

Classification
Physics Abstracts
7.130

ON THE MICROSCOPIC INTERPRETATION OF FLEXOELECTRICITY

J. PROST and J. P. MARCEROU

Centre de Recherche Paul-Pascal, Domaine Universitaire, 33405 Talence, France

(Reçu le 15 juillet 1976, révisé le 22 novembre 1976, accepté le 29 novembre 1976)

Résumé. — La prise en compte des densités quadrupolaires électriques permet de proposer une nouvelle interprétation du phénomène de flexoélectricité. Nous discutons aussi le modèle de Meyer et certains effets de charge.

Abstract. — Recognition of the importance of electric quadrupoles allows a new interpretation of the flexoelectric phenomenon to be proposed. Meyer's model and the influence of charge are also discussed.

1. Introduction. — Since Meyer's invention of flexoelectricity [1], it has been thought that such an effect described the long range deformation resulting from the dipolar orientation of asymmetric molecules in an electric field. Although Helfrich did generalize this idea to polarizable molecules [2] no attempt to use different concepts has been made to our knowledge. The relevant free energy of a uniaxial phase can be written [1] :

$$F = F_0 + F^e - \int_v \left(f_{ij} E_i \partial_k S_{jk} + \frac{\varepsilon_{ij}}{8\pi} E_i E_j \right) dv. \quad (1.1)$$

In this relation F_0 is the free energy at zero strain and applied electric field. F^e is the elastic free energy, $S_{ij} = (n_i n_j - \frac{1}{3} \delta_{ij})$ in which \mathbf{n} gives the direction of the local symmetry axis, and f_{ij} is the flexoelectric tensor. Although one should start from a fourth rank tensor, it is possible to show that one can use this form without loss of generality. In Meyer's notation, $f_{\parallel} = e_{11}$ and $f_{\perp} = e_{33}$. ε_{ij} is the usual dielectric tensor. In the smectic phase there is an additional coefficient [3] which we will discuss later. One of the consequences of (1.1) is that the electric displacement is a function of the strains :

$$D_i = -4\pi \frac{\partial F_u}{\partial E_i} = +4\pi f_{ij} \partial_k S_{jk} + \varepsilon_{ij} E_j \quad (1.2)$$

F_u stands for the free energy density. In his original paper, Meyer gave a purely dipolar interpretation of this relation [1]. We will see that this is not the only possibility, since quadrupole density gradients may

be shown to be equivalent to dipolar densities [4]. The symmetric relations linking the stress field to strains and electric fields have been well described in the nematic and smectic phases [1, 5, 6, 7].

Another aspect of flexoelectricity has however been less emphasized; integrating (1.1) by parts and making use of $\text{Curl } \mathbf{E} = 0$, one gets :

$$F - F'_0 = F^e - \int_v \delta S_{ik} \left(\frac{\varepsilon_a}{8\pi} E_i E_k - \frac{f}{2} \partial_k E_i \right) dv \quad (1.3)$$

$$(f = f_{\perp} + f_{\parallel}).$$

In this expression, we keep only angular dependent parts under the integral. $\delta S_{ik} = S_{ik} - S_{ik}^0$ in which S_{ik}^0 stands for the unperturbed value of S_{ik} (for the rest of the paper \mathbf{n}^0 coincides with the z axis) ⁽¹⁾. Inspection of (1.3) shows that flexoelectricity describes the torque exerted on the director by electric field gradients, just as the anisotropic part of the dielectric tensor ε_a describes the torque exerted by the electric field itself. This is perhaps a stronger indication that molecular quadrupoles might be important, since it has been known for a long time that birefringence, for instance, could be induced in gases by electric field gradients [8, 9, 10, 11].

For clarity, in the second section we review the

⁽¹⁾ To understand the occurrence of δS_{ik} in (1.3), one must note that in a linear theory, devoted to the study of small variations of the director around its unperturbed value, the term $\partial_k S_{jk}$ of (1.1) could have been written as well $\partial_k (\delta S_{jk})$. Then (1.3) is the corresponding linear term, and higher order contributions have been neglected.

electrostatics of uniaxial media. This allows us to recognize where the link between polarization and strain comes in and simultaneously to introduce quadrupole densities. In the third section we discuss Meyer's model of flexoelectricity, and in the fourth we emphasize the new results obtained by taking quadrupole densities into consideration. An appendix is added which is devoted to the possible role of charge carriers.

2. Electrostatics of uniaxial phases. — The current macroscopic description of the electrostatics of condensed phases results from a model conception of matter which takes into account only dipolar densities. However, uniaxial phases have a symmetry such that non-zero electric quadrupolar densities are allowed in the ground state :

$$\Theta_{ij} = \frac{1}{u} \sum_n \theta_{ij}^n \neq 0. \quad (2.1)$$

The summation is performed over a suitable macroscopic volume u and θ_{ij}^n is the quadrupole of the n th molecule defined by :

$$\theta_{ij}^n = \frac{1}{2} \int_{\text{mol}} dv' \rho^{\text{mic}}(\mathbf{r}') \times \\ \times [3(r'_i - r'_{0i})(r'_j - r'_{0j}) - (r'_i - r'_{0i})(r'_k - r'_{0k})\delta_{ij}] \quad (2.2)$$

in which $\rho^{\text{mic}}(\mathbf{r}')$ is the microscopic charge density and the integration is performed over the volume of the molecule. \mathbf{r}'_0 is an effective quadrupole centre defined in the appendix C. Note that although θ_{ij} is a small number (typically 10^{-25} e.s.u.) the density itself is not, since all particles in the volume considered act cooperatively. In other words :

$$\Theta_{ij} = N S \theta_a S_{ij} = \Theta_a S_{ij}. \quad (2.3)$$

where N is the number of molecules per unit volume and θ_a is the anisotropic part of the molecular quadrupole, for instance

$$\theta_a = \theta_{cc} - \frac{\theta_{bb} + \theta_{aa}}{2}$$

a, b, c being the principal axis of the molecular quadrupole tensor θ , if we suppose the molecule to rotate uniformly around c . $S = \frac{1}{2} \langle 3 \cos^2 \alpha - 1 \rangle$ is the orientational order parameter, α being the angle between c and the macroscopic symmetry axis.

