Ion-director coupling in a ferroelectric liquid crystal

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The coupling between the motion of ionic impurities and the bend-type director distortion in a ferroelectric liquid crystal is examined theoretically. We calculate the relaxation rate of the (fast) director mode to lowest order in the ion concentration. Moreover, we calculate the ratio $K_{fast}(\tau=0)/K(\tau=0)$, where $K(\tau)$ is the amplitude of the temporal autocorrelation function for director fluctuations, τ is the correlation time, and $K_{fast}(\tau)$ is the corresponding value for the quickly decaying component of this quantity. The ratio, which can be measured in a light-scattering experiment, yields the inverse Debye-Hückel screening length κ.

Since their invention in 1975 [1] ferroelectric liquid crystals have played a central role in both the physics of low-symmetry systems and in the technologically important electro-optics industry. In consequence, the behavior of the Goldstone and soft modes in the chiral smectic-C (Sm-C^*) phase has been of particular interest, generating substantial activity on both the experimental and theoretical fronts [2–5]. In a recent paper [6] we showed experimentally that, for a bend-type Goldstone mode, the spontaneous polarization $\mathbf{P}_0$ gives rise to a space charge; the ensuing electrostatic energy adds a contribution to the effective elastic constant B_1^{eff}, thereby resulting in an effectively stiffer system. As noted in this paper, *two* relaxation processes were observed in the light-scattering autocorrelation function: a fast mode dominated by thermally driven director fluctuations, and a much slower mode caused by ionic diffusion. (The slow mode is observable in a depolarized light-scattering experiment because the local director very rapidly reorients in order to establish a $\nabla\cdot\mathbf{P}_0$ to partially screen the ions.) Since relaxation rates for the fast process are of order 1000 times larger than for the slow, the fast mode could effectively be analyzed without regard to ionic motion. Our experiments showed a very nice linear relationship between P_0^2 and this polarization contribution to B_1^{eff}, as predicted by theory, and revealed that the effective elastic constant is, in fact, completely dominated by this polraization contribution; the bare elastic constant B_1^0 of the racemate is much smaller than B_1^{eff}. Nevertheless, despite our neglect of ionic motion, the role of ionic impurities remains an important issue both fundamentally and in electro-optic devices. In earlier light-scattering experiments on free-standing ferroelectric films, for example, director fluctuations had been too rapid for observation of ionic screening [7–9]; on the other hand, ionic impurities completely overwhelm the polarization term in the much slower process of domain-wall formation [10]. In bulk, ionic motion can clearly result in interesting mode-coupling phenomena in the Sm-C^* phase, as witnessed by the existence of the slow relaxation in Ref. [6]. In this paper we theoretically investigate the coupling between the bend-type director mode and charge motion in the bulk. We calculate the screening correction to the fast (primarily Goldstone) contribution to the correlation function, the relative amplitudes of this fast mode and slow ionic diffusion mode(s), and suggest a means of measuring the Debye-Hückel screening length κ^{-1}. With appropriate assumptions about the ionic charge and a relatively simple measurement of electrical conductivity, the result will also yield the average ionic mobility.

Consider a chiral Sm-C^* system with n species of ionic impurities, such that the equilibrium concentration of the ith type of impurity is c_i and the local concentration fluctuation (the difference between the actual concentration and the equilibrium concentration) is $\delta c_i(x)$. The geometry is the same as in Ref. [6] (Fig. 1). In the smectic A phase the molecular director $\mathbf{n}$ is aligned homotropically, parallel to the z axis. In the Sm-C^* phase the molecules tilt by a polar angle θ that precesses azimuthally about the z axis with a pitch P; the local polarization vector $\mathbf{P}_0$, which lies in the x-y plane perpendicular to $\mathbf{n}$, precesses accordingly. A sufficiently large electric field $\mathbf{E}$ applied along the y axis will couple to the ferroelectric polarization, thereby unwinding the helix and producing a monodomain structure with a macroscopic polarization $\mathbf{P}_0$ parallel to $\mathbf{E}$.

