Alignment and phase transition induced by surface action in lyotropic nematic liquid crystals

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The alignment properties of lyotropic nematic liquid crystals (LNLC) on treated substrates were studied. Hydrophobic vs hydrophilic surfaces as well as rubbed vs nonrubbed surfaces were used to investigate the influence of the boundary surfaces on the spontaneous alignment of LNLC. It was found that the nematic particles can follow the anchoring direction imposed by the surface only when the LNLC material is strongly confined. We also observed a phase transition induced by surface action in the case of strong confinement. The reorientation and relaxation processes of the nematic director at the treated boundary surfaces were also studied. The characteristic times of these processes were found to be dependent on the sample thickness and the surface properties.

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I. INTRODUCTION

The bulk properties of lyotropic nematic liquid crystals (LNLC's) have been intensively studied during the last decades [1–3]. The main results reported show strong similarities between these materials and their thermotropic cousins. The features of the nematic phase of these materials (flow, orientation by a magnetic field or by surface action) are treated in the same way as for thermotropic nematic liquid crystals (TNLC's). Nevertheless, it is well worth underlying that the building elements (or particles) of LNLC's are formed by the aggregation of hundreds of amphiphilic molecules into large anisotropic micelles, whereas for TNLC's the particles are isolated molecules. Experimental evidence [4,5] showed that the elastic constants (bend, twist, and splay) of lyotropic nematic phases are of the same order of magnitude as for thermotropic nematic phases. Such behavior could be explained by the fact that the micelles can be easily deformed, and should therefore not be treated like rigid particles [4,5]. Indeed, the phase transitions in LNLC's can be accompanied simultaneously by fluctuations of the nematic order and by a change in the shape of the micelles. Assuming the hypothesis of nonrigid particles, the interactions of a lyotropic nematic phase with a boundary surface (i.e., their anchoring properties) may be quite different compared to thermotropic nematic LC's. In fact, the influence of the boundary surfaces on LNLC's has not, up to now, been well understood. Under the application of an external magnetic field, strong anchoring is generally assumed, giving rise to the existence of two surface regions where the nematic director experiences a strong distortion. These surface regions have a thickness that corresponds to the magnetic coherence length, $\xi=(1/H)\sqrt{k/\chi_a}$, where k is the elastic constant and χ_a is the anisotropy of the magnetic susceptibility. Under the application of a strong magnetic field of 10 kG, the surface layer can be estimated to be about 10 μm thick (taking $K=10^{-6}$ dyn and $\chi_a=10^{-8}$). Thus, in order to study the magneto-optical effect in lyotropic nematic phases, one may be constrained to use quite thick cells.

Recently, it was reported that, for a nematic calamitic phase confined in a microslide 200 μm thick, in addition to the usual bulk director reorientation, a reorientation process of the director in the surface layer can be induced by an external magnetic field [6–8]. A phenomenological model was proposed to explain such a surface reorientation process, where we consider, together with a dry-friction-type interaction of the micelles with the boundary surface, an anchoring contribution [8]. It was found that the anchoring strength of the LNLC particles on the microslide surface is of about 10^{-5} erg/cm, which corresponds to quite a weak anchoring.

In this paper we present a study on the influence of the surface on the orientational state of a nematic calamitic phase. Up to now, to our knowledge, no evidence of a spontaneous alignment of lyotropic calamitic nematic on treated surfaces has been reported. Such a lack of investigation may be related to the fact that lyotropic mesophases do not present any interest for use in LC displays. In any case, such a study may be helpful in obtaining a better understanding of the interactions involved between LNLC particles and a solid surface. We have studied the effect of the physicochemical features of the surface (hydrophilic against hydrophobic), the geometrical shape of the surface (rubbed vs nonrubbed), and the influence of the confinement (cell thickness d) on the spontaneous alignment. We have also investigated the surface layer reorientation by applying a strong magnetic field, and the relaxation process when the field is removed, in order to estimate the anchoring strength of a nematic calamitic phase (N_c). The characteristic time for the surface reorientation process, as well as the relaxation time, are obtained by fitting the experimental curves of the transmittance of the sample recorded as a function of time while a magnetic field was applied and then removed, respectively.

