Very strong azimuthal anchoring of nematic liquid crystals on uv-aligned polyimide layers

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(Received 29 January 2007; published 21 May 2007)

The azimuthal anchoring energy of the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB) on a uv-aligned polyimide substrate with in-plane order parameter $S'=0.2$ is measured. The measurements are performed at temperature $T=24\ ^\circ\mathrm{C}$ using simultaneously a high accuracy reflectometric method and a high accuracy transmitted light method. With both the methods, we observe an apparent surface director rotation opposite to the orienting torque that would correspond to a negative extrapolation length. It is shown that this unusual behavior is due to the relatively high birefringence of the uv-aligned polyimide layers. Taking into account for this birefringence, we find a small but positive extrapolation length. The experimental results are interpreted in terms of a simple mesoscopic model where the nematic molecules are assumed to be rigidly attached on the polymer surface and the measured extrapolation length is entirely due to the order parameter variation in a thin interfacial layer where the nematic order parameter passes from the surface value to the bulk value within a few nematic correlation lengths. Assuming the surface order parameter is $S_0=0.37$, the correlation length of the nematic liquid crystal is estimated to be $\xi_c'=2.4\pm1$ nm. The corresponding thermodynamic extrapolation length is $d_e=2.8\pm1.2$ nm that corresponds to a very strong azimuthal anchoring.

DOI: 10.1103/PhysRevE.75.051704 PACS number(s): 61.30.Hn

I. INTRODUCTION

Interfacial phenomena in nematic liquid crystals (NLC) are an object of a lot of attention both for their relevance to basic physics and for the applications in the optoelectronic industry. The orientation of the director $\mathbf{n_s}$ [1] at the interface is characterized by the zenithal angle θ_s with the normal z axis and the azimuthal angle ϕ_s with a x axis on the surface plane. In the absence of external torques, the director is aligned along the easy axis $\mathbf{n_e}$ that minimizes the anchoring energy $W(\mathbf{n_s})$ [1,2]. For strong anchoring [1,2] we write

$$W=\frac{W_a}{2}(\phi_s-\phi_e)^2, \tag{1}$$

where W_a is the azimuthal anchoring energy coefficient and ϕ_e is the easy azimuthal angle. If an electric field $\mathbf{E}$ much greater than the Freederickz threshold field is applied in the surface plane along the x axis, a bulk director twist occurs with characteristic length $\xi=\sqrt{K_2/(\epsilon_0\epsilon_a)}/E$, where K_2 is the twist elastic constant, ϵ_0 is the vacuum permittivity, and ϵ_a is the dielectric anisotropy [1]. For strong anchoring, the director surface rotation is [1,2],

$$\delta\phi_s=-\frac{\sqrt{K_2\epsilon_0\epsilon_a}\sin(\phi_e)E}{W_a}, \tag{2}$$

where $\delta\phi_s=\phi_s-\phi_e$. Then, W_a can be obtained from the measurement of $\delta\phi_s$. Transmitted light methods [3–11] and reflected light methods [12–15] are currently used to measure the azimuthal anchoring energy. However, only a few of these methods can provide reliable measurements of strong azimuthal anchoring energies. Indeed, if there is strong anchoring, high external fields must be applied to the NLC in order to induce an appreciable surface director rotation. In these conditions, a strong director twist is present in the bulk of the NLC that can greatly affect the optical measurements especially in the case of transmitted light methods [9]. In two recent papers [16,17] we have shown that the reflectometric method proposed in [13] and the transmitted light method proposed in [9] provide accurate measurements of strong azimuthal anchoring because they are poorly sensitive to the bulk director twist. Recently, another high accuracy transmitted light method that is poorly affected by the bulk twist has been also proposed by Janossy [11].

In this paper, we use simultaneously both the transmitted light and the reflectometric methods to measure the azimuthal anchoring energy at the interface between the NLC 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and a polyimide layer aligned by irradiation with polarized uv light [18]. This substrate induces a homogeneous planar director orientation with a zero pretilt angle. The anchoring is determined switching on an in-plane electric field at 80° with respect to the easy axis and measuring the consequent surface rotation of the director. A very small apparent surface director rotation opposite to the surface torque [$\delta\phi_s>0$ in Eq. (2)] is found that would correspond to a negative anchoring coefficient and to a negative extrapolation length $d_e=K_2/W_a$ [1,2]. This behavior is observed with both the reflectometric and the transmission light methods. Furthermore, it is also observed if a magnetic field is applied in place of the electric field. Using a numerical procedure based on the optical Berreman theory of the anisotropic stratified media, we show that the apparent negative surface rotation is the consequence of a strong azimuthal anchoring and of a somewhat high optical anisotropy of the uv-aligned polyimide. By taking

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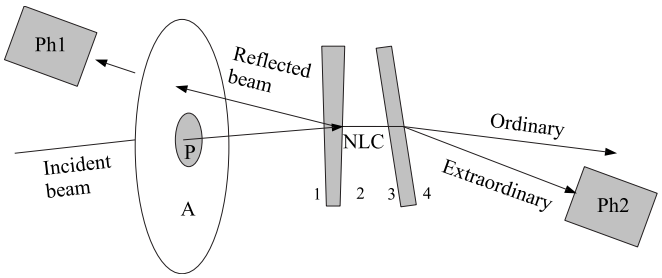

FIG. 1. Schematic draft of the optical method. P denotes polarizer, A denotes analyzer, Ph_1 and Ph_2 denote photodiodes, NLC denotes the wedge cell containing the NLC. System P-A is made by two concentric crossed polarizers glued together.

into account for this anisotropy, the measured surface director rotation is found to be very small but positive. The resulting extrapolation length measured with the reflectometric method is $d_e^R = 3.6 \pm 1.6$ nm, where suffix R denotes the reflectometric method. Then, the uv-aligned polyimide investigated here is characterized by a very strong azimuthal anchoring.

According to Yokoyama [19] (see also Sec. IV of the present paper), the extrapolation length that is measured with any experimental method, does not coincide with the thermodynamically defined extrapolation length. To obtain the correct value of the thermodynamic extrapolation length, the reflectometric or the transmitted light experimental results must be analyzed using a microscopic or mesoscopic model of the interfacial layer. Here, we show that the very small extrapolation length that is measured in our experiment is satisfactorily explained by a simple mesoscopic model of the interfacial interactions. In this model, the nematic molecules in contact with the polymeric layer are assumed to be rigidly anchored on the substrate (strong microscopic anchoring) and the extrapolation length is entirely due to the variation of the nematic order parameter in a thin interfacial layer of characteristic thickness comparable to the nematic correlation length ξ_c'. As shown in Sec. IV, the thermodynamic extrapolation length that reproduces our experimental results is $d_e = 2.8 \pm 1.2$ nm that corresponds to the nematic correlation length $\xi_c' = 2.4 \pm 1$ nm.

II. EXPERIMENTAL METHOD

The theoretical basis of the reflectometric method and of the wedge transmission method have been discussed extensively in Refs. [13,9], respectively, while the experimental apparatus, the experimental procedures, and the main error sources have been discussed in Refs. [16,17]. Then, here we only describe shortly the main features of both these methods. Measurements with both the methods can be performed simultaneously with the same experimental apparatus as shown schematically in Fig. 1. The simultaneous use of two different experimental techniques is very important when strong azimuthal anchoring is measured. In fact, in this case, the maximum surface director rotation is very small and there are many possible noisy effects that can affect the experimental results [16,17]. Then, the comparison between the results of the two different techniques provides a direct check of the reliability of the experimental results.

