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Dynamics of the nematic-electroclinic effect

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The effective response time τ_{eff} of the nematic-electroclinic effect was determined as a function of driving frequency and temperature. Near the nematic–smectic-*A* transition temperature $T_{N\text{-Sm-}A}$, τ_{eff} was found to be a function of driving frequency, indicating the existence of more than one physical process. Several degrees above $T_{N\text{-Sm-}A}$, τ_{eff} was found to be frequency independent up to 100 kHz. At these temperatures, moreover, the effective response times are quite small, of order 100 ns.

In the traditional electroclinic effect,[1,2] chiral molecules in the smectic-*A* phase are subject to an applied electric field **E** parallel to the smectic layers. A polar tilt is obtained, such that the molecules tilt in a plane perpendicular to **E** by an angle proportional to $|\mathbf{E}|$. Recently we discovered[3,4] that smectic layering is not essential for the existence of an electroclinic effect and, in particular, observed such an effect in the liquid-crystalline nematic phase.

In an optical experiment the quantity actually measured is θ, the tilt angle of the principle eigenvector of the optical dielectric tensor $\overleftrightarrow{\epsilon}$. As a function of temperature, we had observed earlier[4] that the electroclinic coefficient $d\theta/dE$ exhibits a cusp at $T_{N\text{-Sm-}A}$ and falls off rapidly with increasing temperature in the nematic phase. Here, $T_{N\text{-Sm-}A}$ is the nematic–smectic-*A* transition temperature. An attempt to fit the critical behavior to a single critical exponent was unsuccessful, however, and we concluded that the apparent pretransitional behavior is sensitive to a number of molecular parameters. In addition, a symmetry-based model for the nematic-electroclinic effect (NECE) was proposed.[3,4] In this model we suggested that at least two tensors are required in order to characterize the orientation of the molecule. In the absence of an electric field the averages of these tensors are codiagonal, owing to rotational invariance about the smectic-*A* layer normal; in the presence of a field E_x, however, rotational symmetry is broken. As a result, the average tensors need not be codiagonal, which may result in off-diagonal elements in $\overleftrightarrow{\epsilon}$, where $\theta \equiv \epsilon_{yz}/(\epsilon_{zz}-\epsilon_{yy})$. We stress that our model is only one of several possible symmetry-based models; in another scheme, for example, optically biaxial smectic-*C* fluctuations are biased by an electric field, giving rise to a nonzero ϵ_{yz}.[5] Given our current understanding, however, there is little reason at this time for one model to be considered preferable to another. Indeed, as our data below suggest, several mechanisms might be operating concomitantly.

The purpose of this paper is to present results for the temporal response of the NECE. By applying an ac electric field and measuring both the in-phase and quadrature (90° out of phase) optical responses, we obtained several results. First, the apparent response time τ_{eff} was found to depend on driving frequency, especially close to $T_{N\text{-Sm-}A}$. Such behavior is indicative of multiple relaxation process, each mechanism having its own characteristic response time. Well above $T_{N\text{-Sm-}A}$, τ_{eff} was found to be independent of frequency, at least up to 100 kHz, the current frequency limit of our apparatus. Finally, in this same temperature region we observed response times of order 100 ns. Since the material used in this study does not have a particularly fast electro-optic response in the smectic phase, we might expect that other materials would have responses significantly faster than 100 ns.

In order to analyze our results, we assume that the system can be described by a Lorentzian with a single relaxation time. This will turn out *not* to be the case, although it serves as a reasonable starting point from which we can develop a better understanding of the dynamics. Thus,

$$\eta\frac{d\theta}{dt}+C^{-1}\theta=E\,, \tag{1}$$

where η is a kinetic coefficient, C is the dc electroclinic coefficient $d\theta/dE$, and E is the applied electric field. For $E=E_0\cos\omega t$, θ is given by

$$\theta=\frac{CE_0}{1+\omega^2\tau^2}(\cos\omega t+\omega\tau\sin\omega t)\,, \tag{2}$$

where the relaxation time $\tau=C\eta$. Thus, by measuring the in-phase component of $d\theta/dE$ and its quadrature component, we can define the quantity

$$R(\omega)\equiv\frac{d\theta/dE|_{\text{in phase}}}{d\theta/dE|_{\text{quad}}}\,. \tag{3}$$

From Eq. (2) we find that $\tau=[\omega R(\omega)]^{-1}$.