As will be shown herein, a spontaneous alignment can be achieved only when the nematic calamitic phase is confined between two rubbed substrates separated by less than 50 μm. Furthermore, we found that a certain anisotropy of the substrate is necessary for surface layer reorientation to take place. It was also found that the characteristic time for the surface layer reorientation seems to depend slightly on

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the cell thickness (d), whereas the relaxation time varies strongly with d. Another important result is the fact that the surface reorientation process can occur even when the cell thickness is smaller than the expected magnetic coherence length (ξ).

II. EXPERIMENT

The lyotropic LC system investigated is a ternary mixture composed of 35.3 wt% of potassium laurate, 4 wt% of decylammonium chloride (DaCl), and 60.7 wt% of water. It presents a hexagonal phase at low temperature, and two uniaxial nematic phases (calamitic N_c and discotic N_d) separated by a biaxial phase N_{bx}. The transition temperatures were precisely determined by birefringence measurements as a function of the temperature; H_α-N_c at 15 °C, N_c-N_{bx} at 30 °C, and N_{bx}-N_d at 35 °C.

The lyotropic material was inserted into glass cells of different thicknesses (10, 40, 100, and 200 μm). The cells were built by sealing two treated glass plates kept distant by Mylar spacers of a given thickness. The glass plates were first carefully cleaned before any specific surface treatment. We have used four different types of substrate: on the one hand, hydrophilic against hydrophobic and, on the other hand, rubbed against nonrubbed. Bare clean glass plates were used as hydrophilic surfaces, whereas to obtain a hydrophobic surface a thin film of poly-methyl-methacrylate (PMMA) was spun coated on the glass plate. Unidirectional rubbing was performed by means of a homemade rubbing machine, which allowed controlled rubbing treatments. The cells were filled with the lyotropic material by capillary action, at room temperature, with the sample in the nematic calamitic phase. The cells were then observed with a polarizing microscope. The surface layer reorientation and relaxation processes were followed by a measurement of the transmittance of the sample as a function of time while the magnetic field was, respectively, switched on and then off.

A. Optical observations

The cells were mounted on a rotating stage of a polarizing microscope, between two crossed polarizers. It was observed that cells 100 and 200 μm thick showed a planar degenerated alignment of the nematic calamitic phase, even when the boundary surfaces were unidirectionally rubbed (see Fig. 1). When the cell thickness is lowered to 40 μm a spontaneous alignment of the LNLC particles can be induced if the surfaces are rubbed. The alignment quality increases even more when the LNLC material is confined in a cell of 10-μm thick (see Fig. 2). This means that, compared to thermotropic NLC, a spontaneous alignment can be induced by surface action only if the LNLC is strongly confined. In order to check if the alignment was not due to the capillary flow during the filling procedure, we rubbed the two glass plates in a direction different from the filling (or flow) direction. It turns out that the LNLC particles orient mainly along the rubbing direction, even if a slight deviation from this direction was observed. Furthermore, when the two boundary substrates are rubbed in two distinct directions, in order to create a twist deformation in the LNLC medium, the director adopts an intermediate uniform orientation between the two imposed alignment directions. The surface action seems not to be sufficient to create a twist deformation in the LNLC medium, independently of the sample thickness. This may be consistent with a weak anchoring of the LNLC particles on the rubbed polymer surface.

