Molecular Crystals and Liquid Crystals. 1971. Vol. 13, pp. 9–15

Comments on Piezoelectric Effect in Liquid Crystals

CHUNGPENG FAN

Rutgers–The State University
New Brunswick, New Jersey, USA

Received August 24, 1970; *in revised form October* 28, 1970

Abstract—A study on Meyer's hypothesis for piezoelectric effect in liquid crystals is made. We find that according to his model the existence of a domain structure in nematic liquid crystals when placed in a constant electric field depends critically upon the magnitude of dielectric anisotropy.† Both positive and negative dielectric anisotropy have inhibitory effect on the appearance of a periodic pattern. There is a critical value in the magnitude of dielectric anisotropy above which no periodicity can occur. Thermal fluctuations from equilibrium orientation pattern are studied by means of linearized dynamical equations. We find that with the piezoelectric coupling there will appear optical modes which are damped oscillations induced by the electromagnetic field besides the ordinary slow mode of relaxation. Under the simplifying assumption that the sum of two piezoelectric coefficients is zero, the change to the spectrum for the slow mode due to the proposed piezoelectric effect is vanishingly small.

It has been demonstrated recently that(1) a nematic liquid crystal may develop domain structure under the influence of a constant electric field. Two different models for explaining this interesting phenomenon were offered by Meyer(2) and Helfrich(3) separately. Meyer, with an analogy of piezoelectricity in ordinary crystal, proposed a coupling scheme between the electric field and the curvature of orientation pattern of the liquid crystal molecules by assuming that either splay or polarization is externally induced by the electric field. Helfrich, on the other hand, emphasized the role of conductivity in liquid crystals and maintained that the orientation pattern is dynamically governed by an interplay of fluid flow, conductivity anisotropy and molecular orientation. We here shall study some

---

† We were told by the referee that this has been discussed by R. Meyer in his unpublished doctoral dissertation, Harvard University, 1970.

consequences of Meyer's model in detail by including the effect of dielectric anisotropy and thermal fluctuations. It will be seen that the existence of a domain-like periodic pattern in Meyer's model is critically influenced by the magnitude of dielectric anisotropy.

The expression for the " electric enthalpy " is given by Meyer.

$$H_E = \tfrac{1}{2}K_{11}S^2 + \tfrac{1}{2}K_{22}(n \cdot \nabla \times n)^2 + \tfrac{1}{2}K_{33}B^2 - e_{1z}E \cdot S - e_{3x}E \cdot B$$
$$- \frac{1}{8\pi}[\epsilon_\perp(E \times n)^2 + \epsilon_\parallel(E \cdot n)^2] \tag{1}$$

where K_{11}, K_{22} and K_{33} are elastic moduli of liquid crystals defined by Frank.(4) S and B are respectively so-called splay and bending related to the curvature of the orientation.

$$S = (\nabla \cdot n)n,$$
$$B = (n \cdot \nabla)n = -n \times (\nabla \times n). \tag{2}$$

e_{1z} and e_{3x} are piezoelectric coefficients, while $\epsilon_\parallel$ and $\epsilon_\perp$ are respectively perpendicular and parallel components of dielectric constant. We shall denote their difference, dielectric anisotropy by $\chi_a = (\epsilon_\parallel - \epsilon_\perp)/4\pi$.

The expression in (1) for the enthalpy can be greatly simplified if we assumed that $e_{1z} = -e_{3x} = e_p$ and $K_{11} = K_{22} = K_{33} = K$. Let $n_x = \cos\theta$, $n_y = \sin\theta$. Then we have from (1) and 12)

$$H_E = \tfrac{1}{2}K\left(\frac{d\theta}{dy}\right)^2 - e_p E \frac{d\theta}{dy} - \frac{\chi_a}{2}E^2\cos^2\theta - \frac{1}{8\pi}\epsilon_\perp E^2. \tag{3}$$

