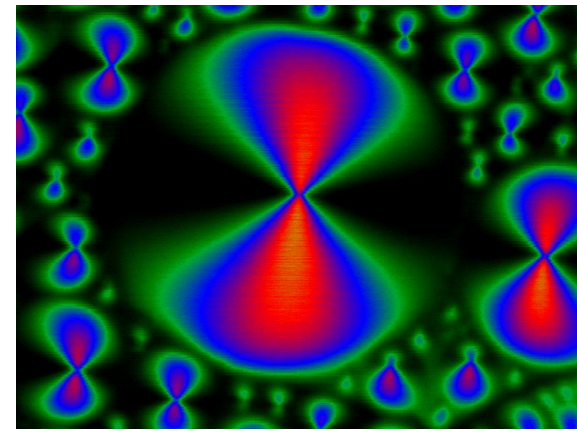


*Ivan I. Smalyukh*

*CU-Boulder & SKCM<sup>2</sup>*



**Topological solitons and knotted vortices in soft matter and magnetic solids**

1. Introduction to topological constructs in condensed matter and their experimental observations

2. Hopfions, heliknotons and other 3D solitons

3. Nonabelian vortices and knots, links and graphs made from them

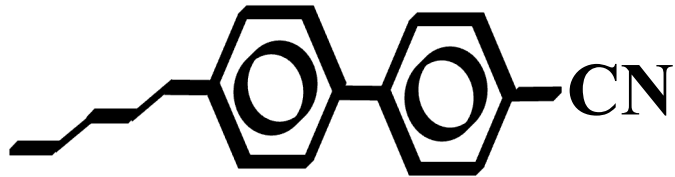
4. Topological meta-atoms and metamaterials made from them

# Hands on “topological protection”



→ Follow the material very closely

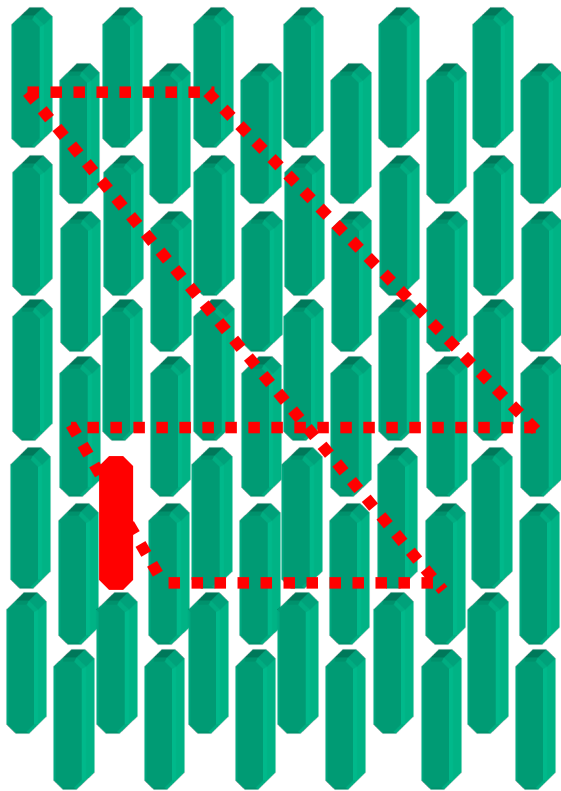
# Liquid Crystals (LCs)



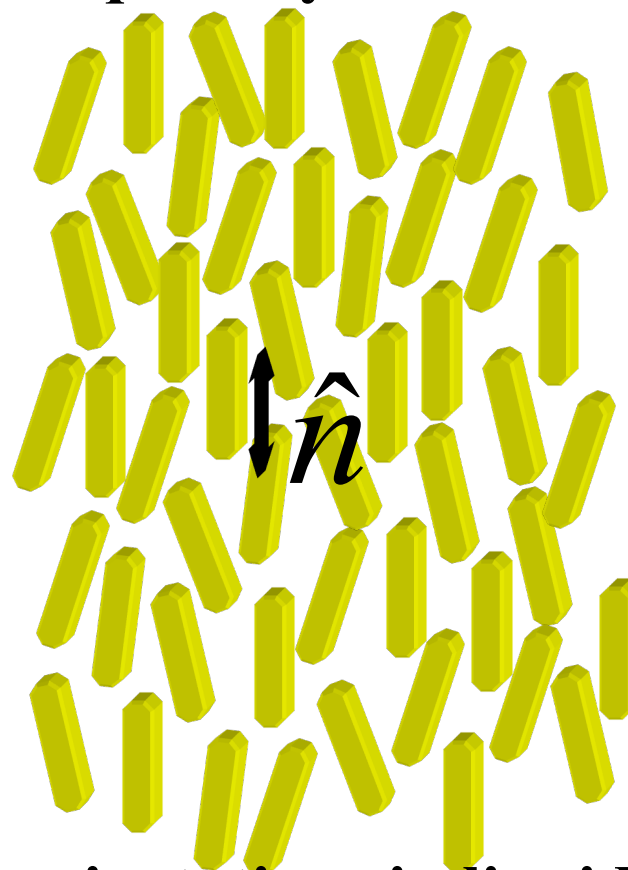
→ Flow like liquids;

→ Anisotropic like solid crystals;

Crystal



liquid crystal



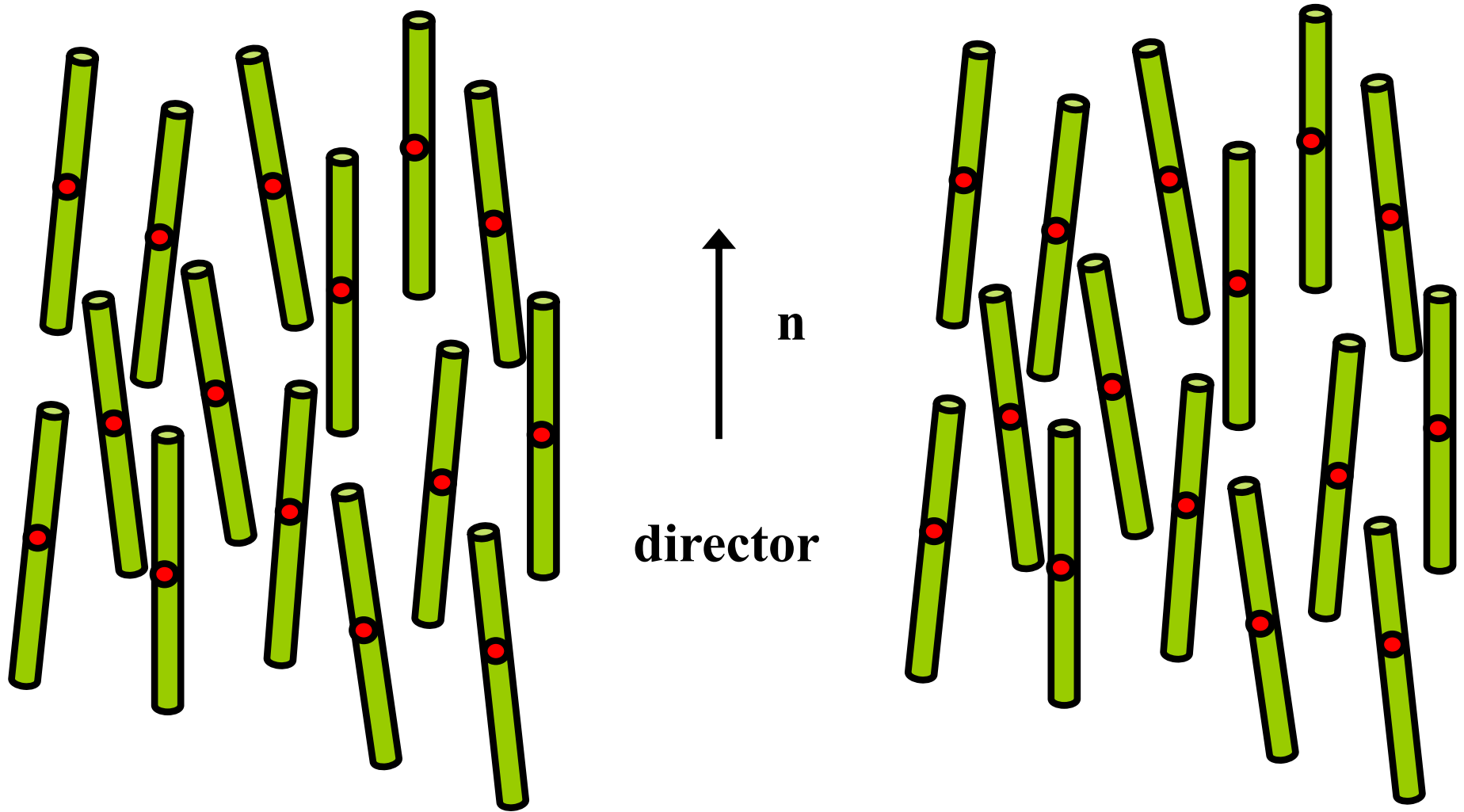
Isotropic fluid



Average local molecular orientations in liquid crystals are described by the director with head-tail symmetry  $\hat{n} \equiv -\hat{n}$

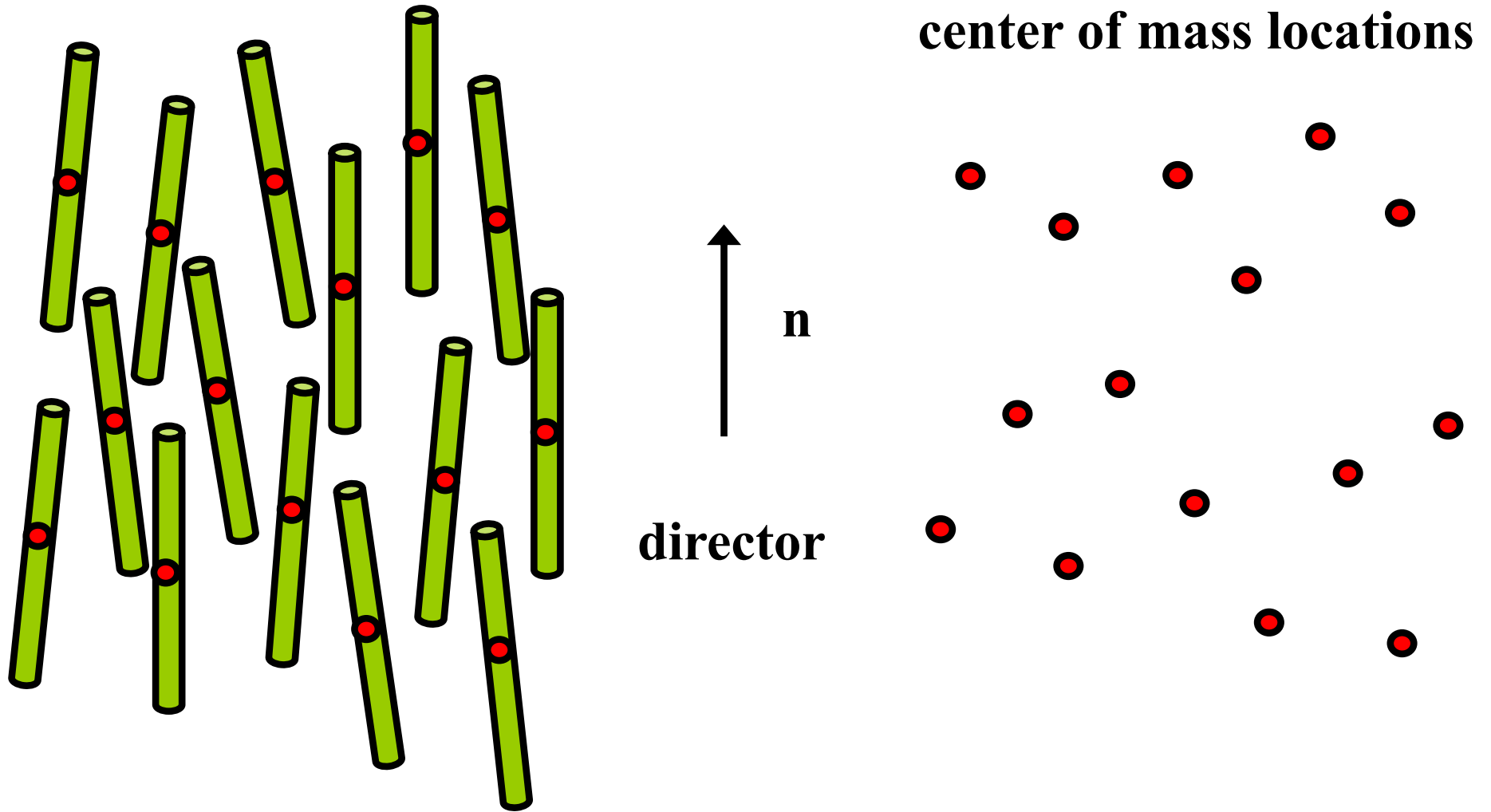
# Nematic liquid crystal

---



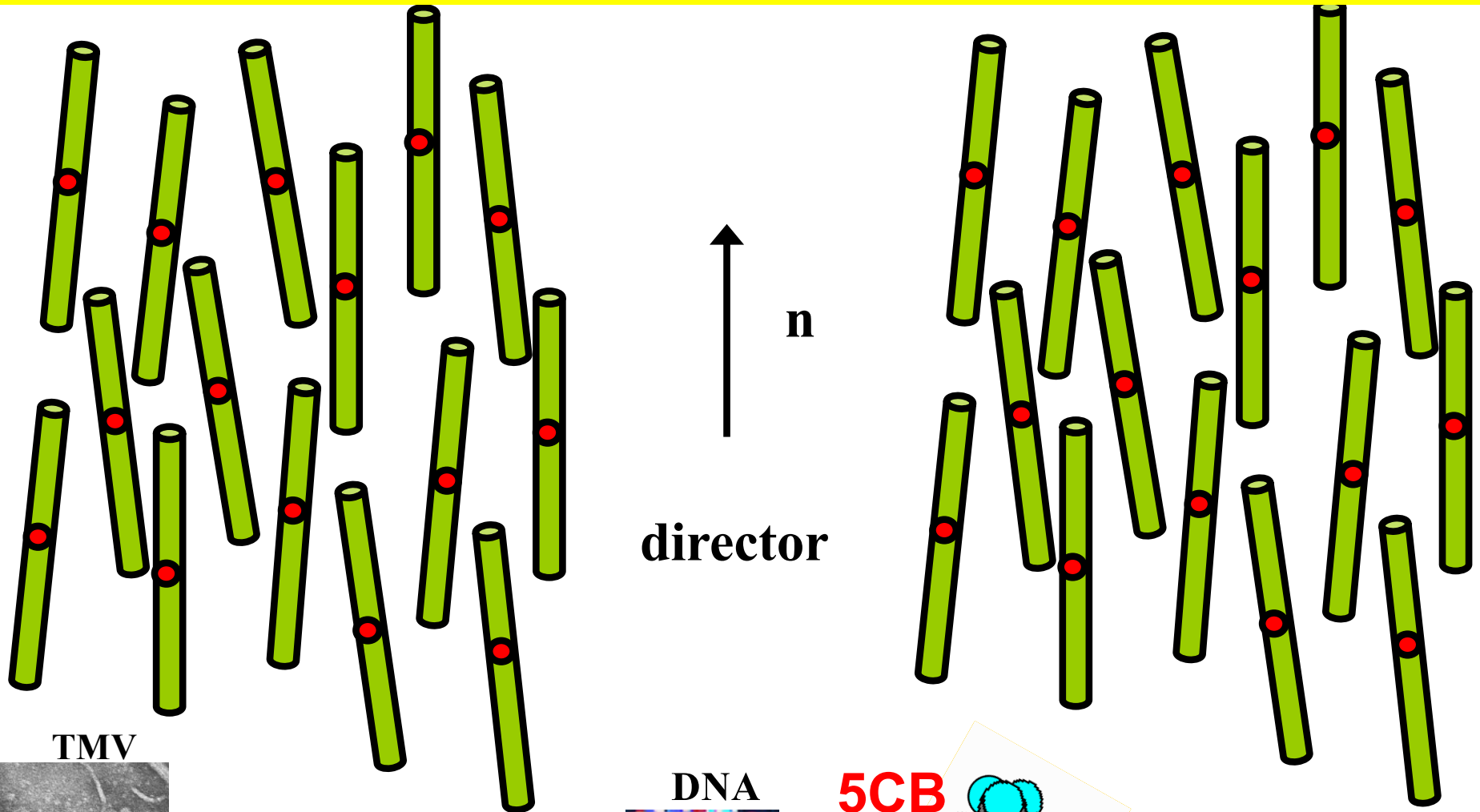
# Nematic liquid crystal

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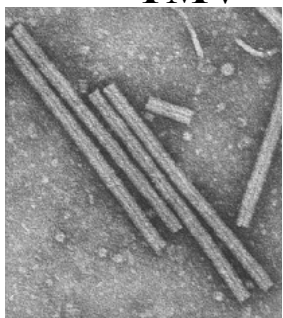


