PHYSICAL REVIEW A VOLUME 40, NUMBER 7 OCTOBER 1, 1989

Molecular theory of the spontaneous polarization in the chiral smectic-*C* phase

W. J. A. Goossens*
Philips Research Laboratories, P.O. Box 80 000, 5600 JA Eindhoven, The Netherlands

(Received 24 April 1989)

It is shown that the specific configuration of a chiral molecule gives rise to a spontaneous polarization in the smectic-*C* phase due to the molecular interaction in terms of the electrostatic quadrupole moments that produces the tilt of the director in the smectic-*C* phase.

In the liquid-crystalline smectic-*C* phase the averaged alignment of the anisotropic molecules constituting the one-dimensional layered structure is tilted with respect to the layer normal $\hat{\mathbf{v}}$.[1] The projection of the director $\hat{\mathbf{n}}$, which is a unit vector along the local direction of alignment, on the two-dimensional fluid layers is denoted by a vector $\mathbf{c}$, $|\mathbf{c}|<1$, called the *C* director. The characteristic parameter for the smectic-*C* phase is the tilt angle ω determined by $\hat{\mathbf{v}}\cdot\hat{\mathbf{n}}=\cos\omega$; cf. Fig. 1.

If the anisotropic molecules of the smectic-*C* phase are chiral, that is, optically active, the *C* director rotates from layer to layer around $\hat{\mathbf{v}}$, resulting in a macroscopic helical structure of the tilted director;[1] the characteristic length p over which the *C* director makes a 2π turn is typically of the order of 1 μm. As predicted by Meyer and also demonstrated experimentally,[2,3] there is in each layer of the chiral smectic-*C* phase a spontaneous polarization $\mathbf{P}=\mu_p\hat{\mathbf{n}}\times\mathbf{c}$; this polarization is only manifest as a homogeneous macroscopic polarization if the twist of the *C* director is suppressed by external means. The magnitude of the piezoelectric coefficient μ_p is typically of the order 10–100 nC/cm^2.

Meyer's symmetry arguments and the chemists' intuition and empirical knowledge[4–8] have not yet led to a clear description of the molecular mechanism responsible for the spontaneous polarization in the chiral smectic-*C* phase. We therefore present a simple elementary picture of the configuration of an anisotropic chiral molecule and its coupling with the layered tilted structure of the smectic-*C* phase, which is of primary importance.

Indeed, to avoid all misunderstanding it should be recognized from the beginning that the molecular interaction that produces the twist from layer to layer cannot be responsible for the polarization in each layer. To illustrate this point, we recall that molecular theories dealing with the twist of the director are essentially based on the dispersive interaction energy between two molecules in terms of the combined action of the molecular dipole-dipole and of the molecular dipole-quadrupole transition.[9–12] The essence of this chiral interaction denoted by V_{ij}^{ch} comes to the fore by noting that[12]

$$V_{ij}^{\mathrm{ch}}=V^{\mathrm{ch}}(\Omega_i,\Omega_j,\mathbf{R}_{ij})\propto(p_\alpha|p_\beta)_i(p_{\alpha'}|q_{\beta'\gamma})_j C_{\alpha\alpha'}D_{\beta\beta'\gamma}\ , \tag{1}$$