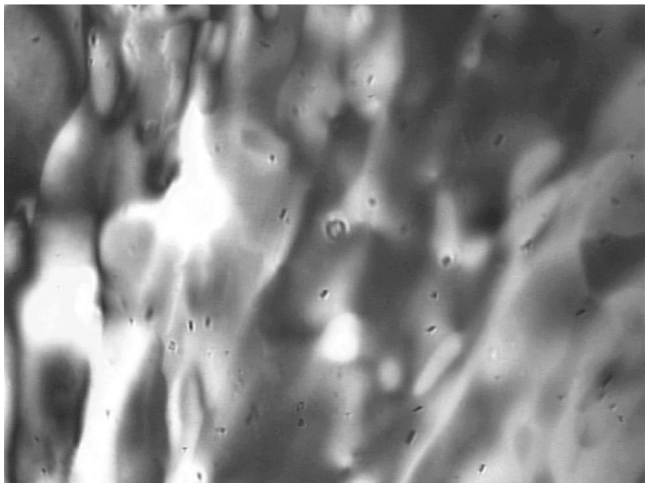

FIG. 1. Texture observed under a polarizing microscope in a lyotropic nematic LC sandwiched between two rubbed PMMA substrates kept apart by a Mylar spacer of 200 μm. A degenerate planar alignment is induced.

It is worth noting that if the boundary surfaces are bare glass surfaces unidirectionally rubbed, the alignment quality is worse than for rubbed PMMA surfaces. A very surprising behavior was also observed in all thin cells of 10 μm independent of the surface treatment: there occurs a transition from a planar texture to a homeotropic texture, as can be seen in Fig. 3. The transmittance of the sample measured as a function of time, in the absence of any external field, shows three regimes; the first is related to the planar texture which remains stable for about 14 h; a second regime with an abrupt decrease of the transmittance taking approximately 3 h is followed by a steady regime where the transmittance reaches a minimum. This regime corresponds to a dark tex-

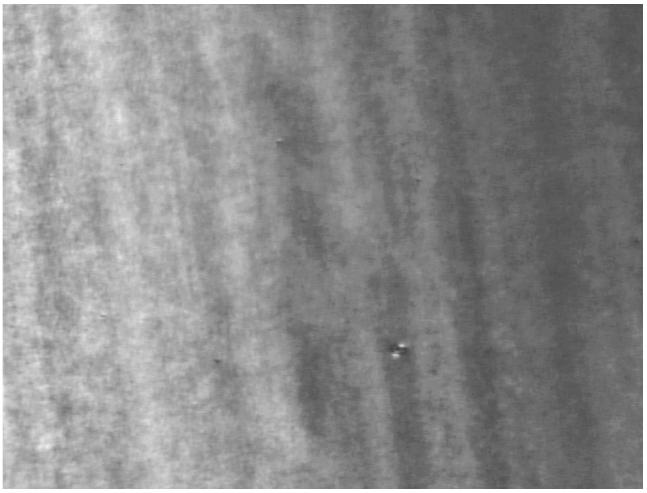

FIG. 2. Texture observed under a polarizing microscope in a lyotropic nematic LC sandwiched between two rubbed PMMA substrates kept apart by a Mylar spacer of 10 μm. A uniform planar alignment is induced.

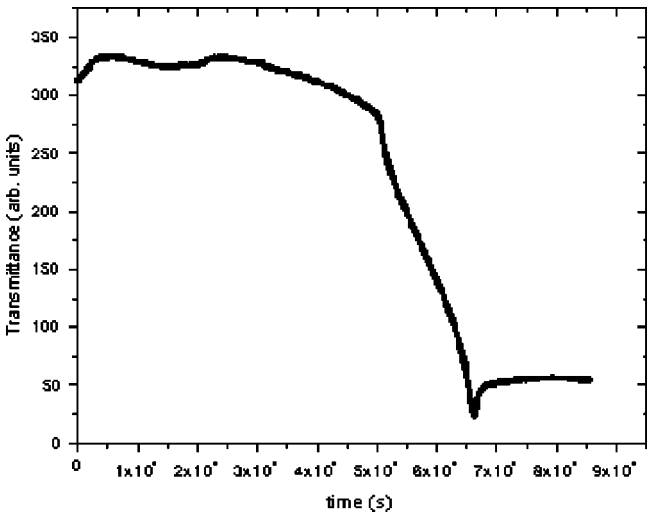

FIG. 3. Transmittance of a sample 10 μm thick between crossed polarizers. Initially the sample is in a planar configuration, and after $\sim$14 h the transmittance decreases and the sample presents a homeotropic texture.