**Only orientational order (crystal), no positional order (liquid)**

# Nematic liquid crystal

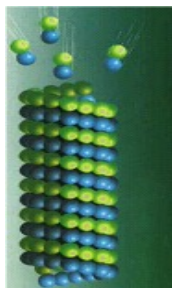


TMV



D=18; l=300 nm

microtubule



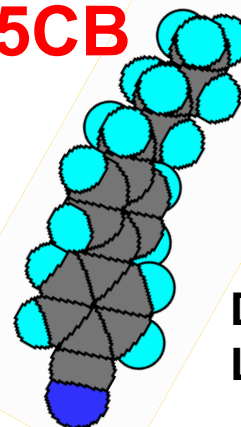
D=25 nm

DNA



D=2 nm

5CB

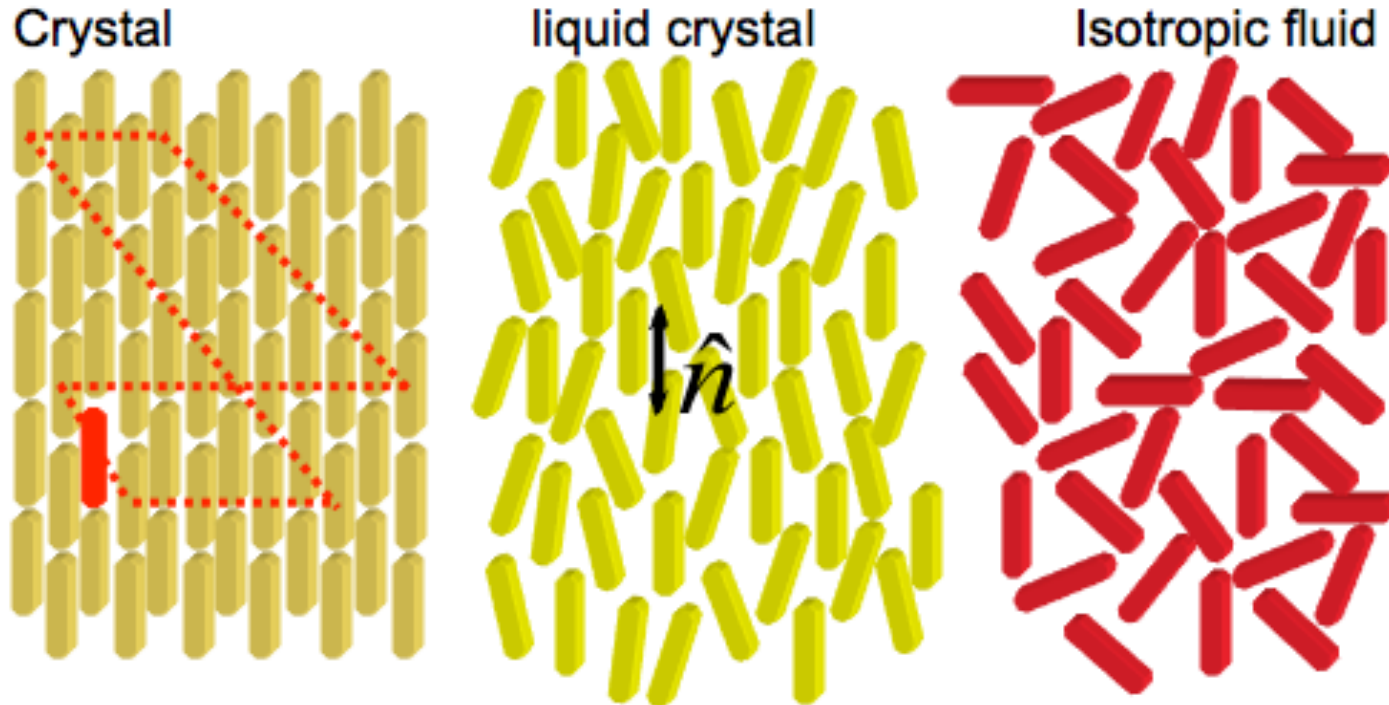


L=1.2 nm

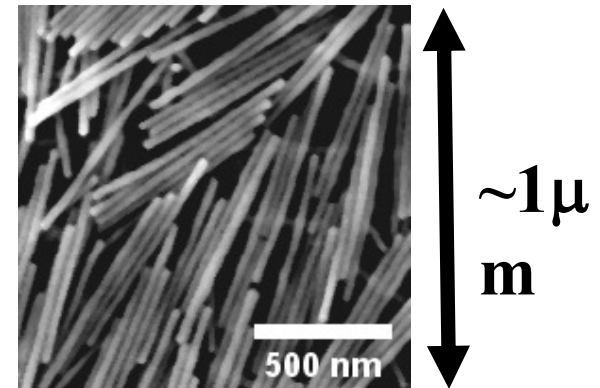
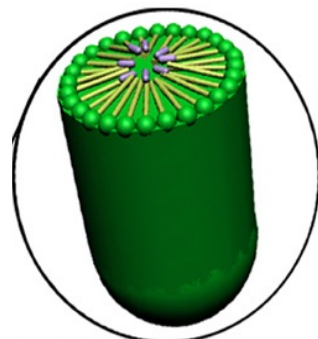
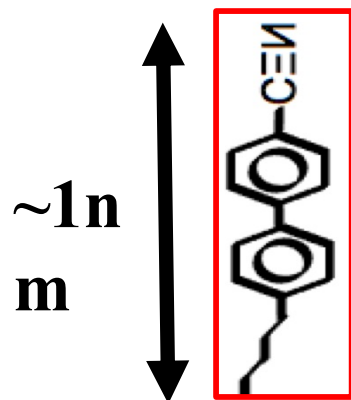
D<1 nm, l>1 nm  
LC molecule

# Nematic Liquid Crystals (LCs)

→ Nematic liquid crystal: flows like liquid, but anisotropic

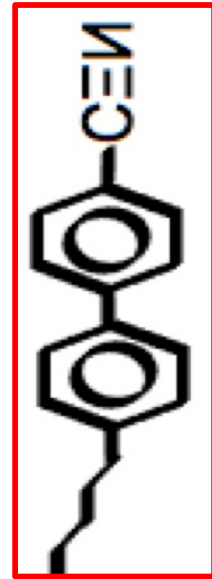
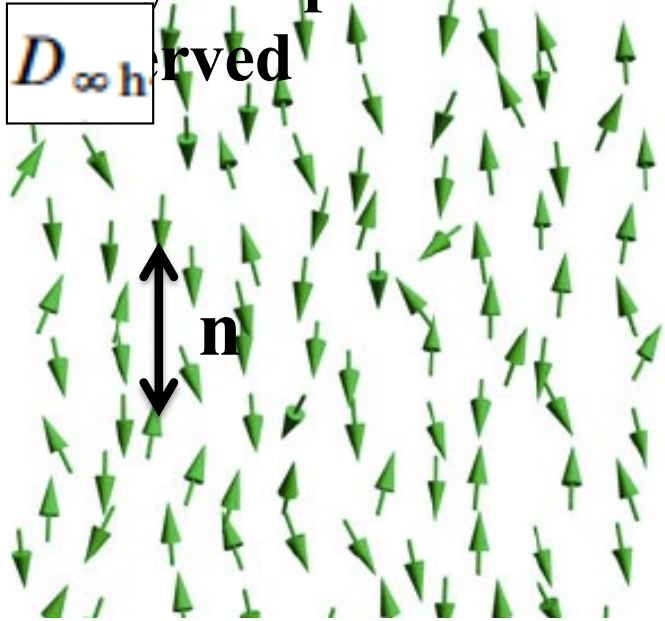


→ Building blocks: molecules, micelles, viruses, inorganic colloidal rods...

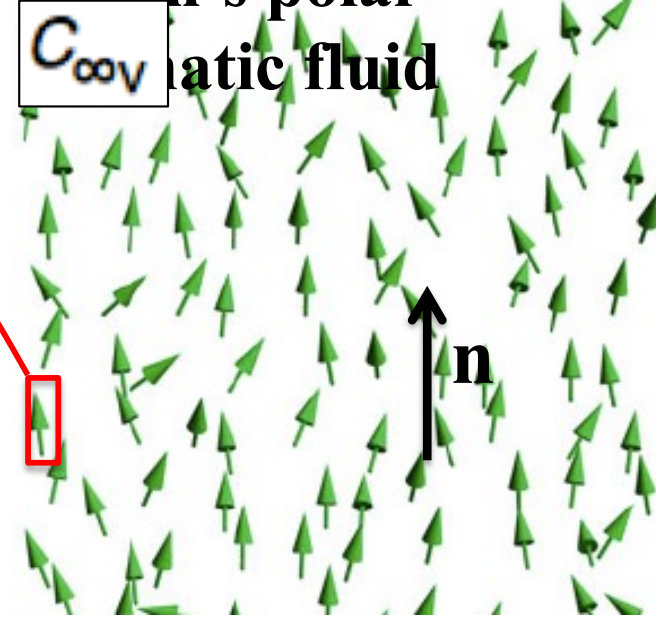


# Fundamental question: how order & fluidity coexist?

Only nonpolar nematic fluid



Born's polar nematic fluid

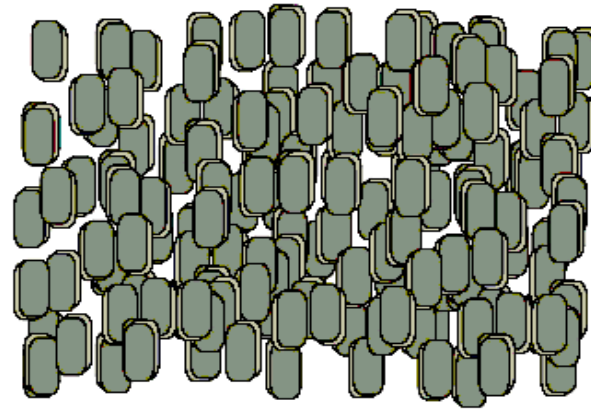
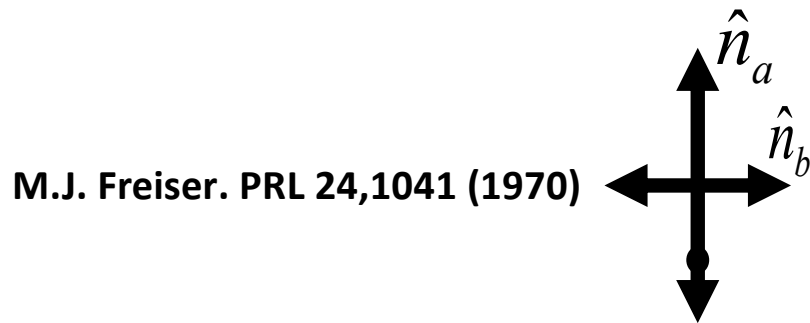


Max Born,  
Nobel Prize  
in Physics

→No polar fluids after a 100-year search - a blunder?

