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Slow mode of the smectic-\(A\)–smectic-\(C^*_a\) phase transition

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Unusual slow fluctuations as revealed recently by dynamic light scattering close to the Sm-\(A\)–Sm-\(C^*_a\) phase transition in the antiferroelectric liquid crystal 4-(1-methylheptyloxy-carbonyl)phenyl 4’-octyloxy biphenyl-4-carboxylate can be explained by the electrostatic coupling between impurity ions and director fluctuations. Within the vicinity of Sm-\(A\)–Sm-\(C^*_a\) transition, the relaxation rate of the slow mode depends linearly on temperature, but with a different slope in each phase. The square root of its intensity shows a clear Curie-Weiss divergence at the phase transition, which is a direct confirmation of the electrostatic coupling mechanism. [S1063-651X(99)06511-3]

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The study of the phase transitions in chiral smectics is fascinating due to the interesting symmetry changes between their subphases [1–5]. Simply by changing the temperature one can observe in one and the same material all para, ferro, ferri, and antiferroelectric phases and the transitions between them. Among them is the Sm-\(A\)–Sm-\(C^*_a\) phase transition which can be observed in the antiferroelectric liquid crystal 4-(1-methylheptyloxy-carbonyl)phenyl 4’-octyloxy biphenyl-4-carboxylate (MHPOBC) [6]. It has been shown by independent NMR [7] and optical experiments [8,9] that the Sm-\(C^*_a\) phase is a tilted smectic phase. From the very small value of the optical rotation in this phase [8,9], it was conjectured and later proved [10] that Sm-\(C^*_a\) is in fact ferroelectric with a very short helical period. It shows antiferroelectric properties close to the Sm-\(A\) phase and changes to a ferrielectriclike structure on approaching the Sm-\(C^*_a\) phase [11,12].

Isozaki et al. and Sun et al. [13,14] developed the discrete Landau model of the Sm-\(C^*_a\) phase, which was based on competing interactions between the nearest- and next-nearest layers. The dynamics of the Sm-\(C^*_a\) phase was then described by Ćepić and Zekš [15] in a simple discrete phenomenological model in which the next-nearest-neighbor interlayer interactions play an important role. In their model, the order-parameter fluctuation spectrum of the Sm-\(A\) phase consists of a single, doubly degenerate branch of excitations with two minima that appear close to the center and close to the boundary of the Brillouin zone, respectively. They also predicted that the Sm-\(C^*_a\) phase is a tilted, short period ferroelectric phase. The order-parameter fluctuations can therefore be decomposed into the fluctuations of the phase and the magnitude of the tilt angle which are called phase and amplitude modes, respectively.

In a recent work we have reported the first dynamic light-scattering measurements in the vicinity of the Sm-\(A\)–Sm-\(C^*_a\) phase transition [16]. In addition to the

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The director contribution to the free energy density is [15]

\[
\begin{align*}
\frac{f_d}{2} &= \frac{1}{2} a_1 (\delta \xi_x^2 + \delta \xi_y^2) + \frac{1}{2} a_2 (\delta \xi_x^2 \delta \xi_{x+1}^2 + \delta \xi_y^2 \delta \xi_{y+1}^2) \\
&\quad + \frac{1}{8} a_2 (\delta \xi_x^2 \delta \xi_{x+2}^2 + \delta \xi_y^2 \delta \xi_{y+2}^2) \\
&\quad + \frac{1}{2} f (\delta \xi_x^2 \delta \xi_{y-x}^2 - \delta \xi_x^2 \delta \xi_{y+x}^2).
\end{align*}
\]

(2)

Here \(\delta \xi_x^j\) and \(\delta \xi_y^j\) are the components of the order-parameter fluctuations in the \(j\)th layer and \(a = \alpha (T - T_c)\) with \(\alpha > 0\) and \(T_c\) the transition temperature. \(a_1\) and \(a_2\) are coefficients that represent the strength of the achiral bilinear interaction between nearest and the next-nearest neighbors, respectively. The last term describes the chiral interaction.

The free-energy density \(f_c\) of the impurity ions can be calculated from the chemical potential of the ionic impurities:

\[
f_c(r) = \frac{1}{2} k_B T \left( \frac{\delta \xi_c(r)}{c_i} \right)^2.
\]

(3)

Here \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(\delta \xi_c(r)\) is the fluctuation of the local impurity concentration \(c_i\).