We choose a light-scattering geometry such that the
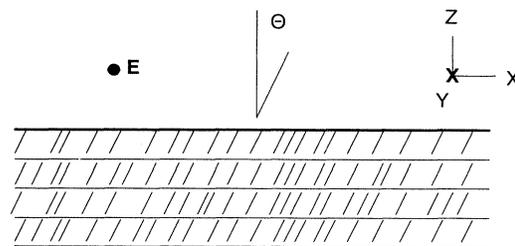
FIG. 1. Schematic representation of sample. Sample cell and smectic layers lie in the x-y plane and molecules tilt by polar angle θ with respect to the z axis.

soft mode is excluded and only the bend-type azimuthal fluctuation, involving the elastic constant B_1, is sampled. In this geometry, which probes variations of the azimuthal director orientation φ along the x axis only, the *bare* distortion Helmholtz free-energy density for small azimuthal angles φ can be written

$$F_b(\vec{x}) = \frac{1}{2}B_1^0\left[\frac{\partial\varphi(\vec{x})}{\partial x}\right]^2 + \frac{1}{2}P_0 E\varphi(\vec{x})^2 \ . \tag{1}$$

Terms involving derivatives of φ with respect to y and z are irrelevant since the light-scattering geometry establishes momentum transfer $\vec{q}=q_x$. Noting that the chemical potential of ionic impurity i is $\mu_i = k_B T \ln c_i = dF_c/dc_i$, the free energy F_c associated with fluctuations of the ionic impurity concentration can be expressed as

$$F_c(\vec{x}) = \frac{1}{2}k_B T \sum_{i=1}^{n}\frac{(\delta c_i(\vec{x}))^2}{c_i} \ , \tag{2}$$

where k_B is the Boltzmann constant and T is the absolute temperature. Note that the indices i and j will always refer to one of the n ionic species. Finally, the electric contribution to the Helmholtz energy, which includes contributions from both polarization charges and ionic impurities, is given by

$$F_e = \frac{1}{2}\rho(\vec{x})V(\vec{x}) \ . \tag{3}$$

V is the overall electric potential which satisfies Poisson's equation $\sum_{\alpha,\beta}\partial_\alpha[\epsilon_{\alpha\beta}\partial_\beta V(\vec{x})] = -4\pi\rho(\vec{x})$, where $\epsilon_{\alpha\beta}$ is the dielectric tensor and ρ is the total charge density:

$$\rho(\vec{x}) = \sum_{i=1}^{n}e_i\delta c_i(\vec{x}) + P_0\frac{\partial\varphi(\vec{x})}{\partial x} \ , \tag{4}$$

where e_i is the charge of ionic species i.

In a light-scattering experiment we measure the autocorrelation function $K_q(\tau)$ [$\equiv\langle\varphi_q(0)\varphi_{-q}(\tau)\rangle$] of the director distortion. In order to compute $K_q(\tau)$ we first calculate the response of φ_q to the time-dependent external field $h_q(t)$:

$$\langle\varphi_q(t)\rangle = \langle\varphi_q(t)\rangle_{\text{equil}} + \int dt'\chi_q(t-t')h_q(t') \ ,$$

where χ_q is the time-dependent susceptibility. From the calculated susceptibility we will then use the fluctuation-dissipation theorem

$$K(\omega) = \int e^{i\omega\tau}K(\tau)d\tau = \frac{2k_B T}{\omega}\chi''(\omega) \ ,$$

where $\chi''(\omega) = \text{Im}\int e^{i\omega t}\chi(t)dt$, to determine the measured quantity $K(\omega)$. Thus introducing the term $-h(x,t)\varphi$ to the Helmholtz potential, we obtain a total free energy

$$F = \int_V d^3\vec{x}\left\{\frac{1}{2}B_1^0\left[\frac{\partial\varphi(\vec{x})}{\partial x}\right]^2 + \frac{1}{2}P_0 E\varphi(\vec{x})^2\right.$$
$$+ \frac{1}{2}k_B T\sum_{i=1}^{n}\frac{[\delta c_i(\vec{x})]^2}{c_i} + \frac{1}{2}\rho(\vec{x})V(\vec{x})$$
$$\left. - h_q(t)e^{-i\vec{q}\cdot\vec{x}}\varphi(\vec{x})\right\} \ . \tag{5}$$

We now introduce the following Fourier transformations:

$$\varphi(\vec{x}) = \int d^3q\,\varphi_q e^{i\vec{q}\cdot\vec{x}}, \quad \delta c_i(\vec{x}) = \int d^3q\,\delta c_i(\vec{q})e^{i\vec{q}\cdot\vec{x}} \ ,$$
$$V(\vec{x}) = \int d^3q\,V_q e^{i\vec{q}\cdot\vec{x}}, \quad \rho(\vec{x}) = \int d^3q\,\rho_q e^{i\vec{q}\cdot\vec{x}} \ .$$