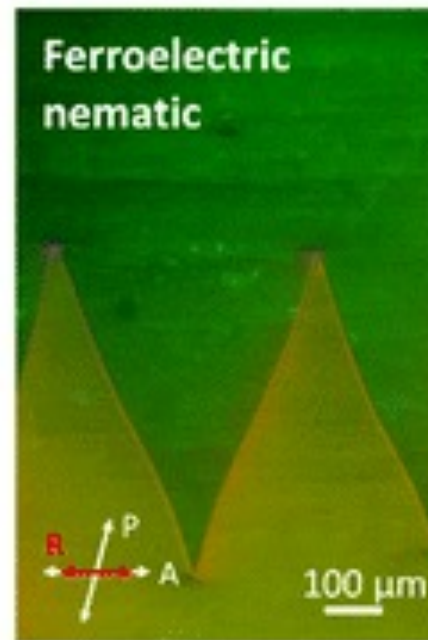
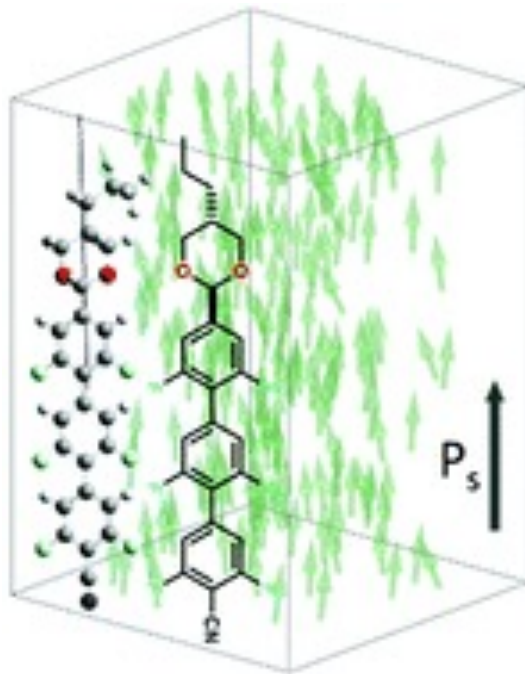
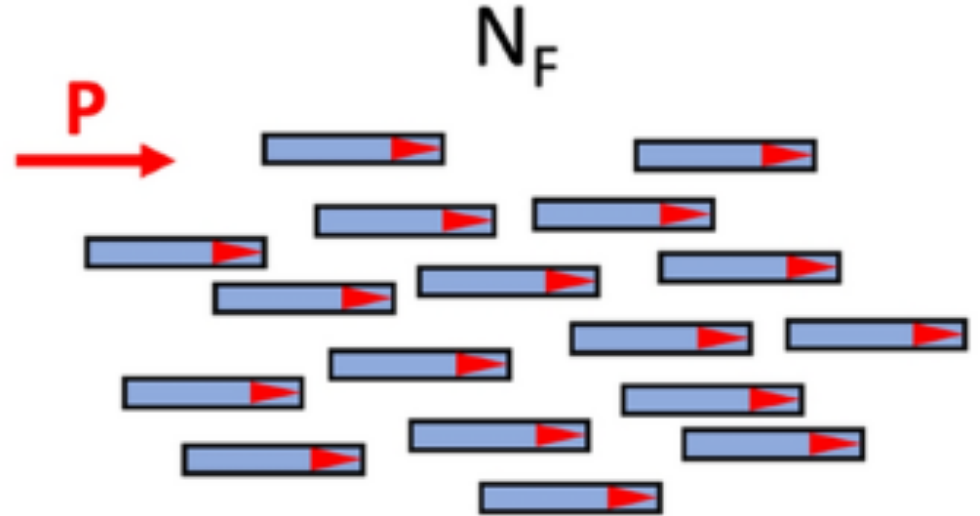
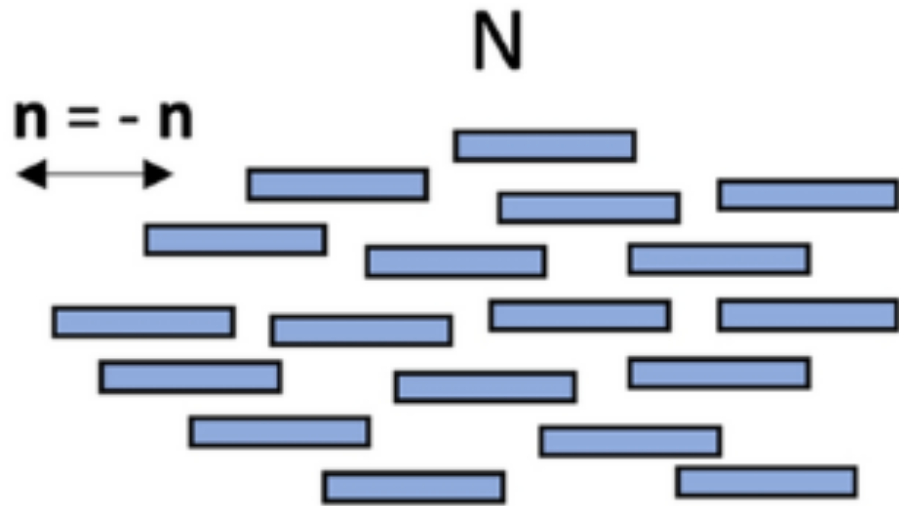
M. Born. Über anisotrope Flüssigkeiten. Sitz Kön Preuss Akad Wiss 30, 614–650 (1916) .

Do biaxial nematic fluids exist?



→Was still elusive after a 50-year search...

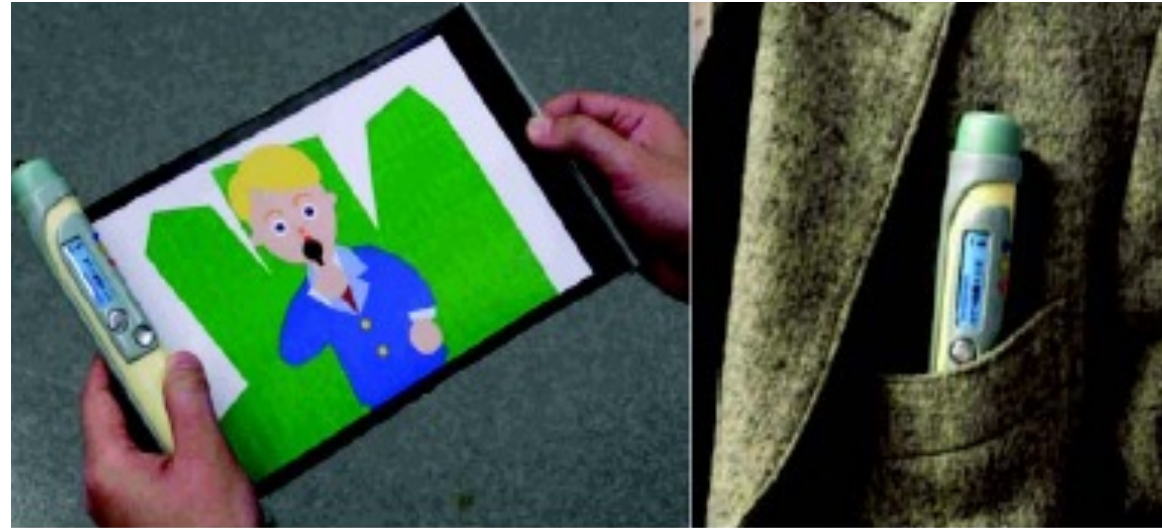
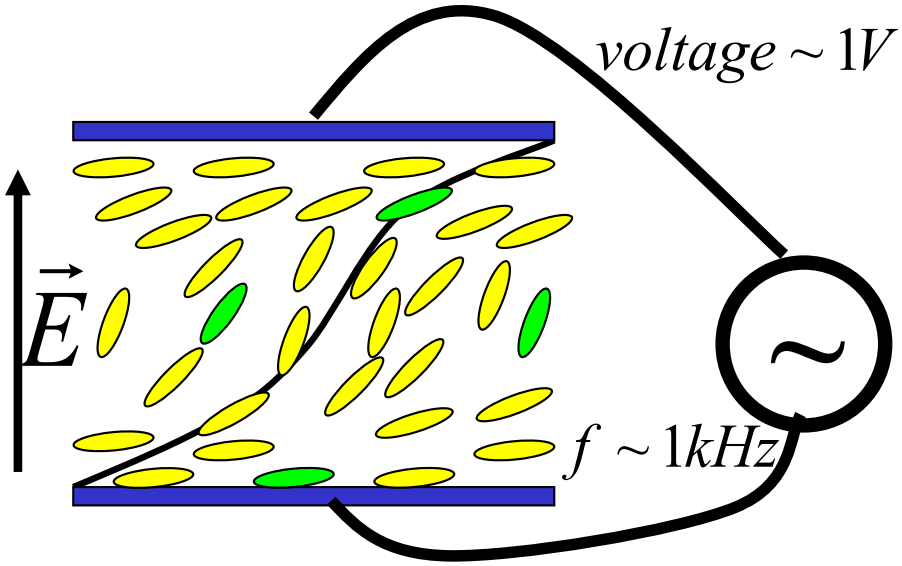
# Polar nature of a ferroelectric nematic



# Very useful soft materials

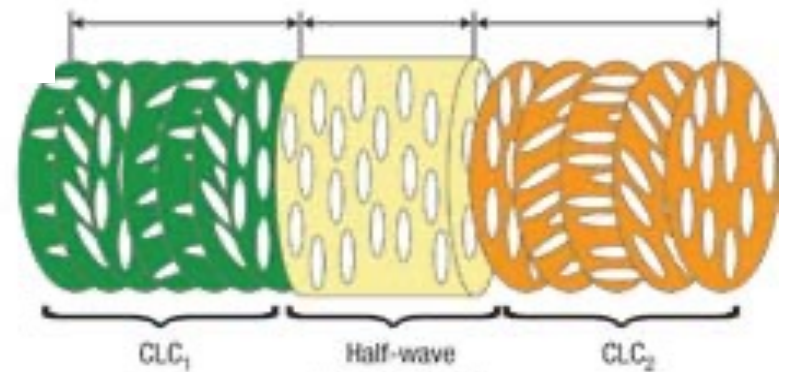
→ Response to tiny external fields

→ Flexible displays



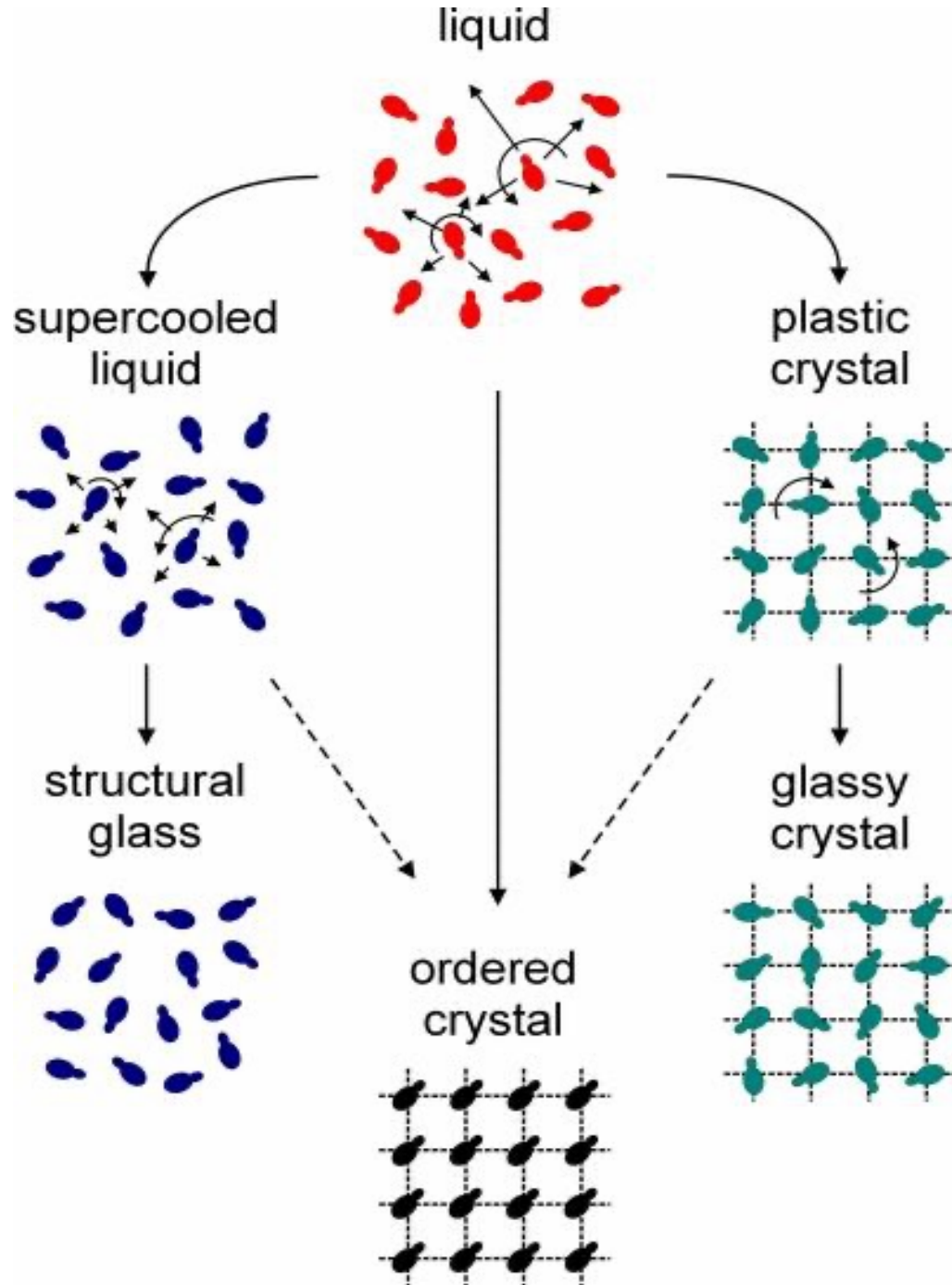
Fujicake, Sato, & Murashige, Tokyo, Japan.

→ Learning from nature: soft materials are useful for a variety of applications;



J. Hwang *et al.*, *Nature materials* **4**, 383 (2005)

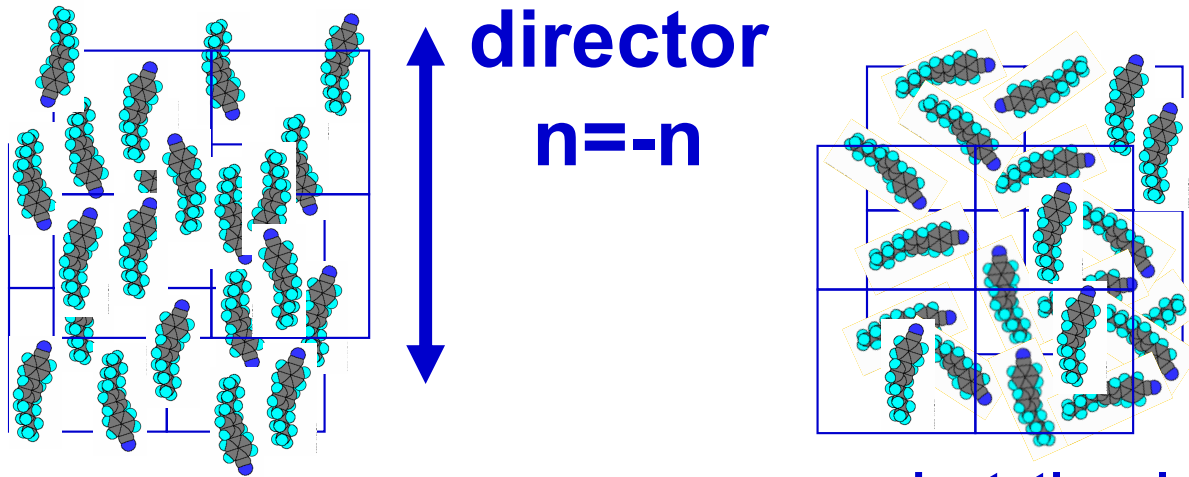
# *Plastic Crystals – no orientational order*



	Positional order	Orientalional order
	yes	yes
	yes	no
	no	yes
	no	no

# Interactions between LC building blocks

- Induced dipole-dipole interactions (thermotropic LCs);

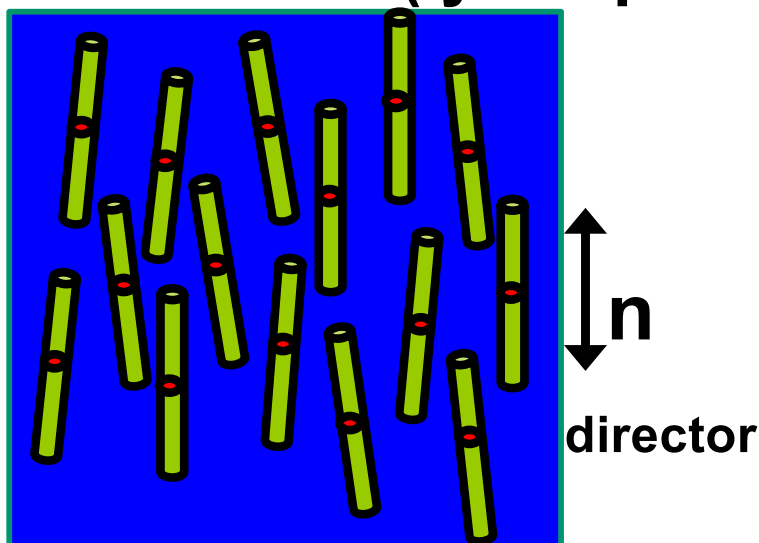


- Order appears upon decreasing temperature

orientational order;  
no positional order (mobility):  
Nematic LC

no orientational and  
no positional order  
Liquid

- Steric interactions (lyotropic LCs formed by hard rods):



- Maximizing Entropy:**
- Orientational and translational entropy
  - Order appears upon increasing concentration
  - Reducing excluded volume due to steric interactions – increasing the number of states and entropy.

