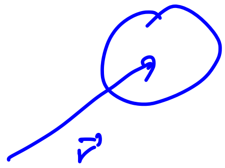
Lecture 10: liquid crystals

In the previous lecture, we have seen that rod-like particles can form a phase for each particle points on average in a preferred direction.

The situation is different from spherical particles:

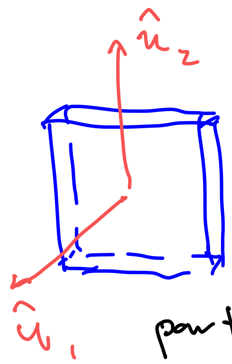
which is described by just translational degrees of freedom.



$\Rightarrow$

gives rise to gas, liquid, crystal phases

mesogen (particles in LC)



3 translational dofs

2 angular dofs

particle biaxiality.

When particle has non-trivial shape:
$\Rightarrow$ anisotropic interactions!

Nematic: No translational order but orientational order along one axis.

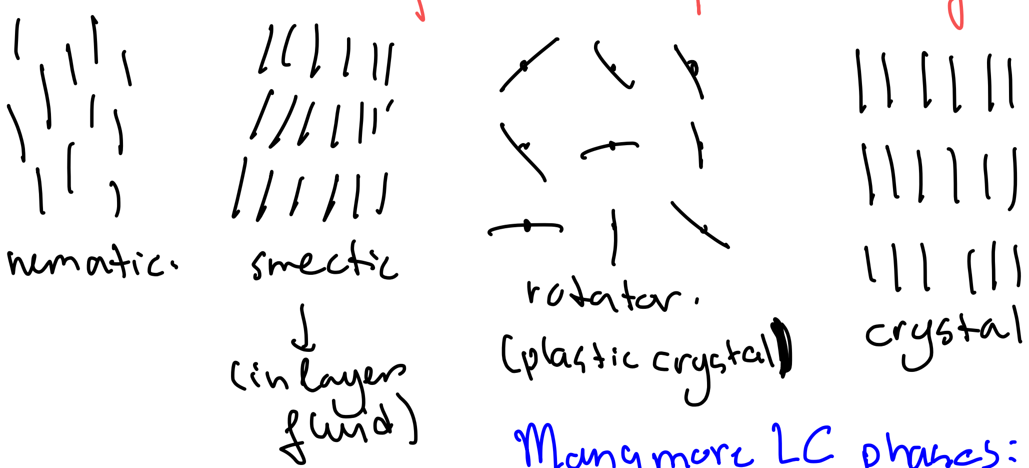
Biaxial nematic: No translational order but orientational order along two axes (phase biaxiality)

Smectic: Translational order along one dimension. Orientational order along one axis.

Rotator: Translational order along all three directions, no orientational order.

Crystal: Translational symmetry and rotational symmetry are completely broken.

Easier to visualise for uniaxial particles (e.g. rods)



Many more LC phases: columnar, hexatic, blue phases, cholesteric, twist-bend nematic etc.

Liquid crystals are so-called mesophases: Partially ordered structures (rotational and translational symmetry is only partly broken). These phases are therefore "in between" liquids and crystals.

We have already seen how to describe liquid crystals from a symmetry breaking perspective: Order parameter $Q_{\alpha\beta} = \frac{3}{2} S (\hat{n}_\alpha \hat{n}_\beta - \frac{1}{3}\delta_{\alpha\beta}) + \frac{P}{2}(e_\alpha^{(1)} e_\beta^{(1)} - e_\alpha^{(2)} e_\beta^{(2)})$

No vectorial order parameter because of up-down symmetry: $\hat{n} \to -\hat{n}$.

How to interpret S_0?

We define the positional and orientational density operator as $\hat{\rho}(\vec{r}, \hat{\omega}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)\,\delta(\hat{u} - \hat{u}_i)$ and $\rho(\vec{r}, \hat{\omega}) = \langle \hat{\rho}(\vec{r}, \hat{\omega}) \rangle$.

Note that $\langle N \rangle = \int d\vec{r} \int d\hat{\omega}\, \rho(\vec{r}, \hat{\omega})$

Note in isotropic phase: $\rho(\vec{r}, \hat{\omega}) = \text{const} \Rightarrow \rho(\vec{r}, \hat{\omega}) = \frac{n}{4\pi}$.

with $n = \langle N \rangle / V$.

