

Gliding anchoring of lyotropic nematic liquid crystals on amorphous glass surfaces

E. A. Oliveira, A. M. Figueiredo Neto, and G. Durand*

Instituto de Física da Universidade de São Paulo, Caixa Postal 20516-01498, São Paulo, Brazil

(Received 11 March 1991)

The interactions of a lyotropic liquid crystal with boundary amorphous glass surfaces are investigated using optical techniques. An unusual phenomenon is observed: the gliding of the director at the surface. A qualitative model is proposed to explain the experimental results.

The anchoring properties of thermotropic nematic liquid crystals have been widely investigated in past years.¹⁻⁴ Many techniques are known for treating surfaces, like rubbing, oblique evaporation, or coating with organic surfactants, resulting in an easy axis along which the molecules align.¹ Models to explain the surface interactions are still not completely understood. To our knowledge, up to now, no gliding of the director on surfaces has been reported.

In lyotropic mixtures there is some evidence of strong anchoring. Despite this, strong magnetic fields are applied in order to orient the director.⁵ In this paper, we investigate the anchoring properties of lyotropic liquid crystals on glass surfaces, without any treatment. The polarizing microscopy is used to determine the director configuration.

The lyotropic sample is a mixture of potassium laurate (28 wt.%), decanol (7 wt.%), and water (5 wt.%). The phases sequence, determined by optical and conoscopy observations, is the following: uniaxial discotic nematic (17°C) → biaxial nematic (19°C) → uniaxial calamitic (40°C) → isotropic. The experiment is performed in the nematic calamitic phase. The sample holder we used was made of microslides 200 μm thick and 4 mm wide. The inner surfaces of these microslides were examined in the interferential microscope. No irregularities or channels greater than 0.1 μm were observed in these microslides, but were observed in microslides with widths smaller than 4 mm.

The laboratory-frame axes are defined with the x axis parallel to the length of the microslides, and the z axis normal to the biggest surfaces. Initially, the sample is uniformly oriented by a strong magnetic field (≈ 17.5 kG), with the direction parallel to the x axis. Then a magnetic field H is applied at 45° from the x axis (perpendicular to the z axis). This geometry is chosen instead of the Fredericksz one because in the former, the director can rotate either to the left or to the right to align parallel to H . The process of orientation of the sample at 45° is studied by measuring the extinction angle φ (from the x axis), in the polarizing microscope, as a function of time. The same measurements are made during the relaxation process when H is switched off.

The measurement of the extinction angle φ gives the mean orientation of the director in the samples. In our experiments, we observe that when H is applied at 45° from the x axis, the sample tends to align with the director parallel to H . A small change in the orientation of the

sample is detected, with a short response time—about 20 s for $H = 2$ kG. Also observed is a slow orientation process, with a response time of hours. The characteristic time of this process depends on $1/H^2$ (Fig. 1).

The relaxation process is investigated, when H is switched off, by measuring the extinction angles for two wavelengths, as a function of time (Fig. 2). The difference between them cannot be explained by a twist along the thickness after such a long time (several hours). The characteristic relaxation time for a distortion with wave vector q ($=2\pi/\lambda$) is $\tau_{rel} = \gamma/q^2K$,⁶ where γ is the viscosity and K is the elastic constant. With $q = 1/200$ μm, $K = 10^{-6}$ dyn (Ref. 7), and $\gamma = 1$ P (Refs. 8 and 9), for lyotropic liquid crystals, one obtains $\tau_{rel} \approx 10^2$ s.

After the relaxation process, the equilibrium is reached to a final orientation at an angle φ_F (different from zero), which depends on the time the magnetic field is applied [Fig. 3(a)]. This means that the director at the surface rotated towards the direction of H , and it does not return to its original orientation (parallel to the x axis) when the magnetic field is switched off. This appears to be a new phenomenon: The director glides at the surface, with a characteristic time proportional to $1/H^2$ [Fig. 3(b)].

The long times observed in the orientation, gliding, and relaxation processes, cannot be explained by the usual models known for thermotropic liquid crystals.

