Ciências ULisboa

# Liquid crystals

## Soft matter physics

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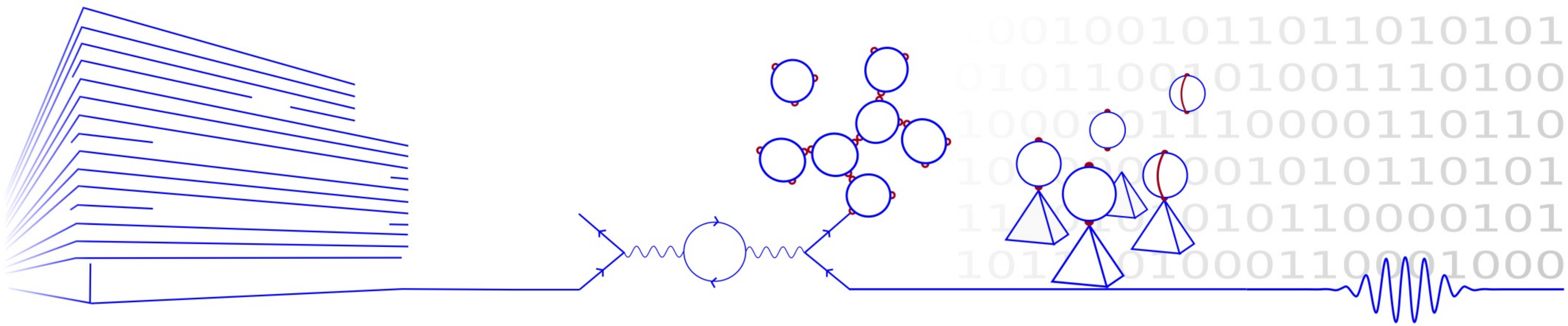
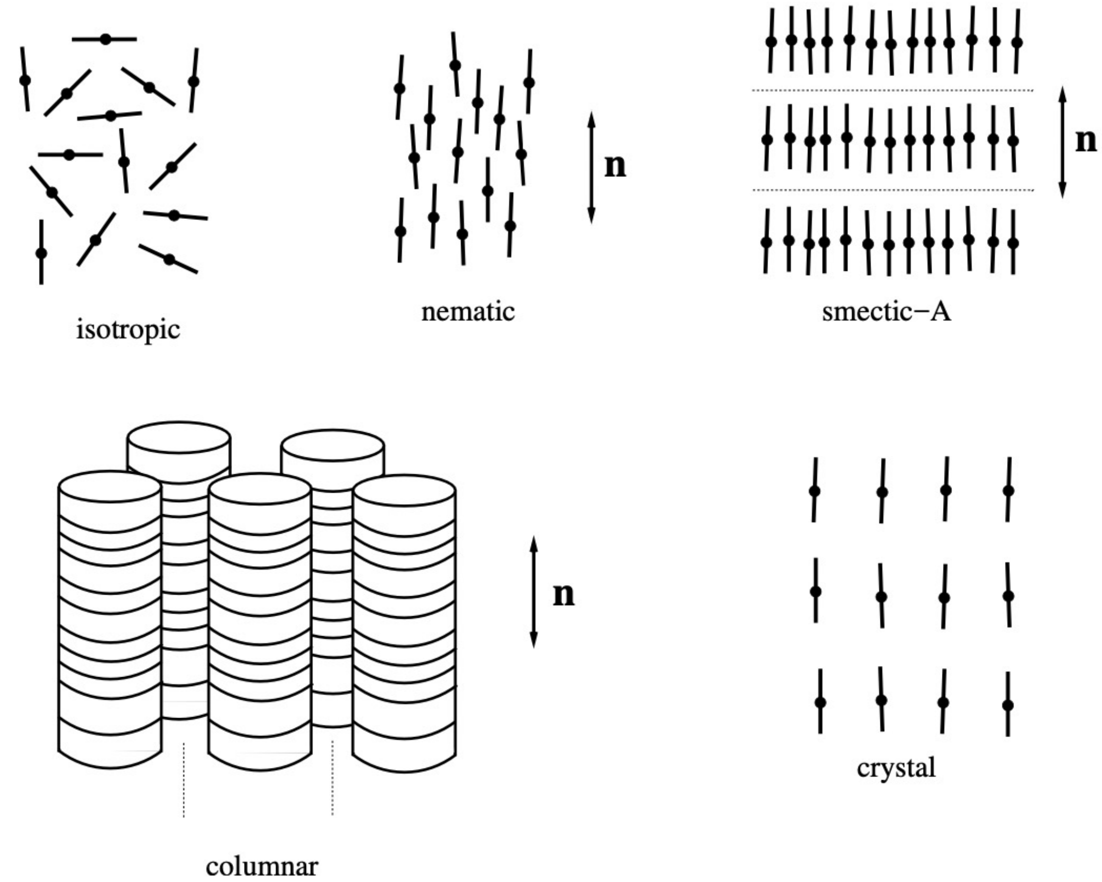
2024



# Introduction

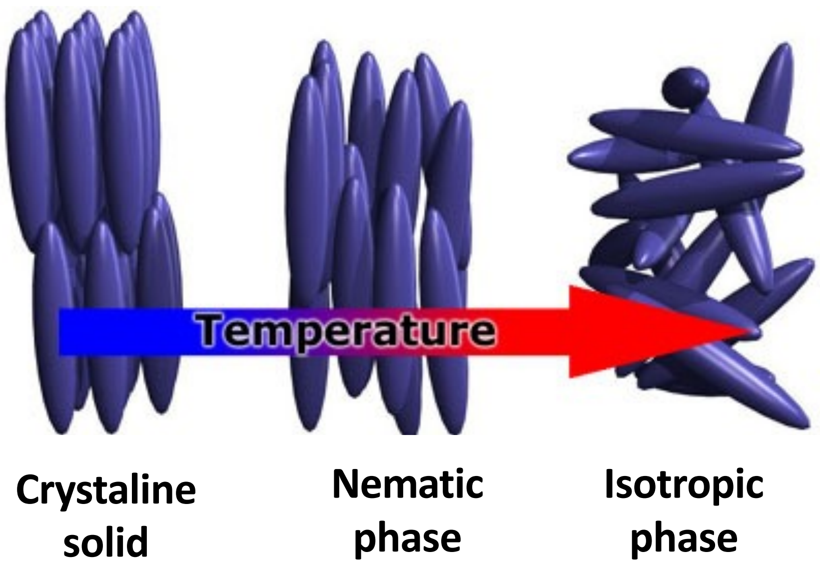
- Liquid crystals can flow like a liquid and are organized in a crystal-like way;
- Their molecular orientation can be controlled by relatively weak external fields;
  - E~MV/mm for usual liquids and E~V/mm for liquid crystals;
  - Application in display technologies;
- Collective behaviour: ordering and flow;
- Order-disorder transition: by temperature (thermotropic) or concentration (lyotropic).

# Phases of a liquid crystal




Nematic phase: the simplest type of LC, but widely used.

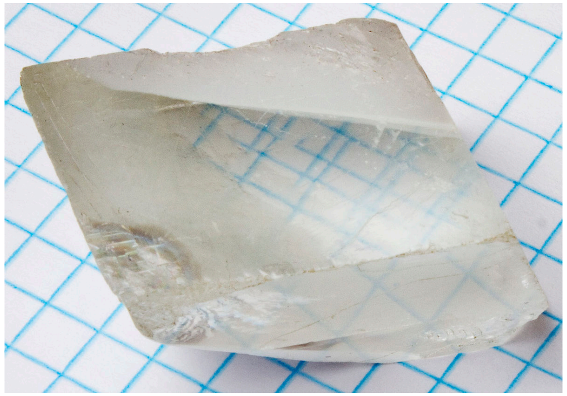
# Liquid crystals

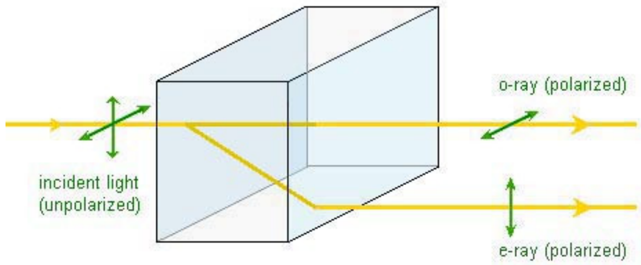



- A liquid crystal flows like a liquid but its particles may be oriented in a crystal-like way;
- In the nematic phase, the particles are aligned;
- The isotropic phase is disordered.

