

## Light-Induced Surface Sliding of the Nematic Director in Liquid Crystals

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We report the effect of light-induced sliding of the nematic director over an isotropic boundary surface in an azo-dye doped liquid-crystal cell. We show that illumination of the cell with polarized laser light induces transient dynamic sliding followed by permanent reorientation of the director. The two effects are in competition and tend to orient the director along mutually orthogonal directions. The sliding can be controlled and even completely quenched by the amount of induced anchoring energy. A physical model is proposed which accounts for the experimental results. [S0031-9007(99)08539-7]

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Light-induced anchoring and reorientation effects in liquid crystals (LC) have been the subject of intense research interests in recent years [1–10].

Optical reorientation was originally concerned with light fields acting on the bulk of a liquid crystal cell, the aligning surface determining only the boundary conditions in the reorientation process. Gibbons *et al.* [2,3] recently demonstrated the surface-mediated alignment of nematic liquid crystals in a cell having one glass substrate spin coated with a photosensitive material. The light-induced transformation of the photosensitive molecules coated over the surface results in the alignment of the LC director perpendicular to the polarization of the impinging light. A different reorientation effect has been reported by Reznikov and co-workers [4,5]. They showed that it is possible to get an easy-orientation axis over an isotropic polymer-coated surface as result of the light-induced excitation of a small quantity of azo-dye (<1%) in the bulk of a LC cell. Here, light absorption leads to a surface reorientation of the molecular director towards a direction parallel to the exciting polarization. After suitable illumination time, the light-induced anchoring becomes strong enough to produce permanent reorientation of the nematic director. This effect has been exploited to record high-resolution intensity [6] and polarization [7] holographic gratings in liquid crystal.

These results stimulated an interest to investigate the possibility of getting free surface sliding of the nematic director under the control of the incident light. In the paper of Marusii *et al.* [8], the authors interpreted the observed molecular reorientation close to the isotropic control surface as an effect of director sliding. However, the impossibility of changing the anchoring energy in their experiment did not allow one to establish definitively the actual nature of the phenomenon.

In this paper we report the first clear demonstration of the effect of molecular director sliding over an isotropic surface endowed with very weak anchoring energy. We

show that illumination with polarized laser light of an azo-dye doped LC cell induces both a transient dynamic sliding and a permanent reorientation of the molecular director. These two effects are regulated by different physical mechanisms and occur on different time scales. The key points of our experimental observations are (i) on a macroscopic scale, i.e., in the frame of the continuum theory, free director sliding over an isotropic boundary surface is possible, and (ii) this effect can be controlled and even completely quenched by the amount of anchoring energy induced on the surface.

The scheme of the experimental setup is shown in Fig. 1. The LC cell, 20  $\mu\text{m}$  thick, was filled by a photosensitive mixture of 4'-*n*-pentyl-4-cyanobiphenyl LC (5CB) and azo-dye methyl red (MR) at a weight concentration of about 1%. The inner surfaces of the two glass substrates limiting the cell were coated by different layers. The reference surface ( $S_r$ ) consists of a mechanically rubbed polyimide layer that provides strong homogeneous uniaxial anchoring. The control surface ( $S_c$ ) is an untreated isotropic layer of polyvinyl-cinnamate-fluoride (PVCN-F) providing a negligibly small azimuthal anchoring on the second boundary. The rubbed surface originally imposes homogeneous planar alignment of the LC molecules in the cell.

