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

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Goal and Approach

Goal:

- To find a ***general route*** for directed self-assembly of nanomaterials (nanotubes, quantum dots, nanorods etc.) over macroscopic dimension.

Approach:

- To exploit the self-organizing anisotropic nature of liquid crystals (LCs) for ***nanotemplating*** purposes.

- To obtain large scale self-assembly of carbon nanotubes (CNTs) and control the long axes of CNTs in a preferred direction –
  - » ***directed self-assembly of CNTs***
  - » ***nano-electromechanical response of CNTs***!

Outline

- Introduction to Liquid Crystal (LC)
    - LC alignment technique
    - Freedericksz transition
- Liquid crystal- carbon nanotube (CNT) functional composite
    - LC-CNT coupling
    - Measurement technique
    - Orientation dynamics in nematic phase
    - Orientation dynamics in isotropic phase
    - Analysis
- Future Direction
- Conclusions

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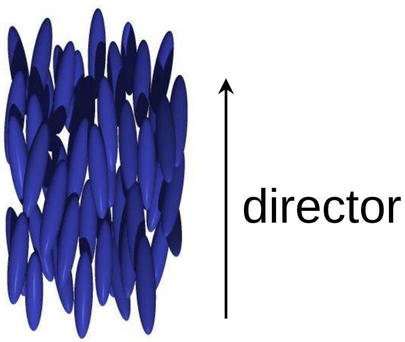
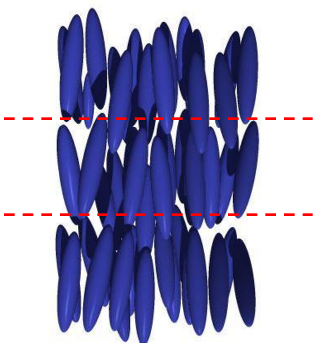
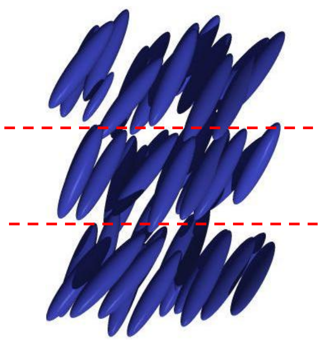
What are Liquid Crystals (LCs)?

Liquid crystals are substances that exhibit a phase of matter that has properties between those of a conventional liquid, and those of a solid crystal.







Nematic

1. long-range orientational order.
2. no long-range positional order.

Smectic A ***Smectic C***

1. one degree of translational order not present in the nematic (more solid-like).
2. general orientational order, but also arrange in layers or planes.
3. Motion is generally restricted to within the planes

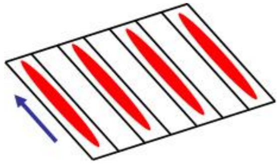
Choosing the preferential direction of the LC molecules

For applications, it is important to obtain a known director distribution.

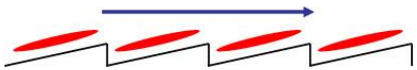
Alignment by rubbing

Planar alignment

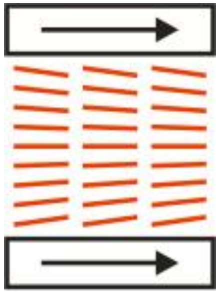
Homeotropic alignment



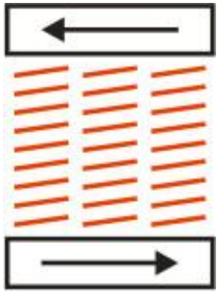
Alignment along the rubbing direction



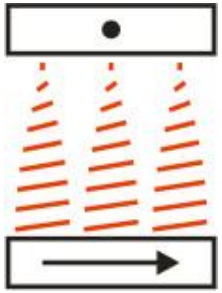
Pretilt originating from the rubbing process



