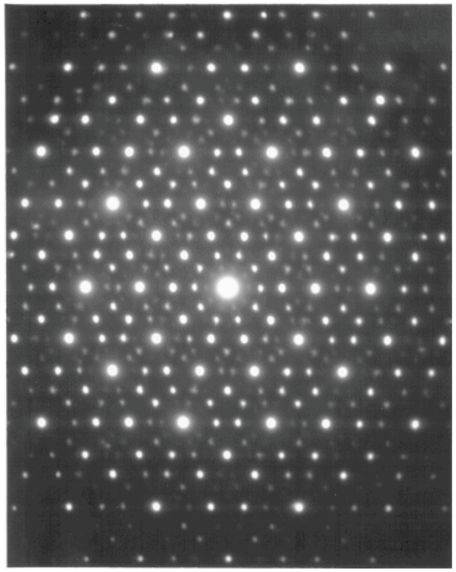
Structure: Lecture 14

- Quasicrystals
- Plastic and liquid crystals – basic concepts
- Liquid crystals: so many exciting options!

Readings:
- Allen and Thomas, *The Structure of Materials*, chapters 3.4-3.5, 4.0-4.1

Quasicrystals



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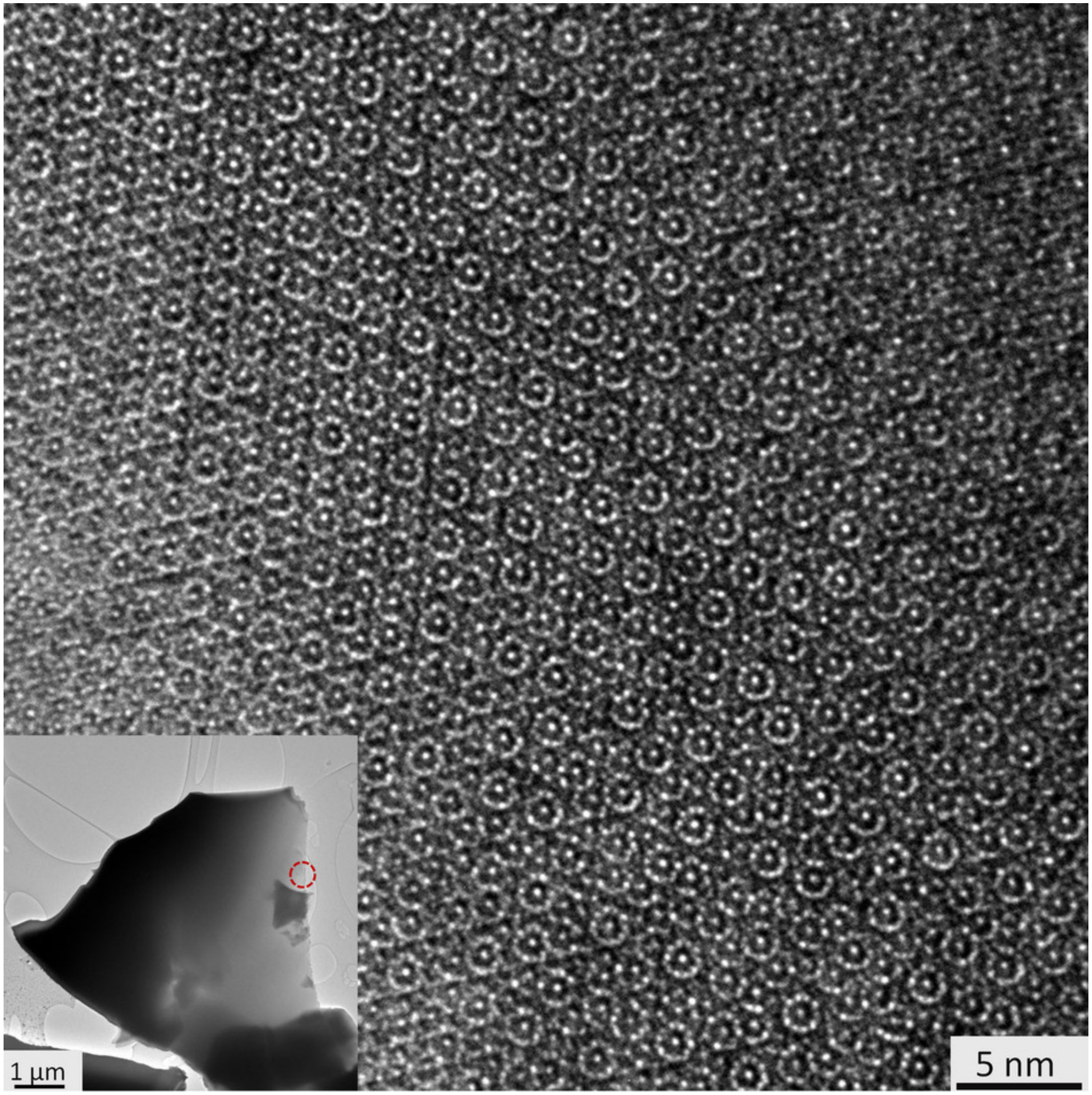
Electron diffraction pattern of Al-Mg

- In 1982, transmission electron microscopy experiments on rapidly cooled aluminum-manganese material showed diffraction patterns with well-defined diffraction spots, but with apparent tenfold symmetry!
- After that, twelvefold and eightfold diffractions have been observed and hundreds of structures with well-defined diffractions, but not obeying the rules of “translational” crystallography have been discovered.

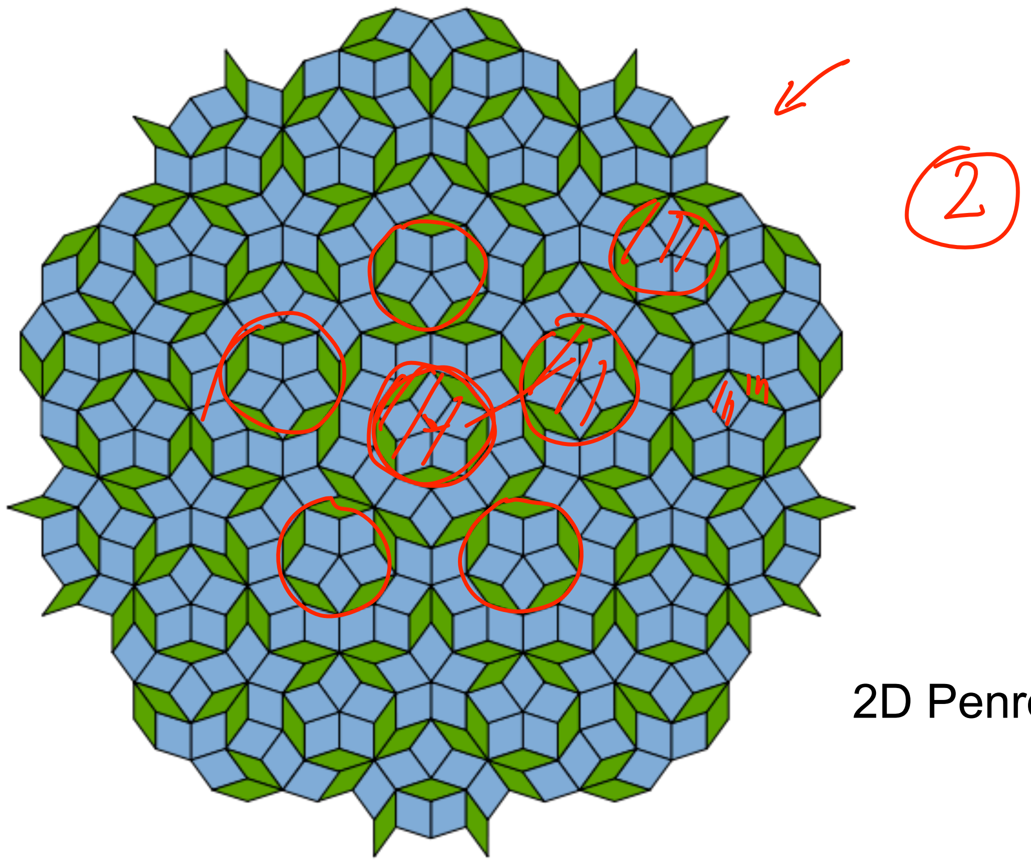
Quasicrystals



https://en.wikipedia.org/wiki/Quasicrystal

Quasicrystals

• Quasi-periodic tiling: the motifs are not periodic in traditional (translational) sense.
• These geometrical (mathematical) structures have been discovered in 1970 by Sir Roger Penrose.
• They consist of 2 basic tiling motifs that completely cover a plane.
• The structures preserve long-range fivefold rotational symmetry, without any translational order.



