

Applicants

Prof. Dr. Uwe Thiele
Westfälische Wilhelms-Universität Münster
Institut für Theoretische Physik
Wilhelm-Klemm-Str., 9
48149 Münster

Mesosopic gradient dynamics models for the (de)wetting dynamics on adaptive substrates

Summary

This project aims at developing and employing a set of generic mesoscopic continuum models for the (de)wetting dynamics on substrates with adaptive wettability and topography. Recently developed thin-film gradient dynamics models for mixtures of simple liquids and dilute solutions and suspensions describe their capillarity- and wettability-dominated (de)wetting dynamics on inert substrates. Here, models are developed that combine these thin-film (or shallow-drop) models with equations describing the dynamics of essential degrees of freedom of the substrate. The latter equations model reversible dynamical processes that change wettability and topography on timescales comparable to the ones of the liquid.

Examples of such substrate degrees of freedom are the amount of physisorbed surfactant at a solid substrate, the swelling grade of a polymeric brush crafted to the substrate or the filling ratio of a porous substrate. For each of these cases, particular energy functionals shall be developed and be introduced into the gradient dynamics framework to directly obtain coupled evolution equations for film height, inner degree(s) of freedom of the liquid and inner degree(s) of freedom of the substrate. The framework automatically gives all relevant cross-couplings between the different acting forces and fluxes and, furthermore, can be extended beyond the shallow drop limit.

The resulting generic models are adapted to particular experimental systems and studied employing large-scale time simulations and path continuation techniques as well as analytical approaches with a focus on the region of the moving three-phase contact line that largely determines the dynamic (de)wetting processes with coupled liquid and substrate dynamics. We envision a close cooperation between theory and several experimental groups within the SPP. The models are also validated against and related to other modelling approaches pursued within the SPP.

1 State of the art and preliminary work

State of the art. Dynamic processes of wetting and dewetting where simple and complex liquids respectively advance onto and recede from various substrates are very common in our daily life and crucial in many technological processes [1, 2, 3, 4]. Most of the performed dedicated experiments, numerical simulations and theoretical considerations of the past decades consider these processes on smooth homogeneous solid substrates or study the influence of static substrate heterogeneities like wettability and topography patterns and defects [5, 6, 7, 8].

However, recent developments in areas like microelectronics or 3D printing have demonstrated a pressing need to also understand cases in which (de)wetting hydrodynamics and substrate dynamics are strongly coupled. This holds true especially on microscopic and mesoscopic length scales, where (non-)equilibrium interface phenomena dominate. For instance, viscous and soft elastic substrates may reversibly change their profile when a drop of liquid is placed on them [9, 10]. In this case, no transport of material takes place across the liquid-solid interface and the substrate changes its topography but not its physico-chemical properties.

In contrast, the adaptive substrates – that are our present focus – change their physico-chemical properties (wettability) and possibly additionally their topography due to the presence of a liquid or through external conditions [12, 13]. This may be induced by direct contact like under a sessile droplet, or it may be mediated through an external phase like the ambient atmosphere or a second liquid. Further, modifications may be mediated through gradual changes of temperature [14, 15, 16, 17], ambient humidity [18] and pH-value [13, 12, 19, 20, 21, 22]. For adaptive substrates, transport of material may take place across the liquid-solid interface and phase boundaries may shift. For instance, polymer brushes and networks, hydrogels and organic multilayers may swell under a drop of liquid or in response to its extending vapour [23, 13]. In a co-nonsolvency transition poly(N-isopropylacrylamide) (PNiPAAm) brushes in aqueous ethanol mixtures show a volume phase transition including a nonmonotonic dependency of brush thickness on solvent concentration [11] (see Fig. 1). Similar effects are observed for hydrogel substrates [?]. A change in temperature may reversibly change a hydrogel from superoleophobic to oleophobic [15] or the phase of a liquid-crystalline substrate implying a change in wettability [24]. Ideally, these changes are reversible and can be repeated arbitrarily often. In all cases, the dynamics of the adaptive substrate and the dynamics of the de(wetting) liquid take place on similar time scales, i.e., their direct coupling results in new phenomena that shall be modeled in this project employing mesoscale continuum models.

A limiting case of ultra-thin adaptive surface layers are the mentioned substrates covered with a polymer brush [17, 25, 26]. For very mobile brushes one can create liquid-like surfaces characterised by very small lateral adhesion forces. A common model system are PDMS-brushes. The mobility results in a relatively fast change of the brush thickness in the three-phase contact line region, i.e., the effective substrate profile is adaptive. One also expects that the contact line motion orders the brush molecules resulting in further anisotropy effects. Therefore the dynamic wetting

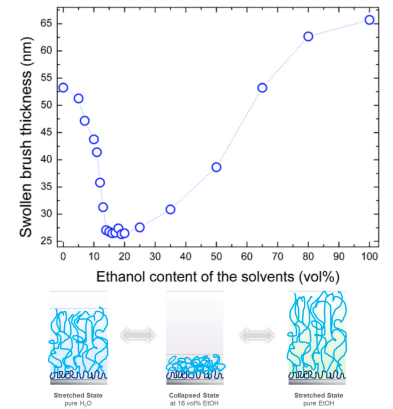


Figure 1: *Non-monotonic dependency of brush thickness on mixture composition and sketch of extended and collapsed brush states. Reproduced from [11].*

behaviour is influenced by the speed of adaptation, i.e. results from the interplay of intermolecular forces of the coating, the vapour pressure of the liquid and the adhesion forces.

If the substrate dynamics is much faster than the one of the liquid, the substrates are not considered as adaptive but as switchable. For instance, switching could be induced by electric or magnetic fields, as well as via changes of pH or temperature. For instance, nematic elastomers or coatings that contain photo-switchable azobenzenes fall into this category. In the present project, switchable substrates are not central, but will only be regarded as a limiting case of the considered adaptive substrates.

