Surface breaking in lyotropic nematic liquid crystals induced by a magnetic field

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The twist deformation induced by a magnetic field H in a lyotropic liquid crystal is analyzed. Our results show the existence of three regimes for the surface deformation related to two critical values for the external magnetic field. The first, for low magnetic field, is an elastic one in which the surface deformation disappears when the field is removed. In a second regime, a permanent deformation of the lyotropic liquid crystal is induced by the distorting field. This regime is characterized by a threshold for H, called H_c^*. In the third regime, the sample is uniformly oriented along H. Also this regime has a well defined threshold value, H_c^{**}, and the alignment remains even when the distorting field is removed. To interpret the experimental data recently published, we proposed a phenomenological model according to which there is an elastic coupling between the surface layer of thickness l and the bulk. This elastic coupling has a saturation for a given value of the deformation of the bulk with respect to the surface layer. [S1063-651X(99)08812-1]

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I. INTRODUCTION

Liquid-crystal (LC) mesophases are present in materials composed of interacting molecules or aggregates of molecules that are anisotropic in shape. These materials can be divided in two categories according to the relevant parameter driving the phase transitions: thermotropic and lyotropic liquid crystals. Thermotropics are composed of elongated organic molecules that present liquid-crystalline mesophases for a certain range of temperature. In lyotropic systems the building blocks are aggregates of amphiphilic molecules dispersed in water. The phase transitions occur by variations of temperature or concentration and are accompanied by simultaneous variations of order and shape of the aggregates.

The simplest mesophase is the nematic phase, characterized by a long-range orientational order of the molecules (or aggregates of molecules). This average molecular orientation is defined by a unit vector **n** called the director. From the crystallographic point of view the nematic medium behaves as a uniaxial crystal whose optical axis coincides with the director **n**. The orientation of **n** in the bulk is sensitive to the presence of external fields (electric or magnetic). The elastic behavior of the bulk nematic can be described by the Frank energy density, proposed long ago by Oseen, Zocker, and Frank [1–3].

However, close to the boundary surfaces the nematic order can be disturbed and a positional order or a particular orientation of the molecules may result. Indeed, it has been reported that a nematic mesophase exhibits a positional order in a thin layer close to the boundary of a solid substrate [4,5]. In the absence of bulk distortions, usually the substrate imposes on the molecules some particular orientation, called the easy axis ($\mathbf{n}_0$) [6], that propagates to the bulk by means of the elastic interactions. This surface effect, known as *anchoring*, becomes more important when the dimensions of the system are reduced. The surface effects have been widely used in the design of liquid-crystal displays and new eletro-optical devices [7]. The investigation of these phenomena is relevant because of the fundamental aspects of physics and applications in microelectronics and medicine.

When a nematic is in contact with a solid substrate, a continuum description is more complicated due to the reduced symmetry of the medium. The interactions of a nematic with the boundary surfaces are usually described, in a phenomenological approach, by an anisotropic surface energy F_s. For thermotropic liquid crystals, the surface energy has an elastic contribution due to the presence of the surface field. It is connected with the geometrical shape of the surface or with the physical anisotropy of the substrate. It is a function of the actual nematic orientation with respect to the easy axis [8]. According to this description, when the distorting effect acting on the liquid crystal is removed, the initial orientation of the system is restored. Most of the experimental results and theoretical models reported on surface properties of liquid crystals concern thermotropic mesophases due to their interest for technological applications. Regarding lyotropic liquid crystals, such an investigation is more recent and a different surface behavior has been observed.

Recently, a gliding effect of a director in the surface layer has been observed in lyotropic nematics [9]. This effect has been interpreted by assuming that the interaction between the nematic and the substrate is of the dry-friction type [10]. According to this model, on an anisotropic substrate all the nematic orientations are equivalent; to pass from one orientation to another one, it is necessary to overcome an energy barrier. To this barrier has been connected a critical torque responsible for the dry-friction interaction [10]. A more detailed analysis of this phenomenon based on thermal relaxation has also been proposed [11]. This shows that the reorientation process of the surface layer can be described in terms of the simple dry-friction model. Furthermore, this model has predicted the existence of a critical magnetic field H_c^*, called *surface critical field*, above which the surface reorientation process takes place. It was also highlighted that for $H > H_c^*$ the surface distortion increases. For high enough

