Dynamics of helicoidal ferroelectric smectic-$\tilde{C}$ liquid crystals

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The order-parameter fluctuation spectrum of a chiral system undergoing a helicoidal ferroelectric smectic-$A \rightarrow$smectic-$\tilde{C}$ phase transition is evaluated both above and below T_c. The transition is produced by a condensation of a coupled tilt-polarization soft mode. The "in-phase" amplitude fluctuations in the tilt and the polarization represent the soft mode of the low-temperature phase, whereas "in-phase" orientational fluctuations represent the Goldstone mode which is recovering the continuous symmetry group broken at T_c.

I. INTRODUCTION

It has been recently shown[1] that the smectic-$\tilde{C}$ liquid crystalline phase is ferroelectric if the molecules are chiral (noncentrosymmetrical) and have a permanent dipole moment transverse to their long molecular axes. In the high-temperature smectic-A phase the molecules are rotating freely around their long axes, which are oriented perpendicular to the smectic layers ($n_z \neq 0$, $n_x = n_y = 0$). The point symmetry of each layer corresponds to the group D_∞. The transition to the ferroelectric smectic-$\tilde{C}$ phase is induced[2] by the two-dimensional representation E_1, and the point symmetry of the layers is reduced to C_2. The order parameters of the transition are the components of the in-plane spontaneous polarization P_x and P_y—describing the ordering of dipoles transverse to the long molecular axes—or the quadratic combinations $\xi_1 = n_z n_x$ and $\xi_2 = n_z n_y$ of the components of the molecular director $\vec{n}$ (describing the orientation of the long molecular axis), which transform as well according to the representation E_1. As far as group theory is concerned, the dipole ordering-type description (P_x, P_y) and the tilt-type description $(n_z n_x, -n_z n_y)$ of this phase transition are equivalent $(P_x = \text{const}\, n_z n_y, P_y = -\text{const}\, n_z n_x)$. In view of the smallness of the observed[3] in-plane spontaneous polarization and the small difference in the smectic-$A \rightarrow$ smectic-$\tilde{C}$ transition temperatures between chiral and nonchiral modifications of the same compounds, it is clear, however, that the tilt of the long molecular axes with respect to the layer normals (which is a consequence of nonzero values of $n_z n_x$ and $n_z n_y$) is the primary and the polarization only a secondary order parameter. The spontaneous polarization is thus induced by the molecular tilt and the ferroelectric smectic-$\tilde{C}$ liquid crystals are improper ferroelectrics.[4]

Indenbom, Pikin, and Loginov have shown[2] that there are no third-order invariants in the expansion of the free energy in terms of the order parameters, so that the transition may be of second order. There is, however, a Lifschitz term[2,4]

$$\xi_1 \frac{\partial \xi_2}{\partial z} - \xi_2 \frac{\partial \xi_1}{\partial z} \tag{1a}$$

or

$$P_x \frac{\partial P_y}{\partial z} - P_y \frac{\partial P_x}{\partial z} \tag{1b}$$

producing a helicoidal distribution of the molecular tilt and the spontaneous polarization as one goes from one smectic layer to another. The periodicity of the helix will be, in the general case, incommensurate with the one-dimensional translational periodicity of the smectic-A phase.

The symmetry properties of the high-temperature phase allow for two types of coupling terms[2] between the molecular tilt and the dipolar ordering: a bilinear "piezoelectriclike" coupling[1,5-8]

$$P_x \xi_2 - P_y \xi_1 \tag{2a}$$

between the polarization and the tilt, which results in

$$P_x = D n_z n_y \tag{2b}$$

and

$$P_y = -D n_z n_x , \tag{2c}$$

and a flexoelectric term[2]

$$P_x \frac{\partial \xi_1}{\partial z} + P_y \frac{\partial \xi_2}{\partial z} , \tag{3a}$$

which results in a proportionality between polarization and the bending and twisting of the molecular director in space,

$$P_x=\tilde{D}\frac{\partial \xi_1}{\partial z}, \quad P_y=\tilde{D}\frac{\partial \xi_2}{\partial z}. \tag{3b}$$

The "flexoelectric" coupling term (3a), which may be more important than the "piezoelectric" term (2a), has so far not been taken into account in phenomenological theories[1,5-8] of ferroelectric liquid crystals.

