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Laser-induced Freedericksz transition in nematic-liquid-crystal films with an air interface: Study of orientational anchoring and damping

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Laser-induced molecular reorientation and the associated Freedericksz transition in nematic films of 4′-*n*-pentyl-4 cyanobiphenyl (5CB) with an air interface are studied. The results indicate that the 5CB-air interface actually behaves like a hard boundary in orienting the liquid-crystal molecules, but it allows an enhanced "backflow" in the medium through the orientation-flow coupling, which significantly speeds up the relaxation of molecular orientation. Theoretical analysis using the continuum theory is shown to be in good agreement with the experimental observations.

Surface effects are of prime importance in the field of liquid crystal (LC) both for basic understanding of physical phenomena and for device applications. It is known that the boundary surface of a solid substrate tends to tie down the LC molecules and orient them in a certain direction (the "easy" direction) even in the presence of long-range orientational correlation among molecules.[1,2] At a LC-air interface, though the existence of an easy direction seems usual,[3] it is possible that both the positional and the orientational anchorings are weak, as the molecules are now free to move on or away from the surface and the anisotropic interactions are solely among the LC molecules. To study such a surface-anchoring effect, the Freedericksz transition,[4] which depends strongly on the boundary conditions, can be utilized.

In this paper, we report our recent experiment using laser-induced Freedericksz transition (LIFT)[5] on two groups of 4′-*n*-pentyl-4-cyanobiphenyl (5CB) samples: one with 5CB films sandwiched between two glass plates coated with *N*,*N*-dimethyl-*N*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) for homeotropic alignment,[6] and the other with one surface exposed to air. The latter case is also the first LIFT experiment on samples other than those of homeotropically aligned films sandwiched between glass plates. We found that the two cases have very similar static properties, but significantly different dynamic behaviors. The results indicate that while the LC-air and the LC-solid interface have similar orientational anchoring strength, their effects on the molecular motion, namely, translation and reorientation, are quite different.

Let us first briefly review the theory of LIFT. Consider a nematic film of thickness d bounded on one side by a strong-anchoring solid surface in the horizontal plane $z=0$, and on the other side by either and LC-air interface or another solid medium at $z=d$. The director $\hat{n}$ (i.e., the average molecular orientation) is assumed to be aligned along $\hat{z}$ by the surface-anchoring forces in the absence of external fields. With the incoming laser beam linearly polarized in the xz plane and propagating in the $\hat{z}$ direction, the reoriented director is described by $\hat{n}=(\sin\theta, 0, \cos\theta)$. In our later discussion, we need to consider only the limit $\theta \ll 1$. For the particular LC-solid interface used in our experiment, a hard-boundary condition, $\theta(z=0)=0$, is assumed, and its validity will be discussed later.

The static properties of LIFT can be determined by minimizing the total excess free energy of the nematic film, which is expressed as

$$F=\int (f_{\mathrm{el}}+f_{\mathrm{opt}}+f_s)d\mathbf{r} \ , \tag{1}$$

with $f_{\mathrm{el}} \approx \frac{1}{2}K(\nabla\theta)^2$, $f_{\mathrm{opt}}=-In_{\mathrm{eff}}/c$, and $f_s \approx \frac{1}{2}A\theta^2 \times \delta(z-d)$ being the elastic, optical, and surface-anchoring free energies, respectively.[2,7] For simplicity, we have adopted the standard one-elastic-constant approximation for f_{el}.[4] In the expression of f_{opt}, c is the speed light, n_{eff} is the local effective refractive index having the form $n_{\mathrm{eff}} \approx n_o[1+(\Delta\epsilon/2n_e^2)\theta^2]$ for $\theta \ll 1$ (n_o and n_e being, respectively, the ordinary and the extraordinary refractive indices; $\Delta\epsilon \equiv n_e^2-n_o^2$), and I denotes the laser intensity. The transverse profile $I(\rho)$ for our laser beam was close to a Gaussian. In order to obtain the analytic solution for $\theta(\rho,z)$, however, we replace the Gaussian profile by an effective profile $I(\rho \le w)=I_0$ and $I(\rho > w)=0$, keeping the power $P=I_0(\pi w^2)$ the same. Since $\theta(\rho \ge w)\approx 0$ near the threshold of LIFT, we impose another boundary condition, $\theta(\rho \ge w)=0$,[8] to further simplify the analysis.

