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Generalization of Meyer’s ferroelectricity to cholesteric phase: electroclinic coupling and prediction of a new ferrocholesteric phase

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Abstract. — We present a generalization of Meyer’s theory of the trilinear coupling between the smectic layers, the tilt angle of the optical axis with respect to the layer normal and the electric polarization which accounts for the spontaneous ferroelectricity in smectic C* liquid crystals. This coupling allows for the description of the electroclinic effect, i.e. the appearance of a polarization and a tilt angle induced by an external electric field in smectic C*, smectic A and N* (cholesteric) phases. A new « ferrocholesteric » phase is expected between C* and N* phases when the local order is smectic C*-like with a small but non-zero polarization. Eventually, a comparison is made with experimental data available in N* phase.

1. Introduction.

In 1975, Meyer [1] used a general symmetry argument to show that in smectic phases made of chiral molecules and belonging to local $C_2$ symmetry group, a spontaneous polarization would develop as soon as the average molecular direction $\mathbf{n}$ is not parallel to the layer normal $\mathbf{q}$. The direction of this polarization is the so-called $C_2$ symmetry axis which is the common normal to $\mathbf{n}$ and $\mathbf{q}$. The purpose of this paper is to show that the same symmetry argument which is known to hold in the SmC* [1] and in the SmA phase in the presence of an electric field (i.e. electroclinic coupling) [2] is also valid in the fluid N* phase when one applies an electric field
normal to the director. One finds, within the framework of mean-field approximation that describes [3-5] the smectic A to smectic C* phase transition, that the inclusion of the electroclinic coupling leads to different predictions about the behaviour of the smectic A phase which becomes a low tilt smectic C* phase and the appearance of a polarized induced ferrocholesteric phase in an electric field. Close to a N*AC* triple point, the possibility of such a new ferrocholesteric phase with local smectic C* order is predicted without any applied field.

In the first part we present a mathematical argument that we use throughout the paper in order to build up odd terms in the free energy and apply it to introduce a coupling between the smectic order parameter and the polarization in the Landau free energy; in the next three parts, we develop our predictions about the polarization susceptibility $\chi_R$; we eventually compare them with already published experimental work on the electroclinic effect in cholesteric phase.

2. Mathematical background.

When molecules are chiral (no mirror symmetry), and the local symmetry group is $D_\infty$ or $C_2$ like in N*, SmA or SmC* phases, odd tensors $T_{ijk}$ are allowed (1) so that trilinear couplings like $T_{ijk} U_i V_j W_k$ (with an implied summation over repeated indices) can enter the free energy. These terms can be written in vectorial notation

$$\Delta F = T U \cdot (V \times W).$$

Two of them are well-known in the physics of chiral liquid crystals as they lead to the helicity of the cholesteric and smectic C* phases, they read

$$\Delta F (N*) = \lambda n \cdot (V \times n)$$
$$\Delta F (C*) = \mu c \cdot (V \times c)$$

where $n$ is the director of the cholesteric phase and $c$ the $c$-director of the smectic C* phase [6].

The original remark of Meyer [1] can be translated as leading to a mixed product of the polarization $P$, the director $n$ and the layer normal $q$ (see e.g. Fig. 1) i.e. to a term proportional to the tilt angle $\theta$ and to the component $P_2$ of the polarization parallel to the $C_2$ axis:

$$\Delta F (RBM) = \tilde{t}P \cdot (n \times q) = -tP_2 \theta.$$

This linear coupling has been shown to describe both the proportionality between the spontaneous tilt angle $\theta_s$ and polarization $P_s$ in smectic C* phase [1, 5] and between these same quantities induced by the electroclinic effect in smectic A and C* phases [2-5]. The coupling coefficient noted $t$ [1, 2] or $C$ in other papers [3, 4, 7] is a direct measure of the chirality of the phase as it is zero for a racemic mixture and changes sign from one enantiomer to the other. One of the most spectacular results of the organic chemistry of ferroelectric liquid crystals in recent years has been to increase this coefficient by a factor of more than 100 from the historical DOBAMBC (with $P_s$ a few nC/cm$^2$ [1]) to the record awarding compounds of today ($P_s > 1000$ nC/cm$^2$ [8]). Recently, an electroclinic effect has been reported in N* phase [9-12] with a surprisingly large dispersion of the apparent or computed tilt angles (from $10^{-5}$ to $10^{-2}$ radian) and with no clear connection to Meyer's argument. We now show that this link can be easily established with a suitable choice of the vectors entering the trilinear coupling term. By a straightforward generalization, one finds that a Meyer's expression valid

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(1) Namely the fully antisymmetric Levi-Civita tensor such that $T_{\nu\mu\lambda} = T_{\mu\lambda\nu} = T_{\lambda\nu\mu} = -T_{\nu\lambda\mu} = -T_{\mu\nu\lambda} = -T_{\lambda\mu\nu}$, all other elements vanishing identically.
Fig. 1. — a) Sketch in real space of the director \( \mathbf{n} \), layer normal \( \mathbf{q} \) and polarization \( \mathbf{P} \) which are coupled linearly so that the amplitudes of \( \mathbf{P} \) and of the tilt angle \( \theta \) between \( \mathbf{n} \) and \( \mathbf{q} \) are spontaneously proportional in SmC* phase. The same coupling leads to the proportionality of \( \theta \) and \( \mathbf{P} \) to an external electric field by means of electroclinic effect. b) Smectic wave vectors in reciprocal space, the amplitude of \( q_x = \theta q_z \) is proportional to the polarization.

in the three phases should include the polarization and the density modulations in the directions parallel and normal to the local director:

\[
\Delta F (\text{RBM}) = -\mathcal{C} \mathbf{P} \cdot (\nabla_{\perp} \Psi \times \nabla_{\perp} \Psi^*)
\]

with

\[
\nabla_{\parallel} \Psi = \mathbf{n} (\mathbf{n} \cdot \nabla \Psi)
\]

and

\[
\nabla_{\perp} \Psi = \mathbf{n} \times (\mathbf{n} \times \nabla \Psi).
\]

We consider here that \( \Psi (r) \) is the smectic order parameter [6] with a preferred wave vector \( \mathbf{q} \) determined, in mean-field approximation, by minimization of the free energy with respect to its components \( q_{\parallel} \) parallel to the director and \( q_{\perp} \) normal to it. Under these conditions, \( \Psi \) and \( \nabla_{\parallel} \Psi \) \(( = i q_{\parallel} \Psi \) in the condensed phase) both account for the smectic A density modulation which fluctuates in the N* phase while \( \nabla_{\perp} \Psi \) \(( = i q_{\perp} \Psi \) measures the smectic C type fluctuations in N* and A phases.

3. Consequences of the electroclinic coupling in cholesteric phase.

Let us write down the free energy density of a N* phase close to a smectic one in the presence of an applied electric field \( E \), it will be the sum of the elastic energy of the N* phase \( F_{N*} \), of the fluctuating smectic Landau energy \( F_{Sm} \) and of electrostatic terms involving the polarization and the electric field \( F_{el} \):

\[
F_{N*} = \frac{1}{2} K_1 (\text{div} \mathbf{n})^2 + \frac{1}{2} K_2 (q_0 + \mathbf{n} \cdot (\nabla \times \mathbf{n}))^2 + \frac{1}{2} K_3 (\mathbf{n} \times (\nabla \times \mathbf{n}))^2
\]

\[
F_{Sm} = \frac{1}{2} (\alpha (T - T_0^{AN}) \Psi^2 - C_1 (\nabla_{\parallel} \Psi)^2 + \gamma (T - T_0^{AC})(\nabla_{\perp} \Psi)^2 + D_{ij\ell \ell} \nabla_{ij}^2 \Psi \nabla_{\ell \ell}^2 \Psi^*)
\]

