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Dynamic wetting phenomena in lattice models for nematic fluids/liquid crystals near switchable substrate potentials

(Name deutsch)

Dynamische Benetzungsphänomene in Gittermodellen für Flüssigkristalle in der Nähe von schaltbaren Oberflächen

Acronyme / Kennwort: **NematoWett**

Proposal Data and Obligations

1 Type of proposal

Programme

Priority Programme SPP 2171

Individual proposal

☒

Coordination proposal

☐

Proposal category

New proposal

☒

Renewal proposal

☐

2 Proposal information

2.1 Title/duration

Title: Dynamic wetting phenomena in lattice models for nematic fluids/liquid crystals near switchable substrate potentials

Duration: 36 months

2.2 Subject classification

2.3 Keywords

2.4 Summary

Using theoretical methods and accompanying simulations, we will investigate liquid crystals near switchable substrates. Of particular interest is the approach to wetting transitions and switches between different wetting states.

As a model system, we consider lattice rods with short-range attractions. We have developed and will further improve classical density functionals for these models as well as formulate a suitable dynamic density functional theory.

Wetting phase diagrams will be computed for nematically ordered (upright or lying-down) and smectic (with possible layering transitions) films. Of particular interest will be the dynamics of smectic layer formation and the switching dynamics between nematic wetting states of different orientation. In these processes, there is little mass transport involved and thus we expect that a lattice dynamics akin to Brownian dynamics can describe these well.

Complementary simulations of grand canonical and kinetic Monte Carlo type will be performed to gauge and validate the theoretical results. Through collaborations with experimental groups the results on time-dependence of smectic layering and of the switching between nematic wetting states shall be tested.

2.5 Zusammenfassung

In diesem Projekt sollen Flüssigkristalle in der Nähe von schaltbaren Substraten mittels theoretischer Methoden und begleitender Simulationen untersucht werden. Von besonderem Interesse sind dabei das Verhalten bei Annäherung an einen Benetzungsübergang und bei Wechsel zwischen verschiedenen Benetzungszuständen.

Als Modellsystem betrachten wir Stäbchen auf einem Gitter mit kurzreichweitigen Attraktionen. Wir haben klassische Dichtefunktionale für diese Modelle formuliert und werden diese verbessern

sowie eine geeignete dynamische Dichtefunktionaltheorie ableiten.

Benetzungsphasendiagramme für nematisch geordnete Filme (senkrecht oder parallel) und smektische Filme (mit möglichen Schichtungsübergängen) sollen berechnet werden. Von besonderem Interesse ist dann die Dynamik einer smektischen Schichtbildung und die Schaltdynamik zwischen nematischen Benetzungszuständen verschiedener Orientierung. Bei diesen Prozessen ist nur ein geringer Massentransport involviert und deswegen erwarten wir, dass eine mit der Brownschen Dynamik verwandten Gitterdynamik die Prozesse gut beschreibt.

Komplementäre Simulationen (großkanonische und kinetisches Monte Carlo) sollen durchgeführt werden, um die theoretischen Resultate zu validieren. In Kollaborationen mit experimentellen Gruppen sollen die Resultate zur Zeitabhängigkeit von smektischer Schichtbildung und bei Schaltprozessen zwischen verschiedenen nematischen Benetzungszuständen getestet werden.

3 Participating individuals

3.1 Applicants

Principal investigator 1

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Project Description

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Applicants:

Prof. Dr. Martin Oettel, Eberhard Karls Universität Tübingen

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1 State of the Art and Preliminary Work

1.1 State of the Art

Wetting transitions are genuine phase transitions in liquids near substrates/walls, accompanied by a sudden change of a thermodynamic potential or one of its derivatives. Undoubtedly, wetting transitions in simple liquids are the ones which have been explored most substantially, for a recent review see [1]. Here, the sudden change takes place in the excess adsorption which itself is a derivative of the excess grand potential (surface free energy) with respect to chemical potential.

Wetting phenomena are not restricted to simple liquids [2]. Their phenomenology is greatly enhanced in systems with richer phase diagrams. In this respect, liquid crystals are the prime example of a still fairly simple fluid (rods instead of spheres from a theorist's perspective) which show a rich subdivision of the region between a fluid and a solid phase into partially ordered phases, such as nematic, biaxial, smectic, cholesteric, blue, ...phases. In principle, wetting transitions near any transition line between two phases can be investigated. Consider the case of a second-order transition between an ordered and a disordered phase. When such a transition is approached from the disordered phase in which the order parameter of the transition is zero, fluctuations of this order parameter appear in the bulk with a correlation length ξ which diverges at the transition. If the system is in contact with an interface favouring the ordered phase, the correlation length at the surface will become infinite in a direction parallel to the surface plane. This creates an ordered layer at the surface in which the order parameter decreases exponentially from a non-zero value at the surface to zero in the bulk over a penetration length ξ_s ; ξ_s is equal to the correlation length ξ and thus diverges at the transition. This phenomenon is called critical adsorption. When the transition is first order, the situation is more complex. Briefly, when the transition between two