$$K\nabla^2\theta + C^{-1}I\theta = 0 \ , \tag{2}$$

with $C=cn_e^2/n_o\Delta\epsilon$, subject to the surface boundary conditions $\theta=0$ at $z=0$ and

$$K(\partial\theta/\partial z)+2A\theta=0 \tag{3}$$

at $z=d$. The lowest-order nontrivial solution of Eq. (2) can be shown to have the form

$$\theta(\rho,z)=\theta_0 J_0(x_1\rho/w)\sin(kz) \ , \tag{4}$$

where θ_0 is a constant, J_0 denotes the Bessel function of order zero, $x_1=2.405$ is the first root of J_0, and k is determined by Eq. (3), or more explicitly,

$$\tan(kd)=-(K/2A)k \ . \tag{5}$$

By substituting Eq. (4) into Eq. (2), and requiring $\theta_0 \neq 0$, an expression for the threshold intensity of LIFT is obtained[9]:

$$I_{\text{th}} = I_0(\text{threshold}) = CK[k^2 + (x_1/w)^2] \ . \tag{6}$$

Equation (5) yields $k = \alpha(\pi/d)$, where α is a real number between 0.5 (for $Ad/K = 0$) and 1 (for $Ad/K \rightarrow \infty$). Therefore, the anchoring energy A can, in principle, be deduced from the value of I_{th}. In practice, however, a boundary with $Ad/K > 50$ leading to an $\alpha > 0.99$ could be experimentally indistinguishable from a hard boundary with an infinite anchoring energy. If we let $K = K_3$ (the bend elastic constant), in the limit $w \rightarrow \infty$, Eq. (6) becomes the exact expression for I_{th}.[7]

The dynamic behavior of LIFT is much more complicated than the static one: Fluid flow and molecular reorientation are generally coupled[10]; at an LC-air interface, shape deformation can happen and affect the molecular reorientation through the anchoring force.[4] All of these, coupled with the finite-size effect of the laser beam, make the solution of the problem extremely difficult. This is particularly true for the switch-on behavior of LIFT, and therefore we shall limit ourselves here to the analysis of the switch-off case. It can be shown theoretically as well as seen from our experimental results that the relaxation of molecular reorientation after the laser excitation is off has only a weak dependence on the beam size (weaker than the static case). This is because in the transverse directions, the influence of elastic restoring forces is partially canceled by that of the orientation-flow coupling.[11] Thus, to illustrate the essential physical picture without much mathematical complexity, we shall ignore the dependence of relaxation on the transverse coordinates. We also assume the surface deformation is negligible for small θ. The coupled equations of motion for the director $\hat{n} \approx [\theta(z,t),0,1]$ and the flow velocity $\mathbf{v} \approx [v(z,t),0,0]$ (for $\rho \sim 0$) can then be simplified as[12]

$$\begin{aligned} &\gamma_1(\partial\theta/\partial t) = K(\partial^2\theta/\partial z^2) - \alpha_2(\partial v/\partial z) \ , \\ &\eta_c(\partial^2 v/\partial z^2) + \alpha_2(\partial^2\theta/\partial z\partial t) = 0 \ , \end{aligned} \tag{7}$$

where γ_1, α_2, and η_c are viscosity coefficients following the notations of Ref. 10. To determine the surface boundary conditions, we assume a rigid orientational anchoring for both the LC-solid interface and the LC-air interface, and a rigid positional anchoring for the former, but no in-plane positional anchoring for the latter. Hence, $\theta(z = 0,d) = 0$, $v(z = 0) = 0$, and either $v(z = d) = 0$ for the LC-solid interface or $(\partial v/\partial z)(z = d) = 0$ (i.e., no shear stress) for the LC-air interface. As seen from our experiment, this set of boundary conditions indeed leads to predictions which are consistent with the behavior of the 5CB films. The solutions of Eq. (7) are

$$\begin{aligned} &\theta(z,t) = \theta_0 \sin(qz)[1 - \tan(qz/2)\cot(qd/2)]\exp(-t/\tau) \ , \\ &v(z,t) = v_0\{\sin(qz)[\cot(qd/2) + \tan(qz/2)] \\ &\qquad - \gamma qz \cot(qd/2)\}\exp(-t/\tau) \ , \end{aligned} \tag{8}$$

where $v_0 = \theta_0\alpha_2(\eta_c\tau q)^{-1}$, $\gamma \equiv \gamma_1\eta_c\alpha_2^{-2}$, and the relaxation time

$$\tau = (1 - \gamma^{-1})\gamma_1 K^{-1} q^{-2} \ , \tag{9}$$

with $q = \pi/d$ for the LC-air interface case, or given by

$$\tan(qd/2) = \gamma(qd/2) \tag{10}$$

for the hard-boundary case. Usually, $\gamma > 0$, and Eq. (10) yields a $q = \beta(\pi/d)$, where $0 < \beta < 1$. Therefore, the relaxation time for the LC-air interface case should always be shorter than for a hard-boundary case. Physically, the LC-air interface allows a finite flow at $z = d$ and consequently an overall enhancement of the "backflow" that effectively increases the speed of the orientational relaxation.[12]

