Lecture I:
Liquid Crystals

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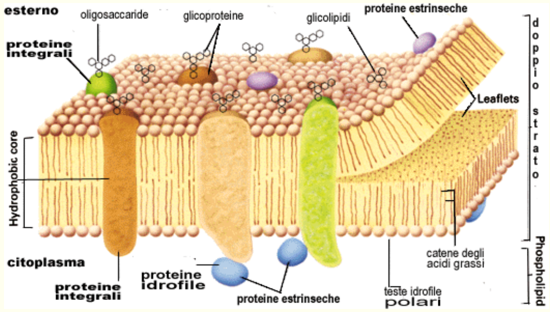
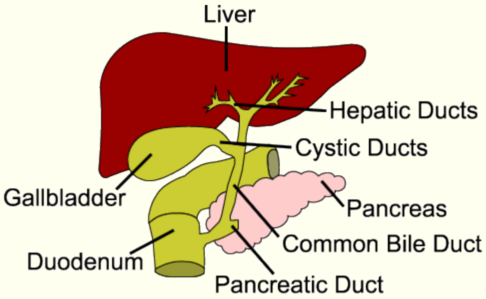
Liquid Crystal Institute
Kent State University

Outline

- history
- orientation & orientational order
- softness
- order parameters, phases
- free energy and phase behavior
- effect of fields

Liquid Crystals around us:



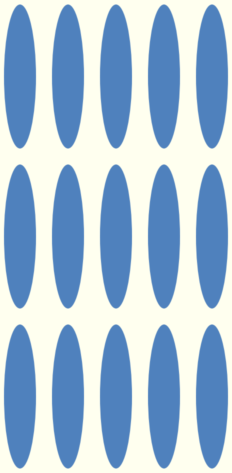


+....

Liquid Crystals: history

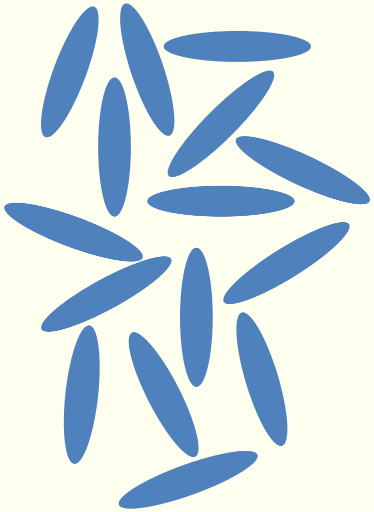
- discovered in 1888
  - botanist Reinitzer observes 2 melting points in cholesteryl benzoate

solid $\xrightarrow{T}$ hazy liquid $\xrightarrow{T}$ clear liquid



solid crystal

?



isotropic liquid

new phase of matter: **liquid crystal phase**

Liquid Crystals: history

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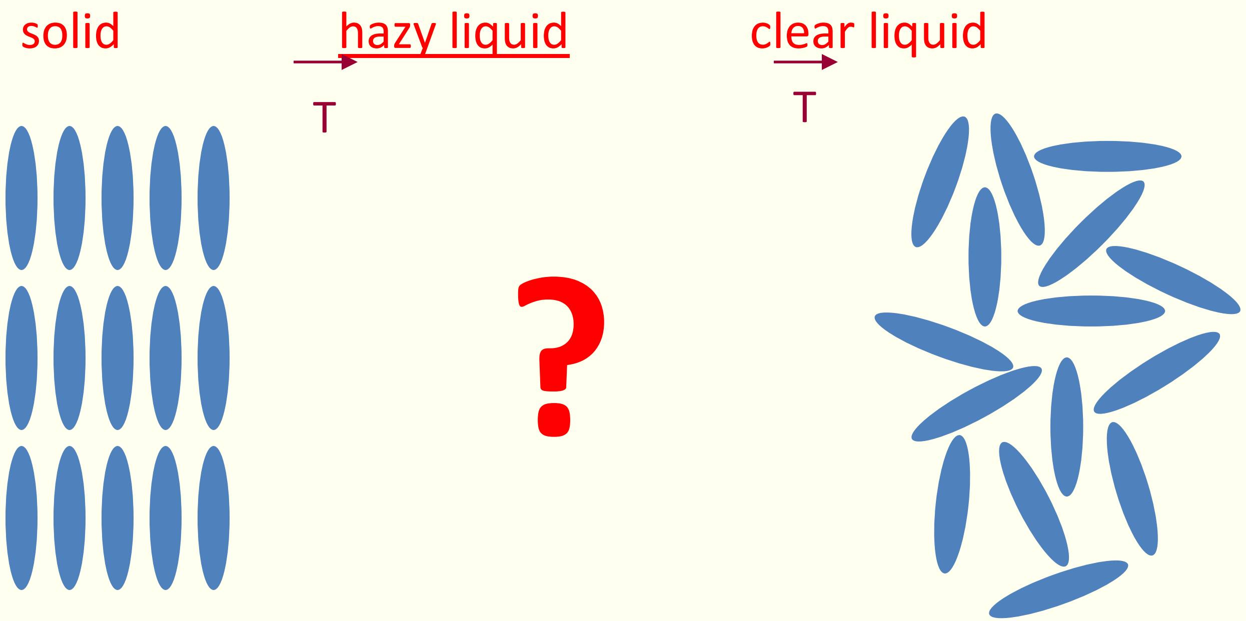


solid $\xrightarrow{T}$ hazy liquid $\xrightarrow{T}$ clear liquid

?

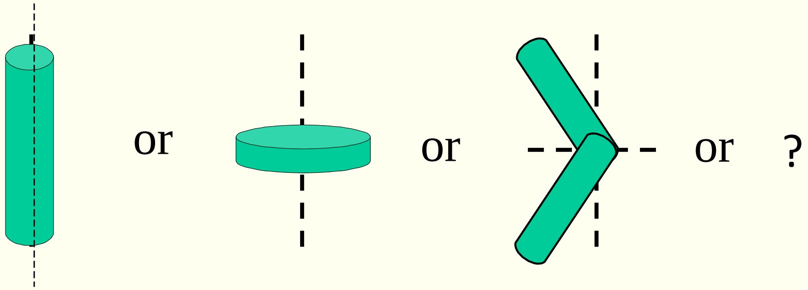
solid crystal

isotropic liquid

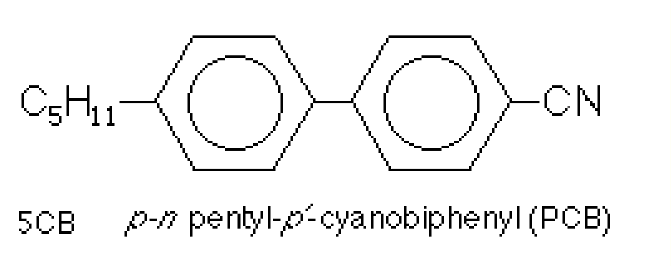
liquid crystal phase: 'mesophase'

Liquid Crystals

- orientationally ordered fluids
  - anisotropic constituents
  - long range orientational order (incomplete positional order)
  - anisotropic physical properties



physicist's picture

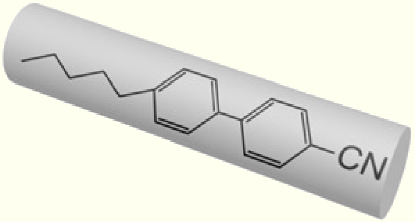


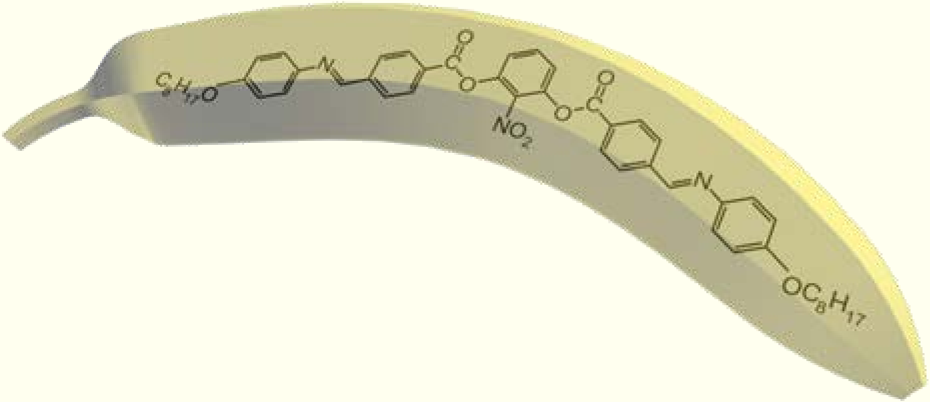
5CB *p-n* pentyl-*p'*-cyanobiphenyl (PCB)

typical chemical structure

Liquid Crystals

- soft materials with orientationally ordered constituents
  - molecules



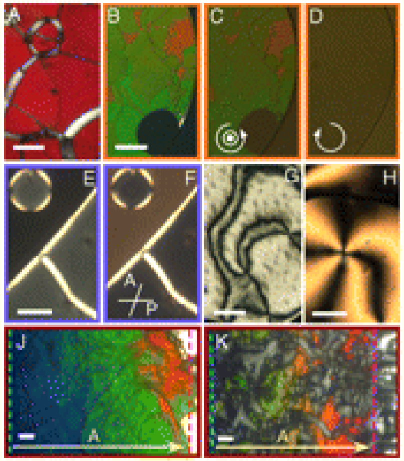


Liquid Crystals

- soft materials with orientationally ordered constituents
  - molecules
  - macromolecules

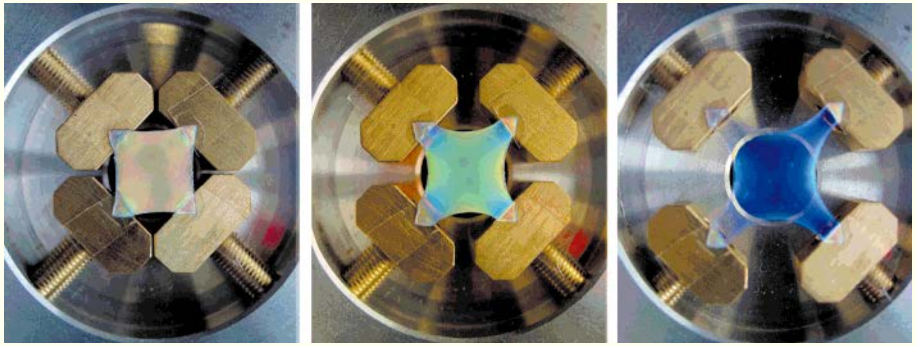
Liquid Crystals

- soft materials with orientationally ordered constituents



textures of DNA oligomers
Clark *et al*., *PNAS* **107** ,17497 (2010)

  - molecules
  - macromolecules



Cholesteric LC elastomer
Finkelmann *et al.* , *Adv. Mat.* **13**, 1069 (2001)

Liquid Crystals

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  - macromolecules
  - molecular aggregates

Liquid Crystals

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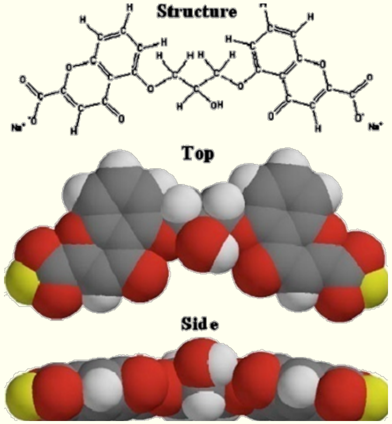

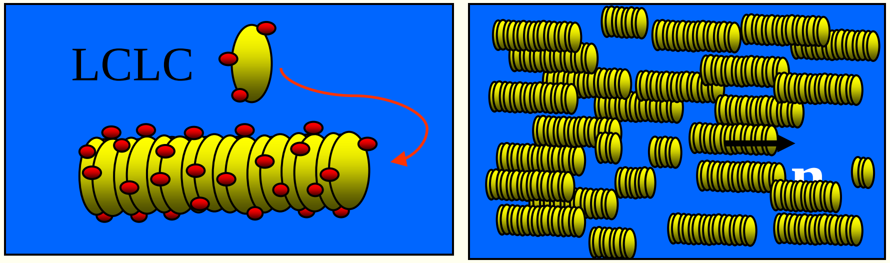

lyotropic chromonic liquid crystals
(J. Lydon, O. Lavrentovich)

Liquid Crystals

- soft materials with orientationally ordered constituents
  - molecules
  - macromolecules
  - molecular aggregates
  - nanoparticles