The relation between \mathbf{D} and \mathbf{E} has then to be implemented :

$$D_i = E_i + 4\pi \{ P_i - \frac{1}{3} \partial_j \Theta_{ij} \}, \quad (2.4)$$

where we introduce the divergence of the quadrupolar density just as one usually introduces the divergence of dipolar density when speaking of total average

charges. (Note that in our case the total charge density is given by :

$$\rho_{\text{tot}} = \rho_{\text{free}} - \partial_i P_i + \frac{1}{3} \partial_i \partial_j \Theta_{ij}. \quad (2.5)$$

The retention of higher multipole moments in (2.4) is clearly not needed since the next density allowed by symmetry in the unperturbed sample is the hexadecapole, the contribution of which is about 10^{-5} or 10^{-6} of the quadrupolar one. The octopole density has to be induced and gives also contributions 10^{-5} or 10^{-6} times smaller than P_i . At this stage, the problem is not fully specified since one does not know anything about P_i . The usual assumption is :

$$P_i = \frac{\epsilon_{ij} - \delta_{ij}}{4\pi} E_j. \quad (2.6)$$

This relation is not general enough for liquid crystals, since not only the electric field but also the strains through Meyer's model and the quadrupole gradients can polarize the medium. Keeping first order terms :

$$P_i = \frac{\epsilon_{ij} - \delta_{ij}}{4\pi} E_j + f_{ij}^M \partial_k S_{jk} + g_{ij} \partial_k \Theta_{jk} \quad (2.7)$$

or :

$$D_i = \epsilon_{ij} E_j + 4\pi \left(f_{ij}^M + \Theta_a \left(g_{ij} - \frac{\delta_{ij}}{3} \right) \right) \partial_k S_{jk} + \\ + 4\pi \left(g_{ij} - \frac{\delta_{ij}}{3} \right) S_{jk} \partial_k \Theta_a. \quad (2.8)$$

In these expressions ϵ_{ij} is the usual dielectric permeability tensor, f_{ij}^M is the Meyer flexoelectric tensor (that is the one corresponding to the dipolar model), and g_{ij} describes the polarization due to quadrupole gradients; we will see that it is linked to the local field problem. Comparison with equation (1.2) gives :

$$f_{ij} = f_{ij}^M + \Theta_a \left(g_{ij} - \frac{\delta_{ij}}{3} \right). \quad (2.9)$$

In this last relation there are clearly two different contributions to flexoelectricity :

— the first term which corresponds to Meyer's model involves asymmetric polar molecules (for example *pear shaped* or *banana like* molecules);

— the second term exists even if one assumes the molecule to be *rodlike* or *cigar shaped* and does not involve any flipping of the molecule. In that sense this is a more general possibility.

The third term of the right hand side of eq. (2.8) is usually unimportant since it is linked to density or order parameter changes. We discuss one of its consequences in section four.

In the next section, we recall the main implications of Meyer's model and in the last one we develop the features which follow from the existence of quadrupolar densities.

3. Dipoles : Meyer's model. — When pear shaped molecules point preferentially in one direction, a microscopic splay of the liquid crystalline structure results; this preferential direction is coupled to electric fields, since the symmetry of such molecules allows them to exhibit a dipole along their long axis. A clear explanation of this effect is to be found in reference [1], and a calculation of the related flexoelectric coefficient in references [5, 6].

The result may be generalized to the smectic phase by using the concept of a monopole type of strain source developed in reference [13]. The detailed calculations are given in the appendix B.

The flexoelectric constant may be expressed in terms of the dielectric permittivity. For instance, for pear-shaped molecules with a longitudinal dipole :

$$f^M = K_{11} \frac{\epsilon_{zz}^0 - \epsilon'_{zz}}{4 \pi \mu} \quad (3.1)$$

μ is a number relating the molecular longitudinal dipole to the steric asymmetry. ϵ_{zz}^0 is the zero frequency dielectric constant and ϵ'_{zz} is the value at frequencies slightly above the first relaxation (i.e. : $\epsilon_{zz}^0 - \epsilon'_{zz}$ is the contribution of the longitudinal dipoles to the dielectric constant).

The part corresponding to the induced dipoles, can be expressed in a similar fashion :

$$f^M = K_{11} \frac{\epsilon_{zz}^\infty - 1}{4 \pi \mu'} \quad (3.2)$$

$\epsilon_{zz}^\infty = n_e^2$ is the optical dielectric constant, and again μ' describes the steric asymmetry resulting from the polarization of the molecule.

In these formulae the only unknown is μ ; for instance if one assumes that the molecules have the form of a truncated cone, the molecular asymmetry is measured by $q \simeq 2 \pi r \alpha$ (see Fig. 1 for the definitions of r and α) and $\mu = p/q$ (where p is the molecular

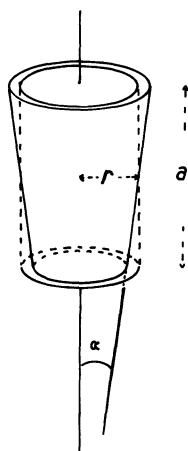


FIG. 1. — The molecular asymmetry is depicted by a truncated cone. The corresponding cylinder would have a vanishing q value; hence, for small α , q which has the dimensions of a surface is proportional to the difference between the top and the bottom surfaces.

longitudinal dipole). For MBBA p is of the order of 0.4 Debye; with $r \sim 2 \times 10^{-8}$ cm, $a \sim 20 \times 10^{-8}$ cm and $\alpha \sim 0.1$ rad (value guessed by Helfrich) one finds $\mu \simeq (1.2) \cdot 10^{-4}$.