Previously[5] we discussed the static and dynamic properties of a spatially homogeneous ferroelectric smectic-C system, where the ferroelectric ordering is induced by the bilinear coupling between the polarization and the tilt. It is the purpose of this paper to perform the same analysis for a helicoidal smectic-$\tilde{C}$ ferroelectric, where terms (1a) and (3a) are present in the free-energy expansion.

II. FREE ENERGY

The nonequilibrium free-energy density above a smectic-$A \rightarrow$ smectic-$\tilde{C}$ transition can be for a spatially inhomogeneous system of chiral molecules with nonzero transverse dipole moments written

$$g=g_A+\frac{1}{2}a(\xi_1^2+\xi_2^2)+\frac{1}{4}b(\xi_1^2+\xi_2^2)^2+\Lambda\left(\xi_1\frac{\partial\xi_2}{\partial z}-\xi_2\frac{\partial\xi_1}{\partial z}\right)+\frac{1}{2}K_{33}\left[\left(\frac{\partial\xi_1}{\partial z}\right)^2+\left(\frac{\partial\xi_2}{\partial z}\right)^2\right]+\eta(\xi_1^2+\xi_2^2)\left(\xi_1\frac{\partial\xi_2}{\partial z}-\xi_2\frac{\partial\xi_1}{\partial z}\right)$$
$$+\frac{1}{2\epsilon}(P_x^2+P_y^2)-\mu\left(P_x\frac{\partial\xi_1}{\partial z}+P_y\frac{\partial\xi_2}{\partial z}\right)+C(P_x\xi_2-P_y\xi_1) \tag{4}$$

Here g_A is the free-energy density of the smectic-A phase in the absence of smectic-C fluctuations, $\xi_1=n_z n_x$, $\xi_2=n_z n_y$, $\vec{n}=(n_x,n_y,n_z)$ is the molecular director, K_{33} is an elastic constant, $a=\alpha(T-T_0)$, $b=\text{const}>0$, and all other coefficients are assumed to be constant. The coupling with the density fluctuations has not been taken into account in the above treatment.

The inhomogeneous fluctuations in the smectic-A phase, induced by the Lifschitz term $\Lambda\neq 0$, will generally take on the form of a "right"- ($q>0$) or a "left"- ($q<0$) handed helicoidal wave. Introducing

$$\xi_1(z)=\sum_q (x_q\cos qz-y_q\sin qz), \tag{5a}$$

$$\xi_2(z)=\sum_q (x_q\sin qz+y_q\cos qz), \tag{5b}$$

$$P_x(z)=\sum_q (-u_q\sin qz-v_q\cos qz), \tag{5c}$$

$$P_y(z)=\sum_q (u_q\cos qz-v_q\sin qz), \tag{5d}$$

we find above T_c the harmonic part of the nonequilibrium free energy per unit volume—averaged over the helix—in the q representation as

$$F=\frac{1}{L}\int_0^L \Delta g\, dz$$
$$=\sum_q\left[\left(\frac{1}{2}a+\Lambda q+\frac{1}{2}K_{33}q^2\right)(x_q^2+y_q^2)+\frac{1}{2\epsilon}(u_q^2+v_q^2)\right.$$
$$\left.-\mu q(x_q u_q+y_q v_q)-C(x_q u_q+y_q v_q)\right]. \tag{6}$$

In view of the cylindrical symmetry of the problem, there are no $x_q y_q$, $u_q v_q$, $x_q v_q$, or $u_q y_q$ cross terms above T_c, and we have for each q two degenerate helicoidal "tilt-polarization" waves, which are shifted in phase for $\frac{1}{2}\pi$: $qz\rightarrow qz+\frac{1}{2}\pi$.