Parallel rubbed

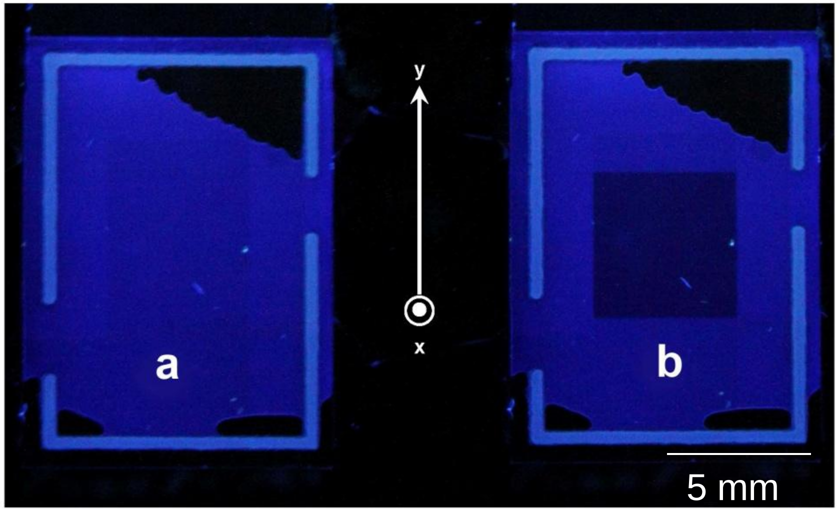


Anti-parallel rubbed



Twisted nematic

Freedericksz transition in nematic LC



Reorientation of LC director on application of electric field

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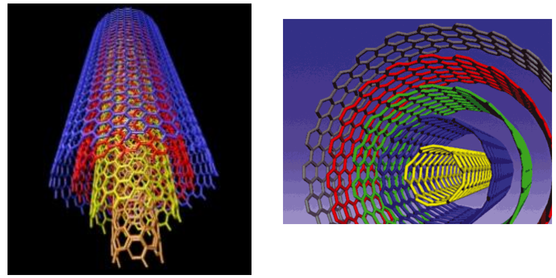
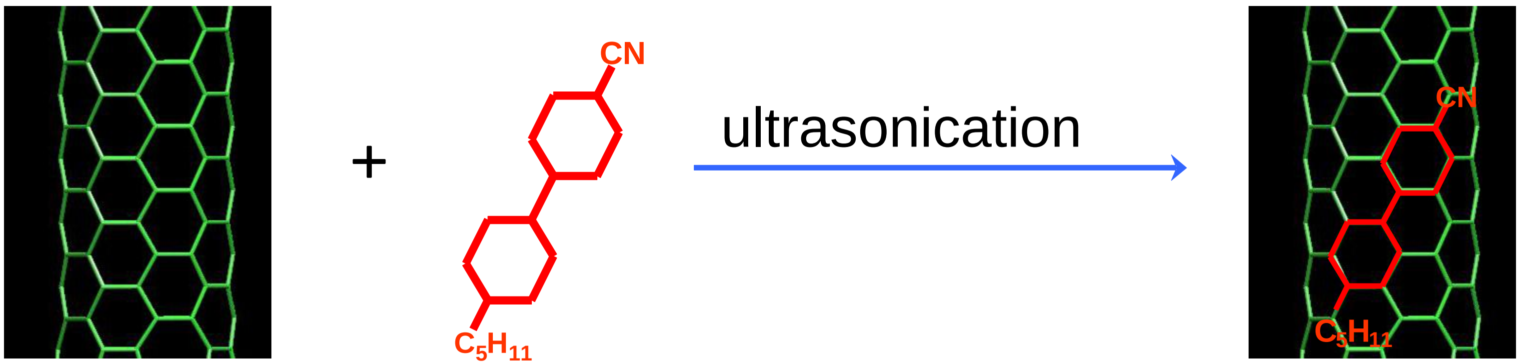
Carbon nanotube (CNT) – LC coupling



Structure of multiwall CNT



CNT

5CB liquid crystal

- ❑The LC molecules tend to anchor *helically* to the CNT wall to enhance π–π stacking by maximizing the *hexagon* – *hexagon* interactions.

- ❑Elastic interactions between the CNT "*strings*" and LC state.

Park et al, *J. Phys. Chem.* C **111**, 1620 (2007); I. Dierking et al, *J. Appl. Phys*. **97**, 044309 (2005).

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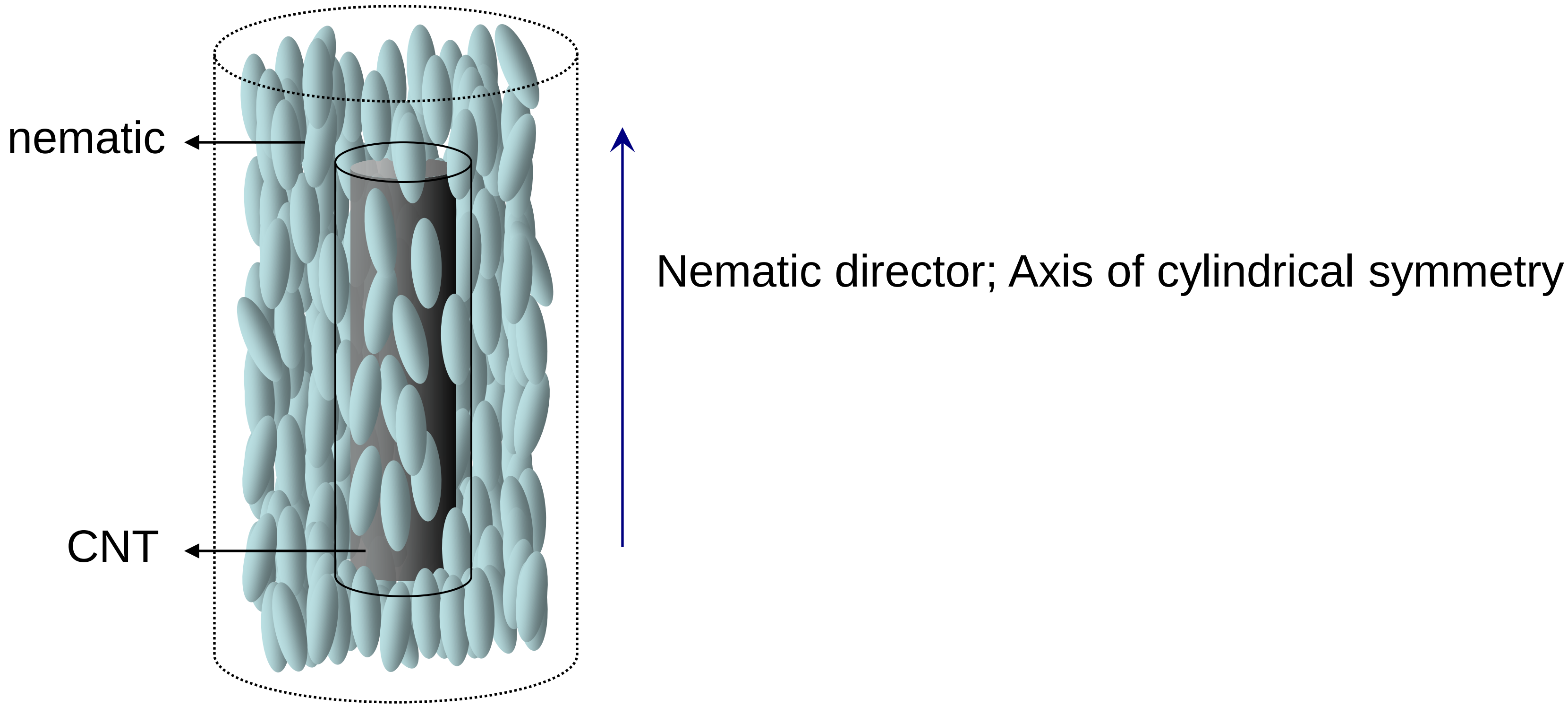
CNT long axis coupling with nematic LC