If several processes are operating simultaneously, we would need to introduce other relaxation parameters in addition to θ, thus requiring two or more coupled dynamic equations analogous to Eq. (1). Based upon the observation of two dielectric relaxations, in fact, we recently discussed[6] the dynamics of the smectic-*A* electroclinic effect[1,2] in terms of two coupled parameters, the *vector* polarization and the *pseudovector* tilt. Solving the resultant equations (assuming that the only important chiral term is the static coupling between these two parameters), we found two relaxations with different signs in the electroclinic effect. These result in a complex tilt susceptibility $\chi_{\theta E}$ in the smectic-*A* phase which is a linear combination of a slow (s) and fast (f) mode:

$$\chi_{\theta E} \propto \frac{a}{i\omega\tau_s+1} - \frac{A_2 b}{i\omega\tau_f+1} , \tag{4}$$

where a, b, and A_2 are coefficients related to the magnitudes of the two processes. In analogy to Eq. (3), the ratio of the real to imaginary parts of Eq. (4) corresponds to $R(\omega)$, from which an effective relaxation time $\tau_{\text{eff}} = [\omega R(\omega)]^{-1}$ was extracted. Owing to the multiple mechanisms involved, τ_{eff} is a function of frequency. Moreover, owing to the minus sign in Eq. (4), τ_{eff} is larger (i.e., slower) than either of the two individual processes, giving rise to the observed anomaly in the smectic-*A* phase. Note that if, for example, b were to vanish, then Eq. (4) would reduce to Eq. (2) and τ_{eff} would be independent of driving frequency ω.

We studied the mixture SCE12, which was kindly supplied to us by British Drug House, Ltd. through EM Industries and used without further purification. The material was inserted in a cell composed of two glass slides, each partially coated with semitransparent indium tin oxide (ITO, ~20 Ω/□), and separated by brass spacers of nominal thickness 30 μm. The ITO was etched so that the overlap of the conducting region was small, approximately 2×3 mm^2. Moreover, the brass spacer also served as a low-resistance conductor to the ITO capacitor region. In consequence the overall *RC* time constant of the cell was small, and did not affect our results. The slides were coated with nylon 6/6 and rubbed undirectionally to give good parallel alignment, as determined by optical microscopy. Details of temperature control and the optical arrangement are described elsewhere.[3,4] For this particular experiment, the laser was focused to a spot of approximately 75 μm on the sample, thus keeping the temperature differential across the face of the sample to less than 0.002 °C.

Since it has already been established that θ is linear in electric field,[3] and it was verified again for the sample under investigation, $d\theta/dE$ was determined by using two values of applied field at each temperature, typically 1.7×10^5 and 3.4×10^5 V/m. Both electric fields gave nearly identical results, as expected. A two-phase lock-in amplifier was first calibrated by using as its input a very low oscillator voltage and zeroing the quadrature component of the lock-in output. Note that the oscillator was driving the sample simultaneously. The voltage was then increased, and the in-phase and quadrature components of signal from a photodiode were measured by the lock-in amplifier. At each frequency, $d\theta/dE|_{\text{in phase}}$ and $d\theta/dE|_{\text{quad}}$ were taken to be proportional to their respective signals divided by the applied field, and were averaged for the two fields used. According to Eq. (3), $R(\omega)$ was defined as the ratio of $d\theta/dE|_{\text{in phase}}$ to $d\theta/dE|_{\text{quad}}$. Note that, by means of an oscilloscope, no phase shift of the oscillator output relative to its synchronized trigger was observed as a function of voltage.