Since $K_{11}^e \sim 7 \times 10^{-7}$ dyne (see for instance ref. [14]) and $\epsilon_{zz}^0 - \epsilon'_{zz} = 0.3$ [15] one estimates :

$$f^M \sim 7 \times 10^{-5} \text{ e.s.u. cm}^{-1}.$$

The contribution from induced dipoles is harder to evaluate. The steric asymmetry resulting from the induced polarization is certainly much smaller, but on the other hand $(\epsilon_{zz}^\infty - 1)$ is known to be of the order of 2. It seems to us reasonable to estimate this contribution to be at most in the 10^{-5} range.

Such orders of magnitude are not very far from the experimental findings [7, 12], but a bit low. However the main difficulty arises from comparing the temperature dependence of K_{11} and f^M : from (3.1) and (3.2) one would expect f to vary essentially like K_{11} (that is S^2 [14]), whereas the experiment on p-butoxybenzal-p-(β -methylbutyl)aniline (BBMBA) agrees better with S (Fig. 2 and ref. [7]; the immediate vicinity of the nematic to isotropic phase transition is not included in this experiment). On the other hand near the nematic to smectic A phase transition, the K_{11}^e value of BBMBA diverges, while f stays constant [7, 15]; this result is not strictly incompatible with (3.1) and (3.2), but its interpretation requires assumptions about the simultaneous behaviour of K_{11} , $\epsilon_{zz}^0 - \epsilon_{zz}^1$ and $\epsilon_{zz}^\infty - 1$ which may not be straightforward.

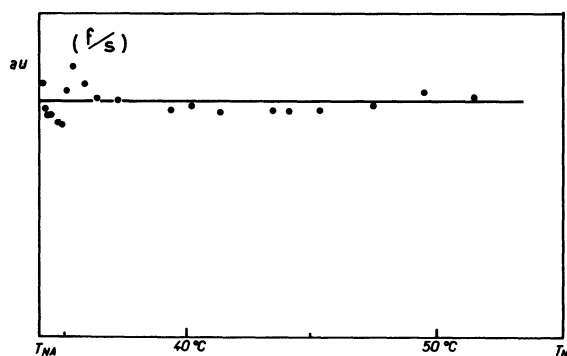


FIG. 2. — Plot of the flexoelectric coefficient of BBMBA (p-butoxybenzal-p-(β -methylbutyl) aniline) divided by the order parameter, as a function of temperature. The solid line is used as a visual aid. Note the constancy of the ratio indicating $f \sim S$, within a few percent.

One can understand that although this mechanism certainly contributes to flexoelectricity, there is room for another molecular mechanism giving rise to a linear coupling between strains and electric fields.

4. Quadrupole densities. — 4.1 QUADRUPOLAR FLEXOELECTRICITY. — At first sight one may be puzzled by the occurrence of these quadrupolar terms and look for a simple picture of what happens physically.

We show in figure 3 a schematic interpretation; let us focus our attention on a volume filling the region 2 :

a) by symmetry there is no charge and no dipole in this volume. Some of the plus charges of the adjacent layers do enter in the region of interest, but this is cancelled out by the fact that part of the plus charges of the quadrupoles considered enter the regions 1 and 3 in the same proportion ;

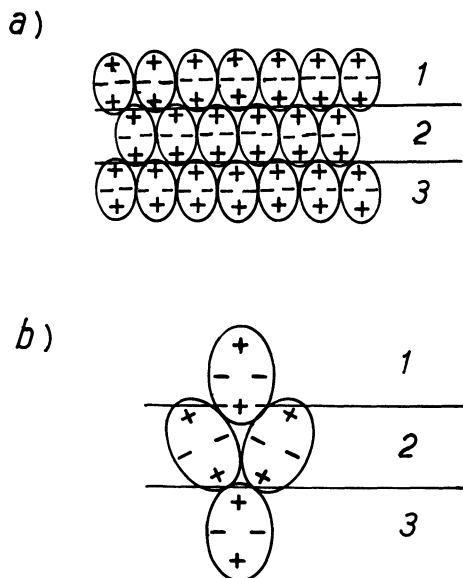


FIG. 3. — Stacking of quadrupoles : a) the symmetry is such that there is no bulk polarization ; b) curving the central plane allows the plus charges of the quadrupoles of the top of the figure to approach this plane, while those of the quadrupoles of the bottom are pushed away from it. This dissymmetry results in a dipole pointing toward the top of the figure.

b) after imposing a splay on the structure, one sees that plus charges have entered the volume, coming from 1, while other plus charges have left it to enter 3. A volume dipole pointing toward the top of the page results. Actually, if the splay is not uniform space charges also arise. What actually happens in liquid crystals arises from similar considerations ; note that this picture is just the transposition to quadrupoles of what is usually accepted for dipoles.

An alternative way of understanding the importance of these terms is to come back to equation (1.3). It is straightforward to note the similarity with the energy of a quadrupole in a field gradient :

$$W = -\frac{1}{3} \theta_{ij} \partial_j E_i^{\text{loc}}. \quad (4.1)$$

In a dense medium the field to be considered is the total local electric field ; however the only contribution to that field which may give on averaging a term similar to (1.3) is the one which depends linearly on E_i , the averaged macroscopic field. This can be written :

$$E_i^{\text{loc}} = L_{ij} E_j + \dots \quad (4.2)$$

L_{ij} is the Lorentz tensor, and is usually assumed to be independent of position :

$$L_{ij} = L\delta_{ij} + L_a(n_i n_j - \frac{1}{3}\delta_{ij}). \quad (4.3)$$

Then.

$$F = F_0 + F^{\text{el}} - \int_v \frac{1}{3} \theta_{ij} L_{ik} \partial_j E_k dv. \quad (4.4)$$

This is compatible with (2.8) provided :

$$g_{ij} = \delta_{ij} \left[\frac{1}{3} - \frac{1}{3} \left(L + \frac{La}{3} \right) \right]. \quad (4.5)$$

In other words, as we have already said, this contribution to the flexoelectric phenomenon describes the behaviour of quadrupoles in a field gradient. In that respect it is the cooperative counterpart of Buckingham's field-gradient-induced birefringence. Furthermore, equation (4.5) justifies our point that the tensor g_{ij} is closely related to the problem of the internal field and constitutes a non-trivial correction to the term $-\delta_{ij}/3$; like the Lorentz tensor it has little temperature dependence [16].

