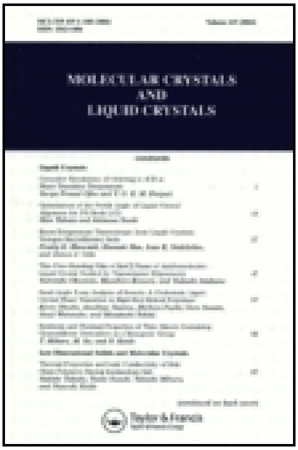

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Flexoelectric Induced Vanishing of the Cholesteric Helix

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Flexoelectric Induced Vanishing of the Cholesteric Helix*

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In the cholesteric liquid crystal helix structure, the director, $\mathbf{n}$, rotates in a plane about an axis, $\mathbf{t}_0 \perp \mathbf{n}$, with a constant twist, $\mathbf{n}\cdot\text{curl}\mathbf{n} = -q$. The inverse helix pitch is defined by $q = 2\pi/\text{pitch}$. Here we show that in the limit of a small electric field, $\mathbf{E}$, applied perpendicular to $\mathbf{t}_0$, a solution to the minimizer of the elastic free energy, including a linear coupling between $\mathbf{E}$ and splay/bend deformations of $\mathbf{n}$ (the flexoelectric term), is one where the director develops a small periodic component parallel to $\mathbf{t}_0$. As the wave number of this distortion is also q, the net effect is a rotation of the optic axis by a small angle relative to $\mathbf{t}_0$. There is no threshold for this effect when the dielectric anisotropy ε_a is greater than $\varepsilon_a > -8\pi e^2/K$. e is the flexoelectric coefficient and K is an elastic constant.

When $\mathbf{E} \| \mathbf{t}_0$ and $\varepsilon_a > 0$, it is well-known that this director configuration can be created by boundary conditions. In which case, above a critical field, E_c, the cholesteric helix transforms to a uniform director field with $\mathbf{n} \| \mathbf{t}_0$, without $q \to 0$ continuously and without introducing defects. As this is similar to solutions presented here when $\mathbf{E} \perp \mathbf{n}$ but $\varepsilon_a < 0$, the suggestion is that flexoelectricity could mediate a similar commensurate defect free vanishing of the cholesteric helix in this case. When $\varepsilon_a > 0$, the conclusion is that a defect free transformation of the cholesteric helix to a uniform director field with $\mathbf{n} \| \mathbf{E}$ requires the assistance of induced flows.

Keywords: Cholesteric liquid crystals; flexoelectricity

In this volume, Brand and Pleiner [1] give a straightforward discussion showing that the original interpretation of Patel and Meyer (PM) of a flexoelectric [2] electro-optic effect they observed in a cholesteric liquid crystal [3] is a surface effect. Here we reinterpret the PM effect and show that when the applied electric field, **E**, is small, so dielectric effects can be

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*With deep respect, this paper is dedicated to Alfred Saupe on the occasion of his birthday. Al carved out a large part of our understanding of liquid crystal physics and material science. His contributions have not only stood the test of time, they have also encouraged the discovery of new physics, the most valuable gift of liquid crystals – and Al's continuing gift to us all.

ignored, a bulk flexoelectric effect could induce a small amplitude periodic component of the director, $\mathbf{n}$, along the undistorted cholesteric twist axis, $\mathbf{t}_0$. The resulting director field is similar to the one determined by boundary conditions and discussed by Berreman and Heffner (BH) [4] for a supertwisted nematic (cholesteric) geometry. These authors showed that when $\mathbf{E} \parallel \mathbf{t}_0$ and the dielectric anisotropy $\varepsilon_a > 0$, pretilt boundary conditions prepare the helix so that it can transform to a uniform state with $\mathbf{n} \parallel \mathbf{t}_0 \parallel \mathbf{E}$ without introducing defects [4]. A striking feature of their model is that the inverse pitch, $q = 2\pi/p$ where p is the helix pitch, does not continuously go to zero above a threshold field: the helix simply vanishes.

