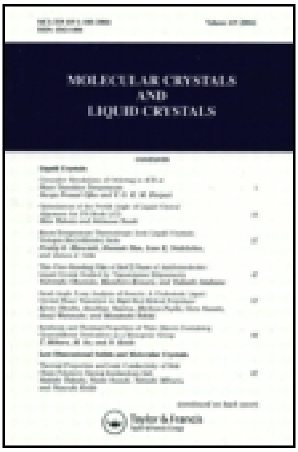

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A LANDAU - de GENNES MODEL FOR THE TEMPERATURE SURFACE TRANSITION IN NEMATICS

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Abstract Recently a surface transition driven by the temperature in nematics has been observed and discussed [K. Flatischler et al., Mol. Cryst. Liq. Cryst. **198**, 119 (1991)]. Such a transition usually appears some degrees below the clearing point: it consists of a change of alignment in the whole nematic layer, from homeotropic to planar, on heating. The transition could be second or first order, depending on surface treatment and bulk properties and is reversible: in the latter case hysteresis takes place. The importance of such a phenomenon is evident, since the temperature surface transition affects the electro-optical properties of a nematic cell. Here we present a new Landau-de Gennes model describing the surface transition which occurs when the cell walls, covered by a thin layer of silicon monoxide, are dipped in a very dilute solution of egg-lecithin in chloroform.

INTRODUCTION

The liquid crystal - solid substrate interactions are usually described in terms of an easy direction $\mathbf{n}_o$ and anchoring strength coefficients. In the absence of bulk torque, the easy direction is coincident with the surface nematic orientation. The phenomenon, "surface transition in nematics", refers to the case where $\mathbf{n}_o$ changes with the temperature. Experimental data of this temperature dependence are available in the literature. Since the pioneering paper of Langevin-Crouchon [1] on the liquid crystal - air interface, other experiments have been performed by different groups [2-4]. The main characteristic of these experiments is that the interface divides the nematic from the isotropic medium.

The aim of these works was to stress that the temperature dependence of the tilt angle at the free surface was a continuous function and that no evidence of sharp transition in the tilt angle orientation was found. A simple phenomenological expression for the surface energy, able to explain the experimental data and to predict a temperature driven surface transition, was proposed a few years ago by Sluckin et al. [5], and more recently in Ref.[6]. In this model, the surface free energy is constructed by taking into account the symmetry of the nematic bulk and the surface; the latter is characterized only by its geometrical normal. The above mentioned phenomenological model can be justified by means of a quasi-microscopic calculation, as shown by Sen et alt. [7]. The most important characteristics of the phenomenological model proposed in Refs. [5-6] are that:

i. it does not contain linear terms in the nematic director, contrary to the model suggested by Parson [8];
ii. the temperature dependence of the easy direction is connected with the dependence of the anchoring strength coefficients on the nematic scalar order parameter S. One of the anchoring parameters is linear in S, whereas the other is quadratic [9].

In this model the important physical properties related to the surface transition are due to the nematic liquid crystal: the nematic liquid crystal can either exhibit a surface transition or not.

An improvement of such a model was presented by Teixeira et al. [10]. The authors allow for spatially varying tilt angle and order parameter (at least close to the surface). The surface transition is explained as a competition between the solid surface and the interface bulk - incipient wetting film of the nematic liquid crystal. Recently a new kind of surface transition induced by the surfactant has been observed and interpreted in terms of a simple model [11-12]. In this case the surface of glass substrate is covered by thin egg-lecithin layer. Our experimental results show that, whatever is the liquid crystal, if the deposited lecithin layer is promoting a homeotropic alignment of the liquid crystal at certain temperature, then a surface induced alignment transition can be detected at higher temperature (see fig.1). This implies that the lecithin is responsible for the surface transition, and the liquid crystal simply indicates it. Such an instability was analysed some years ago by Safran et al. [13], in the case of a lecithin monolayer deposited on the glass substrates.