where the indices α, β, etc. refer to the coordinates X,Y,Z of a macroscopic coordinate system; $p_\alpha=p_\alpha(\Omega)$ and $q_{\beta\gamma}=q_{\beta\gamma}(\Omega)$ are the corresponding components of the induced molecular dipole and quadrupole transitions $e\mathbf{r}$ and $e\mathbf{rr}$, respectively, which are a function of the orientation of a molecular fixed coordinate system (x,y,z) with respect to the (X,Y,Z) coordinate system. This orientation denoted by one symbol Ω can be described in terms of the Euler angles ϕ,θ,ψ indicated in Fig. 1; $\Omega=\Omega(\phi,\theta,\psi)$. The tensor elements $C_{\alpha\alpha'}$ and $D_{\beta\beta'\gamma}$ describe the dependence of V_{ij}^{ch} on the relative position $\mathbf{R}_{ij}=(R_X,R_Y,R_Z)$ of two molecules in terms of products of the corresponding components R_α, R_β, etc.; repeated indices in Eq. (1) indicate a summation. The product $C_{\alpha\alpha'}D_{\beta\beta'\gamma}$ contains only odd powers of the components of $\mathbf{R}_{ij}$. The averaging of V_{ij}^{ch} over all relative positions $\mathbf{R}_{ij}$ yields therefore nonzero only if the relative orientation of the molecules is also an odd function of $\mathbf{R}_{ij}$; this is the characteristic of V_{ij}^{ch}. Indeed, it has been shown[12] that the orientationally averaged value of the sum of terms like $(p_\alpha|p_\beta)_i(p_\alpha|q_{\beta\gamma})_j$, proportional to $\cos\theta_{ij}\sin\theta_{ij}$, in a molecular field approach can be written as $\langle P_2(\cos\theta)\rangle^2\sin(2\pi R_\gamma/p)$, where the order parameter $\langle P_2(\cos\theta)\rangle$ is the orientationally averaged value of the second-order Legendre polynomial P_2 of the argument $\cos\theta_i=\hat{\mathbf{z}}_i\cdot\hat{\mathbf{n}}$ and $2\pi R_\gamma/p$ is the angle of rotation of $\hat{\mathbf{n}}$ over a distance R_γ around the γ axis which is perpendicular to $\hat{\mathbf{n}}$; when considering the chiral smectic-*C* phase the γ axis is along $\hat{\mathbf{v}}$, i.e., perpendicular to $\mathbf{c}$.[13] The actual value of the pitch p is found by minimization of the full potential energy.[12,13]

This brief recapitulation shows that the chiral interaction which produces the twist vanishes when the molecules have on average the same orientation; V_{ij}^{ch} is then an odd function of the relative position of the molecules which vanishes on average. This applies to all molecules in each layer and in the whole of the sample when the twist is suppressed; this proves the assertion of Meyer that the interaction giving rise to the twist is not the cause of the spontaneous polarization. Indeed, to explain the latter one has primarily to consider the molecular interaction that gives rise to the tilt of the director in the smectic-*C* phase.

We therefore consider the interaction V_{ij}^{qq} between the electrostatic molecular quadrupole moments described in

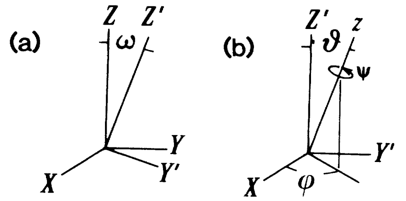

FIG. 1. The relative orientations of the coordinate systems involved. (a) The Z axis is along the layer normal to $\hat{\mathbf{v}}$, the Z' axis is along the director $\hat{\mathbf{n}}$; $\hat{\mathbf{v}}\cdot\hat{\mathbf{n}}=\cos\omega$. (b) Schematic representation of the Euler angles ϕ, θ, ψ which describe the orientation of the molecular coordinate system (x,y,z) with respect to the (X,Y',Z') coordinate system; the primes are only relevant for the smectic-C phase, that is, $\cos\theta=\hat{\mathbf{z}}\cdot\hat{\mathbf{n}}$.

terms of the quadrupole tensor $q_{\alpha\beta}=\sum_\nu e_\nu r_{\nu\alpha} r_{\nu\beta}$, that is

$$V_{ij}^{qq}=V^{qq}(\Omega_i,\Omega_j,\mathbf{R}_{ij})=q_{\alpha\beta}(\Omega_i)q_{\alpha'\beta'}(\Omega_j)T_{\alpha\beta\alpha'\beta'} \tag{2}$$