In nematic phase: $\rho(\vec{r}, \hat{u}) = \rho(\theta)$ in smectic phase $\rho(\vec{r}, \hat{\omega}) = \rho(z, \theta)$ etc.

$$\hat{Q}_{\alpha\beta} = \frac{3}{2N} \sum_{i=1}^{N} \left(u_{i\alpha} u_{i\beta} - \frac{1}{3}\delta_{\alpha\beta} \right)$$

$$Q_{\alpha\beta} = \langle \hat{Q}_{\alpha\beta} \rangle = \left\langle \frac{3}{2N} \sum_{i=1}^{N} \left(\hat{u}_{i\alpha} \hat{u}_{i\beta} - \frac{1}{3}\delta_{\alpha\beta} \right) \right\rangle$$

$$= \left\langle \frac{3}{2N} \int d\vec{r} \int d\hat{\omega} \sum_{i=1}^{N} \left(\hat{\omega}_\alpha \hat{\omega}_\beta - \frac{1}{3}\delta_{\alpha\beta} \right) \delta(\hat{\omega} - \hat{\omega}_i)\, \delta(\vec{r} - \vec{r}_i) \right\rangle$$

$$= \frac{1}{N} \int d\vec{r} \int d\hat{\omega}\, \frac{3}{2} \left(\hat{\omega}_\alpha \hat{\omega}_\beta - \frac{1}{3}\delta_{\alpha\beta} \right) \langle \hat{\rho}(\vec{r}, \hat{\omega}) \rangle$$

$\rho(\vec{r}, \hat{\omega}) = \rho(\hat{\omega})$

$\Rightarrow$

$$= \frac{1}{n}\int d\hat{\omega}\, \frac{3}{2}\left(\hat{\omega}_\alpha \hat{\omega}_\beta - \frac{1}{3}\delta_{\alpha\beta}\right)\rho(\hat{\omega})$$

Define angular distribution

$$\varphi(\hat{\omega}) = \frac{\rho(\hat{\omega})}{n}.$$

$$= \left\langle \frac{3}{2}\left(\hat{\omega}_\alpha \hat{\omega}_\beta - \frac{1}{3}\delta_{\alpha\beta}\right)\right\rangle_\Omega .$$

with $\langle \ldots \rangle_\Omega = \int d\hat{\Omega}\, (\ldots)\, \varphi(\hat{\Omega})$

Largest eigvalue of $\underline{\underline{Q}}$ is S with eigvector $\hat{n}$.

$\hat{n}\cdot\underline{\underline{Q}}\cdot\hat{n} = \hat{n}\cdot(S\hat{n}) = S.$ $\qquad \hat{\omega}\cdot\hat{n} = \cos\theta.$

$$S = n_\alpha Q_{\alpha\beta} n_\beta = \left\langle \frac{3}{2}\left((\hat{u}\cdot\hat{n})^2 - \frac{1}{3}\right)\right\rangle_\Omega = \left\langle \frac{3}{2}\left(\cos^2\theta - \frac{1}{3}\right)\right\rangle_\Omega$$

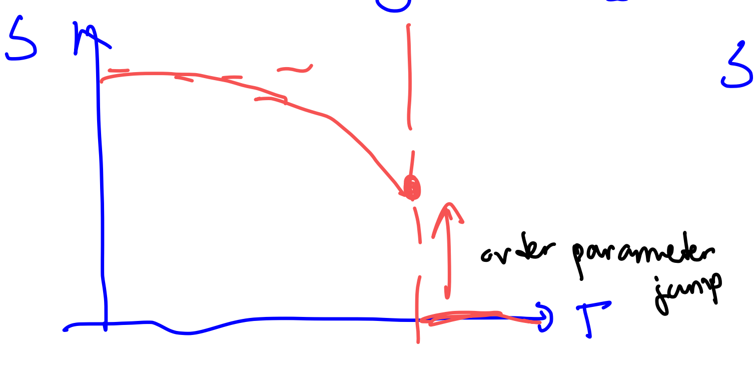
$= \langle P_2(\cos\theta)\rangle_\Omega .$ $\Rightarrow$ S is the angular average over second order Legendre polynomial.

This is because one can expand

$$\varphi(\theta) = \sum_{l=0}^{\infty} \frac{2l+1}{4\pi} S_l P_l(\cos\theta) \quad (l \text{ even})$$

$S_l = \langle P_l \cos\theta\rangle$ $\Rightarrow$ first non-trivial (i.e. angular dependent) moment of the angular distribution.