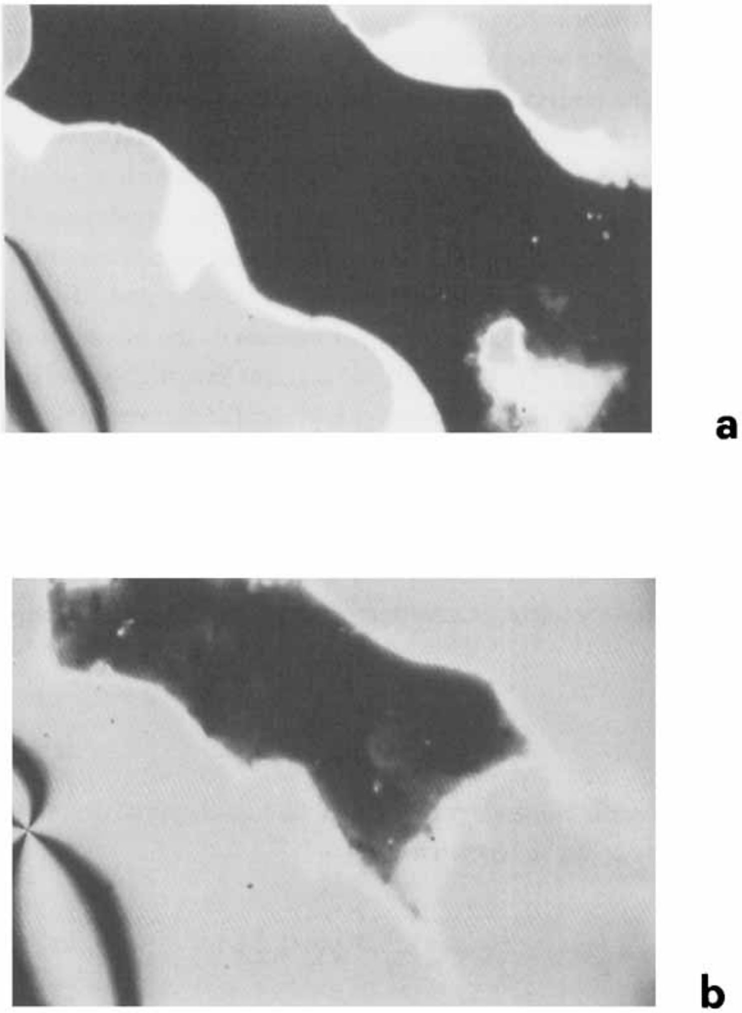

Fig.1 Surface transition from a homeotropic to a planar alignment occurring on heating a few degrees (a) 93.3°C, b) 93.8°C) below the clearing point (99.5°C). The cell, 12μm thick, with inner surfaces covered by thin lecithin layer, was filled with ZLI2806. The black area corresponds to homeotropic alignment. See Color Plate IV.

In Ref.[13] it is shown that the energy of the surfactant monolayer can be evaluated as a function of the orientation of the flexible tails of the molecules at the surface. The structure of the orienting monolayer is determined by a competition between the spacing preferred by the polar heads and the non-polar tails. Analysis shows that, by varing the temperature, the stable orientation of the surfactant changes, and as does the nematic alignment in the bulk, which is driven by the surface layer. In the present experimental arrangement, we were not able to control the number of monolayers of lecithin onto the glass surface, since lecithin deposition was made by dipping the glass substrates into a solution of lecithin in chloroform. Consequently the model of Ref. [13] has to be changed. To interpret our experimental data, we present a modified version of the model proposed a few years ago by Känel et al. [14], by taking into account the order - electric polarization [15]. According to Ref.[14] a smectic order is present at the nematic - solid substrate interface, whose density wave amplitude ψ [16] decreases exponentially with distance. In our model the smectic ordering is relevant essentially to the layer of the lecithin molecules: the nematic phase in the bulk is then oriented by steric interactions. Below we will propose and discuss our model, which explains the observed temperature surface transition due to surface smectic ordering.

THEORY

The excess distortion free energy density in the liquid crystal due to the presence of the smectic layer can be written as

$$f = \frac{1}{2} a \, (T - T^{*}) \, \psi^{2} + \frac{1}{4} b \, \psi^{4} - \frac{1}{2} c \, \psi^{2} Q + \frac{1}{2} r^{2} \, \psi^{2} Q^{2} + \frac{1}{2} B \, \psi_{z}^{2} \qquad (1)$$

as shown in Ref. [17] by using phenomenological arguments.

Eq. (1) can be justified from a more fundamental point of view, as discussed recently by Teixeira et al. [18]. In Eq.(1) ψ denotes the maximum amplitude of the smectic wavevector and ψ_z the first derivative of ψ with respect to the normal z to the boundary. T^{*} is the asymptotic nematic- smectic A transition temperature, a, b, c are Landau coefficients and $Q \equiv Q_{zz}$ is the zz component of the nematic tensor order parameter and

$$Q = S\left(\cos^2\theta - \frac{1}{3}\right) \tag{2}$$

where θ is the tilt angle made by the lecithin axis of molecules with the surface normal (**k**) and S is the nematic scalar order parameter. The parameter r^2 takes into account the order-electric properties of the lecithin molecules in the layer [19], which are connected with the molecular quadrupoles. Finally, the last term in Eq.(1) takes into account the elastic properties of the smectic-like surface layer close to the surface. We note again that the source of the instability is the lecithin layer and not the liquid crystal, as observed in our experiment. The smectic excess free energy density may be written, stressing the dependence on ψ^2 and on ψ_z^2, as

