

### Optical phase shift of polymer-dispersed liquid crystals

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We report a detailed study of the optical phase shift induced by a polymer-dispersed liquid crystal subjected to a low-frequency electric field. A relationship between the optical phase shift and the droplet and sample order parameters  $S_d$  and  $S_f$  is worked out in order to explain the experimental data obtained using an ellipsometric technique. The measurements taken for several incidence angles are in very good agreement with the expected behavior if an increase of the droplet order parameter is also considered when increasing the field. The method appears suitable to study reorientation phenomena in polymer-dispersed liquid crystals overcoming the problems due to light scattering in these materials.

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#### I. INTRODUCTION

Recently there has been increasing interest in polymer-dispersed liquid crystals (PDLC): materials where nematic microdroplets are embedded in a polymeric matrix. The droplets randomly dispersed in the polymer may have a size close to the light wavelength, thus producing strong light scattering. They have strong optical anisotropy which depends on the liquid crystal's orientation inside the droplets. Therefore, since the liquid-crystal molecules can be reoriented by external fields, it is possible to induce a matching of the refractive index of the droplets with the one of the matrix, thus switching the sample to a transmission state [1]. This well-known effect is the basis of many applications presently being studied for these materials. From a fundamental point of view, they are interesting because many physical properties of liquid crystal are strongly influenced by the confinement of the material in a small cavity. Furthermore, the interfacial interaction polymer-liquid crystal must play a very important role in every physical phenomenon because of the very high surface over volume ratio in the liquid-crystal droplet.

Up to now, known measurements of optical properties in PDLC have been restricted to light-intensity transmission [1-4] and, more recently, to light scattering [5]. No measurement of induced optical phase shift has been reported and discussed yet. Nevertheless, this kind of analysis may be interesting because this phenomenon is directly related to droplet reorientation and liquid-crystal reorientation inside the droplets.

In this paper, we report the study of the optical phase shift induced by a PDLC sample when a low-frequency electric field is applied to it. In Sec. II we present a method that allows us to calculate the optical phase shift produced by a PDLC sample. In Sec. III we present the experimental data and discussion based on the above-mentioned method.

#### II. THEORY

According to a model recently introduced by Kelly and Palfy-Muhoray [6] to describe the droplet reorientation in PDLC, we write the elastic part of the free-energy den-

sity for a nematic droplet as

$$\mathcal{F}_{el}^d \simeq -\frac{1}{3} \frac{1}{R_{eff}^2} \xi^2 S S_d P_2(\hat{\mathbf{N}}_d \cdot \hat{\mathbf{L}}). \tag{1}$$

Here,  $R_{eff}$  is an effective radius of the droplet,  $S$  is the usual scalar order parameter of the liquid-crystal dependent on temperature, and  $S_d$  is the droplet order parameter defined as

$$S_d = \langle \frac{1}{2} \{ 3[\hat{\mathbf{N}}_d \cdot \hat{\mathbf{n}}(\mathbf{r})]^2 - 1 \} \rangle_{V_d} = \langle P_2[\cos \vartheta_d(\mathbf{r})] \rangle_{V_d}, \tag{2}$$

where  $\hat{\mathbf{n}}(\mathbf{r})$  is the liquid-crystal director,  $\hat{\mathbf{N}}_d$  is the droplet's director, i.e., the symmetry axis of the nematic distribution inside the droplet, and  $\vartheta_d$  is the angle between these two vectors.

The average is made over the droplet's volume  $V_d$ . With such a definition  $S_d$  takes into account the liquid-crystal orientation with respect to the droplet's axis;  $S_d=1$  when all the molecules are parallel to  $\hat{\mathbf{N}}_d$  and  $S_d=0$  for a random distribution (isotropic droplet). Then the product  $SS_d$  in Eq. (1) takes into account the overall orientational order of the liquid crystal in the droplet.  $P_2$  is the second-order Legendre polynomial which depends on the angle between the geometrical axis  $\hat{\mathbf{L}}$  of the droplet and  $\hat{\mathbf{N}}_d$ . Finally,  $\xi^2$  is a parameter which has been introduced by the authors as an eccentricity of the droplet, but actually it takes into account the shape effects of the droplet as well as the anchoring effects on the droplet's walls. When a low-frequency electric field is applied to a PDLC sample, the droplet orientation along the field axis  $E$  can be described by a sample order parameter

$$S_f^E = \langle P_2(\hat{\mathbf{N}}_d \cdot \hat{\mathbf{E}}) \rangle, \tag{3}$$

where the average is taken over the total number of droplets. According to this definition, it has been shown [6] that the free-energy density due to the interaction with the electric field can be written as

$$\mathcal{F}_d^E = \frac{F_E^d}{V_d} = -\frac{1}{3} g(S_f^E) S S_d \Delta \epsilon E^2 P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{N}}_d^i), \tag{4}$$

where

$$g(S_f^E) = \frac{3\epsilon_p}{\epsilon_{LC} + 2\epsilon_p - \nu_{LC}(\epsilon_{LC} - \epsilon_p)}, \tag{5}$$

and  $v_{LC}$  is the volume fraction of liquid crystal in the sample,  $\epsilon_p$  is the dielectric constant of the polymer, and  $\epsilon_{LC}(S, S_d, S_f^E)$  is the effective scalar dielectric permeability of the liquid crystal. The sample order parameter is expressed by

