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Nematic electroclinic effect in a carbon-nanotube-doped achiral liquid crystal

Rajratan Basu,[1] Rolfe G. Petschek,[1] and Charles Rosenblatt[1,2]
[1]*Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079, USA*
[2]*Université Pierre et Marie Curie–Paris 6, Laboratoire F.A.S.T., Bâtiment 502, F-91405 Orsay, France*

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A small quantity of carbon nanotubes (CNTs) dispersed in an achiral liquid crystal (LC) matrix transmits chirality a short distance into the LC, and the LC+CNT mixture is found to exhibit a bulklike electroclinic effect in the nematic phase. The magnitude of the effect increases rapidly on cooling, showing significant pretransitional behavior on approaching the nematic-smectic-*A* transition temperature (T_{NA}) from above. The variation of the electroclinic coefficient is negligible over the frequency range 100 Hz to 100 kHz in the in the nematic phase well above $\mathrm{T_{NA}}$ and in the smectic-*A* phase, whereas the electroclinic coefficient falls off significantly with increasing frequency just above $\mathrm{T_{NA}}$.

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I. INTRODUCTION

The physical interactions between carbon nanotubes (CNTs) [1] and liquid crystals (LCs) in a LC+CNT colloidal dispersion have drawn a great deal of interest in recent years. These mixtures exhibit a variety of fascinating phenomena, such as the interaction between the CNT-long axis and the LC director, improvement of the electrooptic response of the LCs, an electromechanical memory effect, and incremental changes in the LC orientational order parameter [2–12]. Previously we demonstrated experimentally [13] that the suspended CNTs in a LC medium impose their inherent surface chirality on the nearby LC molecules, and therefore an achiral LC doped with CNTs manifests an electroclinic effect (ECE) in the smectic-*A* phase, a phenomenon first demonstrated by Garoff and Meyer in a bulk, single-component chiral LC molecules [14,15]. In the smectic-*A* electroclinic effect an electric field E applied parallel to the chiral smectic layers induces a polar tilt θ [$\propto E$] of the director in a plane perpendicular to the applied field. The dc tilt susceptibility $d\theta/dE$ for the chiral smectic-*A* ECE, also known as the dc electroclinic coefficient e_c^0, diverges on cooling toward the chiral smectic-C^* phase. Garoff and Meyer showed [14,15] that the ECE involves the reduced C_2 symmetry of the lower temperature smectic-C^* phase and is absent when the system is achiral or racemic. For our *achiral* LC + chiral CNT mixture in the smectic-*A* phase we also have observed a diverging, mean-fieldlike electroclinic coefficient on cooling toward the smectic-*A* to smectic-*C* transition temperature [13].

But the electroclinic effect need not be limited to the smectic-*A* phase and has been demonstrated in a chiral nematic phase as well [16–18]. The bulk nematic electroclinic effect seems to be strongly increased by—or even to result from—smectic fluctuations within the nematic phase [19]. A *surface* nematic electroclinic effect can occur when an achiral LC is in contact with a chiral wall, even in the absence of smectic layer fluctuations [20,21]. But it is important to note that every type of nematic electroclinic effect (NECE) requires the breaking of mirror symmetry. Here we show that the addition of chiral CNTs, which can impart their chirality to the adjacent achiral LC [13], results in an electroclinic effect having physical properties both similar to, and different from, the bulk NECE. CNTs are macromolecules of carbon and, under appropriate conditions, can exhibit different chiral strengths depending on the wrapping angle of the graphene sheet [22]. Multiwalled carbon nanotubes (MWCNTs) can have diameters of tens of nanometers and lengths of hundreds to thousands of nanometers, much larger than LC dimensions, and thus can serve as local alignment surfaces for the LC molecules. In fact, it is because of their large diameters that we chose multiwalled as opposed to single-walled CNTs to examine this chiral surface effect, as the single-walled CNTs have a characteristic diameter not much larger than the LC and therefore have much less of an extended surfacelike character than the MWCNTs. The surface chirality of the multiwalled CNTs can be transmitted into the LC media, thereby allowing the mixture to exhibit a bulklike spatially averaged electroclinic effect in the smectic-*A* phase [13] and a very long pitch (>1 mm) helical twist in the nematic phase [23]. The purpose of this paper is to examine the existence, temperature behavior, and dynamics of the NECE in a mixture of MWCNTs and the achiral LC 4-n-pentylphenylthiol-4′-n-octyloxybenzoate ($\bar{8}S5$). We studied both the temperature and frequency behaviors in the neighborhood of the nematic-smectic-*A* transition temperature T_{NA}, finding a sharp increase in the magnitude of the quasi-dc response near T_{NA} that is reminiscent of the bulk NECE enhanced by the presence of smectic layer fluctuations [19].

