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SOFT MODES IN FERROELECTRIC LIQUID CRYSTALS

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The order parameter fluctuation spectrum of a chiral system undergoing a helicoidal ferroelectric smectic A → 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. The frequency and the dielectric strength of the Goldstone mode for the wave vector q=0 are determined.

I. Introduction

The smectic $\tilde{C}$ liquid crystalline phase is ferroelectric if the molecules are chiral (non-centrosymmetrical) and have a permanent dipole moment transverse to their long molecular axes[1]. In the high temperature smectic A phase the long axes of the molecules are oriented perpendicular to the smectic layers. 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). In view of the smallness of the observed[3,4] in plane spontaneous polarization and the small difference in the smectic A → smectic $\tilde{C}$ transition temperatures between chiral and non-chiral modifications of the same compound, it is clear that the tilt of the long molecular axes with respect to the layer normals (which is a consequence of a non-zero value of $n_z n_x$ and $n_z n_y$) is the primary order parameter and the polarization only a secondary order parameter. Thus, the spontaneous polarization is induced by the molecular tilt, and the ferroelectric smectic $\tilde{C}$ liquid crystals are improper ferroelectrics[5].

Indenbom, Pikin and Loginov[2] have shown that there are no third order invariants in the expansion of the free energy density in terms of the order parameters so that the transition may be of second order. However, there is a Lifshitz term[5,2] producing a helicoidal distribution of molecular tilt and the spontaneous polarization as one goes from one smectic layer to another.

The symmetry properties of the high temperature phase allow for two types of bilinear coupling terms[2] between the molecular tilt and the dipolar ordering:

A piezoelectric coupling[1,2,6-10]

$$P_x\xi_2 - P_y\xi_1 \tag{1}$$

between the polarization and the tilt, and a flexoelectric term[2]

$$P_x \frac{\partial \xi_1}{\partial z} + P_y \frac{\partial \xi_2}{\partial z} \tag{2}$$

Previously[11] we discussed the static and dynamic properties of a helicoidal smectic $\tilde{C}$ ferroelectric with both the "piezoelectric" and flexoelectric coupling terms present in the free energy density expansion. We have shown that the flexoelectric coupling term qualitatively changes neither the static properties of the system nor the behaviour of the fluctuations with the critical wave vector q_o.

The aim of this paper is to analyse the low frequency dynamical properties of the system for the non-critical wave vector $q = 0$ corresponding to the dielectric measurements. We will show that $q = 0$ relaxational eigenfrequencies and dielectric strengths for $T \leq T_c$ depend strongly on the flexoelectric coupling. Because of this we believe that the analysis of dielectric data could give us the relative strengths of piezoelectric and flexoelectric couplings in ferroelectric liquid crystals.

II. Static properties

The non-equilibrium free energy density can be written in the vicinity of the phase transition between a smectic A → smectic $\tilde{C}$ phase as[2]

$$g(z) = g_A + \frac{1}{2}a(\xi_1^2 + \xi_2^2) + \frac{1}{4}b(\xi_1^2 + \xi_2^2)^2 + \Lambda(\xi_1\frac{\partial\xi_2}{\partial z} - \xi_2\frac{\partial\xi_1}{\partial z}) + $$
$$+ \frac{1}{2}K_{33}|(\frac{\partial\xi_1}{\partial z})^2 + (\frac{\partial\xi_2}{\partial z})^2| + \frac{1}{2\varepsilon}(P_x^2 + P_y^2) -$$
$$- \mu(P_x\frac{\partial\xi_1}{\partial z} + P_y\frac{\partial\xi_2}{\partial z}) + C(P_x\xi_2 - P_y\xi_1) \qquad (3)$$

Here g_A is the free energy density of the smectic A phase in the absence of smectic C fluctuations, K_{33} is an elastic constant, $a = \alpha(T - T_o)$, b = const. > 0 and all other coefficients are assumed to be constant.