$$\begin{aligned} S_f^E &= \frac{1}{4\pi} \int P_2(\hat{\mathbf{N}}_d \cdot \hat{\mathbf{E}}) \sin \vartheta_L d\vartheta_L d\varphi_L \\ &= \frac{1}{4} + \frac{3}{4} \frac{e_a^2 - 1 + 2(\hat{\mathbf{E}} \cdot \hat{\mathbf{L}})^2}{[(e_a^2 - 1)^2 + 4e_a^2(\hat{\mathbf{E}} \cdot \hat{\mathbf{L}})^2]^{1/2}}, \end{aligned} \quad (6)$$

where the reduced field is given by

$$e_a = \left[ \frac{R_{\text{eff}}}{\zeta} \left( \frac{g(S_f^E) \Delta \epsilon}{K} \right)^{1/2} \right] E, \quad (7)$$

with  $K$  being the elastic constant (one-constant approximation). From Eqs. (6) and (7) it is possible to work out the value of  $S_f^E$  as a function of the different parameters  $R_{\text{eff}}$ ,  $\zeta$ , and  $K$ .

By considering the above recalled description as our starting point, we now proceed in the calculation of the optical phase shift. First of all, we need to work out the ordinary and extraordinary refractive indices of the droplet  $n_{od}$  and  $n_{ed}$  and their dependence on the droplet's order parameter  $S_d$ .

We will calculate these indexes by an appropriate averaging over the droplet size. This procedure is the usual one [7,8] when one is concerned with the optical phase shift. In fact, this quantity is sensitive only to the average refractive indexes encountered by the waves along their path. If we consider, for instance, a medium with variable refractive indexes  $n_x(z)$  and  $n_y(z)$  depending on the location along the propagation direction  $z$ , the phase shift introduced between two waves of wavelength  $\lambda$  polarized along  $x$  and  $y$ , respectively, is given by

$$\Phi = \frac{2\pi}{\lambda} \int_0^L [n_x(z) - n_y(z)] dz,$$

i.e.,

$$\Phi = \frac{2\pi}{\lambda} L (\bar{n}_x - \bar{n}_y),$$

where

$$\bar{n}_x = \frac{1}{L} \int_0^L n_x(z) dz, \quad \bar{n}_y = \frac{1}{L} \int_0^L n_y(z) dz,$$

and  $L$  is the crossed thickness. Choosing the droplet's refractive indexes through an averaging procedure over the droplet size might create problems when one is concerned with scattering of radiation at the interface of the droplets; nevertheless, average quantities (even if they were not calculated) were considered successfully in the theory of light scattering by polymer-dispersed liquid crystals [9].

Let us consider in the droplet a small volume of liquid crystal with uniform orientation given by  $\hat{\mathbf{n}}(\mathbf{r})$ . In Fig. 1 we have just shown the local index ellipsoid with major axis  $n_e$  and minor axis  $n_o$  ( $n_e$  and  $n_o$  are the liquid-crystal refractive indexes). In this figure, the droplet director  $\hat{\mathbf{N}}_d$  is chosen along  $n_z$ ; therefore, the wave with wave vector  $\hat{\mathbf{k}}_1$  and electric displacement  $\mathbf{D}_1$  is affected by the ordi-

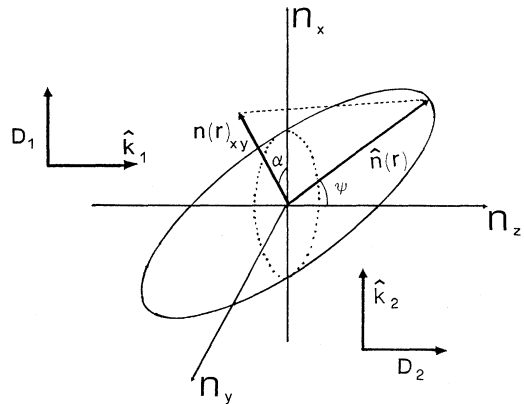


FIG. 1. Local-index ellipsoid for a small volume of liquid crystal in a droplet.  $\hat{\mathbf{N}}_d$  lies along  $n_z$ , so that the wave corresponding to the wave vector  $\hat{\mathbf{k}}_1$  is affected by the ordinary index of the droplet, while the one corresponding to  $\hat{\mathbf{k}}_2$  experiences its extraordinary index.  $\psi$  is the angle between  $\hat{\mathbf{n}}(\mathbf{r})$  and  $\hat{\mathbf{N}}_d$ , while  $\mathbf{n}(\mathbf{r})_{xy}$  is the projection of  $\hat{\mathbf{n}}(\mathbf{r})$  on the  $(n_x, n_y)$  plane.

nary index of the droplet, while the wave with wave vector  $\hat{\mathbf{k}}_2$  and electric displacement  $\mathbf{D}_2$  experiences the extraordinary index. We define the extraordinary index  $n_{od}$  of the whole droplet as the index experienced by a wave traveling in a direction perpendicular to  $\hat{\mathbf{N}}_d$ , with polarization parallel to it. Such a wave impinging on our small volume of liquid crystal is affected by a local index which depends on the angle  $\psi$  between  $\hat{\mathbf{n}}(\mathbf{r})$  and the polarization direction.

$$n_e(\mathbf{r}) = \frac{n_o n_e}{[n_o^2 \sin^2 \psi + n_e^2 \cos^2 \psi]^{1/2}}. \quad (8)$$

Therefore, the extraordinary index of the droplet is simply given by averaging the former expression over the droplet volume,

$$\begin{aligned} n_{ed} &= \langle n_e(\mathbf{r}) \rangle_{V_d} \\ &= \int_{V_d} n_e(\mathbf{r}) f(r, \psi, \alpha) r^2 \sin(\psi) dr d\alpha d\psi, \end{aligned} \quad (9)$$

where  $f(r, \psi, \alpha)$  is the distribution function of the molecular director, which depends on the liquid-crystal orientation in the droplet. For small droplets ( $R_{\text{eff}} = 100-500$  nm), the most likely configuration is the bipolar one [10], with cylindrical symmetry around  $\hat{\mathbf{N}}_d$  and uniform with respect to the angle  $\alpha$ .