Beside the adaptation of a substrate in response to a pure liquid of low molecular weight, substrates may respond to one component of a complex liquid. This brings new aspects into the (de)wetting dynamics as the dynamics of internal degrees of freedom of the liquid (i.e., concentration) may then interact with the substrate dynamics. An example is the already mentioned response to pH-value that is normally related to the degree of ionisation of a polyelectrolytic liquid that interacts with conformation and organisation of the constituents of thin organic surface coatings [13]. The evaporative dewetting of polymer solutions or nanoparticle suspensions may result in irreversible changes of the substrate through (patterned) solute deposition [A1] [29]. – such irreversible processes are not considered. However, a component of a liquid mixture or the solute in a dilute suspension or surfactant (tenside) solution may, by action of surface forces, get enriched close to the moving contact line, be adsorbed to the substrate underneath the liquid or diffuse along the ‘dry’ substrate in front [behind] the advancing [receding] contact line. This includes the cases of dry [30] and liquid-infused [31] porous substrates. In the latter case, the infused liquid might correspond to one component of a mixture while in the former case imbibition acts like substrate adaptation. Even the equilibrium wetting behaviour of homogeneous mixtures or solutions on classic inert substrates may differ from expectations. The reason is that surface forces may induce a local phase separation close to the contact line even for miscible liquids and result in a precursor film consisting of only one component (leak-out transition in [27, 28], see Fig. 2). Related phenomena observed for surfactant solutions are ‘autophobic behaviour’ [32] and ‘substrate-induced condensation’ [33, 34]. If components of the mixture are volatile, one encounters additional interactions between wetting dynamics, partial evaporation, and Marangoni fluxes (driven by surface tension gradients) [18, 35, 36, 37]. Note that the occurring ultrathin adsorption layers also result in an adaptive substrate.

The consistent theoretical description and numerical simulation of wetting processes on micro-, meso- and macroscales is in the case of simple liquids on inert solid substrates quite well developed. The range of applied approaches includes Molecular Dynamics (MD) simulations [38, 39], lattice Boltzmann simulations [39], phase-field models [40], classical hydrodynamics (Navier-Stokes equations) [41] and asymptotic approaches as mesoscopic thin-film (or long-wave) models [42, 43]. Comparative studies, parameter passing approaches and consistency conditions connect these approaches into a multiscale framework [39, 41, 44, 45, 46].

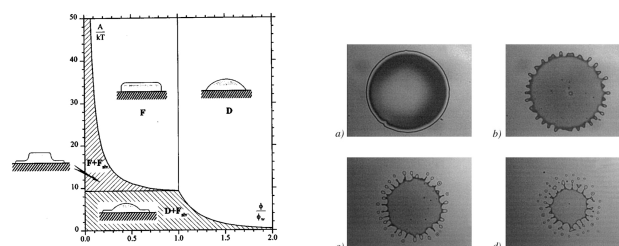


Figure 2: (left) Wetting diagram for a solution showing regions of different equilibrium states: drop (D), Film of solution (F), Film of pure solvent (F_{slv}). Coexistence regions are hatched. (right) Dynamics of corresponding stable spreading and unstable receding process where spreading, leak-out, evaporation and Marangoni flows interact. Reproduced from [27, 28].

In a macroscopic description, an equilibrium three-phase contact line on a smooth substrate is characterised by Young's equation $\gamma \cos \theta_e = \gamma_{sg} - \gamma_{sl}$. It relates the interfacial energies γ , γ_{sl} and γ_{sg} of liquid-gas, solid-liquid and solid-gas interface, respectively, with the macroscopic equilibrium contact angle θ_e . In contrast, in a mesoscale description, wettability is modeled by a film height-dependent wetting energy (or binding potential) $f(h)$. Macro- and mesoscale description are consistent if $\gamma \cos \theta_e = \gamma + f(h_a)$ where h_a is the thickness of the equilibrium adsorption layer [47, 48, 49, 50]. Wetting energies $f(h)$ are obtained by asymptotic considerations (for typical expressions see [48, 42]) or are extracted from microscopic approaches as Density Functional Theory (DFT) [51, 52] and MD [53, 44]. In macroscopic hydrodynamic models, polymeric brushes are often considered as flexible (viscoelastic) layers without adaptability [54]. A macroscopic dynamical model incorporating the effect of an adaptive substrate has been presented in [55] based on exponentially relaxing equilibrium contact angles. A versatile asymptotic method to study nonequilibrium thin films and shallow drops are thin-film equations derived via a long-wave expansion from the governing equations and boundary conditions of hydrodynamics [42, 56]. The equations can often be brought into gradient dynamics form [57]. For a simple nonvolatile liquid that dewets a flat solid substrate we have the mass-conserving dynamics

$$\partial_t h = \nabla \cdot \left[Q(h) \nabla \frac{\delta \mathcal{F}}{\delta h} \right] \quad \text{with} \quad \mathcal{F}[h] = \int \left[\frac{\gamma}{2} (\nabla h)^2 + f(h) \right] d^2 r \quad (1)$$

where the energy functional $\mathcal{F}[h]$ (sometimes called “interface hamiltonian”) contains surface and wetting energies, $Q(h) = h^3/3\eta$ is the mobility function in the case without slip at the substrate, and η is the dynamic viscosity. For volatile liquids, a non-conserved contribution to the dynamics is added to Eq. (1) [58]. In general, different descriptions of a moving contact line are still under debate (see, e.g., [59] and other contributions in the corresponding discussion volume). In the context of thin-film models the two major approaches are slip models that assume the liquid slips at the solid substrate resulting in an amended mobility Q [60] and precursor film models that assume an ultrathin adsorption layer exists on the macroscopically ‘dry’ substrate [61] as determined by the wetting energy.

For selected complex liquids, a systematic theoretical description of the interaction of (de)wetting dynamics and the dynamics of the internal degrees of freedom of the liquid is under development. For instance, there exist mesoscopic thin-film models for films and drops of mixtures of simple liquids and surfactant solutions on homogeneous, solid and inert substrates [62, 63, 64]. Such models can often be reformulated as gradient dynamics on an underlying energy functional [A2], then allowing for systematic and fully thermodynamically consistent extensions [A3, A4]. These are able to capture the full extent of the interface-dominated dynamics in cases where the various diffusive and advective transport channels couple, e.g., in the case of surfactant-dependent wettability. Further, the gradient dynamics approach provides a simple criterium to assess the validity of other long-wave models. To our knowledge the coupled dynamics of an adaptive substrate, the (de)wetting liquid and of the latter's internal degrees of freedom has not yet been considered. It is the aim of the present project to develop such models within a gradient dynamics framework for simple liquids, mixtures of simple liquids and dilute surfactant solutions on adaptive substrates.

Preliminary work. An important part of the activities of the group of Prof. Thiele at the *Institut für Theoretische Physik (ITP)* focuses on theoretical and numerical investigations of nonlinear dynamics and pattern formation in out-of-equilibrium interface-dominated soft matter and fluidic systems. This includes the development and application of a class of gradient dynamics models for thin films and shallow droplets of simple and complex liquids on solid substrates. For simple

liquids, variants of Eq. (1) were recently studied employing advanced numerical path-continuation algorithms and large-scale direct time simulations to determine bifurcation diagrams of single sliding drops [A5], and to analyse the behaviour of large ensembles of drops [A6]. The underlying methods are now being developed for thin-film models of complex liquids [A7, A8][65] and will be available for the project.

