

Wetting of switchable solid substrates: A molecular dynamics study

Proposal for a research project within the priority program

“Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces” (SPP 2171)

Scientific discipline

Theoretical physics (statistical physics, soft matter)

Principal investigators

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Summary

Confining a liquid through surfaces (or interfaces) alters its bulk properties and induces structural forces that underlie wetting. These forces depend crucially on the chemical and physical properties of the surface, which can be tuned through, *e.g.*, coatings such as polymer brushes. Changing these properties externally leads to a change of the surface's wettability and induces a dynamic response of the liquid. A better theoretical understanding of such wetting dynamics is not only interesting from a fundamental physics perspective but also a prerequisite for the development of novel responsive materials. Here we propose to study through numerical simulations a minimal model for an asymmetric binary mixture in contact with a flat surface. The interactions with the wall are determined by a single length, which can be used to tune the contact angle over the full range from completely wet to completely dry. Using this generic model, we will study the dynamics of wetting/dewetting after a sudden change of the control parameter, the evolution of the morphology of a dewetting film, contact angle hysteresis for a periodic protocol, and the impact of a droplet falling on a surface. In addition to these molecular dynamics simulations of the wetting dynamics we will perform static free energy calculations of the interfacial tension and binding potential. These are passed as input to coarse-grained continuum descriptions like the thin-film equation, which we will compare in detail to the microscopic results and available experimental data.

1 State of the art and preliminary work

Surfaces and surface forces are ubiquitous in our everyday lives. These forces are the result of unbalanced microscopic forces close to both (hard) surfaces and interfaces between different phases (typically liquid and vapor). The arguably most prominent manifestation of this force imbalance is wetting, the spreading of a liquid across a surface (for general reviews, see Refs. 1,2). The physics of wetting underlies natural phenomena like the lotus effect^{3,4} but also numerous technical applications like superhydrophobic coatings,⁵ inkjet printing,⁶ membranes for fuel cells and water purification,⁷ as well as applications in microfluidics.⁸

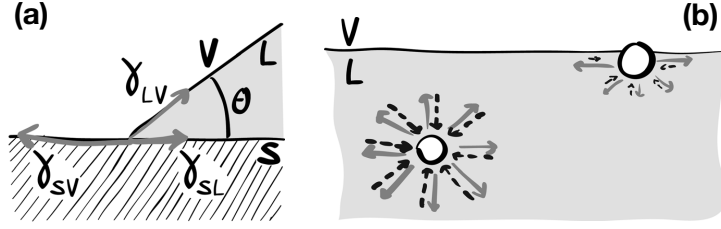


Figure 1: (a) Sketch of the force balance at the contact line between solid substrate, liquid, and vapor. (b) Imbalance of forces at the vapor-liquid interface (black arrows: repulsive, gray arrows: attractive). Drawings from Ref. 16.

A static, macroscopic liquid drop is basically described by a single quantity, the contact angle θ_{eq} . It can be understood from mechanical equilibrium and is expressed through Young's equation

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_{eq}, \quad (1)$$

where γ_{SV} is the solid-vapor tension, γ_{SL} the solid-liquid tension, and γ_{LV} the liquid-vapor tension, cf. Fig. 1(a). One distinguishes completely wet ($\theta_{eq} = 0$) and dry ($\theta_{eq} = \pi$) surfaces from surfaces that are partially wet. The microscopic underpinning of wetting comes from statistical physics, where it is understood as the coexistence of liquid and vapor. This coexistence, however, is strongly influenced and shifted by the interactions with the solid surface, which also determines the nature of the wetting and drying transition as shown recently in Refs. 9–11. Much effort has been directed towards the engineering and the design of surfaces with the desired wetting properties, *e.g.*, mechanically through arrays of microposts¹² and chemically through coating the surface with polymer brushes. Adsorption of molecules (surfactants) at the interface can dramatically change the interfacial tension,¹³ and nanoscopic details at the surface are known to influence static and dynamical aspects of wetting.¹⁴ In this context, numerical studies of model systems^{9–11,15,P6} provide essential tools for the understanding of wetting-related phenomena and their causes.

Dynamic wetting

Tilting a surface with a resting drop, the drop will eventually start to slide down. The onset of this motion is captured by the roll-off angle. Moreover, the drop will deform with typically two (apparent) contact angles, θ_+ for the advancing and θ_- at the receding side of the drop. These angles are different, which is known as contact angle hysteresis. Within a simple hydrodynamic theory,¹⁷ one obtains

$$\theta_{\pm}^3 = \theta_{eq}^3 \pm 9Ca \ln(\ell/b), \quad (2)$$

where ℓ is the capillary length, b is the slip length, and the non-dimensional parameter

$$Ca = \frac{\eta u}{\gamma_{LV}} \quad (3)$$

is called capillary number. Here, η is the viscosity of the liquid (colloidal-rich phase) and u is the speed of the contact line. The corresponding dynamics of the contact line has been studied extensively.²