ture typical of the uniform homeotropic orientation of the nematic director. Two hypotheses could be drawn: an orientational transition of the N_c phase from a planar alignment to a homeotropic alignment or a phase transition from N_c to N_d, even if it seems difficult to stabilize a homeotropic orientation of the N_c phase in the absence of any external magnetic field. To discriminate between these two hypotheses, we applied a strong magnetic field (10 kG) in the plane of the boundary surfaces, and measured the transmitted intensity of a laser beam crossing the sample at normal incidence. No change was observed in the transmitted intensity; this shows that we are not in the presence of a homeotropically oriented N_c phase, but a N_d phase with the director uniformly aligned along the sample thickness. In Fig. 4 we report the transmittance curves of the sample submitted to a magnetic field of 10 kG applied at two distinct angles ($\theta_H = 20°$ and $\theta_H = 45°$) with respect to the plane of the boundary surfaces. It can be seen that the reorientation of the director in the bulk follows the field direction; the resulting deformation is not stable, since once the field is removed a relaxation process takes place.

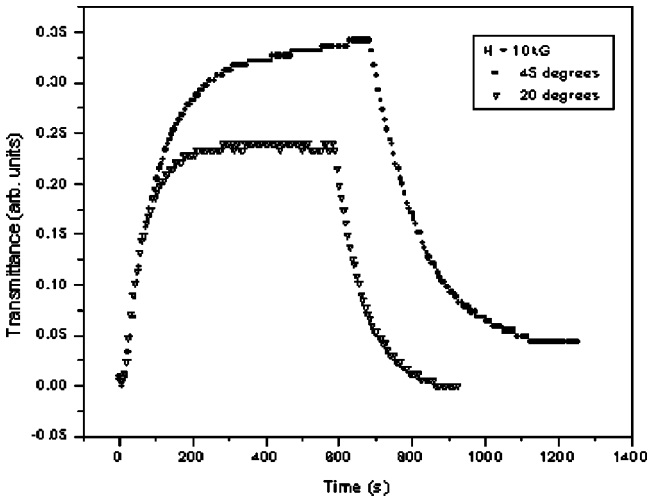

FIG. 4. Experimental curves of transmittance showing the director orientation induced by a magnetic field of 10 kG in a sample of 10 μm, which has experienced a N_c-N_d phase transition due to the surface action. (a) For $\theta_H = 20°$, (b) $\theta_H = 45°$.

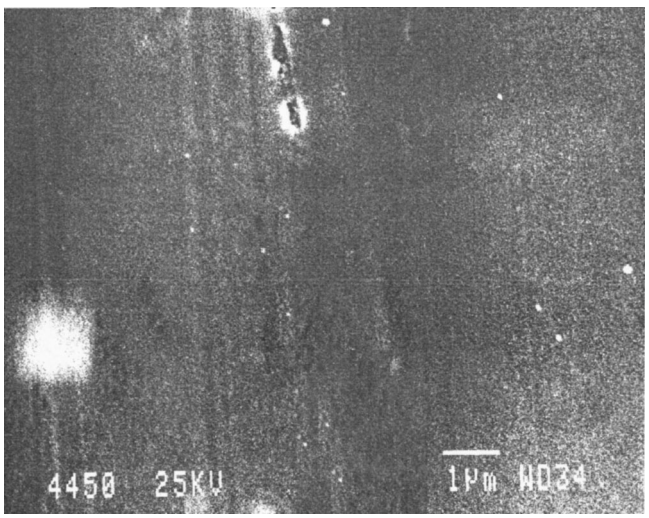

FIG. 5. Electron microscope picture of a rubbed PMMA film deposited on a glass substrate.

