

# Carbon nanotube dispersed liquid crystal: A nano electromechanical system

Rajratan Basu and Germano S. Iannacchione<sup>a)</sup>

Order-Disorder Phenomena Laboratory, Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, USA

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Electric field induced director orientation of a nematic liquid crystal (LC)+carbon nanotube (CNT) system reveals insights on switching behavior for this anisotropic composite. Once the field goes off, the LC+CNT system relaxes back to the original orientation through a mechanical rotation, revealing the intrinsic dynamics. LC molecules and CNTs cooperatively form local *pseudonematic* domains in the isotropic phase due to strong LC-CNT interactions. These field-responsive anisotropic domains do not relax back to the original orientation on switching of the field off, which could find potential applications in memory devices. © 2008 American Institute of Physics.

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Carbon nanotubes (CNTs) dispersed nematic liquid crystal (LC) represents a versatile functional composite that has gained interest in recent years for inducing parallel alignment of CNTs and improving electro-optic effect of LCs.<sup>1-6</sup> This LC+CNT system is a unique assemblage of an anisotropic dispersion (CNTs) in an anisotropic media (LC). This makes it an attractive anisotropic physical system to study the electric field induced switching behavior and nanodynamic response of LC and CNTs. After a field induced *director* (average direction of LC molecules) orientation of the nematic LC+CNT system,<sup>1-3</sup> the LC molecules, as well as the CNTs dynamically reorient back into their original orientation on turning the electric field off, revealing the intrinsic dynamics. However, the reorientation and relaxation mechanisms of CNTs are strongly influenced by the surrounding LC media, such as nematic phase or isotropic phase. In this letter, we report the dynamic response of the average dielectric constant ( $\bar{\epsilon}$ ) for multiwall CNTs (MWCNTs) dispersed in 4-cyano-4'-pentylbiphenyl (5CB) LC as a function of applied ac-field in both the nematic and isotropic phases.

Both the LC and CNTs systems show dielectric anisotropy due to their structural anisotropy. For a positive dielectric anisotropic system, planar configured molecules being perpendicular to the measuring field show smallest dielectric constant  $\epsilon = \epsilon_{\perp}$ . When the director rotates, the dielectric constant increases until the system is homeotropically aligned (parallel to the measuring field) and the dielectric constant reaches its largest value  $\epsilon_{\parallel}$ . However, the values of  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$  depend on the frequency of the measuring field.

A small amount (0.005 wt %) of MWCNT sample (containing nanotubes <8 nm in diameter and 0.5–2  $\mu\text{m}$  in length) was dispersed in 5CB ( $T_{\text{nematic-isotropic}}=35^{\circ}\text{C}$ ) and the mixture was ultrasonicated for 5 h to reduce the bundling tendency of CNTs. Strong interaction with a binding energy of about  $-2$  eV between LC-CNT (Refs. 4 and 7) makes the long axes of CNTs follow the nematic LC director.<sup>1-3</sup> After ultrasonication, the mixture was filled into a cell (5  $\times$  5  $\text{mm}^2$  indium tin oxide coated area and 20  $\mu\text{m}$  spacing)

by capillary action, housed in a temperature controlled bath. Surface treatment inside the LC cell imposes the planar alignment to the nematic director. Empty LC cells<sup>8</sup> were measured first in order to extract the absolute  $\bar{\epsilon}$ . The relax-