To get the order of magnitude and sign, it is reasonable to write :

$$f \simeq -\frac{2}{3} \theta_a = -\frac{2}{3} NS\theta_a. \quad (4.6)$$

Taking again $N \sim 2 \times 10^{21} \text{ cm}^{-3}$, $S \sim 0.5$ and the typical experimental value $f \sim 3 \times 10^{-4} \text{ e.s.u. cm}^{-1}$ [7, 12], one gets :

$$\theta_a \sim -45 \times 10^{-26} \text{ e.s.u.} \quad (4.7)$$

Although we could not get any direct information in the literature on the molecular quadrupoles of mesogenic molecules we think that this number is plausible. A good hint of the validity of this comparison is obtained by using the formula linking the quadrupole (of $^1\Sigma$ molecules) to the magnetic anisotropy [18, 19, 20]

$$\frac{2}{3} \theta_a = -\frac{4mc^2}{e} (\chi_{\parallel} - \chi_{\perp}) + \frac{\beta_n}{2\pi B_0} g_j. \quad (4.8)$$

In this relation, m is the electron mass, c the velocity of light, e the proton charge, $(\chi_{\parallel} - \chi_{\perp})$ the molecular magnetic anisotropy,

$$\beta_n = \frac{e}{2M_p c}$$

the nuclear magneton, B_0 the rotational constant in wave numbers and g_j the molecular g value. The contribution of the magnetic part alone is

$$-105 \times 10^{-26} \text{ e.s.u.}$$

(we take $\chi_{\parallel} - \chi_{\perp} \sim 60 \times 10^{-6} \text{ e.m.u.}$ [21]). The second part is not known so accurately, but to take account of the difference between -45 and -105 one has to assume $g_j/B_0 \sim 0.5 \text{ cm}$ which is typical

of the values found experimentally in smaller molecules [19, 22] (note that the value of -45×10^{-26} for a liquid crystal molecule is not surprisingly large since for instance one finds for cyclohexane which is a much smaller molecule $\theta \sim 16 \times 10^{-26}$ e.s.u. [23]).

Let us furthermore point out that all experiments to date have led to a positive f value [7, 17, 24] which we could understand with the $(\chi_{\parallel} - \chi_{\perp})$ sign.

The next interesting point is the temperature dependence : the proportionality to S in the case of BBMBA [7] is in agreement with formula (4.6) or (2.9) in which f^M is small compared to the second term.

In summary, the order of magnitude and the temperature dependence of the flexoelectric coefficient of BBMBA favor this new interpretation of the flexoelectric phenomenon.

4.2 ADDITIONAL TERM OF THE SMECTIC PHASE. —

In his original paper on the dynamics of smectics A, De Gennes introduces an additional term linking the layer compression gradients to an electric field along the unperturbed optical axis : ($i = x, y$) [3]

$$F - F_0 = \frac{1}{2} \int_v \left\{ b(\partial_z u)^2 + K_{11}(\partial_{ii}^2 u)^2 + 2fE_z \partial_{ii}^2 u + 2f_2 E_z \partial_{zz}^2 u + \frac{\epsilon_a}{2\pi} \partial_i u E_i E_z \right\} dv. \quad (4.9)$$

While we have not been able to give a dipolar interpretation of this term, the quadrupolar one follows directly from (2.8). We first need to remark that at low frequency, the density adjusts to its equilibrium value determined by $\partial_z u$:

$$\theta = -\frac{C}{A} \partial_z u. \quad (4.10)$$

In this relation we keep the notation of De Gennes' book [14] : $\theta = -\delta\rho/\rho$ is the bulk dilation, A^{-1} is the compressibility, and C is an elastic constant describing the coupling between the bulk and the layer compressibilities. This allows us to rewrite the last term of (2.8) the following way :

$$D_z = 4\pi \frac{2}{3} \left(g_{zz} - \frac{1}{3} \right) \frac{C}{A} \Theta_a \partial_{zz}^2 u + \dots \quad (4.11)$$

or :

$$f_2 = \frac{2}{3} \left(\frac{1}{3} - g_{zz} \right) \frac{C}{A} \Theta_a \quad (4.12)$$

f_2 is expected to be smaller than f , essentially by the factor C/A which is many cases is smaller than one [25]. Note that the coupling with density gradients and order parameter gradients exists in nematics as well (and in the x and y directions too), but is obscured by the quasi-incompressibility of these dense fluids on one hand, and the very weak response function of the order parameter on the other.

4.3 SURFACE TERMS. — In deriving equation (2.3) we have neglected the surface terms ; taking account of them gives the additional surface integral :

$$\frac{1}{3} \int_s \Theta_{ij} dS'_j \partial_i \frac{1}{|r - r'|} \quad (4.13)$$

(we make the implicit assumption that the exterior of the volume considered is filled with an isotropic dielectric). That is, a discontinuity in the quadrupole density is equivalent to a surface polarization :

$$P_i^S = \frac{1}{3} \Theta_{ij} s_j \quad (4.14)$$

(s_j is the normal pointing outward the considered volume).

