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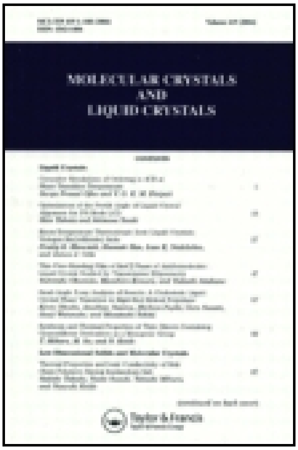

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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SURFACE-INDUCED PHASES IN SMECTOGENIC COMPOUNDS

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Version of record first published: 07 Jan 2010

To cite this article: I. Lelidis & P. Galatola (2004): SURFACE-INDUCED PHASES IN SMECTOGENIC COMPOUNDS, Molecular Crystals and Liquid Crystals, 413:1, 145-150

To link to this article: http://dx.doi.org/10.1080/15421400490437213

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Mol. Cryst. Liq. Cryst., Vol. 413, pp. 145/[2281]–150/[2286], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490437213

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By using a Landau-de Gennes mean-field phenomenological model, we discuss the possibility of inducing parasmectic and surface smectic phases in a smectogenic compound in contact with a rough substrate enhancing the nematic order. A rich variety of behaviors is obtained, depending in particular on the bulk coupling between the nematic and the smectic order. Such transitions are reminiscent of the bulk transitions that can be induced by the application of an external electric or magnetic field.

PACS numbers: 64.70.Md, 68.35.Md, 64.10.+h

I. INTRODUCTION

Surface effects in liquid crystals, such as anchoring [1] and wetting [2], are of great interest both from an applicative and a fundamental point of view. Amongst a rich variety of wetting effects, surface-induced phase transitions have attracted considerable attention since the seminal theoretical works of Ping-Sheng [3,4]. He predicted that a suitable substrate, enhancing the nematic order, could induce a surface nematic transition at a temperature higher than the bulk clearing point. According to this model, the penetration length of the surface nematic phase can remain finite or

Dated 14 November 2002.
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diverge at the bulk clearing point. These two regimes correspond to partial or complete wetting, respectively. They are separated by a prewetting transition terminating at a critical point. The first observation of a substrate-induced nematic phase was reported by Miyano [5], while the prewetting transition has been observed only recently [6]. The surface couples to the bulk by means of an effective potential that is reminiscent of an external electric or magnetic field. This suggests a correspondence between surface and field-induced transitions. In fact, a field-induced paranematic-nematic transition, terminating at a critical point, has been experimentally observed [7]. Moreover, in the case of smectogenic compounds, it was observed the possibility to induce a *non-spontaneous* nematic phase by means of an external electric field [8]. For higher fields, a smectic phase is induced. A complete theoretically analysis of the various possible transitions was performed in [9]. The above-cited correspondence between field and surface-induced transitions suggests that similar non-spontaneous phases could be induced by a surface. In the field case, the transitions are induced by a direct coupling between the external field and the nematic order-parameter S, the direct coupling with the smectic order-parameter ψ, corresponding to electrostriction, being negligible. In the surface case, such a coupling with S might be achieved by a rough surface: this case has not been analyzed yet.

Since the pioneering experimental works of Ocko and coworkers [10] on the smectic layering transitions, the interaction of a smectogenic compound with a substrate has been extensively studied both from an experimental and a theoretical point of view (see e.g., Refs. [11] and [12] and references cited in [13] and [14]). The attention has been focused on microscopically flat substrates favoring the epitaxial growth of smectic layers. Here, on the other hand, we analyze the case of a rough substrate that does not couple to the smectic order, to analyze the role of the coupling between the smectic and the nematic order in the bulk on interfacial transition. In the following we will analyze some of the possible scenarios, concentrating our attention to the case in which the bulk presents a direct isotropic-smectic-A transition.

II. LANDAU-DE GENNES MODEL

In the absence of elastic distortions, we describe the degree of nematic order by means of the scalar order parameter S. When a smectic-A phase appears, the additional positional ordering is characterized by the order-parameter ψ, which gives the amplitude of the modulation of the molecular density. In the following, we will suppose that the smectic ordering does not interact directly with the substrate, such that the phase of the smectic

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order will not intervene. In the bulk, we take the free-energy of the system in the form of the mean-field Landau-de Gennes expression [15]

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

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. They are given by

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

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

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

where T_N^* and T_A^* are the temperatures of the virtual second-order transitions toward the nematic and smectic phase, respectively. In order to induce a direct isotropic-smectic-A transition, a sufficiently strong coupling constant γ is required [9]. The saturation term proportional to λ allows for reentrant nematic behavior. The elastic constants L_N and L_A are proportional to the nematic elastic constants and to the smectic compressibility modulus. Since they are of the same order of magnitude [13], for simplicity in our analysis we will set $L_A = L_N$.

