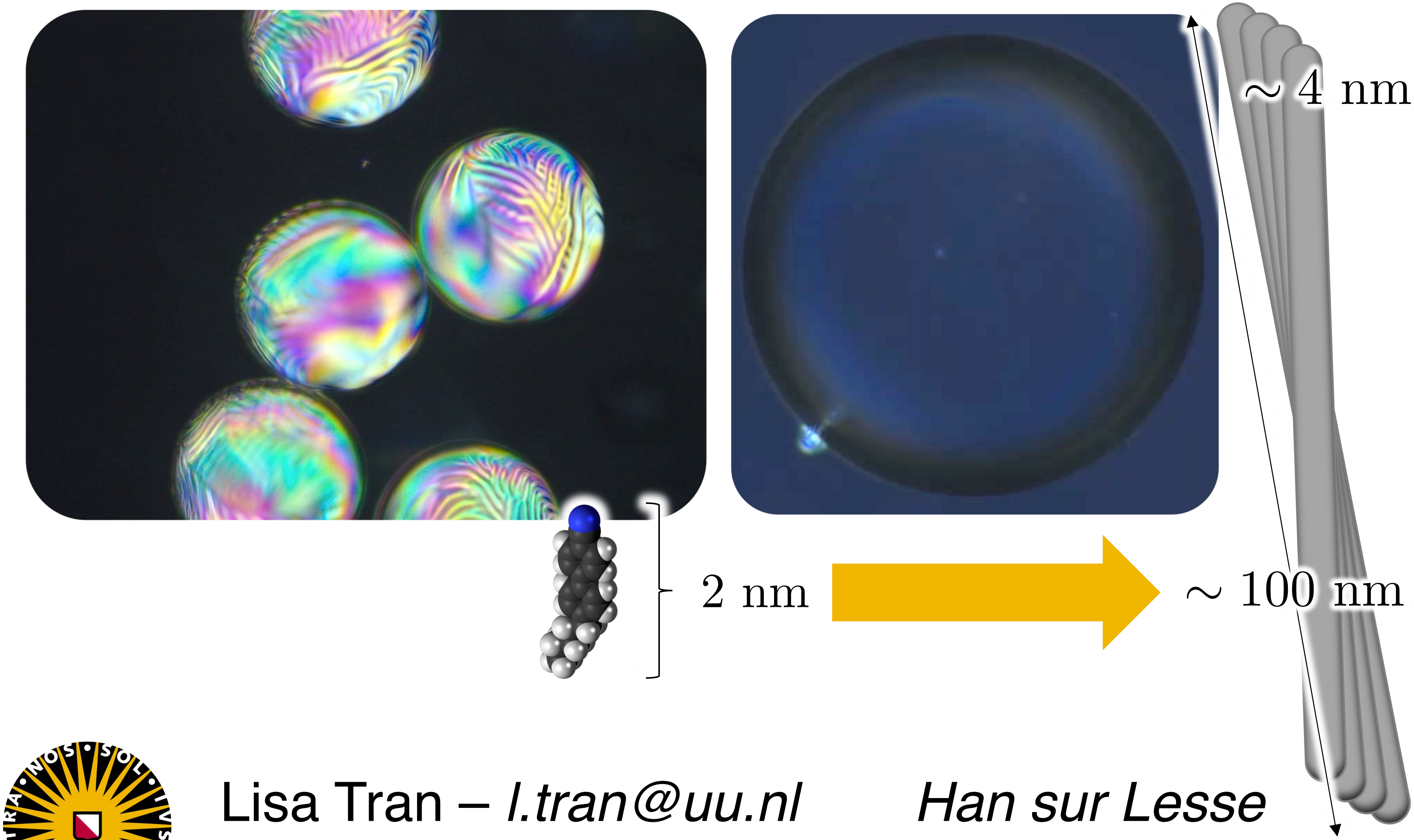
Liquid Crystals



Lisa Tran – *l.tran@uu.nl*
Utrecht University

Han sur Lesse
June 2023

Liquid crystals

Lisa Tran

Day 1: Displays and droplets

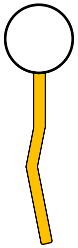
Optical properties
Order: elasticity & defects
LCDs
Research highlights

Day 2: Colloidal liquid crystals

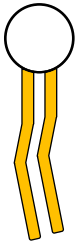
Hard rods - Zwanzig model (2D)
Onsager theory & other interactions
Colloidal liquid crystals in biology
Research highlights

Soft Matter Context

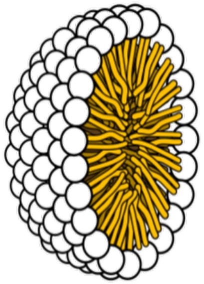
Complex fluids



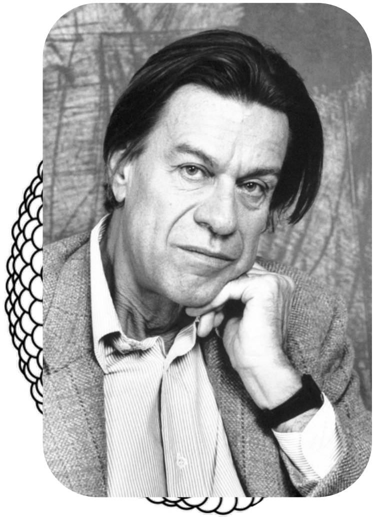
surfactant



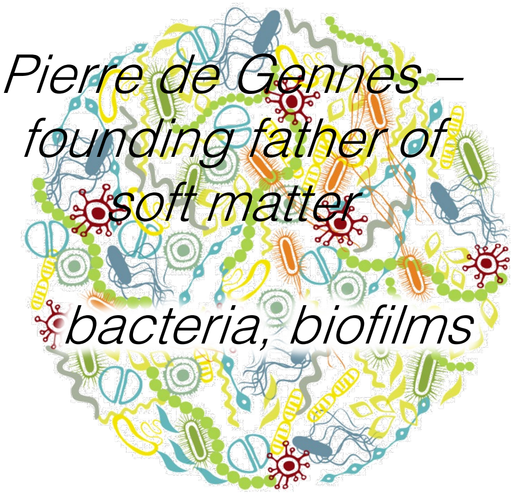
lipid



micelle

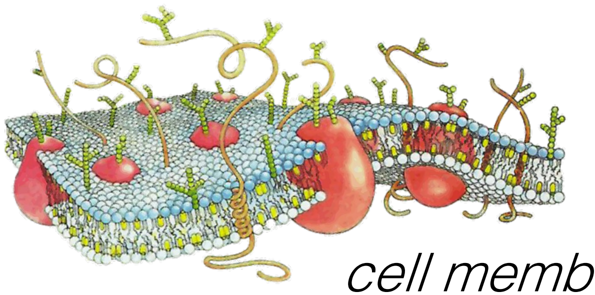


liposome

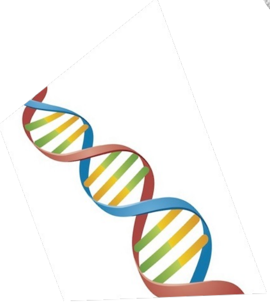


Pierre de Gennes – founding father of soft matter

bacteria, biofilms



cell membrane



polymers, DNA

Liquid crystals

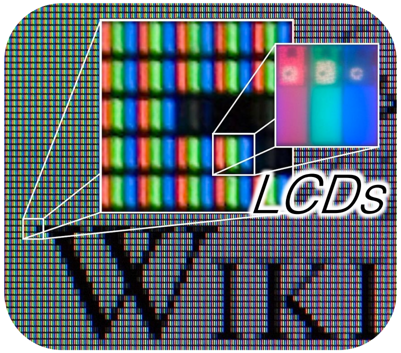
epithelial tissue

T.B. Saw, et al, Nature, 544, 212-216 (2017)

colloids

paint drying

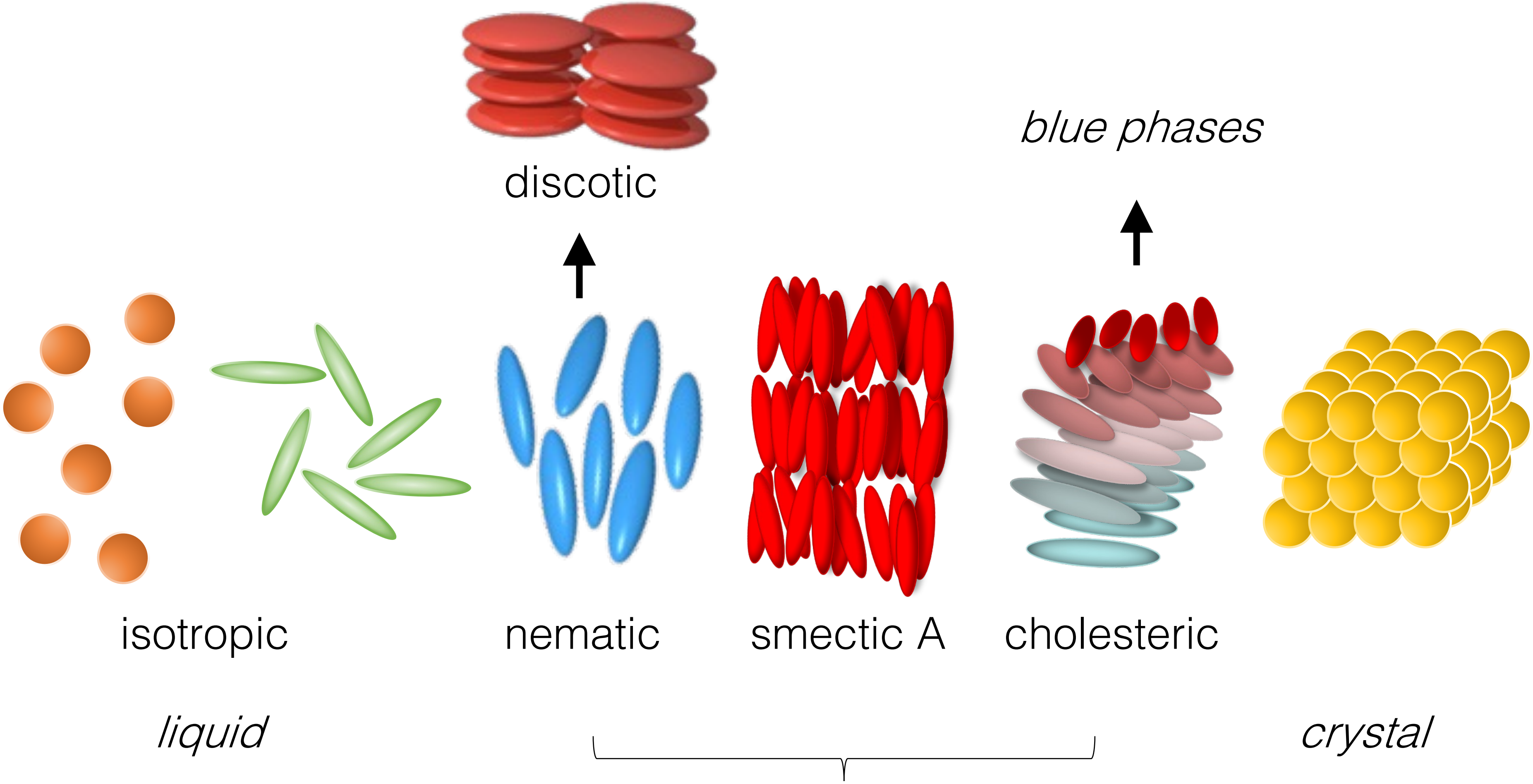
Youtube: Biobus



LCDs

Self-assembly

What are liquid crystals?



discotic

blue phases

isotropic

nematic

smectic A

cholesteric

liquid

crystal

liquid crystal

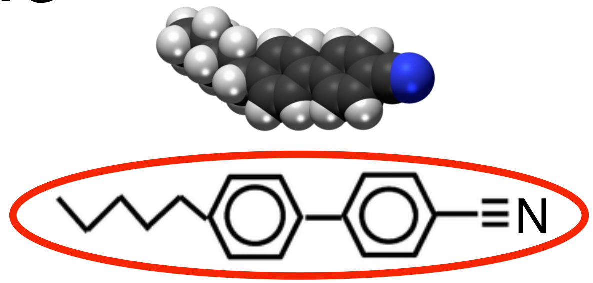
Blue phase video: H. Yoshida, Youtube

Liquid crystals – small molecule

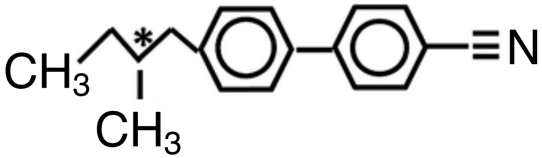
isotropic

nematic

cholesteric

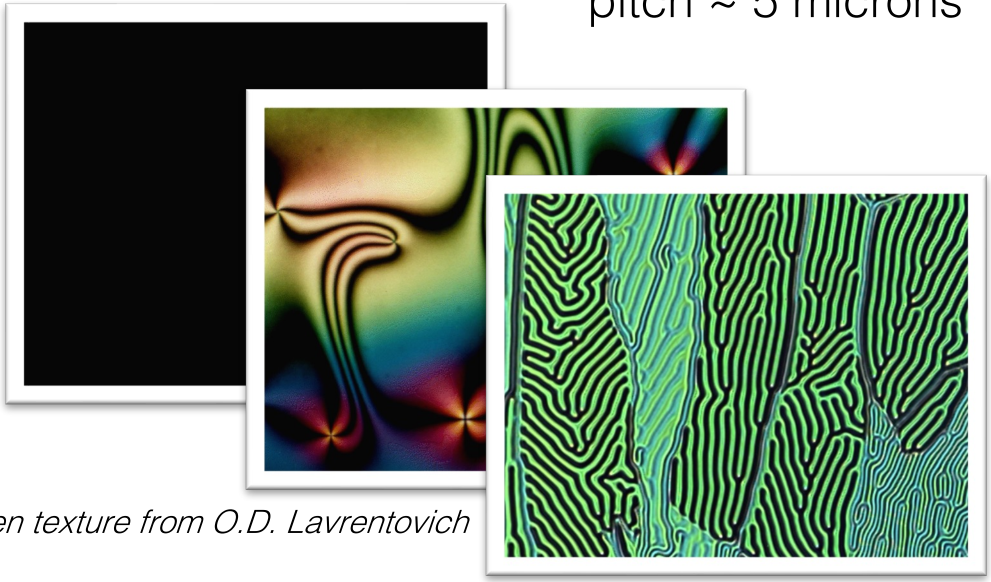


5CB



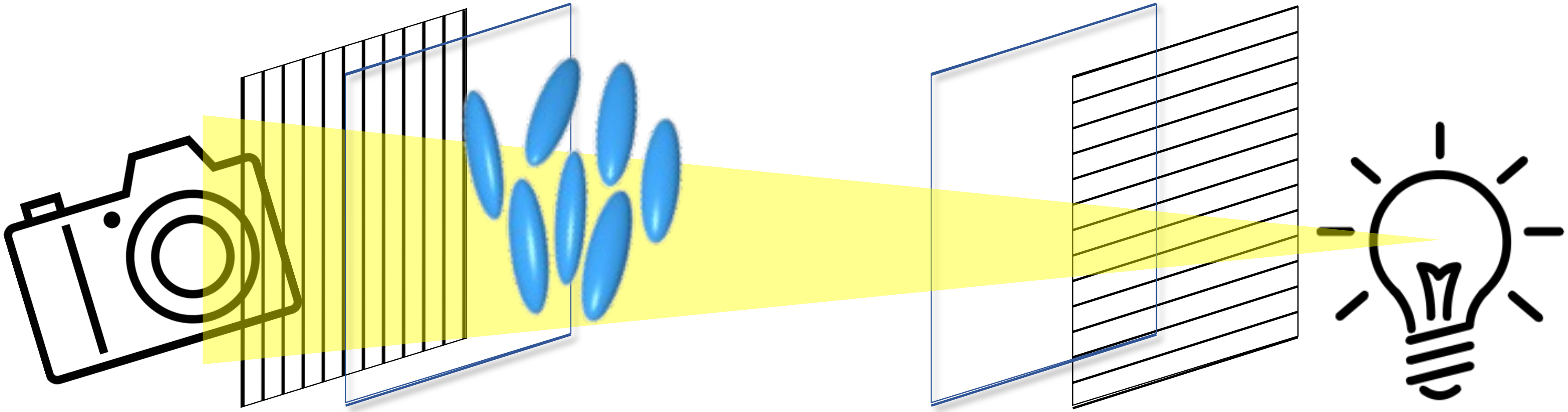
2.8 wt-% CB15

pitch ~ 5 microns



Schlieren texture from O.D. Lavrentovich

Liquid crystal optics

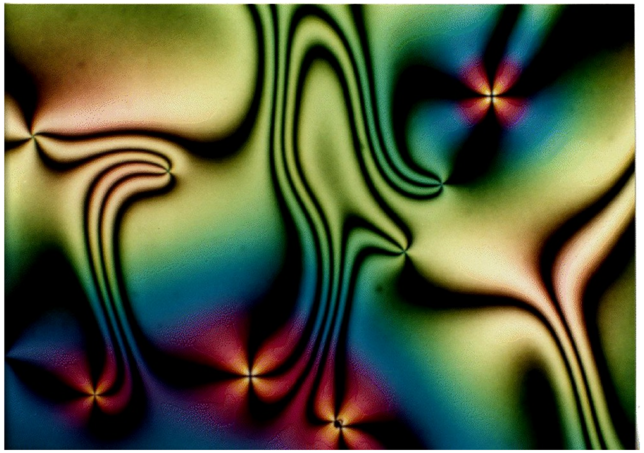


polarizer

glass plate

glass plate

analyzer

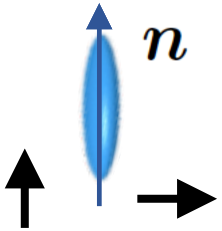


schlieren texture

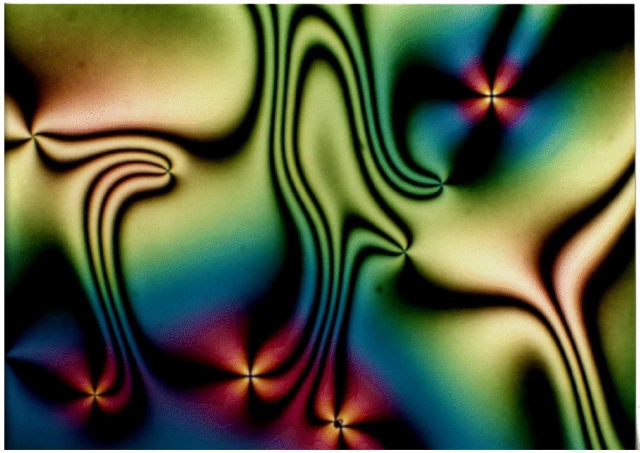
Liquid crystal optics

Dielectric tensor

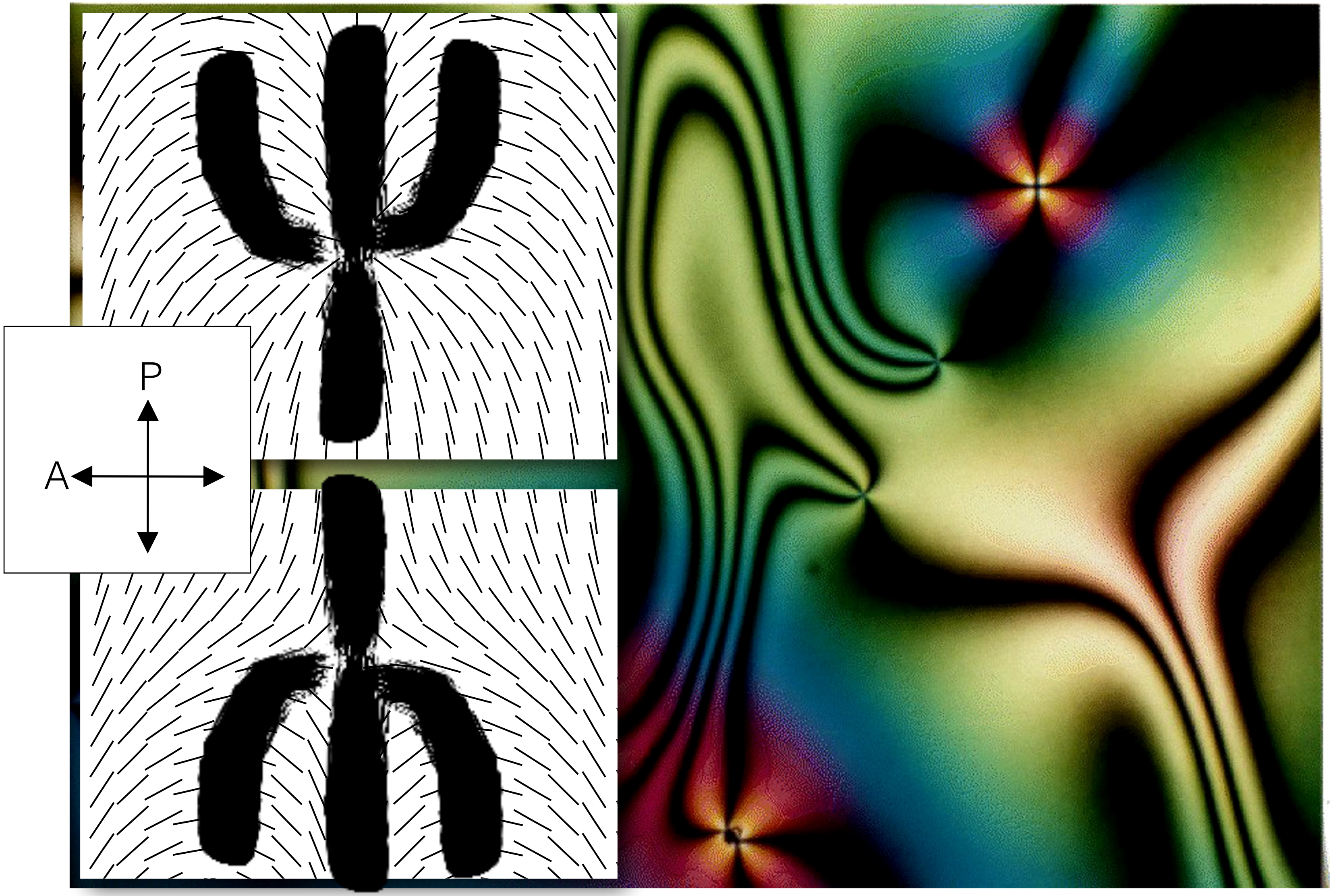
$$\varepsilon_{ij} = \underbrace{\frac{\mathrm{Tr}\,\boldsymbol{\varepsilon}}{d}}_{=\ \text{dielectric constant}}\delta_{ij} + \overbrace{\Delta\varepsilon}^{\text{dielectric anisotropy}}\underbrace{Q_{ij}}_{\substack{\text{dielectric anisotropy tensor}\\ \text{symmetric, traceless}}}$$



$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$$



Schlieren texture – construct director field



Schlieren textures courtesy of O.D. Lavrentovich: http://www.nsf.gov/news/mmg/mmg_disp.jsp?med_id=59511
*and I. Dierking: **Textures of Liquid Crystals**, John Wiley & Sons (2003)*
LC director field schematic courtesy of R.D. Kamien

Liquid crystal optics

$$S = \underset{\uparrow}{f} - (1 - f)$$

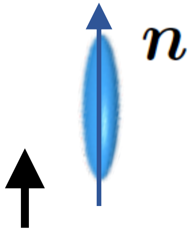
= # molecules aligned along $\boldsymbol{n}$

Dielectric anisotropy from macroscopic order parameter

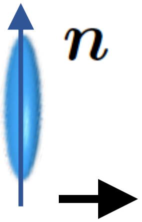
$$\varepsilon_{ij} = \frac{\mathrm{Tr}\,\boldsymbol{\varepsilon}}{d}\delta_{ij} + \Delta\varepsilon Q_{ij}$$

$$f = {}^1\!/\!{}_2(1 + S)$$

$$1 - f = {}^1\!/\!{}_2(1 - S)$$



$$\begin{aligned} \varepsilon_{ij}^{along} &= \varepsilon_{\|} n_i n_j + \varepsilon_{\perp}(\delta_{ij} - n_i n_j) \\ &= \underbrace{\frac{\varepsilon_{\|} + \varepsilon_{\perp}}{2}\delta_{ij}}_{\textit{diagonal}} + \underbrace{\Delta\varepsilon\left(n_i n_j - \frac{1}{2}\delta_{ij}\right)}_{\textit{traceless}} \end{aligned}$$



$$\varepsilon_{ij}^{perp} = \frac{\varepsilon_{\|} + \varepsilon_{\perp}}{2}\delta_{ij} - \Delta\varepsilon\left(n_i n_j - \frac{1}{2}\delta_{ij}\right)$$

From R.D. Kamien's Liquid Crystals: An Entree into Broken Symmetries, Materials Geometry, and Elasticity (in preparation)

Liquid crystal optics

Dielectric anisotropy from macroscopic order parameter

$$S = f - (1 - f)$$

= # molecules aligned along $\boldsymbol{n}$

$$f = {}^{1}\!/_{2}(1 + S)$$

$$1 - f = {}^{1}\!/_{2}(1 - S)$$

$$\boldsymbol{\varepsilon} = f\boldsymbol{\varepsilon}^{along} + (1 - f)\boldsymbol{\varepsilon}^{perp}$$

$$\varepsilon_{ij} = \frac{\varepsilon_{\|} + \varepsilon_{\perp}}{2}\delta_{ij} + S\Delta\varepsilon(n_i n_j - \frac{1}{2}\delta_{ij})$$

compare to before…

$$\varepsilon_{ij} = \frac{\mathrm{Tr}\,\boldsymbol{\varepsilon}}{d}\delta_{ij} + \Delta\varepsilon Q_{ij}$$

$$\boxed{Q_{ij} = S(n_i n_j - \frac{1}{2}\delta_{ij})}$$

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Maier-Saupe theory

$$\boxed{Q_{ij} = S(n_i n_j - \frac{1}{2}\delta_{ij})}$$

Determining the <u>microscopic</u> order parameter

direction of the α^{th} *molecule denoted by* $\boldsymbol{\nu}^\alpha$

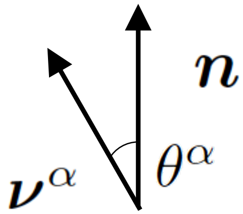
total # of molecules

$$Q_{ij} = \frac{1}{N}\sum_{\alpha=1}^{N}\left[\nu_i^\alpha \nu_j^\alpha - \frac{1}{d}\delta_{ij}\right]$$

system dimension

equate above two, after some manipulation:

$$S\left(1 - \frac{1}{d}\right) \quad = \quad \langle\,(\mathbf{n}\cdot\boldsymbol{\nu})^2\,\rangle - \frac{1}{d}$$



overall average direction

molecular direction

$$\mathbf{n}\cdot\boldsymbol{\nu}^\alpha = \cos\theta^\alpha$$

microscopic

$$\boxed{S = \frac{d}{d-1}\langle\,\cos^2\theta\,\rangle - \frac{1}{d-1}}$$

W. Maier and A. Saupe, "Eine einfache molekulare theorie des nematischen kristallinflüssigen zustandes," Zeitschrift für Naturforschung, ***13A****:564–566 (1958)*

Maier-Saupe theory

microscopic scalar order parameter

$$\boxed{S = \frac{d}{d-1}\langle\,\cos^2\theta\,\rangle - \frac{1}{d-1}}$$

$$S_{2D} = \langle\, 2\cos^2\theta - 1\,\rangle$$

$$S_{3D} = \langle\, \frac{3}{2}\cos^2\theta - \frac{1}{2}\,\rangle$$

Essential for determining phase transitions and for building elastic free energy

W. Maier and A. Saupe, "Eine einfache molekulare theorie des nematischen kristallinflüssigen zustandes," Zeitschrift für Naturforschung, ***13A****:564–566 (1958)*