A circularly polarized laser beam (He-Ne, $\lambda = 632.8$ nm) passes through a polarizer P that rotates with angular velocity $\omega = 61$ rad/s and impinges at nearly normal incidence (about 1°) on a nematic wedged cell thermostated better than 0.1 °C. An electric field can be applied in the cell plane along the x axis. The easy axis makes the angle $\phi_e = 80°$ with the electric field. The first glass plate of the cell is wedged with a 1° wedge. The beam reflected by the first nematic-polyimide interface (surface 2 in Fig. 1) passes through the crossed analyzer A that rotates solidally with P and is focused on photodiode Ph_1. The extraordinary transmitted beam is collected by photodiode Ph_2. The intensity of the reflected laser beam is a periodic function with the $4-\omega$ contribution [13],

$$I^r(t) = A \cos 4(\omega t - \delta\phi_s - \phi_{\text{app}}^R), \tag{3}$$

where A is a suitable coefficient, ϕ_{app}^R is a contribution due to the bulk director twist, and $\delta\phi_s$ is the director surface rotation with respect to the easy axis. The clock is synchronized with the polarizer rotation in such a way that $t=0$ when polarizer P is parallel to the easy axis [20]. The intensity of the extraordinary beam is also a periodic function of time with the $2-\omega$ harmonic contribution [9],

$$I^t(t) = B \cos 2(\omega t - \delta\phi_s - \phi_{\text{app}}^T), \tag{4}$$

where B is a coefficient and ϕ_{app}^T is the contribution of the bulk twist. It must be emphasized here that the surface director angle ϕ_s, that appears in the expressions of the reflected and transmitted intensities [see Eqs. (3) and (4)], corresponds to the azimuthal director angle at the same polyimide-nematic interface (surface 2 in Fig. 1). This important feature of these experimental methods was shown in detail in Refs. [9,13]. Then, the two methods are measuring the surface director orientation at the same interface. The outputs of the two photodiodes Ph_1 and Ph_2 are sent to a PC computer that makes the Fourier transform of the two signals at the angular frequencies 4ω and 2ω, respectively, and calculates amplitudes and phases for both of them (Labview). The azimuthal rotation $\delta\phi_s$ can be obtained from the measurement of the phase coefficient of the reflected intensity I^r,

$$\Phi^R = 4(\delta\phi_s + \phi_{\text{app}}^R), \tag{5}$$

or from the measurement of the phase coefficient Φ^T of the intensity I^t of the extraordinary beam

$$\Phi^T = 2(\delta\phi_s + \phi_{\text{app}}^T). \tag{6}$$

For the interface between a NLC and an isotropic medium, ϕ_{app}^R and ϕ_{app}^T are proportional to $1/\xi^2$ and, thus, to E^2. With the maximum electric field used in the present experiment ($E \approx 0.2$ V/μm), ϕ_{app}^R can be disregarded because it is smaller than 0.002°. Then, in the reflectometric case, $\delta\phi_s$ can be directly obtained from the measurement of the experimental parameter $\Phi_A^R = \Phi^R/4$. In the transmission case, ϕ_{app}^T is not negligible, but we can exploit the fact that $\delta\phi_s$ is proportional to E [see Eq. (2)] while ϕ_{app}^T is proportional to E^2. If we define the apparent surface rotation $\Phi_A^T = \Phi^T/2$, we get

$$\Phi_A^T = \alpha_T E + \gamma_T E^2, \tag{7}$$

where $\alpha_T E = \delta\phi_s$ with

$$\alpha_T = \frac{-\sqrt{K_2 \epsilon_0 \epsilon_a}\sin(\phi_e)}{W_a}. \tag{8}$$

Coefficient α_T and, thus, W_a can be obtained experimentally performing the polynomial best fit of the experimental values of Φ_A^T versus E [see Eq. (7)]. The main advantage of both these experimental methods is that the surface director rotation is simply obtained from the measurement of the phase of an oscillating signal and no knowledge of the bulk material parameters is needed to obtain $\delta\phi_s$. Note that the reflectometric measurement is much more accurate than the transmitted light one because it is virtually insensitive to the macroscopic bulk director twist and does not require the polynomial fitting procedure.

The 1° wedge and the flat BK7 glass plates of the cell are separated by two brass stripes of different thicknesses ($d_1 = 50$ μm and $d_2 = 150$ μm) that produce a wedge with angle $\Delta\theta \approx 2°$. The internal glass surfaces of the cell are covered by a 11 nm thick photoaligned polyimide film. The polyimide contains azobenzene in the backbone structure, whose molecular structure is shown in Fig. 1 of Ref. [18]. Its in-plane orientation can be controlled by exposing the corresponding precursor (polyamic acid) film to linearly polarized uv light (LPUVL) at normal incidence. The average orientation direction of the polyimide backbone structures, which defines the easy axis, is perpendicular to the polarization direction of the LPUVL and lies in the film plane [18]. The detailed preparation procedure of the photoaligned film is described elsewhere [21]. The in-plane molecular orientation was evaluated from the polarization angle dependence of a strong absorption band centered at 351 nm. This band is assigned to the π-π^* transition of azobenzene [22] which is polarized along the polyimide backbone structure. The absorbance ratio, $S' = (A_\parallel - A_\perp)/(A_\parallel + A_\perp)$, of the polyimide films used in this study was 0.20, where $A_\parallel$ and $A_\perp$ are the absorbance for light polarized parallel and perpendicular to the easy axis, respectively. The absorbance ratio S' corresponds to the "in-plane order parameter" of the polyimide backbone structure [23,24]. The NLC is 4-pentyl-4′-cyanobiphenyl (5CB) purchased by Merck and having the clearing temperature $T_c = 35$ °C. It is inserted by capillarity in the cell under vacuum. The two brass stripes make an angle of 10° with the easy axis and their distance is $D = 2.45$ mm. An ac high voltage V at frequency $\nu = 1$ kHz can be applied between the two stripes in a symmetric configuration ($V_+ = -V_- = V/2$) in such a way to generate an electric field at 80° with the easy axis. In these conditions, the electric field is almost uniform with the value $E = 0.9V/D$ (see, Fig. 2 in [17]) in the central region between the electrodes where it impinges the laser beam (beam diameter ≈ 0.6 mm). The maximum applied electric field is $E \approx 0.2$ V/μm having an orienting effect comparable to that of a 2.1 T magnetic induction.

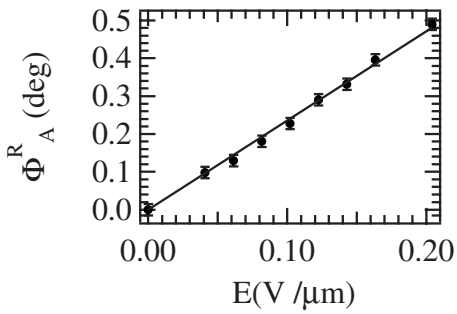

FIG. 2. Full points: apparent surface rotation angle Φ_A^R versus the rms of the electric field measured with the reflectometric method. The full line corresponds to the best linear fit with function $y = \alpha_R E$ [see Eq. (2)] with $\alpha_R = 2.35°$ μm/V. The sample temperature is $T = 24$ °C.

III. EXPERIMENTAL RESULTS

In this section, we report the experimental results obtained using the two experimental methods.

Figure 2 shows the apparent surface director rotation Φ_A^R measured with the reflectometric method versus the rms value of the electric field. The director rotation is proportional to the electric field in agreement with the prediction of Eq. (2). However, Φ_A^R is positive, that is in the opposite sense with respect to the bulk director rotation. This unusual behavior is observed only with uv-aligned polyimide films having an in-plane order higher than $S' = 0.11$. According to Eq. (2), a positive value of $\delta\phi_s$ would correspond to a negative value of the anchoring energy coefficient and to a negative extrapolation length $d_e = K_2/W_a$. Substituting in Eq. (2) the experimental values $K_2 = 4.05 \times 10^{-12}$ N [25] and $\epsilon_a = 13.4$ [26] at temperature $T = 24$ °C and the best-fit linearity coefficient $\alpha_R = \delta\phi_s/E = 4.1 \times 10^{-2}$ rad μm/V of Fig. 2 we get the apparent negative extrapolation length $d_e^{\text{meas}} = -7.6 \pm 0.6$ nm [1]. The same kind of measurements were repeated in other regions of the nematic cell and the same positive rotation was observed with amplitude variations from point to point lower than ±15%. Positive rotations were measured for any value of the temperature in the whole nematic range.

