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Polar electro-optic switching in droplets of an achiral nematic liquid crystal

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A polar electro-optic response is observed in droplets of an achiral nematic liquid crystal in coexistence with the isotropic phase. Between crossed polarizers each pancake-shaped droplet shows extinction brushes in the form of a centred cross aligned with the polarizer axes. An applied electric field **E** induces a rotation of the crosses about the field direction, with about half the droplets switching clockwise and the other half anticlockwise. The sense of rotation in each droplet changes when **E** is reversed. We propose that a twisted bipolar director structure is stabilized in the droplets by a relatively large splay elastic constant and tangential boundary conditions. The molecules twist along the diameter of the droplets, perpendicular to the applied field, which results in a linear rotation of the director by the inverse flexoelectric effect. Since the molecules are achiral, the handedness of the twist, and hence the sense of the switching, in any droplet is arbitrary.

1. Introduction

In liquid crystals, curvature strains may result in an induced polarization of the medium. This phenomenon is called the flexoelectric effect and is analogous to the piezoelectric effect in solids. There is also an inverse flexoelectric effect in which an external electric field may induce a flexoelectric deformation of the medium. A striking example of the latter was described by Meyer [1] in his first paper on flexoelectricity. He proposed that certain combinations of shape polarity (specifically, drop- and/or bow-shaped molecules) and directions of the net molecular dipole moments enable an applied electric field **E** to induce a periodic structure with alternating regions of splay and bend deformation, see figure 1 (*a*).

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A space-filling splay–bend structure, however, requires a continuous rotation of the director in space. Moreover, a transformation from a uniform orientation into one with a periodic splay–bend structure, because it involves the creation and motion of defects, is energetically very costly and has not been observed. In a helicoidal (twisted) director structure, such as a cholesteric liquid crystal, the situation is very different. If we make a cut through the medium, at an oblique angle to the twist axis, the projection of the continuously rotating director onto the cut-plane describes a periodic arc-pattern which is in fact a splay–bend. The origin of this pattern was first explained by Bouligand [2], and we therefore refer to this plane as the 'Bouligand cut' or the 'Bouligand plane'. Evidently, if we turn the director around an axis perpendicular to the helix until it is aligned along the Bouligand plane, we will obtain this same periodic

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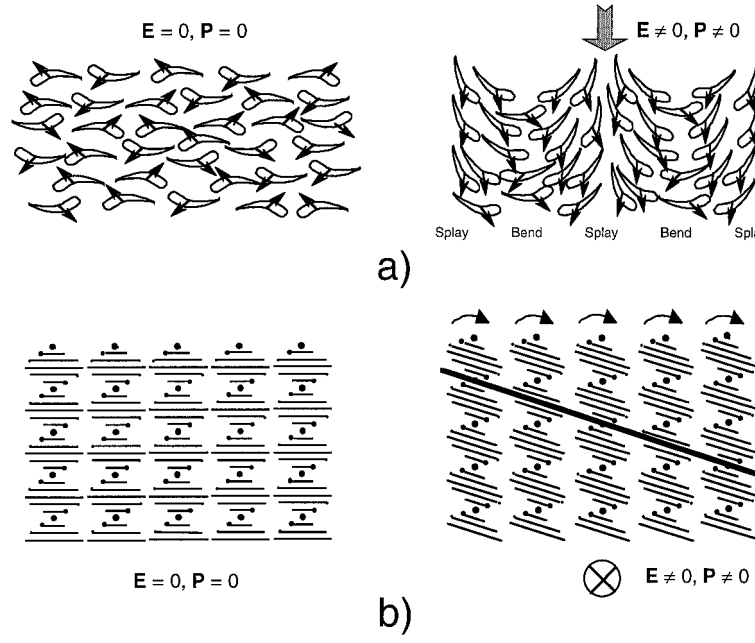

Figure 1. (*a*) Field-induced periodic splay–bend deformation in a nematic liquid crystal. (*b*) The flexoelectro-optic effect in a cholesteric liquid crystal. A periodic splay–bend deformation appears in the Bouligand plane (marked with thick line) when an electric field is applied normal to the helix axis.

splay–bend deformation, and hence an average flexoelectric polarization **P** oriented perpendicular to the helix axis and in the Bouligand plane. The inverse flexoelectric effect can thus be achieved easily in cells containing a helix: an electric field **E** applied normal to the twist axis of a cholesteric (or any twisted nematic structure) will couple to the molecular dipoles and induce a periodic splay–bend deformation by uniformly turning the director to be along a certain Bouligand cut, see figure 1 (*b*).