In order to extract the sample response time τ_{eff} it was necessary to deconvolute τ_{eff} from the response time τ_e of the electronic circuitry, which is dominated by the response of the detector. Using a Pockels cell, we determined τ_e to be $(1.14\pm0.15)\times10^{-7}$ s. Assuming τ_e represents a single exponential decay, it can easily be shown that

$$\tau_{\text{eff}} = \frac{1-R\omega\tau_e}{\omega(R+\omega\tau_e)} . \tag{5}$$

Measurements were first performed at a number of temperatures as a function of driving frequency ω ($\equiv 2\pi\nu$) up to our experimental limit of $\omega = 6.28\times10^5$ s^{-1}, corresponding to $\nu = 100$ kHz. Figure 1 shows the in-phase and quadrature components of $d\theta/dE$ at two temperatures, where the signals were deconvoluted from the detector response in a manner analogous to Eq. (5). The quantity $R(\omega)$ was obtained from the raw data as described above, and the apparent NECE response time τ_{eff} was determined using Eq. (5). τ_{eff} vs ω is shown in Fig. 2 for two of these temperatures, where it is seen that the apparent relaxation times are functions of ω. Closer to $T_{N\text{-Sm-}A}$ moreover, the relative change in τ_{eff} over the observed frequency range is larger than the relative change deeper into the nematic phase. At still higher temperatures the curve becomes even flatter, although experimentally it becomes more difficult to measure τ_{eff} at low frequencies owing to the relatively small size of the quadrature component of the signal. We thus conclude that at least two relaxation processes govern the NECE. In addition, since τ_{eff} is a decreasing function of driving frequency ω, we conclude that the processes must *add,* unlike the behavior observed in the smectic-*A* phase[6] in which the processes compete [see Eq. (4)]. It is not clear at this time, however, how such a crossover can be accomplished at the transition, unless at least two parameters describing local biaxiality (such as the biaxial molecular-orientational distribution[3,4] and the smectic-*C* fluctua-

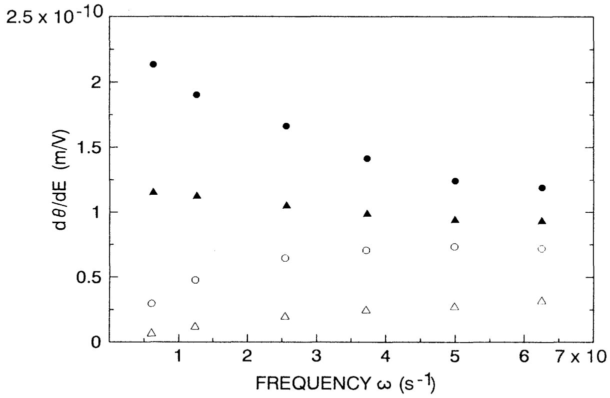

FIG. 1. In-phase and quadrature components of $d\theta/dE$ vs driving frequency ω ($=2\pi\nu$) at $T=80.74$ °C [(●), in phase; (○), quadrature] and at $T=81.08$ °C [(▲), in phase; (△), quadrature]. Error bars are comparable to or smaller than the data points. Note that at the lower temperature, $d\theta/dE|_{\text{quad}}$ seems to reach a maximum in the neighborhood of $\omega \approx 5\times10^5$ s^{-1}, indicating that one (or more) slower process is comparable to our driving frequencies.

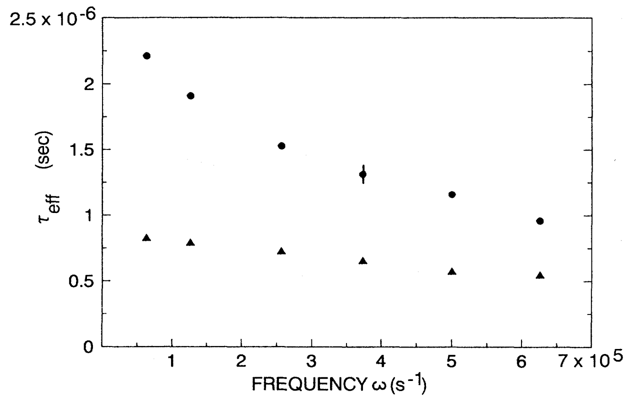

FIG. 2. Apparent relaxation time τ_{eff} vs angular driving frequency ω at $T=80.74\,^{\circ}\mathrm{C}$ (●) and at $T=81.08\,^{\circ}\mathrm{C}$ (▲). Typical error bars are shown.

