

Lecture 6

Liquid Crystals

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Liquids have neither translational nor orientational order.

They have highest possible symmetry.

Crystals have both translational and orientational order.

They have lowest symmetry compatible with regular filling.

Continuous groups of rotations and translations are reduced to the discrete subgroups.

In general, order = absence of symmetry

Liquid crystals are states that have symmetries intermediate between crystals and liquids.

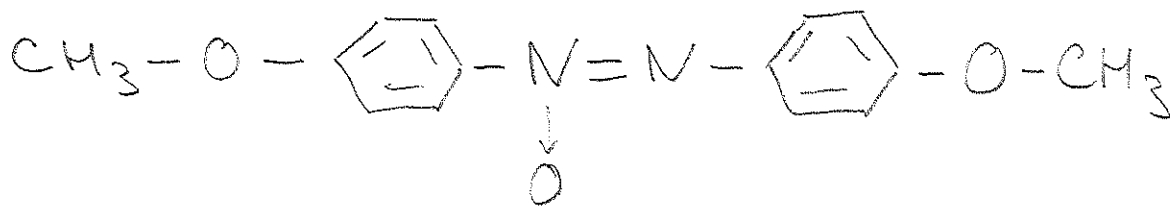
Liquid order is present at least in one direction.

Some degree of anisotropy is also present.

Sometimes there is a crystalline order along some direction.

Some organic materials do not show a single solid - liquid transition. Instead there is a sequence of transitions involving new phases

Building blocks of liquid crystals - rod like molecules ⁽²⁾
p-azoxyanisole (PAA)



It has length $\sim 20 \text{ \AA}$, width $\sim 5 \text{ \AA}$

Nomenclature

Phase transitions due to change of temperature - "thermotropic"
due to change of concentration - "lyotropic"

If only rotational symmetry is broken - nematic

$\downarrow \eta \mu \alpha$ - thread (because of the thread like defects)

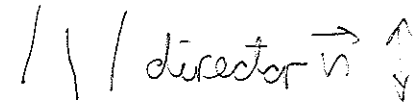
Names are due to G. Friedel ~ 1920

If there is a crystalline order in one dimension -
smectic, $\exists \mu \epsilon \gamma \mu \alpha$ - soap.

Liquid crystals made from plate-like molecules are called discotic nematics (if these plates are aligned). If in addition there is 2d crystalline order - columnar phases

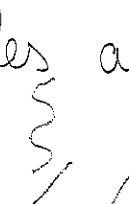
Liquid crystals with helicoidal structure (pitch ~ few thousands Å) - cholesterics, they are made from chiral (no mirror plane) molecules.

When cooling liquid first transition is from the liquid to the nematic (pure entropic).

It has one preferable axis  director \vec{n}

But \vec{n} and $-\vec{n}$ are equivalent (even if the molecules are not symmetric!). It has not the same symmetry as ferrimagnet.

With further decrease of temperature one may have transition to the smectic-A - periodicity in one direction that is along the direction of molecules (\vec{n})

If molecules are tilted with respect to periodicity direction  - smectic-C

Cooling smectic-C one may get the smectic B = hexatic - hexagonal orientational order (it is not due to the symmetry of molecules but due to not complete destruction of the crystalline order)