A different class of dynamic phenomena, which has been investigated less extensively, is generated by surface properties that can be switched, *e.g.* hydrophobic molecules that can be switched by

light,¹⁸ or stimuli-responsive polymers that change their radius of gyration in response to a change of pH or temperature. For example, for a completely wetting polymer film such a change of wettability leads to complex dynamic behavior and morphologies of the detaching film.¹⁹ Wetting properties can also be "modified" by transferring a film onto another substrate, which again can lead to a wealth of interesting dynamical phenomena.²⁰

In this project, we aim to numerically investigate a generic minimal model in response to changing its interactions with a solid substrate. The model is originally motivated by colloid-polymer suspensions,²¹ in which small, soft polymer coils act as depletents and induce entropic forces between the larger colloidal particles. Conceptually, this model exhibits the same phase behavior as a one-component fluid with vapor replaced by the polymer-rich phase, and liquid replaced by the colloid-rich phase. The difference to atomic liquids lies in the fact that attractive interactions are controlled by the polymer size and concentration, which are thus weaker and of short, finite range. Within this model, the (possibly very complicated) interactions of particles with the substrate are described through a repulsive interaction with a single free parameter. Changing the length scale of this repulsive interaction is sufficient to tune the contact angle over the full range from completely wet to completely dry.

Continuum modeling

A well-established approach to model wetting dynamics on mesoscopic lengths is the thin-film equation

$$\partial_t h = \nabla \cdot \left[M(h) \frac{\delta \mathcal{F}}{\delta h} \right], \quad \mathcal{F}[h] = \int_{\tilde{A}} d^2 \mathbf{r} \left[\frac{1}{2} \gamma_{LV} (\nabla h)^2 + \phi(h) \right] \quad (4)$$

with "binding potential" $\phi(h)$ (*i.e.*, the excess free energy density to bring two flat interfaces from infinity to a separation h) and mobility $M(h)$. Eq. (4) is an evolution equation for the two-dimensional height profile $h(\mathbf{r}, t)$ of an interface above a substrate (with contact line given by $h \rightarrow 0$). The integral is over the projected area \tilde{A} of the droplet. The thin-film equation describes a down-hill evolution of the height profile in a landscape prescribed by the free energy functional \mathcal{F} , which resembles the Landau-Ginzburg functional well known from the study of phase transitions. Both $\phi(h)$ and $M(h)$ are in principle unknown and depend on microscopic details, although in typical cases a Taylor-expansion of $\phi(h)$ together with $M(h) \approx h^3/(3\eta)$ for no-slip boundaries might prove sufficient.

For a microscopic model, both γ_{LV} and $\phi(h)$ can be calculated from the interfacial free energy, for example within the framework of classical density functional theory.²⁷ Going further requires to resolve the particulate constituents (atoms, molecules, or colloidal particles), for which computer simulations have proven to be well suited. There is now a wealth of advanced numerical techniques that allow the exact calculation of static quantities and free energy differences,²⁸ such as umbrella sampling. In particular, the systematic study of finite-size effects allows to determine macroscopic quantities with high precision.

Previous work

Both applicants have a long-standing experience in the theoretical modeling of soft matter with complementing sets of skills. In particular, both applicants have worked on the dynamics of nucleation, which shares strong similarities with dynamic wetting.

Peter Virnau has investigated with numerical simulations the phase behavior,^{P6,P7,29} dynamics^{P7,30}

and wetting^{P6,P10} of colloidal suspensions and crystals³¹ using molecular simulations, and has studied homogeneous^{32,P8} and heterogeneous^{P9} nucleation in various systems. He has developed methods to determine phase diagrams³³ and interfacial properties³⁴ of colloidal crystals and studied the influence of hydrodynamic interactions on spinodal decomposition of confined colloid-polymer mixtures. He is also interested in high performance computing and scientific computations on Graphic Processing Units (GPUs),³⁵ which will become relevant in the course of this project when large systems sizes need to be simulated efficiently.

Thomas Speck has been working on the numerical study of phase transitions with an emphasis on their kinetics,^{P1} and non-equilibrium phase transitions of kinetically arrested materials^{P2} and active particles^{P3,P4}. In particular, recently we have extensively studied the nucleation of the solid phase from a supersaturated hard-sphere fluid.^{36,P1} The techniques developed and employed therein will be useful to elucidate microscopic pathways in the dynamic wetting scenario studied here. For example, initiation of dewetting for certain parameters might be a nucleation-like, activated process (metastable state). This calls for advanced numerical methods such as forward-flux sampling (FFS).^{37,P1} Moreover, extensive experience has been gathered in systematically bridging between microscopic particulate models and the continuum level (so far mainly in the context of the phase separation kinetics of active particles^{38,P5}), which will become relevant for the thin-film equation to be studied in this project.

Both applicants have already collaborated recently on a number of projects in the context of microswimmers.^{39–41} In particular they have investigated phase and critical behavior of various model systems for active particles. Beyond the work directly relevant for the proposed project, T. Speck has been involved in the formulation of stochastic thermodynamics a theoretical framework to describe general soft matter systems far from thermal equilibrium. The central elements of this framework are fluctuation theorems for various thermodynamic quantities such as work and heat and the generalized fluctuation-dissipation theorem. P. Virnau is also interested in the investigation of entanglements and knots in polymers, DNA and proteins⁴² and the development of coarse-grained models⁴³ for biomolecular systems.