Liquid Crystals

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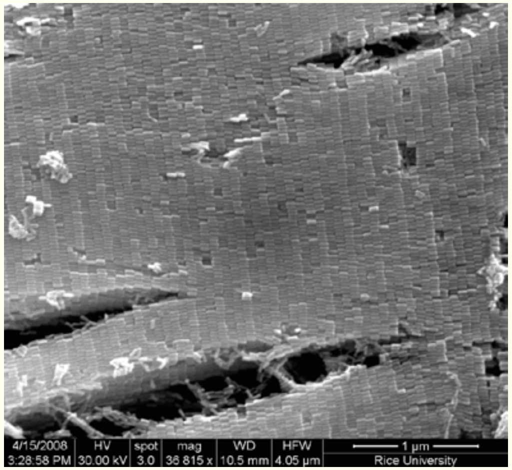
  - nanoparticles

gibbsite platelets

van der Beek, *J. Chem. Phys*. **121,** 5423(2004)



Au nanorods
N. Kotov, U. Mich. ,
E. Zubarev, Rice U. (2008)

Liquid Crystals

- soft materials with orientationally ordered constituents
  - molecules
  - macromolecules
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  - microparticles

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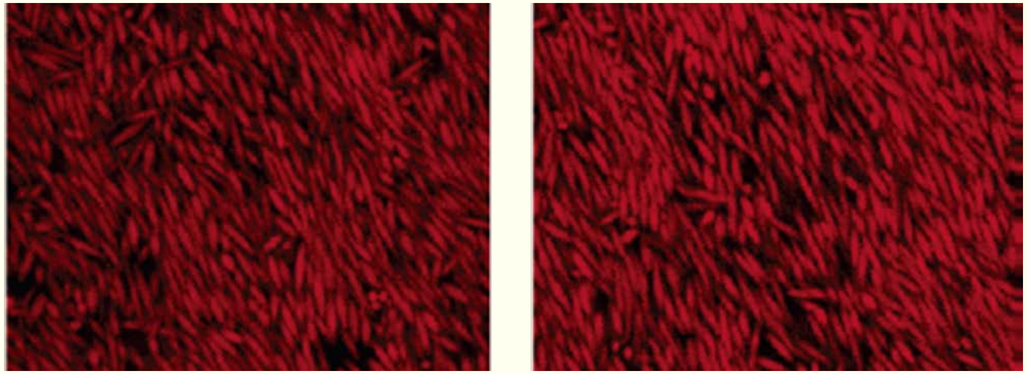

soft colloidal PMMA ellipsoids, *3.3* x *0.6 μm*
A. Mohraz and M. Solomon,
Langmuir **21**, 5298 (2005).

Liquid Crystals

- soft materials with orientationally ordered constituents
    - molecules
    - macromolecules
    - molecular aggregates
    - nanoparticles
    - microparticles
    - active nematics

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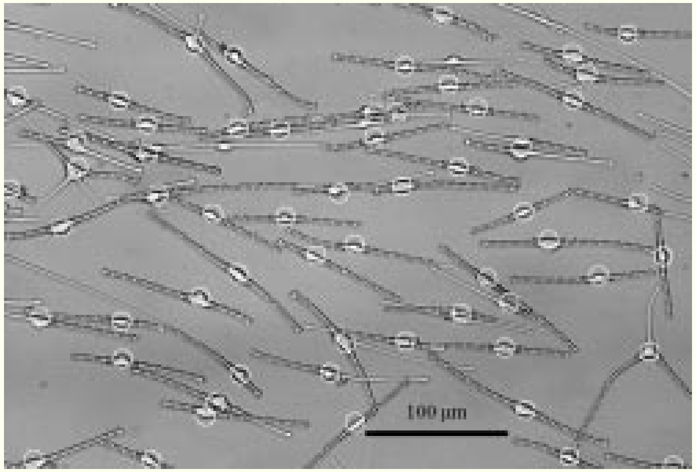

human melanocyte
(cell+dendrites)

Liquid Crystals

- soft materials with orientationally ordered constituents

  - rod/slab shaped nuclei in the mantles of neutron stars
  - molecules
  - macromolecules
  - molecular aggregates
  - nanoparticles
  - microparticles
  - active nematics

Liquid Crystals

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  - rod/slab shaped nuclei in the mantles of neutron stars
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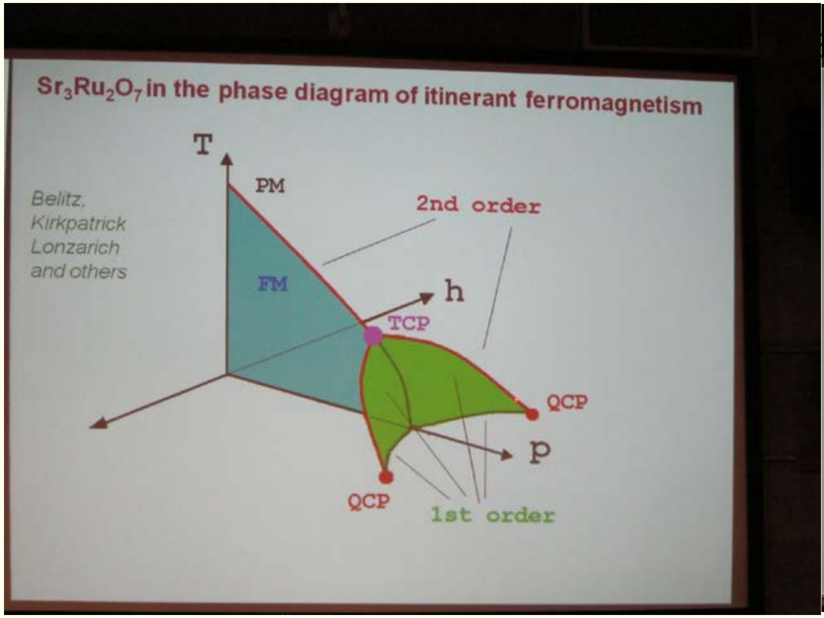
starquake in neutron star – artists' rendition
property of mantle depends on nematic order

Liquid Crystals

- soft materials with orientationally ordered constituents
  - correlated electrons: spin nematics in quantum magnets
  - rod/slab shaped nuclei in the mantles of neutron stars
  - molecules
  - macromolecules
  - molecular aggregates
  - nanoparticles
  - microparticles
  - active nematics

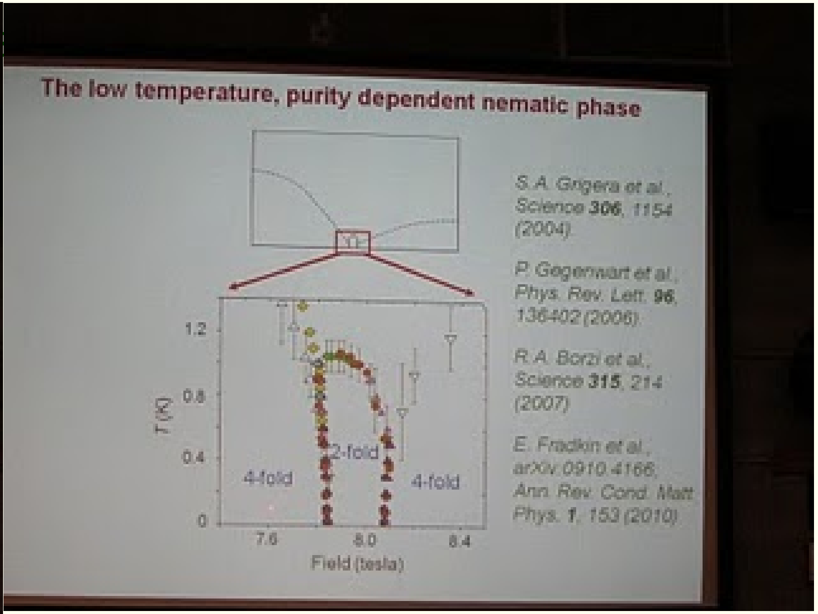
Liquid Crystals

- soft materials with orientationally ordered constituents
  - correlated electrons: spin nematics in quantum magnets



$Sr_3Ru_2O_7$ in the phase diagram of itinerant ferromagnetism

Belitz,
Kirkpatrick
Lonzarich
and others



The low temperature, purity dependent nematic phase

S.A. Grigera et al., Science **306**, 1154 (2004)

P. Gegenwart et al., Phys. Rev. Lett. **96**, 136402 (2006)

R.A. Borzi et al., Science **315**, 214 (2007)

E. Fradkin et al., arXiv 0910.4166, Ann. Rev. Cond. Matt. Phys. **1**, 153 (2010)

low Tc ferromagnet under pressure;
electronic nematic phase.
Lonzarich *et al.*

  - active nematics

Liquid Crystals

- soft materials with orientationally ordered constituents
  - correlated electrons: spin nematics in quantum magnets
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  - molecules
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  - nanoparticles
  - microparticles
  - active nematics

orientational order

Orientational Order

- liquid crystals: systems with orientational order

Goldstone's theorem:

*Broken continuous symmetry → low energy excitations**

→ responsive

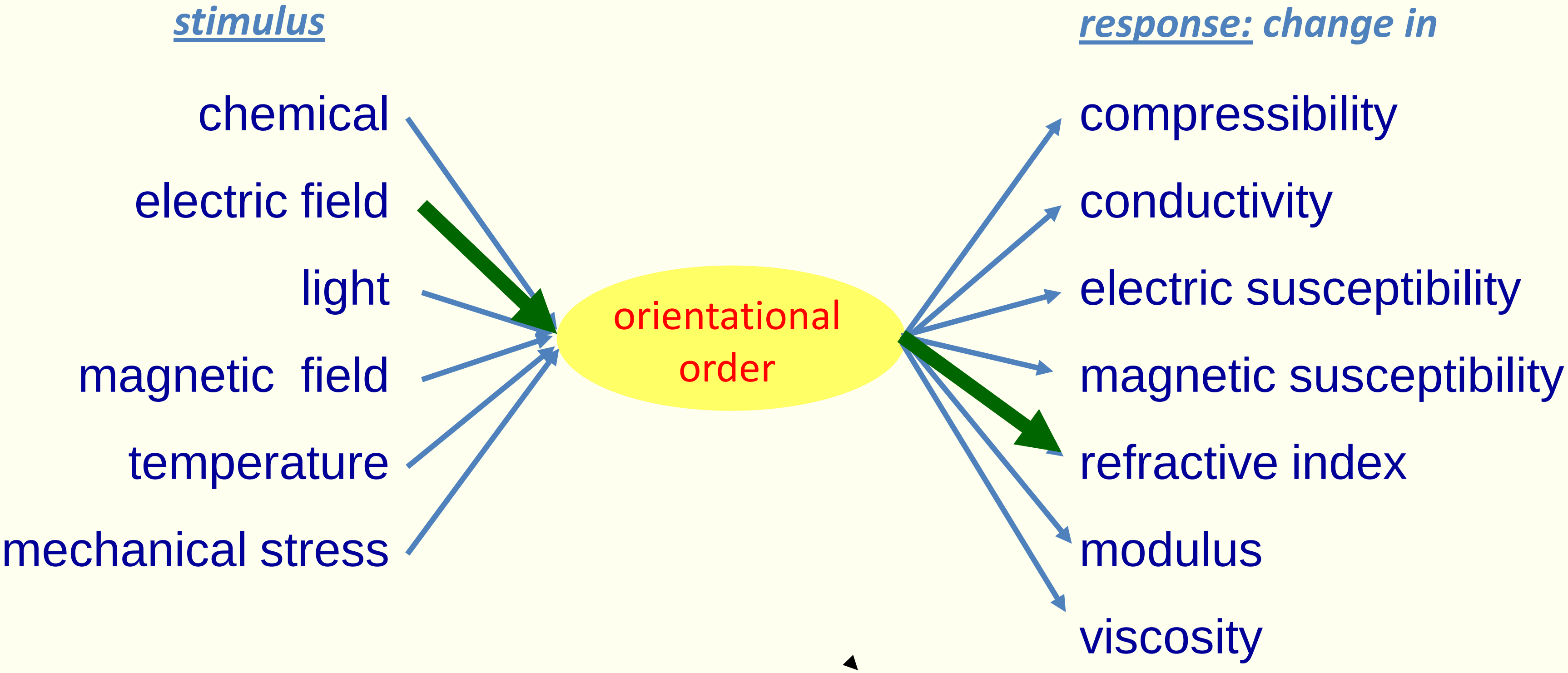
- anisotropic

- soft materials

-unique responsivity

Liquid Crystals

- responsivity: result of coupling via orientational order



stimulus

chemical
electric field
light
magnetic field
temperature
mechanical stress

orientational
order

response: *change in*

compressibility
conductivity
electric susceptibility
magnetic susceptibility
refractive index
modulus
viscosity