- CNT long axis follows 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

P.P.A.M. van der Schoot, V. Popa-nita, S. Kralj, *J. Phys. Chem. B*, **112**, 4512, (2008)

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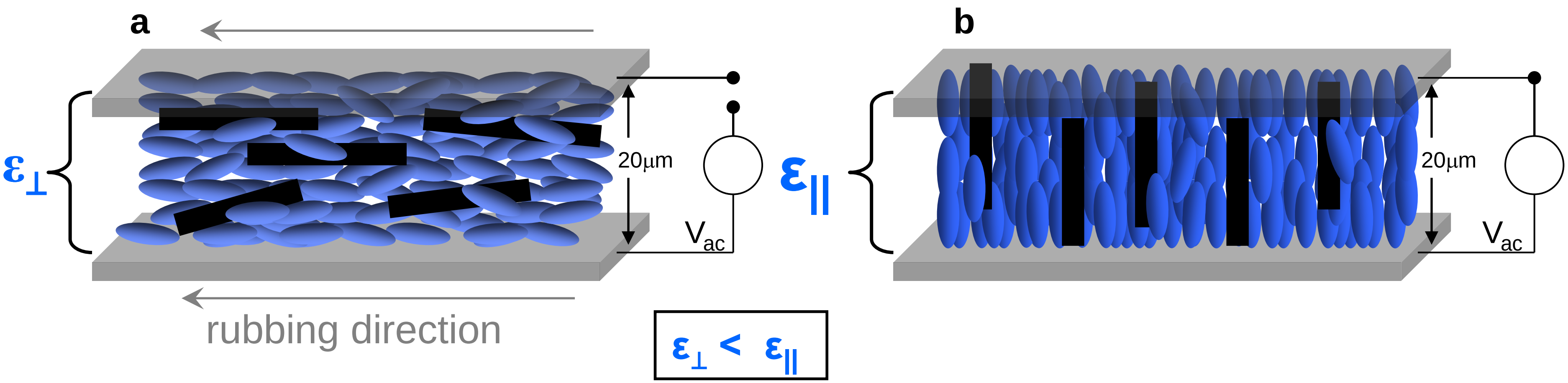
CNT alignment in nematic LC matrix



E_{ac} field off

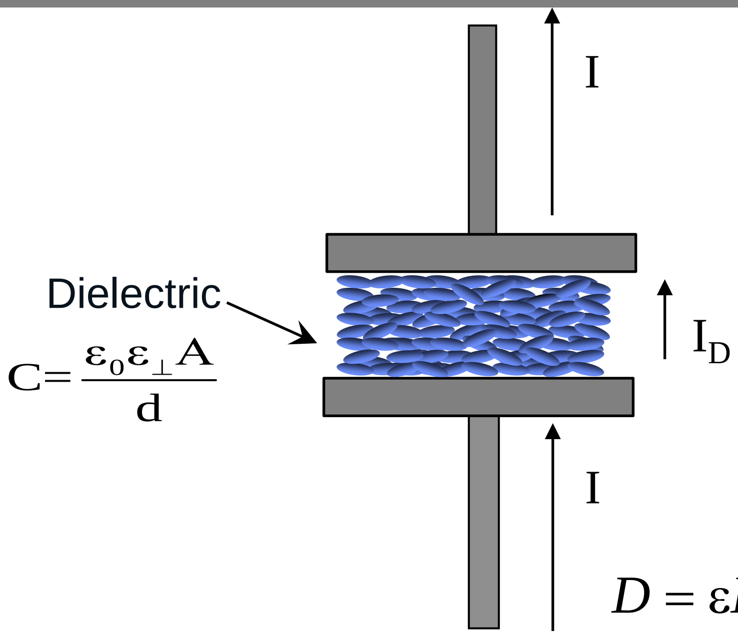
E_{ac} field on

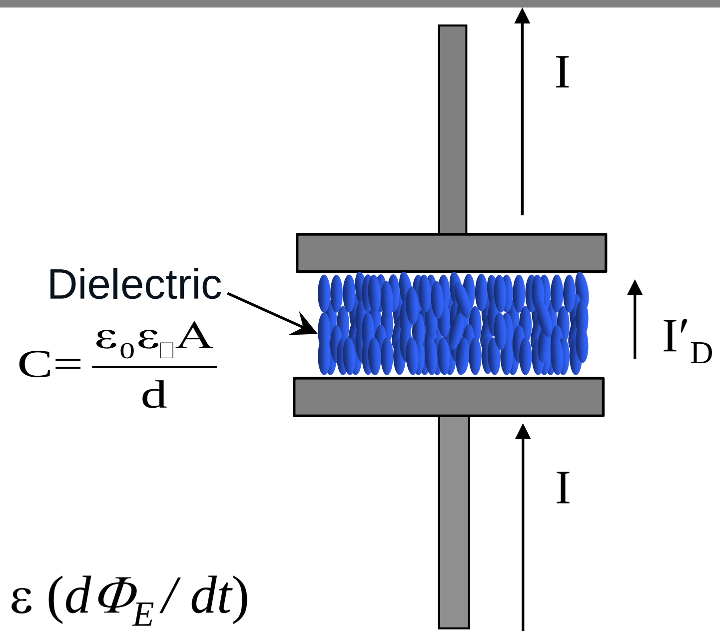
CNT	LC
d = 4-8 nm	d = 1 nm
L = 0.5-2 μm	L = 3 nm

0.005 wt% of CNT in LC

Dielectric measurements!