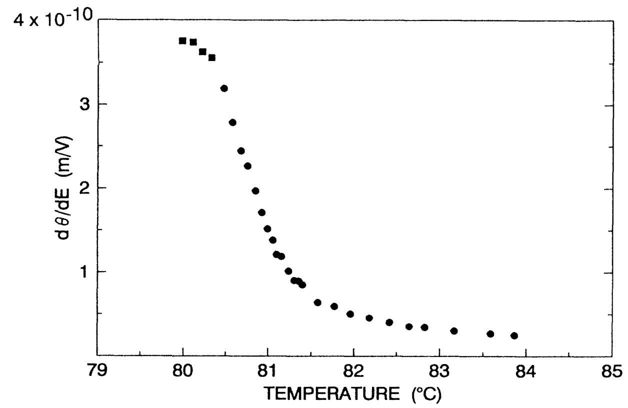

FIG. 3. dc electroclinic coefficient C ($\equiv d\theta/dE$) vs temperature based upon results at $\omega=3.14\times10^4$ s^{-1}. (■) represents points in the smectic-A phase, (●) represents points in the nematic phase, with some uncertainty in the first nematic point.

tions^5) become important above $T_{N\text{-Sm-}A}$. Moreover, for the relaxations of chiral and nonchiral processes in this off-diagonal susceptibility term to add, the *chiral* kinetic coefficients (which, for example, couple tilt and polarization) must be significant. Nevertheless, a necessary consequence of summing the responses is that the apparent relaxation time τ_{eff} must lie between the extremes of the various mechanisms involved. From the behavior of the higher-temperature curve in Fig. 2, one might be tempted to conclude that the faster process is decreasing more rapidly than the slower process on increasing temperature. This conclusion, which may or may not be correct, is not supported by the available data, which is taken over a limited frequency range. All that one can surmise is that the processes become very fast far above $T_{N\text{-Sm-}A}$, such that any evolution in the response time cannot be resolved below $\nu=100$ kHz.

We then performed measurements at many more temperatures at two separate frequencies, $\omega=3.14\times10^4$ s^{-1} ($\nu=5$ kHz) and $\omega=6.28\times10^5$ s^{-1} ($\nu=100$ kHz). At the lower frequency the NECE could easily follow the driving voltage; thus, the in-phase signal was always found to be much larger than the quadrature component, corresponding to $R\gg1\gg\omega\tau_e$. Using the in-phase component of the signal at $\omega=3.14\times10^4$ s^{-1} ($\nu=5$ kHz), along with Eqs. (2)–(4), we determined the magnitude of the dc electroclinic coefficient C as a function of temperature; this is shown in Fig. 3. The squares indicate points which are clearly in the smectic-A phase, although it is not certain whether the first circle above is nematic or smectic A. We note two additional items. First, at 5 kHz, $d\theta/dE|_{\text{in phase}}$ is virtually identical to its dc value. Second, we find that the electroclinic coefficient near $T_{N\text{-Sm-}A}$ approaches the transition with a somewhat shallower slope than observed previously,^{4} where the prior slope was essentially infinite. In order to maintain consistency with previous experiments we have used the remaining material from our original batch of SCE12. This sample had been held at elevated temperatures for several months resulting in some degradation of the sample and an attendant decrease in the transition temperature. Since the pretransitional behavior is very sensitive to molecular properties, such changes in the pretransitional characteristics are not unexpected. The main point of this work, however, is the dynamics of the NECE, and we do not believe that these variations in the pretransitional behavior close to $T_{N\text{-Sm-}A}$ reflect changes which would affect our conclusions.