Inverse flexoelectricity produces a strong linear electro-optic response called the *flexoelectro-optic effect* in cholesterics [3, 4]. The induced rotation of the director ϕ is given for moderate electric fields [3] by

$$\phi = \frac{e\mathbf{E}}{Kk} \qquad (1)$$

where e is the average flexoelectric coefficient, K the average elastic constant for splay and bend, and k the helical wave vector. Since the angle of induced rotation is proportional to the electric field, so is the orientation of the Bouligand plane relative to the helix axis. As can be seen from equation (1), the sign of the electro-optical response depends on the sign of k, i.e. whether the twist is right- or left-handed. We emphasize that it is the helical or twisted director structure rather than chirality that is necessary for the flexoelectro-optic effect: even if molecular chirality is often the reason for helical ordering, as in cholesterics, the flexoelectro-optic effect may be observed with *any* helical nematic structure, even one formed by non-chiral molecules. In this paper we describe such a case, in which a twisted arrangement of achiral nematic molecules is imposed by confined geometry effects.

2. Experimental

The material used in these experiments was a 3:1 molar mixture of *p*-octyloxybenzoic acid (Isotropic $\overset{154\,^{\circ}C}{\longleftrightarrow}$ Nematic $\overset{113\,^{\circ}C}{\longleftrightarrow}$ Smectic $\overset{107\,^{\circ}C}{\longleftrightarrow}$ Crystal; from Finton Laboratories) with 1,10-phenanthroline (melting point 101–105°C; from Aldrich Chemical Company). In the mixture, two kinds of dimer, shown in figure 2, are stabilized by hydrogen bonding and we observed the following phase sequence: Isotropic $\overset{100\,^{\circ}C}{\longleftrightarrow}$ (Isotropic/Nematic) $\overset{90\,^{\circ}C}{\longleftrightarrow}$ Nematic $\overset{85\,^{\circ}C}{\longleftrightarrow}$ Smectic C.

A sandwich cell of thickness 4 μm was filled with the liquid crystal mixture in its isotropic phase. On cooling to $T \approx 100$°C circular nematic regions 10 to 50 μm in diameter appeared which coexisted with the isotropic phase over about a 10°C temperature range.

With the sample between crossed polarizers, extinction crosses could be seen in many of these pancake-shaped droplets, figure 3 (*a*). In the absence of an electric field the brushes of the crosses were oriented essentially parallel to the polarizers. An electric field **E** applied perpendicular to the bounding glass plates of the cell caused the crosses to rotate through an angle $\phi(E)$ about the field direction. The domains with crosses appeared to be of two types, A and B, distinguished by their handedness. In type A the crosses rotated clockwise for $\mathbf{E} > 0$, while in type B they rotated anticlockwise, figure 3 (*b*).

