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Critical orientational states in lyotropic liquid crystals induced by a magnetic field

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The existence of a critical state in a lyotropic liquid crystal has been recently predicted, induced by a magnetic field and corresponding to a uniform orientation parallel to the magnetic field, but not reversible. In this paper we report the observation of two critical states, differing by the final orientation with respect to the magnetic field. We discuss the surface interaction that could explain the experimental results. [S1063-651X(98)50904-X]

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Liquid crystalline phases are observed in materials composed of interacting molecules or aggregates of molecules that are anisotropic in shape. In the nematic phases the molecules tend to align parallel to each other with a long-range orientational order. The average molecular orientation defines a unit vector **n** called the director [1]. The orientation of the director can be fixed by external fields or by the surfaces. The existence of a limiting surface introduces a perturbation in the order of the molecules imposing some preferential orientation, which propagates to the bulk, by means of elastic interactions.

The interactions of the liquid crystal with the boundary surfaces are usually described, in a phenomenological approach, by means of an anisotropic surface energy F_S. It is characterized by an anchoring strengh w and an easy-axis $\mathbf{n}_0$, which corresponds to the preferential orientation of the nematic phase, imposed by the boundary surface, in the absence of bulk distortions. The simplest expression of F_S was proposed long ago by Rapini and Papoular [2]. According to these authors F_S is given by $F_S=-(w/2)(\mathbf{n}\cdot\mathbf{n}_0)^2$, with typical values of w in the range of 10^{-3} to 10^{-1} erg/cm^2, for thermotropic liquid crystals [3].

However, the validity of the Rapini-Papoular formula is contested by some authors [4,5]. Some other expression for F_S has been proposed including terms of higher order in the expansion of F_S in terms of $(\mathbf{n}\cdot\mathbf{n}_0)$, to take into account other effects like polar interactions [6] or the flexo-eletric effect [5].

It has been recently shown that lyotropic liquid crystals exhibit anchoring properties very different with respect to thermotropic liquid crystals. In particular, the easy axis can be altered by an external magnetic field [7,8]. Two orientation processes have been observed under the action of a magnetic field **H**; a fast one related to the orientation of the director in the bulk, parallel to **H**, and a slow one, with a characteristic time of about 10^3 s, related to the orientaction of the director in the surface layer. If the surface orientation process is completed, the final orientation is uniform and the field can be removed without any significant change of orientation of the sample, and the final state is stable.

Some attempts have been made to obtain a theoretical description of both static [9] and dynamical properties [10] for the experimental results. In a recent experiment [11] a Freedericksz transition was used to estimate the anchoring energy of a lyotropic system in a planar configuration, assuming that the surface energy F_S is described by the Rapini-Papoular expression. The anchoring strength w obtained from such an experiment [11] is about 10^{-3} erg/cm^2 and the extrapolation length $L\approx 6\ \mu$m. This description is not completly satisfactory, because according to this, there should exist a relaxation process by removing the field, due to the surface energy. However it gives some idea of the magnitude of the surface interactions.

This problem was also analyzed in analogy to the dry-friction phenomenon that takes place between one body and a solid substrate [9]. According to the dry-friction model the nonreversible orientation induced by the magnetic field on the nematic liquid crystal can be described as follows. The director at the surface tends to align parallel to the field, (if the anisotropy of the diamagnetic susceptibility χ_a is positive) due to the elastic torque coming from the bulk, where **n** is already oriented parallel to **H**. The reorientation of the director at the surface is possible only when the elastic torque acting on it is large enough to break the physical ''bonds'' of the micelles in contact with the substrate. This takes place for a certain magnetic field higher than H_c^*, called the *surface critical field*. For fields lower than H_c^*, there is no reorientation of the surface and the orientation of the bulk is reversible. This means that if the field is removed the director in the bulk aligns again parallel to $\mathbf{n}_0$. For $H>H_c^*$ the reorientation of the director in the surface takes place, and the director tries to align parallel to **H**. The final orientation will be dependent on the intensity of the magnetic field, and for fields very large the director in the surface can be oriented parallel to **H**.

