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Surface Polarization and Flexoelectricity in Nematic Liquid Crystals

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We propose a technique for the measurement of the surface electric polarization in nematic liquid crystals from the birefringence variations of the texture under weak vertical electric field. We study experimentally 5CB aligned on SiO layer with strong tilted anchoring. We show that in this system the surface polarization is one order of magnitude stronger than the bulk flexoelectric polarization of 5CB reported before. We discuss the sign and the magnitude of the surface polarization and the reliability of the proposed method.

Keywords: Surface polarization; flexoelecticity; nematic liquid crystal; electrooptical effect

INTRODUCTION

The orientational order in the nematic phase is usually described by the tensorial order parameter $\mathbf{Q} = \frac{3}{2} S(\mathbf{nn} - \frac{1}{3}\mathbf{I})$, where S is the scalar order parameter, $\mathbf{n}$ the nematic director and $\mathbf{I}$ the unitary isotropic tensor ($I_{ij} = \delta_{ij}$). By symmetry, the average macroscopic dipolar moment of the nematic is zero, even if the molecules have large permanent dipoles. In 1969 Meyer[1] demonstrated, that some nematic distortions break the symmetry of the phase and give rise to a flexoelectric polarization : the asymetric mesogen

molecules are oriented by the distortion field and the average of their permanent dipoles is no more zero. Later, Prost and Marcerou[2] demonstrated that the flexoelectric polarization is mainly of quadrupolar origin and it exists also for symmetric molecules : the spatial variation of the molecular quadrupoles, related to the director distortion, creates a macroscopic polarization. By symmetry, for both the dipolar and quadrupolar contributions the flexoelectric polarization density is[1,2]:

$$\mathbf{P}_f = e_1 \mathbf{n}\, div\mathbf{n} + e_3 curl\mathbf{n} \times \mathbf{n} \qquad (1)$$

where e_1 and e_3 are the flexoelectric coefficients associated with splay and bend.

Another way of breaking the nematic symmetry is to vary in the space the scalar order parameter S, for example in the vicinity of a boundary surface, imposing surface order parameter $S_s \neq S$. Barbero et al. demonstrated[3], that in this case the spacial variation of $\mathbf{Q}$ gives rise to an ordoelectric polarization density, mainly of quadrupolar origin :

$$\mathbf{P}_o = e_o \nabla \bullet \mathbf{Q} = e_o \frac{3}{2} (\nabla S) \bullet (\mathbf{nn} - \frac{1}{3}\mathbf{I}) \qquad (2)$$

where $-e_o = -\dfrac{(e_1 + e_3)}{3S}$ is the quadrupolar density of completely aligned nematic. The ordoelectric polarization is concentrated only close to the surface[3], in a region comparable to the correlation length of the nematic phase. Integrating, we obtain that the surface density $\mathbf{P}_o$ of the ordoelectric polarization is proportional to $(\mathbf{Q} - \mathbf{Q}_s) \bullet \mathbf{N}$, where $\mathbf{Q}$ and $\mathbf{Q}_s$ are respectively the nematic order parameters in the bulk and on the surface and $\mathbf{N}$ is the external normal to the surface.

More generally, the bulk symmetry is always broken at the surface separating two different media. Even for isotropic liquids this can create a "contact" surface dipole density $\mathbf{P}_{iso}$, by symmetry $\mathbf{P}_{iso} // \mathbf{N}$. This surface polarization is due to the different electric properties on both sides of the surface and to the orientation of the permanent dipoles along $\mathbf{N}$. This trivial isotropic contact contribution exists also for nematics, but we are not interested in it because it is decoupled from the nematic order and orientation.

To the lowest order in $\mathbf{Q}$, the anisotropic term is $\mathbf{P_{an}} = p_{an}\mathbf{Q}\bullet\mathbf{N}$, with the same symmetry as the ordoelectric term and it is difficult to separate from it. In the following, we will consider only this surface polarization term, assuming that the ordoelectric contribution is already included in it.