II. EXPERIMENTAL

The MWCNTs were obtained from Nanostructured & Amorphous Materials, Inc., and had an outer diameter in the range 8−15 nm, inner diameter 3−5 nm, and length 500−2000 nm. Dispersion of the CNTs, mixing with the LCs, and filling of the $d = 5\ \mu$m thick commercially available cells in which the LC is oriented in the planar direction with a 1° pretilt angle are described in detail elsewhere [13]. According to the manufacturer, the sample contains nanotubes having a distribution of different chiral strengths [22,24,25], and previously we have shown [13,23] that there is a nonzero enantiomeric excess e. Here e is a chiral-strength-weighted algebraic average of the relative concentration of the different enantiomers; right- and left-handed enantiomers would contribute to e with opposite signs. We note that great care was taken to ensure the absence of chiral impurities, including energy dispersive x-ray spectroscopy analysis that suggested no chiral impurities, washing the nanotubes in chiral contaminant-free acetone, and washing the nanotubes in chiral contaminant-free toluene [13]. Two cells were filled: one having LC only and the other containing a mixture of LC and 0.002 wt fraction CNTs, corresponding to a CNT number density of approximately 10^{13} cm^{-3}. Both cells were filled in the isotropic phase above the nematic-isotropic transition temperature T_{NI}, which is 85.8 °C for the pure LC and 84.2 °C for the mixture. They then were cooled into the nematic phase and held above the nematic—smectic-*A* phase transition temperature T_{NA}, which is 65.3 °C for the pure LC [26] and 64.4 °C for the mixture. That the transition temperatures for the mixture were lower than for the pure LC suggests that the CNTs acted as well-dispersed dissolved impurities rather than undissolved colloids. Additionally, the small cell spacing tends to filter out any nanotube aggregates larger than *d*, and polarizing optical microscopy showed no indication of CNT aggregates, at least on length scales comparable to and larger than visible wavelengths. In a separate work [23] in which we examined the helical pitch versus CNT concentration C_w, we found that the inverse pitch P^{-1} is proportional to C_w out to weight fraction ~0.0015–0.002 before saturation of P^{-1} begins to set in, again suggesting that the CNTs remain well dispersed at lower concentrations. (Near complete saturation of P^{-1} occurred when $C_w \sim 0.004$.) Finally, optical micrographs of the mixed LC+CNT system revealed a uniform nematic texture, like that of the pure LC cell, indicating a uniform, nearly planar director field.

The optical setup consisted of a beam from a 5-mW He-Ne laser at wavelength 633 nm that passed through a polarizer, the cell, a crossed analyzer, and into a detector. The beam was polarized at an angle of $\pi/8$ with respect to the cells' rubbing direction; this is the classical "electroclinic geometry" [27]. The output of the detector was fed into both a lock-in amplifier that was referenced to the driving frequency *f* of the applied electric field and to a dc voltmeter, allowing us to measure the ac intensity I_{ac} at frequency *f* and the dc intensity I_{dc}, respectively. The setup was computer controlled and data acquisition was performed using LabVIEW software. From the measured intensities the field-induced spatially averaged tilt angle θ was obtained from the formula $\theta = I_{\text{ac}}/4I_{\text{dc}}$ [27].