where the tensor $T_{\alpha\beta\alpha'\beta'}$ describes the dependence of V_{ij}^{qq} on the relative position $\mathbf{R}_{ij}$ of the molecules. It is straightforward to show[14] that this interaction in the smectic phase gives rise to an averaged mean field $\langle V_C(\omega)\rangle$, $V_C(\omega)=\langle V_{ij}^{qq}\rangle$, defined in terms of the relevant order parameters $\langle cP_2\rangle=\langle\cos(qR_Z)P_2(\Omega)\rangle$ and $\langle cQ\rangle=\langle\cos(qR_Z)Q(\Omega)\rangle$ and of the tilt angle ω by

$$\langle V_c(\omega)\rangle=-(\Gamma^2\langle cQ\rangle^2+10\Gamma\Delta\langle cQ\rangle\langle cP_2\rangle\sin\omega)3\overline{cP'_4} \tag{3}$$

where $\Delta=q_{zz}-\frac{1}{2}q_{yy}$ and $\Gamma=2q_{yz}$ are the anisotropy and "diagonal flatness" of the molecular quadrupole distribution, respectively, defined in a molecular coordinate system (x,y,z), cf. Fig. 2; $\overline{cP'_4}$ is a weighted average of the tensor $T_{\alpha\beta\alpha'\beta'}$ over all relative positions $\mathbf{R}_{ij}$ which being even in $\mathbf{R}_{ij}$ is harmless. The quantities in angle brackets of Eq. (3) are averaged values defined by

$$\langle cP_2\rangle=\int dR_Z\int d\Omega\, f(\Omega,R_Z)\cos(qR_Z)P_2(\Omega)\ , \tag{4}$$

where the normalized one-particle distribution function $f(\Omega,R_Z)=\exp(-V/kT)/\int dR_Z\int d\Omega\exp(-V/kT)$ is defined in terms of the molecular field $V=V(\Omega,R_Z)$ of the smectic phase given by

$$V=V_R+V_C(\omega)+\delta V_A\sin^2\omega\ ; \tag{5}$$

V_A is the molecular field for the smectic-A phase[1] and $V_C(\omega)$ is the molecular field arising from V_{ij}^{qq} defined above. The additional term $\delta V_A\sin^2\omega$ ensures the stability of the smectic-A phase against a tilt of the director; for the discussion it suffices to note that this term arises in a natural way by taking into account the anisotropy of the excluded volume when calculating V_A.[14]

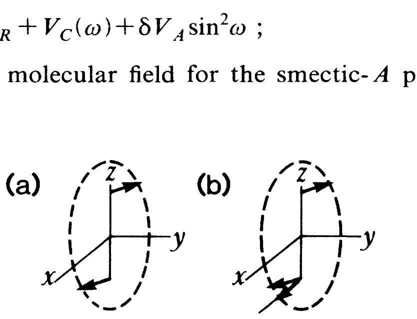

FIG. 2. (a) An anisotropic molecule with a quadrupole moment $\vec{q}$ in terms of two eccentric dipoles $\pm\mathbf{p}=(0,p_y,p_z)$. (b) A chiral variant by the mere addition of a dipole $\mathbf{p}=(p_x,0,0)$.

The order parameter $\langle\cos(qR_Z)P_2(\Omega)\rangle$ is the mixed order parameter of the smectic phase[1] which is a measure for the uniaxial orientational order with respect to $\hat{\mathbf{n}}$, $P_2(\Omega)=P_2(\hat{\mathbf{z}}\cdot\hat{\mathbf{n}})$, in combination with the one-dimensional translational order along $\hat{\mathbf{v}}$; R_Z denotes the relative position of the molecules along $\hat{\mathbf{v}}$ which defines the Z axis, whereas the thickness d of the layers determines the wave number $q=2\pi/d$. To appreciate the meaning of the order parameter

$$\langle cQ\rangle=\langle\cos(qR_Z)Q(\Omega)\rangle$$

it is relevant to note that $Q(\Omega)$ has come out as[14]

$$Q(\Omega)=y_{Y'}z_{Z'}=\cos\phi\cos\psi\cos\theta-\sin\phi\sin\psi\cos^2\theta\ , \tag{6}$$

where $y_{Y'}=\cos\phi\cos\psi-\sin\phi\sin\psi\cos\theta$ and $z_{Z'}=\cos\theta$ are the direction cosines of the molecular y (z) axis with respect to the macroscopic Y' (Z') axis; the Z' axis is along $\hat{\mathbf{n}}$ and the Y' is perpendicular to $\hat{\mathbf{n}}$ in the plane of $\hat{\mathbf{v}}$ and $\hat{\mathbf{n}}$; cf. Fig. 1.

