Dynamical behavior of a nematic lyotropic liquid crystal in flat confined samples

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We investigate the dynamical behavior of the director in the surface layer of lyotropic nematic liquid crystals in an external magnetic field. The characteristic time of the orientation process is obtained from optical measurements for samples of different thickness (200, 50, and 10 μm). The boundary surfaces are glass plates coated with rubbed polymer [polymethylmethcrylate (PMMA)], to introduce an easy axis. Drastic changes in the dynamical behavior are observed when the thickness is decreased and the experimental results indicate a uniaxial to biaxial transition due to the confinement of the nematic sample.

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I. INTRODUCTION

Liquid crystalline phases are present in materials composed of interacting molecules or aggregates of molecules that are anisotropic in shape. The molecules tend to align parallel to each other and the average direction of orientation is characterized by a unit vector, called the director **n**. The particular orientation adopted by the molecules can be fixed by external fields (electrical or magnetic) or by boundary conditions. If the anisotropy of the diamagnetic susceptibility is positive, the director tends to align parallel to an applied magnetic field and the equilibrium configuration will be determined by the competition between the boundary effects and the interaction with the magnetic field. The combination of such effects is useful in designing magneto- or electro-optical devices using liquid crystals.

Lyotropic liquid crystals are formed by aggregates of amphiphilic molecules dispersed in a solvent (usually water), and they present liquid crystalline structures within a certain range of temperature and concentration. Two different orientation processes have been observed in nematic lyotropic liquid crystals under the action of a magnetic field H [1], a fast one, related to the orientation of the director in the bulk, and a slow one (about 10^2 times larger than the bulk one), which has been associated to the orientation of the director in the surface layer. The dynamical behavior of the surface layer of a lyotropic nematic phase in an external magnetic field has been experimentally and theoretical investigated for a lyotropic liquid crystal in the nematic phases (uniaxial and biaxial), and it was shown that the characteristic time of this process, τ, is proportional to the inverse of H^2 [1,2]. A phenomenological model had been proposed considering the particularities of the lyotropic systems and it predicted the possibility of three different equilibrium orientational states characterized by the orientation of the director in the surface layer with respect to the bulk director [3,4].

In this paper we investigate the orientation process of the surface layer in a lyotropic liquid crystal submitted to an external magnetic field. The characteristic time of the orientation process is determined by optical measurements for samples of different thickness and we observe drastic changes in the dynamical behavior due to the confinement of the nematic sample. The results obtained are discussed in the light of the phenomenological model presented in Refs. [3] and [4].

II. DYNAMICAL BEHAVIOR OF THE SURFACE LAYER

In this section we will present the main assumptions and predictions of the phenomenological model developed to explain the dynamical properties of the surface layer of a lyotropic liquid crystal. It is considered that the interactions of the molecular aggregates with the solid substrate leads to the formation of a surface layer with a two-dimensional orientational order with a finite thickness. Let us call $\mathbf{e}_+$, $\mathbf{e}_-$, and **c** the principal axes of the biaxial molecular aggregates (micelles) with **c** parallel to the smallest dimension, which is approximately the bilayer thickness and $\mathbf{e}_+$ related to the biggest dimension of the micelles. The presence of a boundary surface tends to fix the orientation of the axis **c** perpendicular to the surface, but the micelles can glide in the plane parallel to the surface, therefore thermal fluctuation around the axis $\mathbf{e}_+$ are restricted close to the surface (Fig. 1). The order in the surface layer is characterized by the order parameter ρ and the eigenvectors of the biaxial order; $\mathbf{e}_+$ and $\mathbf{e}_-$. Due to its finite thickness the surface layer interacts directly with the magnetic field by means of a coupling con-

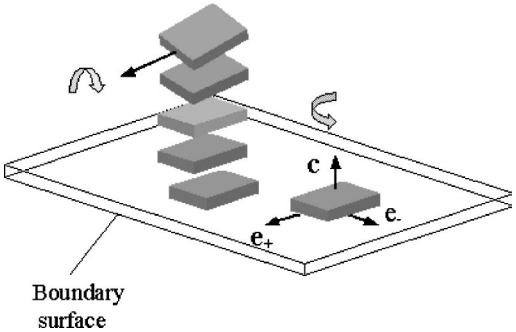

FIG. 1. Organization of the biaxial micelles with principal axes $\mathbf{e}_+$, $\mathbf{e}_-$, and **c** close to a flat boundary surface. Thermal fluctuations around the axis parallel to the plane of the surface are restricted close to the surface.