Why Dielectric measurements?





$$D = \varepsilon E \; ; \; I_D = \varepsilon \, (d\Phi_E / dt)$$

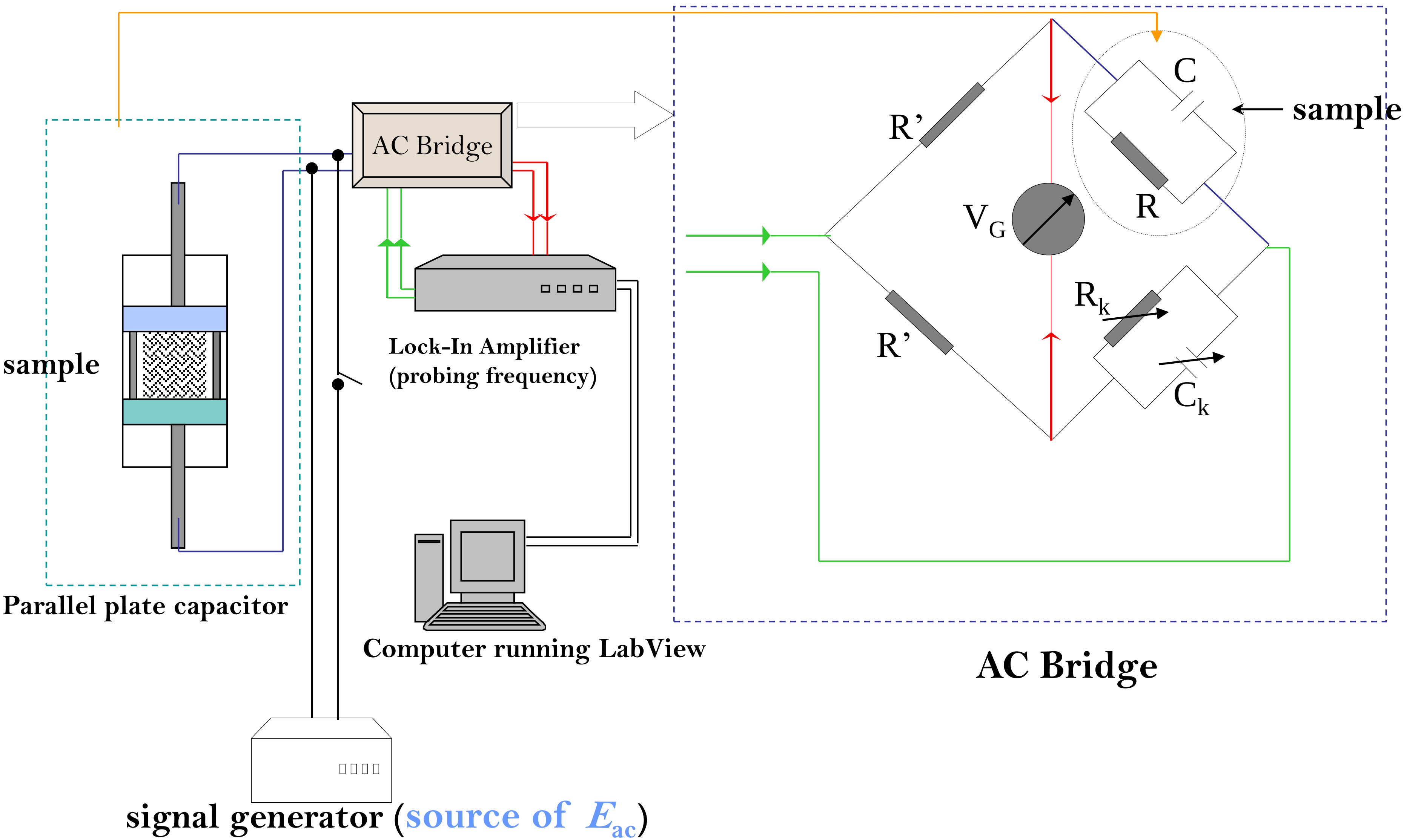
ε_0 = free space permittivity

ε = permittivity of the sample, so Dielectric constant $\varepsilon_r = \varepsilon / \varepsilon_0$

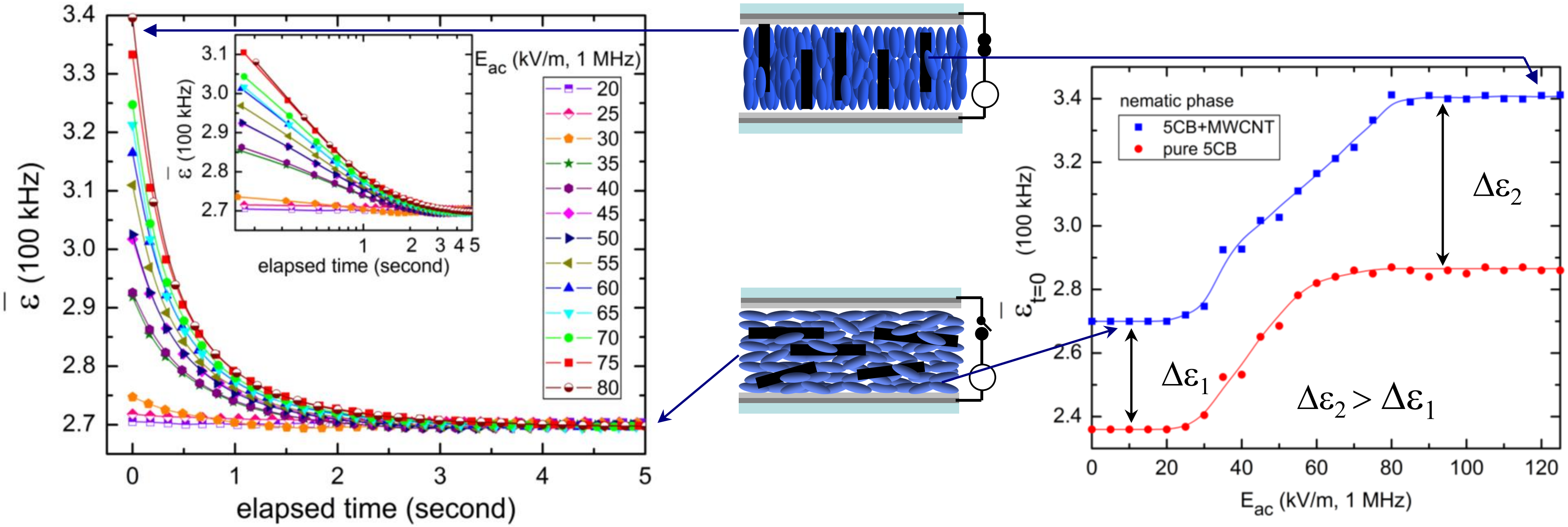
<u>Dielectric constant provides information about</u>