Names of smectics ^(A, B, C) are purely historical, have nothing from symmetry

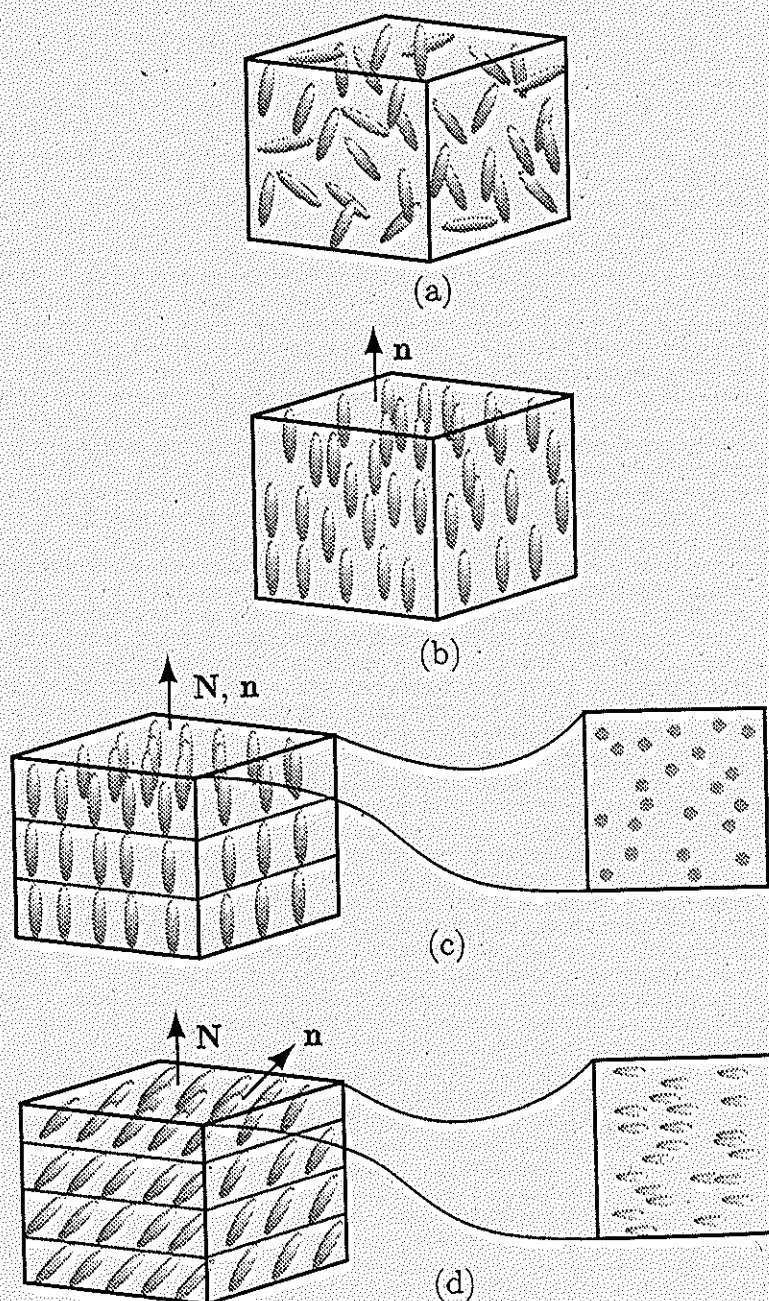


Fig. 2.7.3. Schematic representation of the position and orientation of anisotropic molecules in (a) the isotropic, (b) the nematic, (c) the smectic-A, and (d) the smectic-C phases. The direction of average molecular alignment in all but the isotropic phase is specified by a unit vector n . The layer normal in the smectic phases is indicated by the unit vector N . In the smectic-A phase, n is parallel to N , whereas in the smectic-C phase, it is not. In the text $N = e_z$ is parallel to the z-axis. (c) and (d) also show the arrangement of molecules in the smectic planes in the smectic-A and -C phases. In the smectic-C phase, the projections of molecular axes onto the plane perpendicular to N align on average along the c-director.

First order nematic-to-isotropic transition

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What is the order parameter? Vector? No $\vec{n} \leftrightarrow -\vec{n}$

Let us try tensor. Order parameter is zero in the isotropic phase \Rightarrow symmetric traceless tensor will be zero after averaging over directions

$$Q = \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}S + \eta & 0 \\ 0 & 0 & -\frac{1}{3}S - \eta \end{pmatrix} \quad \begin{array}{l} \text{if } \eta \neq 0 \text{ - biaxial} \\ \text{usually uniaxial and } \eta = 0 \Rightarrow \end{array}$$

$$Q_{ij} = S \left(n_i n_j - \frac{1}{3} \delta_{ij} \right), \text{ where } \vec{n} \text{ - unit vector-director}$$

Landau energy

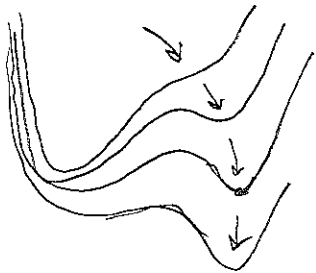
Should be invariant under rotations \Rightarrow

$$F = \sum_P A_P \text{Tr}(Q^P) = A_1 Q_{\alpha\alpha} + A_2 Q_{\alpha\beta} Q_{\beta\alpha} + A_3 Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + A_4 Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\delta} Q_{\delta\alpha}$$

$$= \frac{1}{2} r S^2 - w S^3 + u S^4 \dots$$

As usual in Landau theory $r = a(T - T_c)$

Because of the tensor properties of Q_{ij} there is always a third order term (would be absent for vector order parameter) \Rightarrow 1-st order phase transition