\[
F_{el} = - \mathcal{C} \mathbf{P} \cdot (\nabla_{\parallel} \Psi \times \nabla_{\perp} \Psi^*) - \mathbf{P} \cdot E + \frac{P_{I}}{2} \varepsilon_0 \chi_{\perp}^I + \frac{P_{\perp}}{2} \varepsilon_0 \chi_{\parallel}^I - \frac{1}{2} \varepsilon_{0}^{I I} E_i E_i.
\]
The elastic energy contains as usual a spontaneous twist term that leads [13] to a first order \(N^*\) to A phase transition in order to compensate for the helix unwinding energy of \(K_2 q_0^2/2\) per unit volume. The smectic term shows the two \(\text{would-be}\)-transition temperatures \(T_{AN}^0\) and \(T_{AC}^0\) for the appearance of the SmA or SmC phases while the negative \(-C_1\) coefficient accounts for the spontaneous tendency to build up layers normal to the nematic director [14]. The fourth rank \(D_{ijkl}\) terms which are required for stability, are in principle five in a uniaxial medium but reduce to three in Fourier space [13]. Within the electrostatic term, the polarization \(\mathbf{P}\) represents the amount of permanent molecular dipoles aligned by the applied electric field and by the Meyer’s electroclinic coupling. The susceptibilities \(\varepsilon_\infty = \varepsilon_\infty (1 + \chi_\infty)\) account for electronic or intramolecular polarizabilities.

Then, if the direction of the applied field is from now on assumed to be Ox parallel to the cholesteric axis, as long as there exists a local fluctuation of \(\Psi\), the appearance of a non trivial (i.e. \(\neq \varepsilon_\infty \chi_{\perp} E_x\)) polarization \(\mathbf{P}_{\perp}\) normal to the local director \(\mathbf{n}(\parallel \mathbf{Oz})\) and of a modulation of \(\Psi\) in the \(y\) direction will be energetically favored so that locally:

\[
P_{\perp} = \varepsilon_0 \chi_{\perp} [E_x + \tilde{C} \nabla \Psi \nabla \Psi^*]. \tag{6}
\]

In fact the situation is more involved as this non trivial polarization must be derived by integrating out the thermal fluctuations of \(\Psi\) in the presence of the applied field \(E_x\). It is thus necessary to express the free energy in Fourier space:

\[
\mathcal{F} = \frac{1}{V} \int_V \left( F_{sm} + F_{el} \right) dV =
\]

\[
\frac{1}{2V} \sum_q \left[ \alpha (T - T_{AN}) + \gamma (T - T_{AC}) q_{\perp}^2 - 2 \tilde{C} q_x P_x + 2 D_1 (q_x^2 - q_\perp^2)^2 + D' (q_x^2 - q_\perp^2) q_{\perp}^2 + D_1 q_x^4 \right] \Psi_q \Psi_{-q} - P_x E_x + \frac{P_x^2}{2 \varepsilon_\infty \chi_{\perp}^2} - \frac{1}{2} \varepsilon_\infty \tilde{E}_x^2. \tag{7}
\]

In this expression, \(z\) is the local direction of the optical axis (that may be held fixed in an unwound sample), \(q\) is summed from \(2 \pi/\sqrt{V}\) to \(2 \pi/d\) where \(d\) is a molecular length in the \(\text{Å}\) range, \(T_{AN} = T_{AN}^0 \quad \text{and} \quad T_{AC} = T_{AC}^0\) are the renormalized \(\text{would-be}\) transition temperatures when the \(D_{ijkl}\) terms are taken into account and reduce to \(D_1, D_\perp\) \((> 0)\) and \(D' \quad (D'^2 < D_1 D_\perp)\); eventually, \(q_\perp = 2 \pi/a\) is the preferred wave vector of the smectic density modulation where \(a \approx 30\ \text{Å}\) is the layer thickness.