2D Penrose tiling

Quasicrystals

If a periodic lattice is modulated with another periodicity that is an irrational fraction or multiple of the underlying periodicity, then an incommensurate superlattice results, which gives rise to the quasi-periodicity.

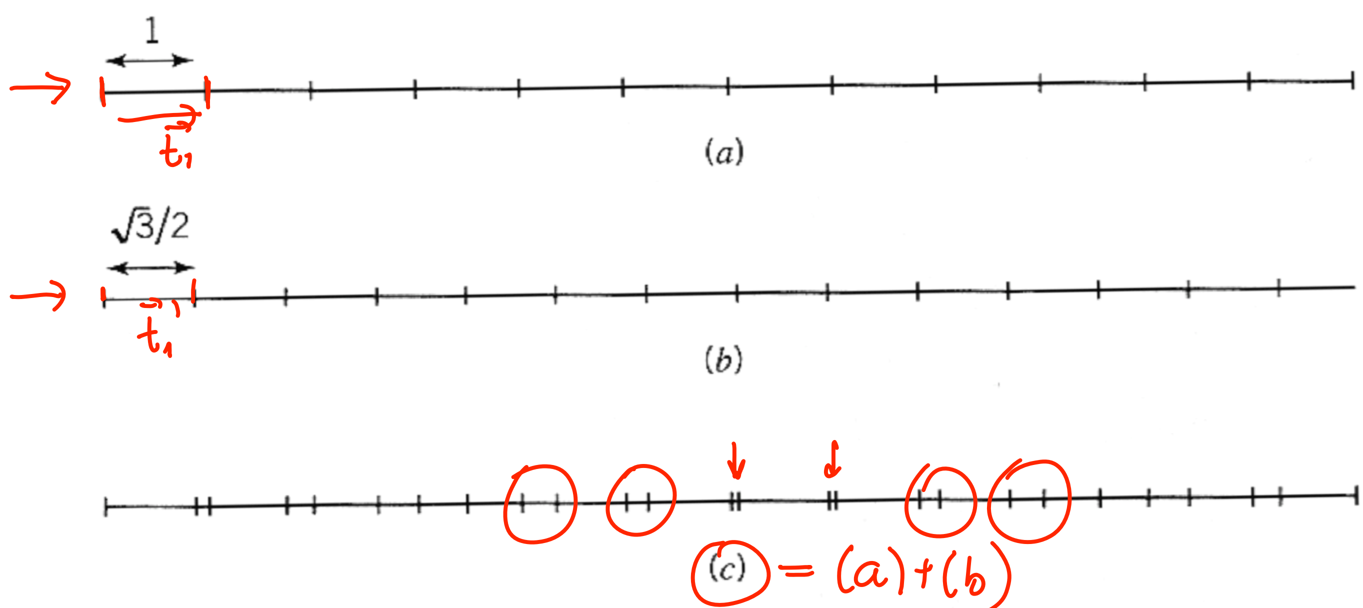


Figure 3.83 Simple one-dimensional example of quasiperiodicity can be constructed by superposition of two one-dimensional periodic arrays if the ratio of respective periods $\lambda_2/\lambda_1 \neq$ rational number: (*a*) one-dimensional array with period λ_1; (*b*) one-dimensional array with period λ_2; (*c*) superposition of the two arrays is an ordered but nonperiodic array because $\alpha \equiv \lambda_2/\lambda_1$ is irrational. Note that this structure is self-similar.

Quasicrystals are popping up everywhere…

octagonal QC:
V-Ni-Si
Cr-Ni-Si
Mn-Si
Mn-Si-Al
Mn-Fe-Si

dodecagonal QC:
Cr-Ni
V-Ni
V-Ni-Si

decagonal QC:
Al-TM
(TM=Ir,Pd,Pt,Os,Ru,Rh,Mn,Fe,Co,Ni,Cr)
Al-Ni-Co *
Al-Cu-Mn
Al-Cu-Fe
Al-Cu-Ni
Al-Cu-Co *
Al-Cu-Co-Si *
Al-Mn-Pd *
V-Ni-Si
Cr-Ni

icosahedral QC:
Al-Mn
Al-Mn-Si
Al-Li-Cu *
Al-Pd-Mn *
Al-Cu-Fe
Al-Mg-Zn
Zn-Mg-RE *
(RE=La,Ce,Nd,Sm,Gd,Dy,Ho,

Ti-TM *(TM=Fe, Mn, Co, Ni)*
Nb-Fe
V-Ni-Si
Pd-U-Si

Quasicrystals – redefining the term crystal

• Inspired by the growing numbers and varieties of quasiperiodic crystals, the *International Union of Crystallography* has redefined the term **crystal** to mean "any solid having an essentially discrete diffraction diagram"

• Interestingly, the essential attribute of crystallinity shifts from position space to Fourier space. → reciprocal space!

• Within the family of crystals one distinguishes between periodic crystals, which are periodic on the atomic scale, and aperiodic crystals which are not.

• This broader definition reflects our current understanding that microscopic periodicity is a sufficient but not a necessary condition for crystallinity (bummer!).

Structure of materials - roadmap

Noncrystalline state
- liquids
- glasses

Crystalline state and symmetry
- lattices
- space groups
- diffraction
- quasicrystals

Liquid-crystalline state
- nematic
- smectic

- Processing and assembly
- Properties
- Applications

Microstructure imperfections
- equilibrium defect
- line defects
- stacking faults
- grain boundaries

A new state of matter!

Short vs. long range order

• We have defined amorphous materials (of which liquids are a sub-class) as materials that possess short-range order
but lack long-range order.

PDF

→ lattice + motif

• Crystalline materials are materials that possess both long- and short-range order.

• In simpler words, we have previously defined a crystal as a material that ideally can be built by translating in all dimension a unit cell with identical steps.

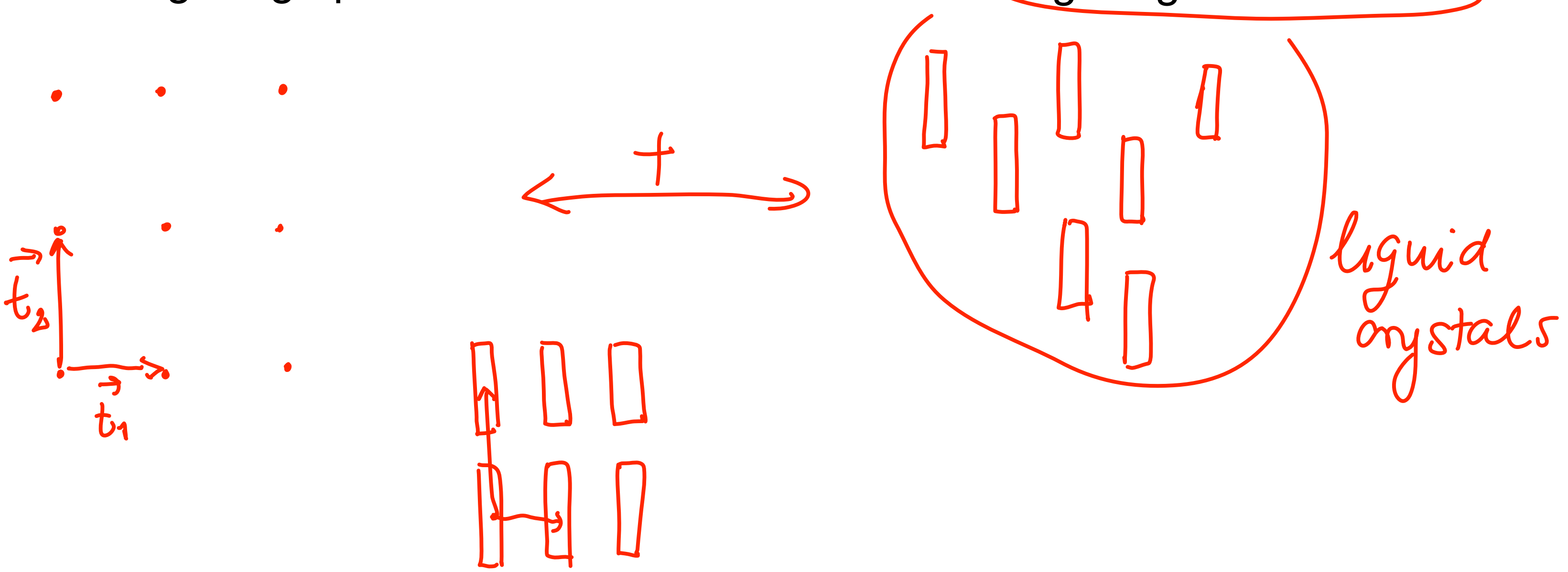
• What are the structural descriptors most frequently used for liquids and crystals? Your answers:
• density, viscosity, PDF, packing coefficient, crystal structure…

Translational vs. orientational order

• This is a fairly strict condition that implies that a crystalline material has *both positional and orientational* long range order.
• Let's decouple these two concepts.