The material 5CB, obtained from British Drug Houses, Inc., was used in the experiment without further purification. LC films with a LC-air interface were prepared by placing an adequate amount of 5CB on an optically flat glass slide mounted horizontally and coated with a monolayer of DMOAP. A flat Mylar O ring, ~125 μm thick and ~1.6 cm in inner diameter, was also placed on the glass slide to confine 5CB as well as to make the LC-air interface flat (5CB does not wet the Mylar surface). The thickness of the LC films was controlled by the amount of 5CB used, and determined by measuring, with the help of a microscope, the vertical distance traveled by a needle tip from the LC-air interface to the LC-glass interface. To form 5CB films bounded by two glass surfaces, a second DMOAP-coated glass slide was brought in contact with 5CB and separated from the bottom slide by a flat Mylar spacer. In both cases, the film thickness ranging from ~125 to 275 μm was determined to within an accuracy of ~ ± 5 μm. The equilibrium structure of these films was homeotropic since both the 5CB-air interface and the DMOAP-coated surface appeared to align molecules normal to the surface.[13,14] During measurements, the sample was enclosed in an oven with temperature stabilized at $25.3 \pm 0.05\,^{\circ}\text{C}$.

The linearly polarized beam from a cw argon-ion laser ($\lambda = 514.5$ nm) was focused to an e^{-1} diameter ($2w$) of 500 μm and normally incident upon the 5CB sample. The occurrence of LIFT leads to a local refractive-index change $\Delta n(\rho,z) = n_{\text{eff}}(\rho,z) - n_o$ in the LC medium and a corresponding phase shift $\Delta\phi$ of the beam traversing the medium:

$$\Delta\phi(\rho) = (2\pi/\lambda)\int_0^d \Delta n(\rho,z)dz \ . \tag{11}$$

If $\Delta\phi_0 \equiv \Delta\phi(\rho = 0) \gg 2\pi$, multiple diffraction rings in the transmitted beam can be observed.[15] In our experiment, the total number of rings $N \cong \Delta\phi_0/2\pi$ was used as a direct measurement of $\Delta\phi_0$ and, hence, the overall molecular reorientation. The relaxation of molecular reorientation was measured by the decay of the number of rings. This was achieved by abrupt attenuation of the laser intensity to a level well below the threshold intensity. The attenuated laser beam then acted only as a passive probe.

For each sample, N as a function of the laser intensity I was obtained first. The threshold intensity I_{th} was then determined (to an accuracy of ~ ± 3%) by extrapolating the $N(I)$ curve to $N(I_{\text{th}}) = 0$. Figure 1(a) shows I_{th} versus the sample thickness in terms of $(\pi/d)^2$ for 5CB films bounded either by a 5CB-air interface and a glass slide, or two glass slides. Within our experimental accura-

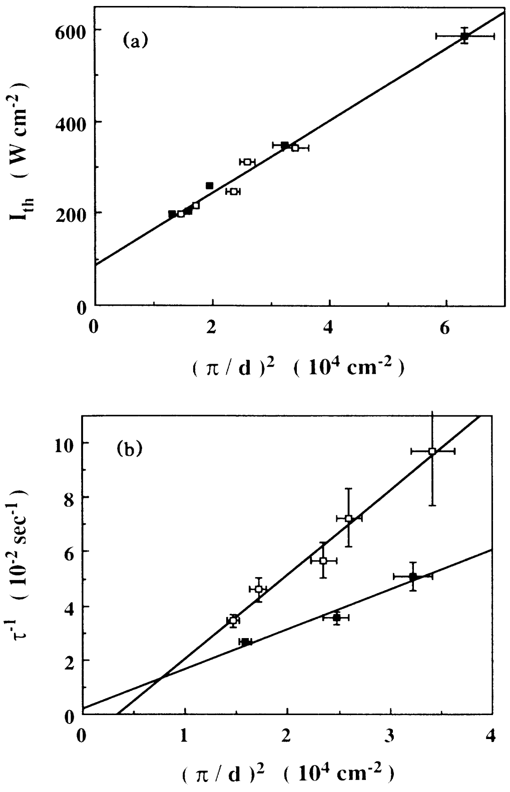

FIG. 1. (a) Threshold intensity (I_{th}) and (b) inverse relaxation time (τ^{-1}) vs $(\pi/d)^2$ for nematic 5CB films bounded by a glass slide and by air (open squares), and by two glass slides (closed squares), where d is the film thickness.