The exciting polarized beam from He-Cd laser ( $\lambda = 0.442 \mu\text{m}$ ;  $P = 1 \text{ mW}$ ) was focused on the cell from the size of the control surface by the lens  $L_1$ . The director reorientation over this surface was detected by checking the polarization state of a He-Ne laser probe beam ( $\lambda = 0.638 \mu\text{m}$ ;  $P = 0.1 \text{ mW}$ ) crossing the cell from the side of the reference surface. The electric field  $\mathbf{E}_p$  of the probe beam was set parallel to the initial director orientation  $\mathbf{n}_0$ , and the signal transmitted through an analyzer crossed to it was detected. In this geometry, any rotation of the molecular director (up to  $90^\circ$ ) over the control surface led to an increase of the transmitted signal. In fact, in our experimental conditions the Mauguin regime was

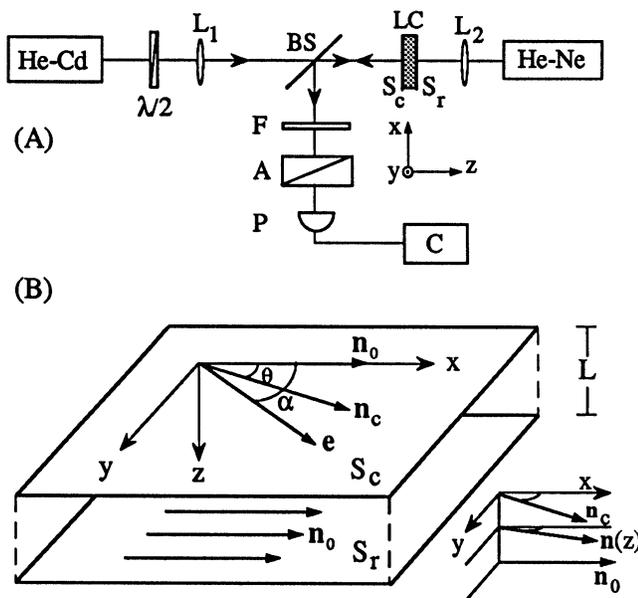


FIG. 1. (A) Experimental setup:  $L_1$  and  $L_2$ , lenses; BS, beam splitter;  $\lambda/2$ , half-wave plate; LC, liquid crystal cell; F, filter; A, analyzer; P, photodetector; C, computer. (B) Detail of the LC cell:  $S_c$ , control isotropic surface;  $S_r$ , reference rubbed surface;  $\mathbf{e}$  is the polarization vector of the incident lightfield.

realized and the field  $\mathbf{E}_p$  followed the director  $\mathbf{n}(z)$  while propagating through the cell [9]. The intensity  $I_d$  measured by the photodiode after the analyzer is then given by the Malus law [10], i.e.,  $I_d = I_0 \sin^2 \theta$ , where  $\theta$  is the angle between  $\mathbf{n}_c = \mathbf{n}(0)$  and  $\mathbf{n}_0$ , and  $I_0$  is the intensity of the probe beam before the analyzer. At the beginning of the experiment  $\mathbf{n}_c$  was parallel to  $\mathbf{n}_0$  and  $I_d = 0$ . Irradiation of the cell resulted in the appearance of a signal on the photodetector while the direction of  $\mathbf{n}_0$  over  $S_r$  did not change during illumination, as revealed by analyzing the light-induced textures with a polarizing microscope. Therefore, the appearance of a signal behind the analyzer indicated that the orientation of  $\mathbf{n}_c$  was changed. The measurement of  $I_d$  as a function of the exposure time allowed us to study the kinetics of the director reorientation at the control surface.

Figure 2 reports the dependence of the modulus of the surface director reorientation angle  $\theta$  versus the time  $t$  of exposure to the exciting light, when the angle  $\alpha$  between the incident polarization  $\mathbf{e}$  and  $\mathbf{n}_0$  is set to  $45^\circ$ . The curve exhibits an initial sharp rise, of the order of one-half a second, followed first by a decay to zero and then by a second slower rise, extending for a few minutes until the limiting value of  $45^\circ$  is reached. The initial fast rise indicates that, as a consequence of the irradiation, the director  $\mathbf{n}_c$  rotates away from  $\mathbf{n}_0$  toward a direction perpendicular to the incident electric vector  $\mathbf{E}$  in the plane of the isotropic surface. This behavior can be explained in terms of a light-induced bulk torque which acts on the LC molecules of the cell [4,11]. The torque is caused by the reorientation of the dye molecules due to the trans-cis photoisomerization process occurring under irradiation