In addition to the low-frequency measurements, data were also collected at our highest experimentally available frequency, $\omega=6.28\times10^5$ s^{-1} ($\nu=100$ kHz). At this frequency $1/\omega$ is significant relative to the fast NECE response time τ_{eff}, rendering $R(\omega)$ considerably smaller and more easily measurable. Equation (5) was used to determine the effective NECE response time at $\omega=6.28\times10^5$ s^{-1}, which is shown in Fig. 4. Two features should be noted. In the smectic-A phase just below $T_{N\text{-Sm-}A}$ the response time appears to be *increasing* with increasing temperature; this is just the smectic-A anomaly discussed above.^{6} In addition, at temperatures well above the nematic–smectic-A phase transition, response times are quite rapid by most liquid-crystal standards. Presumably, τ_{eff} can be reduced further by appropriate molecular engineering, although this is beyond the scope of the present work.

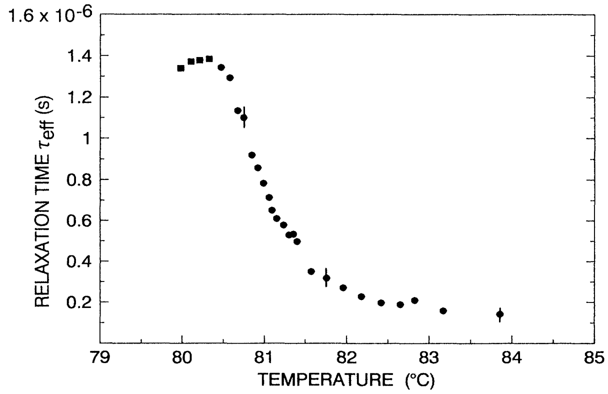

FIG. 4. NECE relaxation time τ_{eff} vs temperature based upon results at $\omega=6.28\times10^5$ s^{-1}. See Fig. 3 for symbols.

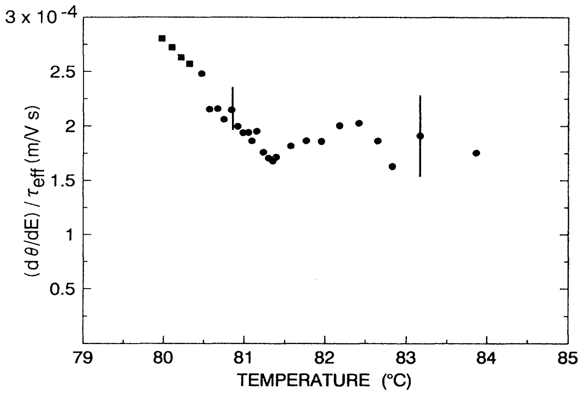

FIG. 5. Ratio of dc electroclinic coefficient C to NECE relaxation time τ_{eff} at $\omega = 6.28 \times 10^5$ s^{-1}.

In Fig. 5 we show the ratio C/τ_{eff} as a function of temperature. (Note that both C and τ_{eff} were extracted simultaneously, thus avoiding problems of sample degradation with time.) This ratio, of course, combines the dc electroclinic coefficient with the effective relaxation time at $\omega = 6.28 \times 10^5$ s^{-1}. If only a single process were involved, excepting experimental scatter the curve would be flat and equal to η^{-1}, the inverse kinetic coefficient. In the nematic phase just above $T_{N\text{-Sm-}A}$ there is an apparent downward trend in this ratio, however, which is another indication of the presence of multiple processes. At higher temperatures the curves does flatten out, although with a large degree of experimental uncertainty. Here the relaxation processes have become so rapid that the driving frequency $\omega = 6.28 \times 10^5$ s^{-1} is effectively dc. In this case, $R \propto \omega^{-1}$ and C/τ_{eff} correspond to some *effective* inverse kinetic coefficient.

In summary, we have investigated the dynamics of the nematic-electroclinic effect up to $\nu = 100$ kHz. It was found that at least two relaxation processes acting cooperatively are involved near $T_{N\text{-Sm-}A}$. Owing to the very rapid response deep into the nematic phase, we cannot yet determine whether only a single process remains, or whether several very fast processes are operative. Presently we are modifying our apparatus to facilitate measurements up to 1 MHz.

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