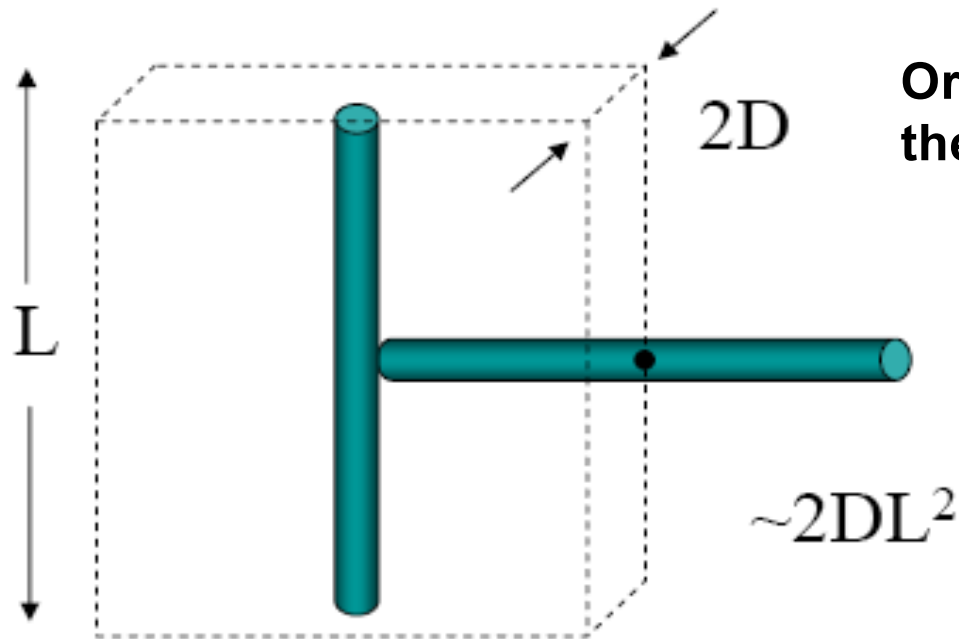
# **Interactions between LC building blocks**

---

**Some of the interaction leading to the LC order:**

- Steric interactions (lyotropic LCs of hard rods)**
- Induced dipole-dipole interactions (thermotropic LCs);**
- Hydrophobic/hydrophilic interactions (surfactant-based lyotropic LCs, chromonic LCs);**
- Screened electrostatic (LCs formed by biopolymers and biomolecular complexes)**
  
- The interactions are usually weak and comparable in strength to thermal fluctuations.**
  
- Will be explored in details for specific LC phases;**

# Excluded Volume Depends on Rod Orientation



Orientalional Entropy is the Packing Entropy

$$\pi D^2 2L$$

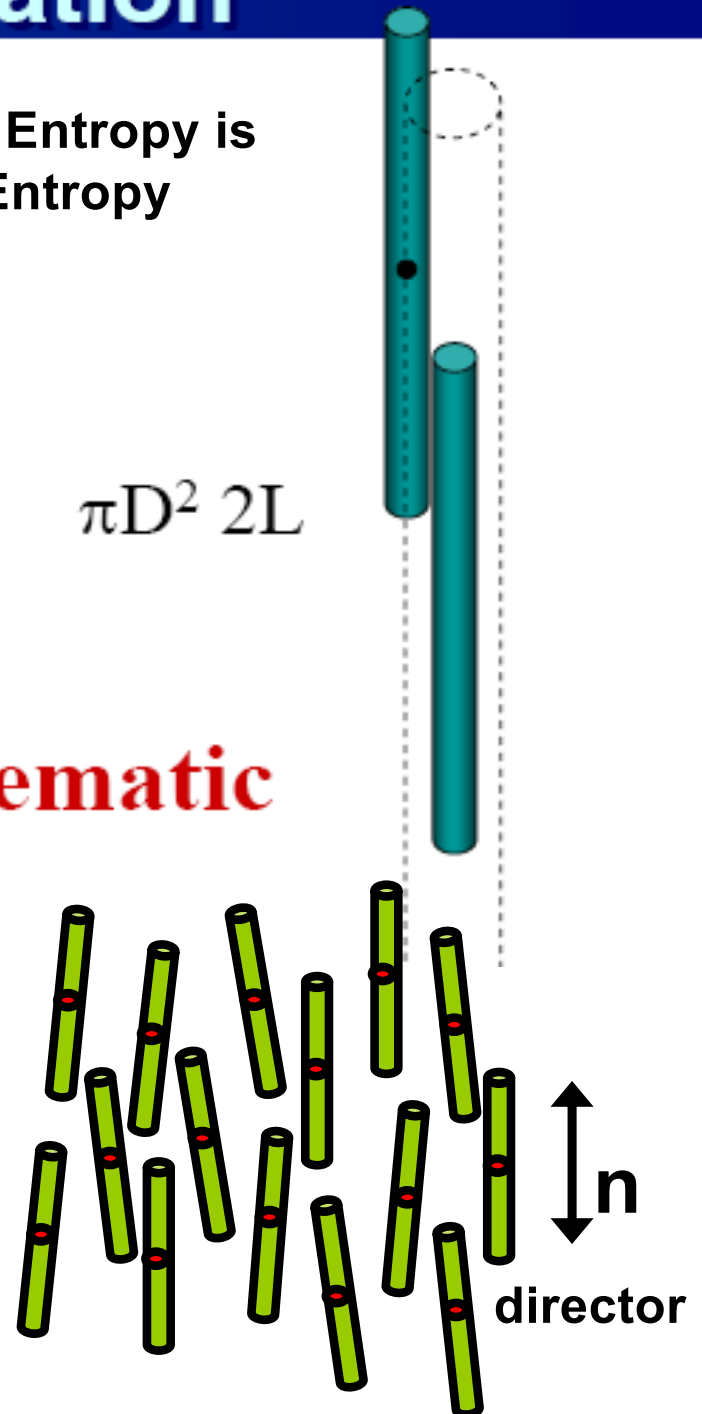
**isotropic**

**nematic**

$$\text{Ratio : } L/\pi D$$

**Lars Onsager:**

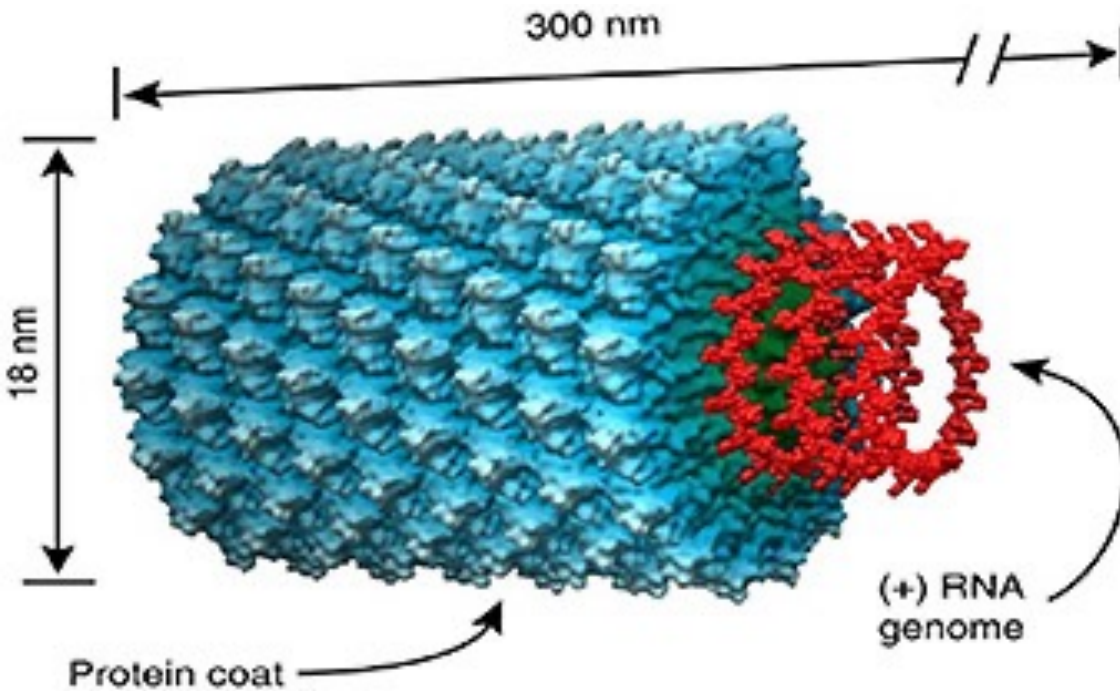
1. Minimize both translational and rotational parts of entropy of rods;
2. Translational entropy favors nematic-like order (due to smaller excluded volume).
3. Obtain nematic order at some critical concentration of the rods



# Liquid Crystal of Rigid Rods of TMV



Tobacco mosaic virus (TMV)

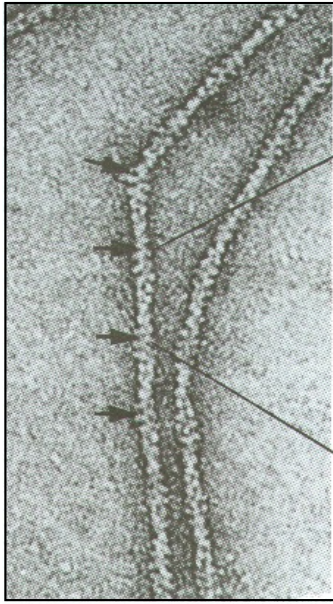


Orientationally-ordered

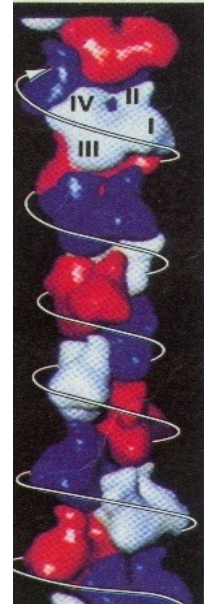


Spaghetti before cooking?

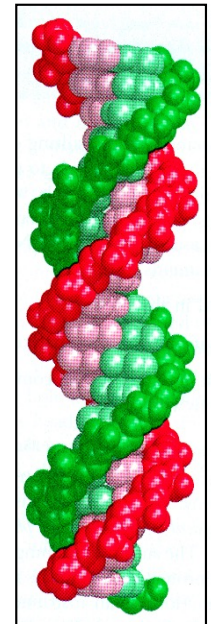
# Actin & DNA as building blocks for LC phases



- **Actin Rods**
- **Charge Density:  $e^-/2.5\text{\AA}$**
- **Diameter:  $D \sim 8\text{ nm}$**
- **Persistence Length:  $\xi_p \sim 10\ \mu\text{m}$**



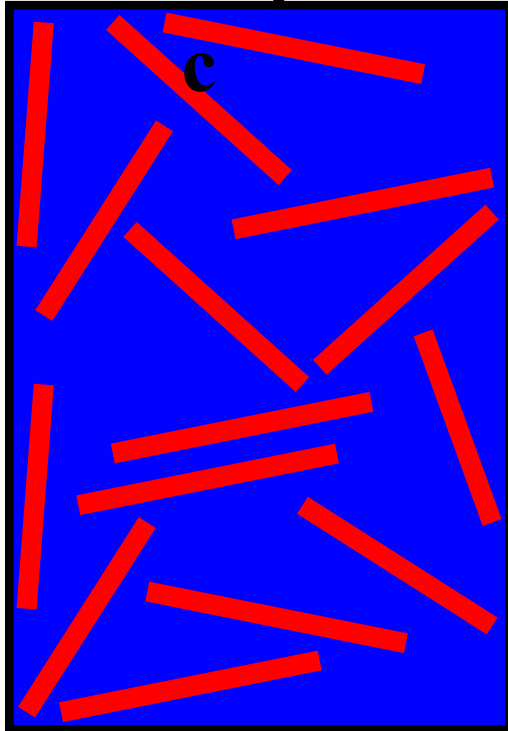
- **DNA chains**
- **Charge Density:  $e^-/1.7\text{\AA}$**
- **Diameter:  $D \sim 2\text{ nm}$**
- **Persistence Length:  $\xi_p \sim 50\text{ nm}$**



**Other biological rods: fd virus, TM virus, microtubules, etc.**

# Onsager criterion for nematic order of rigid rods

**Isotropi**



**Nematic**

→ **Critical concentration**

$$\phi_{NI} \sim 4 \frac{D_{rod}}{l_{rod}} \quad \text{when} \quad \frac{l_{rod}}{D_{rod}} \gg 1$$

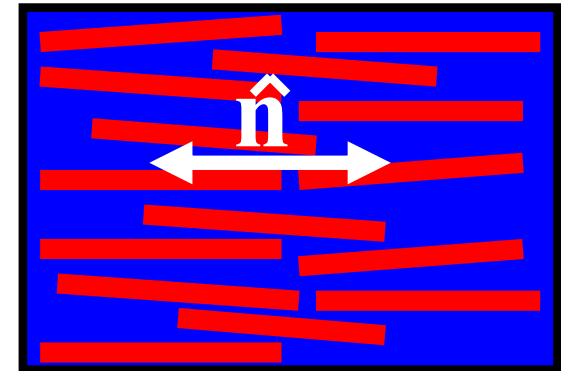
**Increasing**

**concentration**

→ **Steric interactions**

→ **Orientalational entropy**

$$\phi_{NI} = (0.3 - 10)\%$$



$$l_{actin} = 300 \text{ nm}$$

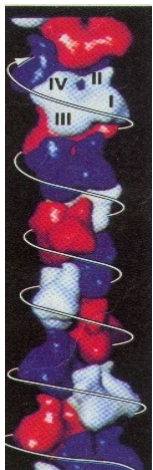
$$l_{actin} \leq \lambda_{actin} = 10 \mu m$$

