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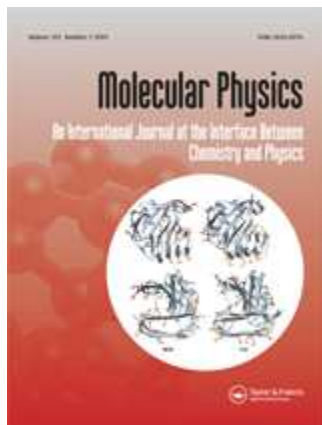
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# Complex fluids at complex surfaces: Simply complicated?

P. Patrício,<sup>1,2</sup> J. M. Romero-Enrique,<sup>3</sup> N. M. Silvestre,<sup>1,4</sup> N. R. Bernardino,<sup>1,4</sup> and M. M. Telo da Gama<sup>1,4,\*</sup>

<sup>1</sup>*Centro de Física Teórica e Computacional, Avenida Professor Gama Pinto 2, P-1649-003 Lisboa, Portugal*

<sup>2</sup>*Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro 1, P-1959-007 Lisboa, Portugal*

<sup>3</sup>*Departamento de Física Atómica, Molecular y Nuclear,*

*Universidad de Sevilla, Apartado de Correos 1065, 41080 Sevilla, Spain*

<sup>4</sup>*Departamento de Física, Faculdade de Ciências da Universidade de Lisboa, P-1749-016 Lisboa, Portugal*

We study wetting and filling of patterned surfaces by a nematic liquid crystal. We focus on three important classes of periodic surfaces: triangular, sinusoidal and rectangular. The results highlight the similarities and differences of nematic wetting of these surfaces and wetting by simple fluids. The interplay of geometry, surface and elastic energies can lead to the suppression of either filling or wetting. The periodic rectangular surface displays re-entrant transitions, with a sequence dry-filled-wet-filled, in the relevant region of parameter space.

## I. INTRODUCTION

Classical Density Functional Theory (DFT) is one of the most powerful theoretical tools in the study of surface and interfacial phenomena of liquids [1]. The application of DFT to simple fluids led to a truly significant discovery by Ebner and Saam: the wetting transition of a simple fluid (argon) on a simple solid (CO<sub>2</sub>) surface [2]. A simple surface is - for the purposes of this paper - one that is flat (structureless) on the mesoscale. The wetting transition was discovered simultaneously by Cahn [3] using a phenomenological square-gradient theory. Bob Evans established the connection between DFT and the square-gradient theory - proposed originally by van der Waals for simple fluid interfaces [1, 4]. Subsequently, Bob Evans and his co-workers made seminal contributions in the field of wetting of simple surfaces, and pioneered the study of simple fluids under confinement [5-7].

In this paper we will shift the focus from simple fluids at simple surfaces to complex fluids at complex surfaces, revisiting the most significant results of simple fluids at complex surfaces and complex fluids at simple surfaces. The aim is to establish general rules for nematic wetting at structured surfaces, based on a systematic investigation of the square-gradient (Landau-de Gennes) theory of nematics at representative periodic surfaces.

The global surface phase diagram of simple fluids at simple surfaces is quite rich but has been well understood for decades [8, 9]. More recently, Parry and co-workers led a systematic investigation of simple fluids at structured surfaces, discovering new phase transitions and elucidating - at last - the role of thermal fluctuations at the critical wetting transition [10]. In the next section we review the most relevant results of this work in preparation for the discussion of nematic wetting of analogous structured surfaces. In section III, we give an overview of the physics of wetting of simple surfaces by nematics, highlighting the role of the elastic free energy of non-

uniform director fields. In the last section, we present the results of our program of systematic investigation of nematic wetting at structured surfaces, emphasising the role of the elastic energy of surface and bulk topological defects.

Throughout this paper we will consider three paradigmatic examples of patterned surfaces: triangular, sinusoidal and rectangular periodic surfaces. We will present our results side by side, and in relation with simple fluids, to stress the similarities and the differences between different fluids and different surfaces. The free energy of a nematic slab includes an elastic term caused by distortions of the director field. The latter may be smooth or 'singular' due to the nucleation of defects in the bulk nematic matrix or at the surface. The interplay of surface geometry, interfacial and elastic energies results in complex (and complicated) phase diagrams with new features. To summarise the most surprising results, we found that: i) For periodic triangular surfaces the singular elastic free energy, due to geometrical surface singularities, is responsible for a drastic increase of the wetting anchoring energy, even in the limit of long wavelengths. The filling transition is suppressed, and a direct transition from the dry to the wet state is observed. ii) For periodic sinusoidal surfaces, the situation appears to be quite different as the defects, if present, are necessarily bulk topological defects. We found that, in general, filling and wetting pre-empt each other. We observed a single transition - filling or wetting - to a phase without topological defects. Whether the stable phase is the wet or filled state depends on a combination of the surface roughness and anchoring conditions at the interfaces. The competing wet and filled phases are metastable over a relatively wide range of parameters but the nucleation of bulk topological defects - required to realise one or the other - is not compensated by a decrease in the anchoring energy in the transitions range of parameters. As a consequence, for a given surface geometry, we have not observed a sequence of filling/wetting transitions for different anchoring strengths. iii) Finally, for periodic rectangular surfaces the scenario is similar to that of periodic sinusoidal surfaces over a wide range of parameters.