For thermotropic liquid crystals it is known that in the

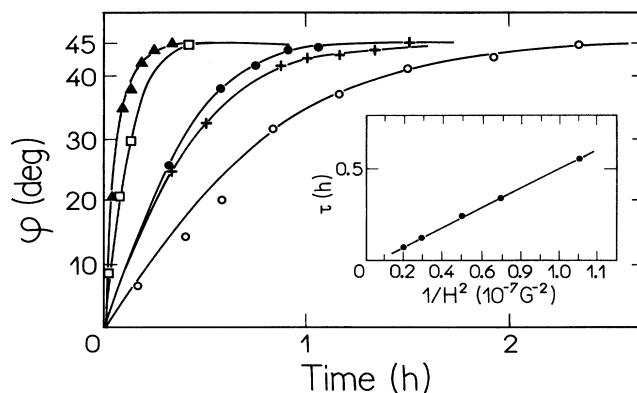


FIG. 1. Orientation of the director as a function of the time. Magnetic-field values: \circ , 3; $+$, 3.8; \bullet , 4.5; \square , 6; \blacktriangle , 8 kG. Inset: the characteristic time for orientation is proportional to $1/H^2$. The lines are only a guide to the eyes.

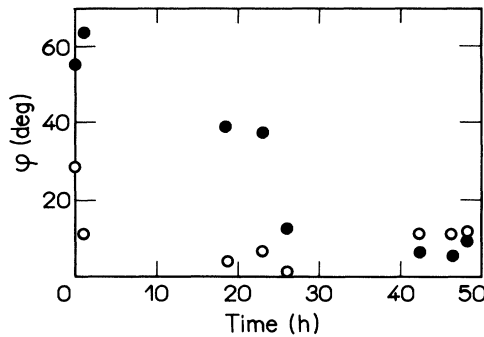


FIG. 2. Relaxation process when H is switched off. The measurements are given for red light (○) and blue light (●), $\lambda = 6328$ and 4880 Å, respectively, after 2 h in $H = 4.5$ kG (45°).

bulk the director aligns parallel to H , at 45° from the x axis. The nematic alignment is perturbed only in a layer near the surface, with thickness of the order $\xi = (K/X_a)^{1/2}/H$,⁶ where X_a is the anisotropy of magnetic susceptibility. If the director at the surface is at angle θ_s , related to the x axis, and at an angle θ in the bulk, there is an elastic torque coming from the bulk which is equilibrated by the surface-anchoring torque. This is written as

$$\frac{K}{L}(\theta_s - \theta_0) \cong K \left. \frac{\partial \theta}{\partial z} \right|_{\text{surf}}, \quad (1)$$

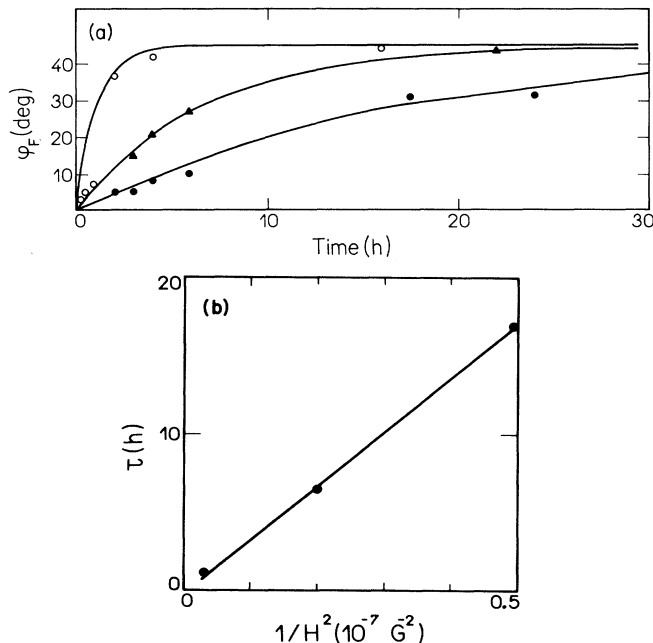


FIG. 3. (a) Final orientation of the samples as a function of the length of time that the magnetic field is applied. The director glides at the surface and does not return to the original configuration when the magnetic field is switched off. The exponential curves are adjusted. (b) The characteristic time of the gliding process is proportional to $1/H^2$.