In order to evaluate the dependence of  $f$  on  $\psi$ , we make the assumption that all the directors form the same angle  $\psi$  with respect to  $\hat{\mathbf{N}}_d$ . This approximation can be justified by noting that a typical order parameter for a bipolar droplet is  $S_d = 0.7$  when no electric field is applied [6], and for such a value of  $S_d$  the average angle between  $\hat{\mathbf{n}}(\mathbf{r})$  and  $\hat{\mathbf{N}}_d$  is quite small. This approximation has the following meaning. We replace the "real" distribution with the simplest one that produces the same value of the droplet's order parameter  $S_d$ . We show in the Appendix that the result we obtain using this approximation introduces, at most, a discrepancy of the order of 1% from the actual value of the optical phase shift. Then we set

$$f(r, \psi, \alpha) = \frac{3}{2} \frac{\delta(\psi - \bar{\psi})}{\pi R^3 \sin \bar{\psi}} = f(\psi), \quad (10)$$

where  $\delta(\psi - \bar{\psi})$  is the Dirac function and the other constants are required by normalization condition.

Since  $\cos^2 \psi = \langle \cos^2 \psi \rangle_{V_d} = \frac{1}{3}(2S_d + 1)$ , we have

$$n_{ed}(S_d) = \frac{n_o n_e}{[n_e^2 + \frac{1}{3}(n_o^2 - n_e^2)(2S_d + 1)]^{1/2}}. \quad (11)$$

The ordinary refractive index of the droplet is obtained by considering a wave traveling in a direction parallel to  $\hat{N}_d$ , with any polarization lying in a transverse plane. The intersection of the local ellipsoid with the wave front ( $xy$  plane) gives

$$n_x^2 \left[ \frac{\cos^2 \psi}{n_o^2} + \frac{\sin^2 \psi}{n_e^2} \right] + \frac{n_y^2}{n_o^2} = 1, \quad (12)$$

where  $\hat{n}(\mathbf{r}) = (n_x, n_y, n_z)$ . Thus the "local" ordinary index  $n_o(\mathbf{r})$  depends on the angle  $\alpha$ ; as it varies from 0 to  $\pi/2$ ,  $n_o(\mathbf{r})$  varies from the maximum value

$$n_{\text{eff}}(\psi) = \frac{n_o n_e}{[n_o^2 \sin^2 \psi + n_e^2 \cos^2 \psi]^{1/2}}$$

to the minimum value  $n_o$ . Averaging over the droplet's volume we get

$$n_{od} = \langle n_o(\mathbf{r}) \rangle_{V_d} = \int_{V_d} n_o(\mathbf{r}) f(\psi) r^2 \sin(\psi) dr d\alpha d\psi, \quad (13)$$

where

$$n_o(\mathbf{r}) = \frac{n_o [n_{\text{eff}}(\psi)]}{[n_o^2 \cos^2 \alpha + [n_{\text{eff}}(\psi)]^2 \sin^2 \alpha]^{1/2}}. \quad (14)$$

Now

$$\begin{aligned} \int_0^{2\pi} n_o(\mathbf{r}) d\alpha \\ = 4n_{\text{eff}}(\psi) \int_0^{\pi/2} \frac{d\alpha}{\left[ 1 + \frac{(n_{\text{eff}}(\psi) - n_o^2)}{n_o^2} \sin^2 \alpha \right]^{1/2}}. \end{aligned} \quad (15)$$

By integration we finally get

$$n_{od}(S_d) \simeq \frac{2}{\pi} n_o F\left(\frac{\pi}{2}, m(S_d)\right), \quad (16)$$

where  $F(\pi/2, m(\psi))$  is the complete elliptic integral of first kind defined as

$$F\left(\frac{\pi}{2}, m\right) = \int_0^1 \frac{dx}{\sqrt{(1-x^2)(1-m^2x^2)}},$$

while

$$m(\psi) = \frac{\sqrt{n_{\text{eff}}^2(\psi) - n_o^2}}{n_{\text{eff}}(\psi)}. \quad (17)$$

In this case

$$m(S_d) = \frac{1}{n_e} \sqrt{\frac{2}{3}(n_e^2 - n_o^2)(1 - S_d)}. \quad (18)$$

Equations (11) and (16) for  $n_{ed}$  and  $n_{od}$  are plotted in Fig. 2 vs the droplet's order parameter  $S_d$ . The figure clearly shows that as  $S_d$  approaches 1,  $n_{ed}$  and  $n_{od}$  approach the values of  $n_o$  and  $n_e$ , since this condition corresponds to perfect alignment of the liquid-crystal director along the droplet axis, while the condition  $S_d = 0$  means random orientation of the liquid crystal in the droplet, that is, an isotropic droplet with refractive index  $n = (2n_o + n_e)/3$ . The curves in Fig. 2 show that the model is quite correct even for  $S_d = 0$ , as discussed in the Appendix. This means that the average refractive index of a droplet depends on  $S_d$ , but it does not depend much on the particular director configuration, i.e., two different configurations that produce the same value of  $S_d$  correspond to the same average refractive indexes.