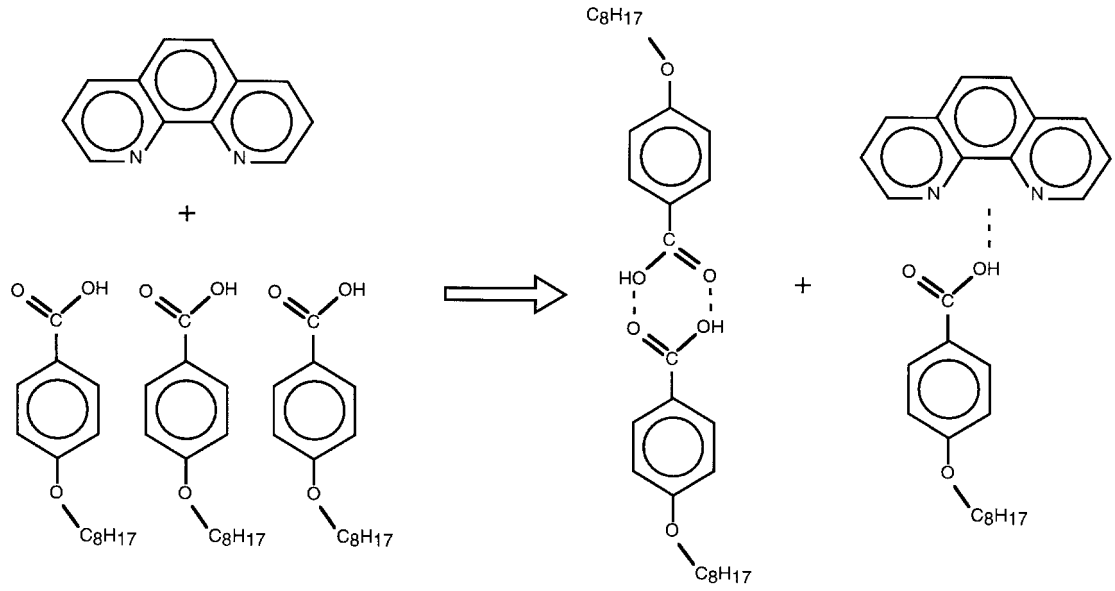

Figure 2. Structural formulae of hydrogen-bonded dimers in the 3:1 molar mixture of *p*-octyloxybenzoic acid (I) with 1,10-phenanthroline (II).

When the electric field was reversed, so also was the sense of rotation in both the A and B domains, figure 3(*c*). In moderate fields, the rotation increased linearly with field strength ($\phi \propto \mathbf{E}$), and in smaller droplets (diameter $\lesssim 30\,\mu m$) the response also increased with droplet size. In larger domains the crosses became strongly distorted during the switching. Typically, ϕ reached values of about 30° for applied fields of $5\,V\,\mu m^{-1}$ in domains about $30\,\mu m$ in diameter. When the analyser was turned slightly clockwise with no field applied, the A domains became reddish and their crosses darker, whereas the B domains became yellowish and brighter and their crosses less distinct, figure 3(*d*). These optical effects were exchanged when the analyser was decrossed anticlockwise, figure 3(*e*).

Above some threshold, the applied field induced electrohydrodynamic instabilities, temporarily destroying the original textures of the droplets and providing a mechanism for changing the sign of their electro-optic response. For example, by briefly applying a high electric field, domains that before showed no crosses (let us call them type O) could be transformed with equal probability into type A or type B, and domains of type A or B could be transformed into type O. Moreover, domains of type A could be transformed into type B and *vice versa*.

3. Proposed model

In liquid crystals in confined volumes, the director configuration is greatly influenced by the presence of surfaces, particularly when the surface-to-volume ratio is large. In nematic droplets these configurations therefore depend both on the relative magnitudes of the Oseen–Frank elastic constants for splay, twist, and bend (respectively, K_{11}, K_{22}, and K_{33}), and on the type and strength of the boundary conditions. Surface anchoring can usually be satisfied at the expense of introducing a certain number of structural defects. In particular, two idealized configurations that accommodate tangential boundary conditions are the bipolar structure, with two surface point defects, and the toroidal configuration, with a line defect along the droplet axis, shown in figures 4(*a*) and 4(*b*). In practice, the director configuration may often be more complicated than in either of these models since the configuration adopted in nature is the one that best accommodates differences in the splay, twist, and bend elastic energies. In our experiments the thickness of the cell ($4\,\mu m$) is much smaller than the droplet diameter ($10–50\,\mu m$), so the droplets are not spheres, but more like pancakes. The fact that we see domains of opposite handedness, and that the switching is sensitive to the sign of **E**, implies that they have neither a simple bipolar nor a toroidal configuration.

Volovik and Lavrentovich [5] and later Xu *et al.* [6] studied spherical nematic droplets with tangential boundary conditions and found evidence in some materials for the formation of a so-called 'twisted bipolar' structure, shown schematically in figure 4(*c*). Williams [7] showed theoretically, using a axisymmetrical approximation, that in a sphere with strong tangential boundary conditions, this twisted bipolar structure is favoured when $K_{11} \gtrsim K_{22} + 0.431 K_{33}$, i.e. when the splay elastic constant is large and/or the twist and bend elastic constants are small.