We consider a semi-infinite sample filling the half space $z \geq 0$, in contact with a solid boundary at $z = 0$ that promotes a nematic order with homogeneous homeotropic anchoring [5]. At lowest order, we describe the enhancement of the nematic order by the surface contribution [4]

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

with $w > 0$. The minimization of the total free-energy $\mathcal{F}_{\mathrm{bulk}} + \mathcal{F}_s$ leads to the Euler-Lagrange equations defining the equilibrium order parameter profiles $S(z)$ and $\psi(z)$

$$L_N \frac{d^2 S}{dz^2} = \frac{\partial f}{\partial S}, \tag{4a}$$

$$L_A \frac{d^2 \psi}{dz^2} = \frac{\partial f}{\partial \psi}, \tag{4b}$$

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with the boundary conditions

$$L_N \frac{ds}{dz}\bigg|_{z=0} = -w, \tag{5a}$$

$$\frac{dS}{dz}\bigg|_{z=\infty} = \frac{d\psi}{dz}\bigg|_{z=0} = \frac{d\psi}{dz}\bigg|_{z=\infty} = 0. \tag{5b}$$

In Eqs. (4), $f = f_N(T,S) + f_A(T,\psi) + f_{AN}(S,\psi)$ is the total bulk homogeneous free-energy density.

III. ANALYSIS

We solve the boundary value problem (4)–(5) numerically; when multiple solutions are present, we chose the one corresponding to the minimum free-energy. A very reach variety of surface phases and surface transitions may be obtained, depending on the surface nematic coupling w and on the bulk nematic-smectic coupling coefficients γ and λ. In particular, a non-spontaneous surface nematic phase has been predicted [14]. Here, we show that, when the bulk nematic-smectic coupling is sufficiently strong, para-smectic and surface smectic phases can be excited, even if the surface does not directly enhances the smectic order.

For a moderate bulk nematic-smectic coupling, we consider in Eq. (2) the typical values: $a_N = 0.2 \times 10^7 \mathrm{erg/K\,cm^3}$, $b_N = -3 \times 10^7 \mathrm{erg/\,cm^3}$, $c_N = 4 \times 10^7 \mathrm{erg/\,cm^3}$, $a_A = 0.05 \times 10^7 \mathrm{erg/K\,cm^3}$, $c_A = 0.3 \times 10^7 \mathrm{erg/\,cm^3}$, $\gamma = -0.25 \times 10^7 \mathrm{erg/cm^3}$, $\lambda = 0.33 \times 10^7 \mathrm{erg/cm^3}$, $T_{NI} - T_A^* = 2\,\mathrm{K}$, where $T_{NI} = T_N^* + 2b_N^2/(9a_N c_N)$ is the nematic-isotropic transition temperature. For this set of parameters, a paranematic to surface-smectic transition appears, followed by the transition to the bulk smectic phase. The corresponding behaviors of the surface nematic order $S_0 = S(z=0)$ and of the surface smectic order $\psi_0 = \psi(z=0)$, as a function of the reduced temperature $t = (T - T_N^*)/(T_{NI} - T_N^*)$ are shown in Figure 1 for two different surface couplings w. For low surface coupling ($w = 0.34\,\mathrm{erg/cm^2}$, lower curves), on cooling a first-order paranematic ($S_0 \neq 0, \psi_0 = 0$) to surface smectic ($S_0 \neq 0, \psi_0 = 0$) phase first occurs. On further cooling, the bulk isotropic-smectic-A transition drives a first-order transition on the surface toward a bulk-like smectic phase. When the surface coupling is larger ($w = 0.5\,\mathrm{erg/cm^2}$, upper curves), the first-order paranematic to surface-smectic transition becomes second order. This indicates the presence of a tricritical point in between.