There are two ways how liquid crystals can form:

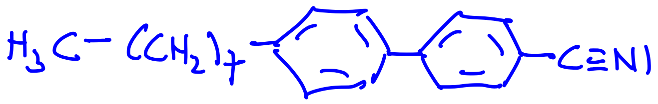


thermotropics

density jump

lyotropics.

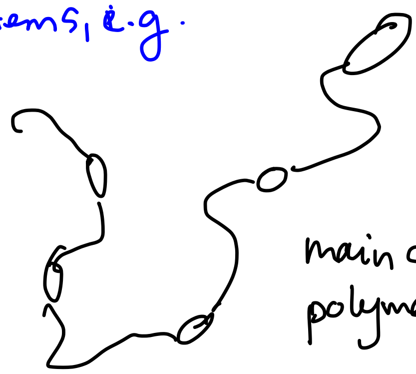
Thermotropics are typically molecular systems, e.g.



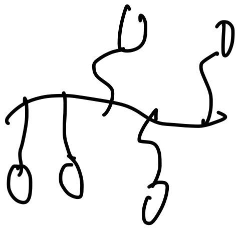
flexible tail

planar and stiff.

often no solvent!
(one component systems)



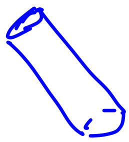
main chain polymer LC



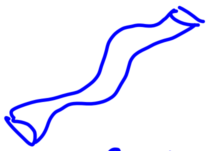
side chain polymer LC.

Lyotropics : concentration is control variable
mixtures (colloidal particles + solvent)

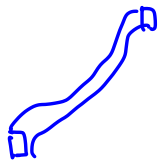
Examples:



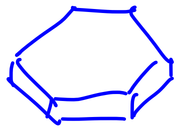
rigid rods (carbon nanotubes, TMV)



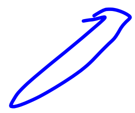
semi-flexible fibers (fd virus, DNA worm-like micelles)



ribbons (V_2O_5, β-sheets)



clays



needles. (cellulose)

Onsager (1949) showed that a system of identical hard rods can undergo an isotropic to nematic phase. In his model he assumed that

(i) each rod with a specific orientation is modeled as a separate chemical species.

(ii) Onsager used the second virial approximation.

(iii) Minimised the resulting free energy.

Although not known at the type, Onsager used implicitly a density functional theory! Generalisation to $\rho(\vec{r}, \hat{\omega})$

$$\Omega[\rho] = \mathcal{F}[\rho] + \int d\vec{r} \int d\hat{\omega}\, \rho(\vec{r}, \hat{\omega}) \left[V_{ext}(\vec{r}; \hat{\omega}) - \mu \right].$$

With $\beta \mathcal{F}[\rho] = \int d\vec{r} \int d\hat{u}\, \rho(\vec{r},\hat{u}) \left[\log \rho(\vec{r},\hat{u})\Lambda^3 - 1 \right]$

$$- \frac{1}{2} \int d\vec{r} \int d\hat{u} \int d\vec{r}\,' \int d\hat{u}'\, f(\vec{r},\hat{u};\vec{r}\,',\hat{u}')\rho(\vec{r},\hat{u})\rho(\vec{r}\,',\hat{u}')$$

with Mayer function $f(\vec{r},\hat{u};\vec{r}\,',\hat{u}') = e^{-\beta\phi(\vec{r},\hat{u};\vec{r}\,',\hat{u}')} - 1$.

Let's focus only on possibility of a nematic phase $\rho(\vec{r},\hat{u}) = \rho(\hat{u})$

$\rho(\hat{u})$ has normalisation: $n = \int d\hat{u}\, \rho(\hat{u})$

Furthermore, we are interested in bulk: $V_{ext} \equiv 0$.

$$\Rightarrow \frac{\beta\Omega[\rho]}{V} = \int d\hat{u}\, \rho(\hat{u}) \left[\log \rho(\hat{u})\Lambda^3 - 1 - \beta\mu \right] + \frac{1}{2} \int d\hat{u} \int d\hat{u}'\, E(\hat{u},\hat{u}')\rho(\hat{u})\rho(\hat{u}')$$