Here we show in a different geometry that flexoelectricity plays a role similar to pretilt boundary conditions for BH [4]. This raises the novel possibility that, when $\varepsilon_a < 0$, the cholesteric helix may transform to a uniform director field with $\mathbf{n} \parallel \mathbf{t}_0 \perp \mathbf{E}$ without introducing line defects or walls. However, to avoid walls and/or disclination lines [5] when $\varepsilon_a > 0$, the transformation from a helix structure to a uniform director field with $\mathbf{n} \parallel \mathbf{E}$ requires a cooperative rotation mediated by back-flow [6] or by a Lehmann coupling [1] not discussed here.

This is an old result [7]. It was originally inspired by the seminal remarks of Helmut Brand and Harald Pleiner [1] in 1987 and Al Saupe's even earlier remark [8] that a twisted nematic structure with pre-tilt may simply vanish in a large enough applied field.

Along with the frame of reference used here, Figure 1 shows (a) the undistorted helix in the concise Friedel-Kléman [9] representation and (b) the PM model as equivalent to a simple shear of the twist axis introducing a new length for $\wp$. To avoid introducing a length for $\wp$, let's consider $\mathbf{n}$ given by $(\cos\theta\cos\delta, \sin\theta\cos\delta, \sin\delta)$ with the ansatz, $\theta = qz + \theta_0$. We take $\theta_0 = 0$ when $\varepsilon_a > 0$ and $\pi/2$ when $\varepsilon_a < 0$ [10] and assume δ is only a function of z. With the electric field, $\mathbf{E}$ given by $\mathbf{E} = (E, 0, 0)$, in the one constant elastic (K) and flexoelectric (e) limit, the cholestéric elastic energy is:

$$F = \int dV \frac{1}{2} K(\mathrm{div}(\mathbf{n})^2 + (\mathbf{n} \times \mathrm{curl}\,\mathbf{n})^2) \tag{1}$$

$$+ \frac{1}{2} K((\mathbf{n}.\mathrm{curl}\mathbf{n} + q)^2 - \mathrm{div}(\mathbf{n}\mathrm{div}\mathbf{n} + \mathbf{n} \times \mathrm{curl}\mathbf{n}))$$

$$- e\mathbf{E}\cdot(\mathbf{n}\mathrm{div}\mathbf{n} + \mathbf{n} \times \mathrm{curl}\mathbf{n}) - \frac{\varepsilon_a}{8\pi}(\mathbf{E}\cdot\mathbf{n})^2.$$

