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Director-charge coupling in a ferroelectric liquid crystal: Experiment

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Quasielastic-light-scattering measurements are reported for a chiral smectic-C^* liquid crystal doped with an organic salt. Two classes of relaxation processes are observed: a fast decay corresponding to azimuthal director fluctuations, and several slow decays corresponding to ionic diffusion, which couples to the director through the local polarization. Based on the theory of Lu, Rosenblatt, and Petschek [Phys. Rev. E **47**, 1139 (1993)], the ion concentration and average mobility are obtained.

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The chiral smectic-C^* (Sm-C^*) phase, which is characterized by a spontaneous polarization perpendicular to the molecule and in the plane of the smectic layer [1], can be switched reversibly with an electric field. In consequence, ferroelectric liquid crystals present not only a tremendous variety of fascinating physical phenomena, but offer a number of display applications as well. Particularly important in any study of these materials are effects arising from charges. In ordinary liquid crystals, ionic motion can give rise to a number of interesting and, on occasion, unwanted phenomena. In ferroelectric liquid crystals there are additional effects, which come about from a coupling between the local polarization and charge density. Recently we performed a calculation which couples ion motion with azimuthal director fluctuations [2]. The bendlike Goldstone mode gives rise to a periodic space charge, which is partially screened on very slow time scales by free ions. Similarly, slow variations in the local charge concentration due to ionic diffusion are rapidly screened by reorientation of the liquid-crystalline dipoles, and therefore by reorientation of the Sm-C^* director. In this manner ionic diffusion should be observable in a depolarized dynamic light-scattering experiment: for n ionic species we predicted one fast mode corresponding principally to director fluctuations, and n slow modes corresponding principally to ion diffusion. The time scales depend on the impurity concentrations, mobilities, and wave vector. If the fast mode is many times faster than the slow modes, the Debye-Hückel screening length can in principle be obtained in two ways: from the amplitudes of the corresponding temporal autocorrelation functions in a light-scattering experiment, or from the relaxation rate Γ_{fast} of the fast mode.

In this Rapid Communication we report on light-scattering measurements which quantitatively demonstrate the predicted coupling between ionic and director modes, an effect that has been observed qualitatively by Pindak *et al.* [3]. A ferroelectric liquid crystal was doped with an organic salt and, based upon the results of our mode-coupling theory, we have been able to determine the ionic concentration c_i from a measurement of the amplitudes. (Although a measurement of Γ_{fast} would ultimately provide the same information, Γ_{fast} is only a weak function of c_i and requires a knowledge of the mobility [2]. Moreover, given the experimental scatter associated with linewidth fits, it is clear that the amplitude ratio method is a far more reliable and easier technique to obtain the ionic concentration.) Finally, a measurement of the conductivity allows us to extract an average charge mobility, which is consistent with typical mobilities in liquid crystals determined by other techniques.

To avoid the complexities associated with charge redistribution in an applied electric field, we employed a surface stabilized homogeneous geometry, different from the homeotropic geometry described in Ref. [2]. In the Sm-C^* phase the director tilts by an angle $\theta(T)$ with respect to the layer normal, where T is temperature; in consequence, we tilted the *sample* by an angle θ in the laboratory frame, such that the director was oriented parallel to the $\hat{\mathbf{z}}$ axis (Fig. 1). Light was incident with wave vector $\mathbf{k}_i$ along the $\hat{\mathbf{x}}$ axis, and was polarized along the $\hat{\mathbf{z}}$ axis, perpendicular to the scattering plane $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$. The depolarized scattered light was polarized in the $\hat{\mathbf{x}}$-$\hat{\mathbf{y}}$ (scattering) plane. For small scattering angles the dominant component of scattering wave vector $\mathbf{q}(\equiv\mathbf{k}_f-\mathbf{k}_i)$ lies along

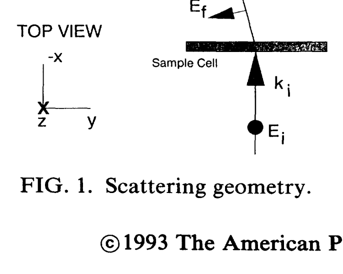

FIG. 1. Scattering geometry.

