Order Electricity and Surface Orientation in Nematic Liquid Crystals

G. Barbero,[a] I. Dozov,[b] J. F. Palierne, and G. Durand
Laboratoire de Physique des Solides, Université de Paris-Sud, 91405 Orsay Cédex, France

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A nematic liquid crystal should present an order electric polarization associated with the gradient of order parameter, in addition to the flexoelectric polarization associated with the gradient of orientation. Using thermodynamical arguments, we show that the order-electricity coefficients are of the same order as the flexoelectric ones. The dielectric energy resulting from the order polarization can explain the unsolved problem of the spontaneous tilted orientation at the nematic-isotropic (or air) interfaces. The core of disclination lines can also present electric multipoles.

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A nematic liquid crystal is characterized by a tensorial order parameter $Q_{ij}=S(n_in_j-\frac{1}{3}\delta_{ij})$, of modulus S and director **n** (**n** is a unit vector usually called director[1]). At thermal equilibrium uniform textures of nematic liquid crystals, i.e., with uniform S and **n**, are centrosymmetric by compensation and then are not ferroelectric. Long ago, Meyer[2] showed that by breaking this symmetry, bend or splay curvature distortions can induce a macroscopic electric polarization $\mathbf{P}_f$. $\mathbf{P}_f$, proportional to the curvature of **n** at constant S, is the well-known flexoelectric polarization. More recently, the idea of inducing an electric polarization by forcing a gradient of S at constant **n** was suggested by Prost and Marcerou[3] and applied to the problem of the orientation of **n** at a nematic-isotropic interface. They predicted that **n** should always align parallel to the interface. This is not in agreement with the experimental data.[4] Faetti and Palleschi, for instance, have recently measured the surface orientation of cyanoderivative.[5,6] In heptyl cyanobiphenyl (7CB), **n** is found to make an angle of 52° with the surface normal.[5] In this paper, we give the first complete analysis of the order polarization connected with the spatial variation of the modulus S of the order parameter in nematic liquid crystals. As an application we show how the surface orientation is connected with the order polarization. We can explain quantitatively the experiments of Faetti and co-workers.[5-8]

We start by generalizing the thermodynamical arguments of Ref. 2. We write the differential of the electric enthalpy density as

$$dH=\nu_i d(S_{,i})+\gamma_{ij}d(n_{i,j})-(1/4\pi)D_i dE_i, \tag{1}$$

where $G_{,i}=\partial G/\partial x_i$. In (1) the first term takes into account the new contribution to the spatial variation of S. The second term represents the elastic contribution from curvature elasticity and the last the usual dielectric contribution (**E** is the electric field). We make a linear expansion of the conjugate quantities ν_i, γ_{ij}, and D_i in terms of our independent variables as

$$\begin{gathered}\partial H/\partial(S_{,i})=\nu_i=\tau_{,ij}S_{,j}+L_{ijk}n_{j,k}+M_{ij}E_j,\quad \partial H/\partial(n_{i,j})=\gamma_{ij}=N_{ijk}S_{,k}+\alpha_{ijkl}n_{k,l}+\beta_{ijk}E_k,\\ -\partial H/\partial E_i=(1/4\pi)D_i=R_{ij}S_{,j}+\mu_{ijk}n_{j,k}+(\epsilon_{ij}/4\pi)E_j;\end{gathered} \tag{2}$$

using the usual Maxwell relations, we can write

$$\tau_{ij}=\tau_{ji},\quad \alpha_{ijkl}=\alpha_{klij},\quad \epsilon_{ij}=\epsilon_{ji},\quad \beta_{ijk}=-\mu_{kij},\quad L_{ijk}=N_{jki},\quad M_{ij}=-R_{ji}. \tag{3}$$

τ_{ij} is related to the L_1 and L_2 gradient elastic constants of the Landau–de Gennes free energy[9]; α_{ijkl} gives the curvature Frank elastic constants[10] $K_{(1,2,3)}$; ϵ_{ij} is the usual dielectric tensor; β_{ijk} and μ_{ijk} give the flexoelectric coefficients[2]; L_{ijk} and N_{ijk} would give the (usually neglected) coupling between change of order and curvature[9]; they depend only on L_2. Finally M_{ij} and R_{ij} give the new "order" electricity effect. H becomes now

$$H=\tfrac{1}{2}\tau_{ij}S_{,i}S_{,j}+\tfrac{1}{2}\alpha_{ijkl}n_{i,j}n_{k,l}-(1/8\pi)\epsilon_{ij}E_iE_j+L_{ijk}S_{,i}n_{j,k}-\mu_{kij}n_{i,j}E_k-R_{ji}S_{,i}E_j. \tag{4}$$