Note that the resulting surface polarization has a component parallel to s and also one perpendicular to it (in the plane defined by s and n). The existence of this second component has been recognized phenomenologically by Meyer and Pershan [26]. Furthermore it can give an anisotropic surface energy ; in a first approximation one could consider it as proportional to $(P_i^S)^2$. Minimizing $(P_i^S)^2$ at constant surface orientation, with respect to the director, would give :

$$n_i s_i = 0. \quad (4.15)$$

This is the case for several liquid crystal molecules at the isotropic-nematic interface, and for PAA at the liquid crystal-air surface ; the MBBA-air interface disagrees with this result [27]. Of course the real problem is more complicated than this : one should consider simultaneously dipolar densities which may at the surface be quite different from the bulk ; the quadrupolar term itself might be more involved.

5. Conclusion. — The description of the electrostatics of uniaxial phases provides a proper framework for discussing the different interpretations of the flexoelectric phenomenon. The relatively large values of the flexoelectric coefficient and its temperature dependence may be understood if one recognizes the importance of the quadrupole densities. Such a conclusion implies that flexoelectricity will exist and have the same order of magnitude in liquid crystals built up of symmetric molecules, and also in phases in which the *flip-flop* phenomenon is strongly hindered as in certain biologically relevant phases. On the other hand, Meyer's effect might be dominant in strongly asymmetric molecules. Finally, one should be able to determine the contribution of each mechanism from the study of the temperature dependence of the flexoelectric coefficient.

Experiments designed to check those features are currently under way in our laboratory. Successful results obtained on the symmetric pp'-hexyloxytolane, will be reported elsewhere.

Acknowledgements. — We are very grateful to J. R. Lalanne who introduced us to the *quadrupolar* literature. It is also a pleasure to acknowledge the constructive reading of our manuscript by P. G. De Gennes, R. B. Meyer and P. S. Pershan.

APPENDIX A

Charge contribution. — It is possible to distinguish three aspects of the possible influence of charges on the strain in liquid crystals. Firstly real charge densities can develop and move in such a way that they shield the applied electric field out, if no current is sustained. We do not consider this case any further since it has been found experimentally that it leads to vanishing flexoelectric signals. Secondly polarization charges have been shown to give rise to non-linear effects [14, 28] and can be omitted here. Thirdly, if electric currents are sustained, a linear coupling can exist which is contained in the hydrodynamics developed by Martin, Parodi and Pershan [29] :

$$\frac{\partial u}{\partial t} - V_z = \lambda_p g + \xi_e E_z \quad (\text{A.1})$$

V_z is the z component of the barycentric velocity field, λ_p the permeation constant and g the force associated with the hydrodynamic variable u . ξ_e which has the dimensions of a mobility describes the difference, due to ionic motion across the layers, between the layer displacement velocity and the barycentric velocity. Further, using the momentum conservation law one gets the following equation for the undulation mode :

$$v_3 \delta \dot{n}_x + \left[b \frac{q_z^2}{q_x^2} + K_{11} q_x^2 \right] \delta n_x = - (\xi_e v_3) \partial_z E_x \quad (\text{A.2})$$

$\delta n_x = - \partial_x u$ and v_3 is a shear viscosity. The term in the right hand side of equation (A.2) has exactly the same structure as if it was derived by minimizing the free energy from equation (1.1) or (1.3) ; whether this effect should be considered as true flexoelectricity or not is not clear to us. For instance, although ξ_e and v_3 appear separately as dissipative coefficients, their product is reactive, just as $\lambda = - \gamma_2/\gamma_1$ is a reactive coefficient in the nematic phase [29]. One can evaluate the magnitude of this term the following way : $\xi_2 \sim (\rho_e/\rho) \mu$ [5] in which ρ_e is the mass density of a given ion, and μ its mobility (for order of magnitude purposes one can neglect the existence of several different ions).

Typically $\rho_e/\rho \sim 10^{-6}$, $\mu \sim 10^{-3} \text{ cm}^2 \text{ s}^{-1} (\text{stat volt})^{-1}$ (which corresponds to a conductivity σ of the order of $10^{-8} (\Omega \text{ cm})^{-1}$) ; that is with $v_3 \sim 1 \text{ P}$ $\xi_e v_3 \sim 10^{-9} \text{ e.s.u. cm}^{-1}$.

In other words, this effect is several orders of magnitude smaller than the experimentally observed one, and is certainly negligible in all practical situations. In the nematic phase, a similar coupling can be introduced, and describes the torque exerted on the director by current gradients :

$$\delta \dot{n}_i = \frac{h_i}{\gamma_1} + \lambda A_{iz} + \xi_e \partial_i E_z$$

$\delta \dot{n}_i$ is the director field, h the director body force, γ_1 the twist viscosity, $\lambda = - \gamma_2/\gamma_1$ and A_{ij} is the symmetric part of the velocity gradient tensor.

$\xi_e \gamma_1$ is equivalent to $\xi_e v_3$ and expected to have the same order of magnitude. Thus the existence of charged impurities is not likely to explain experimental observations relating a linear coupling between an electric field and curvature, as already pointed out by Helfrich [30].

APPENDIX B

The calculation of Meyer's flexoelectricity we propose here uses the concept of *monopole type* of strain source developed in reference [13].

We use notations relevant to the smectics A although the conclusions will hold in the nematic phase. The free energy can be expanded in the following way [1, 3] :

$$F - F_0 = \frac{1}{2} \int_v \left\{ b(\partial_z u)^2 + K_{11}(\partial_{ii}^2 u)^2 + 2 f E_z \partial_{ii}^2 u + \frac{\epsilon_a}{2\pi} \partial_i u E_i E_z \right\} dv \quad (\text{B.1})$$

u is the layer displacement taken along the unperturbed optical axis z , b and K_{11} are the compressional and splay elastic constants. f and ϵ have the same meaning as in the first section ($i = x, y$).