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\*Electronic address: margarid@cii.fc.ul.pt

We have, however, observed re-entrant filling transitions, with a sequence of states dry-filled-wet-filled as the anchoring strength increases, in a restricted but relevant range of parameters.

## II. SIMPLE FLUIDS AT COMPLEX SURFACES

We start by reviewing wetting and adsorption of simple fluids at complex surfaces. As alluded to above, a complex surface is one that is geometrically structured on the mesoscale.

At the level of thermodynamics, a liquid droplet deposited on a planar solid surface will form a spherical droplet, defining a contact angle  $\theta$  of the liquid with the surface. The cornerstone of wetting phenomena [8, 9, 11–15], Young’s equation, relates the contact angle with the surface tensions of the solid-vapour  $\sigma_{sv}$ , solid-liquid  $\sigma_{sl}$ , and liquid-vapour  $\sigma$  interfaces:

$$\cos \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma}. \quad (1)$$

When the contact angle is zero, the liquid spreads to cover the surface and we say that the liquid *wets* the solid. A *wetting transition* occurs when the contact angle changes from a finite value to zero, as the temperature or the surface properties vary [8, 9, 11, 12, 14, 15].

The macroscopic droplet is accompanied by a microscopic film of adsorbed liquid. In wetting studies, it is convenient to focus on the amount of adsorbed liquid. A wetting transition now corresponds to the divergence of the adsorption, which is equivalent to the presence of a macroscopic liquid film. This phase transition is very sensitive to the details of the interactions within the fluid and of the fluid with the surface. Even the character of the transition, continuous or discontinuous, depends on these details [10, 16]. The adsorption can also diverge if we approach the liquid-vapour coexistence line from the vapour side, typically by changing the vapour pressure. This is the route usually followed in experiments [8, 9, 11, 12, 14, 15, 17–19], and is called a *complete wetting transition*.

On structured surfaces the most obvious difference is that the effective surface area increases due to the surface structure. The roughness  $r$  is defined as the ratio of apparent, i. e. projected, to real surface area. On a rough surface the interfacial free energies of the solid-vapour and solid-liquid interfaces increase by the same amount, leading to a modified Young equation

$$\cos \theta = r \cos \theta_0 \quad (2)$$

where  $\theta_0$  is the contact angle at the planar surface. This is known as Wenzel equation and results from simple thermodynamic arguments [13]. Eq. (2) implies that mesoscopic surface structure or roughness amplifies the surface wetting properties: hydrophilic surfaces become more hydrophilic, and hydrophobic surfaces become more hydrophobic.

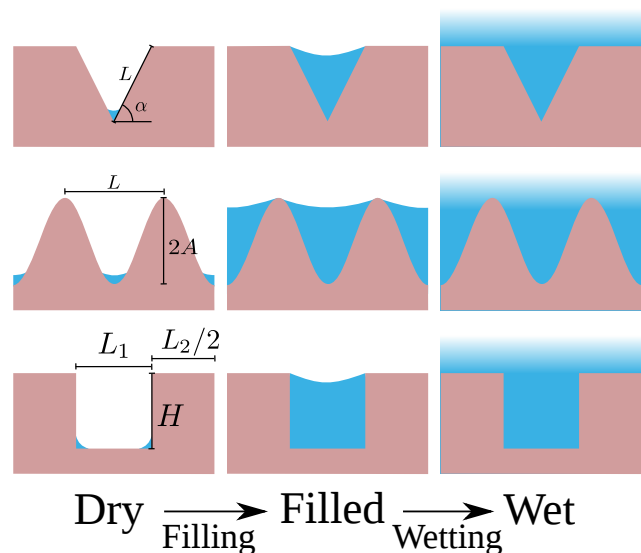


FIG. 1: The three wetting states of structured surfaces: dry, filled and wet, separated by filling and wetting “transitions”. In certain geometries these are true phase transitions. The relevant length scales are defined for each geometry. See the text for details.

