*2010 TAPPI Intl Conf. on Nano for the Forest Product Industry*

# Ultra Thin Films of Oriented Cellulose Nanocrystals by Electric Field-Assisted Convective Assembly

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# Objective

- Ultra-thin films of cellulose nanocrystals (CNCs) produced by controlled assembly have gained recent attention:
  - understanding complex interactions
  - fabricating advanced materials

# Introduction

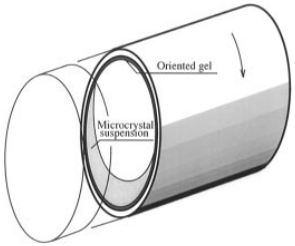
- Self-assembly can be facilitated by:
  - geometry of particles (aspect ratio)
  - dimensions
  - surface and intermolecular interaction forces
  - their response to electric or magnetic fields

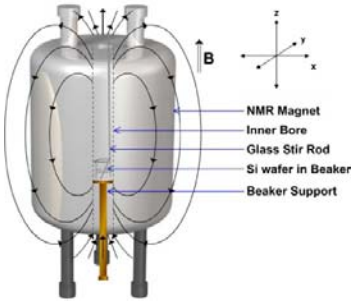
# Methods for alignment of cellulose materials

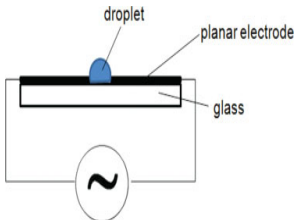
| Methods | Cellulose Source | Reference |
|---|---|---|
| Magnetic field | Tunicate cellulose **microcrystals** | Sugiyama, J.; Chanzy, H.; Maret, G. *Macromolecules* **1992**, 25, 4232 |
| Magnetic field | **Microcyrstals** from filter paper and bleached SW kraft fiber | Revol, J.-F.; Godbout, L.; Dong, X. M.; Gray, D. G.; Chanzy, H.; Maret, G. Liq. Cryst. **1994**, 16, 127 |
| Shear alignment | **CNX** from Green alga *Cladophora sp* | Y. Nishiyama, S. Kuga, M. Wada, T. Okano, *Macromolecules* 30, **1997**, 6395 |
| Magnetic and Shear alignment | **Microfibrils** from black spruce bleached Kraft pulp | WJ Orts, L Godbout, RH Marchessault, JF Revol, *Macromolecules*, **1998**, 31, 5717 |
| Shear alignment | Cotton **microcrystals** | Ebeling, T.; Paillet, M.; Borsali, R.; Diat, O.; Dufresne, A.; Cavaille, J-Y.;Chanzy, H. *Langmuir* **1999**, 15, 6123 |
| Magnetic field | Tunicate cellulose **microfibrils** | Kimura, F.; Kimura, T.; Tamura, M.; Hirai, A.; Ikuno, M.; Horii, F. *Langmuir* **2005**, 21, 2034 |
| Electric field alignment | Ramie and Tunicate **CNXs** | Bordel, D.;Putaux, J. L.;Heux, L. *Langmuir*, **2006**, 22, 4899 |

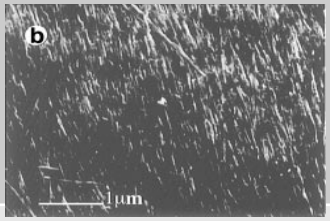
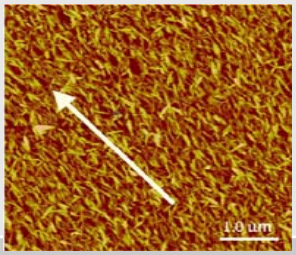
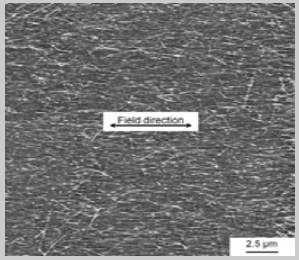
# Alignment of CNXs

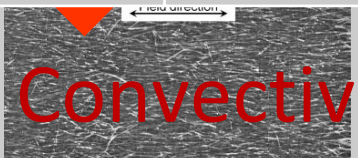
| Methods | Cellulose Source | Alignment evidence | Reference |
|---|---|---|---|
| Rotational shearing of a gel | G<br>C | | yama, S. Kuga, M.<br>T. Okano,<br>nolecules **1997**,<br>5 |
| Magnetic Field | C | | nston, D.G. Gray.<br>and Technology<br>nced Materials ,<br>, 319 |
| Electric Field | T<br>R | | D.;Putaux, J.<br>, L. Langmuir,<br>2, 4899<br>Habibi et al. Journal of Polymer Science B, **2008**, 46, 1430 |




| Methods | Alignment evidence | Disadvantage |
|---|---|---|
| Rotational shearing of a gel |  | Time 12 h. High Viscosity; Difficult thin film manufacture |
| Magnetic Field |  | Time 24 h. Nuclear magnetic resonance. 7 Tesla magnetic field. |
| Electric Field |  | High electric field: Voltage: 2.5 – 20V (2-10 kV/cm) Frequency: 1kHz – 2MHz |