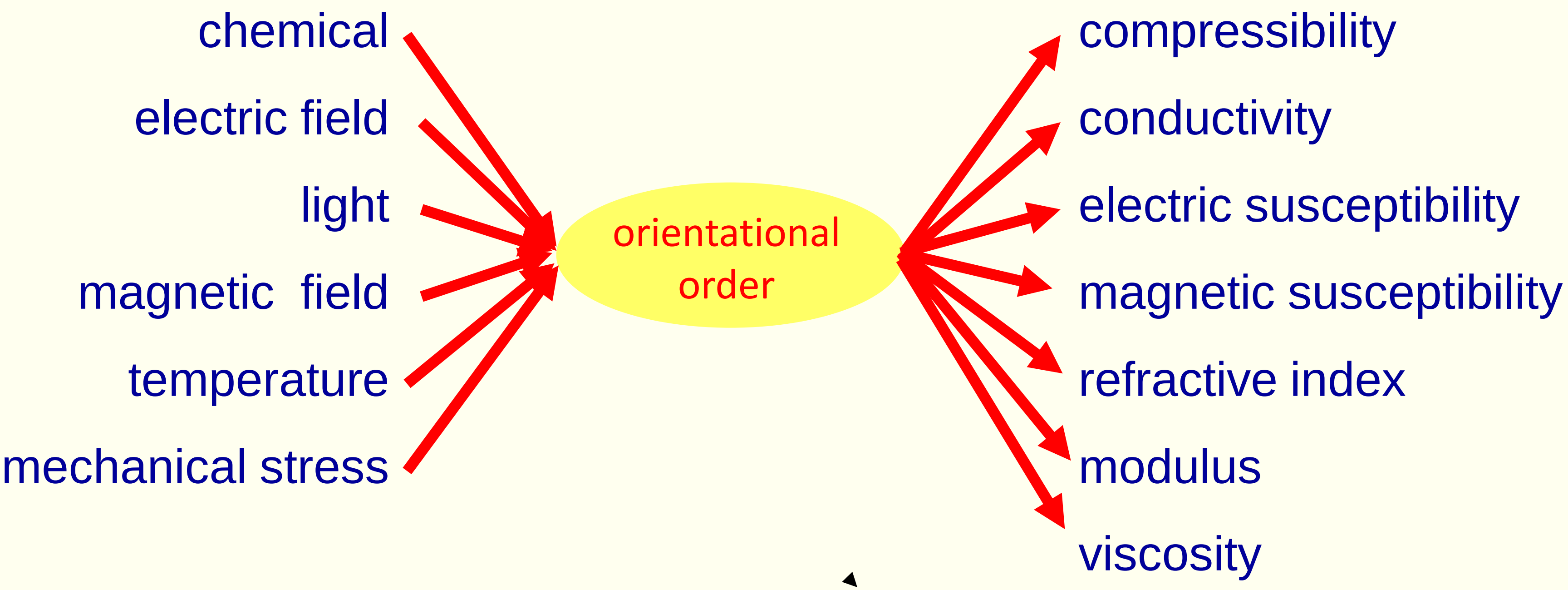
multi-billion dollar LCD industry is based on only *ONE* such coupling,

Liquid Crystals

- responsivity: result of coupling via orientational order

excitation

response: change in



chemical
electric field
light
magnetic field
temperature
mechanical stress

orientational
order

compressibility
conductivity
electric susceptibility
magnetic susceptibility
refractive index
modulus
viscosity

multi-billion dollar LCD industry is based on only *ONE* such coupling,

many possibilities to explore!

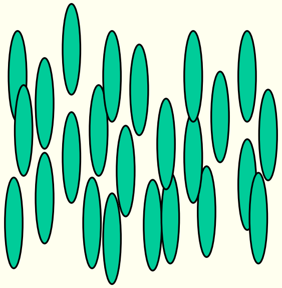
Two types of LC:

- thermotropic (temperature dependent)
  - only 'mesogenic' constituents
    - typical low molecular wt. LCs

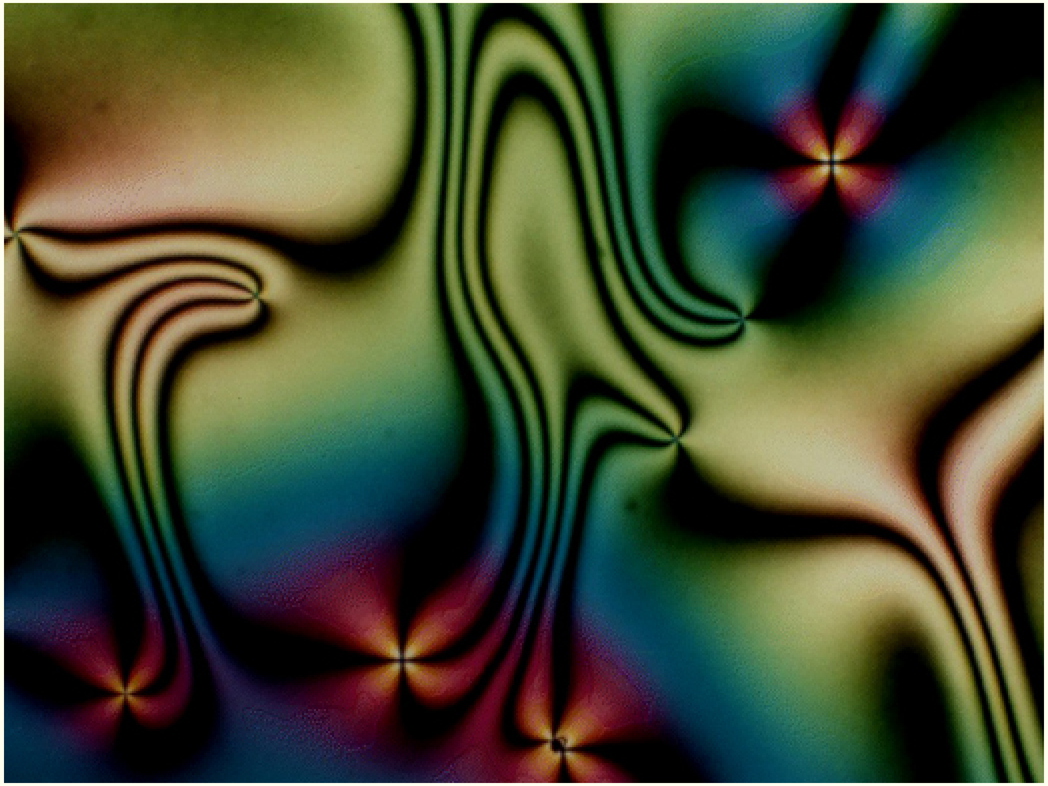
- lyotropic (solvent concentration dependent)
  - 'mesogenic' constituents in a solvent
    - amphiphilics (soaps, myelin...)

Liquid Crystal Phases

- most common:



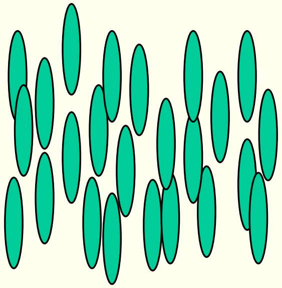
nematic



nematic film with schlieren texture

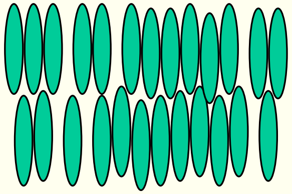
Liquid Crystal Phases

- most common:



Why? - energy: anisotropic attraction
- entropy: pack better

nematic

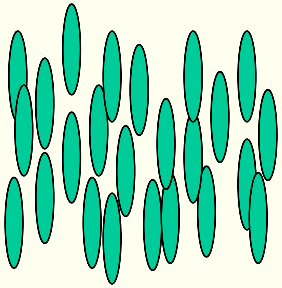


Why? - energy: better pairing
- entropy: more available volume

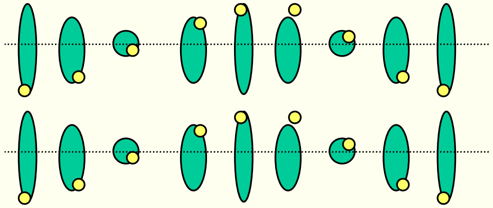
smectic A

Liquid Crystal Phases

- if constituents are chiral:

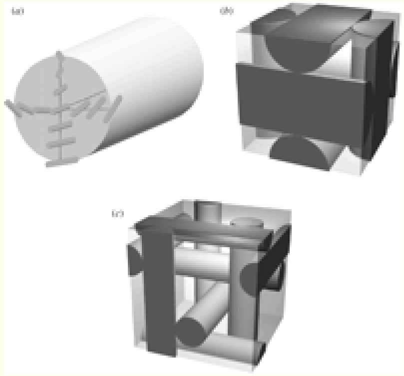


nematic

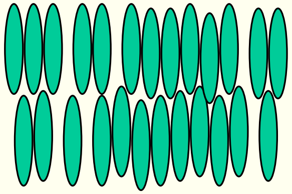


helical cholesteric

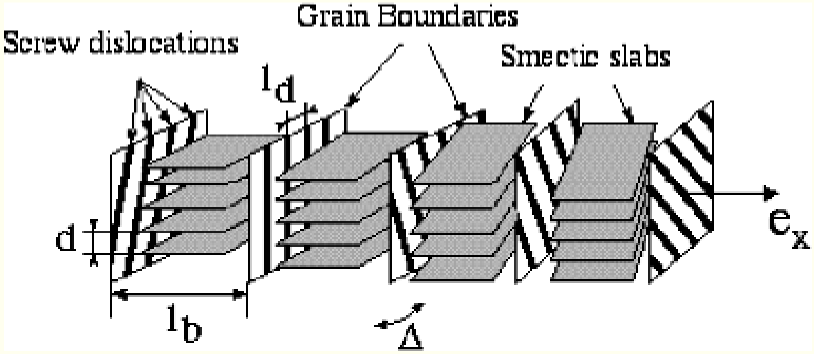
or



cholesteric blue



smectic A



Liquid Crystal Phases

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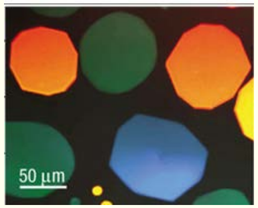
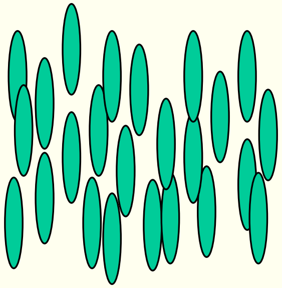
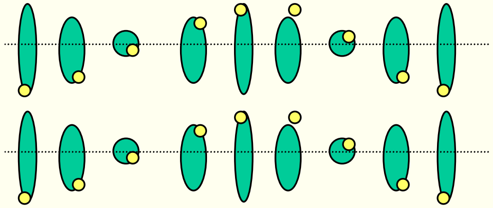
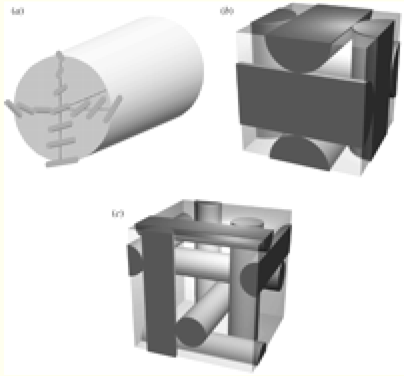






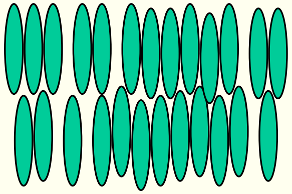
or



nematic

helical cholesteric

cholesteric blue



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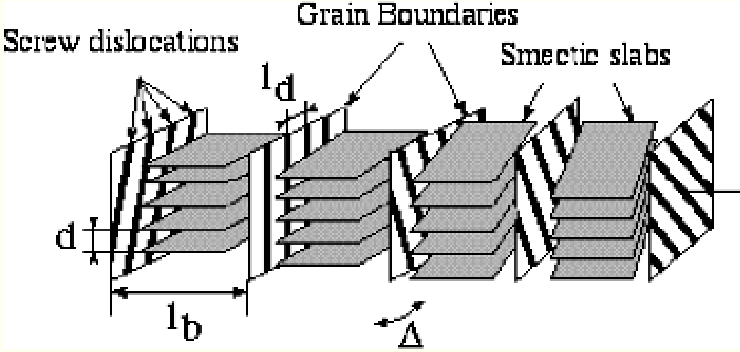
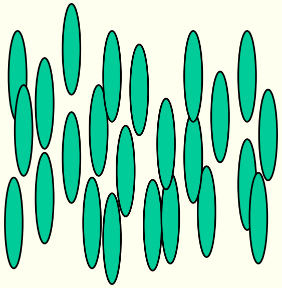


Liquid Crystal Phases

- large variety of phases:



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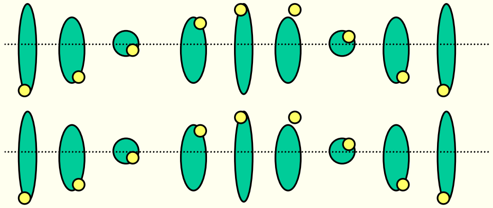
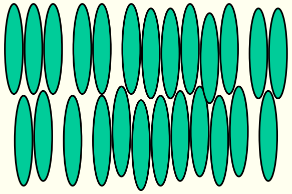


cholesteric



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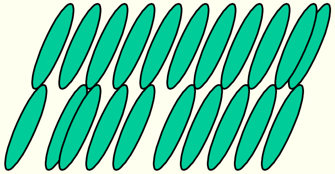


smectic C

+ ferroelectic,
blue, TGB,
bananas,
etc...