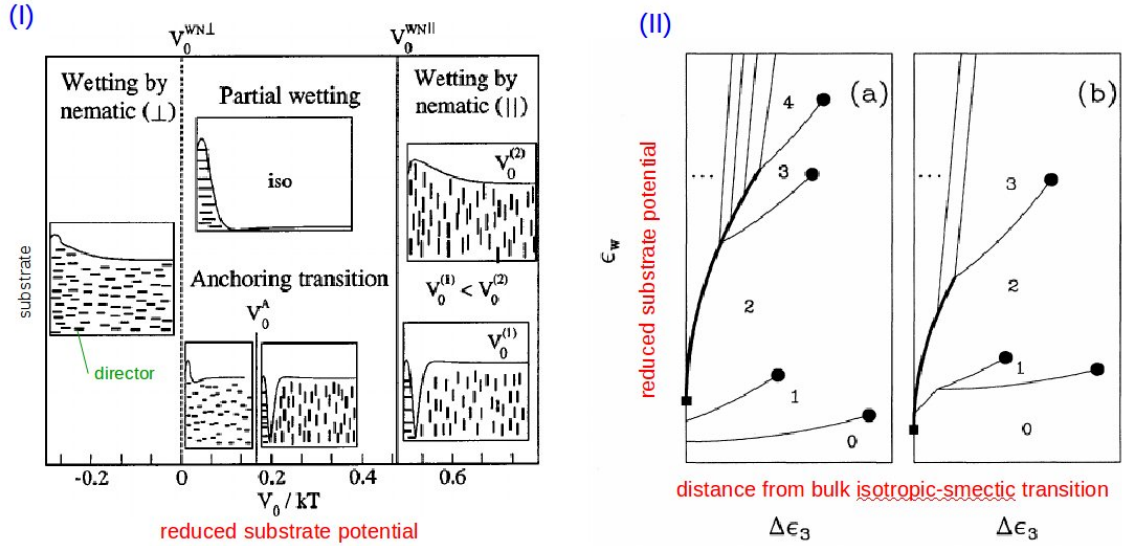


Figure 1: (I) Possible wetting types for a nematic model system of hard spherocylinders on the nematic–isotropic coexistence line. Depending on the anchoring strength of a substrate potential, the system shows wetting of the isotropic–wall interface by a perpendicular nematic phase (left) or a parallel nematic phase (right). Partial wetting and the appearance of a thin perpendicular (anchoring) layer are also possible. Figure adapted from Ref. [9]. (II) Layering and prewetting transitions for a smectic model system near isotropic–smectic coexistence. Layering transitions (thin lines) may or may not originate from a prewetting line (which signifies coexistence of a few smectic layers with a thick smectic layer). (a) and (b) differ by the location in the overall phase diagram (density, temperature). Figure adapted from Ref. [10].

phases I and II is approached, say from phase I, a layer of phase II can form at the surface: phase II is said to wet the surface. If the thickness of the phase II layer becomes infinite at coexistence, wetting is complete; if the thickness remains finite at coexistence wetting is partial. When one explores the coexistence curve between phases I and II, one can go from a partial wetting regime to a complete wetting regime via a wetting transition. This wetting transition can be first- or second-order. If it is first order, there is a line of first-order surface transition extending off coexistence, where the wetting film exhibits a jump in thickness (thin-thick film transition); this line is called the prewetting line and ends at a prewetting critical point. A variant of the prewetting transition is the layering transition which can be present also in simple liquids [3] but is present more prominently in smectic systems [4].

Classical density functional theory (DFT) has proved to be a versatile tool to study wetting phase diagrams both of simple liquids and liquid crystals [5]. DFT uses the fact that there exists a unique functional for the grand potential $\Omega[\rho]$ in terms of the inhomogeneous density ρ and that the equilibrium density profile minimizes Ω . Thus in DFT any excess adsorption (needed for assessing the wetting phase diagram) is directly computed. The grand potential functional is further split according to $\Omega[\rho] = \mathcal{F}^{\text{id}}[\rho] + \mathcal{F}^{\text{ex}}[\rho] + \int d\mathbf{r}(V^{\text{ext}}(\mathbf{r}) - \mu)\rho(\mathbf{r})$ where μ is the chemical potential, $V^{\text{ext}}(\mathbf{r})$ an arbitrary external potential (e.g. exerted by a substrate) and $\mathcal{F}^{\text{id}}[\rho]$ is the free energy functional of the ideal gas. The core ingredient of DFT is the excess free energy functional $\mathcal{F}^{\text{ex}}[\rho]$. In general, excess functionals for hard-body interactions have a high degree of accuracy, especially those derived from Fundamental Measure Theory (FMT) [6]. For anisotropic particles in the continuum, these are rather recent achievements [7, 8]. On the other hand, attractive interactions are mostly treated in mean-field approximation. However, experience has shown that the computation of sensible wetting phase diagrams does not require the most sophisticated functionals - what is required are the correct insights for $\mathcal{F}^{\text{ex}}[\rho]$ to give a qualitatively correct phase diagram. Therefore, earlier (pre-FMT) work has already demonstrated the rich phenomenology of wetting transitions in liquid crystals, for which we show examples in Fig. 1.