A large number of techniques has been applied so far to measure the flexoelectric coefficients[4-13] and some of them enable also the study of the surface dipole density[14-18]. In most of the cases, the flexoelectric contribution can be integrated to give a surface term and weak anchorings are needed to measure it. As a result, the separation and the interpretation of the different polar surface terms are difficult. Several other difficulties arise in this kind of experiment : the ionic screening of the flexopolarization, the sensitivity to the field gradients created by the space charge accumulation, the electrochemical reactions on the electrodes, the difficulties to control and reproduce the weak anchoring, the competition with the much stronger dielectric coupling to the applied field. This explains the large number of discrepancies in the values and even in the sign of the experimentally measured flexocoefficients.

Here we propose a new technique to study the polar effects in nematics. The method is based upon measurement of small birefringence variations when a weak electric field is applied across a thin sample. Even for large dielectric anisotropy ε_a the quadratic dielectric effect is dominated by the linear polar effects. The surface polarization is measured on only one of the plates, chosen to have tilted and relatively strong anchoring. We present our experimental results for the surface polarization of 5CB on SiO_x showing polar effects of one order of magnitude stronger than those reported in the literature.

MEASUREMENT PRINCIPLE

Let us suppose that a dielectrically positive ($\varepsilon_a>0$) nematic liquid crystal is contained in a thin sandwich cell of thickness d. We choose the z-axis perpendicular to the plates, as in figure 1. The easy axes are tilted on the plates, respectively at angles Ψ_1 and Ψ_2, supposed arbitrary at the time being.

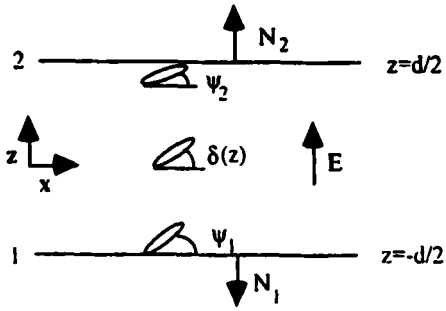

FIGURE 1 Geometry of the cell

A vertical electric field **E** is applied across the cell, parallel to the plates normals N_1 and N_2. Both substrates align the molecules in the (xz) plane and no azimuthal torques are applied. We suppose then that the director remains everywhere in the vertical plane (xz), and its orientation is described by the angle δ(z), where $cos\,\delta = \mathbf{n} \bullet \mathbf{x}$ (Figure 1). We suppose that the tilt of the director is small across the cell ($\delta^2(z) << 1$) and we assume $sin\,\delta \approx \delta$.

The total energy of the system can be written as the sum of the bulk (F_b), polar (F_p) and anchoring (F_{a_i}) terms:

$$F = F_b + F_p + F_{a_1} + F_{a_2} \tag{3}$$

The bulk energy due to the dielectric and elastic contributions is

$$F_b = \frac{1}{2} K_1 \int_{-\frac{d}{2}}^{\frac{d}{2}} (\delta'^2 - \frac{1}{\xi^2}\delta^2)dz \tag{4}$$

where K_1 is the splay curvature elastic constant, ξ is the electric field correlation length $\xi = \sqrt{\frac{4\pi K}{\varepsilon_a E^2}}$ and $\delta' = \frac{d}{dz}\delta$.

For small deviations $(\delta_i - \psi_i)$ of the surface director from the easy axis, the surface anchoring energy is given by:

$$F_{a_i} = \frac{1}{2}\frac{K_1}{L_i}(\delta_i - \psi_i)^2 \qquad i = 1, 2 \tag{5}$$

where L_i is the extrapolation length of the anchoring on the surface i.
The polar energy can be also integrated to give just a surface term:

$$F_p = -E\left[e\left(\delta_2^2 - \delta_1^2\right) - p_1\delta_1^2 + p_2\delta_2^2\right] + const. \quad (6)$$

where $e = \frac{1}{2}(e_1 + e_3)$ is the quadrupolar flexocoefficient and the surface polarization terms are taken in the simplest symmetry allowed approximation: $P_i = p_i \mathbf{N} \bullet (\mathbf{nn} - \frac{1}{3}\mathbf{I})$.