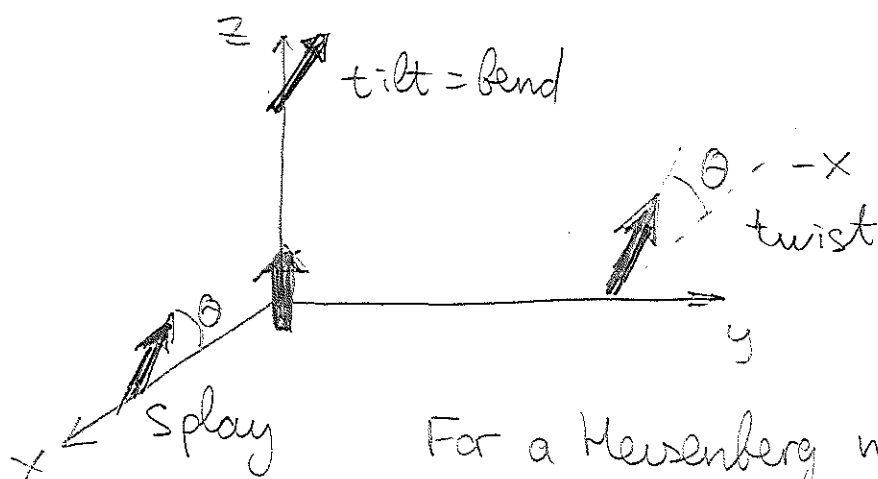
Interaction with external field

$$\int dV \times Q_{ij} H_i H_j = \int dV \times S \left[(\vec{H} \cdot \vec{n}) - \frac{1}{3} H^2 \right]$$

Elastic energy of nematics

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Different modes of deformations



For a Heisenberg magnet all the interactions of the central spin have the same energy. $\Rightarrow (\nabla_\alpha M_\beta)^2$ since rotations in the spin and coordinate spaces (\vec{M} and \vec{r}) are different operations

Liquid crystals are different because rotations of \vec{n} and \vec{r} are produced by the same operator.

The invariant gradient terms (including $\vec{n} \rightarrow -\vec{n}$, $\vec{r} \rightarrow -\vec{r}$)

$$F = \frac{1}{2} \int dV \left\{ K_1 (\nabla \cdot \vec{n})^2 + K_2 (\vec{n} \cdot [\nabla \times \vec{n}])^2 + K_3 [n \times [\nabla \times \vec{n}]]^2 \right\}$$

splay
twist
bend

Frank energy, $K_1, 2, 3$ - Frank constants.

Typical values $K \sim \frac{400 \text{ K}}{20 \text{ \AA}} \sim 10^{-4}$ (elastic moduli for solids)

! Since: $n^2 = 1 \Rightarrow \nabla n^2 = 0 \Rightarrow \vec{n} \times \text{rot } \vec{n} = -(\vec{n} \cdot \nabla) \vec{n}$

For cholesterics one has term $K_2 (\vec{n} \cdot [\nabla \times \vec{n}] + g)^2$

Minimizing energy $\Rightarrow \text{div } \vec{n} = 0$, $\vec{n} \times \text{rot } \vec{n} = 0$, $\vec{n} \cdot \text{rot } \vec{n} = -\vec{g} \Rightarrow$

$$\Rightarrow n_x = \cos g z, n_y = \sin g z, n_z = 0, \vec{g} \parallel z$$

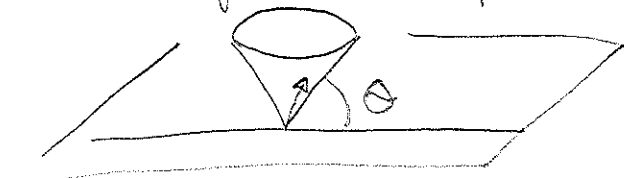
Since $\vec{n} = -\vec{n}$ then the pitch = $\frac{\pi}{g}$

Boundary effects

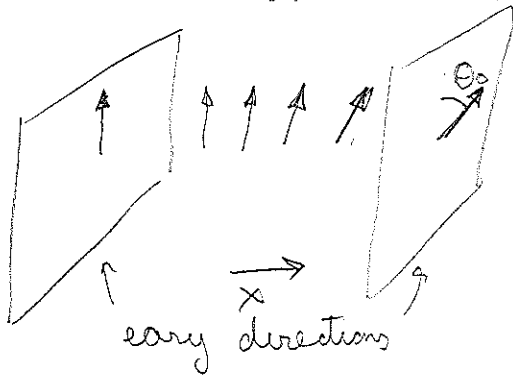
easy direction

for anisotropic surface - one direction (in the plane or at some angle)

for isotropic medium - normal to it (rare case) (degenerate) or at some angle



section to the surface



- twist

$$n = [0, \sin\theta(x), \cos\theta(x)] \Rightarrow$$

$$F = \frac{1}{2} K_2 \int dx \left(\frac{\partial \theta}{\partial x} \right)^2 \Rightarrow$$

$$\theta'' = 0 \Rightarrow \theta = \theta_0 \frac{x}{L}, \quad F = \frac{K_2}{2} \frac{\theta_0^2}{L}$$

Nematics can transfer torque!