B. Surface reorientation and relaxation processes

As already highlighted, when a magnetic field is applied to a lyotropic nematic LC in the calamitic phase, in addition to the usual bulk reorientation process there occurs a reorientation of the director in the surface layer. More recently, we reported a phenomenological model to explain such a surface reorientation process, where together with a dry-friction type contribution we considered a contribution from the anchoring energy of the nematic particles on the boundary surfaces. In this section, we will present some preliminary results on the influence of surface features on the surface reorientation process, which may help us to obtain a better understanding of the anchoring contribution to the surface layer reorientation process.

Samples of 100 and 200 μm that did not show any spontaneous alignment were submitted to a strong magnetic field **H** (typically 10 kG). It was found that the magnetic field induces a uniform stable orientation of the director along **H** only if the confining glass or polymer surfaces were unidirectionally rubbed in the same direction as the applied field. This implies that a certain anisotropy of the surface is necessary for the surface layer orientation to take place, and then to give rise to a uniform and stable alignment of the sample. To try to gain an insight into the mechanism involved in the surface orientation process, we performed an analysis of the surface topography by means of a scanning electron microscope. It was found that for bare glass, rubbing does not provoke any significant surface deformation, such as microgrooves. We have to underline that we used a soft velvet cloth to rub the substrates. Regarding the polymer-coated glass substrate, rubbing induces the formation of microgrooves (Fig. 5) about 0.04 μm wide along the rubbing direction. Both types of rubbed substrates give rise to a surface orientation process, and we believe that the presence of microgrooves at the surface is not the main feature that controls

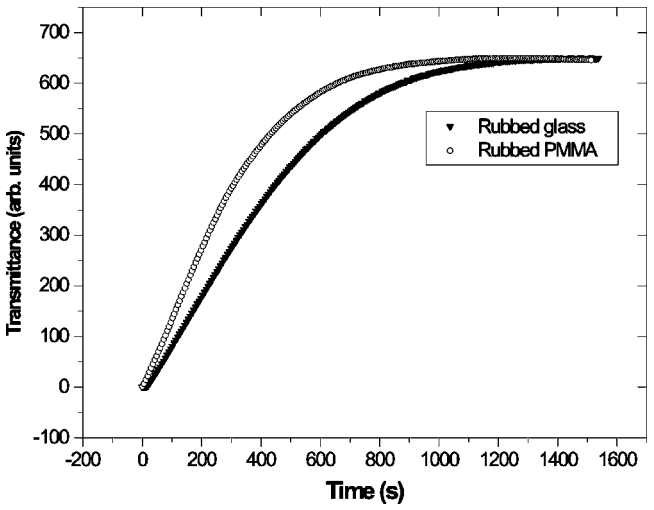

FIG. 6. Experimental curves of transmittance of a LNLC confined in a cell of 200 μm, built up from two rubbed glass plates and two rubbed PMMA substrates, respectively.

the occurrence of this process. Nevertheless, the most important fact is that rubbing creates a certain surface anisotropy which seems necessary for the surface orientation to take place.

To investigate the effect of a magnetic field on an initially aligned LNLC sample, the field was applied at an angle of 45° with respect to the initial orientation. A reorientation of the director takes place at a characteristic time that depends strongly on the field intensity [6–8]. Figure 6 shows the transmittance curve for the surface reorientation process that takes place when a field intensity of 10 kG is applied to a sample 200 μm thick built of, rubbed glass plates and rubbed PMMA-coated glass plates, respectively. The characteristic time for the surface reorientation process is slightly different for both kinds of substrate used. It therefore seems that the hydrophobic or hydrophilic character of the surface has a certain influence on the surface reorientation process.