→ **Semi-flexible rods**

→ **Critical number density**  $4.48 / (\pi D_{rod} l_{rod}^2 / 4)$

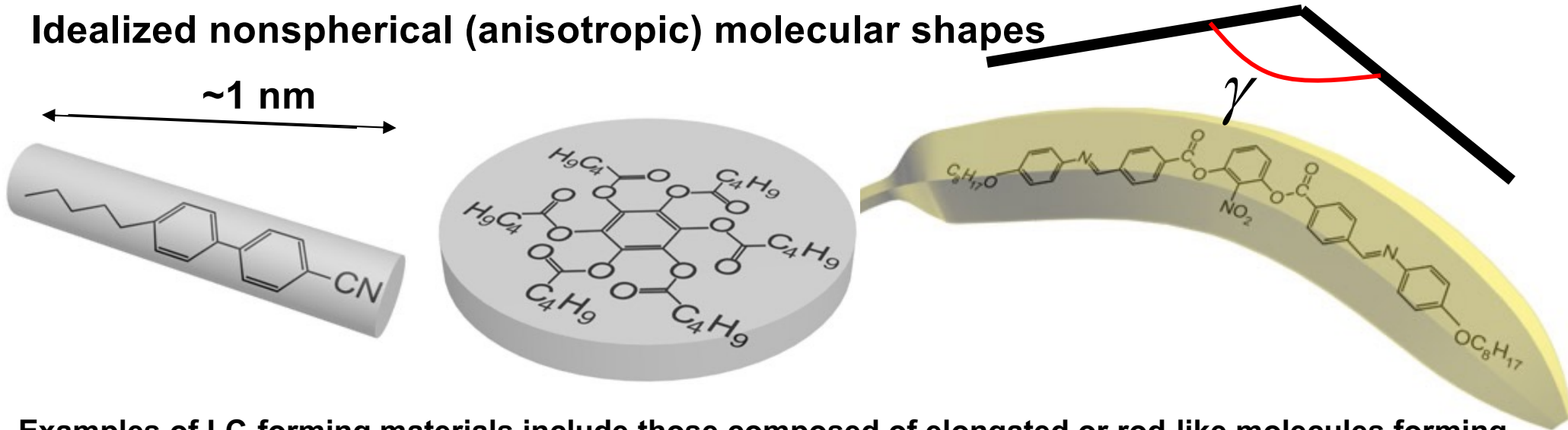
→ **For rods of**  $l_{actin} = 300 \text{ nm}$  **one needs**  $3.4 \cdot 10^{23} \text{ rods/m}^3$

→ **Charged rods have effective diameter**  $D_{eff} > D_{rod}$



# From anisotropic molecules to mesophases

Idealized nonspherical (anisotropic) molecular shapes

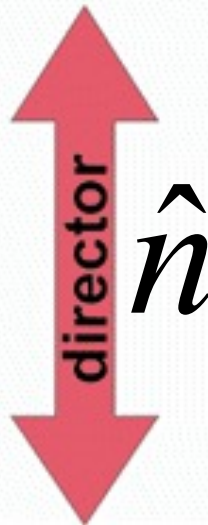


Examples of LC-forming materials include those composed of elongated or rod-like molecules forming *calamitic* LCs and disk-like molecules forming *discotic* LCs, as well as banana-shape molecules and building blocks with more complicated shapes forming exotic thermotropic LC phases.

liquid-crystalline  
phases

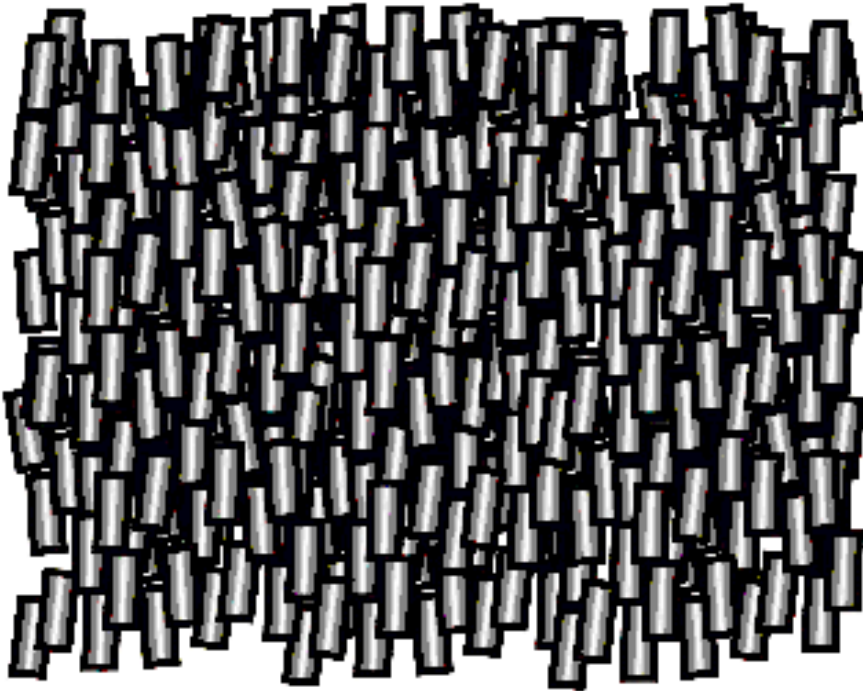


Molecular self-assembly into LC  
phases

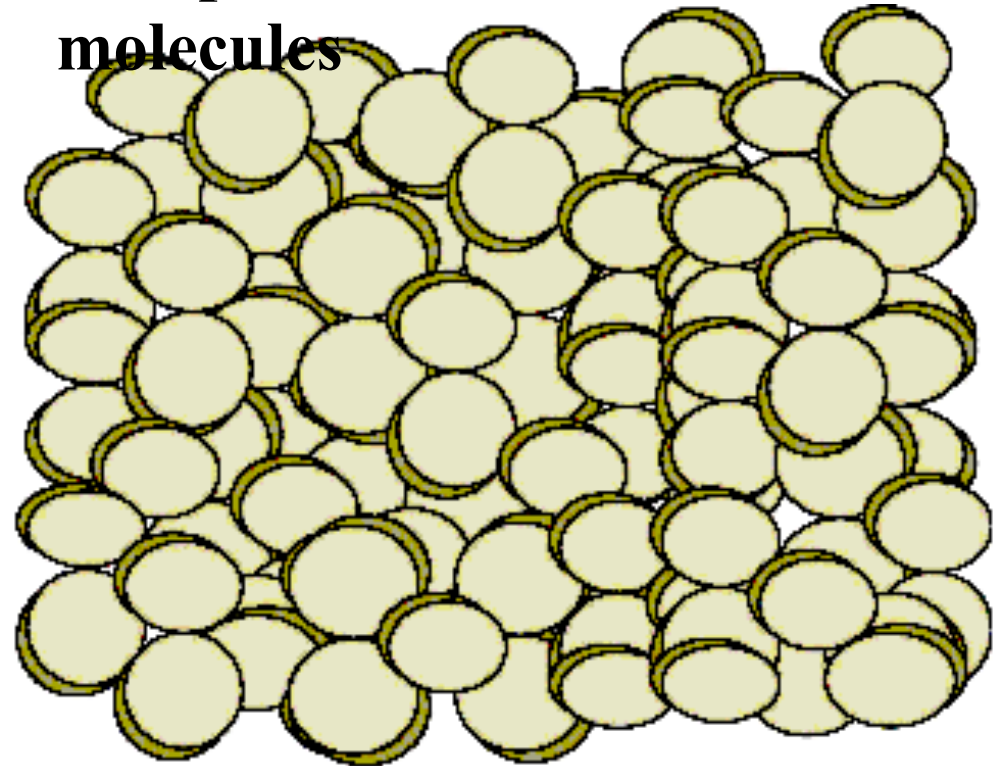


# Nematic liquid crystals

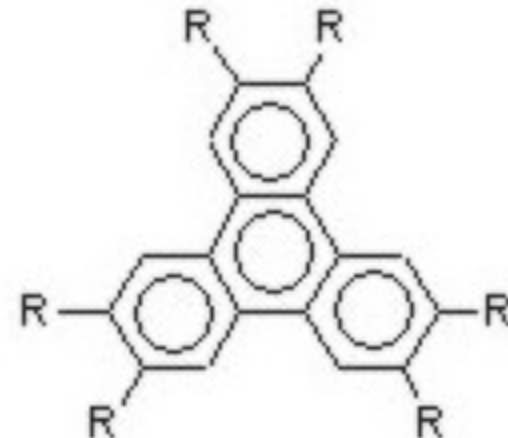
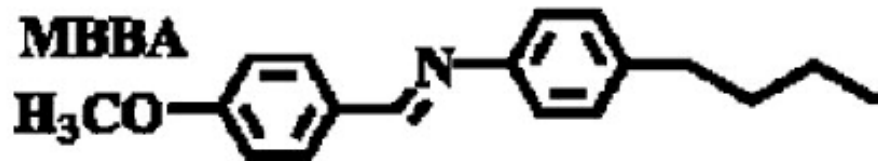
Composed of rod-like molecules



Composed of disk-like molecules

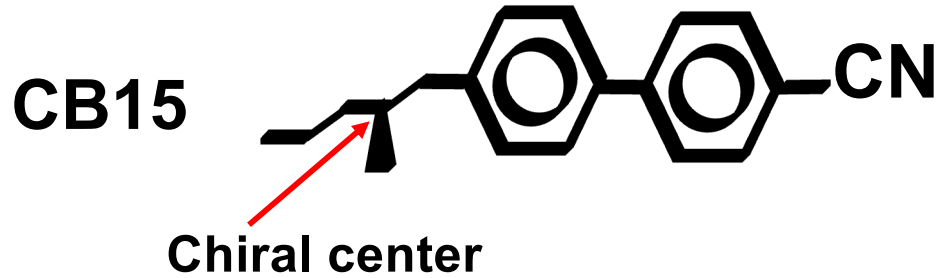
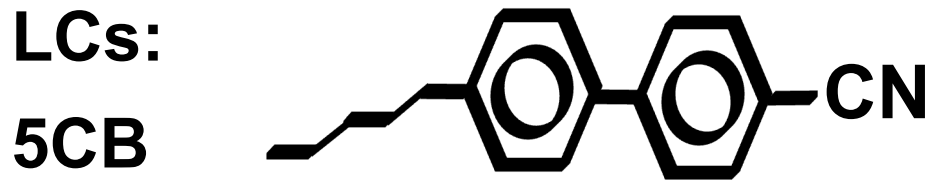


Typical rod-like and disk-like LC molecules



# Chiral nematic LCs: twisted ground states

Chiral & ordinary nematic LCs:



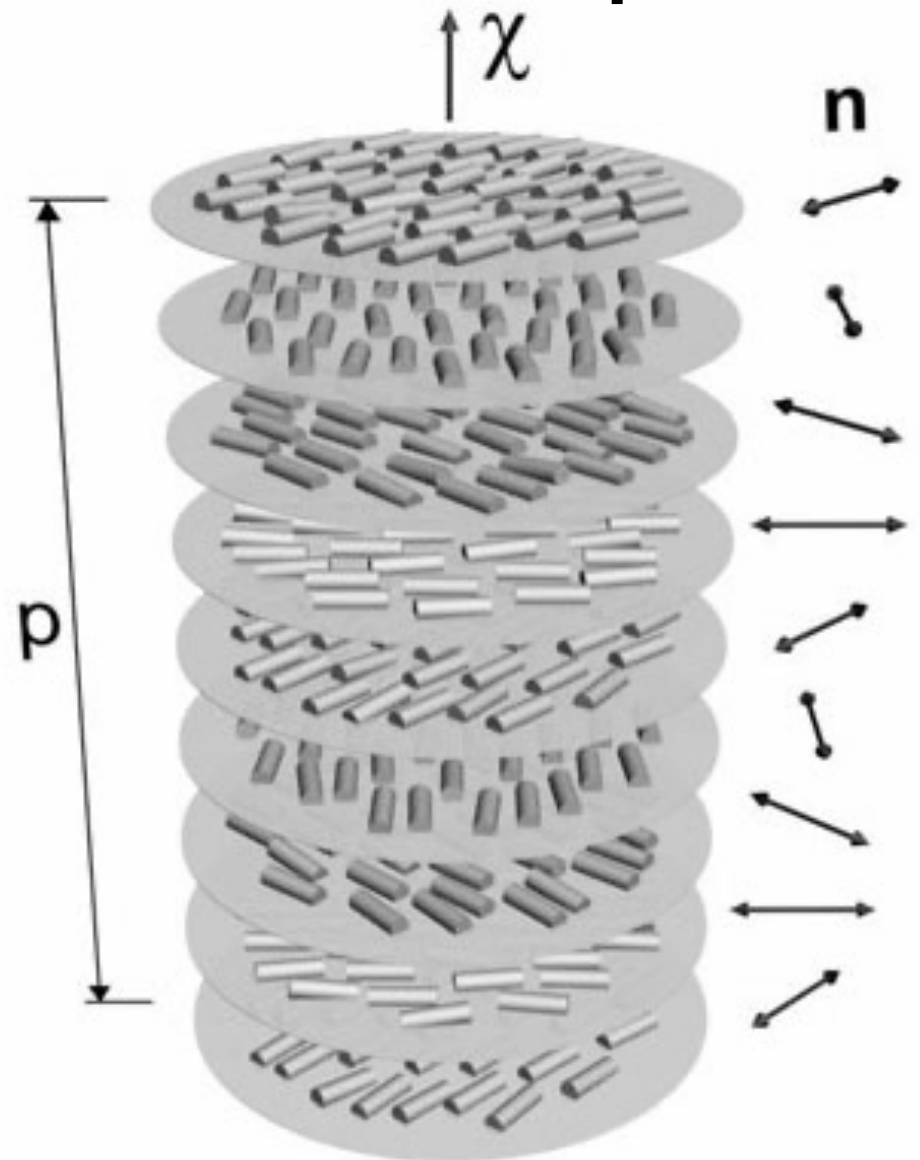
Chiral Dopant	$HTP$ ( $\mu\text{m})^{-1}$
S-811	-14
IS-4651	-13.6