Orientation & Orientational Order

- need to quantify orientation & orientational order to
  - construct statistical description
  - relate physical properties of orientational order
  - predict materal response to excitations

- need orientational descriptor & order parameter

- how to define these?

Orientation & Orientational Order

- orientation of rigid body is defined by Euler angles; orientational distribution fn. $P(\theta,\phi,\psi)$ has all info.
- may not respect symmetry
- too much information

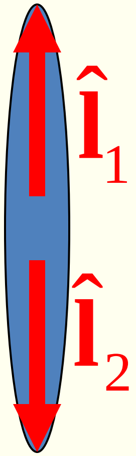
- Examples of orientational order parameters:
  - Ferromagnetics: $\uparrow\mathbf{m}$ magnetization $\mathbf{M} = \rho < \mathbf{m} >$
  - Ferroelectrics: $\uparrow\mathbf{p}$ polarization $\mathbf{P} = \rho < \mathbf{p} >$

vectors – related to the symmetry of constituents

Nematic liquid crystals

- orientational order parameter?

- two equivalent directions:



- expressions which treat these the same:

$$\xcancel{\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2} \qquad = 0!$$

$$\frac{1}{2}(\hat{\mathbf{l}}_1\hat{\mathbf{l}}_2 + \hat{\mathbf{l}}_2\hat{\mathbf{l}}_1) \quad = -\hat{\mathbf{l}}_1\hat{\mathbf{l}}_1 = -\hat{\mathbf{l}}_2\hat{\mathbf{l}}_2 = -\hat{\mathbf{l}}\hat{\mathbf{l}}$$

$$\xcancel{\hat{\mathbf{l}}_1\hat{\mathbf{l}}_1\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2\hat{\mathbf{l}}_2\hat{\mathbf{l}}_2} \qquad \text{not necessary}$$

use $\hat{\mathbf{l}}\hat{\mathbf{l}}$

Nematic Liquid Crystals

- orientation descriptor:
  - second rank tensor

$$\boldsymbol{\sigma} = \frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I})$$

$$\boldsymbol{\sigma} = \begin{bmatrix} \frac{1}{2}(3l_x{}^2 - 1) & \frac{3}{2}l_x l_y & \frac{3}{2}l_x l_z \\ \frac{3}{2}l_y l_x & \frac{1}{2}(3l_y{}^2 - 1) & \frac{3}{2}l_y l_z \\ \frac{3}{2}l_z l_x & \frac{3}{2}l_x l_y & \frac{1}{2}(3l_z{}^2 - 1) \end{bmatrix}$$

- orientational order parameter:
  - traceless symmetric

$$\mathbf{Q} = < \frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I}) >$$

Representation

$$\mathbf{Q} = \begin{bmatrix} -\frac{1}{2}(S-P) & 0 & 0 \\ 0 & -\frac{1}{2}(S+P) & 0 \\ 0 & 0 & S \end{bmatrix}$$

eigenvectors: $\hat{\mathbf{j}}, \hat{\mathbf{m}}, \hat{\mathbf{n}}$

$$S =< \frac{1}{2}(3(\hat{\mathbf{l}}\cdot\hat{\mathbf{n}})^2 - 1 >$$

$$P = 3((\hat{\mathbf{l}}\cdot\hat{\mathbf{j}})^2 - (\hat{\mathbf{l}}\cdot\hat{\mathbf{m}})^2)$$

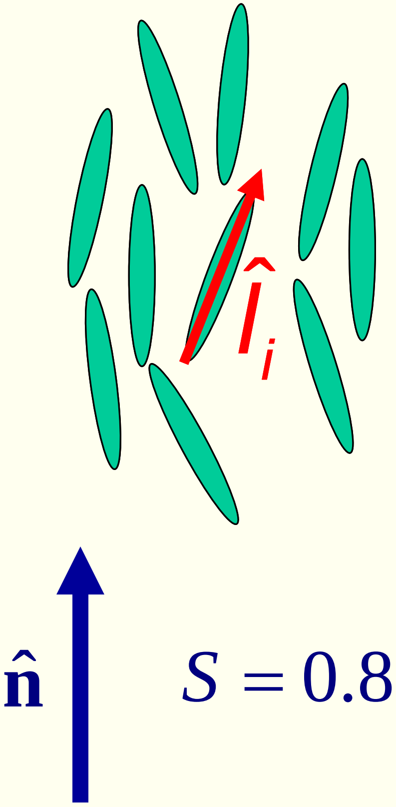
- *S* and *P* are scalar order parameters

- eigenvalue decomposition:

$$\mathbf{Q} = P(\hat{\mathbf{j}}\hat{\mathbf{j}} - \hat{\mathbf{m}}\hat{\mathbf{m}}) + S\frac{1}{2}(3\hat{\mathbf{n}}\hat{\mathbf{n}} - \mathbf{I})$$

usually, *P* = 0!

Nematic liquid crystals



$$S = 0.8$$

- order parameter:
  - symmetric traceless tensor

$$\mathbf{Q} = < \frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I}) >$$

- eigenvectors:
  - direction of alignment: nematic director $\hat{\mathbf{n}}$

$$\mathbf{Q} = S\frac{1}{2}(3\hat{\mathbf{n}}\hat{\mathbf{n}} - \mathbf{I})$$

- eigenvalues:
  - degree of alignment: order parameter S

$$S = < \frac{1}{2}(3(\hat{\mathbf{l}} \cdot \hat{\mathbf{n}})^2 - 1 >$$

3 levels of description:

- director: $\hat{\mathbf{n}}$
  - direction of average orientation
- Q-tensor: $\mathbf{Q} = < \frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I}) >$
  - direction and degree of average orientation
- probability density: $\rho(\boldsymbol{\sigma})$
  - complete description of the distribution

Frank - Oseen free energy density

- first phenomenological description:

$$\mathcal{F} = \frac{1}{2}K_1(\nabla\cdot\hat{\mathbf{n}})^2 + \frac{1}{2}K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + \frac{1}{2}K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2$$

splay twist bend

- elastic constants have units of *force*

- deformations are Goldstone modes (unstable?)*

- does not have right symmetry (problem at defects)*

Smectic -superconductor analogy

- layered structure is not consistent with curl or bend

- layers without defects: must have

$$\oint \hat{\mathbf{n}} \cdot d\mathbf{l} = 0$$

Smectic -Superconductor analogy

- layers without defects: must have

$$\oint \hat{\mathbf{n}} \cdot d\mathbf{l} = \int (\nabla \times \hat{\mathbf{n}}) \cdot d\mathbf{A} = 0$$

- so elastic constants K_2 , K_3 diverge at $\mathrm{S_A}$ transition

- $\hat{\mathbf{n}}$ corresponds to magnetic potential

- $\nabla \times \hat{\mathbf{n}}$ is expelled (Meissner effect)

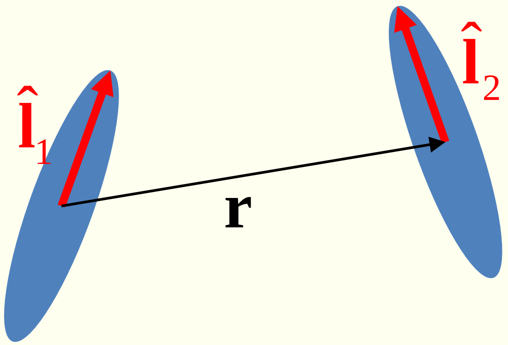
P.G. de Gennes, Sol. Ste. Commun. **10**, 753, (1972).

Mean Field Theories of Liquid Crystals

- Max Born:
  - first mean field theory of liquid crystals
  - assumed vector order parameter $<\hat{\mathbf{l}}>$
  - unsuccessful

Mean Field Theories of Nematics

- Maier-Saupe theory:



- Van der Waals interaction:

$$\mathcal{E}_{1,2} = \mathcal{E}_{iso} - \frac{u\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2}{r^6}$$

- single particle potential:

$$\mathcal{E} = -\rho U\boldsymbol{\sigma}\mathbf{Q} + \frac{1}{2}\rho U\mathbf{Q}\mathbf{Q}$$

  - second term corrects for overcounting

Free Energy

- partition function: $Z = \frac{1}{N!}\left[V \int e^{-\mathcal{E}/kT} d\Omega \right]^N$

- free energy density: $\mathcal{F} = -\frac{kT}{V} \ln Z = -\rho kT \ln \int e^{-\mathcal{E}/kT} d\Omega$

$$\boxed{\mathcal{F} = \frac{1}{2}\rho^2 U \mathbf{Q}^2 - \rho kT \ln \int e^{\rho U \boldsymbol{\sigma}\mathbf{Q}/kT} d\Omega}$$

Equilibrium value of $Q_{\alpha\beta}$ minimizes $\mathcal{F}$.

Self-consistent equation

- Minimizing the free energy $\frac{\partial \mathcal{F}}{\partial Q_{\alpha\beta}} = 0$ gives the self-consistent equation

$$\mathbf{Q} = \frac{\int \boldsymbol{\sigma} e^{\rho U \boldsymbol{\sigma} \mathbf{Q}/kT} d\Omega}{\int e^{\rho U \boldsymbol{\sigma} \mathbf{Q}/kT} d\Omega}$$

This can be solved numerically.

Landau Theory of Nematics

- The Maier-Saupe free energy

$$\mathcal{F}_{MS} = \frac{1}{2}\rho^2 U\mathbf{Q}^2 - \rho kT \ln \int e^{\rho U \boldsymbol{\sigma}\mathbf{Q}/kT} d\Omega$$

- can be expanded in $\mathbf{Q}$:

$$\boxed{\mathcal{F}_L = \frac{1}{2}A_o(\frac{T}{T_c} - 1)\mathbf{Q}^2 - \frac{1}{3}B\mathbf{Q}^3 + \frac{1}{4}C\mathbf{Q}^4 + ..}$$

Maier-Saupe Theory

- minimizing $\mathcal{F}_{MS}$ gives $P=0$ so

$$\mathcal{F}_{MS} = \frac{1}{2}\rho^2 US^2 - \rho kT \ln \int e^{\rho US \frac{1}{2}(3\cos^2\theta - 1)/kT} d\Omega$$

- and

$$S = \frac{\int \frac{1}{2}(3\cos^2\theta - 1) e^{\rho US \frac{1}{2}(3\cos^2\theta - 1)/kT} d\cos\theta}{\int e^{\rho US \frac{1}{2}(3\cos^2\theta - 1)/kT} d\cos\theta}$$