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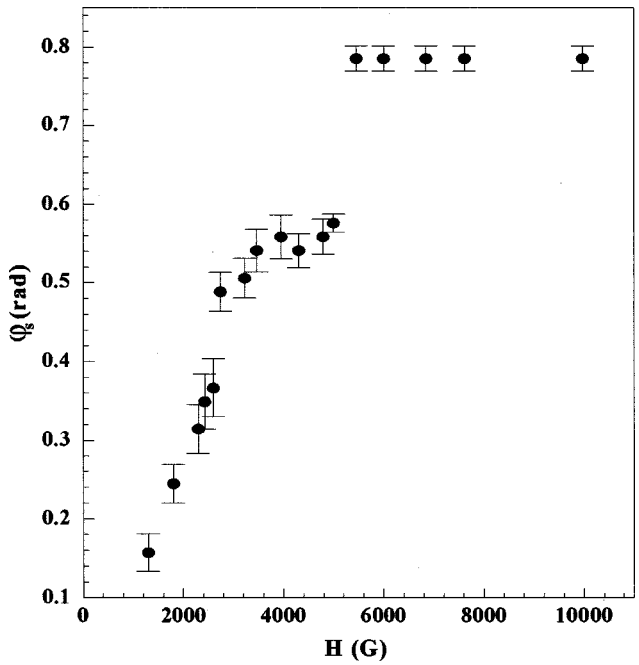

FIG. 1. The experimental curve of the equilibrium orientation φ_s of the surface director as a function of the magnetic field intensity H [12].

fields, there is a saturation regime that corresponds to the director oriented along the applied external field direction.

In a recent publication [12], we reported some experimental results on the equilibrium states of a lyotropic nematic LC in the presence of a magnetic field. The experiment consists of applying a magnetic field to a uniform oriented sample in the nematic calamitic phase, in a planar geometry. The magnetic field is applied parallel to the boundary surfaces and induces a twist deformation in the sample, along the thickness. By measuring the transmittance of the sample between crossed polarizers, as a function of the time, it is possible to fit the experimental curves for a given dynamical profile of the director along the thickness. With this fitting one can determine the characteristic reorientation time and the final configuration of the director. It was found that there exists a critical field, H_c^*, above which an irreversible deformation of the surface layer occurs. By increasing the field intensity, we observed that the director in the surface layer tends to align along the direction imposed by the applied field, but the saturation regime is reached with a discontinuity. Indeed, if H overcomes a second critical value $H_c^{**} > H_c^*$, the surface director jumps to the external field direction (see Fig. 1). This shows that there is a kind of breaking at the surface for $H = H_c^{**}$. Such a behavior could not be explained either in terms of the dry-friction model, or by considering also an anchoring contribution to the surface reorientation process.

In this paper, we develop a more elaborate phenomenological model to interpret the complete surface reorientation process. We propose a simple two-layer model for the interface nematic substrate. We assume that there is a first surface layer of the nematic which interacts with the substrate giving elastic and dry-friction contributions to the surface energy. Such an assumption is based on the fact that lyotropic LC's are self-organizing systems. When a nematic lyotropic LC is in physical contact with a solid surface, the interactions involved are not only of the particle (micelle) -surface interactions type, but mainly of the amphiphilic molecule-surface interactions type. The last interactions may give rise to the formation of a bilayer structure of amphiphilic molecules at the substrate. The thickness of this surface layer depends on the hydrophilic properties of the substrate. In the case of a highly hydrophilic substrate, the surface layer may be seen as a broken lamellar structure, whereas if the substrate is hydrophobic, a more compact reverse bilayer organization may be stabilized. The experimental results reported here were obtained on a hydrophilic glass substrate.

This surface layer is coupled to the bulk by means of an elastic energy. The surface energy depends on the orientation of the surface layer with respect to the bulk one [13]. The functional form of the energy describing the interaction of the bulk with the surface is assumed to have a saturation behavior. This means that if the deformation at the interface is larger than a given quantity, this energy becomes independent of the deformation; consequently, the transmitted torque vanishes. This functional dependence is similar to the surface energy proposed by Blinov *et al.* [14]. To the saturation is connected the existence of the second critical field H_c^{**}.