- indicates left twist sense

$$p = \frac{1}{HTP * c}$$

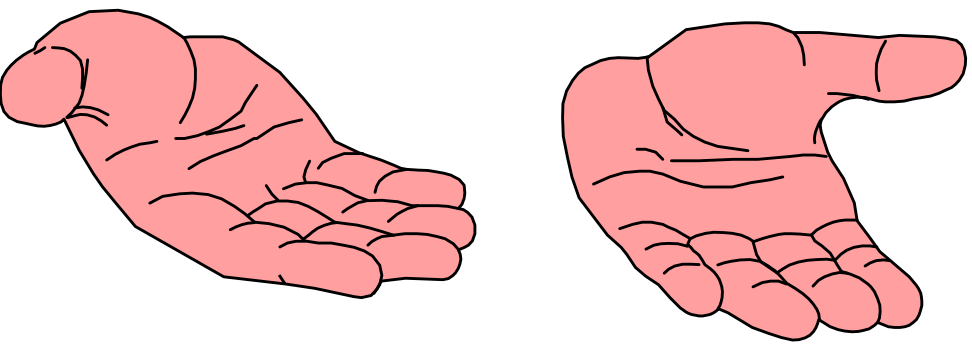
C – dopant concentration

Cholesteric phases



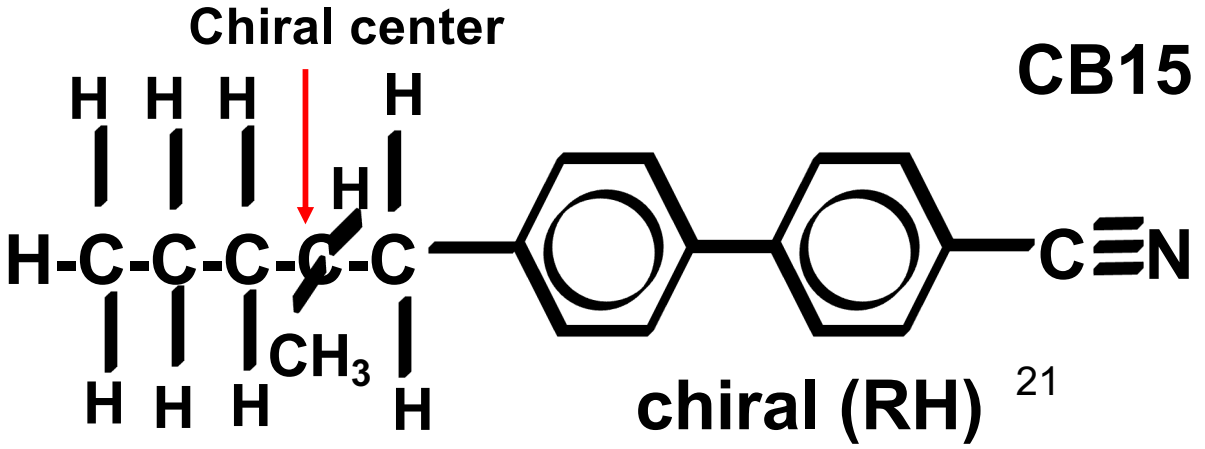
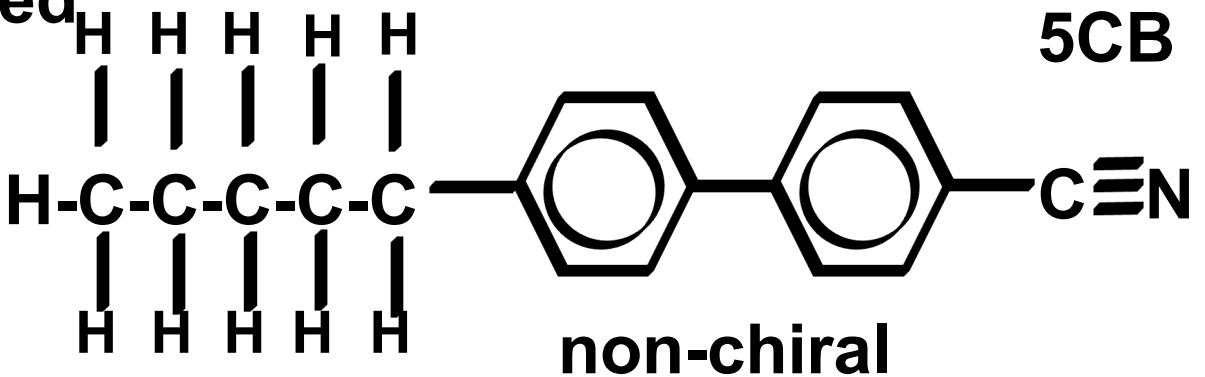
One can obtain a cholesteric (chiral nematic) material by doping a conventional nematic with a chiral dopant.

# Effects of chirality on LC self-organization

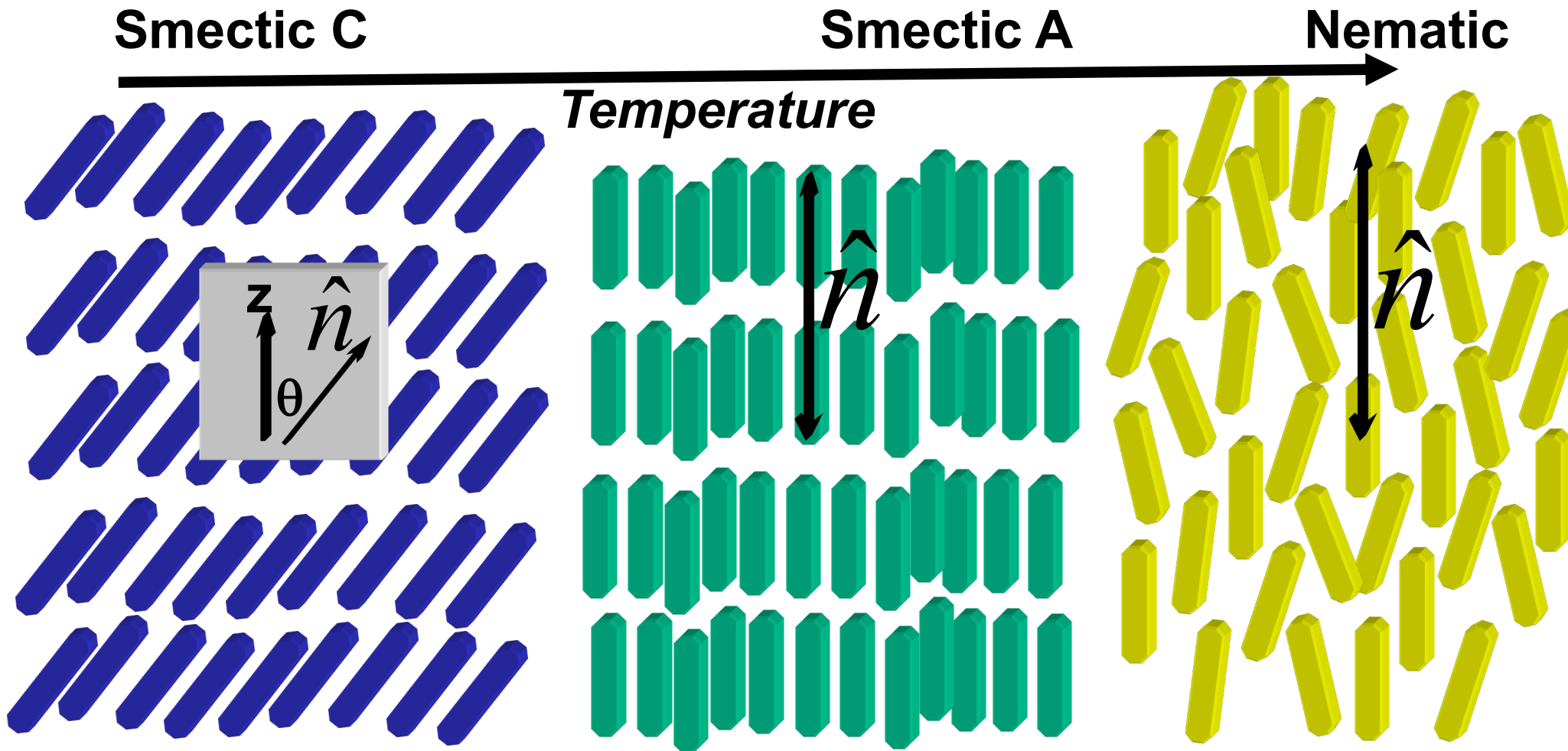


left-handed right-handed  
mirror images

The methyl group on the 2nd carbon atom on the alkyl chain of the molecules extends out of the plane of the paper and the hydrogen atom extends into the plane of the paper. Therefore the 2nd carbon can be thought of as a right or left handed coordinate system



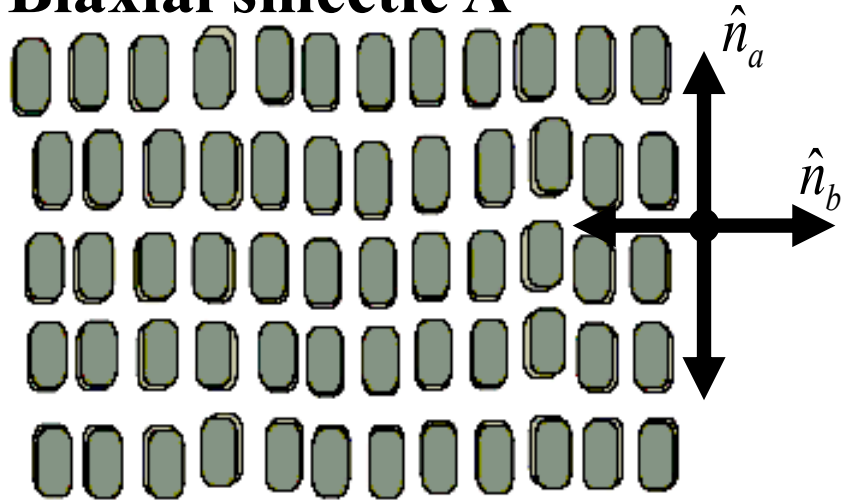
# Smectic A, smectic C, and phase transitions



The word "smectic" is derived from the Greek word for soap. This seemingly ambiguous origin is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually a type of smectic liquid crystal. The phase transitions between nematic and smectic phases can be observed at different temperatures on heating and cooling. Molecules in the smectic phases show a degree of *translational order* not present in the nematic. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted to within these planes, and separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic.

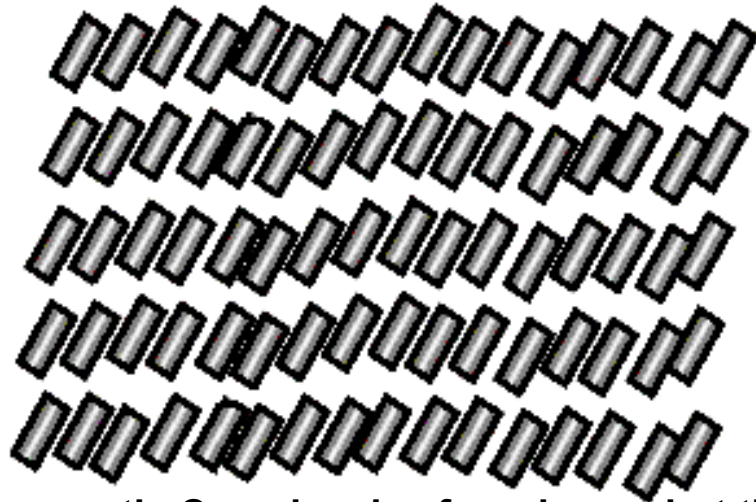
# Biaxial nematic & smectic liquid crystals

## Biaxial smectic A



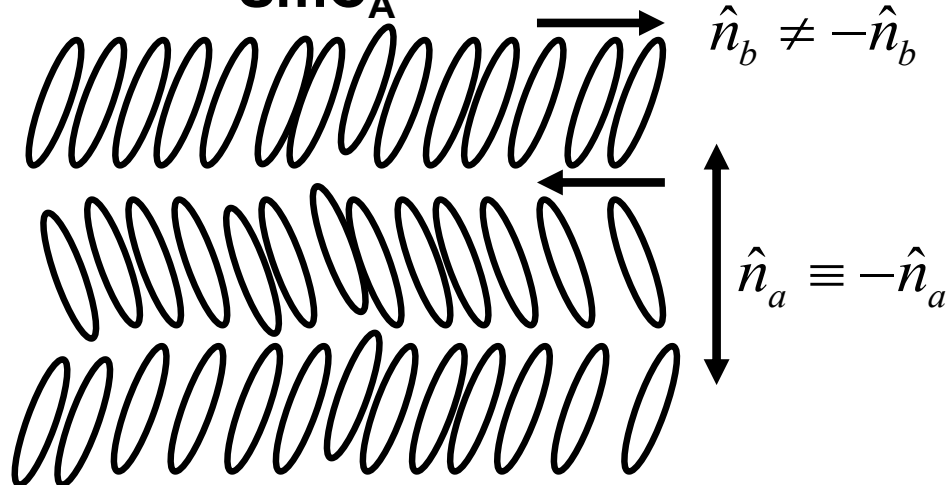
Orientalional order described by more than one directors;

## Biaxial smectic C



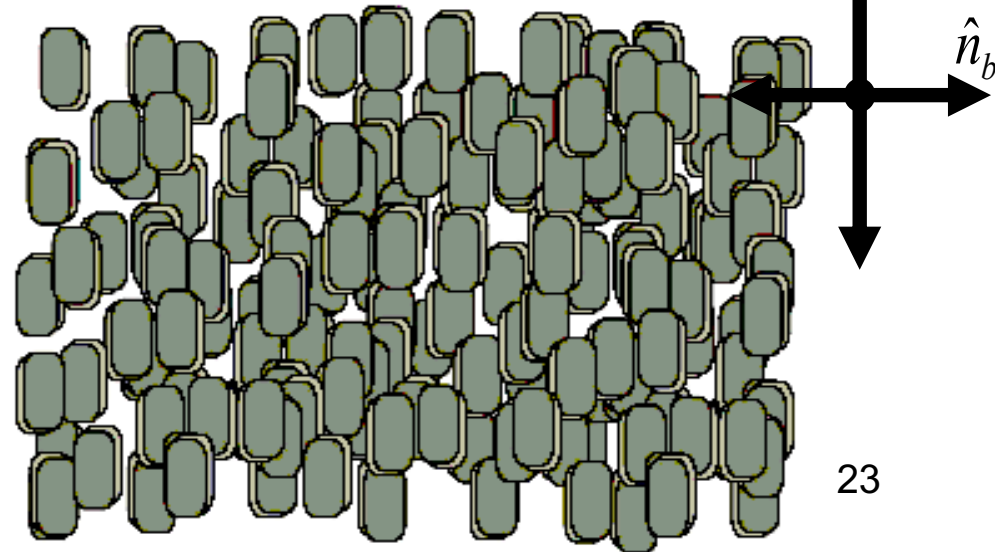
In the smectic C, molecules form layers but the director is tilted from the normal. This angle is temperature dependent if a smectic C to A transition occurs with increasing temperature.