Figure 3 shows the apparent surface rotation $\Phi_A^T = \Phi^T/2$ measured with the transmitted light method versus the electric field. As discussed above, the bulk director twist produces a quadratic contribution in E that becomes dominant at high electric fields. For this reason, the maximum electric field reported in Fig. 3 is appreciably smaller than that of the reflectometric measurements (Fig. 2). Points in Fig. 3 correspond to the experimental results, while the full line represents the best fit with Eq. (7). In Fig. 3 it is evident that the linear contribution is opposite with respect to the quadratic contribution that is related to the bulk twist. This means that the apparent surface rotation is opposite to the surface torque in agreement with the reflectometric results. The best-fit coefficient α_T is $\alpha_T = 2.33°$ μm/V that corresponds to a positive surface rotation and is close to the coefficient $\alpha_R = 2.35°$ μm/V obtained with the reflectometric method. The dotted line in Fig. 3 represents the linear contribution. The apparent extrapolation length that is obtained from the transmitted light measurement is $d_e^{\text{meas}} = -7.6 \pm 3$ nm. Then, in this

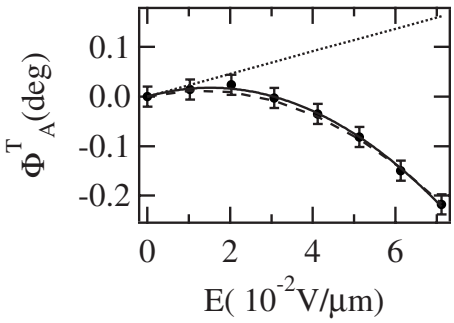

FIG. 3. Full points: Apparent surface rotation Φ_A^T measured with the transmission method versus the rms of the electric field. The full line corresponds to the parabolic best fit with function $\Phi_A^T = \alpha_T E + \gamma_T E^2$ in Eq. (7). The dotted line represents the linear best-fit contribution due to the surface director rotation $\delta\phi_s = \alpha_T E$ where $\alpha_T = 2.33°$ μm/V. The sample temperature is 24 °C. The broken line represents the best fit that is obtained with coefficient α_T of the linear term fixed at the value $\alpha_T = 1.84°$ μm/V and coefficient γ_T as a free parameter.

case too, we get a negative extrapolation length. The somewhat high uncertainty of the extrapolation length measured with the transmitted light method is due to the fact that the true surface rotation is obtained in an indirect way by making a polynomial fit in a restricted range of applied electric fields. This is evident if we look at the broken curve in Fig. 3 that is obtained by making the best polynomial fit holding fixed the linearity coefficient at the value $\alpha_T = 1.84°$ μm/V that corresponds to the extrapolation length $d_e^{\text{meas}} = -6$ nm. Measurements have been also performed using an orienting magnetic field ($B < 0.75$ T) in place of the electric field. Using the reflectometric method, we still find an apparent negative anchoring with the azimuthal extrapolation length $d_e^{\text{meas}} = -7.9 \pm 1$ nm in a satisfactory agreement with the electric field measurements. This means that electric field contributions not taken into account in the theory (flexoelectricity, small nonuniformity of the electric field, surface polarization, *etc.*) do not play an important role in our experiment.

So far, we have considered the interface between a nematic liquid crystal and an isotropic substrate. In our experiment, the orienting polyimide layer has a relatively high in-plane order parameter ($S' = 0.2$) and, thus, it is expected to have an appreciable optical birefringence. In fact, we find that the extraordinary and the ordinary index of this polyimide are $n_{ep} = 2.184$ and $n_{op} = 2.040$, respectively. This corresponds to the refractive indices anisotropy $\Delta n_p = 0.144$ that is comparable to the NLC anisotropy ($\Delta n = 0.183$ [27]). Then, the effect of the polymer anisotropy on the reflectometric and transmitted light measurements can be important. The contributions of the polymer anisotropy to transmitted and reflected light measurements is analyzed in Appendixes A and B, respectively [28]. Using numerical programs based on the Berreman approach [29] to the optics of stratified anisotropic media, we show that the anisotropy of the polymeric layer affects the reflected and transmitted light measurements. In particular, the extrapolation lengths that are measured with these methods are related to the actual extrapolation lengths through the simple relation:

$$d_e^{\text{meas}} = d_e(1 - \chi) - d_{ep}, \tag{9}$$

where d_e^{meas} is the measured extrapolation length and d_e is the actual extrapolation length. $\chi \ll 1$ is a dimensionless positive coefficient and d_{ep} is a positive characteristic length. These latter parameters depend on the material parameters of the NLC and of the polymer layer and on the kind of measurement (reflected or transmitted light). Both of them vanish if the anisotropy of the polymer layer is zero. Then, the true extrapolation length of the NLC can be obtained using the relation

$$d_e = \frac{d_e^{\text{meas}} + d_{ep}}{1 - \chi}. \tag{10}$$

The order of magnitude of d_{ep} is $\Delta n_p d_p / \Delta n$ where Δn and Δn_p are the anisotropies of the refractive indices of the NLC and of the polymer, respectively (see Appendix A). The standard rubbed polyimide layers are characterized by a somewhat small optical dephasing ($\delta_p \ll 0.5°$) and, thus, the spurious extrapolation length is $d_{ep} \ll 4$ nm. In particular, for the rubbed polyimide layers that were investigated in Refs. [16,17], the spurious extrapolation length d_{ep} was lower than 1 nm. On the contrary, for uv-aligned polyimide layers with high in-plane order parameter, the optical dephasing is appreciably higher. The extraordinary and ordinary refractive indices of our polyimide layer are $n_{ep} = 2.184 \pm 0.004$ and $n_{op} = 2.040 \pm 0.003$, respectively. Using these parameters together with the other material parameters of the 5CB at temperature $T = 24$ °C we can calculate numerically the parameters χ and d_{ep} for the transmitted and reflected light methods (see the appendixes). In the case of the reflectometric method we find $\chi = 0.065 \pm 0.006$ and $d_{ep} = 10.94 \pm 1$ nm, where the uncertainties are mainly due to the uncertainty on the anisotropy of the refractive indices of the polymer layer ($\approx 5\%$) and on the uncertainties on the elastic and dielectric constants of the NLC ($\approx 5\%$). Substituting in Eq. (10) these values together with the experimentally measured extrapolation length $d_e^{\text{meas}} = -7.6 \pm 0.6$ nm we obtain $d_e^R = 3.6 \pm 1.6$ nm, where R denotes the reflectometric method. In the case of the transmitted light method we find $\chi \approx 0$ and $d_{ep} = 8.96 \pm 1$ nm. Then, using these values we get $d_e^T = 1.84 \pm 4$ nm, where T denotes the transmitted light method. The very small extrapolation lengths measured with the two methods are in agreement within the estimated experimental uncertainty. This is also evident if we look at the broken curve in Fig. 3. This curve represents the result of the polynomial best fit of the experimental transmitted light when coefficient α_T of the contribution linear in E is held fixed at the value corresponding to the extrapolation length d_e^R measured with the reflectometric method while the γ_T coefficient of the quadratic term is the only free parameter. Since the reflectometric result is more accurate than the transmitted light result, here and below we will consider only the reflectometric value $d_e^R = 3.6 \pm 1.6$ nm.

IV. ANALYSIS OF THE EXPERIMENTAL RESULTS

The experimental value of the extrapolation length is appreciably smaller but of the same order of magnitude as that

measured by some authors at the interface between a nematic liquid crystal and a strongly rubbed polyimide layer [10,11,16,17]. The very small extrapolation length $d_e^R = 3.6$ nm that is measured in our experiment is consistent with other indirect experimental observations on nematic-polyimide interfaces. Indeed, as pointed out by Chen *et al.* [30], the molecules in contact with a rubbed polyimide are rigidly adsorbed on the surface through the polar end group (-CN). The alignment of the first molecular layer remains stable also if the temperature is increased well above the clearing temperature so suggesting that the short-range aligning interactions with the polymer layer are very strong. Chen *et al.* concluded that the azimuthal anchoring on rubbed polyimides is mainly due to the short-range interaction between the polymeric aligned chains and the nematic molecules. This situation should hold also for photoaligned films where it has been shown that the in-plane molecular order of an adsorbed monolayer deposited by evaporation is almost equal to that of the photoaligned film [31,32]. These experimental results suggest that the first nematic molecular layer is strongly anchored on the polyimide surface (strong microscopic anchoring).