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the "1" direction used in Ref. [2]. (The "1" direction lies in the $\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$ plane and is parallel to the smectic layers.) In principle we would need to include elastic terms in the free energy associated with the other components of **q** as well, including the cross terms such as $B_{13}q_1q_3$. From previous experiments [4], however, we know that the elastic contribution to the free energy is much smaller than the polarization term, and that all relevant elastic moduli are of the same magnitude [5]. In consequence we are able to use the single elastic constant approximation B. For the case at hand, where the fast relaxation mode is considerably faster than slow modes, we find from Eq. (26) of Ref. [2]

$$R \equiv \frac{a_{\text{fast}}}{\sum_{k=1}^{n+1} a_k} = \frac{Bq^2 + \dfrac{4\pi P_0^2 \frac{q_1^2}{q^2} q^2}{\varepsilon_q(\kappa_q^2+q^2)}}{Bq^2 + \dfrac{4\pi P_0^2 \frac{q_1^2}{q_2}}{\varepsilon_q}} , \tag{1}$$

where the inverse Debye-Hückel screening length κ is

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

The first correction term to Eq. (1) (due to charge mobility) would modify our results by the order 1%, and will be neglected. The experimentally measured quantity R corresponds to the ratio of the fast decay amplitude a_{fast} of the heterodyne autocorrelation function to the sum over *all* decay amplitudes $\sum_{k=1}^{n+1} a_k$, which includes the one fast mode and the n slow modes. P_0 is the temperature-dependent polarization in the Sm-C^* phase, q_1 the bend-like component of **q** along the "1" direction, ε_q the wave-vector-dependent dielectric constant, e_i and c_i the charge and concentration of species i, and k_B Boltzmann's constant. Note that because the scattering geometry differs from Ref. [2], the polarization P_0 in Eq. (1) must now be scaled by the factor q_1^2/q^2, where q_1 is a well-defined function of **q**. Also, no external electric field E is required in the surface stabilized geometry. Thus a light-scattering measurement of the quantity R yields the ion concentration, which, in connection with a measurement of the conductivity, yields an effective mobility.

The sample cells consisted of a pair of indium-tin-oxide (ITO) coated glass slides separated by Mylar spacers of nominal thickness, 3 μm. The slides were treated with nylon 6/6 and rubbed unidirectionally to achieve homogeneous alignment. Three cells were filled with liquid crystal in the isotropic phase by means of capillary action. One cell consisted of the chiral mixture SCE12 (E. Merck), and was used without further purification. The other two cells consisted of SCE12 doped with sodium dodecyl sulfate (SDS), such that the number concentration X of SDS was $X=2.2\times10^{18}$ cm^{-3} in one cell and $X=8.2\times10^{18}$ cm^{-3} in the other cell. A given sample was placed in a light-scattering oven that was temperature controlled to 0.05 K. The cell was tilted with respect to the $\hat{\mathbf{z}}$ axis in the $\hat{\mathbf{y}}$-$\hat{\mathbf{z}}$ plane by $\theta=11°$ (Fig. 1), which corresponds to the molecular tilt angle of SCE12 at 4 °C below the smectic-A-smectic-C^* transition temperature. A small electric field was applied using the ITO electrodes to achieve a uniform monodomain, then removed. Since the cell thickness was approximately 3–5 μm, the sample was unwound and surface stabilized after removal of the field. Thus at $T=T_{AC^*}-4$ °C, the temperature at which the experiment was performed, the director was oriented along the $\hat{\mathbf{z}}$ axis in the laboratory frame (Fig. 1). In practice the sample could be treated as a tilted uniaxial, with ordinary and extraordinary refractive indices of $n_0=1.491$ and $n_e=1.671$ at wavelength $\lambda=5145$ Å [6].

