The Strength of Piezoelectricity in Liquid Crystals

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A simple method combining macroscopic and microscopic features is proposed to calculate approximate values for Meyer's piezoelectric coefficients. The numerical result suggests that the piezoelectricity of liquid crystals is weak and its effect on alignment fluctuations mostly negligible.

About two years ago MEYER [1] proposed that liquid crystals may display a peculiar kind of piezoelectricity which is associated with curvature strains or distortions of the natural orientation pattern. Prerequisites for this piezoelectricity are that the constituent molecules possess an electric dipole moment and have a certain asymmetrical shape. All liquid crystals are made up of rodlike or elongated molecules which are aligned parallel to each other. Splay, i. e. slightly diverging orientation lines, will cause conical molecules to orient preferentially with their thicker ends in the direction of the divergence. The consequence is a polarization parallel to the orientation lines, if the molecular dipole has a nonvanishing component pointing, for instance, towards the thicker end. Bend will lead to a polarisation normal to the orientation lines and within the plane of bending, if the molecules are bananalike and have a dipole whose component in the plane of the crescent and perpendicular to the long molecular axis does not vanish. Conversely, an electric field may produce splay and bend, provided a polarization ensues which lowers the free energy.

Meyer has pointed out a few situations in which piezoelectric effects may come into play. The possible influence of the piezoelectric self-energy on alignment fluctuations in nematic liquid crystals has been discussed by the Orsay Liquid Crystal Group [2]. The light scattering connected with these fluctuations offers a method to determine viscosity coefficients and elastic moduli, and a knowledge of the strength of piezoelectricity would be desirable for their evaluation. However, no measurements of the piezoelectric coefficients have as yet been reported. Such studies are difficult, particularly since the piezoelectric polarization may be screened by space charge.

In the following we wish to derive the approximate magnitude of liquid-crystalline piezoelectricity by theoretical means. Our approach involves the curvature-elastic properties of the liquid crystal [3], the molecular size, shape, and dipole moment, and a Boltzmann factor.

Following Meyer we write the differential form of the internal free energy density f as

$$\mathrm{d}f = t_i \,\mathrm{d}a_i + \frac{1}{4\pi} E_n \,\mathrm{d}D_n \qquad (i = 1, \ldots, 6;\ n = x, y, z)$$

which takes account of curvature elasticity and polarization but neglects volume changes. E and D are the electric field and displacement, the a_i FRANK's [3] curvature strains, and the t_i the conjugate couple stresses. One now defines an "electric" Gibbs free energy density

$$g_\mathrm{E} = f - E_n D_n / 4\pi$$

and views it as a function of the a_i and E_n, thus having to lowest order

$$\begin{aligned}\mathrm{d}g_\mathrm{E} &= t_i \,\mathrm{d}a_i - (D_n/4\pi)\ \mathrm{d}E_n \\ &= [K_{ij}\, a_j - e_{\mathrm{in}}\, E_n]\,\mathrm{d}a_i - [e_{\mathrm{in}}\, a_i + (\varepsilon_{nm}/4\pi)\, E_m]\,\mathrm{d}E_n\end{aligned}$$

The e_{in} are the piezoelectric coefficients introduced by Meyer. The reduced form adequate for the uniaxial character of nematic liquid crystals is

$$\begin{aligned}\mathrm{d}g_\mathrm{E} = {} & K_{11}(s_1 + s_2)\ \mathrm{d}(s_1 + s_2) + K_{22}(t_1 + t_2)\ \mathrm{d}(t_1 + t_2) \\ & + K_{33}(b_1\,\mathrm{d}b_1 + b_2\,\mathrm{d}b_2) \\ & - e_{11} E_z\,\mathrm{d}(s_1 + s_2) - e_{33}(E_x\,\mathrm{d}b_1 + E_y\,\mathrm{d}b_2) \\ & - e_{11}(s_1 + s_2)\ \mathrm{d}E_j - e_{33}(b_1\,\mathrm{d}E_x + b_2\,\mathrm{d}E_y) \\ & - (\varepsilon_{\parallel}/4\pi)\ E_z\,\mathrm{d}E_z - (\varepsilon_{\perp}/4\pi) \\ & \cdot (E_x\,\mathrm{d}E_x + E_y\,\mathrm{d}E_y).\end{aligned}$$

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[1] R. B. MEYER, Phys. Rev. Letters **22**, 918 [1969].