Let us just recall that using a Green's function technique, analogous to the dipolar expansion in electrostatics, one can introduce two sources of strain field in a smectic. The first one (dipoles P_3) which represents the number of layers pushed away from their unperturbed position cannot be linearly coupled to an electric field. The second type of strain field source (*monopoles* q_{ij}) corresponds precisely to molecules having a vectorial symmetry along the z direction (*pear* parallel or antiparallel to z) and a tensorial symmetry (second rank) in the xy plane.

We modify the definition given in reference [13] in such a way that it can be used continuously across the smectic A to nematic phase transition :

$$q_{lm} = -\frac{1}{2} \int dA_i \{ x_l x_m [-\lambda^{-2} \delta_{iz} \partial_z u + \partial_{i\alpha\alpha}^2 u] - [\delta_{il} x_m + \delta_{im} x_l] \partial_{jj}^2 u + 2 \partial_i u \delta_{lm} \} \quad (\text{B.2})$$

$\lambda = \sqrt{K_{11}/B}$ diverges at the $S_A \rightarrow N$ transition so that λ^{-2} vanishes; ijl and m run over x and y , whereas α runs over xy and z . The summation is performed on a surface surrounding the strain source considered, but its choice is unimportant since the divergence of the expression under the integrand vanishes.

For the same reasons as those explained in reference [13], we will consider only the case of isotropy in the xy plane; that is: $q_{ij} = q\delta_{ij}$. q has the dimensions of a length squared and is a measure of the asymmetry of the source considered: for instance, an ellipsoidal impurity would not give any contribution to q . On the other hand, in a pure sample, an excess of pear-shaped molecules pointing one way will lead to a non-vanishing q value. This is the case of interest for the discussion of Meyer's flexoelectricity. The free energy of a smectic, containing a non-zero Q density (that is $Q = nq$ in which $n = (n_+ - n_-)$ denotes the excess) can be written in a number of different ways. From averaging (3.20) of reference [13] or equivalently (3.21) one knows the interaction energy of Q with the stress field :

$$\delta E^i = \int_v K_{11} (\partial_{ii}^2 u + Q) Q \, dv. \quad (\text{B.3})$$

One has then to add a term such that the relation :

$$\Phi_i = \frac{\partial F}{\partial (\partial_i u)} - \partial_z \left(\frac{\partial F}{\partial (\partial_{iz}^2 u)} \right)$$

is compatible with (3.23) of reference [13]. This is easily fulfilled with :

$$F - F_0 = \frac{1}{2} \int_v \{ b(\partial_z u)^2 + K_{11} (\partial_{ii}^2 u)^2 + 2 K_{11} (\partial_{ii}^2 u + Q) Q \} \, dv. \quad (\text{B.4})$$

One should still add a term quadratic in Q to obtain the full free energy; its significance is more apparent if one writes :

$$F - F_0 = \frac{1}{2} \int_v \left\{ b(\partial_z u)^2 + K_{11} (\partial_{ii}^2 u + Q) \partial_{jj}^2 u + K_{11} (\partial_{ii}^2 u + Q) Q + \frac{1}{\chi} Q^2 \right\} \, dv. \quad (\text{B.5})$$

If we maintain $\partial_{ii}^2 u = 0$, and increase Q from zero to a given value, one can realize that the second term is the self energy of the Q s. in the long range stress field they create. The third term then describes essentially the decrease in entropy due to the resulting order. Comparison with an Ising model gives :

$$-T \delta S = k_B T \frac{n^2}{N} \quad \text{that is} \quad \frac{1}{\chi} = \frac{k_B T}{Nq^2} \quad (\text{B.6})$$

(N is the number of molecules per unit volume and q is defined by (B.2)).

The next step is to remark that a pear-shaped molecule is allowed to have a longitudinal dipole P . Since both the polarization density and the Q density are proportional to n , they are linearly related :

$$\mathcal{P} = \mu Q \quad (\text{B.7})$$

μ which has the dimensions of a charge per unit length like the flexoelectric coefficient, is the ratio p/q . It depends both in sign and magnitude on the molecule considered, but is expected to have little temperature dependence.

When an electric field is applied in the z direction, the free energy therefore takes the form :

$$F - F_0 = \frac{1}{2} \int_v \left\{ b(\partial_z u)^2 + K_{11} (\partial_{ii}^2 u)^2 + 2 K_{11} (\partial_{ii}^2 u) Q + \left(\frac{1}{\chi} + K_{11} \right) Q^2 - 2 \mu Q E_z - \frac{\epsilon_{zz}}{4\pi} E_z^2 \right\} \, dv. \quad (\text{B.8})$$

Minimizing with respect to Q , one obtains :

$$F - F_0 = \frac{1}{2} \int_v \left\{ b(\partial_z u)^2 + K_{11}^e (\partial_{ii}^2 u)^2 + 2 f^M (\partial_{ii}^2 u) E_z - \frac{\epsilon_{zz}^e}{4\pi} E_z^2 \right\} \, dv \quad (\text{B.9})$$

with :

$$K_{11}^e = \frac{K_{11}}{1 + K_{11} \chi} \quad f^M = \frac{K_{11} \mu}{\left(\frac{1}{\chi} + K_{11}\right)} = K_{11}^e \mu \chi \quad \varepsilon_{zz}^e = \varepsilon_{zz} + \frac{4 \pi \mu^2 \chi}{1 + K_{11} \chi}. \quad (\text{B.10})$$

The contribution that one could expect from the induced dipoles obeys the same equations. However, in that case the response function χ describes the polarization energy, and the relation $p = \mu' q$ has a significance at a molecular level : the dipole value is a measure of the induced charge asymmetry, which is, to the lowest order, linearly coupled to an induced steric asymmetry.