Elastic free energy

Energetic cost to pointing away from $\boldsymbol{n}$

Can be written in gradients of $\boldsymbol{Q}$ *or of* $\boldsymbol{n}$

Rotational invariants of $\partial_i Q_{jk}$

$$\partial_i Q_{jk}\partial_i Q_{jk}, \qquad \partial_i Q_{ik}\partial_j Q_{jk}, \qquad \partial_i Q_{jk}\partial_j Q_{ik}$$

Plug in $Q_{ij} = S\left[n_i n_j - \delta_{ij}/3\right]$

$$\begin{aligned}
\partial_i Q_{jk}\partial_i Q_{jk} &= S^2\left(n_j\partial_i n_k + n_k\partial_i n_j\right)\left(n_j\partial_i n_k + n_k\partial_i n_j\right) = 2S^2\partial_i n_k\partial_i n_k \\
\partial_i Q_{ik}\partial_j Q_{jk} &= S^2\left[\left(\partial_i n_i\right)^2 + \left(\left[n_i\partial_i\right]n_k\right)^2\right] \\
\partial_i Q_{jk}\partial_j Q_{ik} &= = S^2\left[\left(\left[n_i\partial_i\right]n_k\right)^2 + \partial_i n_j\partial_j n_i\right]
\end{aligned}$$

From R.D. Kamien's Liquid Crystals: An Entree into Broken Symmetries, Materials Geometry, and Elasticity (in preparation)

Elastic free energy

Energetic cost to pointing away from $\boldsymbol{n}$

A few useful identities to help write into vector notation…

$$\begin{aligned}
(\nabla \times \boldsymbol{n})^2 &= \epsilon_{ijk}\partial_j n_k \epsilon_{ilm}\partial_l n_m \\
&= \partial_i n_j \partial_i n_j - \partial_i n_j \partial_j n_i \\
&= \partial_i n_j \partial_i n_j - \partial_i \left[n_j \partial_j n_i - n_i \partial_j n_j \right] - \left(\partial_i n_i\right)^2
\end{aligned}$$

$$\boldsymbol{n} \times [\nabla \times \boldsymbol{n}] = \frac{1}{2}\nabla \boldsymbol{n}^2 - (\boldsymbol{n} \cdot \nabla)\,\boldsymbol{n}$$

Plug in $Q_{ij} = S\left[n_i n_j - \delta_{ij}/3\right]$

$$\begin{aligned}
\partial_i Q_{jk} \partial_i Q_{jk} &= S^2 \left(n_j \partial_i n_k + n_k \partial_i n_j\right)\left(n_j \partial_i n_k + n_k \partial_i n_j\right) = 2S^2 \partial_i n_k \partial_i n_k \\
\partial_i Q_{ik} \partial_j Q_{jk} &= S^2 \left[\left(\partial_i n_i\right)^2 + \left(\left[n_i \partial_i\right] n_k\right)^2\right] \\
\partial_i Q_{jk} \partial_j Q_{ik} &= = S^2 \left[\left(\left[n_i \partial_i\right] n_k\right)^2 + \partial_i n_j \partial_j n_i\right]
\end{aligned}$$

From R.D. Kamien’s Liquid Crystals: An Entree into Broken Symmetries, Materials Geometry, and Elasticity (in preparation)

Elastic free energy

Putting it all together:

$$\begin{aligned}
\partial_i Q_{jk}\partial_i Q_{jk} &= 2S^2\left\{(\nabla\cdot\boldsymbol{n})^2+(\nabla\times\boldsymbol{n})^2+\underline{\nabla\cdot\left[(\boldsymbol{n}\cdot\nabla)\,\boldsymbol{n}-\boldsymbol{n}\nabla\cdot\boldsymbol{n}\right]}\right\}\\
\partial_i Q_{ik}\partial_j Q_{jk} &= S^2\left\{(\nabla\cdot\boldsymbol{n})^2+\left[\boldsymbol{n}\times(\nabla\times\boldsymbol{n})\right]^2\right\}\\
\partial_i Q_{jk}\partial_j Q_{ik} &= \partial_i Q_{ik}\partial_j Q_{jk}-S^2\underline{\nabla\cdot\left[(\boldsymbol{n}\cdot\nabla)\,\boldsymbol{n}-\boldsymbol{n}\nabla\cdot\boldsymbol{n}\right]}
\end{aligned}$$

- *total derivative, integrates to the surface*
- *called the saddle-splay*
- *will not discuss in detail today*

$$F=\int d\boldsymbol{r}\,\{k_1\partial_i Q_{jk}\partial_i Q_{jk}+k_2\partial_i Q_{ik}\partial_j Q_{jk}\}$$

$$\begin{aligned}
F &= \int_V d\boldsymbol{r}\left\{\frac{1}{2}K_1(\nabla\cdot\boldsymbol{n})^2+\frac{1}{2}K_2\left[\boldsymbol{n}\cdot(\nabla\times\boldsymbol{n})\right]^2+\frac{1}{2}K_3\left[\boldsymbol{n}\times(\nabla\times\boldsymbol{n})\right]^2\right\}\\
&\quad + K_{24}\int_{\partial V} d\boldsymbol{A}\cdot\left[(\boldsymbol{n}\cdot\nabla)\,\boldsymbol{n}-\boldsymbol{n}\nabla\cdot\boldsymbol{n}\right]
\end{aligned}$$

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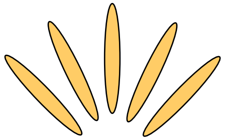
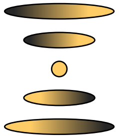
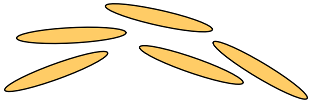
Elastic free energy

Putting it all together – Frank Free Energy







$$F = \int_V d\boldsymbol{r} \left\{ \frac{1}{2}K_1 \left(\nabla \cdot \boldsymbol{n}\right)^2 + \frac{1}{2}K_2 \left[\boldsymbol{n} \cdot \left(\nabla \times \boldsymbol{n}\right) \underset{+\,q_0}{} \right]^2 + \frac{1}{2}K_3 \left[\boldsymbol{n} \times \left(\nabla \times \boldsymbol{n}\right)\right]^2 \right\}$$

$$+ K_{24} \int_{\partial V} d\boldsymbol{A} \cdot \left[\left(\boldsymbol{n} \cdot \nabla\right)\boldsymbol{n} - \boldsymbol{n}\nabla \cdot \boldsymbol{n}\right]$$

saddle-splay

additional term for cholesteric for helical ground state

$$q_0 = \frac{2\pi}{p}$$

where p *is the pitch, which measures how much the cholesteric twists*

However, when deformation is very large, discontinuities in the director field will be introduced, called <u>defects</u>.

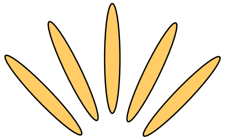
Splay deformations

Note: squaring keeps that $\boldsymbol{n} \to -\boldsymbol{n}$ but for the splay vector to have this symmetry, you have to write it as:

$$\boldsymbol{s} = \boldsymbol{n}\nabla\cdot\boldsymbol{n}$$

Important for the splay flexoelectric effect! (triangle particles)

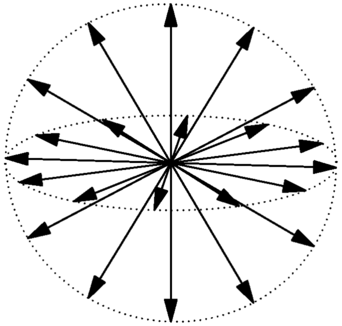
splay



$$F = \int_V d\boldsymbol{r}\left\{\frac{1}{2}K_1\left(\nabla\cdot\boldsymbol{n}\right)^2 + \frac{1}{2}K_2\left[\boldsymbol{n}\cdot\left(\nabla\times\boldsymbol{n}\right)\right]^2 + \frac{1}{2}K_3\left[\boldsymbol{n}\times\left(\nabla\times\boldsymbol{n}\right)\right]^2\right\}$$

$$+ K_{24}\int_{\partial V} d\boldsymbol{A}\cdot\left[\left(\boldsymbol{n}\cdot\nabla\right)\boldsymbol{n} - \boldsymbol{n}\nabla\cdot\boldsymbol{n}\right]$$

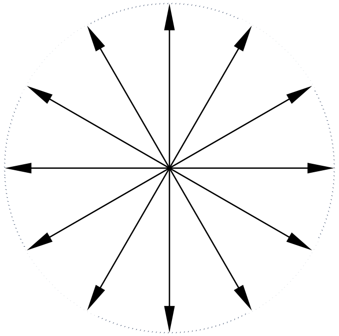
3D splay



$$\boldsymbol{n} = \frac{\boldsymbol{r}}{|\boldsymbol{r}|} \qquad \nabla\cdot\boldsymbol{n} = \frac{2}{|\boldsymbol{r}|}$$

Both are positive contributions!

2D splay



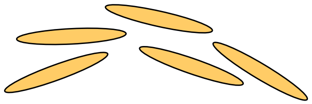
$$\boldsymbol{n} = \frac{[x, 0, z]}{\sqrt{x^2+z^2}} \qquad \nabla\cdot\boldsymbol{n} = \frac{1}{\sqrt{x^2+z^2}}$$

Bend deformations

From vector identities for unit vectors: $\boldsymbol{n} \times (\nabla \times \boldsymbol{n}) = -\underbrace{(\boldsymbol{n} \cdot \nabla)\boldsymbol{n}}$

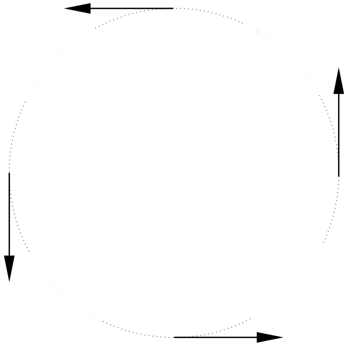
rate of change of the director,
along the direction of the director

bend



$$F = \int_V d\boldsymbol{r} \left\{ \frac{1}{2} K_1 (\nabla \cdot \boldsymbol{n})^2 + \frac{1}{2} K_2 \left[\boldsymbol{n} \cdot (\nabla \times \boldsymbol{n})\right]^2 + \frac{1}{2} K_3 \left[\boldsymbol{n} \times (\nabla \times \boldsymbol{n})\right]^2 \right\}$$

$$+ K_{24} \int_{\partial V} d\boldsymbol{A} \cdot \left[(\boldsymbol{n} \cdot \nabla)\, \boldsymbol{n} - \boldsymbol{n} \nabla \cdot \boldsymbol{n}\right]$$



$$\boldsymbol{n} = \frac{[-z, 0, x]}{\sqrt{x^2 + z^2}}$$

bend vector points radially with magnitude $1/r$

$$\boldsymbol{n} \times (\nabla \times \boldsymbol{n}) = \boldsymbol{n} \times \frac{[0, -1, 0]}{\sqrt{x^2 + z^2}} = \frac{1}{\sqrt{x^2 + z^2}} \frac{[x, 0, z]}{\sqrt{x^2 + z^2}}$$

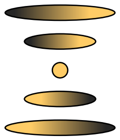
Important for the bend flexoelectric effect!
(banana particles)

measures curvature of lines tangent to $\boldsymbol{n}$

Twist deformations

Twist is necessarily 3D!

$$\boldsymbol{n} = [\cos qz, \sin qz, 0]$$



$$\begin{aligned} F &= \int_V d\boldsymbol{r} \left\{ \frac{1}{2} K_1 \left(\nabla \cdot \boldsymbol{n}\right)^2 + \frac{1}{2} K_2 \left[\boldsymbol{n} \cdot \left(\nabla \times \boldsymbol{n}\right)\right]^2 + \frac{1}{2} K_3 \left[\boldsymbol{n} \times \left(\nabla \times \boldsymbol{n}\right)\right]^2 \right\} \\ &\quad + K_{24} \int_{\partial V} d\boldsymbol{A} \cdot \left[\left(\boldsymbol{n} \cdot \nabla\right) \boldsymbol{n} - \boldsymbol{n} \nabla \cdot \boldsymbol{n}\right] \end{aligned}$$

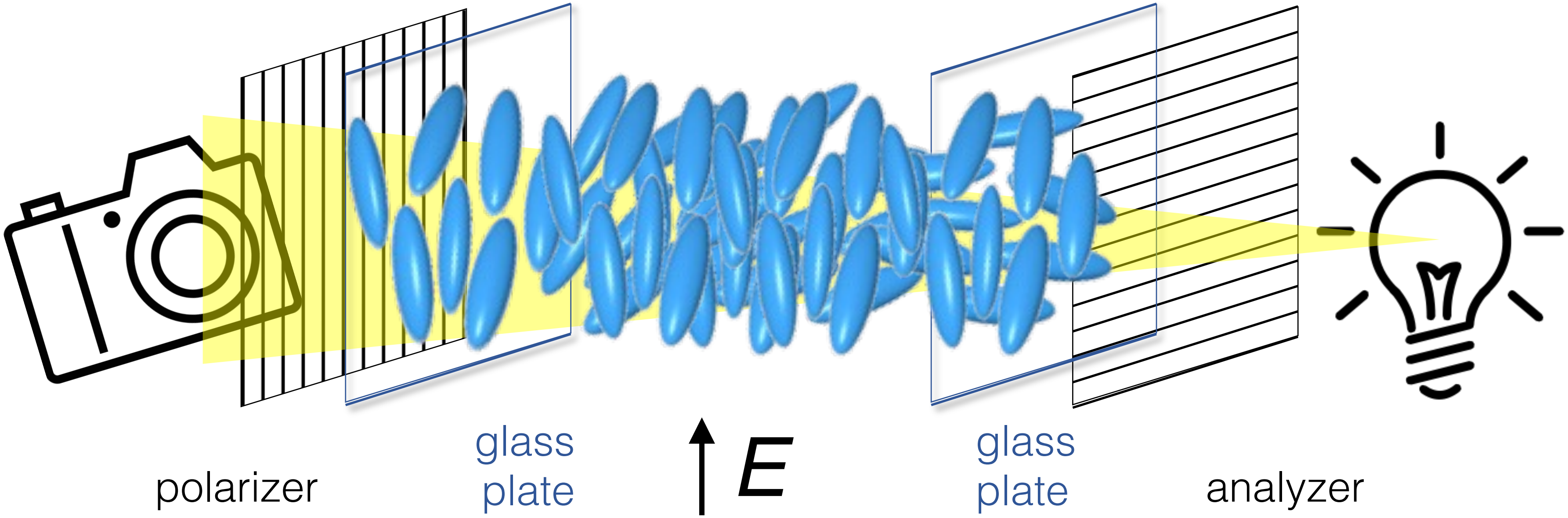
Note that this texture is pure twist!
Both splay and bend are zero.

$$\nabla \cdot \boldsymbol{n} = 0$$

$$\nabla \times \boldsymbol{n} = -q\boldsymbol{n}$$

$$\boldsymbol{n} \times \left(\nabla \times \boldsymbol{n}\right) = 0$$

The twisted nematic display

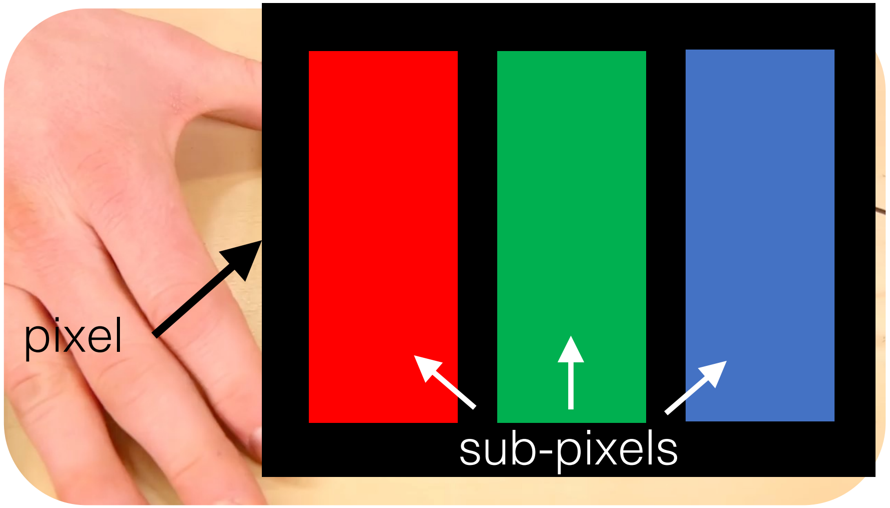

polarizer

glass plate

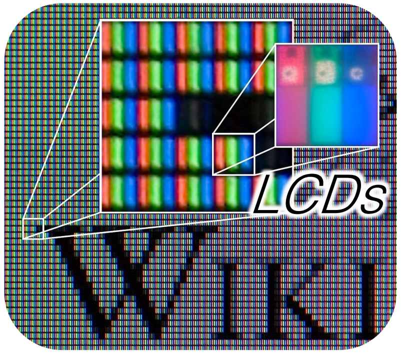
E

glass plate

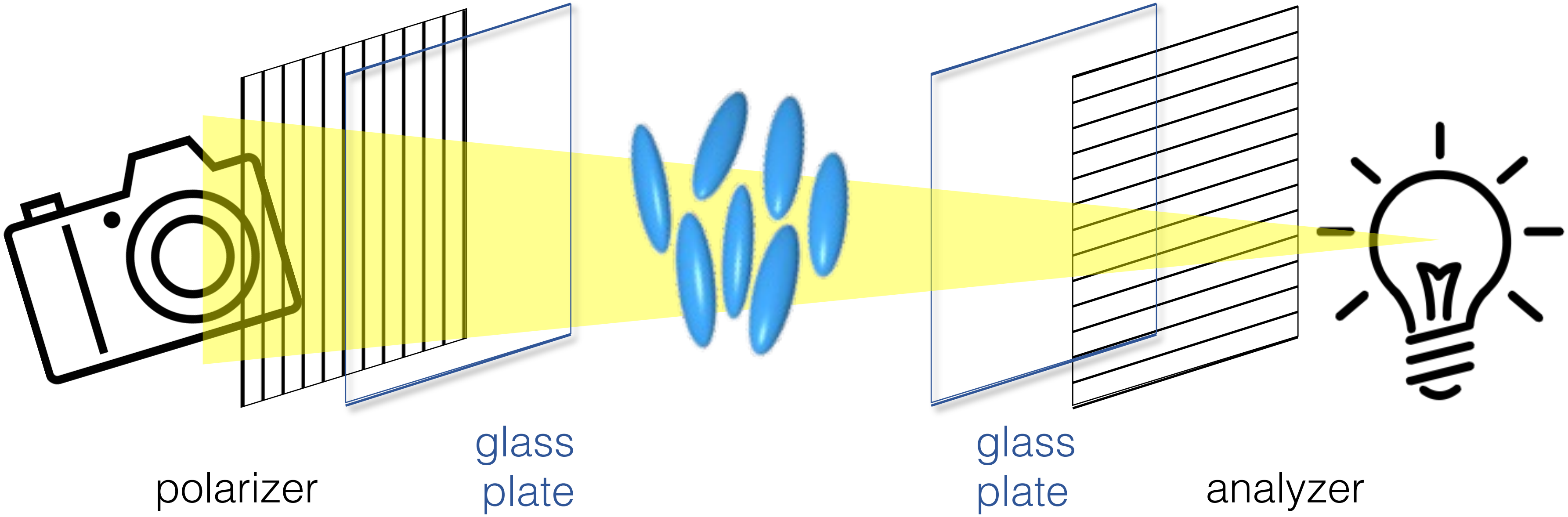
analyzer

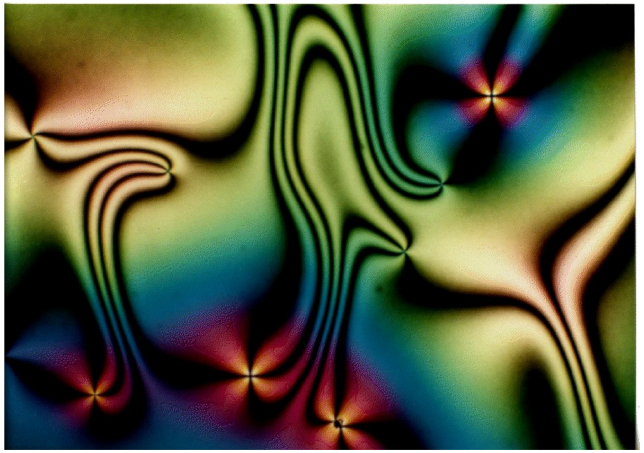

pixel

sub-pixels



Liquid crystal defects

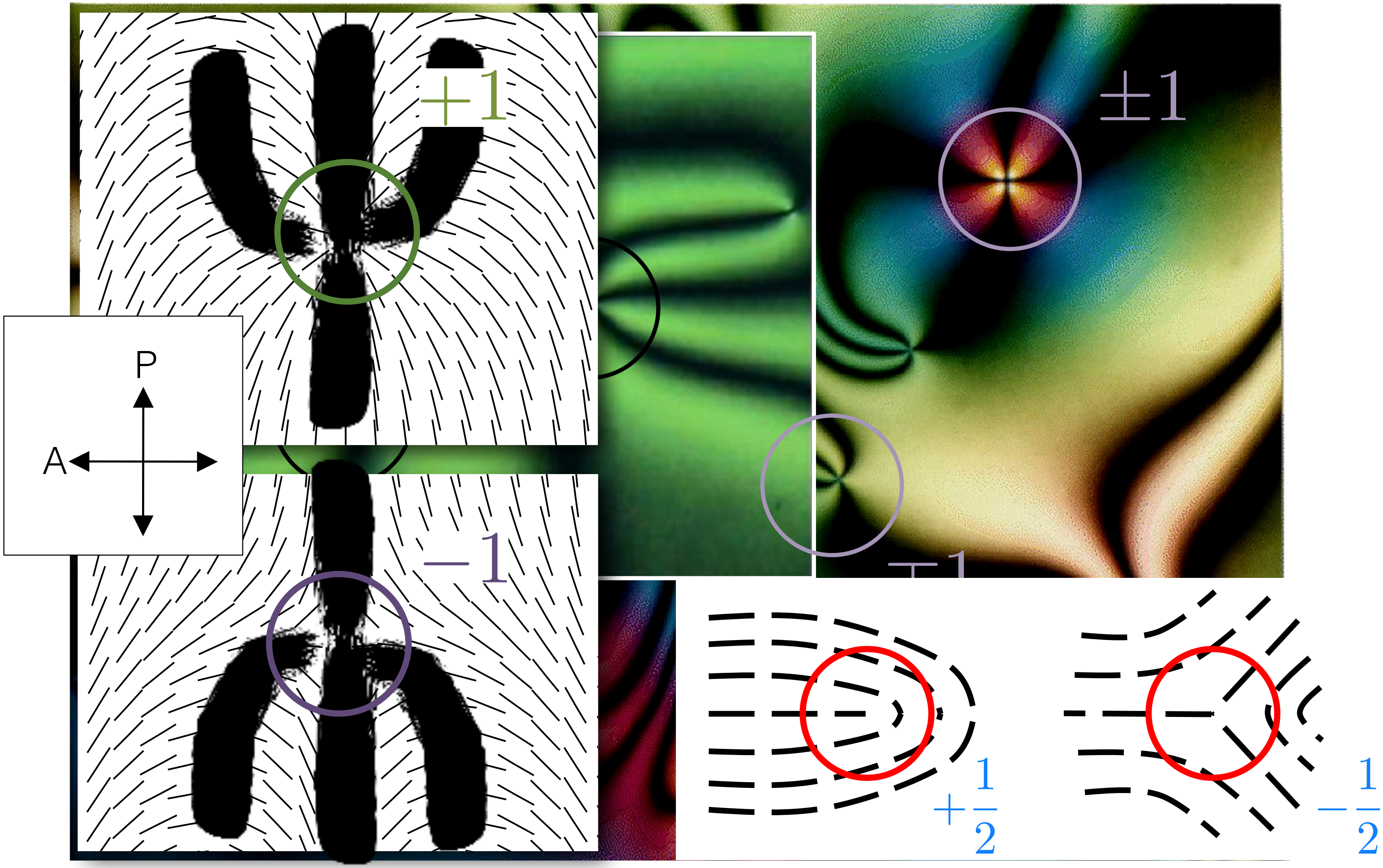




schlieren texture

Schlieren texture - defects

$$w = \frac{1}{2\pi}\int_0^{2\pi} d\phi \frac{df}{d\phi}$$



Schlieren textures courtesy of O.D. Lavrentovich: http://www.nsf.gov/news/mmg/mmg_disp.jsp?med_id=59511
and I. Dierking: ***Textures of Liquid Crystals****, John Wiley & Sons (2003)*
LC director field schematic courtesy of R.D. Kamien

Boundary effects on defects – topology

System boundary geometry/topology can necessitate defects

$K_{Gauss} = {}^{1}\!/_{R_1 R_2}$ *Gaussian curvature of a surface, local geometry*

Gauss-Bonnet theorem – relate local geometry to global geometry/topology

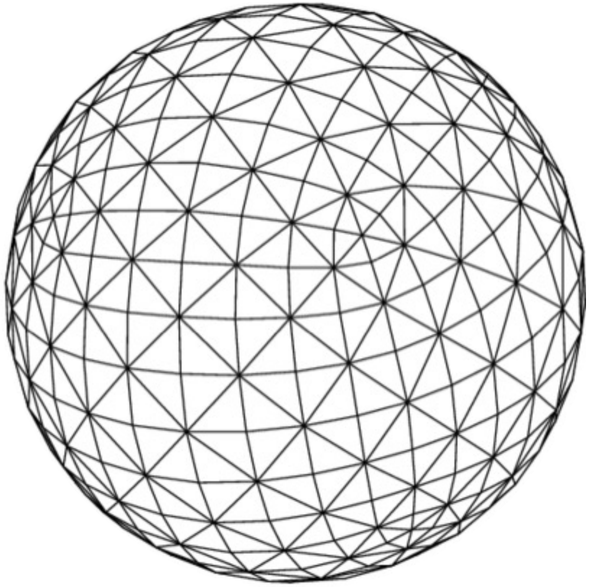
Consider a triangulation of an arbitrary surface:

$$2\pi V = \pi F + \oiint_S K_{Gauss}\, dS$$

$$3\mathrm{F} = 2\mathrm{E}$$

$$V - E + F = \chi = \frac{1}{2\pi} \oiint_S K_{Gauss}\, dS$$

Euler characteristic

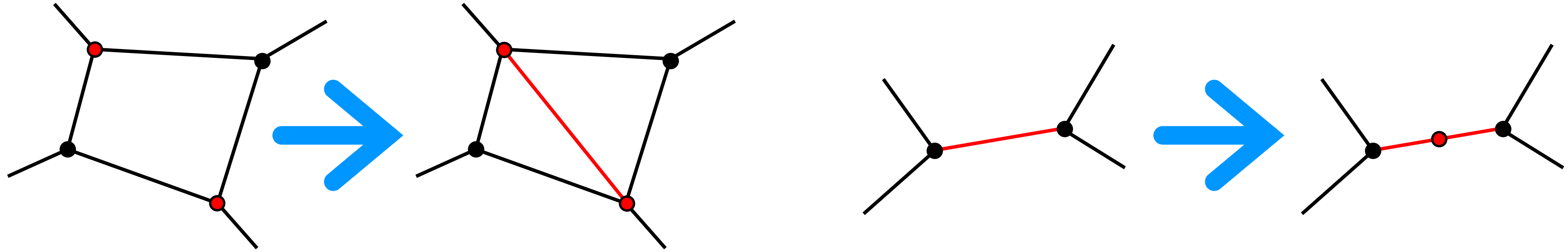


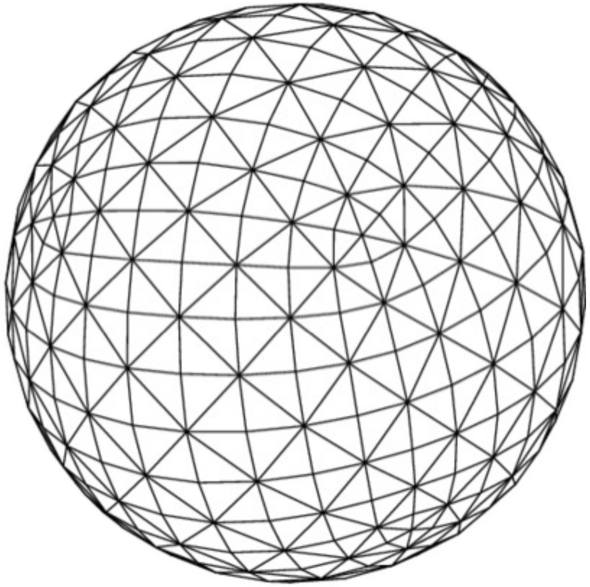
R. Montenegro, et al., Proc. 15th International Meshing Roundtable, (2006)

