Carbon Nanotube Dispersed Liquid Crystal : A Nanoelectromechanical System and Non-volatile Memory Effect

Rajratan Basu and Germano S. Iannacchione

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

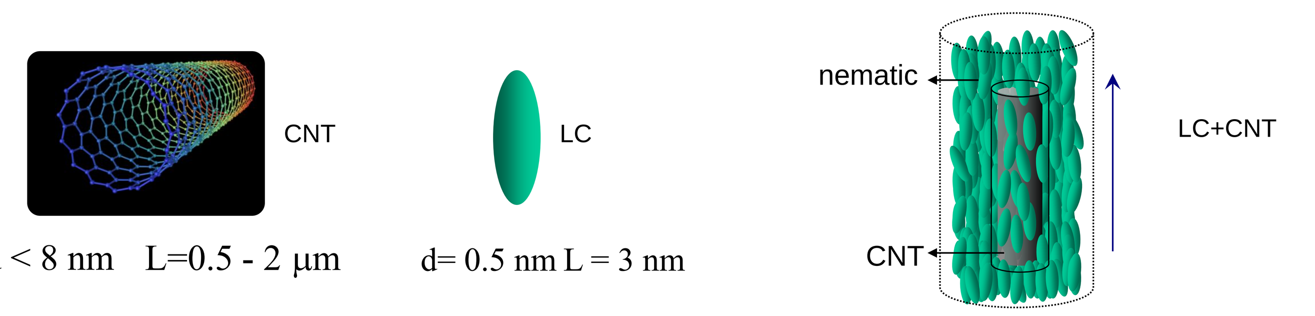
Introduction

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 *pseudo-nematic* 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.

Goals:

- To exploit the self-organizing anisotropic nature of liquid crystals (LCs) for ***nanotemplating*** purposes.
- Self-assembly of carbon nanotubes (CNTs) and control the long axes of CNTs in a preferred direction – ***directed self-assembly*** !
- To exploit the switching behavior of liquid crystals for a ***nano-electromechanical response***.

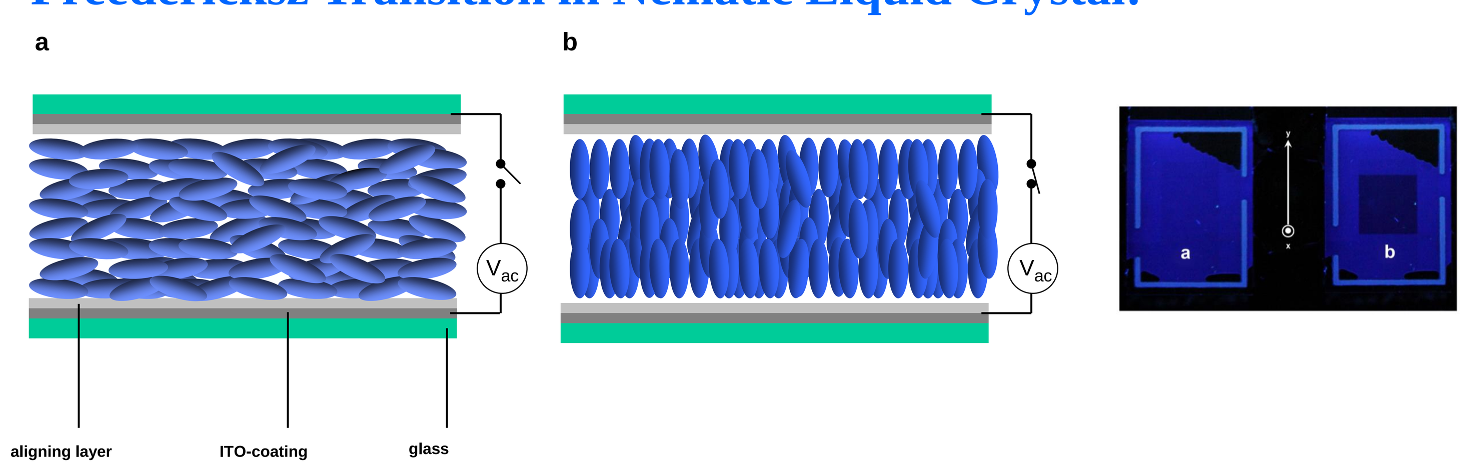
Structural Anisotropy of Carbon Nanotube and Liquid Crystal:



d < 8 nm L=0.5 - 2 µm d= 0.5 nm L = 3 nm

- In LC+CNT mixture, CNT long axis follow the nematic director without perturbing the nematic symmetry
- This configuration costs the lowest amount of energy
- The excluded volume is the smallest for this configuration

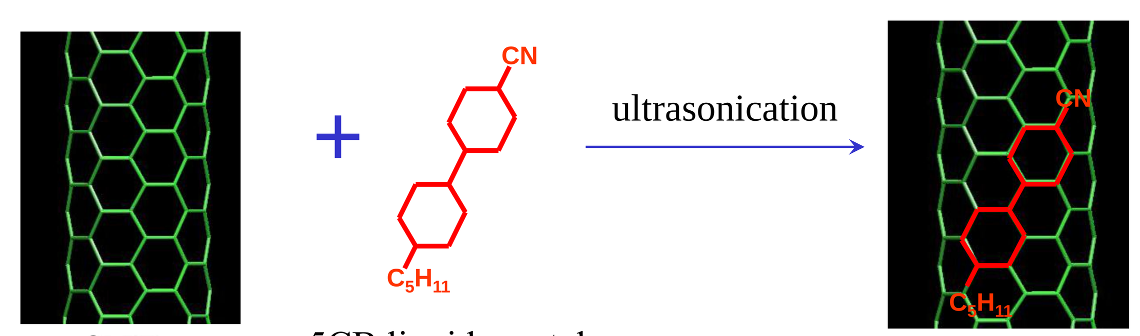
Freedericksz Transition in Nematic Liquid Crystal:



(a) Nematic phase of the liquid crystal confined between parallel plates maintains a uniform director, ***n***, due to plate boundary conditions.
(b) External electric field, above the Freedericksz-threshold, forces the director to reorient along the field (perpendicular to the plates).

Dynamic response of dielectric constant: Dielectric constant of an anisotropic material is orientation dependent. Planar LC molecules, being perpendicular to the measuring field, show small dielectric constant ($\varepsilon_\perp$), but when the molecules start reorienting the dielectric constant starts to increase until the LC is homeotropically reoriented (parallel to the measuring field) and the dielectric constant reaches its saturation value ($\varepsilon_\parallel$).

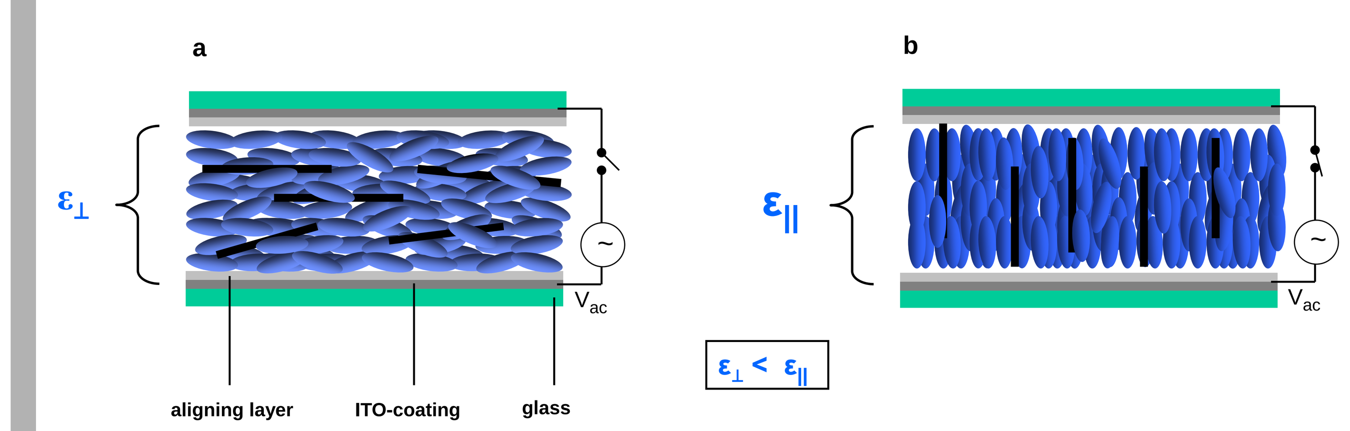
Liquid Crystals + Carbon Nanotube Mixture:



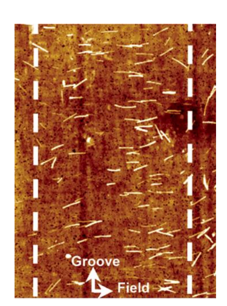
CNT 5CB liquid crystal

- ❑ Surface anchoring of LC molecules helically to the CNT wall to enhance π-π stacking by maximizing the **hexagon-hexagon** interactions between two species.
- ❑ Elastic interaction between CNT and LC molecules.

LC+CNT Orientation Coupling:



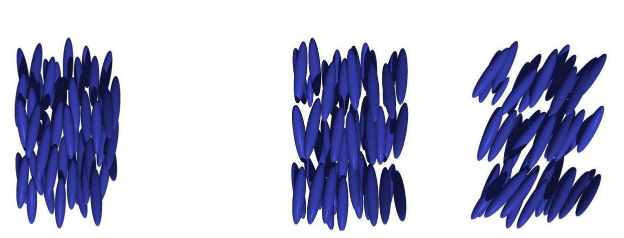
Schematic diagram of LC+CNT in the nematic phase. **(a)** CNT suspended in the nematic matrix, align along the LC director.
(b) External electric field, above the Freedericksz-threshold, reorients the LC director and , through elastic interactions, the long axis of the CNTs.
- On switching the field off, the LC+CNT system relax back to the original state-electromechanical response at nanoscale level.



Electric field induced alignment. Microscopic patterning of CNT alignment can be achieved using local electric fields and LCs. This AFM image shows oriented MWCNTs deposited from 5CB in a 20 µm channel defined by two copper electrodes whose boundaries are indicated by dashed lines. A 1.8 V µm^{-1} electric field was strong enough to overwhelm the orientational influence of the grooves, which were perpendicular to the electric field in the channel.

Michael D. Lynch and David L. Patrick, *Nano Letters*, Vol. **2**, No. **11**, 1197 (2002)

Liquid Crystal Phases:

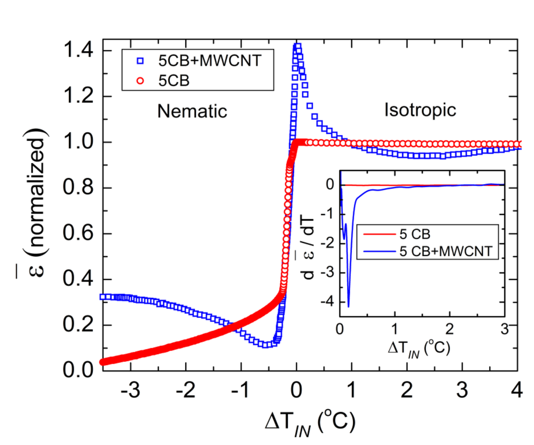


(a) Nematic **(b) Smectic-*A* and Smectic-*C***

(a) Nematic
1. Molecules align parallel to each other, i.e., long-range orientational order.
2. Center of mass positions of each molecule are completely random, i.e., no long-range positional order.