## SmC<sub>A</sub>

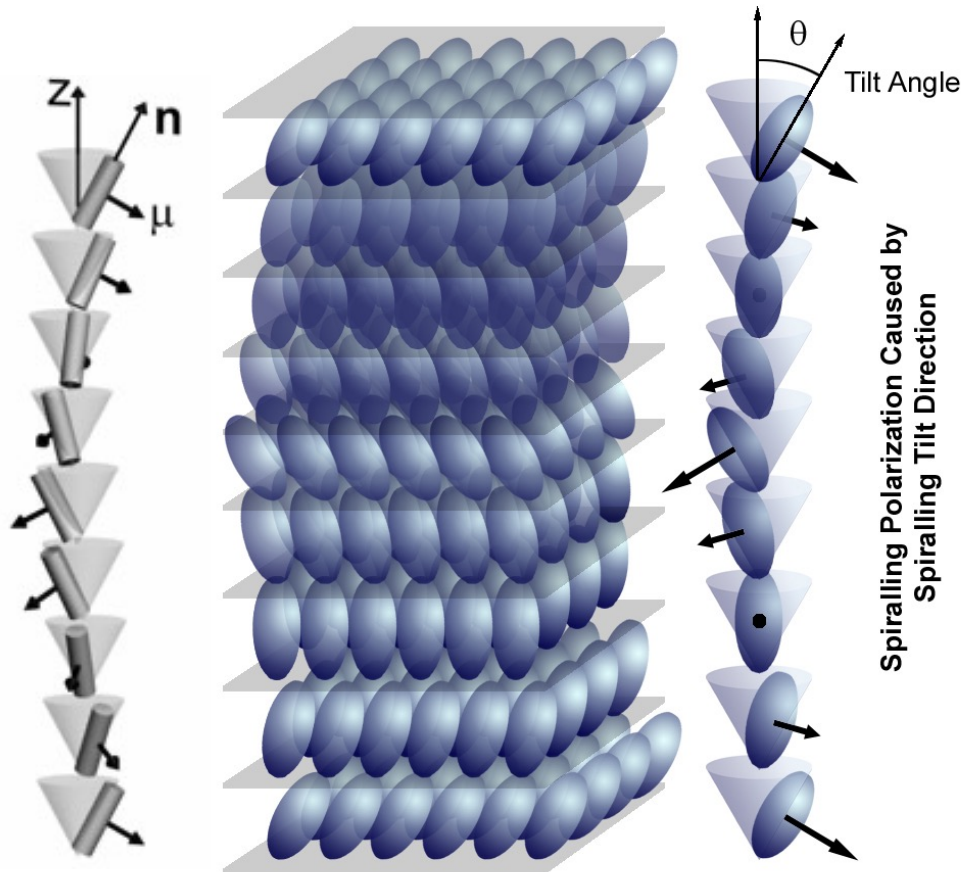


anticlinic SmC<sub>A</sub>: molecules are tilted within each layer with the direction of tilt alternating from layer to layer

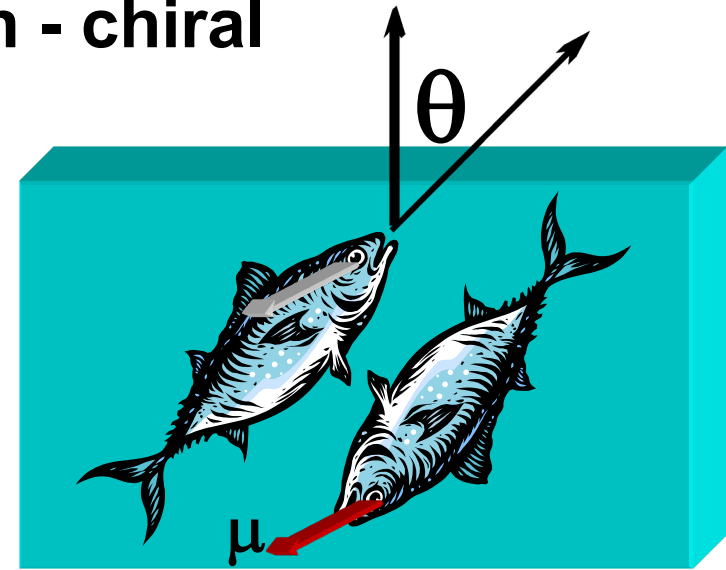
## Biaxial nematic



# The Chiral Smectic C



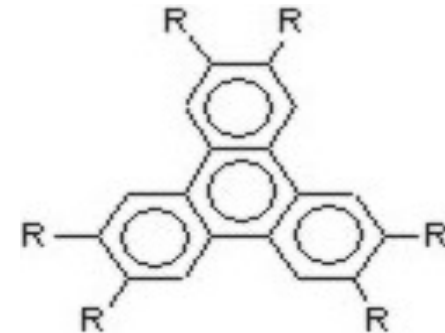
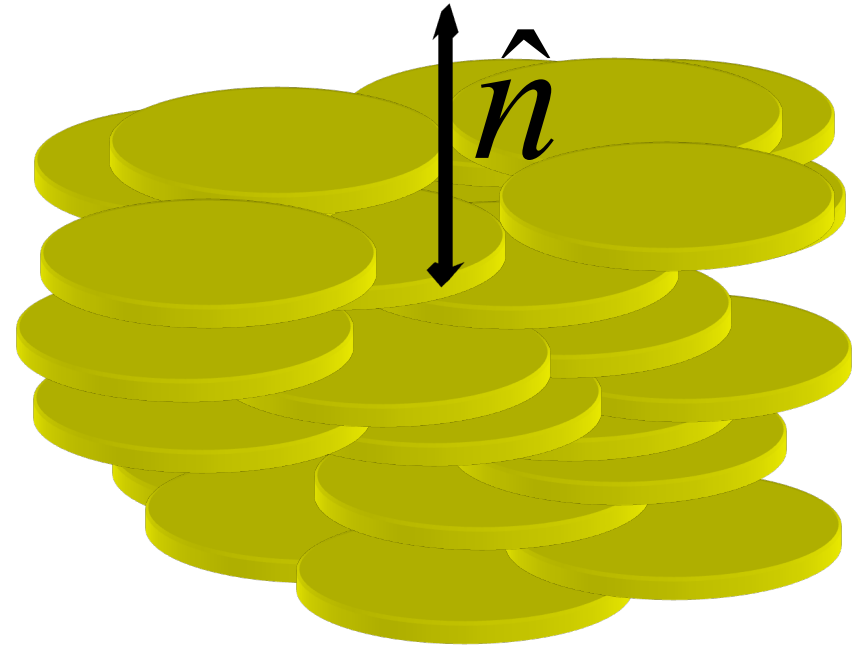
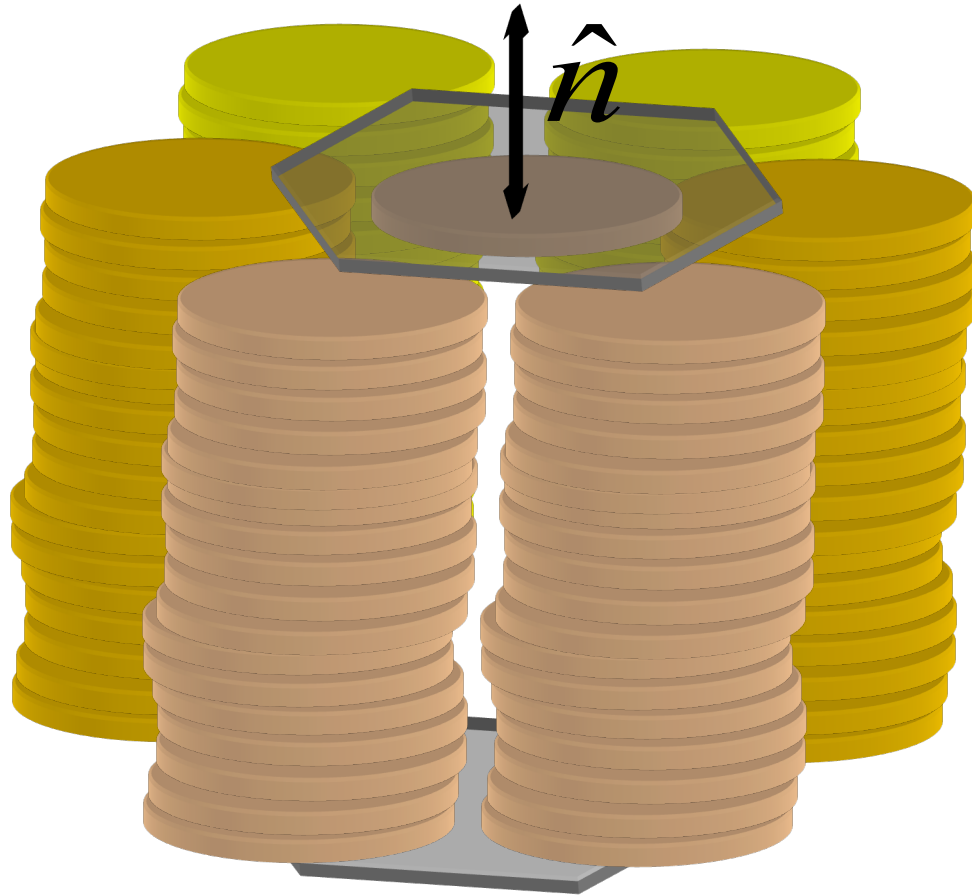
Eye - dipole moment  $\mu$   
fin - chiral



When the molecule is chiral, successive smectic C layers show a gradual change in the direction of tilt, such that the director precesses about the layer normal from layer to layer, always lying on the surface of a hypothetical cone illustrated in the cartoon. This creates a helical structure in the chiral smectic C (SmC\*) mesophase with the pitch being the distance along the z axis needed to reach the same molecular orientation. Ferroelectric smectic C\* LC has a dipole moment perpendicular to the molecule's long axis and contained in the layer plane.

# Discotic LCs: columnar and nematic

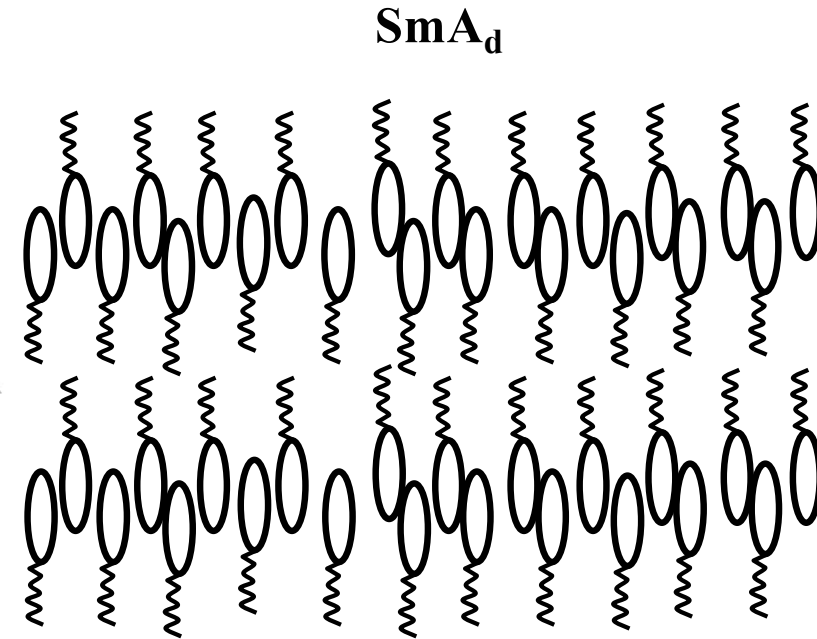
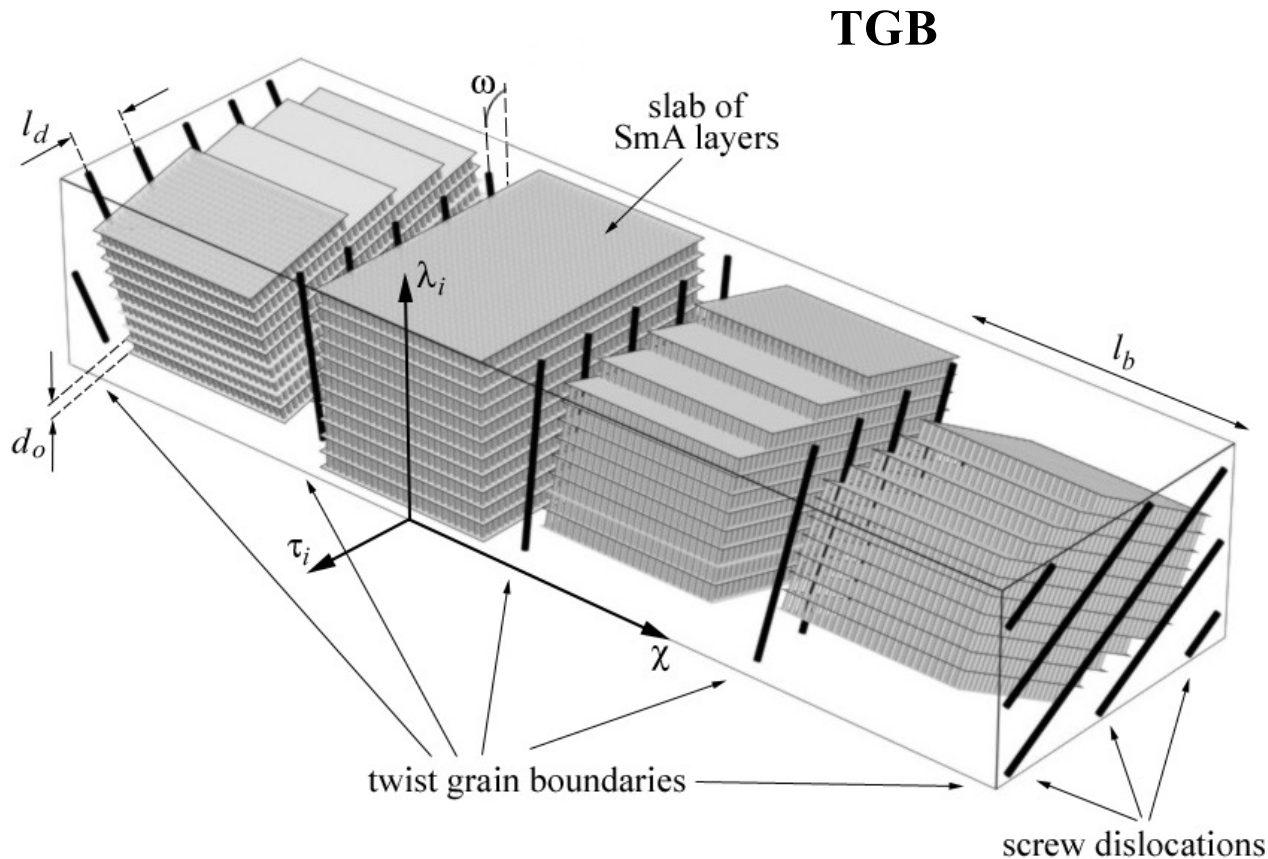
**Columnar: columns of molecules in hexagonal lattice**      **Nematic discotic phase**



**Typical molecule**

Columnar liquid crystal molecules are shaped like disks instead of long rods. The columnar mesophase is characterized by stacked columns of molecules. The columns are packed together to form a two-dimensional crystalline array. Existence of long-range orientational and 2D translational order is characteristic for columnar mesophases. The arrangement of the molecules within the columns and the arrangement of the columns themselves leads to new mesophases.