We consider a planar nematic sample of thickness d, where **n** is parallel to the boundary surfaces everywhere, and the surfaces are located at $z=\pm d/2$. The initial orientation is described by the vector $\mathbf{n}_0$, parallel to the x axis. Since **H** is parallel to the surfaces of the slab, the deformation induced on the nematic is a pure twist. Let φ be the angle formed by **n** with the x axis. The orientation of the director at the surface is given by the angle $\varphi_s=\varphi(z=\pm d/2)$ and in the middle of the sample by $\varphi_v=\varphi(z=0)$. The magnetic field is

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at an angle θ with respect to the direction of $\mathbf{n}_0$. According to the dry-friction model, the orientation of the director in the surface is $\varphi_s(H)$ [9]:

$$\varphi_s = \theta - \arcsin\left(\frac{H_c^*}{H}\right), \tag{1}$$

where the value of H_c^* can be calculated from

$$H_c^* = \left(\frac{d\Gamma_c}{\pi K}\right) H_c . \tag{2}$$

In Eq. (2) H_c is the usual critical field for a Freedericksz transition ($H_c = (\pi/d)\sqrt{K/\chi_a}$), derived from strong anchoring assumptions, K is the elastic constant associated with the induced distortion and Γ_c is the critical torque that must be applied in the surface to allow the surface reorientation process.

We have experimental access to the values of φ_s and φ_v by measuring the transmittance of the nematic sample between crossed polarizers, as a function of the time (t) when the magnetic field is applied. The experimental setup is described in detail in Ref. [8]. The lyotropic mixture consists of potassium laurate (29.4 wt %), decanol (6.6 wt %), and water (64 wt %), that for such composition has a calamitic nematic phase in the range of 15–50 °C, followed by an isotropic phase for higher temperatures. The sample holders are glass microslides (Vitrocom, 200 μm thick, 4 mm wide, and $\sim$2 cm long) and the director tends to align parallel to its length. The geometry of the experiment is such that the normalized transmittance is maximum at $\varphi = 0$ and minimum when the director is parallel to the field.

The experimental curves of transmittance are compared to calculated curves for some profile of the director, $\varphi(z,t)$, by assuming that the nonuniform and optically anisotropic sample can be divided into many thin layers, with a uniform orientation in each layer. The propagation of the light through this medium can be calculated using the Jones matrix where in each layer there is a phase shift between the ordinary and extrordinary ray, and a rotation of the direction of polarization of the light. Since the orientation of the director in the bulk is fast compared to the orientation in the surface, we can assume that the dependence of φ on time comes only from the dependence of φ_s on time. The orientation of the director at the surface as a function of the time is given by

$$\varphi_s(t) = \varphi_f(1 - e^{-t/\tau_S}), \tag{3}$$

where φ_f is the final orientation of the director at the surface, with respect to the x axis, and $0 < \varphi_f < \theta$.

The profile of the director can be obtained from the minimization of the free energy, considering the elastic and magnetic interactions in the bulk. For $H < H_C^*$, $\varphi_s = 0$, $\varphi(z)$ is given approximatively by [1]

$$\varphi(z) = \varphi_f - \arctan\left[\exp\left(\frac{|z| - d/2}{\xi}\right) tg(\varphi_f)\right], \tag{4}$$

where ξ is the magnetic correlation length; $\xi = (1/H)\sqrt{K/\chi_a}$.