(b) Smectic-*A* and Smectic-*C*
1. Molecules in this phase show one degree of translational order not present in the nematic (hence more solid-like, 1-dimensional order).
2. Molecules maintain the general orientational order, but also arrange in layers.
3. Motion is generally restricted to within the planes, and separate planes can flow past each other.

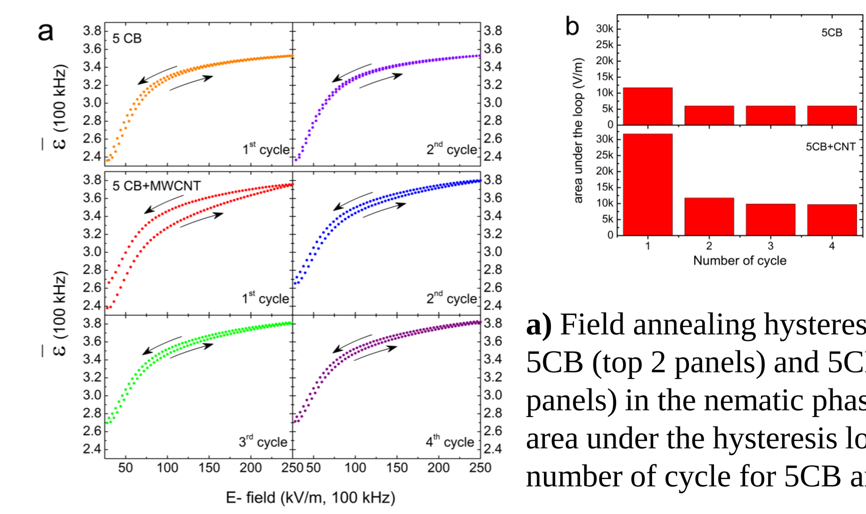
I-N Phase Transition:



$\bar{\varepsilon}_{iso}$ for pure LC is independent of T
$\bar{\varepsilon}_{iso}$ for LC+CNT depends on T

$\Delta T_{IN} = T - T_{IN}$; 5CB T_{IN} = 35.1 °C and for 5CB+MWCNT T_{IN} = 34.67 °C.

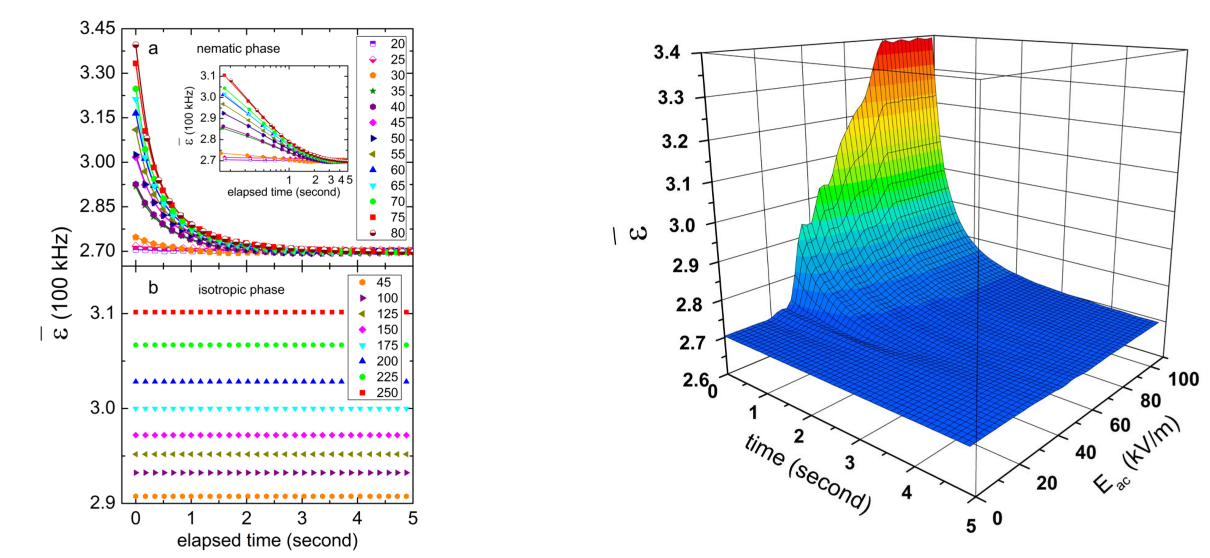
Probing Field Annealing: Hysteresis effect:



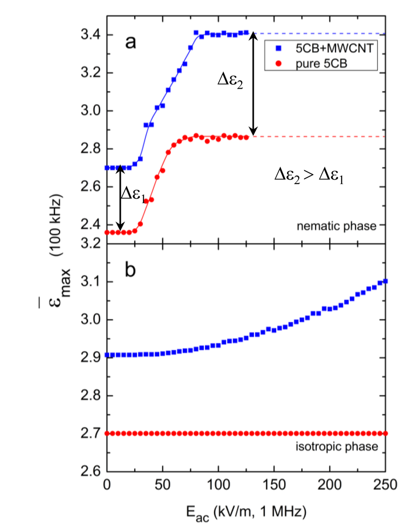
a) Field annealing hysteresis cycles, $\bar{\varepsilon}$ vs. ***E***, for 5CB (top 2 panels) and 5CB+MWCNT (bottom 4 panels) in the nematic phase (T = 25°C). **b)** The area under the hysteresis loop as a function number of cycle for 5CB and 5CB+MWCNT.

- This ferroelectric-type hysteresis effect clearly indicates that the spontaneous polarization of the nematic LC system increases by a considerable amount due to the presence of a small amount of CNTs.
- It is possible that LC-CNT coupling makes some local ordering better in the nematic matrix, and this leads to an increment in the spontaneous polarization of the whole system.
- Also, the multiple field-annealing results in a reduction of the presence defects in the nematic LC and LC+CNT, improving the nematic ordering.

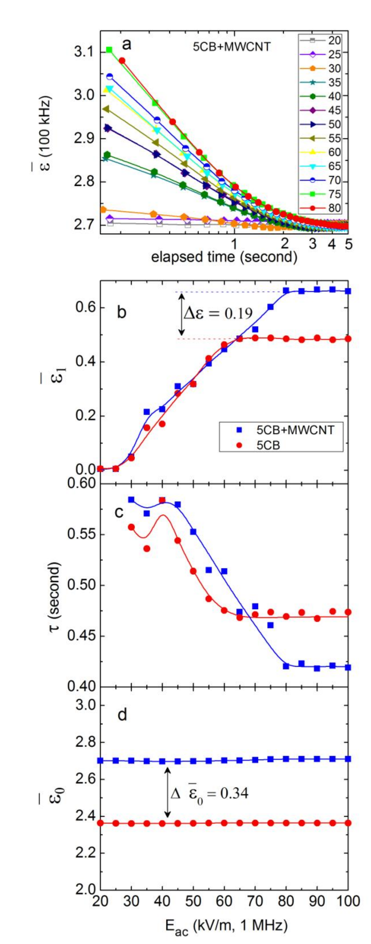
Dynamic Response: Dielectric Relaxation of LC+CNTs System – nano electromechanical system



a) Dynamic response of the average dielectric constant $\bar{\varepsilon}$ for the LC+CNT system in the nematic phase (T = 25°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 $\bar{\varepsilon}$ for LC+CNT system in the isotropic phase (T = 45°C) after E_{ac} = 0. The legends in both the panels represent the magnitude of E_{ac} (kV/m, 1MHz).