The static properties of the model can be obtained[11] by minimizing the free energy $F = \frac{1}{L}\int_o^L g(z)dz$. The spontaneous polarization can be expressed as

$$\xi_1 = \theta_o \cos q_o z \quad , \qquad \xi_2 = \theta_o \sin q_o z \qquad (4a)$$

$$P_x = - P_o \sin q_o z \quad , \qquad P_y = P_o \cos q_o z \qquad (4b)$$

where θ_o and P_o are the absolute values of the spontaneous tilt and polarization which are given by

$$P_o = \varepsilon(\mu q_o + C)\theta_o \qquad (5a)$$

$$\theta_o^2 = \frac{\alpha}{b}(T_c - T) \qquad (5b)$$

for $T < T_c$. Above T_c in the smectic A phase, P_o and Θ_o are equal to zero. The transition temperature T_c is obtained from

$$T_c = T_o + \frac{1}{\alpha} \left| \varepsilon C^2 + \frac{(\varepsilon\mu C - \Lambda)^2}{K_{33} - \varepsilon\mu^2} \right| \qquad (6)$$

and the critical wave vector which determines the pitch of the helix in the smectic $\tilde{C}$ phase is given by

$$q_o = \frac{\varepsilon\mu C - \Lambda}{K_{33} - \varepsilon\mu^2} \qquad (7)$$

and is temperature independent in this approximation.

III. Dynamic properties

$\underline{T > T_c}$. - Neglecting interial terms, we get the Landau--Khalatnikov equations of motion as

$$\frac{d\xi_1}{dt} = - \Gamma_1 \frac{\partial F}{\partial \xi_1} \quad , \quad \frac{d\xi_2}{dt} = - \Gamma_1 \frac{\partial F}{\partial \xi_2} \qquad (8a)$$

$$\frac{dP_x}{dt} = - \Gamma_2 \frac{\partial F}{\partial P_x} \quad , \quad \frac{dP_y}{dt} = - \Gamma_2 \frac{\partial F}{\partial P_y} \qquad (8b)$$

where F is the free energy and the kinetic coefficients for tilt (Γ_1) and for polarization (Γ_2) vary only slightly with temperature. We assume that the polarization frequencies are much higher than the tilt frequencies. Introducing the Fourier transform

$$\xi_1 = \sum_q (\delta\Theta_{1q} \cos qz - \delta\Theta_{2q} \sin qz) \tag{9a}$$

$$\xi_2 = \sum_q (\delta\Theta_{1q} \sin qz + \delta\Theta_{2q} \cos qz) \tag{9b}$$

$$P_x = \sum_q (-\delta P_{1q} \sin qz - \delta P_{2q} \cos qz) \tag{9c}$$

$$P_y = \sum_q (\delta P_{1q} \cos qz - \delta P_{2q} \sin qz) \tag{9d}$$

and linearizing the equations of motion (8) we obtain for each wave vector, q, two - doubly degenerate - solutions for relaxational frequencies $(1/\tau)_{\pm}$ of the above system, which describe the exponential approach of the fluctuations in the tilt angle and in the polarization to the equilibrium[11]. For the critical wave vector $q = q_o$ and $T \to T_c^+$ we find that $1/\tau_- \propto (T - T_c)$ and $1/\tau_+ = \text{const}$. Thus, $1/\tau_-$ is the doubly degenerate "soft" and $1/\tau_+$ the doubly degenerate "hard" mode in the smectic A phase.

For the non-critical wave vector $q = 0$ the relaxational frequency $1/\tau_-$ decreases when approaching T_c from above but has a finite value at T_c. The soft mode frequency $1/\tau_-$ is an even function of $(q - q_o)$ in the absence of the flexoelectric coupling ($\mu = 0$) and the frequency for $q = 0$ is the same as the one for $q = 2q_o$. For $\mu \neq 0$, this symmetry does not exist. It is possible to show that in this case $1/\tau_{-,q=0}$ is always bigger than $1/\tau_{-,q=2q_o}$.

The dielectric response can be calculated adding $- EP_x \cdot \exp(-i\omega t)$ term to the free energy density (eq.3.). Here E and ω are the amplitude and the frequency of the homogeneous external electric field applied in the x-direction. Only $q = 0$

fluctuations contribute to the dielectric susceptibility, which can be expressed as a sum of two Debye terms with characteristic relaxation frequencies $1/\tau_{-,q=0}$ and $1/\tau_{+,q=0}$. The dielectric strength of the low frequency part ($1/\tau_{-,q=0}$) has a soft mode behaviour. It is increasing when approaching T_c from above but does not diverge at T_c, because $q = 0$ is not the critical wave vector. If the piezoelectric coupling is not present ($C = 0$), the soft mode for $q = 0$ does not have any dielectric strength. The flexoelectric coupling does not essentially influence the dielectric response for $T > T_c$.