Another way of presenting the results is suggested by the following remark :

$$\frac{4 \pi \mu^2 \chi}{1 + K_{11} \chi}$$

is nothing but the contribution of the longitudinal dipoles (in the case of dipolar molecules) to the dielectric constant. In other words, if we call ε^0 the zero frequency dielectric constant value, and ε^1 the value obtained after the relaxation of the longitudinal dipoles (as discussed by Maier and Meier and for instance measured by Rondelez [15]), one can write :

$$\varepsilon_{zz}^0 - \varepsilon_{zz}^1 = \frac{4 \pi \mu^2 \chi}{1 + K_{11} \chi}$$

and hence

$$f^M = K_{11} \frac{\varepsilon_{zz}^0 - \varepsilon_{zz}^1}{4 \pi \mu}. \quad (\text{B.11})$$

The case of the induced contribution is similar

$$f^M = K_{11} \frac{(\varepsilon_{zz}^\infty - 1)}{4 \pi \mu'}. \quad (\text{B.12})$$

[Note that the formulae correspond to the clamped situation, which is the experimentally relevant one. The unclamped limit is obtained by setting the stress equal to zero, that is imposing $Q = \mu \chi E_z$. In that case one finds :

$$\varepsilon_{zz}^f = \varepsilon_{zz} + 4 \pi \mu^2 \chi$$

which is consistent with $\varepsilon^e - \varepsilon^f = -4 \pi f^{M^2}/K_{11}^e$ as pointed out by the Sofia group and Helfrich.]

APPENDIX C

Effective quadrupole centre. — One way of getting equation (2.4) is by averaging the molecular contributions to the macroscopic electric potential assuming that the molecules have both dipoles and quadrupoles.

The contribution of a small volume u to the potential V at the observation point \mathbf{r} reads :

$$V_u(\mathbf{r} - \mathbf{r}') = \sum_{(n \in u)} \left\{ p_i^n \partial_i \frac{1}{|\mathbf{r} - \mathbf{r}_0^n|} + \frac{1}{3} \theta_{ij}^n \partial_i \partial_j \frac{1}{|\mathbf{r} - \mathbf{r}_0^n|} \right\}. \quad (\text{C.1})$$

The summation extends over all particles contained in the volume u . \mathbf{p}^n is the molecular dipole and \mathbf{r}_0^n the quadrupole centre of the n th particle. Since we assume the molecules to be neutral, the \mathbf{p}^n value does not depend on the choice of \mathbf{r}_0^n whereas the θ^n value depends non-trivially on this choice.

Actually, although the observation point is defined in this expression, the value of the vector \mathbf{r}' is not ; one must implement (C.1) by :

$$\mathbf{r}' = \frac{1}{u} \int_u \mathbf{r}^0 dv = \frac{1}{u} \sum_{n \in u} \mathbf{r}_0^n v \quad (\text{C.2})$$

in which v is the molecular volume. Developing $1/|\mathbf{r} - \mathbf{r}_0|$ around \mathbf{r}' and keeping terms up to the relevant order one finds :

$$V_u(\mathbf{r} - \mathbf{r}') = \left[\sum_{n \in u} p_i^n \right] \partial_i \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{3} \left[\sum_{n \in u} 3 p_i^n (r_{0j}^n - r'_j) - p_k^n (r_{0k}^n - r'_k) \delta_{ij} + \theta_{ij}^n \right] \partial_i \partial_j \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{C.3})$$

The second term of (C.3) exhibits some amount of mixing between quadrupolar and dipolar contributions but does not depend on the choice of \mathbf{r}_0^n (which is legitimate since $V(\mathbf{r} - \mathbf{r}')$ is of course independent of \mathbf{r}_0^n).

The effective centre we use in the definition of θ_{ij} is such that the quadrupolar and dipolar contributions are decoupled. that is :

$$R_{ij} = \sum_{n \in u} [3 p_i^n (r_{0j}^n - r_j') - p_k^n (r_{0k}^n - r_k') \delta_{ij}] = 0. \quad (C.4)$$

Introducing the molecular inertia centres : \mathbf{r}_g^n , one can write (with the obvious notation for $R_{ij}(\mathbf{r}_g)$) :

$$R_{ij} = R_{ij}(\mathbf{r}_g) - \sum_{n \in u} \{ 3 p_i^n (r_{gj}^n - r_{0j}^n) - (r_{gk}^n - r_{0k}^n) p_k^n \delta_{ij} \}. \quad (C.5)$$

By doing that, we split R_{ij} into two different contributions : the first one is determined by the correlation between translational and rotational degrees of freedom, whereas the second is orientational only. Following De Gennes [14] we introduce a molecular reference frame : $[\hat{\alpha}, \hat{\beta}, \hat{\gamma}]$ such that :

$$\begin{aligned} (r_{gi} - r_{0i}) &= \delta r_i = \delta r_\alpha \alpha^i \\ p_i &= p_\alpha \alpha^i \end{aligned} \quad (C.6)$$

(α^i is the i th component of the molecular unit vector $\hat{\alpha}$). Then :

$$R_{ij} = R_{ij}(\mathbf{r}_g) - 2 \delta r_\alpha p_\beta \langle S_{\alpha\beta}^{ij} \rangle \quad (C.7)$$

with :

$$S_{\alpha\beta}^{ij} = \frac{1}{2} (3 \alpha^i \beta^j - \delta_{ij} \delta_{\alpha\beta}). \quad (C.8)$$

The macroscopic symmetry leads to one independent component only :

$$R_{zz} = R_{zz}(\mathbf{r}_g) - 2 \delta r_\alpha p_\beta \langle S_{\alpha\beta}^{zz} \rangle. \quad (C.9)$$

The condition $R = 0$ is equivalent to :

$$R_{zz}(\mathbf{r}_g) = 2 \delta r_\alpha p_\beta \langle S_{\alpha\beta}^{zz} \rangle. \quad (C.10)$$

This can always be fulfilled by a suitable choice of δr_α , since $\langle S_{\alpha\beta}^{zz} \rangle$ is different from zero. Furthermore this choice is not unique. since δr_α comes in only through a scalar product. There is an infinite number of effective quadrupole centres. This may be at first sight puzzling since the molecular quadrupole depends on this point. However this is unimportant because the average quadrupole does not depend on it, provided it lies precisely in the plane defined by (C.11) since :

$$\Theta_0 = \Theta_g + 2 \delta r_\alpha p_\beta \langle S_{\alpha\beta}^{zz} \rangle \quad (C.11)$$

(Θ_0 and Θ_g are the quadrupole densities defined from any effective centre, and the centre of inertia respectively).