Beyond thermodynamics, at the microscopic level, surface geometry has a profound effect on wetting transitions: the nature of the transition may change and new kinds of transitions, e.g. filling, may occur [20].

It is convenient to unify and simplify the notation for the remaining of the paper. We distinguish three “wetting states”: *dry*, *filled* and *wet* (see Fig. 1). We call *filling* the process through which a dry state becomes filled, and *wetting* the process through which a dry or filled state becomes wet. This classification does not imply that the “states” are distinct thermodynamic surface phases, i.e., that they are separated by phase transitions. In some cases the filling process is indeed smooth and there is no phase transition. Our classification is not unique, for example, Rascón et al. [21] called *unbending* (of the interface) to the filling of a sinusoidal surface, and *unbinding* (of the interface from the surface) to the wetting transition of the same surface.

There are numerous theoretical predictions for wetting on a wedge [20, 22–27]. The filling transition of wedges occurs before wetting of flat surfaces. Indeed, the latter occurs when the contact angle vanishes ( $\theta = 0$ ) while for a wedge with opening angle  $\alpha$  a filling transition occurs when  $\theta = \alpha$ . One of the most surprising results is that the filling transition may be continuous when the wetting transition is discontinuous [23]. There are also hidden symmetries between filling on wedges and wetting of planar surfaces, known as *wedge covariance* [20]. Unlike critical wetting at planar surfaces the theoretical results for wedge filling are in very good agreement with both simulations [28] and experiments [17].

On sinusoidal surfaces there are both similarities and

differences with wetting and filling of wedges [21]. There is filling of the sinusoidal cavities accompanied by a thermodynamic transition when the surface roughness is above a certain threshold. The filling transition, or the smooth crossover below the threshold, are then followed by the wetting transition of the sinusoidal surface. On a capped capillary, filling of the surface turns condensation into a continuous phase transition [29]. Again there is filling of the capillary followed by the wetting of the surface. Related results have been published for arrays of posts and pits [30, 31].

More generally, Rascón and Parry [32] have used a simple geometric construction to study a parametrised family of surfaces that goes smoothly from a planar surface to a capillary slit, with linear and parabolic wedges as particular cases. This study illustrates the role of geometry and the relation between wetting, filling, and capillary condensation. Many of the novel theoretical results have been confirmed by experiments [17–19].

### III. COMPLEX FLUIDS AT SIMPLE SURFACES

Since their discovery, *liquid crystals* (LC) provided a fertile ground for the development of new theoretical methods and ideas. Wetting is no exception [33, 34]. In this section, we review nematic wetting of simple surfaces emphasising the similarities and differences with simple fluid wetting.

The nematic phase is characterised by long-range orientational order and positional disorder. The direction of molecular alignment, the nematic director  $\mathbf{n}$ , is arbitrary in bulk nematics but the presence of surfaces and interfaces selects a particular direction, known as surface anchoring. Typical situations include homeotropic (orientation perpendicular to the surface), random planar (random orientation parallel to the surface) and planar (orientation along a direction in the surface). Nematic wetting was predicted in the framework of the Landau-de Gennes (LdG) theory [35–42] and has been observed experimentally using a variety of techniques [43–47]. At nematic-isotropic (NI) coexistence, the quantity of interest is the adsorption of the orientational order parameter  $\mathbf{Q}$  (defined below), as the densities of the coexisting liquid phases are very close and their spatial variations may be neglected [48–52]. Although there are quantitative discrepancies between the full DFT and LdG, and some qualitative ones [53], the overall picture of the wetting phase diagram is described adequately by the simpler LdG theory and this is the theory that will be used here.

Within the LdG theory, the isotropic and nematic phases are characterised by a traceless, symmetric order-parameter tensor with components  $Q_{ij}$ , which may be represented as

$$Q_{ij} = \frac{3}{2}S[n_i n_j - \frac{1}{3}\delta_{ij}] + \frac{1}{2}B[l_i l_j - m_i m_j], \quad (3)$$

where  $n_i$  are the Cartesian components of the director

field  $\mathbf{n}$ ,  $S$  is the nematic order parameter, which measures the degree of orientational order along the nematic director, and  $B$  is the biaxiality, which measures the degree of orientational order along the directions perpendicular to  $\mathbf{n}$ , characterized by the eigenvectors  $\mathbf{l}$  and  $\mathbf{m}$ . The corresponding LdG free energy may be written as