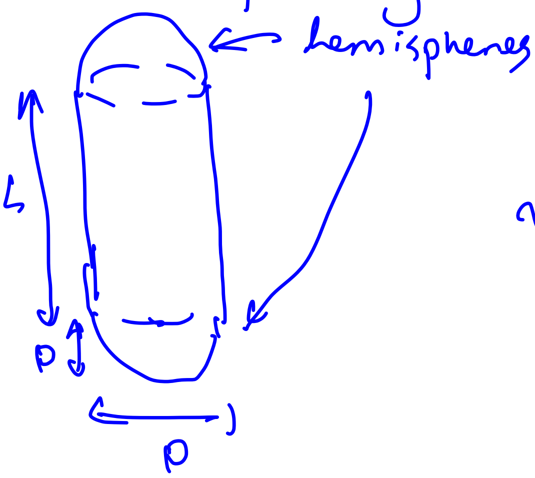
$$E(\hat{u},\hat{u}') = -\int d\vec{r}_{12}\, f(\vec{r}_1,\hat{u};\vec{r}_2,u') \qquad \vec{r}_{12} = \vec{r}_1 - \vec{r}_2.$$

excluded volume between two rods.

So we find the Euler-Lagrange equation.

$$\log \rho(\hat{u})\Lambda^3 + \int d\hat{u}'\, E(\hat{u},\hat{u}')\rho(\hat{u}') = \beta\mu.$$

For hard spherocylinders: Onsager found:



$$E(\hat{u},\hat{u}') = \underbrace{2L^2 D\, |\sin\gamma|}_{\mathcal{O}(L^2D)} + \underbrace{8 v_0}_{\mathcal{O}(LD^2)}.$$

$v_0 = (\pi/4)LD^2 + \pi/6\, D^3$ (volume of single spherocylinder),

and $\cos\gamma = \hat{u}\cdot\hat{u}'$

In the limit $\frac{L}{D} \to \infty$ (needle limit) we can neglect second term in $E(\hat{u},\hat{u}')$.

Now writing that $\rho(\hat{u}) = \rho(\theta)$

$$\ln\rho(\theta)\Lambda^3 + 2L^2 D \int d\theta' \sin\theta' \, K(\theta,\theta')\rho(\theta') = \beta\tilde{\mu}$$ ~> numerical.

$$\int_0^{2\pi} d\phi \, E(\hat{\omega},\hat{\omega}')/L^2 D$$

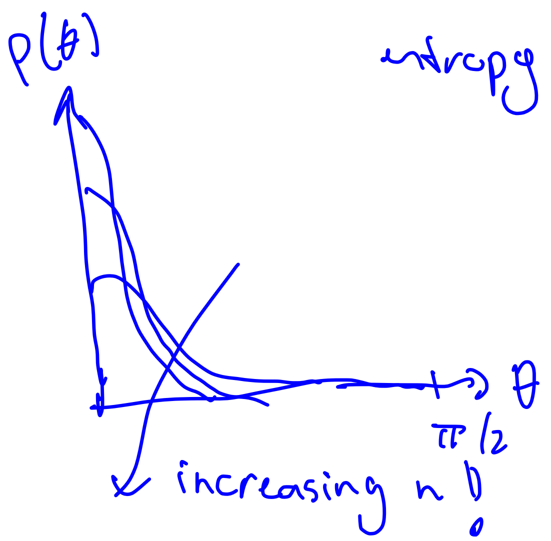
At low n this term dominates $\Rightarrow$ $\rho(\theta) L^2 D = e^{\beta\mu}$.

At higher n becomes of similar order as first term!

So we have a phase transition:

At low density: system maximises its orientational entropy & translational entropy.

At high density: Net entropy increase by alignment: although orientational entropy is lower, center-of-mass entropy increases!



(Note $\rho(\theta) = \rho(\pi - \theta)$)

How good is the second virial approximation?

$$\beta p = \rho + B_2\rho^2 + B_3\rho^3 = \rho\left(1 + B_2\rho + \frac{B_3}{B_2^2}(B_2\rho)^2 + \dots\right)$$

So good when $B_3/B_2^2 \ll 1$.

Spheres: $B_2 \propto \sigma^3$, $B_3 \propto \sigma^6$ $\Rightarrow \frac{B_3}{B_2^2} = \mathcal{O}(1)$.

For rods Onsager showed that: $\frac{B_3}{B_2^2} \approx \frac{D}{L} \log\left(\frac{L}{D}\right) \to 0$ (for $L/D \to \infty$)

In the needle limit Onsager theory is exact!

Why is it called liquid crystal?