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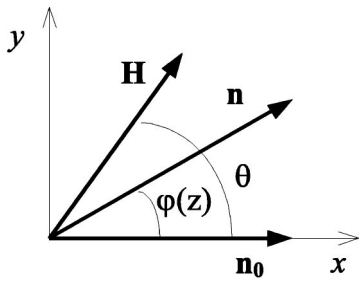

FIG. 2. At $t=0$ the nematic sample is homogeneously oriented with the director **n** parallel to the x axis. The magnetic field is applied at angle θ with respect to the x axis inducing a twist of the director in the bulk, characterized by φ(z), the angle between the director and the x axis. In the surface layer the orientation of the director is characterized by the angle Φ(t).

stant D, $D>0$, which means that the orientation of $\mathbf{e}_+$ parallel to the direction of H is favored. In addition, the surface layer interacts with the bulk by an elastic torque due to their different orders (uniaxial in the bulk), by means of a coupling constant C, which can be either positive or negative, depending on the relative orientation of the eigenvectors to the director in the bulk; $C>0$ corresponds to $\mathbf{e}_+$ aligned parallel to H and $C<0$ corresponds to $\mathbf{e}_-$ parallel to H.

Let us consider a semi-infinite sample, with the boundary surface in $z=0$. The initial orientation, at $t=0$ corresponds to the director (**n**) uniformly oriented along the x axis and the eigenvector in the surface layer $\mathbf{e}_+$ parallel to **n**. A magnetic field, is then applied to the sample, parallel to the boundary surface, making an angle θ with respect to x axis (Fig. 2). Considering that the orientation of the director in the bulk is much faster than in the surface layer, for $z\to\infty$, it is expected that **n** is parallel to H; $\varphi(z\to\infty)=\theta$, where φ describes the orientation of the director in the bulk with respect to x axis and $\varphi=\varphi(z)$. In the surface layer, the orientation of the eigenvector $\mathbf{e}_+$ with respect to the x axis is given by the angle $\Phi=\Phi(t)$ and in the border of the bulk, the orientation of the director is given $\varphi\ (z\to 0)=\varphi_0$. The free energy per unity area can be written as [3]

$$f=F_{V0}+F_{S0}+\frac{1}{2}\int_0^\infty K\left(\frac{d\varphi}{dz}\right)^2+\frac{1}{2}\int_0^\infty \chi_a H^2\cos^2(\theta-\varphi)dz$$

$$-\frac{1}{2}DH^2\rho\cos^2\Phi-Cr\rho\cos^2(\Phi-\varphi_0), \qquad (1)$$

where F_{V0} and F_{S0} are the bulk and surface energies of the unperturbed state, K is the bulk twist elastic constant, r and χ_a are the amplitude of the order parameter and the anisotropic diamagnetic susceptibility in the bulk, respectively. The time evolution of the director in the surface will be given by $\Phi(t)$, that can be obtained from the Landau-Khalatnikov equations [3,4] resulting in

$$\Phi(t)=\theta(1-e^{-t/\tau}), \qquad (2)$$

where τ is the characteristic time of the surface orientation process, given by

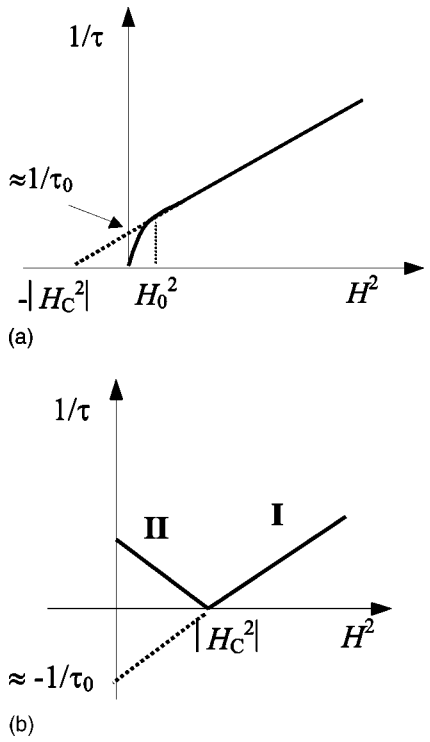

FIG. 3. Dynamics of the orientation process in the biaxial surface layer. Theoretical dependence of the orientation frequency $1/\tau$ as a function of H^2. (a) C>0 and D>0, the equilibrium state I corresponds to the eigenvector $\mathbf{e}_+$ and is oriented parallel to H. (b) A transitional orientation can occur when C<0 and D>0. The equilibrium state II corresponding to $\mathbf{e}_-$ parallel to H becomes stable for $H<H_c$.