In Fig. 7 we show the transmittance curves for the reorientation and relaxation of the surface director when a magnetic field of 10 kG is applied and then removed, respectively, in cells of 10, 100, and 200 μm. The characteristic time for the process increases slightly when the cell thickness decreases. Such a behavior seems consistent with an increase of the surface contribution when the LNLC is more and more confined; the anchoring plays the role of a resistance to the reorientation of the director in the surface layer in the field direction. We have to underline that the effect is not so strong as one would expect. This may be due to the quite weak anchoring of lyotropic particles on the boundary surfaces. Regarding the relaxation process, at 10 μm, a quite a rapid relaxation of the surface director takes place, giving rise to a complete recovery of the initial orientation. When the lyotropic material is confined in a cell of 200 μm, however, the initial orientation is not recovered even after a quite long time. The relaxation time τ_s was determined by fitting the relaxation curves using a simple exponential decay function. τ_s decreases with decreasing cell thicknesses. Nevertheless, this result is consistent with the fact that the relaxation process involves mainly surface contributions. As could be expected, the relaxation process becomes faster when the cell thickness decreases, due to the fact that the anchoring contribution of the nematic particles on the boundary surfaces is higher for a smaller cell thickness.

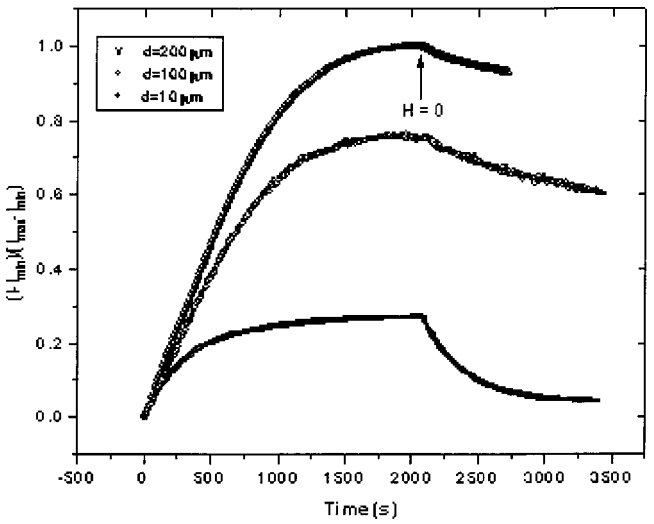

FIG. 7. Experimental curves of the transmittance of a LNLC material sandwiched between cells of different thicknesses (10, 100, and 200 μm).

III. DISCUSSION AND CONCLUSION

As one may guess, the anchoring properties of lyotropic NLC's are quite different from their thermotropic cousin. It was found that to obtain a surface action on the anisometric micelles, which are the building particles of a bulk lyotropic NLC, it is necessary to confine the LC material inside quite thin cells (typically 10 μm). Furthermore, it was observed that, in the experimental conditions used, it is hard to introduce a twist deformation into such a system. Such a surprising feature, together with the possible gliding of the nematic director at the surface by the application of a magnetic field, seems consistent with the existence of a weak anchoring of the lyotropic particles at the boundary surfaces. Nevertheless, the experiments performed here do not give any access to the type of interactions involved in the anchoring of the anisometric micelles onto the surface. If we assume that the micelles are nonrigid bodies, and can therefore be easily deformed by the boundary surface, we can argue that a surface layer may be built up by amphiphilic molecules in contact with the solid substrate. The thickness and compactness of this surface layer may depend on the physical shape of the substrate as well as the related physicochemical features. It is well known that in the case of thermotropic NLC's, in contact with a solid substrate, the rodlike molecules form a smectic structure at the surface that arises from symmetry breaking [9]. It has been shown that this smectic layer does not influence the macroscopic anchoring properties of the nematic particles. Nevertheless, in the case of lyotropic NLC's, the surface layer may be much thicker than that present in thermotropic LC's due to the amphiphilicity, and thus the self-organizing nature of the molecules in the aqueous medium. We may indeed obtain a lamellar structure at the surface formed by one or more bilayers. In the case of hydrophobic substrates, we believe that a compact reverse