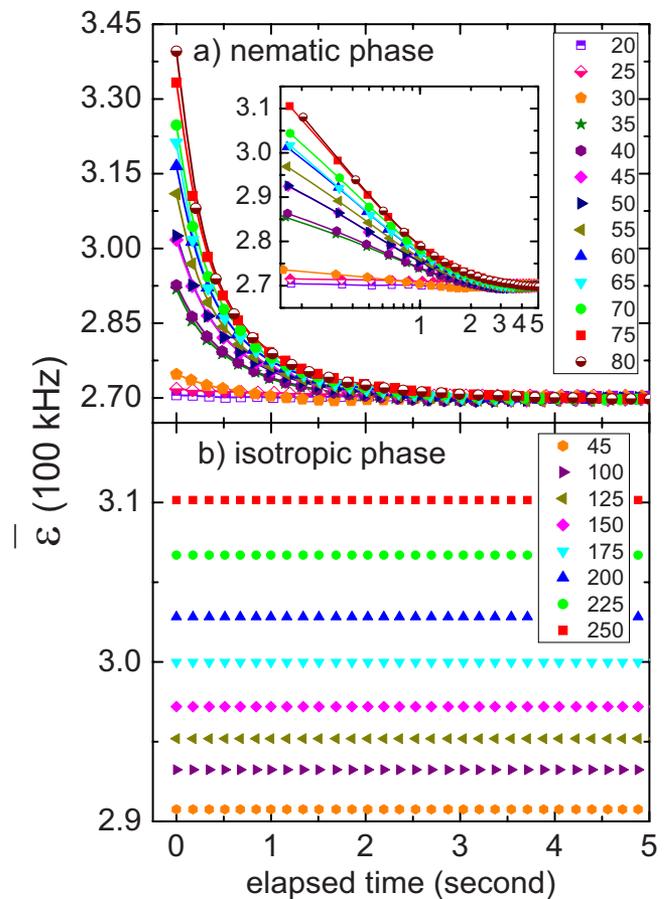


FIG. 1. (Color online) (a) Dynamic response of the average dielectric constant  $\bar{\epsilon}$  for the LC+CNT system in the nematic phase ( $T=20^{\circ}\text{C}$ ) after  $E_{ac}=0$ . The inset (same main graph axes) represents the same relaxation in log-time scale to show the single exponential decay. Lines represent the fitting according to a single exponential decay function, see text for details. (b) Dynamic response of the average dielectric constant  $\bar{\epsilon}$  for LC+CNT system in the isotropic phase ( $T=45^{\circ}\text{C}$ ) after  $E_{ac}=0$ . The legends in both the panels represent the magnitude of  $E_{ac}$  (kV/m, 1 MHz).

<sup>a)</sup>Electronic address: gsiannac@wpi.edu.

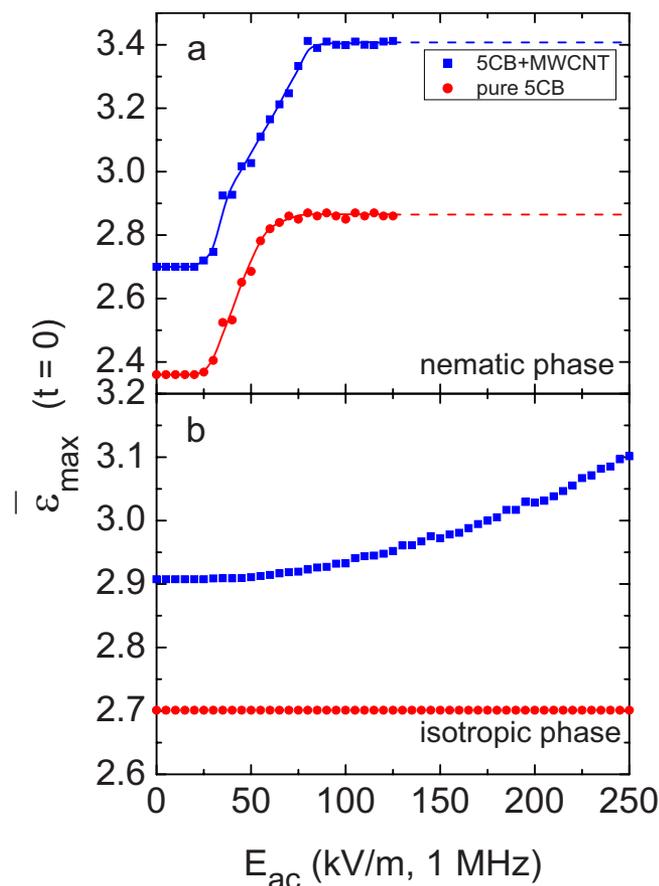


FIG. 2. (Color online) (a) Field-saturated dielectric constant  $\bar{\epsilon}_{\max}$  ( $\bar{\epsilon}$  at  $t=0$ ) as a function  $E_{ac}$  in the nematic phase ( $T=20$  °C). Lines represent guide to the eye. (b) Field-saturated dielectric constant  $\bar{\epsilon}_{\max}$  ( $\bar{\epsilon}$  at  $t=0$ ) as a function  $E_{ac}$  in the isotropic phase ( $T=45$  °C).

ation dynamics also depend on cell configuration; for comparisons, the same type of cells was used for both pure 5CB and 5CB+MWCNT.