$$\frac{1}{\tau}=\frac{1}{\tau_0}\left[\frac{H^2}{H_c^2}-\frac{H}{H_0-H}\right] \qquad (3)$$

and $1/\tau_0=2Cr\rho/\gamma$, $H_0=(2Cr\rho)/(K\chi_a)^{1/2}$, and $H_c^2=2Cr/D$. For high intensities of applied magnetic field or for small values of H_0 we expect that $1/\tau$ is proportional to H^2, as is shown in Fig. 3(a). If we extrapolate the linear behavior of $1/\tau$ as a function of H^2 to the region of low magnetic fields we find the values of $1/\tau_0$ and $|H_c^2|$, which are related to the phenomenological constants C and D. The configuration of the director in the bulk can be obtained from Eq. (1), by imposing the equilibrium of the elastic and magnetic torques in the bulk, and assuming that the distortions are small; $\sin\varphi\approx\varphi$. Then, the twist in the bulk is described by $\varphi(z)$;

$$\varphi(z)=\theta-2\arctan\left[\exp\left(-\frac{z}{\xi}\right)\tan\left(\frac{\theta-\varphi_0}{2}\right)\right], \qquad (4)$$

where $\xi=(K/\chi_a)^{1/2}/H$ is the magnetic correlation length.

An interesting behavior is observed when we consider the competition between the elastic interaction of the surface layer with the bulk and the magnetic torque in the surface layer. The magnetic torque tends to induce the orientation of $\mathbf{e}_+$ parallel to H, however the elastic interaction of the surface layer with the bulk depends on the signal of C; when

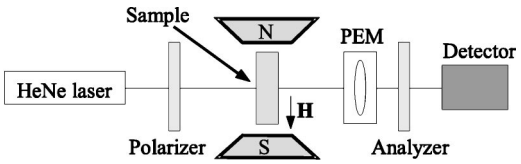

FIG. 4. Sketch of the experimental setup.

$C>0$ the elastic torque in the surface layer is the same sense of the magnetic torque, and the equilibrium state (I) corresponds to a homogeneous state, with $\mathbf{e}_+$ parallel to H, everywhere in the sample. When $C<0$, the elastic torque tries to orient $\mathbf{e}_-$ parallel to H, which corresponds to the direction of the smallest dimension of the biaxial object in the plane parallel to the boundary surfaces. This situation can occur in the bulk biaxial phase, when the three bulk directors $\mathbf{n}_i$ are oriented. The equilibrium state (II) corresponds then, to $\mathbf{e}_-$ parallel to the H and there is no twist. Therefore, there are two homogeneous equilibrium states, distinguished by the orientation of the eigenvector with respect to the magnetic field with the possibility of an orientational transition from one state to another [4], as is shown is Fig. 3(b). These predictions were confirmed by observing qualitative changes in the behavior of $1/\tau$ by variation of the temperature through the calamitic to biaxial phase transition in the bulk transition [4]. The effects of confinement were also previously discussed [4,5], and it is expected that in the surface layer, there is a suppression of the micellar fluctuations around the axes parallel to the boundary surfaces, leading to the formation of a biaxial interface of finite thickness and two-dimensional orientation order. In this paper we investigate the effects of confinement by changing the thickness of the cells containing the lyotropic sample.

III. EXPERIMENT

The lyotropic liquid crystal consists of potassium laurate (35.3 wt. %), decylammonium chloride (4 wt. %), and water (60.7 wt. %), and for such composition it presents a nematic calamitic phase between 15 and 30 °C. The transition temperatures were determined by birefringence measurements. The sample is introduced by capillarity into cells 200, 50, and 10 μm thick, whose inner surfaces are flat glass plates coated with thin films of polymethyl-methcrylate (PMMA) by spin coating. Furthermore, the films are unidirectionally rubbed and we observe that such treatment induces a homogeneous planar orientation on the nematic sample in the rubbing direction.