- and

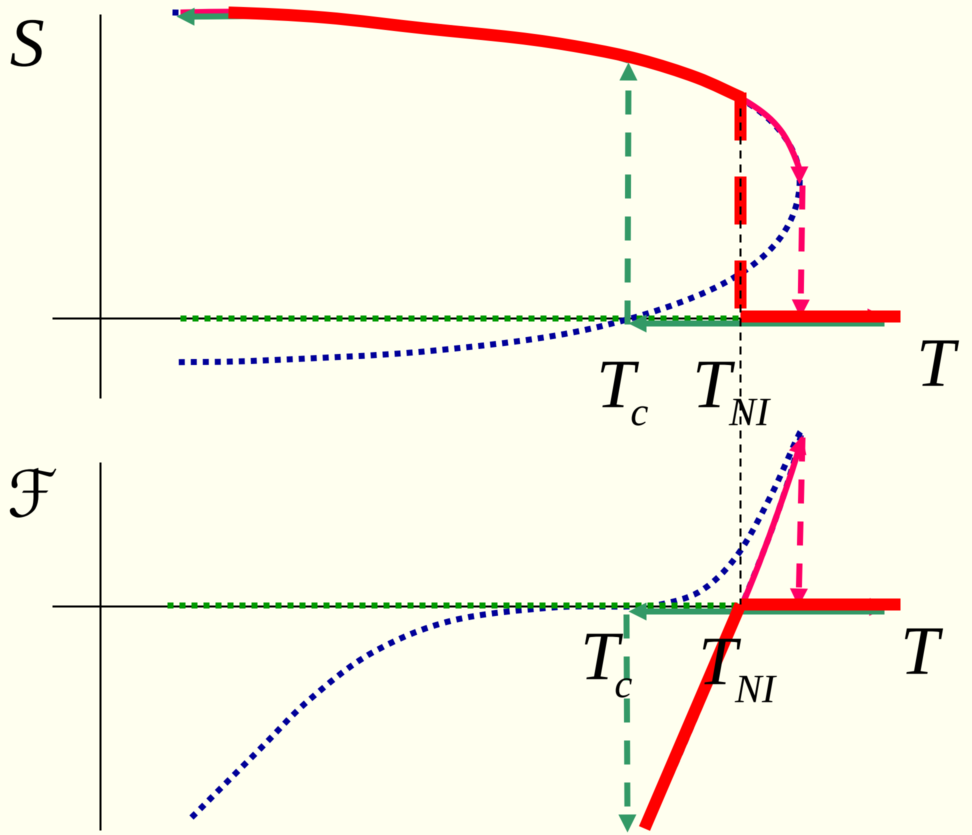
$$S = < \frac{1}{2}(3\cos^2\theta - 1 >$$

Maier-Saupe Theory

- S scalar order parameter
- $\hat{\mathbf{n}}$ nematic director

$$S = < \frac{1}{2}(3\cos^2\theta - 1 >$$

first order
phase transition



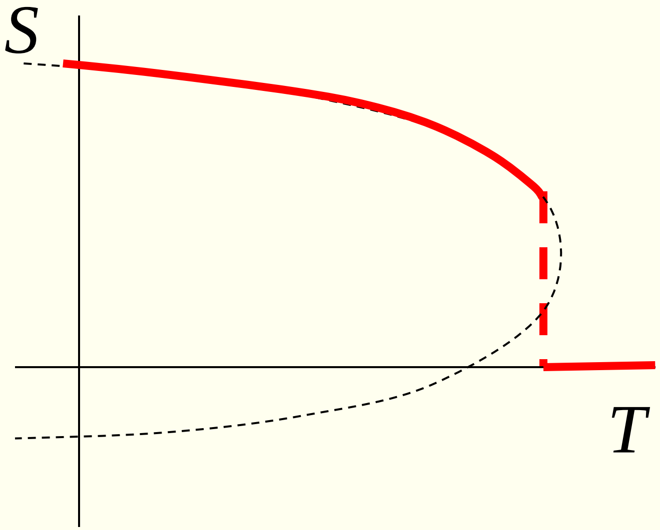
Landau Theory

- minimizing $\mathcal{F}_L$ gives $P=0$ so

$$\mathcal{F}_L=\frac{1}{2}a_o(\frac{T}{T_c}-1)S^2-\frac{1}{3}bS^3+\frac{1}{4}cS^4+..$$

- and

$$S=\frac{b}{2c}\pm\sqrt{(\frac{b}{2c})^2-\frac{a_o}{c}(\frac{T}{T_c}-1)}$$

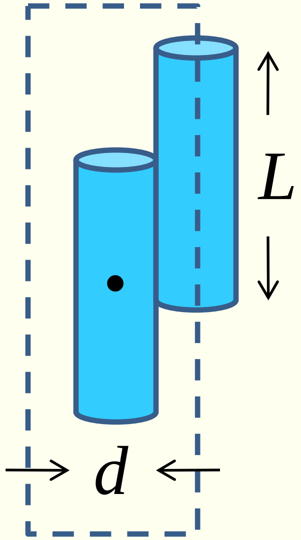


Steric Interactions

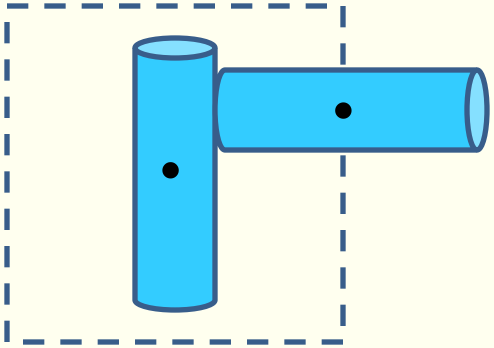
- Lars Onsager
  - developed theory of packing of hard rods
  - found that sufficiently dense assemblies of hard rods had orientational order

Excluded volume

- one particle makes volume V_{ex} unavailable to the center of another



$$V_{\|} \simeq 2\pi d^2 L$$



$$V_{\perp} \simeq 2dL^2$$

$$V_{ex} = (\frac{V_{\|} + 2V_{\perp}}{3}) + \frac{4}{3}(V_{\|} - V_{\perp})\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$$

Excluded volume

- volume exclude by one particle with orientation $\boldsymbol{\sigma}$

$$V_{ex} = (\frac{V_{\|} + 2V_{\perp}}{3}) + \frac{4}{3}(V_{\|} - V_{\perp})\boldsymbol{\sigma}\mathbf{Q} = v_o(1 + \Delta\boldsymbol{\sigma}\mathbf{Q})$$

- volume per molecule, on average

$$v_m = \frac{1}{2}v_o(1 + \Delta\mathbf{Q}^2)$$

- similar to attractive part of potential!

Steric Interactions: van der Waals approach

- free energy density:

$$\mathfrak{F} = \rho E - \rho T S_{pos} - \rho T S_{or}$$

- define pseudopotential $\mathcal{E}$ which contains steric effects

$$\mathfrak{F} = \rho E - \rho kT \ln\left[\frac{V - v_m}{N}\right] - \rho < \mathcal{E} > - \rho kT \ln \int e^{-\mathcal{E}/kT} d\Omega$$

- if $E(Q)$ and $v_m(Q)$ are known, $\mathcal{E}(Q,\sigma)$ can be determined self-consistently.

Steric Interactions: Van der Waals approach

- average energy:

$$E = -\frac{1}{2}\rho\gamma(1+uQ^2)$$

- average volume:

$$v_m = \frac{1}{2}v_o(1-\Delta Q^2)$$

- self-consistency:

$$\mathcal{E} = -\left[\rho\gamma u + \frac{\Delta kT}{\frac{1}{\rho v_o} - \frac{1}{2}(1-\Delta Q^2)}\right] Q_{\alpha\beta}\sigma_{\alpha\beta}$$

- single particle potential contains steric contribution*.

Equation of State

- the pressure is

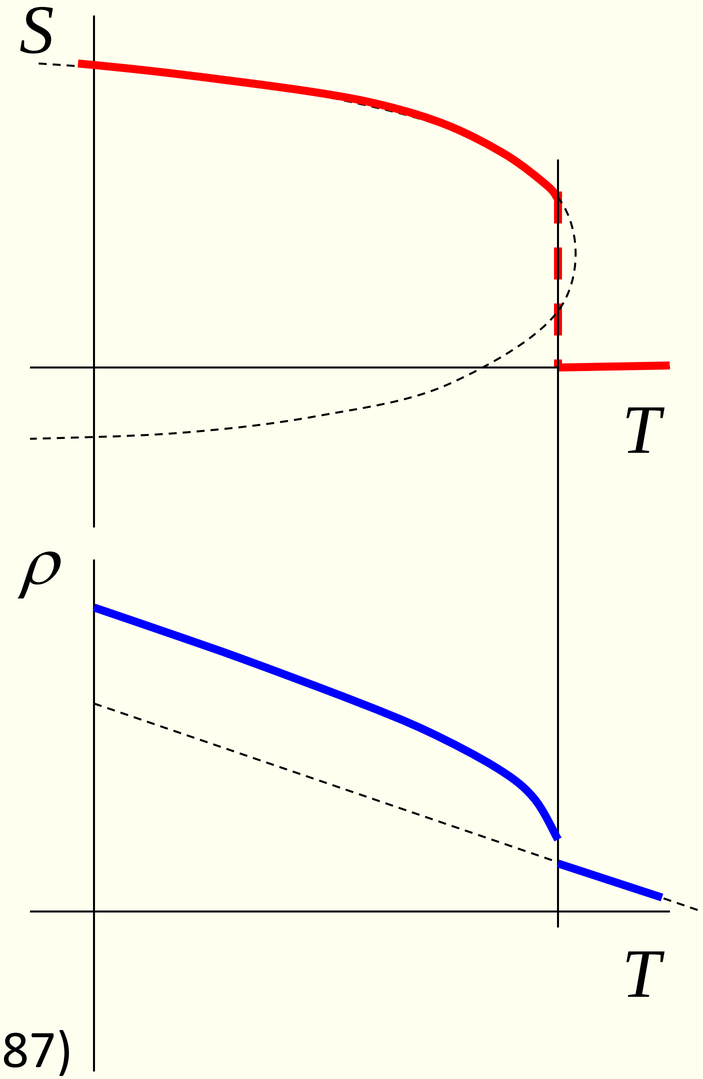
$$P = -\frac{\partial \mathcal{F}}{\partial \rho}$$

$$P = -\rho^2\gamma(1+uQ^2) + \frac{kT}{\frac{1}{\rho} - \frac{1}{2}v_o(1-\Delta Q^2)}$$

- where

$$\mathrm{Q} = \frac{\int \sigma e^{-\mathcal{E}/kT}\, d\Omega}{\int e^{-\mathcal{E}/kT}\, d\Omega}$$

Steric Effects:



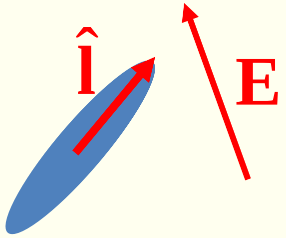
- order parameter:

- density change:

P.P-M, B. Bergersen, *Phys Rev. E* **53,** 2704 (1987)

Electric & Magnetic Susceptibilities

- fundamental importance!



- induced dipole moment:

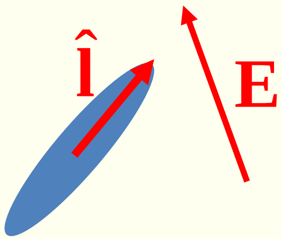
$$\mathbf{p} = \alpha_{\|}(\mathbf{E}\cdot\hat{\mathbf{l}})\hat{\mathbf{l}} + \alpha_{\perp}(\mathbf{E} - (\mathbf{E}\cdot\hat{\mathbf{l}})\hat{\mathbf{l}})$$

$$\boldsymbol{\alpha} = (\frac{\alpha_{\|} + 2\alpha_{\perp}}{3})\mathbf{I} + \frac{2}{3}(\alpha_{\|} - \alpha_{\perp})\frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I})$$

$$< \boldsymbol{\alpha} >= \alpha_{av}\mathbf{I} + \Delta\alpha\mathbf{Q}$$

Electric & Magnetic Susceptibilities

- dielectric tensor:



$$\mathbf{D} = \boldsymbol{\varepsilon}\mathbf{E} = \varepsilon_o \mathbf{E} + \mathbf{P}$$

$$\boldsymbol{\varepsilon}\mathbf{E} = (\varepsilon_o \mathbf{I} + \rho \boldsymbol{\alpha})\mathbf{E}$$

$$\boldsymbol{\alpha} = \alpha_{av}\mathbf{I} + \Delta\alpha \mathbf{Q}$$

$$\boxed{\boldsymbol{\varepsilon} = (\varepsilon_o + \rho\alpha_{avg})\mathbf{I} + \rho\Delta\alpha\mathbf{Q}}$$

- but

$$\mathbf{Q} = S\frac{1}{2}(3\hat{\mathbf{n}}\hat{\mathbf{n}} - \mathbf{I})$$

- and

$$\boldsymbol{\varepsilon} = \varepsilon_o[\varepsilon_\perp \mathbf{I} + (\varepsilon_{||} - \varepsilon_\perp)\hat{\mathbf{n}}\hat{\mathbf{n}}]$$