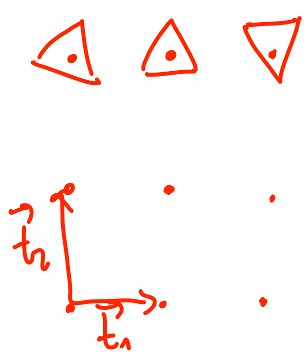
What is long range positional order?

What is long range orientational order?



Plastic crystals

• In terms of interactions, orientational and translational orders may have substantially different strength of the determining forces.
• For example if a crystal constituent is mostly spherical, its orientational order will be determined by very weak forces.
• Therefore, a range of temperatures will exist where the material will have long range translational, but no long range orientational order.
• These materials are called *plastic crystals.*

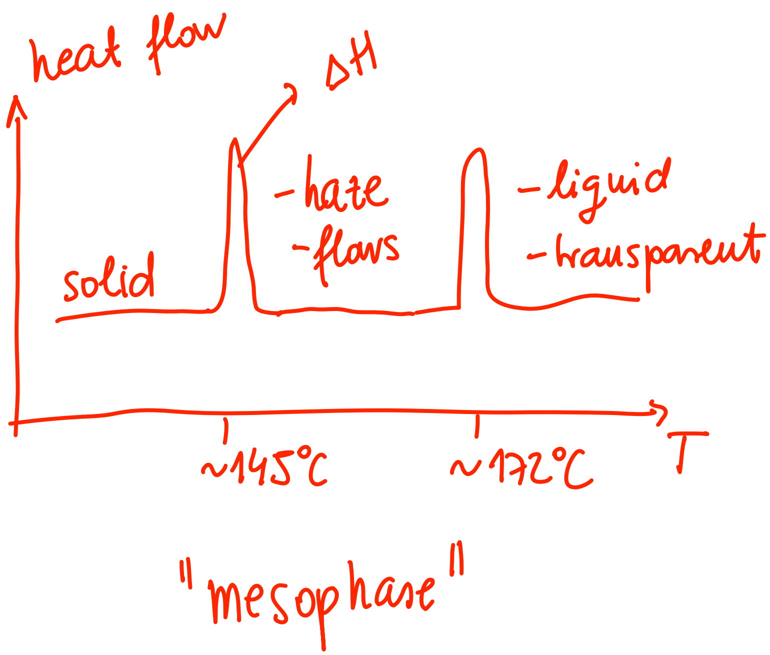


"spherical"- like shapes

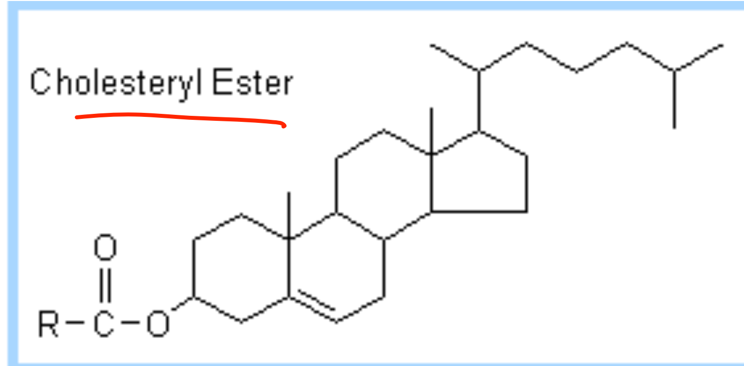
Liquid crystals

Let's start with a bit of history…

1889: Freidrich Reinitzer – melting of cholesterol ester
Unique state over a 33°C range



DSC



Liquid crystals

• While plastic crystals are limited in natural occurrence and have little to no application, materials that have long range orientational order and no long range translational order are very common and have a truly large number of applications.

• These are called **liquid crystals**.

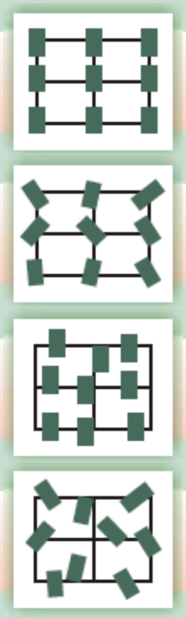
• The key structural requirement: **molecular shape anisotropy**

– rod-like : calamitic LC

– disc-like : discotic

Ordering: summary

Classification of condensed matter on the basis of long-range order



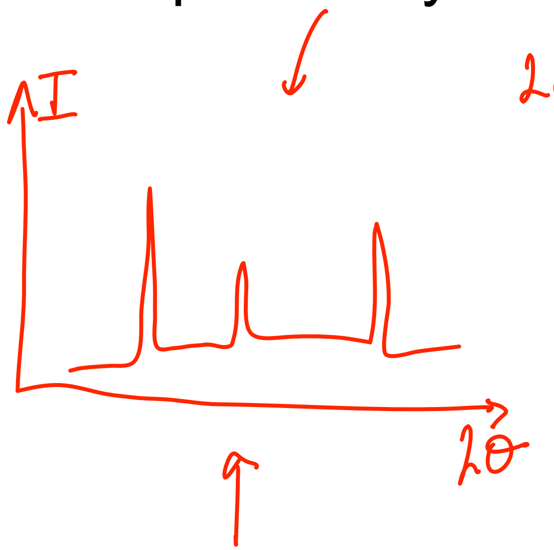
	Positional order	Orientational order
Solid crystal	✓	✓
Plastic crystal	✓	✗
Liquid crystal	✗	✓
Isotropic liquid	✗	✗

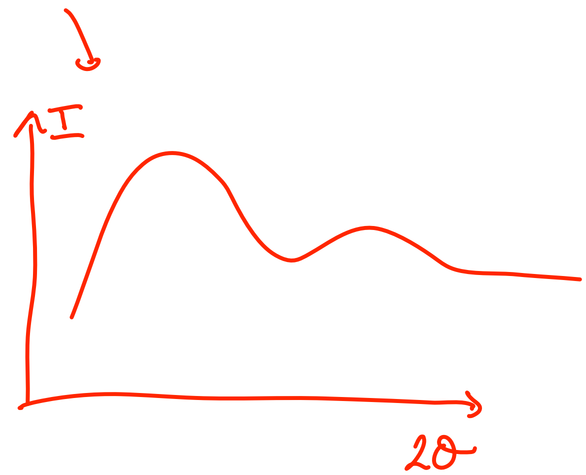
- Before we move on, we should point out that orientational order in liquid crystal is defined in a loose way, liquid crystals are fluid and posses a high degree of molecular mobility, hence the position of their components varies with time over a certain range.
- A snapshot of a liquid crystal would not readily show a rigorous orientational order, but a time average one would.

Check point

How would the diffraction patterns look like for plastic crystals and liquid crystals?

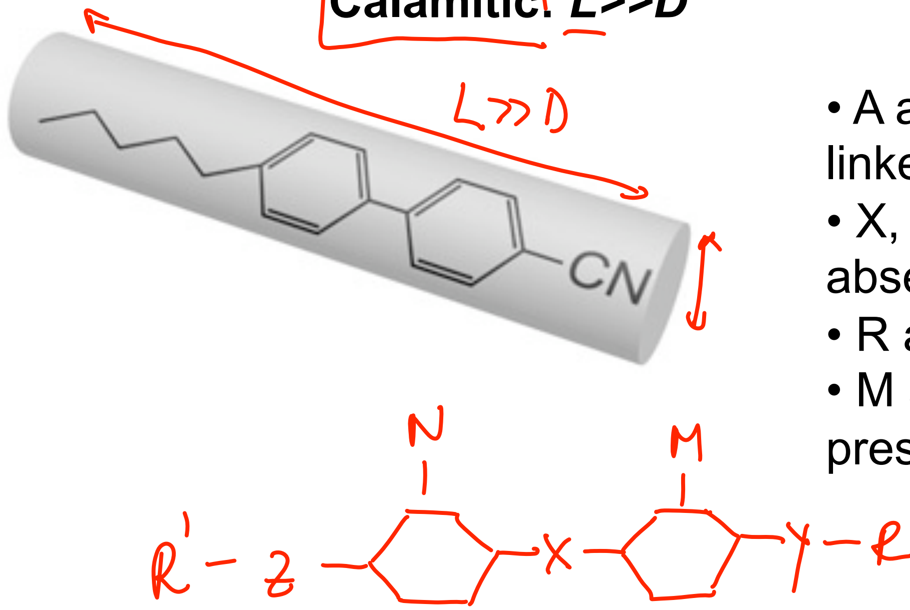
$$2d\sin\theta = n\lambda$$





Calamitic liquid crystals

Calamitic: ***L>>D***



- A and B: core units consisting of linearly linked aromatic or alicyclic rings
- X, Y and Z: linking groups which are often absent (direct links)
- R and R' : terminal functional groups
- M and N: lateral substituents which are not present for all systems

What would be an appropriate structural descriptor for liquid crystals?