A. The meaning of the extrapolation length and the Gibbs dividing surface

It is important to emphasize here that the surface director rotation $\delta\phi_s$ that enters Eq. (2) does not correspond to the actual rotation $\delta\phi_{\rm act}$ of the nematic molecules in contact with the polyimide film. Indeed, in the continuum theory of NLCs, the nematic material is assumed to behave bulklike everywhere up to the Gibbs dividing surfaces that are implicitly assumed to coincide with the position of the surfaces of the solid orienting plates. This means that the elastic, the magnetic, and the dielectric constants and any other material parameter are assumed to have the same values in any point of the NLC. With this assumption, the free energy density F of the NLC is represented everywhere by the bulk Frank-Oseen expression. The variations of the bulk material parameters that occur in a thin interfacial layer close to the surfaces of the NLC lead to a surface excess of free energy. Then, according to the Gibbs thermodynamics of the interfaces, the total free energy can be written as follows:

$$G = \int_S \Gamma dS + \int_V F dV, \tag{11}$$

where Γ is the surface free-energy density and the two integrals are extended to the whole surface and to the whole volume of the NLC, respectively. The anchoring energy W represents the director-dependent contribution to the surface free-energy density Γ. If an electric field much higher than the Freederickz threshold is applied along the x axis, the director azimuthal angle that minimizes the bulk free energy is [1]

$$\phi(z) = 2\arctan\left[\tan\left(\frac{\phi_s}{2}\right)\exp(-z/\xi)\right], \tag{12}$$

where $\xi = \sqrt{K_2/(\epsilon_0\epsilon_a)}/E$ is the electric coherence length, $\phi_s = \phi(0)$ and the Gibbs dividing surface is at $z = z_G = 0$. Of course, the material parameters of the NLC are different from the bulk ones in a thin interfacial layer close to the interface and the actual director field in the interfacial layer can differ appreciably from that in Eq. (12) as schematically shown in Fig. 4. Then, the actual surface angle $\phi_{\rm act}$ can be different from angle ϕ_s that appears in the definition of the surface anchoring energy and in the boundary condition (2). The extrapolation length is $d_e = z_G - z_e = -z_e$, where z_e represents the z coordinate of the point where the extrapolation of the bulk distortion (broken line in Fig. 4) approaches the easy angle ϕ_e.

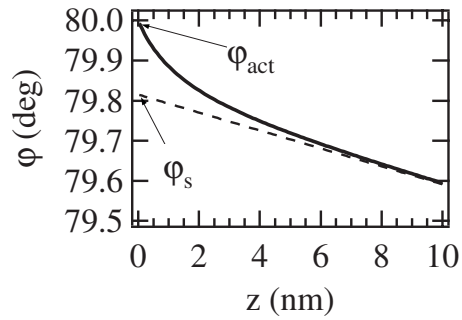

FIG. 4. The broken line shows the azimuthal director angle $\phi(z)$ [see Eq. (26)] that solves the continuum bulk Frank-Oseen equation versus distance z from the Gibbs dividing surface when the electric coherence length is $\xi = 906$ nm. The full line represents the actual director angle $\phi_{\rm act}(z)$ [see Eq. (23)] in the interfacial layer when the characteristic interfacial length is $\xi_c = 2.9 \pm 1.3$ nm. The surface extrapolated angle ϕ_s differs appreciably from the actual surface angle $\phi_{\rm act}$.

According to the analysis above, angle ϕ_s in Eq. (1) is a macroscopic thermodynamic parameter that corresponds to the extrapolation of the bulk director angle up to the Gibbs dividing surface $z = z_G = 0$. In a very interesting paper, Yokoyama [19] showed that any experimental method used to measure the anchoring energy measures the extrapolated surface angle on an ideal reference surface $z = z_R$ that characterizes the specific method and, in general, does not coincide with the Gibbs dividing surface $z = z_G = 0$. Then the extrapolation length that is measured with a given experimental method corresponds to $z_R - z_e$ and not to the thermodynamic value $d_e = -z_e$. $|z_R|$ is expected to be of the order of the characteristic thickness ξ_c of the interfacial layer. If the true extrapolation length is much greater than the thickness of the interfacial layer (weak anchoring), all the experimental methods provide a substantially unambiguous measurement of the thermodynamic extrapolation length. On the contrary, for strong anchoring, as occurs in our experiment, the measured extrapolation length can differ appreciably from the thermodynamically defined value. For each experimental method, the position z_R of the reference surface depends on the specific microscopic structure of the interfacial layer. Then, its precise position z_R can be only determined using a specific microscopic or mesoscopic model of the interfacial layer. In particular, in the case of our optical reflectometric and transmitted light methods, the position of the reference surface will depend on the specific shape of the local director angle $\phi_{\rm act}(z)$ and on the spatial variation of the NLC refractive indices $n_e(z)$ and $n_o(z)$ in the interfacial layer.

B. The model of the interfacial layer

According to Usami *et al.* [31], an adsorbed monolayer of 8CB deposited by evaporation on a uv-aligned polyimide has an in-plane surface order parameter comparable to the in-plane order parameter $S'=0.2$ of the polymeric layer. We emphasize here that the order parameter of polyimide and 8CB that was determined in [31] is not the uniaxial order parameter $S=(A_{\parallel}-A_{\perp})/(A_{\parallel}+2A_{\perp})$ but the in-plane order parameter $S'=(A_{\parallel}-A_{\perp})/(A_{\parallel}+A_{\perp})$. Since a single deposited 8CB monolayer has a biaxial character [31,33,34], we cannot use the uniaxial order parameter S. One must use a tensor order parameter to exactly describe its molecular order, instead of S or S'. However, for simplicity, in the following theoretical treatment we ignore the biaxiality and we use the uniaxial order parameter S to describe the molecular order in the interfacial layer. Furthermore, it must be emphasized here that the theoretical model that will be discussed below involves variation of macroscopically defined quantities (refractive indices and elastic constants) on a length scale comparable with a molecular length. This should be considered only as a rough approximation of the real situation which is much more complicated. The important parameter in our model is the uniaxial surface order parameter S_0 of the first nematic monolayer that corresponds to the measured in-plane order parameter $S'=0.2$. To obtain this parameter, we follow the Zhuang *et al.* treatment [34] assuming that the distribution function $f(\theta',\phi')$ of the NLC molecules can be expressed as the product of two independent functions $F(\theta')$ and $Q(\phi')$ with

$$F(\theta')=F_0\exp\left[-\left(\frac{\theta'-\theta_0}{\sigma}\right)^2\right], \tag{13}$$

$$Q(\phi')=\frac{\left(1+\sum_{n=1}^{\infty}d_n\cos(n\phi')\right)}{2\pi}, \tag{14}$$

where θ' is the polar angle of the molecular long axis with respect to axis z' orthogonal to the substrate and ϕ' is the azimuthal angle with respect to axis x' parallel to the director. F_0 is a normalization constant and θ_0, σ, and d_n are coefficients characterizing the surface molecular distribution. Using the distribution function $f(\theta',\phi')=F(\theta')Q(\phi')$ we find that the uniaxial surface order parameter S_0 and the in-plane order parameter S' are (see also [34])

$$S'=\frac{\langle\sin^2\theta'\cos(2\phi')\rangle}{\langle\sin^2\theta'\rangle}=\frac{d_2}{2}, \tag{15}$$

$$S_0=\frac{\langle 3\sin^2\theta'\cos^2\phi'-1\rangle}{2}=\beta-\frac{1}{2}+\frac{\beta d_2}{2}, \tag{16}$$