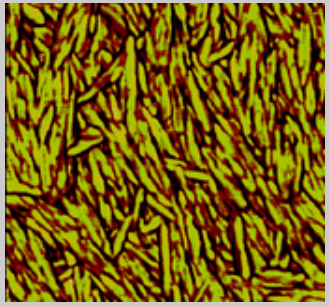


Shear Rate with Convective Assembly

# Recent advances of alignment of CNXs

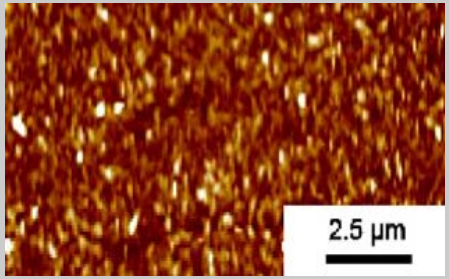
- Ultra thin films of cellulose nanocrystals (CNs) can be made using (isotropic films):

*Langmuir-Schaeffer lifting*:

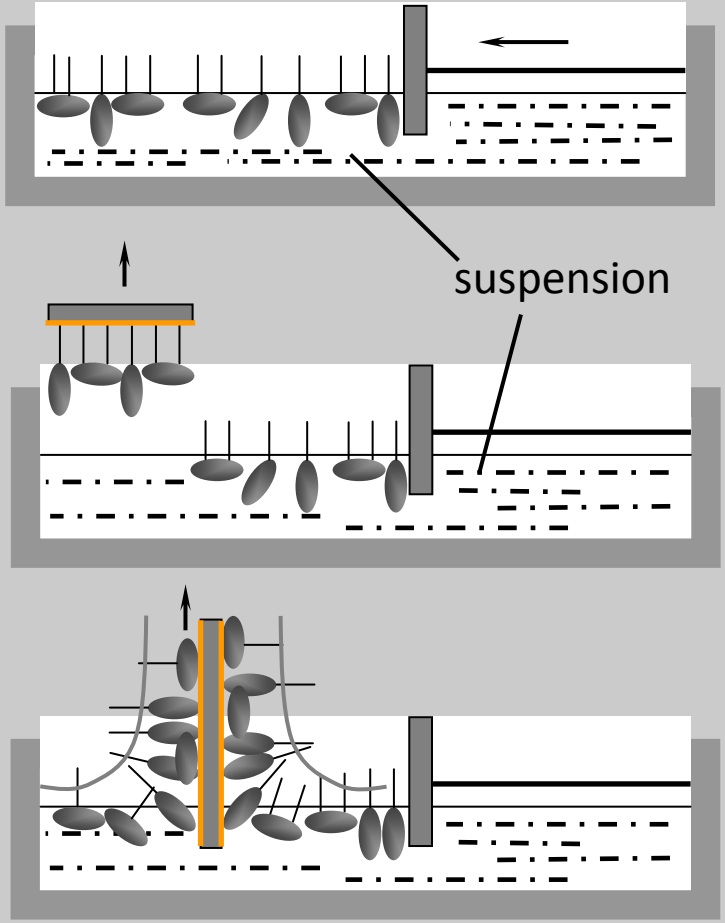


Rojas and co-workers, *Langmuir* 26, 990 (2010)

*Langmuir-Blodgett lifting:*



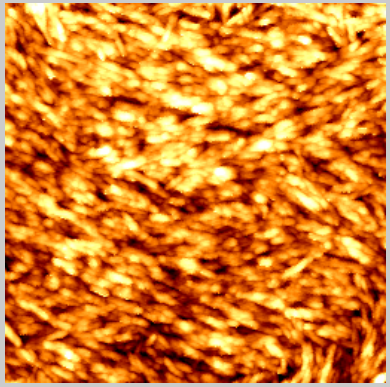

Habibi et al. *JCIS*, 316,388 (2007)

