

Self Assembly of Gold-Nanorods in Cellulose Liquid Crystals

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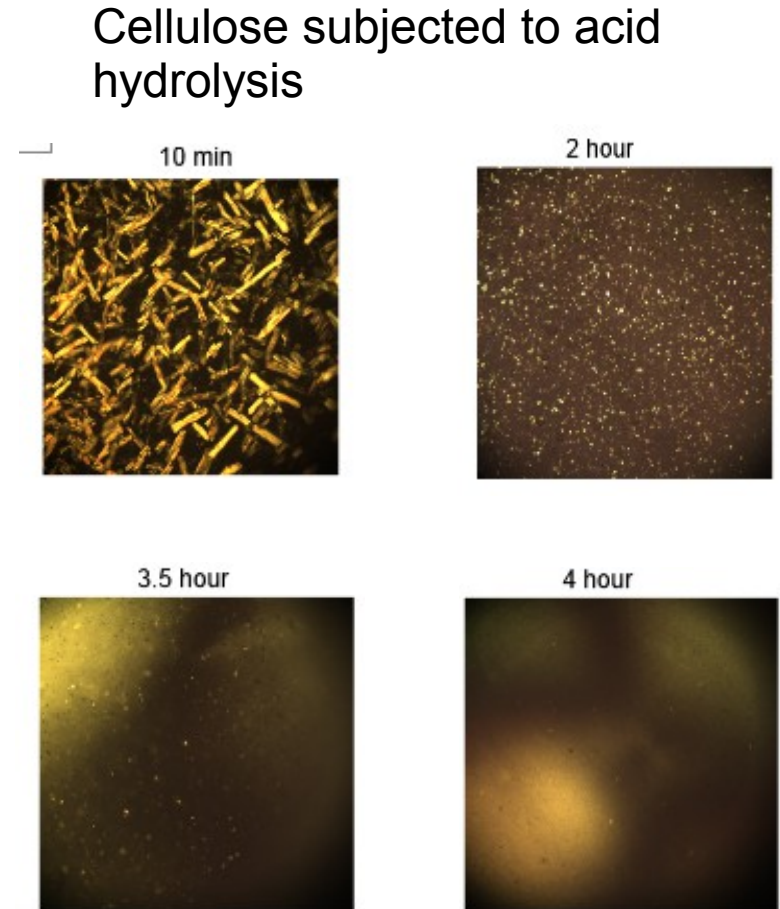
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Abstract: Liquid Crystal Media can be used as a host material which can provide control over large scale self organization of nanometer sized particles. In this work, we used cellulose nanocrystal based nematic and cholesteric liquid crystals to disperse and align gold nanorods along the far-field LC director. In the nematic phase, the liquid crystal mediated alignment results in a polarization-sensitive plasmon resonance, different from that of the same nanoparticles in isotropic media.

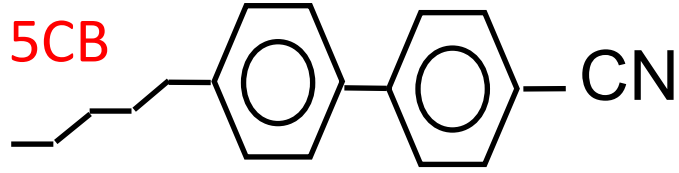
Cellulose Nanorods

- Cellulose consists of both crystalline and amorphous regions. The crystalline regions are typically 5-10nm wide and 100-200 nm long
- When cellulose is subjected to hydrolysis by sulfuric acid, the amorphous regions will dissolve leaving highly ordered cellulose nanocrystals (CNC).
- Sulfate groups will bind to the CNC during hydrolysis. These sulfate groups cause the cellulose to disperse in water and form liquid crystal phase.



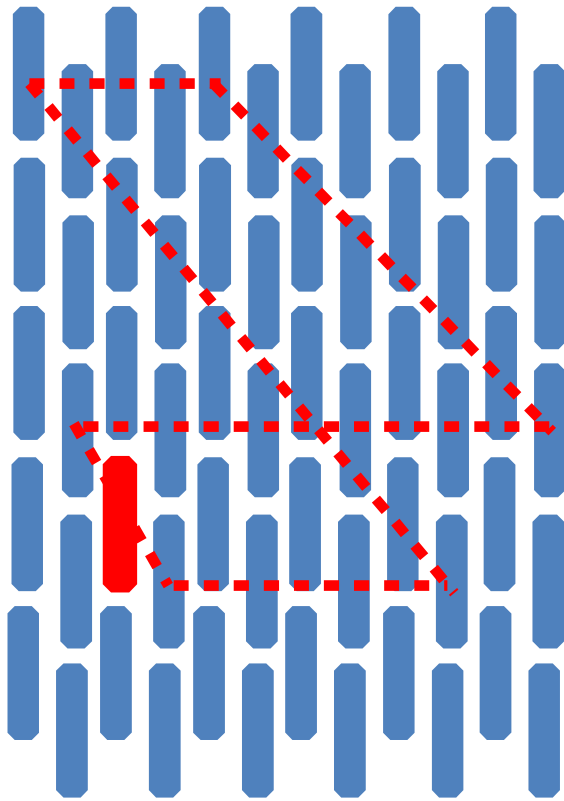
Liquid Crystals (LCs)

