Capillary and anchoring effects in thin hybrid nematic films and connection with bulk behaviour

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Abstract

By means of a molecular model, we examine hybrid nematic films with antagonistic anchoring angles where one of the surfaces is in the strong anchoring regime. If anchoring at the other surface is weak, and in the absence of wetting by the isotropic phase, the anchoring transition may interact with the capillary isotropic–nematic transition in interesting ways. For general anchoring conditions on this surface we confirm the existence of the step–tilt, biaxial phase and the associated transition to the linear, constant–tilt–rotation, configuration. The step–like phase is connected with the bulk isotropic phase for increasing film thickness so that the latter transition is to be interpreted as the capillary isotropic–nematic transition. Finally, we suggest possible global surface phase diagrams.

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Frustration effects associated with confinement of liquid crystals by competing surface fields continue to attract interest. Hybrid nematic cells, where a nematic material is exposed to two surfaces with strong but opposing anchoring tendencies, are commonly used experimentally to determine anchoring properties of substrates [1,2] and may be important in the context of display device technologies, especially in the case of hybrid twist nematic cells [3]. The two configurations observed in hybrid homeotropic/planar cells are (Fig. 1): (i) uniform director along the direction favoured by the substrate with the highest anchoring energy (U phase), and (ii) linearly–rotating director between the two antagonistic surfaces (L phase). Elastic and surface effects play opposite roles and determine the equilibrium director configuration. A confinement–induced anchoring transition (between the L and U phases) is expected for sufficiently thin cells [4]. However, a third possible configuration was proposed by Palffy–Muhoray et al. [5] (and a few years before by Schopohl and Sluckin [6] in the context of disclination defects), consisting of two contiguous slabs of nematic material with uniform but opposite director orientations, each following the orientation favoured by each substrate; macroscopically the directors in the two slabs cannot be continuously connected. This phase will be called step–like (S) phase (see Fig. 1), but is also known as director–exchange phase, biaxial phase, etc. Although the S phase, predicted by the phenomenological Landau–de Gennes theory [5,9,10], has been confirmed by Monte Carlo simulation on a (lattice–spin) Lebwohl–Lasher model [8], no experimental evidence seems to exist as yet (see however Ref. [19]), presumably because the step–to–linear (SL) phase transition will take place very close to the bulk isotropic–nematic transition and for a cell thickness of a few tens of nanometers [10], challenging experimental verification. Also, an understanding of the role of the different phases in the surface phase diagram and of the relation of the capillary isotropic–nematic transition in hybrid cells to bulk behaviour (in particular, to the anchoring transition for a single substrate) is, we believe, still lacking.

In this Letter we establish the connection between capillary and anchoring effects, on the one hand, and clarify the role of the SL transition in the surface phase diagram, on the other, in an asymmetric nematic film confined between dissimilar, parallel substrates. In addition, we discuss possible scenarios, in the weak anchoring regime, for how this connection may be realised. In contrast with previous theoretical works based on mesoscopic models, the problem is analysed using a mean–field molecular theory applied to an athermal fluid of hard anisotropic particles that undergoes an isotropic–nematic transition with respect
to chemical potential (which plays the role of an inverse temperature in a thermotropic liquid crystal). The model, extensively tested previously [12, 13], consistently describes bulk and interfacial properties, allowing for a microscopically-based assessment of the effects of surface interactions, wetting properties and elastic free energies, on the formation of the S phase. Our analysis indicates that the SL transition corresponds in fact to the usual capillary isotropic–nematic transition, well described, in the limit of thick planar cells, by the Kelvin equation, which relates the transition to the wetting conditions of the substrates. In addition, we relate the capillary transition to the anchoring transition in the confined system when one of the substrates is in the weak anchoring regime, and provide several possible scenarios for the global surface phase diagram.