The dynamics of the approach to a wetting transition has been investigated far less frequently. In fact, the term “wetting dynamics” is often associated with the dynamics of droplets on surfaces

only (i.e. of a liquid in a partially wetted state but away from a transition) [1]. Overall, the time-dependence of a system near a wetting transition should have the character of phase transition dynamics but for an inhomogeneous system. Especially in the case of prewetting/layering, the dynamics involves the formation of a two-dimensional phase at the boundary of a three-dimensional system which should be distinctly different from bulk phase separation dynamics. Since the wetting state and the location of the wetting transitions are determined by the properties of the substrate, switchable substrates offer the possibility to approach wetting transitions and to switch between different wetting states. The investigation of the time-dependence of such processes for a lattice model for liquid crystals is the topic of this proposal.

Switchable substrates for changing the anchoring strength offer interesting applications in liquid crystal technology. From a theorist's perspective, the easiest switch is temperature (see Fig. 1(I)) for the effect on wetting transitions. Experimentally much more interesting are contactless methods like photoswitching. Here, surfaces are decorated with photosensitive molecules (azo—dendrimers) which upon illumination change conformation from *trans* (favoring orthogonal anchoring) to *cis* (favoring parallel anchoring). See Refs. [11, 12] from the Magdeburg group of Eremin and Stannarius (participating with a SPP proposal) for more details.

1.2 Preliminary Work

Our group has substantial experience in constructing and applying density functional theory to inhomogeneous soft condensed matter, in particular phase transitions and interfacial properties. We have worked extensively on the description of colloidal crystals, see e.g. Refs. [A1, A2] for benchmark results on hard sphere crystals and the crystal–fluid interface.

Investigating the statics and dynamics for phase transitions in lattice models has often helped in formulating general concepts in phase transition theory, if not initiating them. Additionally, lattice models often take up the role of a simplified version of a continuum model of interest, in the hope they retain the basic physics, e.g. the type of phase transition. One of the most popular examples is using the lattice gas model to explore the liquid–vapor and wetting transitions.

The straightforward extension of the lattice gas (particles occupying one lattice site with nearest-neighbor attractions) to a model for liquid crystal appears to be hard rods of variable length L with possible nearest-neighbor attractions which in principle allows to study the effects of both density and of temperature variation on the phase diagram and which could be this called the “Ising model for a liquid crystal”. Schematically, the model is depicted in Fig. 2. Surprisingly, such a type of model has been studied far less intensive than the lattice gas, presumably owing to the difficulties associated with the hard body constraint which precludes the use of several analytic techniques developed for lattice models. For 2D hard rods, the existence of nematic-like transition for $L \geq 6$ has been established only in 2007 [13], effects of temperature for attracting rods have been studied in Ref. [14]. Phase diagrams in 3D and on surfaces were analyzed in our group during the past years (see below).

We have started to work on equilibrium and dynamics in these models in the context of studying film growth with anisotropic particles (such as relevant for the fabrication of organic solar cells). Such experiments have a possible connection to the topic of wetting transitions in liquid crystals since the appearance of thin film phases is well documented in these systems (resembling layering transitions).

Equilibrium properties:

- **Density functionals:** Building on the general FMT framework of constructing lattice functionals by Lafuente and Cuesta [15, 16], we have derived hard rod functionals \mathcal{F}_{FMT} for 2D and 3D [A3]. The FMT functionals give nematic transitions in 2D (second order) and 3D (first order) but the tendency to the formation of nematic order is overestimated in comparison to simulations. For attracting rods, we used the idea of representing the attractive interactions via depletion interactions and derived an FMT-like functional \mathcal{F}_{AO} [A4] as was done for the Asakura–Oosawa (AO) model of colloid–polymer mixtures [17]. For attracting rods,

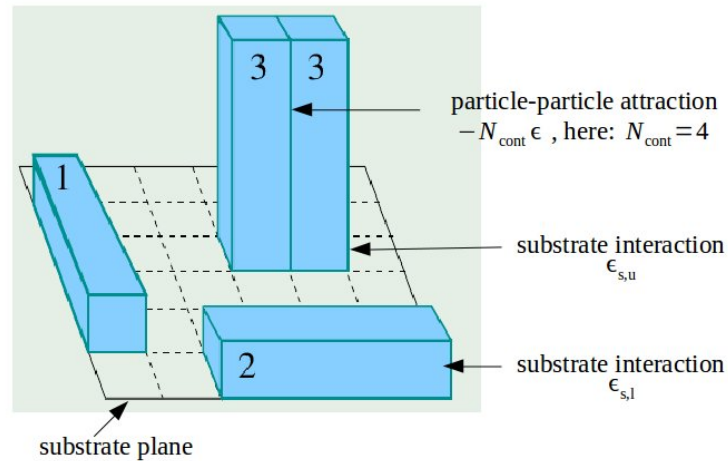


Figure 2: Simple lattice model for a liquid crystal. Particles are hard rods of length L defined on a cubic lattice. Rods attract each other proportionally to the number N_{cont} of touching sites. Additionally, there is a contact interaction with a substrate which might be different for lying and standing rods.

liquid–vapor separation competes with nematic ordering and FMT predicts the formation of a tricritical point (2D) and widening of the isotropic–nematic coexistence region (3D) upon lowering the temperature, see Fig. 3.