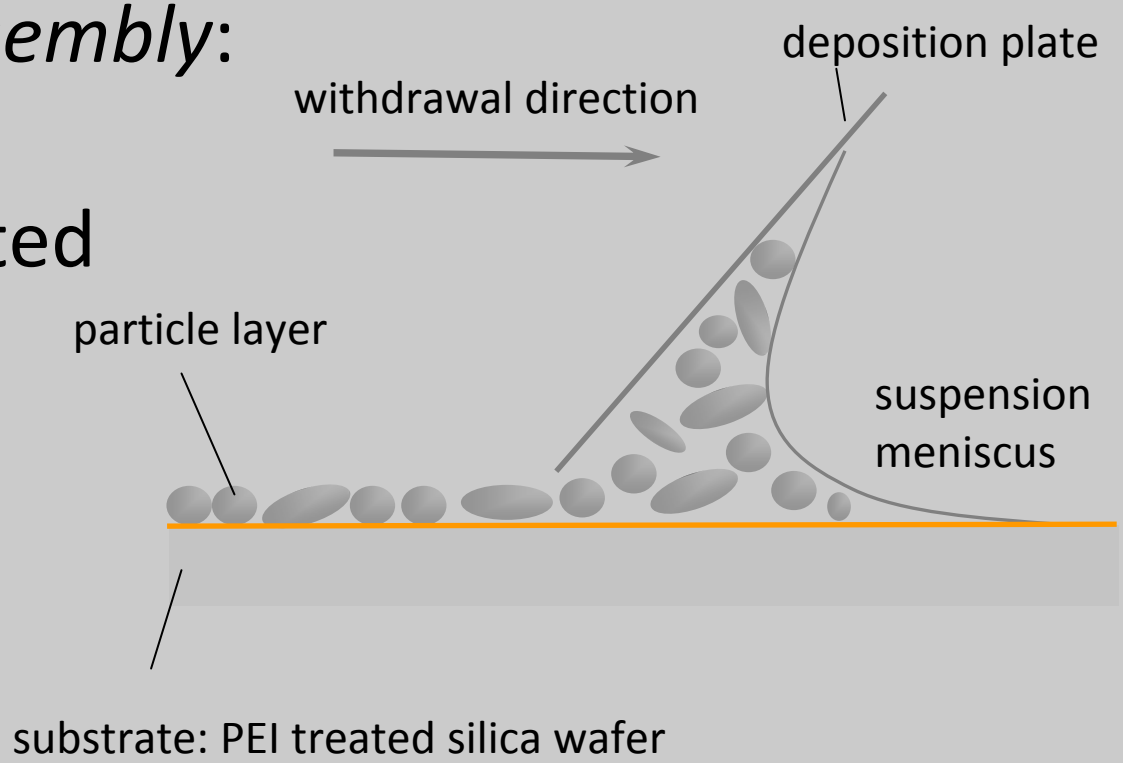


# Convective self assembly

*Convective self-assembly*:

The film is oriented

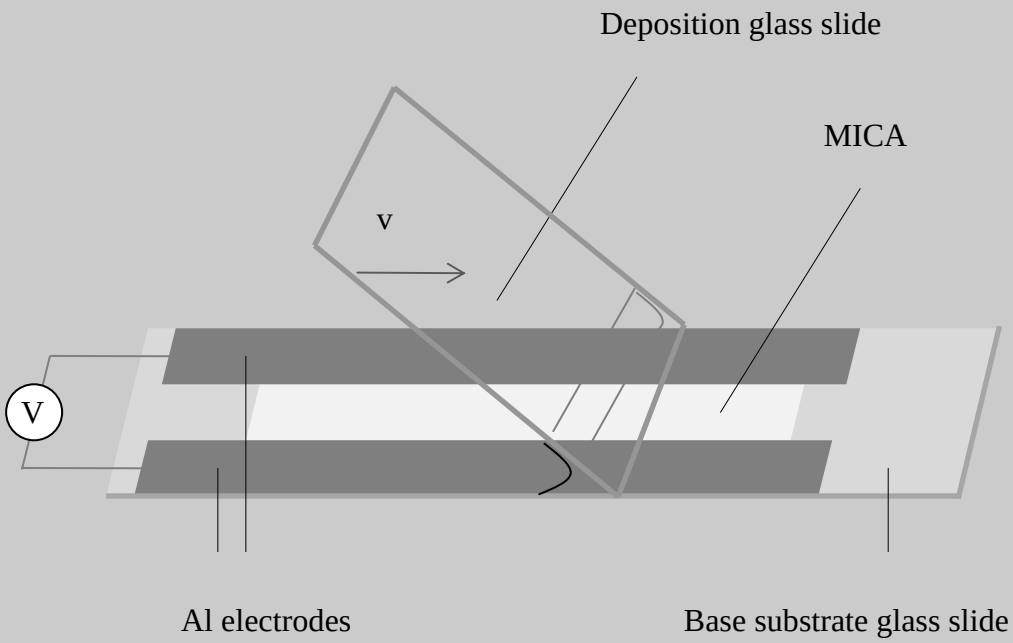





Rojas and co-workers,
*ACS Nano*, submitted

# Aim

- Aim of this presentation:
  - Demonstration of the fabrication of higly ordered structured CNC films by using:
    - electric field-assisted convective self-assembly



# Materials

- Ramie fibers were used in the production of cellulose nanocrystals (CNCs)
- They were hydrolyzed with 65 % sulfuric acid at 55 °C for 30 min
- Dialysis against deionized water followed and then against Milli-Q water (for a few weeks)
- The dimensions of the CNs were 185± 25 nm in length and 6.5 ± 1 nm in width (88% CrI)