The breaking of the cylindrical symmetry below T_c will remove the degeneracy of the above two modes.

III. STABILITY CONDITIONS

The equilibrium values of the polarization and the tilt are obtained from

$$\frac{\partial F}{\partial x_q}=\frac{\partial F}{\partial y_q}=\frac{\partial F}{\partial u_q}=\frac{\partial F}{\partial v_q}=0, \tag{7}$$

where, for $T<T_c$, the quartic terms in the tilt have to be included.

One solution of this system, which corresponds to the smectic-A phase, exists at all temperatures:

$$x_q^{(0)}=y_q^{(0)}=u_q^{(0)}=v_q^{(0)}=0, \tag{8a}$$

whereas another, which corresponds to a helicoidal ferroelectric smectic-C phase with either $P_y\neq 0$ or $P_x\neq 0$ at $z=0$,

$$x_q^{(0)},u_q^{(0)}\neq 0, \quad y_q^{(0)},v_q^{(0)}=0,$$
or
$$y_q^{(0)},v_q^{(0)}\neq 0, \quad x_q^{(0)},u_q^{(0)}=0, \tag{8b}$$

will exist only below a certain temperature T_c.

To see which of these two solutions—(8a) or (8b)—represents a stable state, we have to find out which corresponds to a minimum of the free energy. The condition for the stability of a given solution can be expressed as the requirement that the inverse susceptibility of the system is a positive definite quantity. To perform this calculation, let us look for the stability limit of the high-temperature phase against a helicoidal fluctuation in the tilt angle ϑ and the polarization P of wave vector q:

$$\xi_1 = \delta\vartheta_q \cos qz\,, \quad P_x = -\delta P_q \sin qz\,, \tag{9a}$$

$$\xi_2 = \delta\vartheta_q \sin qz\,, \quad P_y = \delta P_q \cos qz\,. \tag{9b}$$

The harmonic part of the nonequilibrium free energy per unit volume, averaged over the helix, now becomes

$$\begin{aligned} F_q &= \frac{1}{L}\int_0^L \Delta g\, dz \\ &= \tfrac{1}{2}a(\delta\vartheta_q)^2 + \Lambda q(\delta\vartheta_q)^2 + \tfrac{1}{2}K_{33}q^2(\delta\vartheta_q)^2 \\ &\quad + (1/2\epsilon)(\delta P_q)^2 - (\mu q + C)\delta\vartheta_q \delta P_q\,. \end{aligned} \tag{10}$$

The first derivatives are

$$\frac{\partial F_q}{\partial \vartheta_q} = (a + 2\Lambda q + K_{33}q^2)\delta\vartheta_q - (\mu q + C)\delta P_q \tag{11a}$$

and

$$\frac{\partial F_q}{\partial P_q} = \frac{1}{\epsilon}\delta P_q - (\mu q + C)\delta\vartheta_q\,, \tag{11b}$$

and the stability limits of the smectic-A phase are determined by this eigenvalue λ of the inverse susceptibility matrix of the high-temperature phase ($T > T_c$):

$$\begin{vmatrix} \dfrac{\partial^2 F}{\partial \vartheta_q^2} - \lambda, & \dfrac{\partial^2 F}{\partial \vartheta_q \partial P_q} \\ \dfrac{\partial^2 F}{\partial \vartheta_q \partial P_q}, & \dfrac{\partial^2 F}{\partial P_q^2} - \lambda \end{vmatrix} = \begin{vmatrix} a + 2\Lambda q + K_{33}q^2 - \lambda, & -(\mu q + C) \\ -(\mu q + C), & 1/\epsilon - \lambda \end{vmatrix} = 0\,, \tag{12}$$

which first becomes zero on lowering the temperature T.