- Change in molecular structure
- Dynamics of molecules

Schematic diagram of dielectric spectrometer

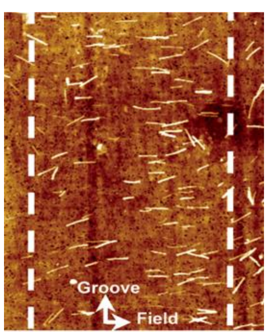


Dynamic response of nematic LC-CNT system



$\Delta\varepsilon_2 > \Delta\varepsilon_1$ confirms the CNT long axes reorientation

R. Basu and G. S. Iannacchione; ***Applied Physics Letters***, vol. 93, 183105 (2008)



This AFM image shows oriented MWCNTs deposited from 5CB in a 20 μm channel

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

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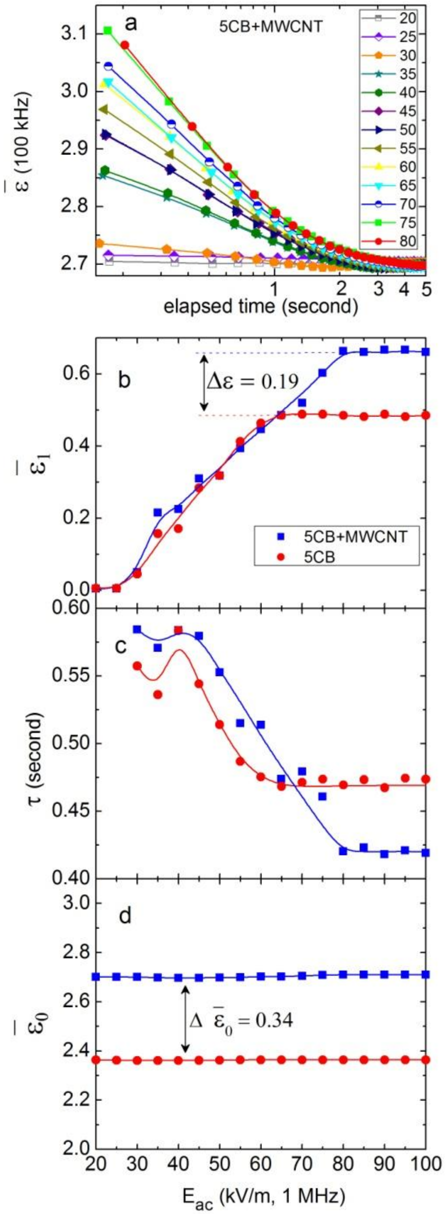
Analysis



$$f(t) = \bar{\varepsilon}_1 \, e^{(-t/\tau)} + \bar{\varepsilon}_0$$ (regression coefficient R = 0.9996)

τ = relaxation decay time

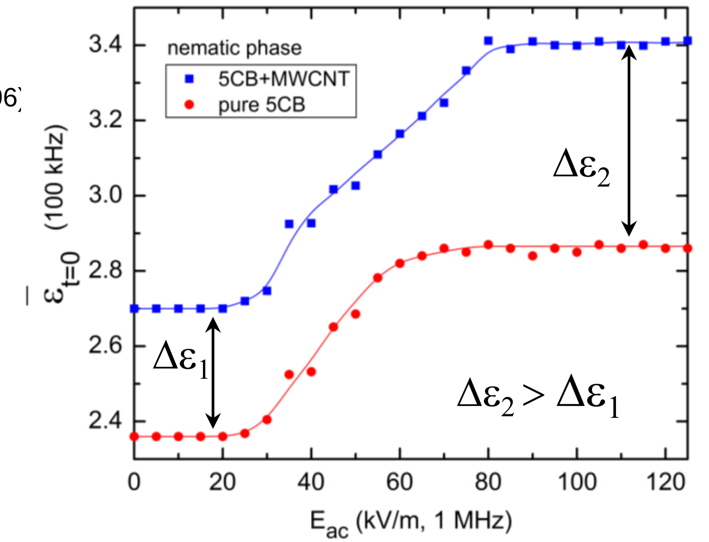
$\bar{\varepsilon}_1$ = field dependent dielectric constant