$$\mathcal{F}_{\text{LdG}} = \int_{\mathcal{V}} (\phi_b + \phi_{\text{el}}) dv + \int_{\mathcal{S}} \phi_s ds \quad (4)$$

where  $\phi_b$  is the bulk free energy density and  $\phi_{\text{el}}$  is the elastic free energy density, given by [54]:

$$\phi_b = a \text{Tr} \mathbf{Q}^2 - b \text{Tr} \mathbf{Q}^3 + c[\text{Tr} \mathbf{Q}^2]^2 \quad (5)$$

$$\phi_{\text{el}} = \frac{\mathcal{L}_1}{2} \partial_k Q_{ij} \partial_k Q_{ij} + \frac{\mathcal{L}_2}{2} \partial_j Q_{ij} \partial_k Q_{ik} \quad (6)$$

where  $a$  depends linearly on the temperature,  $b$  and  $c$  are positive constants, and  $\mathcal{L}_1$  and  $\mathcal{L}_2$  are positive parameters related to the elastic constants. The first integral in (4) is over the volume,  $\mathcal{V}$ , while the second is over the surface area,  $\mathcal{S}$ . The surface free energy,  $\phi_s$ , is assumed to take the form [55]:

$$\phi_s = \frac{w}{3} \text{Tr}[\mathbf{Q} - \mathbf{Q}_s]^2 \quad (7)$$

where  $\mathbf{Q}_s$  is the tensor order parameter favoured by the surface:  $\mathbf{Q}_s = S_s(3\boldsymbol{\nu} \otimes \boldsymbol{\nu} - 1)/2$ , with  $\boldsymbol{\nu}$  the surface director,  $S_s$  the surface nematic order parameter, and  $w$  the anchoring strength. In the strong anchoring regime, the nematic order parameter will take the value  $\mathbf{Q}_s$  at the surface.

By rescaling the variables as in [56]:  $\tilde{\mathbf{Q}} = 6c\mathbf{Q}/b$ ,  $\tilde{\mathbf{r}} = \mathbf{r}/\xi$ , where the nematic bulk correlation length  $\xi$  is  $\xi^2 = 8c(3\mathcal{L}_1 + 2\mathcal{L}_2)/b^2$ , and  $\tilde{\mathcal{F}}_{\text{LdG}} = 24^2 c^3 \mathcal{F}_{\text{LdG}}/\xi^3 b^4$ , we find  $\tilde{\mathcal{F}}_{\text{LdG}} = \int_{\tilde{\mathcal{V}}} (\tilde{\phi}_b + \tilde{\phi}_{\text{el}}) d\tilde{V} + \int_{\tilde{\mathcal{A}}} \tilde{\phi}_s d\tilde{s}$ , where the rescaled free energy densities are:

$$\tilde{\phi}_b = \frac{2}{3}\tau \text{Tr} \tilde{\mathbf{Q}}^2 - \frac{8}{3} \text{Tr} \tilde{\mathbf{Q}}^3 + \frac{4}{9}[\text{Tr} \tilde{\mathbf{Q}}^2]^2 \quad (8)$$

$$\tilde{\phi}_{\text{el}} = \frac{1}{3 + 2\kappa} [\tilde{\partial}_k \tilde{Q}_{ij} \tilde{\partial}_k \tilde{Q}_{ij} + \kappa \tilde{\partial}_j \tilde{Q}_{ij} \tilde{\partial}_k \tilde{Q}_{ik}] \quad (9)$$

$$\tilde{\phi}_s = \frac{1}{3} \tilde{w} \text{Tr}[\tilde{\mathbf{Q}} - \tilde{\mathbf{Q}}_s]^2 \quad (10)$$

Here  $\tau = 24ac/b^2$  is a dimensionless temperature,  $\kappa = \mathcal{L}_2/\mathcal{L}_1$  a dimensionless elastic parameter ( $\kappa > -3/2$ ) and  $\tilde{w} = 16wc/b^2\xi$  a dimensionless anchoring strength. From now on we consider rescaled variables only, and will drop the tildes to simplify the notation.

At  $\tau = 1$ , the bulk free-energy density has two minima  $\phi_b = 0$  for rescaled scalar order parameters  $S_I = 0$  (isotropic phase) and  $S_N = 1$  (nematic phase). The sign of the elastic parameter  $\kappa$  determines the anchoring at the NI interface: homeotropic for negative  $\kappa$  and planar for positive  $\kappa$ .