In small δ^2 approximation, the Euler Lagrange equation becomes $\delta'' = -\frac{1}{\xi^2}\delta$, giving:

$$\delta = \frac{1}{\sin\frac{d}{\xi}}\left[\delta_2 \sin\frac{d+2z}{2\xi} + \delta_1 \sin\frac{d-2z}{2\xi}\right] \quad (7)$$

and

$$F_b = \frac{1}{2}K_1 \frac{1}{\xi \sin\frac{d}{\xi}}\left[\left(\delta_1^2 + \delta_2^2\right)\cos\frac{d}{\xi} - 2\delta_1\delta_2\right] \quad (8)$$

In general, now we can find δ_1 and δ_2 as functions of the applied field from the surface torque equilibrium on the two plates, for arbitrary Ψ_i.

We note, however, that for $\delta_2 = \pm\delta_1$ the linear coupling with the field disappears due to the symmetry of the system. To have the strongest possible polar effect, we choose then $\psi_2 = 0$, i.e. the anchoring on the upper plate is planar, without pretilt, and the surface polarization on it is zero. This enables us to study separately the surface polarization on the pretilted lower plate. From the equilibrium equations, we obtain approximately, for low fields ($\frac{d}{\xi} << 1$) and for strong anchorings ($L_i << d$):

$$\delta_2 \approx 0 \quad \text{and} \quad \delta_1 \approx \psi_1 - 2\frac{L_1}{K_1}(p_1 + e)\psi_1 E \quad (9)$$

Equation (9) enables us to obtain $(p_1 + e)$ from the δ_1 variation under electric field. However, the direct measurement of δ_1 is a difficult experimental task. What can be measured much more precisely (and easily) is the integrated birefringence of the cell as a function of the applied field:

$$l(E) = \int_{-\frac{d}{2}}^{\frac{d}{2}} \left[\frac{n_o n_e}{\sqrt{n_o^2 \cos^2\delta + n_e^2 \sin^2\delta}} - n_o \right] dz \approx$$

$$\approx (n_e - n_o)d - \frac{1}{2} n_e \frac{n_e^2 - n_o^2}{n_o^2} \int_{-\frac{d}{2}}^{\frac{d}{2}} \delta^2 dz \qquad (10)$$

Substituting equations (7) and (9) in (10) and integrating, we obtain:

$$\Delta l(E) = l(E) - l(-E) = \frac{4}{3} n_e d \frac{n_e^2 - n_o^2}{n_o^2} \frac{L_1}{K_1} \psi_1^2 E(p_1 + e) \quad (11)$$

Note that the quadratic effects (dielectric coupling or higher terms in the polar couplings, neglected in the previous equations) do not contribute to this formula.

RESULTS AND DISCUSSION

We apply this measurement method to the nematic liquid crystal n-pentyl cyanobiphenyl (5CB) contained between two transparent indium tin oxyde (ITO) coated glass plates. To induce an alignment, the two electrodes have a silicon monoxyde (SiO) grazing evaporation coating. Depending of the evaporation angle, planar or oblique anchoring is achieved[19,20,21]. For the upper electrode, to ensure a planar alignment, the angle of evaporation is of 60°. The lower plate is evaporated at 82.5° to ensure an oblique anchoring of the nematic molecules. The pretilt on this plate, $\psi_1 = 20° \pm 1°$, was measured by the comparison of the twin domains birefringence[22] in separate experiment.

We use thin cells of variable thickness ($1\mu m \leq d \leq 10\mu m$) obtained by changing the spacers but remaining physically on the same two plates and in the same area.