Finally, we point that all theories such as that of Maier and Saupe, in which translation-rotation cross correlations are neglected, would allow us to choose as an effective quadrupole centre the centre of inertia. Their reasonable success in describing the nematic order suggests that $(\Theta_0 - \Theta_g/\Theta_0)$ might not be too large.

References

- [1] MEYER, R. B., *Phys. Rev. Lett.* **22** (1969) 918.
- [2] HELFRICH, W., *Mol. Cryst.* **26** (1974) 1.
- [3] DE GENNES, P. G., *J. Physique Colloq.* **30** (1969) C 4-65.
- [4] LAUDET, M., *C.R. Hebd. Séan. Acad. Sci.* **233** (1951) 20.
- [5] HELFRICH, W., *Z. Naturforsch.* **26a** (1971) 833.
- [6] DERZHANSKI, A., PETROV, A. G., *Phys. Lett.* **36A** (1971) 483 ;
PETROV, A. G., Thesis Sofia (1974).
- [7] PROST, J., PERSHAN, P. S., *J. Appl. Phys.* **47** (1976) 2298.
- [8] DEBYE, P., *Physik Z.* **22** (1921) 302 ;
BUCKINGHAM, A. D., *J. Chem. Phys.* **30** (1959) 1580.
- [9] BUCKINGHAM, A. D. and LONGUET HIGGINS, H. C., *Mol. Phys.* **14** (1968) 63.
- [10] BUCKINGHAM, A. D. and DISCH, R. L., *Proc. R. Soc. (London)* **A 273** (1963) 275.
- [11] BUCKINGHAM, A. D., DISCH, R. L. and DUNMUR, D. A., *J. Am. Chem. Soc.* **90** (1968) 3104.
- [12] DERZHANSKI, A. I., MITOV, M. D., *C.R. Acad. Bulg. Sci.* **28** (1975) 1331.
- [13] PERSHAN, P. S., PROST, J., *J. Appl. Phys.* **46** (1975) 2343.
- [14] DE GENNES, P. G., *The Physics of liquid crystals* (Clarendon Press, Oxford) 1974.
- [15] MAIER, W., MEIER, G., *Z. Naturforsch.* **16a** (1961) 1200 ;
RONDELEZ, F. and MIRCEA-ROUSSEL, A., *Mol. Cryst.* **28** (1974) 173 ;
For dielectric measurements on BBMBA, see : CHEUNG, L. and MEYER, R. B., *Phys. Lett.* **43A** (1973) 261.
- [16] JEN, S., CLARK, N. A., PERSHAN, P. S. and PRIESTLY, E. B., *Phys. Rev. Lett.* **31** (1973) 1552 ;
See also : MADHUSUDANA, N. V., SHASHIDHAR, R. and CHANDRASEKHAR, S., *Mol. Cryst. liq. cryst.* **13** (1971) 61.
- [17] DERZHANSKI, A. I., PETROV, A. G., KHINOV, Ch., MARKOVSKI, B. L., *Bulg. J. Phys.* **2** (1974).
- [18] ESHBACH, J. R. and STRANDBERG, M. W. P., *Phys. Rev.* **85** (1952) 24.
- [19] HÜTTNER, W., LO, M. K. and FLYGARE, W. H., *J. Chem. Phys.* **48** (1968) 1206.

- [20] BUCKINGHAM, A. D., *Phys. Chem.* « An advanced treatise », vol. IV, Mol. Properties Chap. 8, p. 349-384 (Acad. Press New York, London) 1970.
- [21] GASPAROUX, H., REGAYA, B. et PROST, J., *C.R. Hebd. Séan. Acad. Sci.* **B 272** (1971) 1168 ;
See also GASPAROUX, H., PROST, J., *J. Physique* **32** (1971) 953.
- [22] FLYGARE, W. H., *J. Chem. Phys.* **42** (1965) 1563.
- [23] LALANNE, J. R., MARTIN, F. B. and KIELICH, S., *Chem. Phys. Lett.* **30** (1975) 73.
- [24] SCHMIDT, D. S., SCHADT, M. and HELFRICH, W., *Z. Naturforsch.* **27a** (1971) 277.
- [25] LIAO, Y., CLARK, N. A. and PERSHAN, P. S., *Phys. Rev. Lett.* **30** (1973) 639 and LE PESANT, J. P., PERSHAN, P. S., to be published.
- [26] MEYER, R. B., PERSHAN, P. S., *Solid State Commun.* **13** (1973) 989 ;
For systematic studies of surface energies, see for instance :
PROUST, J., TER MINASSIAN-SARAGA, L., *J. Physique Colloq.* **36** (1975) C 1-77.
- [27] BOUCHIAT, M. A., LANGEVIN, D., *Phys. Lett.* **34** (1971) 331 ;
See also : PROST, J., Thesis, Bordeaux n° 392 (1973).
- [28] HELFRICH, W., *J. Chem. Phys.* **51** (1969) 4092.
- [29] MARTIN, P. C., PARODI, O., PERSHAN, P. S., *Phys. Rev. A* **6** (1972) 2401.
- [30] HELFRICH, W., *Phys. Lett.* **35A** (1971) 393.
-