R.D. Kamien, The Geometry of Soft Materials: A Primer, Rev. Mod. Phys. (2002)

Boundary effects on defects - topology

System boundary geometry/topology can necessitate defects





$$V - E + F = \chi = \frac{1}{2\pi} \oiint_S K_{Gauss}\, dS$$

Euler characteristic

is topologically invariant

$\chi = 2$ for the sphere

R.D. Kamien, The Geometry of Soft Materials: A Primer, Rev. Mod. Phys. (2002)

Boundary effects on defects - topology

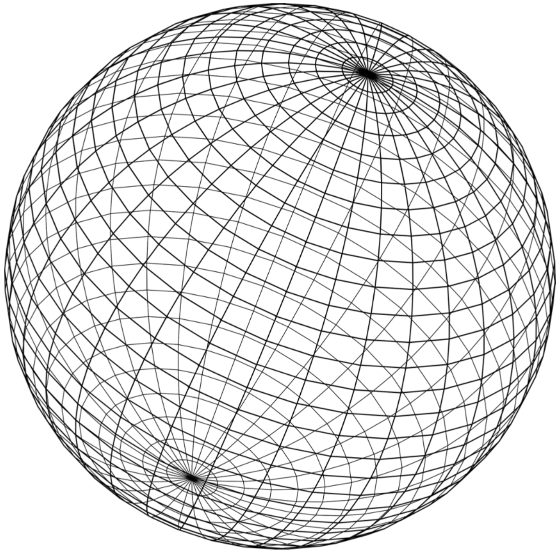
System boundary geometry/topology can necessitate defects

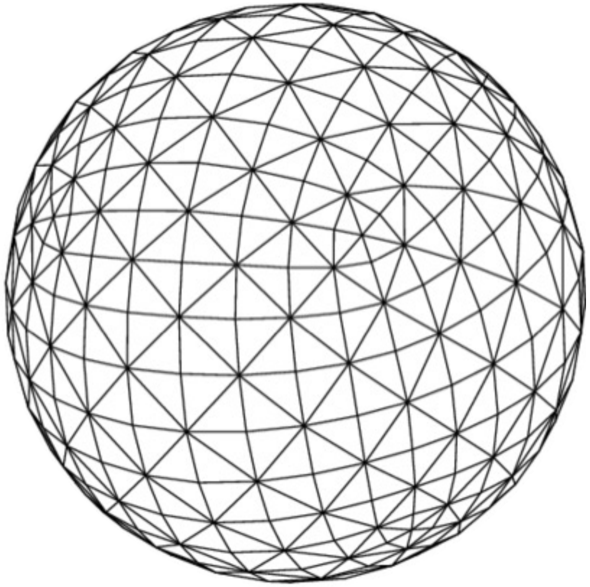
*Anything ordered on a surface obeys **Poincaré-Hopf** theorem*

$$\sum_i m_i = \chi$$

total topological charge

*Holds for liquid crystals with **planar anchoring***





$\chi = 2$ for the sphere

R.D. Kamien, The Geometry of Soft Materials: A Primer, Rev. Mod. Phys. (2002)

Boundary effects on defects - topology

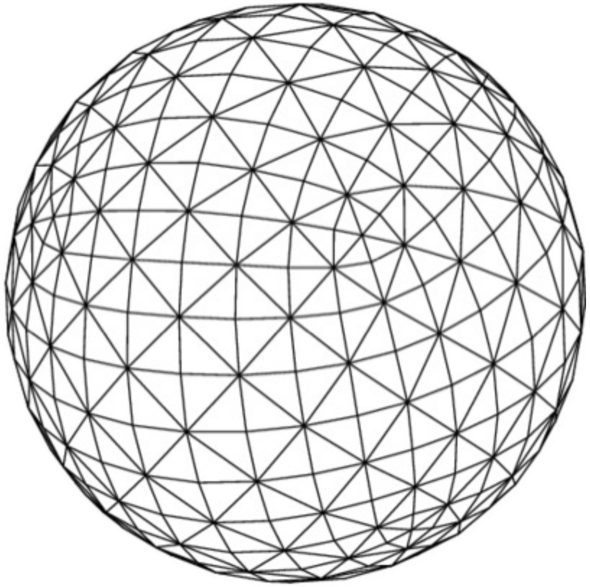
System boundary geometry/topology can necessitate defects

For homeotropic (perpendicular) anchoring to a surface, must consider full 3D field

3D ordering obeys **Gauss** *theorem*

$$\sum_i m_i = {}^1\!/_2\,\chi$$

total topological charge



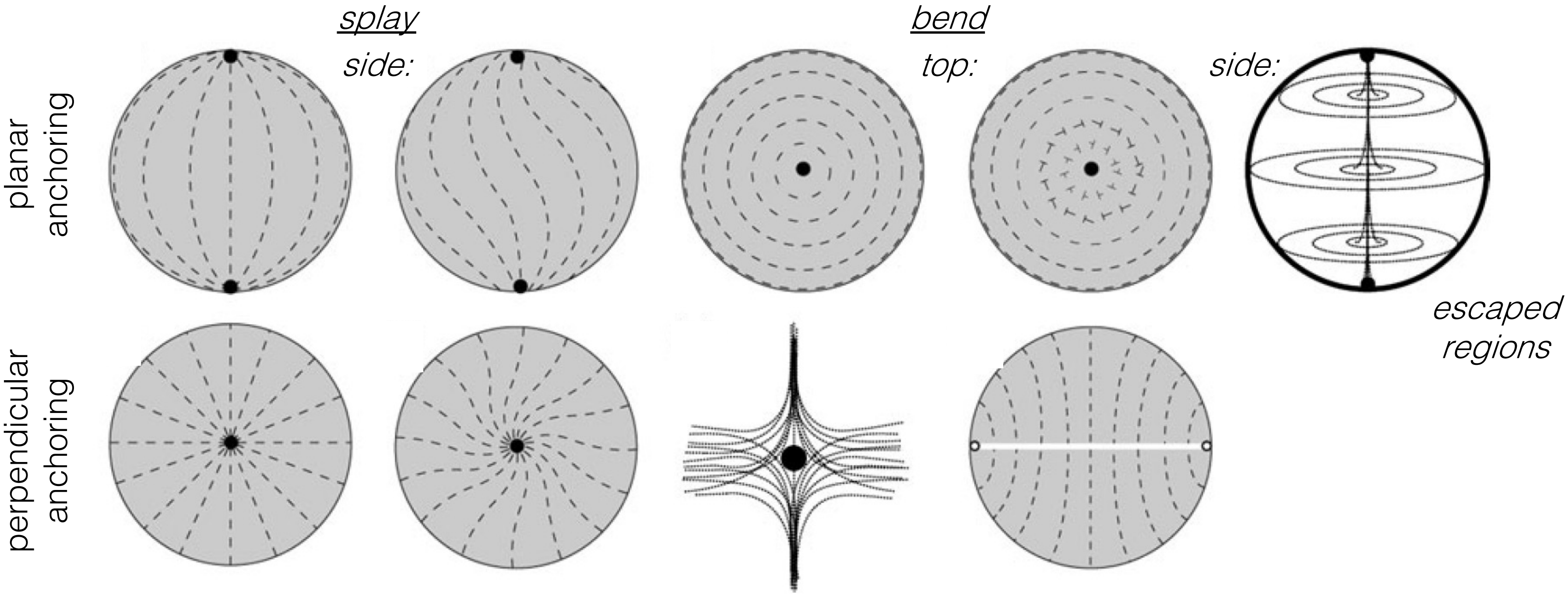
$\chi = 2$ for the sphere

R.D. Kamien, The Geometry of Soft Materials: A Primer, Rev. Mod. Phys. (2002)

Nematics in spheres

Poincaré-Hopf –

total index 2 for spherical topology with surface ordering



Gauss –

with perpendicular boundary conditions total index = ½ χ = 1 for sphere (ordering in volume)

D.L. Stein, *Phys. Rev. A* (1979), **19**:1708

T, Lopez-Leon, A. Fernandez-Nieves, *Colloid Polym Sci (2011)* **289**:345-359

Liquid crystals

Lisa Tran

Day 1: Displays and droplets

- Optical properties
- Order: elasticity & defects
- LCDs
- Research highlights

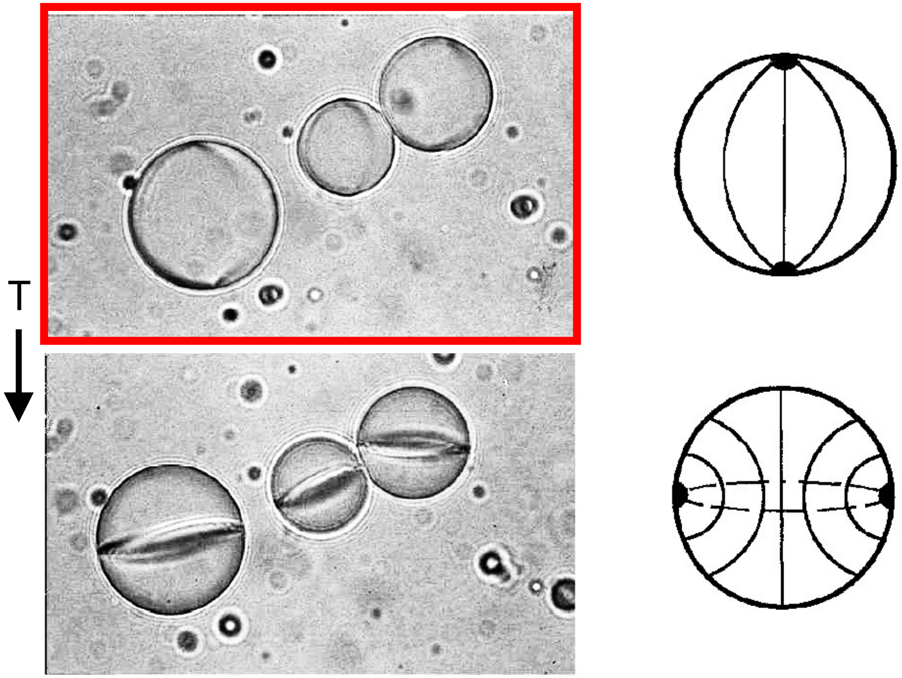
Day 2: Colloidal liquid crystals

- Hard rods - Zwanzig model (2D)
- Onsager theory & other interactions
- Colloidal liquid crystals in biology
- Research highlights

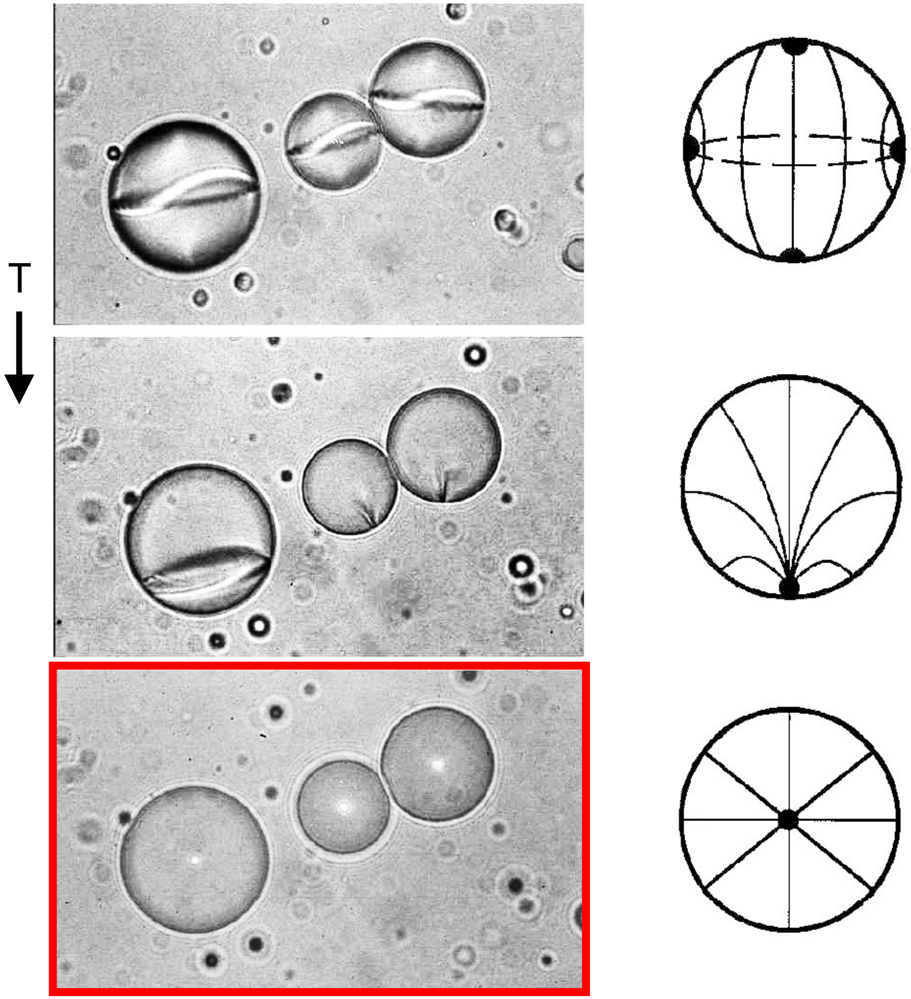
Nematic droplets

Topological dynamics of defects in nematic spherical droplets suspended in a glycerin-lecithin matrix. Temperature increases from top-down, left to right. Bright field images.

planar anchoring



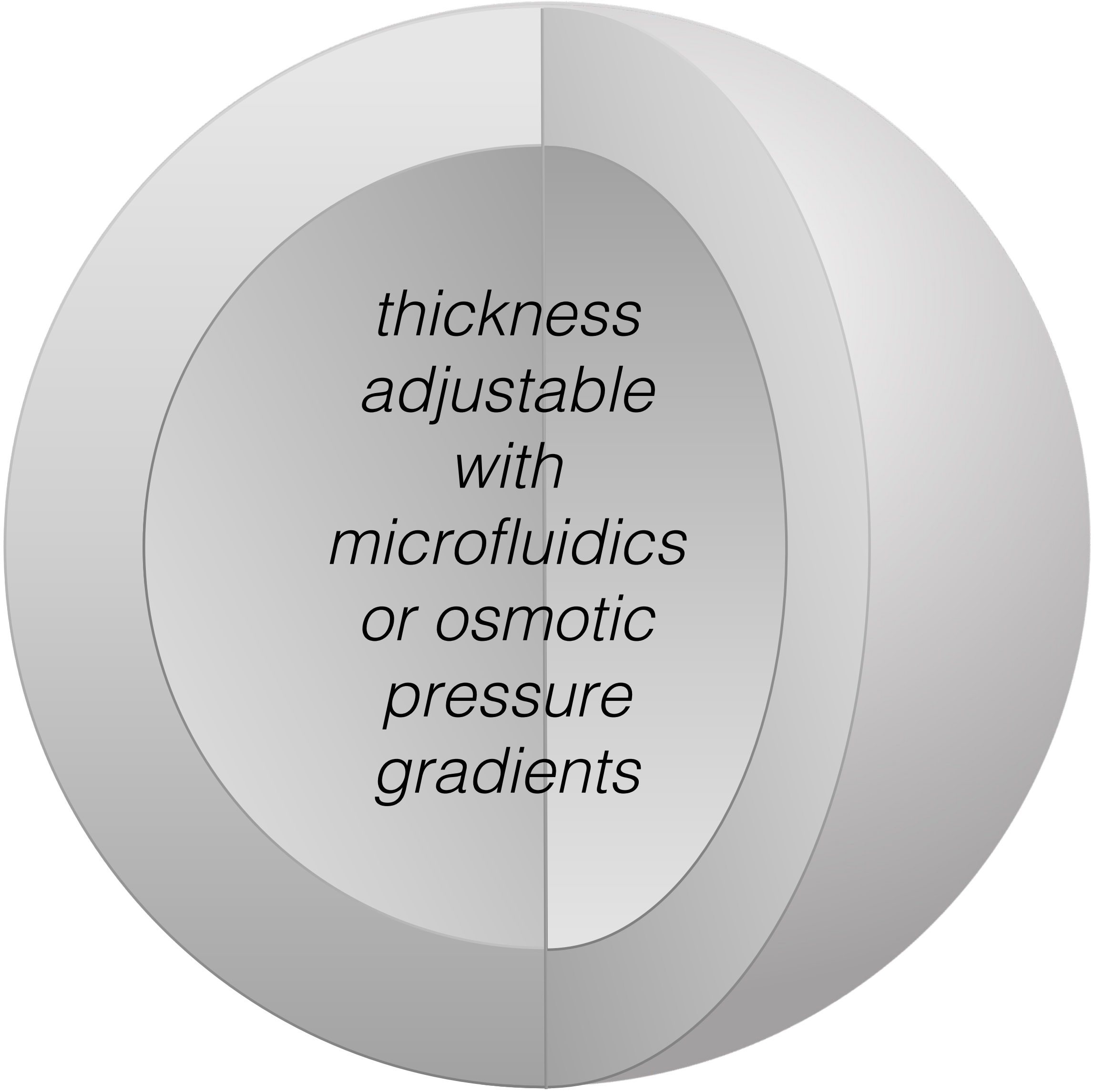
red = equilibrium



perpendicular anchoring

O.D. Lavrentovich *Liquid Crystals (1998)* **24:1**, 117-126

Controlling the liquid crystal environment



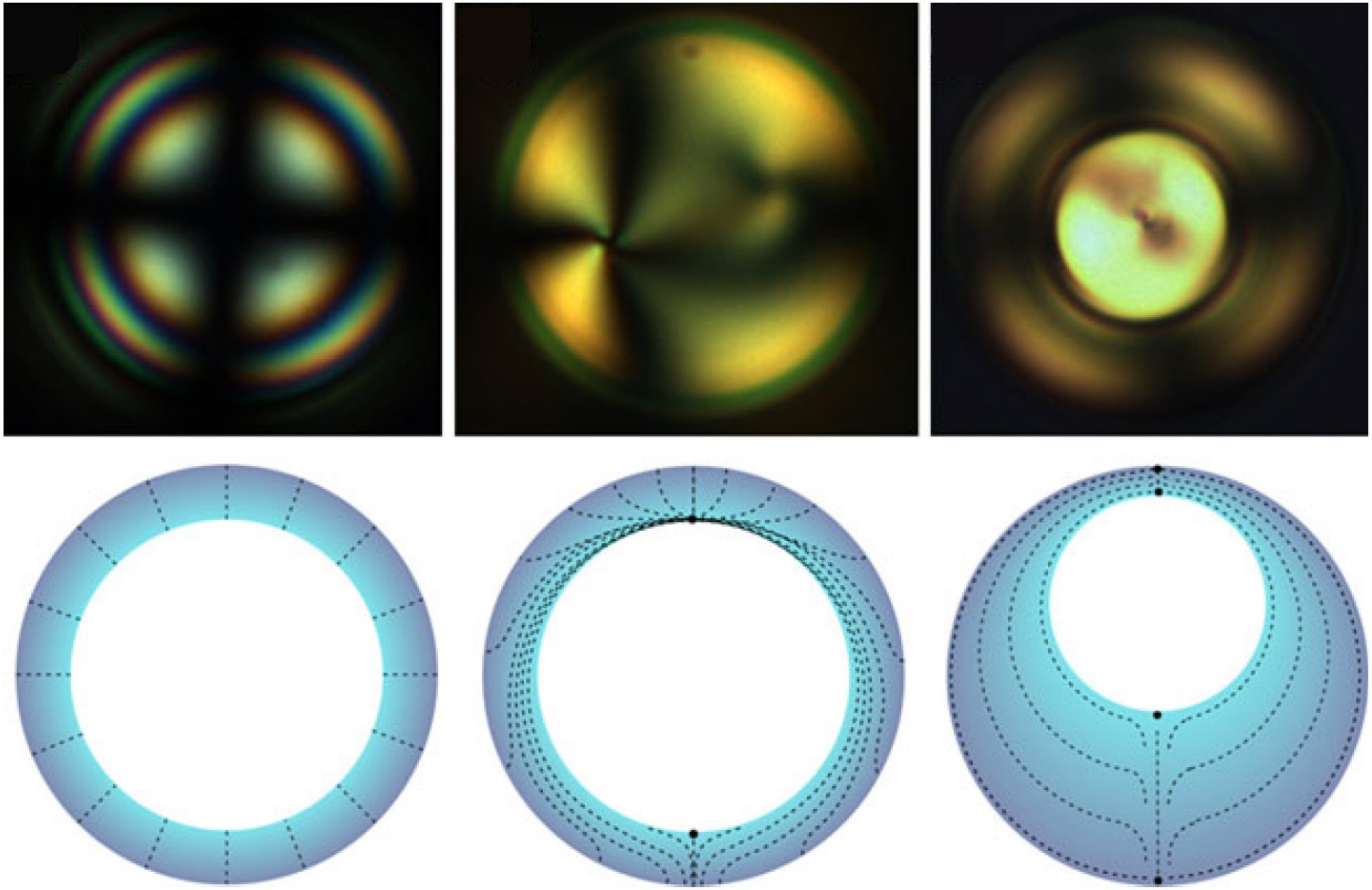
thickness adjustable with microfluidics or osmotic pressure gradients

Small molecule liquid crystal in shells

DOI:
10.1103/
PhysRevX.
7.041029

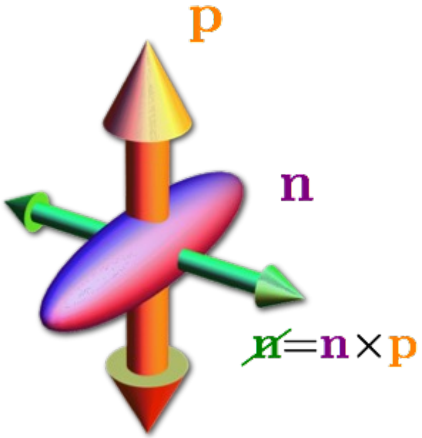
From Guillaume Durey

Nematic shells

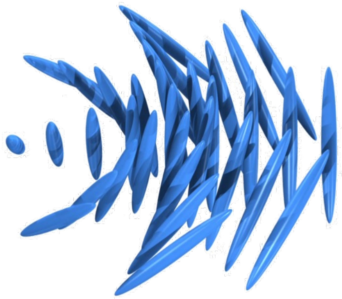


T, Lopez-Leon, A. Fernandez-Nieves, *Colloid Polym Sci (2011)* **289**:345-359

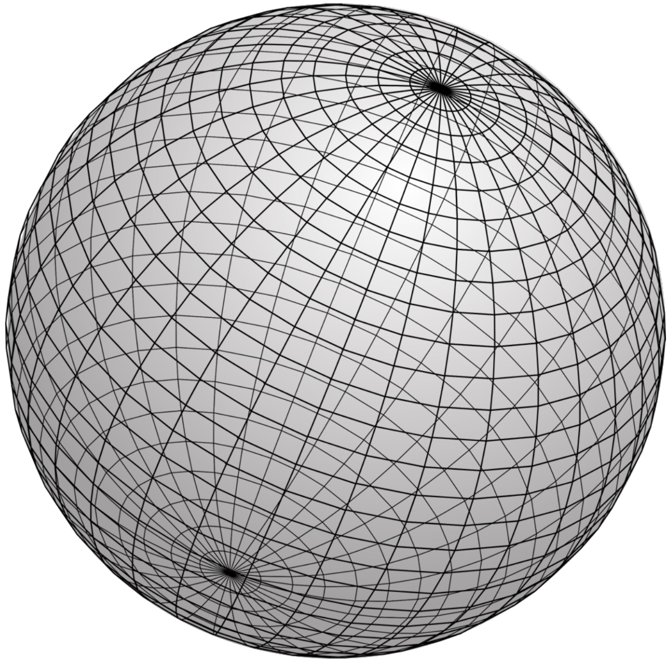
Cholesterics are more complex

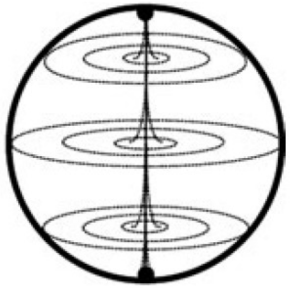


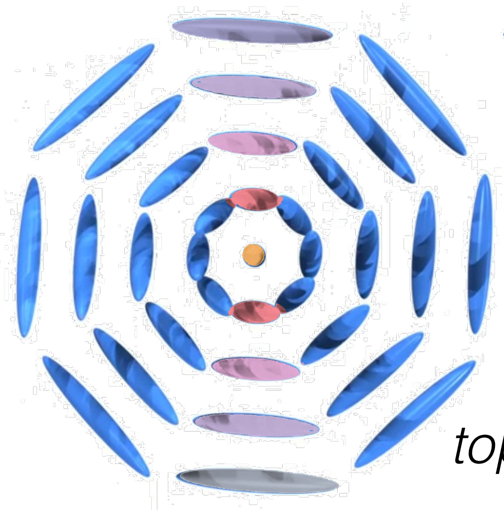
Poincaré-Hopf – line field on a sphere has total index +2



side view







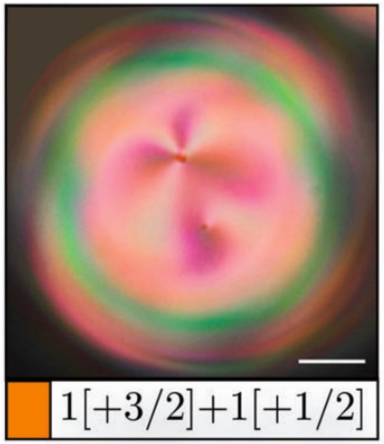
top view

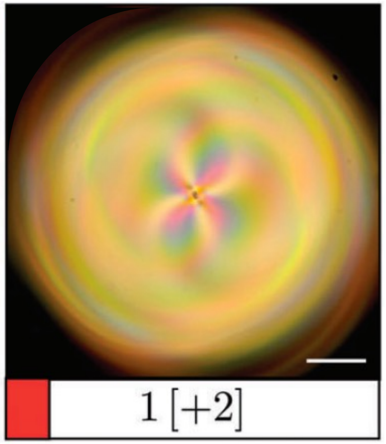
``baby'' skyrmion – λ^{+1}

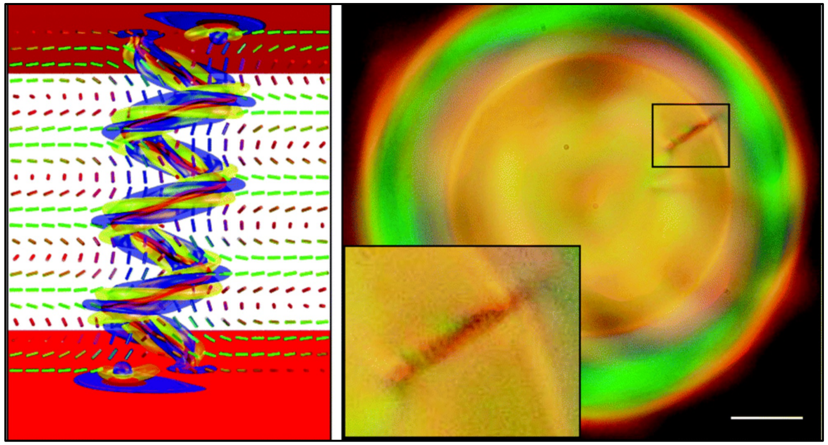
Nematics can escape into 3D
Cholesterics ***cannot escape***

There must be a defect in $\boldsymbol{n}$ *or in* $\boldsymbol{p}$

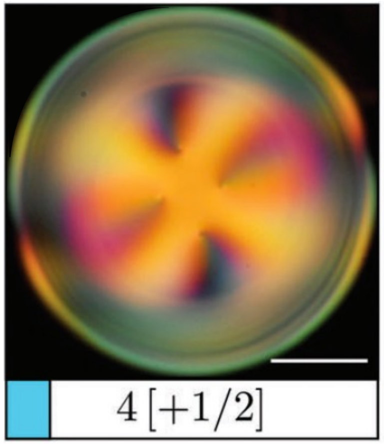
Planar cholesteric shells

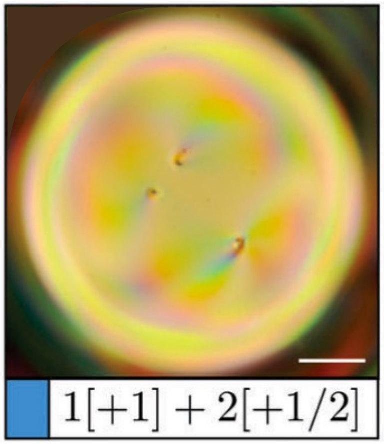


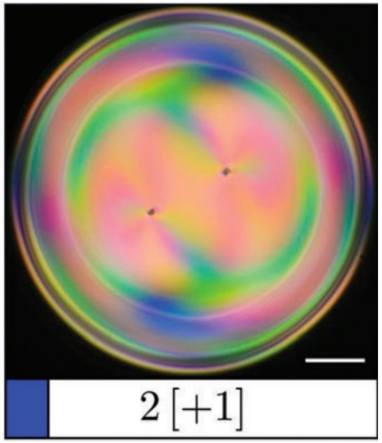




Scale bars are 20 μm.