With respect to the model presented in [12], this model also considers (i) the presence of a surface layer where the order parameter and the structure of the lyotropic liquid crystal are different from the bulk; (ii) the elastic energy describing the interaction of the bulk with this surface layer.

As will be shown in the following, all the experimental data can be interpreted in terms of this model.

II. THE MODEL

We suppose that the boundary surface induces a positional order and the amphiphilic molecules are organized as in lamellar structure. When a magnetic field (**H**) is applied to the amphiphilic molecules, it is known that the aggregates tend to orient with their biggest axis parallel to the field direction, due to the anisotropy of the diamagnetic susceptibility. The average orientation of the parafinic chains is perpendicular to H.

In the experiments cited above, the sample is initially in a planar configuration, therefore the average orientation of the parafinic chains is perpendicular to the boundary surfaces. If at the surface the lamellar structure is not compact, but presents defects such as channels, the amphiphilic aggregates may be larger than the micelles in the bulk. There is a possibility that these aggregates can also be anisotropic, and in this case they would orient with their biggest axis parallel to the direction of the magnetic field, however this process would take a longer time than for the micelles in the bulk. If the large aggregates in the lamellar structure are not anisotropic, the anisotropy of the diamagnetic susceptibility is zero for the surface layer.

In the following we propose the existence of a surface layer of thickness l of the order of a few molecular dimensions as shown in Fig. 2. As we consider that the order parameter and the structure of the surface layer are different from the bulk, it results that $k_s \neq k_b$, where k_s and k_b are the surface and the bulk elastic constants, respectively.

In our two-layer model we assume that (i) the surface layer interacts with the substrate by means of an ''elastic''

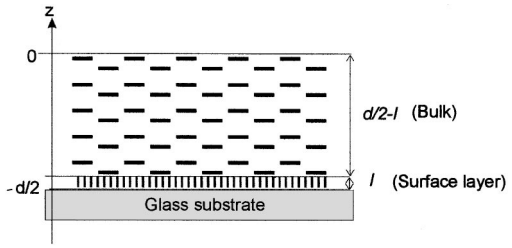

FIG. 2. The two layers system. l is the thickness of the surface layer (of molecular dimensions); d is the sample thickness.

bulk surface energy density of strength w and by means of dry-friction-like energy of critical torque τ_c, (ii) the bulk interacts with the surface layer with an interface energy of the type $\frac{1}{2}u(\varphi_b^*-\varphi_l^*)^2$, where φ_b^* and φ_l^* are the angles of the bulk director and the surface layer director at the interface (see Fig. 3).

Note φ is not continuous, only the torque has to be continuous at the interface.

The torque at the interface is

$$\tau_I = u(\varphi_b^*-\varphi_l^*) \leqslant \tau_t .$$

At $\tau_I=\tau_t$ the interface is broken and the bulk is free to move under the action of the magnetic field. The total energy of the sample, per unit area, is given by

$$F=\int_{-d/2}^{-d/2+l}[\tfrac{1}{2}k\varphi'^2-\tfrac{1}{2}\chi_a H^2\cos^2(\theta_H-\varphi)]dz + \int_{-d/2+l}^{0}[\tfrac{1}{2}k\varphi'^2-\tfrac{1}{2}\chi_a H^2\cos^2(\theta_H-\varphi)]dz + \tfrac{1}{2}u(\varphi_b^*-\varphi_l^*)^2+F_s , \quad (1)$$

where $\varphi'=d\varphi/dz$ and $F_s=-(1/2)w\sin^2\varphi_s$ is the surface energy; θ_H defines the magnetic-field direction with respect to the surface easy axis; χ_a is the anisotropy of the magnetic susceptibility. Since l is of the order of a few molecular dimensions, φ does not change too much in the first integral which appears in Eq. (1), but its derivative is finite. A change of φ modifies the cosine function near its maximum value and this modification would be much smaller than the term connected to φ'. This implies that the magnetic contribution in the first integral can be considered as a constant term. In other words, the torque of magnetic origin can be neglected with respect to the elastic torque. In this context, the minimization of Eq. (1) gives the torque balance, for the Euler-Lagrange equations: in the surface layer $(-d/2<z\leqslant -d/2+l)$:

$$k\varphi' = \text{const}$$

in the bulk $(-d/2+l\leqslant z\leqslant 0)$:

$$\tfrac{1}{2}k_b\varphi'^2=\tfrac{1}{2}\chi_a H^2\sin^2(\theta_H-\varphi).$$

The torque in the bulk is $\tau_b=(k_b/\xi)\sin(\theta_H-\varphi_b)$, where ξ is the magnetic coherence length, whereas in the surface layer the torque is $\tau_s=k_s[(\varphi_l^*-\varphi_s)/l]$.

At the interface the equilibrium imposes

$$\frac{k_b}{\xi}\sin(\theta_H-\varphi_b^*)=u(\varphi_b^*-\varphi_l^*), \quad (2)$$

$$k_s\frac{\varphi_l^*-\varphi_s}{l}=u(\varphi_b^*-\varphi_l^*), \quad (3)$$

showing that the torque at the interface is continuous.

Let us consider that $\theta_H-\varphi_b^*$ is very small. In this approximation, Eqs. (2) and (3) become

$$\frac{k_b}{\xi}(\theta_H-\varphi_b^*)=u(\varphi_b^*-\varphi_l^*), \quad (4)$$

$$k_s\frac{\varphi_l^*-\varphi_s}{l}=u(\varphi_b^*-\varphi_l^*). \quad (5)$$

From Eqs. (4) and (5), we obtain

$$\varphi_b^*=\frac{\frac{k_b}{\xi}\theta_H\left(\frac{k_s}{l}+u\right)+u\frac{k_s}{l}\varphi_s}{\frac{k_bk_s}{\xi l}+u\left(\frac{k_b}{\xi}+\frac{k_s}{l}\right)}, \quad (6)$$

$$\varphi_l^*=\frac{\frac{k_s}{\xi}\varphi_s\left(\frac{k_b}{\xi}+u\right)+u\frac{k_b}{\xi}\theta_H}{\frac{k_bk_s}{\xi l}+u\left(\frac{k_b}{\xi}+\frac{k_s}{l}\right)}. \quad (7)$$

The torque equilibrium at the interface between the first layer and the surface imposes

$$-\frac{k_s}{l}(\varphi_l^*-\varphi_s)+\frac{w}{2}\sin(2\varphi_s)+\tau_D=0. \quad (8)$$

For $H>H_c^*$, the surface reorientation process can take place only if the torque associated to the dry friction is equal to the critical torque τ_c; the above equation can then be rewritten as

$$-\frac{k_s}{l}(\varphi_l^*-\varphi_s)+\frac{w}{2}\sin(2\varphi_s)+\tau_c=0. \quad (9)$$

From Eq. (7) we evaluate φ_l^* and Eq. (9) is rewritten as

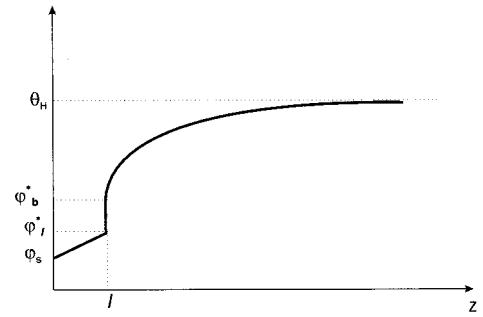

FIG. 3. Azimuthal angle profile in the two-layer system. φ_s is the surface angle; φ_l^* and φ_b^* are the angles at the interface; θ_H defines the magnetic field direction.

$$-\frac{u}{1+u\left(\frac{l}{k_s}+\frac{\xi}{k_b}\right)}(\theta_H-\varphi_s)+\frac{w}{2}\sin(2\varphi_s)+\tau_c=0. \quad (10)$$

To obtain the second threshold for which the surface breaking takes place, we evaluate the torque at the interface $\tau_I=u(\varphi_b^*-\varphi_l^*)$.