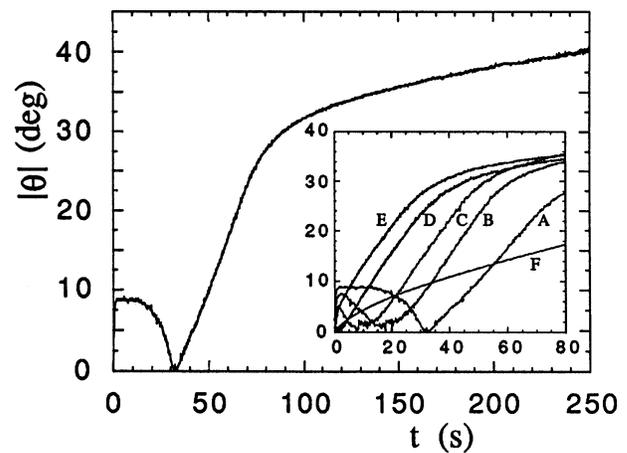


FIG. 2. Modulus of the surface director reorientation angle  $\theta$  versus the exposure time  $t$  when  $\alpha = 45^\circ$ . The inset shows that  $|\theta|$  vs  $t$  curves measured with different preillumination times  $t_0$ : (A)  $t_0 = 0$  s; (B)  $t_0 = 10$  s; (C)  $t_0 = 20$  s; (D)  $t_0 = 50$  s; (E)  $t_0 = 120$  s; (F)  $t_0 = 360$  s.

in the absorption band of the dye [12]. Because of the very small anchoring energy, the LC molecules over the isotropic surface rotate quasifreely away from  $\mathbf{n}_0$  toward a direction perpendicular to the exciting electric field. Because of the strong anchoring imposed by the rubbed surface, this reorientation results in a twisted director configuration in the bulk. This effect is not permanent because the cell spontaneously recovers its initial planar configuration after the exciting beam is switched off.

The behavior of  $|\theta(t)|$  after the initial rise is a consequence of the anisotropy induced by the light on the control surface, which results in the formation of an easy-orientation axis parallel to the exciting field [4,5]. The most probable mechanism responsible for this process seems to be the adsorption on the isotropic surface of the phototransformed MR molecules [5,6]. As the exposure time increases, the director rotates over the control surface toward the easy-orientation axis  $\mathbf{e}$  and finally reorients parallel to it. The consequent twisted director configuration which sets up in the cell is extremely stable: no change in the irradiated area was found after several months. Surface reorientation of the LC director involves a continuous rotation of the director towards the direction of the exciting electric field, starting from the position reached after the fast initial sliding. Accordingly, at first  $\theta$  reduces crossing the zero value when the director  $\mathbf{n}_c$  becomes parallel to  $\mathbf{n}_0$ ; then, after changing sign, it increases again up to  $45^\circ$  (i.e., the angle between  $\mathbf{n}_0$  and the incident polarization  $\mathbf{e}$ ).

This interpretation of the experimental results in terms of a competition between sliding and capturing is confirmed by measurements in which the anchoring energy of the easy axis was varied by preillumination (PI) of the sample before irradiation. The inset of Fig. 2 shows the  $|\theta|$  vs  $t$  curves measured after preilluminating the sample for different PI times  $t_0$ . Preillumination was achieved by submitting the sample to an incident light field (from He-Cd laser) parallel to  $\mathbf{n}_0$ . This induces an easy axis