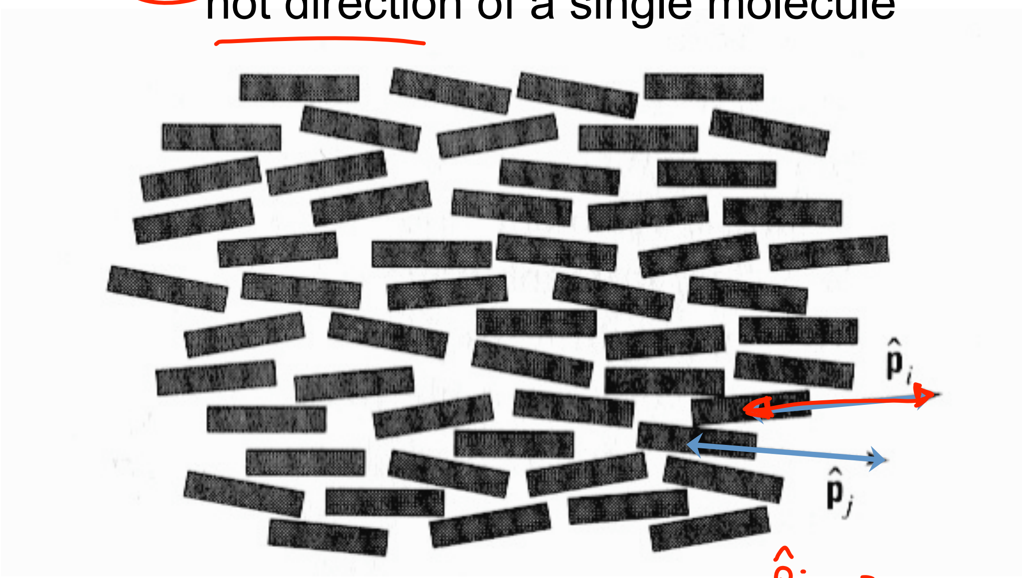
Your answer(s): long-range orientational order

Liquid crystals: director

• Very useful concept of describing structure of liquid crystals: **director** – a preferred axis of LC molecular orientation

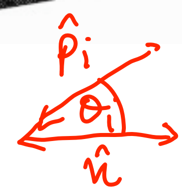
• A monodomain is a region of space where all of the molecular directors are aligned to this axis.

$\hat{\mathbf{p}}_i$: *nonpolar vector* indicates orientation, but not direction of a single molecule



$\hat{n}(\vec{r})$: director line

$\hat{n}(\vec{r}) = \langle \hat{p}_i \rangle_V$ → average over volume



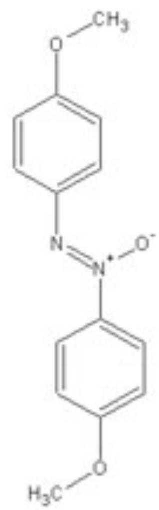
Nematic liquid crystals

• There are many structural classes of liquid crystals, but only some of them are common.

Nematic liquid crystals (N):

• No positional order

• Long-range orientational order

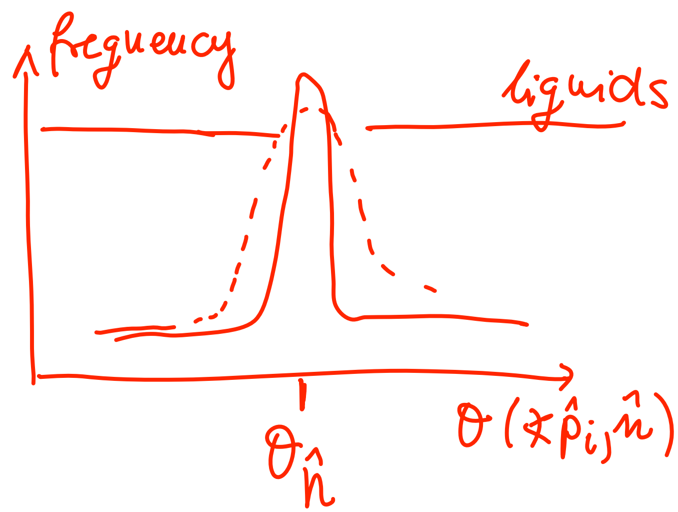


e.g. para-azoxyanisole

• In nematic liquid crystals molecules are typically oblong – calamitic or rod-like molecules.

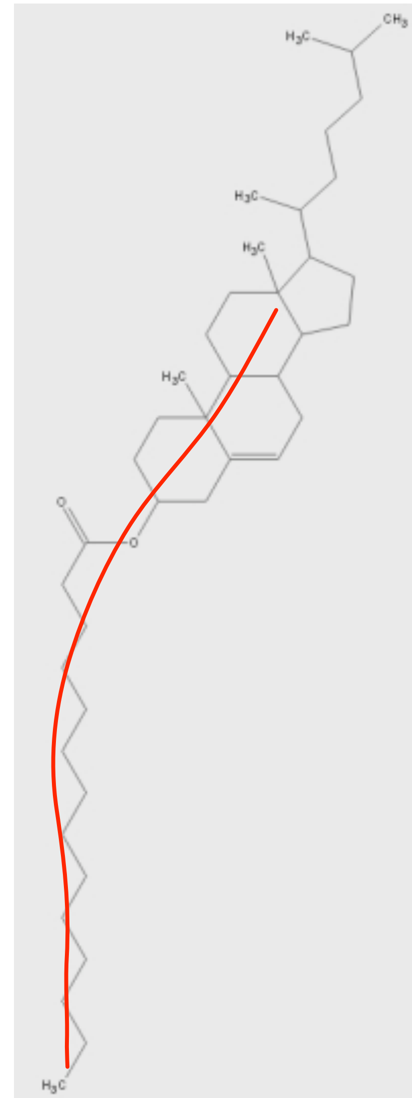
• Greek "nematos"=thread

• **Their director is more or less aligned to a common axis.**



Chiral nematic liquid crystals

e.g. cholesteryl myristate



- In **chiral nematic liquid crystals (N*) or cholesteric**
- If a nematic liquid crystal is inherently chiral, then adjacent mesogens will have a preferential twist with respect to one another, which leads to the larger-scale twisting of the internal order.
- The director $\hat{\mathbf{n}}(\mathbf{r})$ changes smoothly forming a helix.
- Remember screw symmetry?

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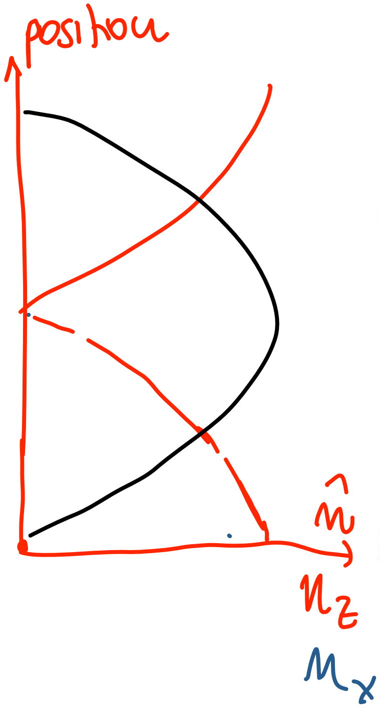
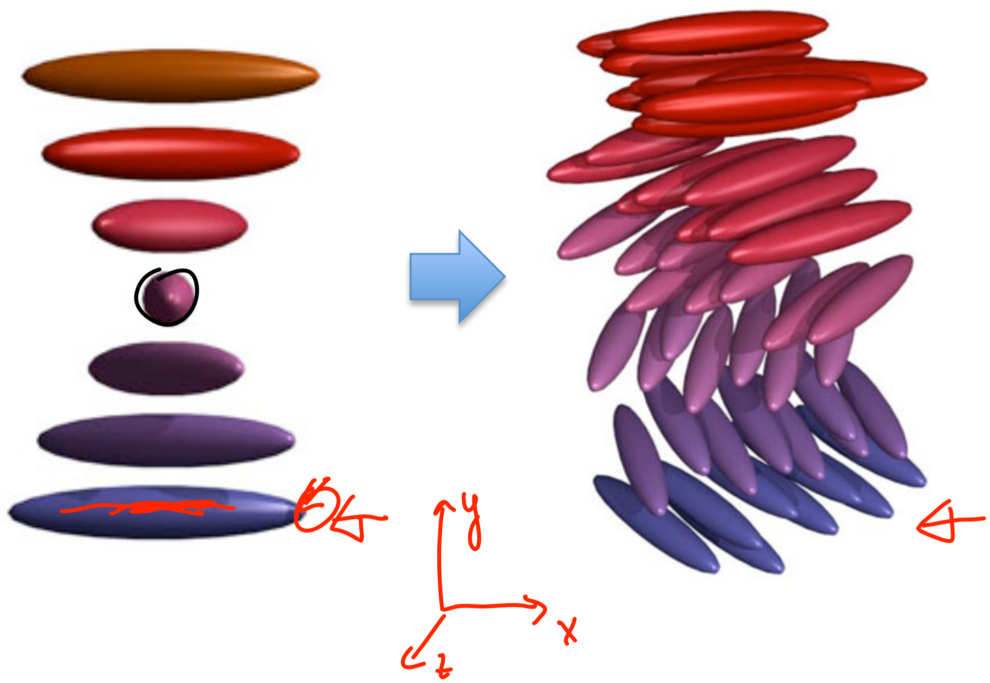
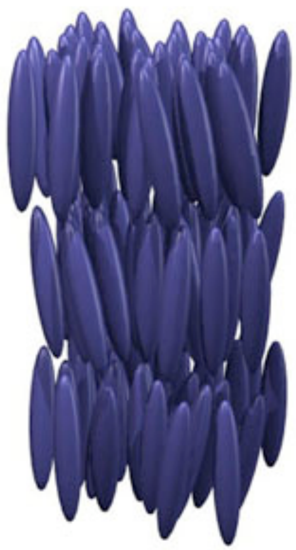