5CB

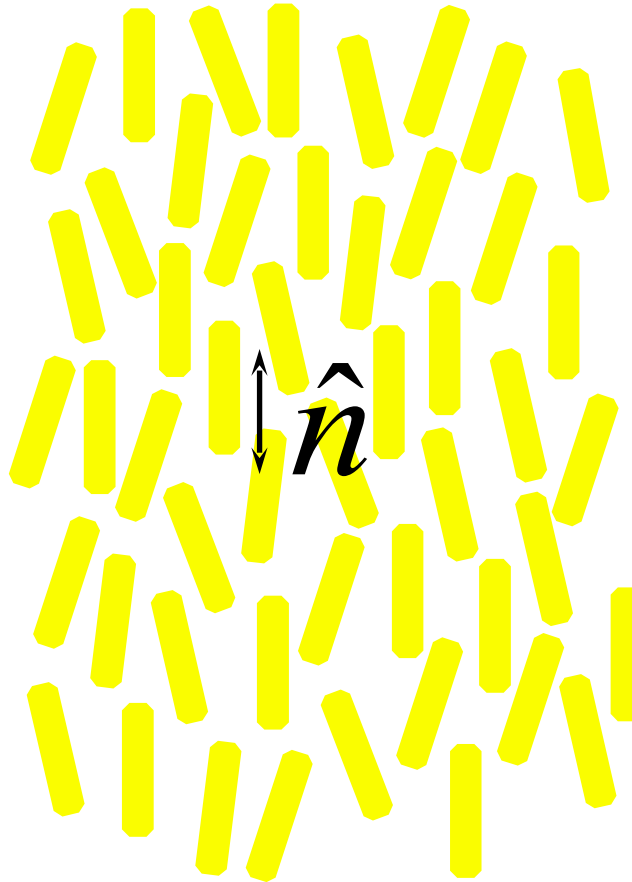


- Flow like liquids;
- Anisotropic like solid crystals;

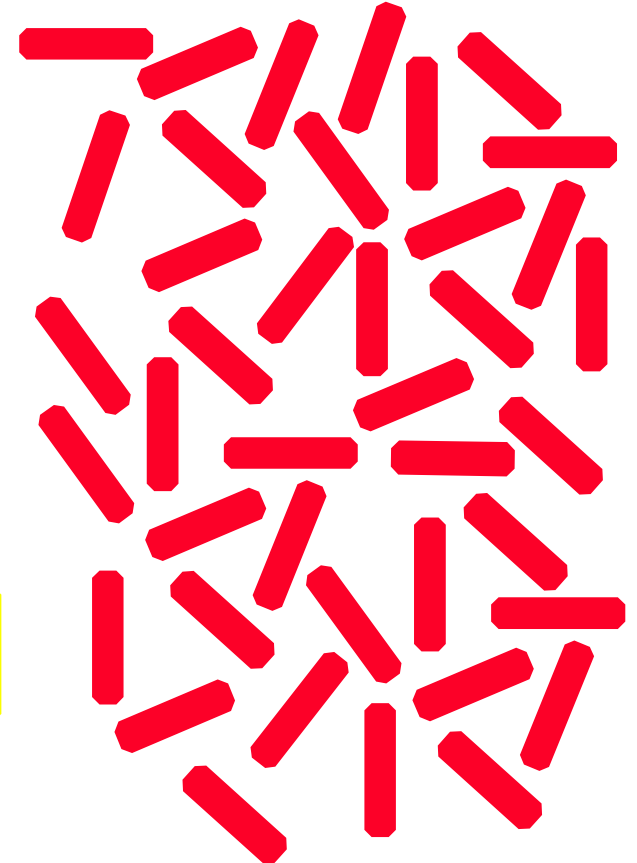
Crystal



liquid crystal (nematic)



