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Nonspontaneous surface-induced nematic phase

I. Lelidis*
Laboratoire de Physique de la Matière Condensée, Université de Picardie, 33 rue Saint-Leu, 80039 Amiens cedex, France

P. Galatola†
LBHP, Université Paris 7—Denis Diderot et Fédération MSC, FR CNRS 2438, Case 7056, 2 place Jussieu,
F-75251 Paris cedex 05, France

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By means of a Landau–de Gennes mean field model, we predict the existence of a nonspontaneous surface nematic phase in a smectogenic compound in contact with a suitable solid substrate. In the bulk the system does not show any nematic phase, the latter being solely induced by the substrate–liquid crystal interaction. Depending on the strength of the surface potential, a prewetting line, terminating at a critical point, may appear. For strong enough coupling, a new surface smectic phase can be induced, accompanied by a reentrant behavior. Our analysis might explain some recent experimental results [T. Moses, Phys. Rev. E **64**, 010702(R) (2001)]: to validate it we suggest possible further experimental investigations.

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Interfacial ordering phenomena, and especially wetting and surface transitions [1,2], have been predicted and observed in many physical systems such as isotropic liquids [3,4], magnetic materials [5,6], superconductors [7], binary mixtures [8,9], binary alloys, ferrofluids [10], polymers, and liquid crystals [11]. In liquid crystals (LC), interfacial phenomena display a rich variety and complexity because of their long-range orientational order, that couples with positional order in smectic phases [12]: roughening, wetting [13,14], dewetting, surface melting [15], anchoring transitions [16,17], memory effects [18], symmetry breaking Berezinskii-Kosterlitz-Thouless (BKT) transitions [19–21], wetting transitions [22], layering transitions [23,24], and other surface phase transitions [25,26]. In recent years, they have attracted special attention because of the variety of exciting physical behaviors and their crucial significance in improving the performance of LC devices [27,28]. Attention has been mostly paid to anchoring and wetting effects. Orientational and positional wetting have been studied at the liquid crystal-solid interface, for homeotropic [29] and planar anchoring conditions [30], and at the free surface [31] of the isotropic (I) phase. Dewetting [32], nonwetting, partial and complete wetting, as well as the prewetting transition from partial to complete wetting [33] and discrete layer by layer transitions have been experimentally observed [23,24,34]. The effects of an external bulk field on wetting and on the prewetting transition have been investigated only theoretically [35,36]. Anchoring [17] and anchoring transitions between states of different tilt angles have been extensively studied [37,38]; here the experimental and theoretical situations are not yet clear: the interplay between anchoring and wetting transitions [39] has only recently started to be elucidated [40,41].

Apart from the wetting and anchoring transitions, LCs may exhibit a variety of *surface phase transitions* that eventually could influence anchoring and wetting effects. As phase transitions in two- and three-dimensional systems are not located at the same place in the phase diagram space, the onset of a lower symmetry LC phase may first appear in a thin surface layer in contact with a substrate, while the bulk remains in a higher symmetry phase. Such a transition is the onset of a surface layer with orientational [13,14] or positional [25] order, while the bulk remains in the isotropic or nematic (N) phase. Another type of surface phase transition is the uniaxial-biaxial nematic BKT transition [19–21]. The interaction potential between the LC and the substrate could also induce *new* phases nonexisting at all in the bulk. These new phases could correspond to bulk nonspontaneous phases induced by an external field. In the case of the I to smectic-A (SmA) bulk phase transition it is now well established that an external field may induce a nonspontaneous nematic (NSN) phase in the sample volume [42,43].

Recently, Moses [44] experimentally studied the interfacial ordering in decylcyanobiphenyl (10CB), undecylcyanobiphenyl (11CB), and dodecylcyanobiphenyl (12CB) above the I-SmA transition, at a rough substrate inducing homeotropic alignment. He found partial wetting for 10CB, with an interfacial ordering significantly lower than the SmA bulk phase. This suggests that in the interfacial region a surface NSN phase is induced. In this work we show how such an NSN phase could be induced by the interface interaction potential. This phase exists only for LC compounds having a not too strong coupling between nematic and smectic order. For higher surface couplings we also find a new smectic surface phase showing a reentrant nematic behavior.