The integration of the thermal fluctuations of \(\Psi\) yields a uniform polarization \(\mathbf{P}_{\perp} = \varepsilon_0 \chi_{R} E_x\) which susceptibility \(\chi_{R}\) is renormalized and larger than the bare one \(\chi_{\perp}\), moreover the optimum wave vector of the density modulation that will be retained at the \(N^*\) to smectic phase transition is modified. As usual, one can assume \(q_x\) to be given by \(q_x = 2 \pi/a\) while the optimum \(q_\perp\) \((T > T_{AN} > T_{AC})\) is non zero in the \(y\) direction in presence of the applied field along \(x\):

\[
q_\perp = \frac{\varepsilon_0 \chi_{R} \tilde{C} q_x}{\gamma (T - T_{AC})} E_x \tag{8}
\]

\((0, + q_x, + q_\perp)\) and \((0, - q_x, - q_\perp)\) represent in the reciprocal space the coordinates of the maxima of the correlation function \(\langle \Psi_q \Psi_{-q} \rangle\) in \(N^*\) phase (see e.g. Fig. 1). Third consequence, replacing \(q_x\) and \(P_{\perp}\) by their optimum value in (7) leads to an increase of the temperature \(T'\) where the coefficient of \(\Psi_q \Psi_{-q}\) vanishes (i.e. to a displacement of the
transition under field):

\[ T' = T_{AN} + \frac{(\epsilon_0 \chi_R q_6 \hat{C})^2}{\alpha \gamma (T_{AN} - T_{AC})} E_i^2. \]  \hspace{1cm} (9)

So applying an electric field in a cholesteric phase transforms it to a kind of induced ferrocholesteric phase with both a polarization \( P_i = \epsilon_0 \chi_R E_i \) and a tilt angle \( \theta = q_6 / q_s \) (Eq. (8)) proportional to the electric field and sensitive to the proximity of the smectic phase via the renormalized susceptibility \( \chi_R \), as apparently reported in recent experimental work [9-12]. In order to improve these predictions, we will then evaluate the susceptibility \( \chi_R \) in a model where the only consequence of the chirality is the onset of the Meyer term we introduced, neglecting the helicity of the director that leads to cholesteric and TGB [13] phases.

4. Mean field derivation of the susceptibility \( \chi_R \) with smectic fluctuations.

Chen and Lubensky [14] have developed the NAC phase diagram as a function of parameters that correspond in our notations to \(- \gamma (T - T_{AC})\) for \( x \)-axis and \(+ \alpha (T - T_{AN})\) for \( y \)-axis. This diagram is reproduced in figure 2 where the physical paths followed when decreasing the temperature from the nematic phase are straight lines of negative slope starting from the upper left corner \( (T \gg T_{AN} \text{ and } T \gg T_{AC}) \). There are two kinds of behavior depending on \( T_{AN} \) and \( T_{AC} \) (the triple point is reached when \( T_{AC} = T_{AN} \)):

i) if \( T_{AN} > T_{AC} \), one encounters a second order nematic to smectic A phase transition at \( T = T_{AN} \) with wave vector of the smectic modulation at \( q_2 = q_s, q_\perp = 0 \), and a second order smectic A to smectic C phase transition at \( T = T_{AC} \);

ii) if \( T_{AN} < T_{AC} \), then there is a direct second order nematic to smectic C phase transition at \( T = T_{NC} = T_{AC} + 2 \delta^2 - 2 \delta (T_{AC} + \delta^2 - T_{AN})^{1/2} \) where the wave vector at the transition is given by \( q_\perp^2 = \gamma (T_{AC} - T_{NC})/2 \tilde{D}_\perp \) and \( q_2^2 = q_s^2 - \gamma D' (T_{AC} - T_{NC})/2 D_\perp D_\parallel \); in these expressions \( \delta^2 = \alpha D_\perp (1 - D^{\perp^2}/D_\parallel D_\perp) \gamma^2 = \alpha \tilde{D}_\perp / \gamma^2 \).