Isotropic fluid



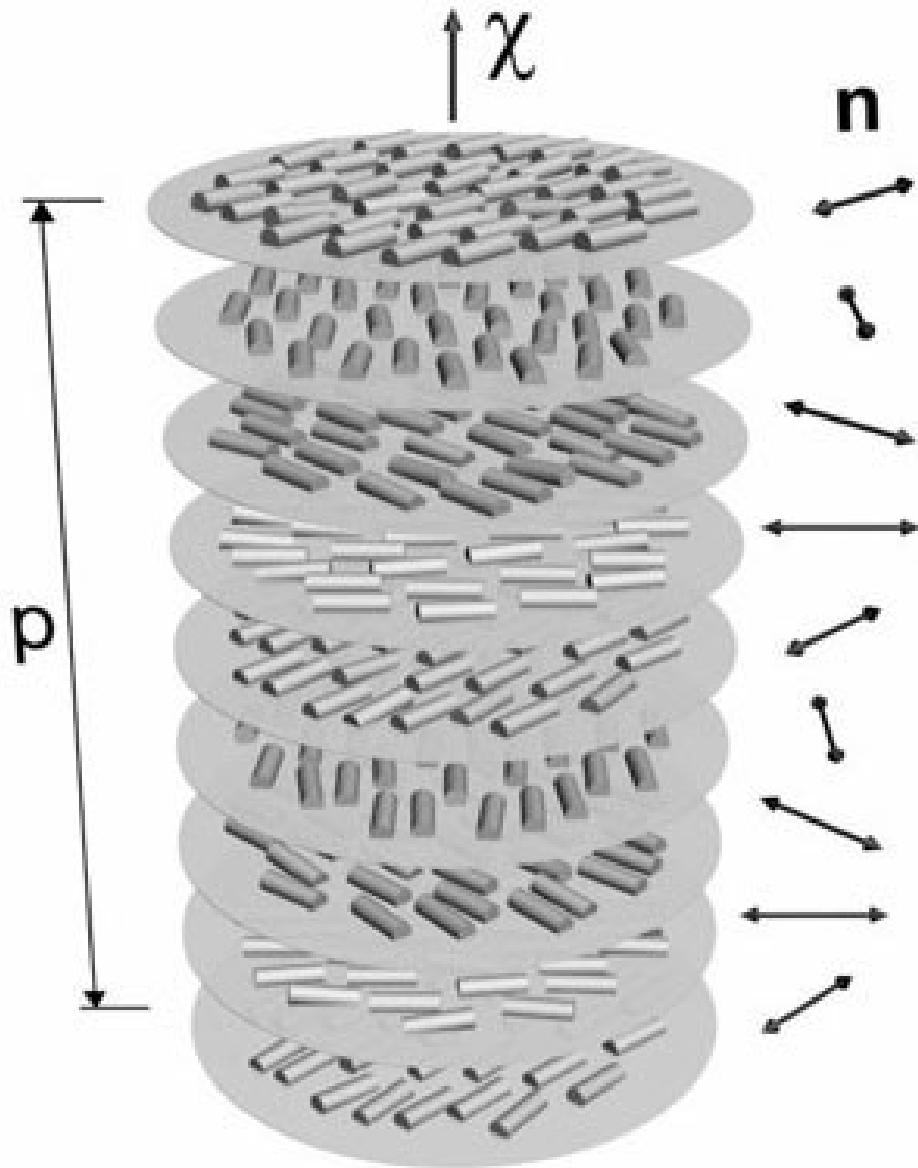
Average local molecular orientations in liquid crystals are described by the director with head-tail symmetry

$$\hat{n} \cdots \leftrightarrow \hat{n}$$

LC is a state of matter intermediate between that of a crystalline solid & an isotropic liquid. LCs possess many of the properties of liquid, e.g. high fluidity, viscosity, formation, and coalescence of droplets. At the same time they are similar to crystals in that they exhibit anisotropy in their optical, mechanical, electrical, and magnetic properties. LCs exhibit a great variety of phases, which differ one from another by their structure and physical properties.

Chiral nematic LCs: twisted ground states

Cholesteric phase



Cellulose

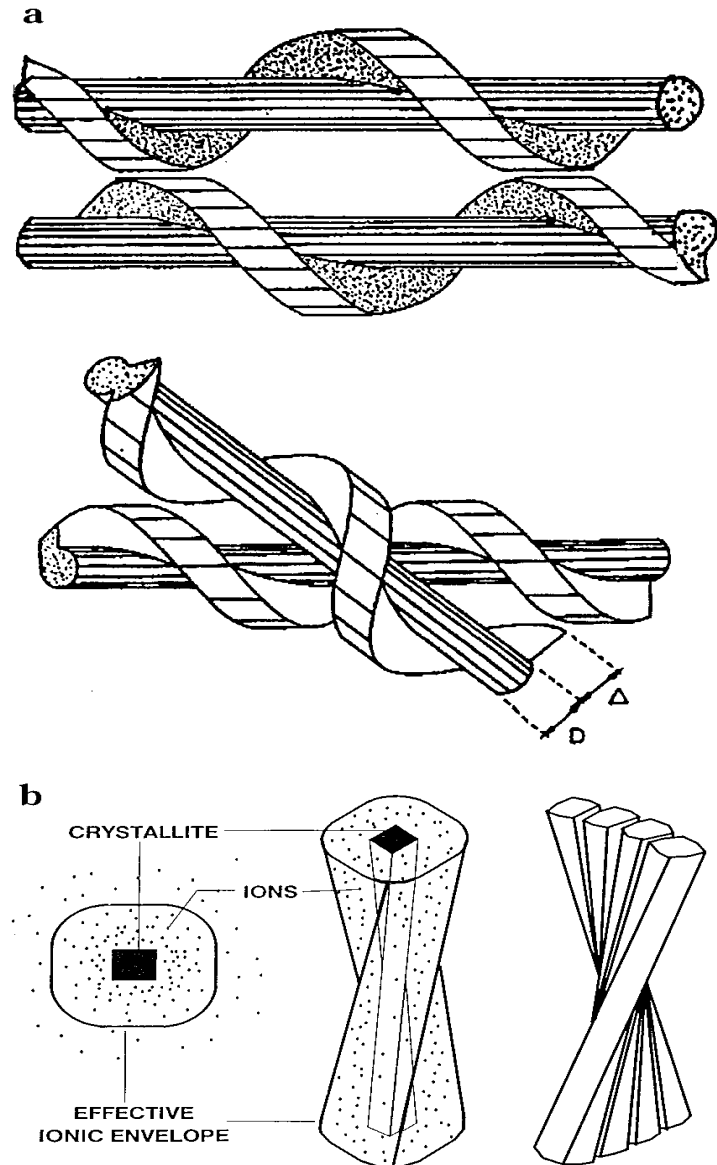
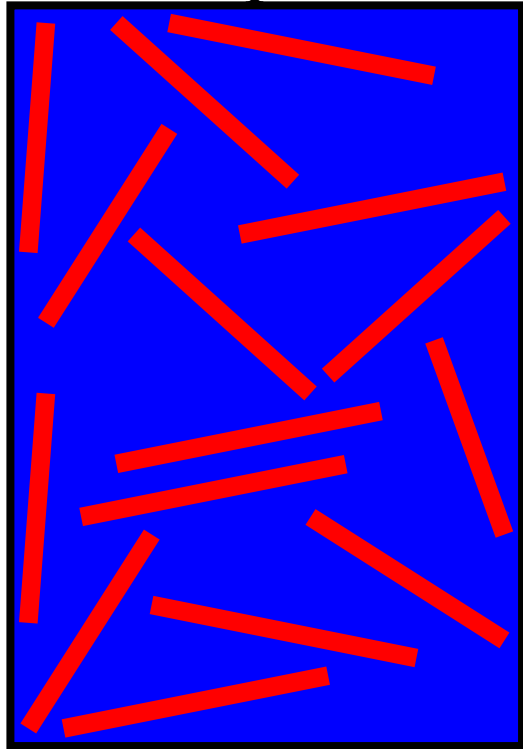