We consider a thermotropic liquid crystal undergoing a direct I-SmA transition on lowering the temperature T. In the SmA phase, elongated molecules with long-range orientational nematic order form layers orthogonal to the average molecular orientation, the nematic director $\mathbf{n}$. In a first approximation, the molecular density ρ is spatially modulated

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*Electronic address: Ioannis.Lelidis@u-picardie.fr

†Electronic address: galatola@ccr.jussieu.fr

according to $\rho=\rho_0[1+(1/\sqrt{2})\,\psi\cos(q_s z-\phi)]$, where ρ_0 is the average density, $2\pi/q_s$ is the layer thickness, and z is an axis parallel to **n**. The complex order parameter $\psi\exp(i\phi)$ gives the amplitude and the phase of the smectic ordering. The orientational nematic order can be described by the symmetric traceless tensor $Q_{ij}=S(3n_in_j-\delta_{ij})/2$, where the n_i $(i=1,2,3)$ are the Cartesian components of **n**, δ_{ij} is the Kronecker delta, and $-1/2\leqslant S\leqslant 1$ is the scalar order parameter that specifies the degree of nematic order.

In the absence of elastic distortions and biaxiality, we describe the system by the mean-field Landau–de Gennes free-energy [12]

$$\mathcal{F}_{\text{bulk}}=\int\left[f_N(T,S)+f_A(T,\psi)+f_{AN}(S,\psi)+\frac{1}{2}L_N(\boldsymbol{\nabla}S)^2+\frac{1}{2}L_A(\boldsymbol{\nabla}\psi)^2\right]d^3r. \tag{1}$$

Here $f_N(T,S)$ and $f_A(T,\psi)$ are the homogeneous nematic and smectic free-energy densities, respectively, and $f_{AN}(S,\psi)$ is a coupling term. We take them in the form

$$f_N(T,S)=\frac{1}{2}a_N(T-T_N^*)S^2+\frac{1}{3}b_NS^3+\frac{1}{4}c_NS^4, \tag{2a}$$

$$f_A(T,\psi)=\frac{1}{2}a_A(T-T_A^*)\psi^2+\frac{1}{4}c_A\psi^4, \tag{2b}$$

$$f_{AN}(S,\psi)=\gamma S\psi^2+\frac{1}{2}\lambda S^2\psi^2, \tag{2c}$$

where T_N^* and T_A^* are the supercooling temperature limits of the isotropic and nematic phases, respectively. In order to induce a direct *I*-Sm*A* transition, a sufficiently strong coupling constant γ is required [43]. The saturation term proportional to λ allows for reentrant nematic behavior. The elastic constants L_N and L_A are related to the nematic elastic constant K and to the smectic compressibility modulus B according to the relations $K=L_NS^2$, $B=L_A\psi^2q_s^2$. Since the characteristic length $\sqrt{K/B}$ is of the order of the interlayer spacing $2\pi/q_s$ [12], then $L_A/L_N\sim(S/\psi)^2\sim 1$. In our analysis we therefore set $L_A=L_N$.

We consider a semi-infinite sample filling the half space $z\geqslant 0$, in contact with a solid boundary at $z=0$ that enhances the nematic order [11]. At lowest order, this enhancement can be described by the surface contribution [14]

$$\mathcal{F}_s=-w\int S(z=0)\,dx\,dy, \tag{3}$$

with $w>0$. We suppose that the surface induces a homogeneous homeotropic anchoring: therefore, no biaxiality nor elastic distortions are excited. In the Sm*A* phase the smectic layer will grow parallel to the surface. For simplicity, we do not take into account surface couplings with the smectic order: this might correspond to the case of a rough surface. In the discussion we will briefly comment on this point.