where symbol $\langle\cdots\rangle$ denotes the average over the distribution function and $\beta=3\langle\sin^2\theta'\rangle/4$. From Eq. (15) we obtain $d_2=2S'=0.4$ for our uv-aligned polyimide. Note that polyimide tends to favor a strong planar anchoring of molecules. Then we expect θ_0 to be close to 90° and, thus, $\beta=3\langle\sin^2\theta'\rangle/4\approx 0.75$. Indeed, using optical second harmonic generation with a 8CB monolayer deposited on a polyimide layer, Zhuang *et al.* [34] found the polar parameters $\theta_0=80°$ and $\sigma=7°$ virtually independent of the rubbing strength. Substituting these values in Eq. (13) we calculate $\beta=3\langle\sin^2\theta'\rangle/4=0.722$ that, substituted in Eq. (15) with $d_2=0.4$, gives $S_0=0.366$. Similar results are also obtained using $\theta_0=81°$ and $\sigma=5°$ measured by Barmentlo *et al.* [24] by optical second harmonic generation. With these values, we obtain $\beta=0.73$ and $S_0=0.375$. Then, it seems to be reasonable to assume that also for 5CB and for our uv-aligned polyimide, the surface uniaxial order parameter is $S_0\approx 0.37$. Above the interfacial layer, the order parameter must approach the bulk uniaxial value at temperature $T=24$ °C that is $S_b=0.57$ [35]. In the interfacial layer, the local twist elastic constant $K_2(z)$ is approximatively proportional to the square of the local order parameter $S(z)$, that is $K_2(z)=K_2S^2(z)/S_b^2$, where K_2 is the bulk elastic constant. As shown by Yokoyama *et al.* [36], if the characteristic interfacial length ξ_c is much smaller than the magnetic coherence length ξ, the surface elastic torque

$$M_z=K_2\frac{S^2(z)}{S_b^2}\frac{d\phi}{dz} \tag{17}$$

remains constant across the interfacial layer. The interfacial variation of the order parameter produces also a change of the local refractive indices that can appreciably affect the transmitted and reflected beams. Neglecting the biaxiality induced by the interface, we write

$$n_o(z)=\bar{n}-\Delta nS(z)/(3S_b), \tag{18}$$

$$n_e(z)=\bar{n}+2\Delta nS(z)/(3S_b), \tag{19}$$

where $\bar{n}=(n_e+2n_o)/3$ is the isotropic refractive index. According to the Landau-De Gennes theory, for S_0 sufficiently close to S_b, the interfacial variation of the surface order parameter is satisfactorily represented by the simple exponential form [36,37]

$$S(z)=S_b+(S_0-S_b)\exp(-z/\xi_c), \tag{20}$$

where ξ_c is a characteristic interfacial length and S_b and S_0 are the bulk and surface order parameters. ξ_c depends on the L_1 and L_2 parameters of the Landau-De Gennes expansion and on the second derivative A_s of the Landau-De Gennes free energy at the equilibrium nematic point ($S=S_b$) and can be written as follows:

$$\xi_c=\sqrt{\frac{3(L_1+L_2/6)}{2A_s}}\approx\sqrt{\frac{3L_1}{2A_s}}, \tag{21}$$

where we have exploited the condition $L_2/6\ll L_1$ [38]. We remind the reader that the correlation length ξ_c' that is obtained from the light scattering measurements in the isotropic phase is

$$\xi_c'=\sqrt{\frac{L_1}{A}}\approx\sqrt{\frac{L_1+L_2/6}{A}}, \tag{22}$$

where $A=a(T-T^*)$ is the known Landau-De Gennes coefficient that represents the second derivative of the free energy at $S=0$. Then, according to Eq. (22), we can define the nem-

atic correlation length ξ_c' by replacing A with A_s as in Eq. (22). Comparing Eq. (21) with Eq. (22), we obtain $\xi_c \approx \sqrt{3/2}\xi_c' = 1.22\ \xi_c'$. Then, the interfacial characteristic length is close to the nematic correlation length. Substituting $S(z)$ of Eq. (20) into Eq. (17) with the boundary condition $\phi(0) = \phi_{\text{act}}$ and with the surface elastic torque $M_z = -K_2 \sin(\phi_e)/\xi$, after simple calculations we get

$$\phi(z) = \phi_{\text{act}} + \frac{\xi_c \sin(\phi_e)}{\xi}\left(-\frac{z}{\xi_c} - \ln(M) + H\right), \tag{23}$$

where

$$M = \frac{S_b - (S_b - S_0)\exp(-z/\xi_c)}{S_0}, \tag{24}$$

$$H = \frac{S_b}{S_b - (S_b - S_0)\exp(-z/\xi_c)} - \frac{S_b}{S_0}, \tag{25}$$

and ϕ_{act} is the actual surface director angle. For $z \gg \xi_c$, $\phi(z)$ must approach the bulk director solution that is

$$\phi(z) \approx \phi_s - \frac{\sin(\phi_e)}{\xi} z, \tag{26}$$

where ϕ_s is the extrapolated surface angle. Comparing Eq. (26) to Eq. (23) for $z \gg \xi_c$, we get the surface extrapolated angle

$$\phi_s = \phi_{\text{act}} - \frac{\xi_c \sin(\phi_e)}{\xi}\left[\ln\left(\frac{S_b}{S_0}\right) + \frac{S_b - S_0}{S_0}\right]. \tag{27}$$

The director distortion that is predicted by Eq. (23) for $\phi_{\text{act}} = 80°$, $\xi_c = 2.9$ nm, and $E = 0.2042$ V/μm is represented by the full line in Fig. 4. According to Eq. (27), the extrapolation length $d_e = \xi(\phi_e - \phi_s)/\sin(\phi_e)$ that corresponds to such a distortion is

$$d_e = d_{\text{act}} + \xi_c\left[\frac{S_b - S_0}{S_0} + \ln\left(\frac{S_b}{S_0}\right)\right], \tag{28}$$

where the first term $d_{\text{act}} = \xi(\phi_e - \phi_{\text{act}})/\sin(\phi_e)$ represents the short-range contribution to the extrapolation length due to the actual surface director rotation while the second term takes into account for the interfacial elastic distortion. Note that the second contribution in Eq. (28) correctly vanishes if $S_0 = S_b$. For $S_0 < S_b$, the elastic contribution is positive, then we infer that the short-range contribution d_{act} is always smaller than the total extrapolation length d_e. As shown above, many experimental observations suggest that the polymer-nematic short-range interactions are very strong. Then, it seems to be reasonable to assume that the first nematic layer is strongly anchored at the polyimide surface [$d_{\text{act}} \approx 0$ in Eq. (28)] and that the surface order parameter S_0 is close to 0.37. In such a case the extrapolation length is entirely due to the elastic interfacial contribution [second term between the square brackets in Eq. (28)].

C. Relation between the measured extrapolation length and the interfacial characteristic length

Now, we have the following question: what is the extrapolation length d_e^R that is measured with our reflectometric method when the interfacial behavior is represented by Eqs. (18), (19), and (23)? To answer this question, we used the numerical Berreman approach to calculate the apparent surface rotation that will be measured with the reflectometric method when the director distortion is that in Eq. (23) with $\phi_{\text{act}} = \phi_e = 80°$ (strong short-range anchoring), the interfacial refractive indices are those in Eqs. (18) and (19) and the NLC is sandwiched between two polyimide anisotropic layers of thickness 11 nm. The other material parameters are those reported in Appendix A. We find that the measured extrapolation length (expressed in nanometers) is a linear function of the characteristic interfacial length ξ_c. Assuming $S_0 = 0.37$, we obtain

$$d_e^{\text{meas}} = -10.94 + 1.14\xi_c. \tag{29}$$

For $\xi_c = 0$ nm we recover the negative apparent extrapolation length $-d_{ep} = -10.94$ due to the anisotropy of the polyimide layer [see Eq. (9)]. Substituting the experimental value $d_e^{\text{meas}} = -7.6 \pm 0.6$ in Eq. (29) we find the characteristic length is $\xi_c = 2.9 \pm 1.3$ nm, where the uncertainty comes from the uncertainty on d_e^{meas} and from the numerical uncertainties due to the material parameters of the NLC and of the interfacial layer. The corresponding value of the nematic correlation length is $\xi_c' = \xi_c/1.22 = 2.4 \pm 1$ nm.