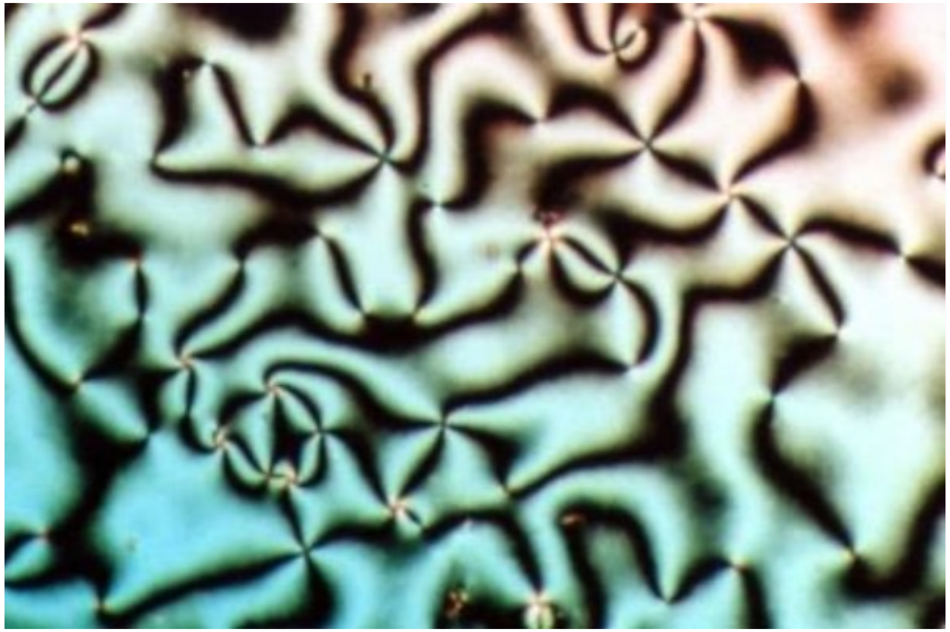
# Anisotropic properties of nematics

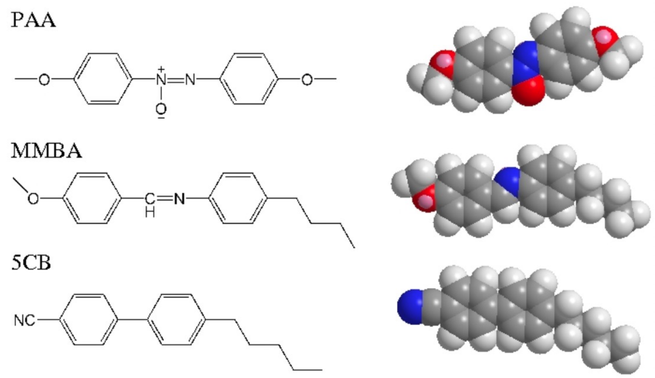
- Electrical, magnetic and optical;
- Mostly uniaxial: can be represented by a director field **n**;
- Birefringence: anisotropy in the transmission of light. Similar to crystals (below), but nematics can flow.





# Rod-like molecules



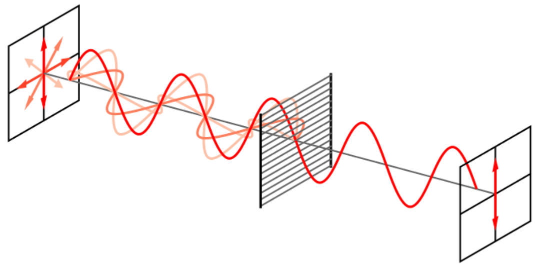


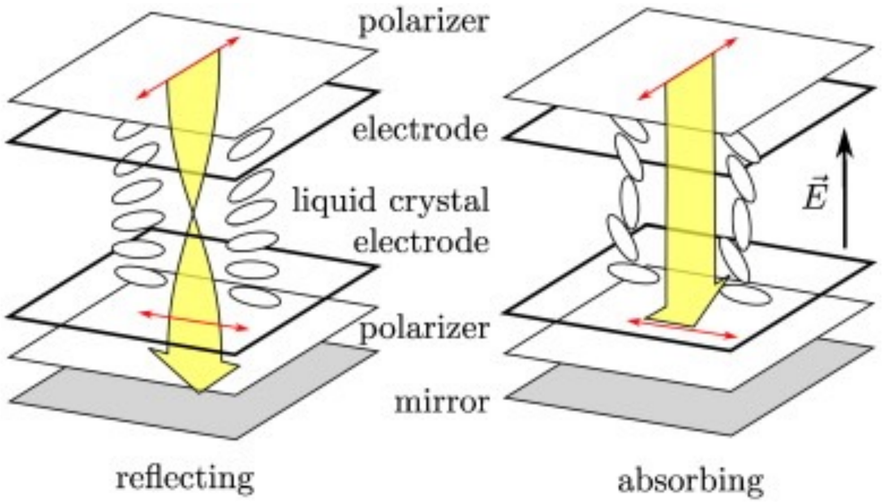

Typical mesogens forming liquid crystalline phases (mesophases). (PAA) p-azoxyanisole. From a rough steric point of view, this is a rigid rod of length ∼ 20 ̊A and width ∼ 5 ̊A. The nematic state is found at high temperatures (between 1160C and 1350C at atmospheric pressure). (MMBA) N-(p- methoxybenzylidene)-p-butylaniline. The nematic state is found at room temperatures (between 200C to 470C). Lacks chemical stability. (5CB) 4-pentyl-4’-cyanobiphenyl. The nematic state is found at room temperatures (between 240C and 350C).

# Displays

Basic LCD display

Applications

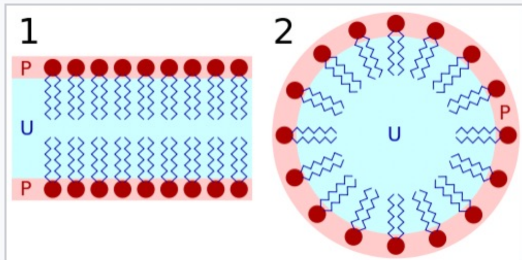





# Nails in a box

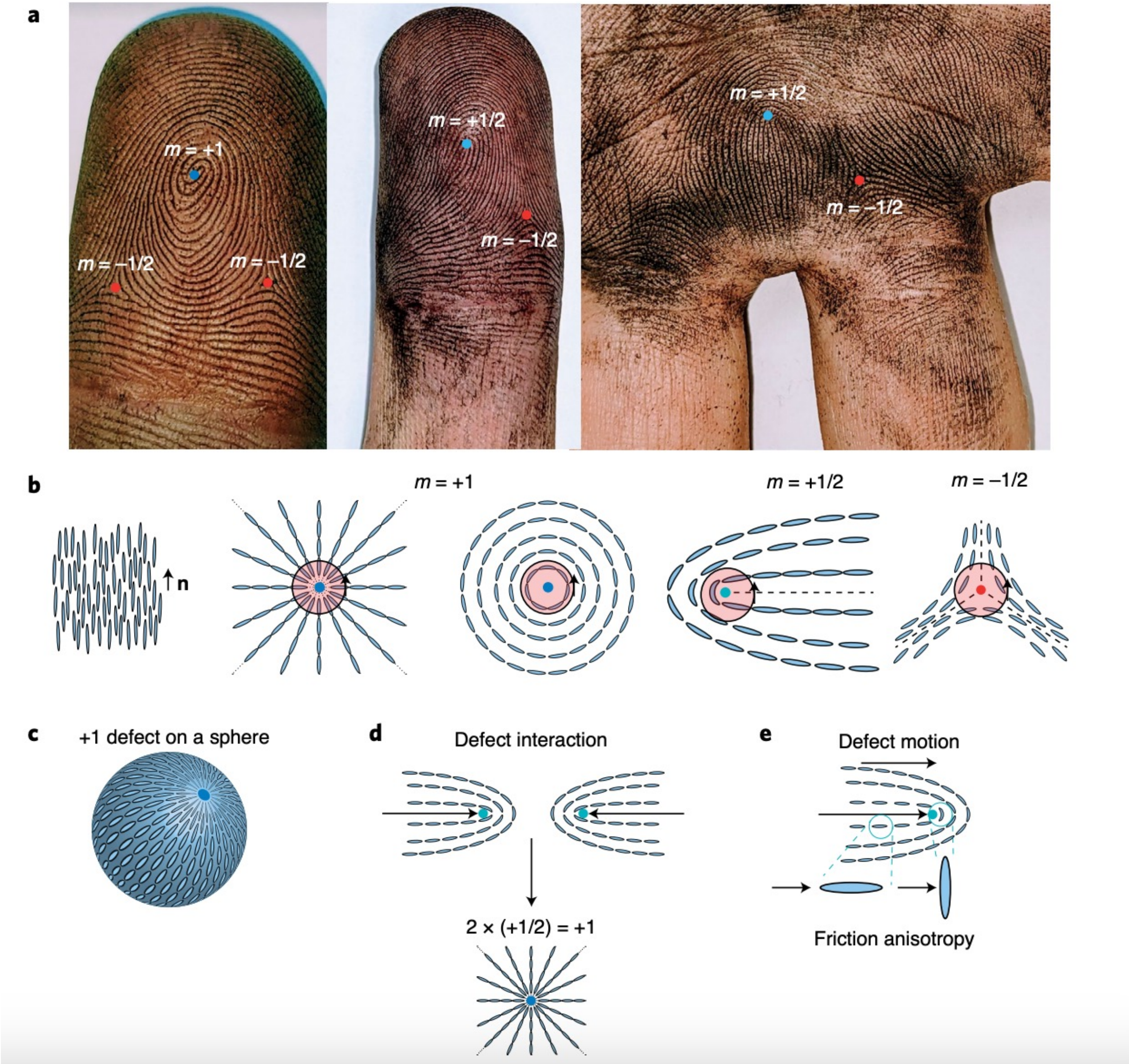
- Maximize packing;
- Volume exclusion;
- Osanger model;
- Analogy with LC: isotropic-nematic transition.