ε_0 = base dielectric constant

$$\bar{\varepsilon}_1 + \bar{\varepsilon}_0 = \bar{\varepsilon}_{t=0}$$

$$\Delta\varepsilon_2 - \Delta\varepsilon_1 = 0.2 \cong \Delta\varepsilon$$

$$\Delta \bar{\varepsilon}_0 = 0.34 = \Delta\varepsilon_1$$

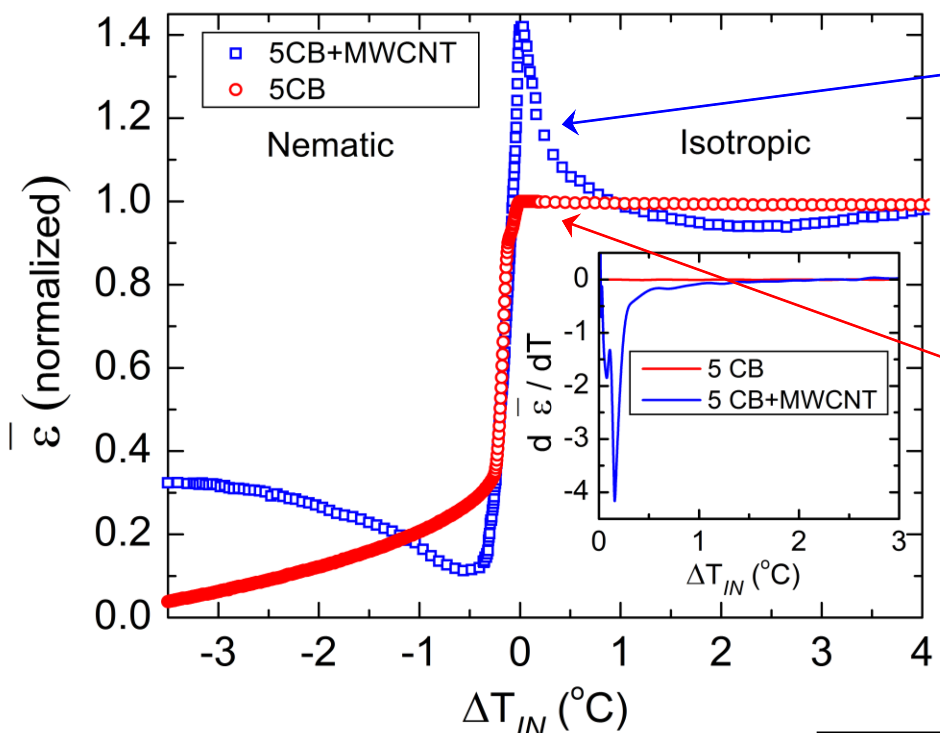


- Nano electromechanical system!
  nano/micro switch with a fast response time

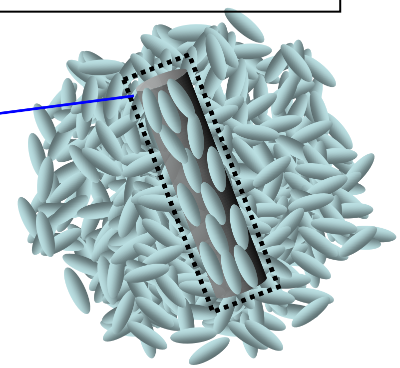
- Improvement in decay time!
  ion catching process of CNTs; application to LCD for image stabilization

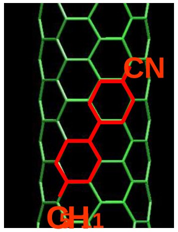
LC+CNT system temperature dependence

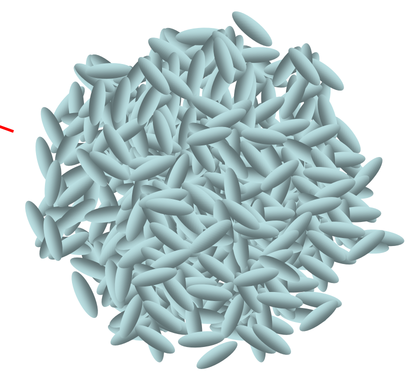
- Classic behavior of $\bar{\varepsilon}$ for pure LC
- Dramatic change in $\bar{\varepsilon}$ for the composite



Pseudo nematic domain







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

$\bar{\varepsilon}_{iso}$ for pure LC is independent of T

$\bar{\varepsilon}_{iso}$ for LC+CNT is *NOT* independent of T

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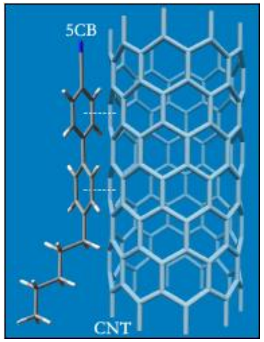
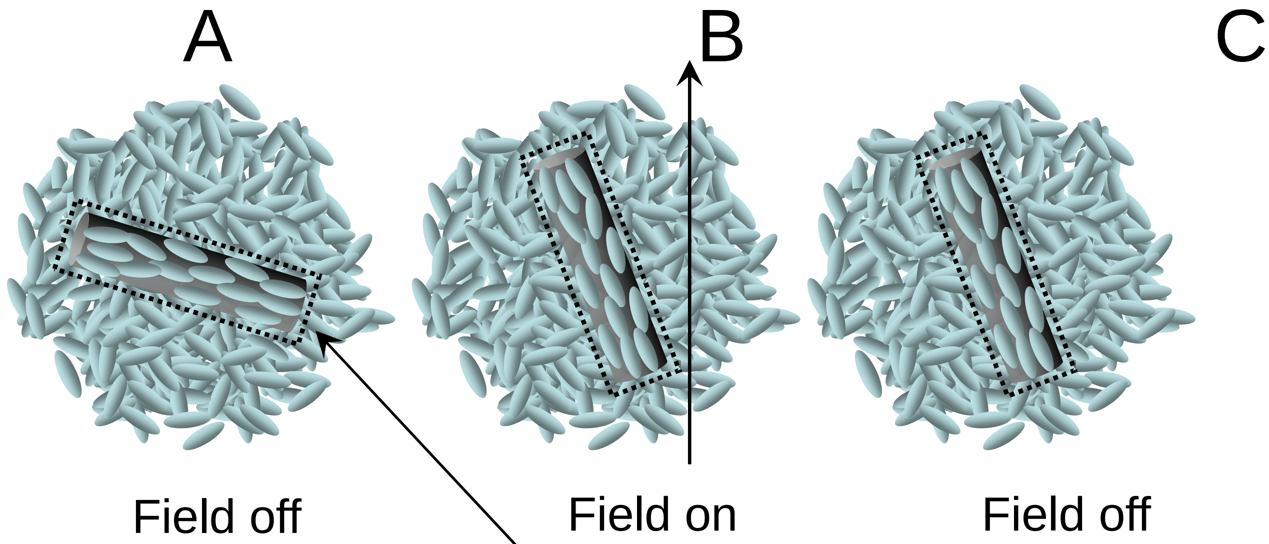
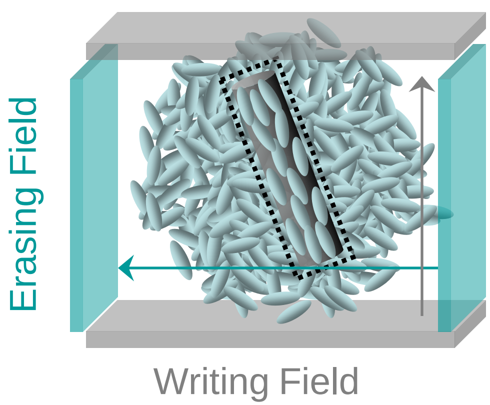
LC+CNT system in isotropic phase