On substituting these expressions into Eq. (5), we obtain after some algebra the Fourier transform of the Helmholtz free energy,

$$F(q) = \frac{1}{2}B_1^0 q_x^2|\varphi_q|^2 + \frac{1}{2}P_0 E|\varphi_q|^2$$
$$+ \frac{1}{2}k_B T\sum_{i=1}^{n}\frac{[\delta c_i(q)]^2}{c_i} + \frac{1}{2}\rho_{-q}V_q - h_q(t)\varphi_q \ , \tag{6}$$

where

$$\rho_q = \sum_{i=1}^{n}e_i\delta c_i(q) + iP_0 q\varphi_q \ . \tag{7}$$

Owing to our choice of geometry, it's understood that $q=q_x$ throughout the remainder of this work. The electrical potential is determined by the Fourier transform of Poisson's equation, viz., $V_q = 4\pi\rho_q/q^2\epsilon$, where $\epsilon\equiv\epsilon_{xx}$. Substituting V_q and ρ_q into Eq. (6), we obtain

$$F(q) = \left[\frac{1}{2}B_1^0 q^2 + \frac{1}{2}P_0 E + \frac{2\pi P_0^2}{\epsilon}\right]|\varphi_q|^2 + \sum_{i=1}^{n}\left[\frac{1}{2}\frac{k_B T}{c_i} + \frac{2\pi}{q^2\epsilon}e_i^2\right]|\delta c_i(q)|^2$$
$$+ \frac{4\pi}{q\epsilon}P_0\sum_{i=1}^{n}e_i\text{Re}[i\delta c_i(-q)\varphi_q] + \frac{4\pi}{q^2\epsilon}\sum_{\substack{i,j=1 \\ i<j}}^{n}e_i e_j\delta c_i(q)\delta c_j(-q) - h_q(t)\varphi_q \ . \tag{8}$$

The third term on the right-hand side of Eq. (8) involves ionic screening of the polarization space-charge buildup due to director fluctuations. The polarization space charge is spatially phase shifted by $\pi/2$ relative to the director distortion [cf. Eq. (7)], and is thus maximum when φ is zero. Thus one also expects a buildup of im-

purity ions at these positions as well, i.e., spatially phase shifted by $\pi/2$ relative to the director fluctuations. This occurs, of course, when $\delta c_i \sim i\varphi$ [cf. Eq. (8)], and is consistent with expectations from the charge induced by a polarization gradient.

We now turn to the dynamics. If we assume a viscosity

η associated with a bend-type director fluctuation, we can write a dynamical equation for φ:

$$\eta \frac{\partial \varphi_q}{\partial t} = -\frac{\partial F(q)}{\partial \varphi_{-q}} . \tag{9}$$

Additionally, we have the condition of charge conservation, viz.,

$$\frac{\partial \delta c_i(q)}{\partial t} = -\vec{\nabla} \cdot \vec{J}_i , \quad i = 1, \ldots, n , \tag{10}$$

where the current $\vec{J}_i$ is given by $\vec{J}_i = m_i c_i \vec{\nabla} [\partial F(q)/\partial \delta c_i(-q)]$, and where m_i is the mobility of the ith ion. Equation (10) can thus be rewritten in the form of a generalized diffusion equation for charge:

$$\frac{\partial \delta c_i(q)}{\partial t} = -m_i c_i q^2 \frac{\partial F(q)}{\partial \delta c_i(-q)}, \quad i = 1, \ldots, n . \tag{11}$$

We now suppose that both $\varphi_q(t)$ and $h_q(t)$ vary as $\exp(i\omega t)$. On substituting Eq. (8) into Eqs. (9) and (11), we find

$$\left[i\eta\omega + B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\epsilon} \right] \varphi_q - i\frac{4\pi}{q\epsilon} P_0 \sum_{i=1}^{n} e_i \delta c_i(q) = h_q(\omega) , \tag{12}$$

$$\frac{4\pi m_i c_i e_i}{\epsilon} \left[iP_0 q \varphi_q + \sum_{j=1}^{n} e_j \delta c_j(q) \right] + (i\omega + m_i k_B T q^2) \delta c_i(q) = 0, \quad i = 1, \ldots, n . \tag{13}$$

Equations (12) and (13) represent a set of $n+1$ linear equations in $n+1$ unknowns. To simplify our task we eliminate the summation over ionic impurity concentration by using Eq. (7) for the total charge density ρ_q. The $n+1$ equations reduce to two equations:

$$(i\eta\omega + B_1^0 q^2 + P_0 E)\varphi_q - i\frac{4\pi}{q\epsilon} P_0 \rho_q = h_q(\omega) \tag{14}$$

and

$$\left\{ \sum_{i=1}^{n} \frac{4\pi m_i c_i e_i^2/\epsilon}{i\omega + m_i k_B T q^2} + 1 \right\} \rho_q - iP_0 q \varphi_q = 0 . \tag{15}$$