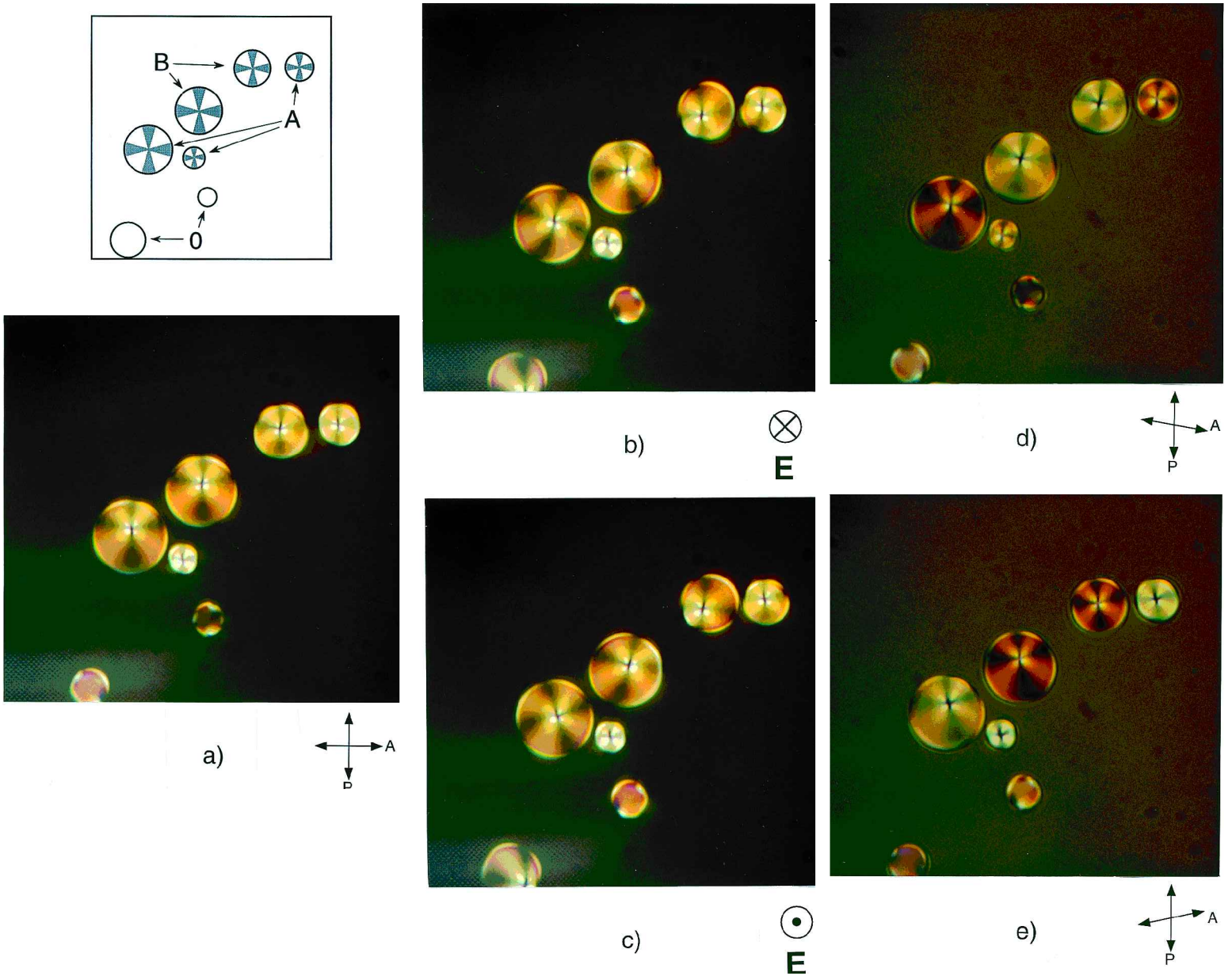

Figure 3. Electro-optic response of nematic droplets. The droplet types, classified according to their structure (A: right-handed, B: left-handed, O: no extinction cross), and the initial polarizer orientations are shown in the sketch. The photomicrographs show the electro-optic response under different conditions: crossed polarizers (*a*) $\mathbf{E} = 0$, (*b*) $\mathbf{E} > 0$, (*c*) $\mathbf{E} < 0$; (*d*) analyser rotated 20° clockwise; (*e*) analyser rotated 20° anticlockwise. The positive field direction is into the page; the largest droplets are about 50 μm in diameter.