The theoretical model is the density–functional theory of Onsager, with Parsons–Lee rescaling (see [12, 13] for a full account of the theory and its numerical implementation), formulated for rigid particles (spherocylinders) with a length–to–breadth ratio $L/D = 5$. In this theory the free energy $F[\rho]$ is minimised with respect to the density distribution, $\rho(z, \hat{\omega})$, with $z$ the normal distance from the left substrate and $\hat{\omega}$ the main axis of the uniaxial rods (Fig. 1). The theory includes interactions from excluded volume effects, which promote nematic ordering at high packing fractions, and entropic contributions from orientational degrees of freedom, which play against those effects. A bulk isotropic–nematic transition is predicted for sufficiently slender rods at a chemical potential $\mu_b$. Four structural quantities are needed to describe ordering: $\rho(z)$, the local number density, $\eta(z)$ and $\sigma(z)$, the uniaxial and biaxial nematic order parameters with respect to the local director $\mathbf{n}$, and $\psi(z)$, the tilt angle of the local director with respect to the substrate normal along the unit vector $\hat{z}$.

Further, the effect of each substrate is accounted for by means of a one–particle external potential, which for the substrate at left is $V^{(1)}_{ext}(z, \hat{\omega}) = \infty$ ($z < 0$) and $W_1 \exp(-\alpha z)P_2(\hat{\omega} \cdot \hat{z})$ ($z > 0$), with a similar expression for the substrate potential $V^{(2)}_{ext}(z, \hat{\omega})$ at right (but with a strength $W_2$). In all our calculations we set the potential range as $\alpha = 0.88(L+D)^{-1}$. This model has been used [12, 13] to explore wetting properties; it also predicts an anchoring transition [12]. Fig. 2 is the (schematic) interfacial phase diagram for a single–substrate system in the $\Delta \mu \equiv \mu - \mu_b$ vs. surface strength $W$ plane. Dashed vertical lines indicate the state of both substrates in the confined case; substrate 1 is fixed to be in the regime of complete wetting by nematic (with homeotropic orientation $\perp$) and in the strong anchoring case, while the state of substrate 2 will be chosen in the regimes of complete wetting (with
planar orientation \( \parallel \) or partial wetting. In the latter case proximity to the anchoring transition will bring about interaction of anchoring and capillary effects in the confined system. The model does not predict a region of wetting by the isotropic phase; consequently, we expect no suppression of the capillary isotropic–nematic transition [16, 18] in our system.

Our first result is Fig. 3(a), which depicts the surface phase diagram in the \( \Delta \mu \) vs. film thickness \( h \) plane. Conditions of wetting by nematic and strong anchoring with homeotropic and planar alignments [states (1) and (2) in Fig. 2] are imposed; therefore no anchoring transition is expected in the nematic region. The line represents a first–order SL phase transition separating two confined structures, the L and S phases. For thin films the line terminates in a critical point. Therefore, the stable director configuration for sufficiently thin films is the S phase (as predicted by Palffy–Muhoray et al. [5]), but only below the critical point (provided the latter is within the stable nematic region). As \( h \to \infty \) (thick films) the transition line approaches the bulk value \( \mu_b \) from below, as corresponds to a preference of the substrate for the nematic phase. The non–monotonic shape of the transition line can be understood from a competition between capillary and elastic effects in the L phase: macroscopically \( \Delta \mu(h) = a_2/h^2 - a_1/h \), where \( a_2 > 0 \) is proportional to the nematic elastic constant \( K \) and \( a_1 > 0 \) to the surface tension difference \( \Delta \gamma = 2\gamma_{\text{WI}} - \gamma_{\text{WN}} - \gamma_{\text{WN}} \) (the last two surface tensions corresponding to planar and homeotropic director configurations, respectively); as \( h \to \infty \) capillary effects [second term in \( \Delta \mu(h) \)] dominate and \( \Delta \mu(h) \to 0^- \), but in the thin–film regime elastic effects are more important and \( \Delta \mu \) becomes positive.