$\varphi_q(\omega)$ can easily be calculated from Eqs. (14) and (15):

$$\varphi_q(\omega) = \frac{h_q(\omega)}{i\eta\omega + B_1^0 q^2 + P_0 E + \dfrac{4\pi P_0^2}{\displaystyle\sum_{i=1}^{n} \frac{4\pi m_i c_i e_i^2}{i\omega + m_i k_B T q^2} + \epsilon}} . \tag{16}$$

Equation (16) can be rewritten in terms of the susceptibility $\chi_q(\omega)$, i.e., $\varphi_q = \chi_q(\omega) h_q(\omega)$. Whence,

$$\chi_q(\omega) = \frac{1}{i\eta\omega + B_1^0 q^2 + P_0 E + \dfrac{4\pi P_0^2}{\displaystyle\sum_{i=1}^{n} \frac{4\pi m_i c_i e_i^2}{i\omega + m_i k_B T q^2} + \epsilon}} . \tag{17}$$

We know from experiments that there are at least two relaxation rates: a very fast rate corresponding principally to director fluctuations, and a much slower rate or combination of slower rates corresponding primarily to ion diffusion. (These latter processes are observable by light scattering because the ion density couples to the polarization, and thus to the director orientation.) For n ionic species, there will be n slow modes, all of order $10^2 - 10^4$ times slower than the fast director mode. In order to make a zeroth-order estimate of the fast and slow relaxation rates, we first assume that only one species of ionic impurity is present ($n = 1$). This, of course, is a completely unphysical assumption, since it would imply a sample with a nonfluctuating charge density compensating this single ionic species. Nevertheless, it serves an important pedagogical purpose in that it allows us to easily separate out the fast mode from the one slow mode. By letting the mobility $m_i \to 0$, we can obtain from Eq. (17) a zero-order approximation for the fast mode relaxation rate Γ_{fast} ($\equiv -i\omega_{\text{fast}}$):

$$\Gamma_{\text{fast}} = \frac{1}{\eta} \left[B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\epsilon} \right] . \tag{18}$$

This is the same expression obtained in Ref. [6]. Similarly, by disregarding director fluctuations and the polarization P_0, we can obtain the slow relaxation rate,

$$\Gamma_{\text{slow}} = m_i k_B T q^2 + \frac{4\pi}{\epsilon} e_i^2 m_i c_i . \tag{19}$$

We note that Γ_{slow} is independent of ion concentration.

We now relax the restriction on the number of ionic species n, allowing values $n > 1$. To obtain the first-order correction to Γ_{fast} which comes about from ionic screening, we assume that $i\omega \gg m_i k_B T q^2$. The last term in the denominator of Eq. (17) can then be approximated by

$$\frac{4\pi P_0^2}{\epsilon} \left[1 - \frac{4\pi}{i\omega\epsilon} \sum_{i=1}^{n} m_i c_i e_i^2 \right] .$$

To first order, Γ_{fast} is thus given by the solution of the equation

$$i\eta\omega + B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\epsilon} - \frac{(4\pi P_0)^2}{i\omega\epsilon^2} \sum_{i=1}^{n} m_i c_i e_i^2 = 0 , \tag{20}$$

which corresponds to

$$\Gamma_{\text{fast}} = \frac{1}{\eta} \left[B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\epsilon} \right]$$

$$+ \frac{\frac{(4\pi P_0)^2}{\epsilon^2} \sum_{i=1}^{n} m_i c_i e_1^2}{B_1^0 q^2 + P_0 E + 4\pi P_0^2 / \epsilon} . \tag{21}$$

Equation (21) represents one of the two central results of this work, for it explicitly shows the effects of ionic screening on the relaxation rate of the Goldstone mode.