parallel to  $\mathbf{n}_0$  whose anchoring energy increases with  $t_0$ . We point out that the sliding effect occurs also during the PI. However, being a transient phenomenon, it does not affect either the easy axis direction or the surface anchoring energy. This behavior of the curves at small  $t_0$  is similar to that obtained at  $t_0 = 0$ . However, both intensity and the extension of the fast rise associated with sliding progressively reduce with increasing  $t_0$  and, finally, this feature completely disappears when  $t_0$  becomes larger than  $\approx 60$  s. As shown by the inset of Fig. 2, the time  $\Delta t$  corresponding to  $\theta = 0$  reduces with increasing PI time. This behavior is explained by considering that increasing the anchoring energy is equivalent to increasing the difficulty for the molecules to slide over the surface. Then, a lower number of molecules slide out of the exciting direction or smaller sliding angles are reached, both effects contributing to reduce the output signal. Further increasing of the anchoring energy leads to a progressive quenching of the sliding. The complete quenching is achieved for PI times larger than  $\approx 60$  s when only the reorientation towards the exciting electric field is observed. Such reorientation becomes more and more difficult with further increases in anchoring energy, which is in agreement with the curve  $F$  in Fig. 2.

A simple phenomenological model is proposed which accounts for the experimental observations. Two different mechanisms contribute to the director reorientation over the control surface: the bulk torque due to the photoinduced reorientation of the MR molecules, which favors director alignment perpendicular to the exciting polarization, and the surface torque associated with the adsorption of the MR molecules, which favors alignment parallel to the incident polarization. The competition between these effects controls the reorientation process. The total free energy of the system can be written as

$$F = \frac{1}{2} K \int [(\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2] dV + \chi \int (\mathbf{n} \cdot \mathbf{e})^2 dV - w \int c_s(\beta) (\mathbf{n}_c \cdot \mathbf{l})^2 d\beta dS, \quad (1)$$

where the three terms represent the elastic, the bulk-reorientation, and the surface-reorientation contributions, respectively. In Eq. (1),  $K$  is the elastic constant of the LC in the one constant approximation [9],  $\mathbf{n} = \mathbf{n}(z)$  is the director in the bulk,  $\mathbf{e}$  is the unit vector of the incident polarization,  $\chi$  ( $\chi > 0$ ) is a quantity measuring the strength of interaction between MR and LC molecules,  $\mathbf{l} = (\cos \beta, \sin \beta, 0)$  is the unit vector giving the local easy axis direction for the surface director reorientation due to MR adsorption,  $c_s(\beta)$  is the anisotropic angular distribution of the surface concentration of adsorbed MR molecules, and  $w$  ( $w > 0$ ) is a quantity characterizing the strength of interaction between LC and adsorbed MR molecules. We point out that the bulk torque is due to the photoisomerization process and the consequent

reorientation of the azo-dye molecules. Its effect is a reorientation of the LC molecules perpendicular to  $\mathbf{e}$  and then the associated free energy contribution is minimum when  $\mathbf{n}$  is orthogonal to  $\mathbf{e}$ . The second term in Eq. (1) just fulfills this requirement. On the other hand, the direct optical torque of the light field on the LC molecules can be neglected because of the small intensity used in the experiments. We assume that the orientation of MR molecules close to the surface is random in the  $xy$  plane [5] and also that their concentration within the LC-PVCN interface is maintained constant by molecular diffusion in the bulk. The rate of adsorption  $P(t)$  of a dye molecule depends on the probability of excitation [10] and on the concentration of MR molecules near the control surface. It depends also on the overall concentration of already adsorbed dye molecules, as suggested by the self-gaining of the holographic gratings recorded with this technique [6]. Assuming a simple proportionality relation and considering that the optical transition moment is parallel to the long molecular axis [12], the rate of adsorption  $P(t)$  can be written as

$$P(t) = c_0 [a' + b' c_{s0}(t)] E^2 \nu k (\mathbf{l}_1 \cdot \mathbf{e})^2, \quad (2)$$