In addition to the usual dielectric term, the electric polarization contains the two terms

$$\mathbf{P}_f=e_1\mathbf{n}\cdot\operatorname{div}\mathbf{n}-e_3\mathbf{n}\times\operatorname{rot}\mathbf{n},\quad \mathbf{P}_o=r_1(\mathbf{n}\cdot\operatorname{grad}S)\mathbf{n}+r_2\operatorname{grad}S. \tag{5}$$

$\mathbf{P}_f$ is the usual flexoelectric polarization. $\mathbf{P}_o$ is the order polarization. To obtain (5) we have decomposed μ_{ijk} and R_{ij} in term of tensors made with n_j and δ_{ij}, using $n_in_j=1$.[11]

In this symmetry-based approach, the flexoelectric (e_1,e_3) and order-electric (r_1,r_2) coefficients seem unconnected, and their temperature dependence unknown. In fact, the true variable which describes the spatial nematic

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behavior is $Q_{ij,k}$, so that the H differential should have been written as

$$dH = A_{ijk}\, d(Q_{ij,k}) - (1/4\pi) D_i\, dE_i. \tag{6}$$

Following the above procedure, we obtain

$$H = \tfrac{1}{2} B_{ijklmn} Q_{lm,n} Q_{ij,k} - \frac{1}{8\pi} \epsilon_{ij} E_i E_j - G_{ijlm} Q_{jl,m} E_j, \tag{7}$$

where $B_{ijklmn} = B_{lmnijk}$ can be decomposed in the usual way, giving the well-known Landau–de Gennes free-energy density.[9,12] Furthermore, in addition to the usual dielectric term, the electric polarization is now

$$P_i = G_{ijlm} Q_{jl,m}. \tag{8}$$

G_{ijlm} can be expanded in terms of Q_{ij} and δ_{ij}.[11] To second order in S,[12] we can write the flexoelectric and order-electric coefficients as

$$\begin{aligned} &e_1 = A_1 S^2 + eS, \quad e_3 = A_3 S^2 + eS, \\ &r_1 = AS + e, \quad r_2 = -\tfrac{1}{3}\{-(A+B)S + e\}, \end{aligned} \tag{9}$$

where $A = A_1 + A_3$.

The coefficients A_1, A_3, and e are known from the temperature analysis of the flexoelectric coefficients e_1 and e_3.[13] We see that the order-electric coefficients r_1 and r_2, expressed in terms of A_1, A_3, and e, are of the same order as the flexoelectric coefficients. The only new term is B which, in absence of any measurement, can be assumed to be comparable with A.

Order electricity must be present each time one deals with a situation implying a spatial variation of S. A good case is the interface between a nematic phase and its isotropic phase, stabilized by a small temperature gradient. We neglect the associated transport phenomena, assuming thermal equilibrium at the transition temperature T_c. We make a one-dimensional analysis along the normal $\mathbf{x}_3$ to the interface. Across the interface, S must vary from S_0 in the nematic phase to 0 in the isotropic phase.[9] We call $\theta(\mathbf{n}, \mathbf{x}_3)$ the polar angle of the director. In principle, θ must also vary through the interface, because of the coupling between $\theta_{,3}$ and $S_{,3}$. We make for the moment the usual uniform-θ approximation through the interface. We consider the pure dielectric case

$$D_3 = \epsilon_{33}(\theta) E_3 + 4\pi (r_1 \cos^2\theta + r_2) S_{,3} = 0,$$

because the Debye screening length is, in general, much larger than the coherence length ξ. This gives

$$H = L(\theta) S_{,3}^2, \tag{10}$$

where

$$L(\theta) = \tfrac{3}{8} L_2 \cos^2\theta + \tfrac{3}{4}(L_1 + \tfrac{1}{6} L_2) + \frac{2\pi}{\epsilon_\perp} \frac{(r_1 \cos^2\theta + r_2)^2}{1 + (\epsilon_a/\epsilon_\perp)\cos^2\theta}. \tag{11}$$