[2] Orsay Liquid Crystal Group in: Liquid Crystals and Ordered Fluids, ed. by J. F. JOHNSON and R. S. PORTER, Plenum Press, New York 1970, pg. 195.

[3] F. C. FRANK, Disc. Faraday Soc. **25**, 19 [1958].

We are using Frank's local coordinate system and his notations for the elastic moduli and curvatures. With $\boldsymbol{L}$ being a unit vector indicating the unique axis and with $\hat{z} \parallel \boldsymbol{L}$ at the considered point, one has the splays

$$s_1 = \partial L_x/\partial x\,, \quad s_2 = \partial L_y/\partial y\,,$$

the twists

$$t_1 = -\partial L_y/\partial x\,, \quad t_2 = \partial L_x/\partial y\,,$$

and the bends

$$b_1 = \partial L_x/\partial z\,, \quad b_2 = \partial L_y/\partial z\,.$$

Also needed here are the dielectric constants ε parallel and perpendicular to the unique axis and the components of the local electric field $\boldsymbol{E}$.

Let us now consider conical molecules and imagine that it is somehow possible to make the polarization complete so that all their thick ends are on the same side. Fig. 1 a shows the geometry of the individual molecule, Θ_0 being its splaying angle

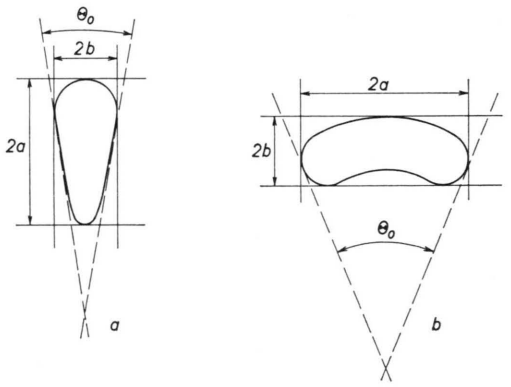

Fig. 1. Sketches of conical and bananalike molecules, as explained in the text.

and a and b the major and minor axes if it is approximated by an ellipsoid of revolution. In the absence of constraints our hypothetical liquid crystal may be expected to assume a characteristic splay s_c being approximately [4, 5].

$$s_c = 2\,\Theta_0 \left(\frac{a}{b}\right)^{1/3} N^{1/3}$$

where N is the density of the molecules. Analogous reasoning gives for the bananalike molecules (Fig. 1 b) a characteristic bend

$$b_c = \Theta_0 \left(\frac{b}{a}\right)^{2/3} N^{1/3}\,,$$

if the bend is restricted to one plane. These characteristic values will be useful below.

Complete polarization is of course impracticable. Even if the curvatures s_c and b_c could be produced, part of the molecules would still be "wrongly" aligned because the distribution among different directions is controlled by a Boltzmann factor. Let us estimate the extent of polarization for zero electric field. We start from the observation that for a given $(s_1 + s_2)$ the splay elastic energy density is

$$K_{11}(s_1 + s_2)^2/2\,.$$

It is natural to assume that molecules of fixed and equal direction with concentration n create the splay $s_1 + s_2 = s_c\, n/N$ in an unrestrained liquid crystal [6]. To uniformly align such a "biased" material should require the same energy as producing this splay in an "unbiased" sample. Couple stresses may therefore arise from external or internal strains or a combination of both. Reasons of energy conservation entail that reversing the direction of one molecule in a liquid crystal with externally generated splay $(s_1 + s_2)$ requires or releases the free energy

$$2\,\varepsilon_M = 2\,K_{11}(s_1 + s_2)\; s_c/N\,.$$

We now define a degree w_z of "directedness"

$$w_z = (N_{+z} - N_{-z})/N$$

where N_{+z} and N_{-z} are the densities of conical molecules whose thick ends point in z or $-z$ direction, respectively $(N_{+z} + N_{-z} = N)$. Obviously, w_z obeys the Langevin formula for bistable systems

$$w_z = \varepsilon_M/k\,T\,.$$

The explicite dependence is

$$w_z = K_{11}(s_1 + s_2)\; s_c/k\,T\,N\,.$$

[4] In our approximations the degree of order is taken to be unity. It would not be difficult to take account of the actual, lesser order.

[5] The factor of 2 reflects that the molecules are conical, not wedgelike.