By means of Eqs. (6) and (7) we deduce

$$\tau_I=u(\varphi_b^*-\varphi_l^*)=u\frac{\frac{k_bk_s}{\xi l}(\theta_H-\varphi_s)}{\frac{k_bk_s}{\xi l}+u\left(\frac{k_b}{\xi}+\frac{k_s}{l}\right)}. \quad (11)$$

The above equation shows that τ_I is a function of the applied magnetic field since φ_s depends on the magnetic field intensity, as can be seen in Fig. 1.

When the external magnetic field strength is larger than a critical value H_c^{**}, the torque at the interface may overcome the critical torque τ_t for which the interface between the bulk and the surface layer is broken. Thus, for $H>H_c^{**}$, the bulk is completely free to move with respect to the interface layer and can follow the direction imposed by the external magnetic field. The nematic sample behaves then like a three-layer system: two boundary layers with uniform orientation along the imposed surface orientation, and the bulk oriented along the external magnetic field direction. The expression of the second threshold H_c^{**} can be calculated as follows.

From Eq. (11) one obtains

$$\theta_H-\varphi_s=\frac{\tau_t}{u}\left[1+u\left(\frac{l}{k_s}+\frac{\xi}{k_b}\right)\right] \quad (12)$$

and introducing Eq. (11) in Eq. (10) gives

$$\xi^{**}=k_b\left\{\frac{1}{\tau_t}\left[\theta_H-\arcsin\left(2\frac{\tau_t-\tau_c}{w}\right)\right]-\frac{1}{u}-\frac{l}{k_s}\right\}. \quad (13)$$

The above equation expresses the dependence of the second critical field H_c^{**} on the surface and bulk parameters, and on the critical torque for the breaking of the interface between the surface layer and the bulk.

III. DISCUSSION AND CONCLUSION

The configuration of the director, when the magnetic field is applied, is determined by optical measurements of the transmittance of the sample between crossed polarizers, as described above. From the experiments, one obtains the characteristic time of the reorientation process of the surface layer and the orientation of the surface layer φ_s, as a function of the applied magnetic field. We will proceed to the fitting of the experimental values of φ_s as a function of H; according to our model, the dependence of φ_s on H can be obtained from Eq. (10). The value of the critical torque was calculated in the previous work [12]; $\tau_c=7\times10^{-5}$ erg/cm^2, from the determination of the first critical magnetic field. However, we have to introduce numerical values for some parameters, such as the elastic constants (k_s and k_b), the thickness of the surface layer (l), and the coupling energy u.

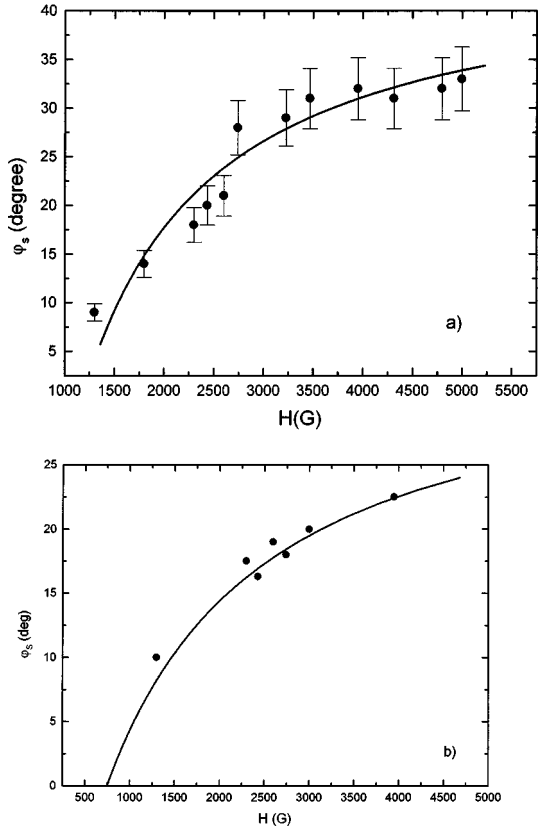

FIG. 4. Final orientation φ_s of the director at the surface as a function of the magnetic field strength H. The solid curve corresponds to the fitting obtained using Eq. (10). (a) $\theta_H=45°$, (b) $\theta_H=35°$.