In order to describe nematic wetting, we have to consider the anchoring *both* at the surface and at the NI interface. In the simplest case, both favour homeotropic

anchoring (i.e.  $\kappa < 0$ ,  $S_s > 0$ ,  $w > 0$  and  $\nu$  perpendicular to the surface). The biaxiality  $B$  vanishes and the nematic director is uniform throughout the system. In this case the LdG functional reduces to the Landau-Ginzburg free-energy functional of a subcritical fluid at a planar surface. The system exhibits a first-order wetting transition for  $w < \sqrt{2}$ , with an associated prewetting line for  $\tau > 1$  [57]. Sheng's limit [35, 36] corresponds to  $w \rightarrow 0$ ,  $S_s \rightarrow \infty$  with  $w = wS_s$  finite. The wetting transition becomes tricritical at  $w = \sqrt{2}$ , and for larger values of  $w$  it is continuous. In this case, isotropic wetting is completely analogous to nematic wetting, and follows by changing  $wS_s$  to  $1 - wS_s$ . This symmetry, characteristic of fluids with scalar order parameters, breaks down in the presence of biaxiality and is absent when the surface and the NI interface are antagonistic, i.e., favour distinct anchorings.

When the surface and the NI interface favour planar anchoring, biaxiality plays a role. The nematic director is still uniform throughout the system but there are two distinct possibilities:  $S_s < 0$  and  $\nu$  perpendicular to the surface (random planar), or  $S_s > 0$  and  $\nu$  parallel to the surface (planar). In the former case, the wetting phase diagram resembles that for homeotropic anchoring with an additional feature, the 'nematization' surface transition between a random planar and a planar nematic film [39].

Finally, when the anchoring at the surface differs from that at the NI interface, the picture changes quite drastically, as the elastic deformations of the director field play a crucial role. As the nematic wetting layers grow, spatial variations of the nematic and biaxial order parameters,  $S$  and  $B$ , remain confined to the neighbourhood of the interfaces, but the nematic director changes linearly from that favoured at the surface to that favoured at the NI interface [42]. Since the associated elastic energy is positive, the wetting transition is always first-order. In addition, wetting by the isotropic phase of the nematic-solid surface may be pre-empted by a pure surface anchoring transition [41].

#### IV. COMPLEX FLUIDS AT COMPLEX SURFACES

Nematic wetting on structured surfaces has attracted little attention [58], although it is of considerable fundamental interest, with relevant applications in bistable liquid-crystal displays. One reason for this is that it is complicated! The surface structure causes orientational frustration that contributes an elastic term to the free energy. Under certain conditions, it may lead to the nucleation of topological defects that will, in turn, affect the nematic order at the surface. The nucleation of defects, with complex structure and dynamics, is a new ingredient, not present in the wetting of simple liquids at structured surfaces nor in nematic wetting at structureless ones.

In this section we will address the interplay between surface geometry (on the order of  $l \sim 10 - 100\xi$ ) and the elastic energy of the distortions caused by the spatially varying surface director field. The role of fluctuations, which is completely unknown for nematic wetting, is left for future work. A few systematic studies based on the LdG theory were carried out for periodic triangular [59, 60] and sinusoidal [61] surfaces, and general rules begin to emerge. In the following, we discuss these rules and present new results, based on the LdG theory, for nematic wetting at periodic rectangular surfaces. The latter have been investigated numerically and experimentally, in the context of zenithal bistable switching of LC devices [62, 63] and exhibit a rich wetting behaviour, due to a large number of metastable ordered states in the wetting range of parameters. Multiple filling transitions may occur, leading to re-entrant behaviour, which has not been observed at the periodic triangular and sinusoidal surfaces.

##### A. Nematic wet states: Thermodynamics

We start with the thermodynamics of nematic wetting. The structured surface is characterised by a spatially varying surface director field, while the director at the NI interface is uniform. There is then an elastic contribution to the thermodynamic free energy of a nematic slab which is long-ranged, repulsive, and dominates the interfacial free energies at large distances. In the wet state, the system has a single length scale,  $l$ , set by the surface. The elastic free energy for smooth distortions is, up to a constant of order 1 which depends on the surface geometry,  $KS/l$ , where  $K$  is the macroscopic Frank elastic constant. The nematic wetting transition is then given by a generalization of Wenzel's law [59]

$$\cos \theta = r \left( \cos \theta_0 - \frac{K\tilde{\mathcal{F}}_{el}}{\sigma_{in}l} \right) \quad (11)$$

where  $\tilde{\mathcal{F}}_{el} = l\mathcal{F}_{el}/KS \sim 1$  and  $\sigma_{in}$  is the NI surface tension.