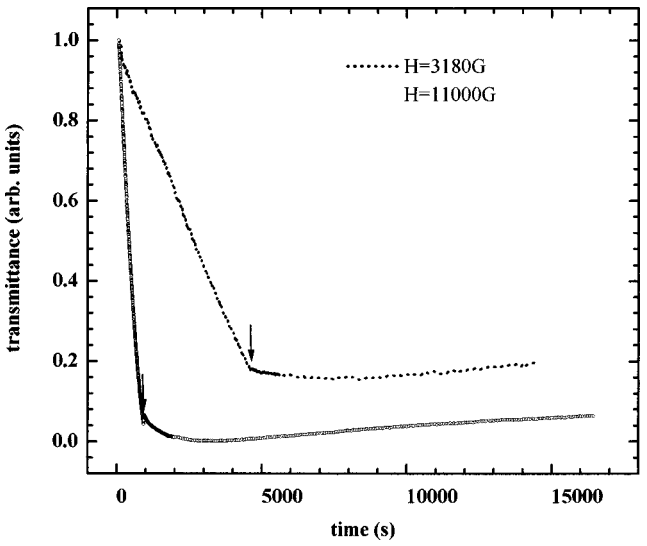

FIG. 1. Experimental curves of transmittance (arbitrary units) for different intensities of the applied magnetic field. The magnetic field is turned on at $t = 0$ and the reorientation process of the surface takes place, resulting in decreasing transmittance. The arrows indicate the instant when the field is removed ($H = 0$), and we notice that there is no significant change in the transmittance.

For $H > H_c^*$, Eq. (4) has to be modified to match the boundary conditions in the surface, $\varphi(d/2,t) = \varphi_s(t)$. The profile is then described by

$$\varphi(z,t) = \left[\varphi_f - \arctan\left(\exp\left(\frac{|z| - d/2}{\xi}\right) tg(\varphi_f)\right)\right] e^{-t/\tau_s} + \varphi_s(t). \tag{5}$$

In the bulk, $\varphi(0,t) = \varphi_f$, independent on t. The calculation of the transmittance is carried out dividing the sample into 50 layers, taking τ_s and φ_f as fitting parameters.

For fields lower than 5000 G it is possible to fit the experimental curves using the profile described by Eq. (5), and we obtain values of τ_s proportional to H^{-2} as expected from the dynamical analysis [10]. We observe that the final orientation of the sample is uniform, with the director at the surface parallel to the director in the bulk.

The reorientation process is nonreversible, as shown in Fig. 1, for field strengths of 11 000 and 3180 G. The arrows in the figure indicate the instant when the magnetic field is removed, and we observe that there is no relaxation. We observe also that for $H = 11\,000$ G the final orientation of the sample is uniform and parallel to the direction of the magnetic field. For $H = 3180$ G the final orientation is also unifom, but not parallel to **H**. This can be noticed from Fig. 1, since the transmittance of the final state for $H = 3180$ is higher than for $H = 11\,000$ G.

For fields higher than 5000 G, it is no more possible to fit the experimental curves using the profile described by Eq. (5), and we adopt a *discountinous* profile, for which we assume that the director is parallel to the magnetic field everywhere, except in the thin boundary layers of thickness ξ. In Fig. 2, it is possible to compare the shape of the curves for high and low fields and the respective fitting to these curves.

The final orientation of the director at the surface, obtained from the fittings of the experimental curves of trans-