III. RESULTS AND DISCUSSION

Figure 1 shows the spatially averaged tilt angle θ as a function of the rms applied field E at $f = 1$ kHz for (a) pure $\bar{8}S5$ at two temperatures—only two temperatures are shown for purposes of clarity, but data at all temperatures have this behavior—and (b) the $\bar{8}S5+$ MWCNT mixture at several representative temperatures in the nematic phase close to T_{NA}. Note that the slopes $d\theta/dE$ are shown for all temperatures in Fig. 2. As expected, the LC in the absence of CNTs does not exhibit a nematic electroclinic effect in the nematic phase, confirming the absence of molecular chirality in pure $\bar{8}S5$. On the other hand, the CNT-doped $\bar{8}S5$ clearly shows a bulk NECE that grows on approaching T_{NA} from above, demonstrating a spatially averaged nonzero chirality in the nematic phase. Examining the pretransitional behavior of the nematic electroclinic effect for the LC+CNT mixture, in Fig. 2 we observe a rapid growth on cooling of the low-frequency ($f=$ 1 kHz) electroclinic coefficient $d\theta/dE$, which we take to be approximately equal to the dc electroclinic coefficient e_c^0, with an apparent plateau below T_{NA}. The shape of the variation of e_c^0 as a function of *T* in Fig. 2 is quantitatively similar to previous results on fully chiral nematic LCs [17,18], even though the magnitudes for the achiral LC+CNT mixture are smaller by three orders of magnitude. This is due to the localization of the induced chirality close to the CNT [13], generally only a few molecular diameters [28], and the spatial averaging of $d\theta/dE$ over the entire sample.

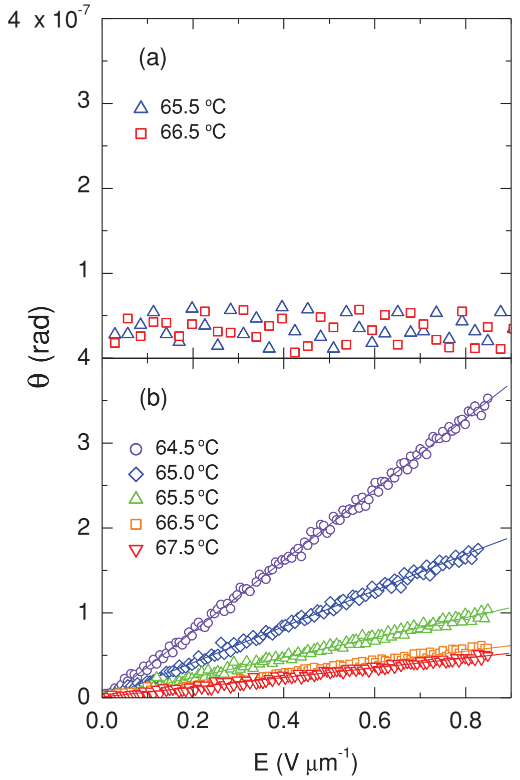

FIG. 1. (Color online) Electroclinic effect in the nematic phase: (a) tilt angle θ vs. E ($f = 1$ kHz) for bulk $\bar{8}S5$ at two different values of *T*, listed in the legend; (b) tilt angle θ vs. E ($f = 1$ kHz) for $\bar{8}S5$+MWCNTs at five different values of *T* listed in the legend.