1.1 Project-related publications

- P1 D. Richard and **T. Speck**, *Crystallization of hard spheres revisited. I. Extracting kinetics and free energy landscape from forward flux sampling*, J. Chem. Phys. **148**, 124110 (2018)
- P2 F. Turci, C.P. Royall, and **T. Speck**, *Non-Equilibrium Phase Transition in an Atomistic Glassformer: The Connection to Thermodynamics*, Phys. Rev. X **7**, 031028 (2017)
- P3 D. Richard, H. Löwen, and **T. Speck**, *Nucleation pathway and kinetics of phase-separating active Brownian particles*, Soft Matter **12**, 5257 (2016)
- P4 J. Bialké, J.T. Siebert, H. Löwen, and **T. Speck**, *Negative Interfacial Tension in Phase-Separated Active Brownian Particles*, Phys. Rev. Lett. **115**, 098301 (2015)
- P5 **T. Speck**, J. Bialké, A.M. Menzel, and H. Löwen, *Effective Cahn-Hilliard Equation for the Phase Separation of Active Brownian Particles*, Phys. Rev. Lett. **112**, 218304 (2014)
- P6 A. Statt, A. Winkler, **P. Virnau**, and K. Binder, *Controlling the wetting properties of the Asakura-Oosawa model and applications to spherical confinement*, J. Phys.: Condens.

Matt. **24**, 464122 (2012)

- P7 J. Zausch, **P. Virnau**, K. Binder, J. Horbach, and R.L. Vink, *Statics and dynamics of colloid-polymer mixtures near their critical point of phase separation: A computer simulation study of a continuous Asakura-Oosawa model*, J. Chem. Phys. **130**, 064906 (2009)
- P8 M. Schrader, **P. Virnau**, and K. Binder, *Simulation of vapor-liquid coexistence in finite volumes: A method to compute the surface free energy of droplets*, Phys. Rev. E. **79**, 061104 (2009)
- P9 D. Winter, **P. Virnau**, and K. Binder, *Heterogeneous nucleation at a wall near a wetting transition: a Monte Carlo test of the classical theory*, J. Phys.: Condens. Matt. **21**, 464118 (2009)
- P10 D. Deb, A. Winkler, **P. Virnau**, K. Binder, *Simulation of fluid-solid coexistence in finite volumes: A method to study the properties of wall-attached crystalline nuclei* J. Chem. Phys. **136**, 134710 (2012)

2 Objectives and work program

2.1 Anticipated total duration of the project

The anticipated total duration of the project is 6 years planned to start in October 2019. This should give as ample time to find a suitable candidate and start in sync with the other projects. Below we outline the objectives and the work schedule for the first funding period of three years.

2.2 Objectives

Our aim is to gain a generic understanding of wetting dynamics as a function of the underlying equilibrium contact angle (which would be reached in the long-time limit). To this end, we will study the dynamics of wetting and dewetting using a computational, particle-based approach. Specifically, a variant of the Asakura-Oosawa-Vrie model with continuous interactions suitable for molecular and Brownian dynamics simulations will be used. In this model, we can tune the equilibrium contact angle θ_{eq} over the full range from no wetting to complete wetting as a function of a single parameter, the range of the repulsive force between substrate and colloidal particles (Fig. 2b). In this way, we can continuously change the contact angle from wetting to drying conditions, and study dynamical processes associated with a switchable substrate.

We plan to investigate several processes: (i) the dynamics of wetting/dewetting after a sudden change of the control parameter, (ii) the evolution of the morphology of a dewetting film, (iii) contact angle hysteresis for a periodic protocol, and (iv) the impact of a droplet splashing on a surface. On one hand, we will use our microscopic approach to make contact with more coarse-grained, macroscopic approaches such as the thin-film equation through, e.g., calculating wetting binding potentials and transport coefficients. On the other hand, we will gauge our model with experimental observations within the SPP.

2.3 Work program incl. proposed research methods

2.3.1 Methods

We will study a continuous variant of the Asakura-Oosawa-Vrie (AO) model^{21,44} suitable for molecular and Brownian Dynamics simulations, which was co-derived by one of us (PV) in Ref. P7. Even though the AO model was originally invented to investigate phenomenologically mixtures of colloids and polymers, it can also be regarded as a generic model system to study phase transitions and related phenomena. In this project, we will use it as a coarse-grained particle-based model system in which wetting properties can be switched easily from wetting to drying conditions and vice versa. The static behavior of this model has already been studied extensively by one of us,^{P6} and the phase diagram for bulk and various forms of confinements as well as conditions for wetting are well-known (Fig. 2). The model thus presents an ideal starting point for the investigation of dynamic wetting.