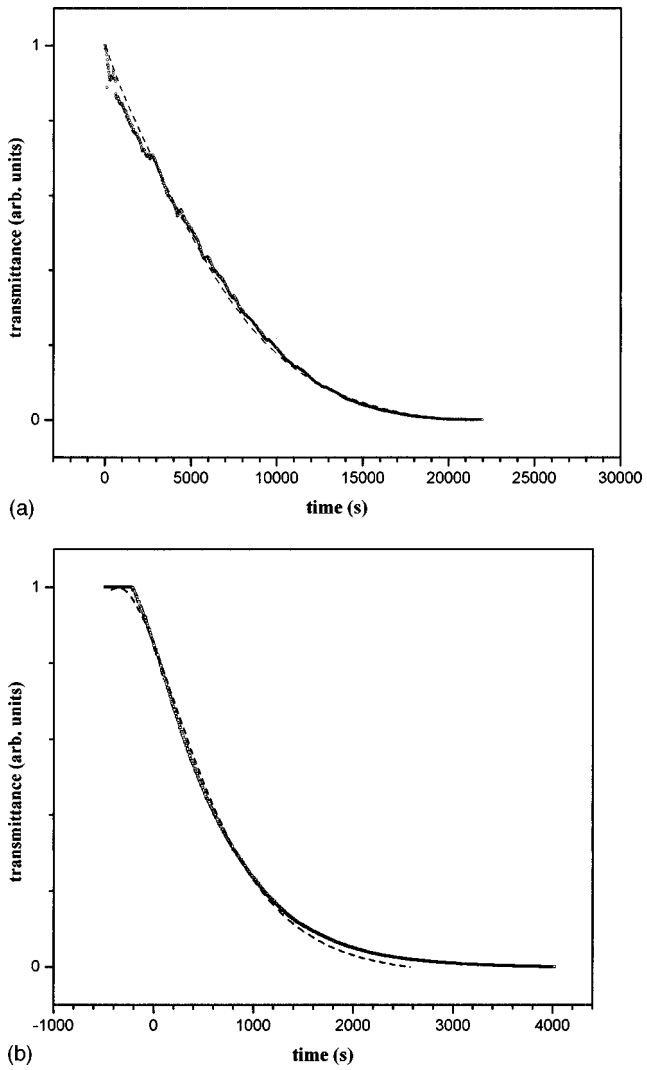

FIG. 2. Experimental and calculated curves for (a) $H=2742$ G. The dashed line corresponds to the calculated transmittance with the profile described by Eq. (5) for $\tau=6700$ s and $\varphi_f=22°$. (b) $H=11\ 110$ G. The dashed line represents the calculated transmittance using the *discontinuous* profile described in the text, with $\tau_s=950$ s and $\varphi_f=0$.

mittance, is plotted as a function of the magnetic field in Fig. 3. Each point corresponds to an average of several measurements, with an uncertainty of 2° in the value of φ_s. We observe a region of low fields corresponding to small values of φ_s, increasing very fast with H, tending to a saturation regime, but with a jump for $H\cong 5000$ G. We observe that, for $H>5000$ G, the final state corresponds always to a uniform orientation of the sample, with the director parallel to H, $\varphi_s=\pi/4$. We can clearly identify three different states.

(I) There is no reorientation of the surface, although it can happen in the bulk. The final state is not uniform and the reorientation phenomenon is reversible. (II) The final orientation is uniform, but the orientation of the director is in some intermediate direction between the easy axis in the surface ($\mathbf{n}_0$) and the direction of H. The reorientation induced by the magnetic field is a irreversible phenomenon. (III) The final orientation is uniform, with the director parallel to H, everywhere in the sample, including the surface layers. The reorientation induced by H is also an irreversible phenomenon.

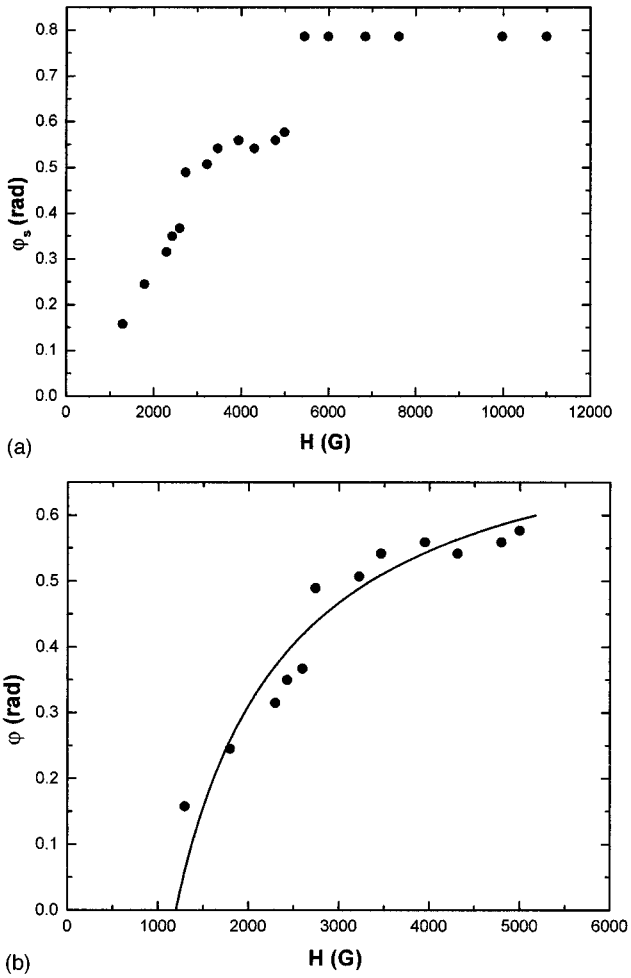

FIG. 3. (a) Final orientation of the director in the surface as a function of the magnetic field. (b) The solid curve corresponds to the fitting obtained from Eq. (10), assuming $H_c^*=1000$ G.