A decisive stepping stone towards gradient dynamics models for complex liquids on adaptive substrates is the development of such models for inert substrates. Literature models are often obtained by ad-hoc amendments of hydrodynamic models for simpler cases what often results in inconsistencies between the various transport channels. In contrast, we have recently developed gradient dynamics models for films and drops covered by insoluble [66] and soluble [A4] surfactants, and non-surface-active mixtures [A3, A9]. Extensions towards laterally driven systems that remain permanently out of equilibrium were also considered [A1] [67]. These shall in our project be coupled to different substrate models.

For instance, the governing equations that describe film flows and surfactant dynamics at low surfactant concentrations with negligible wettability influence had been well established (see [A4] for review). Typically, the dynamics is described using a film-height evolution equation like Eq. (1) - adding a concentration-gradient driven Marangoni flux - coupled to a thin-film advection-diffusion equation for the surfactant concentration [43]. We have proposed how to develop such models as gradient dynamics on an underlying appropriate energy functional that allows, e.g., for a thermodynamically consistent incorporation of concentration-dependent surface and wetting energies [A4]. In WP 3 we will use this as a base for models that incorporate adaptive substrates. The model for a film with insoluble surfactant is an example of the case of two coupled scalar fields. Excluding evaporation and other nonconserved processes, all these two-field models can be brought into the gradient dynamics form

$$\begin{aligned}\partial_t h &= \nabla \cdot \left[Q_{hh} \nabla \frac{\delta \mathcal{F}}{\delta h} + Q_{h\psi} \nabla \frac{\delta \mathcal{F}}{\delta \psi} \right] \\ \partial_t \psi &= \nabla \cdot \left[Q_{\psi h} \nabla \frac{\delta \mathcal{F}}{\delta h} + Q_{\psi\psi} \nabla \frac{\delta \mathcal{F}}{\delta \psi} \right]\end{aligned}\quad (2)$$

where h and ψ are two fields with conserved dynamics. The Q_{ij} form the symmetric mobility matrix

$$\mathbf{Q} = \frac{1}{\eta} \begin{pmatrix} h^3/3 & a h^2 \psi \\ a h^2 \psi & b h \psi^2 + c(\psi) \psi \end{pmatrix}, \quad (3)$$

where η is a viscosity, and the respective energy functionals \mathcal{F} normally contain entropic and/or interaction terms as well as terms penalising strong gradients. For the film of binary mixture [A3], h and ψ correspond to the thickness of the film and the effective solute layer height $\psi = h\phi$ (where ϕ is the height-averaged concentration), respectively, and the particular mobilities in (3) have $a = b = 1/3$ and $c(\psi) = \tilde{D}$ is the solute's diffusive mobility. For the film with insoluble surfactant [66], h and ψ correspond to the thickness of the film and the surfactant concentration projected onto the cartesian plane, and in (3) $a = 1/2$, $b = 1$ and $c(\psi) = \tilde{D}$ is the diffusive mobility of the surfactant. Ref. [A9] develops a symmetric mixture model that is valid at all concentrations. It has a mobility matrix that is cubic in the fields as (3) but also symmetric with respect to an exchange of the two components. For films/drops with soluble surfactant we have developed a three-field gradient dynamics model that accounts for solvent evaporation and desorption/adsorption of surfactant at the free surface [A4].

In this project, the developed methodology shall be expanded by incorporating the substrate dynamics using an adapted energy functional that accounts for interaction and adhesion properties

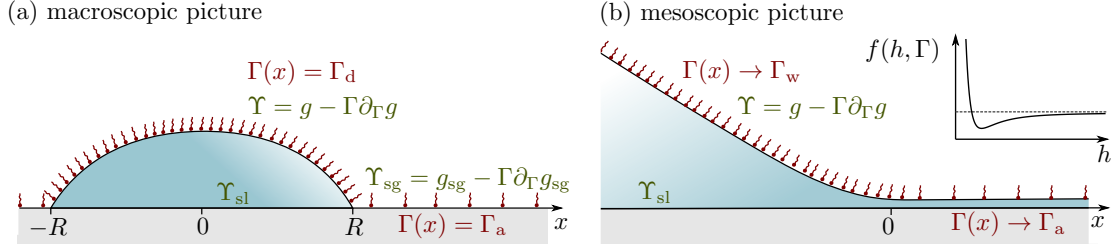


Figure 3: (a) Quantities that determine the macroscopic description for a static surfactant-covered drop are the surfactant-dependent interface tensions γ , γ_{sl} and γ_{sg} depending on surfactant concentrations Γ_a and Γ_d through the interface free energies $g_{sg}(\Gamma)$ and $g(\Gamma)$, respectively. (b) In the mesoscopic description the wetting energy f depends on film height h and surfactant concentration Γ in a way consistent with the macroscopic picture. Incorporated in a gradient dynamics model as Eqs. (3) the dynamics of autophobing due to surfactant adsorption can be determined [A8]. Effectively, this corresponds to an adaptive substrate.

of the substrate, i.e., models like (2) will form a core part of models for (de)wetting on adaptive substrates.

Recently, it turned out that consistency conditions of macroscopic and mesoscopic descriptions of wettability as introduced above for simple liquids had not yet been discussed in the case with surfactants (see Fig. 3). This was accomplished in [A8] for the case of a liquid covered by an insoluble surfactant. At equilibrium, the surfactant is spatially inhomogeneously distributed implying a non-trivial dependence of θ_e on surfactant concentration. We show that macroscopic and mesoscopic descriptions are only consistent for a particular dependence of the wetting energy on the surfactant concentration. This is illustrated by a simple example of dilute surfactants, for which we show excellent agreement between mesoscopic and macroscopic equilibrium theories and time-dependent numerical simulations [A8].

The presented overview of our preliminary work illustrates how the proposed project will be based on significant preliminary work in thin-film modelling of (de)wetting thin films and shallow drops of simple and complex liquids. Our objectives and particular plans are laid out next.

1.1 List of project-related publications

- [A1] U. **Thiele**. Patterned deposition at moving contact line. *Adv. Colloid Interface Sci.*, 206:399–413, 2014.
- [A2] U. **Thiele**. Recent advances in and future challenges for mesoscopic hydrodynamic modelling of complex wetting. *Colloids Surf. A*, 553:487–495, 2018.
- [A3] U. **Thiele**, D. V. Todorova, and H. Lopez. Gradient dynamics description for films of mixtures and suspensions: Dewetting triggered by coupled film height and concentration fluctuations. *Phys. Rev. Lett.*, 111:117801, 2013.
- [A4] U. **Thiele**, A. Archer, and L. Pismen. Gradient dynamics models for liquid films with soluble surfactant. *Phys. Rev. Fluids*, 1:083903, 2016.
- [A5] S. Engelnkemper, M. Wilczek, S. V. Gurevich, and U. **Thiele**. Morphological transitions of sliding drops - dynamics and bifurcations. *Phys. Rev. Fluids*, 1:073901, 2016.
- [A6] M. Wilczek, W. Tewes, S. Engelnkemper, S. V. Gurevich, and U. **Thiele**. Sliding drops - ensemble statistics from single drop bifurcations. *Phys. Rev. Lett.*, 119:204501, 2017.