\[
\begin{align*}
N & \quad \text{ELECTROCLINIC EFFECT IN } N^*, \text{ SmA AND SmC* PHASES} \\
T_{AN} & \quad \text{SmA} \\
T_{AC} & \quad \text{SmC*}
\end{align*}
\]

Fig. 2. — Chen-Lubensky phase diagram in the vicinity of the NAC point. If \( T_{AN} > T_{AC} \), one follows the dashed line when decreasing the temperature from N to A and C phases. If \( T_{AN} < T_{AC} \), then one goes directly from N to C at \( T_{NC} \) (\( T_{AN} < T_{NC} < T_{AC} \)).
We have then to derive the effective susceptibility $\chi_R$ when approaching the N to smectic phase transition from above. For this we will define the effective free energy obtained by integrating out $\Psi_q$ fluctuations in equation (7):

$$f \equiv \frac{F_{\text{eff}}}{V} = -\frac{kT}{V} \ln \text{Tr} \left( e^{-\frac{\mathcal{H}}{kT}} \right)$$

$$= -P_x E_x + \frac{P_x^2}{2 \epsilon_0 \chi_\perp} - \frac{1}{2} \epsilon_\infty E_x^2 + \frac{1}{2} kT \int \frac{d^3q}{(2 \pi)^3} \ln G^{-1}(q, P_x)$$

where

$$G^{-1}(q, P_x) = \alpha (T - T_{AN}) + \gamma (T - T_{AC}) q_\perp^2 - 2 \tilde{\mathcal{C}} q_x q_y P_x +$$

$$+ D_1 (q_x^2 - q_y^2)^2 + 2 D' (q_x^2 - q_y^2) q_\perp^2 + D_\perp q_\perp^4$$

minimizing (10) with respect to $P_x$, yields the equation of state for the polarization:

$$\frac{P_x}{\epsilon_0 \chi_\perp} - E_x - I(P_x) = 0$$

where

$$I(P_x) = kT \int \frac{d^3q}{(2 \pi)^3} \tilde{\mathcal{C}} q_x q_y G(q, P_x).$$

This equation can be solved graphically as shown in figure 3. First in the presence of the applied electric field, one sees that there always exists an intersection of the straight line $(P_x/\epsilon_0 \chi_\perp - E_x)$ with the curve $I(P_x)$. At sufficiently low field, there is a linear relationship $P_x = \epsilon_0 \chi_R E_x$ between the position $P_x$ of the intersection and the value of the field.

Without field, the trivial solution that corresponds to a paraelectric phase yields $P_x = 0$. One may see graphically that this will happen as long as the initial slope of $I(P_x)$ for $P_x = 0$ is smaller than $1/\epsilon_0 \chi_\perp$. On the contrary, i.e. high enough initial slope, one predicts the existence of a ferrocholesteric phase which could be ferroelectric without a fully developed smectic layering (see e.g. Fig. 4).

Fig. 3.—The graphical solution of the equation of state for the polarization $P_x$ is given by the intersection of the straight line $(P_x/\epsilon_0 \chi_\perp - E_x)$ and the integral $I(P_x)$. One easily checks that the solution $P_x \neq 0$ corresponds to a minimum of the effective energy $f$. 
Fig. 4. — a) First kind of ferrocholesteric phase where the layer normal rotates around the cholesteric axis Ox like in a TGB phase [13]. The polarization is always parallel to the axis, this configuration should be retained in the induced ferrocholesteric when the field is applied along Ox as it is assumed in the text.

b) Second possibility where the polarization $P$ (that may require a more involved definition with modulus and phase like the smectic order parameters) rotates together with $n$ while the layer normal $q$ processes making an angle of $\pi/2 - \theta$ with the helix axis.