The two eigenvalues of Eq. (12) are

$$\begin{aligned} \lambda_{1,2} = \tfrac{1}{2}\{&(a + 2\Lambda q + K_{33}q^2 + 1/\epsilon) \\ &\pm [(a + 2\Lambda q + K_{33}q^2 - 1/\epsilon)^2 + 4(\mu q + C)^2]^{1/2}\} \end{aligned} \tag{13}$$

and have to be positive for any q for the high-temperature phase to be stable.

It is clear that for $\epsilon > 0, \lambda_1 > 0$, and that it is λ_2 which determines the stability limit of the smectic-A phase. The temperature at which λ_2 vanishes depends on q:

$$\begin{aligned} T_c(q) = T_0 + (1/\alpha)[&(\epsilon\mu^2 - K_{33})q^2 \\ &+ 2(\epsilon\mu C - \Lambda)q + \epsilon C^2]\,. \end{aligned} \tag{14}$$

The critical wave vector q_0, for which $T_c(q)$ is highest is obtained from

$$\left(\frac{dT_c(q)}{dq}\right)_{q_0} = 0 \tag{15}$$

as

$$q_0 = \frac{\epsilon\mu C - \Lambda}{K_{33} - \epsilon\mu^2}\,. \tag{16}$$

It should be noted that $\epsilon\mu^2 < K_{33}$ and, in view of the magnitude of the coupling constants C and Λ, q_0 is rather small.

The smectic-$A \to$ smectic-$\tilde{C}$ transition temperature is thus obtained as

$$T_c(q_0) = T_0 + \frac{1}{\alpha}\left(\epsilon C^2 + \frac{(\epsilon\mu C - \Lambda)^2}{K_{33} - \epsilon\mu^2}\right) \tag{17}$$

and is always higher than T_0. The difference between $T_c(q_0)$ and T_0 measures the effect of the coupling of the tilt to the in-plane polarization. Below this temperature, ϑ_0 and P_0 are different from zero. For $\eta = 0$, the pitch of the helix and q_0 are temperature independent and we find

$$P_0 = \epsilon(\mu q_0 + C)\vartheta_0\,, \quad T < T_c \tag{18a}$$

and

$$\vartheta_0^2 = (\alpha/b)(T_c - T)\,, \quad T < T_c\,. \tag{18b}$$

Thus we find the equilibrium values of our order parameters as

$$\xi_1^{(0)} = \vartheta_0 \cos(q_0 z)\,, \quad P_x^{(0)} = -P_0 \sin(q_0 z)\,, \tag{19a}$$

$$\xi_2^{(0)} = \vartheta_0 \sin(q_0 z)\,, \quad P_y^{(0)} = P_0 \cos(q_0 z)\,. \tag{19b}$$

For $\eta \neq 0$, the pitch of the helix and q_0 will be temperature dependent:

$$\begin{aligned} q_0(T) = \frac{1}{3}\Bigg\{ &q_0(T_c) - \frac{2b}{\eta} + \Bigg[4\left(q_0(T_c) + \frac{b}{\eta}\right)^2 \\ &- \frac{3\alpha(T_c - T)}{K_{33} - \mu^2\epsilon}\Bigg]^{1/2}\Bigg\}\,, \end{aligned} \tag{19c}$$

where $q_0(T_c)$ is given by Eq. (16). The relation between P_0 and ϑ_0 as given by expression (18a) is still valid, though in view of $q_0 = q_0(T)$ the temperature dependence of these two quantities will not be exactly the same.

In the following we shall put $\eta = 0$.