Coupling to fields

- dielectric permittivity:

$$\boldsymbol{\varepsilon} = \varepsilon_o[\varepsilon_\perp \mathbf{I} + \Delta\varepsilon \hat{\mathbf{n}}\hat{\mathbf{n}}]$$

$$(\varepsilon_\perp \approx 10, \qquad \Delta\varepsilon \approx 10)$$

- diamagnetic permeability:

$$\boldsymbol{\mu} = \mu_o[\mu_\perp \mathbf{I} + \Delta\mu \hat{\mathbf{n}}\hat{\mathbf{n}}]$$

$$(\mu_\perp \approx 1, \qquad \Delta\mu \approx 10^{-4})$$

$$\mathcal{F}_L = \frac{1}{2}A\mathbf{Q}^2 - \frac{1}{3}B\mathbf{Q}^3 + \frac{1}{4}C\mathbf{Q}^4 + .. - \frac{1}{2}\Delta\varepsilon'\mathbf{QEE} - \frac{1}{2}\Delta\mu'\mathbf{QBHH}$$

or

$$\mathcal{F}_L = \frac{1}{2}aS^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 + .. - \frac{1}{2}\Delta\varepsilon(\mathbf{E}\cdot\hat{\mathbf{n}})^2 - \frac{1}{2}\Delta\mu(\mathbf{B}\cdot\hat{\mathbf{n}})^2$$

Symmetry arguments:

- linear coupling?
  - no; cannot make scalar from tensor $Q_{\alpha\beta}$ and vector E_α

- coupling is quadratic: $Q_{\alpha\beta}E_\alpha E_\beta$

or

$$D_\alpha E_\alpha = \varepsilon_{\alpha\beta}E_\beta E_\alpha = (\bar{\varepsilon}\delta_{\alpha\beta} + \Delta\varepsilon Q_{\alpha\beta})E_\beta E_\alpha$$

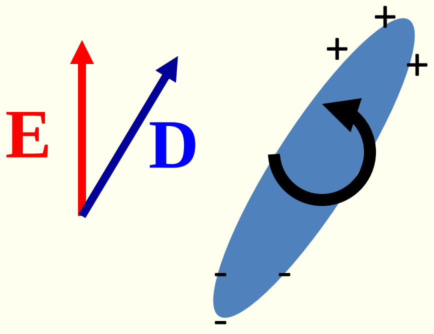
$$\mathfrak{F} = \frac{1}{2}a_o(\frac{T}{T_c} - 1)\mathbf{Q}^2 - \frac{1}{3}b\mathbf{Q}^3 + \frac{1}{4}c(\mathbf{Q}^2)^2 + .. \quad -\frac{1}{2}\Delta\varepsilon\mathbf{QEE}$$

- free energy is minimized if molecules/director align with field

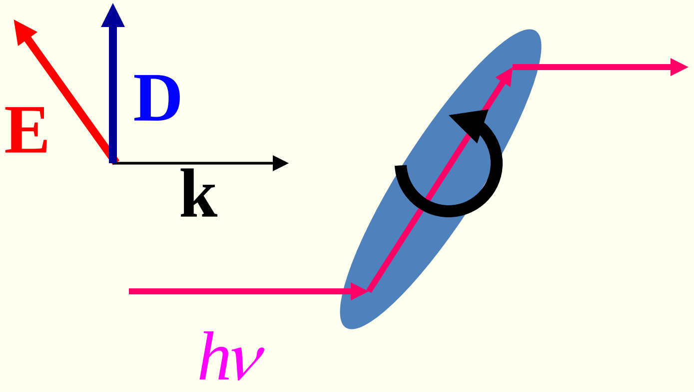
Torque Density

- If **D** and **E** are not parallel, a torque is exerted on the material,

$$\boldsymbol{\tau} = \mathbf{D} \times \mathbf{E}$$

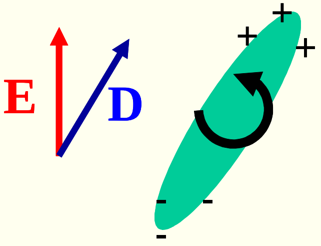


DC field

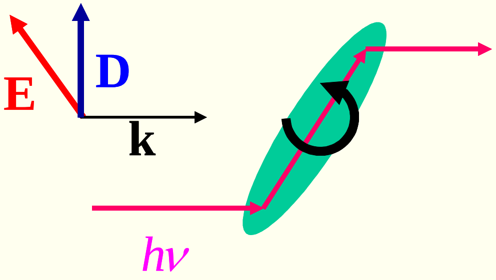


optical field

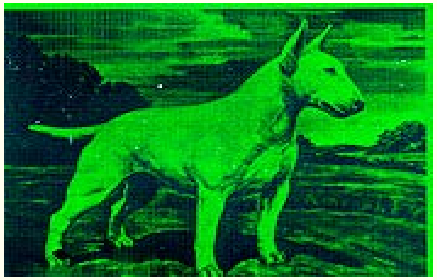
Applications



DC field



optical field



laser written
image in CLC cell

Gradients

- What if **Q** varies in space?

$$\mathcal{F} = \mathcal{F}_o + L_1 \frac{\partial Q_{\alpha\beta}}{\partial x_\alpha}\frac{\partial Q_{\gamma\beta}}{\partial x_\gamma} + L_2 \frac{\partial Q_{\alpha\beta}}{\partial x_\gamma}\frac{\partial Q_{\alpha\beta}}{\partial x_\gamma} + L_3 \frac{\partial Q_{\alpha\beta}}{\partial x_\gamma}\frac{\partial Q_{\alpha\gamma}}{\partial x_\beta}$$

$$\mathcal{F}_L = \frac{1}{2}aS^2 - \frac{1}{3}bS^3 + \frac{1}{4}cS^4 + ..\frac{1}{2}L(\nabla S)^2$$

$$+\underbrace{\frac{1}{2}K_1(\nabla\cdot\hat{\mathbf{n}})^2 + \frac{1}{2}K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + \frac{1}{2}K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2}_{\text{Goldstone Modes}}$$

Dimensional Analysis

- how large are *a,b,c,…?*

$$b \simeq \frac{kT_{NI}}{l_{mol}{}^{3}}$$

- how large are *K’s?*

$$K \simeq \frac{kT_{NI}}{l_o}$$

(de Gennes)

- cost of varying *S*:

$$\Delta\mathcal{F}_S \simeq \frac{kT_{NI}}{l_{mol}{}^{3}}$$

- cost of varying $\hat{\mathbf{n}}$:

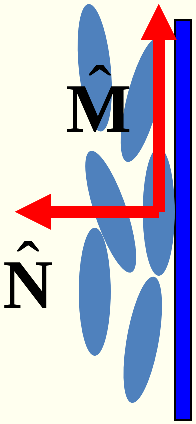
$$\Delta\mathcal{F}_{\hat{\mathbf{n}}} \simeq \frac{kT}{l_{mol}} q^2$$

$$\frac{\Delta\mathcal{F}_{\hat{\mathbf{n}}}}{\Delta\mathcal{F}_S} = q^2 l_{mol}{}^{2}$$

small!

Surface interactions

- surface free energy density



$$\mathcal{F}_S = \frac{1}{2} w_1 \mathbf{Q}\hat{\mathbf{N}}\hat{\mathbf{N}} + \frac{1}{2} w_2 \mathbf{Q}\hat{\mathbf{M}}\hat{\mathbf{M}}$$

$$\mathcal{F}_S = \frac{1}{2} W_1 (\hat{\mathbf{n}} \cdot \hat{\mathbf{N}})^2 + \frac{1}{2} W_2 (\hat{\mathbf{n}} \cdot \hat{\mathbf{M}})^2$$

Rapini-Papular

Surface interactions

- bulk and surface contributions in sample of size *R*:

$$F = F_o + \int \frac{1}{2} K (\nabla \cdot \hat{\mathbf{n}})^2 \, dV + \int \frac{1}{2} W (\hat{\mathbf{n}} \cdot \hat{\mathbf{N}})^2 \, dA$$

$$\sim R \qquad\qquad\qquad \sim R^2$$

For large samples, *surface* dominates!

Surface preparation

- spin-coat polyimide on surface

- rub with rubbing machine

- can also use:
  - lecithin, siloxane, smoke, (carbon), paper,..

- corrugate surface

- photosensitive materials: azo dyes in polymer
  - use light for photoalignment

Dynamics

- basic idea:

$$T\dot{S} = -\frac{dF}{dt}$$

$$\gamma \dot{\mathbf{Q}}^2 = -\frac{\delta \mathcal{F}}{\delta \mathbf{Q}} \dot{\mathbf{Q}}$$

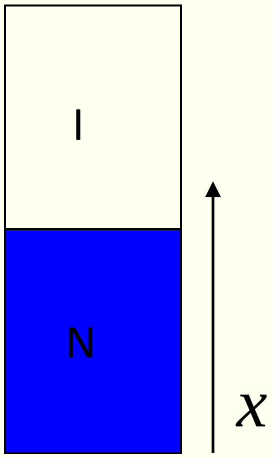
- and

$$\gamma \frac{\partial Q_{\alpha\beta}}{\partial t} = -\frac{\delta \mathcal{F}}{\delta Q_{\alpha\beta}}$$

switching
front propagation
defect dynamics,
etc.

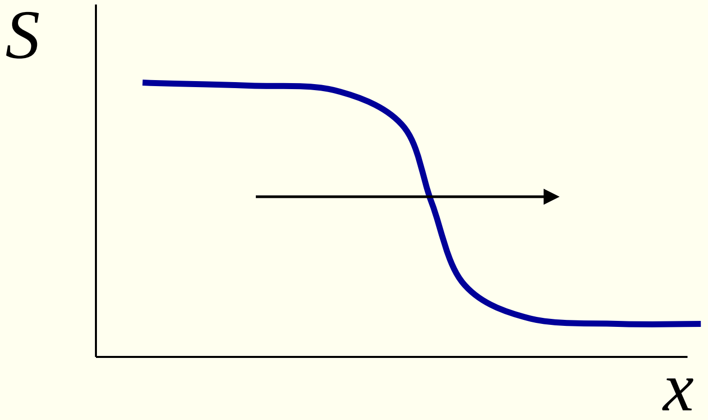
Dynamics: Examples

- interface dynamics



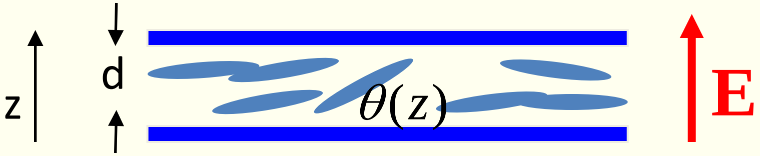
$$\gamma \frac{\partial S}{\partial t} = \kappa \frac{\partial^2 S}{\partial x^2} - aS + bS^2 - cS^3$$

$$S = \frac{1}{2} S_o (1 - \tanh(x - vt))$$



Dynamics: Examples

- nematic cell in E-field



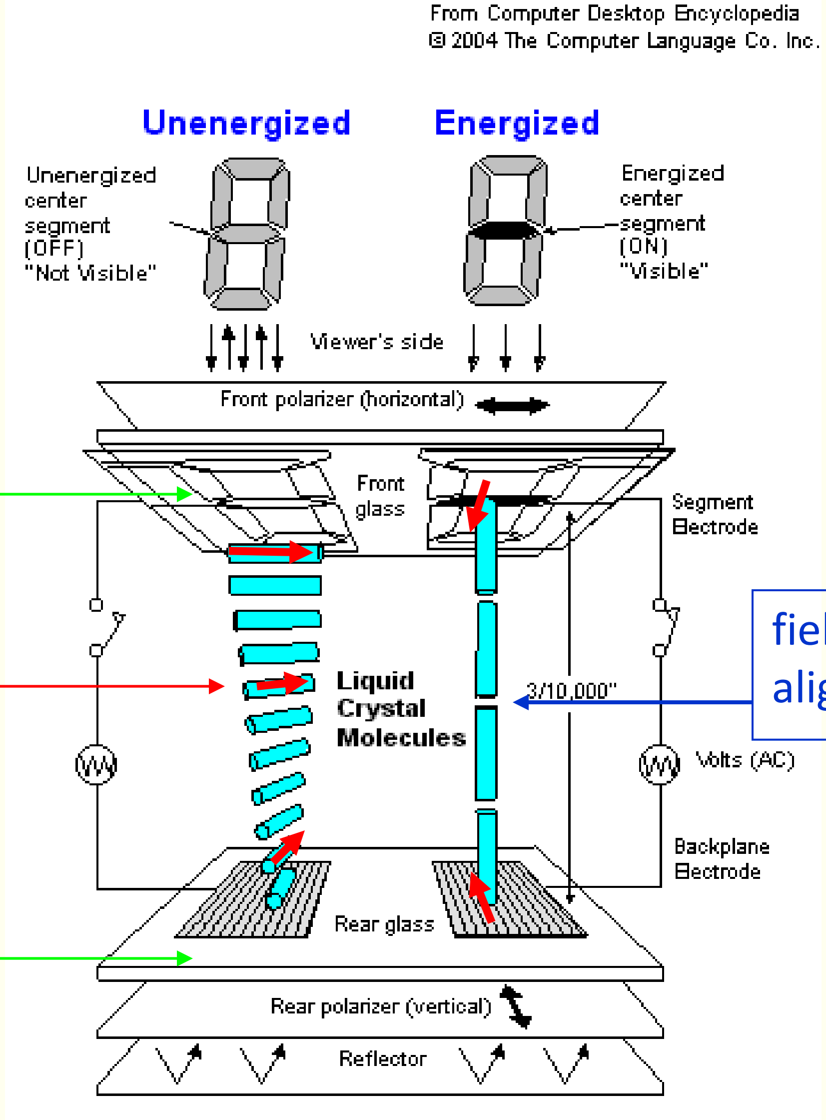
$$\gamma \frac{\partial \theta}{\partial t} = K \frac{\partial^2 \theta}{\partial z^2} + \varepsilon_o \Delta \varepsilon E^2 \sin\theta \cos\theta$$

  - switching time:

$$\tau = \frac{\gamma d^2}{\pi^2 K (1 - (E / E_c)^2)}$$

Twisted Nematic Cell

- how a TN cell works:



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surface alignment layer

polarization of light follows director

field induced alignment

surface alignment layer

Some symmetry considerations

- symmetry arguments have played an important role

- what is allowed by symmetry, is observed experimentally!