- [A7] S. Trinschek, K. John, S. Lecuyer, and U. **Thiele**. Continuous vs. arrested spreading of biofilms at solid-gas interfaces - the role of surface forces. *Phys. Rev. Lett.*, 119:078003, 2017.
- [A8] U. **Thiele**, J. Snoeijer, S. Trinschek, and K. John. Equilibrium contact angle and adsorption layer properties with surfactants. *Langmuir*, 35:7210–7221, 2018.
- [A9] X. Xu, U. **Thiele**, and T. Qian. A variational approach to thin film hydrodynamics of binary mixtures. *J. Phys.: Condens. Matter*, 27:085005, 2015.
- [A10] H. Yin, D. Sibley, U. **Thiele**, and A. Archer. Films, layers and droplets: The effect of near-wall fluid structure on spreading dynamics. *Phys. Rev. E*, 95:023104, 2017.

2 Objectives and work programme

2.1 Anticipated total duration of the project

36 Months

2.2 Objectives

In this project we aim at developing and employing a set of generic mesoscopic continuum models for the (de)wetting dynamics of liquids on substrates with adaptive topography and wettability. This shall allow us to gain a deeper understanding of the fundamental physics behind the dynamic (de)wetting of simple (volatile) low-molecular-weight liquids, their mixtures, dilute suspensions or surfactant solutions on substrates with reversible adaptive wettability and topography that show a strong coupling between liquid hydrodynamics and reversible substrate dynamics.

In particular, thin-film gradient dynamics models for simple and complex liquids on inert substrates recently developed by us shall be amended by coupling them to equations describing the dynamics of essential degrees of freedom of the substrate. The resulting models for the coupled liquid and substrate dynamics will describe reversible dynamical processes that can change wettability and topography on timescales comparable to the ones of the liquid and in response to processes in the liquid or gas phase.

In the framework of the developed generic gradient dynamics models, particular energy functionals and sets of mobilities are used allowing us to derive sets of coupled evolution equations for film height, inner degree(s) of freedom of the liquid and inner degree(s) of freedom of the substrate. The framework automatically gives all relevant cross-couplings between the different acting forces and fluxes and, furthermore, can be extended beyond the thin-film limit. The resulting specific models are then studied employing large scale time simulations and path continuation techniques as well as analytical approaches with a focus on the region of the moving three-phase contact line that largely determines the dynamic (de)wetting processes with coupled liquid and substrate dynamics.

After developing and analysing a number of generic models, they are adapted to specific experimental systems in close cooperation between theory and several experimental groups within the SPP. The models are also validated against and related to other modelling approaches pursued within the SPP. Examples of specific substrate degrees of freedom considered in detail can be, e.g., the amount of physisorbed surfactant at a solid substrate, the swelling grade of a polymeric brush crafted to the substrate or the filling ratio of a porous substrate.

2.3 Work programme including proposed research methods

Work Package 1. Simple liquid on adaptive substrate

WP 1.1. Model development - nonvolatile case. A generic long-wave model is developed describing thin films/shallow drops of simple liquid on adaptive substrates. Thereby the substrates are characterised by a single order parameter field $\psi(x, t)$ that is then related to, e.g., the local stretching state of a polymer brush covering the bare substrate (see Fig. 4). In all cases, a generic quantity ‘substrate-absorbed liquid’ that represents the liquid absorbed into the surface layer of the substrate is used as ψ . It can be directly related to the stretching state of a grafted polymer brush or to the filling ratio of a porous layer. This absorption is a proper thermodynamic quantity allowing for a coupled gradient dynamics description of liquid and substrate dynamics that has the form of Eqs. (2). The absorbed liquid may diffuse or flow within the substrate layer.

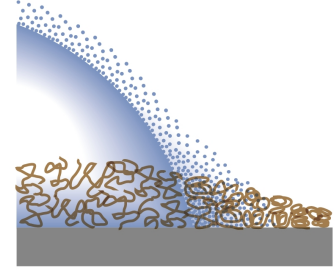


Figure 4: *Polymer brush swollen by contact with liquid drop (WP 1.1) or by diffusing vapour (WP 1.2).*

In the nonvolatile case, the local substrate state ψ can only start to change after the contact line has past the respective position. Then a changing ψ may generically result in adaptation of wettability or topography or both. In the former case, the wetting energy ($f(h)$ in Eq. (1)) also depends on ψ which itself follows, e.g., a Langmuir-like isotherm. Encoding all energetic and entropic influences into a single free energy (similar to [A8]) automatically accounts for all cross couplings.

WP 1.2. Model development - volatile case. Next, a volatile liquid is considered that allows for the transport of vapour through the ambient atmosphere (see Fig. 4). The vapour may then absorb into the adaptive substrate and therefore change it already in front of an advancing contact line. To bring this setting into the reach of thin-film gradient dynamics models a small-gap geometry is introduced that allows for a long-wave description of the dynamics of film, vapour and substrate dynamics. The introduced vapour dynamics is then coupled to the approach to substrate dynamics developed in WP 1.1, now triggered by absorption of the vapour and liquid underneath the drop into the substrate layer. The resulting three-field model is analysed adapting analytical and numerical methods from WP 1.1.

WP 1.2.M Evaporation modi in volatile case (Master project). The novel set-up allows for a description of diffusion-limited and phase transition-limited evaporation and of their crossover. As a side branch of our project, this transition shall be investigated in a Master thesis.

WP 1.3. Application to experiments The generic gradient dynamics models for (de)wetting on adaptive substrates developed in WPs 1.1 and 1.2 are adapted to specific experimental systems, namely, substrates with a porous upper layer where liquid can absorb changing the effective wettability and substrate covered by a polymer brush or a layer of hydrogel that swell when they absorb liquid, thereby changing their effective wettability and topography. Beside the energies and mobilities from WPs 1.1 and from the literature, further specific expressions shall be extracted from experiments and molecular simulations performed within the SPP. In particular, we plan to adapt our models to experiments on wetting and moving drops on substrates with various adaptive polymer brushes, polymer carpets and hydrogels (Berger/Butt, v. Klitzing, Vollmer/Schmid),

and experiments on drop spreading on and imbibition of paper sheets (Biesalski/Meckel) and nanoporous surfaces (Huber). As a limiting case, we plan to consider the switching of wettability by irradiation with light. Here it shall be investigated how the interface dominated (de)wetting dynamics reacts to instantaneous switching and if the optical focusing due to the free surface profile can result in an effectively adaptive substrate (e.g., respective experimental SPP projects by Braunschweig and Haag consider the effects of light-switchable self-assembled arylazopyrazole layers and light-switchable spiropyran-to-merocyanine coatings). Note that this WP will be continuously ongoing till the end of the project.