# Theoretical considerations

- Dielectric: *ability to store energy in an applied electric field* *(depend on frequency, temperature, orientation, mixture, molecular structure)*
- Permittivity: *interaction of a material with an electric field*

$$\bar{\varepsilon} = \varepsilon - i\frac{\sigma}{\varepsilon_0 \omega}$$

I - how dissipative or lossy the material is

R - how much energy from an external field is stored

# Polarization

- <u>Materials have</u> an *arrangement of charge carriers that can be displaced by electric fields*

the charges become polarized

To describe the complex CNC-water suspension system the *Maxwell-Wagner* permittivity model must be redefined!

$$\varepsilon^*_{p,MW}(\omega_e) = \varepsilon_p - j\frac{\sigma_p}{\varepsilon_0 \cdot \omega_e}$$

$$\varepsilon^*_{c,MW}(\omega_e) = \varepsilon_c - j\frac{\sigma_c}{\varepsilon_0 \cdot \omega_e}$$

# Dipole moment of an ellipsoid

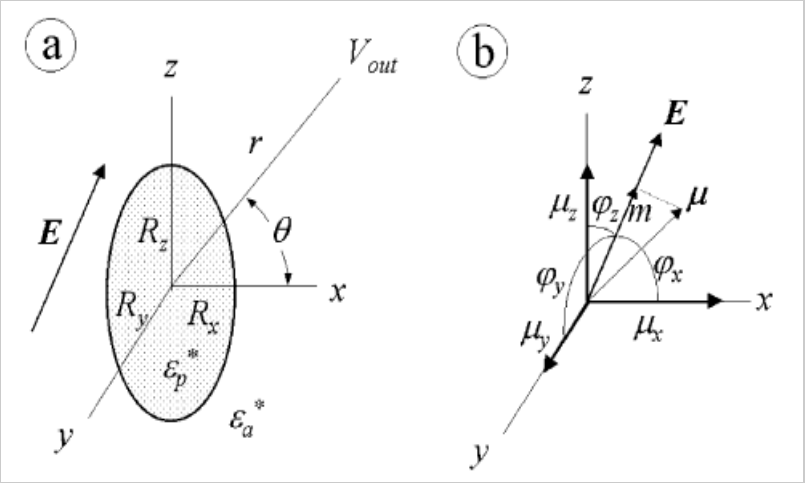
<u>Dipole moment</u>: a measure of the separation of *positive* and *negative* electrical charges, a measure of the charged system's overall polarity

$$p_i = 4\pi a^2 b \overline{\varepsilon_m} K_i E_i$$

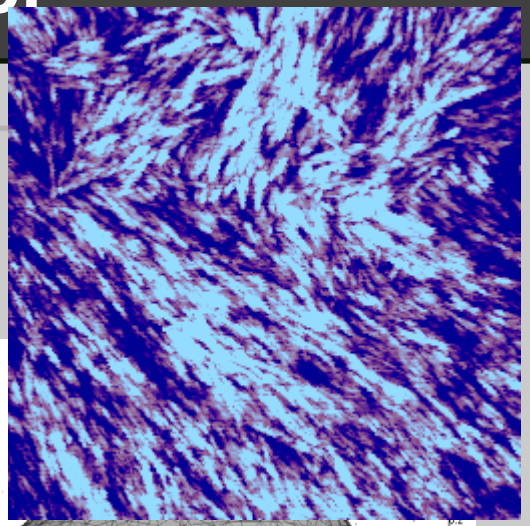
Clausius-Mossotti factor

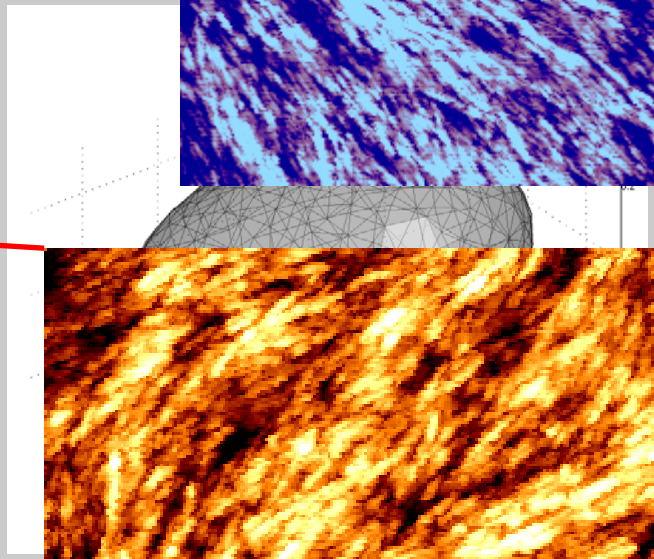
$$K_i(\omega) = \frac{1}{3}\frac{(\overline{\varepsilon_p} - \overline{\varepsilon_m})}{\overline{\varepsilon_m} + A_i(\overline{\varepsilon_p} - \overline{\varepsilon_m})}$$