LC-CNT interactions still exist in isotropic phase!

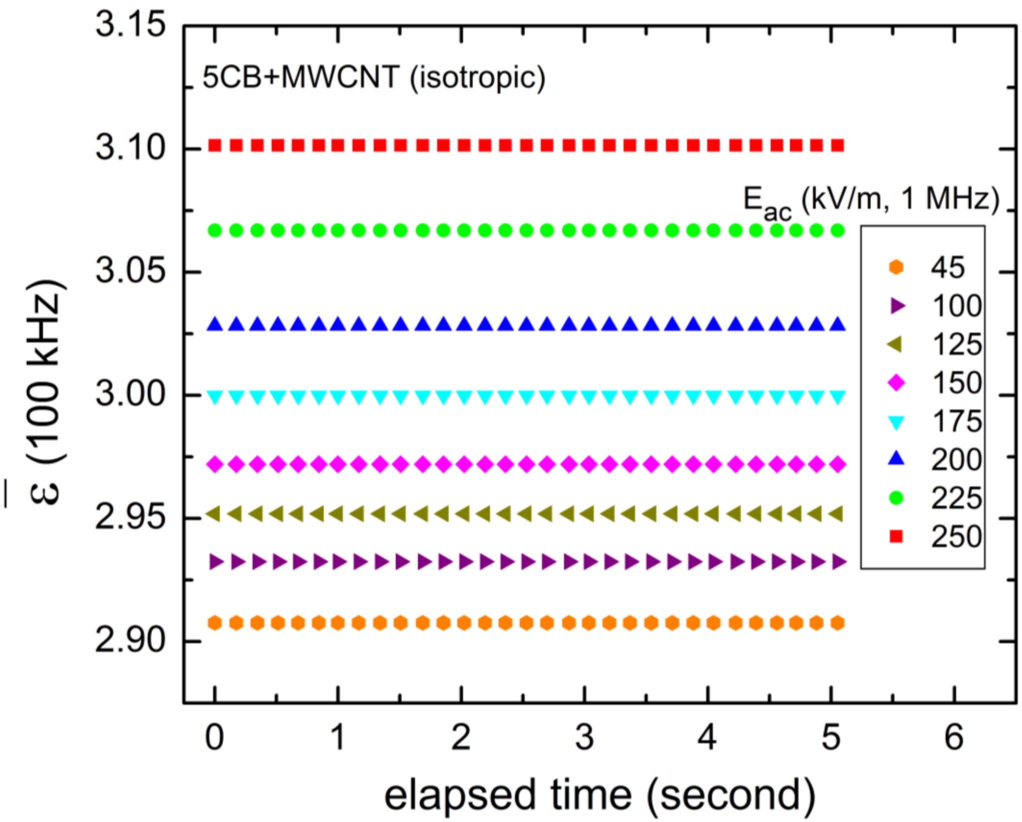


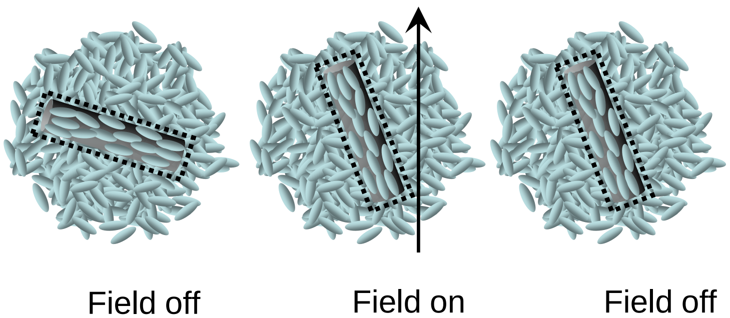
- Presence of anisotropic domains in an isotropic media
- No restoring force to torque the domains back to the original orientation after the field goes off

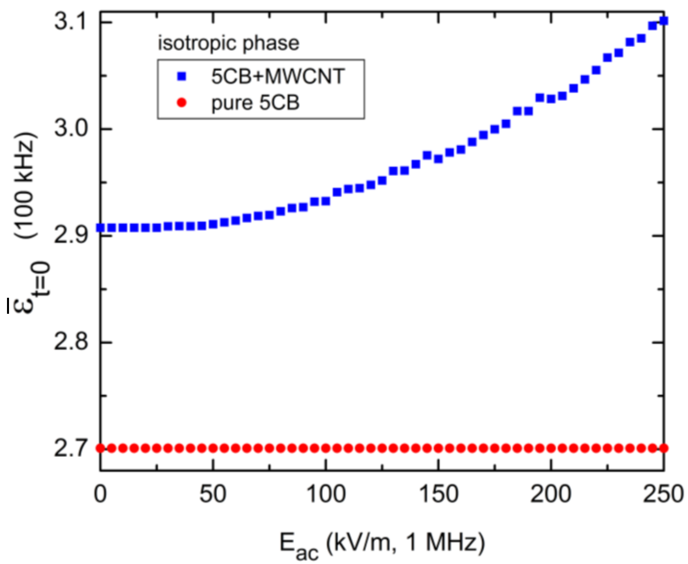


A model of a four-electrode field induced memory device

Dielectric response of isotropic LC-CNT system







T = 45 ^oC

Field-responsive anisotropic domains do not relax back to the original orientation on switching of the field off. **Non-volatile memory effect**!

