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Inherent Bounds to the Elasticity and Flexoelectricity of Liquid Crystals

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Phenomenological and molecular considerations indicate certain limitations to the elastic moduli and flexoelectric coefficients of liquid crystals.

Some years ago R. B. Meyer has pointed to the possible polarization of liquid crystals by a distortion of the orientation pattern.[1] Originally named piezoelectricity, this effect is also called curvature electricity or flexoelectricity. It may be expressed by the following formula for the free energy density g which includes the elastic and dielectric contributions

$$\begin{aligned} g = {} & \frac{1}{2} K_{11} (\operatorname{div} \mathbf{n})^2 - e_{11} \operatorname{div} \mathbf{n} (\mathbf{n}\cdot\mathbf{F}) - \frac{1}{8\pi} \epsilon_{\parallel} (\mathbf{n}\cdot\mathbf{F})^2 + \frac{1}{2} K_{22} (\mathbf{n}\cdot\operatorname{curl} \mathbf{n})^2 \\ & + \frac{1}{2} K_{33} (\mathbf{n}\wedge\operatorname{curl} \mathbf{n})^2 - e_{33} (\mathbf{n}\wedge\operatorname{curl} \mathbf{n}) (\mathbf{n}\wedge(\mathbf{n}\wedge\mathbf{F})) - \frac{1}{8\pi} \epsilon_{\perp} (\mathbf{n}\wedge(\mathbf{n}\wedge\mathbf{F}))^2 \end{aligned} \tag{1}$$

We have the elastic moduli of splay (K_{11}), twist (K_{22}), and bend (K_{33}), the nematic director (unit vector **n**), Meyer's flexoelectric coefficients (e_{11} and e_{33}), the principal dielectric constants ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$) parallel and penpendicular to the director, and the electric field **F**.

Another, quite instructive representation is

$$\begin{aligned} g = {} & \frac{1}{2} K_{11} \left(\operatorname{div} \mathbf{n} - \frac{e_{11}}{K_{11}} \mathbf{n}\cdot\mathbf{F}\right)^2 - \frac{1}{8\pi} \left(\epsilon_{\parallel} + 4\pi \frac{e_{11}}{K_{11}}\right) (\mathbf{n}\cdot\mathbf{F})^2 \\ & + \frac{1}{2} K_{22} (\mathbf{n} \cdot \operatorname{curl} \mathbf{n})^2 \end{aligned} \tag{2}$$

$$+\frac{1}{2}K_{33}\left((n\wedge\text{curl } n)-\frac{e_{33}}{K_{33}}\,n\wedge(n\wedge F)\right)^2-\frac{1}{8\pi}\left(\epsilon_\perp+4\pi\frac{e_{33}^2}{K_{33}}\right)(n\wedge(n\wedge F))^2$$

We may regard

$$\frac{e_{11}}{K_{11}}\,n\cdot F \qquad \text{and} \qquad -\frac{e_{33}}{K_{33}}\,n\wedge(n\wedge F) \tag{3}$$

as the splay and bend induced by the electric field, comparable to the spontaneous twist of cholesteric liquid crystals. Also, we can interpret

$$\epsilon_\parallel^f=\epsilon_\parallel+4\pi\frac{e_{11}^2}{K_{11}} \qquad \text{and} \qquad \epsilon_\perp^f=\epsilon_\perp+4\pi\frac{e_{33}^2}{K_{33}} \tag{4}$$

as the free dielectric constants, to be observed with an "unclamped" orientation pattern which is free to assume the splay or bend minimizing g. That the free dielectric constants are larger than the ordinary or "clamped" ones has already been noted (with a slight mistake) by Derzhanski and Petrov.[2] These authors estimated the strength of flexoelectricity from the difference $\epsilon_{\text{isotropic}}-(\frac{1}{3}\epsilon_\parallel+\frac{2}{3}\epsilon_\perp)$ at the nematic-isotropic clearing point. The difference seems to be often of the order of a few percent. It follows from (4) that

$$e_{11}^2<K_{11}\frac{\epsilon_\parallel^f-1}{4\pi}, \qquad e_{33}^2<K_{33}\frac{\epsilon_\perp^f-1}{4\pi} \tag{5}$$

For instance, with an assumed value $\epsilon^f=5$ and typically $K=10^{-6}$ dyne one has $|e|<6\cdot10^{-4}$ dyne$^{1/2}$. The only known measurement, that of e_{33} in MBBA,[3] yielded $e_{33}\approx4\cdot10^{-5}$ dyne$^{1/2}$, not very far below this limit and in fair agreement with a theoretical estimate.[4]

Next we consider a deformation in the absence of an applied electric field. The flexoelectric polarization can produce an intrinsic electric field (or "back field") which depends on the sample geometry. If the director is a function of only one coordinate, z, and there is no dielectric displacement, one has $F_z=-4\pi P_z$, P being the total polarization. If in addition the director is restricted to a plane containing the z axis, the density of deformational energy and flexoelectric self-energy is

$$g=\frac{1}{2}\left[K_{11}\sin^2\varphi+K_{33}\cos^2\varphi+\frac{4\pi(e_{11}+e_{33})^2\cos^2\varphi\sin^2\varphi}{\epsilon_\parallel\cos^2\varphi+\epsilon_\perp\sin^2\varphi}\right]\left(\frac{d\varphi}{dz}\right)^2 \tag{6}$$

where φ is the angle made by the z axis and the director. The square bracket may be viewed as an effective elastic modulus. Arguing as above, one expects that the third term in the bracket, although it can predominate in principle, will rarely do so in practice.