Work Package 2. Liquid mixture and adaptive substrates.

WP 2.1. Modelling a liquid mixture on inert substrates. A gradient dynamics model for a thin film/shallow drop of a binary mixture of simple liquids is developed. First, we consider an inert substrate and account for consistently concentration-dependent surface and wetting energies, the resulting Marangoni and Korteweg forces, convective and diffusive transport. This amounts to improving the symmetric model of [A9] by employing aspects of [A3] and section IV.B of [A4]) and taking into account findings of [A8]. The resulting model of form (2) is used in WP 2.2 to study substrate-induced decomposition effects amounting to substrate adaptability.

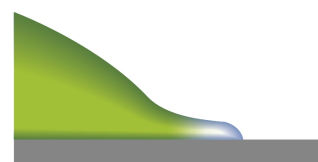


Figure 5: *Local decomposition induced by surface forces (WP 2.2).*

WP 2.2. Substrate-induced decomposed precursor. The model developed in WP 2.1 is employed to study the equilibrium features and dynamics of substrate-induced decomposition that, e.g., may result in the development of a single-component adsorption layer (see sketch in Fig. 5) that may be drawn out of the drop of mixture by convection and/or diffusion. As a result the drop experiences effective substrate properties that differ from the bare substrate, as it adapts to the particular mixture placed on it.

WP 2.3. Adaptive substrate. Next, the model developed in WP 2.1 is combined with the different couplings to an adaptive substrate developed for a simple liquid in WP 1. However, now the substrate reacts differently to the individual components of the mixture, i.e., its dynamics distinctively couples to the inner degrees of freedom of the liquid. Energy functionals that account for the coupling are developed as well as the gradient dynamics form of the evolution equations (three-field model in non-volatile case).

WP 2.4. Application to experimental systems The generic gradient dynamics models developed in WPs 1.1 and 1.3 are applied to specific experimental systems, namely, mixtures on inert and adaptive substrates investigated in the literature and within the SPP. A very interesting application is to model the wetting dynamics induced by the concentration-dependent swelling and collapse of PNIPAA brushes (Fery/Auernhammer) and the concentration-dependent swelling of hydrogels (v. Klitzing) in water/ethanol mixtures. This includes studies of the influence of the partial pressure of the different components in the gas phase where we incorporate the modelling methodology developed in WP 1.2. Experimentally obtained equations of state for the brush and gel layer and dependencies of equilibrium contact angles on their state [11] shall be fed into the generic gradient dynamics. We also expect other SPP experiments involving wetting on brushes to progress towards liquid mixtures.

Work Package 3. Surfactant solutions and adaptive substrates.

WP 3.1. Modelling a surfactant solution on inert substrates. Next, a generic gradient dynamics model for a thin film/shallow drop covered by an (in)soluble surfactant on an inert substrate is considered that consistently accounts for surfactant-dependent surface and wetting energies as well as for the resulting cross-couplings via convective and diffusive transport. That is, our recent general results for coupled surfactant-dependent energies [A8] are incorporated into the generic model of [A4]. The resulting model is used to study the spreading of surfactant-laden drops, in particular, to elucidate the conditions for and dynamics of autophobing. Note, that autophobing, i.e., the receding of a contact line after an initial spreading stage, can be seen as an effect of substrate adaptation. A radially-symmetric (1d) geometry is investigated as well as spreading stability on a 2d substrate. Continuation techniques for steady states are combined with linear stability analyses and time stepping algorithms to identify regions of stable and unstable spreading and autophobing.

WP 3.1.M Transversal spreading front instability (Master project). If transversal instabilities of the spreading fronts are encountered in WP 3.1 or 3.2 (similar to Fig 2 (right)), this effect shall be investigated in an independent Master thesis (months 25-36). This is particularly interesting close to the onset of autophobing as such an instability would strongly differ from the hydrodynamic instabilities of moving ridges discussed in the literature for surfactant-driven spreading on thick liquid films [43].

WP 3.2. Surfactant adsorption as substrate adaptation. In the next step, adsorption of surfactant at the solid-liquid interface, i.e., at the substrate, is incorporated into the model from WP 3.1 in the case of soluble surfactant. We expect that this results in a richer autophobing behaviour than observed in WP 3.1 as then both, the solid-gas and solid-liquid interface, adapt (on different timescales) to the suspension placed on the substrate. Note, that the necessary relation between concentration-dependent interface energies and the concentration-dependent wetting energy has already been sketched in [A8]. This relation will be made specific by first assuming low surfactant concentrations at all interfaces (i.e., purely entropic free energies) and a simple product ansatz for the height- and concentration-dependencies of the wetting energy. These energies are incorporated into a four-field gradient dynamics model for film height, liquid-gas and solid-liquid surfactant concentrations and dissolved surfactant amount that automatically accounts for all adsorption and desorption fluxes based on fluxes proportional to differences of the appropriate chemical potentials. The model is employed in a parameter study of the spreading/autophobing dynamics that will show under which conditions the simple product ansatz breaks down.

WP 3.3. Coupling to intrinsically adaptive substrates. Next, the model developed in WP 3.2 is coupled to a further degree of freedom of the substrate as developed for a simple liquid in WP 1. However, now the substrate may react to the adsorbing surfactant as well as to the solvent. Energy functionals that account for the coupling are developed as well as the gradient dynamics form of the evolution equations. An example is a grafted brush that changes its properties in response to adsorbed surfactant and as well in response of solvent absorbed into the brush.

WP 3.4. Application to experimental systems The generic gradient dynamics models developed in WPs 3.1 to 3.3 are adapted to specific experimental systems, namely, surfactant solutions on

inert and brush-covered substrates investigated in the literature and within the SPP (advanced stage of project by v. Klitzing). Beside the concentration-dependent surface tension of the liquid, adsorption isotherms, remaining interfacial energies and diffusive mobilities are extracted from experiments and microscopic models (collab. Archer, UK). The project by Hardt considers the dynamics of height and concentration profiles for surfactant-laden drops on liquid-infused substrates - this shall be studied with our model in the limiting case of very thick adsorption layers.