Using our dynamic-light-scattering apparatus, which is described in detail elsewhere [7], we performed series of depolarized vertical-horizontal (VH) experiments at several scattering angles. Exploiting the multi-τ capability of our digital autocorrelator, the first 64 and last 72 channels were set for different acquisition times, thereby allowing us to observe simultaneously decay processes on widely different time scales. Data were collected at scattering angles ranging from 5° to 12° in the laboratory frame, and static sample defects provided a local oscillator for purposes of heterodyning. As expected from the model [2], both fast and slow modes were observed [8]. In Fig. 2 we show the correlation function $K(\tau)$ versus correlator channel, where the acquisition time changes from 10 to 160 μs per channel at channel no. 64. The apparently linear tail of the rapid decay (beginning at approximately channel no. 40) actually corresponds to the early part of the slow relaxation; this behavior is plainly apparent when the acquisition time is identical (at 10 μs) for all 136 correlator channels [4]. To aid the reader and avoid the temporal discontinuity and resulting cusp in $K(\tau)$, we show in Fig. 3 the same data plotted against the logarithm of time.

As there are two monovalent ionic species present

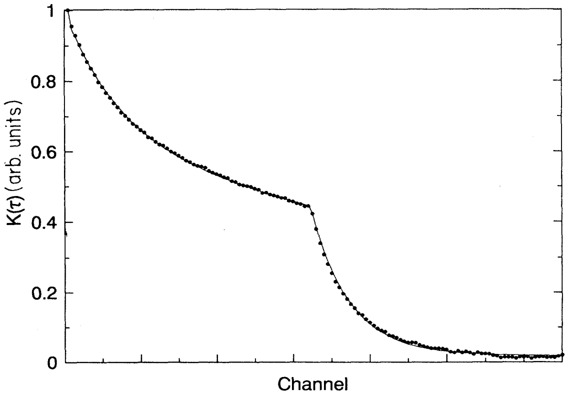

FIG. 2. Typical autocorrelation profile, in this case for the $X=2.2\times10^{18}$ cm^{-3} sample at $q=2.7\times10^4$ cm^{-1}. The autocorrelation function $K_q(\tau)\equiv\langle\varphi_q(0)\varphi_{-q}(\tau)\rangle$, where φ_q is the azimuthal angle of the director. The first 64 channels correspond to an acquisition time of 10 μs per channel, and the last 72 correspond to 160 μs per channel. The double exponential fit is shown, such that $R=0.32$, $\tau_{\text{fast}}(=1/\Gamma_{\text{fast}})=1.4\times10^{-4}$ s, and $\tau_{\text{slow}}^{\text{eff}}=1.6\times10^{-3}$ s.

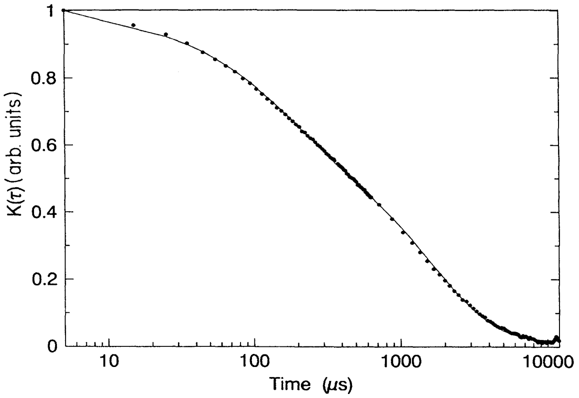

FIG. 3. Same as Fig. 2, except the data is plotted against the logarithm of time.

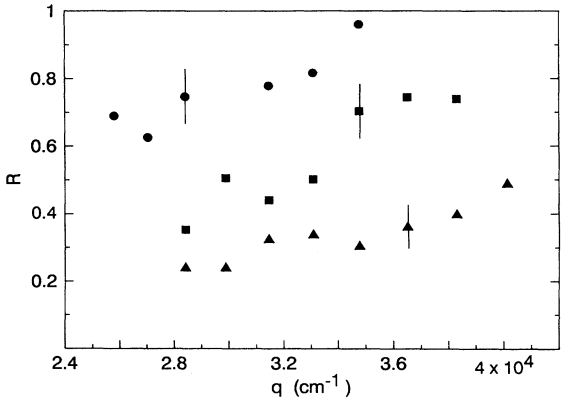

FIG. 4. The quantity R [cf. Eq. (1)] vs scattering wave vector. The triangles ▲ correspond to the $X=8.2\times10^{18}$ cm^{-3} sample, the squares (■) to the $X=2.2\times10^{18}$ cm^{-3} sample, and the circles (●) to the undoped $X=0$ material. Typical error bars are shown.