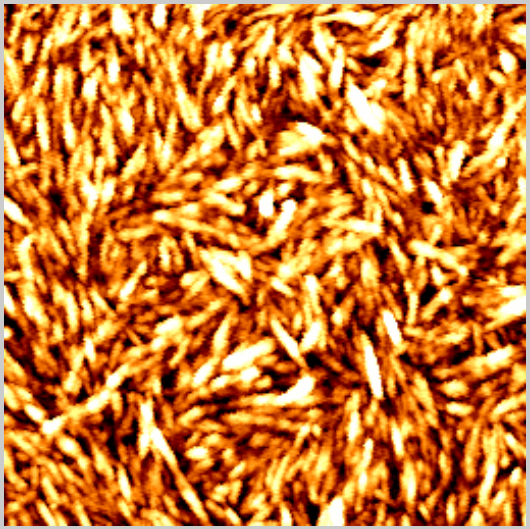
depolarization factor



# Depolarization factor

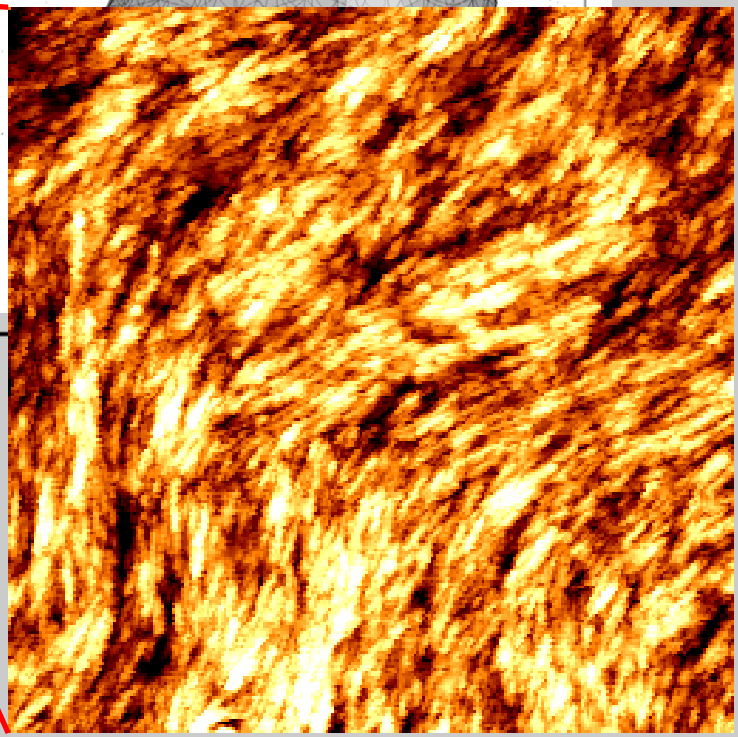






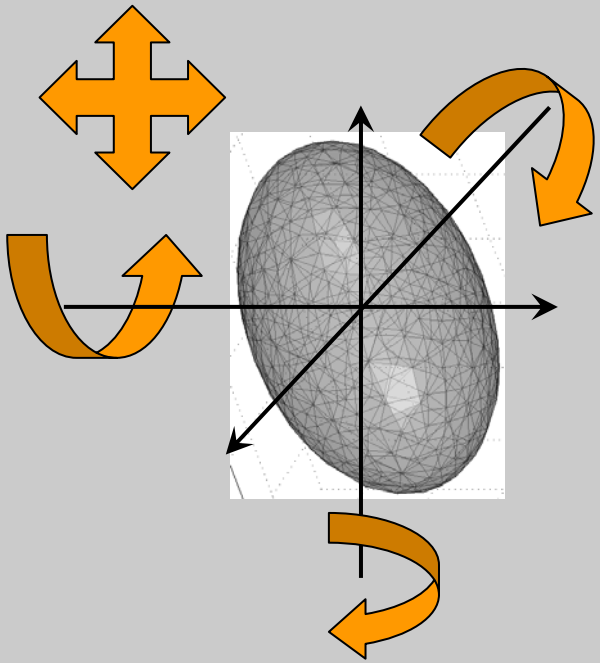
eccentricity

$$e = \sqrt{1 -}$$



# Dielectrophoresis

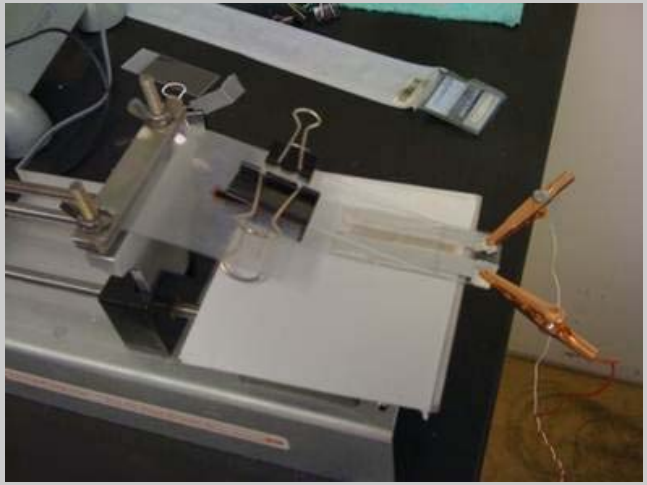