Figure taken from Orts et. al
Macromolecules, 1998, 31, 5717-5725

Onsager criterion for nematic order of rigid rods

Isotropic



Nematic

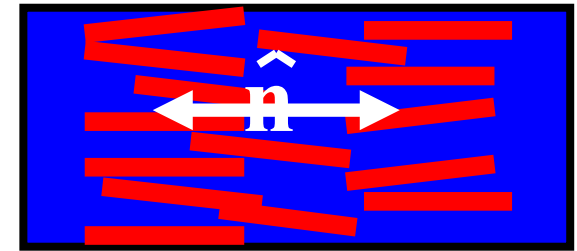
→ **Critical concentration**

$$\eta_{NI} \sim 4 \frac{D_{rod}}{l_{rod}} \quad \text{when} \quad \frac{l_{rod}}{D_{rod}} \uparrow \uparrow 1$$

Increasing
concentration

→ **Steric interactions**
→ **Orientalional entropy**

$$\eta_{NI} \downarrow (0.3 \div 10)\%$$



→ **Semi-flexible rods** $l_{cellulose} = 300\text{nm}$

→ **Critical number density** $4.48 / (-D_{rod} l_{rod}^2 / 4)$

→ **For rods of** $l_{cellulose} = 300\text{nm}$ **one needs** $3.4 \cdot 10^{23} \text{rods/m}^3$

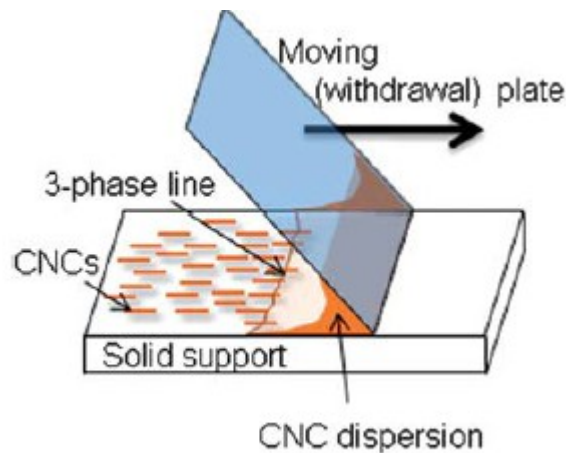
→ **Charged rods have effective diameter** $D_{eff} \uparrow D_{rod}$

→ **Charged rods will twist, forming chiral nematic phase**

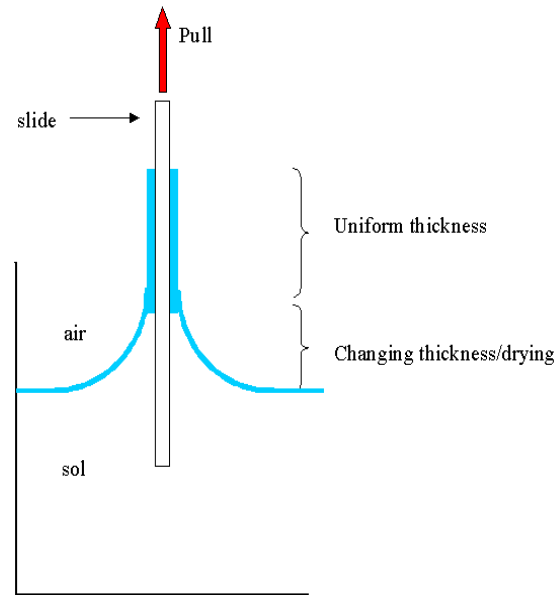
Nematic order

- Cellulose nanocrystals may also form a nematic like order when they are subjected to shearing, or when the rods flow.