After the LC+CNT sample was loaded into the cell, an external ac electric field pulse,  $E_{ac}$  (1 MHz) of 30 s duration was applied across the cell at magnitudes ranging from 0 to 250 kV/m. The reason for applying the ac field (not dc) is to avoid the affect of ion migration on the dielectric relaxation measurements. Once  $E_{ac}$  was turned off (at  $t=0$  s), isothermal average dielectric ( $\bar{\epsilon}$ ) measurements were carried in the nematic ( $T=20$  °C) and isotropic ( $T=45$  °C) phases as a function of time, see Fig. 1. The dielectric measurements were performed by the ac capacitance bridge technique,<sup>9–11</sup> operating with a probing field far below the reorientation threshold field and at 100 kHz frequency. The LC 5CB does not exhibit any tumbling mode<sup>12</sup> and MWCNTs show no space charge or dipole orientation dynamics at this probing frequency.<sup>13</sup> Thus, the observed dynamics should be driven mainly by a mechanical relaxation mechanism of the director after  $E_{ac}$  is switched off.

Figure 1 shows the average complex dielectric constant,  $\bar{\epsilon}$  (100 kHz) as a function of time after  $E_{ac}$  was tuned off for 5CB+MWCNT sample. In the nematic phase ( $T=20$  °C), CNTs and LC molecules cooperatively relax back to the planar orientation after the field goes off, clearly seen in Fig. 1(a). Field induced director orientation occurs when the torques, due to the external electric field, overcome the elastic interactions between LC molecules and, through surface

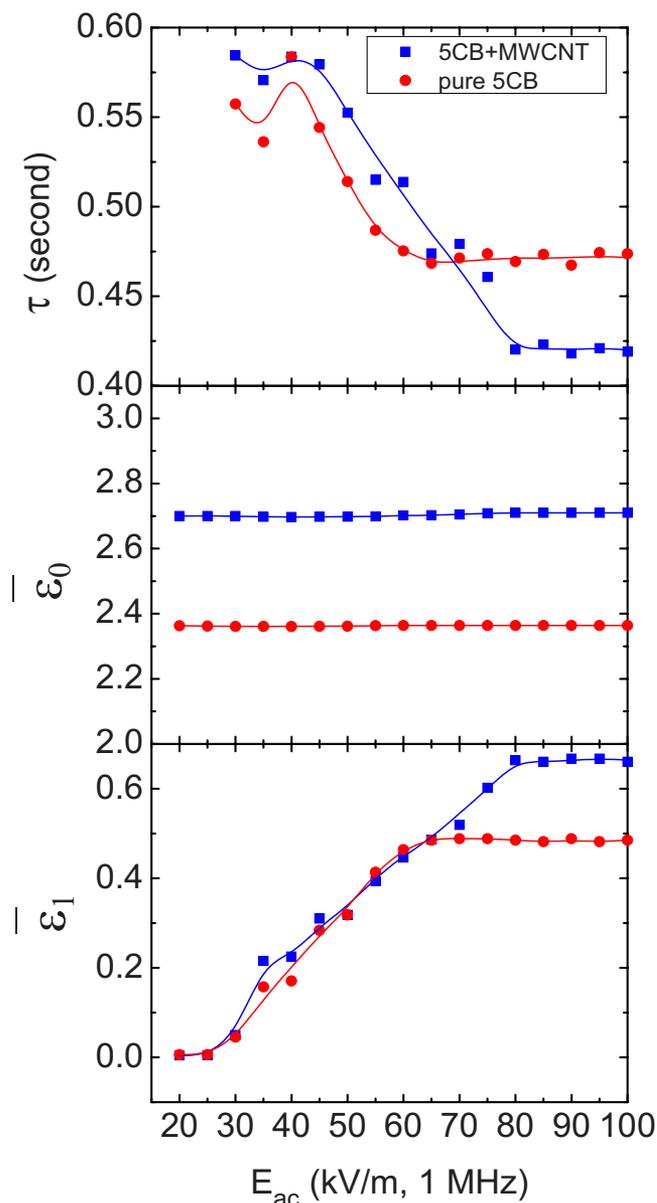


FIG. 3. (Color online) Fitting parameters according to a single-exponential decay [ $f(t)=\bar{\epsilon}_1 e^{-t/\tau} + \bar{\epsilon}_0$ ] function for pure 5CB and 5CB+MWCNT system. Lines represent guide to the eye.