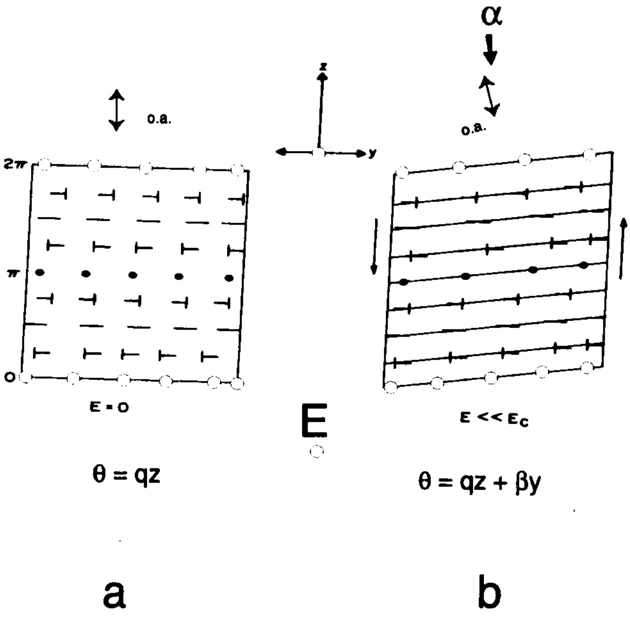

FIGURE 1 The helix phase, θ, is shown on the left. (a) A right-handed helix with a constant pitch ($p = 2\pi/q$), $\theta = qz$, is shown using the Friedel-Kléman representation [9]. The drawing is in the (y, z) plane, the plane perpendicular to the applied field. In this right-handed coordinate system, the positive $\hat{x}$ direction, shown with open circles, is towards the viewer. The negative $\hat{x}$ direction is shown with filled circles. $\mathbf{t}_0$ is the optic axis (o.a.) for the uniform helix. (b) The PM model: [3] $\mathbf{n} = (\cos\theta, \sin\theta, 0)$ with $\theta = qz + \beta y$ ($\beta < 0$ in the figure). The flexoelectric effect rotates the optic axis by an angle $\alpha = -\beta/q$ relative to $\mathbf{t}_0$. It can be obtained from the uniform helix (Fig. 1a) by applying a shear in the (y, z) plane. Here α is exaggerated to illustrate their point [3]. The observed α in their compound is small: $\alpha \sim 5 - 8°$.

The corresponding Euler-Lagrange equation is

$$\left(\frac{\cos^2\theta}{\xi^2} + q^2\right)\cos\delta\sin\delta - \frac{d^2\delta}{dz^2} = 2\alpha q^2\cos^2\delta\sin\theta \tag{2}$$

where $\alpha = eE/Kq \equiv E/E_f$, a number. $\xi = (4\pi K/\varepsilon_a E^2)^{1/2}$, a coherence length, is a measure of the dielectric coupling (the term quadratic in E in Eq. 1). When this length is comparable to the pitch, p, the cholesteric helix unwinds with $q \to 0$ continuously in increasing field [11].

It is interesting to note that $\delta = \pi/2$ is a trivial solution to Eq. 2. This corresponds to the case where $n_z \equiv 1$ and the helix structure has vanished. In contrast, $\delta = 0$ is a solution to Eq. 2 if and only if $\alpha = 0$. As soon as E is turned on ($\alpha \neq 0$), the director develops a small periodic component along $\mathbf{t}_0$

($n_z \neq 0$) commensurate with the undistorted helix even when $\xi > 1/q$ i.e. before conventional ($\varepsilon_a > 0$) helix unwinding takes place [11].

In the limit $\xi \gg q^{-1}$ and to first order in δ, a solution to Eq. 2 is:

$$\delta = \alpha \sin\theta \tag{3}$$

showing a periodic component for n_z with amplitude, α, linear in E and the pitch and wavenumber determined by q. For comparison, Figure 2a shows the director configuration with $\delta = 0$ and Figure 2b with $\delta \neq 0$. While δ follows $\theta = qz$, the director has the same inclination relative to $\mathbf{t}_0$ resulting in a net rotation of the optic axis relative to $\mathbf{t}_0$ given by [12] $\sqrt{\langle n_z^2 \rangle} = \alpha/\sqrt{2}$, i.e., is linear in E as observed [3]. Figure 2b also shows this director configuration to be similar to the Berreman-Heffner tilted half pitch state which they showed can transform to a uniform state (in the reference frame used here this corresponds to $\delta \equiv \pi/2$) without introducing defects [4].

Eq. 3 is valid when $\alpha < 1$ or $E < Kq/e \equiv E_f$. Taking $K \sim 1 \times 10^{-6}$ dynes, $e \sim 1 \times 10^{-4}$ cgs units [13], for a material with a 0.5 μm pitch [3], $E_f \sim 400$ kV/cm (using 300 volts = 1 volt esu). We conclude, therefore, that $E \ll E_f$ (hence $\alpha \ll 1$) in the range of fields where this effect was first observed [3].