# Soap bubble




Structure of lyotropic liquid crystal. The red heads of surfactant molecules are in contact with water, whereas the tails are immersed in oil (blue): bilayer (left) and micelle (right).

# Defects in liquid crystals

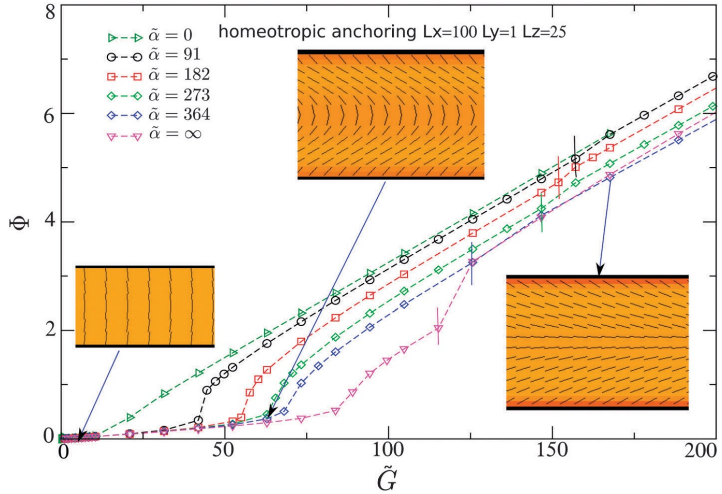



Fardin, MA., Ladoux, B., *Nat. Phys.* **17**, 172–173 (2021)

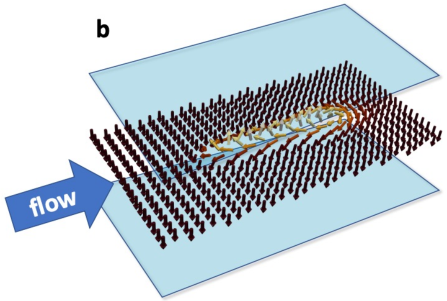
# Liquid crystals and flows

Poiseuille-like flow of a nematic LC

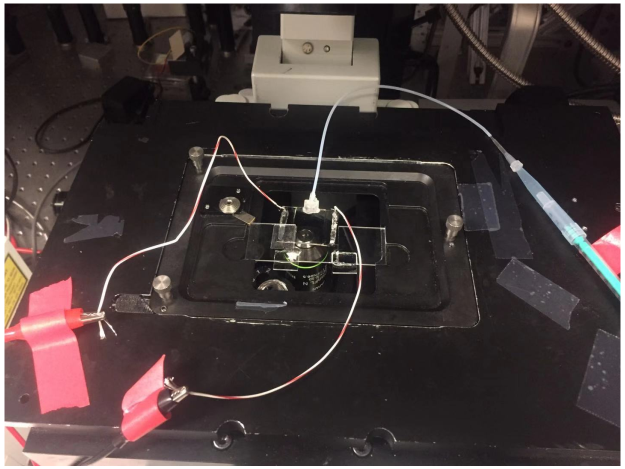
***Soft Matter***, 2015,**11**, 4674-4685




Flowing skyrmions



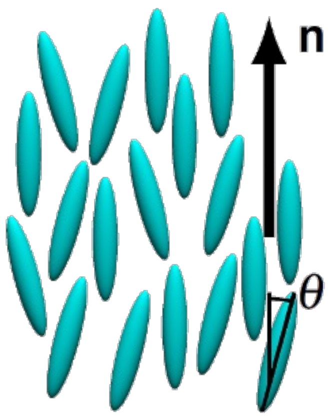

Microfluidic setup



240µm/s

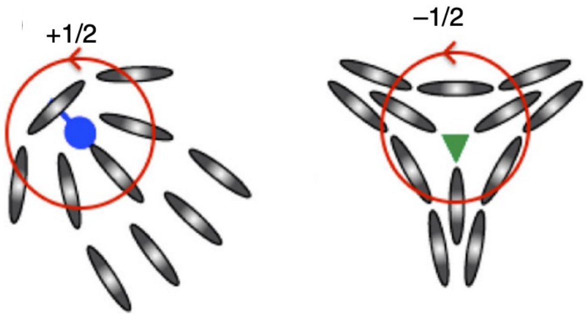
# Active nematics

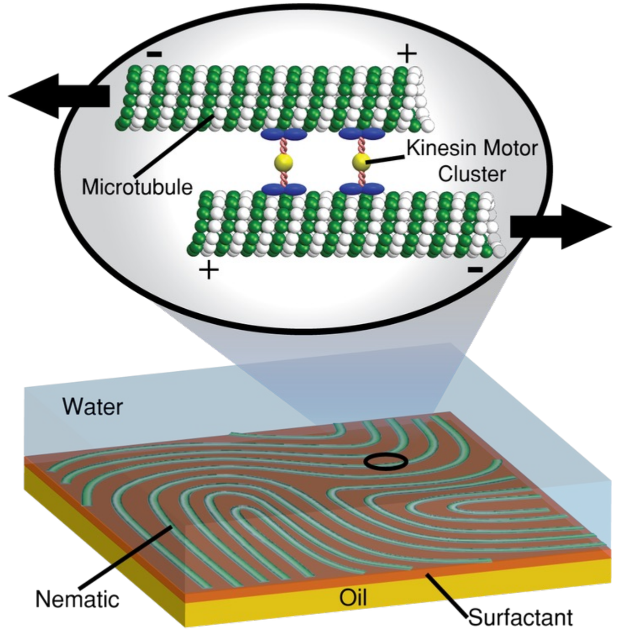
- The particles transform energy from the environment in directed motion;
- Elongated particles like in liquid crystals;
- Examples: mixtures of microtubule-kinesin, dense suspensions of bacteria and shoals of fish.