- Dielectrophoresis: is the motion of particles due to the interaction of a non-uniform applied electric field and the moments induced in particles

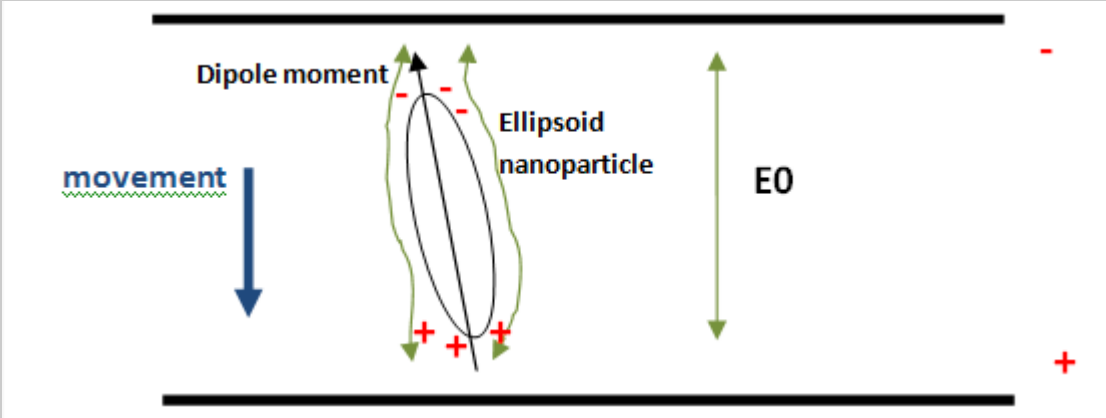


# Energy of an ellipsoid particle

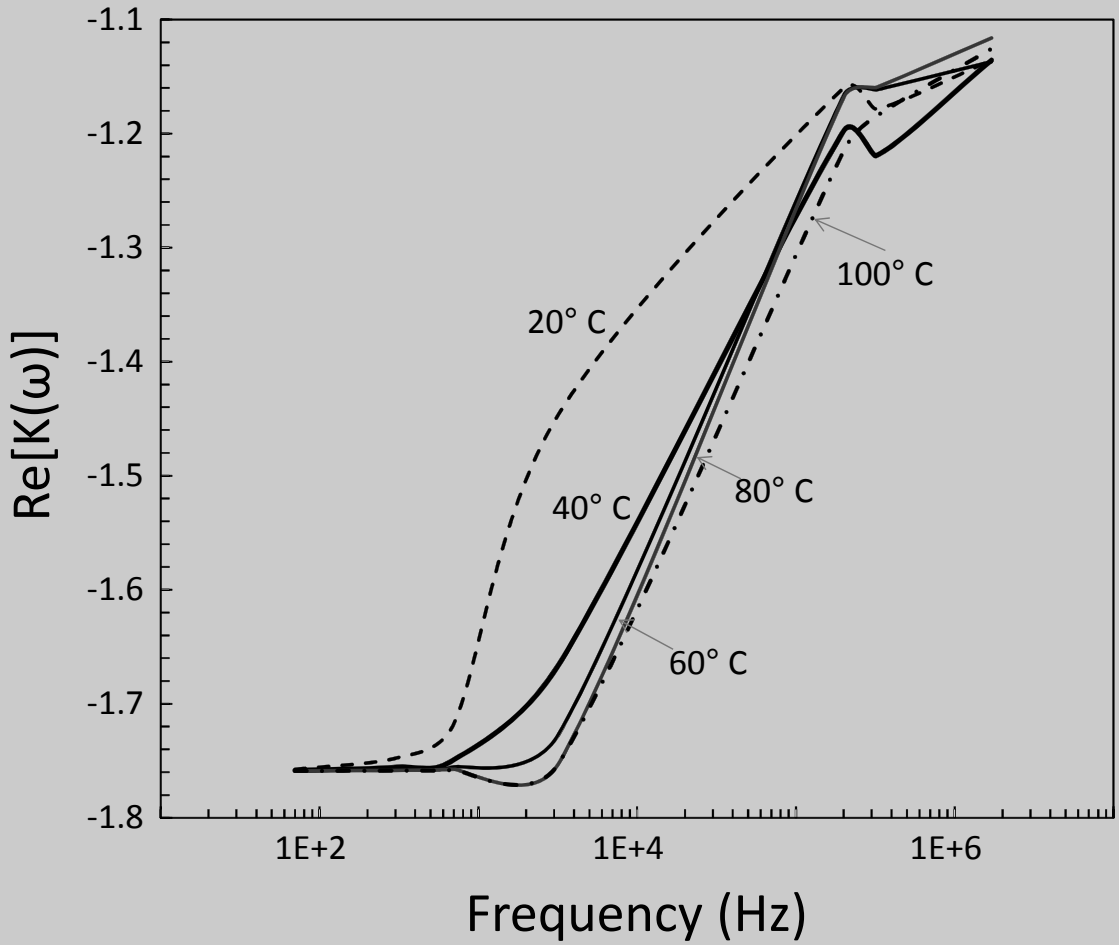
- with dipole moment *p* and
- electric field *E*