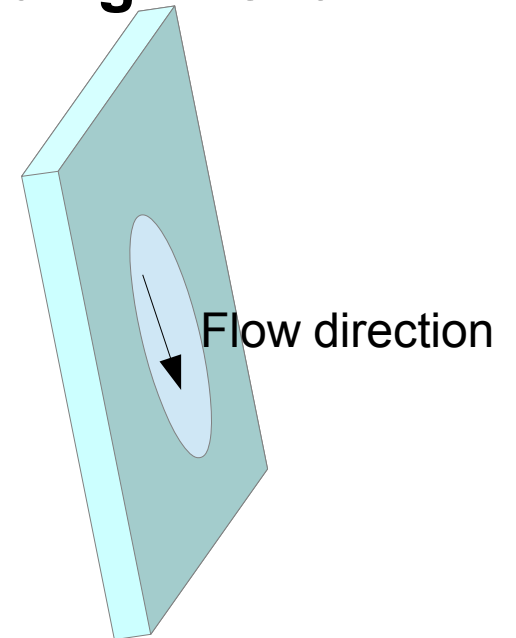
Shearing



Dipcoating



Gravity assisted alignment

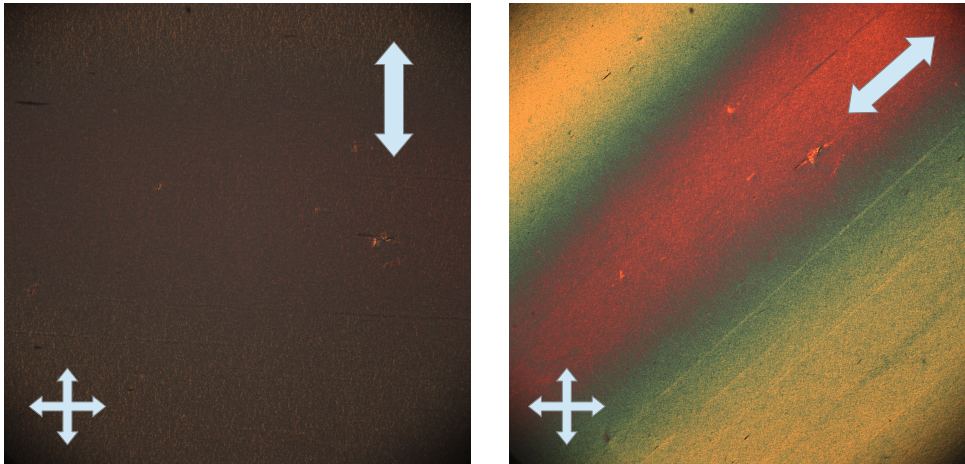


Hoeger et. al Soft Matter, 2011, 7, 1957-1967

http://www.phy.davidson.edu/StuHome/shmeidt/talk/thin_films.htm

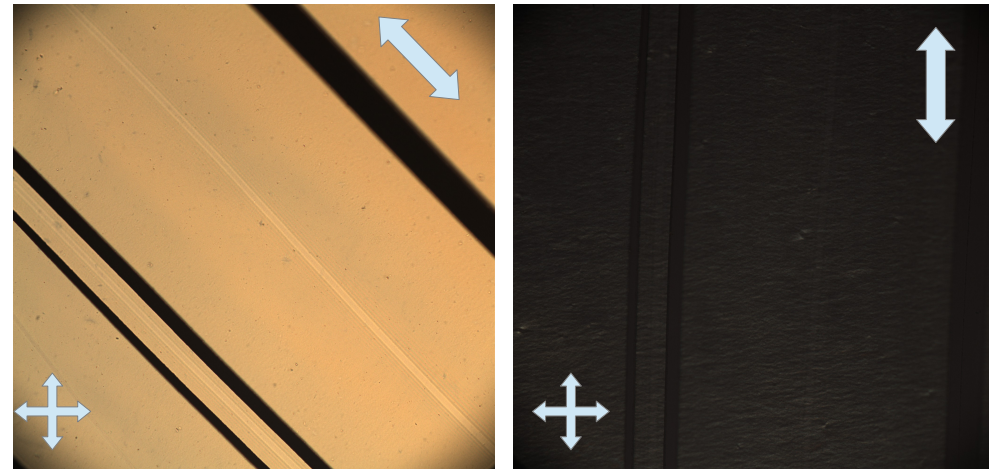
Nematic like order

Dipcoating



Dipcoating alignment of CNC. Images taken from cross polarized microscopy with 10x objective.