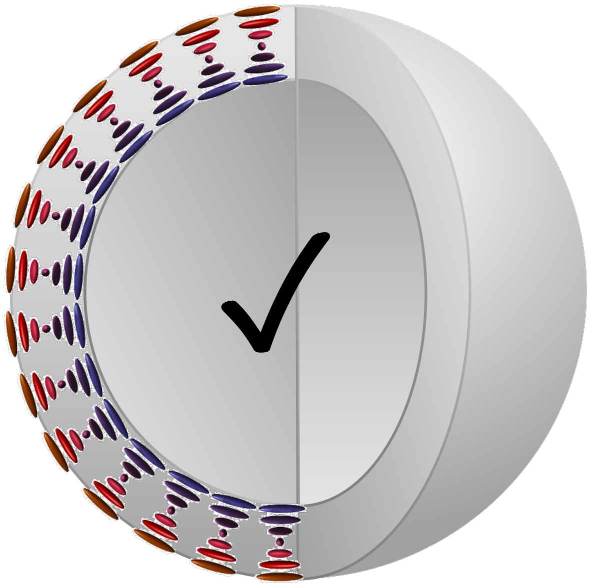




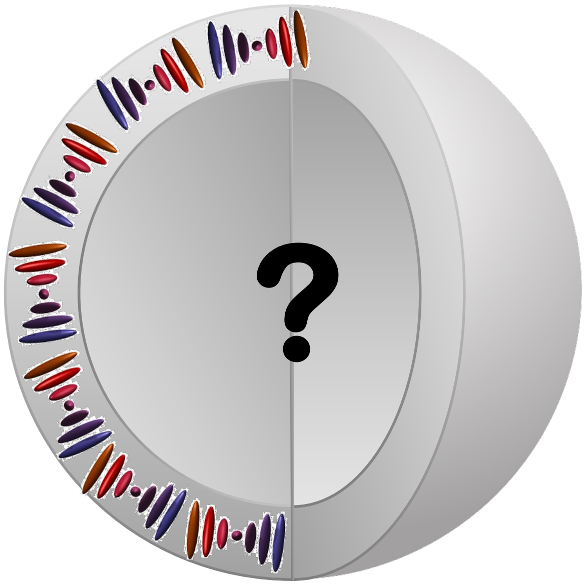


Topological defects in cholesteric liquid crystal shells. A Darmon, M Benzaquen, S Čopar, O Dauchot, T Lopez-Leon. *Soft Matter* **12**: 9280-9288 (2016)

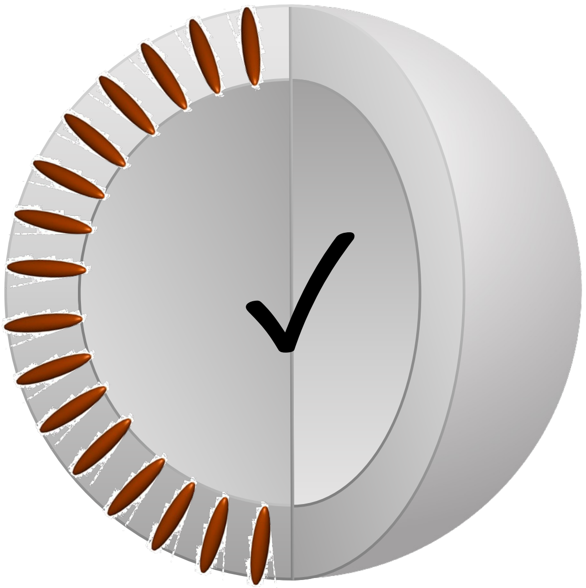
Cholesterics in shells



planar anchoring



weak perpendicular anchoring



strong perpendicular anchoring

Simulations setup – Landau-de Gennes model

Energy of the system:

Q *is the tensor order parameter*
S *is the scalar order parameter*
The director is the eigenvector of ***Q****.*
S₀ *is preferred eigenvalue of* ***Q****.*

$$f = f_{\mathrm{pot.}}[\boldsymbol{Q}] + f_{\mathrm{grad.}}[\nabla \boldsymbol{Q}, \boldsymbol{Q}] + f_{\mathrm{surf.}}[\boldsymbol{Q}|_S]$$

Potential energy –
of the system, with A, B, and C being the material constants

$$f_{\mathrm{pot.}} = \frac{A}{2}\operatorname{tr}\boldsymbol{Q}^2 + \frac{B}{3}\operatorname{tr}\boldsymbol{Q}^3 + \frac{C}{4}(\operatorname{tr}\boldsymbol{Q}^2)^2$$

Gradient energy –
corresponds to the energy corresponding to specific deformations, can be rewritten as the Frank Free Energy

$$f_{\mathrm{grad}} = \frac{L_1}{2}\left[\nabla \times \boldsymbol{Q} + 2q_0\boldsymbol{Q}\right]^2 + \frac{L_2}{2}(\nabla \cdot \boldsymbol{Q})^2$$

chiral term

Surface energy –
or the anchoring energy, which is equal to the energy from planar degenerate anchoring plus homeotropic anchoring

$$f_{\mathrm{surf.}} = f_{\mathrm{deg.}} + f_{\mathrm{hom.}}$$

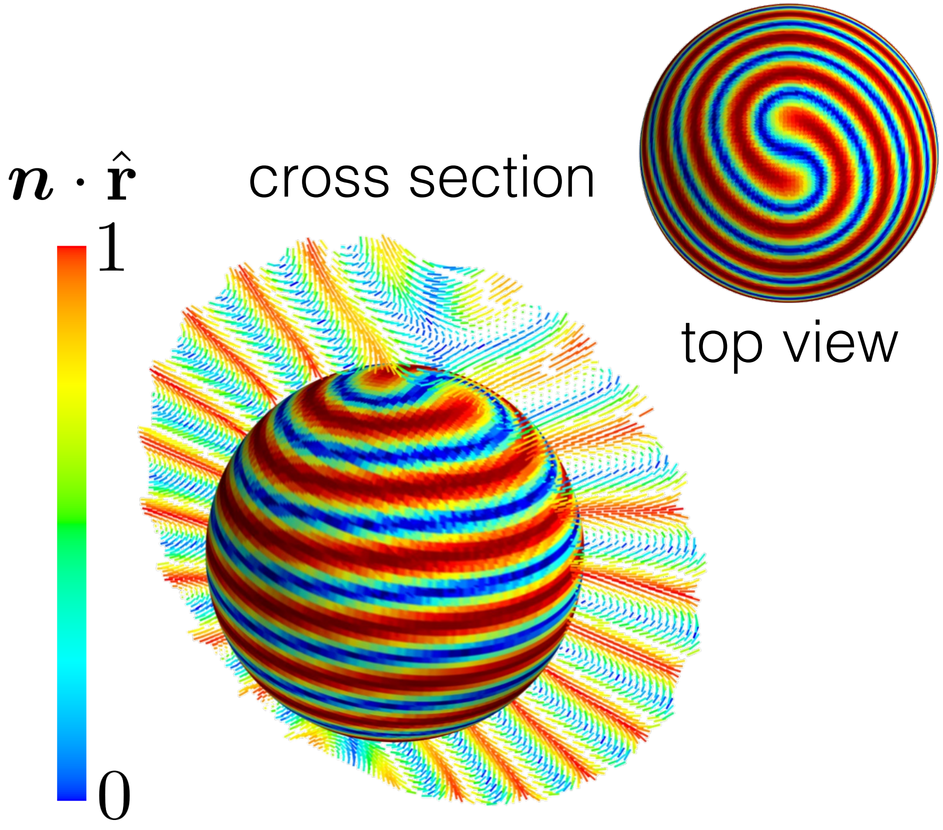
matrix of surface normals

$$f_{\mathrm{hom.}} = W_0 \int_S \mathrm{d}A \operatorname{tr}\left[\boldsymbol{Q} - \frac{3S_0}{2}\left(\boldsymbol{\nu} - \frac{\boldsymbol{I}}{3}\right)\right]^2$$

Projection operator: $P = I - \nu$

$$f_{\mathrm{deg.}} = \int_S \mathrm{d}A \left\{W_1 \operatorname{tr}\left[(\boldsymbol{Q} + S_0\boldsymbol{I}/2 - \boldsymbol{P}(\boldsymbol{Q} + S_0\boldsymbol{I}/2)\boldsymbol{P})^2\right] + W_2\left[\operatorname{tr}(\boldsymbol{Q} + S_0\boldsymbol{I}/2)^2 - (3S_0/2)^2\right]^2\right\}$$

Cholesteric stripes – simulations



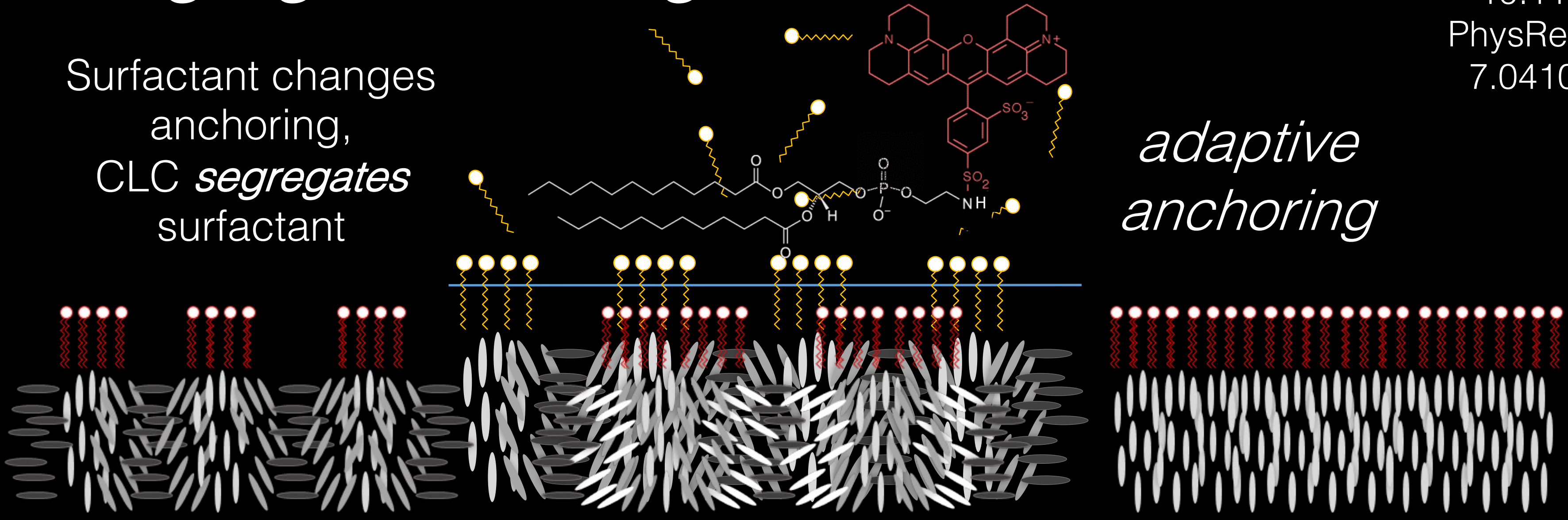
No director defects

Pitch defects
satisfy the spherical
topology

published in PRX
DOI: 10.1103/PhysRevX.7.041029

Changing anchoring with surfactant

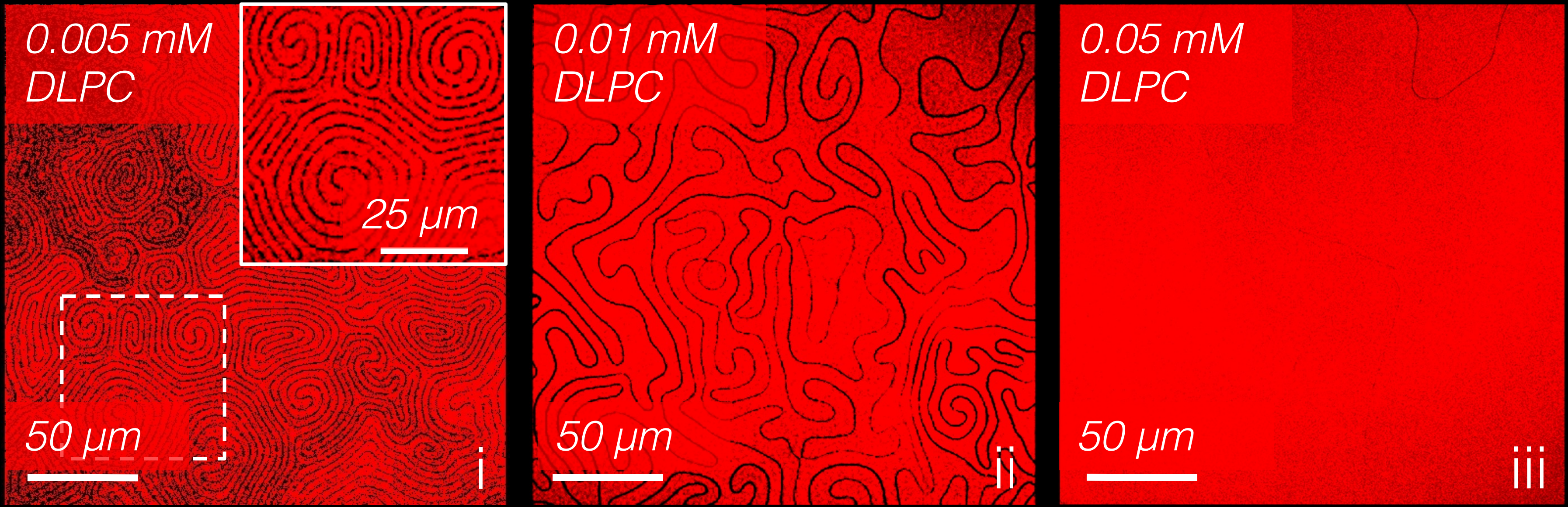
DOI:
10.1103/
PhysRevX.
7.041029

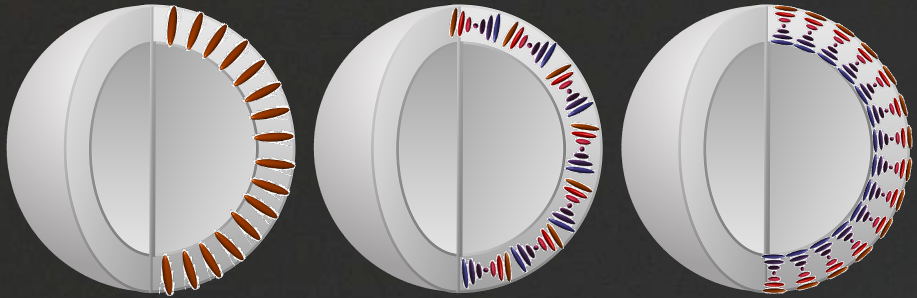


Surfactant changes
anchoring,
CLC *segregates*
surfactant

*adaptive
anchoring*

Flat cholesteric film: Fluorescently labeled lipid





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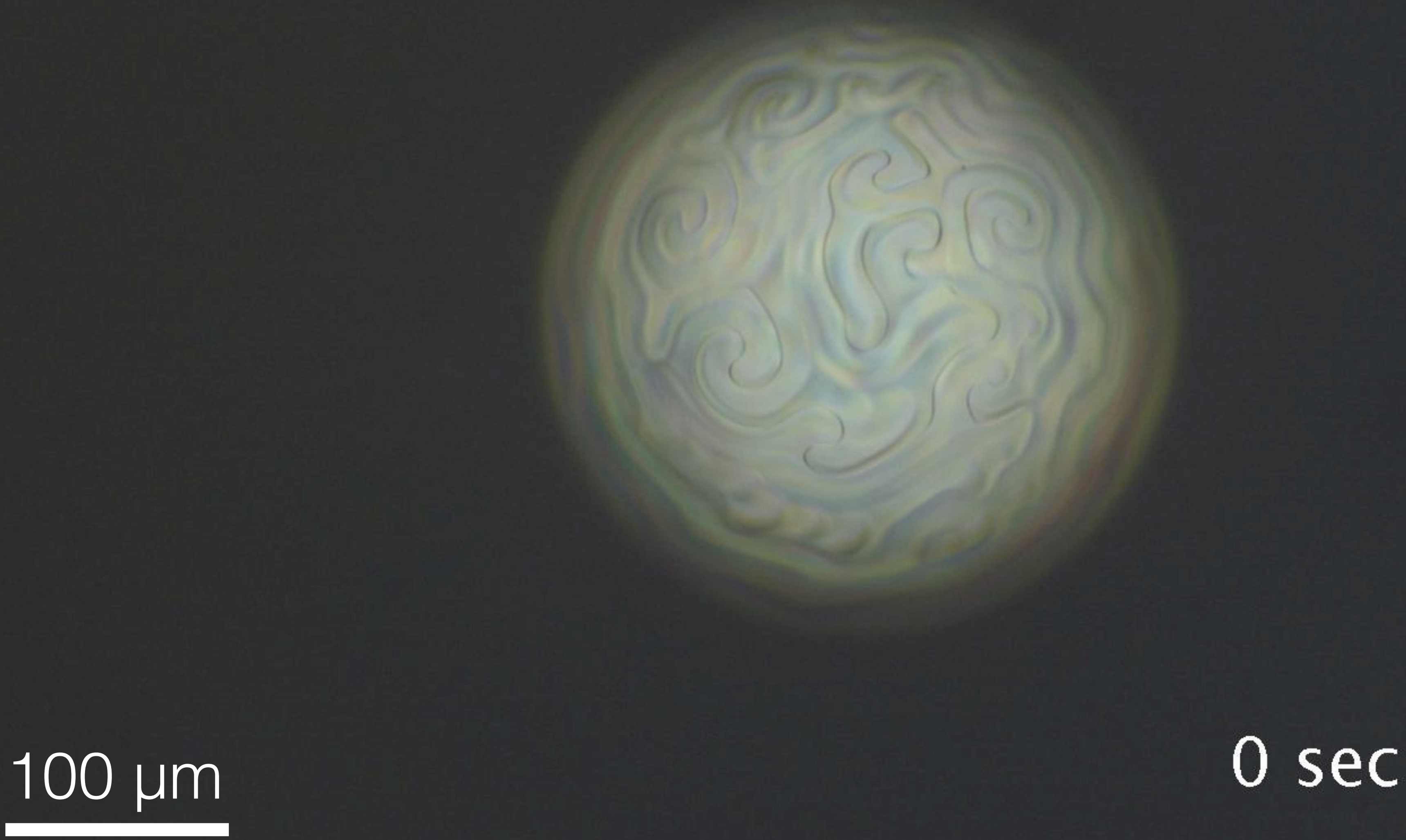
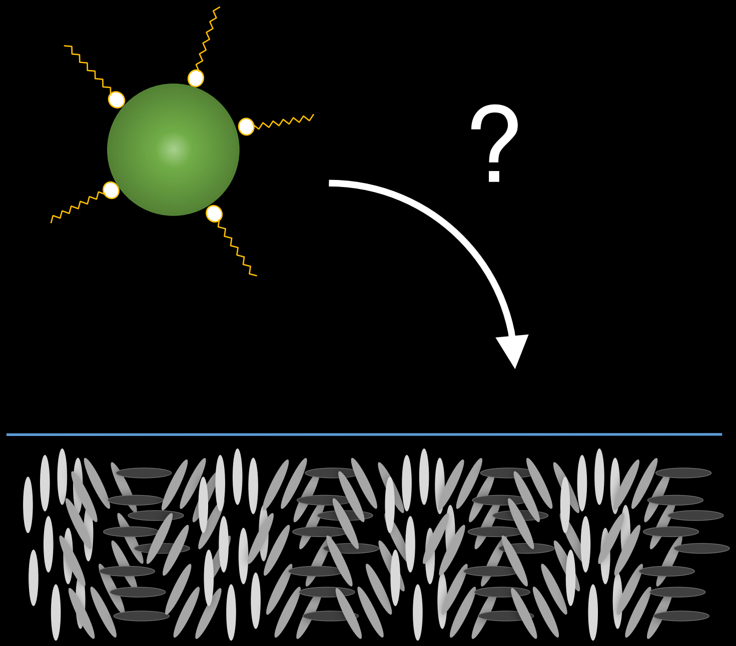
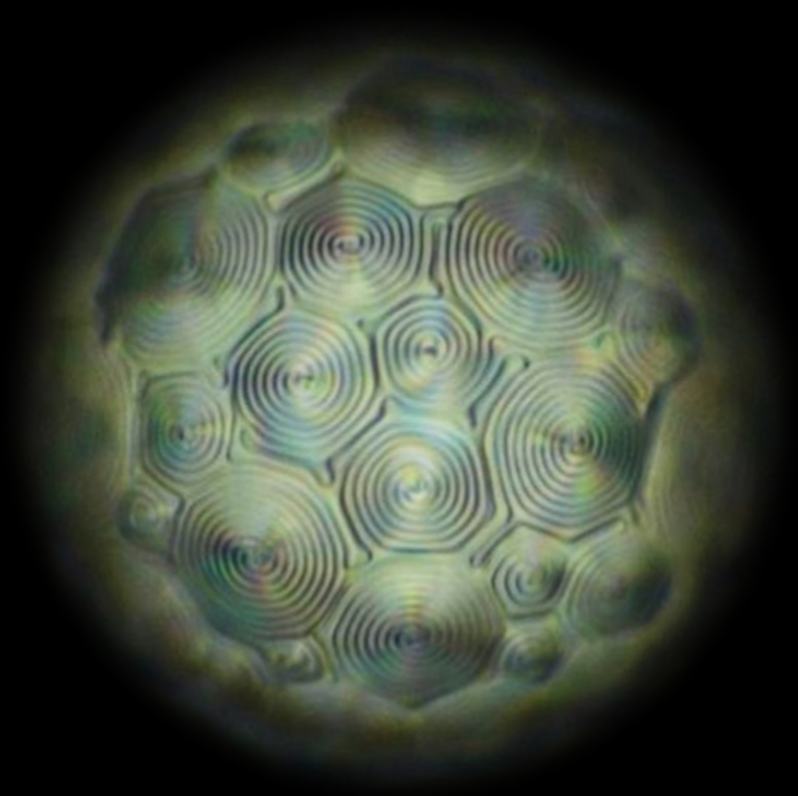


Nanoparticle ordering in cholesterics

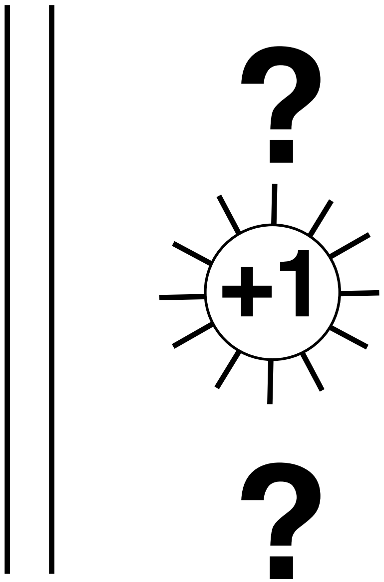
DOI:
10.1126/
SciAdv.
aat8597

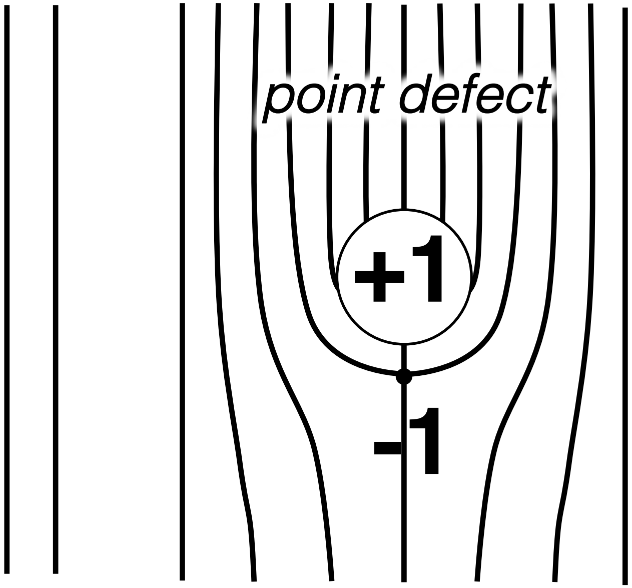


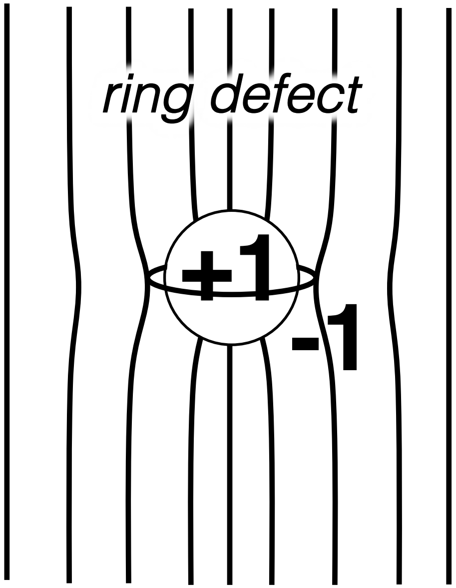


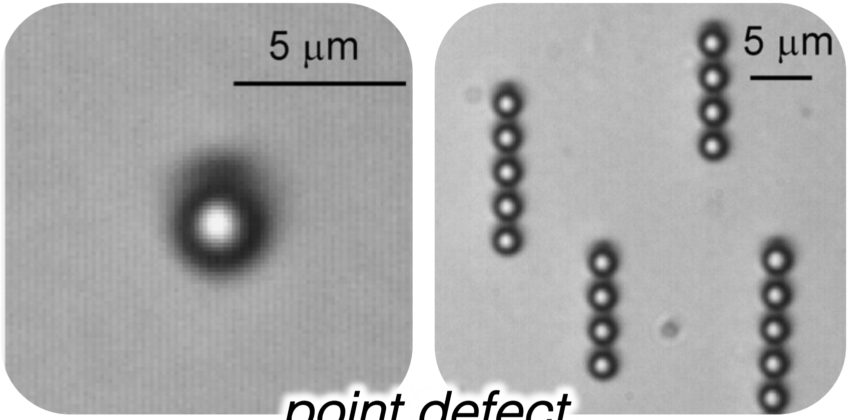
elastic fluids for directed self-assembly