A standard calculation gives for the interfacial energy the value[9,14]

$$\gamma(\theta) = \{\tfrac{3}{4} a L_0(\theta)\}^{1/2} (T_c - T)^{1/2} S_0^2 + O(S_0^4), \tag{12}$$

where $\frac{1}{2} a (T_c - T) S^2$ is the first term of the de Gennes free energy. At equilibrium, $\gamma(\theta)$, and hence $L(\theta)$, must be minimum with respect to θ. This leads to

$$\left\{ \frac{3}{8} L_2 + \frac{2\pi}{\epsilon_\perp} (r_1 \cos^2\theta_0 + r_2) \frac{(\epsilon_a/\epsilon_\perp) r_1 \cos^2\theta_0 + 2r_1 - (\epsilon_a/\epsilon_\perp) r_2}{[1 + (\epsilon_a/\epsilon_\perp)\cos^2\theta_0]^2} \right\} \sin 2\theta_0 = 0, \tag{13}$$

which defines the mean interface orientation θ_0. Note that for $L_2 = 0$ (i.e., in absence of $\theta_{,3}$-$S_{,3}$ coupling), and close to the transition ($S \rightarrow 0$), θ_0 tends towards the "magic" angle defined by $\cos^2\theta_0 = \frac{1}{3}$ [see Eq. (9), giving $r_1 \rightarrow e$ and $r_2 \rightarrow -e/3$]. Physically this corresponds to simply minimizing the order-electric polarization proportional to $(P_3)^2$ (and not P^2, as suggested in Ref. 3). Close to the transition, a departure from the magic angle should give a direct measurement of L_2, responsible for the difference, at T_c, between $k_1 = k_3$ and k_2. For finite S, and L_2 arbitrary, Eq. (13), in the case, for instance, of a nematic-air interface, gives the temperature dependence of θ_0. If the bracket has no zero, θ_0 is 0 or $\pi/2$, according to de Gennes's[14] prediction. If the bracket can become zero, θ_0 depends on S, i.e., varies with temperature. It may be possible to find some temperature T_0 where θ_0 goes from one regime to the other one. Close to T_0, a trivial calculation shows that θ_0 (or $\pi/2 - \theta_0$) will vary according to $|T - T_0|^{1/2}$.

We can now estimate the deviation $\Delta\theta = \theta - \theta_0$ across the interface. We use the simplified Landau–de Gennes energy,[9] in the absence of flexoelectricity, for the two-constants approximation. Writing $S_{,3} \simeq S_0/2\xi$, we obtain for θ the equilibrium equation

$$3(L_1 + \tfrac{1}{2} L_2) S_0^2 \theta_{,33} + \tfrac{1}{4} L_2 \sin 2\theta (S_0/2\xi)^2 = 0,$$

i.e.,

$$\Delta\theta \simeq \{L_2/[12(L_1 + \tfrac{1}{2} L_2)]\} \sin 2\theta_0. \tag{14}$$

L_2 is generally smaller than L_1 (see Ref. 9); consequently Eq. (14) shows that $\Delta\theta$ is usually small enough for the uniform approximation to be valid.

Knowing θ_0, we can estimate γ_e and the surface anchoring energy W, defined as[5,7] $\gamma_e = \gamma(\theta_0)$ and

$$W = \frac{1}{2}\left\{\frac{d^2\gamma}{d\theta^2}\right\}_{\theta_0} = \left\{\frac{3}{4}a\frac{(T_c - T)}{L(\theta_0)}\right\}^{1/2} S_0^2 \frac{\pi}{\epsilon_\perp} \frac{[r_1 - (\epsilon_a/\epsilon_\perp)r_2]^2}{[1 + (\epsilon_a/\epsilon_\perp)\cos^2\theta_0]^3} \sin^2 2\theta_0. \tag{15}$$

This anchoring energy is of the order of $W \simeq e^2 S_0^2/\xi$. As $e^2 \sim K$, we can write W as $W \simeq K/\lambda$, where the extrapolation length λ characterizing the anchoring strength is $\lambda(T_c) \sim \xi/S_0^2$. Using the classical Landau mean field model, we can write immediately

$$\lambda(T) \sim \xi_0[T_c/(T^* - T)]^{3/2},$$

where $T^* - T_c$ is of the order of 1 °C and the bare correlation length ξ_0 compares with a molecular length.[9] The surface anchoring must become very strong far below T_c.