The dynamical behavior of the surface layer is investigated by applying a magnetic field (H) making an angle $\theta = 45\,°\mathrm{C}$ with the initial orientation $\mathbf{n}_0$, parallel to the boundary surfaces, inducing a pure twist in the nematic sample. We follow the orientation process by measuring the transmittance of the sample between crossed polarizers as a function of the time, when the magnetic field is turned on. A sketch of the experimental setup is shown in Fig. 4, where the orientation of the polarizers, with respect to the initial orientation of the sample, is chosen to start with a minimum of transmittance. The propagation of the light through the optical

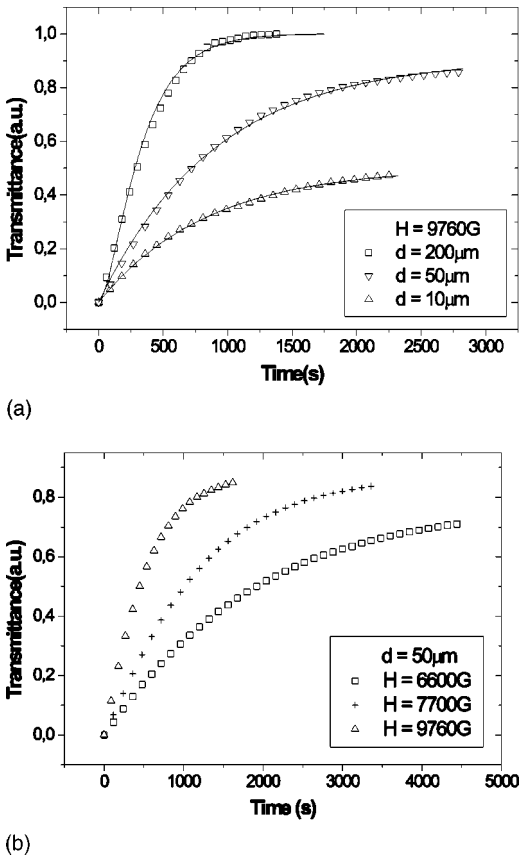

FIG. 5. Experimental curves of transmittance for (a) different sample thicknesses and (b) different strengths of magnetic field. The magnetic field is turned on for $t=0$. The solid lines represent the best fitting for the experimental curves.

elements as well as through the sample is simulated by using Jone's matrix method; the sample is considered as built of thin layers, with uniform orientation in each layer, where a phase shift and a rotation of the direction of polarization take place. The magnetic field is turned at $t=0$, inducing a twist in the bulk and the reorientation of the director in the surface layer, which are described by Eqs. (4) and (2), respectively. The experimental curves of transmittance are then fitted using Jone's matrix and considering the evolution of the orientation of the surface layer described by Eqs. (2) and (4), taking τ as the fitting parameter [2]. The experiments are performed at room temperature ($22\pm2\,°\mathrm{C}$), which corresponds to the maximum birefringence of the sample in the nematic calamitic phase.

IV. RESULTS AND DISCUSSION

The magnetic field is turned at $t=0$, inducing a reorientation of the director and a change in the transmittance of the sample, as can be seen in Fig. 5(a), for samples of different thickness. From this figure, we note that there is an increasing in the transmittance reaching a saturation regime. The maximum limiting value of transmittance is lower for the thinner samples indicating that the amplitude of the distortion induced by the magnetic field is also smaller. The same effect is observed for the sample, when the field strength is

decreased, as illustrated in Fig. 5(b). Using the procedure described above to simulate the propagation of the light through the nematic sample, we obtained the values of the characteristic time (τ) for the orientation of the surface layer, for the 200 μm thick sample. However, for the thinner samples, 50 and 10 μm thick, it was not possible to fit the experimental curves of transmittance using Eq. (4) to reproduce the twist in the sample. Such samples were examined in a polarizing microscope after a long time submitted to the magnetic field and we observed a uniform planar texture, rotated from the initial orientation. The direction of the final orientation depends on the intensity of the magnetic field. However, even for fields as high as 10 kG, the orientation does not match the direction imposed by the magnetic field. The experimental curves of transmittance could be well fitted considering that the sample rotates as a whole in the direction of the magnetic field with a characteristic time τ. The orientation of the director in the sample is assumed to be described by Eq. (2). This means that if there is a surface layer, it is so thin compared to the light wavelength that it cannot be detected in this experiment. In Fig. 5(a) we present experimental curves of transmittance and the respective fitting curves.