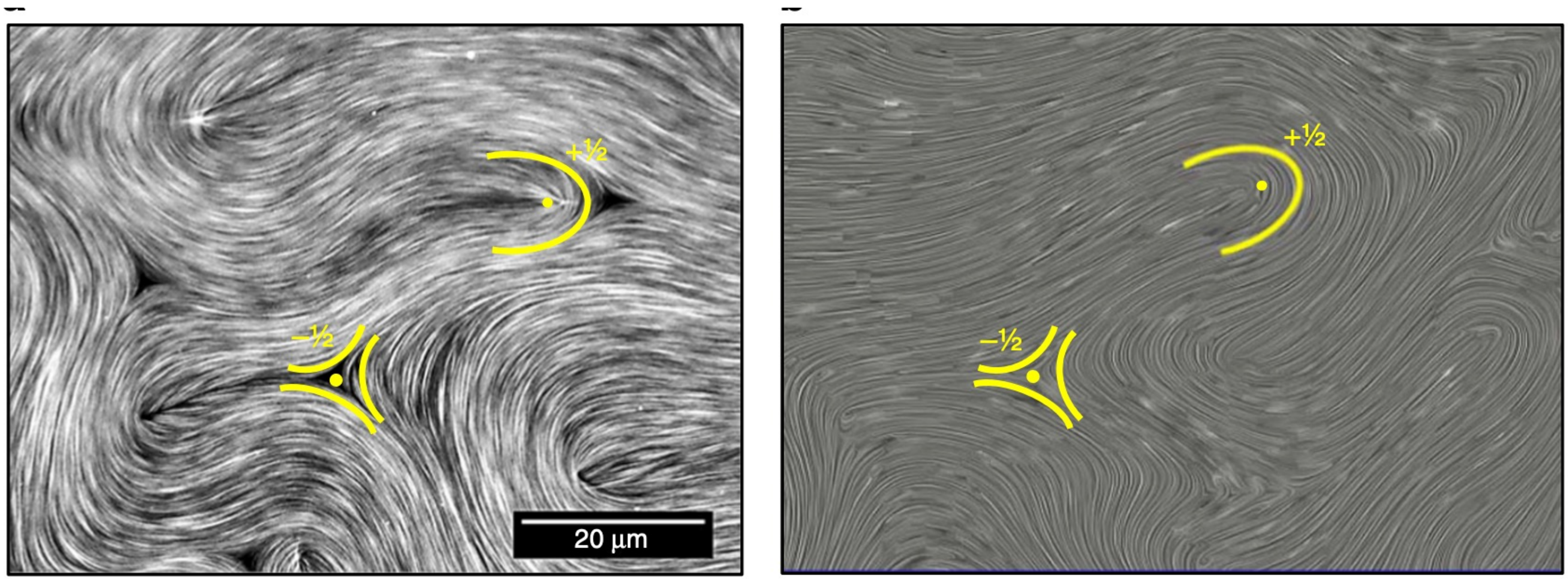

Marchetti et. al., Rev. Mod. Phys. **85**, 1143

# Microtubule-kinesin



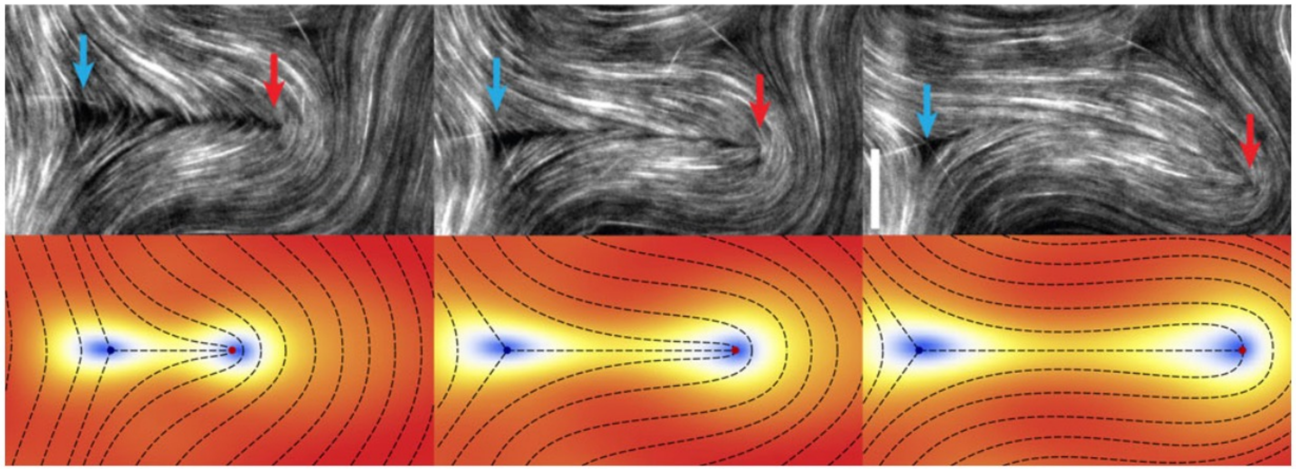

T. Sanchez et al. Nature **491**, 431–434 (2012)



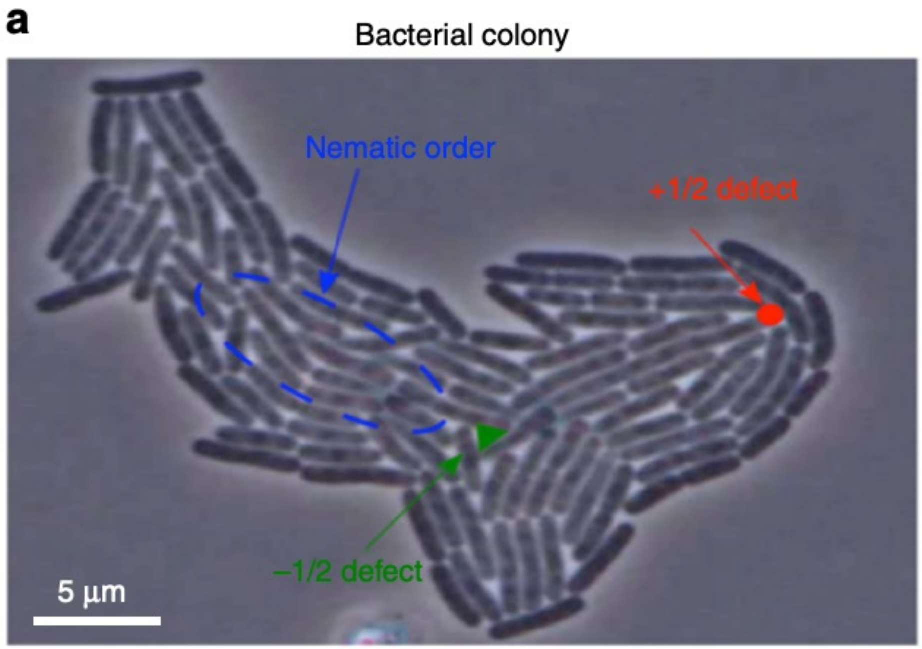

Experiments

Continuum simulations

Doostmohammadi, A., Ignés-Mullol, J., Yeomans, J.M. *et al.* Active nematics. *Nat Commun* **9**, 3246 (2018)



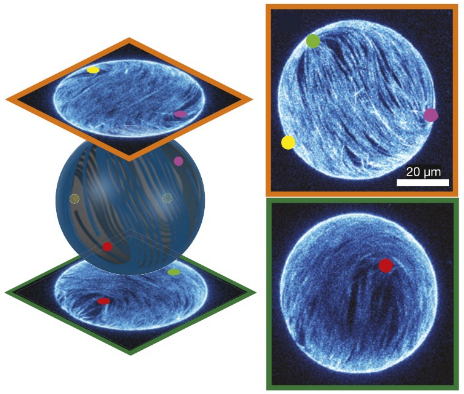
Giomi et al. .Phil.Trans.R.Soc. A372: 20130365 (2014)

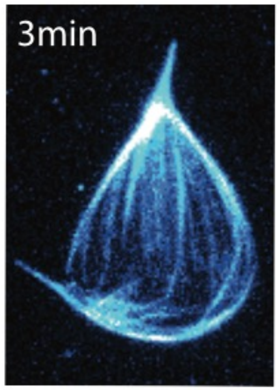


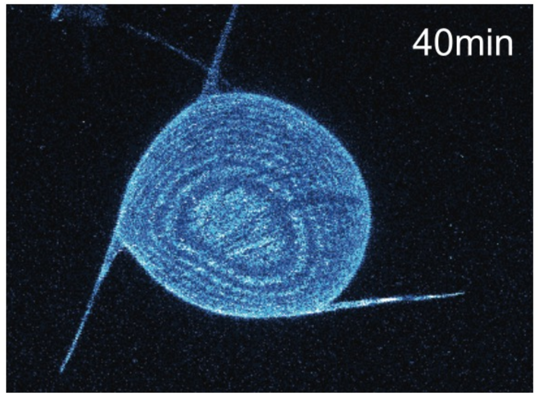

Doostmohammadi, A., Ignés-Mullol, J., Yeomans, J.M. *et al.* Active nematics. *Nat Commun* **9**, 3246 (2018)

# Active nematic droplets

## Active vesicle of microtubule-kinesin

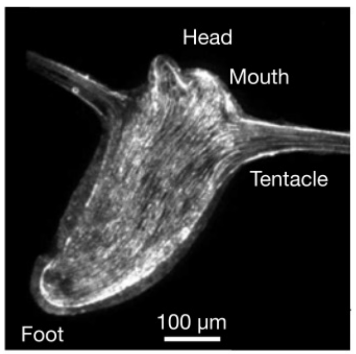


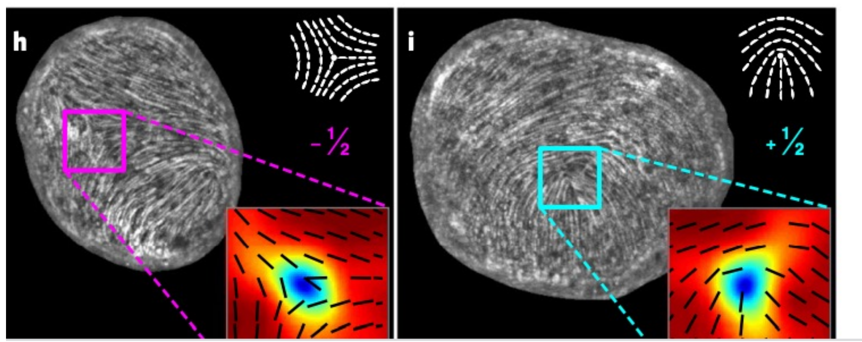




Felix C. Keber *et al. Science* **345**, 1135 (2014)