We will use the calculated  $n_{od}$  and  $n_{ed}$  to work out the optical phase shift induced by the sample. Looking at Fig. 3, let us call  $\mathbf{D}$  the dielectric induction in the medium and  $\eta_d$  and  $\psi_d$  the Euler angles determining the orientation of  $\hat{N}_d$  in the laboratory frame  $x, y, z$  when the wave vector is parallel to  $z$ .

The two components of  $\mathbf{D}$ , parallel and perpendicular to  $\hat{N}_d$ , are

$$\begin{aligned} \mathbf{D}_\perp &= \mathbf{D} \sin(\eta_d - \alpha), \\ \mathbf{D}_\parallel &= \mathbf{D} \cos(\eta_d - \alpha), \end{aligned} \quad (19)$$

where  $\alpha$  is the polarization angle with respect to the  $x$  axis. The phase shift between  $\mathbf{D}_\perp$  and  $\mathbf{D}_\parallel$  after traveling through a droplet is

$$\bar{\varphi}(S_d; \psi_d) = \frac{2\pi}{\lambda} \langle l \rangle_{V_d} [n_{\text{def}}(S_d) - n_{od}(S_d)], \quad (20)$$

where

$$n_{\text{def}}(S_d) = \frac{n_{od}(S_d) n_{ed}(S_d)}{[n_{ed}^2(S_d) \cos^2 \psi_d + n_{od}^2(S_d) \sin^2 \psi_d]^{1/2}} \quad (21)$$

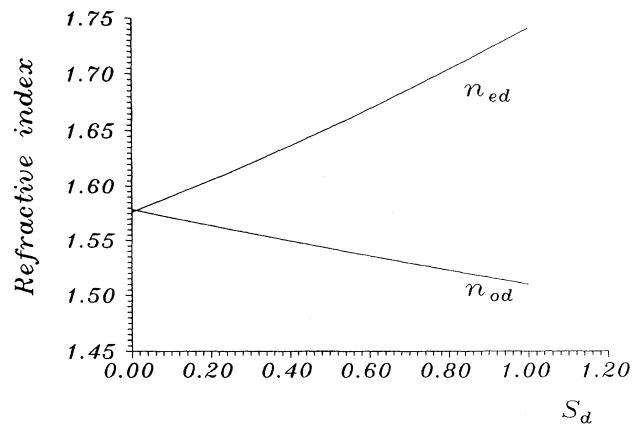


FIG. 2. Ordinary and extraordinary indexes for a nematic droplet vs its order parameter  $S_d$ .

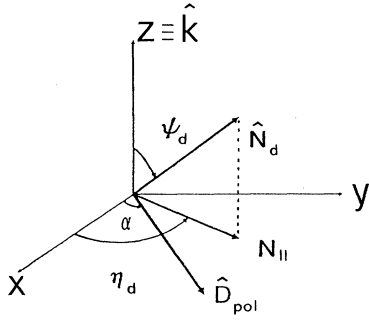


FIG. 3. Frame of reference used for the evaluation of the optical phase shift that an impinging monochromatic wave propagating along the  $z$  axis experiences in crossing a nematic droplet.

and  $\langle l \rangle_{V_d}$  is the average path inside the droplet,

$$\langle l \rangle_{V_d} = \frac{4}{3}R \quad (22)$$

for a spherical cavity of radius  $R$ . Transforming this into the laboratory frame

$$D_x(t) = a \cos(\omega t + \delta_x), \quad (23)$$

$$D_y(t) = b \cos(\omega t + \delta_y),$$

where

$$a = [(\mathbf{D}_\perp \sin \eta_d)^2 + (\mathbf{D}_\parallel \cos \eta_d)^2 + \mathbf{D}_\parallel \cdot \mathbf{D}_\perp \cos \tilde{\varphi} \sin(2\eta_d)]^{1/2}, \quad (24)$$

$$b = [|\mathbf{D}_{\text{pol}}|^2 - a^2]^{1/2},$$

and

$$\sin \delta_x = \frac{\mathbf{D}_\parallel}{a} \sin \tilde{\varphi} \cos \eta_d, \quad (25)$$

$$\cos \delta_x = \frac{1}{a} (\mathbf{D}_\perp \sin \eta_d + \mathbf{D}_\parallel \cos \eta_d \cos \tilde{\varphi}),$$

$$\sin \delta_y = \frac{\mathbf{D}_\parallel}{b} \sin \tilde{\varphi} \sin \eta_d,$$

$$\cos \delta_y = \frac{1}{b} (-\mathbf{D}_\perp \cos \eta_d + \mathbf{D}_\parallel \sin \eta_d \cos \tilde{\varphi}).$$

In this way it is possible to work out the phase shift induced by a single droplet,

$$\varphi_d(\alpha, S_d; \psi_d, \eta_d) = \delta_y - \delta_x \quad (26)$$

using the above relationships.