- **Grand-canonical simulations:** Lattice hard rods show a very weak first order transition between isotropic and nematic states [A5]. This is different from longer continuum rods where the transition is first order with a noticeable density jump between the isotropic and nematic state. Results from a bachelor thesis [18] and ongoing master thesis work suggest that the weak first order character persists for attracting rods (this behavior is not captured well by FMT yet). In 2D, a tricritical point is found as in FMT.
- **Application: Monolayers of rods** Hard rods show a rather abrupt “standing-up” transition (from initially lying molecules) when the coverage is increased. This phenomenon is known from experiments in self-assembled monolayers [19] and with rod-like π -conjugated molecules like pentacene (PEN) or diindenoperylene (DIP) [20, 21] and is also seen in an all-atom simulation for monolayer growth of PEN on C60 [22]. We could establish that this transition is continuous and stays so for arbitrarily attractive substrates (although for strongly attractive substrates it may look like a true discontinuous phase transition). Furthermore we proved that these findings also hold for hard rods (spherocylinders) in the continuum [A3]. For rods with mutual attractions the FMT density functional predicts that in general there is a first-order transition between a dilute, possibly lying-down phase and a dense, upright-oriented phase below a critical temperature. For an aspect ratio of 2, however, the monolayer exhibits two critical points, one associated with a gas–liquid transition between states of unoriented rods and one associated with a transition between a weakly and strongly upright-oriented phase.

Dynamic properties: In the context of our film growth studies, we performed an extensive study of hard rod monolayer growth dynamics in the lattice and the continuum picture [A6]. It turns out that the dynamics of the standing-up process is mainly governed by the equilibrium equation of state. For further quantification we have developed a novel variant of dynamic density functional theory for lattice models (see below). We could identify a genuine out-of-equilibrium effect occurring for attractive substrates: here, the initial propensity for the rods to lie down leads to jammed, fully packed states which are then slowly transformed to a fully upright monolayer.

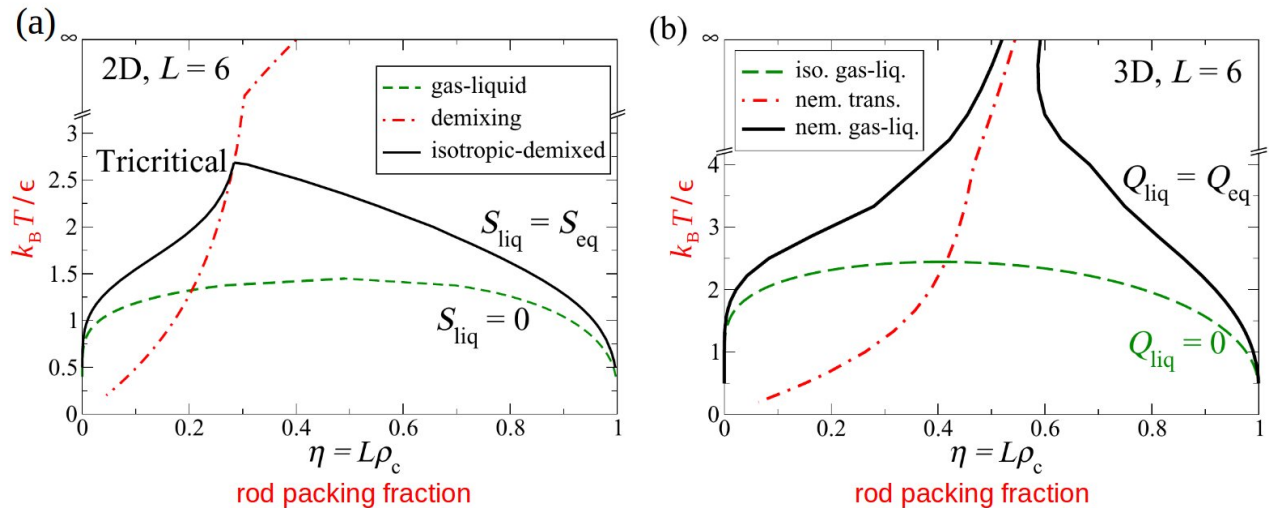


Figure 3: FMT phase diagrams for attracting rods ($L = 6$) in the packing fraction–reduced temperature plane. (a) Two dimensions. The red dot–dashed line shows the second order nematic transition (demixing between horizontal and vertical rods) which meets the vapor–liquid binodal at a tricritical point. (b) Three dimensions. The isotropic–nematic binodal (black line) widens upon lowering the temperature. The red dot–dashed line shows the onset of nematic metastability.