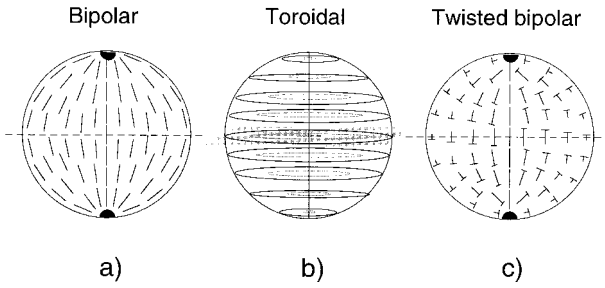

Figure 4. Vertical cross sections of (*a*) bipolar, (*b*) toroidal, and (*c*) twisted bipolar director configurations of spherical droplets with tangential boundary conditions.

We propose that the domains of type A and B in our experiments have a twisted bipolar director configuration similar to that found in spherical droplets. A vertical cross-section of this configuration in a pancake-shaped droplet with azimuthal symmetry is shown schematically in figure 5.

Let us correlate the features of the bipolar twisted configuration to our experimental observations. Along the diameter of the droplet there is, according to the model, a twist of the director field. If we now apply an electric field **E** parallel to the vertical symmetry axis of the droplet, we have essentially the same situation as in figure 1 (*b*): the field couples to the molecular dipoles and starts to orient them along **E**. The flexoelectric coupling leads to a splay–bend deformation achieved by locally reorienting the director, as shown in figure 6. This in turn is manifested as a rotation of the extinction cross observed in polarized light.

The analogue of the Bouligand plane in the droplets is a curved surface which forms a double spiral as shown in figure 7. By symmetry this Bouligand 'ribbon' begins and ends at diametrically opposite positions on the edge of the droplet. For small angles of induced director rotation, the double spiral makes several revolutions N around the droplet axis, with $N \to \infty$ as $\mathbf{E} \to 0$, and $N \to 0$ as $\mathbf{E} \to \infty$.

Since the liquid crystal material studied here is itself achiral, droplets with either handedness of radial twist (types A and B) should appear with the same probability.

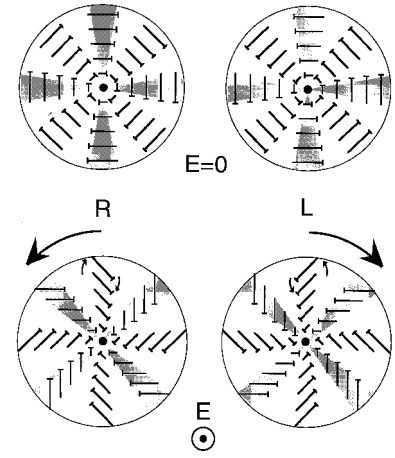

Figure 6. Field-induced rotation of the extinction crosses in circular droplets with a bipolar twisted director configuration. The sense of switching for a given direction of the applied electric field is governed by the sign of the radial twist [R (right-handed) with $k > 0$, or L (left-handed) with $k < 0$] according to equation (1). Note that the cross rotates in the opposite direction to the local director reorientation.

The sense of field-induced director rotation in the flexoelectro-optic effect is dependent on the sign of the twist wave vector k, so that type A and type B domains have opposite responses. The birefringence colour changes observed by decrossing the analyser prove that there is a twist of the director from the bottom to the top of the droplets, and that this twist sense is also different in type A and type B domains. The director structure in figure 5 shows a slight twist (II) from top to bottom of the droplet, with a handedness opposite to that of the radial twist (I).