In a light-scattering experiment we measure the autocorrelation function $K_q(\tau)$ of the director distortion. The relaxation rates of $K_q(\tau)$ will be the same as those for the susceptibility, corresponding to Eqs. (19) and (21). Thus the ionic correction to the fast mode [Eq. (21)] can, in principle, be examined in a light-scattering measurement. Moreover, since we can measure the total *amplitude* of the correlation function at $\tau = 0$, as well as separate out the amplitude of the fast component, we will now calculate these quantities in terms of physical parameters. First, we note that the *susceptibility* can be written as the partial fraction expansion

$$\chi_q(\omega) = \sum_{k=1}^{n+1} \frac{a_k}{\frac{i\omega}{\Gamma_k} + 1} , \tag{22}$$

where a_k is the amplitude of the kth mode comprising the susceptibility and Γ_k is the relaxation rate of this mode. Note that the summation over the index k refers to a summation over *all* modes, the one fast mode and the n slow modes. It follows that

$$K_q(\tau) = \sum_{k=1}^{n+1} k_B T a_k \exp(-\Gamma_k |\tau|) . \tag{23}$$

To obtain the amplitude of the fast mode we make a partial fraction expansion of Eq. (17) and find

$$\frac{1}{a_{\text{fast}}} = \left[B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\epsilon} \right]$$

$$+ \eta \frac{\frac{(4\pi P_0)^2}{\epsilon^2} \sum_{i=1}^{n} m_i c_i e_i^2}{B_1^0 q^2 + P_0 E + 4\pi P_0^2 / \epsilon} . \tag{24}$$

Moreover, from Eqs. (17) and (22) we note that

$$\chi(\omega = 0) = \sum_{k=1}^{n+1} a_k = \frac{1}{B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\sum_{i=1}^{n} \frac{4\pi e_i^2 c_i}{k_B T q^2} + \epsilon}} . \tag{25}$$

Retaining only the zeroth-order terms in Eq. (24), we find

$$\frac{a_{\text{fast}}}{\sum_{k=1}^{n+1} a_k} = \frac{B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2 q^2}{\epsilon(\kappa^2 + q^2)}}{B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\epsilon}} , \tag{26}$$

where the inverse Debye-Hückel screening length κ is

$$\kappa = \left[\frac{4\pi}{\epsilon k_B T} \sum_{i=1}^{n} e_i^2 c_i \right]^{1/2} . \tag{27}$$

We now need to express the ratio of *susceptibility* amplitudes given by Eq. (26) in terms of a measurable quantity derived from the time autocorrelation function $K(\tau)$. The Fourier transform $K(\omega)$ of the temporal autocorrelation function $K(\tau)$ can be expressed in terms of the susceptibility. We see immediately from Eqs. (23) and (26) that

$$\frac{K_{\text{fast}}(\tau = 0)}{K(\tau = 0)} = \frac{k_B T a_{\text{fast}}}{k_B T \sum_{k=1}^{n+1} a_k}$$

$$= \frac{B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2 q^2}{\epsilon(\kappa^2 + q^2)}}{B_1^0 q^2 + P_0 E + \frac{4\pi P_0^2}{\epsilon}} . \tag{28}$$

Equation (28) corresponds to the second major result of this work. In a previous experiment [6] we measured the bare elastic constant B_1^0. Moreover, the polarization P_0 can easily be obtained using a standard capacitance cell. Thus a measurement of the ratio of correlation function amplitudes allows us to determine the inverse Debye-Hückel screening length κ. From the standpoint of applications this is an extremely important quantity for which, to our knowledge, there is no other convenient means of determining. Since our earlier experiments showed that in the material SCE12 (BDH, Ltd.) the P_0^2 term completely dominates the elasticity, the ratio of correlation function amplitudes in Eq. (28) reduces to approximately $q^2/(\kappa^2 + q^2)$ for $q < 10^5$ cm^{-1}. Since we found this ratio to be of order 0.5 for $q \approx 3 \times 10^4$ cm^{-1}, our results would imply a not unreasonable screening length κ^{-1} of several thousand angstroms.

Equation (28) now gives us a way to directly measure κ in ferroelectric materials. Additionally, one could dope the sample with an appropriate salt. A measurement of κ would then yield the equilibrium ionic concentrations c_i [cf. Eq. (27)]. Then, since the conductivity is proportional to the product of the concentration and the ionic mobility, a measurement of the conductivity σ will yield an effective mobility. In principle a detailed analysis of the slow relaxation modes would also permit a separate measurement of the mobilities of different ions when many species are present. However, as we expect these mobilities to be comparable, and the resulting exponential decays difficult to sort out, we do not pursue this possibility here. Owing to a variety of experimental difficulties, there is a paucity of data for either Debye lengths or mobilities [11] in the literature; now we have shown that

these quantities can be determined experimentally in a very straightforward manner.

To summarize, we have examined the coupling between the Goldstone mode and ionic impurities in a ferroelectric liquid crystal. We have calculated the temporal autocorrelation function for director fluctuations and related the result to the Debye-Hückel screening length κ^{-1}, and have determined the relaxation rate of the Goldstone mode to lowest order in ionic concentration.

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