Magnetic (electric) correlation length

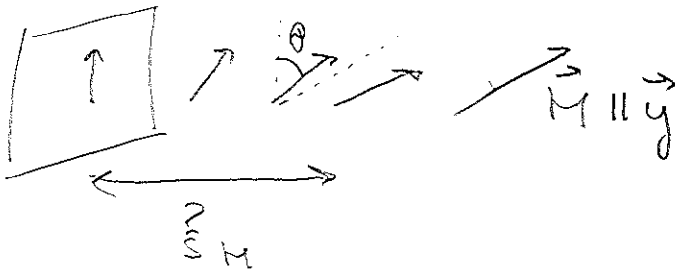
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In a field H additional term

$$F_{\text{ext}} = - \frac{\chi_a}{2} \int (\vec{H} \cdot \vec{n})^2 dV - \frac{\epsilon_a}{2} \int (\vec{E} \cdot \vec{n})^2 dV$$

tends to align along the field

Near the surface



$$\frac{F}{S} = \frac{1}{2} \int dx \left[K_2 \left(\frac{d\theta}{dx} \right)^2 - \chi_a H^2 \sin^2 \theta \right]$$

$$\frac{d^2 \theta}{dx^2} = -\frac{1}{2} \frac{d \sin^2 \theta}{d\theta}, \quad \xi_H = \left(\frac{K_2}{\chi_a H^2} \right)^{1/2}$$

$$\frac{d^2 \theta}{dx^2} = -\sin^2 \theta + C = \cos^2 \theta \quad (x \rightarrow \infty \theta = \frac{\pi}{2}, \theta|_0 = 0)$$

defining $\beta = \frac{\pi}{2} - \theta$ ($\beta \rightarrow 0$ $x \rightarrow \infty$) \Rightarrow

$$\Rightarrow \frac{d\beta}{\sin \beta} = -\frac{dx}{\xi_H} \Rightarrow \ln \tan \beta/2 = -\frac{x}{\xi_H} \Rightarrow$$

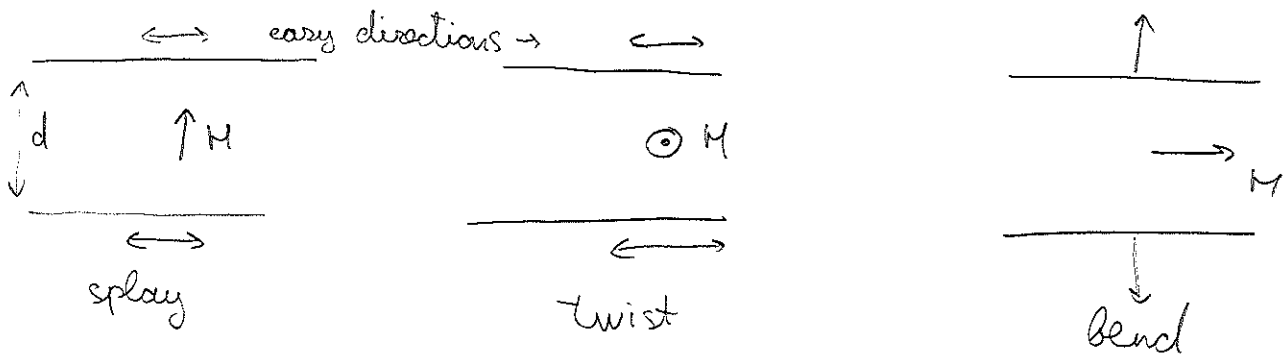
$$\beta = 2 \arctan e^{-\frac{x}{\xi_H}}$$

Since 3 elastic constants - 3 lengths for different modes, usually of the same order.