To find the equilibrium orientation pattern we minimize the enthalpy (3) with respect to θ and obtain the equation

$$K\frac{d^2\theta}{dy^2} - \chi_a E^2 \sin\theta\cos\theta = 0. \tag{4}$$

We note that this equation, except for a sign, is identical to an equation found by de Gennes(5) in his work on cholesteric liquid crystals in magnetic field. Using the same analysis we can draw the following conclusions:

(a) The domain width is expressible as follows

$$Z = \left(\frac{2}{\pi}\right)^2 \frac{\pi K}{e_p E_0} K(k)\, E(k). \tag{5}$$

Where $E(k)$ and $K(k)$ are complete elliptical integrals of first and second kinds and the eccentricity k is determined by

$$\frac{(K\chi_a)^{1/2}}{e_p} = \frac{(\pi/2)k}{E(k)}. \tag{6}$$

This certainly reduces to the relation given by Meyer for $\chi_a = 0$ where $k = 0$,

$$Z = \frac{\pi K}{e_p E_0}. \tag{7}$$

(b) The periodicity of the domain structure only depends upon the magnitude of dielectric anisotropy $|\chi_a|$ but not on its sign. This can be seen from the following reasoning. For negative χ_a Eq. (4) remains invariant when we change θ into $\theta+\pi/2$ while Eq. (3) will be changed into the form

$$H_E = \tfrac{1}{2}K\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2 - e_p E\frac{\mathrm{d}\theta}{\mathrm{d}y} - \frac{|\chi_a|}{2}E^2\cos^2\theta - \frac{1}{8\pi}\epsilon_\parallel E^2. \tag{8}$$

This expression (8) is the same as (3) except for a constant in the last term. Since the eccentricity k is determined from (4) by minimizing the enthalpy the difference of a constant term in (8) does not have any effect. Therefore, the orientation pattern for negative χ_a is obtainable from positive χ_a by changing θ into $\theta+\pi/2$.

(c) From Eqs. (5) and (6) we observe that there is a critical value for $|\chi_a|$ beyond which the domain structure cannot exist. i.e.

$$Z = \infty, \quad k = 1 \qquad \text{for} \qquad |\chi_a| \geqslant |\chi_a|_c \tag{9}$$

where

$$|\chi_a|_c = \frac{((\pi/2)e_p)^2}{K}.$$

This is a distinct feature in Meyer's model that dielectric anistropy, either positive or negative inhibits the formation of a domain pattern. On the contrary it has been found that in Helfrich's model positive anistropy has inhibitory effect while negative anistropy will stimulate the onset of an instability which will manifest itself in the form of a stationary convective flow at the marginal state.$^{(16)}$ So far experimental results seem to agree closely with Helfrich's model.

We shall study further the effect of piezoelectricity on the frequency spectrum of the orientation fluctuation when it is perturbed from the equilibrium pattern. We assume for simplicity that dielectric anistropy χ_a is zero, fluctuation in n only occur in x–y plane and that all the dynamical variables depend upon x and y only. The equations of motion for the orientation n can be obtained from the hydrostatic and hydrodynamic theories of liquid crystals by Oseen,(7) Frank,(4) Erickson,(8) Leslie(9) and Stephen.(10) Since we have complications here due to the coupling between electric field and orientation through the piezoelectric effect we have to supplement those hydrodynamic equations with the complete set of Maxwell's equations for electro-magnetic fields. In fact, if we want to obtain the exact dispersion relation for the thermal excitation, we have to solve the whole set of coupled electro-magneto-hydrodynamic equations for liquid crystals in a self-consistent fashion. Instead, we shall here content ourselves with a study on the relationship between the electromagnetic fields and orientation alone. The effect of viscous flow is summarily represented by a term of relaxation for the director n. In this approximation indeed the fast mode is neglected while only the slow mode of molecular relaxation is retained.(11) In light of the fact that in both nematic(11) and cholesteric(12) liquid crystals for $e_p = 0$ only the slow mode contributes to the light scattering spectrum and that these two modes are widely separated, we feel quite convinced that this is not too bad an approximation. With this we have the following self-consistent equations:

$$n \times \Big[K\nabla^2 n + e_p((\nabla \cdot n)E - \nabla(E \cdot n) + \nabla \times (E \times n) - E \times (\nabla \times n)) - \gamma \frac{\partial n}{\partial t} \Big] = 0 \tag{10}$$

$$D = 4\pi e_p[(\nabla \cdot n)n + n \times (\nabla \times n)] + \epsilon E \tag{11}$$

$$\nabla \cdot D = 4\pi\rho, \qquad \nabla \times E = -\frac{1}{c}\frac{\partial B}{\partial t} \tag{12}$$

$$\nabla \cdot B = 0, \qquad \nabla \times H = \frac{4\pi}{c} J + \frac{1}{c}\frac{\partial D}{\partial t} \tag{13}$$

$$B = H, \qquad J = \sigma E \tag{14}$$

$$\nabla \cdot J + \frac{\partial \rho}{\partial t} = 0 \tag{15}$$

where γ is the viscosity coefficient, ρ, J, D, E, B and H are respectively the electric charge, current, electric displacement, electric field, magnetic flux density and magnetic field in the system, σ and ϵ are the conductivity and permittivity of the liquid crystal, and c is the velocity of light. We have here assumed that the electric current consists only of conduction current. Diffusion current is entirely neglected.

The equations are linearized into the following version:

$$\left[\nabla^2 - \frac{i\omega}{c^2}(4\pi\sigma + i\omega\epsilon)\right](\nabla \times E)_z - 4\pi e_p \frac{\omega^2}{c^2}\nabla^2 \tilde{n} = 0 \tag{16}$$

$$[K\nabla^2 - \gamma i\omega]\tilde{n} - e_p(\nabla \times E)_z = 0 \tag{17}$$

where ω is the frequency for the excitation, $\tilde{n}$ is the fluctuating component of director, i.e. $\tilde{n} = n_x \sin ay - n_y \cos ay$, $a = e_p E_0/K$ and E_0 being the constant applied field.

Substituting (17) into (16) we obtain the dispersion relation as follows:

$$(\gamma i\omega - Kq^2)(\epsilon(i\omega)^2 + 4\pi\sigma(i\omega) + c^2q^2) - 4\pi e_p{}^2(i\omega)^2q^2 = 0 \tag{18}$$

where q is the wave number.

This expression clearly shows that in the spectrum for the orientation fluctuation there exist optical modes besides the ordinary slow mode. The optical modes are induced by the electromagnetic fields and they are mixed with the slow mode by the piezoelectric coupling. We can easily show that the last term in (18) is vanishing small and the slow mode is entirely decoupled from the optical modes. We do this by first transforming Eq. (18) into a dimensionless form using the units for frequency and wave number:

$$\omega \Rightarrow \frac{K}{\gamma d^2}$$

$$q \Rightarrow \frac{1}{d}$$

where d is the spacing between the parallel plates across which the constant electric field E_0 is applied.

$$(i\omega - q^2)\left((i\omega)^2 + \left(\frac{4\pi\sigma}{\epsilon}\frac{\gamma d^2}{K}\right)i\omega + \frac{c^2}{\epsilon}\left(\frac{\gamma^2 d^2}{K^2}\right)q^2\right) - \frac{4\pi e_2^p}{K\epsilon}(i\omega)^2 q^2 = 0. \tag{19}$$

We estimate the value of e_p by using the expression for the domain width in (7) and the experimental values for K, E_0 and Z for p-azoxyanizole given by Heilmeier *et al.*(1) and Helfrich.(3) We find $e_p \sim 10^{-4}$ in cgs unit. Taking values $K \sim 10^{-6}$ dyne, $\sigma \sim 10^3$, $\gamma \sim 0.05$, $\epsilon \sim 5$, $d \sim 10^{-4}$. The three characteristic numbers in (19) are respectively:

$$\frac{4\pi\sigma}{\epsilon}\frac{\gamma d^2}{K} \sim 10$$

$$\frac{c^2}{\epsilon}\frac{\gamma^2 d^2}{K^2} \sim 10^2$$

$$\frac{4\pi e_p}{K\epsilon} \sim 10^{-2}$$

Since these numbers differ largely in orders of magnitude, we can conclude that the last term in (19) is almost negligible, and that the hypothesis for a piezoelectric effect in liquid crystals does not bring significant change to the frequency spectrum except for adding a constant wave vector due to Bragg scattering from the periodic distorted structure.