where θ_0 is the angle between the director and the easy axis at the surface, and L is the extrapolation length.^{6,10}

The elastic torque at the surface can be derived from the equilibrium condition of the torques in the volume,

$$K \frac{\partial^2 \theta}{\partial z^2} + \frac{1}{2} X_a H^2 \cos 2\theta = 0. \quad (2)$$

From Eq. (2) one obtains

$$K \left. \frac{\partial \theta}{\partial z} \right|_{\text{surf}} = \frac{K}{\xi} \left(\frac{\pi}{4} - \theta_s \right). \quad (3)$$

Assuming that the magnetic field can induce some gliding of the director in a surface layer of thickness D , the simplest model one can build is to suppose that at the surface there is only the elastic torque coming from the bulk, which is equilibrated by a viscous torque:

$$\frac{K}{\xi} \left(\frac{\pi}{4} - \theta_s \right) \cong \gamma \dot{\theta}_s D. \quad (4)$$

The solution of this equation gives an exponential increasing of θ_s , with a characteristic time proportional to $1/H$. If we assume D to be equal to ξ , the correct dependence on $1/H^2$ is obtained, $\tau = \gamma/(X_a H^2)$. With the typical values of γ and X_a for lyotropic liquid crystals ($X_a = 10^{-8}$),⁷ one obtains τ of the order of 10^2 s. To fit the experimental values ($\tau = 17$ h for $H = 4.5$ kg), one should admit a viscosity 10^4 times larger.

We propose, then, an alternative model. Let us make the hypothesis that at the surface, there is a bilayer of amphiphilic molecules, with defects or channels, like in a lamellar structure.^{9,11,12} Initially, the micelles in the bulk are uniformly oriented at 45° and the alignment is perturbed in a layer of thickness ξ near the surface. The defects at the surface layer can be interpreted as large anisotropic objects that can glide and align parallel to H if they have surface dimensions of order ξ . If they are smaller, the competition between the elastic torque coming from the volume does not favor this gliding. Because these objects are larger (their dimensions in the x - y plane are a few micrometers) than the micelles (dimensions of 100 Å), there is an apparent larger viscosity near the surface.

These larger objects are subjected to the elastic torque coming from the micelles in the bulk. This torque is equilibrated by the viscous torque. To rotate an object with dimensions of L , l , and thickness d (about the bilayer thickness), it is necessary to exert a torque that is $T = \gamma \theta l L d$. The total number of objects is $\alpha A \xi / d$, where A is the surface area and α is the number of objects per unit area. The torque per unit area is then $T = \gamma \theta \xi \alpha$. The balance of the torque at the surface gives

$$\gamma \dot{\theta}_s \alpha \xi = \frac{K}{\xi} \left(\frac{\pi}{4} - \theta_s \right). \quad (5)$$

The solution of this equation gives an exponential increasing of θ_s , or the gliding process, with a characteristic time:

$$\tau = \frac{\xi^2 \gamma \alpha}{K}. \quad (6)$$

The dependence of τ on $1/H^2$ is obtained. The product

$\alpha\gamma$ can be interpreted as an apparent viscosity. If the dimensions of the objects are about ξ ($\xi \approx 20 \mu\text{m}$ for $H=4$ kG), α can be estimated to be no more than 10^6 when the objects occupy the whole surface. From our experimental values of τ , α is estimated to be 10^4 , which indicates that these objects do not fill the surface.

Indeed, some kinds of defects (such as grains) were observed in the textures. It was also observed that the size of these grains depends on the magnetic field. In Fig. 4, the typical dimensions of the defects are about $30 \times 80 \mu\text{m}^2$, for $H=4.5$ kG. The value of α can be calculated, and one obtains $\alpha \sim 10^4$, in good accordance with the estimation from the experimental values of τ . Small dimensions of the defects were observed with a stronger magnetic field, which confirms the hypothesis of the dimensions of the grains about ξ .