4. Discussion

Linear electro-optic effects are rare in liquid crystals and when they exist they are usually related to the chirality of the molecules. Examples are the electroclinic effect in chiral smectic A and surface-stabilized ferroelectric liquid crystals, and the deformed helix mode in chiral smectic C materials. By linear we mean that

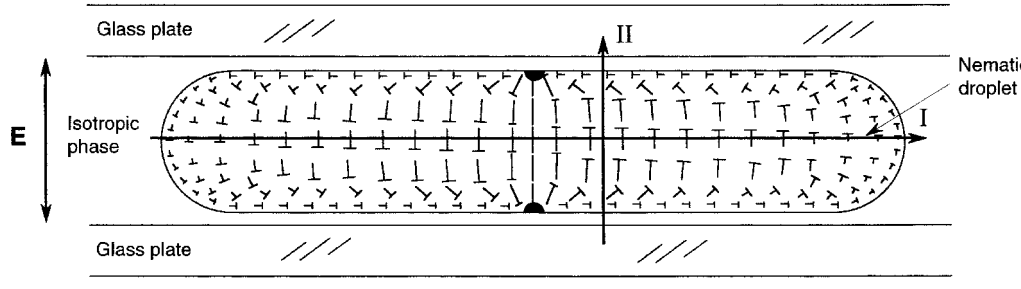

Figure 5. Vertical cross section of twisted bipolar director configuration in a flattened droplet. Note the two directions of twist: I, the (horizontal) twist axis along the droplet radius, and II, the (vertical) twist from top to bottom of the droplet.

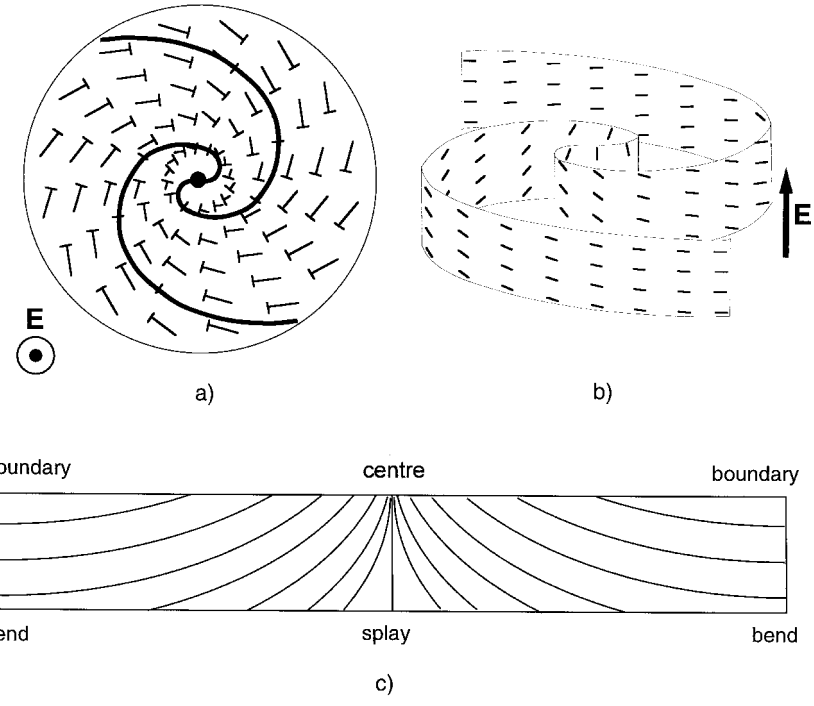

Figure 7. Bouligand plane in nematic droplets. The analogue of the flexoelectrically-induced Bouligand plane in the case of circular droplets is a double-spiralled ribbon. An idealized ribbon is drawn for the director field in the vicinity of the equatorial plane of the droplets.

the polarization **P**, whether spontaneous or induced, couples linearly to the electric field (free energy density $\sim -\mathbf{P}\ \mathbf{E}$), so that the electro-optic response depends on both the magnitude and the sign of **E**. Dielectric coupling, in contrast, is not linear, being quadratic in the field (free energy density $\propto \mathbf{E}^2$), and the electro-optic response is dependent on the magnitude, but not the sign of the applied field. The polar switching observed in the nematic droplets under study can therefore not be a dielectric effect. Neither is it electroclinic in origin since the molecules are achiral. Flexoelectricity, on the other hand, has (at least to first order) nothing to do with chirality and is moreover a polar effect. Whenever there is an intrinsic twist of the medium whether as a consequence of chirality or of the boundary conditions, a large linear electro-optic effect may result from inverse flexoelectricity.