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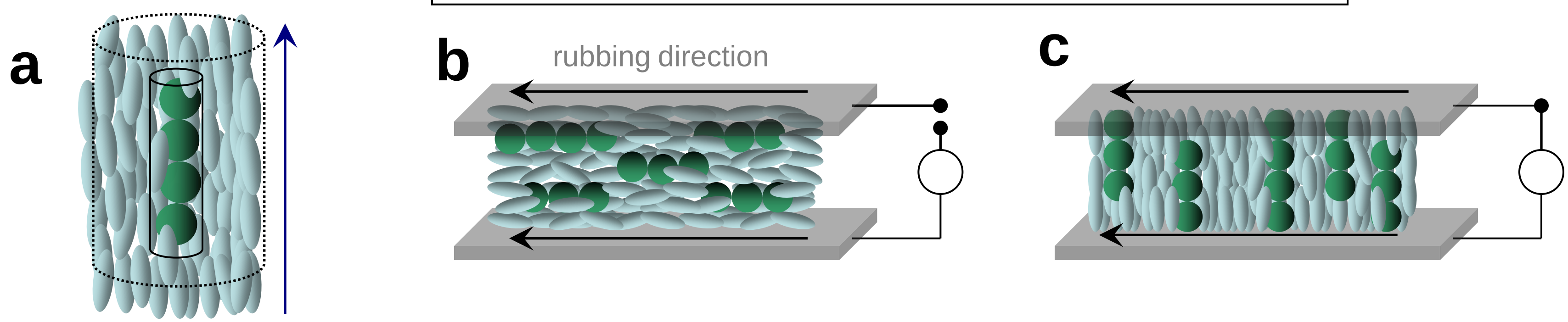
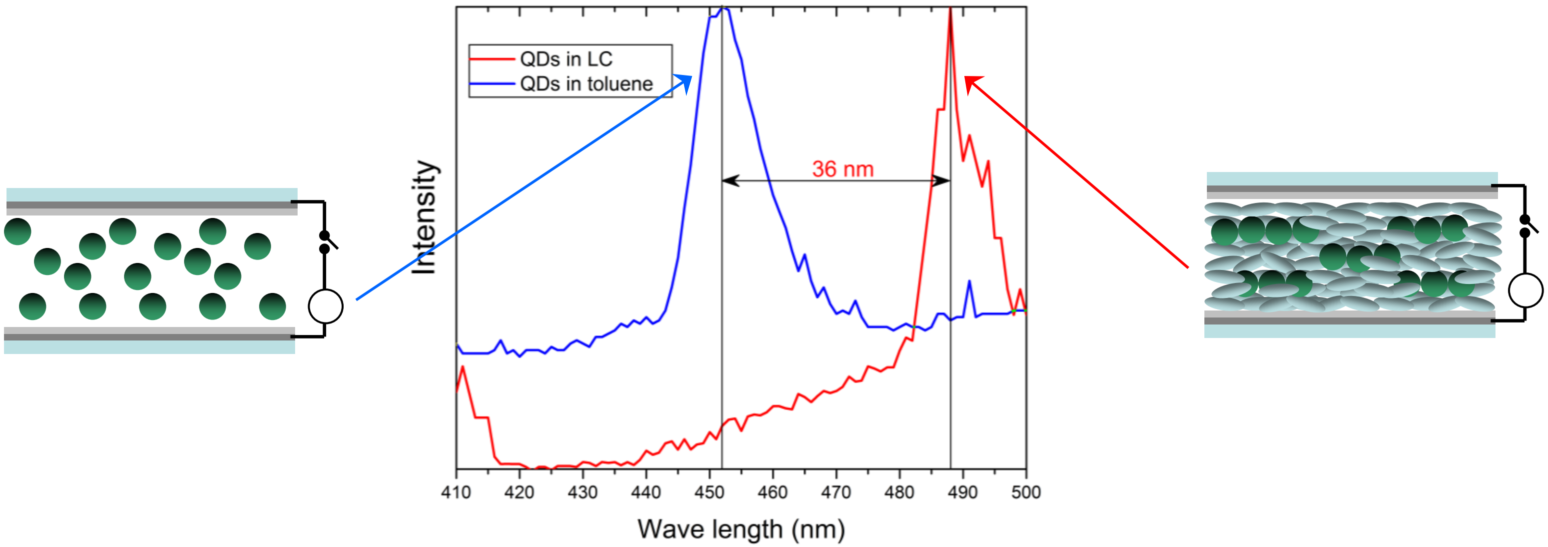
Future directions

Directed self-assembly of Quantum Dots





Fluorescence emission spectra also show red-shift

Conclusions

- Nematic LC phase transfers the orientational order onto dispersed nanotubes

- LC+CNT system shows nano-electromechanical response, and can be used as a micro-switch exploiting the high conductivity of CNTs along the long axis.

- In the nematic phase, the composite system results in an improvement in relaxation decay time for $E_{ac} > 80$ kV/m; which might be an application for LC display technology.

- In the isotropic phase, the presence of local *pseudo-nematic* domains demonstrates a promising field induced memory storage device application.

- Precise control of the long axes of CNTs enables possibility of using CNTs as *molecular wire* in *nano-electronics*.

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