It is interesting to compare the value of the correlation length ξ_c' that is obtained here with some results reported in the literature. The correlation length ξ_c' of 5CB has been recently measured by Krich *et al.* [39] in the isotropic phase. They found $\xi_c' \approx 5$ nm at the clearing temperature and $\xi_c' \approx 2$ nm 11 °C above the clearing point. To the best of our knowledge, the correlation length in the nematic phase of 5CB has not been measured directly but an estimation for this parameter has been obtained by Lelidis *et al.* [40]. In their experiment, the authors measured the change of the order parameter induced in the nematic phase by a strong electric field applied parallel to the nematic director. This kind of measurement provides the experimental value of coefficient A_s in Eq. (21). Using this value together with the value of L_1 that can be estimated from the known values of the elastic constants and of the order parameter of 5CB, the authors found $\xi_c' = 4.7 \pm 0.5$ for $T_c - T = 0.1$ °C and $\xi_c' = 1.7 \pm 0.2$ nm for $T_c - T = 3.8$ °C. A comparable value of ξ_c' was calculated using the analogous experimental data obtained by Malraison *et al.* [41] for 7CB using a high magnetic field (B = 12 T). The agreement between these values of ξ_c' and our estimated value $\xi_c' = 2.4 \pm 1$ nm is satisfactory. It must be noted that, in a recent paper, Shao *et al.* [42] measured the average order parameter of a 5CB NLC sandwiched between two polyimide films versus the thickness of the NLC. From this thickness dependence, they were able to obtain the characteristic thickness ξ_c of the interfacial layer for $T_c - T = 4$ °C. They found $\xi_c = 10$ nm that is much higher than our experimental result. Similar results were also obtained for the interface between a PVA rubbed film and the NLC mixture GR-41 (Chisso Co. Ltd.) [43]. It is evident that the disagreement between our estimated value of the interfacial thickness and that obtained in Ref. [42] is very high and cannot be justified by the different temperatures of the two measurements. A possible reason for the high value of the

interfacial characteristic thickness measured in [42] could be related to the rubbing procedure. This method generates grooves on the polymer layer with a typical depth of some nanometers [33,44]. Grooves can affect appreciably the measured thickness of the interfacial layer because they simulate a smoother transition from the polymer film to the NLC. Since the surface of uv-aligned polyimides is expected to be much more flat than that of rubbed polyimides, direct measurements of the interfacial layer thickness for these materials would be very interesting.

As expected by the analysis above, the reference surface $z=z_R$ for the reflectometric method is expected to not coincide with the Gibbs dividing surface $z_G=0$. It is interesting to obtain the value of z_R for the interfacial distortion investigated here. The measured extrapolation length that corresponds to this distortion is given in Eq. (29). Substituting this expression in Eq. (10) with $\chi=0.065$ and $d_{ep}=10.94$ we obtain the reflectometric extrapolation length $d_e^R=1.22\ \xi_c$. According to the discussion above, this extrapolation length corresponds to z_R+d_e, where $d_e=0.97\ \xi_c$ is the thermodynamic extrapolation length [d_e in Eq. (28) with $d_{\mathrm{act}}=0$, $S_0=0.37$, and $S_b=0.57$]. Then, the reflectometric reference surface is at $z_R=0.25\ \xi_c$ inside the interfacial layer. The displacement of the optical reference surface from the Gibbs dividing surface is very small and, thus, the reflectometric method is confirmed to be a very efficient technique to measure strong azimuthal anchoring. Similar conclusions can be reached analyzing the transmitted light method.

V. CONCLUSIONS

In this paper, we have investigated the azimuthal anchoring at the interface between a 5CB NLC and a thin uv-aligned polyimide layer having the in-plane order parameter $S'=0.2$. The experimental results clearly show that the measurements of strong anchoring energies are somewhat complex and require special care. In particular, the anisotropy of the polymeric layer plays a very important role in the anchoring energy measurements on these substrates that are characterized by a strong anchoring and a high birefringence. It has been shown that the optical anisotropy of our uv-aligned polymer layer simulates a negative extrapolation length whose absolute value is comparable to the thickness $d_p=11$ nm of the anisotropic film. This effect is particularly relevant for highly oriented uv-aligned polymeric layers, while it is usually negligible for rubbed polymeric layers. Taking into account for this effect, we find that the extrapolation length measured with the reflectometric method at the nematic-polyimide interface is $d_e^R=3.6\pm1.6$ nm. The experimental value of the extrapolation length is appreciably smaller but of the same order of magnitude as that measured by some authors at the interface between a nematic liquid crystal and a strongly rubbed polyimide layer [10,11,16,17]. It must be noted, however, that much greater extrapolation lengths and, thus, much smaller anchoring energies, have been often reported in the literature for rubbed polyimide films [6,45,46]. In our opinion, these latter weak azimuthal anchoring energies are probably due to a very small rubbing of the investigated substrates or to some drawback of the experimental methods. Indeed, measurements of strong anchoring energies require special experimental methods and very great care [9,19].

As clearly stated by Yokoyama [19], the extrapolation length that is measured by any experimental method does not correspond to the correct thermodynamic definition of the extrapolation length because the reference surface for the experimental method is virtually coincident with the Gibbs dividing surface only in the special case where the thickness of the interfacial layer is completely negligible with respect to the extrapolation length. Such an effect can be disregarded for weak anchoring, but it can become important in the case of strong anchoring. For strong anchoring substrates, a reliable value of the thermodynamic extrapolation length can be only obtained comparing the experimental results with the predictions of a specific microscopic or mesoscopic model of the interfacial layer (the so-called structure-model perspective [19]). Using this mesoscopic procedure, we showed that the experimental results are in agreement with the prediction of a simple interfacial model where the director is assumed to be rigidly anchored on the polymeric layer and the measured finite extrapolation length is only due to the presence of an interfacial layer where the local order parameter passes from the surface value $S_0=0.37$ to the bulk value $S_b=0.57$ within a few correlation lengths. The correlation length that is estimated from our experimental results 11 °C below the clearing point is $\xi_c'=2.4\pm1$ nm which is in satisfactory agreement with some previous experimental results. Furthermore, the true thermodynamic extrapolation length is $d_e=2.8\pm1.3$ nm that is close to the reflectometric measured value $d_e^R=3.6\pm1.6$ nm. However, it must be emphasized that our model of the interfacial layer is somewhat rough because we disregard completely the biaxiality of the interfacial layer and we assume that the microscopic anchoring is much greater than the macroscopic one. A more detailed analysis of our experimental results would need a more complex theoretical procedure where the biaxiality of the interfacial layer is taken into account and the surface potential of the polymer-nematic interface is considered [36,47].

ACKNOWLEDGMENTS

One of the authors (S.F.) acknowledges the Ministero dell' Istruzione, dell'Universita' e della Ricerca of Italy (MIUR) for financial support (PRIN 2004: 2004024508003). The authors would like to thank S. Murata, N. Narita, and J. Yokota of Chisso Co. Ltd. for supplying the polyamic acid solution used in this study and I. Dozov of Nemoptics for arranging the collaboration between our groups.

APPENDIX A: EFFECT OF THE POLYMER ANISOTROPY ON THE TRANSMITTED BEAM

Here we discuss the contribution of the anisotropy of the orienting polymeric layer to the transmitted light measurements. We consider a NLC layer of extraordinary and ordinary refractive indices n_e and n_o, respectively, sandwiched between two anisotropic polymeric layers of thickness d_p and refractive indices n_{pe} and n_{po}. The polymer layers are

coated on isotropic glass plates of refractive index n. The polymers extraordinary axes are aligned along the easy axes of the NLC interfaces. The director at the first surface (2 in Fig. 1) makes angle $\delta\phi_s$ with the easy axis. According to [9], the beam transmitted through a twisted NLC is separated into a "generalized" extraordinary beam that propagates with velocity c/n_e and a "generalized" ordinary beam that propagates with velocity c/n_o. Due to the bulk director distortion, the polarizations of these beams are not the standard extraordinary and ordinary polarizations. For sufficiently small director distortions, the transmission through the NLC is satisfactorily described by the perturbative Oldano approach [5]. In this approach, reflections at the interfaces are disregarded and the transmitted beam is described by the 2×2 Jones matrix. The transmission matrix is written in a rotating basis that follows the director rotation. Then, the base vectors (1,0) and (0,1) represent an electric field that remains parallel or orthogonal to the local director, respectively. The base vectors are normalized in such a way that they correspond to extraordinary and ordinary beams of unitary intensity. We define the perturbative parameters