The results obtained for the sample 200 μm thick are presented in Fig. 6(a) where we observe a linear dependence of $1/\tau$ as a function of H^2, in the region of high magnetic fields as expected. However, we observe that for low magnetic fields the dependence is also linear, but with a change in the slope. The parameters obtained for a linear fitting in the two regions are listed in Table I, where the data $F1$ and $F2$ refer to the low and high magnetic fields, respectively, and the values of $1/\tau_0$ and H_c^2 are obtained from the extrapolation of the linear behavior. Comparing the two fittings, we observe that in the region of low magnetic fields, the slope of the line ($s=D\rho/\gamma$), is larger with respect to the region of high magnetic fields ($\gtrsim$ 6 kG) while the value of $1/\tau_0$ ($1/\tau_0=2Cr\rho/\gamma$), is two orders of magnitude smaller. Such a large variation in $1/\tau_0$ cannot be explained by variations of r and ρ (that are restricted between 0 and 1), therefore we speculate about the influence of the magnetic field on the others parameters; C, D, and γ. High magnetic field may increase the order in the surface layer, which could result in an increasing viscosity, and smaller values of both $1/\tau_0$ and s. Therefore, we think that the changes in the slope should be related to the influence of the magnetic field on C and D.

In Figs. 6(b) and 6(c) the values of $1/\tau$ are plotted as a function of H^2 for samples 50 and 10 μm thick, respectively. In both cases it is possible to fit a straight line and the related parameters are listed in Table I. In Fig. 6(b), there are two points in the region of low magnetic field that were not included in the fitting because they could belong to another line, as was sketched in Fig. 3(b). This result indicates the possibility of an orientational transition, as was discussed above, and this situation corresponds to the existence of a bulk biaxial phase. The two points, that can be connected by a straight line with negative slope, would correspond to the equilibrium state II, where the axis $\mathbf{e}_-$ is parallel to the magnetic field. It is important to note, that this transition is due only to the decreasing of the cell thickness, as was predicted [4].

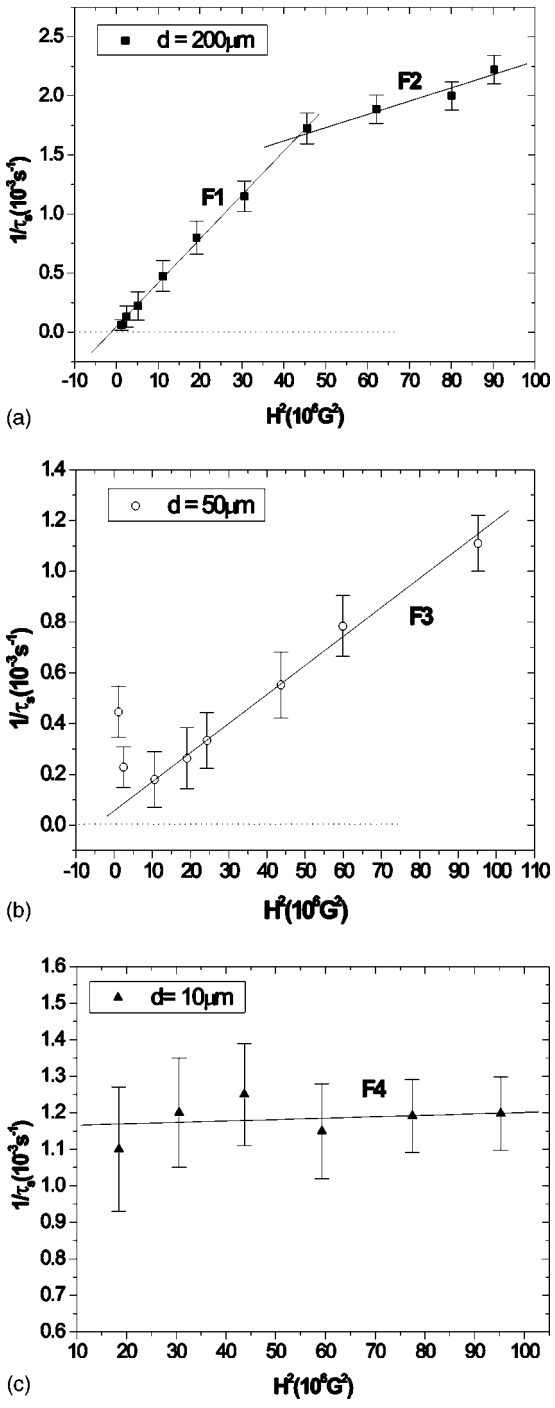

FIG. 6. Experimental results for $1/\tau$ as a function of H^2 for different cell thicknesses, (a) 200 μm, (b) 50 μm, and (c) 10 μm. The solid lines correspond to a linear fitting using Eq. (3), where the related parameters obtained from the fitting are listed in Table I.