The Fredericksz (Frederiks) - transition

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different modes



For $d \ll \xi_H$ $\vec{n} \parallel$ easy direction and does not change

For $d \gg \xi_H$ \vec{n} rotates towards the field

Phase transition at $d \sim \xi_H \sim \sqrt{\frac{K_i}{\chi}} \frac{1}{H} \Rightarrow$

$$\Rightarrow H d = \text{const} \sim \sqrt{\frac{K_i}{\chi}}$$

Second order transition

$$\vec{n} = \vec{n}_0 + \delta \vec{n} \quad (\delta \vec{n} \parallel \vec{M} \perp \vec{n}_0)$$

- easy direction

$$F = \frac{1}{2} K_i \left(\frac{\partial \delta n}{\partial z} \right)^2 - \frac{\chi_a}{2} H^2 \delta n^2$$

at the boundaries $\delta n = 0 \Rightarrow \delta n = \sum \delta n_k \sin \frac{\pi k}{d} z =$

$$F = \frac{d}{4} \sum (\delta n_k)^2 \left(K_i \left(\frac{\pi k}{d} \right)^2 - \chi_a H^2 \right)$$

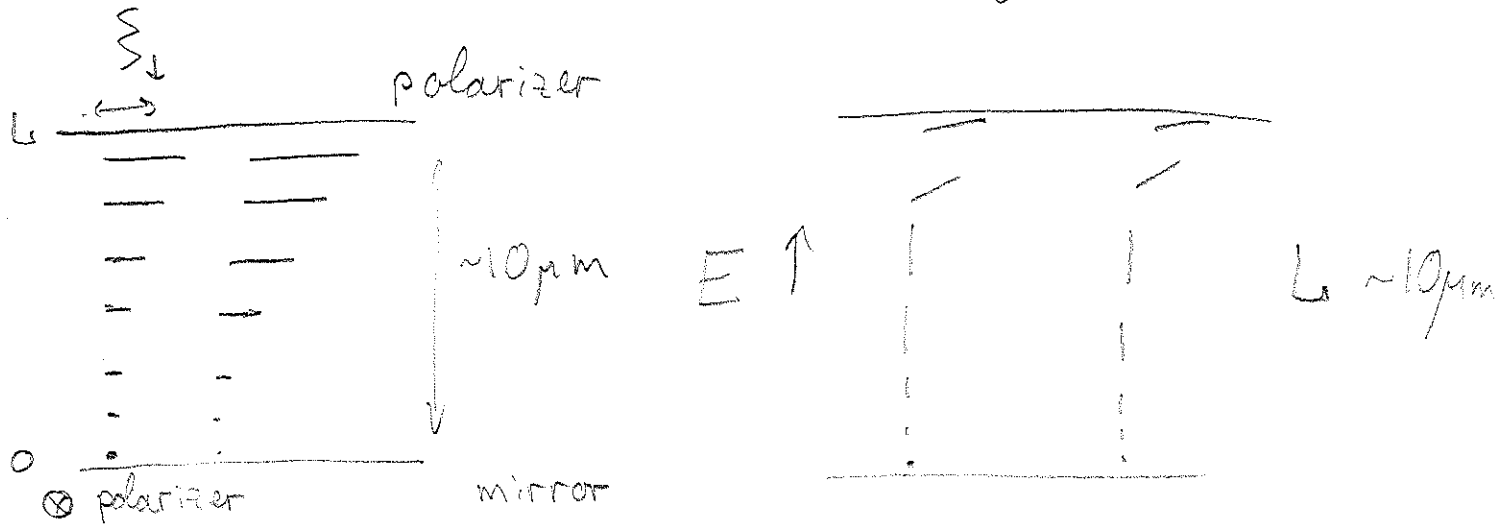
Phase transition: when first harmonic ($k=1$) appears \Rightarrow

$$\Rightarrow \xi_H = \frac{\pi}{d} \Rightarrow H_{ci} = \frac{\pi}{d} \left(K_i / \chi_a \right)^{1/2}$$

Problem Find configuration for $H = K_c + \delta H$ (10)

($F = K_1 \left(\frac{\partial \theta}{\partial z} \right)^2 = X M^2 \sin^2 \theta$)
 expand $\theta^2 - \theta^4 + \dots$

The twisted nematic display



$$V_c = 2\pi^{3/2} \left[K_1 + \frac{1}{4} (K_3 - K_2) + \frac{K_2}{2} \right]^{1/2} \epsilon_a^{-1/2} \sim 1V$$

Without the field pitch length $= 4L \gg \lambda$ (light wavelength)
 and the direction of polarization of light adiabatically follows director (even after reflection),
 light can leave the sample - shiny.

With voltage - most of the molecules \perp plane
 \Rightarrow can not change polarization \Rightarrow light is blocked \Rightarrow dark color