IV. DYNAMIC PROPERTIES

A. $T > T_c$

Neglecting inertial terms, we get the Landau-Khalatnikov equations of motion as

$$\frac{d\xi_1}{dt} = -\Gamma_1 \frac{\partial F}{\partial \xi_1}, \quad \frac{d\xi_2}{dt} = -\Gamma_1 \frac{\partial F}{\partial \xi_2}, \tag{20a}$$

$$\frac{dP_x}{dt} = -\Gamma_2 \frac{\partial F}{\partial P_x}, \quad \frac{dP_y}{dt} = -\Gamma_2 \frac{\partial F}{\partial P_y}, \tag{20b}$$

where $F = (1/L)\int_0^L g\,dz$ and the kinetic coefficients Γ_1 and Γ_2 vary only weakly with temperature. Expressing ξ_1, ξ_2, P_x, and P_y in terms of "amplitude" $\delta\vartheta_1 \parallel \vartheta_0$, $\delta P_1 \parallel P_0$ and "orientational" $\delta\vartheta_2 \perp \vartheta_0$, $\delta P_2 \perp P_0$ fluctuations,

$$\xi_1(t) = \vartheta_0 \cos(qz) + \delta\vartheta_1(t)\cos(qz) - \delta\vartheta_2(t)\sin(qz), \tag{21a}$$

$$\xi_2(t) = \vartheta_0 \sin(qz) + \delta\vartheta_1(t)\sin(qz) + \delta\vartheta_2(t)\cos(qz), \tag{21b}$$

$$P_x(t) = -P_0 \sin(qz) - \delta P_1(t)\sin(qz) - \delta P_2(t)\cos(qz), \tag{21c}$$

$$P_y(t) = P_0 \cos(qz) + \delta P_1(t)\cos(qz) - \delta P_2(t)\sin(qz), \tag{21d}$$

and linearizing the above system, we see that for $T > T_c$ (where $\vartheta_0 = P_0 = 0$) the "amplitude" and "orientational" fluctuations are uncoupled for all q vectors and are degenerate.

In this case we can use expressions (9a) and (9b), and the linearized equations (20a) and (20b) simplify to

$$\frac{1}{\tau}(\delta\vartheta_q) = \Gamma_1 \frac{\partial F_q}{\partial \vartheta_q}, \tag{22a}$$

$$\frac{1}{\tau}(\delta P_q) = \Gamma_2 \frac{\partial F_q}{\partial P_q}, \tag{22b}$$

where F_q is given by expression (10). The two (doubly degenerate) solutions $(1/\tau)_\pm$ of the above system, describing the exponential approach of the fluctuations in the tilt angle and the polarization to equilibrium, are

$$(1/\tau)_\pm = \tfrac{1}{2}\big(\left[\Gamma_1(a + 2\Lambda q + K_{33}q^2) + \Gamma_2(1/\epsilon)\right] \pm \{\left[\Gamma_1(a + 2\Lambda q + K_{33}q^2) - \Gamma_2(1/\epsilon)\right]^2 + 4\Gamma_1\Gamma_2(\mu q + C)^2\}^{1/2}\big). \tag{23}$$

For the critical wave vector $q = q_0$ [see Eq. (17)] and $T \to T_c^+$ we find

$$\frac{1}{\tau_-} = \frac{\Gamma_1\Gamma_2 \alpha/\epsilon}{\Gamma_1\epsilon(\mu q_0 + C)^2 + \Gamma_2(1/\epsilon)}(T - T_c), \quad T > T_c \tag{24a}$$

and

$$\frac{1}{\tau_+} = \Gamma_1\epsilon(\mu q_0 + C)^2 + \Gamma_2\frac{1}{\epsilon}, \quad T > T_c. \tag{24b}$$

$1/\tau_-$ is thus the doubly degenerate "soft" and $1/\tau_+$ the doubly degenerate "hard" mode of the smectic-A phase. The eigenvector of $1/\tau_-$ describes the "in-phase" fluctuation in the polarization and the tilt of wave vector q_0,

$$\left(\frac{\delta P}{\delta\vartheta}\right)_{-,\,T=T_c,\,q=q_0} = \epsilon(\mu q_0 + C), \tag{25a}$$

whereas the eigenvector of the "hard" mode $1/\tau_+$

$$\left(\frac{\delta P}{\delta\vartheta}\right)_{+,\,T=T_c,\,q=q_0} = -\frac{\Gamma_2}{\Gamma_1}\frac{1}{\epsilon(\mu q_0 + C)} \tag{25b}$$

describes the "out-of-phase" fluctuations of the same quantities.