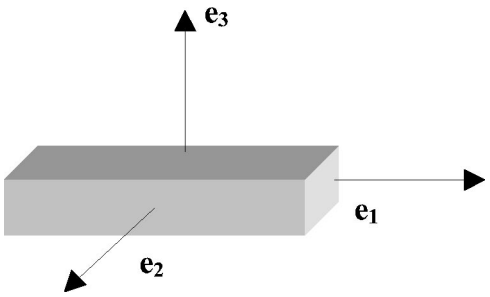

FIG. 8. Sketch of the biaxial molecular aggregates. In the biaxial phase there is a positional order along the three directions of space. Orientational fluctuations around the e_1 axis result in a calamitic (N_c) phase, and around the e_3 axis results in a discotic (N_d) phase.

bilayer of amphiphilic molecules is formed with the aliphatic chains came into contact with the surface. For hydrophilic substrates, however, the amphiphilic molecules organize into a bilayer, with the polar heads in contact with the surface, which allows the inclusion of water (holed bilayer). This surface layer may not screen the substrate properties, that can then propagate toward the bulk, composed of anisometric micelles (nematic particles). Regarding the anchoring behavior of the LNLC on such substrates, the experimental observations show a slight difference in the alignment quality and in the characteristic time of the surface reorientation process. At present, it is not obvious how to discriminate between the different surface effects that dominate the anchoring of LNLC particles. In the case of the hydrophilic substrate used, i.e., a rubbed glass plate, no microgrooves are present. However, in the case of the hydrophobic substrate (the PMMA coated-plate), microgrooves are created at the surface. Nevertheless, the contact surface for the nematic particles may be the surface layer of the lamellar structure instead of the solid substrate. The structure of this surface layer may also influence the anchoring behavior of the LNLC. New experiments are in progress to try to obtain a better understanding of the anchoring properties of LNLC's, and will be published elsewhere.

Regarding the phase transition from nematic calamitic (N_c) to nematic discotic (N_d) that was observed in the thin samples (10 μm), one must consider the particularities of lyotropic systems. Molecular aggregates are biaxial objects that can be destroyed and rebuilt due to the diffusion of the amphiphilic molecules through the solution [10]. The biaxial nematic phase is characterized by a orientational order along the three directions, whereas orientational fluctuations around the longest or shortest axis lead to the calamitic or discotic nematic phases, respectively (Fig. 8) [11]. Let us consider a nematic calamitic phase in contact with a boundary surface, in the x-y plane. Due to symmetry breaking, close to the boundary surface the aggregates tend to align with the shortest axis (e_3) perpendicular to the surface, and this order extends to the next neighbors. The transition to a N_d phase indicates that fluctuations around the e_1 axis are suppressed due to the surface imposed alignment direction and the strong confinement, favoring fluctuations around the e_3 axis. This could occur if the shape anisotropy is weak, and this is the case in this system; x-ray experiments have shown that the ratios of the repetition distances (e_1/e_3 and e_2/e_3) are 1.5 and 1.4 [12]. It is worth underlining that the hypothesis of a chemical process has been omitted to explain the transition from N_c to N_d, due to the fact that care was taken to obtain hermetically sealed cells, and that esterification was avoided by using DaCl instead of Decanol.

In conclusion, we have shown that surface action can align a lyotropic NLC only if the material is confined into a thin cell. The occurrence of a gliding of the surface director, as well as the impossibility of generating a twist deformation in such systems, seem consistent with the existence of a weak anchoring of the nematic particles on the treated substrates we used. Furthermore, a phase transition from N_c to N_d was observed in the strongly confined sample, underlying the influence of the surface layer to organization of the micelles in the bulk. The experimental results presented in this work raise important questions about the nature of the interface interactions, and how these interactions influence self-organized systems such as lyotropics. New experiments are in progress with the objective to obtain a more complete description of the anchoring properties of lyotropic liquid crystals.

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