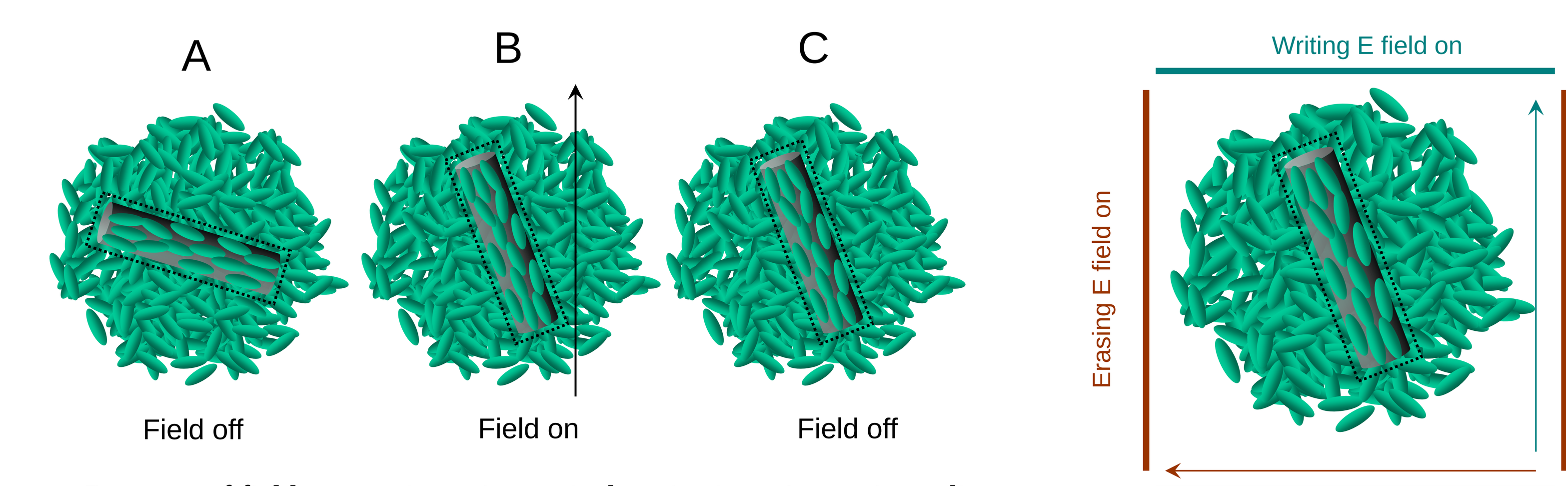


a) Field-saturated dielectric constant, $\bar{\varepsilon}_{max}$ ($\bar{\varepsilon}$ at t = 0) as a function E_{ac} in the nematic phase (T = 25°C). Lines represent guide to the eye; **b)** Field-saturated dielectric constant, $\bar{\varepsilon}_{max}$ ($\bar{\varepsilon}$ at t = 0) as a function E_{ac} in the isotropic phase (T = 45°C).



Fitting parameters according to a single-exponential decay ($f(t) = \varepsilon_1\, e^{(-t/\tau)} + \varepsilon_0$) function for pure 5CB and 5CB+MWCNT system. Lines represent guide to the eye. Note that faster decay for E_{ac} > 75 kV/m

Isotropic LC-CNT system as a non-volatile memory storage device



- Presence of field-responsive anisotropic domains in an isotropic media.
- No restoring force to torque the domains back to the original orientation after the field goes off.

Conclusions:

- The nano-dynamics of LC+CNT system has been studied to understand the stability of these systems.
- Nematic Phase: The dielectric relaxation can be described by a single exponential decay. Faster decay and enhanced average permittivity for E_{ac}> 75 kV/m = 0.075 V/mm. Broader switching region: an application for LC display technology.
- Isotropic Phase: Permanent enhancement of the permittivity with increasing Eac. Suggests presence of local anisotropic *pseudo-nematic* domains surrounding MWCNT strings: A a promising field induced memory storage device application.
- This versatile nano-scale electro-mechanical system can be used as micro-switch and molecular wire in nano-electronics.

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