## Hydra morphogenesis driven by nematic defects



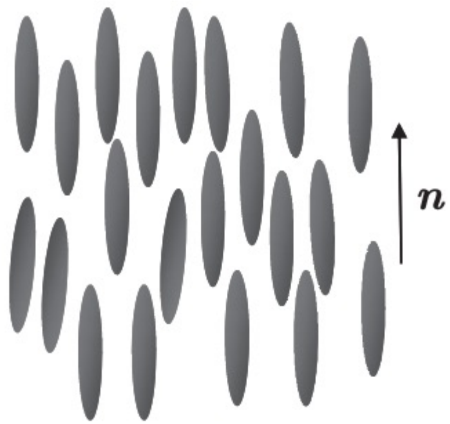

Maroudas-Sacks, Y., Garion, L., Shani-Zerbib, L. *et al*. *Nat. Phys.* **17**, 251–259 (2021).

# Question

How to quantify the order and the preferential alignment (if any) of elongated particles with head-tail symmetry?

# Order parameter for nematics


isotropic liquid




nematic liquid

Distribution function

$$\int d\boldsymbol{u}\ \psi(\boldsymbol{u}) = 1$$

Isotropic: $\psi(\boldsymbol{u}) = \dfrac{1}{4\pi}$

Averages:

$$\langle \cdots \rangle = \int d\boldsymbol{u} \cdots \psi(\boldsymbol{u})$$

The first moment of u is not a good candidate for the order parameter as it does not takes into account the symmetry u / -u.

Second moment

Isotropic state $\langle u_\alpha u_\beta \rangle = \frac{1}{3}\delta_{\alpha\beta}$

Perfect nematic $\langle u_\alpha u_\beta \rangle = n_\alpha n_\beta$

Order parameter:

$$Q_{\alpha\beta} = \left\langle u_\alpha u_\beta - \frac{1}{3}\delta_{\alpha\beta} \right\rangle = S\left( n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta} \right)$$

$$\left\langle (\boldsymbol{u} \cdot \boldsymbol{n})^2 - \frac{1}{3} \right\rangle = n_\alpha n_\beta Q_{\alpha\beta} \qquad S = \frac{3}{2}\left\langle (\boldsymbol{u} \cdot \boldsymbol{n})^2 - \frac{1}{3} \right\rangle$$

# Mean field theory for the isotropic–nematic transition

$$F[\psi] = E[\psi] - TS[\psi]$$

Potential energy

$$w(\boldsymbol{u}, \boldsymbol{u}') = -\tilde{U}(\boldsymbol{u} \cdot \boldsymbol{u}')^2$$

$$E[\psi] = \frac{zN}{2} \int d\boldsymbol{u} \int d\boldsymbol{u}' \; w(\boldsymbol{u}, \boldsymbol{u}')\psi(\boldsymbol{u})\psi(\boldsymbol{u}')$$

Entropy

$$\begin{aligned} S &= k_B \ln W \\ &= k_B \left[ N(\ln N - 1) - \sum_i N_i(\ln N_i - 1) \right] \\ &= -Nk_B \sum_i (N_i/N) \ln(N_i/N) \end{aligned}$$

$$S[\psi] = -Nk_B \int d\boldsymbol{u} \; \psi(\boldsymbol{u}) \ln \psi(\boldsymbol{u})$$

Free energy functional for the orientational distribution function

$$U = z\tilde{U}.$$

$$F[\psi] = E[\psi] - TS[\psi]$$
$$= N\left[k_BT\int d\boldsymbol{u}\ \psi(\boldsymbol{u})\ln\psi(\boldsymbol{u}) - \frac{U}{2}\int d\boldsymbol{u}\int d\boldsymbol{u}'\ (\boldsymbol{u}\cdot\boldsymbol{u}')^2\psi(\boldsymbol{u})\psi(\boldsymbol{u}')\right]$$

Find the minimum energy with respect to $\psi$

$$\frac{\delta}{\delta\psi}\left[F[\psi] - \lambda\int d\boldsymbol{u}\psi(\boldsymbol{u})\right] = 0$$

$$k_BT\left[\ln\psi(\boldsymbol{u}) + 1\right] - U\int d\boldsymbol{u}'\ (\boldsymbol{u}\cdot\boldsymbol{u}')^2\psi(\boldsymbol{u}') - \lambda = 0$$

$$\boxed{\psi(\boldsymbol{u}) = C\exp[-\beta w_{mf}(\boldsymbol{u})]}$$

where:

$$w_{mf}(\boldsymbol{u}) = -U\int d\boldsymbol{u}'\ (\boldsymbol{u}\cdot\boldsymbol{u}')^2\psi(\boldsymbol{u}')$$

$$\beta = 1/k_BT$$

# Self-consistent equation

$$w_{mf}(\boldsymbol{u}) = -U \int d\boldsymbol{u}' \ (\boldsymbol{u} \cdot \boldsymbol{u}')^2 \psi(\boldsymbol{u}') \ = -U u_\alpha u_\beta \langle u'_\alpha u'_\beta \rangle = -U u_\alpha u_\beta \langle u_\alpha u_\beta \rangle$$

Assuming n in the z direction

$$S = \frac{3}{2} \left\langle (\boldsymbol{u} \cdot \boldsymbol{n})^2 - \frac{1}{3} \right\rangle \ = \frac{3}{2} \left\langle u_z^2 - \frac{1}{3} \right\rangle$$

$$\langle u_z^2 \rangle = \frac{1}{3}(2S+1)$$

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \frac{1}{2} \left(1 - \langle u_z^2 \rangle\right) = \frac{1}{3}(-S+1)$$

Mean field potential

$$\begin{aligned} w_{mf}(\boldsymbol{u}) &= -U\left[u_x^2\left\langle u_x^2\right\rangle + u_y^2\left\langle u_y^2\right\rangle + u_z^2\left\langle u_z^2\right\rangle\right] \\ &= -U\left[\frac{1}{3}(-S+1)\left(u_x^2+u_y^2\right) + \frac{1}{3}(2S+1)u_z^2\right] \\ &= -U\left[\frac{1}{3}(-S+1)\left(1-u_z^2\right) + \frac{1}{3}(2S+1)u_z^2\right] \\ &= -USu_z^2 + \text{constant} \end{aligned}$$

Thus:

$$\psi(\boldsymbol{u}) = Ce^{\beta USu_z^2}$$

Self-consistent equation

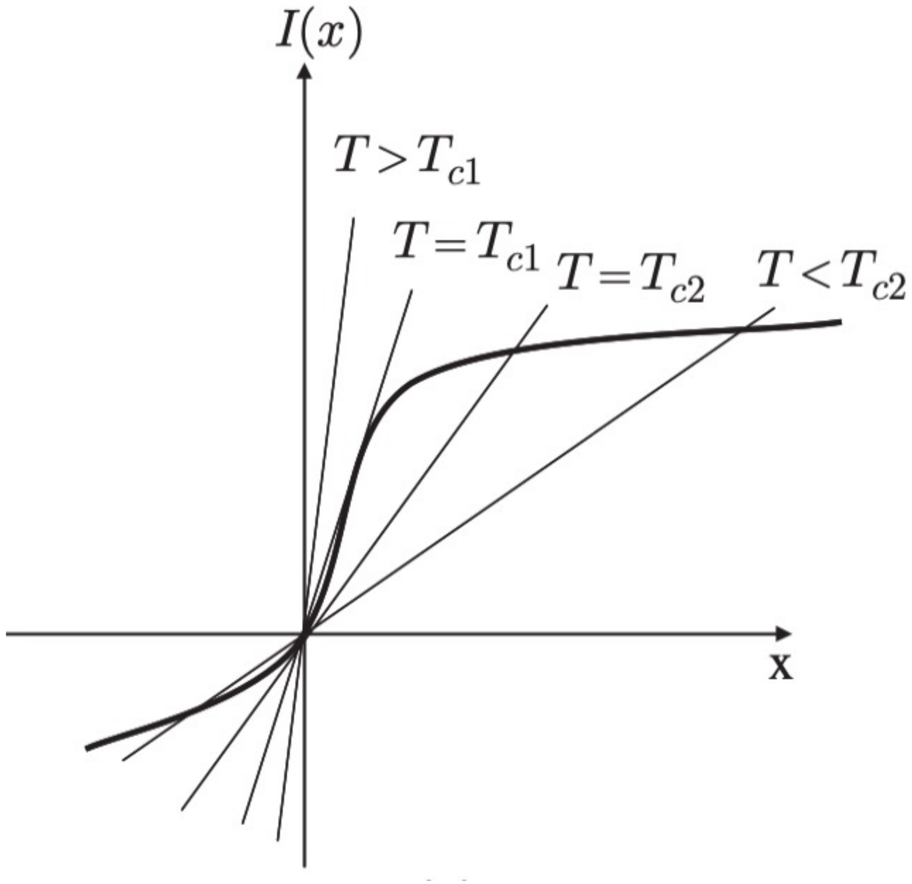
$$S = \frac{3}{2}\left\langle u_z^2 - \frac{1}{3}\right\rangle = \frac{\int d\boldsymbol{u}\,\frac{3}{2}\left(u_z^2-\frac{1}{3}\right)e^{\beta USu_z^2}}{\int d\boldsymbol{u}e^{\beta USu_z^2}}$$