Defects from particles in liquid crystals

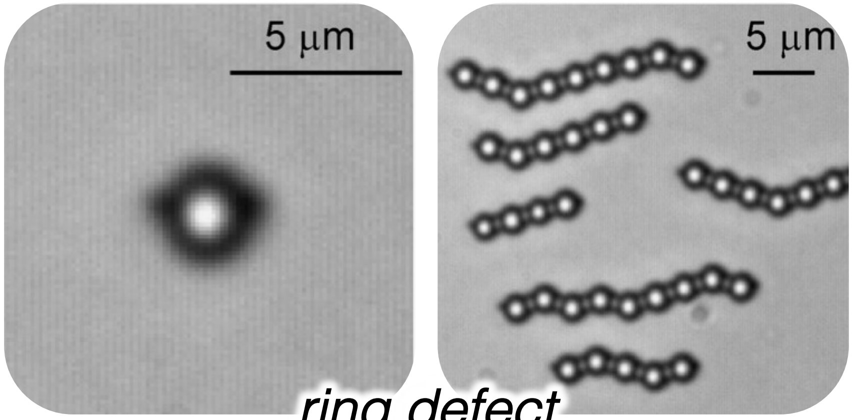








point defect



ring defect

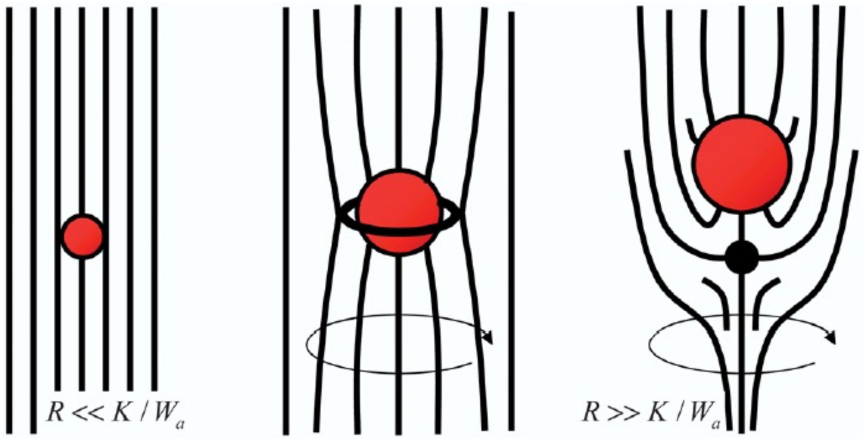
Liquid crystal assembles colloids from elastic distortions

I. Muševič, *et. al. Science* (2006)

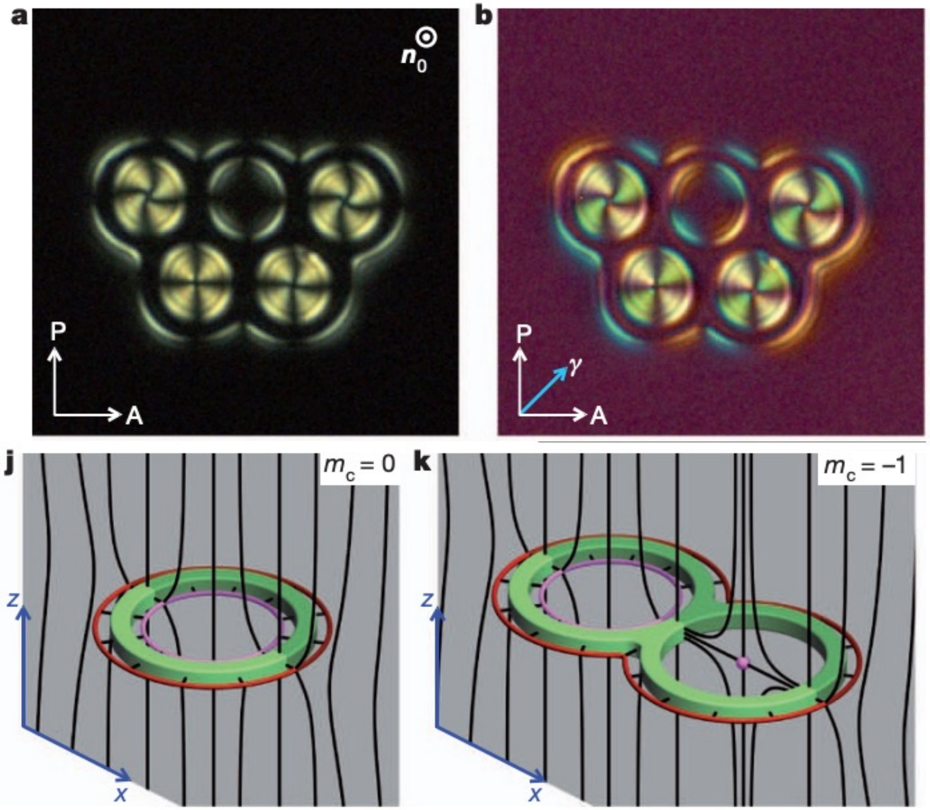
Effect of size and shape

Colloid size and shape

$$f_{\text{anch}} = \frac{1}{2} W_{\text{a}} \sin^2(\theta - \theta_0)$$



Lavrentovich, O. D. (2014). Transport of particles in liquid crystals. Soft Matter, 10(9), 1264-1283.



Senyuk, B., Liu, Q., He, S., Kamien, R. D., Kusner, R. B., Lubensky, T. C., & Smalyukh, I. I. (2013). Topological colloids. Nature, 493(7431), 200-205.

Beller, D. A., Gharbi, M. A., & Liu, I. B. (2015). Shape-controlled orientation and assembly of colloids with sharp edges in nematic liquid crystals. Soft Matter, 11(6), 1078-1086.

Nanoparticle ordering in cholesterics

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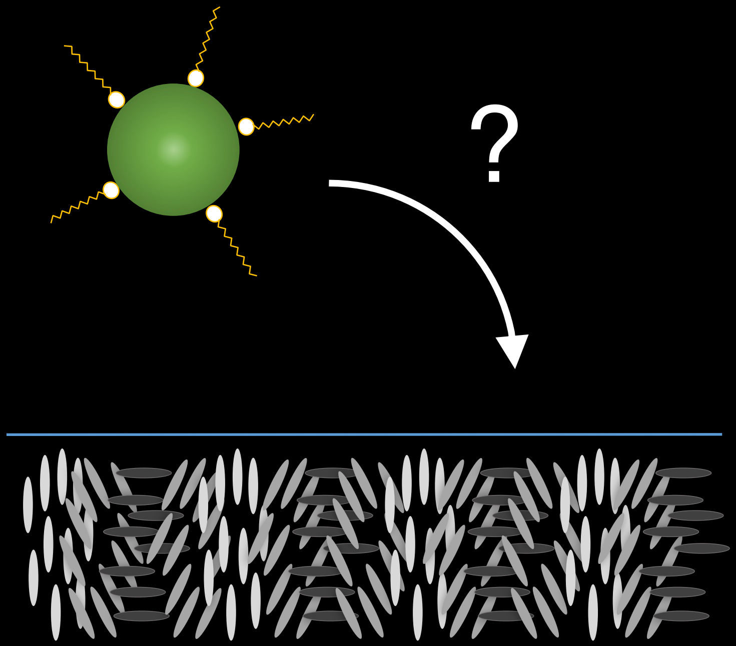
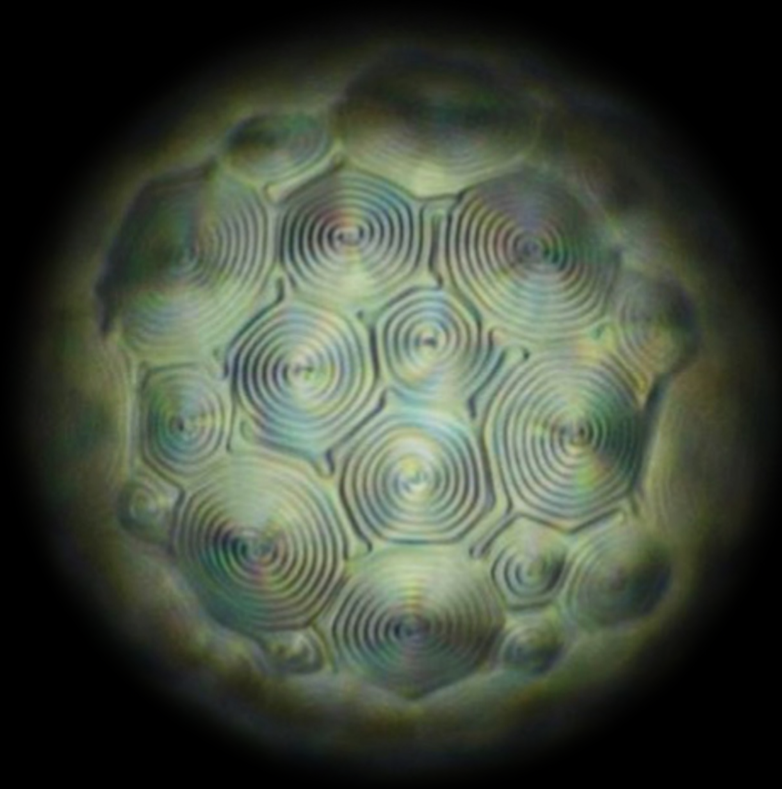
10.1126/
SciAdv.
aat8597

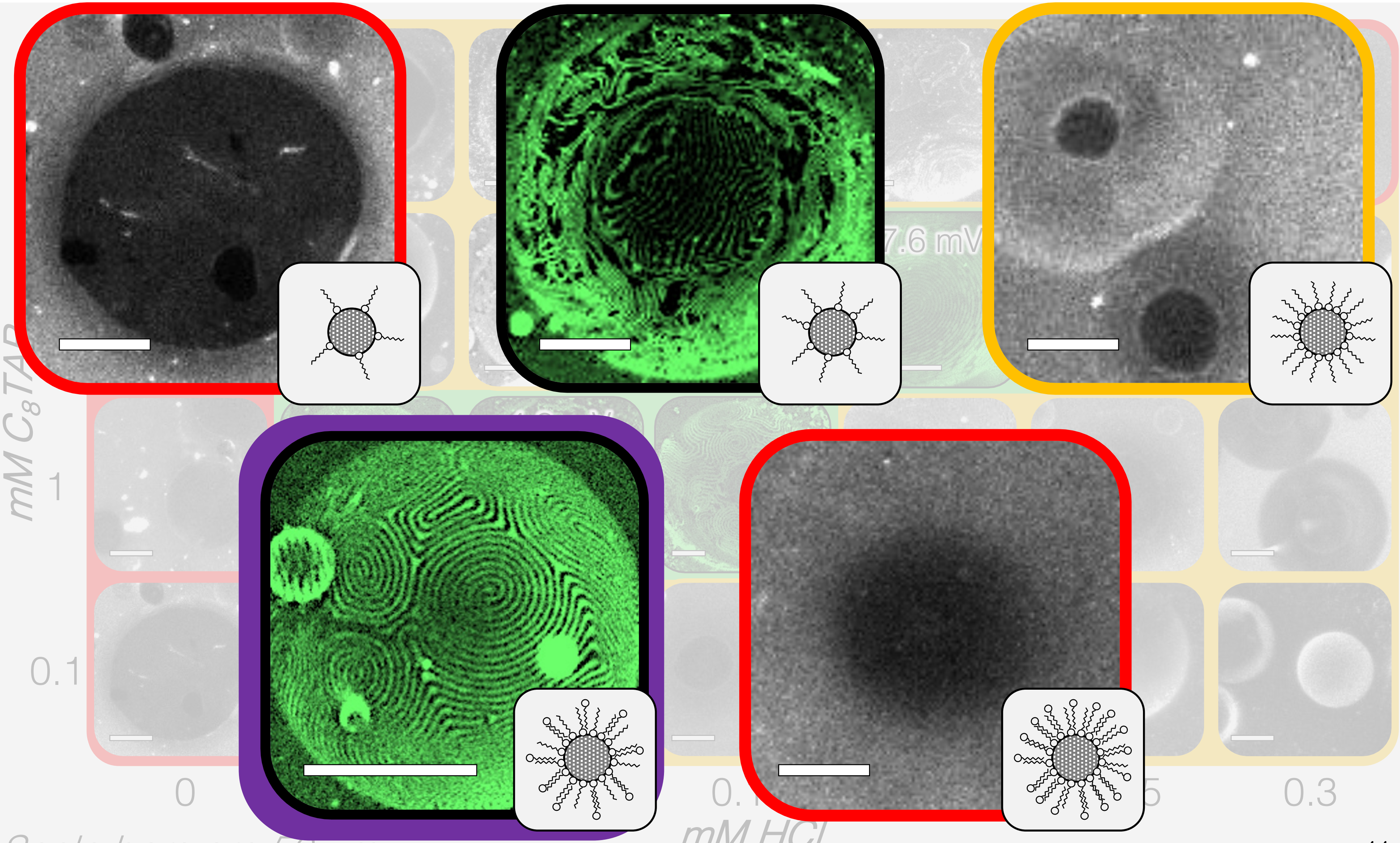




elastic fluids for directed self-assembly

C_8TAB and 30 nm silica Particle chemistry sweet spot

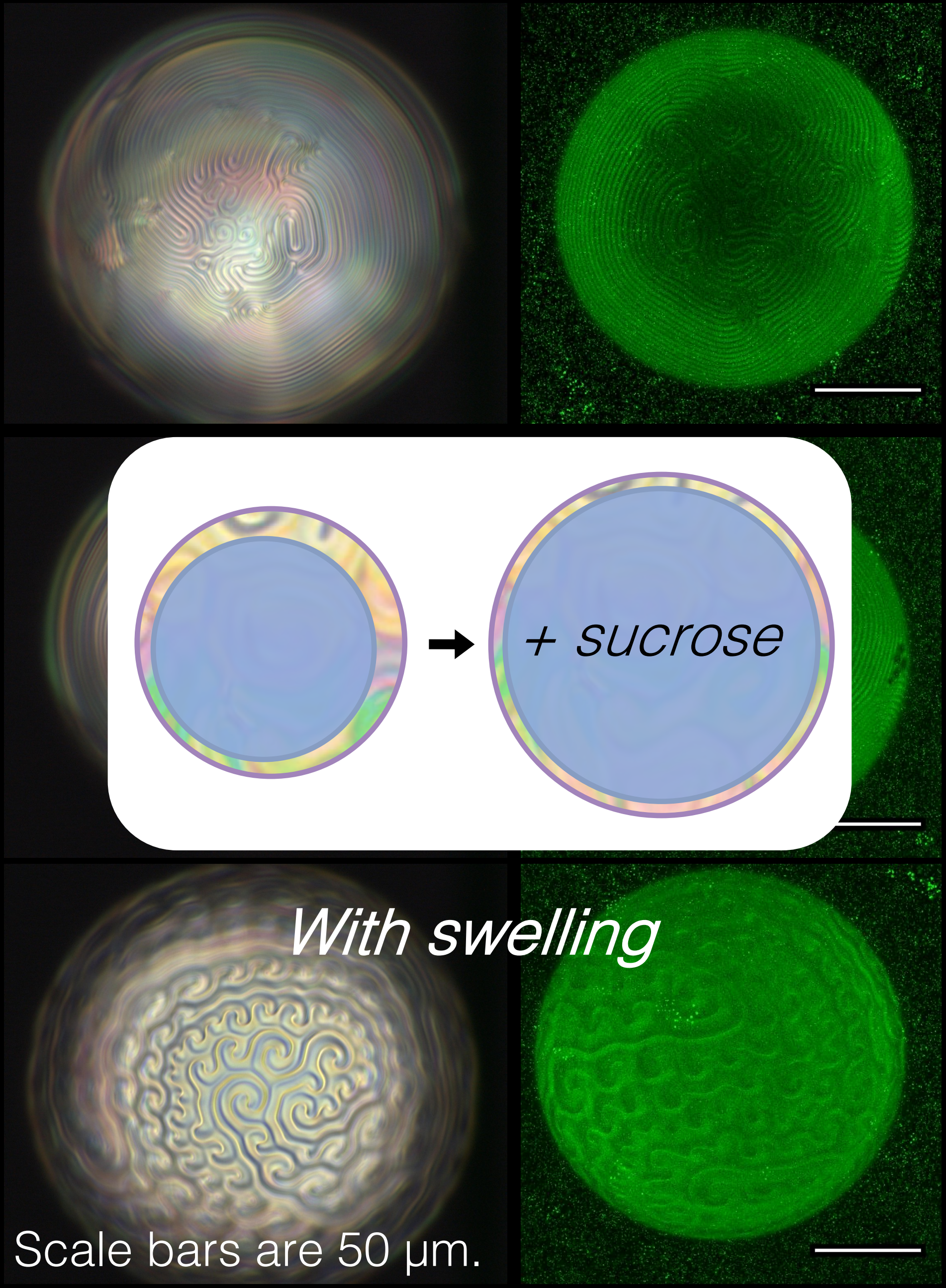
DOI:
10.1126/
SciAdv.
aat8597



Scale bars are 50 μm.

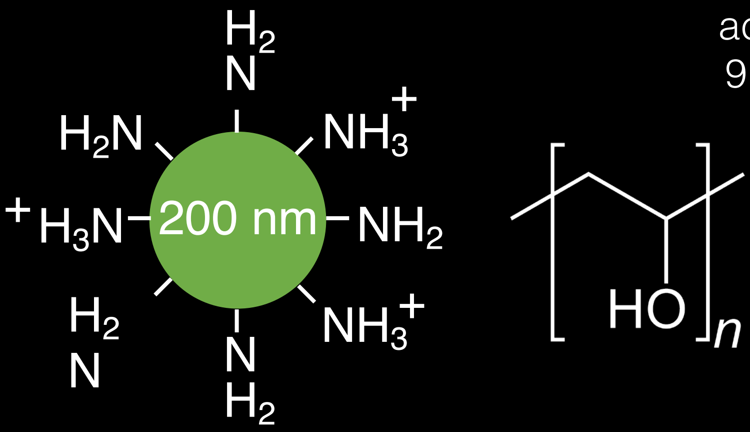
Controlling assembly with geometry

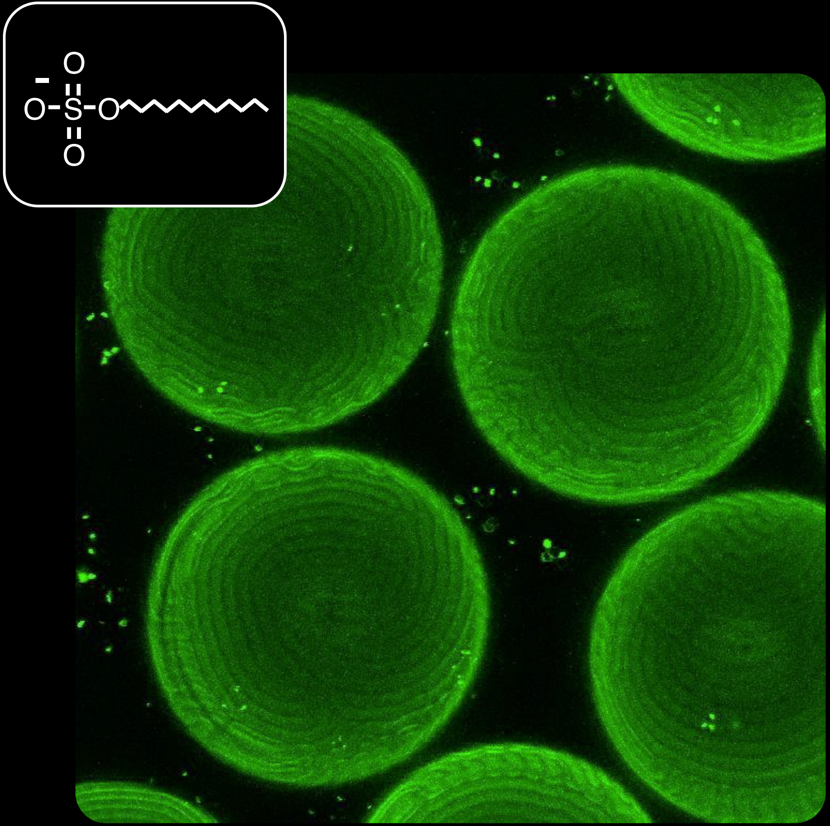
DOI: 10.1021/ acsnano. 9b09441



With swelling

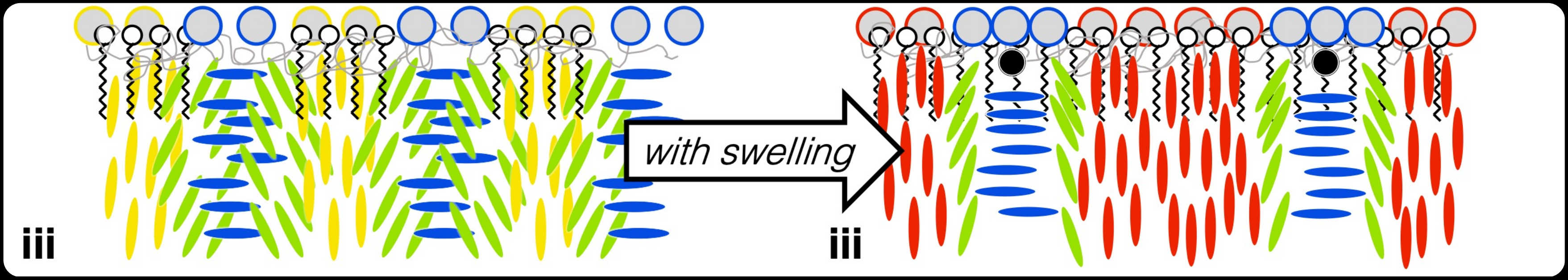
Scale bars are 50 µm.