For the cell 10 μm thick within the experimental uncertainties, it is observed that τ is independent on the intensity of the applied magnetic field and the plot of $1/\tau$ as a function of H^2 results in a straight line with a very small slope; $s \approx 3.8\times10^{-13}\,\mathrm{s}^{-1}\,G^2$, which is two orders of magnitude smaller than the values obtained for the other cells (see Table

TABLE I. Values obtained from the fitting of the experimental data.

d (μm)	Linear fit	$1/\tau_0$ (10^{-5} s^{-1})	H_c^2 (units of 10^6) G^2	s (10^{-11} s$^{-1}G^{-2}$)	C (units of 10^{-3})	D (units of 10^{-10})
200	F1	4.13	−1.11	3.70	0.82	8
	F2	124	−120.4	1.03	24.8	2.1
50	F3	5.53	−4.87	1.13	1.4	2.3
10	F4	116	−2993	0.038	23.2	0.076

I). Such low value of s can be due to a decreasing in the value of D, which means that the direct interaction of the surface layer and the magnetic field has a weaker contribution to the total energy, compared to the other cells. It is worthwhile to note that the magnetic field is applied making an angle of 45° with respect to the initial orientation, but the maximum deformation observed for such a thin cell is only $\approx$10°, for $H\approx 10$ kG.

Concerning the experimental results the first point we must discuss is the existence of two lines with different slopes for the thicker cell (200 μm). In fact, we proceeded to the fitting assuming two independent lines, and we argued that this should be related to changes in the phenomenological parameters C and D. Considering the values of $1/\tau_0$ and s listed in Table I and assuming $r\approx\rho\approx 0.5$ and $\gamma\approx 10$ P [6], which are reasonable values for such parameters, we estimate the values of C and D. Such values introduced in Eq. (3) were used to simulate the curves presented in Fig. 7, introducing small variations on both parameters C and D. We observe that keeping C constant and allowing D to assume different values it is possible to obtain two lines connected with different slopes, however, the break occurs for very low values of H. It was not possible to fit all the experimental points using Eq. (3), for unique values of C and D; the data must be separated in two independent lines, as we have done.

The second important point to be discussed concerns the fact that in the regions of high magnetic fields the slope of the curve is smaller. We argued that this could be related to a lower value of D, which means that the coupling of the surface layer to the magnetic field is weaker. This may be due to the fact that increasing the intensity of the magnetic field a larger portion of the sample is oriented in the direction of the magnetic field, reducing the thickness of the surface layer. For thin cells we observe also a decreasing of D, which is consistent with the fact that we had to change the profile of the director in order to fit the experimental curves of transmittance, neglecting the thickness of the surface layer, and considering a uniform orientation in the sample. The extremum situation is illustrated for the thinner cell (10 μm thick), where we obtained $D\approx 0$. In fact, assuming strong anchoring conditions (which are not the observed for lyotropic liquid crystals), the magnetic correlation length would be $\approx$10 μm for $H=10$ kG, which is comparable to the thickness of the sample, and we would not expect any effect of the magnetic field [5].

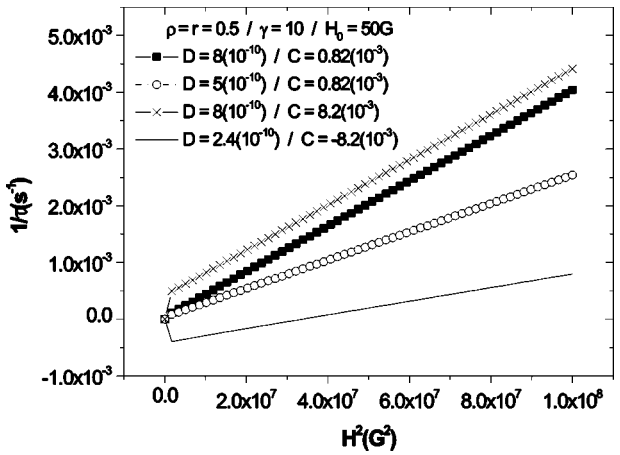

FIG. 7. Simulation of Eq. (3), assuming constant values for the parameters r, ρ, K, and γ and allowing C and D to assume different values, to illustrate their influence on the behavior of $1/\tau$ vs H^2.