However, when $\varepsilon_a > 0$, the threshold field to unwind the helix [11] is given by $E_c = \pi/2q\,[4\pi K/\varepsilon_a]^{1/2}$. It is possible that for the compound used in the original study [3] that ε_a is a small positive number. For an estimated $\varepsilon_a \sim 1$, then, the threshold field to unwind the helix would be $E_c \sim 200$ kV/cm $< E_f$. Thus, the condition, $E < E_c < E_f$ is consistent with the criterion of small δ when ε_a, is order one or smaller [14]. For larger positive ε_a, E_c decreases reducing the range of applied fields where this effect may be observed. This is because when $E \sim E_c$, even if δ is still small, the dielectric term in Eq. 2 can no longer be neglected: the uniform helix ansatz ($\theta = qz + \theta_0$) breaks down.

The energy density averaged over one pitch for this solution (Eq. 3) is (from Eq. 1):

$$\frac{F}{p} = -\frac{e^2E^2}{2K}\left[1 + \frac{\varepsilon_a K}{8\pi e^2}\left(1 - \frac{\alpha^2}{4}\right)\right]. \tag{4}$$

Using the same values for the material constants as above: $\varepsilon_a K/8\pi e^2 \equiv \varepsilon_a X \sim 4\varepsilon_a$. The energy density monotonically decreases with increasing field as the director develops a periodic small amplitude $\hat{z}$-component when $\varepsilon_a > -1/X \sim -0.25$. In this case the effect is observable for fields $0 < E < E_c$

i.e. without a threshold. A larger negative dielectric anisotropy (i.e. $\varepsilon_a < -1/X$) suppresses this effect until E is greater than $E_c^- > 2E_f\ (1 + 8\pi e^2/K\varepsilon_a)^{1/2}$. Thus, while a threshold field can be defined, it implies a value for $\alpha > 1$ which is outside the scope of effects discussed here.

When $-1/X < \varepsilon_a < 0$, the Berreman-Heffner defect free unwinding process [4] may apply. This then could be an interesting geometry to explore helix vanishing in materials with small negative dielectric anisotropy [15], a phenomenon that, as far as we know, has not yet been observed.

Figure 2 shows a possible scenario for helix vanishing when $\varepsilon_a > 0$. Between Figures 2b and 2c, the large bracket covers the part of the pitch that must be rotated to convert the "frustration" at the helix phase $\theta = \pi$ to a splay/bend deformation symmetric about π. This avoids the creation of a twist wall at π. Once this takes place (Fig. 2c), the splay/bend deformation