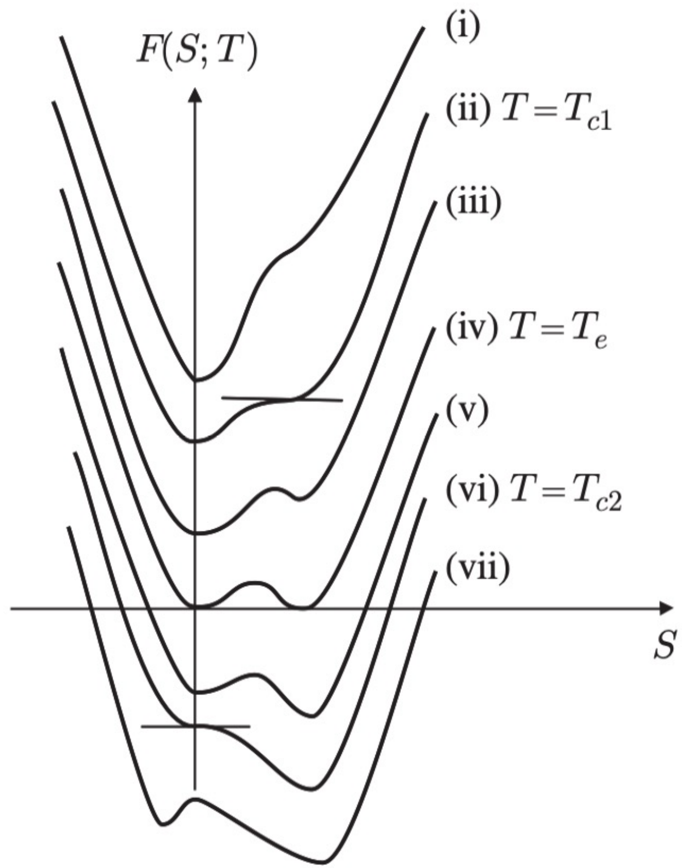
Replacing $x = \beta U S$

$$\Rightarrow \quad \frac{k_B T}{U} x = I(x)$$

$$I(x) = \frac{\int_0^1 dt \ \frac{3}{2}\left(t^2 - \frac{1}{3}\right) e^{xt^2}}{\int_0^1 dt \ e^{xt^2}}$$

Graphic solution



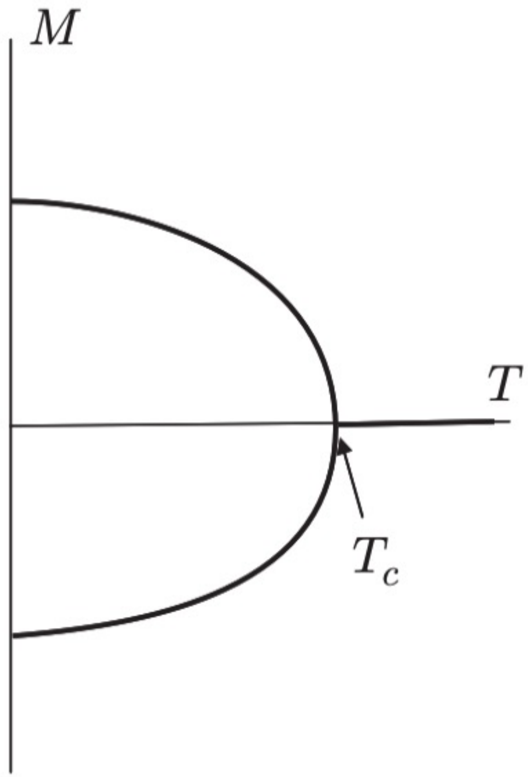
# Landau-de Gennes theory

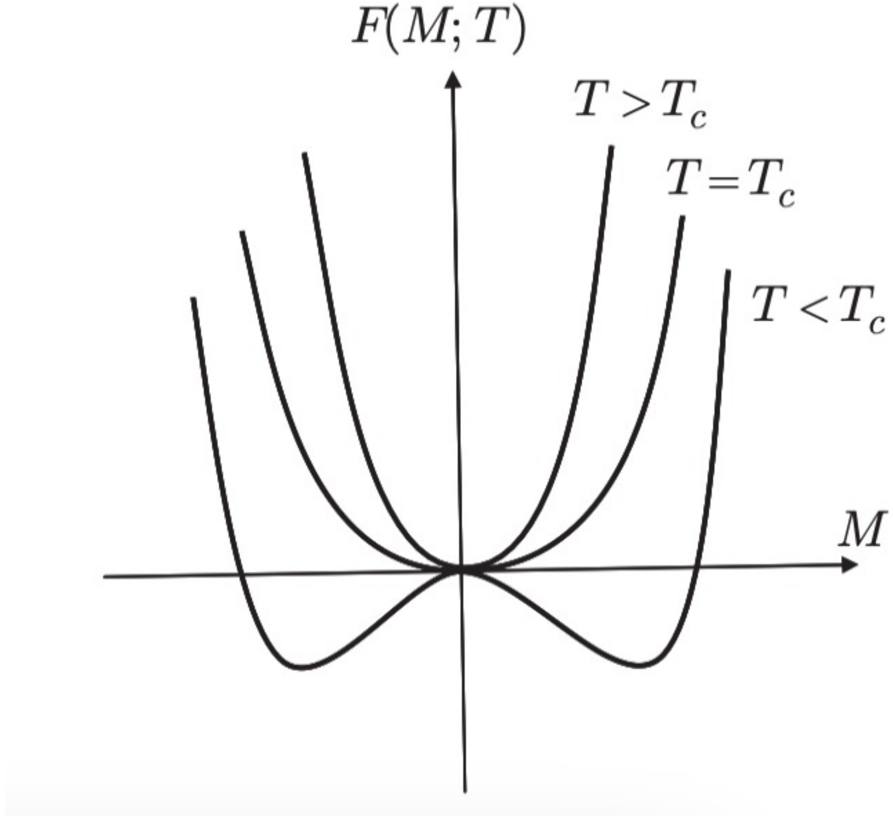
- Nematic-isotropic (NI) transition in liquid crystals;
- Driven by temperature;
- Analogous to the transition in magnetic materials, but the NI is of first order;
- Order parameter: S. Polynomial expension of the free energy.

$$F(x;T) = a_0(T) + a_1(T)x + a_2(T)x^2 + a_3(T)x^3 + a_4(T)x^4 + \cdots$$

$$a_2(T) = A(T - T_c),$$

Analogy with magnetic materials



Free energy for the NI transition:

$$F(\xi, T) = A(T - T_c)\,\xi^2 + A_3\,\xi^3 + A_4\,\xi^4$$

More generically:

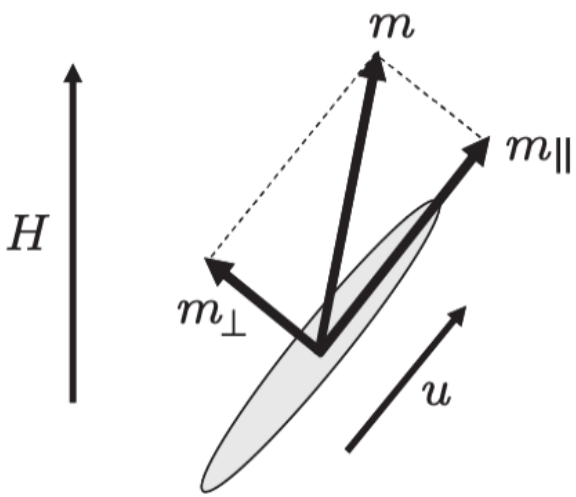
$$F(Q_{\alpha\beta}, T) = a(T - T_c)\,Q_{\alpha\beta}^2 - a_3\,Q_{\alpha\beta}\,Q_{\beta\gamma}\,Q_{\gamma\alpha} + a_4\,Q_{\alpha\beta}^4$$

The above free energy does not depend on the directors, only on S.