Work Package 4. Development of methodology.

WP 4.1. Advancing numerical tools for long-wave modelling within SPP. The development of thin-film (gradient dynamics) models for systems that involve substrate and liquid degrees of freedom in WPs 1 to 3 advances our methodology for systems with a lack of generally accepted macroscopic models. We will advance from two-field models (film height and substrate state) of form (2) that have already been specified for other cases (review in [A2]) to four-field models where this is not the case. Thereby, we will gain a systematic understanding of the structure of energetic cross-couplings and mobility matrices of conserved and non-conserved fluxes.

This is accompanied by progress in model analysis as we expand the analytical and numerical techniques now available for one- and two-field models towards three- and four-field models. This includes linear stability analyses of homogeneous states and advancing or receding fronts, numerical path-continuation of steady states and time-simulation. Here we will develop algorithms within the toolboxes AUTO07P and PDE2PATH and within DUNE for large-scale time simulations. The resulting algorithms shall be shared with other groups within the SPP and beyond (see WP 5).

Our gradient dynamics approach can be applied to many related systems and also allows for the incorporation of certain lateral driving forces [A2]. Therefore, we envision a vivid exchange with other projects that pursue mesoscopic models for coupled substrate and liquid dynamics for related systems. This includes the projects on wetting and imbibition on deformable porous substrates (Gambaryan-Roisman), on wetting on switchable prestructured substrates (Gurevich/Heuer), and effective dynamics for surfactant-laden systems with dissipative substrate-flow interaction (Peschka), and the thin-film limit of phase-field models for dewetting mixtures and surfactant suspensions (Voigt). Note that we can also provide the project of Müller/Tanaka on the wetting behaviour of vesicles on brushes with an effective mesoscopic model by incorporating a bending energy into our formalism.

WP 4.2. Full-curvature models and simulations within SPP. Often, experiments are performed for material combinations that result in contact angles that are not small. In contrast, standard asymptotic thin-film models are only strictly valid at small angles. Nevertheless, often they show quite good agreement with experiments/simulations at moderate angles. Within the gradient dynamics approach, this can sometimes be strongly improved by employing better approximations for the energy functional (e.g., ‘full curvature trick’) while keeping the mobilities of the asymptotic model (see, e.g., [46] and discussion in [A2]).

Here, we plan to extend the models of WPs 1 to 3 using exact interface energies instead of their long-wave approximation. This allows us to better match our models and results with macroscopic approaches pursued within the SPP, e.g., Stokes-based analyses of drops on light-switchable substrates (Stark) and of surfactant-laden drops on finite-support (Peschka), dissipative-particle dynamics models for wetting on brushes with free chains (Vollmer/Schmid), coupled finite-element/lubrication model approach for the wetting of porous structures (Gambaryan-

Roisman), Lattice-Boltzmann simulations of drops on Janus-particle covered liquid substrates (Harting), and the already mentioned phase-field models (Voigt). We also plan to collaborate with microscopic modelling projects within the SPP. In particular, wetting and surface energies shall be extracted from corresponding kinetic Monte-Carlo (Gurevich/Heuer) and Molecular Dynamics (Müller/Tanaka) simulations building on experiences in parameter passing [A2, A10][44, 51]. This will allow us to embed our project into a SPP-wide multiscale framework. For WPs 2 and 3, furthermore, a collaboration with Archer (UK) is planned (see sec. 2.7).

Work Package 5. Creation of hands-on Tutorials. Hands-on tutorials are created that detail how the numerical results are obtained allowing, e.g., bachelor and master students to easily reproduce results and kick-start their thesis projects. The tutorials are shared within the wider community enabling groups working experimentally or with other model/simulation types to nearly instantaneously master the pursued gradient dynamics modelling approach and to implement their own versions of thin-film models for adaptive substrates. For this WP a dedicated Student Research Assistant (wissenschaftliche Hilfskraft) shall be employed (see sec. 4.1).

Time line of the project. Figure 6 represents the tentative time line of the project and the dependencies between the work packages.

2.4 Data handling

The research data gained from the project will be handled according to the guidelines of the University of Münster. All scientific results will be published in international peer-reviewed journals and be presented at international conferences. Following our past best practice, parallel to journal submission all manuscripts will be uploaded to the preprint server *arXiv* guaranteeing full open access to our results. The data behind all publications and theses related to the project will be archived in a structured way. Furthermore, we plan to bring essential parts of the developed numerical algorithms into tutorial form and make them available to the wider international community (see WP 5). Short project descriptions and regularly updated main results will be provided on the websites of the SPP and ITP.

2.5 Other information

Not applicable.

2.6 Explanations on the proposed investigations

No experiments on humans, human materials and animals are planned.

2.7 Information on scientific and financial involvement of international cooperation partners

Close collaboration with Prof. A. Archer (Loughborough University, UK) is planned on aspects of WPs 2 and 3: An important input for our gradient dynamics models are consistently concentration-