For an applied sinusoidal electric field $E = E_0\cos\omega t$, the induced tilt angle θ can be written as [18], $\theta = e_c^0 E_0(\cos\omega t + \omega\tau \sin\omega t)/(1+\omega^2\tau^2)$, assuming a single relaxation process with a relaxation time $\tau = \eta e_c^0$, where η is a kinetic coefficient and ω is the angular frequency of the applied field, i.e., $\omega = 2\pi f$. In Fig. 3 we plot $e_c(\omega)$ at several temperatures in the nematic phase and at the upper end of the smectic-*A* phase region. At temperatures in the nematic phase well above T_{NA} and in the smectic-*A* phase, there is very little variation of $e_c(\omega)$ with frequency, whereas there is a significant decrease of $e_c(\omega)$ with ω in the nematic phase close to the transition temperature T_{NA}. This shape of the electroclinic coefficient vs. frequency curves in this region is reminiscent of the dynamics of the bulk NECE in an undoped chiral LC [18], for which it was concluded that

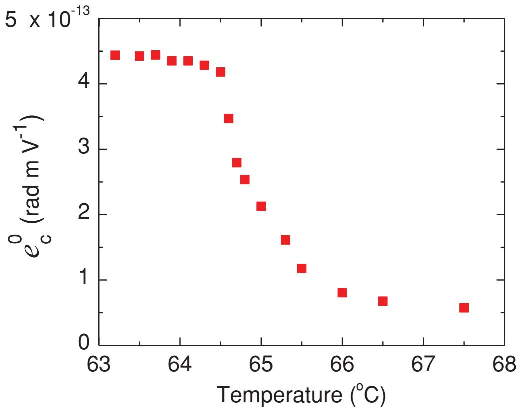

FIG. 2. (Color online) Electroclinic coefficient e_c^0 vs. T, where we have taken the value measured at $f = 1$ kHz to be the approximate dc value.

multiple relaxation processes were operative in the region near T_{NA}; the same apparently applies here as well. Quantitatively, however, the *fractional* falloff of $|e_c(\omega)|$ with increasing ω for the CNT-doped LC is much smaller (by well more than an order of magnitude) than that of the bulk NECE for a chiral LC in Ref. [18], suggesting much faster process(es) in the in the CNT-induced effect compared to the bulk NECE.

How can this difference in frequency response be explained? One possibility involves rotation of the CNTs. The reorientation time of a CNT about an axis perpendicular to the long axis of the CNT in a nematic LC host can be estimated to be $\sim 10^{-2}$ s, assuming the CNT is subjected to a restoring torque $W_2\theta LD$ arising from the field-induced tilt θ of the director. Here we have used a CNT length $L \sim 1000$ nm, diameter $D \sim 10$ nm, LC viscosity ~ 0.1 P [29], and quadratic anchoring strength coefficient $W_2 \sim 0.1$ erg cm^{-2} [30–32] for the LC at the CNT wall. This time is slow compared to ω^{-1} in our experiment, and therefore we do *not* believe that rotation of the CNT is an important mechanism in the NECE. Turning to the LC, we propose two possible mechanisms. In mechanism 1 the chiral CNTs facilitate an electric field-induced tilt in the nematic LC close to the CNT walls. Smectic fluctuations, which can be enhanced by the surface, tend to increase the electroclinic effect near the wall but also tend to quench the tilt as one moves away from the wall. In mechanism 2 the chiral CNT surfaces facilitate an electroclinic effect in the LC close to the surface, similar to that observed in Ref. [21] and not requiring smectic layering. Thus, in the absence of smectic fluctuations the resulting tilt would propagate elastically, but temporally slowly, deep into the bulk [21]. Although both of these chiral symmetry breaking effects are possible, both the similarity of the sharp increase in e_c^0 near T_{NA} and the fast dynamics strongly suggest that mechanism 1 dominates the NECE in our system. Examining mechanism 1 more closely, we note that there are several length scales of importance. One length is t, the distance from the CNT over which chirality is induced in the LC; this corresponds to at most 2–3 nm [13,28] and is expected to be relatively independent of temperature. (Two other length scales that will be discussed later are $\xi_\perp$ and $\xi_{||}$, the smectic layer correlation lengths perpendicular and parallel to the director, respectively, in the nematic phase. $\xi_\perp$ tends to be at least 5 nm and $\xi_{||}$ at least 10 nm approximately 3 °C above T_{NA}; both diverge on cooling toward the transition temperature, but with different critical exponents [33].) While there is no analytic theory, it is reasonable to expect that the observed faster response in this experiment (Fig. 3) compared to that in a bulk chiral NECE, i.e., in the absence of a surface (Fig. 1 in Ref. [18]) is due in part to the small size t of the chiral region near the CNT walls. Additionally, since it has been shown that nematic order is enhanced near the CNTs [9], this likely will increase the degree of smectic order in that region as well. Thus, the fast relaxation time will be further enhanced by the increased smectic order near the CNTs. A signature of the faster response time for the CNT-doped system is $|e_c(\omega)|$, which falls off slowly with increasing ω, as observed in Fig. 3.