coupling, the CNT long axis follows the director orientation. Soon after the field goes off, these restoring forces between the planar surface state and LC director drive the system back to the original orientation through a mechanical rotation. The field-saturated dielectric constant  $\bar{\epsilon}_{\max}$  [ $\bar{\epsilon}$  at  $t=0$ , from Fig. 1(a)] for each relaxation is plotted as a function of  $E_{ac}$  in Fig. 2(a) and is directly associated with the director orientation. The value of  $\bar{\epsilon}_{\max}$  starts to increase above  $E_{ac}=20$  kV/m for both pure 5CB and 5CB+MWCNT samples, confirming the director reorientation from planar to homeotropic, but  $\bar{\epsilon}_{\max}$  saturates at a higher field for the composite sample than pure 5CB, see Fig. 2(a). This is probably due to the higher aspect ratio of CNTs that require higher fields to fully reorient.

A dramatic change in the field induced orientation mechanism has been observed in the isotropic phase ( $T=45$  °C). Due to the absence of elastic interactions in the isotropic phase, the LC molecules no longer form long range

orientation order. So, it is expected to have no field induced director reorientation for pure 5CB, as also experimentally observed in Fig. 2(b). However, the composite shows an increment in  $\bar{\epsilon}$  on application of electric field which does not relax back over time on switching the field off, as seen in Fig. 1(b). Even though there are no long-range nematic interactions in the isotropic phase, the coupling between LC-CNT (Ref. 4 and 7) still exists. Due to this coupling, the CNT induces local short-range orientation order of LC surrounding the CNT, which can be visualized as presence of isolated pseudonematic domains in an isotropic media. These local anisotropic pseudonematic domains are also field responsive and can be reoriented on application of  $E_{ac}$ . However, after the field goes off, there is no restoring force in the isotropic LC media to mechanically torque these domains back into the original orientation. Figure 2(b) depicts that in the isotropic phase there is no sharp threshold field to start the reorientation and  $\bar{\epsilon}_{max}$  does not seem to saturate in the field range studied. The field induced reorientations of these anisotropic domains can only be erased by slowly cooling the system down to the nematic phase and then heating it up again to the isotropic phase.

Dielectric relaxation curves for 5CB and 5CB +MWCNT composite were fitted according to a single exponential decay function  $f(t) = \bar{\epsilon}_1 e^{-(t/\tau)} + \bar{\epsilon}_0$  with a typical regression coefficient of  $R=0.9996$ . Here,  $\tau$  is the relaxation decay time and  $\bar{\epsilon}_1 + \bar{\epsilon}_0 = \bar{\epsilon}_{max}$ . The inset in Fig. 1(a) shows the linear dependency of  $\bar{\epsilon}$  at small  $t$  with logarithmic time scale. The values for the three fitting parameters  $\tau$ ,  $\bar{\epsilon}_0$ , and  $\bar{\epsilon}_1$  as a function of  $E_{ac}$  are shown in Fig. 3. Generally, the relaxation time decreases as  $E_{ac}$  increases and, for the composite, saturates at a higher field than that of pure 5CB, which is consistent with the behaviors of  $\bar{\epsilon}_{max}$  shown in Fig. 2(a). For  $E_{ac}$  larger than the saturation point, the composite system relaxes back faster than pure 5CB, as seen in Fig. 3. It is possible that the dispersed CNTs attract ions present in the LC media,<sup>4</sup> which may influence this result. The presence of ions would slow down the elastic-force driven mechanical relax-

ation of the nematic domains. The presence of CNTs would lower the free ion concentration and allow the composite system relax faster. If true, this could be an interesting application for image stabilization in LC displays.

In summary, the nanodynamics of LC+CNT system has been studied to understand the stability of these systems. In the nematic phase, the composite system results in an improvement in relaxation decay time for larger  $E_{ac}$ , which might be an application for LC display technology. The presence of local anisotropic pseudonematic domains in the isotropic phase in the system demonstrates a promising field induced storage memory device application. This versatile nanoscale electromechanical system might reveal interesting individual molecular dynamics of LC and CNTs in high frequency gigahertz dielectric measurements. Future work involves field-induced frequency dependent dielectric studies for different CNT concentrations in LC media for both the nematic and isotropic phases.

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