$$f = \frac{1}{2}\tilde{A}\ \psi^2 + \frac{1}{4}b\ \psi^4 + \frac{1}{2}B\ \psi_z^2 \tag{3}$$

where

$$\tilde{A} \equiv a\ (T - T^*) - c\ Q + r^2\ Q^2 \tag{4}$$

The first contribution in Eq.(4) prevents the material from being smectic everywhere in the cell for $T \geq T^*$ in the absence of nematic order in the case of materials exhibiting smectic - isotropic transition, provided a is positive. The second term describes the smectic - nematic dipolar coupling, and assumes the form, even in the bulk, of the Rapini-Papoular interaction [20], favoring the homeotropic alignment, if $c > 0$. We note that this must be so, since a flat solid surface with no distinguished in-plane easy directions, forces the director $\mathbf{n}_o$ to be normal to the surface with Smectic A layers parallel to the boundary.

The third contribution gives the smectic - nematic quadrupolar coupling [17]: this effect competes with the previous one, since a quadrupolar distribution close to the boundary favors a planar alignment. We stress that b must be positive for the stability of the smectic phase, and B also must be positive, since the presence of gradients of ψ is energetically unfavorable. Since we are interested in the role of the surface smectic ordering in the temperature anchoring transition, we assume that the tensor order parameter Q describing the nematic order is not positiondependent. Then, considering the cell as a semi - infinite slab of liquid crystal, bounded by the plane z=0, which is the interface with a solid substrate, the Landau - de Gennes free energy of the cell is

$$F = \int_0^{+\infty} f dz + F_s \tag{5}$$

where

$$F_s \equiv \frac{1}{2} W_o \psi_o^2 \tag{6}$$

is the surface energy associated with the smectic ordering, and $\psi_o \equiv \psi(z = 0)$ is the amplitude of the smectic wavevector at the boundary. Eq.(6) is obtained by expanding $F_s(\psi)$ around $\psi = \psi_o$, and keeping only terms up to second order. When W_o is positive, surface smectic ordering is not favored. Minimizing [21] the free energy of Eq.(5) gives

$$\psi_{zz} - \frac{\tilde{A}}{B}\psi - \frac{b}{B}\psi^3 = 0 \tag{7}$$

Despite of the non-linearity of (7), it admits a first integral, since it can be put into the form

$$\psi_{zz} - \frac{1}{B}\frac{df_u}{d\psi} = 0 \tag{7'}$$

where f_u is the uniform part of the excess free energy density f. Hence

$$\psi_z^2 - \frac{2}{B}[f_u(\psi) - f_u(\psi_\infty)] = 0 \tag{8}$$

where $\psi_\infty(T)$ is the equilibrium value of the smectic wavevector amplitude in the bulk.

Since ψ_∞ has to minimize f_u, then

$$\psi_\infty^2 = -\frac{\tilde{A}}{b} \tag{9}$$

and $\tilde{A}$ must be negative, for $T < T^*$, when the smectic phase is present in the bulk. It follows that $f_u(\psi_\infty) = 1/4\ \psi_\infty^2 \tilde{A}$ and finally

$$f_u(\psi) - f_u(\psi_\infty) = \frac{1}{4} b(\psi^2 - \psi_\infty^2)^2 \tag{10}$$

substitution into Eq.(8) gives

$$\psi_z^2 = \frac{b}{2B}(\psi^2 - \psi_\infty^2)^2 \tag{11}$$

Let us suppose that at the boundary the smectic order is higher than in the bulk, $\psi_o > \psi(z)$; in this case, from Eq.(11) we have:

$$\psi_z = -\left\{\frac{b}{2B}\right\}^{1/2} (\psi^2 - \psi_\infty^2) \tag{11'}$$

which can be easily integrated. In fact, we are interested in the case when $T \geq T^*$, and the smectic phase disappears in the bulk; $\psi_\infty = 0$. Then, the solution of Eq.(11') is given by

$$\psi = \frac{\psi_o}{z/\xi + 1} \tag{12}$$

when the smectic penetration length is

$$\xi \equiv \left(\frac{2B}{b}\right)^{1/2} \frac{1}{\psi_o} \tag{13}$$

In fact, expression (12) is an approximation, rigorously valid only for $T > T^*$, with T close to T^*. The actual solution for a finite temperature gap $T - T^* > 0$ is a bilinear function of $\exp(-z/\xi)$, that does not produce substantial changements in the results of the calculation.

The boundary condition $-(\partial f/\partial\psi_z) + \partial F_s/\partial\psi\,|_{z=0} = 0$ gives

$$-B\psi_{zo} + W_o\psi_o = 0 \tag{14}$$

which provides the condition

$$W_o = -\left(\frac{bB}{2}\right)^{1/2} < 0 \tag{15}$$

for favoring smectic order at the solid substrate.