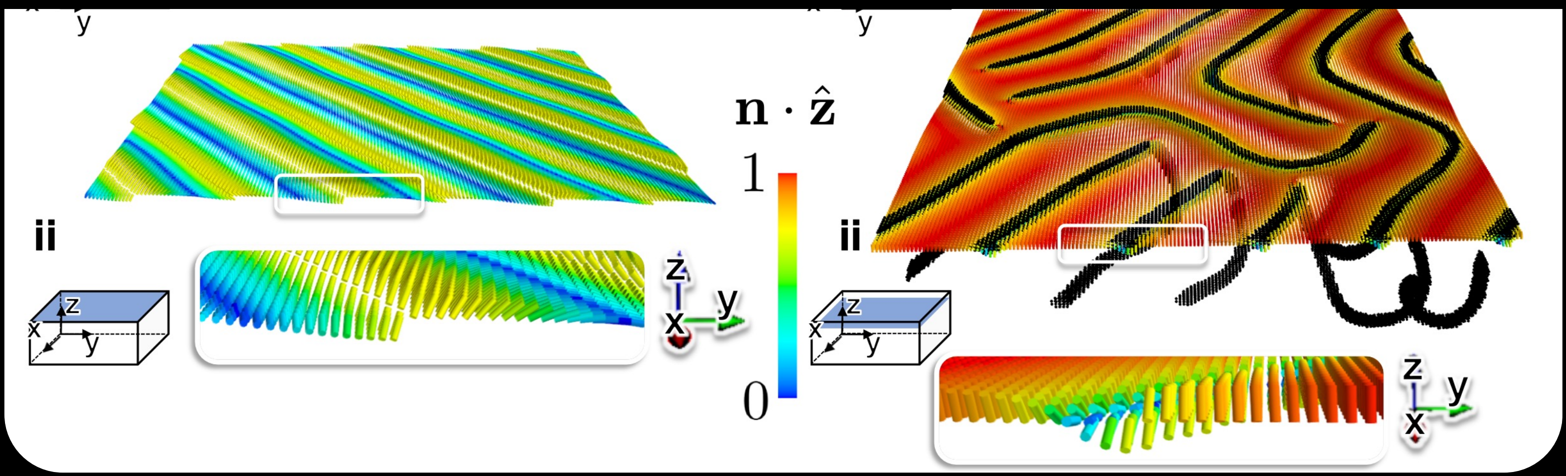




Mechanism for ordering transition

DOI:
10.1021/
acsnano.
9b09441



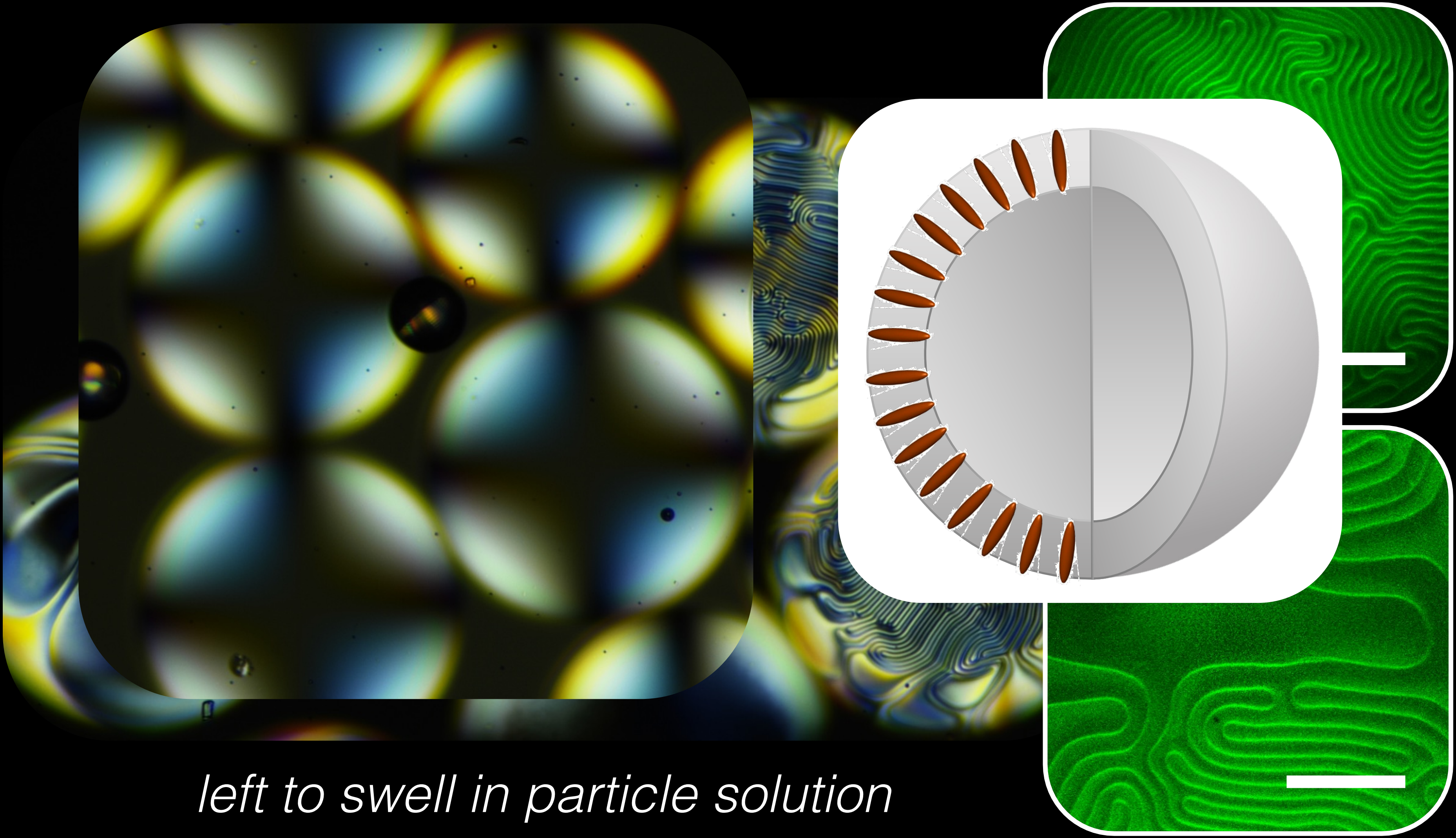


swelling changes energy landscape, introduces defects

particles get pushed into and stabilize defects

Nanoparticles <u>stabilize</u> defects

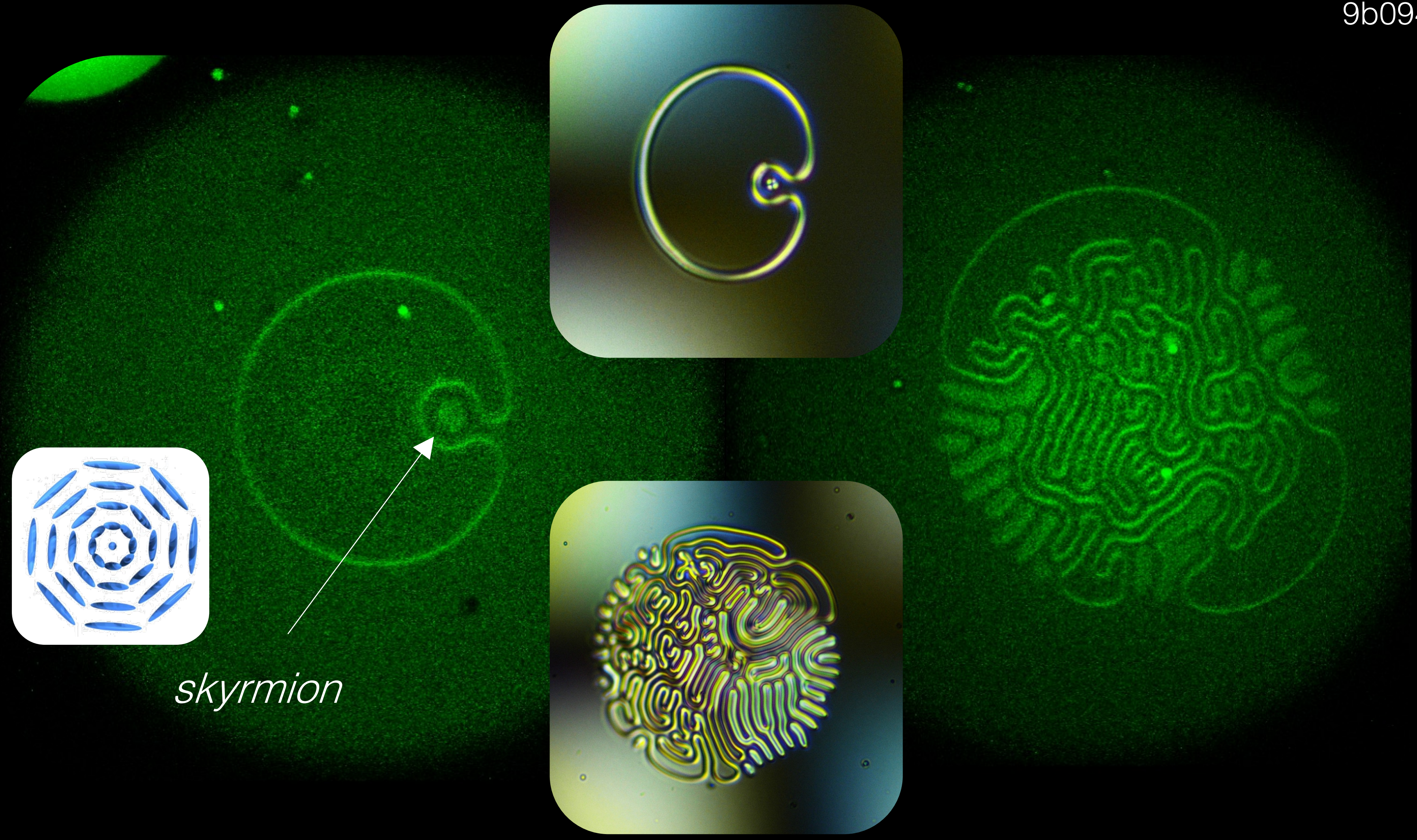
DOI:
10.1021/
acsnano.
9b09441



left to swell in particle solution

Nanoparticles map out defects

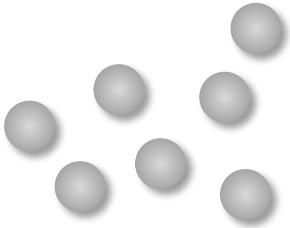
DOI:
10.1021/
acsnano.
9b09441



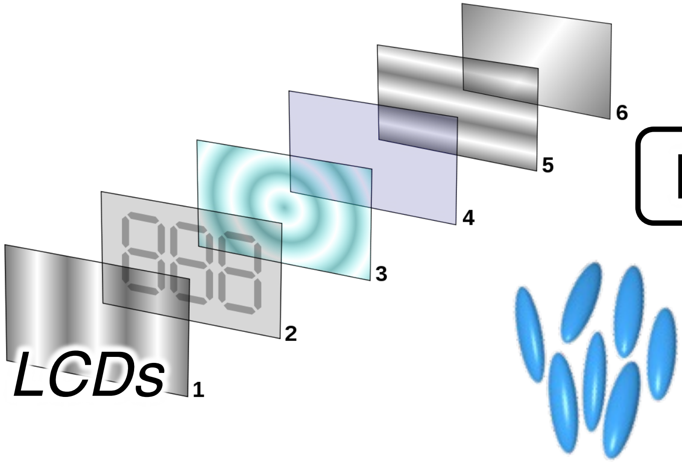
skyrmion

reduced outer particle concentration

Relevance to Tech



optical & electronic properties



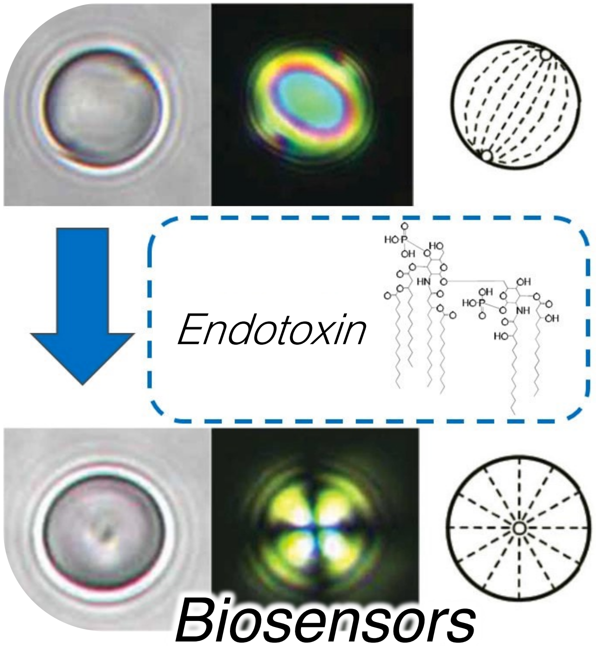
LCDs

Liquid Crystals ⟺ Nanoparticles

elastic, dielectric material

reconfigurable & responsive

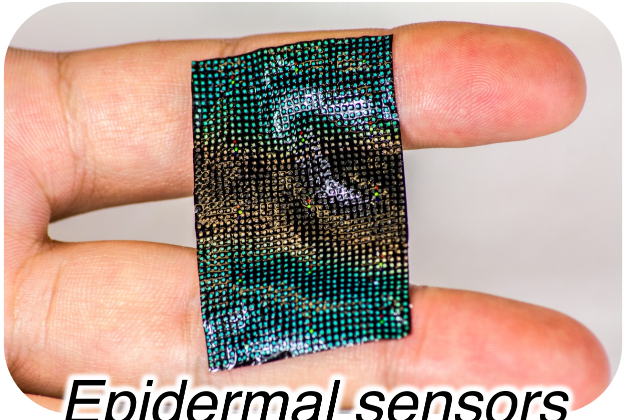
Plasmonics



Endotoxin

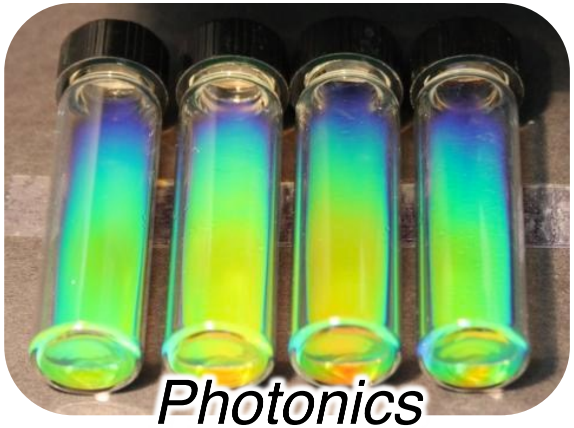
Biosensors

Abbott group, Cornell



Epidermal sensors

Rogers group, Northwestern

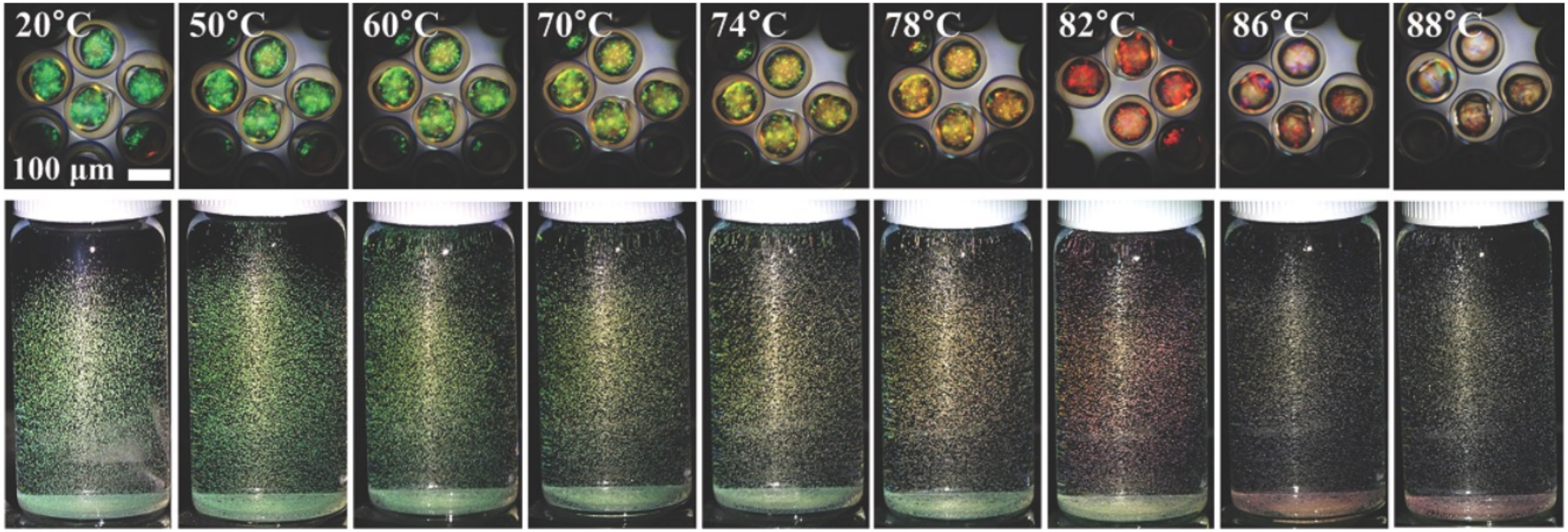


Photonics

nanoComposix

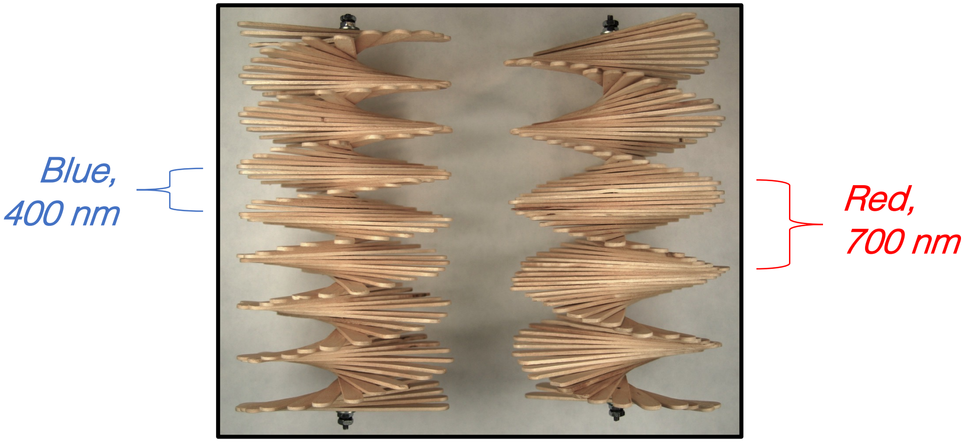
Applications of small molecule cholesterics

Sensors: macroscopic difference with microscopic change



Photonic ink capsules as temperature sensors

S.S. Lee,B. Kim, S.K. Kim, J.C. Won, Y.H. Kim, S-H. Kim, *Advanced Materials* **27** (2014): 627-633



Liquid crystals

Lisa Tran

Day 1: Displays and droplets

Optical properties
Order: elasticity & defects
LCDs
Research highlights

Day 2: Colloidal liquid crystals

Hard rods - Zwanzig model (2D)
Onsager theory & other interactions
Colloidal liquid crystals in biology
Research highlights

Special case of depletion

2-dimensional!

Let’s write it out together…

Statistical Mechanics Review (Brief)

Partition function and free energy

$$Z = e^{-F/k_BT} = \sum e^{-E/k_BT} \qquad F = -k_BT\ln Z$$

Free energy of an ideal gas

$$\frac{F}{k_BT} = N\ln(n\lambda_T^3) \qquad n = \frac{N}{V}$$

Getting pressure from the free energy – recover the ideal gas law!

$$p = -\frac{\partial F}{\partial V}|_{N,T} = -\frac{\partial n}{\partial V}|_{N,T}\frac{\partial F}{\partial n}|_{N,T} = \frac{N}{V^2}\frac{\partial F}{\partial n}|_{N,T} = \frac{N}{V^2}\frac{Nk_BT}{n} = k_BTn$$

Corrections to ideal gas: Virial Expansion for 1-component

$$\frac{p}{k_BT} = n + \underbrace{B_2}n^2 + \ldots$$

We will only keep up to the second virial coefficient…

Statistical Mechanics Review (Brief)

Corrections to ideal gas: Virial Expansion for 1-component

$$\frac{p}{k_B T} = n + \underbrace{B_2 n^2} + \ldots \qquad B_2 = \frac{1}{2} V_{\mathrm{exc}}$$

is related to the excluded volume for indistinguishable particles…!

Can see this from chemical potential, considering virial expansion…

$$\mu = \frac{\partial F}{\partial N} \qquad \frac{F}{k_B T} = N \ln(n\lambda_T^3) + \frac{N^2}{V} B_2 + \ldots \qquad \mu = \mu_{\mathrm{ideal}} + nV_{\mathrm{exc}}$$

$$n = \frac{N}{V}$$

Virial Expansion for 2-components

$$\frac{p}{k_B T} = n_1 + n_2 + B_{1,1} n_1 n_2 + B_{2,0} n_1^2 + B_{0,2} n_2^2 + \ldots$$

Statistical Mechanics Review (Brief)

Virial Expansion for 2-components

$$\frac{p}{k_B T} = n_1 + n_2 + B_{1,1} n_1 n_2 + B_{2,0} n_1^2 + B_{0,2} n_2^2 + \ldots$$

Let $f = \frac{N_1}{N_1 + N_2}$ *and* $1 - f = \frac{N_2}{N_1 + N_2}$

$$p = \frac{N}{V^2} \frac{\partial F}{\partial n} \Big|_{N,T,\underbrace{f}}$$

constant f, same as constant N_1 & N_2

Rewrite this in terms of f *We will minimize with respect to f later…*

$$n_1 = f n \qquad N_1 = f N$$

$$n_2 = (1 - f) n \qquad N_2 = (1 - f) N$$

After some massaging…

$$\frac{p}{k_B T} = n + n^2 [B_{2,0} f^2 + B_{1,1} f (1 - f) + B_{0,2} (1 - f)^2] + \ldots$$

Statistical Mechanics Review (Brief)

Let’s also get the free energy (to be minimized…) more massaging…

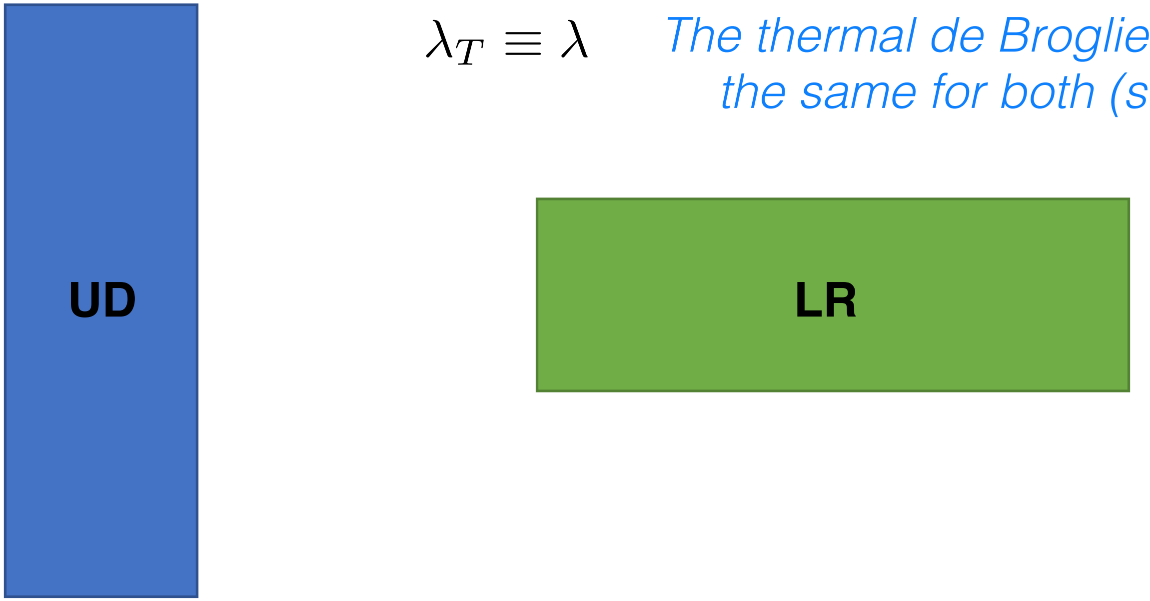
★

$$\frac{F}{k_B T N} = f \ln f + (1-f)\ln(1-f) + \ln n$$
$$+ f \ln \lambda_1^3 + (1-f)\ln \lambda_2^3$$
$$+ n[B_{2,0} f^2 + B_{1,1} f(1-f) + B_{0,2}(1-f)^2] + \ldots$$

Consider 2 species: rods pointing NS and rods pointing EW

$$\lambda_T \equiv \lambda$$

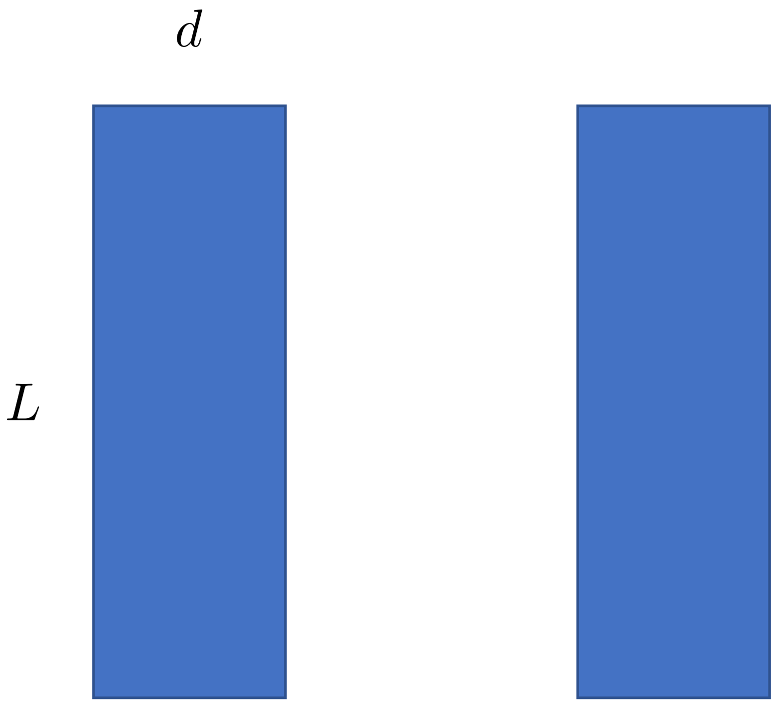
The thermal de Broglie wavelength is the same for both (same mass).



Zwanzig Model

Let's determine the second virial coefficient(s)…

$$B_2 = \frac{1}{2} V_{\mathrm{exc}}$$



$$B_{[2,0]} = \ ?$$

$$V_{\mathrm{exc}} = \ ?$$

$$V_{\mathrm{exc}} = 2L(2d)$$

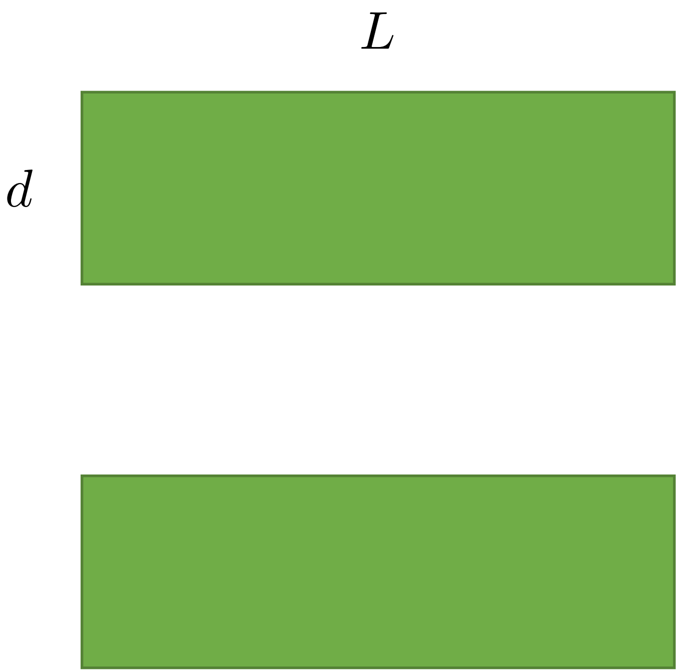
$$\boxed{B_{[2,0]} = 2Ld}$$

Zwanzig Model

Let's determine the second virial coefficient(s)…

$$B_2 = \frac{1}{2} V_{\text{exc}}$$

$$B_{[0,2]} = \ ?$$



$$V_{\text{exc}} = \ ?$$

$$V_{\text{exc}} = 2L(2d)$$

$$\boxed{B_{[0,2]} = 2Ld}$$

Zwanzig Model

Let's determine the second virial coefficient(s)…

$$B_2 = \frac{1}{2} V_{\mathrm{exc}}$$

$$B_{[1,1]} = \ ?$$

$$V_{\mathrm{exc}} = \ ?$$

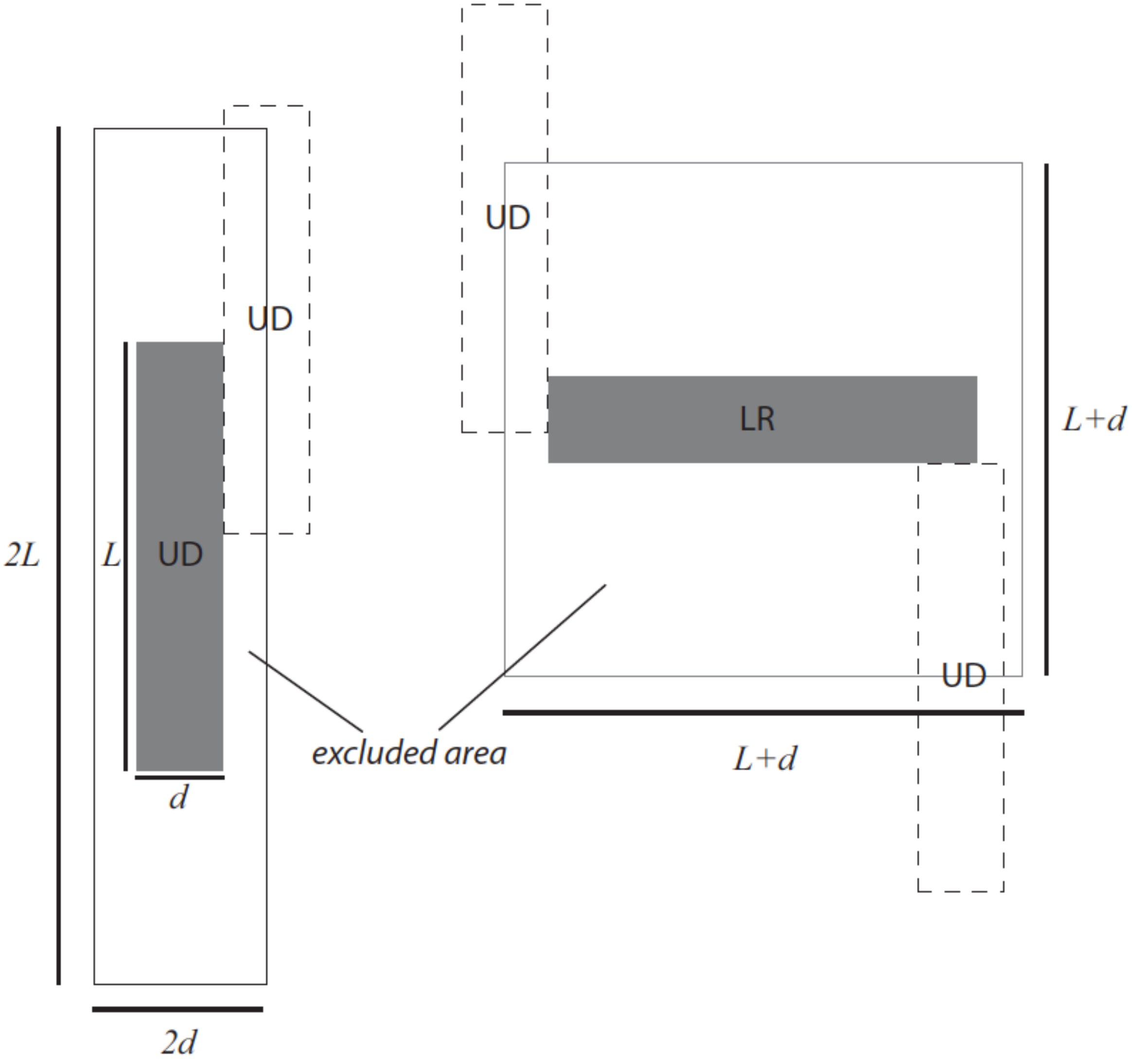
$$V_{\mathrm{exc}} = (L + d)^2$$

$$\boxed{B_{[1,1]} = (L + d)^2}$$

Not divided by 1/2 because the two are distinguishable!