We introduce the normalized temperature

$$t=\frac{T-T_N^*}{T_{NI}-T_N^*}, \tag{4}$$

where $T_{NI}=T_N^*+2b_N^2/(9a_Nc_N)$ is the nematic-isotropic transition temperature, and the normalized nematic surface coupling constant

$$h=\frac{w}{\sqrt{2a_NL_N(T_{NI}-T_N^*)}}. \tag{5}$$

Then, scaling lengths to the nematic coherence length

$$\xi=\sqrt{\frac{L_N}{2a_N(T_{NI}-T_N^*)}}, \tag{6}$$

the minimization of the total free energy $\mathcal{F}_{\text{bulk}}+\mathcal{F}_s$ leads to the Euler-Lagrange equations defining the equilibrium order parameter profiles $S(z)$ and $\psi(z)$,

$$\frac{d^2S}{dz^2}=\frac{1}{2}\left[tS+\frac{9}{2}\gamma_NS^2+\frac{9}{2}\gamma_N^2S^3+\Gamma\psi^2+\Lambda S\psi^2\right], \tag{7a}$$

$$\frac{d^2\psi}{dz^2}=\frac{1}{2L}\left[\alpha(t-t_A^*)\psi+\gamma_A\psi^3+2\Gamma S\psi+\Lambda S^2\psi\right], \tag{7b}$$

with the boundary conditions

$$\left.\frac{dS}{dz}\right|_{z=0}=-h, \tag{8a}$$

$$\left.\frac{dS}{dz}\right|_{z=\infty}=\left.\frac{d\psi}{dz}\right|_{z=0}=\left.\frac{d\psi}{dz}\right|_{z=\infty}=0. \tag{8b}$$

The normalized parameters appearing in Eqs. (7) are defined as follows:

$$\gamma_N=\frac{c_N}{b_N}, \tag{9a}$$

$$\gamma_A=\frac{c_A}{a_N(T_{NI}-T_N^*)}, \tag{9b}$$

$$t_A^*=\frac{T_A^*-T_N^*}{T_{NI}-T_N^*}, \tag{9c}$$

$$\alpha=\frac{a_A}{a_N}, \tag{9d}$$

$$\Gamma=\frac{\gamma}{a_N(T_{NI}-T_N^*)}, \tag{9e}$$

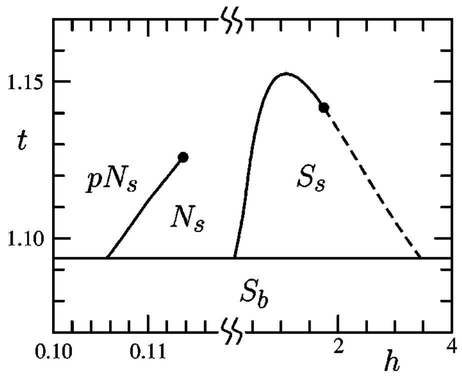

FIG. 1. Surface phase diagram in the plane of the reduced surface nematic coupling h and of the reduced temperature t. pN_s, surface paranematic phase; N_s, nonspontaneous surface nematic phase; S_b, bulk smectic phase; S_s, surface smectic phase. The continuous lines correspond to first-order transitions, the dashed one to a second-order transition.

$$\Lambda=\frac{\lambda}{a_N(T_{NI}-T_N^*)}, \tag{9f}$$

$$L=\frac{L_A}{L_N}. \tag{9g}$$

We solve the boundary value problem (7),(8) numerically, by means of a finite difference scheme with deferred correction and Newton iteration [26,45]. When multiple solutions are present, we chose the one corresponding to the minimum free energy.