We have proposed that in order to minimize the total free energy of the system, the liquid crystal adopts a bipolar twisted configuration inside the flattened nematic droplets, a structure with radial twist. The electric field is applied perpendicular to this twist, which is the correct geometry for flexoelectro-optic switching. The handedness of the radial twist determines the sign of the response. There is also twist along the vertical axis in the droplets, which apparently has little unfluence on the switching, but is responsible for the observed reduction in extinction when the sample is between crossed polarizers. As can be seen from figure 5, the vertical twist always has the opposite sign from the radial twist. This fact allows us to determine the sign of the average flexoelectric coefficient e in the liquid crystal material as follows. Since we can determine the handedness of the axial twist from the rotation of the plane of polarization of the incident light [8], we therefore know the handedness of the radial twist, i.e. the sign of k. The sense of field-induced rotation of the extinction crosses then reveals the sign of e. In our mixture, e was determined to be negative.

In 1991, Komitov *et al.* [9] reported a huge linear electro-optic effect in circular droplets of chiral nematic liquid crystals embedded in the isotropic phase in temperature regions where the helical pitch of the materials diverged. The characteristics of the observed effect were qualitatively similar to those described here (an electric field perpendicular to the glass plates of the cell caused the extinction crosses to rotate), but in this case although the sign of the rotation was dependent on the sign of the field, all droplets switched in the same direction. Since no cross rotation was observed in droplets of an achiral nematic, the response was attributed to an electromechanical coupling made possible by the chiral symmetry of the molecules. Furthermore, it was pointed out that a helical structure was neither present nor necessary, chirality itself being sufficient to produce the observed effect.

As shown experimentally by Volovik [5] and theoretically by Williams [7], molecular chirality is not essential to get bipolar twisted structures in confined geometries. It is the relative magnitudes of the elastic constants that makes the twisted structure favourable. This means that in a chiral nematic with a very low

twisting power (where the pitch is much longer than the diameter of the droplets), the bipolar twisted configuration could spontaneously appear just as in the case of a non-chiral nematic. The two bipolar twisted structures A and B should, however, in the chiral nematic case, have slightly different energies and thus all droplets would tend to adopt the same minimum energy structure, and give the same sign of the electro-optic effect. To test this hypothesis, we added a tiny amount of a chiral dopant [10] to our achiral mixture: in the chiralized mixture only one handedness and sign of switching was now observed. This conforms with our proposed model of the observed polar electro-optic effect.

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References

[1] Meyer, R. B., 1969, *Phys. Rev. Lett.*, **22,** 918.
[2] Bouligand, Y., 1969, *J. Physique (Fr)*, **30,** C4-90.
[3] Patel, J. S., and Meyer, R. B., 1987, *Phys. Rev. Lett.*, **58,** 1538.
[4] Rudquist, P., Komitov, L., and Lagerwall, S. T., 1998, *Ferroelectrics*, **213,** 53.
[5] Volovik, G. E., and Lavrentovich, O. D., 1983, *Sov. Phys. JETP*, **58,** 1159.
[6] Xu, F., Kitzerow, H.-S., and Crooker, P. P., 1988, *Phys. Rev. E*, **49,** 3061.
[7] Williams, R. D., 1986, *J. Phys. A. Math., Gen.*, **19,** 3211.
[8] Mauguin, M. C., 1911, *Bull. Soc. Fr. Minér. Crist.*, **34,** 71.
[9] Komitov, L., Lagerwall, S. T., Stebler, B., Andersson, G., and Flatischler, K., 1991, *Ferroelectrics*, **114,** 167.
[10] We used the chiral liquid crystal compound W314, which is (*S*)-[4-(1-methylheptyloxy)-5-nitro-]phenyl 4′-decyloxybiphenyl-4-carboxylate: see Walba, D. M., Blanca Ros, M., Clark, N. A., Shao, R., Robinson, M. G., Liu, J.-Y., Johnson, K. M., and Doroski, D., 1991, *J. Am. chem. Soc.*, **113,** 5471.