<u>$T < T_c$</u>. - In the low temperature ferroelectric smectic C phase we transform at first the coordinates ξ_1, ξ_2, P_x and P_y into the new coordinate system rotating with the helix

$$\xi_1(z) = |\theta_o + \delta\theta_1(z)| \cos q_o z - \delta\theta_2(z) \sin q_o z \quad (10a)$$

$$\xi_2(z) = |\theta_o + \delta\theta_1(z)| \sin q_o z + \delta\theta_2(z) \cos q_o z \quad (10b)$$

$$P_x(z) = -|P_o + \delta P_1(z)| \sin q_o z - \delta P_2(z) \cos q_o z \quad (10c)$$

$$P_y(z) = |P_o + \delta P_1(z)| \cos q_o z - \delta P_2(z) \sin q_o z \quad (10d)$$

Here $\delta\theta_1$ and δP_1 represent the "amplitude" fluctuations while $\delta\theta_2$ and δP_2 describe the "orientational" fluctuations. After linearizing the equations of motion (8) and after introducing the Fourier transforms, we obtain a system of coupled equations for the fluctuations with the wave vector k and with the wave vector (- k) in the rotating frame. In the laboratory coordinate system this corresponds to the coupling between the fluctuations with the wave vector $(k + q_o)$ and the ones with $(-k + q_o)$.

For the wave vector $k = 0$, which corresponds to the critical wave vector q_o in the laboratory frame, the equations of motion separate into the "amplitude" fluctuations part and the "orientational" fluctuations part. The two eigenfrequencies of the "amplitude" fluctuations are given by the same expression as $1/\tau_{\pm,q=q_o}$ for $T > T_c$ only replacing $\alpha(T - T_c)$ by $2\alpha(T_c - T)$. The "out of phase" amplitude fluctuation mode is the "hard" mode, and the "in phase" amplitude fluctuation mode is the soft mode which vanishes at T_c. The "in phase" orientational fluctuations represent the Goldstone mode of the transition. The eigenvector of this mode describes the rotation of the helix, and its frequency identically equals zero.

Since we are interested in dielectric response, we have to analyse the equations of motion in the rotating frame for $k = q_o$. This corresponds in the laboratory system to the coupled fluctuations with the wave vector $q = o$ and $q = 2q_o$. Only these degrees of freedom contribute to the dielectric response. For $\mu = 0$ the equations of motion for $k = q_o$ separate again into amplitude and orientational part. The orientational part is temperature independent and consists of the "hard" orientational mode and of the low frequency Goldstone mode with temperature independent frequency $1/\tau_1$ which is finite because of the non--critical wave vector. The dielectric strength of the Goldstone mode is also temperature independent. The low frequency part of the amplitude fluctuations has a soft mode behaviour. Its relaxational frequency decreases and dielectric strength increases when approaching T_c from below. Both stay finite at T_c because of the non-critical wave vector. At the transition temperature we have

$$\frac{1}{\tau_1} = \frac{1}{\tau_2}(T = T_c^-) = \frac{1}{\tau_-}(T = T_c^+, q = 0) = \frac{1}{\tau_-}(T = T_c^+, q = 2q_o) \quad (11)$$

The Goldstone mode dielectric strength (I_1) is temperature independent, while the soft mode strength (I_2) increases with temperature to a finite maximal value at T_c. Only very close to T_c is $I_2 > I_1$.

For $\mu \neq 0$ the equations of motion for $k = q_o$ do not separate into amplitude and orientational part. This means that in contrast to $\mu = 0$ case the elementary excitations have a mixed character. Now, the Goldstone mode frequency is only approximately temperature independent with a small decrease close to T_c.

The dielectric strength of the Goldstone mode (I_1) and its temperature dependence have changed more than its frequency. The intensity of the Goldstone mode can be expressed approximately as

$$I_1 = \frac{A(T_c - T)^2}{\mu^2 + B(T_c - T)^2} \quad (12)$$

where A and B are temperature independent constants. From eq. 12 we see that I_1 is constant for $\mu = 0$, but it shows a critical behaviour for $\mu \neq 0$.

Since the experimental results show this kind of behaviour, we can conclude that the flexoelectric coupling is essential for the understanding of the dielectric response of ferroelectric liquid crystals.

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