In Eq. (26) we have underlined the dependence of  $\varphi_d$  on the light polarization ( $\alpha$ ), on the liquid crystal's orientation inside the droplet ( $S_d$ ), and on the droplet's orientation ( $\psi_d, \eta_d$ ). By applying the electric field  $\mathbf{E}_a$  with amplitude  $E_a$  the droplet directors try to reorient along the field direction. Also in this case we assume an average angle  $\gamma$  so that  $\cos^2 \gamma = \langle (\hat{\mathbf{N}}_d \cdot \mathbf{E}_a)^2 \rangle_{V_d}$ , which gives the droplet orientation at a given value of the field

$$\cos^2 \bar{\gamma} = \langle \cos^2 \gamma \rangle_{V_c} = \frac{1}{3}(2S_f + 1), \quad (27)$$

$$S_f \in [0, 1].$$

Now let us consider a thin layer of PDLC so that the radiation travels at most through one droplet's layer, with the beam cross section being much larger than the droplet size. When, in zero field, we have a random droplet orientation, the average phase shift experienced by the wave is zero. When an orienting field is applied we assume the droplets to be aligned along a conical surface forming an angle  $\gamma(E_a)$  with respect to the field direction. Also in this case we replace the real distribution with the simplest one that produces the same value of the order parameter  $S_f$ . In the Appendix we show that this approximation affects in a negligible way the calculation of the optical phase shift. Therefore, we use the following normalized distribution function:

$$f_s(\gamma) = \frac{1}{2} \frac{\delta(\gamma - \bar{\gamma}(E_a))}{\pi \sin \bar{\gamma}(E_a)}. \quad (28)$$

It is then easy to work out the phase shift induced by a single droplet's layer in a local reference  $x', y', z'$  where  $y' = y$  and  $z' = \mathbf{E}_a$ , where the angle between  $z'$  and  $z$  is the incidence angle  $\vartheta_i$ . In this frame

$$\varphi_{ml} = \int_0^{2\pi} \int_0^{\pi/2} \varphi_d(\xi, \gamma) f_s(\gamma) \sin(\gamma) d\xi d\gamma, \quad (29)$$

where  $\xi$  and  $\gamma$  are related to  $\psi_d$  and  $\eta_d$  by the following relationships:

$$\begin{aligned} \sin \psi_d &= \sin^2 \gamma (1 + \sin^2 \vartheta_i \sin^2 \xi) \\ &\quad + \frac{1}{2} \sin(2\gamma) \sin(2\vartheta_i) \cos \xi + \sin^2 \vartheta_i \cos \xi, \\ \cos \psi_d &= \cos \gamma \cos \vartheta_i - \sin \gamma \cos \xi \sin \vartheta_i, \end{aligned} \quad (30)$$

$$\sin \eta_d = \frac{\sin \gamma \sin \xi}{\sin \psi_d},$$

$$\cos \eta_d = \frac{\cos \gamma \sin \vartheta_i + \sin \gamma \cos \xi \cos \vartheta_i}{\sin \psi_d}.$$

Now we need to evaluate the layer thickness. By supposing that a uniform spatial distribution of the droplets in the polymeric matrix, which is an optically isotropic medium,  $v_{\text{LC}}$  (volume fraction of liquid crystal in the polymer) is also the fraction of total optical path of the radiation which is done through the droplets, which are responsible for the phase shift. Therefore, the layer thickness may be written as

$$\bar{d}(\vartheta_i) = \frac{R_{\text{eff}} \cos \vartheta_i}{v_{\text{LC}}}, \quad (31)$$

where the factor  $\cos(\vartheta_i)$  is due to the increase of the optical path in the polymer by increasing the incidence angle.

Finally, the whole PDLC sample must be considered to be made out of many single layers, each of them described by the same values of  $S_d$  and  $S_f$  and the same applied field. Then the total phase shift will be given by the sum of the phase shift of each single layer.

If the sample thickness is  $d_0$ , the number of elementary layers is

$$N_s(\vartheta_i) = \frac{d_0}{\bar{d}(\vartheta_i)} = \frac{d_0 v_{\text{LC}}}{R_{\text{eff}} \cos(\vartheta_i)} \quad (32)$$

and the total phase shift induced by the samples is

$$\Delta\varphi = N_s(\vartheta_i)\varphi_{ml}. \quad (33)$$

We emphasize that  $\Delta\varphi = \Delta\varphi(\alpha, \vartheta_i, S_d, S_f)$ , namely, the induced phase shift depends on the light polarization ( $\alpha$ ) and propagation direction ( $\vartheta_i$ ), on the liquid-crystal orientation inside the droplet ( $S_d$ ), and on the droplet orientation with respect to the applied field. In Fig. 4 we show the expected behavior of  $\Delta\varphi$  vs the applied voltage at different values of  $\vartheta_i$ , using  $d_0 = 36 \mu\text{m}$ ,  $R_{\text{eff}} = 150 \text{ nm}$ ,  $\zeta = 0.16$ . In the Figs. 5 and 6 we show the influence of the materials parameters  $R_{\text{eff}}$  and  $\zeta$  which affect  $S_d$  and, consequently,  $\Delta\varphi$ . The curves have been calculated at  $\vartheta_i = 20^\circ$ . It can be seen that both  $\zeta$  and  $R_{\text{eff}}$  strongly affect the droplet reorientation and, consequently, the slope of the phase shift from the low field to the saturation value.