For the Landau coefficients in Eqs. (2) we use the typical values given in Ref. [42]: $a_N=0.2\times10^7$ erg/K cm^3, $b_N=-1.85\times10^7$ erg/cm^3, $c_N=2.5\times10^7$ erg/cm^3, $a_A=0.13\times10^7$ erg/K cm^3, $c_A=0.25\times10^7$ erg/cm^3, $\gamma=-0.5\times10^7$ erg/cm^3, $\lambda=0.65\times10^7$ erg/cm^3, and $T_N^*-T_A^*=0.5$ K. For this choice of parameters, in the bulk a *direct I*-Sm*A* transition occurs, *without any intervening nematic phase*. Considering the reduced temperature t and the reduced surface nematic coupling h as free parameters, we obtain the surface phase diagram shown in Fig. 1. At high enough temperature, a paranematic order appears close to the surface and vanishes on a thickness of the order of ξ: on the surface the bulk isotropic phase is replaced by a surface paranematic phase. Therefore, the surface field h somehow acts like an external (electric or magnetic) orienting field [42]. For low nematic coupling h, by reducing t a direct paranematic–smectic-A transition occurs at the surface, at the same temperature as the bulk transition. By increasing the surface coupling h, a *nonspontaneous* surface nematic phase is induced. This phase corresponds to a jump of the surface nematic order $S_0\equiv S(z=0)$ as the temperature is decreased, while the smectic order parameter $\psi(z)$ remains zero, as shown in Fig. 2. The surface paranematic phase and the nonspontaneous surface nematic phase are separated by a prewetting line that terminates at a critical point. This is reminiscent of the prewetting behavior of the direct isotropic-nematic bulk transition [14,33]. Further reducing t, we retrieve the bulk transition toward the smectic phase. For higher nematic coupling h, a surface smectic phase appears. It is induced by the $S\psi^2$ bulk coupling term in Eq. (2c). This surface smectic phase disappears for even higher values of h, giving rise to a reentrant nonspontaneous surface nematic phase. This behavior originates from the saturation bulk term $S^2\psi^2$, which is known to be responsible for reentrant nematic behavior in the bulk [43]. The reentrancy appears either through a second-order or a first-order transition, as it can occur in the bulk [46]. The character of the transition changes at a surface tricritical point.

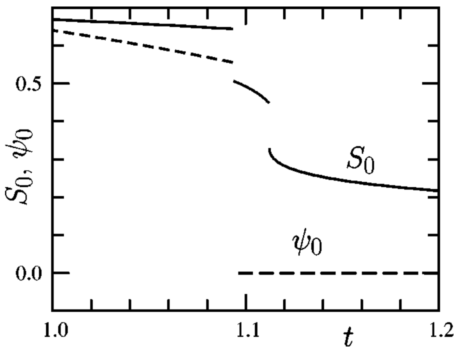

FIG. 2. Behavior of the surface order parameters $S_0=S(z=0)$ (full line) and $\psi_0=\psi(z=0)$ (dashed line) as a function of the reduced temperature t for the surface field $h=0.11$ in Fig. 1.

The appearance of a nonspontaneous nematic phase due to the surface coupling is similar to the nonspontaneous nematic phase induced in the bulk by an external field. In particular, as in the bulk case, the prewetting line disappears when the bulk coupling between the two order parameters becomes too strong.

The above predictions about the existence of a surface nonspontaneous nematic phase might explain the experimental results of Moses [44]. A possible candidate for observing these various surface transitions is an octylcyanobiphenyl (8CB)-10CB mixture with varying concentrations, in order to continuously change the surface coupling. In fact, this choice of mixture is known to give rise to a field-induced nonspontaneous nematic phase [42] and allows us to avoid even-odd alkyl-chain length effects. The surface properties may also be varied by, e.g., depositing a controlled number of surfactant monolayers.

We note that in our analysis we have not taken into account any direct coupling between the surface and the smectic order that might either enhance or suppress the smectic order. As a consequence, we find that the isotropic–smectic-A transition in the bulk is always accompanied by a corresponding smectic transition at the surface. Including this coupling, we expect a temperature shift between the bulk and the surface transition [26], the latter eventually disappearing at, e.g., a tricritical point. Such an analysis is beyond the scope of our work and should not qualitatively alter the surface phase diagram. Finally, we note that the prewetting line is preempted by the bulk isotropic–smectic-A transition when the $S\psi^2$ bulk coupling term is too strong.

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