As representative parameters for a system having a larger bulk nematic-smectic coupling we choose $a_A = 0.02 \times 10^7 \mathrm{erg/cm^3}$, $c_A = 0.5 \times 10^7 \mathrm{erg/\,cm^3}$, $\gamma = -0.2 \times 10^7 \mathrm{erg/cm^3}$, $\lambda = 0.27 \times 10^7 \mathrm{erg/cm^3}$, with the other

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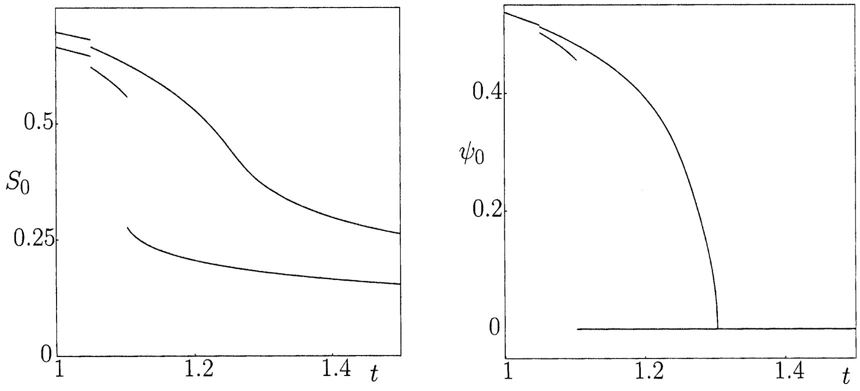

FIGURE 1 Surface nematic order-parameter S_0 and surface smectic order ψ_0 as a function of the reduced temperature t for moderate bulk nematic-smectic coupling. A paranematic to surface smectic transition appears: for $w = 0.34\,\text{erg/cm}^2$ (lower curves) it is first-order; for $w = 0.5\,\text{erg/cm}^2$ (upper curves) it becomes second-order.

parameters as before. With this set of parameters, the bulk isotropic-smectic-A transition occurs for a slightly higher temperature than the previous case. The corresponding sequence of surface transitions is shown in Figure 2. When the surface coupling is low ($w = 0.3\,\text{erg/cm}^3$, lower curves), on cooling a second-order paranematic to surface parasmectic

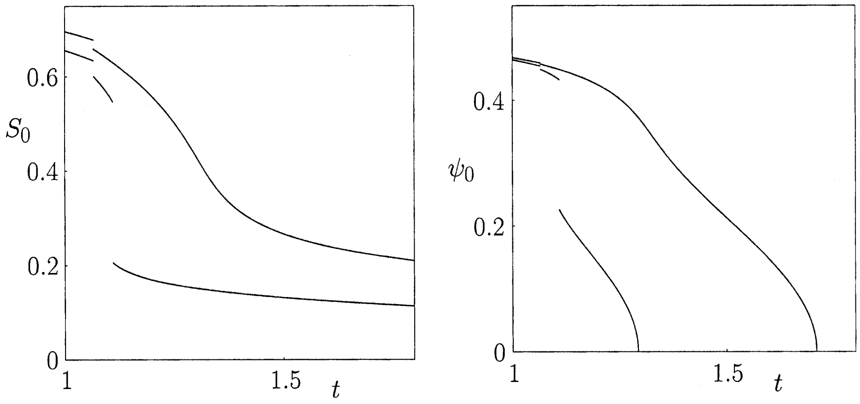

FIGURE 2 As Figure 1 but for stronger bulk nematic-smectic coupling. Lower curves: $w = 0.3\,\text{erg/cm}^2$; a first-order parasmectic to surface transition occurs on cooling. Upper curves: $w = 0.5\,\text{erg/cm}^2$; the first-order parasmectic to surface smectic transition has disappeared.

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transition occurs. Cooling further, a first-order transition to a surface smectic phase takes place. Finally, the bulk smectic transition drives a first-order smectic transition at the surface. Increasing the surface coupling $w = 0.5\,\mathrm{erg/cm^2}$, upper curves, the first-order parasmectic to surface smectic transition disappears. This indicates the existence of a critical point in between.

IV. CONCLUSIONS

To conclude, we have shown that a compound showing a direct isotropic-smectic-A transition in the bulk, when in contact with a substrate enhancing the nematic order can display a rich variety of surface phases. In particular, a surface parasmectic phase and a surface smectic phase can appear. When the surface smectic phase is followed at higher temperature by a paranematic phase, a surface transition always occurs. The order of the transition changes from first to second-order as the surface coupling is increased. When the surface smectic phase is followed at higher temperature by a parasmectic phase, a first-order transition can only be present at most. It terminates at a critical point as the surface coupling is increased. The parasmectic phase appears only for a sufficiently strong bulk nematic-smectic coupling. Similar behaviors have been predicted for bulk phases in the presence of an external electric or magnetic field [9] and partially observed [8]. Up to now, no parasmectic phases have been observed: mixtures of nCB compounds with $n \geq 10$ might be good candidates.

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