1.3 Project-related peer-reviewed publications (limited to 10)

- [A1] M Oettel, S Görig, A Härtel, H Löwen, Marc Radu, and Tanja Schilling. Free energies, vacancy concentrations, and density distribution anisotropies in hard-sphere crystals: A combined density functional and simulation study. *Physical Review E*, 82(5):051404, 2010.
- [A2] A. Härtel, M. Oettel, R. E. Rozas, S. U. Egelhaaf, J. Horbach, and H. Löwen. Tension and stiffness of the hard sphere crystal–fluid interface. *Phys. Rev. Lett.*, 108:226101, 2012.
- [A3] M. Oettel, M. Klopotek, M. Dixit, E. Empting, T. Schilling, and H. Hansen-Goos. Monolayers of hard rods on planar substrates: I. Equilibrium. *J. Chem. Phys.*, 145:074902, 2016.
- [A4] M. Mortazavifar and M. Oettel. Phase diagrams for sticky rods in bulk and in a monolayer from a lattice free-energy functional for anisotropic particles with depletion attractions. *Phys. Rev. E*, 96:032608, 2017.
- [A5] A. Gschwind, M. Klopotek, Y. Ai, and M. Oettel. Isotropic-nematic transition for hard rods on a three-dimensional cubic lattice. *Phys. Rev. E*, 96:012104, 2017.
- [A6] M. Klopotek, H. Hansen-Goos, M. Dixit, T. Schilling, F. Schreiber, and M. Oettel. Monolayers of hard rods on planar substrates: II. Growth. *J. Chem. Phys.*, 146:084903, 2017.
- [A7] M. Oettel. Integral equations for simple fluids in a general reference functional approach. *J. Phys.: Condens. Matter*, 17:429, 2005.
- [A8] J. Bleibel, A. Dominguez, and M Oettel. A dynamic dft approach to generalized diffusion equations in a system with long-ranged and hydrodynamic interactions. *J. Phys.: Condens. Matter*, 28:244021, 2016.

2 Objectives and Work Programme

2.1 Anticipated duration of the project

36 months

2.2 Objectives

The aim of the project is to use the conceptually very simple lattice model for liquid crystals depicted in Fig. 2 and to study thoroughly time-dependent wetting phenomena near switchable substrates, i.e. substrates whose anchoring strength can be modulated. In contrast to simple liquids where a wetting transition is commonly only associated with the formation of a film of denser material, liquid crystals can wet substrates with films in different phase state: nematically ordered (upright or lying-down), smectic (with possible layering transitions) or cholesteric (not investigated here). The anchoring strength at the substrate essentially governs the type of wetting. Switching the anchoring strength allows for a transition between different wetting states.

The simplicity of the lattice model will allow for a microscopic, theoretical treatment using time-dependent density functional theory (DFT). Additionally, simulations will be performed using a type of lattice Brownian Dynamics. Central aims of the project are:

1. Full derivation and testing of an explicit time-dependent DFT for hard rods with short-ranged attractions
2. Establishing the phase diagram for all wetting transitions in the model
3. Investigating the dynamics of the formation of a wetting film of a specific kind (nematic, smectic)
4. Investigating the switching dynamics between different wetting states

The equilibrium transitions occurring in liquid crystals maybe of first-order, weakly first-order or second-order type. Therefore we expect also the corresponding dynamics to show crossovers between nucleation dynamics, spinodal behavior and critical dynamics. Lattice models exhibit these different types of equilibrium transitions, so we also expect that they are useful in bringing out also the different dynamic features.

We consider the proposed investigations as a fundamental contribution to the statics and dynamics in a basic lattice model for liquid crystals. At the same time, through studying the dynamics of transitions to and between wetting states, we hope to contribute to the rich field of surface transition dynamics.

2.3 Work programme incl. proposed research methods

The lattice model used is schematically depicted in Fig. 2 and has already been introduced in Sec. 1.2. As described, for hard rods we have derived a free energy functional \mathcal{F}_{FMT} from FMT and for attractive rods a corresponding free energy functional \mathcal{F}_{AO} using techniques for treating effective attractions as in AO models.

The central aims of Sec. 2.2 define associated work packages:

1. **WP 1: Full derivation and testing of an explicit time-dependent DFT for hard rods with short-ranged attractions**

Time-dependent DFT (dynamic DFT, DDFT) in continuum models has been derived through various routes (see e.g.) and its density evolution equation is given by

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -D \nabla \cdot \mathbf{j} \quad (1)$$

$$\mathbf{j}(\mathbf{r}, t) = -\rho(\mathbf{r}, t) \nabla \frac{\delta \mathcal{F}[\rho(\mathbf{r}, t)]}{\delta \rho(\mathbf{r}, t)} . \quad (2)$$

Here, \mathbf{j} is the particle current which is obtained as the gradient of a nonlocal chemical potential $\mu = \frac{\delta \mathcal{F}}{\delta \rho}$ where the free energy contains also the contribution of (time-dependent) external

potentials. The identification of \mathcal{F} with the equilibrium free energy functional is equivalent to an adiabatic approximation.