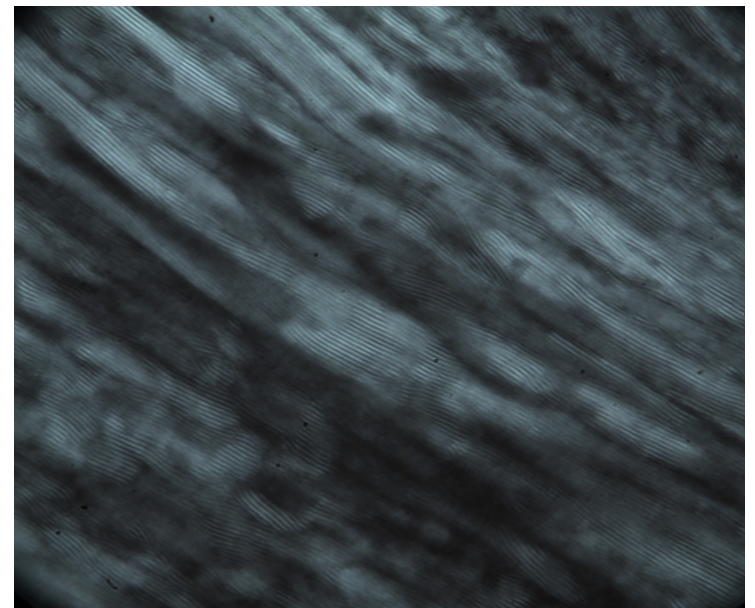
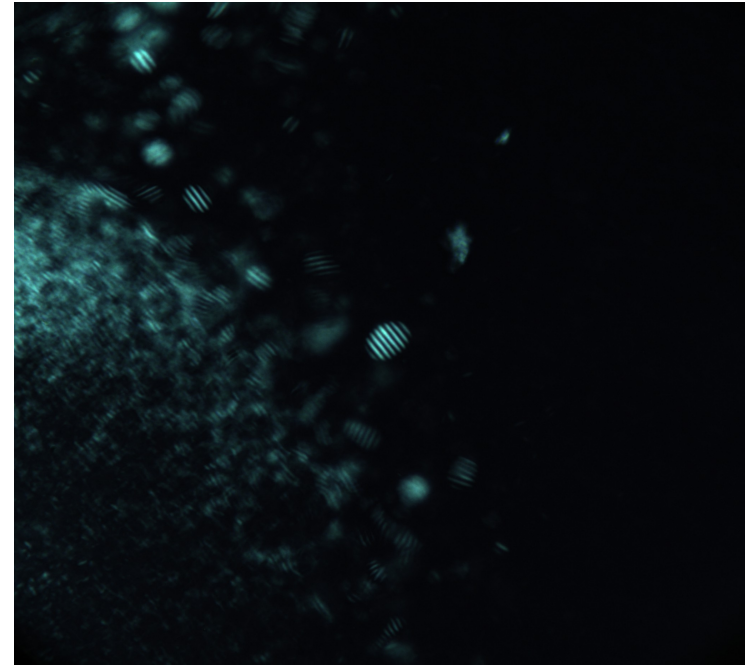
Shearing



Shearing Allingment of CNC, images taken from cross polarized microscopy with 10x objective

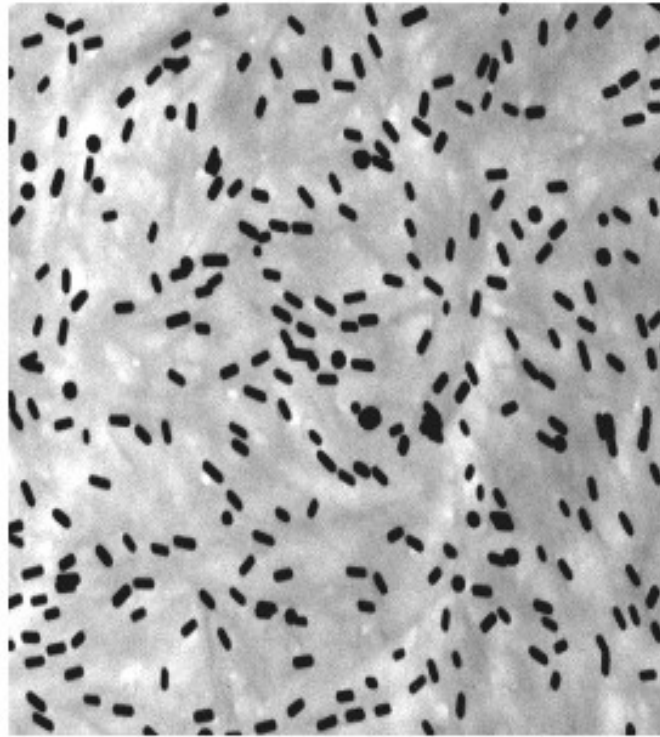
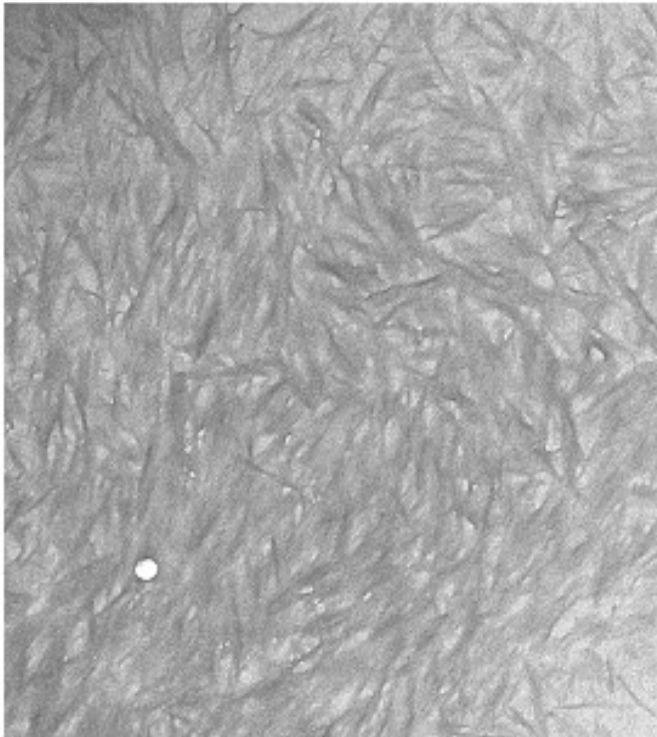
Cholesteric phase

- CNC will naturally form a cholesteric phase.
- As concentration increases, the amount of the solution in a cholesteric phase will increase.
- As the concentration increases, the solution forms droplets of large pitch cholesteric. As time progresses, these spheres merge, while the pitch contracts.