At this stage we are in a position to consider the points at issue. The first point is that the tilt angle ω introduced as the characteristic parameter for the smectic-C phase is determined by the order parameter $\langle cQ\rangle$.[14] Indeed, it may be seen from Eqs. (5) and (3) that minimization of the averaged mean field $\langle V\rangle$ with respect to ω yields

$$\sin\omega\propto\Gamma\Delta\langle cQ\rangle\ . \tag{7}$$

By the mere definition of $Q(\Omega)$, cf. Eq. (6) and Fig. 1, it is obvious that a nonzero value of $\langle cQ\rangle$, or of the tilt ω, requires that the symmetry of the smectic-C phase is confined to a twofold rotation around the X axis perpendicular to $\hat{\mathbf{v}}$ and $\hat{\mathbf{n}}$, a reflection with respect to the plane of $\hat{\mathbf{v}}$ and $\hat{\mathbf{n}}$ and the inversion. This restricted symmetry corresponds to the monoclinic symmetry first assigned to the smectic-C phase by Meyer.

The second point is the specific consequence for the smectic-C phase as compared with the nematic phase when the anisotropic molecules constituting the phase are also chiral. The fact that the lack of a mirror plane and inversion center on a molecular level eliminates the mirror and inversion symmetry on a macroscopic level has been considered before[2–4] and will not be discussed. It is, however, essential to consider the actual molecular configuration in connection with chirality. One could of course try to study and classify all possible conformations of such molecules consistent with the more or less hindered rotations around covalent bonds and other specific intramolecular interactions to find the most probable configuration compatible with a nonvanishing chirality.[15] Such detailed analysis,[5–8] though essential for the understanding of the activity of each specific molecular compound, is beyond the scope of this paper and not relevant for the argument. Indeed, it suffices to recognizes that the effective chiral configuration of a molecule with respect to an asymmetric substituted carbon atom is in fact a system of at least two dipoles 1 and 2 at a distance r_{12} such that not only $\mathbf{p}_1\cdot\mathbf{p}_2$ but also $(\mathbf{p}_1\times\mathbf{p}_2)\cdot\mathbf{r}_{12}$ is nonzero; this picture is reminiscent of the classic theories and descriptions of the optical rotatory power.[16,17] In order to make the molecular depicted in Fig. 2(a) chiral, it is then necessary and sufficient to rotate one of the dipoles out of the *yz* plane, or equivalently to attach to the molecule a dipole directed along the *x* axis, making $(\mathbf{p}_1\times\mathbf{p}_2)\cdot\mathbf{r}_{12}=p_x q_{yz}$ nonzero; cf. Fig. 2(b). This model is quite different from previous models,[18,19] which describe chiral molecules as molecules with just one single dipole. This manifestation of chirality on a molecular level leads in the smectic-*C* phase inevitably to a molecular dipole p_x, effective on a macroscopic level, that is $p_X=p_x\langle c x_X\rangle\neq 0$. Indeed, the existence of the *C* phase due to the mutual coupling of the quadrupole components Γ and Δ requires a nonzero $\langle c y_{Y'} z_{Z'}\rangle$; this implies that $\langle c x_X\rangle$ is zero nonzero. To illustrate this point we note that $x_X=\cos\phi\cos\psi\cos\theta-\sin\phi\sin\psi$, that is $x_X=y_{Y'}z_{Z'}-\sin\phi\sin\psi\sin^2\theta$; cf. Eq. (6).