The coefficient can be calculated using mean free theory. $A \simeq Nk_B, \quad B \simeq Nk_BT_c, \quad C \simeq Nk_BT_c$

Exercise: a) relate A, $A_3$ and $A_4$ with a, $a_3$ and $a_4$ ; b) Find the transition temperature.

# Magnetic field




Projection

$$\boldsymbol{H}_{\parallel} = (\boldsymbol{H} \cdot \boldsymbol{u})\boldsymbol{u}$$

$$\boldsymbol{H}_{\perp} = \boldsymbol{H} - \boldsymbol{H}_{\parallel}$$

Magnetic moments

$$\boldsymbol{m}_{\parallel} = \alpha_{\parallel}\boldsymbol{H}_{\parallel} = \alpha_{\parallel}(\boldsymbol{H} \cdot \boldsymbol{u})\boldsymbol{u}$$

$$\boldsymbol{m}_{\perp} = \alpha_{\perp}\boldsymbol{H}_{\perp} = \alpha_{\perp}[\boldsymbol{H} - (\boldsymbol{H} \cdot \boldsymbol{u})\boldsymbol{u}]$$

Potential energy for one molecule: $-\boldsymbol{m} \cdot \boldsymbol{H}/2$

$$\begin{aligned} w_H(\boldsymbol{u}) &= -\frac{1}{2}\alpha_{\parallel}(\boldsymbol{H} \cdot \boldsymbol{u})^2 - \frac{1}{2}\alpha_{\perp}[\boldsymbol{H} - (\boldsymbol{H} \cdot \boldsymbol{u})\boldsymbol{u}]^2 \\ &= -\frac{1}{2}\alpha_{\parallel}(\boldsymbol{H} \cdot \boldsymbol{u})^2 + \frac{1}{2}\alpha_{\perp}(\boldsymbol{H} \cdot \boldsymbol{u})^2 + \text{terms independent of } \boldsymbol{u} \\ &= -\frac{1}{2}\alpha_d(\boldsymbol{H} \cdot \boldsymbol{u})^2 + \text{terms independent of } \boldsymbol{u} \end{aligned}$$

$$\alpha_d = \alpha_{\parallel} - \alpha_{\perp}$$

$\alpha_d > 0$ The molecules align parallel to the magnetic field

Total potential energy

$$F_H = -\frac{N}{2}\alpha_d \left\langle (\boldsymbol{H}\cdot\boldsymbol{u})^2 \right\rangle = -\frac{N}{2}\alpha_d \boldsymbol{H}\cdot\boldsymbol{Q}\cdot\boldsymbol{H} = -\frac{N}{2}\alpha_d S(\boldsymbol{H}\cdot\boldsymbol{n})^2$$

Total free energy

$$F(\boldsymbol{Q};T) = \frac{1}{2}A(T-T_c)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 - \frac{SN}{2}\alpha_d(\boldsymbol{H}\cdot\boldsymbol{n})^2$$

In the presence of a magnetic field, the direction of the molecules matter. The response to a magnetic field will also depend on the degree of order S.

# Response in the isotropic phase

In the presence of a magnetic field, S becomes different form zero, but small. Thus:

$$F(\boldsymbol{Q};T) = \frac{1}{2}A(T-T_c)S^2 - \frac{SN}{2}\alpha_d \boldsymbol{H}^2$$

$\hat{m} \parallel \vec{H}$

Minimization with respect to S:

$$\frac{\delta F}{\delta S} = 0 \Rightarrow \quad S = \frac{N\alpha_d \boldsymbol{H}^2}{2A(T-T_c)}$$

$\uparrow S$ if $T \to T_c$ (critical phenomena)

$\uparrow S$ if $H \uparrow$

# Response in the nematic phase

- The effect in S is small ($S=S_N$), of the order of

$$\alpha_d H^2 / k_B T_c$$

- Because the molecules align with the neighbours, the main effect of a magnetic field in the nematic phase is in the director field;
- To rotate the molecules in the isotropic state, one needs: $\alpha_d H^2 > k_B T$
- In the nematic phase: $S_{eq} N \alpha_d H^2 > k_B T$ .So, the necessary magnetic field to rotate all the particles is relatively small

# Effect of a spatial gradient on the nematic order

- Consider Q=Q(x) due to anchoring or external fields for instance;

$$F_{tot} = \int d\boldsymbol{r}[f(\boldsymbol{Q}(\boldsymbol{r})) + f_{el}(\boldsymbol{Q}, \boldsymbol{\nabla Q})]$$

- The elastic term can be expanded in powers of $\nabla Q$, but the smallest term is the squared one due to the symmetry;

$$f_{el}(\boldsymbol{Q}, \boldsymbol{\nabla Q}) = \frac{1}{2} K_{\alpha\beta\gamma,\alpha'\beta'\gamma'} \nabla_\alpha Q_{\beta\gamma} \nabla_{\alpha'} Q_{\beta'\gamma'}$$

# Effect of the gradient terms in the disordered phase

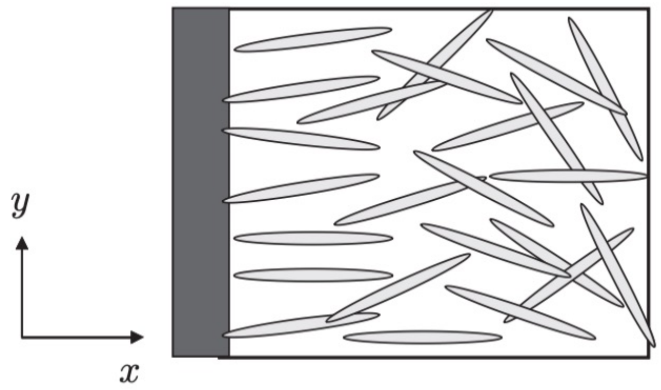
Possible terms (the other possibilities are equivalent):

$$f_{el} = \frac{1}{2}K_1 \nabla_\alpha Q_{\beta\gamma} \nabla_\alpha Q_{\beta\gamma} + \frac{1}{2}K_2 \nabla_\alpha Q_{\alpha\gamma} \nabla_\beta Q_{\beta\gamma}$$

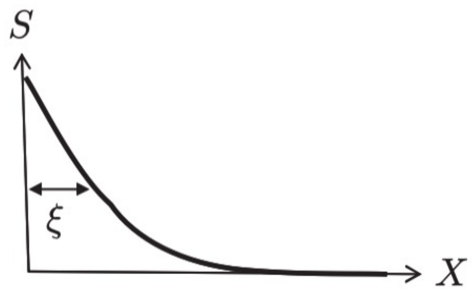
Free energy:

$$F_{tot} = \int d\boldsymbol{r} \left[ \frac{1}{2}A(T - T_c)S^2 + \frac{1}{2}K_1 \nabla_\alpha Q_{\beta\gamma} \nabla_\alpha Q_{\beta\gamma} + \frac{1}{2}K_2 \nabla_\alpha Q_{\alpha\gamma} \nabla_\beta Q_{\beta\gamma} \right]$$

Application: local ordering induced by a wall of solid substrate.




(a)




(b)

$$Q_{xx} = \frac{2}{3}S, \quad Q_{yy} = Q_{zz} = -\frac{1}{3}S, \quad Q_{xy} = Q_{yz} = Q_{zx} = 0$$

$$F_{tot} = \int d\boldsymbol{x} \left[ \frac{1}{2}A(T - T_c)S^2 + \frac{1}{3}K_1 \left(\frac{dS}{dx}\right)^2 + \frac{2}{9}K_2 \left(\frac{dS}{dx}\right)^2 \right]$$
$$= \frac{1}{2}A(T - T_c) \int d\boldsymbol{x} \left[ S^2 + \xi^2 \left(\frac{dS}{dx}\right)^2 \right]$$

Correlation length

$$\xi = \sqrt{\frac{2(3K_1 + 2K_2)}{9A(T - T_c)}}$$

Diverges for T -> Tc.