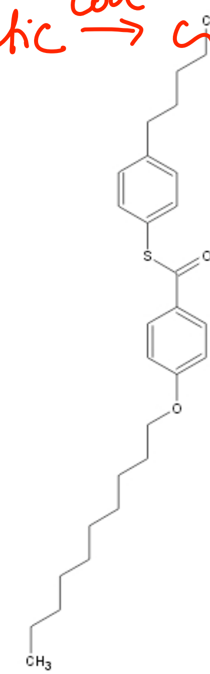


Smectic liquid crystals

- In **smectic liquid crystals (SM)** there is a planar alignment of the liquid crystals molecules that leads to the formation of planes.
- Orientational and 1D translational order.

nematic $\xrightarrow{cool}$ smectic $\xrightarrow{cool}$ cryst.





Smectic A:
layers oriented at 90° to the director

Smectic C:
a director tilted with respect to the layers

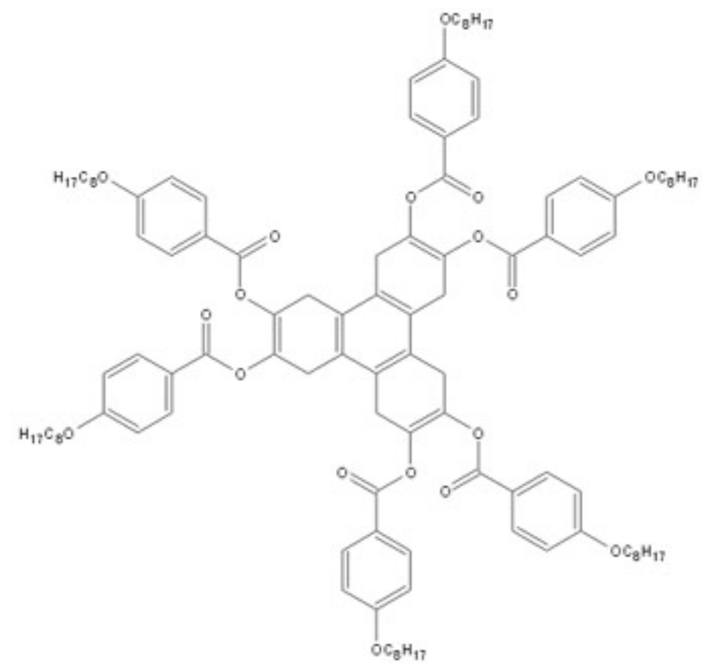
Note: smectic phase is more ordered than a nematic phase. Some materials can exist in both phases, depending on temperature.

Smectic liquid crystals

• Example of smectic phases: amphiphilic molecules - have both hydrophilic and hydrophobic properties.

• Although these molecules are not necessarily highly anisotropic, they assembly due to polar nature of the molecules.

Discotic liquid crystals

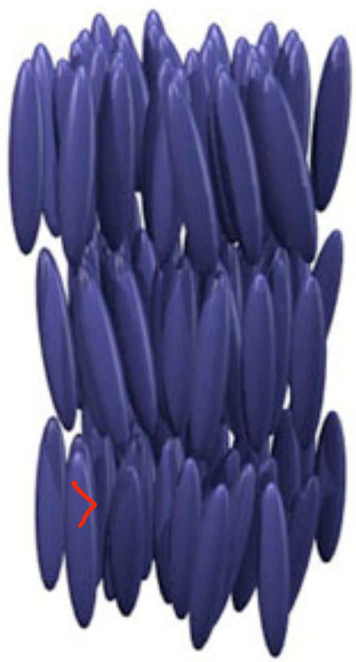


Disc-shaped molecules have a tendency to lie on top of one another forming either discotic nematic phases (with discs oriented similarly) or columnar phases.

Liquid crystals: descriptors

Liquid crystal structural descriptors:

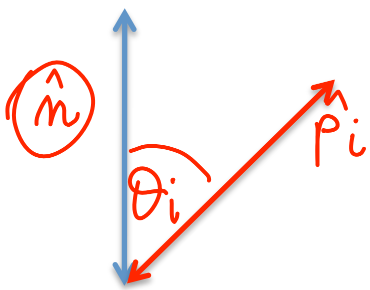
1. Orientational order parameter *S*
2. Translational order parameter *S*
3. Pair distribution function



Liquid crystal structural descriptors:

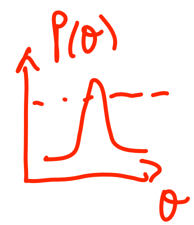
1. Orientational order parameter *S* in 2D

$\hat{n}\cdot\hat{p}_i = |\hat{n}|\cdot|\hat{p}_i|\cdot\cos\theta = \cos$ (with $|\hat{n}| = 1$, $|\hat{p}_i| = 1$)



$S = 2\cdot\langle(\hat{n}\cdot\hat{p}_i)^2\rangle_V - 1$

$= 2\cdot\langle\cos^2\theta\rangle_V - 1$



$$S = \begin{cases} 1 & \text{crystals} \\ 0\text{-}1 & \text{liq. cry.} \\ 0 & \text{liquids} \end{cases}$$

$$\langle\cos^2\theta\rangle_V = \frac{\int_0^\pi \cos^2\theta\cdot P(\theta)\,d\theta}{\int_0^\pi P(\theta)\,d\theta}$$

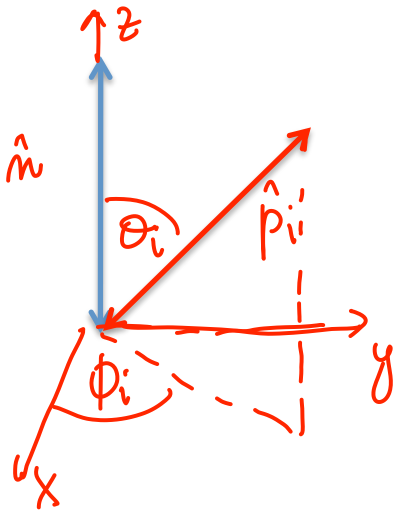
1. solid, perfect. orient. $P(\theta) = \begin{cases} 0 ; & \theta \neq 0° \\ 1 ; & \theta = 0° \end{cases}$: $\langle\cos^2\theta\rangle = 1 \Rightarrow S = 2\cdot 1 - 1 = 1$

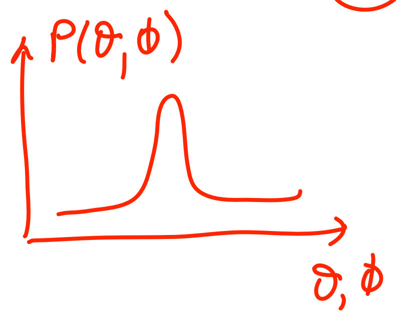
2. liquids : $P(\theta) = K$ (const.) $\Rightarrow \langle\cos^2\theta\rangle_V = \frac{\frac{1}{2}\pi}{\pi} = \frac{1}{2} \Rightarrow S = 2\cdot\frac{1}{2} - 1 = 0$

Liquid crystals: descriptors

Liquid crystal structural descriptors:

1. Orientational order parameter S in 3D





$$S = \frac{1}{2}\left(3\cdot\langle(\hat{n}\cdot\hat{p})^2\rangle - 1\right) = \frac{1}{2}\left(3\cdot\langle\cos^2\theta\rangle_V - 1\right)$$

$$\langle\cos^2\theta\rangle_V = \frac{\int_0^{\pi}\int_0^{2\pi}\cos^2\theta\cdot P(\theta,\phi)\sin\theta\, d\theta}{\int_0^{\pi}\int_0^{2\pi}P(\theta,\phi)\,d\theta\, d\phi}$$

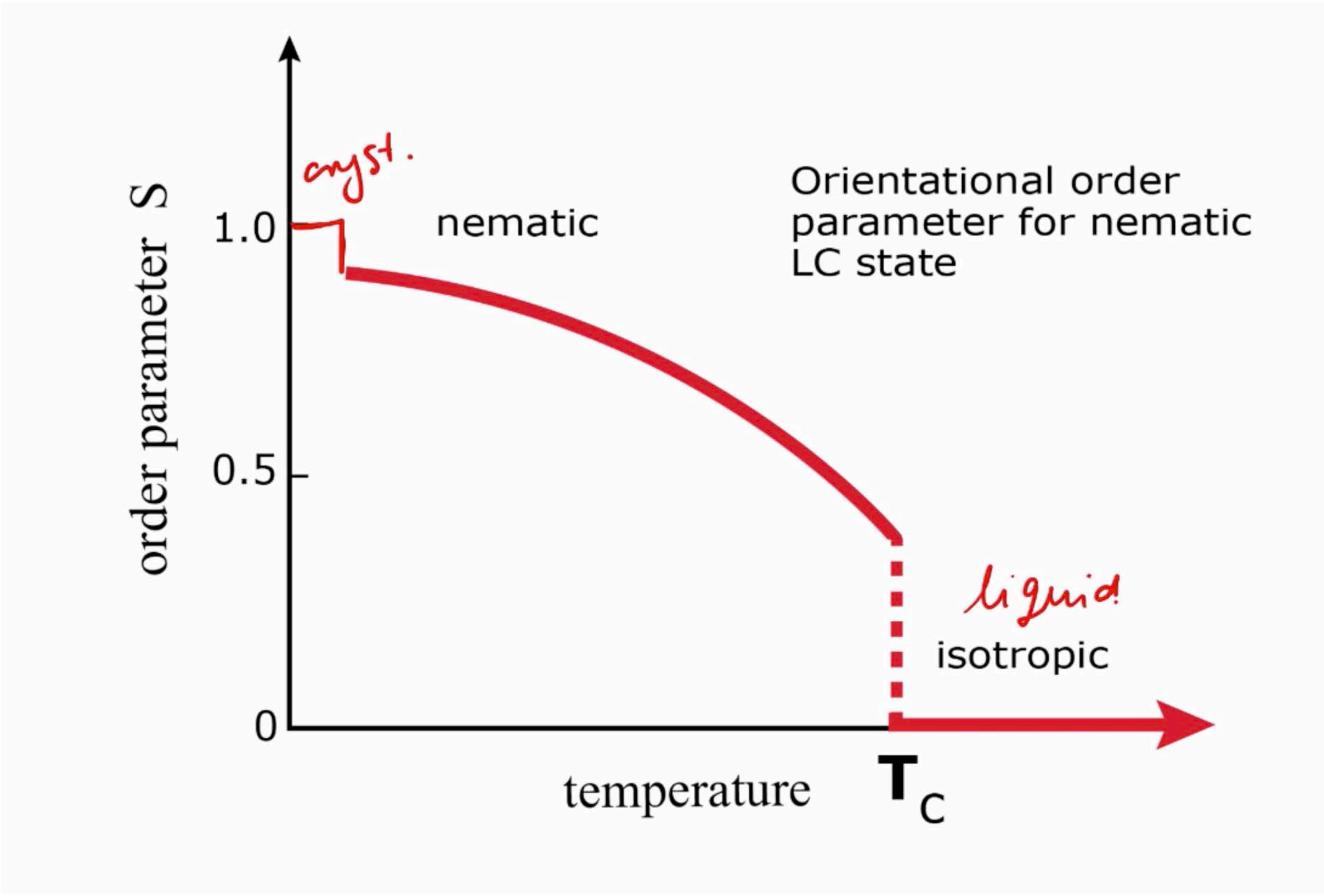
$$d\Omega = \sin\theta\, d\theta\, d\phi$$

$$S = \begin{cases} 1 & \text{cryst} \\ 0.3\text{–}0.7 & \text{LC} \\ 0 & \text{liq.} \end{cases}$$

Liquid crystals: descriptors

Liquid crystal structural descriptors:

1. Orientational order parameter *S*



Liquid crystals: descriptors

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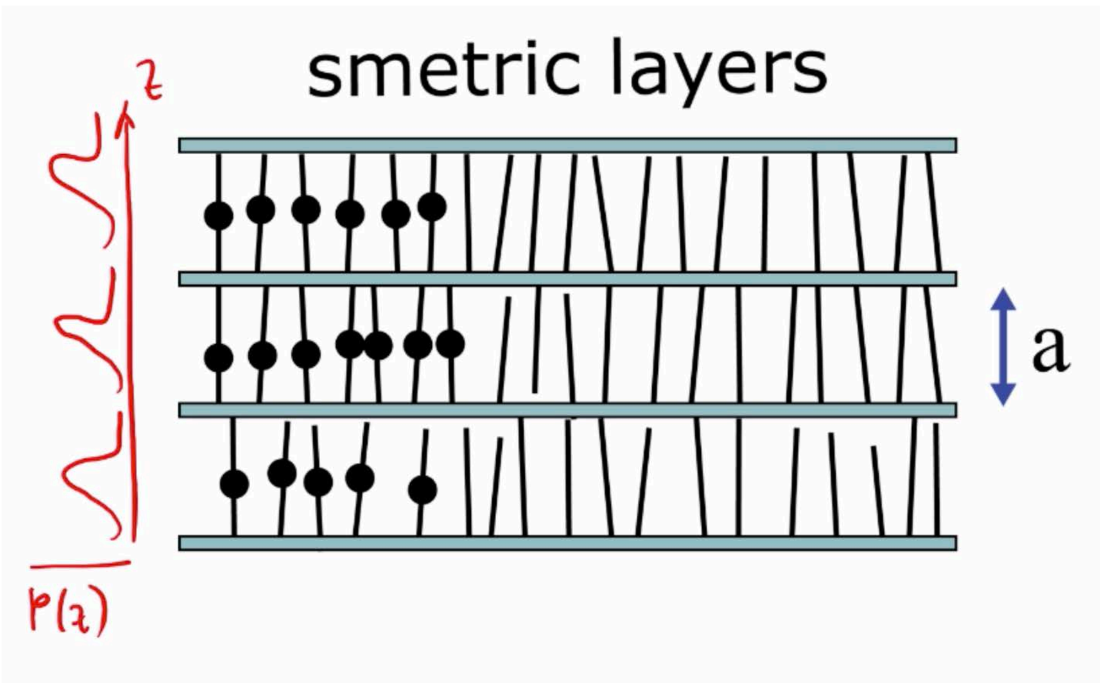
Liquid crystal structural descriptors:

2. Translational order parameter S – relevant for the smectic phase



$$\Sigma_{SM} = \left\langle \cos\frac{2\pi z}{a} \right\rangle_V = \frac{\int_{-a/2}^{a/2} \cos\frac{2\pi z}{a} P(z)\,dz}{\int_{-a/2}^{a/2} P(z)\,dz}$$