$$a = \eta_1 \lambda \frac{d\phi/dz|_2}{2\pi\Delta n} \tag{A1}$$

and

$$b = \eta_1 \lambda \frac{d\phi/dz|_3}{2\pi\Delta n}, \tag{A2}$$

where $\Delta n = n_e - n_o$ is the anisotropy of the refractive indices of the NLC, $d\phi/dz|_2$ and $d\phi/dz|_3$ are the director derivatives at the polymer-nematic interfaces 2 and 3 of the cell (see Fig. 1) and $\eta_1 = \sqrt{(n_o/n_e)} + \sqrt{(n_e/n_o)} = 1.002 \approx 1$ for 5CB at room temperature. The perturbative expansion of the transmission matrix of the NLC at the first order in the parameters a and b leads to the Oldano matrix that can be written in the form [9]

$$\bar{O} = e^{i\delta_e} \begin{vmatrix} 1 & ia \\ ib & 0 \end{vmatrix} + e^{i\delta_o} \begin{vmatrix} 0 & ib \\ ia & 1 \end{vmatrix} \tag{A3}$$

where $\delta_{e,o} = 2\pi n_{e,o} d/\lambda$ with d=thickness of the NLC. The first matrix term on the right-hand side of Eq. (A3), that we will denote by $\overline{O^e}$, describes the propagation of the generalized extraordinary wave in the NLC, while the second term describes the propagation of the generalized ordinary wave. The transmission matrixes $\overline{P_2}$ and $\overline{P_3}$ of the polymer layers written in the local reference systems where the x axis is parallel to the director at each surface are $\overline{P_i} = \overline{R_i P_0 R_i^t}$, where $\overline{R_i}$ with $i=2,3$ is the rotation matrix from easy axis to the director axis at the ith interface while $\overline{P_0}$ is the diagonal matrix

$$\overline{P_0} = \begin{vmatrix} e^{i\delta_{pe}} & 0 \\ 0 & e^{i\delta_{po}} \end{vmatrix}, \tag{A4}$$

where $\delta_{pe,o} = 2\pi n_{pe,o} d_p/\lambda$. The total transmission matrix for the generalized extraordinary beam is

$$\bar{T} = \overline{P_3 O^e P_2}. \tag{A5}$$

According to the analysis given in Ref. [9], the apparent rotation angle ϕ_{app}^T in eq. (4) at the first order in a and b is obtained using the theoretical expression

$$\phi_{\text{app}}^T = \frac{1}{2}\arctan\left(\frac{c_I}{a_I - b_I}\right) \approx \frac{1}{2}\left(\frac{c_I}{a_I - b_I}\right), \tag{A6}$$

where

$$a_I = T_{11}T_{11}^* + T_{21}T_{21}^*,$$

$$b_I = T_{12}T_{12}^* + T_{22}T_{22}^*,$$

$$c_I = 2\,\text{Re}(T_{11}T^*{}_{12} + T_{21}T^*{}_{22}), \tag{A7}$$

where the asterisk denotes the conjugate of a complex number, Re is the real part, and T_{ij} are the components of matrix $\bar{T}$. By retaining only contributions up to the first order in a and b we get

$$\phi_{\text{app}}^T = \frac{2ac_2 \sin\delta_p - s_4 \sin^2(\delta_p/2)}{2[1 - 2(s_2)^2 \sin^2(\delta_p/2) + 2as_2 \sin\delta_p]}, \tag{A8}$$

where $\delta_p = \delta_{pe} - \delta_{po} = 2\pi\Delta n_p d_p/\lambda$ is the optical dephasing across the polymeric layer, $c_2 = \cos(2\delta\phi_s)$, $s_2 = \sin(2\delta\phi_s)$, and $s_4 = \sin(4\delta\phi_s)$. ϕ_{app}^T correctly vanishes for a zero anisotropy of the polymer layer ($\delta_p = 0$). Note that ϕ_{app}^T does not depend on the director angle at the second interface of the cell (3 in Fig. 1). In fact, the director angle at the second interface appears only in the polymer matrix $\overline{P_3}$ in Eq. (A5). It can be easily shown that this matrix does not affect the intensity of the transmitted beam but only the transmitted electric field because it is a unitary and symmetric matrix. In our experimental method, we are only interested to the contributions that are proportional to the external field E [α_T term in Eq. (7)]. Both the perturbative parameter a and the director rotation angle $\delta\phi_s$ [see Eq. (2)] are proportional to the external field. Then, only those contributions in Eq. (A8) that are linear in a and $\delta\phi_s$ can affect our experimental measurement of the director rotation angle. Evidencing these contributions we have

$$\phi_{\text{app}}^T = a\sin(\delta_p) - 2\sin^2(\delta_p/2)\delta\phi_s + 0(E), \tag{A9}$$

where $0(E)$ are the higher order contributions in the electric field. Then, the total phase signal measured with the transmission method is

$$\phi_A^T = \delta\phi_s + a\sin(\delta_p) - 2\sin^2(\delta_p/2)\delta\phi_s + 0'(E), \tag{A10}$$

where $0'(E)$ denotes any higher order contribution (also those disregarded in the Oldano approach). The second and third terms on the left-hand side of Eq. (A10) are proportional to the electric field and, thus, are equivalent to a positive apparent surface director rotation,

$$\delta\phi = a\sin(\delta_p) - 2\sin^2(\delta_p/2)\delta\phi_s, \tag{A11}$$

that is to a negative apparent contribution d_e^{app} to the extrapolation length. For an electric field that is much higher than

the Freederickz threshold field, the bulk director twist is very accurately described by the semi-infinite sample approximation $d\phi/dz|_2 = -\sin(\phi_e)/\xi$ and the apparent extrapolation length $[-\xi\delta\phi/\sin(\phi_e)]$ results,

$$d_e^{\text{app}} = -d_{ep} - \chi d_e, \tag{A12}$$

where d_{ep} and χ are the two positive coefficients,

$$d_{ep} = \frac{\eta_1 \lambda \sin(\delta_p)}{2\pi\Delta n}, \tag{A13}$$

$$\chi = 2\sin^2(\delta_p/2). \tag{A14}$$

The extrapolation length that is measured with the transmitted method is the sum of the true extrapolation length d_e and of the apparent one d_e^{app}. Then

$$d_e^{\text{meas}} = (1-\chi)d_e - d_{ep}. \tag{A15}$$

The χ term renormalizes the extrapolation length, while d_{ep} is an additive contribution. Note that, in standard conditions $\chi \ll 1$ since $\delta_p \ll 1$ and, thus, it can be completely disregarded. Then, the most important contribution comes from d_{ep}, that is of the order of magnitude as the thickness of the anisotropic uv-aligned polymer layer. Indeed, for $\delta_p \ll 1$, Eq. (A13) becomes

$$d_{ep} \approx \frac{\Delta n_p}{\Delta n} d_p = \frac{\Delta l_{\text{opt}}}{\Delta n}, \tag{A16}$$

where Δl_{opt} is the optical path difference across the polymer layer. It must be emphasized here that, for the standard rubbed polyimide layers, the optical dephasing is appreciably smaller than that of photoaligned polyimide films and this leads to a smaller contribution to the measured extrapolation length (typically $d_{ep} \ll 4$ nm). In particular, in the case of the rubbed polyimide films investigated in Refs. [16,17], the optical dephasing was $<0.1°$ that corresponds to a spurious extrapolation length d_{ep} lower than 1 nm. The main reason for the important contribution of the polymeric layer in our experiment is the relatively high average refractive index of the photoaligned Azo-PI films compared to the conventional polyimides films (e.g., $\bar{n}=1.74$ for PMDA-ODA at 632.8 nm, while $\bar{n}=2.088$ for Azo-PI) and its large in-plane anisotropy.