According to the dry-friction model, only one critical state was expected, state (II). However we observe that there are two critical states. The discontinuity between states (II) and (III) seems to indicate that there is no more an elastic coupling between the surface layer and the bulk.

We will reanalyze this problem, considering that, in addition to the dry-friction-like interaction at the surface, there is also an elastic interaction, given by the Rapini-Papoular expression. Therefore, the torque in the surface due to the surface interactions can be written as

$$\Gamma_s=\frac{d\mathcal{F}_s}{d\varphi_s}=\frac{w}{2}\sin(2\varphi_s)+\Gamma_d, \tag{6}$$

where Γ_d is the dry torque at the surface and $\mathcal{F}_s$ is the total surface energy.

The magnetic field induces a distortion of the director in the bulk, resulting in an elastic torque that is transmitted to the surface.

The expression of the elastic torque is

$$K\frac{d\varphi}{dz}=\frac{K}{\xi}[\cos^2(\theta-\varphi_v)-\cos^2(\theta-\varphi_s)]^{1/2}. \tag{7}$$

The equilibrium at the surface is obtained by the balance of the surface and elastic torques:

$$\Gamma_d + \frac{w}{2}\sin(2\varphi_s) = \frac{K}{\xi}\sin(\theta-\varphi_s) = K\left(\frac{d\varphi}{dz}\right)_{z=+d/2}. \quad (8)$$

The reorientation of the director at the surface is possible only if Γ_d is smaller than a certain critical torque. Assuming that, for $H<H_c^*$, $\varphi_s=0$, the critical torque Γ_c is given by

$$\Gamma_d=\Gamma_c=\frac{K}{\xi^*}\sin\theta, \quad (9)$$

which defines the value of H_c^*. For $H>H_c^*$ the values of φ_s can be obtained as a function of H, from Eq. (8) and the calculated value of Γ_d:

$$\frac{1}{\xi}=\frac{\left(\frac{w}{2K}\right)\sin 2\varphi_s+\frac{1}{\xi^*}\sin\theta}{\sin(\theta-\varphi_s)}. \quad (10)$$

This equation shows that for $H\to\infty$ (which implies $\xi\to 0$), $\varphi_s\to\theta$. If H is removed, the final state is stable and homogeneous along φ_s (given by the above equation) if the elastic torque in the surface is smaller than the critical one:

$$\frac{w}{2}\sin 2\varphi_s<\Gamma_c. \quad (11)$$

If the above condition is not fulfilled, the final state is not homogeneous and the final orientation will be along φ_s' defined by

$$\frac{w}{2}\sin 2\varphi_s'=\Gamma_c. \quad (12)$$

From the experimental results it is possible to estimate the value of $H_c^*=(1000\pm 100)$ G, and from the threshold condition in Eq. (9), one obtains the value of the critical torque $\Gamma_c=7\times10^{-5}$ erg/cm^2. In Fig. 3(b), the curve $\varphi_s(H)$ calculated from Eq. (10) is fitted to the experimental data. The first part of the curve can be reasonably fitted, for $w=8\times10^{-5}$ erg/cm^2. However, it is not possible, with this model, to explain the discontinous behavior of φ_s for $H=5000$ G.

The values of Γ_c and w are of the same order of magnitude and of the order of $\sim10^{-5}$ erg/cm^2, which corresponds to a weak anchoring at the surface. The discontinuity observerd at $H\simeq 5000$ G seems to be connected to the breakdown of the elastic interaction between the surface layer and the bulk, probably because the distortions of the director in the surface layer become very large, corresponding to a limit value of $\varphi_s=0.57$ rad (12°). In this case, the value of the second critical field (related to the jump in the value of φ_s) can depend on the thickness of the sample.

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