In all these curves,  $S_d$  has been considered to be not dependent on the field,  $S_f$  being the only parameter varying with the field. Actually, we will show in Sec. III that our experimental data can be fit taking into account an increase of  $S_d$  by increasing the applied voltage, which means a better orientation of the liquid-crystal molecules along the droplet axis.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

The samples were prepared by the phase-separation method using fluid prepolymer EPON 815 (Shell Chemical Co.) and MK107 (Wilmington Chemical Corporation) and as curing agent Capcure 3-800 (Shell Chemical Co.) and B-component BOSTIK (Boston s.p.A.). The liquid crystal was E7 from the British Drug House, with refractive indexes  $n_o = 1.511$ ,  $n_e = 1.740$  at  $25^\circ\text{C}$ , and density  $\rho = 1.03 \text{ g/cm}^3$ . The polymeric matrix (cured) has a density  $1.3 < \rho_p < 1.4 \text{ g/cm}^3$  and a refractive index  $n_p = 1.55$ . Each sample ( $36 \mu\text{m}$  thickness) was bounded by two conducting glasses.

The optical phase shift was measured by a conventional ellipsometric technique using a  $\lambda/4$  wave plate and an

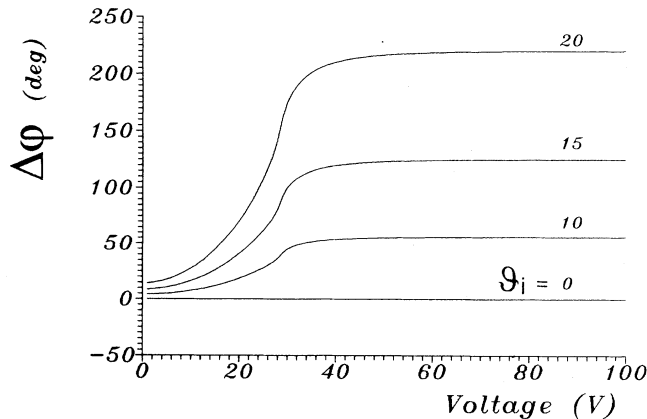


FIG. 4. Expected behavior of the optical phase shift  $\Delta\varphi$  for a PDLC sample vs the applied voltage, at different values of  $\vartheta_i$ . The sample thickness is  $36 \mu\text{m}$  and the parameters used for the plot are  $R_{\text{eff}} = 150 \text{ nm}$  and  $\zeta = 0.16$ .

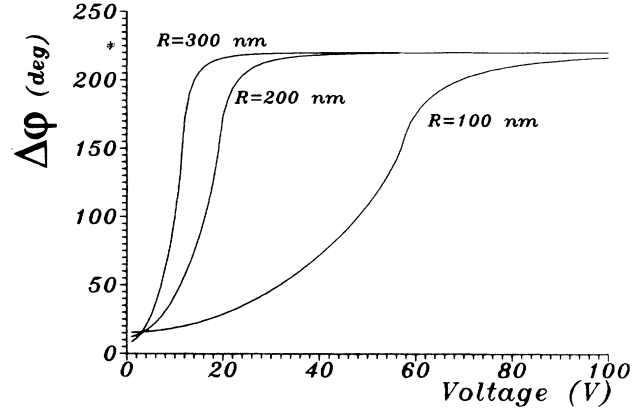


FIG. 5. Expected behavior of the optical phase shift  $\Delta\varphi$  for a PDLC sample vs the applied voltage, at different values of  $R_{\text{eff}}$ . The sample thickness is  $36 \mu\text{m}$  and the parameters used for the plot are  $\vartheta_i = 20^\circ$  and  $\zeta = 0.16$ .

analyzer after the sample in order to determine the parameters of the elliptical radiation coming out of the sample. The impinging radiation of a He-Ne laser was linearly polarized in a direction at  $45^\circ$  in the  $xy$  laboratory plane.

A lock-in detection system allowed a good resolution with an uncertainty lower than  $0.5^\circ$  on the phase shift. Measurements were taken at different voltages applied to the sample and for different incidence angles  $\vartheta_i$ . The direct measurements of the rotation angles of the  $\lambda/4$  plate and of the analyzer that give signal extinction on the detector are used to work out the phase shift induced between the waves traveling with polarization along the  $x$  axis and the  $y$  axis, respectively.

Measurements were possible only at voltages higher than a threshold voltage that switches the sample into the transmission state (which, in our case, was  $V_{\text{th}} = 35 V_{\text{rms}}$ ) (Fig. 7). In Fig. 8 we report experimental data obtained for an incidence angle  $\vartheta_i = 20^\circ$  together with the results of the calculation for different values  $S_d$  (full lines) worked

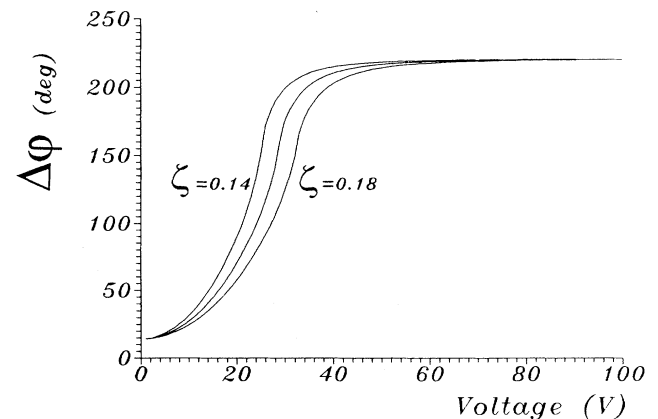


FIG. 6. Expected behavior of the optical phase shift  $\Delta\varphi$  for a PDLC sample vs the applied voltage, at different values of  $\zeta$ . The sample thickness is  $36 \mu\text{m}$  and the parameters used for the plot are  $\vartheta_i = 20^\circ$  and  $R_{\text{eff}} = 150 \text{ nm}$ .