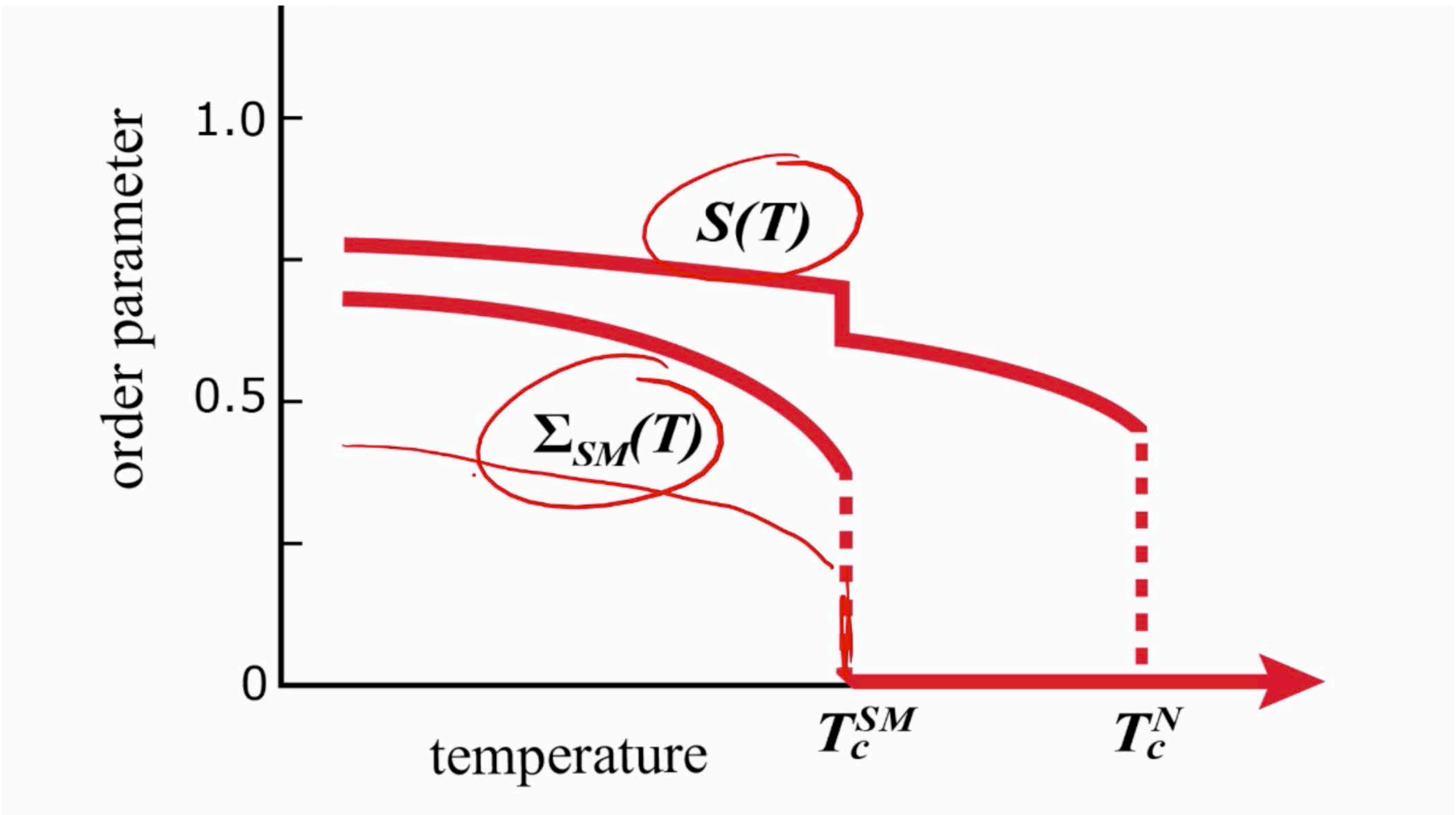
$$\Sigma_{SM} = \begin{cases} 0 & \text{nematic} \\ \neq & \text{smectic} \end{cases}$$

Liquid crystals: descriptors

smectic ord. / translat. ord.

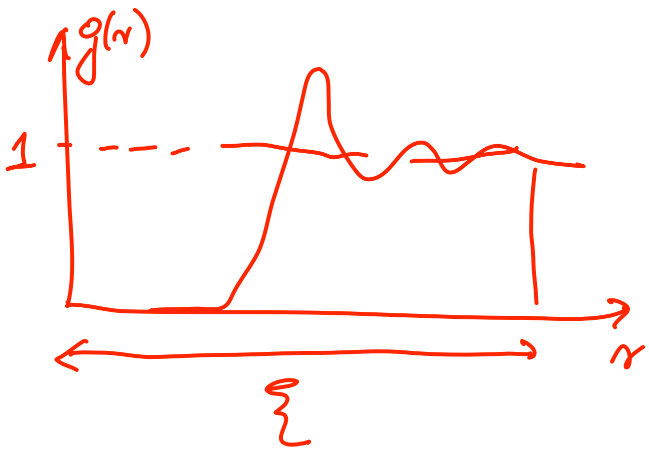
$$S_{SM} = \Sigma_{SM} \cdot S$$

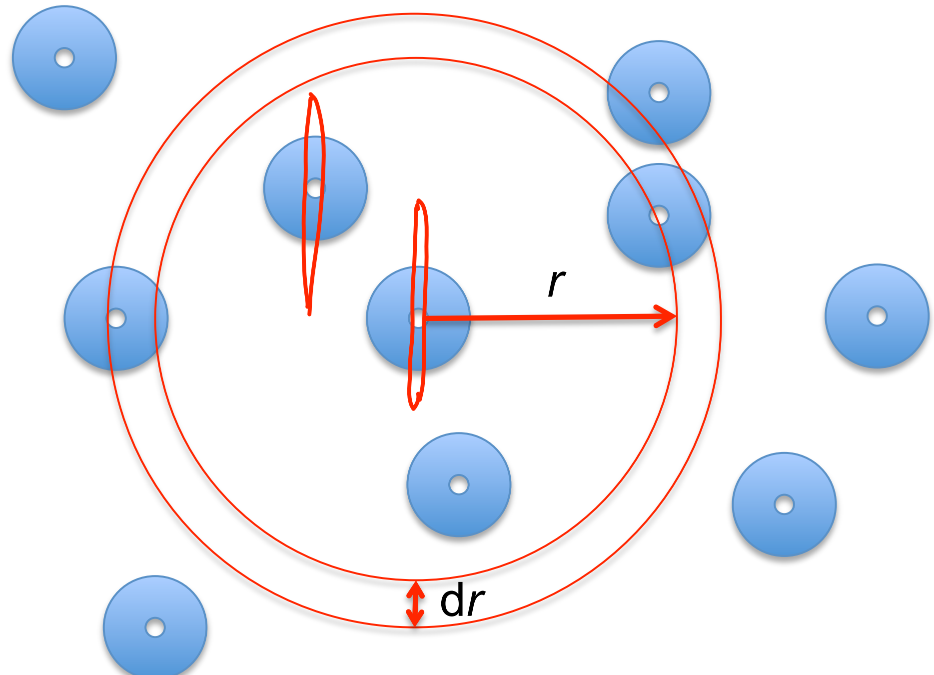
orient. ord. par.



Liquid crystals: descriptors

3. Pair distribution function
– general definition





Pair distribution function: $$g(r) = \frac{1}{\langle \rho \rangle} \frac{dn(r, r+dr)}{dv(r, r+dr)}$$

local density of atoms around an average atom

dn: number of atoms in a spherical shell
dv: spherical shell volume
r: distance of the shell from an arbitrary atom selected as the origin
<*ρ*>: average particle density

Liquid crystals: descriptors

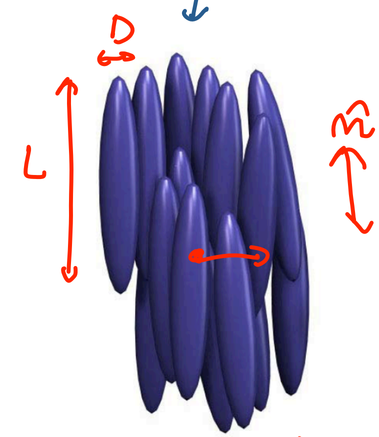
Liquid crystal structural descriptors:

3. Pair distribution function for liquid crystals

A more complex pair distribution function: dependence on both distance and mutual orientation of units

Nematic state:

- *intra*molecular correlation along molecular axis $\xi \simeq L$
- *inter*molecular correlation between molecules $\xi_{\parallel}$, $\xi_{\perp}$ → 2-5 L, 2-5 D

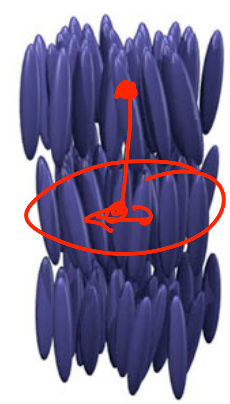


Smectic state:

- *intra*molecular correlation along molecular axis ↳ same as nematic
- *inter*molecular correlation between molecules