We measure the birefringence variations using a Leitz polarizing microscope. The cell thickness is determined using a compensator and

measuring the birefringence of the cell when no field is applied. The optical signal is detected by a photo-multiplier and analyzed with a differential amplifier connected to an oscilloscope. The applied voltage is of square profile, which allows us to average on a large number of accumulated data and to have directly the optical response as a function of the time. In order to optimise the sensitivity and to have the best precision, when measuring the small variations Δl under electric field we work in the linear ($\lambda/4$) regime : by the compensator we introduce the phase difference needed to make the total phase difference equal to $(2m+1)\frac{\lambda}{4}$, where m is an arbitrary integer. By this way, good precision and sensitivity is achieved (much better than 1Å).

For 5CB, n_O=1.6, n_e=1.75[23], K_1=6.10^{-12}N[24] and we estimate L_1=20nm from the anchoring breaking threshold[25]assuming that the energy is of Rapini Papoular form.

Experimentally, we have measured the phase difference as a function of the voltage at fixed cell thickness. Just after the pulse, we observe fast response with relaxation time τ_1 in the order of (1-10 ms) depending on the cell thickness. This fast response is characteristic for the field induced texture change. At longer time scale the optical signal goes back to zero with much slower characteristic relaxation time τ_2. This slow process may be attributed to parasitic effects, such as ionic screening of the field, volume charge accumulation and electrochemistry. To avoid complications, we choose the pulse duration of the order of few times τ_1, much faster than the ionic effects. Moreover, we apply an alternative square electric signal with zero mean value in order to avoid at long term any cell damage due to electrochemical reactions or ions adsorption. We have also measured the current through the cell during the experiment. We observe that for "high" field (100mV/μm), the current becomes asymetric with the voltage polarity. We attribute this effect to electrochemical reactions. To avoid them, the field used in our measurements was limited to values inferior to this electrochemical threshold.

The fast contribution to the optical phase difference is presented on figure 2 as a function of the applied voltage.

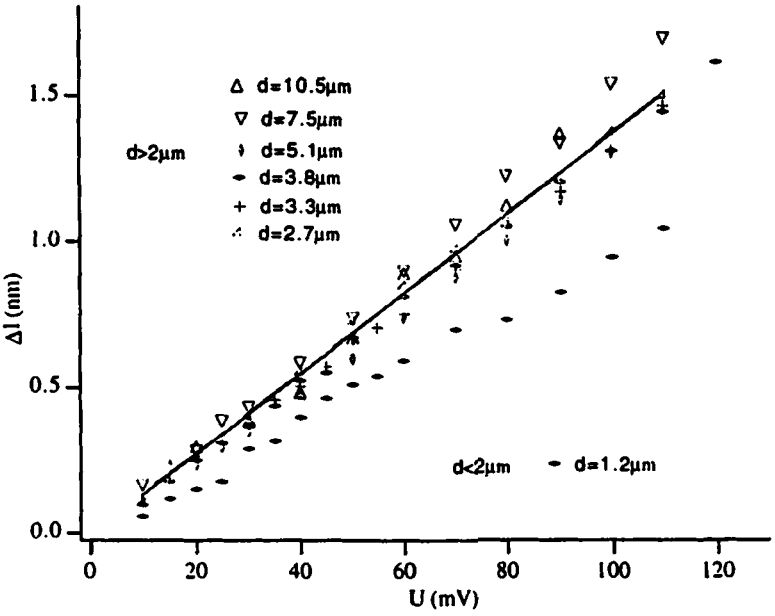

FIGURE 2 Birefringence variation of the cell

We observe, up to U≈150mV, linear dependence of Δl on the applied voltage U. The slope of Δl(U) for all thicknesses d larger than about 2μm is independent on d, in good agreement with eq. (11). For d<2μm, we obtain typically 20-30% smaller Δl/U slopes, showing that for thin cells our approximations are no more well satisfied. In particular, some parasitic ionic effects neglected in our model can be very important in thin cells, e.g. the ions adsorption in the SiO aligning layer[26], screening partially the field and changing the field profile close to the plates.