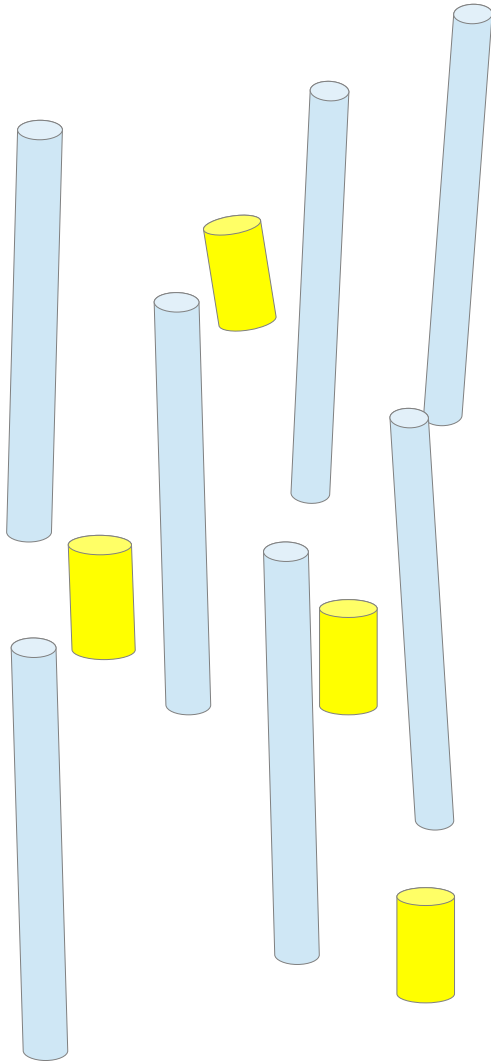


Gold nanorods in CNC

- Gold nanorods will disperse easily in a solution of CNC and H₂O.



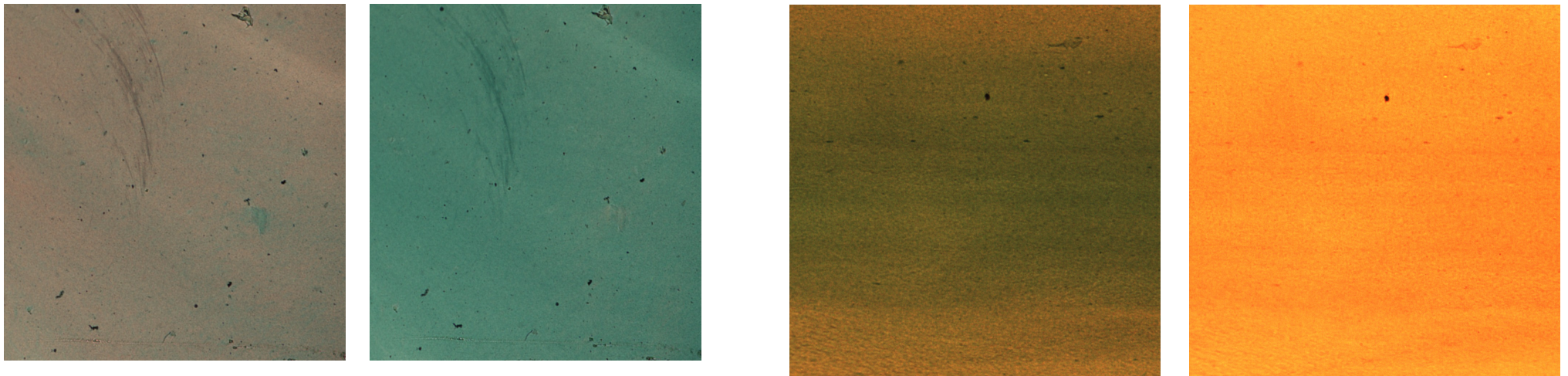
GNR in CNC



- Gold nanorods will align along the director in order to minimize the excluded volume and maximize entropy.
- MPEG capping on the gold nanorods prevents aggregation.
- At low concentrations of CNC the gold nanorods will be in the isotropic state. After a critical threshold, beyond the cellulose isotropic to nematic transition, the gold nanorods will align with the cellulose to maximize translational entropy.

Aligned gold nanorods.