Quantitatively, equation (11) may be used to compute the effective susceptibility $\chi_R$ in the cholesteric phase. In the linear approximation (i.e. low field without any bias), $E_\perp = P \epsilon_0 \chi_R$ and $I(P_\perp)$ are proportional to $P_\perp$, so that:

$$\frac{1}{\epsilon_0 \chi_R} = \frac{1}{\epsilon_0 \chi_\perp} - 2 \tilde{C}^2 kT \int \frac{d^3q}{(2 \pi)^3} q^2 \bar{q}^2 G^2(q, 0).$$

So, the susceptibility will diverge as soon as the derivative of $I(P_\perp)$ is large enough. Let us now check this by means of a numerical estimate using reasonable values for the coefficients involved in the calculation.

5. Numerical simulation of $\chi_R(T)$ in the vicinity of NAC point.

Estimating first the tilt angle in a smectic C phase at 3 K below the transition gives:

$$\frac{q_\perp}{q_s} = \sqrt{\frac{\gamma(T_{AC} - T)}{2 D_\perp q_s^2}} \approx \frac{1}{8} \Rightarrow \frac{\gamma}{q_s^2} \approx \frac{D_\perp}{100}.$$

Using now X-rays scattering results [15, 16] in the vicinity of a nematic to smectic A phase transition, to evaluate $G^{-1}(q)$ leads to:

$$G^{-1}(q, 0) \sim \alpha' \left( \frac{T - T_{AN}}{T_{AN}} \right)^\gamma (1 + \xi_1^2(q_z - q_s)^2 + \xi_\perp^2 q_\perp^2)$$
estimating roughly that \( \alpha (T - T_{AN}) = \alpha' [(T - T_{AN})/T_{AN}]^y \) at \( T = T_{AN} + 3 \text{ K} \), and using \( \gamma' \approx 2 \nu_1 \approx 2 \nu_\perp \approx 1.3 \); \( \xi_0^0 q_s \approx 1 \) and \( \xi_0^0 q_s \approx 0.5 \) \([15]\); one may express all the coefficients as functions of \( D_\perp \) alone: \( \gamma/q_s^2 = D_\perp /100 \), \( \alpha/q_s^4 = D_\perp /3 \, 000 \), \( D_1 = D_\perp /10 \); \( D' \) being arbitrarily taken equal to \( D_\perp /200 \) in the calculation.

Introducing the dimensionless variables \( u = q_s^2 /q_s^2 \) and \( x = q_s /q_s^2 \), equation (12) becomes:

\[
\frac{\varepsilon_0 X_\perp}{\varepsilon_0 X_R} = 1 - N \int_0^\infty u \, du \int_0^\infty x^2 \, dx \, g^2(u, x)
\]

with

\[
g^{-1} = \frac{T - T_{AN}}{30} + 10(x^2 - 1)^2 + 100 \, u^2 + u[T - T_{AC} + x^2 - 1]
\]

and

\[
N = 10^4 \times \frac{\varepsilon_0 X_\perp \, kT \tilde{C}^2}{4 \pi^2 D_\perp^2 \, q_s^2}
\]

eventually, the ratio \( \tilde{C}/D_\perp \) can be extracted from the measurements of the Meyer coefficient \( C \) and the elastic constant \( B_\perp \) in smectic phases \([3, 4]\):

\[
\frac{\tilde{C}}{D_\perp} = \frac{C q_s^2 (T - T_{AC})}{100 B_\perp}
\]

so that with \( \varepsilon_0 = 1/36 \, \pi \times 10^9 \), \( X_\perp = 5 \), \( kT = 4 \times 10^{-21} \text{ J} \), \( q_s = 2 \, \pi /3 \times 10^{-9} \text{ m}^{-1} \), \( C = 3.8 \times 10^7 \) and \( B_\perp / (T - T_{AC}) = 4 \times 10^4 \); one finally estimates the numerical factor \( N \) to be \( 23 \) in equation (13). This means that the integral in this equation has to reach a value of 0.044 in order to describe a cholesteric to ferrocholesteric phase transition.