The electrical contribution to the free energy \(f_c\) originates from the electrostatic Coulomb interaction of both real charges \(p_i(r)\) (ionic impurities) and fluctuation-induced polarization charges \(\rho_P = -\nabla \cdot \mathbf{P}(r, t)\) and is given by

\[
f_c = \frac{1}{2} \rho(r) V(r).
\]

(4)

Here, \(\rho(r) = \rho_i(r) + \rho_P(r) = \epsilon \delta \xi_c(r) - \nabla \cdot \mathbf{P}\). \(V(r)\) is the local electric potential that satisfies the Poisson equation

\[
\frac{\partial}{\partial x^\alpha} [\epsilon_{\alpha \beta} \partial \delta \xi_c(r)] = -\frac{\rho(r)}{\epsilon_0}.
\]

(5)

\(\epsilon_{\alpha \beta}\) is the dielectric tensor for high frequencies and \(\epsilon_0\) is the permittivity of free space. The spontaneous polarization is \(P(x, y) = -P_0 \xi_x(r) \hat{x} + P_0 \xi_y(r) \hat{y}\) and \(P_0\) is the magnitude of the spontaneous polarization in the Sm-\(C_{a^*}\) phase. Note that \(P_0\) is replaced by the fluctuation-induced polarization \(P_f = C \epsilon\) in the Sm-A phase. \(C\) is the flexoelectric coefficient and \(\epsilon\) is dielectric constant of the Sm-A phase.

Due to the helical symmetry of the Sm-\(C_{a^*}\) phase it is more convenient to expand the fluctuations of the order parameter as helicoidal fluctuations with wave vector \(q = (q_x, q_y, q_z)\)

\[
\delta \xi_x^j(r) = \sum_q \delta \xi_{q_x} e^{iq_x} e^{iq_y} e^{iq_z},
\]

\[
\delta \xi_y^j(r) = \sum_q \delta \xi_{q_x} e^{iq_x} e^{iq_y} e^{iq_z}.
\]

(6)

Here \(d\) is the layer thickness. The total free energy of the fluctuations \(F = \int f(r) d^3r\) with a wave vector \(q\) is then given by \(F(q) = F_d(q) + F_c(q) + F_e(q)\) and can be represented as

\[
F(q) = \frac{1}{2} \sum_q \delta \xi_q \delta \xi_q.
\]

(7)

where \(\delta \xi_q = [\delta \xi_{q_x}, \delta \xi_{q_y}, \delta \xi_{q_z}, \delta \xi_c(q)]\) and \(F_c(q)\) and \(F_e(q)\) are the corresponding Fourier transforms. The dynamical matrix \(D(q)\) is

\[
D(q) = \begin{bmatrix} A & -B & iD \\ -B^* & A' & -iD' \\ -iD & iD' & E \end{bmatrix}
\]

(8)

with the elements

\[
A = a + a_1 e^{iq \cdot d} + \frac{a_2}{4} e^{2iq \cdot d} + \frac{p_0^2}{2 \epsilon_0 q_z^2},
\]

\[
A' = a + a_1 e^{iq \cdot d} + \frac{a_2}{4} e^{2iq \cdot d} + \frac{p_0^2}{2 \epsilon_0 q_z^2},
\]

\[
D = \frac{e P_0 q_z}{2 \epsilon_0 q_y}, \quad D' = \frac{e P_0 q_z}{2 \epsilon_0 q_y},
\]

\[
B = \frac{P_0}{2 \epsilon_0 q_z} + i 2 q y (\sin q_x d), \quad E = \frac{k_B T}{c_1} + \frac{e^2}{2 \epsilon_0 q_z^2}.
\]

(9a)

(9b)

(10)

We use the Landau-Khalatnikov equations for director fluctuations to study the dynamics of the system

\[
\frac{\partial \delta \xi_c(q)}{\partial t} = -\gamma \frac{\partial \delta \xi_q}{\partial t},
\]

(11)

where \(\gamma\) is the rotational viscosity and \(\bar{F}_d\) is the contribution of the director fluctuations to the dynamical tensor. For the dynamics of the ionic impurities we use the continuity equation

\[
\frac{\partial \delta \xi_c(q)}{\partial t} = -\nabla \cdot \mathbf{J}_i = -\nabla \cdot \mathbf{m}_i \mathbf{c} \nabla \left( \frac{\partial F(q)}{\partial \delta \xi_c(q)} \right),
\]