In the limit of large  $l$ ,  $l \gg K/\sigma_{in}$ , the elastic contribution is irrelevant, and Wenzel's law is recovered. However, the orientational frustration, due to the geometrical surface pattern, may lead to the nucleation of topological defects close to the surface, with a cut-off length (defect size) set by the bulk correlation length  $\xi$ . The presence of bulk and/or surface defects will contribute a singular  $\ln(l/\xi)$  term to the rescaled elastic free energy  $\tilde{\mathcal{F}}_{el}$  [60], which is dominant at large  $l$ . While for simple fluids the wetting transition at structured surfaces occurs always before the wetting transition at structureless ones (as the temperature or the surface field increase), for nematics, the wetting transition will occur before if the geometrical structure dominates or after if the elastic energy dominates. In systems where the elastic energy

dominates, large deviations from Wenzel's law are still found at large  $l$ , and nematic wetting may be suppressed.

Beyond thermodynamics, at the microscopic level, surface geometry has an even more profound effect on nematic wetting. As for simple fluids it may lead to new transitions such as filling. However, nematic wetting does not necessarily follow filling, as the pinned NI interface in the filled state may prevent the nucleation of topological defects in the bulk nematic, which would increase the elastic energy by an amount that is not compensated by the decrease in the surface anchoring energy.

### B. Nematic wet states: LdG theory for periodic triangular surfaces

Having set the stage, we proceed to discuss nematic wetting at structured surfaces, based on the mesoscopic LdG theory. Systematic work along these lines was pioneered by Patrício et al. [59–61].

We start with nematic wetting at periodic triangular surfaces, characterised by an opening angle  $\alpha$  and length  $L$  (see Fig. 1). The surface periodicity has wave number  $q = \pi/L \cos \alpha$  in the azimuthal plane and is translationally invariant in the perpendicular direction. The roughness parameter is  $r = 1/\cos \alpha \geq 1$ . The surface anchoring was assumed homeotropic and linear (see [59, 60]) while the anchoring at the NI interface is planar ( $\kappa = 2 > 0$ ). The LdG free energy minimization (using adaptive meshing) yields equilibrium in-plane nematic textures only, for the range of parameters relevant in the wetting regime.

The numerical results further show that the nematic texture with the lowest free energy changes from 'homeotropic' to 'planar', as  $\alpha$  increases, at  $\alpha = \pi/4$  (see Fig. 2) and the system exhibits bi-stability for opening angles close to  $\pi/4$ . Inspection of the textures also reveals that, in general, there are no disclination lines in the bulk nematic, but large distortions of the director field were observed close to the surface singularities (lines along the vertices of the triangular section). These distortions signal the presence of surface disclination lines that contribute a term, to the elastic free energy, which scales with the wave number  $q$ , as  $-q \ln q$  for small  $q$  and  $w > q$ . Although stable disclination lines in bulk three dimensions have half-integer winding numbers, the surface disclination lines have (arbitrary) winding numbers related to the surface geometrical parameters [60].

This conclusion is quantified in Fig. 2, where the results of the LdG theory for the wetting transition anchoring strength  $w_t$  are plotted as a function of opening angle  $\alpha$ , for different surface lengths,  $L$ . In the same figure, we have plotted the result of the generalized Wenzel's law, where the leading singular elastic contribution from the surface disclination lines is taken into account (see [60] for details). This contribution introduces a very slow decay of the surface free energy at large  $L$ , and explains the large deviations from Wenzel's law observed in [59, 60].

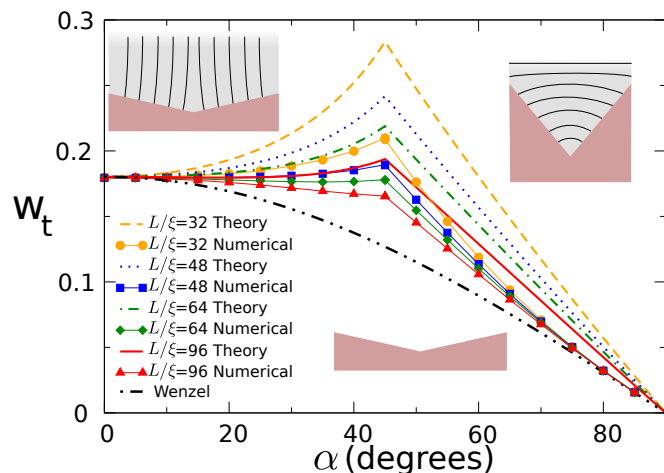


FIG. 2: Wetting phase diagram - anchoring strength  $w_t$  versus opening angle  $\alpha$  - of periodic triangular surfaces and typical nematic textures of each phase. Symbols correspond to the results of LdG theory [59], and lines to the generalized Wenzel's law, Eq. 11, where the leading contribution to the elastic free energy from surface disclination lines, proportional to  $\ln L/\xi$ , is accounted for (see Ref. [60] for more details).