where  $c_0$  is the volume concentration of MR,  $a'$  and  $b'$  are proportionality constants,  $c_{s0}(t) = \int c_s(\beta, t) d\beta$  is the total concentration of adsorbed MR molecules,  $\mathbf{l}_1 = (\sin \varphi \cos \beta, \sin \varphi \sin \beta, \cos \varphi)$  is the unit vector giving the orientation of MR molecules in the interfacial region near the control surface,  $\nu$  is the quantum efficiency of the adsorption process, and  $k$  is the absorption coefficient along the dye molecular axis [5,10]. Because of the low dye concentration, guest-guest interactions are negligible and  $k$  can be considered independent on  $c_0$ . We note also that the linear dependence of  $P(t)$  on  $c_{s0}$  is valid only until saturation phenomena related to the adsorption process begin to operate. Accordingly, the model does not describe the asymptotic behavior of the reorientation process with increasing irradiation time. The probability for the adsorbed dye molecules to have orientation  $\mathbf{l}$  on the control surface is proportional to  $\int P(t, \varphi, \beta) \sin \varphi d\varphi$ . Within these assumptions and after integrating over  $\varphi$ , the kinetic equations for  $c_s$  and  $c_{s0}$  are

$$\begin{aligned} \frac{dc_s(\beta, t)}{dt} &= c_0 (a + b c_{s0}(t)) E^2 \nu k (\mathbf{l} \cdot \mathbf{e})^2, \\ \frac{dc_{s0}(t)}{dt} &= c_0 (a + b c_{s0}(t)) \pi E^2 \nu k, \end{aligned} \quad (3)$$

with  $a = 4a'/3$ ,  $b = 4b'/3$ . The solution of the coupled equations (3) with the initial condition  $c_s(\beta, 0) = 0$  gives  $c_s(\beta, t) = a(b\pi)^{-1} [\exp(t/\tau) - 1] \cos^2(\alpha - \beta)$ , where  $\tau = (c_0 b \pi \nu E^2 k)^{-1}$ . If we preilluminate the sample for a time  $t_0$  with light polarized parallel to the  $x$  axis ( $\alpha = 0$ ) and then irradiate the cell with light polarized at an angle  $\alpha$ , the angular distribution of adsorbed dye molecules at time  $t$  ( $t > t_0$ ) becomes

$$c_s(\beta, \alpha, t)_{t \geq t_0} = a(b\pi)^{-1} \{ [\exp(t_0/\tau) - 1] \cos^2 \beta + [\exp(t/\tau) - \exp(t_0/\tau)] \cos^2(\alpha - \beta) \}. \quad (4)$$

Substituting Eq. (4) into the last integral of Eq. (1), one obtains the expression of surface free energy

$$F_S = WS \{ [\exp(t_0/\tau) - 1] \cos^2 \theta + [\exp(t/\tau) - \exp(t_0/\tau)] \cos^2(\alpha - \theta) \}, \quad (5)$$

where  $W = wa/2b$  and  $S$  is the area of the control surface. According to Eq. (5), preillumination results in the formation of an easy axis parallel to  $x$  and characterized by anchoring energy density proportional to  $W[\exp(t_0/\tau) - 1]$ , whereas the following exposure to the exciting light produces an easy axis at an angle  $\alpha$ , with anchoring energy density proportional to  $W[\exp(t/\tau) - \exp(t_0/\tau)]$ . This latter increases with time, and the resulting easy axis direction turns from  $\mathbf{n}_0$  to  $\mathbf{e}$ .