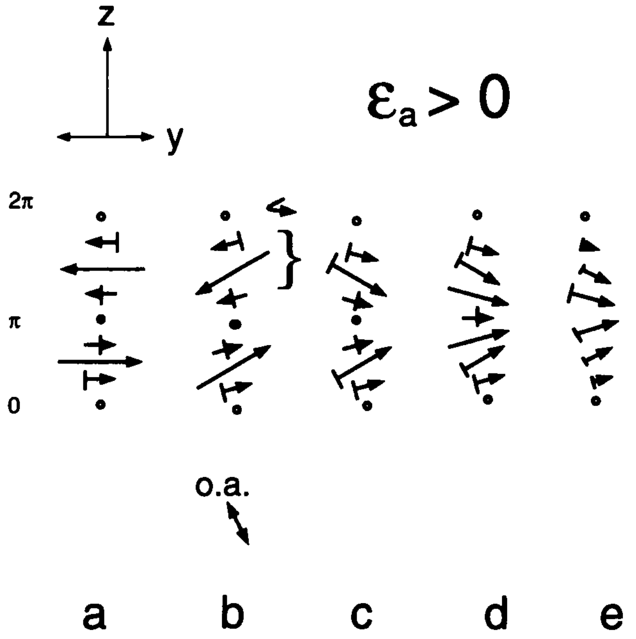

FIGURE 2 The helix phase, θ, is shown on the left. (a) A right-handed uniform helix, $\delta = 0$. The arrows are an aid to follow the evolution of this three dimensional structure and do not represent new symmetries. (b) $\delta \neq 0$: A right-handed helix periodically perturbed following Eq. 3. Attention is drawn to the effective tilt in the optic axis (o.a.). A flow field is required to rotate half the pitch (the bracketed region) to clear twist "frustration" at $\theta = \pi$. (c) The frustrated region is replaced by a splay/bend deformation symmetric about $\theta = \pi$. (d) The symmetric splay/bend deformation anneals. (e) Transformation to a uniform state with $\mathbf{n} \parallel \mathbf{E}$ is now defect free. The arrow missing at π illustrates reduction in splay/bend gradients after annealing.

(Fig. 2d) may anneal (Fig. 2e) and the transition to the uniform state with $\mathbf{n} \parallel \mathbf{E}$ is defect free. While elastic torques alone cannot account for the director rotation to go from Figure 2b to Figure 2c, it is well-known that transient splay/bend deformations couple to velocity gradients (backflow) [16]. The suggestion is that a feature of the effects discussed here (and perhaps also conventional helix unwinding in cholesterics) involves macroscopic induced flows.

These ideas may help better understand electro-optic processes in polymer stabilized cholesteric textures [17] and polymer dispersed cholesteric liquid crystals. It also suggests new display applications if negative dielectric anisotropy materials can be found with a much larger flexoelectric coefficient. One could test some of these ideas on cholesteric droplets floating in the isotropic liquid. But that seems too obvious. Rather, in homage to Al Saupe's genius for connecting subtle optical observations to deep truths, more recently in lyotropic liquid crystals, we propose a speculative experiment using the beautiful single crystals involving sugar-water-transmembrane protein aggregates [18]. In solution, sugar aggregates are well known to form lyotropic liquid crystal phases [19] and structural studies show the transmembrane protein crystals contain a large volume of water in a unit cell [20]. While protein crystals are typically solids, these protein/sugar/water single crystals may be soft lyotropic liquid crystals.

We are particularly interested in the needle crystals of bR (bacteriorhodopsin) solubilized with octylglucoside (a sugar). These crystals exhibit an optical absorption (560–580 nm) maximum along the long crystal axis but compatible with rotation of the chromophore on the surface of a 13° cone [18]. The flexoelectric effect predicts that in a dc electric field, the maximum along the optical absorption axis will be slightly off the crystal symmetry axis (the $\hat{z}$-axis) in either the plus or minus y-direction, as shown in e.g. Figure 2b. If, in addition, the crystal shape distorts (Fig. 1b), one has evidence of the surface flexoelectric effect (Fig. 1b) [3]. As the surface energy of cholesterics in contact with their isotropic liquid is small in thermotropic liquid crystals [21], no change in crystal shape could mean that a bulk effect (Eq. 3) has been observed (Fig. 2b). It could also mean that lyotropic liquid crystals are not "soft" enough so the effect will be too small to observe–unless Al Saupe comes up with a way.

In conclusion, a global minimum has been found when an electric field, E, linearly couples to elastic distortions of a cholesteric liquid crystal. In this solution, the director, $\mathbf{n}$, develops a small amplitude periodic component, with wave number q, parallel to the zero field twist axis, $\mathbf{t}_0$. The amplitude of this deformation is linear in E and the pitch. Single crystals of the purple membrane which exhibit a maximum in optical absorption parallel to the long crystal axis may be an interesting lyotropic system to test the existence of flexoelectricity in biologically relevant liquid crystals. Finally, numerical solution to Eq. 2 may shed light on intermediate steps connecting a field induced uniform director configuration ($\mathbf{n} \parallel \mathbf{t}_0$) to the low field periodic state (Eq. 3) when $-8\pi e^2/K < \varepsilon_a < 0$.

Acknowledgements

It is a pleasure to thank H. R. Brand for drawing my attention to this problem in 1987 as well as many useful discussions on this and other topics.

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