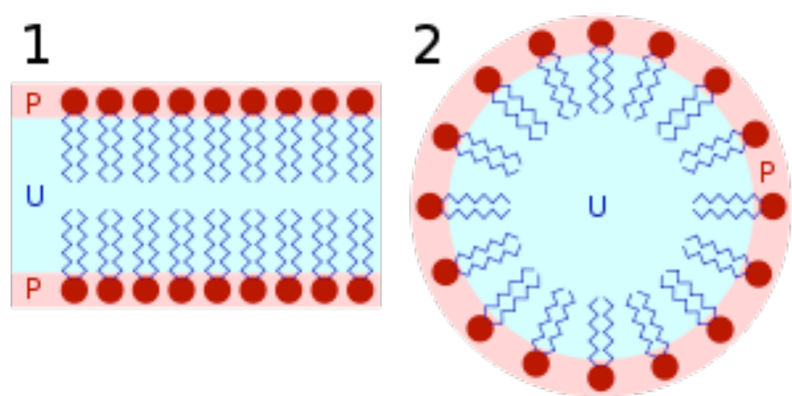
$\xi_{\perp}$ same as nematic

$\xi_{\parallel}$ long range



Surfactants

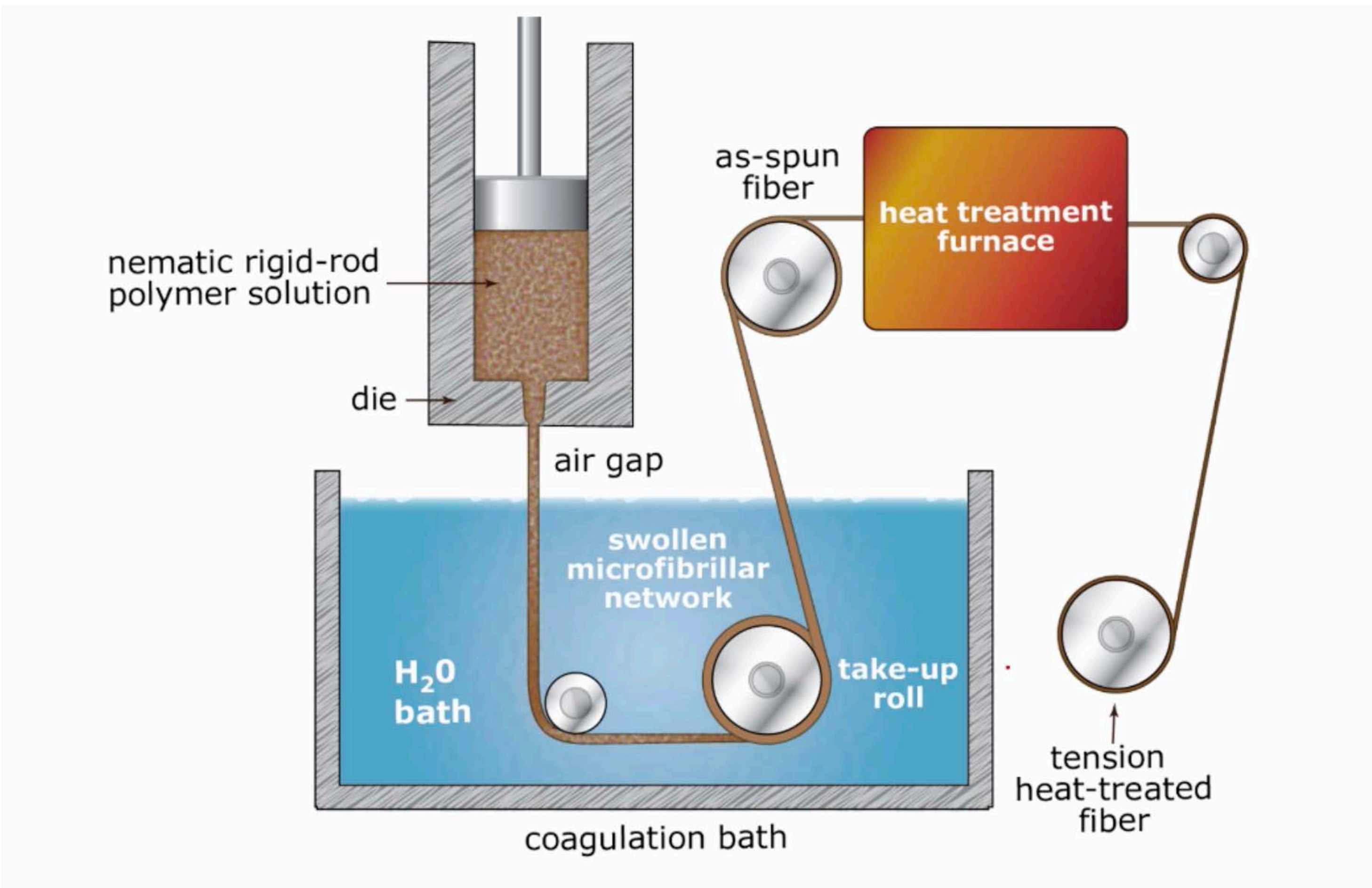
- Surfactants: Molecules that segregate at the interfaces between immiscible fluids
- Surfactants (e.g. soap molecules) can form a variety of liquid crystalline phases in water due to hydrophobic/hydrophilic competitions.
- The hydrophilic (ionic) portion of the surfactant is more stable when solubilized by water, whereas the hydrophobic (alkane) portion of the surfactant is more stable when surrounded by other organic chains.
- Hence, the materials self-assemble in the liquid phase, giving it a higher than isotropic order.



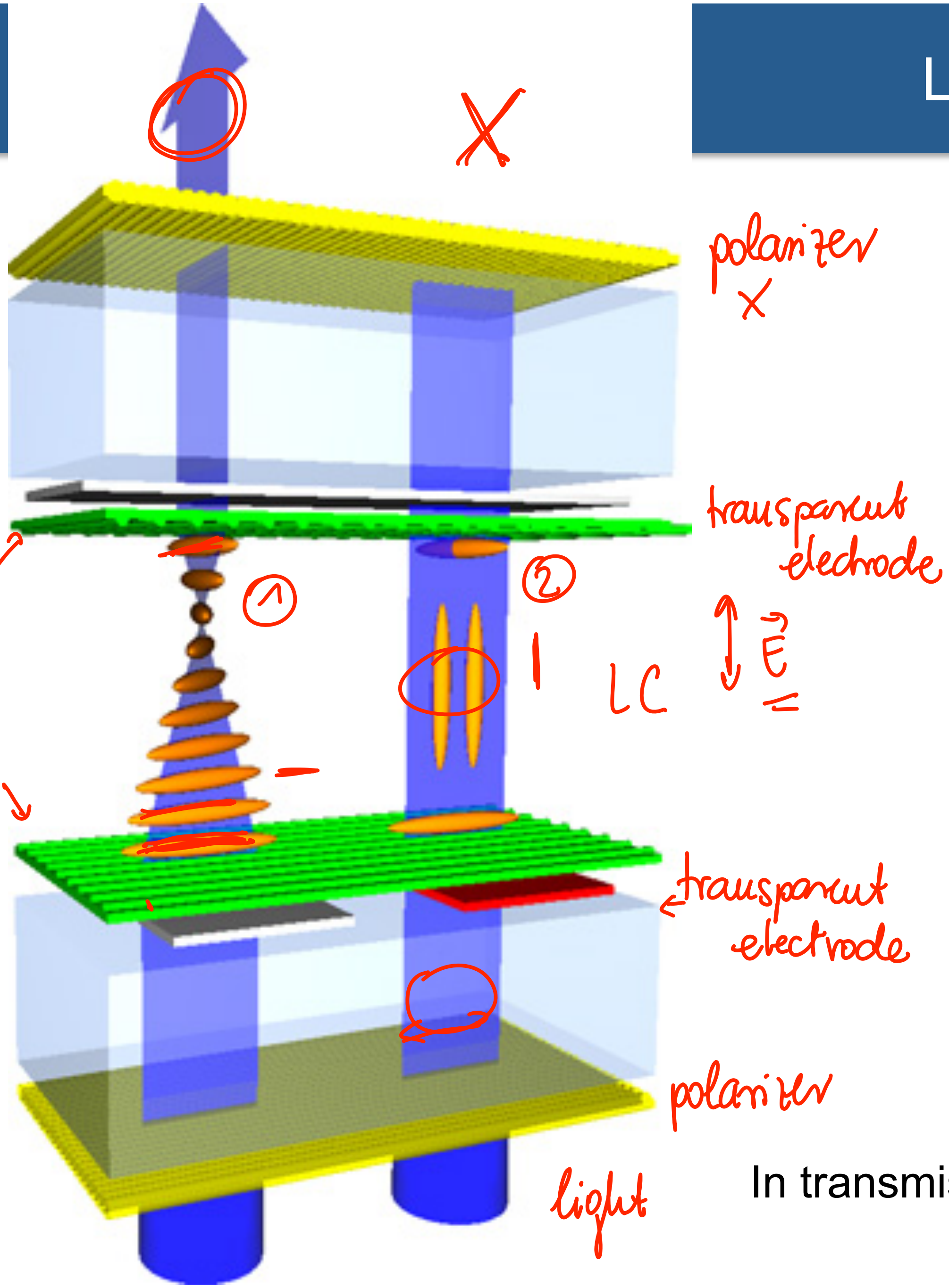
Lipid bilayers and micelles

Liquid crystal polymers

• Liquid crystal polymers are extremely unreactive, inert, and resistant to fire.
• Liquid crystallinity in polymers may occur either by dissolving a polymer in a solvent or by heating.
• The most famous lytropic liquid crystal polymer is **kevlar**.



Liquid crystal displays



$\vec{\tau} = \vec{\mu} \cdot \vec{E}$

In transmission