Can also be used in the ordered phase

$$\delta F_{tot}/\delta S = 0 \quad \Rightarrow \quad \xi^2 \frac{d^2 S}{dx^2} = S \quad \Rightarrow \quad S = S_0 e^{-x/\xi}$$

# Effect of the gradient terms in the ordered phase

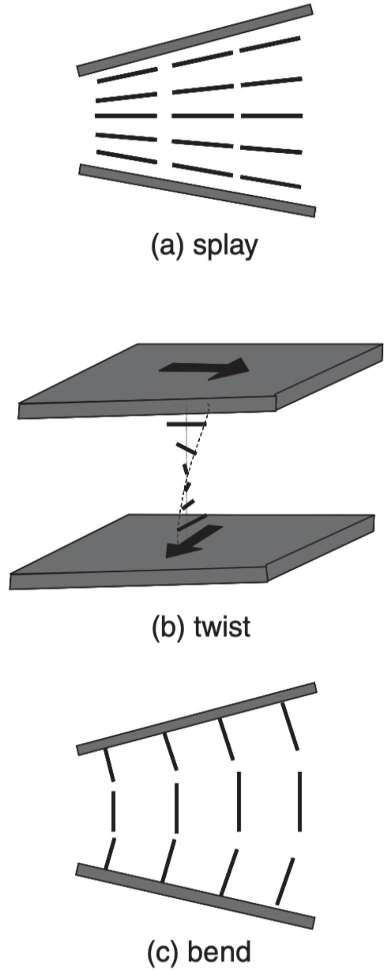
Assume a constant S

$$\boldsymbol{Q}(\boldsymbol{r}) = S_{eq}\left[\boldsymbol{n}(\boldsymbol{r})\boldsymbol{n}(\boldsymbol{r}) - \frac{1}{3}\boldsymbol{I}\right]$$

Rewrite the elastic term for the tensor Qab (exercise):

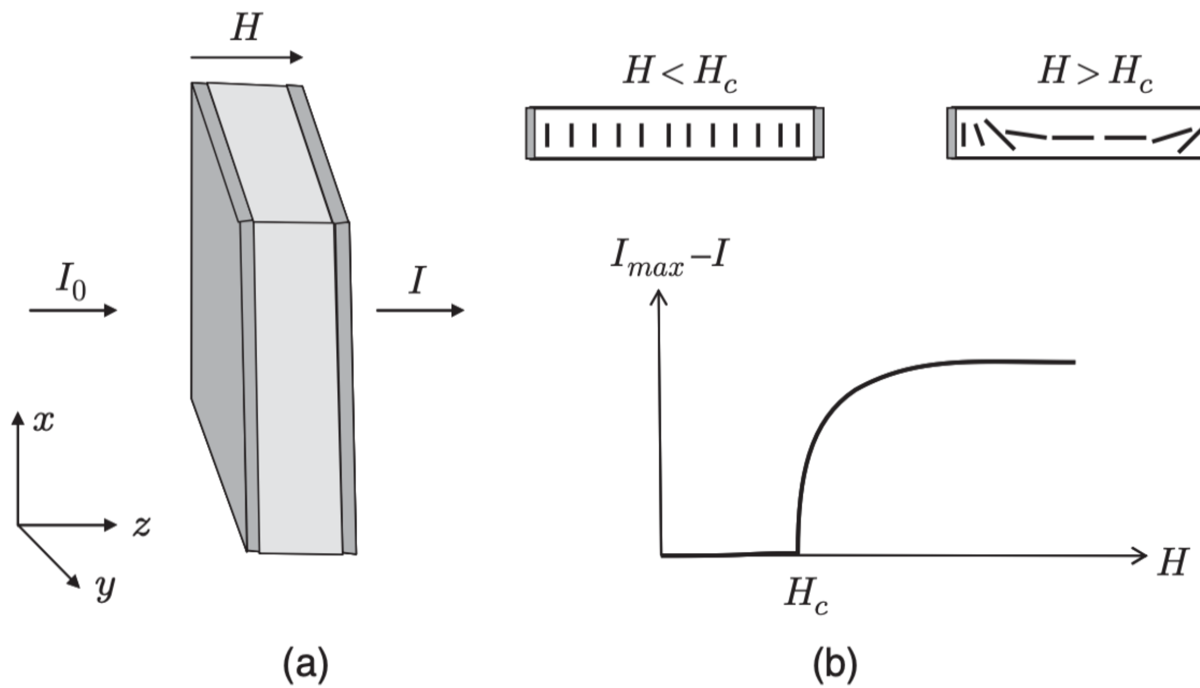
$$f_{el} = \frac{1}{2}K_1(\boldsymbol{\nabla}\cdot\boldsymbol{n})^2 + \frac{1}{2}K_2(\boldsymbol{n}\cdot\boldsymbol{\nabla}\times\boldsymbol{n})^2 + \frac{1}{2}K_3(\boldsymbol{n}\times\boldsymbol{\nabla}\times\boldsymbol{n})^2$$

K1 – splay
K2 – twist
K3 – bend
Units: J/m or N



# Fredericks transition

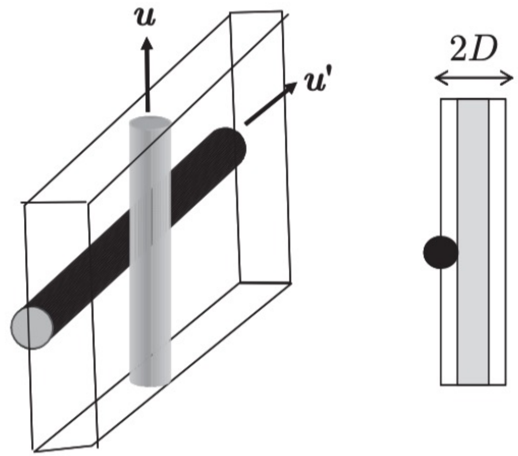
See section 5.4.4 of Doi's book



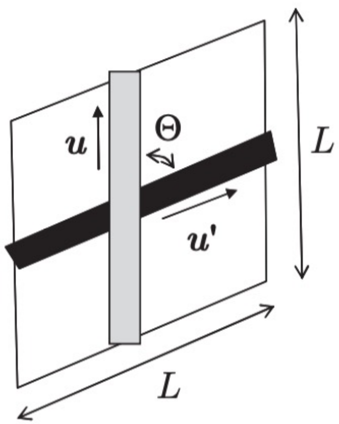

$$H_c = \sqrt{\frac{K_1 \pi^2}{\Delta\chi L^2}}$$

Mechanism to measure the elastic constants (K1 in this case).

# Onsager's theory for the isotropic–nematic transition of rod-like particles




(a) (b)




- Nematic isotropic transition;
- Rod-like particles (L>>D);
- Lyotropic liquid crystals: transition driven by the concentration;

The volume occupied by a particle 1 that cannot be occupied by another particle:

$$v_{ex}(\boldsymbol{u}, \boldsymbol{u}') = 2DL^2 \sin\Theta = 2DL^2|\boldsymbol{u} \times \boldsymbol{u}'|$$

Consider N particles.

Probability of particle j do not overlap particle i:

$$1 - v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)/V$$

Small Θ's are entropically more favourable. This is why rod-like particles form a nematic phase at high concentrations.

The probability $\psi(\boldsymbol{u})$ that particle 1 points in the direction $\boldsymbol{u}$ is equal to the probability that all other particles do not overlap particle 1:

$e^x \approx 1 + x$

$$\psi(\boldsymbol{u}) \propto \Pi_{j=2}^{N} \left[1 - \frac{v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)}{V}\right] = \exp\left[-\sum_{j=2}^{N} \frac{v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)}{V}\right]$$

but $$\sum_{j=2}^{N} \frac{v_{ex}(\boldsymbol{u}, \boldsymbol{u}_j)}{V} = n \int d\boldsymbol{u}' v_{ex}(\boldsymbol{u}, \boldsymbol{u}')\psi(\boldsymbol{u}')$$

Self-consistent equation

$$\psi(\boldsymbol{u}) = C \exp\left[-n \int d\boldsymbol{u}' v_{ex}(\boldsymbol{u}, \boldsymbol{u}')\psi(\boldsymbol{u}')\right]$$

$n = N/V$

Interaction potential:

$$w_{eff}(\boldsymbol{u}, \boldsymbol{u}') = n k_B T v_{ex}(\boldsymbol{u}, \boldsymbol{u}') = 2\underbrace{nDL^2}_{\text{Interaction strength}} k_B T |\boldsymbol{u} \times \boldsymbol{u}'|$$

If $n\ D\ L^2$ exceeds a a critical value, the isotropic state becomes unstable.

Transition (numerical solution of the self consistent equation):

$$nDL^2 > 5.1$$

Corresponding volume fraction

$$\phi_{c2} = \frac{5.1\pi}{4}\frac{D}{L} \simeq 4\frac{D}{L}$$

Above this concentration, the isotropic state cannot be stable, and the system turns into the nematic state.