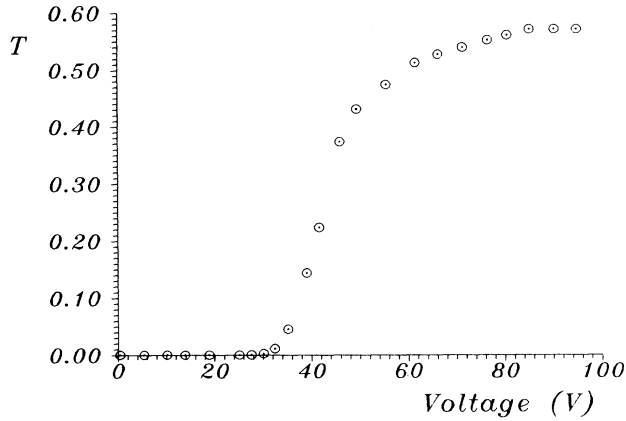


FIG. 7. Transmittivity of the PDLC sample vs applied voltage, for normal impinging light.

out from Eq. (33) using  $\zeta=0.16$ ,  $R_{\text{eff}}=150$  nm, and the measured value  $v_{\text{LC}}=0.5$ . One can observe a qualitative agreement between theory and experiment (the shape of the curve), however the experimental data cross (at high voltages) the theoretical curves. The effect cannot be due to the approximations of our calculations because they can at most shift the calculated values by 1–2% and, moreover, our approximations are expected to work better in the high-voltage region where the discrepancy between experiment and theory is relevant from a quantitative point of view. From this figure it is clear that the weak point of the theory lies in keeping constant the droplet order parameter. In fact, the data can be fitted in an excellent way by taking into account the effect of re-orientation of the liquid crystal inside the droplet using the following empirical expression:

$$S_d = 1 - \frac{\tilde{k}(1 - S_d^m)}{\tilde{k} + (1 - S_d^m)V}, \quad (34)$$

which fulfills the conditions  $\lim_{V \rightarrow \infty} S_d(V) = 1$ , which means complete alignment of the liquid-crystal molecules

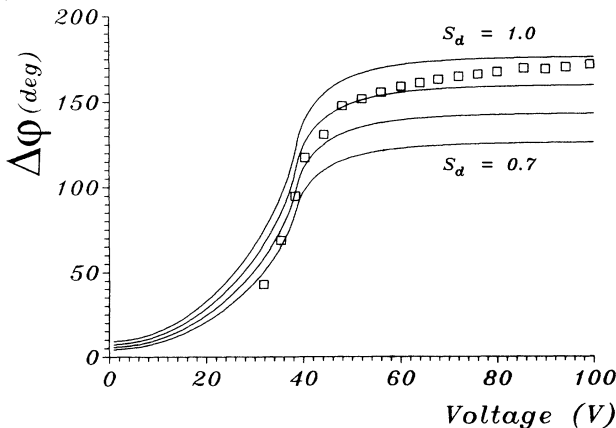


FIG. 8. Measured optical phase shift vs applied voltage at  $\vartheta_i = 20^\circ$ . The full lines represent the result of the theory for different values of  $S_d$ . Parameters used:  $\zeta=0.16$ ,  $R_{\text{eff}}=150$  nm.

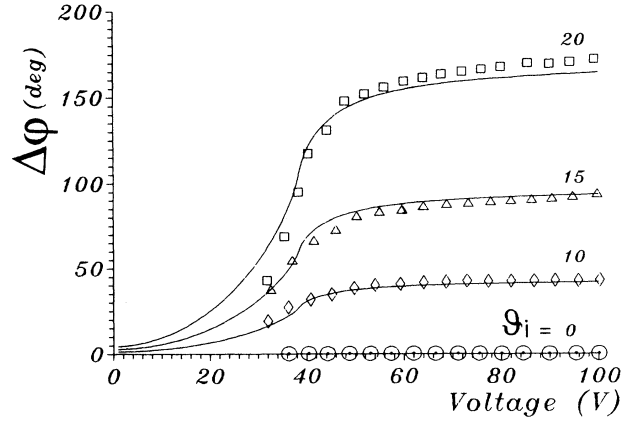


FIG. 9. Measured optical phase shift vs applied voltage for different values of  $\vartheta_i$ . The full lines represent the result of the theory corrected according to Eq. (34).

along the field direction, and  $\lim_{E_a \rightarrow 0} S_d(E_a) = S_d^m$ , where  $S_d^m$  is the minimum value of the droplet's order parameter for a bipolar configuration.