On a lattice, continuous variables become discrete lattice vectors, $\mathbf{r} \rightarrow \mathbf{s}$. The three discrete orientations of rods are equivalent to the introduction of three rod species, thus $\rho(\mathbf{r}, t) \rightarrow \rho_i(\mathbf{s}, t)$ ($i = 1..3$). The rate of change $\frac{\partial \rho_i(\mathbf{s})}{\partial t}$ fulfills a Master equation

$$\frac{\partial \rho_i(\mathbf{s})}{\partial t} = \underbrace{\sum_{\mathbf{s}'} (\rho_i(\mathbf{s}') P_{\mathbf{s}', \mathbf{s}}^i - \rho_i(\mathbf{s}) P_{\mathbf{s}, \mathbf{s}'}^i)}_{\text{hopping events to neighboring lattice sites } \mathbf{s}'} + \underbrace{\sum_j (\rho_j(\mathbf{s}) P_{ji}(\mathbf{s}) - \rho_i(\mathbf{s}) P_{ij}(\mathbf{s}))}_{\text{local rod reorientation events}} \quad (3)$$

is now determined by averaged hopping rates $P_{\mathbf{s}, \mathbf{s}'}^i$ of rods at \mathbf{s} to neighboring lattice sites \mathbf{s}' as well as averaged local reorientation rates $P_{ij}(\mathbf{s})$ (effectively, rods changing their species). Our studies of the orientation dynamics in rod monolayers [A6] lead us to propose as a generic expression for such averaged rates

$$P_{\alpha\beta} \propto \exp(\min(0, \beta\mu_{\alpha}^{\text{ex}} - \beta\mu_{\beta}^{\text{ex}})) , \quad (4)$$

where α stands for a certain rod species i located at point \mathbf{s} . Here, $\mu_{\alpha}^{\text{ex}} = \frac{\delta \mathcal{F}^{\text{ex}}}{\delta \rho_i(\mathbf{s})}$ is the excess chemical potential for species i at point \mathbf{s} and β is the inverse temperature. In the continuum limit, standard DDFT is recovered. Our proposal appears to be a generalization of previously proposed mean-field dynamics in lattice models for point particles [23].

We will use this idea as the starting *ansatz* for our lattice DDFT and explore in more detail the consequences of the underlying adiabatic assumption. This adiabatic assumption is encoded in Eq. (4) which looks like an ensemble-averaged rate of a combined removal/insertion move in grand canonical simulations.

2. WP 2: Establishing the phase diagram for all wetting transitions in the model

Bulk phase diagrams of the model have been computed in Refs. [A3, A4] (DFT) and in Refs. [A5] (simulations). DFT phase diagrams in general predict nematic transitions at too low densities and too short rod lengths. To eliminate this, we will improve the functional on the level of the direct correlation function. More precisely, for the case of sticky rods we will improve the AO functional \mathcal{F}_{AO} in the form

$$\mathcal{F}_{\text{sticky}} = F(\rho_{0,i}) + \sum_{i, \mathbf{s}} (\mu_i - \mu_{i, \text{AO}}) \rho_i(\mathbf{s}) - \frac{1}{2\beta} \sum_{ij, \mathbf{s}\mathbf{s}'} (c_{ij}^{(2)} - c_{ij, \text{AO}}^{(2)}) \rho_i(\mathbf{s}) \rho_j(\mathbf{s}') + \mathcal{F}_{\text{B, AO}} . \quad (5)$$

Here, $\mu_{i, \text{AO}}$ and $c_{ij, \text{AO}}^{(2)}$ are the chemical potential and the direct correlation function as contained in \mathcal{F}_{AO} . The new improved μ_i and $c_{ij}^{(2)}$ at the reference density $\rho_{0,i}$ are obtained via self-consistent integral equations with the closure derived from Eq. (5). The so-called bridge function, the central element of the closure, is generated by the bridge functional $\mathcal{F}_{\text{B, AO}}$ (which is the AO functional Taylor expanded around the reference state $\rho_{0,i}$ with all terms up to second order subtracted). This is known as the test-particle consistent functional, we have shown that for simple liquids it gives an excellent description of the equation of state and of wetting [A7]. Therefore we expect also a very good performance for the rod model.

The improved functional will be used to establish the wetting phase diagram as a function of the substrate interaction strengths $\epsilon_{\text{s}, \text{l}}$ (for lying rods) and $\epsilon_{\text{s}, \text{u}}$ (for standing, upright rods). We expect [24, 10, 9]

- layering transitions with layers of upright rods when $\epsilon_{\text{s}, \text{l}}$ is sufficiently weak (formation of smectic membranes)

- wetting with a nematic phase with ordering parallel to the substrate plane when $\epsilon_{s,l}$ is sufficiently strong which also might appear as
- possible anchoring transitions of a biaxial phase

3. WP 3: Investigating the dynamics of the formation of a wetting film of a specific kind (nematic, smectic)

Clearly, the onset of wetting is determined by the substrate strengths $\epsilon_{s,u/l}$ or, indirectly, by temperature. We assume now that the substrate strengths are externally controllable by “smart surfaces”, thus they can be functions of time. As briefly discussed before, it has been shown that covering surfaces with light-responsive molecules one can indeed switch between parallel and homeotropic anchoring.

A basic scenario is now quenching the system to a point where a wetting transition occurs. For a specific wetting state, the first smectic layering transition, say, this can be achieved by a “smart switching” as described above or by a temperature quench. Although it is presumably difficult to experimentally control the exact location of the wetting transition and thus the final point of the quench, it is feasible to perform a quench which crosses a wetting transition.