Zwanzig Model

Let's determine the second virial coefficient(s)…



Zwanzig Model

Let's simplify our star equation a little and plug in the B_2's

★

$$\frac{F}{k_B T N} = f\ln f + (1-f)\ln(1-f) + \ln n$$

$$\lambda_T \equiv \lambda$$

$$\left. + f\ln\lambda_1^3 + (1-f)\ln\lambda_2^3 \right\} = \ln\lambda^3$$

$$+n[B_{2,0}f^2 + B_{1,1}f(1-f) + B_{0,2}(1-f)^2] + \ldots$$

$$= \ln n\lambda^3$$

… which is independent of f, so I will drop it since we will minimize soon…

$$\frac{F}{k_B T N} = f\ln f + (1-f)\ln(1-f)$$

$$+n\{2Ld[f^2 + (1-f)^2] + (L+d)^2 f(1-f)\} + \ldots$$

Rewrite this last term using $(f + 1 - f)^2 = 1 = f^2 + (1-f)^2 + 2f(1-f)$

$$\frac{F}{k_B T N} = f\ln f + (1-f)\ln(1-f)$$

$$+n[2Ld - 4Ldf(1-f) + (L+d)^2 f(1-f)] + \ldots$$

… drop terms independent of f again…

Zwanzig Model

After all this our star equation becomes:

★ $$\frac{F}{k_B T N} = f \ln f + (1-f)\ln f + n[(L-d)^2 f(1-f)] + \dots$$

1. Entropy of mixing! (E_{mix})

2. interaction term

1. Minimize mixing term

$$0 = \frac{\partial}{\partial f}(E_{\mathrm{mix}}) = 1 + \ln f - 1 - \ln(1-f) = \ln\left(\frac{f}{1-f}\right)$$

perfectly mixed!

$$f = 1 - f$$

$$\boxed{f = \frac{1}{2}}$$

2. Minimize interaction term

$$0 = \frac{\partial}{\partial f}[f(1-f)] = 1 - 2f$$

$$\boxed{f = \frac{1}{2}}$$

Question: Is this a minimum?

$$\frac{\partial^2}{\partial^2 f}E_{\mathrm{mix}} = \frac{1}{f} + \frac{1}{1+f} > 0$$

minimum

$$\frac{\partial^2}{\partial^2 f}[f(1-f)] = -2 < 0$$

maximum!!!

Zwanzig Model

We have ourselves a classic battle between two terms!

★ $$\frac{F}{k_B T N} = f \ln f + (1 - f) \ln f + n[(L - d)^2 f(1 - f)] + \ldots$$

1. Entropy of mixing! (E_{mix})　　*2. interaction term*

What happens when L = d?

The interaction term vanishes, and everything is well-mixed.

You can control n, which is the density/concentration.

By changing the concentration, you go from mixed to aligned.

This is a phase transition!

Zwanzig Model

Mini Landau theory…

Let's rewrite f in terms of a scalar order parameter S.

$$f = \frac{1}{2} + S$$

When S = 0, everything is randomly oriented.

$$f(1-f) = \frac{1}{4} - S^2$$

$$E_{\text{mix}} = f \ln f + (1-f)\ln(1-f)$$

$$= (\frac{1}{2} + S)\ln(\frac{1}{2} + S) + (\frac{1}{2} - S)\ln(\frac{1}{2} - S)$$

Note that $S \rightarrow -S$
Expand in powers of S^2

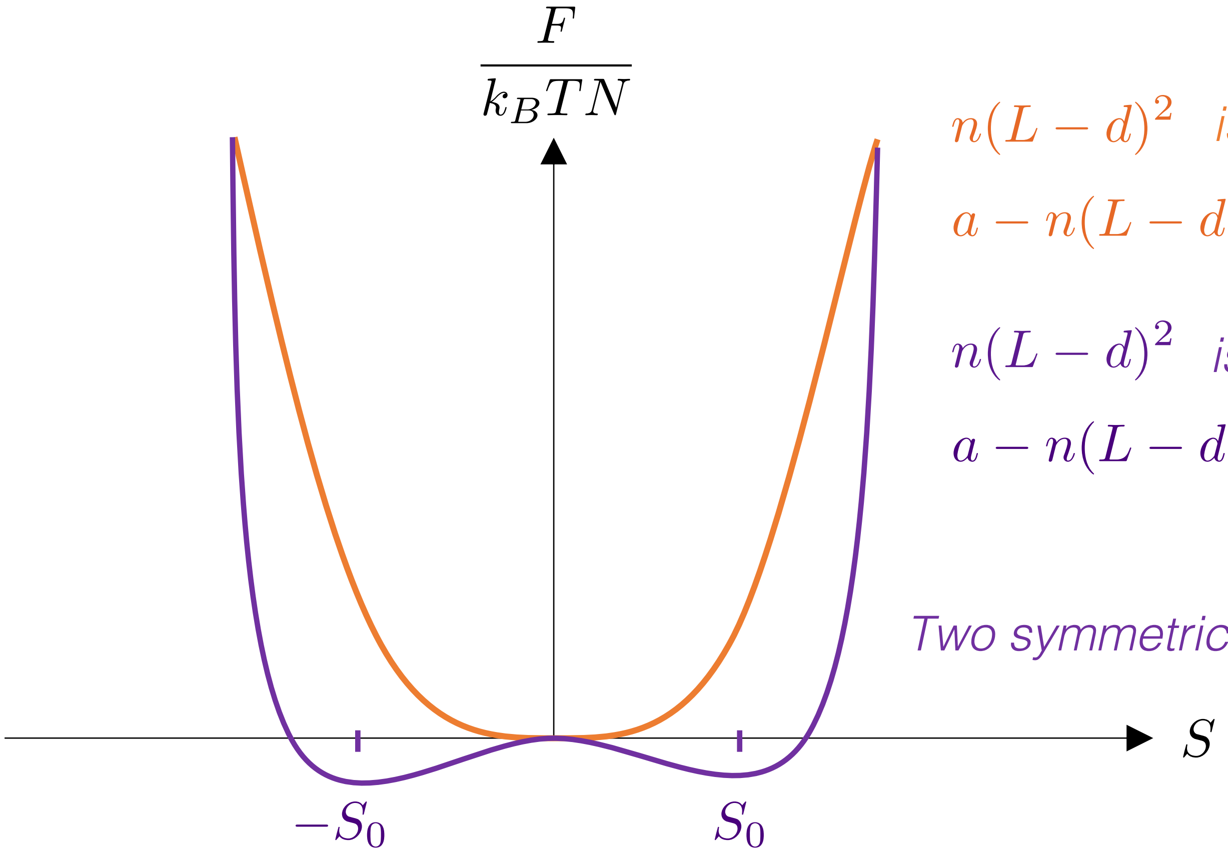
$$E_{\text{mix}} = -\ln 2 + aS^2 + bS^4 + cS^6 + \ldots$$

Let's plug this into the free energy and consider only the leading powers…

Zwanzig Model

Mini Landau theory…

$$\frac{F}{k_B T N} = -\ln 2 + aS^2 + n(L-d)^2(1/4 - S^2) + bS^4 + \ldots$$



$n(L-d)^2$ *is small*

$a - n(L-d)^2 > 0$

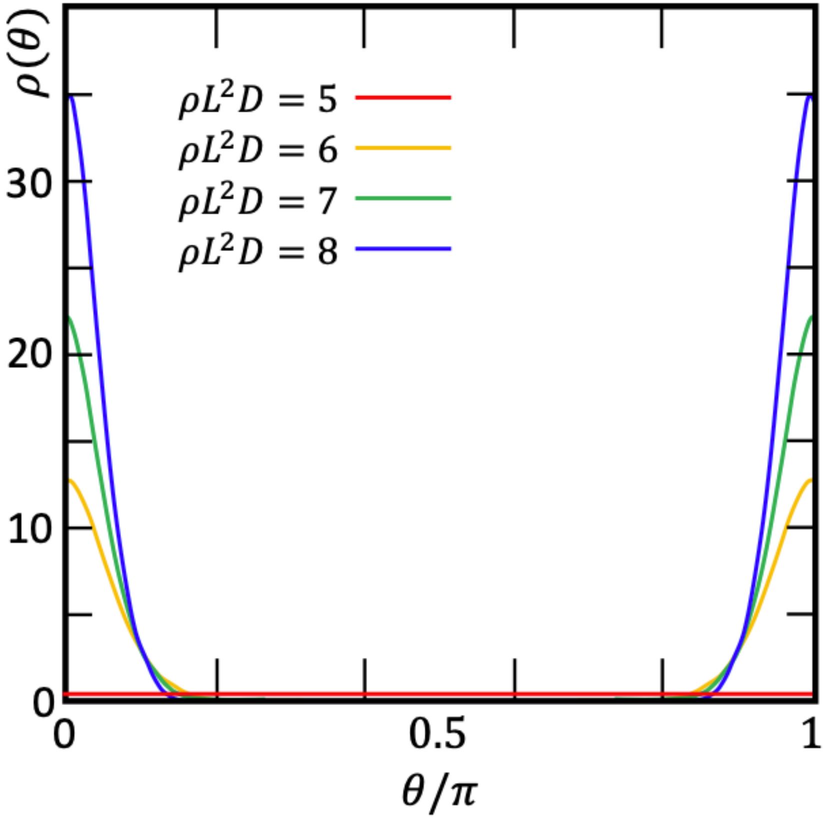
$n(L-d)^2$ *is large*

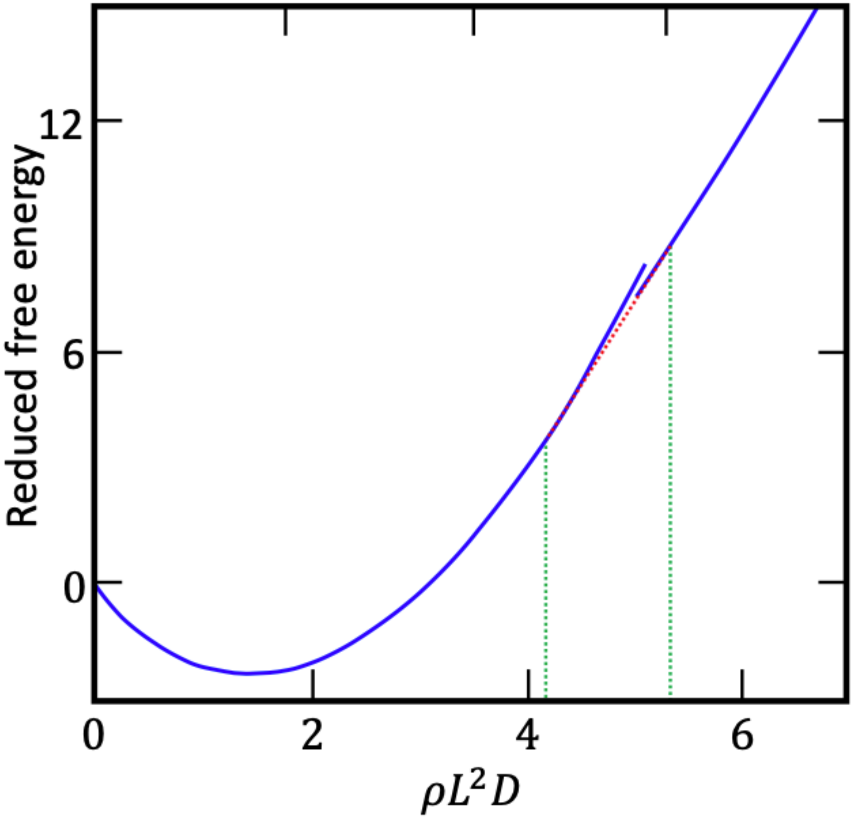
$a - n(L-d)^2 < 0$

Two symmetric minimum!

Symmetry breaking → a classic signature of a phase transition.

Onsager theory, 3D & plotted $L >> d$





From Joost de Graaf

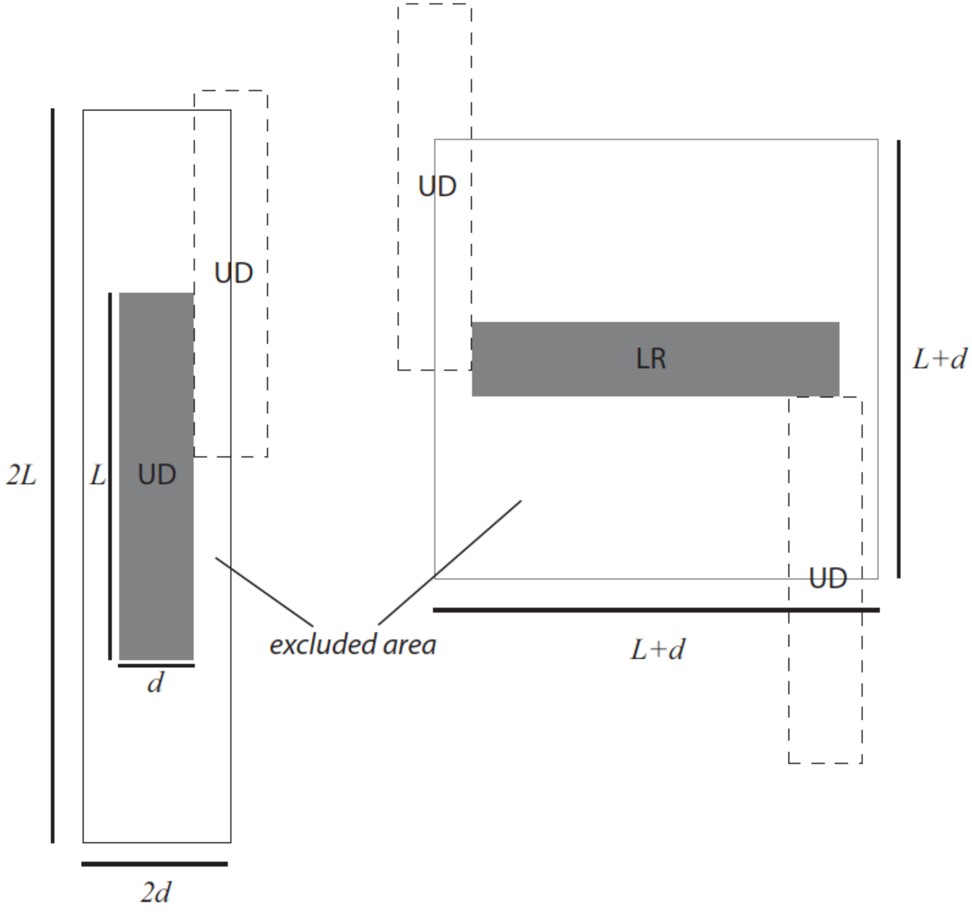
Colloids as Liquid Crystals

Overview

Assembly into liquid crystal phases due to entropic interactions, excluded volume

Reducing excluded volume gives more freedom of motion, increases entropy.

Phase transitions occur which minimize excluded volume.



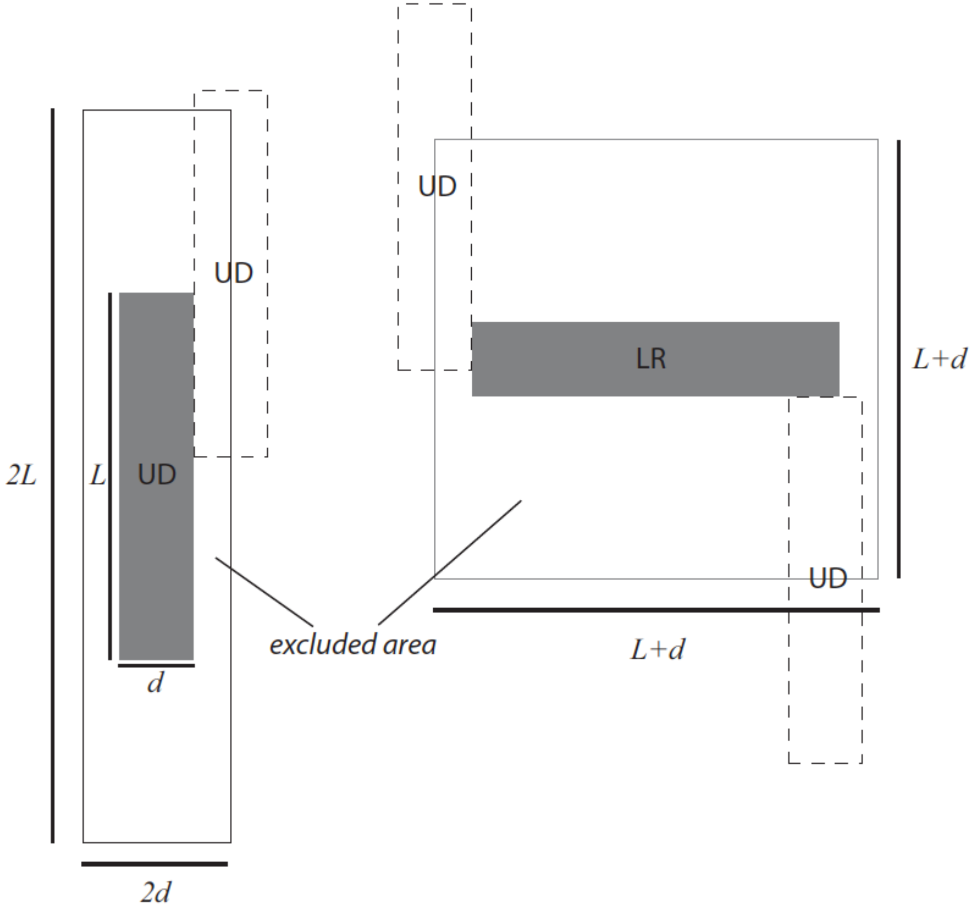
Colloids as Liquid Crystals

Some Open Questions (not exhaustive)

Role of molecular shape and heterogeneity in stabilizing phases? Which phases and why?

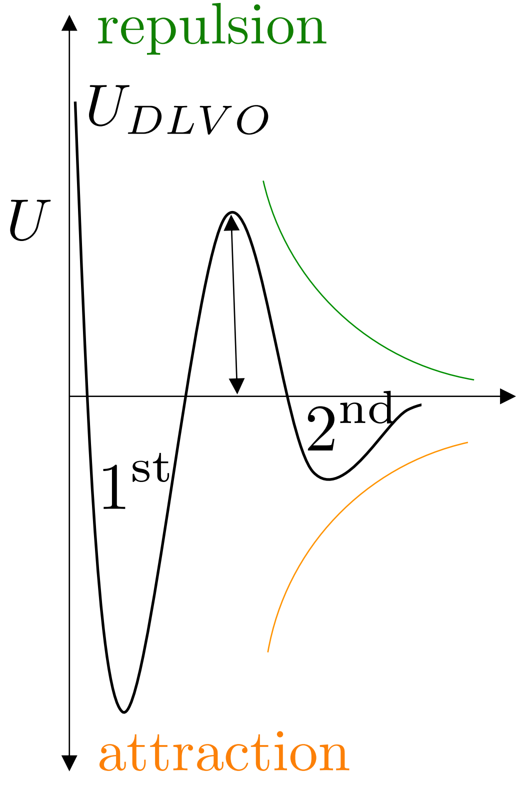
Diffusion behavior of individual components in phases?

Controlling assembly in biological, colloidal liquid crystals



Beyond entropy…

Controlling interparticle interactions



Considerations…

Steric repulsion (adsorbed polymer)

Electrostatic interactions (solvent, salts)

Depletion effects (nonadsorbing polymer)

Liquid crystals

Lisa Tran

Day 1: Displays and droplets

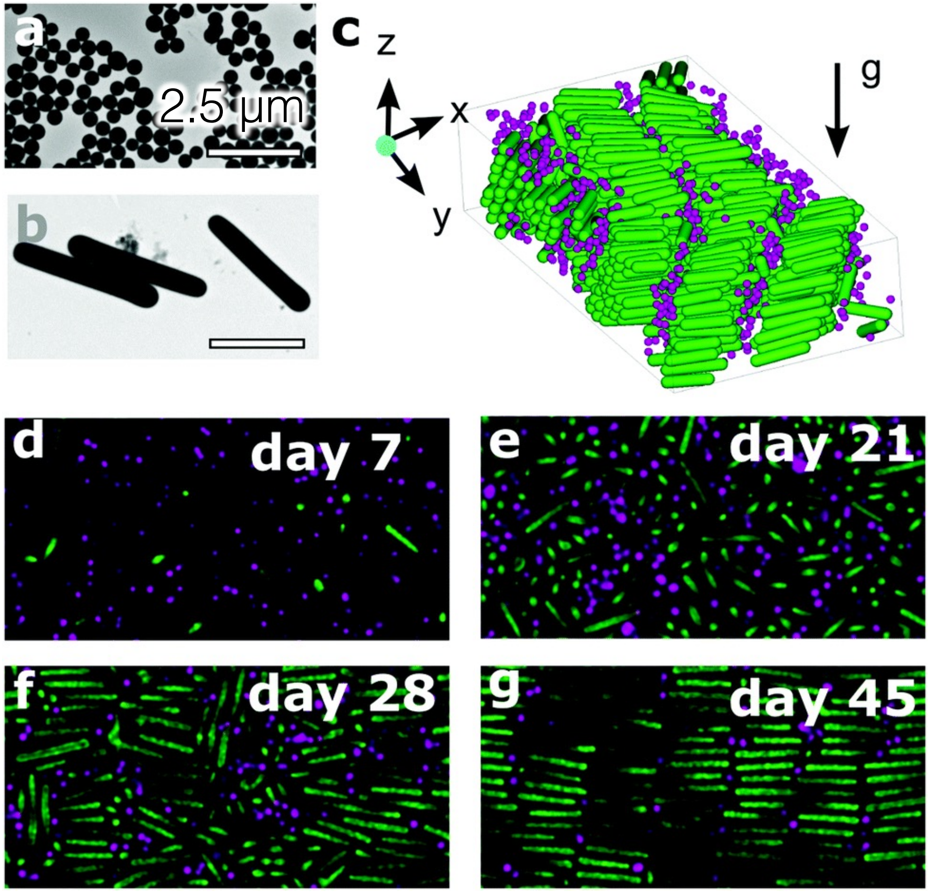
- Optical properties
- Order: elasticity & defects
- LCDs
- Research highlights

Day 2: Colloidal liquid crystals

- Hard rods - Zwanzig model (2D)
- Onsager theory & other interactions
- Colloidal liquid crystals in biology
- Research highlights

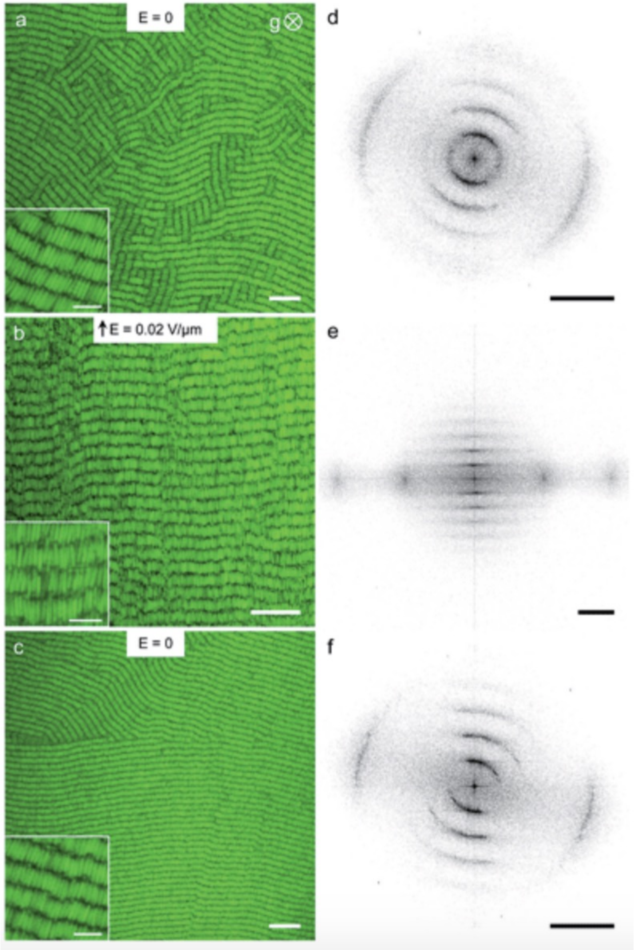
Experimental methods…

Sedimentation



Bakker, H.E., Dussi, S., Droste, B.L., Besseling, T.H., Kennedy, C.L., Wiegant, E.I., Liu, B., Imhof, A., Dijkstra, M. and van Blaaderen, A., 2016. Soft Matter, 12(45), pp.9238-9245.

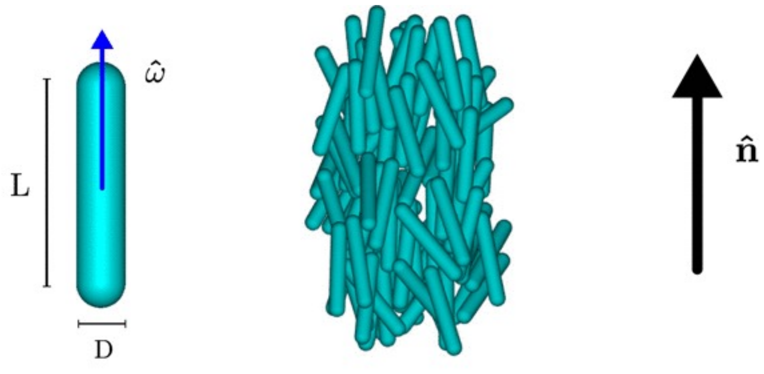
External fields

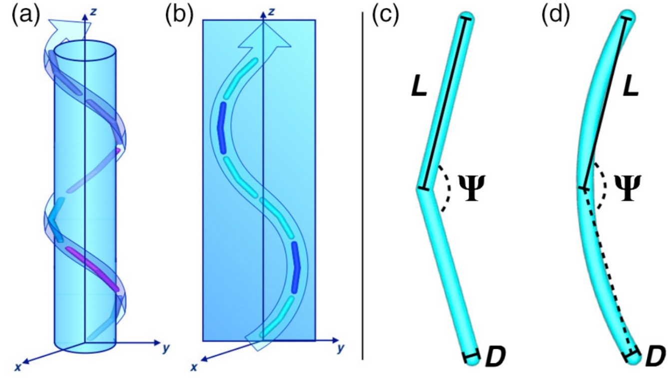


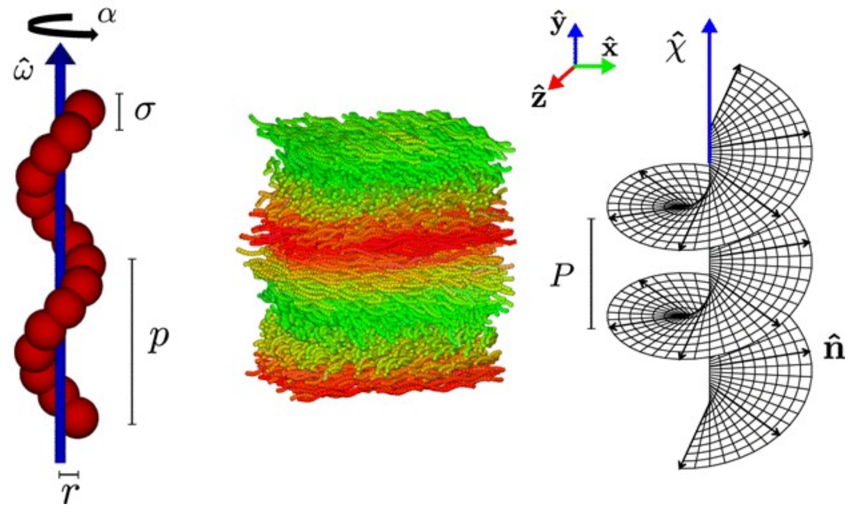
Kuijk, A., Troppenz, T., Filion, L., Imhof, A., Van Roij, R., Dijkstra, M., & Van Blaaderen, A. (2014). Effect of external electric fields on the phase behavior of colloidal silica rods. Soft Matter, 10(33), 6249-6255.