Somewhat surprisingly, the results also show that filled states are suppressed, as they are found to be metastable over the wetting range of parameters.

### C. Nematic wet states: LdG theory for periodic sinusoidal surfaces

A periodic sinusoidal surface is characterised by a wave number,  $q = 2\pi/L$ , and amplitude,  $A$ , in the azimuthal plane and is translationally invariant in the perpendicular direction (see Fig. 1). The surface roughness is a monotonic increasing function of  $Aq$ . Sinusoidal surfaces are interesting as for simple fluids, and roughness above a certain threshold, they exhibit a sequence of filling and wetting transitions [21]. Recently, using the LdG theory and the numerical techniques used for triangular surfaces, nematic wetting of sinusoidal surfaces was also investigated [61].

For linear surface potentials and homeotropic anchoring [61], it is found that when the NI interface favours parallel anchoring, a wetting transition from the dry to 'homeotropic' nematic occurs at small values of  $Aq$ . The filled states appear at larger anchoring strengths but are found to be metastable. At large  $Aq$  (large roughness) the transition is from the dry to a filled state (as in simple fluids) but the wet states, found at higher anchoring strengths, are always metastable. Indeed, the filled states where the NI interface is pinned at the surface crests have always a lower free energy than the wet states, where a periodic array of defect lines is nucleated at the sinusoidal crests (see Fig. 3).

Detailed results over a wide range of parameters show that the filling-wetting transition sequence, observed

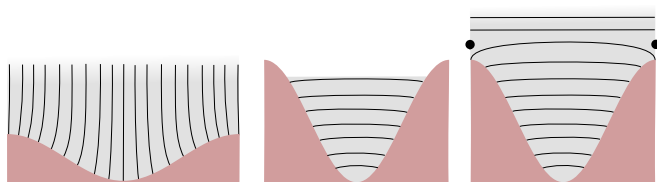


FIG. 3: Typical nematic textures at sinusoidal surfaces. From the left: wetting by ‘homeotropic’ nematic, filling and wetting by a ‘planar’ nematic. The latter, characterised by topological defects along the crests of the sinusoidal pattern (black dots), was found to be metastable.

for simple fluids on sinusoidal surfaces, does not occur for nematics [61]. The phase diagrams - transition anchoring strength  $w_t$  versus  $Aq$  - are cusped, resembling those found for periodic triangular surfaces. While in the latter, the two branches correspond to wetting by ‘homeotropic’ (small angle/roughness) and ‘planar’ (large angle/roughness) nematics, at sinusoidal surfaces the transitions are wetting by ‘homeotropic’ nematic at small roughness and filling by ‘planar’ nematic in the opposite regime. The results, however, depend on the anchoring conditions at both interfaces and the situation is somewhat reversed if the anchoring at the surface and at the NI is homeotropic. The detailed analysis of these results will be published elsewhere [61].

#### D. Nematic wet states: LdG theory for periodic rectangular surfaces

We now turn our attention to periodic rectangular surfaces. Like the triangular surface, these have geometrical singularities, but unlike the triangular case, they may exhibit a sequence of nematic filling and wetting transitions. Periodic rectangular surfaces are characterised by two lengths,  $L_1$  and  $L_2$  (wave number  $q = 2\pi/(L_1 + L_2)$ ) and depth,  $H$ , in the azimuthal plane and are translationally invariant in the perpendicular direction (see Fig. 1). The roughness is  $r = 1 + 2H/(L_1 + L_2)$ . In order to restrict the number of parameters, we have first set  $L_1 = L_2 = 10\xi$ .

We consider homeotropic surface anchoring and planar anchoring at the NI interface, as in the previous studies. The anchoring strength at the transition,  $w_t$ , is plotted as a function of roughness,  $r$  in Fig. 4. The nematic textures representative of the various surface phases are also illustrated in the diagram. At small and large roughnesses,  $r$ , the wetting behaviour is similar to that found at sinusoidal surfaces. There is wetting but no filling of nearly flat surfaces ( $r \sim 1$ ), and filling but no wetting of highly rough ones ( $r \gg 1$ ). At intermediate values of the roughness novel wetting behaviour is observed.