From the more reliable thick sample values on figure 2, we find $(p_1 + e) = +2.6.10^{-3}$c.g.s.u (statvolts). This result is one order of magnitude larger than the usually reported flexocoefficient values. For example, Maheswara Murthy et al.[5] report for the same nematic 5CB:

$\frac{e_1 + e_3}{K} = +108.10^{-2} Cm^{-1} N^{-1}$, giving in our notations

$e = 1.1.10^{-4}$ *c.g.s.u.*, factor of 20 smaller than our results. This discrepancy cannot be attributed to our experimental uncertainties, like the approximate estimation of the anchoring extrapolation length. A systematic underevaluation of the reported flexocoefficients by one order of magnitude is not very realistic, taking into account the large variety of measurement methods. Most probably, our results show the very important role of the surface polarity, much larger than the flexoelectric polarization, our $(e + p_1)$ value is similar to the one reported recently[16] for another system ($e + p_1 \approx 1.10^{-3}$c.g.s.u. in our notations).

The large value of the surface polarization coefficient p_1 can be due in our case to the strongly polar molecule of 5CB. By our definition of p_1 it is the surface dipole density of homeotropically oriented nematic. We can estimate the upper limit of the surface polarization due to the molecular permanent dipole as $\mathbf{P_{lim}} = N_m \mu$ where N_m is the surface numerical density of the nematic molecules (i.e. we suppose that the surface is covered with dense monomolecular layer, with perfect polar ordering). Taking $\mu \approx 4$ debye and $N_m = 4.10^{14}$cm^{-2} (area per molecule: 25Å^2), we obtain $P_{lim} \approx 1.4.10^{-3}$ c.g.s.u. (statcoul.) compatible with our experimental value for p_1. This estimated P_{lim} value is of the same order of magnitude than the measured value, but slightly weaker. We can attribute this difference to the high porosity of SiO, the effective surface is larger than the plane surface.

From the same reasonement we can find easily also the sign of p_1, related to the sign of the molecular dipole moment and to the biphilic affinity of the molecules with the surface. Due to the large polarizability of the SiO evaporated surface, we expect the first layer of 5CB molecules to be oriented with their polar heads to the surface, as on fig. 3a, giving negative sign of p_1, in drastic disagreement with our measurements. To understand this discrepancy, we should take into account that the first layer is strongly adsorbed on the SiO surface and its molecules cannot reorient, even under very strong torques. Therefore, the dipole moment of this layer is "invisible" for our experiment, much as the dipole moment of the substrate itself (in fact, the adsorbed layer becomes a part of the substrate). The first, properly speaking, nematic layer is on the top of the adsorbed layer with tail-to-tail orientation (fig. 3b) due to the large affinity of the hydrophobic molecular tails. Our measurement gives the

dipole moment density of this layer, which is free to vary its orienation under external torque.

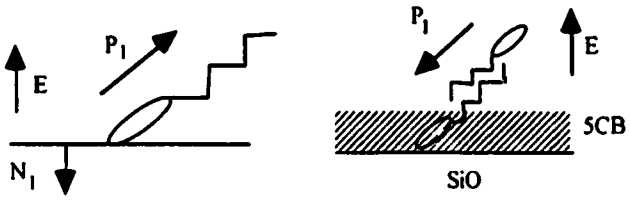

FIGURE 3 a) Arrangement of the surface layer expected by the polarity of the nematic molecule, in disagreement with the experimental result. b) Possible explanation of the observed molecules in the first layer does not rotate under the field

Further experiments are needed to separate better the p_1 and the e terms in our measurements. For example, one can study the change of the sign of the polar coefficient when changing the biphilic affinity of the surface or nematic. Another approach is to vary the surface (i.e. p_1) remaining with the same nematic (i.e. same e). Finally, by similar technique, but in symmetric cell, tilted to the observation axis, one can measure separately e, without any surface polarization influence.

To conclude, we propose a simple technique to study the polar effects in nematics using thin cells, low voltages and weak deformations we avoid the influence of the dielectric coupling and the parasitic ionic effects. For SiO - 5CB system we measure polar coupling coefficient 20 times larger than the reported flexoelectric contribution. We explain qualitatively the sign and the large value of the polar coefficient by the orientation of the large 5CB permanent dipoles on the surface.

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