It should be emphasized that the conclusions we have drawn here is by no means contrary to what was given by the Orsay Group regarding a related problem.(13) They have discussed the frequency spectrum for fluctuations from a *uniform* orientation pattern with *no* equilibrium distortion, and reached the conclusion that if the sum of the two coefficients $e_{1z}+e_{3x}$ is nonzero and large enough, then the piezoelectric effect may contribute a noteable change in the slow mode. In fact, what they have considered is an experimental situation quite different from what was being discussed above. They assumed that the nematic liquid crystal is placed in a static *magnetic field* instead of an electric field. They have further assumed that the fluctuating electric field is irrotational and thus neglected any coupling of the slow mode with the optical mode. On the other hand, we have adopted directly the simplifying assumption made by Meyer(2) that $e_{1z} = -e_{3x} = e_p$(14) and studied the fluctuation from the equilibrium *distorted* structure which is caused by the applied *electric* field through the piezoelectric effect. Whether the hypothesis for a piezoelectric effect in liquid crystals is relevant to the experimental observation of domain-like structure and significantly changes the fluctuation spectrum can only be clarified by further experiments on nematics with large values of $e_{1z}+e_{3x}$ as suggested by the Orsay Group.(13) So far, no apparent experimental evidence has been offered in support of such an hypothesis.(15,16)

Acknowledgement

The author wishes to thank Professor M. J. Stephen and Dr. L. Kramer for valuable discussions and the referee for kindly pointing out a large error in the estimate of numerical parameters.

REFERENCES

1. Heilmeier, G. H., Zanoni, L. A. and Barton, L. A., *Proc. IEEE* **56,** 1162 (1968).
2. Meyer, R. B., *Phys. Rev. Letters* **22,** 918 (1969).
3. Helfrich, W., *J. Chem. Phys.* **51,** 4092 (1969).
4. Frank, F. C., *Disc. Faraday Soc.* **25,** 1 (1958).
5. deGennes, P. G., *Solid State Comm.* **6,** 163 (1968).
6. Fan, C., unpublished.
7. Oseen, C. W., *Trans. Faraday Soc.* **29,** 883 (1933).
8. Erickson, J. L., *Arch. Ratl. Mech. Anal.* **4,** 231 (1960).
9. Leslie, F. M., *Quart. J. Mech. Appl. Math.* **19,** 357 (1966).
10. Stephen, M. J., *Phys. Rev.* **A2,** 1558 (1970).
11. Groupe d'Etude des Cristaux Liquides (Orsay), *J. Chem. Phys.* **51,** 816 (1969).
12. Fan, C., Kramer, L. and Stephen, M. J., to be published in *Phys. Rev.* November (1970).
13. Orsay Liquid Crystal Group, p. 195 in "Liquid Crystals and Ordered Fluids", edited by J. F. Johnson and R. S. Porter, Plenum Press, 1970.
14. Notice the difference in the definition for the piezoelectric coefficient e_p. In our notation $e_p = e_{1z} = -e_{3x}$, while in Orsay Group's work $e_p = e_{1z}+e_{3x}$.
15. Orsay Liquid Crystal Group, p. 447 in "Liquid Crystals and Ordered Fluids", edited by J. F. Johnson and R. S. Porter, Plenum Press, 1970.
16. Durand, G., Veyssie, N., Rondelez, F. and Leger, L., *Compt. Rend.* **270B,** 97 (1970).