when SDS dissociates, as well as a small but measurable concentration of impurity species, it is difficult if not impossible to separate out the many slow modes. Therefore, since only *amplitudes* are required for purposes of data analysis, we have chosen to perform a double exponential least-squares fit to the data. This allows us to extract an amplitude and decay time for the fast mode and an effective amplitude $a_{\rm slow}^{\rm eff}$ and decay time for the slow modes. $a_{\rm slow}^{\rm eff}$ is in principle the desired sum of the individual amplitudes of the slow modes $\sum_{k=1}^{n} a_k$, although one might expect a small error from fitting the sum of n decay processes to a single relaxation. It is important to realize that although the decay times obtained from a double exponential fit are very sensitive to small variations in the data, the amplitudes are not. In consequence, the fitted amplitudes are extremely reliable. Figure 4 shows the amplitude ratio R [cf. Eq. (1)] as a function of q for the three samples. The presence of additional charges is expected to increase the amplitude of the slow modes, which corresponds to ionic diffusion, relative to the fast mode; this can be seen in Eq. (1), where R decreases with increasing ionic strength. Figure 4 clearly demonstrates this behavior. One disturbing feature, of course, is the presence of *any* slow modes associated with the non-SDS doped ($X=0$) material. From Eq. (1) we obtain the inverse Debye-Hückel length κ as a function of q; the results are shown in Fig. 5. Taking $\kappa\sim(2.0\pm0.6)\times10^{4}$ cm^{-1} for the $X=0$ material and $\varepsilon\sim6$ [4], we find from Eq. (2) an ionic strength $\sum_{i=1}^{n} e_i^2 c_i \sim (9\pm5)\times10^{-6}$ esu^2 cm^{-3}. If the impurity consists of two monovalent species, the concentration of each species would be approximately 2×10^{13} cm^{-3}. This represents a tiny number fraction, approximately one ion in 10^{8} liquid-crystalline molecules, a figure extremely difficult to separate out in a multicomponent liquid-crystal mixture. For the $X=8.2\times10^{18}$ cm^{-3} material, $\kappa\sim(6\pm1)\times10^{4}$ cm^{-1}, corresponding to a total ionic strength $\sim(8\pm2)\times10^{-5}$ esu^2 cm^{-3}, and therefore to a concentration c_i of each of the anion and cation of 1.5×10^{14} cm^{-3}. Again this is a small concentration and represents dissociation of only two of every 10^{5} SDS molecules. For the $X=2.2\times10^{18}$ cm^{-3} material, with $\kappa\sim(3.5\pm0.8)\times10^{4}$ cm^{-1}, we find an ionic strength of $\sim(2.5\pm1.2)\times10^{-5}$ esu^2 cm^{-3} and a concentration for each ionic species of $\sim3.5\times10^{13}$ cm^{-3}. These results clearly demonstrate the high sensitivity to ion concentration of this probe.

We note in passing that κ appears to be a weakly decreasing function of $|\mathbf{q}|$ (see Fig. 5). There are several possible sources for this behavior. For example, the development of Eq. (1) (see Ref. [2]) assumed that ionic diffusion is isotropic in $\mathbf{q}$, an assumption made by necessity for calculational purposes. A corollary of this approximation is that the inverse Debye-Hückel length κ is also independent of direction aside from the factor ε_q. In reality, however, κ does depend on direction. The q axes in Figs. 4 and 5 correspond to the *magnitude* $|\mathbf{q}|$; for larger $|\mathbf{q}|$ the momentum transfer has a larger component parallel to the smectic layers, thus allowing for anisotropic diffusion and an anisotropic κ. Another effect enters at higher concentrations c_i (and correspondingly larger κ), the polarization term in the numerator Eq. (1) no longer overwhelms the elastic contribution. In consequence, the single elastic constant approximation may break down, especially at larger $|\mathbf{q}|$, giving rise to an elastic contribution in Eq. (1) that depends upon the *direction* of the wave vector. Finally, we have to consider a possible ex-