What is the structure of the L and S phases? This is shown in Fig. 4 where the order parameter profiles of the two structures coexisting at point p (a and c) and point q (b and d) on the transition line depicted in Fig. 3(a) are shown. Particularly interesting is the behaviour of \( \eta \) in the S phase in the central region of the cell; it drops almost to zero symmetrically with respect to the step, Fig. 4(a). One can interpret this profile as indicating the presence of a planar defective region sandwiched between two finite–thickness nematic films with opposite director orientations, i.e. a ‘true’ S phase. However, in the S–type structure of point q [Fig. 4(b)], this region has evolved into a well–developed isotropic slab whose thickness \( l \) depends on the departure from the bulk, \( \Delta \mu \): if \( l_1 \) and \( l_2 \) are the thicknesses of the incipient wetting nematic layers, then [see Fig. 4(b)] \( l = h - l_1 - l_2 \sim -\Delta \mu^{-1} \) according to Kelvin equation (large \( h \)); it follows that \( l \) is an increasing function of \( h \) as \( h \to \infty \) for the coexisting S phase and, for large values of \( h \), the isotropic slab completely decouples.
the two nematic films with opposite director orientations [7], the situation being identical to the usual capillary isotropic–nematic transition in symmetric or nearly symmetric cells. Therefore, the S phase is in fact a confined phase connected with the bulk isotropic (I) phase, whereas the L phase corresponds to the confined phase connected with the bulk nematic (N) phase: we are observing the usual capillary IN transition line.

The S phase, therefore, is not a genuine phase different from the confined I phase: whether the two nematic films are in contact or not will depend on conditions such as wetting strength and departure from bulk coexistence (determining film thickness) of the particular material/surface. What we can say is that the optimum conditions to observe a ‘true’ S phase, with an intervening defective region of molecular thickness where the tilt angle changes abruptly (see Fig. 1), involve nematic wetting at both substrates, sufficiently narrow pore widths and sufficiently developed nematic layers adsorbed at the two substrates (or equivalently, closeness to the bulk phase transition). Both conditions may play against univocal experimental verification. These observations are implicit in the recent paper by Chiccoli et al. [8] who performed Monte Carlo simulations on a (lattice) Lebwohl–Lasher model. However, the authors established a maximum cell thickness in which the S phase could be found. Our results rather suggest that: (i) the S phase can be found for any value of cell thickness, (ii) the SL transition continues to bulk as the true capillary transition, and (iii) wetting properties, along with closeness to bulk transition and pore width, determine whether a ‘true’ step–like phase can be observed or not.

The central result of our analysis is that the SL transition line may in some cases interact with the anchoring phase transition occurring in the semiinfinite case, in the weak anchoring regime, when the chemical potential is varied [state (2’) in Fig. 2]. In our model, the anchoring transition in substrate 2 becomes a UL phase transition in the confined system, but this transition is genuinely different from the SL transition; the two can be present at the same time and may in fact interact in some cases in the regime of very narrow pores. This is illustrated in Fig. 3(b), which shows the phase diagram for a case pertaining to complete and partial wetting by nematic, respectively, but with an anchoring transition occurring in the latter substrate. In this case a ULS triple point actually occurs. However, other scenarios, where e.g. the SL and UL lines do not meet, may be possible. Also, in the strong anchoring regime, where no anchoring transition exists in the semiinfinite system, a confinement–induced anchoring (UL) transition could exist for narrow pores [4]; Fig. 5.
presents a summary of possible scenarios that can actually be obtained by our theoretical model.

Rodríguez–Ponce et al. [16, 17] have analysed a related system using a simplified version of density–functional theory. However, their system is crucially different in that the isotropic phase wets the substrate that undergoes the anchoring transition; the result is that the capillary isotropic–nematic phase transition is suppressed, and capillary and anchoring transitions never occur at the same time in the weak anchoring regime: no interaction between the two is possible. For the same reason, the U phase is never stabilised and the transition in the confined system always proceeds between the S and L phases. Suppression of the capillary transition is expected whenever the isotropic phase preferentially adsorbs on (or wets) one of the substrates [16] (so that one of the nematic phases, either homeotropic or planar, becomes irrelevant) or the director orientation of the planar nematic film is random [18], the phenomenology being similar to that in magnetic systems [15] (with some variations related to elastic effects).