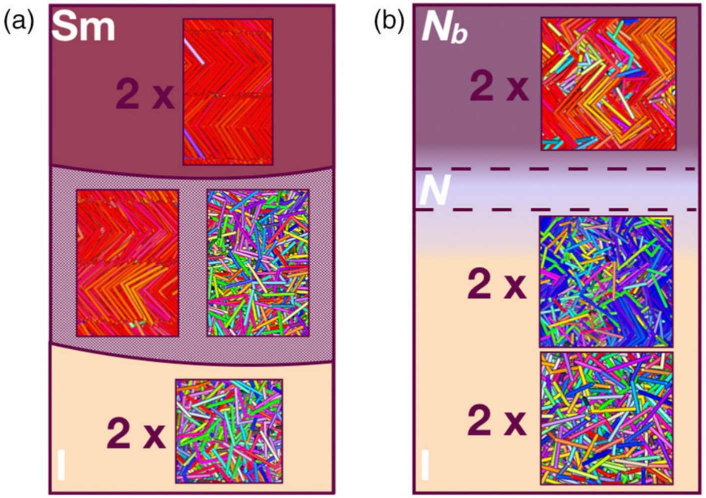
Phase Behavior

Phases from particle shape





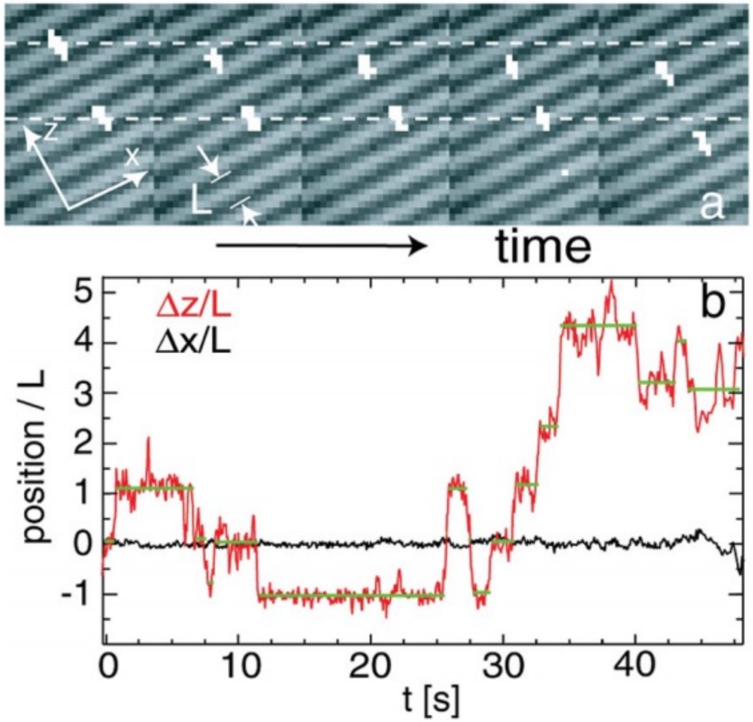




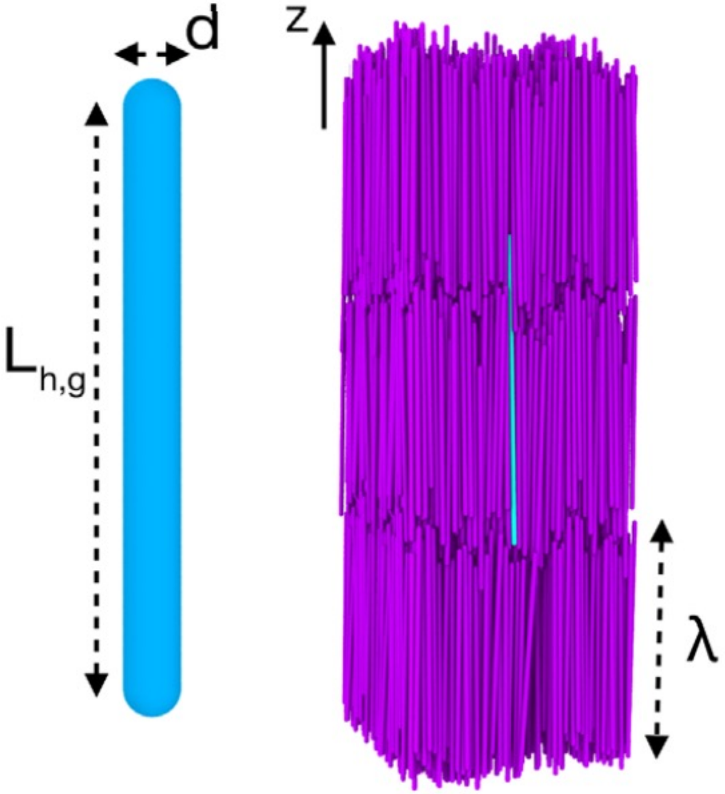
Dussi, S., Belli, S., Van Roij, R., & Dijkstra, M. (2015). Cholesterics of colloidal helices: Predicting the macroscopic pitch from the particle shape and thermodynamic state. The Journal of chemical physics, 142(7), 074905.

Chiappini, M., Drwenski, T., Van Roij, R., & Dijkstra, M. (2019). Biaxial, Twist-bend, and Splay-bend Nematic Phases of Banana-shaped Particles Revealed by Lifting the “Smectic Blanket”. Physical review letters, 123(6), 068001.

Diffusion behavior



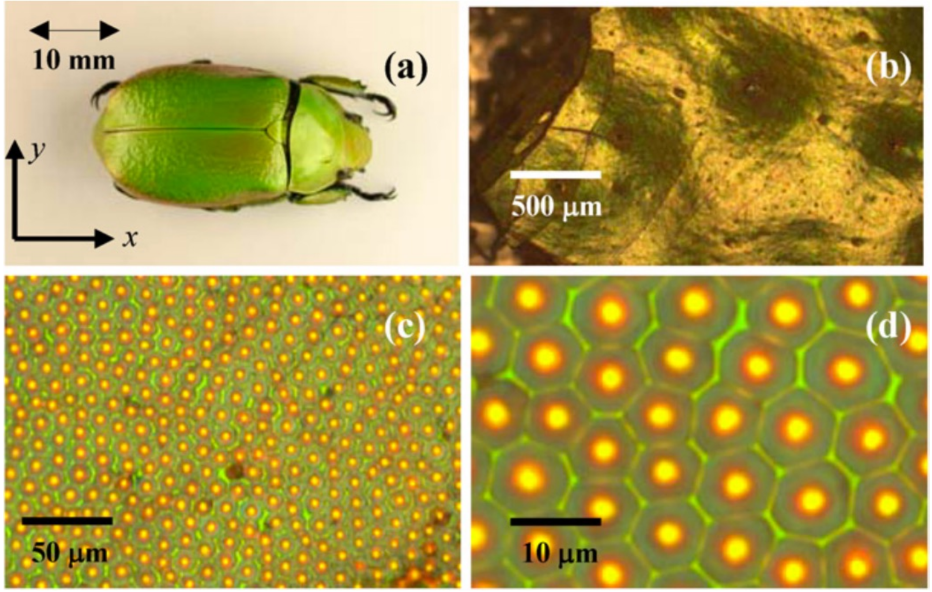
Lettinga, M. P., & Grelet, E. (2007). Self-diffusion of rodlike viruses through smectic layers. Physical review letters, 99(19), 197802.



Chiappini, M., Grelet, E., & Dijkstra, M. (2020). Speeding up Dynamics by Tuning the Noncommensurate Size of Rodlike Particles in a Smectic Phase. Physical Review Letters, 124(8), 087801.

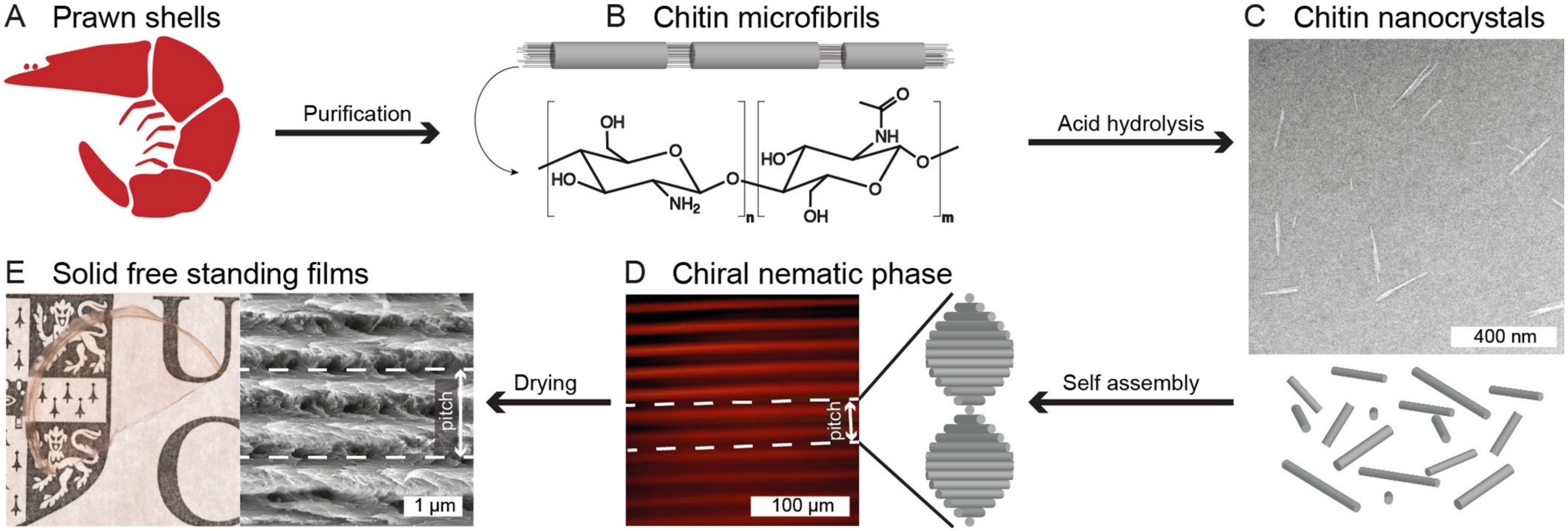
Biologically Sourced Colloids

Chitin



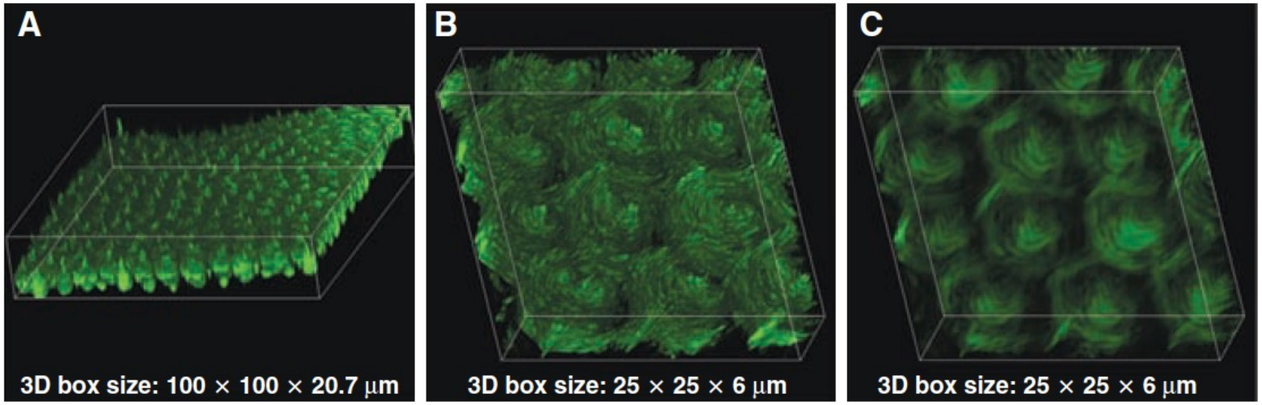
V. Sharma, M. Crne, J. O. Park, M. Srinivasarao, *Science* **325** (2009): 449-451

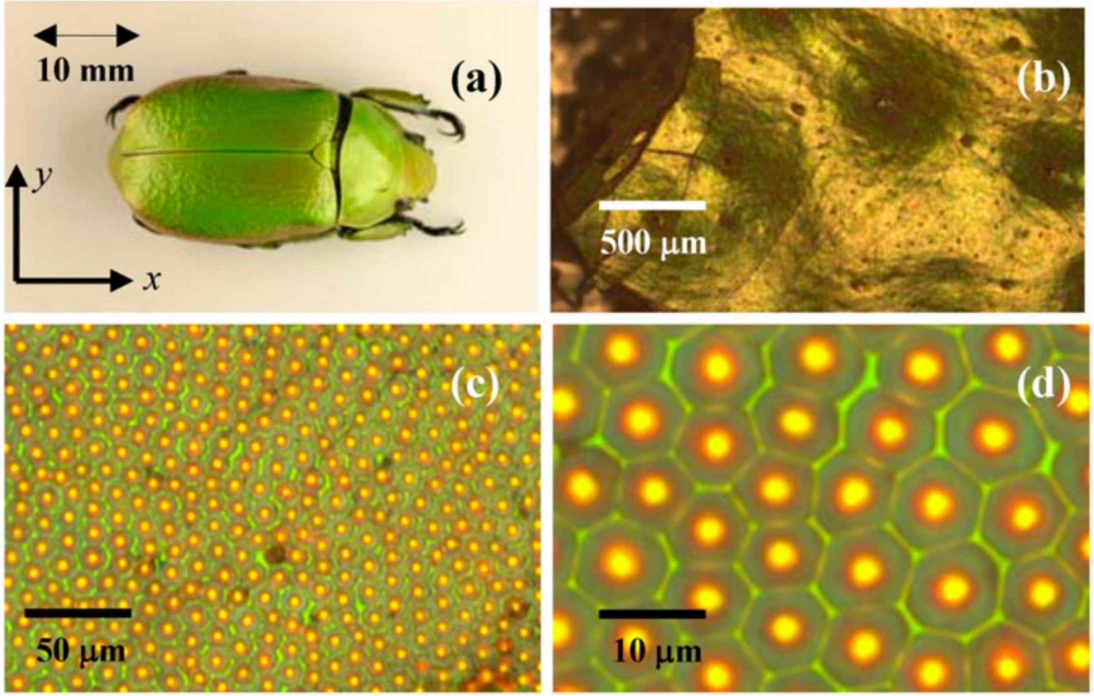
Narkevicius, A., Steiner, L. M., Parker, R. M., Ogawa, Y., Frka-Petesic, B., & Vignolini, S. (2019). Biomacromolecules, 20(7), 2830-2838.

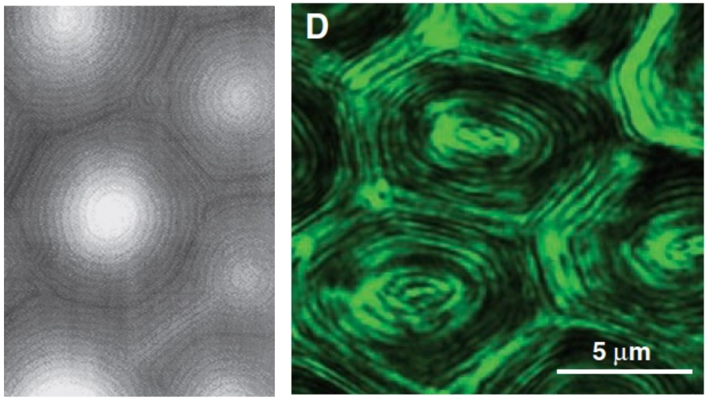


Cholesterics in the natural world

Structural color



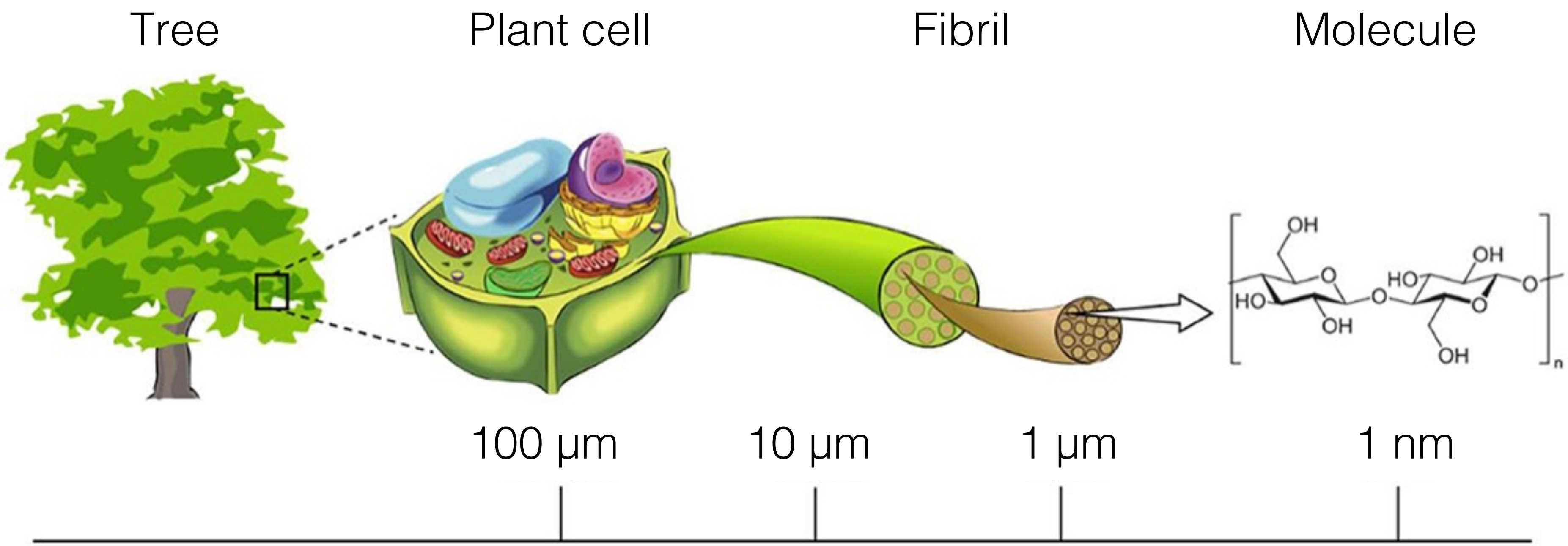




V. Sharma, M. Crne, J. O. Park, M. Srinivasaro, *Science* **325** (2009): 449-451

S. A. Jewell, P. Vukusic, & N. W. Roberts, *New Journal of Physics* **9** (2007) 99

Cellulose nanocrystals (CNCs)



Tree

Plant cell

Fibril

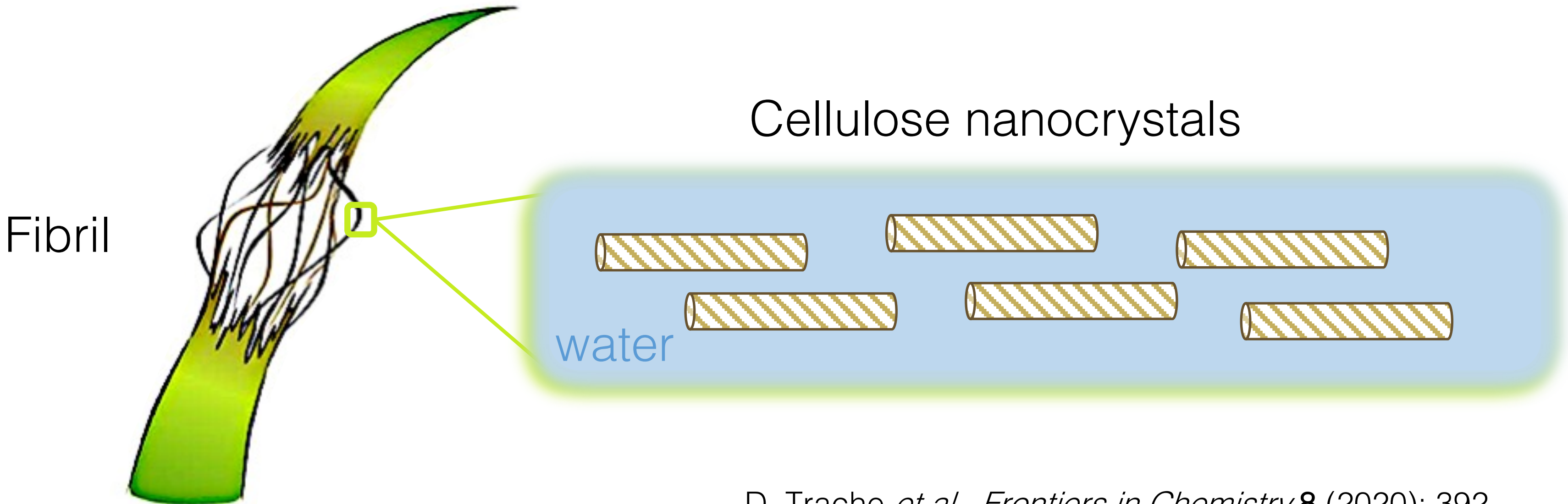
Molecule

100 μm

10 μm

1 μm

1 nm



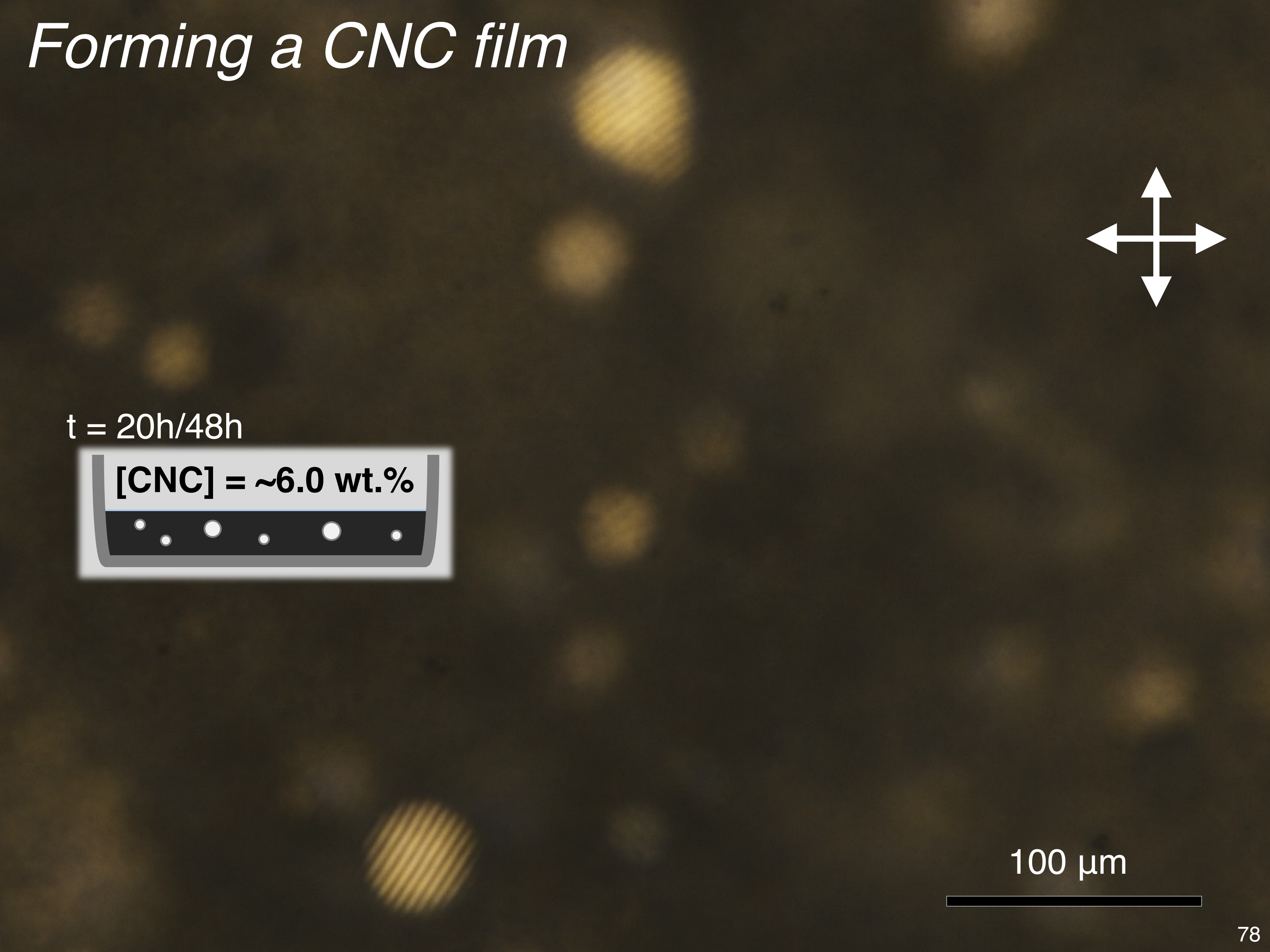
Fibril

Cellulose nanocrystals

D. Trache *et al.*, *Frontiers in Chemistry* 8 (2020): 392

Forming a CNC film

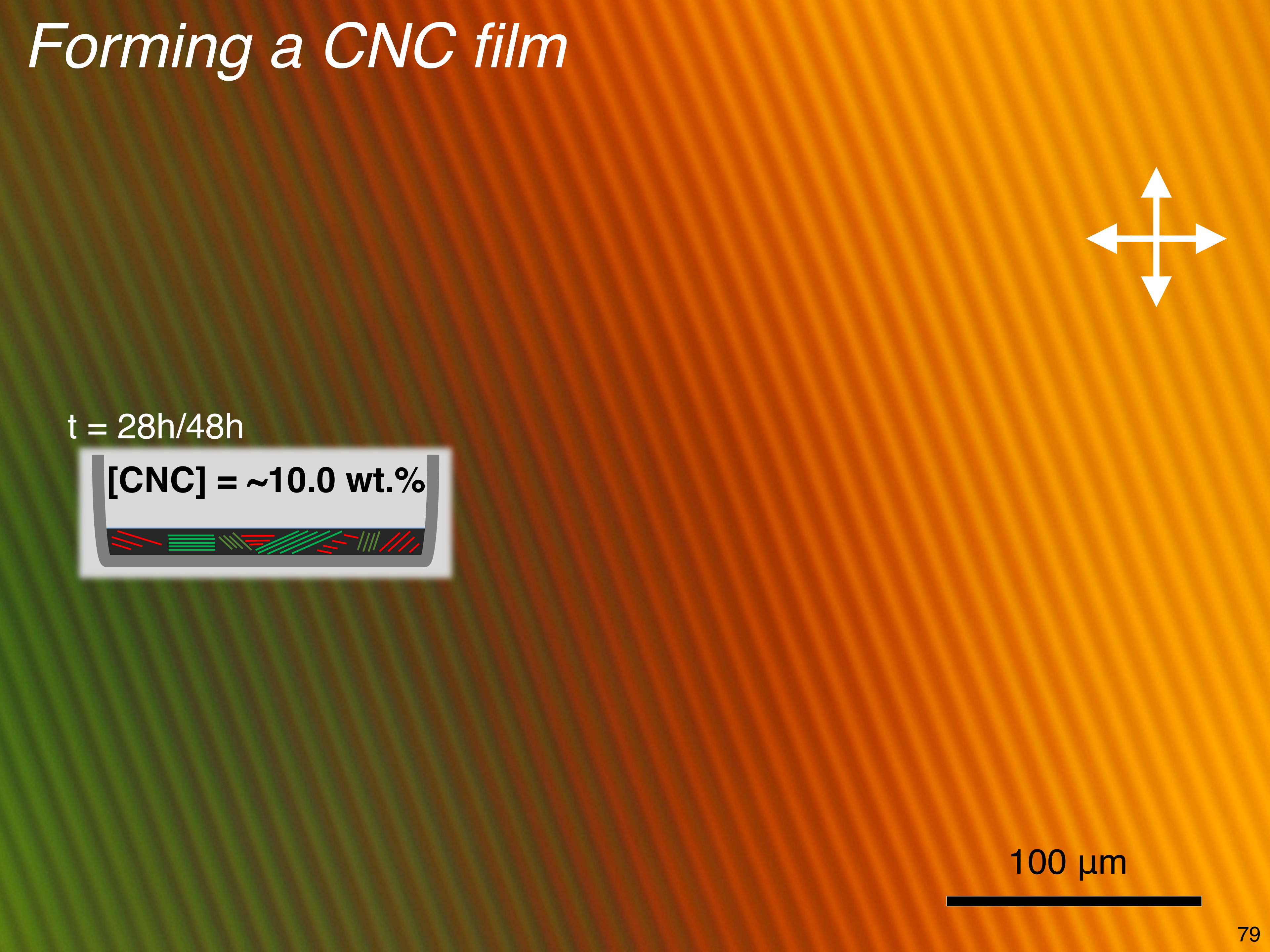
Forming a CNC film



t = 20h/48h

[CNC] = ~6.0 wt.%

Forming a CNC film


t = 28h/48h

[CNC] = ~10.0 wt.%

Liquid crystals

Lisa Tran

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