Flexoelectricity

- Coupling between Q and E is quadratic – cannot make linear term in E which is a scalar.

$$Q_{\alpha\beta} E_\alpha E_\beta$$

- CAN make a linear coupling if gradients are allowed!

$$\frac{\partial Q_{\alpha\beta}}{\partial x_\alpha} E_\beta$$

- coefficient of linear E in free energy must be P
  - distortion induced polarization: ‘flexoelectricity’

Flexoelectricity

- consider the vector

$$\frac{\partial}{\partial x_\alpha}\varepsilon_{\alpha\beta} = \frac{\partial}{\partial x_\alpha}(\bar{\varepsilon}\delta_{\alpha\beta} + \Delta\varepsilon Q_{\alpha\beta}) = \Delta\varepsilon\frac{\partial}{\partial x_\alpha}Q_{\alpha\beta}$$

$$= \Delta\varepsilon(S(\nabla\bullet\hat{\mathbf{n}})\hat{\mathbf{n}} + S(\nabla\times\hat{\mathbf{n}})\times\hat{\mathbf{n}} + (\hat{\mathbf{n}}\bullet\nabla S)\hat{\mathbf{n}})$$

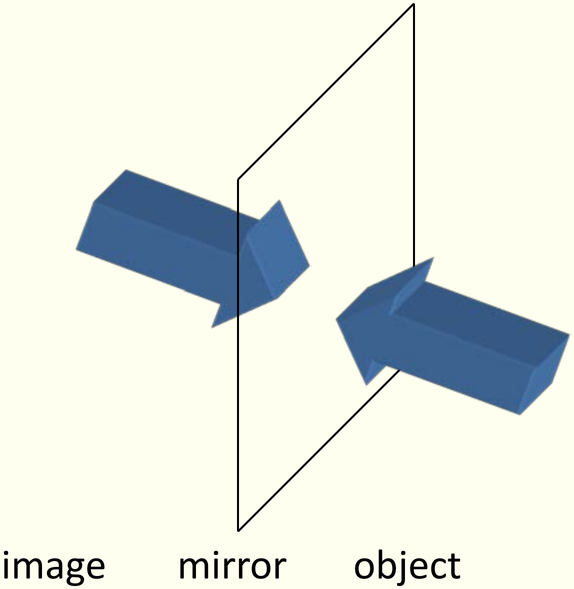
- must result in electric polarization;

$$\mathbf{P} \sim (\nabla\bullet\hat{\mathbf{n}})\hat{\mathbf{n}} + (\nabla\times\hat{\mathbf{n}})\times\hat{\mathbf{n}}$$ flexoelectricity (R.B. Meyer, 1969)

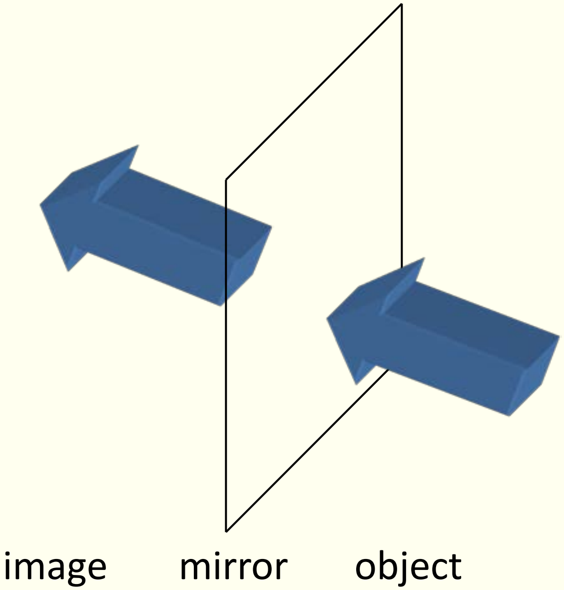
$$\mathbf{P} \sim (\hat{\mathbf{n}}\bullet\nabla S)\hat{\mathbf{n}}$$ order electricity (G. Durand, 1986)

Vampires and pseudovectors

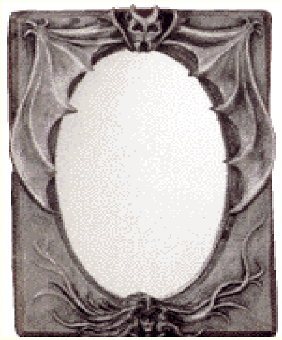
- to detect a vampire, look at him/her through a mirror….



proper (polar) vector



pseudo (axial) vector



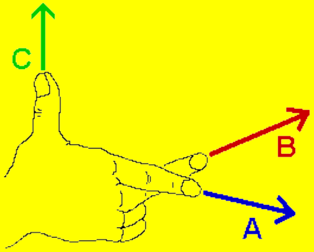
Proper- and pseudo-tensors

tensor rank	0	1	2	3	4
proper	$\pi\ ,\quad x$	$\mathbf{E},\ \mathbf{P},\ \mathbf{D}$	$\delta_{\alpha\beta},\ Q_{\alpha\beta}$ $\varepsilon_{\alpha\beta},\ \mu_{\alpha\beta}$	$d_{\alpha\beta\gamma}$	etc.
pseudo	$\mathbf{A}\bullet(\mathbf{B}\times\mathbf{C})$	$\mathbf{H},\ \mathbf{M},\ \mathbf{B}$	$\Gamma_{\alpha\beta}$	ε_{ijk}	

scalar vector

🟧 changes sign on inversion

🟦 does not change sign on inversion

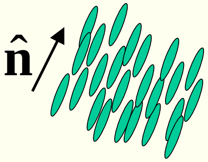


handedness = pseudoscalar c*!

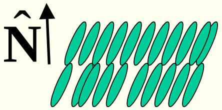
,

Ferroelectricity in liquid crystals

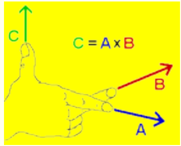
- in nematics, have director $\hat{\mathbf{n}}\hat{\mathbf{n}}$



- in smectics, have, in addition, layer normal $\hat{\mathbf{N}}\hat{\mathbf{N}}$



- and if material is chiral, have pseudoscalar c^*



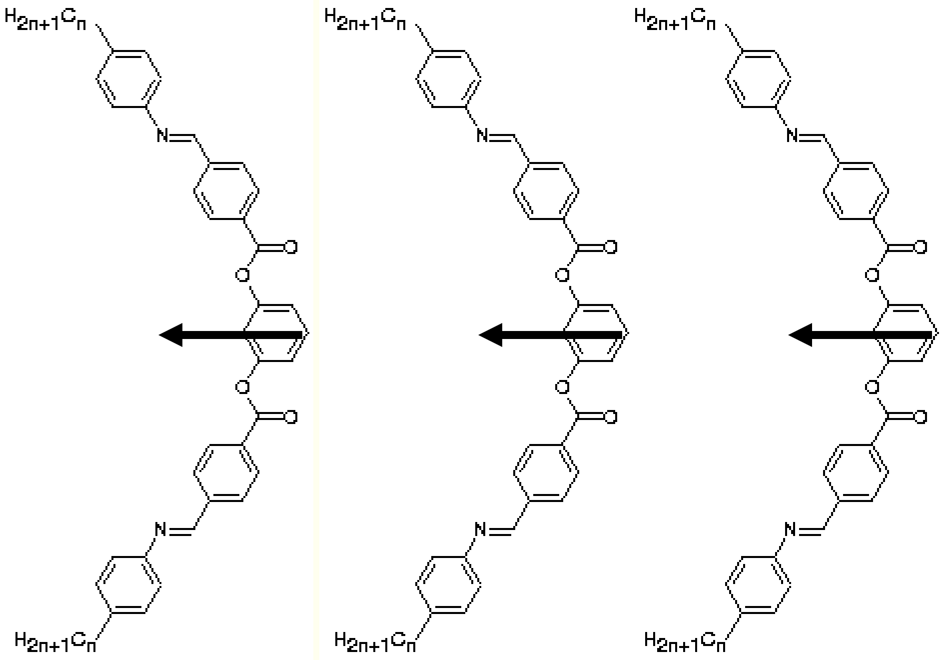
- can therefore form a proper vector $(\hat{\mathbf{n}}\bullet\hat{\mathbf{N}})(\hat{\mathbf{n}}\times\hat{\mathbf{N}})c^*$

$\therefore$ spontaneous polarization & ferroelecticity!

R.B. Meyer predicted the possibility of ferroelectric liquid crystals in 1974, and demonstrated this in 1975 with Liebert, Strzelecki and Keller. To date, over 50,000 ferroelectric liquid crystal compounds have been synthesized.

Banana liquid crystals

- banana shaped molecules
    - *achiral*, polar
- form *chiral* smectic phases!



- in nematics, have director
- in smectics, have, in addition, layer normal
- have polarization vector
- can form pseudoscalar

∴ chiral!

$$\hat{\mathbf{n}}\hat{\mathbf{n}}$$

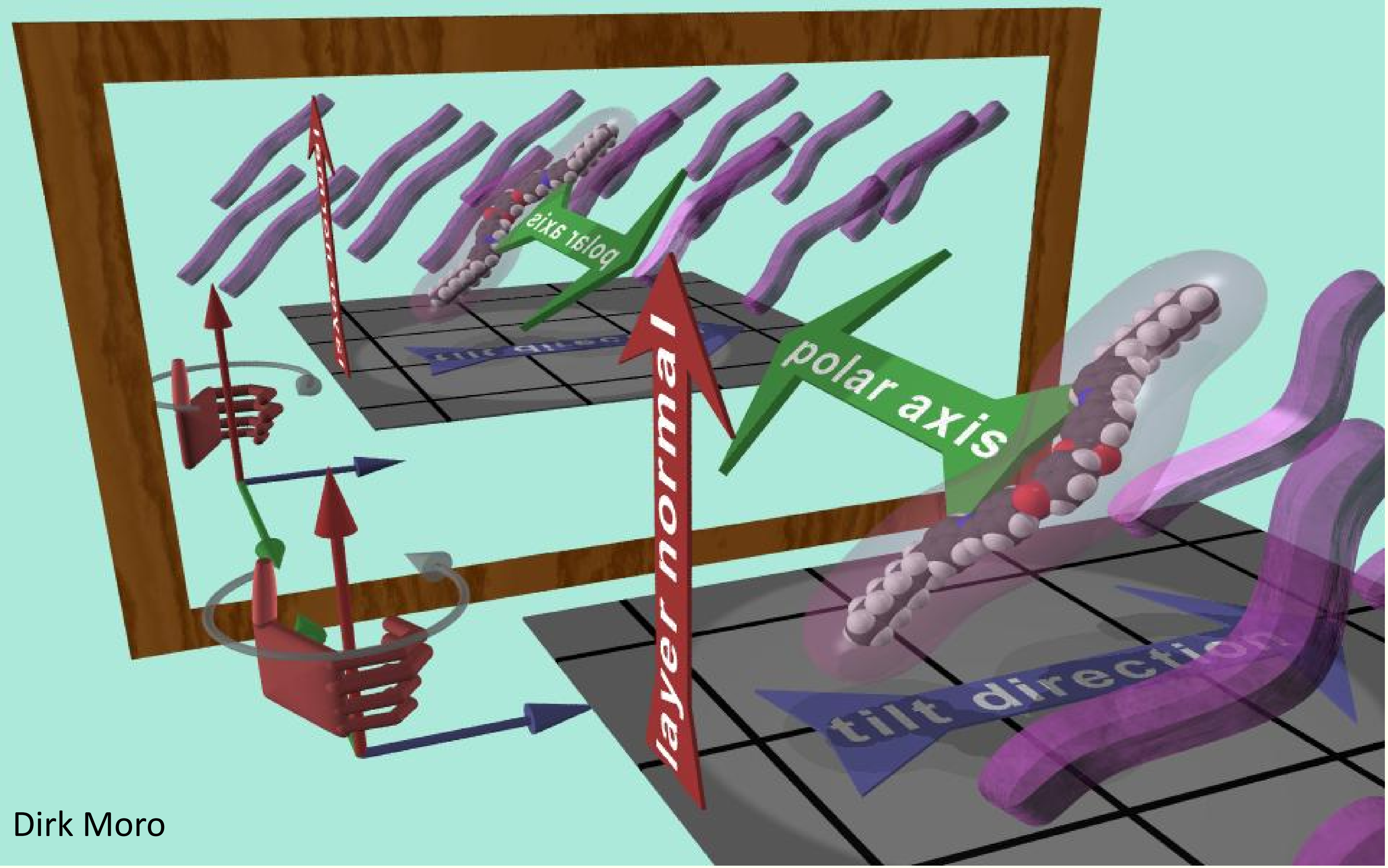
$$\hat{\mathbf{N}}\hat{\mathbf{N}}$$

$$\mathbf{P}$$

$$c^* = [\hat{\mathbf{N}} \bullet (\mathbf{P} \times \hat{\mathbf{n}})](\hat{\mathbf{N}} \bullet \hat{\mathbf{n}})$$