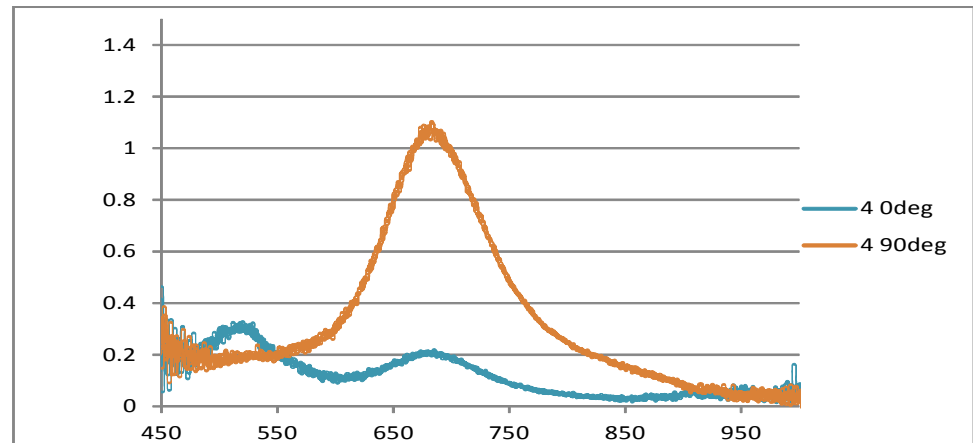
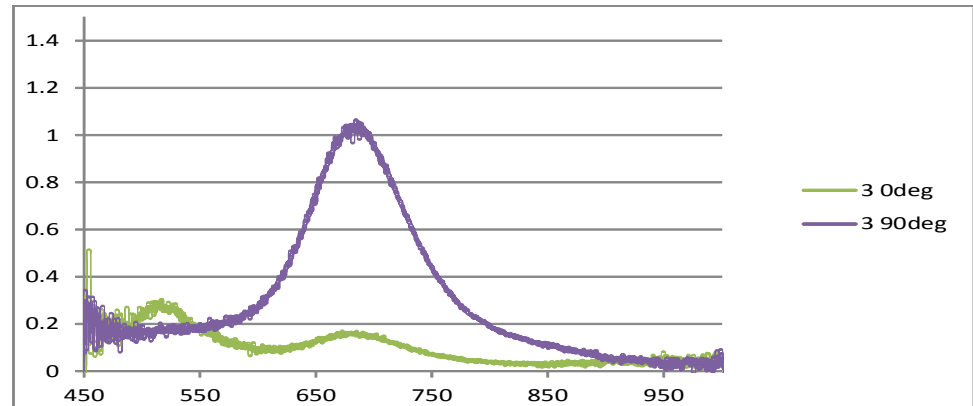
- By using a shearing, dip-coating, or gravity assisted alignment, we can force the cellulose to nematically align, which causes the gold nanorods to align in a nematic like order.



Images taken with analyzer at 0 and 90 deg with respect to the director

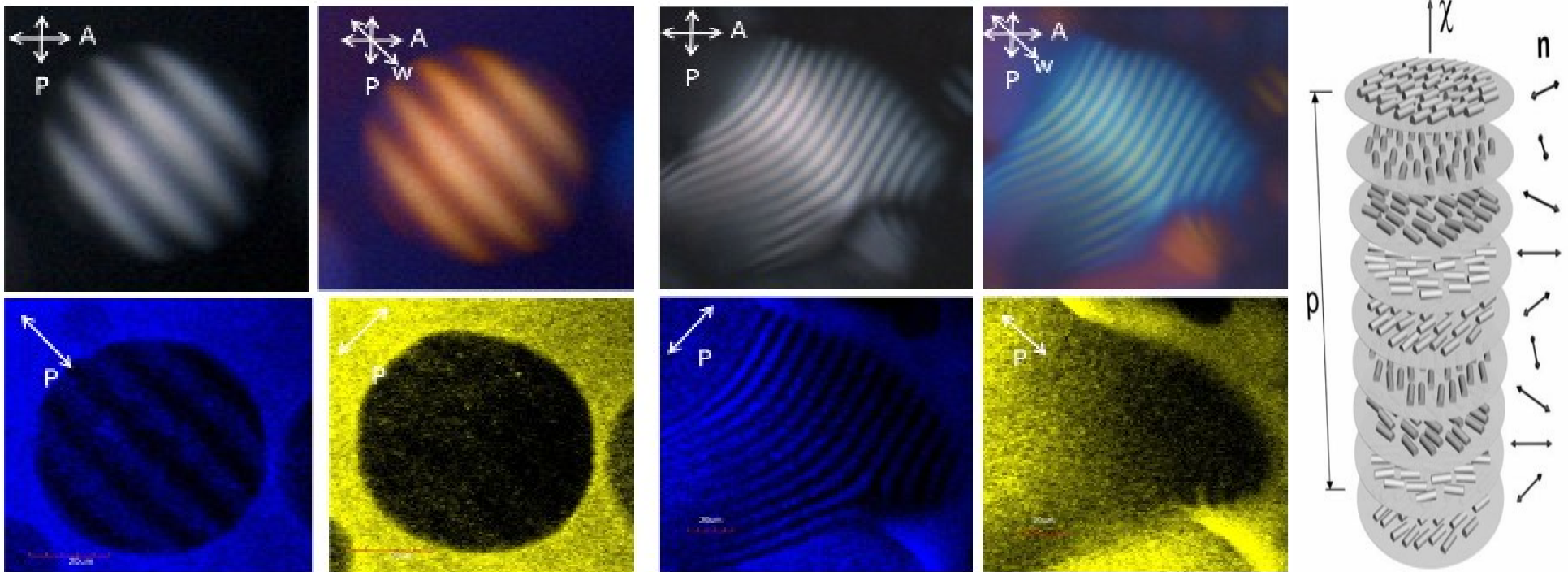
Polarization Dependent Plasmon Resonance.

- When gold nanorods are aligned in parallel, they create a large polarization dependent plasmon resonance.



Cholesteric Alignment of GNR

- Gold nanorods tend to aggregate outside of cholesteric regions.
- However, by forcing a fast phase transition, we can temporarily align rods within large pitch cholesteric regions.



Conclusion

- Gold nanorods and cellulose nanocrystals can self assemble into thin films orientation order.
- These thin films have unique optical properties not found in GNR or CNC.
- Potential applications include plasmonic polarizers, optical metamaterials

Funding

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