Saupe and co-workers [15] determined the bend and splay elastic constants as a function of temperature, for a lyotropic mixture in the nematic domain close to transition to the lamellar phase. According to these authors, the bend elastic constant is about 2×10^{-6} dyn in the middle of the nematic domain and is 100 times larger close to the transition to the lamellar phase. As was mentioned in the preceding section, we consider that the order in the surface layer is different from the bulk, with a positional order similar to a lamellar structure. This order extends to the bulk, within a few molecular dimensions. We assume that the elastic constant in the surface layer is one order of magnitude greater than the bulk one; $k_s\approx10^{-5}$ dyn and $k_b\approx10^{-6}$ dyn.

Experiments of x-ray scattering perfomed in lyotropic samples have shown that the amphiphilic aggregates present are positionally correlated in the three nematic phases (the two uniaxial phases and the biaxial phase), which has been called a pseudolamellar order [16]. The correlation length is about 40 nm, which corresponds to eight lamellar distances. Therefore, we will assume that the thickness of the surface layer can vary from $\approx$20 nm up to 50 nm, which corresponds to approximately five to ten bilayers, including the water between them.

The experimental data are fitted using Eq. (10) and ORIGIN 5.0 software. We start fixing the values of the following parameters: $l=5\times10^{-6}$, $k_b=10^{-6}$ dyn, $k_s=10^{-5}$ dyn,

and $\tau_c = 7 \times 10^{-5}$ erg/cm^2, and we allow w and u to vary from 10^{-5} up to 1 erg/cm^2. This results in $w = 6 \times 10^{-5}$ erg/cm^2 and $u = 1$ erg/cm^2 and the χ^2 is 54. The resulting value of w corresponds to a weak anchoring. We expect that $U \sim ua$, where U is the energy of the interaction between the surface layer and the bulk and a is the area of the aggregate. Taking $a \sim (10^{-6})^2$ cm^2 and the calculated value of u, we obtain $U \sim 10^{-12}$ erg, which is comparable to energy of the interactions between the aggregates in the bulk [17].

If we proceed to fit starting with u and w in the above best-fitting values and allow all parameters, expect k_b, to vary imposing the following constrains to l, k_s, and τ_c: $10^{-5} \leqslant k_s \leqslant 10^{-4}$ dyn, $10^{-6} \leqslant l \leqslant 10^{-2}$ cm, $10^{-6} \leqslant \tau_c \leqslant 10^{-2}$ erg/cm^2, we obtain as best values $k_s = 10^{-4}$ dyn, $l = 10^{-6}$ cm, and $\tau_c = 9 \times 10^{-5}$ erg/cm^2, with almost the same χ^2. Therefore, we can conclude that the values of w, u, l, and τ_c do not change too much, remaining with the same order of magnitude. However, for k_s we arrive at a larger value than the initial one, but still compatible with the experimental value of the elastic constant in the nematic phase close to the transition to the lamellar phase.

In Fig. 4 are reported the experimental data of the surface angle versus H with the best-fitting curve. From the experimental data in Fig. 1, we estimate the value of the second critical magnetic field $H_c^{**} \approx 5000$ G, and this value can be used in Eq. (13) to evaluate the critical torque at the interface, τ_I. The corresponding values are $\tau_I \approx 10^{-4}$ erg/cm^2 and $\tau_I \approx 6 \times 10^{-5}$ erg/cm^2 for $\theta_H = 45°$ and $\theta_H = 35°$, respectively. We expect that the weaker the deformation introduced by the magnetic field is, the smaller is the torque at the interface. The experimental results follow this tendency, since for smaller value of θ_H we obtained a smaller value of τ_I.

In this paper we have analyzed the effect induced by an external magnetic field H on planarly oriented lyotropic nematic liquid crystals. According to the model presented, in the first two regimes the surface energy has elastic and dry-friction-like contributions. The third regime exists when the torque at the interface between the bulk and the surface layer overcomes a critical value.

To explain the existence of the two thresholds for H, a phenomenological model based on the presence of a surface layer coupled to the bulk by means of an elastic energy has been developed.

It was found that our model is in good agreement with the experimental results recently observed on lyotropic nematic liquid crystals.

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