Depending on the type of wetting transition described above, we expect different scenarios for such a quench.

- layering transitions (formation of smectic membranes). Presumably these are first-order transitions. For the first layer, this might be viewed as an effective phase separation in 2D, associated with nucleation of islands of standing particles and subsequent growth. However, if a quench crosses too fast over several layering transitions, the evolution might proceed via the formation of 3D droplets of standing particles.
- wetting with a nematic phase with ordering parallel to the substrate plane.
- possible layering transitions of a biaxial phase. If these occur, we expect them to be of second order, since they correspond to a demixing of rods in the substrate plane which is a second order transition. Here, a quench to the wetting transition has the character of a critical quench with associated slow, critical dynamics. Our proposed DDFT captures the mean-field dynamics of such a process and certainly misses out fluctuations. Here, comparison to simulations shall clarify the extent of the missing contributions.

The formation of smectic membranes will be investigated experimentally in the project by Stannarius/Eremin in Magdeburg. There, droplets will be brought onto a smectic membrane and their coverage with smectic layers will be monitored. This is akin of smectic layering on a liquid–vapor interface. Such a process could be studied also in our lattice model in a mixture of rods and a standard lattice gas where the liquid–vapor interface is formed by the lattice gas.

The idea of considering rod/lattice gas mixtures would also enable us to study the time-dependence of the liquid–vapor surface tension upon adsorption of a smectic layer. A similar problem is also studied in the project by Stannarius/Eremin. There, fresh smectic films are created in a solution with surfactant. The surfactant will partially adsorb at the smectic layer and change its surface tension.

Since our simulations have shown that already the bulk ordering transitions are only weakly first order, it might well be that also some first-order wetting transitions as predicted by DFT become weak, or are even “washed out” by fluctuations. Therefore we will perform complementary kinetic Monte Carlo (KMC) simulations of quenches. KMC simulations speed up dynamic simulations since they keep track of the allowed hopping and reorientation moves in the system. Over the past few years, we have developed efficient codes for these simulations (as described in [A6]). We will offer suitable Master thesis projects on KMC simulations of quenches.

4. WP 4: Investigating the switching dynamics between different wetting states

Consider the wetting diagram of Fig. 1(I). At isotropic–nematic coexistence (or very close to it), the substrate may be switched from perpendicular anchoring (left side of Fig. 1(I)) to parallel anchoring (right side of Fig. 1(I)). Since this process involves mainly the change of order and only to a minor extent material transport it will be governed by orientational dynamics. If an intermediate state is a partially wetted state, the process is akin to “dewetting” of a film (without material transport) which will be followed by complete wetting. Here it is interesting to compare the laterally averaged dynamics of order and density with explicit 3D solutions which include the formation of (order parameter) “holes” for dewetting and “droplets” for subsequent wetting. The explicit 3D solutions can then be laterally averaged over different realizations or runs. It is indeed not clear that “pre–averaged” and “post–averaged” dynamics as obtained from a dynamic DFT should give the same result. This has been noted first in a 2D study for a colloidal fluid phase separating near a wall [25]. A similar problem has been noted by us in the study of the capillary collapse of a colloidal monolayer [A8] and we are currently working on a theoretical solution of this problem considering the correct implementation of noise and ensemble average in dynamic DFT.

The group of Santer (Potsdam) can realize topographical changes in surfaces containing azobenzene by appropriate light stimulus. This can be used to manipulate the anchoring conditions for a colloidal rod fluid and switch between the two different parallel orientations or between parallel and perpendicular anchoring. The orientational dynamics of the rods can be observed by optical methods and offers the possibility to compare with our results.

The main working steps are again summarized in the following table which details also the anticipated time to solve the respective tasks.

	DFT (M. Oettel + PhD)	Simulation (M. Oettel + MSc students)
6 months	Getting started with lattice DFT WP 1: Dynamic DFT, tests on monolayers WP 2: Wetting diagram FMT	Thesis 1: Cursory GCMC test of layering transitions (no full wetting diagram)
6 months	WP 2: tp improved FMT, new wetting diagram	Adapting existing KMC code for 3D simulations
	SPP workshop Advanced school	
6 months	WP 3: dynamics of wetting transition, dynamic smectic layering	Thesis 2: Quenches to smectic layering transition
	Cross-check with simulations	
	Cross-check with Stannarius/Eremin (Magdeburg) Visit to Magdeburg	
6 months	WP 3: other transitions	
	SPP workshop PhD workshop	
6 months	WP 4: dynamic switching between wetting states	
	Cross-check with Santer (Potsdam) Visit to Potsdam	
6 months	Finishing WP 3 and 4 Write-up of thesis	
	Final SPP conference	

2.4 Data handling

The project will produce moderate amounts of data. In Tübingen, professionally managed redundant data storage solutions are in place, allowing to store several TB of data for at least 10 years in accordance to data handling guidance rules. A project-internal online repository will be installed.

Raw data (such as individual snapshots for selected times) from the simulation runs will be stored to allow later re-analysis by the PhD student working on the DFT part. Computer codes for the simulations and analyses will be stored in versioned repositories (as, for instance, with GitLab – gitlab.com).