The model consists of two types of particles, colloids (A-particles) and polymers (B-particles). Interactions between two A-particles and an A- and a B-particle is hard-sphere like and mediated via a Weeks-Chandler-Andersen (WCA) potential:

$$U_{\text{WCA}}(r; \sigma, \varepsilon) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right]. \quad (5)$$

Here, r is the distance between two particles, σ is the pair interaction range and ε is the interaction amplitude. For distances larger than $r_c = 2^{1/6}\sigma$ the potential is set to zero. Interactions between particles and walls are also modelled with Eq.(5) using $\sigma_{\text{AW},\text{BW}} = 0.5\sigma_{\text{AA},\text{BB}}$ and $\varepsilon_W = 1$.

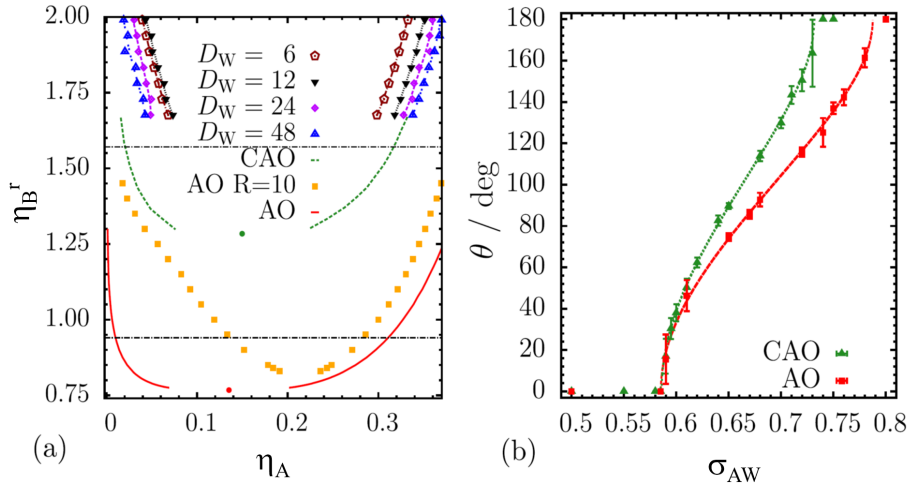


Figure 2: (a) Phase diagrams of the original and the continuous (CAO) variant of the Asakura-Oosawa model. Full lines correspond to bulk while symbols denote confinement between two plates at distance D_W for the continuous model and spherical confinement for the regular AO model (yellow squares). Dashed horizontal lines denote reservoir packing fractions of B-particles at which wetting properties were determined. (b) Contact angle as a function of interaction range σ_{AW} between A-particles as determined from Young's equation (at $\eta_B^r = 1.5711$ for the CAO model). Adapted from Ref. P6.

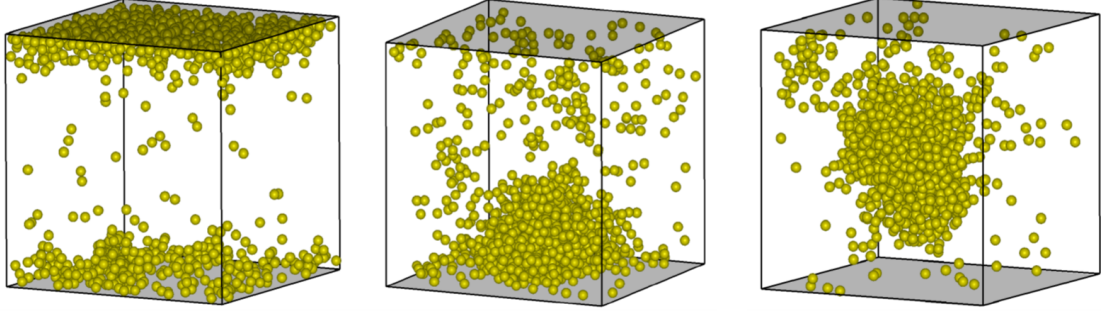


Figure 3: Snapshots of AO simulations corresponding to contact angles of 0° , 90° , and 180° as obtained from adjusting σ_{AW} . (Only A-particles are depicted for clarity.) Note that system sizes shown here are rather small and will be increased significantly for investigations of dynamics. From Ref. 45.

Interactions between two B-particles are rather soft and given by:

$$U_B(r; \sigma, \epsilon) = 8\epsilon \left[1 - 10 \left(\frac{r}{2^{1/6}\sigma} \right)^3 + 15 \left(\frac{r}{2^{1/6}\sigma} \right)^4 - 6 \left(\frac{r}{2^{1/6}\sigma} \right)^5 \right] \quad (6)$$

for $r < r_c = 2^{1/6}\sigma$ and zero otherwise. Interaction ranges and amplitudes are chosen to be the same as in Ref. P7, namely $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.9$, $\sigma_{BB} = 0.8$, $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.0$, $\epsilon_{BB} = 0.0625$. In essence, these potentials preserve the basic form and properties of the original AO-model. Particularly, B-particles act as depletents for A-particles promoting phase separation in bulk and confinement even though all potentials are purely repulsive. However, hard core repulsions are replaced by somewhat softer potentials and interactions between depletents are now finite and differentiable instead of being set to zero, thus enabling computations of forces.