Our data have been fitted using  $S_d^m = 0.7$  and  $k = 10$  V. In Fig. 9 we report experimental data obtained for different values of the incidence angle with the correspondent theoretical curves with the empirical correction made on  $S_d$  as explained above. The agreement is remarkable, since it is satisfactory for each value of  $\vartheta_i$  using the same parameters  $\zeta$  and  $R_{\text{eff}}$ . It must also be noted that, as expected, our data confirm that no phase shift is present for normal incidence since in this case the sample appears isotropic. This result demonstrates that it is necessary to take into account the increase of the droplet order parameter with the field. Therefore, the theory introduced by J. R. Kelly and P. Palffy-Muhoray should be corrected accordingly.

In conclusion we have presented measurements of a phase shift induced by an applied electric field in PDLC samples. Carrying out a calculation of the droplet's refractive indexes, we have shown that these measurements can be used to study the effects of liquid-crystal reorientation in the droplet disregarding the scattering phenomena that strongly affect any measurement of light intensity in these samples. In our opinion this method can also be applied to investigate also nonlinear optical effects in PDLC.

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#### APPENDIX

We want to discuss here the approximations used in choosing  $\delta$  functions for the director distribution into a droplet [Eq. (10)] and for the droplet director distribution in the sample [Eq. (28)]. We will justify these approxima-

tions by showing that the error introduced by them in the calculation of the optical phase shift is of the order of 1%. Let us start with the distribution in the single droplet and compare the result of our theory to the one that can be obtained independently, in the extreme case, of isotropic distribution of the director, namely, the distribution farthest from a  $\delta$  function. This is the case where the introduced approximation should give rise to the maximum discrepancy between the calculated and the actual value of the optical phase shift. The error we will find will be an upper limit for us, since we deal with bipolar droplets when the minimum order parameter is about 0.7. The isotropic director distribution means  $S_d=0$ . According to our calculation, we have from Eq. (11)

$$n_{ed} = \frac{n_o n_e}{[n_e^2 + \frac{1}{3}(n_o^2 - n_e^2)]^{1/2}}. \quad (\text{A1})$$

For the liquid-crystal E7 ( $n_o=1.511$ ,  $n_e=1.740$ )  $n_{ed}=1.576$ . Eq. (17) gives

$$n_{od} = \frac{2}{\pi} n_o F\left[\frac{\pi}{2}, m(0)\right], \quad (\text{A2})$$

where

$$m(0) = \frac{1}{n_e} \left[\frac{2}{3}(n_e^2 - n_o^2)\right]^{1/2}.$$

For E7 we get  $m(0)=0.4057$  and  $F(\pi/2, m(0))=1.6390$ , then  $n_{od}=1.578$ . On the other hand, the exact calculation of the isotropic refractive index would give  $n_{iso}=(n_e+2n_o)/3=1.587$ . Therefore, using our model we have a maximum discrepancy given by

$$(\Delta n)_{\max} = n_{iso} - n_{ed} = 0.011.$$

The influence of this error on the phase shift given by a single droplet can be easily worked out. From Eq. (20) we have

$$\tilde{\varphi}_d = \frac{2\pi}{\lambda} \frac{4}{3} R \left[ \frac{n_{od} n_{ed}}{(n_{ed}^2 \cos^2 \psi + n_{od}^2 \sin^2 \psi)^{1/2}} - n_{od} \right]. \quad (\text{A3})$$

By setting  $n_{ed}=x$ ,  $n_{od}=y$ , the total error on  $\varphi_d$  is

$$\Delta \varphi_d = \left| \frac{\partial \tilde{\varphi}_d}{\partial x} \right| \Delta x + \left| \frac{\partial \tilde{\varphi}_d}{\partial y} \right| \Delta y. \quad (\text{A4})$$

Therefore an upper limit, actually a real overestimation of the relative error, is given by

$$\left| \frac{\Delta \tilde{\varphi}_d}{\tilde{\varphi}_d} \right|_{\max} < \frac{1}{xy} \left| \frac{x^3 \cos^2 \psi + y^3 \sin^2 \psi}{x^2 \cos^2 \psi + y^2 \sin^2 \psi} + (x^2 \cos^2 \psi + y^2 \sin^2 \psi)^{1/2} \right| (\Delta n)_{\max}. \quad (\text{A5})$$

By setting  $x=y=1.577$  we get

$$\left| \frac{\Delta \tilde{\varphi}_d}{\tilde{\varphi}_d} \right|_{\max} < 0.014. \quad (\text{A6})$$

We notice that this result has been obtained using the parameters of the E7 compound, which is a nematic liquid crystal with a rather high optical anisotropy ( $n_e - n_o = 0.23$ ); then the relative maximum error will be, in general, smaller for other nematic liquid crystals. The result we have just obtained may be surprising, since it demonstrates that our approximation is quite good (error of the order of 1%) even at  $S_d=0$  (as shown in Fig. 2). The same arguments can be carried on to justify the approximation made for the droplet director distribution [Eq. (28)].

Following the same procedure, we could define the average refractive indexes  $n_{os}$  and  $n_{es}$  of a layer of droplets and we would get the same analytical results as for  $n_{od}$  and  $n_{ed}$  just replacing  $S_d$  with  $S_f$ . Then one can consider the extreme situation when  $S_f=0$  (zero field), comparing the results of our theory to the one given by an isotropic distribution. Again we would find an upper limit for the error in the phase shift, which, summed to the former one, give 2.8% as the maximum relative error introduced by the two approximations. Actually the extreme conditions corresponding to  $S_d=0$  and  $S_f=0$  are not considered in our experiment. Therefore, in our case the error introduced by the two approximations is much smaller than the maximum.

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