In summary, we have presented a scenario, based on a microscopic model, for the phase equilibria of a liquid–crystal film subject to opposite anchoring energies in a planar cell. The different possible director structures, their phase boundaries and their relation to the bulk and anchoring transitions of the corresponding system adsorbed on a single substrate, have been discussed. We believe our work clarifies recent analyses on the hybrid cell, based on phenomenological approaches, Monte Carlo simulation on a lattice spin model, and density–functional theory. Therefore our work presents a unified picture of the capillary phenomena occurring in a hybrid cell, linking phenomena such as the SL transition to capillary nematicization, wetting and anchoring.

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In our system anchoring at the free isotropic–nematic interface is planar, and the homeotropically–oriented nascent wetting nematic film will change to a linearly distorted configuration, with a faster growth rate (from logarithmic to power law) on approaching coexistence; of course this does not invalidate our argument. See D. E. Sullivan and R. Lipowsky, Can. J. Chem. 66, 553 (1988); T. J. Sluckin and A. Poniewierski, Mol. Cryst. Liq. Cryst. 179, 349 (1990); F. N. Braun, T. J. Sluckin and E. Velasco, J. Phys.: Condens. Matter 8, 2741 (1996).

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The S phase may have been observed already in the recent surface–force–apparatus measurements of Zappone et al. [11], who probed nematic films under homeotropic/planar hybrid conditions. At very short film thicknesses (< 10 nm) the force between the surfaces becomes strongly attractive, a signature that, according to the authors, may point to a film reconstruction into a step–like phase.
FIG. 1: Geometry used for the calculations and director configurations for the three possible phases inside a hybrid cell. The U phase, here represented with homeotropic orientation, may also have planar orientation, depending on the relative anchoring energies of the two antagonistic substrates.
FIG. 2: Interfacial phase diagram of the single–substrate model. ∆µ is the chemical potential relative to bulk coexistence and W the surface strength. ⊥ and || indicate nematic bulk director configurations perpendicular (homeotropic) and parallel to substrate, respectively. Thick lines are wetting transitions. Thin lines are anchoring and prewetting transitions for substrate 2. (1) is the state chosen for substrate 1 (complete wetting and strong anchoring) whereas (2) and (2') are two states for substrate 2 considered in the text.

FIG. 3: Interfacial phase diagram in the chemical potential ∆µ vs. pore width h plane, for values of the surface strengths (a) \( W_1 = -1kT, W_2 = 3kT \), and (b) \( W_1 = 0, W_2 = 0.35kT \). Points p and q in (a) are the two coexistence points for which order–parameter and tilt–angle profiles are shown in Fig. 4 as discussed in the text. Open circles are surface critical point.
FIG. 4: Uniaxial order–parameter $\eta(z)$ and tilt–angle $\psi(z)$ profiles for the two film structures that coexist at points p (a and c) and q (b and d) in the phase diagram of Fig. 3(a). Continuous line: S phase; dotted line: L phase. In (d) the tilt angle profile in the isotropic region is not plotted since it cannot be defined.
FIG. 5: Possible phase diagrams for confined films in hybrid cell (schematic). (a) Single SL transition with strong anchoring conditions on both surfaces. (b) Additional U phase and associated UL (confinement–induced) anchoring transition when one anchoring energy weaker than the other. (c) Additional anchoring transition when corresponding substrate is in weak anchoring regime. (d) Two anchoring transition lines, UL and U’L, the first continued from the bulk and the second induced by confinement when at least one substrate is in weak anchoring regime. Fig. 3(b) pertains to case (c) where the two transition lines meet at a triple point.