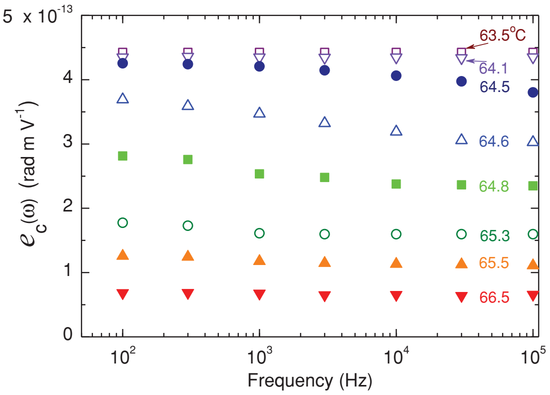

FIG. 3. (Color online) Electroclinic coefficient, $e_c(\omega)$ vs. frequency at different values of T listed in the legend. Note that $T = 63.5$ and 64.1 °C are in the smectic-A phase.

We note that t is smaller than both smectic-A correlation lengths $\xi_{||}$ and $\xi_\perp$over the entire temperature range studied [13,28]. In consequence, the elastic propagation of the NECE tilt beyond distance t into the internanotube (bulk) region is suppressed by the smectic-A fluctuations. Thus there is no measureable tilt in the internanotube region to contribute to the measured signal. This is inherently different than the observed surface electroclinic effect induced by a chirally patterned substrate in the LC methoxybenzylidine butylanaline (MBBA) [21], in which the director tilt propagates far into the bulk. There are two reasons for this. First, because MBBA has no smectic-A phase and, as a result, any incipient smectic fluctuations have extremely small correlation lengths, the field-induced tilt of the director at the chiral substrate is not suppressed by the fluctuating smectic layers and *can* propagate elastically into the bulk. Second, in the chirally patterned surface-MBBA experiment the surface pattern is scribed on length scales $\sim$100 nm, which is to say length scales large in comparison to the smectic correlation lengths.

Finally, we note that at very low driving frequencies there is an anomalous increase in the noise in the nematic phase, but not in the smectic-A phase. We find that the rms noise ($\sqrt{\chi^2}$) from a linear least-squares fit of θ versus E (Fig. 1) is nearly constant above 100 Hz, but increases by some two orders of magnitude on decreasing the frequency from 100 to 30 Hz. This sharp variation of $\sqrt{\chi^2}$ with frequency argues against a rotation of the

CNT as the cause of the noise. Rather, we believe that this noise is due to some other phenomenon—i.e., not the NECE (which is the subject of this paper)—that occurs at low frequencies in this system, perhaps a hydrodynamic instability or perhaps a dielectrophoretic effect. Both are beyond the scope of the present paper but will be considered in future work.

IV. SUMMARY

To summarize, we have examined the electroclinic effect in a nematic mixture of an achiral LC and chiral CNTs. The temperature dependence suggests that the CNTs induce chirality a short distance into the neighboring LC, and that the resulting NECE is due primarily to the local physical interactions between the LC and the chiral surface of the CNTs, whose interactions are enhanced by smectic fluctuations. The weak frequency dependence of the effect above 100 Hz is a result of the small spatial extent of the chirally induced region.

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