2.5 Other information

Broader Impact. In Sec. 1.2, we briefly discussed an application of our preliminary work on the statics and dynamics of rod lattice models to the growth of monolayers. In fact, most of our results on which the current proposal is based have been obtained in a joint DFG project on

thin film growth with organic molecules (OE 285/3-1, finishing date March 2019) together with an experimental group (Frank Schreiber, Tübingen) and a simulation group (Tanja Schilling, Freiburg). We expect that the investigations on dynamic wetting in lattice models are additionally relevant for the formation of ordered films with elongated organic molecules. This is a field with considerable activity given the possible applications of such films in organic electronics. Our work would add a thermodynamic perspective to thin film formation.

2.6 Description of proposed investigations involving experiments on humans, human materials or animals **n/a**

2.7 Information on scientific and financial involvement of international cooperation partners **n/a**

2.8 Information on embedding and scientific cooperation within SPP 2171

A central goal of the PP is formulated as

The Priority Programme aims at establishing a deeper understanding of the fundamental physics behind the dynamic (de)wetting of flexible, adaptive and switchable substrates combining experimental and theoretical perspectives.

This project is situated at the microscopic, theoretical side and aims to contribute to our fundamental understanding of dynamic surface phenomena in liquid crystals. This is different from the physics of bulk switching liquid crystal devices (described by mesoscale nematodynamics), underlying most existing technical applications. The general phase behavior in liquid crystals is understood very well and the chosen lattice models model certain aspects of this general phase behavior. The wetting state of the material may be dynamically controlled by switchable surfaces. A physical realization of such a switchable surface is provided by interfaces coated with light-responsive azo-dendrimers as investigated by the group of Stannarius/Eremin from the University of Magdeburg.

Collaboration and mutual exchange is planned with the project of Stannarius/Eremin. As described in Sec. 2.3, our work package 3 (Dynamics of formation of a wetting film) has a direct connection to the dynamics of smectic film formation and time-dependent surface tensions which will be investigated there.

Likewise, we plan to establish a collaboration/exchange with the project of Santer (Potsdam). They will employ photoresponsive materials to change the topography of surfaces which directly translates into changing anchoring conditions for fluids with colloidal rods. In this way, the approach to wetting (work package 3) or the switching between wetting states (work package 4) can be experimentally tested.

3 Bibliography

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4 Requested Modules/ Funds

4.1 Staff		€ 145 125	
PhD student, TV-L E13 75%, € 48 375 p.a., 3x	€ 145 125		
4.2 Consumables and Instrumentation		€ –	
publication costs	€ —		
4.3 Travel		€ 6 000	
TOTAL (DFG)			€ 151 125

4.1 Funding for staff

We ask for funding of one PhD student (E13 75%). The PhD student will develop equilibrium and dynamic DFT methods and apply them to the dynamics of wetting transitions as described.

4.2 Funding for consumables and instrumentation **n/a**

4.3 Direct project costs

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

4.3.2 Travel expenses

- Two SPP workshops (4 days each, participation of PI, PhD student, MSc student) : 1800 Euro
- One Advanced school (5 days) and one PhD workshop (4 days) for the PhD student : 1000 Euro
- Final SPP conference (5 days, participation of PI and PhD student) : 1200 Euro
- Visit to Magdeburg (3 days, participation of PI, PhD student, MSc student) : 1000 Euro
- Visit to Potsdam (3 days, participation of PI, PhD student, MSc student) : 1000 Euro

5 Project Requirements

5.1 Employment status information

Applicant: Prof. Martin Oettel Employment Status: permanent

5.2 First-time proposal data **n/a**

5.3 Composition of the project group

Summary table of the persons involved in the project			
Name	Position	field of work	type of funding
Oettel, Martin	Prof., permanent	PI	core
N.N.	MSc thesis students	GCMC and KMC simulations	n.a.

5.4 Cooperation with other researchers

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

Ralf Stannarius, Alexey Eremin (TU Magedeburg)
Svetlana Santer (Uni Potsdam)

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

J.W. Bartha [TU Dresden, Germany], **S. Dietrich** [MPI Stuttgart, Germany], **A. Dominguez** [University of Sevilla, Spain], **H. Emmerich** [University of Bayreuth, Germany], **R. Evans** [University of Bristol, UK], **T. Franosch** [University of Innsbruck, Austria], **D. Raabe** [MPI Düsseldorf, Germany], **F. Roosen–Runge** [University of Lund, Sweden], **R. Roth** [University of Tübingen, Germany], **T. Schilling** [University of Freiburg, Germany], **F. Schreiber** [University of Tübingen, Germany], **F. Zhang** [University of Tübingen, Germany],

5.5 Scientific equipment

The following scientific equipment is available for use within the project:

- (Oettel group) The group owns a dedicated multi-thread, high-memory machine for cDFT calculations and has access to small GPU clusters with high-memory cards. For GCMC simulations, access to the BW cluster is possible.

5.6 Project-relevant cooperation with commercial enterprises **n/a**

5.7 Project-relevant participation in commercial enterprises **n/a**

6 Additional Information