For this model, we have already demonstrated that by switching the interaction range of A-particles with the repulsive wall (σ_{AW}) we can drive the system from wetting conditions to drying or any state in between (see Figs. 2b,3). To this end, we have determined the equilibrium interfacial tensions of A and B particles (at a given reservoir packing fraction of B particles) with respect to the each other and with respect to the wall (using the so-called ensemble switch method³⁴), and thus the contact angle as a function of σ_{AW} via Young's equation. Conceptually, A-particles are gradually being replaced by B-particles close to the wall once the repulsion range for A-particles σ_{AW} increases while the corresponding range σ_{BW} remains constant for interactions with B-particles. This not only enables fine control over wetting conditions close to the wall, but also allows us to stabilize single droplets.

Note that in finite-size systems, one observes system-size dependent (first-order like) transitions from a homogeneous gas phase to a droplet to a cylinder and eventually a slab and vice versa as density increases in the two-phase region. This is exemplified for a simple Lennard-Jones liquid without walls in Fig. 4. In the presence of walls spherical capped droplets and cylindrical capped droplets (at somewhat higher densities) form close to a wall. Hence, knowledge of the location of the so-called evaporation-condensation transition^{P8,P9} is important to determine the density range at which droplets are stable.

Large-scale simulations of wetting and dewetting dynamics will be performed using the Molecular Dynamics package HOOMD on graphic processing units.^{46,47} In addition to simulations of dynamics we will also determine free energy differences by performing a thermodynamic integration^{48,P6}

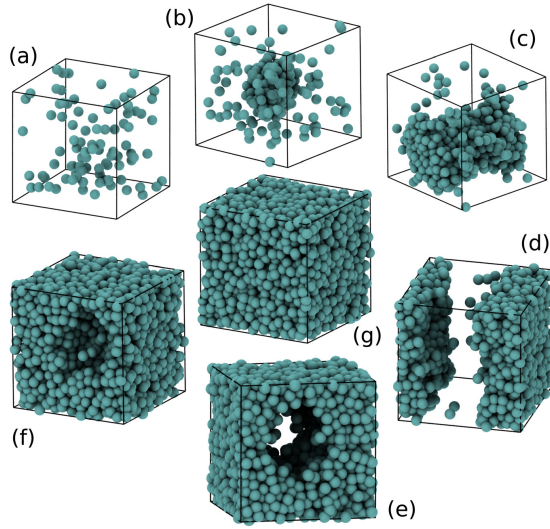


Figure 4: Simulation snapshots of a one-component Lennard-Jones fluid increasing the density: (a) gas, (b) droplet, (c) cylindrical droplet, (d) slab, (e) cylindrical bubble, (f) bubble, and (g) liquid.

from the wetted state to the dry state by increasing σ_{AW} in discrete steps. Should the necessity arise to consider higher or lower densities of embedding B particles, additional grand-canonical Monte Carlo simulations will be undertaken by our external collaborator Antonia Statt.

2.3.2 Work schedule

The work program is split into 4 interconnected work items. The following chart shows the order and projected duration of the single work items:

year 1/1	year 1/2	year 2/1	year 2/2	year 3/1	year 3/2
WP1					
	WP2				
			WP3		
				WP4	
					Thesis

WP1: Setting up the simulations

The PhD student will first have to become familiar with the HOOMD programming package and set up first simulations. In this phase, we will also undertake additional simulations with our own grand-canonical Monte Carlo code to assess small changes in the polymer density during dewetting (since the free volume accessible to the polymers changes in a finite simulation box). We expect that this introductory phase takes about six months.

WP2: Spreading and drying dynamics

First, we will equilibrate a system with σ_{AW}^0 corresponding to partial wetting conditions. Exploiting finite-size transitions,^{P8} we will tune the box geometry in order to obtain an elongated cylindrical droplet along one axis [cf. Fig. 5 and Fig. 4(c) in the absence of a substrate], which will drastically simplify the analysis since we can determine one-dimensional profiles. We then

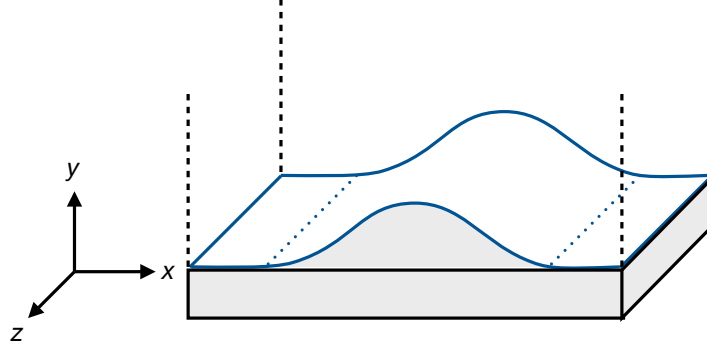


Figure 5: Sketch of the box geometry used in the simulations of WP2. By varying the ratio between L_x and L_z , one obtains an elongated droplet so that we can treat the system basically as one dimensional, which facilitates analysis and comparison with predictions of the thin-film equation. After switching the substrate interactions, the droplet spreads over the surface. The dotted lines indicate the position of the contact line.