This integral is evaluated in two steps, first the integration over \( u \) variable can be done analytically then the second integration over \( x \) is made numerically using a Romberg method. The \( T_{AN} \) transition temperature has been held arbitrarily at 310 K while the integral was computed for \( T_{AC} \) ranging from 300 to 330 K and for \( T \) ranging from \( T_{AN} \) (resp. \( T_{NC} \)) + 0.001 to + 10 K. The result of the most divergent integral (that corresponds to the NAC point where \( T_{AN} = T_{AC} \)) is sketched in figure 5. One can see that the maximum value is larger than 0.4 so that the 0.044 limit for a transition to ferrocholesteric phase is reached about 0.1 K before \( T_{NAC} \). One sees more precisely in figure 6 the plot of the integral as a function of \( T_{AC} \) on one axis \((309.4 < T_{AC} < 310.5)\) and of the distance \( \Delta T \) to the nematic-smectic phase transition.

\[\text{Fig. 5.} \quad \text{Plot of the most diverging integral (Eq. (13)) at the NAC point (} T_{AN} = T_{AC} \text{).}\]
transition on the second axis. Then, the cholesteric to ferrocholesteric phase boundary is given by the plane with an elevation of $1/N$ (0.044 in our estimation), the contours 0.15 and 0.3 are represented in figure 6 showing that the extent of the ferrocholesteric phase would be a small closed domain around the NAC point.

Using this simulation, one can predict the behavior of the susceptibility $\chi_R$ from equation (13) in two cases:

i) if one reaches the ferrocholesteric phase, $\chi_R$ will diverge as shown in figure 7;

ii) if not, $\chi_R$ will increase at the N-Smectic transition from $\chi_\perp$ to a finite value.

These predictions are useless if not compared to experiments, so we will now give a short discussion about already reported and possible future experiments.

6. Discussion.

Let us first recall that the calculation has been done under the assumption [17] that the initial NAC phase diagram is the Chen-Lubensky one (without chirality) [14]. We have not taken into account the further refinements of Renn and Lubensky [13], who first showed the displacement of NA and AC phase boundaries due to chirality, neither did we for the AC shift due to Meyer’s term [2, 5] nor for the possible appearance of TGB phases [13] in the same area of the phase diagram. These results have to be joined together in order to place the ferrocholesteric phase in a more realistic phase diagram, with hopefully a greater existence domain.
Nevertheless, the structures sketched in figure 4 may be revealed by some accurate X-rays scattering or polarization sensitive experiments.

Returning to the $\chi_R$ calculation, an immediate check of its validity should use dielectric spectroscopy techniques. A series of experiments done in pure compounds close to a NAC point has been reported by Legrand (Fig. 9 of Ref. [12]) and shows that the dielectric strength $\epsilon = 1 + \chi_R$ increases when approaching the N to A phase transition as expected. The interpretation of optical experiments reported by most other authors [9-11] is more involved. First we do not compute a tilt angle but a dielectric susceptibility, the link between these quantities has to be expressed like in equation (8) which gives the most probable angle between the fluctuating smectic modulation and the optical axis at a given temperature in N phase. Then, assuming that the fluctuating layer normal is fixed in the direction of the optical axis at rest, one may think that the light intensity modulation is directly proportional to $\chi_R$ and that optical experiments are again a proof of Meyer's ferroelectricity in cholesteric phases.

7. Summary.

We have generalized the symmetry argument due to R. B. Meyer which is at the origin of the invention of ferroelectric liquid crystals. We have shown that, as long as three elements meet together, namely smectic layering, tilt of the optical axis and electric polarization, one can derive, in mean-field approximation, a theory of electroclinic coupling that covers cholesteric, smectic A and smectic C* phases and is consistent with experimental results. We have then shown that a spontaneously ferroelectric phase is likely to appear close to a NAC point as long as the Meyer's coupling is strong enough.

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References

[17] One must remark however, that most of the optical measurements have been done with commercial mixtures designed to have a compensated pitch (i.e. diverging for alignment purpose) just above the N to A phase transition. So the N to A phase boundary is not too different from the Chen-Lubensky one.