Let us now compare these predictions with existing data. First, consider the results from Refs. 5 and 6 on the 7CB nematic-isotropic interface. θ_0 is 52.6° ±0.6°, i.e., the magic angle. This means that for 7CB, in the limit of small S, the three curvature elastic constants should be equal. This fits very well with the analysis of the S dependence for this compound reported in Ref. 8. Furthermore, assuming $a \simeq 12 \times 10^5$ cgs,[15] $L_1 \simeq 10^{-6}$ cgs,[9] $T^* - T_c \simeq 1$ °C,[9] $S_0 \simeq 0.25$,[16] $e \simeq 5 \times 10^{-4}$ cgs,[17] $\epsilon_\parallel = 11$, and $\epsilon_\perp = 7$,[18] we can estimate the interfacial tension $\gamma_e \simeq 5 \times 10^{-2}$ erg/cm^2. The experimentally estimated value is 2×10^{-2} erg/cm^2,[5] of the same order of magnitude. With the same parameters, we estimate for the anchoring energy $W \simeq 5 \times 10^{-3}$ erg/cm^2. The two measured values[5,6] are $W = 1 \times 10^{-3}$ erg/cm^2 and $W = 2 \times 10^{-3}$ erg/cm^2, in reasonable agreement.

We now consider the case of MBBA (methoxybenzylidene butylaniline). θ_0 is found to become zero within 1.2 K of T_c (Ref. 8); it increases as $(T_0 - T)^{1/2}$ below T_0. For this compound we can write

$$\cos^2\theta_0 = \frac{1}{3} - \frac{3\epsilon_\parallel L_2}{32\pi e^2} + \left\{\frac{3\epsilon_\parallel L_2 A}{16 e^3} - \frac{2A + B}{3e}\right\} S,$$

which fits the data far from T_0 ($\theta_0 \simeq 35°$) and close to T_0 if we use the values $\epsilon_\parallel \simeq \epsilon_\perp \simeq 5$, $e \simeq 0.5 \times 10^{-3}$ cgs, $A_1/e \simeq A_3/e \simeq B/e \simeq 0.12$, and $L_2 < 0$ with $|L_2| \simeq 1.5 \times 10^{-6}$ cgs.

Note that the few measurements which give the L_1 and L_2 values[19,20] are based on the Landau-de Gennes model, ignoring the large contribution from the order electricity. These experiments should be reanalyzed to give the correct values. Note, for instance, that in Ref. 20 it is not possible to fit the data with a constant L_2. The temperature dependence of the surface angle in MBBA appears to fit qualitatively with our model. The last experiment to quote is the observation[21] of a free surface undulation under the application of a magnetic field. The surface distortion (instead of the director tilt) is an obvious consequence of the large increase of W far from T_c.

Finally, we can describe other situations where order electricity can be important. In the core of disclination lines, S must go continuously to zero. The associated order electricity must build intrinsic electric multipoles on the lines. This contribution must be added to the one already calculated for the distorted volume around the core.[22] Lines of order $\frac{1}{2}$, for instance, should bear a charge $\pm eS$ and an electric dipole $\pm eS\xi$ per unit length, normal to the line, in the plane of symmetry. One can also predict the existence of a potential difference between an electrode and the bulk, if the surface order parameter is different from the bulk one. These effects will be described in a forthcoming paper.

To conclude, we have generalized the idea of Meyer on the flexoelectric polarization, associated with spatial curvature distortion of the nematic. One can also associate an electric order polarization with the spatial gradient of the modulus of the order parameter. The associated order coefficients are the same as the flexoelectric ones except for a new one to be measured. Order electricity must be important close to boundaries, or disclination lines. In particular, we have shown that the problem of director orientation at a free surface can now be solved. In addition to the de Gennes model, which predicted only molecular orientation parallel or perpendicular to the interface, we can explain the observed tilted orientation and its temperature dependence. In the simplest case, where the surface energy is totally of electric origin, the molecules align along the magic angle, to suppress the normal component of the order polarization. In general, the elastic anisotropy must also be taken into account and allows for a different, and temperature-dependent, surface orientation. More generally, we can predict an intrinsic electric multipolar property for all situations which imply a change of order parameter, for instance in the core of disclination lines.

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[a] Also at Dipartimento di Fisica, Politechnico, Corso Duca degli Abruzzi 24, 10129 Torino, Italy, and Gruppo Nazionale di Struttura della Materia, Unità di Cosenza, Università della Calabria, Arcaracata di Rende, Italy.

[b] Permanent address: Institute of Solid State Physics, Bvd. Lenin 72, Sofia, Bulgaria.

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