decrease instantaneously the value of σ_{AW} to reach complete wetting [see Fig. 2(b)], and study the dynamics of the spreading droplet as a function of time. We will repeat these simulations and calculate an average density $\rho(\mathbf{r}, t)$, from which we extract the height profile $h(\mathbf{r}, t)$ as an isodensity surface. In contrast to the equilibrium contact angle, which is well-defined through Eq. (1), it is notoriously difficult to determine contact angles from such profiles. Nevertheless, we will try to extract such an (apparent) instantaneous angle $\theta(t)$ through interpolating the height profile, e.g., with splines. We will also determine the contact line and its speed u . This cycle will be repeated for partial wetting/dewetting scenarios as Fig. 2(b) provides us with fine control over our switchable surface. We expect that the dynamics are to some extent governed by the finite size of the droplet, which will also be studied in detail.

In the next step, we will turn to drying dynamics through suddenly increasing σ_{AW} . We will compare the dynamics of $\theta(t)$ with the spreading case. Finally, we will combine both situations into the periodic protocol

$$\sigma_{AW}(t) = \sigma_{AW}^0 + a \sin(2\pi t/\tau), \quad (7)$$

which is defined by the time-scale τ . This allows us to study in detail the contact angle hysteresis and its dependence on the driving time scale τ .

After studying the dynamics wetting and dewetting on one-dimensional profiles in cylindrical geometry (which will form the basis for investigations in WP3), we will extend our simulations and analyses to the conceptually more challenging case of a spherical droplet (which will also be investigated in WP4).

Our system investigates a scenario in which a liquid droplet of A-particles is embedded in a liquid of B-particles. By increasing the density of A-particles (while keeping σ_{AW} fixed) we can also reverse the scenario and embed a droplet of B-particles in a liquid of A-particles, which should alter the dynamics considerably. Further extensions to a liquid or a crystalline droplet embedded in a gas (as opposed to a liquid) will be considered at a later stage of the project (and potentially in the next funding period). The former can be implemented with a simple Lennard-Jones model for which a relation similar to Fig. 2b was determined by Evans et al^{10,11}, namely the contact angle (ranging from complete wetting to complete drying) as a function of wall attraction as determined

by Young's equation. Contact angle as a function of wall attraction was also determined by the same group for the SPC/E water model.⁹ Crystalline droplets can be realized with an effective AO model as studied in Ref. P¹⁰.

Morphology. Finally, we will try to gain some insights into the morphology of a drying film (initially at complete wetting) after a sudden quench to dry conditions. While for a sessile drop there are basically two modes of evaporation (constant contact angle, constant contact radius, or mixed), we expect that an extended film will develop a complex morphology (*i.e.*, regular "holes" that at latter stages connect to leave single droplets) and more complex dynamics. We will look into suitable order parameters to describe the morphology and its evolution in our particle-based simulations. Moreover, depending on the state point, the film might be in a metastable state and initiating the dewetting process is a rare event. To study this situation, we will employ forward-flux sampling.^{P1} A modular implementation of forward-flux sampling as a "wrapper" is available in the group of TS, which calls HOOMD to generate molecular dynamics trajectories.

WP3: Comparison with thin-film equation

To reach a more complete understanding, we will then turn to the mesoscopic thin-film equation [Eq. (4)]. We aim to systematically derive such a coarse-grained description through a direct calculation of the interfacial tension and binding potential from the numerical simulations. Such a coarser description allows to study dynamics and morphologies on larger length and time scales than accessible in the particulate simulations, and to analytically study instabilities.

In our setup it is sufficient to consider the one-dimensional case $h(x, t)$ governed by Eq. (4), which will be solved using standard methods for partial differential equations (finite-difference schemes). As input, we require the binding potential $\phi(h)$ and the liquid-vapor interfacial tension γ_{LV} . The latter has already been determined applying grand-canonical Monte Carlo simulations in combination with Successive Umbrella Sampling³³ (at $\eta_B^r = 1.5712$). From the resulting probability distribution of the density of A particles at coexistence, one can derive the free energy difference between the two homogeneous gas and liquid phases and a phase in between in which a slab with two interfaces is present (like in Fig. 4d), and thus $\gamma_{LV} = \Delta F/(2L^2)$. Further state points at higher or lower densities of B particles could be generated by our external collaborator Antonia Statt.

The binding potential has been calculated from density functional theory calculations.^{23,49} In this work package, we aim to develop methods to calculate $\phi(h)$ from molecular dynamics simulations. We will first try a direct approach in which we perform a thermodynamic integration in bins of width Δx . Denoting U_i the potential energy in bin i , we calculate the local free energy differences

$$\Delta F_i(\sigma_{AW}) = \int_{\sigma_{AW}^0}^{\sigma_{AW}} d\sigma'_{AW} \left\langle \frac{\partial U_i}{\partial \sigma_{AW}} \right\rangle_{\sigma'_{AW}}, \quad (8)$$

where the parameter σ'_{AW} is changed in small steps from completely wet to a dry state. Recording at the same time the average height profile h_i allows to reconstruct the binding potential $\phi_i = \phi(h_i)$. We will compare the predictions at the continuum level with the detailed dynamic results obtained in WP2. We will also investigate more advanced sampling schemes from which a spatially resolved free-energy (*i.e.*, the binding potential) can be extracted.