[6] The splay or bend produced by holding a fraction of the molecules in a fixed direction may also be estimated on the basis of calculations by F. Brochard and P. G. DeGennes, J. Physique **31**, 691 [1970]. Their work deals with the local orientational distortion around suspended particles, and they showed how an overall twist depends on the concentration and chirality of such centers. Extending their method to splay and bend, one obtains about $s_c\, n/N$ (or $s_b\, n/N$) for the induced strain, in agreement with our estimate. Common to both approaches are poorly defined boundary conditions (or short-range order) and the neglect of possible nonlinear elastic effects.

The situation is a little more complicated for bend as the molecules are allowed to rotate around the unique axis. Choosing the coordinates such that there is only one bend, one obtains for the corresponding degree of "directedness"

$$w_x = K_{33}\, b_1\, b_c/2\, k\, T\, N\,.$$

Here $w_x = \overline{\cos\varphi}$, φ being the rotation angle.

These results permit us to calculate the polarization produced by a given curvature strain. The only further quantity needed is the molecular dipole moment. It may have a component $p_{\parallel}$ in the direction of the thick end and another $p_{\perp}$ pointing into the crescent. (The third component which is perpendicular to the plane of the crescent should vanish in molecules which are both conical and crescent-like, if the liquid crystal is not to be cholesteric.) The polarizations P_z and P_x are [4]

$$P_z = N\, p_{\parallel}\, w_z \quad \text{and} \quad P_x = N\, p_{\perp}\, w_x\,.$$

On the other hand we take from the expression for $\mathrm{d}g_{\mathrm{E}}$

$$P_z = e_{11}(s_1 + s_2) \quad \text{and} \quad P_x = e_{33}\, b_1\,.$$

Consequently,

$$e_{11} = p_{\parallel}\, K_{11}\, s_c/k\,T \quad \text{and} \quad e_{33} = p_{\perp}\, K_{33}\, b_c/2\, k\, T\,.$$

Inserting the formulas for the characteristic strains, one arrives at

$$e_{11} = (2\, p_{\parallel}\, K_{11}/k\,T)\ \Theta_0 (a/b)^{1/3}\, N^{1/3}$$

and

$$e_{33} = (p_{\perp}\, K_{33}/2\, k\, T)\ \Theta_0 (b/a)^{2/3}\, N^{1/3}\,.$$

To make a numerical estimate of e_{11} we take $p_{\parallel} = 1$ debye, $K_{11} = 10^{-6}$ dyn, $k\,T = 5 \cdot 10^{-14}$ erg, $\Theta_0 = 0.1$ ($\approx 10^{\circ}$), $a/b = 1$, and $N = 10^{21}$ cm^{-3}. The result is

$$e_{11} = 4 \cdot 10^{-5} \text{ cgs units}\,.$$

For a typical splay of $s = 10^3$ cm^{-1} this corresponds to

$$P_z = 4 \cdot 10^{-2} \text{ stat. coulomb/cm}^2$$

which is equivalent to $8 \cdot 10^7$ elementary charges per cm^2. Similar values may be anticipated for e_{33} and P_x. The discussion is easily extended to cholesteric and smectic liquid crystals.

The similarity of our numbers with an estimate by MEYER [1] is accidental. He did not use a Boltzmann factor but assumed "close packing". This approach would imply that the polarization produced by a given curvature is the larger the smaller the asymmetry of the molecules, which does not appear reasonable.

It is interesting to insert $e_{11} = e_{33} = 4 \cdot 10^{-5}$ cgs in the formula [2] for the mean piezoelectric self-energy density in alignment fluctuations,

$$\frac{\pi\,[(e_{11}+e_{33})\ q_z\, q_x]^2}{\varepsilon_{\parallel}\, q_z^2 + \varepsilon_{\perp}\, q_x^2}\ \delta^2$$

where δ is the amplitude and q the wave vector of the fluctuation. K_{11} and K_{33} being about 10^{-6} dyn, this energy should be negligible compared to the corresponding elastic energy density,

$$\tfrac{1}{2}\ (\tfrac{1}{2}\, K_{33}\, q_z^2 + \tfrac{1}{2}\, K_{11}\, q_x^2)\ \delta^2\,.$$

The comparison suggests that it is difficult to find a liquid crystal whose piezoelectricity is measurable through its effect on alignment fluctuations, even if there is no screening by space charge.

FRANK's [3] saddle-splay term

$$-\,(K_{22} + K_{24})\,(s_1\, s_2 + t_1\, t_2)$$

of the elastic energy has been omitted in our calculation. This may be justified in the same way as in other problems. It can also be proved directly and for loose wall alignment that inclusion of the term, although changing the elasticity and the characteristic splay, does not affect e_{11}.