$$V(\theta) = -A\Re(p.E)$$

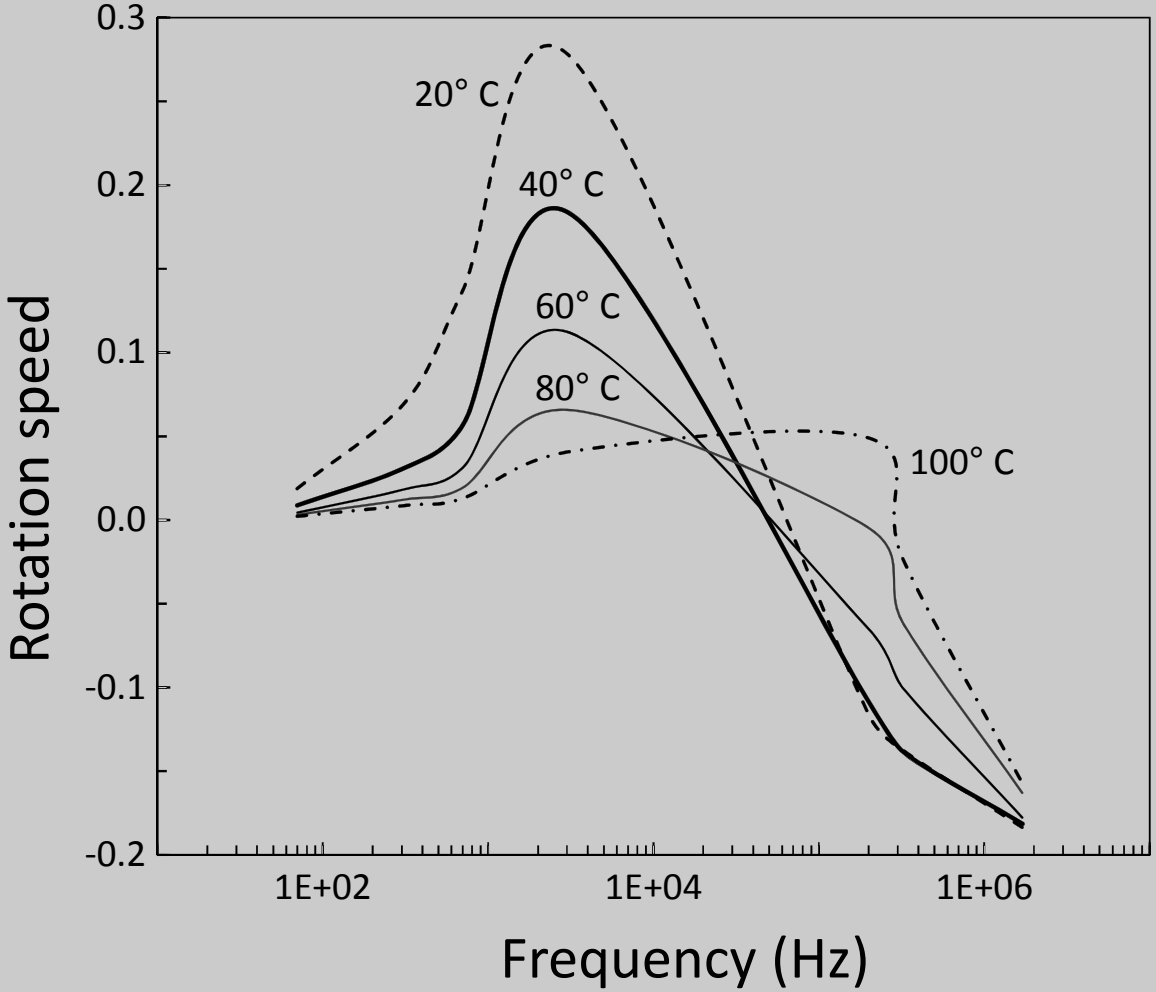




# Calculated spectra for homogeneous prolate ellipsoids at different water and cellulose conductivities



# Rotation speed $Im[f_{CM}]$ spectra of nanocrystalline cellulose



# Probability distribution

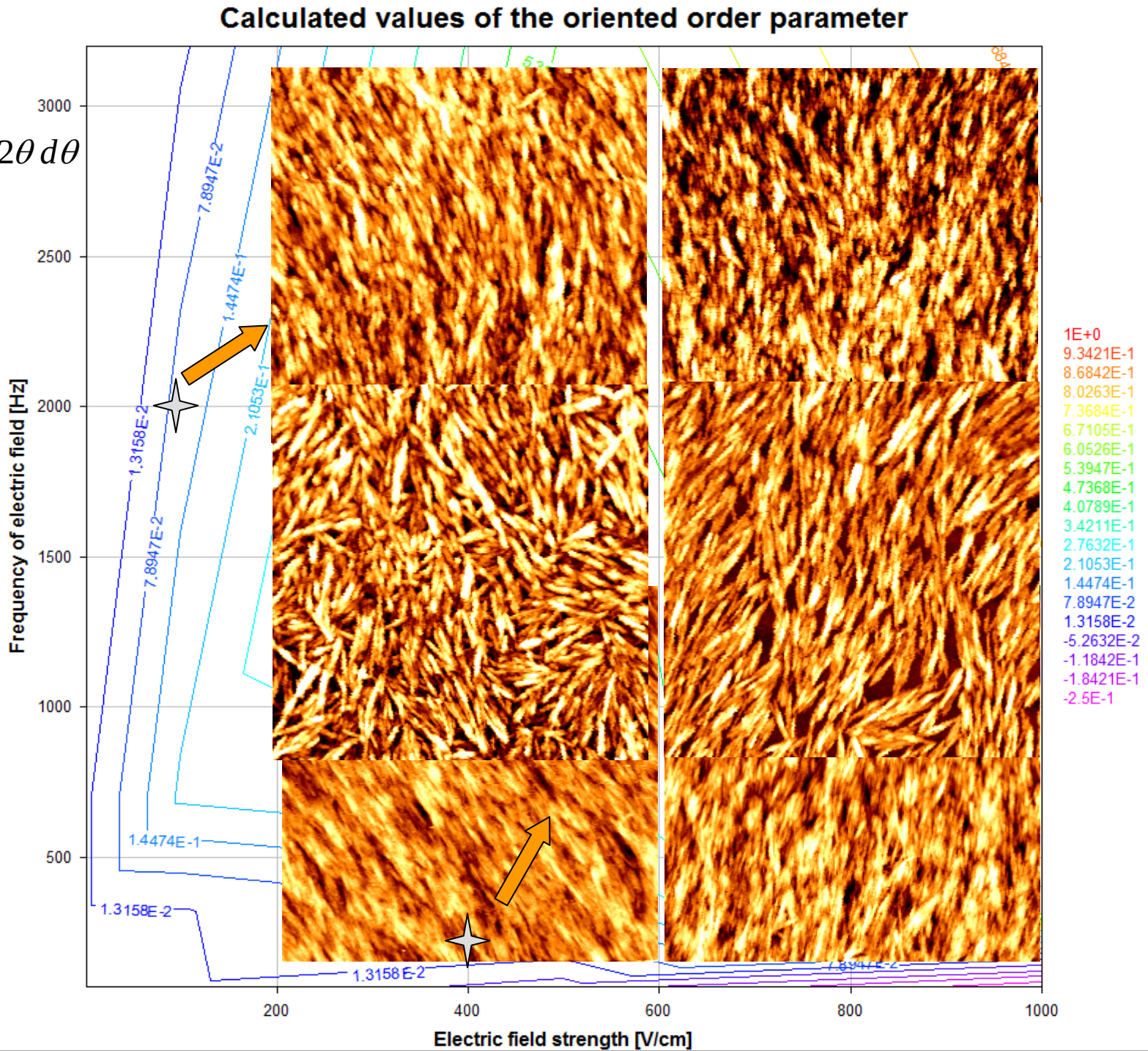
- Probability *Maxwell-Boltzmann* distribution function $P$ of the orientation of ellipsoid nanocrystals in an electric field:

$$P_{MBd} = \frac{e^{-\frac{V(\theta)}{kT}}}{\int_0^{\pi/2} e^{-\frac{V(\theta)}{kT}} d\theta} \Rightarrow O_p = \int_0^{\pi/2} P_{MBd} \cos 2\theta \, d\theta$$

where: *k*-Boltzmann constant,

*T*-temperature

$$O_p = \int_0^{\pi/2} P_{MBd} \cos 2\theta \, d\theta$$



# Conclusions

- Comprehensive literature review
- Polarization of CNCs
- Alignment

# Thank you for your attention!