At this stage, we will also compare results with experimental data obtained within the Priority Program for the different switchable substrates studied (for details, see Sec. 2.8). We will in

particular evaluate whether the simple repulsive wall potential employed so far is sufficient are should be replaced by a more complicated form in order to model the experiments more closely. We will then repeat the calculation of the binding potential and compare predictions like the contact angle and large-scale dynamics obtained from solving the thin-film equation with the experimental results.

WP4: Droplet impact

If time allows, we will employ an equilibrated colloidal droplet from WP2 and drive it towards the surface by a constant velocity v_0 or force f_0 . (Technically, the velocity (or force) is applied to all beads in the cluster in a steered molecular dynamics simulation.) We will study the impact of the colloidal droplet for various contact angles (as defined by σ_{AW}), impact velocity v_0 (or force f_0), and droplet size. The droplet may either stick to the wall or splash,^{50–52} and a corresponding phase diagram will be constructed as a function of the aforementioned variables. As in WP2, we will also consider extensions to liquids and crystallites embedded in a gas. This work package as well as extensions of prior packages to specific substances and surfaces used in the SPP may also become a focus for the second funding period.

2.4 Data handling

In the course of this project, an extensive amount of data is generated through computer simulations. However, this data is reproducible and we will ensure that the code is documented and archived. Nevertheless, any data that is used for publications will also be backed up on external hard drives and securely stored.

2.8 Interactions within the priority program

The goal of our project is the theoretical underpinning of many-body effects based on a statistical physics approach. To this end, we will examine dynamics of wetting on switchable substrates with a computational particle based-approach employing a generic coarse-grained model system. Our investigations will thus form a basis for a variety of specific systems with switchable surfaces and connects with many other efforts in this Priority Program. Several experimental groups are interested in switchable substrates, and we will explore to which extends our model is applicable and helpful in predicting dynamic wetting behavior.

Specifically, we have agreed to collaborate with the following groups: The project by **Müller and Tanaka** investigates wetting of vesicles on stimulus-responsive polymer brushes. This system will also be modelled with a complementary coarse-grained approach, which can be compared to our more generic ansatz. Particularly, we plan to exchange results about the response to a sudden change or time-periodic modulation of the wetting properties as well as simulation techniques. The project by **Vollmer and Schmid** will undertake GPU-based coarse-grained simulations of partial wetting of water or alkanes on various polymer brushes. Again, we believe that a comparison with our more generic model will be interesting. In addition, we have agreed to collaborate on technical issues arising from implementing large-scale systems on graphic processing units. Another approach to switchable, polymer-coated surfaces controlled by temperature and pH is studied in the **von Klitzing** group, and we will test our model against their experimental data for

contact angles and the dynamics of the contact line.

Heuer and Gurevich will follow a comparable theoretical approach to the wetting dynamics on switchable, pre-structured substrates combining microscopic Kinetic Monte Carlo and Molecular Dynamics simulations with the mesoscopic thin-film equation. The specific systems studied in their and our project are complementary. We will exchange results and ideas on the technical implementation and on the coupling of, and the passing of parameters between, the different scales. Finally, we will collaborate with **Varlamova and Borgia**, who plan to study drop dynamics on pre-structured substrates modeled using phase-field simulations, which is closely related to the thin-film equation but employs a simplified ansatz for the free energy.

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4 Requested modules/funds

4.1 Basic module

4.1.1 Funding for staff

For the first funding period, we apply for one PhD position.

One PhD position (75%, employed for the duration of the project):

Thomas Speck:	$3 \times 0.75/2 \times \text{€}64,500 =$	€72,563
Peter Virnau:	$3 \times 0.75/2 \times \text{€}64,500 =$	€72,563
		total = €145,126

4.1.2 Direct project costs

Equipment up to 10,000, software and consumables

For hard disks needed for long-time storage of simulation data in accordance with DFG regulations, we apply for:

Thomas Speck:	€250
Peter Virnau:	€250
<hr/>	
total =	€500

For local code development, Peter Virnau applies for a high-performance graphic card (RTX 2080Ti or equivalent) for the PhD student:

Peter Virnau:	€1000
<hr/>	
total =	€1000

Travel expenses

To present our results at national and international conferences (one per year for TS and PV), to visit collaborators and events related to the priority program in Germany, and enable the PhD student to attend the yearly DPG meetings and one international conference in three years, we apply for funding to cover travel expenses:

Thomas Speck:	€2,000/year =	€6,000
Peter Virnau:	€2,000/year =	€6,000
		total = €12,000