To get a solution in closed form, we restricted the analysis to the limit of small reorientation angles and assumed the light field in the cell to be constant. The validity of this assumption can be justified (as far as small reorientation angles are involved) on the basis of the results which we got with alternative approaches, such as the solution of the Maxwell equations in the Mauguin limit or the geometrical optics approximation. We also assumed that the bulk concentration of reoriented dye molecules (i.e., oriented perpendicular to the light polarization) varies with time as  $c_v = c_{v0}[1 - \exp(-t/\tau_1)]$ , where  $\tau_1 \ll \tau$  and both  $c_{v0}$  and  $\tau_1$  depend on the intensity of the incident electric field. Finally, we limited our analysis to the experimental geometry, i.e., we put  $\alpha = \pi/4$ . Within these assumptions, minimization of the total free energy, linearization of the Euler-Lagrange equation, and the solution with the appropriate boundary conditions gave

$$\theta(t, t_0) = -\frac{\chi_0 c_v L^2}{K} \frac{1}{1 - 2\xi_1(t_0)} - \frac{\xi_2(t, t_0)}{1 - 2\xi_1(t_0)}, \quad (6)$$

where  $\xi_1(t_0) = 2WLK^{-1}[\exp(t_0/\tau) - 1]$  and  $\xi_2(t, t_0) =$

$2WLK^{-1}[\exp(t/\tau) - \exp(t_0/\tau)]$  are the anchoring parameters and  $\chi = \chi_0 c_v$ .

Equation (6) provides a satisfactory reproduction of the experimental results. The first term describes reorientation perpendicular to the light polarization ( $\theta < 0$ ) while the second term describes reorientation towards the exciting polarization ( $\theta > 0$ );  $\theta = 0$  corresponds to the mutual compensation of the bulk and surface torques. Figure 3 shows the best fit of Eq. (6) to the experimental data at  $t_0 = 10$  s; the values of the fit parameters are  $\chi_0 c_{v0} L^2 / K = 0.159$ ,  $\tau_1 = 0.522$  s,  $\tau = 51.356$  s,  $2WL/K = 0.314$ . Similar good quality fits were obtained for the other PI times, with only slight differences in the fit parameters. By assuming a typical value of the elastic constant for nematics [9]  $K \approx 10^{-11}$  N/m and taking  $L = 20 \mu\text{m}$ , the value  $W \approx 10^{-7}$  J/m<sup>2</sup> is obtained for the surface anchoring energy density, which is in agreement with previous determinations in similar LC cells [5,7]. As shown in the inset of Fig. 3, Eq. (6) also reproduces the reduction of  $\Delta t$  with increasing  $t_0$ . The difference in the slopes between the experimental and the theoretical curves could be due to secondary additional effects, such as surface viscosity or irreversible changes in the conformation of MR molecules, which have been neglected in our simple mode.

In conclusion, we have demonstrated the possibility of light-induced free director sliding over an isotropic boundary surface in liquid crystals. The additional possibility shown, of regulating the dose of the anchoring energy under the control of the incident light, seems to be very attractive for all of those applications where the operational characteristics of the devices are determined by this quantity.

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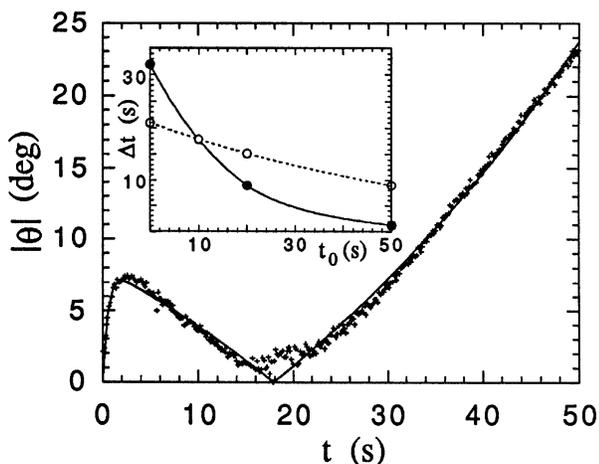


FIG. 3. The  $|\theta|$  vs  $t$  curve at  $t_0 = 10$  s. The continuous line is the best fit of Eq. (6) to the experimental data (+). The inset shows the dependence of  $\Delta t$  on the preillumination time  $t_0$ : (●) experiment; (○) theory. The theoretical points are calculated using the best fit parameters obtained at  $t_0 = 10$  s.

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