Eq. (6) holds for the well-known Freedericksz transitions of homeotropic and planar textures where a deformation is produced by magnetic or electric fields.[5] Of course, the flexoelectric term drops out whenever the polarization is screened by space charge. For measuring flexoelectricity the elastic response of the sample must be faster than space charge relaxation. Conductivities of 10^{-13} to 10^{-14} ohm^{-1} cm^{-1} which can be achieved by careful purification should be low enough.

Let us now discuss the case of asymmetric molecules (pear-shaped or banana-shaped) without an electric dipole moment or, equivalently, with full screening of the flexoelectric polarization by space charge. The molecules tend to relieve the torque stresses due to splay or bend by suitably adjusting their orientation to the strain field. This may result in a reduction of the elastic moduli as compared to the values they would have with symmetric molecules. With reference to an earlier article[4] we may write in the case of splay

$$\Delta E = \frac{2(2\alpha)N^{1/3}}{N}\, t \tag{7}$$

for the molecular energy difference between the orientations of higher and lower energy. We assume perfect nematic order; N is the density of molecules, t the applied torque per unit area, and the angle α to be expressed in radians a measure for the conical character of the molecules. The degree of preferential alignment is $\Delta w = (N\uparrow - N\downarrow)/N = \Delta E/2k_BT$. The product of Δw and $(2\alpha)N^{1/3}$ corresponds to an induced splay.

Accordingly we have

$$t = K_{11}\,\mathrm{div}\,\mathbf{n} = \bar{K}_{11}\left(\mathrm{div}\,\mathbf{n} - \frac{(2\alpha)^2N^{-1/3}}{k_BT}\,t\right) \tag{8}$$

where $\bar{K}_{11}$ is the elastic modulus without molecular adjustment to the strain. The actual modulus is then

$$K_{11} = \frac{\bar{K}_{11}}{1 + (2\alpha)^2N^{-1/3}(\bar{K}_{11}/k_BT)} \tag{9}$$

Clearly, for large enough α the modulus becomes independent of $\bar{K}_{11}$, being given by $(2\alpha)^{-2}N^{1/3}k_BT$. For $\alpha = 0.1$, $N = 10^{22}\,\text{cm}^{-3}$, and $k_BT = 4 \cdot 10^{-14}$ erg (room temperature) one computes $2 \cdot 10^{-5}$ dyne. This is near enough the typical value of 10^{-6} dyne to anticipate, with markedly conical molecules, an appreciable influence of orientational adjustment on K_{11}.

For bend and banana-shaped molecules one may write

$$\Delta E = \frac{2\beta N^{1/3}}{N} t \tag{10}$$

and

$$K_{33} = \frac{\bar{K}_{33}}{1 + \beta^2 N^{-1/3} (\bar{K}_{33}/2k_B T)} \tag{11}$$

where the angle β expresses the curvature of the molecule. The factor 2 in front of $k_B T$ takes account of the free rotation of the molecule about its long axis. A comparison of (9) and (11) suggests that the self-limitation of elasticity should tend to be more pronounded with splay than with bend.

Expressing the ϵ's and e's in terms of molecular properties, we finally show that the phenomenological inequalities (5) can also be obtained from a microscopic theory. We use

$$\epsilon_{\parallel}^{f} = 1 + 4\pi \frac{N p_{\parallel}^2}{k_B T}, \qquad \epsilon_{\perp}^{f} = 1 + 4\pi \frac{N p_{\perp}^2}{2k_B T} \tag{12}$$

and, from Ref. 4

$$e_{11} = \frac{p_{\parallel} K_{11}}{k_B T} (2\alpha) N^{1/3}, \quad e_{33} = \frac{p_{\perp} K_{33}}{2k_B T} \beta N^{1/3} \tag{13}$$

where $p_{\parallel}$ and $p_{\perp}$ are the components of the molecular dipole parallel and perpendicular to the long molecular axis. Upon inserting the asymptotic formulas for K_{11} and K_{33} we indeed obtain (5).

It should be noted that the microscopic formulas (9), (11), (12) and (13) are only approximate and could be improved, for instance, by incorporating Onsager's internal field correction, the elongated shape of the molecules, and the degree of order in the nematic liquid crystal. We also remark that flexoelectricity does not necessarily require a permanent molecular dipole moment as the strain field itself can probably polarize the molecules. Liquid crystals made up of symmetrically shaped molecules may thus display flexoelectricity without the elastic self-limitation of the type indicated.

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References

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5. Flexoelectric and dielectric free energy densities are clearly independent of each other for AC fields. They are also uncoupled if a DC voltage effects a Freedericksz transition. For a prove it is important to note that the flexoelectric contribution to the dielectric displacement is identical to zero. The deformations to be expected if Eg. (6) applies have been computed by H.J. Deuling, Mol. Cryst. Liq. Cryst., in the press.