Visiting researchers

We will collaborate with Antonia Statt (Princeton University, USA), who will contribute with grandcanonical Monte Carlo simulations as detailed below in Sec. 5.4. For a successful collaboration and to coordinate our activities, we would like to invite Dr. Statt to come to Mainz at least twice. As her host, Peter Virnau applies for funding to cover travel costs and accommodation:

Air fare from US:	2×€1,500 =	€3,000
Accommodation and per diem:	28 days×€150 =	€4,200
		<hr/>
		total = €7,200

Project-related publication expenses

To publish our results in open access and interdisciplinary high-profile journals (*e.g.*, Nature Physics), we apply for:

Thomas Speck:	€375/year =	€1,125
Peter Virnau:	€375/year =	€1,125
		<hr/>
		total = €2,250

5 Project requirements

5.1 Employment status information

- Prof. Dr. Thomas Speck, Johannes Gutenberg-Universität Mainz
Permanent position: Yes (W2)
- PD Dr. Peter Virnau, Johannes Gutenberg-Universität Mainz
Permanent position: Yes (Akademischer Oberrat)

5.2 First-time proposal data

N/A

5.3 Composition of the project group

- T. Speck, Principal Investigator
will coordinate the project and jointly supervise PhD student (in particular mesoscopic modeling), carry out literature searches, and take responsibility of publication writing.
- P. Virnau, Principal Investigator
will coordinate the project and jointly supervise PhD student (in particular numerical simulations), carry out literature searches, and take responsibility of publication writing.
- N.N., PhD student
will work on the project according to the work plan outlined above.
- William Janke, PhD student, DFG funded (SP 1382/5-1)
works on molecular dewetting of organic molecules on dielectric substrates and multiscale modelling.
- Florian Dittrich, PhD student, DFG funded (SPP 1726)
works on GPU-based simulations of active particles. He will support the student to set up his/her simulations with HOOMD.

- Additional Bachelor and Master students will work on single aspects of the project proposed here.

5.4 Cooperation with other researchers

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

We have agreed to collaborate with the following groups within the priority program (for details see Sec. 2.8):

- Prof. Dr. Friederike Schmid, University of Mainz; Prof. Dr. Doris Vollmer, MPIP Mainz
- Prof. Dr. Marcus Müller, University of Göttingen
- Prof. Dr. Regine von Klitzing, University of Darmstadt
- Prof. Dr. Andreas Heuer and Dr. Svetlana Gurevich, University of Münster
- Dr. Radica Borgia and Dr. Olga Varlamova, BTU Cottbus-Senftenberg

In addition, outside of the priority program we plan to collaborate with:

- Prof. Dr. (emer.) Kurt Binder, University of Mainz (wetting)
- Dr. Antonia Statt, Princeton University (AO model, grandcanonical simulations)

The long-term goal of our project is to advance the understanding of wetting dynamics in response to a switchable surface. To this end we intend to collaborate with **Kurt Binder**, who is a longtime expert in area of wetting, computer simulations and Statistical Mechanics. We will also work together with **Antonia Statt**. Dr. Statt has already performed simulations with the model on which this proposal is based, and will support our Molecular Dynamics simulations with accompanying grandcanonical Monte Carlo simulations.

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

- Thomas Speck:
Angelika Kühnle (University of Bielefeld, Germany); Clemens Bechinger (University of Konstanz, Germany); Hartmut Löwen (University of Düsseldorf, Germany); C. Patrick Royall (University of Bristol, UK); Robert L. Jack (University of Cambridge, UK); Michael E. Cates (University of Cambridge, UK); Udo Seifert (University of Stuttgart, Germany);
- Peter Virnau:
K. Daoulas (MPIP Mainz, Germany); R. Potestio (University of Trento, Italy); N. Emami (Uni Stuttgart, Germany); A. Milchev (Bulgarian Academy of Sciences, Bulgaria); H. Meyer (CNRS Strasbourg, France); S. Das, (J. Nehru Center for Adv. Sci. Res., India); J. Sulkowska (University of Warsaw, Poland); E. Laue, T. Stevens (Cambridge University, UK); A. Statt (Princeton University, USA); S. Egorov (University of Virginia, USA);

5.5 Scientific equipment

Adequate computational resources to perform the simulations are available at the University of Mainz in the form of the high-performance computing cluster "Mogon" (35520 AMD Interlagos cores at 2,1 Ghz) and "Mogon 2" (49432 Intel Xeon Processors at 2.1 Ghz). The central computing facility also provides access to around 200 GPUs (mostly GTX 1080Ti). In addition, we have a small local cluster with about 800 cores.

The PhD student would greatly benefit from a high-performance graphic card (RTX 2080 Ti or equivalent) in his/her desktop computer for local code development. Production runs will take place on the graphic card cluster of Mogon2.

6 Additional information

We have not requested funding for this project from any other sources. In the event that we submit such a request, we will inform the Deutsche Forschungsgemeinschaft immediately. In submitting a proposal for a research grant to the DFG, we agree to adhere to the DFG's rules of good scientific practice. In preparing the proposal, we have adhered to the guidelines for publication lists and bibliographies.