On the other hand, the smectic phase at the surface exists when

$$\frac{\partial F}{\partial\psi_o} = 0 \tag{16}$$

We now calculate the smectic contribution to the free energy F as a function of ψ_o. By substituting Eq.(12) into Eq.(5) and integrating over the entire cell, we obtain for the bulk free energy F_B

$$F_B = \frac{1}{2}\xi\tilde{A}\ \psi_o^2 + \frac{1}{12}\xi b\psi_o^4 + \frac{1}{6\xi}B\psi_o^2 \tag{17}$$

which, making use of Eq.(13), gives

$$F = \left(\frac{B}{2b}\right)^{1/2}\left\{\tilde{A}\psi_o + \frac{1}{3}b\psi_o^3\right\} + \frac{1}{2}W_o\psi_o^2 \tag{18}$$

Minimizing F and using Eq.(15) gives:

$$\frac{\partial F}{\partial\psi_o} = \frac{1}{4}\left(\frac{bB}{2}\right)^{1/2}\left\{\psi_o^2 - 4\psi_o + 4\frac{\tilde{A}}{b}\right\} = 0 \tag{19}$$

i.e.

$$\psi_o = 2\{1 + (1 - \tilde{A}/b)^{1/2}\} \tag{20}$$

for

$$0 \le \tilde{A} \le b \tag{21}$$

When $\tilde{A} = 0$, the smectic phase disappears in the bulk, and at the surface $\psi_o = 4$. As $\tilde{A}$ approaches b, ψ_o approaches to its critical value $\psi_{oc} = 2$, for $\tilde{A} > b$, $\psi_o = 0$.
Hence the temperature of the smectic - nematic transition in the bulk is given by

$$T^{SN} = T^* + \frac{1}{a}(cQ - r^2Q^2) \tag{22}$$

whereas at the surface it is

$$T_o^{SN} = T^{SN} + \frac{b}{a} > T^{SN} \tag{23}$$

The transition is first order. It is remarkable that both transitions depend on the nematic order.
Let us now investigate the orientational transitions. The stability of the homeotropic alignment $\theta = 0$ is characterized by the condition

$$T < T_o^{SN} \tag{24}$$

whereas the planar alignment $\theta = \pi/2$ is stable in the range

$$T_o^{SN} < T < T^{NI} \tag{25}$$

where T^{NI} is the clearing point.
For solving the general problem, the strategy is to minimize the cell free energy $F(\psi, \theta, S)$ with respect to ψ, θ, assuming for S the usual approximate behavior [17]:

$$S = S_o \tau \tag{26}$$

where the reduced temperature τ is given by

$$\tau \equiv \left(1 - \frac{T}{T^{NI}}\right)^{1/2} \tag{27}$$

We obtain

$$\frac{\partial F}{\partial \theta} = -\left(\frac{B}{2b}\right)^{1/2} \psi_o \,(2r^2 Q - c)\, S \sin 2\theta = 0 \tag{28}$$

which implies that $\theta = 0$, $\theta = \pi/2$ are extremals, as is the "magic" angle θ^*, for which $Q = c/2r^2$. The last case just describes the possibility of a smectic C phase, which is not relevant here. Instead, we are looking for the stability of the homeotropic and of the planar alignment.

For this, the behavior of the second derivatives has to be investigated. We obtain

$$\frac{\partial^2 F}{\partial \psi_o^2} = -\frac{1}{2} W_o \psi_o + W_o > 0 \tag{29}$$

in the range $2 < \psi_o \leq 4$, approching zero at the critical point $\psi_{oc} = 2$. Moreover, $\partial^2 F/\partial\psi_o \partial\theta = 0$ identically, whereas

$$\frac{\partial^2 F}{\partial \theta^2} = -\left(\frac{B}{2b}\right)^{1/2} \psi_o \,(2r^2 Q - c)\, 2S \cos 2\theta \tag{30}$$

which provides

$$\frac{\partial^2 F}{\partial \theta^2} > 0 \tag{31}$$

only if $\theta = 0$. In fact, in this case

$$Q = \frac{2}{3} S < \frac{c}{2r^2} \tag{32}$$

So, the polar orientation $\theta = \pi/2$ is unstable in all the range $T < T_o^{SN}$, and will become metastable just at the critical point T_o^{SN}.

CONCLUSIONS

The experimental evidence of a surface orientational transition form homeotropic to planar alignment upon heating was investigated by means of a Landau - de Gennes phenomenological approach, taking into account smectic order induced by a lecithin layer distributed at the boundary. The present model simply explains the observed stability of the homeotropic alignment at lower temperature and the transition to planar alignment at a certain temperature T_o^{SN}, which in our experiment was close to the clearing point T^{NI}. Such a critical temperature T_o^{SN} corresponds to the temperature at which the smectic phase at the surface is destroyed.

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