The dispersion relations of the two modes, $1/\tau_-$ and $1/\tau_+$, are as well significantly different. For $T = T_c$ and $q \to q_0$ we find for the "soft" mode a "spin-wave-like" dispersion relation:

$$\frac{1}{\tau_-} = -\frac{\Gamma_1\Gamma_2\Lambda}{q_0[\Gamma_1\epsilon^2(\mu q_0 + C)^2 + \Gamma_2]}(q - q_0)^2, \tag{26a}$$

whereas the hard mode is "opticlike":

$$\frac{1}{\tau_+} = \Gamma_2\frac{1}{\epsilon} + \Gamma_1\epsilon(\mu q_0 + C)^2 + \frac{2\Gamma_1(\mu q_0 + C)^2(q - q_0)}{q_0}. \tag{26b}$$

It should be noted that in contrast to the homogeneous case,[5] treated previously, $1/\tau_-$ is finite at $T = T_c$ for $q = 0$, if $q_0 \neq 0$. In the absence of coupling between the polarization and the tilt, the "hard" mode would become the T-independent polarization rotation mode, whereas the "soft" mode would become a pure "tilt" mode.

B. $T < T_c$

In view of the nonzero value of $\vec{P}_0 = (P_x^{(0)}, P_y^{(0)}, 0)$ and $\vec{\vartheta}_0 = (\xi_1^{(0)}, \xi_2^{(0)}, 0)$ [see Eqs. (19a) and (19b)] the symmetry of the high-temperature phase is broken below T_c and the degeneracy between the "amplitude" and "orientational" fluctuations is removed. Inserting expressions (21a)–(21d) for fluctuations $\xi_1(t)$, $\xi_2(t)$, $P_x(t)$, $P_y(t)$ with the critical wave vector q_0 into expression (4) we find

$$\Delta F = \tfrac{1}{2}[2\alpha(T_c - T) + \epsilon(\mu q_0 + C)^2]\delta\vartheta_1^2 + \tfrac{1}{2}\epsilon(\mu q_0 + C)^2\delta\vartheta_2^2 + (1/2\epsilon)(\delta P_1^2 + \delta P_2^2) - (\mu q_0 + C)(\delta P_1\delta\vartheta_1 + \delta P_2\delta\vartheta_2), \tag{27}$$

where we used $\vartheta_0^2 = (\alpha/b)(T_c - T)$ and $P_0 = \epsilon(\mu q_0 + C)\vartheta_0$.

It is clear that for $q = q_0$ the amplitude fluctuations ($\delta\vec{P}_1 \parallel \vec{P}_0$, $\delta\vec{\vartheta}_1 \parallel \vec{\vartheta}_0$) are uncoupled from the orientational fluctuations ($\delta\vec{P}_2 \perp \vec{P}_0$, $\delta\vec{\vartheta}_2 \perp \vec{\vartheta}_0$), so that the 4×4 secular matrix, resulting from Eqs. (20a) and (20b), factorizes into two 2×2 matrices. One of these matrices describes the orientational and the other the amplitude fluctuations. For $q = q_0$, such a factorization does not seem to occur.

The eigenfrequencies of the amplitude fluctuation modes $\delta\vartheta_1$ and δP_1 are obtained as

$$(1/\tau)_{3,4} = \tfrac{1}{2}\big[\Gamma_1[2\alpha(T_c - T) + \epsilon(\mu q_0 + C)^2] + \Gamma_2(1/\epsilon) \pm (\{\Gamma_1[2\alpha(T_c - T) + \epsilon(\mu q_0 + C)^2] - \Gamma_2(1/\epsilon)\}^2 + 4\Gamma_1\Gamma_2(\mu q_0 + C)^2)^{1/2}\big] \tag{28a}$$

for $q = q_0$, $T < T_c$. These frequencies for $q = q_0$ are the same as $(1/\tau)_\pm$ above T_c if only $\alpha(T - T_c)$ is replaced by $2\alpha(T_c - T)$. This is, of course, the usual "molecular-field-approximation" result. The "out-of-phase" amplitude tilt-polarization fluctuation mode is the "hard" mode $(1/\tau_3)$, and the "in-phase" amplitude fluctuation mode is the "soft" mode

$$1/\tau_4(q_0) = 2\Gamma_1\alpha(T_c - T) \tag{28b}$$

which vanishes at $T = T_c^-$.