Over a narrow range of the roughnesses ( $1.4 < r < 1.5$ ) the system exhibits a sequence of transitions, from dry  $\rightarrow$  filled  $\rightarrow$  wet, as in simple fluids. However, as the anchoring strength increases, the system exhibits a tran-

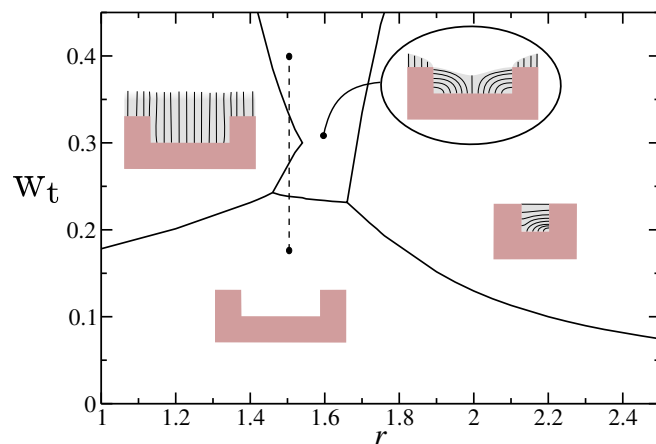


FIG. 4: Wetting phase diagram - anchoring strength  $w_t$  versus roughness  $r$  - of periodic rectangular surfaces and typical nematic textures of each phase. Along the dashed path the system exhibits a re-entrant filling transition, with a sequence of states: dry-filled-wet-filled.

sition from the wet to a filled state (see Fig. 4). In this phase, pinning of the NI interface is energetically favourable when compared with the wet nematic phase, where topological disclination lines appear at the top corners of the rectangular surface. This re-entrant behaviour is robust and similar diagrams are obtained for rectangular surfaces characterised by different geometrical parameters.

#### V. CONCLUSION

The wetting of complex surfaces by complex liquids is complex and complicated. This is hardly surprising, in view of the large number of parameters involved. Nevertheless, a simpler picture emerges from the results obtained.

Like with simple fluids, nematic wetting phenomena is essentially an interplay of three possible states: dry, filled and wet. In nematics, there can be a number of different textures in each of these states (‘homeotropic’, ‘planar’, with or without defects...) but the basic phenomenology is the same. That said, each of the surfaces studied has its own set of interesting and unique wetting behaviour.

The triangular is perhaps the simplest of geometrically structured surfaces, but even in this case, the elastic free energy and the effect of topological defects manifest themselves: bistable nematic states are found for opening angles close to  $\alpha = \pi/4$  and the approach to the wetting transition predicted by Wenzel’s law, for rough surfaces, is extremely slow. Rather surprisingly, the filled state is found to be always metastable and thus the filling transition is pre-empted by wetting.

Sinusoidal surfaces exhibit a phase diagram that looks, superficially, similar to that of triangular surfaces. However, at sinusoidal surfaces both filling and wetting may



be suppressed. For a given roughness, the transition is either from dry-to-wet or dry-to-filled and we do not observe the sequence dry-filled-wet found in simple fluids. The analysis of the textures sheds some light on this behaviour: the sinusoidal surface is not singular and thus wet states on sufficiently rough surfaces lead to the nucleation of topological defects. The energy to create these defects is usually so high that the filled state is always energetically favourable. In effect, the NI interface becomes pinned by the emerging defects of the nematic wet phase.

Rectangular surfaces once again have similarities with the other surfaces. At low and high roughnesses, the results are similar to the sinusoidal surface: There is a transition from dry-to-wet at low  $r$  and a dry-to-filled transition in the opposite limit. Interestingly, for intermediate roughness, we find re-entrant filling transitions, with a sequence dry-filled-wet-filled states.

The following table summarises the main results:

Geometry	Main Result
Triangular	No filling, wetting only.
Sinusoidal	Either filling or wetting. The transitions pre-empt each other.
Rectangular	Re-entrant filling transitions: sequence of dry-filled-wet-filled states.

The study of wetting of complex surfaces by complex fluids is work in progress and the interpretation of the

results is still somewhat complicated! We hope that, as more results become available, a simpler picture will emerge, with a better understanding of the role of elasticity and topological defects. This will provide a framework - or generic behaviour - to guide and/or interpret detailed studies of the phase diagrams of individual systems.

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It is a great pleasure to contribute this paper to the special issue of Molecular Physics to honour Professor Robert Evans's sixty fifth birthday. Bob has taught and influenced us all by the high intellectual standards used in his work and which he has also demanded of everybody else. We wish him many more years of productive research.

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