(12)

which can be rewritten in the form of a generalized diffusion equation for charge:

\[
\frac{\partial \bar{F}_c(q)}{\partial \delta \xi_c(q)} = \gamma \frac{\partial \delta \xi_c(q)}{\partial t}, \quad \gamma' = \frac{1}{m_i c \bar{q}^2}.
\]

(13)

Here \(\bar{F}_c\) is the contribution of the ionic impurities to the free energy. Note that the \(m_i\) of the impurity mobility is connected to the ionic mobility \(\mu_i\) in an external electric field by the equation \(\mu_i = e \bar{m}_i\) where \(e\) is the electric charge of an ion.

After considering the time dependence of the fluctuations as \(\delta \xi_q = \delta \xi_{q, 0} \exp(-t/\tau(q))\), the dynamics of the system reduces to a set of coupled linear equations. These have non-trivial solutions if the corresponding determinant vanishes:
To obtain the slow fluctuations we insert the unperturbed D which represent three branches of the excitation spectrum. In the absence of coupling (D = D\* = 0), the determinant [Eq. (14)] gives us two director (phase and amplitude) modes and a single diffusion mode of the ionic impurities:

\[
\begin{vmatrix}
A - \frac{\gamma}{\tau(q)} & B & iD \\
-B^* & A' - \frac{\gamma}{\tau(q)} & -iD' \\
-iD & iD' & E - \frac{\gamma'}{\tau(q)}
\end{vmatrix} = 0.
\]  

For a given wave vector we obtain three relaxation rates, which represent three branches of the excitation spectrum. In the absence of coupling (D = D\* = 0), the determinant [Eq. (14)] gives us two director (phase and amplitude) modes and a single diffusion mode of the ionic impurities:

\[
\tau_{\text{am}} = \frac{1}{2\gamma} \left( a + a_1 e^{i\eta_d} + \frac{a_2}{4} e^{2i\eta_d} + 2 \sin(q_d) \right),
\]
\[
\tau_{\text{ph}} = \frac{1}{2\gamma} \left( a + a_1 e^{i\eta_d} + \frac{a_2}{4} e^{2i\eta_d} - 2 \sin(q_d) \right),
\]
\[
\tau_{\text{ion}} = \frac{1}{m} k_B T q^2 + \frac{e_i^2 m \mu c_1}{2 \epsilon e_0}.
\]  

The intensities of these modes can be calculated from the equipartition theorem. This gives a Curie-Weiss law for the intensity of the soft (amplitude) mode and a slight temperature dependence of the amplitude of the fluctuations of the impurity concentration. It is important to note that in this limit of uncoupled modes, we can observe only the two director modes in a light-scattering experiment because the ionic modes cause no fluctuations of the direction of the optical axis.

The situation is completely different when we include an electrostatic interaction. This has two consequences: (i) the eigenfrequencies are renormalized due to the coupling and (ii), the director and ionic modes become mixed such that the latter become visible in light-scattering experiments.

The general problem of diagonalizing the dynamical matrix is rather cumbersome. We have chosen a perturbation approach because there is a large difference in the relaxation rates: around 1 MHz for the relaxation rates of the soft mode and around 100 Hz for the ionic mode. Furthermore, one can choose the scattering geometry such that only fluctuations in the direction of q_3 can be observed. Therefore, we can safely let q_y = q_x = 0 (and therefore B = D = 0) without losing the generality of the problem. Equation (14) then reduces to

\[
(A - \frac{\gamma}{\tau(q)})[D' - (A' - \frac{\gamma}{\tau(q)})][E - \frac{\gamma'}{\tau(q)}] = 0.
\]  

Now D' is the only coupling coefficient which we assume to be small enough that it can be considered as a perturbation. The unperturbed solutions (D' = 0) are given by

\[
\tau_{\text{am}} = \frac{A}{\gamma}, \quad \tau_{\text{ph}} = \frac{A'}{\gamma}, \quad \tau_{\text{ion}} = \frac{E}{\gamma'}.
\]  