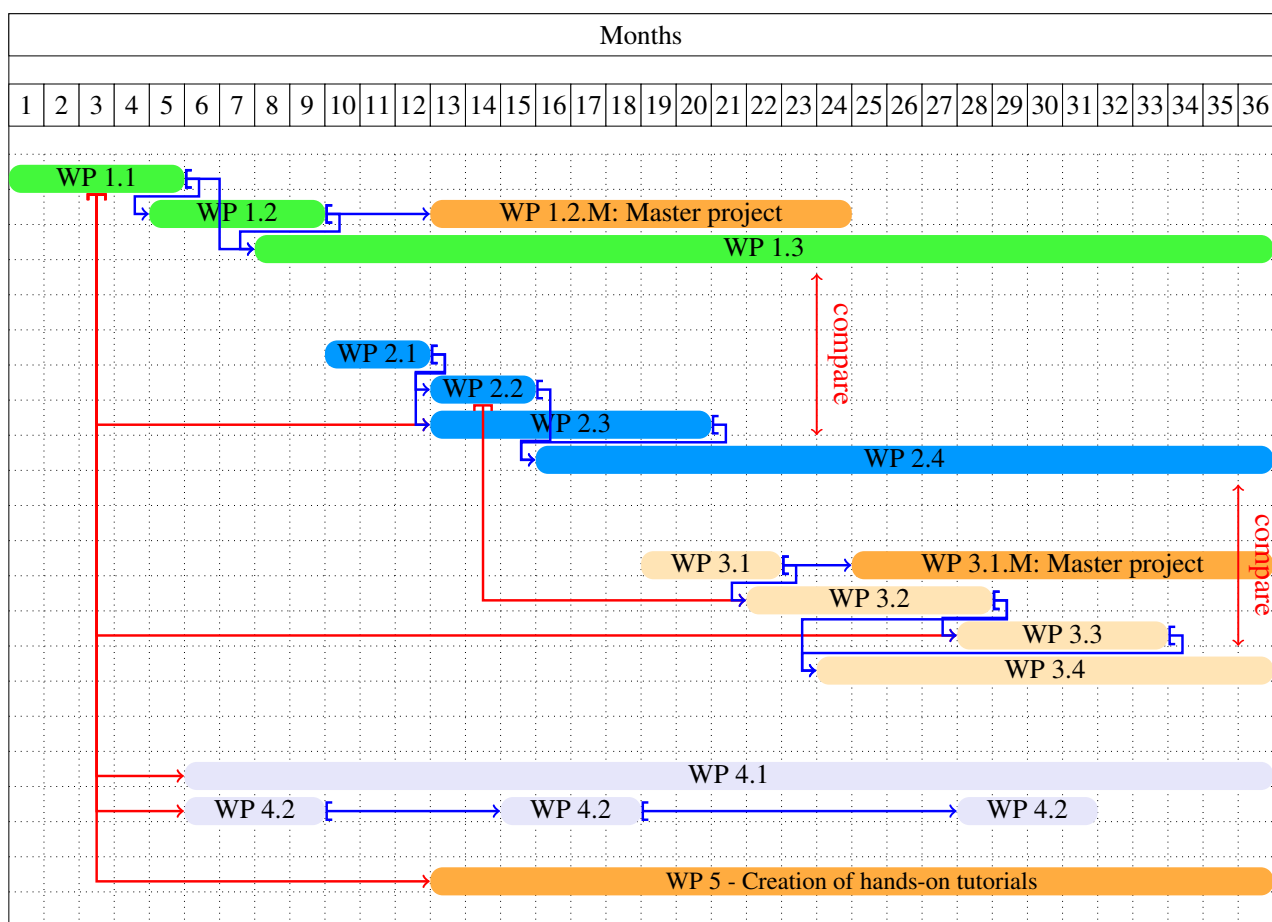


Figure 6: Tentative time line and main data flow in the project. For clarity we do not include all connections into WPs 4 and 5. Exchange with experiments (WPs 1.3, 2.4 and 3.4) is continuously ongoing in the indicated timespan as is the interaction with the other modelling projects (WP 4.1). WP 4.2 is on/off supplementing WP 4.1 at several instances.

dependent interface and wetting energies. In WPs 2.1, 3.1 and 3.2 we first use the simple product ansatz proposed in [A8]. Prof. Archer is developing a DFT model for films of mixtures and surfactant solutions and plans to extract interface and wetting energies thereby extending the together developed methodology [52, 51]. These shall then be used to progress beyond the product ansatz. At Loughborough a PhD candidate will work on the DFT model within the recently established Loughborough mini Centre of Doctoral Training (mini-CDT) ‘Designed Self-assembly of Nanoparticles within Fluids and at Interfaces’ that is coordinated by Prof. Archer.

We expect that the PI and PhD candidate working in Münster and the PhD candidate and Prof. Archer working in Loughborough will have a meeting in year one of the SPP project. Further, we plan for an exchange of the PhD candidates, i.e., they shall spend up 2-4 weeks per year at the partner group. For all these activities each side will fund the local costs and their own travel costs.

2.8 Information on scientific cooperation within SPP 2171

We plan for versatile collaborations with partners within SPP 2171 at all stages of the project (see sec. 2.3 and scheme in Fig. 7). This includes connections to (i) experiments (WPs 1.3, 2.4 and

3.5), (ii) mesoscopic models for related systems (WP 4.1), and (iii) complementary microscopic and macroscopic approaches for similar systems (WP 4.2).

(i) The generic mesoscopic continuum models developed in WPs 1.1-1.2 (simple liquids), 2.1-2.3 (mixtures) and 3.1-3.2 (surfactant suspensions) shall be adapted to experiments pursued within the SPP in WPs 1.3, 2.4 and 3.5, respectively. Main targets are experiments on wetting dynamics of different simple and complex liquids on various types of brushes and porous media (Auernhammer/Fery, Berger/Butt, Biesalski/Meckel, Braunschweig, Haag, Hardt, Huber, v. Klitzing, Vollmer/Schmid) that adapt their wettability and/or topography to the deposited liquid. Beside adaptive substrates this also involves certain switchable substrates as limiting case.

(ii) Our gradient dynamics modelling approach [A2] allows for many extensions and therefore a vivid exchange with other projects that pursue mesoscopic models for coupled substrate and liquid dynamics in related systems (Gurevich/Heuer, Peschka, Thiele/Snoeijer, Voigt). We will give our expanded numerical algorithms into a pool of tools available to all projects and can act as a corresponding training site. See WP 4.1.

(iii) Our mesoscopic models and results shall on the one hand at moderate contact angles be matched with several macroscopic approaches pursued within the SPP for related systems: Navier-Stokes, Lattice-Boltzmann, Stokes, dissipative-particle dynamics, coupled finite-element/lubrication models, phase-field models (Gambaryan-Roisman, Harting, Peschka, Stark, Voigt, Vollmer/Schmid). On the other hand we plan to obtain wetting and interface energies via parameter passing from microscopic models: kinetic Monte-Carlo, Molecular Dynamics, Density Functional Theory (e.g., Gurevich/Heuer, Müller/Tanaka within the SPP and Archer, UK).

Further, to foster the exchange between theoretical groups working with continuum-theoretical approaches within the SPP, we have initiated an informal network, which includes the groups of Brinkmann, Gurevich, Peschka, Snoeijer, Stark, Thiele, Voigt and Wagner and is open to others. There, we will coordinate aspects of the training of the involved young researchers within the SPP, and meet sporadically to discuss details of our approaches and ongoing work.