Thus we find that the macroscopic polarization in each layer, which is directed along the local symmetry axis, can be written as

$$P_X=\rho p_x(\langle cQ\rangle-\langle c\sin\phi\sin\psi\sin^2\theta\rangle)=\rho p_x\langle cQ\rangle\ , \tag{8}$$

where ρ is the number density N/V and p_x the effective molecular dipole along the *x* axis; since it is not essential for the argument, we have disregarded the term $\langle c\sin\phi\sin\psi\sin^2\theta\rangle$, which, in view of the almost perfect orientational order in the smectic-*C* phase, can be expected to be vanishingly small. Equations (7) and (8) show that the connection between P_X and ω found experimentally is due to their relation with the order parameter $\langle cQ\rangle$, which below the smectic-*A*–smectic-*C* phase transition temperature T_{AC} varies as $(T_{AC}-T)^{1/2}$. Equation (8) also shows that the maximum obtainable value of P_X is apart from p_x limited by the actual value of $\langle cQ\rangle$. Maximization of P_X therefore requires a molecular configuration in which not only p_x but also Γ and Δ are optimum, the latter two to optimize the coupling of the molecules with the layered tilted structure.

In conclusion, we have shown that the coupling of a chiral molecule, depicted as an asymmetric three-dimensional system of coupled dipoles, to the monoclinic environment of the smectic-*C* phase in terms of the molecular interaction that gives rise to the tilt of the director in the *C* phase leads inevitably to a macroscopic polarization in each layer of the *C* phase, twisted or not.

---

*Deceased.

[1] E. Priestly, P. J. Wotjowicz, and Sheng Ping, *Introduction to Liquid Crystals* (Plenum, New York, 1975).

[2] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris) **36**, L69 (1975).

[3] R. B. Meyer, Mol. Cryst. Liq. Cryst. **40**, 33 (1977).

[4] G. W. Gray and D. G. MacDonnel, Mol. Cryst. Liq. Cryst. **34**, L211 (1977).

[5] J. W. Goodby and T. M. Leslie, Mol. Cryst. Liq. Cryst. **110**, 175 (1984).

[6] J. W. Goodby, E. Chin, T. M. Leslie, J. M. Geary, and J. S. Patel, J. Am. Chem. Soc. **108**, 4729 (1986).

[7] J. W. Goodby and E. Chin, J. Am. Chem. Soc. **108**, 4736 (1986).

[8] D. M. Walba, S. C. Slater, W. N. Thurmes, N. A. Clark, M. A. Handschy, and F. Supon, J. Am. Chem. Soc. **108**, 5210 (1986).

[9] G. Chilaya and L. Lisetski, Mol. Cryst. Liq. Cryst. **140**, 243 (1986).

[10] H. Kimura, M. Hosino, and H. Nakano, J. Phys. (Paris) Colloq. **40**, C3-174 (1979); J. Phys. Soc. Jpn. **51**, 1584 (1982).

[11] B. W. v. d. Meer, G. Vertogen, and H. Schroder, in *The Molecular Physics of Liquid Crystals,* edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979).

[12] W. J. A. Goossens, Mol. Cryst. Liq. Cryst. **12**, 237 (1971); J. Phys. (Paris) Colloq. **40**, C3-159 (1979).

[13] W. J. A. Goossens, Liq. Cryst. **1**, 521 (1986).

[14] W. J. A. Goossens, Europhys. Lett. **3**, 341 (1987); Mol. Cryst. Liq. Cryst. **150b**, 419 (1987).

[15] J. W. Brewster, J. Am. Chem. Soc. **81**, 5475 (1959).

[16] T. Martin Lowry, *Optical Rotatory Power* (Dover, New York, 1964).

[17] D. J. Caldwell and H. Eyring, *The Theory of Optical Activity* (Wiley, New York, 1971).

[18] R. G. Priest, J. Chem. Phys. **65**, 408 (1976).

[19] M. A. Osipov and S. A. Pikin, Mol. Cryst. Liq. Cryst. **103**, 57 (1983).