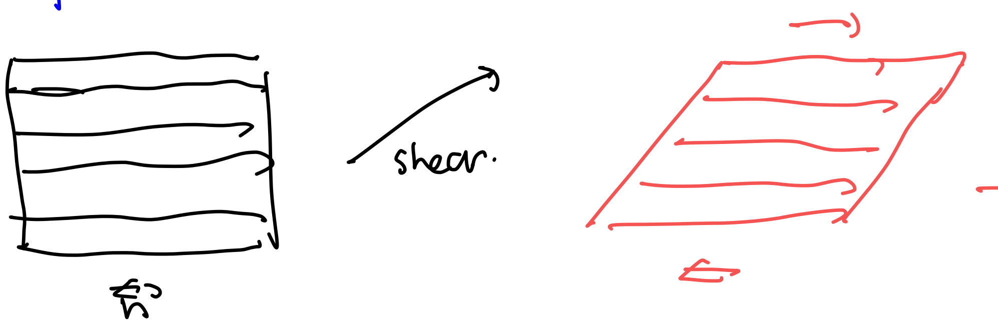
Liquid: no long range order.

$\to$ static deformation leads to flow.

Crystal: Long-range positional order $\to$ static deformation leads to elastic response.

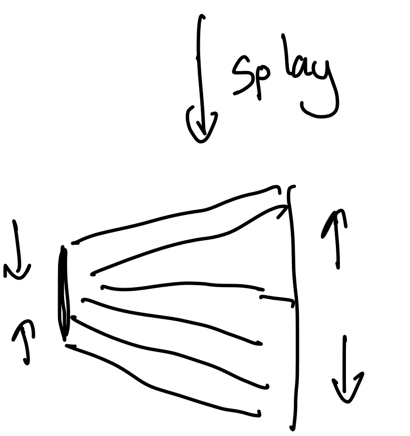
Liquid crystal: Liquid-like short-range positional order, but long range orientational order $\to$ certain types of deformations lead to elastic response, some to flow.

Example:



orientational order unaffected

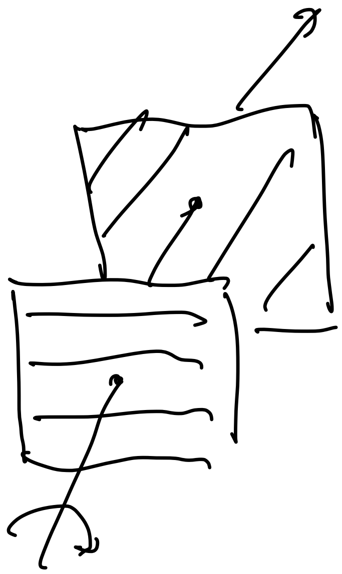
$\to$ flow.



perturbation of director field

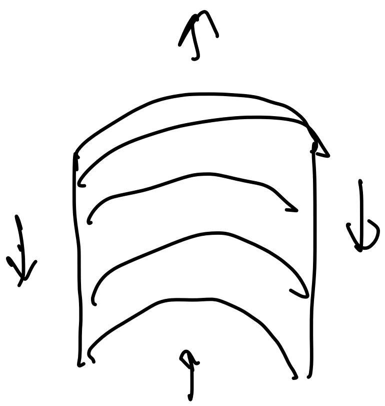
$\Rightarrow$ elastic responce

elastic const K_1.



twist deformation

elastic constant K_2.



bend deformation

elastic constant K_3.

Deformed state leads to higher free energy. This is captured in the Frank elastic free energy F_E:

$$F_E[\vec{n}] = \frac{1}{2}\int d\vec{r}\left[K_1(\nabla\cdot\vec{n})^2 + K_2(\vec{n}\cdot(\nabla\times\vec{n}))^2 + K_3|\vec{n}\times(\nabla\times\vec{n})|^2\right].$$

$$= \int d\vec{r}\, f_E(\vec{r})$$

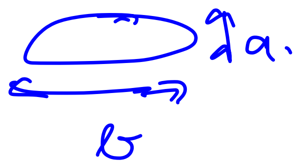
Note that for uniform state $F_E[\hat{n}]$!

Remarks

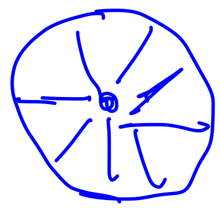
(i) $F_E[\hat{n}]$ derivable from LdG free energy! Add gradient terms that are symmetry allowed, e.g. $\sim \partial_\alpha Q_{\beta\gamma}\,\partial_\alpha Q_{\beta\gamma}$ etc.
Then use uniaxial approximation $\Rightarrow K_i = K_i(S)$!