The relaxation process can be understood as a relaxation process at the surface. Different orientations of the objects at the surface layer gives rise to an elastic torque that is equilibrated by the viscous torque. The viscous torque per unit area is $T = \gamma\theta l\alpha$, where θ is the angle between the objects. The equilibrium condition is written as

$$\gamma\alpha\theta l = \frac{K}{\xi} \theta. \quad (7)$$

As l is comparable to ξ and $\alpha = 1 \text{ cm}^2/ll$, one finds the characteristic relaxation time

$$\tau_r \sim \gamma/K. \quad (8)$$

With the typical values of K and γ for lyotropic liquid crystals, we obtain $\tau_r \sim 10^5$ s. The experimental values are about 20 h, which is 10^5 s. The difference observed between the extinction angles measured for different wavelengths can be explained by the nonuniform orientation in the surface layer.



FIG. 4 Observation of defects in the texture seen in the polarizing microscope during the relaxation process after 45 min in $H=4.5$ kG at 45° from the x axis.

With the qualitative model presented here we can explain the long times observed and the correct dependence of τ on $1/H^2$. The gliding of the director at the surface is an interesting phenomenon that is probably related to the particular characteristic of the lyotropic systems. It has never been observed in thermotropic systems. In lyotropic systems, the amphiphilic molecules at the surface probably cannot move, but in the bilayer structure the defects on channels can be destroyed and rebuilt with a new orientation, due to the finite lifetime of the micelles.

The authors want to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazil) and CNRS (France) for financial support.

*Permanent address: Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France.

¹J. Cognard, *Mol. Cryst. Liq. Cryst. Suppl. Series* **1**, 14 (1982).

²K. H. Yang, *Appl. Phys. Lett.* **43**, 62 (1983).

³S. Faeti, M. Gatti, V. Palleschi, and T. T. Sluckin, *Phys. Rev. Lett.* **55**, 1681 (1985).

⁴R. Barbieri and G. Durand, *Phys. Rev. A* **41**, 2207 (1990).

⁵T. Kroin, Ph.D. thesis, Instituto de Física, Universidade de São Paulo, 1990.

⁶P. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

⁷T. Kroin and A. M. Figueiredo Neto, *Phys. Rev. A* **36**, 2987 (1987).

⁸E. Zhou, M. Stephanov, and A. Saupe, *J. Chem. Phys.* **88**, 5137 (1988).

⁹A. Saupe, *Nuovo Cimento* **30**, 16 (1984).

¹⁰A. Rapini and M. Papoular, *J. Phys. (Paris) Colloq.* **30**, C4-54 (1969).

¹¹M. C. Holmes and J. Charvolin, *J. Phys. Chem.* **88**, 810 (1984).

¹²J. Charvolin and Y. Hendrikx, *J. Phys. (Paris) Lett.* **41**, L597 (1980).

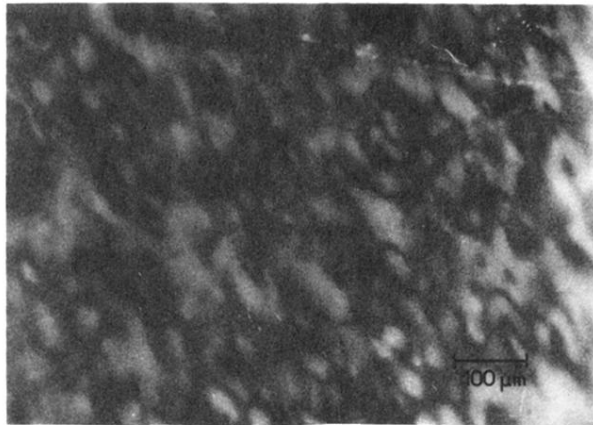


FIG. 4 Observation of defects in the texture seen in the polarizing microscope during the relaxation process after 45 min in $H = 4.5$ kG at 45° from the x axis.