de Gennes, 1974

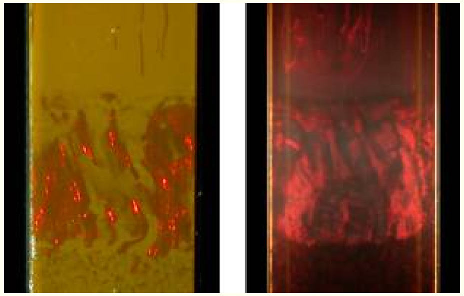
Chiral phase of banana liquid crystal



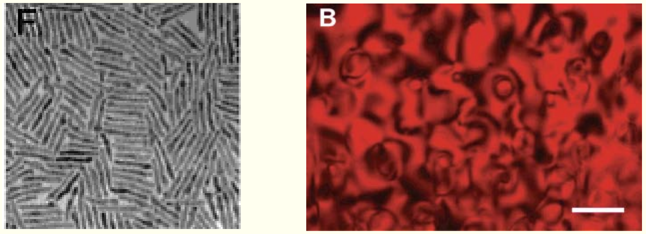
Dirk Moro

Nanoparticle Liquid Crystals

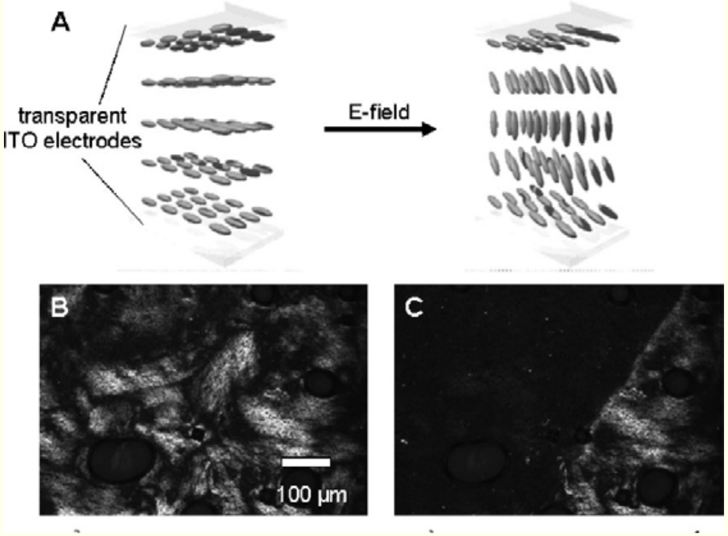
- goethite (alpha-FeOOH) nanorods form nematic phases
  - Davidson, Orsay



- semiconductor nanorods form nematic phases
  - Alivisatsos, Berkeley

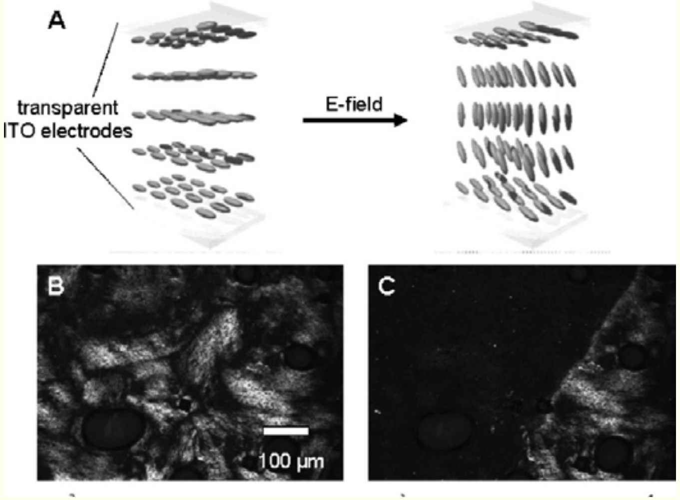


Nanoparticle liquid crystals



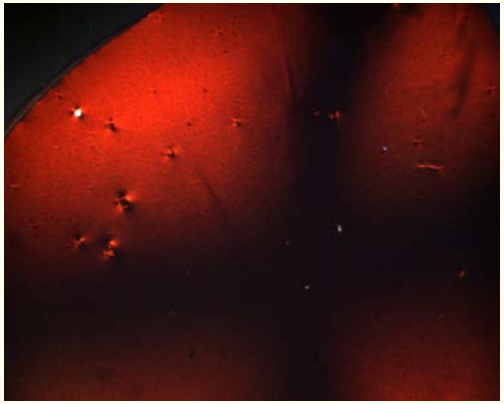
Nanoparticle Liquid Crystals: switchable

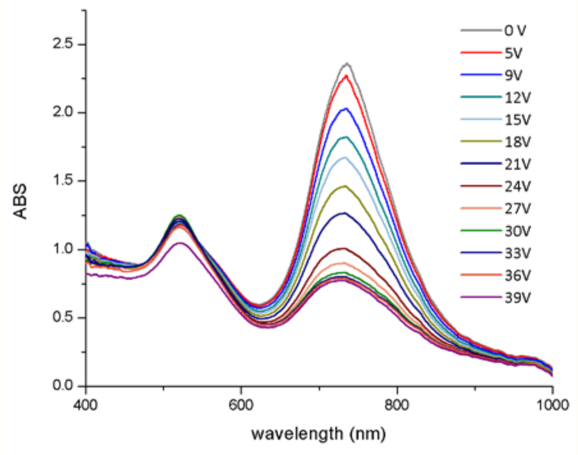
- ZnO nanorods



M. Zorn, M. Tahir, B. Bergmann W. Tremel, C. Grigoriadis, G. Floudas and R. Zentel, , *Macromol. Rapid Comm.* **31**, 1101 (2010)

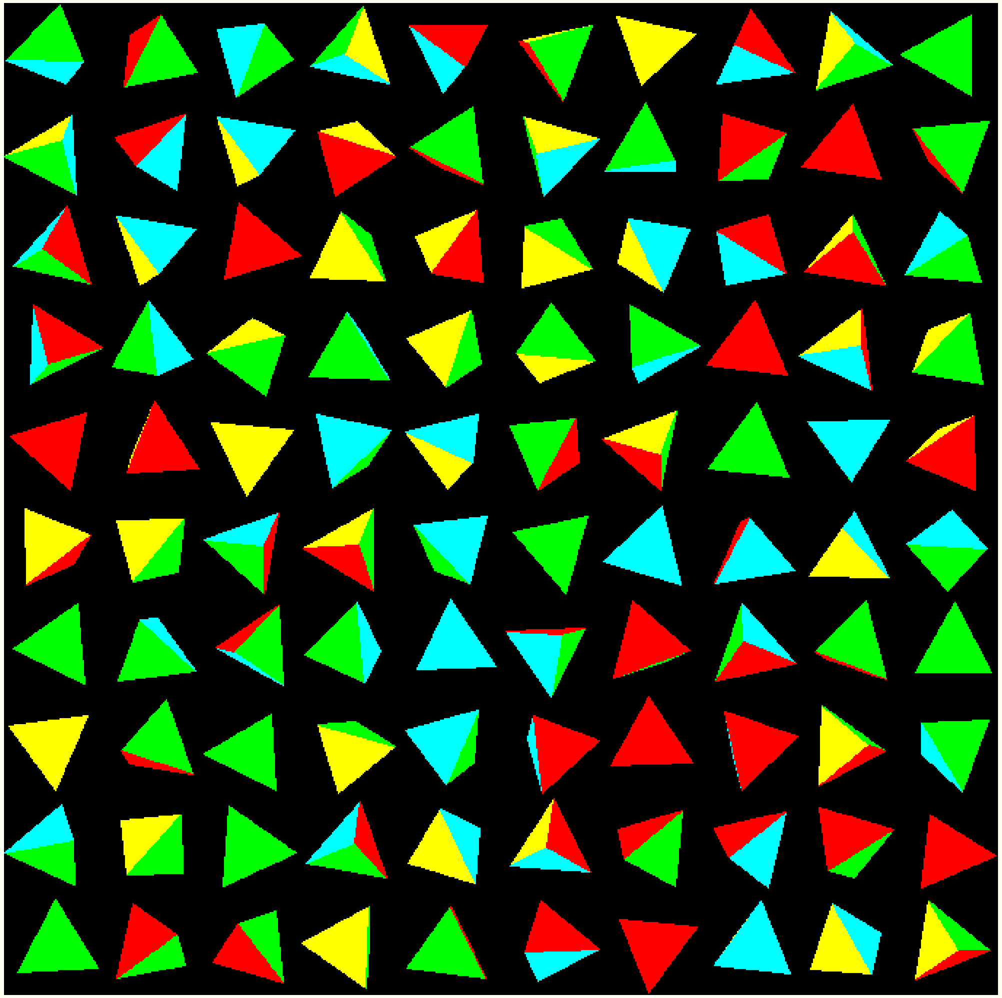
- Au nanorods





P.P-M., unpublished

Nanoparticles – other symmetries?



orientationally ordered?

how do we know?

Order parameter?

$$Q_t = < \hat{\mathbf{l}}\hat{\mathbf{l}}\hat{\mathbf{l}} >$$

Theory?

L.G. Fel, *Phys. Rev. E* **52**, 702–717 (1995)

L. Radzihovsky and T. C. Lubensky 2001 *Europhys. Lett.* **54** 206

Summary

- orientational order is ubiquitous
  - many new systems on the horizon
- liquid crystals are ‘soft’
  - respond readily to excitations
- symmetry considerations give insights
  - predictions based on symmetry arguments
- prospects:
  - new responses in existing materials
  - new materials, new symmetries

What to remember:

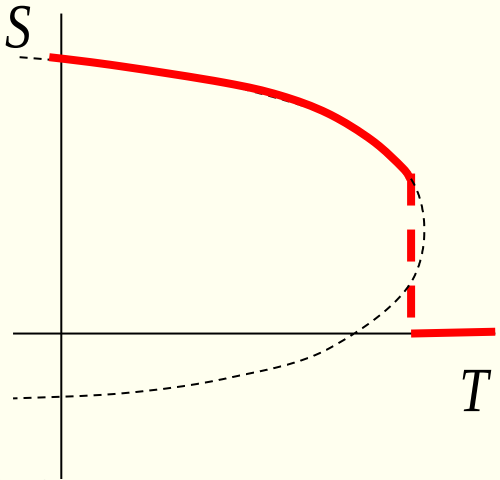
- order parameter

$$\mathbf{Q} = < \frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I}) >$$

$$\mathbf{Q} = S\frac{1}{2}(3\hat{\mathbf{n}}\hat{\mathbf{n}} - \mathbf{I})$$

- free energy

$$\mathfrak{F}_L = \frac{1}{2}A_o(\frac{T}{T_c} - 1)\mathbf{Q}^2 - \frac{1}{3}B\mathbf{Q}^3 + \frac{1}{4}C\mathbf{Q}^4 + .. - \frac{1}{2}\Delta\varepsilon\mathbf{QEE}$$



$$B \simeq \frac{kT_{NI}}{l_{mol}{}^3}$$