cies, the same linear dependence was followed in both cases. By using Eq. (6) and assuming $\alpha=1$, with $C \cong 9.0\times10^{10}$ cm/sec deduced from the literature values[16] of n_o (1.54) and n_e (1.74), a linear least-squares fit of the data yields $K \cong 8.8\times10^{-7}$ dyne and $x_1 \cong 2.6$, which are in very good agreement with the literature value of $K_3(8.7\times10^{-7}$ dyne) (Ref. 17) and the theoretical value of $x_1(2.405)$. Since K_3 is the largest among the three elastic constants of 5CB, we do not expect the effective elastic constant K to be larger than K_3. Therefore, any value $\alpha<1$ that yields a larger K may be ruled out. The results, therefore, indicate that both the 5CB-air interface and the 5CB-glass interface behave like a hard boundary as far as the orientational anchoring is concerned. This roughly sets a lower limit for their anisotropic anchoring energies: $A>3\times10^{-3}$ erg/cm^2. We notice that in the literature, a value, $A\sim8\times10^{-3}$ erg/cm^2, has been reported for the 5CB-air interface.[13] Studying LIFT in thinner LC films or under strong intensities ($\gg I_{th}$) can improve our sensitivity in determining A.[18,19] However, it is more difficult to prepare uniform thin films with a LC-air interface; and very strong intensities require tight focusing of the laser beam which can also introduce undesirable effects such as local heating.

The measured relaxation times τ in the two cases were substantially different; as expected, for the same film thickness, τ was always shorter in the LC-air interface case. The experimental data of τ^{-1} vs $(\pi/d)^2$ are shown in Fig. 1(b), where the solid lines are obtained by the linear least-squares fits using Eqs. (9) and (10). From the slopes of these lines, we have deduced $\gamma_1 \cong 0.67$ P and $\gamma \cong 1.74$. These values are in fair agreement with the literature values: $\gamma_1=0.79$ P and $\gamma \equiv \gamma_1\eta_c\alpha_2^{-2}=1.25$,[17] considering the simplifications made in the analysis. The slight offsets at $(\pi/d)^2=0$ in Fig. 1(b) are not accounted for by Eq. (9); they could result from the finite beam profile that we have neglected in the theory.

In the LC-air interface case, immediately following the application of the laser field ($I>I_{th}$), the induced molecular reorientation usually exhibited transient oscillation which persisted for several hours before the equilibrium state was reached. The period of oscillation was fairly long, of the order of a few tens of minutes. The oscillation could be eliminated by increasing the laser intensity in very small steps so that the system approached a quasistationary state in each step. Since the oscillatory transient behavior was not observed in the hard-boundary case, it is most likely related to the shape deformation of the LC-air interface that couples strongly with the molecular reorientation through the surface anchoring force. Further studies are needed to pin down the mechanism and achieve a good understanding of this transient behavior.

In conclusion, we were able to use LIFT as a simple tool to study the boundary conditions of different LC interfaces. In spite of the absence of molecule-substrate interactions, the 5CB-air interface still possesses a very strong surface-induced orientational anchoring force, practically indistinguishable from a rigid anchoring. This indicates that the intrinsic structure of the 5CB-air interface is homeotropic. It is then likely that the anchoring of a 5CB-solid interface always tends to give strong homeotropic alignment, unless the solid surface is specially treated for planar or tilt alignment to compete with the intrinsic anchoring force of 5CB. The essential differences between the 5CB-air interface and a rigid, homeotropic boundary of 5CB lie in their dynamic behavior. Because of the lack of positional anchoring, the LC-air interface can enhance the backflow in the LC, which effectively reduces the orientational damping and hence speeds up the relaxation of molecular reorientation. The shape deformation of a LC-air interface adds an extra degree of freedom to the motion of the LC molecules at the surface, and could also lead to intriguing dynamic phenomena.

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[10] Reference 4, Chap. 5.

[11] A rigorous proof is rather difficult. However, a qualitative proof can be obtained by considering a "ribbon" optical intensity profile, $I(|x| \leq w,y) = I_0$; $I(|x| > w,y) = 0$. The deviation is similar to that given by E. Guyon, R. Meyer, and J. Salan, Mol. Cryst. Liq. Cryst. **54**, 261 (1979).

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