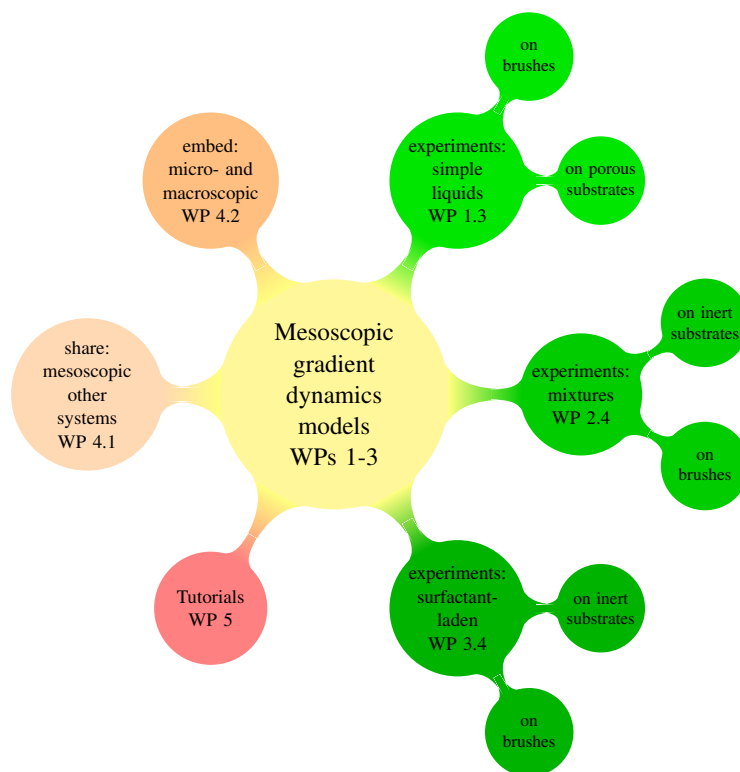


Figure 7: Scheme of WPs that relate to other SPP projects on (i) experiments, (ii) mesoscopic models for related systems, and (iii) micro- and macroscopic approaches to similar systems.

3 Bibliography concerning the state of the art, the research objectives, and the work programme

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4 Requested modules/funds

4.1 Scientific personnel

1. Doctoral Candidate, who will realise the main part of the WPs of the project: 36 Months, 75% TVL (DFG flat rate E 13 level 2 to E 14 level 1)

Justification

Together with the PI, the doctoral candidate will develop the theoretical models in WPs 1.1 to 3.2, analytically analyse the models and implement them into time stepping and path continuation algorithms, validate the numerical method and perform the numerical investigations possibly supported by Master students (WPs 1.2.M and 3.4.M). The junior researcher will organise the exchange with the collaborators in Loughborough, and keep close contact with the collaborating experimental and theoretical groups within the SPP (as part of WPs 1.3, 2.4, 3.4, 4.1 and 4.2). (S)he will organise project collaboration meetings in Münster. The position is needed for the complete duration of the project.

2. Student Research Assistant (Studentische Hilfskraft), who will in month 12-36 create the hands-on tutorials (WP 5). (24 Months, 10hrs/week SHB, monthly 542€, **in total 13.008€**)

Justification

In current publications, results are often presented in a rather compact manner and dissemination of novel techniques etc. to students and young researchers entering into interdisciplinary fields has high thresholds. The planned creation of detailed hands-on tutorials shall lower these threshold

for entry into gradient dynamics modelling - a field where knowledge from several areas must be quickly acquired. The SPP shall provide a platform for the creation and sharing of these tutorials allowing all groups within the SPP and the wider community (including groups working experimentally or with other model/simulation types) to nearly instantaneously master the gradient dynamics modelling approach and to easily implement their own multi-field thin-film models.

4.2 Travel costs¹

SPP Advanced School 2019 (10 person days [pd])	1.200 €
SPP PhD candidate Workshop 2020 (4 pd)	520 €
SPP Workshops 2019 & 2020 (16 pd)	2.080 €
SPP International Conference 2021 (10 pd)	1.200 €
Cooperation stays within SPP and at Loughborough	5.280 €
11th Liquid Matter Conf., Prague 2020 (10 pd)	2.600 €
35th Conf. of European Colloid and Interface Society, Crete 2021 (10 pd)	2.600 €
Overall sum for all three years	15.480 €

Justification

- The junior researcher (JR) has to attend all SPP events, the PI attends all SPP events with the exception of the PhD Workshop, (in total 40 person days a 80€ and 9 times return travel within Germany).
- Visits of JR and PI to collaborating groups (2 visits each year, PI 2 days each, JR 4 days each), in total 36 days and 12 times return travel within Germany or to Loughborough (at 200€).
- The *Liquid Matter Conf.* (tri-annual conference of the Liquid Physics Section of EPS) and *Conf. of European Colloid and Interface Society* (yearly) provide ideal interdisciplinary audiences to present our results to the liquid, soft matter and interface communities. The PI and JR shall both attend (each 5 days a 80€, travel 400€ and conference fees of about 500€).

4.3 Publication costs

750 € per year Σ 2250 €

5 Project requirements

5.1 Employment status information

- Prof. Dr. Uwe Thiele: Full Professor, permanent W3 position.

¹For all travel we estimate accommodation costs as 60€ per night and 20€ daily subsistence. Normally, we assume average travel costs of 200€ within Germany, of 400€ within Europe and of 800€ overseas.

5.2 First-time proposal data

n.a.

5.3 Composition of the project group

1. **Prof. Uwe Thiele**, ITP, is responsible for the overall project and contributes to model development, interaction with collaborators, and interpretation of results (paid by the university).
2. **Tobias Frohoff-Hülsmann**, ITP, PhD candidate, uses 10% of his time to supports the implementation of the numerical path continuation approach and bifurcation analysis (paid by the university).

5.4 Cooperation with other researchers

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

International collaboration with Prof. AJ Archer, Loughborough University (UK) as laid out in sec. 2.7. Collaboration with partners within the SPP as summarised in sec. 2.8 and further detailed for experiments in WPs 1.3, 2.4, 3.4 and for alternative modelling approaches in WPs 4.1 and 4.2 (sec. 2.3).

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

Prof. AJ Archer, Loughborough University (UK); Prof. T Betz, Univ. Münster; Dr. A Chervanyov, Univ. Münster; Prof. L Chi, Shuzhou Univ. (China); Prof. H Gomez, Univ. A Coruna (Spain); Dr. SV Gurevich, Univ. Münster; Prof. A Hazel, Univ. Manchester; Prof. A Heuer, Univ. Münster; Dr. K John, Univ. Grenoble; Prof. E Knobloch, Univ. California, Berkeley (USA); Prof. T-S Lin, National Chiao Tung Univ. Hsinchu (Taiwan); Profs. O Manor & L Pismen, Technion Haifa (Israel); Dr. DN Sibley, Loughborough University (UK); Prof. J Snoeijer, Twente Univ. (Netherlands); Prof. H Stark, TU Berlin; Dr. D Tseluiko, Loughborough University (UK); Prof. H Uecker Univ. Oldenburg;

5.5 Scientific equipment available for the project

- Local Computing Cluster at ITP, WWU
- High Performance Computing (Palma 2 at WWU)
- All necessary licences for the needed software

5.6 Project-relevant interests in commercial enterprises

There are no connections between the project and an enterprise.

6 Additional information

This proposal has not been submitted to a third party.