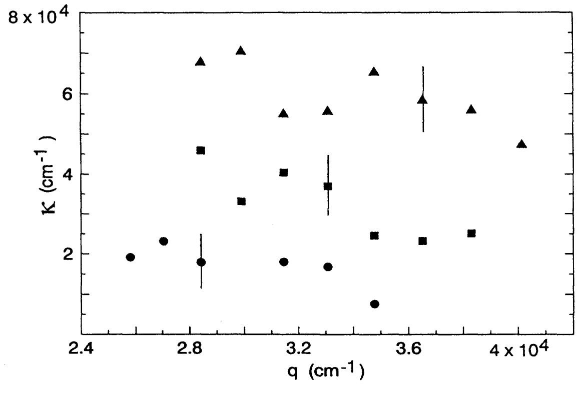

FIG. 5. The inverse Debye-Hückel screening length κ vs scattering wave vector. Symbols are the same as in Fig. 3.

perimental artifact. At larger scattering angles the intensity at the detector may not be a pure heterodyne signal, but may contain a small but observable homodyne component as well. The effect is not large, but may contribute to the behavior in Fig. 5. Despite these issues, however, one should not lose sight of the fact that this evolution in κ is relatively small, and we are able to determine the ionic strength to approximately 25%, well within the correct order of magnitude. Given the small degree of dissociation of SDS and the concommitant tiny ion concentrations, this is no mean feat.

To determine an average mobility, we measured the conductivity of the high concentration $X=8.2\times10^{18}$ cm^{-3} material. The capacitance of an empty cell of well-defined ITO overlap area was measured with a high-resolution, 1-kHz capacitance/loss bridge and found to be $C=36$ pF. The $\pi/2$-out-of-phase resistance of the filled, homogeneously aligned cell just above T_{AC^*} (to avoid the polarization reversal current) was $R=38$ MΩ, from which we derive the conductivity $\sigma=\varepsilon_0/RC$. We find $\sigma\sim6.5\times10^{-9}$ $\Omega^{-1}\,\mathrm{m}^{-1}$, corresponding to 60 s^{-1}. We note that $\sigma=\sum_{i=1}^{n}c_i e_i \mu_i$, where μ_i is the mobility of species i, and we define the effective number averaged mobility $\bar{\mu}\equiv\sum_{i=1}^{n}c_i\mu_i/\sum_{i=1}^{n}c_i$. (Note that the mobility μ defined here differs by a factor of charge e from the mobility m used in Ref. [2], i.e., $\mu=em$.) We thus obtain $\bar{\mu}=\sigma/(e\sum_{i=1}^{n}c_i)$ for monovalent charges, corresponding to $\bar{\mu}\sim3.5\times10^{-4}$ $\mathrm{cm}^3\,\mathrm{esu}^{-1}\,\mathrm{s}^{-1}$ in cgs, or $10^{-10} m^2 V^{-1} s^{-1}$ in SI units. We have obviously overlooked the conductivity anisotropy in this calculation, although for the chosen geometry the error introduced into the mobility by this approximation is well under 10%. Our value for $\bar{\mu}$ is consistent with those obtained for typical materials using a field-reversal and/or time-of-transit technique in a capacitor cell [9,10], giving further credence to our results. We note in passing that in ferroelectric liquid crystals the spontaneous polarization would contribute an extra component to the current in the field-reversal technique, and thus a noninvasive technique such as light scattering must be employed to determine the mobility.

In conclusion, we have demonstrated the existence of a coupling between director and charge motion in ferroelectric liquid crystals. Our light-scattering results are consistent with the theoretical predictions of Ref. [2], revealing that the slow relaxations are due to ionic diffusion and concommitant reorientation of the local molecular polarization, and the fast process is due to partially screened director fluctuations. In addition, we are able to determine the ionic strength of the liquid crystal, as well as a number of averaged mobilities for the charge carriers.

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