(ii) Various approximations, e.g.: one-constant approximation. ($K_2 = K_3 = 0$)
Or equal-constant approximation $K_1 = K_2 = K_3 = K$.
$\Rightarrow f_E = \frac{1}{2}K\left[(\nabla\cdot\hat{n})^2 + (\nabla\times\hat{n})^2\right]$.

(iii) $K_i \sim 10^{-12}$ N (estimate by $K_i \approx \frac{k_B T}{b}$)



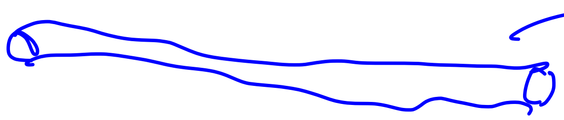
Consequences: Topological defects: high-energy excited structures in uniform ground state.



Radial hedgehog defect

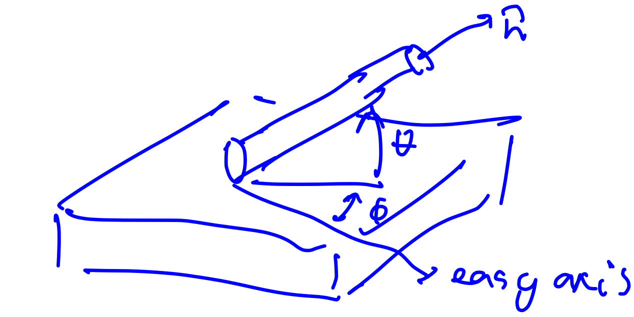
$f_E \sim \frac{1}{r} \Rightarrow$ diverges in the center.

$\Rightarrow$ core of topological defect melts



$\rightarrow$ defect lines can form in liquid

Interaction with surfaces



preference to align a mesogen close to particle surface.

$$\gamma = \sigma_s + W_p \sin^2\theta + W_a \sin^2\phi$$

(Rapini-Papoular anchoring)

γ: surface free energy.

planar anchoring

$W_p > 0$

homeotropic anchoring.

$W_p < 0$

Interaction with external fields (magnetic electric)

$\epsilon \longrightarrow \underline{\underline{\epsilon}}$ dielectric tensor (similar for magnetic properties)

$$\underline{\underline{\epsilon}} = \epsilon_\perp \mathbb{I} + \Delta\epsilon\, \hat{n}\hat{n}. \qquad \Delta\epsilon = \epsilon_{\parallel} - \epsilon_\perp.$$

$\Delta\epsilon$ can be positive or negative.

Dielectric anisotropy results in an additional free energy contribution

$$f_E = -\frac{\epsilon_0 \Delta\epsilon}{2} (\vec{n}\cdot\vec{E})^2$$

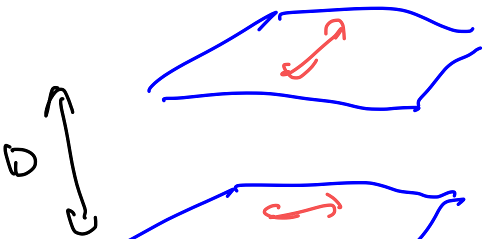
$\vec{E}$: external electric field.

In other words $\Delta\epsilon > 0$: $\vec{n} \parallel \vec{E}$ lowers free energy.

$\Delta\epsilon < 0$: $\vec{n} \perp \vec{E}$ lowers free energy.

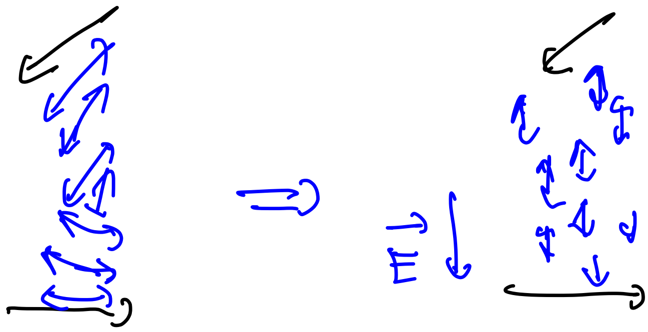
Suppose we have a positive dielectric anisotropy.

Consider geometry:



perpendicular easy axes.

Twisted nematic cell



Frederiks transition!

Alignment in direction of $\vec{E}$ for $E \geq E_c = \sqrt{K/(\Delta\epsilon D)}$

$\rightsquigarrow$ This is a mechanism exploited in liquid-crystal displays! (LCDs)

$\square$