The results above were obtained using the Oldano perturbative approach that disregards any reflected beam. The "exact" optical behavior of the NLC can be obtained using the optical approach developed by Berreman [29] and the complex numerical procedure described in Ref. [9]. Using this numerical procedure, we calculated the optical dephasing ϕ_A^T for different values of the electric field and for a strongly anchored NLC ($d_e=0$). Then, we made the polynomial best fit of $\phi_A^T(E)$ and we extracted the contribution $\alpha_T E$ that is linear in the electric field and that corresponds to the apparent surface rotation $\delta\phi$. The full line in Fig. 5 represents the numerically calculated value of the best-fit coefficient α_T versus the surface easy angle for $d_p=11$ nm, $n_{pe}=2.184$, $n_{po}=2.040$, $n_e=1.711$, $n_o=1.528$ and using the BK glass refractive index $n=1.515$. The elastic constant and the dielectric anisotropies of the NLC at $T=24\,°\text{C}$ are $K_2=4.05 \times 10^{-12}$ N and $\epsilon_a=13.4$, respectively. The extrapolation length is assumed $d_e=0$, that is $\delta\phi_s=0$. We have also verified that, as expected [see Eq. (A11)], the correction due to a finite value of the extrapolation length [$\delta\phi_s \neq 0$ in Eq. (A11)] is completely negligible. The broken line in Fig. 5 corresponds to the surface rotation predicted by Eq. (A11). The agreement between the numerical results and the analytical approximated expression is satisfactory. The small discrepancies are due to the reflections at the interfaces that were disregarded in the perturbative approach. In fact, we have verified that these discrepancies become vanishingly small if the refractive indices of the polymer layer are chosen the same as those of the NLC so eliminating multiple reflections in the polymeric layer.

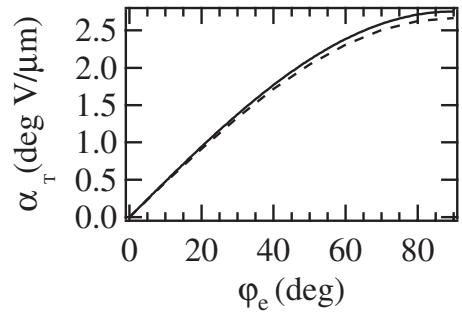

FIG. 5. Apparent surface rotation per unit electric field (1 V/μm) versus the angle ϕ_e between the easy axis and the electric field. The full line represents the apparent surface rotation calculated numerically using the Berreman approach for $d_e=0$. The broken line represents the approximated value given by Eq. (A11).

APPENDIX B: EFFECT OF THE POLYMER ANISOTROPY ON THE REFLECTOMETRIC METHOD

Here we discuss the influence of a residual anisotropy of the substrates on the reflectometric measurements of the surface director rotation $\delta\phi_s$ and of the extrapolation length d_e. In this case, we make only a numerical analysis based on the Berreman algorithm. The numerical procedure has been already described in detail in the appendix of Ref. [13], then we only report here the numerical results. The numerical procedure allows us to calculate the apparent rotation angle

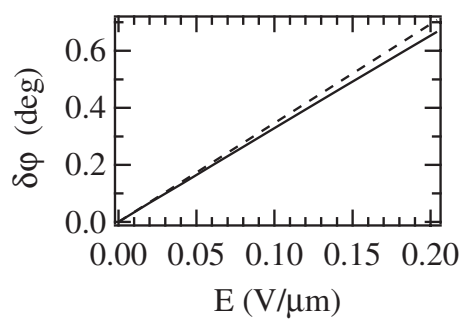

FIG. 6. Apparent surface director rotation due to the anisotropy of the polymeric layer in the case of reflectometric measurements. The full line represents the apparent surface rotation versus the rms of the electric field for a strongly anchored NLC ($d_e=0$). The broken line represents the spurious rotation for $d_e=10$ nm.

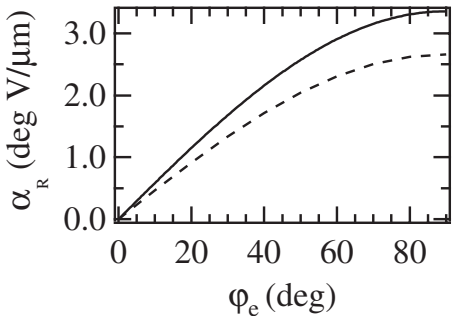

FIG. 7. The full line represents the apparent surface rotation per unit electric field ($E=1$ V/μm) versus the easy angle ϕ_e in the case of the reflectometric method and for $d_e=0$. The broken line represents the spurious rotation predicted by Eq. (A11) in the transmitted light case.

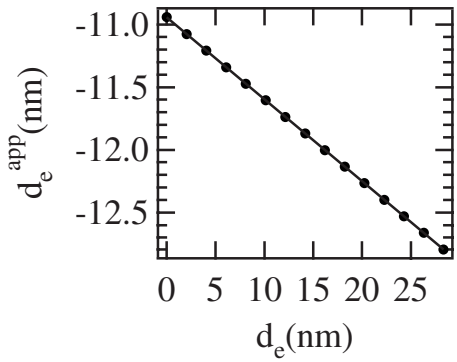

FIG. 8. Points represent the contribution of the layer anisotropy to the measured extrapolation length versus the actual extrapolation length. The easy angle is $\phi_e=80°$. The full line represents the linear best fit with Eq. (B2).

$\phi_A^R=\phi^R/4$ and, thus, the spurious rotation angle $\delta\phi=\phi_A^R-\delta\phi_s$ due to the polymer and to the bulk distortion. Here we are interested in the beam reflected at the first polymer-nematic interface (2 in Fig. 1) passing through the crossed analyzer. The calculation of the spurious director rotation due to the anisotropic layer was already reported by one of the authors in Ref. [13]. However, in Ref. [13] we disregarded the director distortion in the NLC and we accounted only for the presence of a finite angle $\delta\phi_s$ between the director axis and the extraordinary axis of the polymer layer. This is equivalent to consider only the term $-2\sin^2(\delta_p/2)\delta\phi_s$ in Eq. (A11) for the transmitted beam. As shown in Ref. [13], in agreement with what happens for the transmitted beam, this contribution leads to a decrease of the measured surface director rotation $\delta\phi_s$ that is negligible in the standard experimental conditions (less than 5%). However, as well as what happens for the transmitted beam, the effect of the director bulk distortion is not negligible for a NLC interface having a strong azimuthal anchoring. For this reason, we repeat here the calculations taking also into account the director twist contributions.

Figure 6 shows the spurious rotation angle $\delta\phi$ versus the rms of the electric field E. The parameters used for calculations are $d_p=11$ nm, $n_{pe}=2.184$, $n_{po}=2.040$, $n=1.515$, $n_e=1.711$, $n_o=1.528$. The elastic constant and the dielectric anisotropy of 5CB are $K_2=4.05\times10^{-12}$ N and $\epsilon_a=13.4$, respectively. The full line in Fig. 6 represents the spurious rotation versus the rms of the electric field E when the extrapolation length of the NLC is $d_e=0$ (the director at the surface remains fixed and $\delta\phi_s=0$) and the easy angle is $\phi_e=80°$ as in our experimental conditions. We see that quadratic contributions in E are completely negligible here and that the apparent surface rotation $\delta\phi$ is proportional to the rms of the electric field. The broken line in Fig. 6 shows the behavior when the extrapolation length of the NLC is $d_e=10$ nm. We see that, in this case, the effect of a finite extrapolation length is small but not completely negligible contrary to what happened for the transmitted light measurements.

The full line in Fig. 7 shows the dependence of the apparent surface rotation per unit electric field ($E=1$ V/μm) on the angle ϕ_e between the easy axis and the director for $d_e=0$ nm. For comparison, the broken line in Fig. 7 represents the surface apparent rotation given by the analytical function obtained in the transmitted light case [Eq. (A11)]. In analogy with the transmitted light case, we expect that the apparent extrapolation length due to the anisotropic layer can be written in the simple form

$$d_e^{\text{app}}=-d_{ep}-\chi d_e, \tag{B1}$$

where d_{ep} and χ are positive coefficients. This is fully confirmed by our numerical calculations. Points in Fig. 8 represent the numerically calculated values of d_e^{app} versus d_e. The line represents the best linear fit. From the best fit we obtain $d_{ep}=10.94$ nm and $\chi=0.0654$. The total extrapolation length that is measured in the experiment is $d_e^{\text{meas}}=d_e+d_e^{\text{app}}$. Then, the extrapolation length d_e of the NLC can be obtained from the reflectometric measured extrapolation length d_e^{meas} using the expression

$$d_e=\frac{d_e^{\text{meas}}-d_{ep}}{1-\chi}. \tag{B2}$$

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