To obtain the slow fluctuations we insert the unperturbed solutions for the director modes into the dynamical equation above [Eq. (16)]. After taking into account (A/\gamma) \approx (E/\gamma') [see Eqs. (9), (10), (14)], we find the perturbed relaxation rate of the ionic impurity mode:

\[
\frac{1}{\tau_{\text{ion}}} = \frac{1}{2} \frac{k_B T \mu c_1^2}{2 \epsilon e_0} - \frac{e_i^2 p_0 d \mu c_1}{4 \epsilon_e e_0 \gamma^0}.
\]  

The dispersion relation for the ionic diffusion shows a finite gap in the limit of small wave vectors, which is characteristic for the Coulomb interaction. The third term in the right-hand side of Eq. (18) gives the correction due to the electrostatic coupling to the director fluctuations. This term is most significant for wave vectors that are parallel to the smectic planes and is proportional to the relaxation time of the first director modes. A similar correction, only with an opposite sign, can be obtained for the fast director modes. Note that as soon as the polarization disappears (i.e., P_0 = 0) the ionic impurity mode is decoupled and unobservable. Note also that for paraelectric systems, like the Sm-A phase, this term is replaced by P_0 = C \epsilon, reflecting the polarizability of this phase.

We have performed the perturbation analysis of the eigenvectors of the fluctuations in a similar way. After a straightforward calculation, we obtain the first-order correction \( \delta \varepsilon^{(1)} \) to the amplitudes of the coupled director-ionic fluctuations:

\[
\delta \varepsilon^{(1)} \approx \frac{D'}{A(T)} |\delta \varepsilon^{(0)}| \approx \frac{1}{\alpha(T-T_c)} |\delta \varepsilon^{(0)}|.
\]  

Note that the Curie-Weiss law for the soft director modes is also reflected in the amplitude of the slow ionic mode. This can be easily understood by remembering that the dielectric susceptibility of the system increases close to the Sm-A - Sm-C_{a*} transition. This results in an increased intensity of the slow ionic mode. One should also note that the intensity of light scattered by this mode \( I \approx (\delta \varepsilon^2) \) is proportional to the inverse square of \( (T - T_c) \).

In our experiments we used 50 \( \mu \)m thick homotropic cells filled with the antiferroelectric liquid crystal MHPOBC. Experiments in MHP8CBC showed similar results. A good homotropic alignment was achieved using silane surfactants and was checked by a polarization microscope. The dynamic light-scattering experiments were performed by measuring the heterodyne autocorrelation functions of the intensity of the scattered light with a multi-tau ALV-5000E autocorrelator. We used a doubled-YAG (\( \lambda = 532 \)nm) laser to expand the experimental range to large scattering wave vectors. The scattering geometry was chosen such that the scattering wave vector remained either close to the plane of the smectic layers (q || q_3) or close to the normal to the smectic layers (q || q_x). Depending on the required measurements. Ordinary polarized light (S polarized) was incident on the sample and extraordinary light (P polarized) was detected. The temperature was controlled with a resolution of 5 mK throughout the experiments. The measured autocorrelation functions of the scattered light intensity were in the heterodyne regime and were then fitted to exponential decay functions. The fit parameters give the amplitude and relaxation rate of the fluctuations in these phases.

Figure 1 shows the critical temperature dependence of the relaxation rate of the soft and slow modes in the Sm-A phase of MHPOBC over a wide temperature range. The slope of
the temperature dependence of the soft mode is 1.6 MHz/K, which is a characteristic value for the soft mode in most ferroelectric liquid crystals like DOBAMBC and CE-8. At $T_c = 396.5$ K, the relaxation rate of the soft mode is close to 3 MHz, which is a clear indication that the experiment was performed at a noncritical wave vector. It is known that for a chiral (helical) system, the relaxation rate of the soft mode at $T_c$ and at a small wave vector is proportional to $\tau^{-1}_{\text{soft}}(T_c, q \approx 0) \approx (K_3 / \gamma) q_c^2$. Here, $K_3$ is the torsional elastic constant and $q_c = 2 \pi / \ell$ is the wave vector of the helix. By taking a typical value for $K_3 / \gamma \approx 3 \times 10^{-6}$ cm$^2$ s$^{-1}$, we obtain an approximate value for the helical period in the Sm-$C_{a*}$ phase $\ell_c \approx 60$ nm, which is indeed a very short helix. The temperature dependence of the relaxation rate of the slow mode far above the transition tends to a saturated value of $\approx 200$ Hz, whereas it nearly critically slows down at the transition. Figure 2 shows the temperature dependence of the relaxation rate of the soft mode close to the Sm-$A$–Sm-$C_{a*}$ phase transition. It can be seen that the relaxation rate of the slow mode has a nearly linear temperature dependence both in the Sm-$A$ and Sm-$C_{a*}$ phase. This is a unique characteristic of these slow fluctuations and can be used to determine the Sm-$A$–Sm-$C_{a*}$ phase transition temperature rather precisely, as illustrated even more clearly in the inset of Fig. 2. The open dots in Fig. 2 show the calculated relaxation rate of the slow mode using the following function:

$$\frac{1}{\tau} = C_1 T + C_2 - C_3 \tau_0^{(0)}(T).$$

Here $\tau_0^{(0)}(T)$ is the measured soft mode relaxation time from Fig. 1 and $C_1$, $C_2$, and $C_3$ are parameters given by [see Eq. (18)]

$$C_1 = \frac{k_B \mu_i}{2 \epsilon_i} q_i^2,$$

$$C_2 = \frac{\epsilon_i \mu_i c_i}{2 e_0 \epsilon_0},$$

$$C_3 = \frac{\epsilon_i \mu_i c_i P_0^2}{4 e_0^2 \epsilon_0^2 \gamma}.$$

One can see that the calculated relaxation times describe the decreasing of the slow relaxation rate with decreasing temperature quite well. Knowing the scattering wave vector $q$, we can calculate the mobility of the impurity ions from $C_1 = 0.54$ s$^{-1}$ K$^{-1}$. If we assume that the ions possess a single elementary charge, the calculated electric mobility is $\mu_i = 8.5 \times 10^{-4}$ m$^2$ V$^{-1}$ s$^{-1}$. This is in excellent agreement with typical electric mobilities reported by other authors [18]. Further, we can use this mobility to obtain an estimate of the ionic concentration of $7 \times 10^{26}$ ions/m$^3$ from $C_2 = 45$ s$^{-1}$. This roughly corresponds to one ion per 10$^7$ liquid crystal molecules, and is of reasonable magnitude. We also calculated the contribution of the first two terms in Eq. (18) for high temperatures. This gives a relaxation rate of 250 Hz, which is very close to the observed high-temperature limit of the slow relaxation rate, shown in Fig. 1. As predicted by theory [Eq. (18)], the third (correction) term vanishes in the high-temperature limit, because the relaxation time of the fast director fluctuations becomes very small.

As a second independent way of checking whether the slow mode indeed originates from the coupling between the ionic and director modes, we analyzed the measured temperature dependence of the intensity of light, scattered by the slow fluctuations. The theory predicts [Eq. (19)] that the inverse square root of the measured scattering intensity is proportional to $(T - T_c)$. This is in contrast to the director soft modes in ferroelectric liquid crystal, where the inverse of the scattering intensity is proportional to $(T - T_c)$. The results are shown in Fig. 3 and are in excellent agreement with the predicted inverse square root dependence. This clearly confirms the origin of the slow fluctuations in the vicinity of the Sm-$A$–Sm-$C_{a*}$: the slow mode arises due to the electrostatic coupling of Brownian ionic motion with the collective excitations of the Sm-$C_{a*}$ order parameter.
the discrete model of the Sm-A-Sm-C*a phase transition [15], taking into account the electrostatic interaction between charges induced by fluctuations of the electric polarization and the impurity ions. These polarization charges originate either from flexoelectric effects in the Sm-A phase or from ferroelectricity in the Sm-C*a phase and are significant in materials with a high spontaneous polarization and a high dielectric susceptibility. These theoretical calculations are confirmed by our dynamic light-scattering measurements.

Due to the coupling to the soft director modes, the relaxation rate of the slow ionic mode is linearly temperature dependent in the vicinity of the Sm-A-Sm-C*a phase transition in both Sm-A and Sm-C*a phases. We have calculated the average mobility of the impurity ions in this system and our results are in good agreement with other experiments. As a final proof, we have presented the nearly Curie-Weiss behavior of the measured intensity of light, scattered by slow ionic modes. This behavior is typical for a noncritical mode, which is linearly coupled with a critical soft mode of the transition and fully supports our theoretical considerations.

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