V. CONCLUSIONS

We must be careful when comparing length scales in thermotropics and lyotropic liquid crystals, because the building blocks present completely different features. In the case of lyotropics, the building blocks are aggregates (or micelles) of amphiphilic molecules that due to self-organization can exhibit simultaneously shape and order variations driven by temperature and/or concentration changes. The micelles present a biaxial shape (Fig. 1) with typical repetition distances; 10, 8, and 5 nm, along the three main directions. The three nematic phases are the macroscopical consequence of orientational fluctuations, which are free rotations around **c** axis and $\mathbf{e}_+$ axis, in the discotic and calamitic phases, respectively, and only small amplitude oscillations in the biaxial phase [7]. Furthermore, there is a pseudolamelar order along the shortest dimension of the micelles (or perpendicular to the bilayer) with a correlation length of about 30 nm, which corresponds to approximately six bilayers, including the water between them. The frequencies related to the orientational fluctuation modes are in the range of 200 Hz for lyotropics [8] while for thermotropics the typical frequency is 5 kHz [9] for thick samples.

The existence of a limiting surface imposes a restriction on the fluctuations of the biaxial micelles around the longest axis, parallel to the boundary surface, although they are free to rotate around **c** axis. If a magnetic field is applied to the calamitic sample, the orientation of the $\mathbf{e}_+$ axis is fixed (parallel to H), leading to a biaxial order close to the surface. The phenomenological model discussed in this paper considers the existence of a surface layer of finite thickness and biaxial order that interacts directly with the magnetic field. This model predicts there are two possible equilibrium states

which are distinguished by the orientation of the longest axis ($\mathbf{e}_+$) of the micelles with respect to the direction of the magnetic field. The experimental data obtained for the cell 200 μm thick presents a behavior similar to what has been predicted when the equilibrium state corresponds to state I, the axis $\mathbf{e}_+$ is parallel to H, both in the surface layer and in the bulk. In fact, this is what is expected in the bulk, since we are dealing with a calamitic nematic sample that tends to align with the director parallel to the magnetic field, and this direction corresponds also to the average orientation of longest axis of the micelles.

The equilibrium state II can occur when the phenomenological constant C is negative, which corresponds to the $\mathbf{e}_-$ axis oriented parallel to the magnetic field in the bulk and in the surface layer. This state is possible when there is a bulk biaxial phase, and the magnetic field is not strong enough to induce the orientation of the longest axis, i.e., for $H<H_c$. It is possible to distinguish the two equilibrium states from the dynamical behavior of the surface layer, as was sketched in Fig. 2(b), where in state II the angular coefficient is negative. According to the experimental results obtained for the cell 50 μm thick there are two points in the region of weak magnetic fields that would be connected by a line of negative angular coefficient. This is consistent with a bulk biaxial order, although the temperature of the sample has not been changed with respect to the thicker sample. Therefore, we believe that the existence of the equilibrium state II characterized by a homogeneous orientation of the director, is a consequence of the reduction of the sample thickness. It is worthwhile to remember that in order to fit the experimental curves of transmittance for the cells 50 and 10 μm thick, we assumed that there is no distortion in the sample induced by the magnetic field and the sample rotates as a whole towards the field. For these cells, it is possible that the thickness of the biaxial layer becomes comparable to the thickness of the sample, and the biaxial order is stable over the whole sample. In this case, there is no discontinuity between bulk and surface layer; they are the same.

In conclusion, the behavior of τ as a function of H^2 observed for the sample 200 μm thick is consistent with a uniaxial nematic (calamitic) bulk phase, while the results obtained for the 50 and 10 μm thick samples are consistent with a bulk biaxial phase. Since the temperature of the sample is the same during the experiments, we believe that the uniaxial-biaxial transition is an effect of the reduction of the thickness of the sample, which restricts the orientational fluctuations in the cell, or in other words, it is a confinement effect.

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