The eigenfrequencies of the "orientation" fluctuation modes $\delta\vartheta_2$ and δP_2 are, on the other hand, obtained for $q = q_0$ from

$$\begin{vmatrix} \Gamma_1\xi(\mu q_0 + C)^2 - 1/\tau, & -\Gamma_1(\mu q_0 + C) \\ -\Gamma_2(\mu q_0 + C), & (1/\epsilon)\Gamma_2 - 1/\tau \end{vmatrix} = 0 \tag{29}$$

as

$$1/\tau_1 = 0, \quad q = q_0, \quad T < T_c \tag{30a}$$

and

$$1/\tau_2 = \Gamma_1\epsilon(\mu q_0 + C)^2 + (1/\epsilon)\Gamma_2, \quad q = q_0, \quad T < T_c. \tag{30b}$$

The in-phase "orientational" fluctuations in the tilt and the polarization $1/\tau_1$ represent the Goldstone mode of the ferroelectric smectic-$A \to$ smectic-$\tilde{C}$ transition, which tries to recover the continuous symmetry group which has been broken $(D_\infty \to C_2)$ at T_c. The eigenvector of this mode is

$$\left(\frac{\delta P_2}{\delta\vartheta_2}\right)_1 = \epsilon(\mu q_0 + C). \tag{31}$$

It costs zero energy to excite this mode for $q = q_0 = 2\pi/L$, or what is the same for $\lambda = L$ where L is the pitch of the helix, at any temperature below T_c.

The frequency of the "hard" orientational mode $1/\tau_2$ is temperature independent below T_c. Its eigenvector represents the "out-of-phase" orientational fluctuations in the tilt and the polarization:

$$\left(\frac{\delta P_2}{\delta\vartheta_2}\right)_2 = -\frac{\Gamma_2}{\Gamma_1\epsilon(\mu q_0 + C)}. \tag{32}$$

The temperature dependence of the helicoidal order fluctuation modes is presented in Fig. 1 for both $q = q_0$ and $q = 0$. The results for $q = q_0$ are similar to those for $q = 0$ in the homogeneous case,[5] where only the bilinear coupling between the polarization and the tilt was taken into account.

V. DIELECTRIC RESPONSE

If one includes in the equations of motion the terms arising from the coupling of the polarization to a time-varying electric field of wave vector q applied parallel to the smectic planes, we can evaluate the dynamic susceptibility $\chi(\omega, q)$.

For a response to a homogeneous external field, we find above T_c the dynamical susceptibility $\chi(\omega, q = 0)$ of our system as

$$\chi(\omega, q = 0) = \chi_+(\omega) + \chi_-(\omega) \approx \frac{-\Gamma_2}{i\omega - 1/\tau_+(0)} + \frac{-\Gamma_1\epsilon C^2}{i\omega - 1/\tau_-(0)} \tag{33}$$

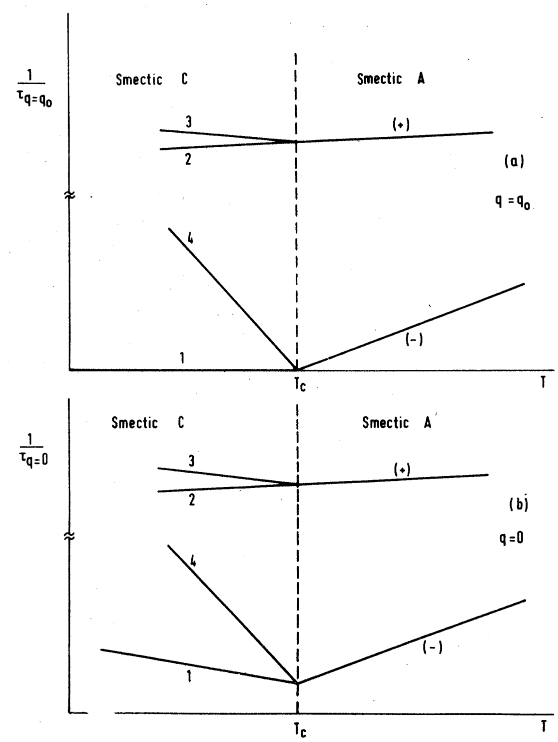

FIG. 1. Temperature dependence of the order fluctuation modes of (a) the critical wave vector $q_0 = 2\pi/L$ and (b) the wave vector $q = 0$ at the helicoidal ferroelectric smectic-$A \to$ smectic-$\tilde{C}$ transition. $1/\tau_1$ represents the Goldstone mode of this transition which recovers the continuous symmetry group broken at T_c $(D_\infty \to C_2)$.

where

$$1/\tau_+(q=0)=\Gamma_2/\epsilon+\Gamma_1\epsilon C^2\,,\quad T>T_c \tag{34a}$$

and

$$1/\tau_-(q=0)=\Gamma_1[\alpha(T-T_c)+(K_{33}-\epsilon\mu^2)q_0^2]\,,\quad T>T_c\,. \tag{34b}$$

The dielectric strength of the "hard" mode is thus obtained as

$$\chi_+(0)=\epsilon\,,\quad T>T_c \tag{35a}$$

and that of the "soft" mode as

$$\chi_-(0)=\frac{\epsilon^2C^2}{\alpha(T-T_c)+(K_{33}-\mu^2\epsilon)q_0^2}\,,\quad T>T_c\,. \tag{35b}$$

The dielectric strength of the soft mode is thus zero, $\chi_-(0)=0$, in the absence ($C=0$) of bilinear coupling between the polarization and the tilt. In contrast to the homogeneous case,[5] there will be, strictly speaking, no Curie-Weiss anomaly in the homogeneous dielectric constant at a helicoidal smectic-$A\to$ smectic-$\tilde{C}$ phase transition, even though $C\neq 0$. In view of the helicoidal distribution of the in-layer polarization in the smectic-$\tilde{C}$ phase, the dielectric response for $T<T_c$ will be given by

$$\chi(\omega,q=0)\propto\{[i\omega-1/\tau_1(0)][i\omega-1/\tau_2(0)]\times[i\omega-1/\tau_3(0)][i\omega-1/\tau_4(0)]\}^{-1}\,,\quad T<T_c\,. \tag{36}$$

At $q=0$,

$$1/\tau_2(0)\simeq 1/\tau_3(0)\simeq 1/\tau_2(q_0)\simeq 1/\tau_3(q_0)\,, \tag{37}$$

whereas both the Goldstone $[1/\tau_1(0)]$ and the soft mode $[1/\tau_4(0)]$ will have nonzero excitation frequencies at $T=T_c$ which will increase with increasing T_c-T in the smectic-C phase (Fig. 1b). The dielectric strength of these two modes, $\chi_1(\omega=0,q=0)$ and $\chi_4(\omega=0,q=0)$, will be zero even below T_c for $C=0$. Dielectric measurements are thus a very sensitive test of the nature of the coupling responsible for the occurence of ferroelectricity in liquid crystals.

The order-parameter fluctuation spectrum derived in this paper could be conveniently measured by laser-light-beating spectroscopy or by dielectric relaxation spectroscopy if $C\neq 0$. No such measurements have been reported so far, though the critical exponent for the fluctuation in the tilt of the molecular director has been recently determined.[9]

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