# Twist grain boundary (TGB) phase and partial bilayer ( $\text{SmA}_d$ ) smectic A phase

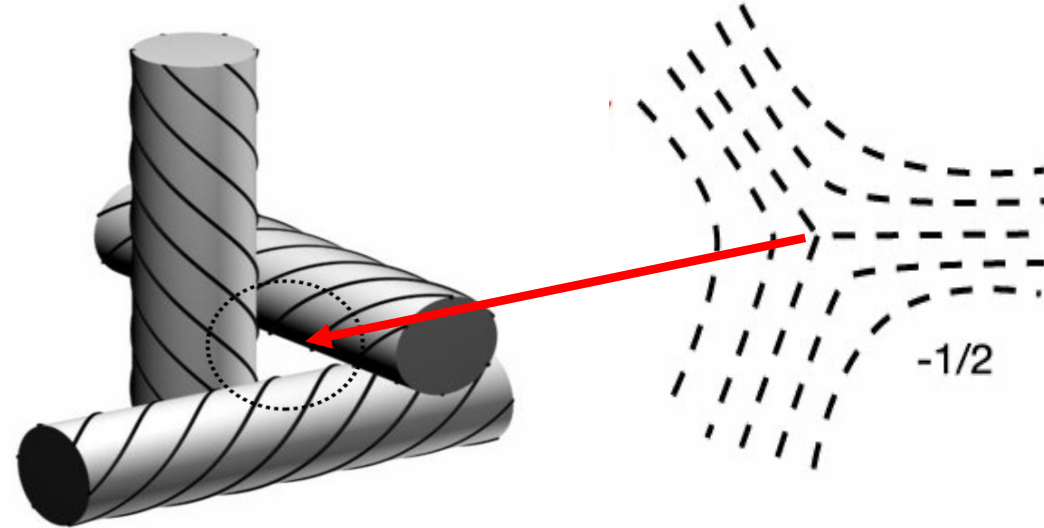
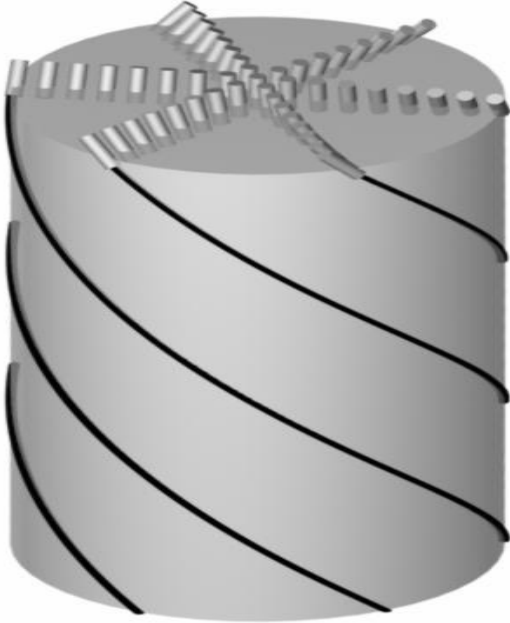


**Layer spacing is larger than the length of one molecule but smaller than that of two molecules**

**Composed of <100nm smectic-like blocks that rotate via arrays of screw dislocations between these blocks.**

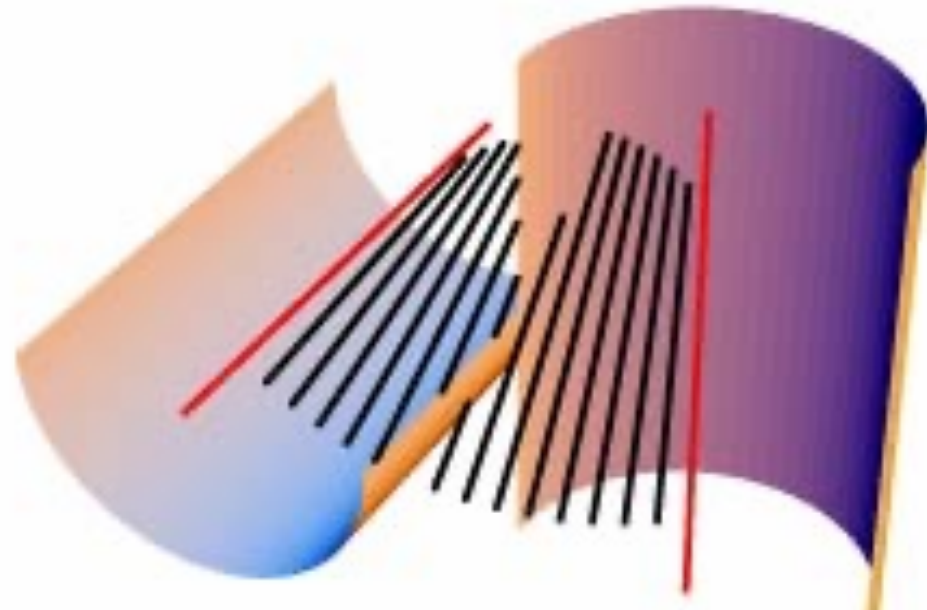
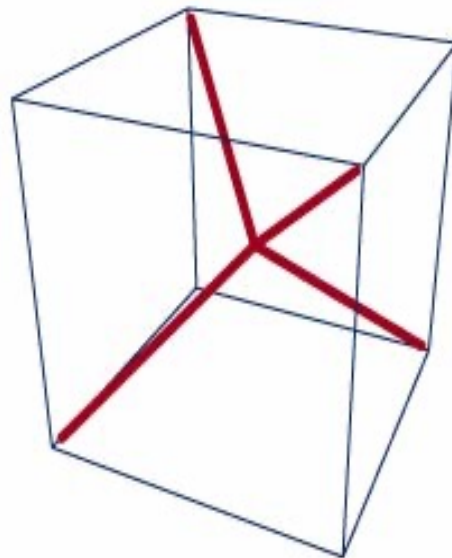
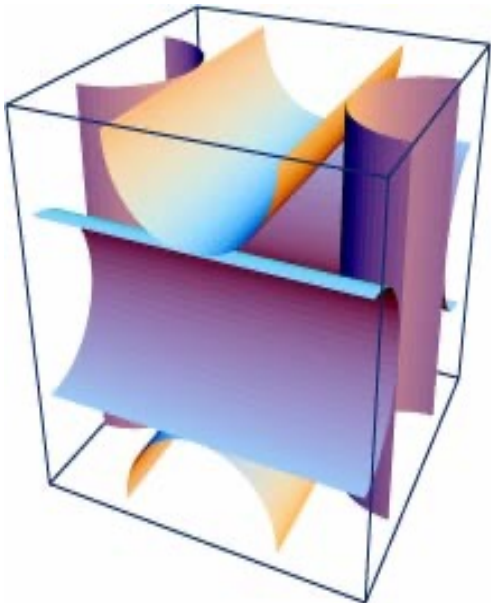
# Double twist and cholesteric Blue Phases

## Double twist cylinder

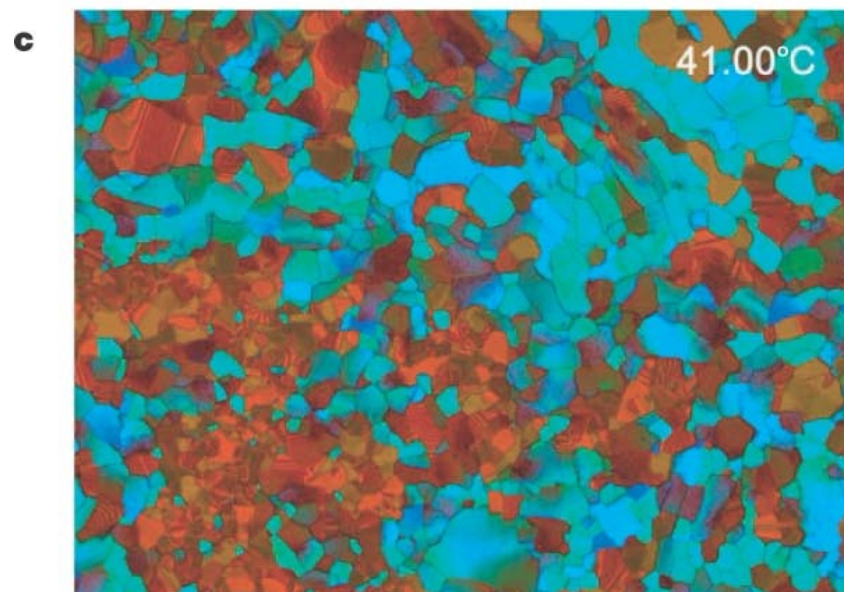
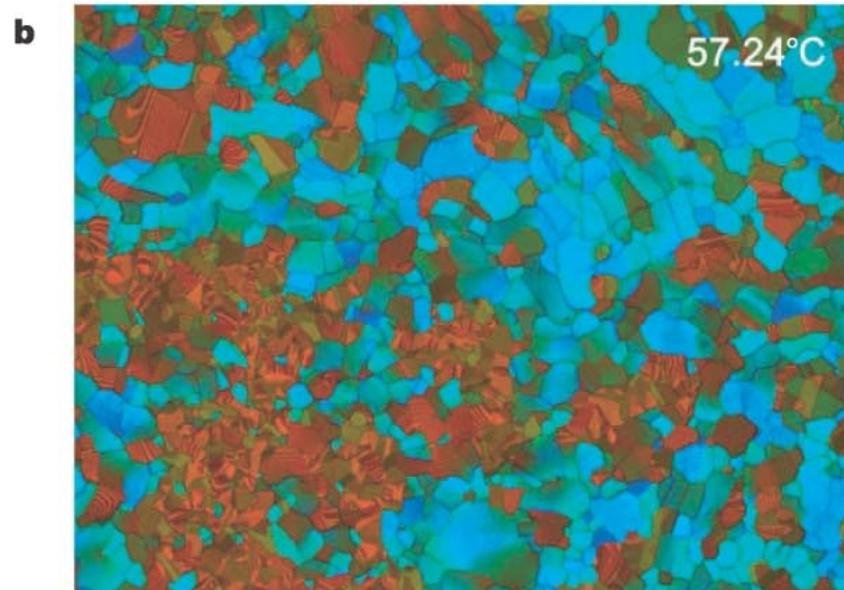
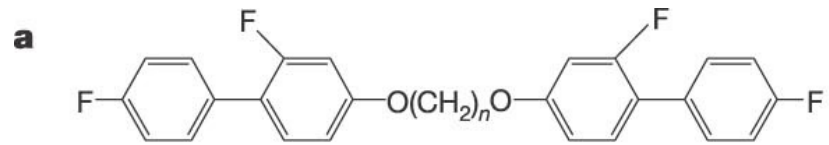
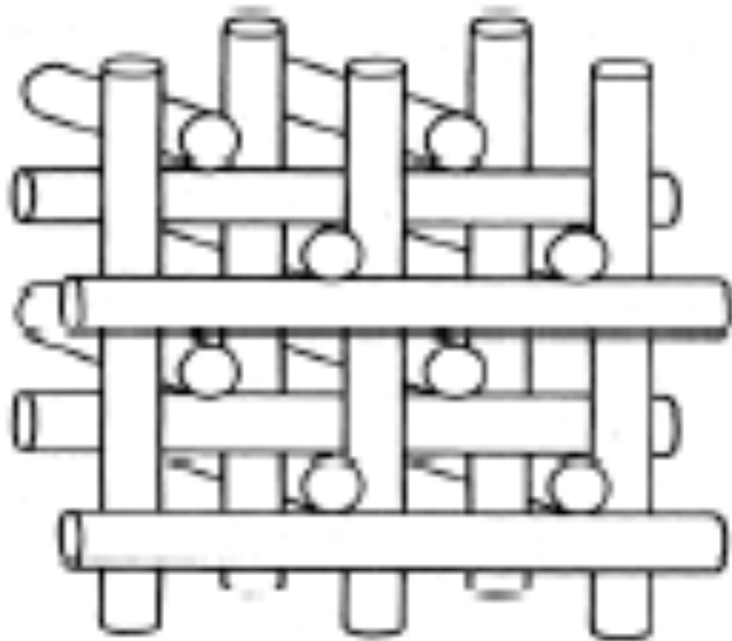
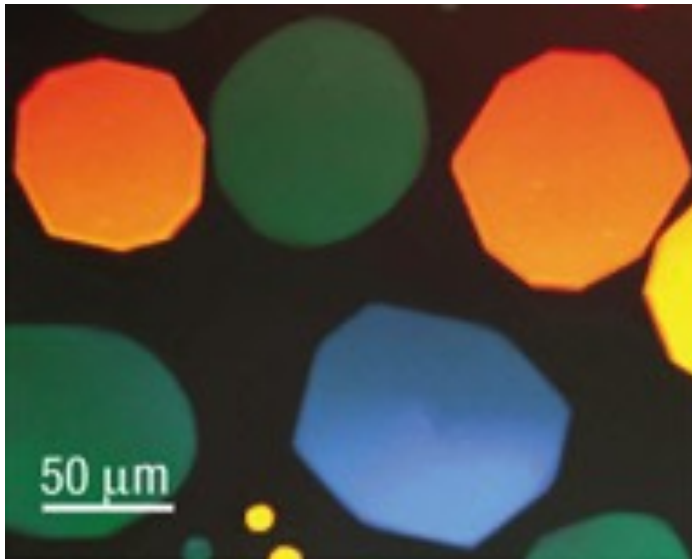


matching of adjacent  
double twist tubes

## Arrangement into a cubic lattice:



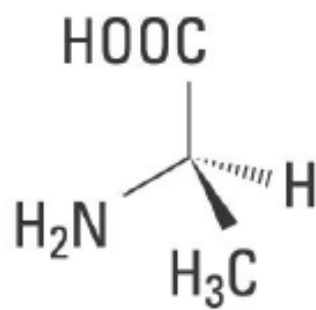
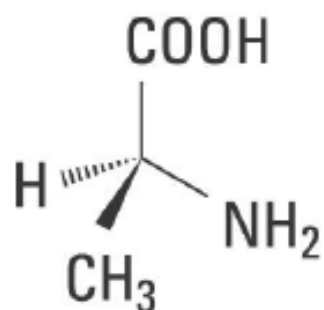
# Blue Phases: selective reflection of light



Coles et al., *Nature* 436, 997 (2005)

W. Cao et al., *Nature Materials*, 111, (2002).

# Chiral molecule (does not overlap with its chiral image)

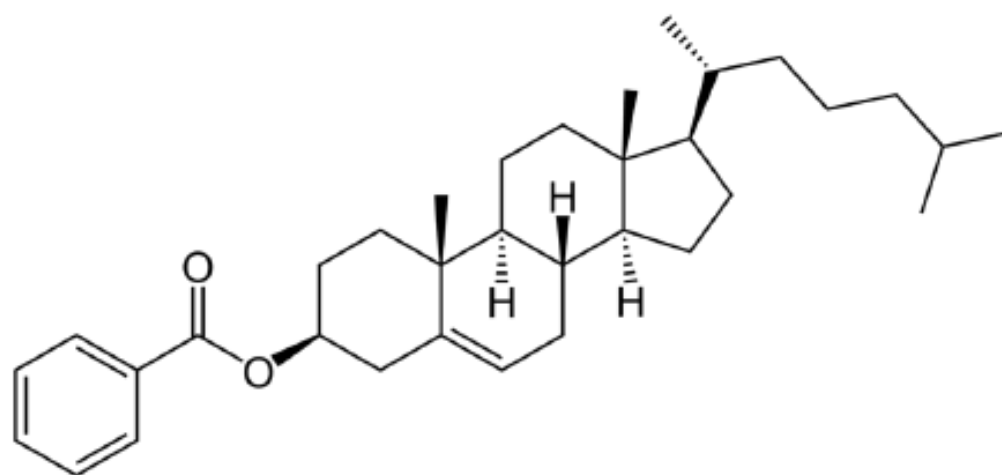


Carbon atom with 4 different attachments

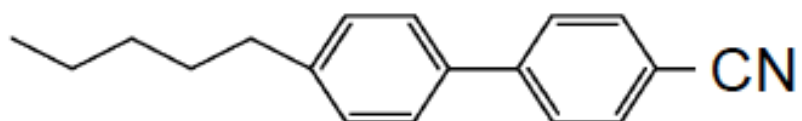
(S)-alanine    mirror plane    (R)-alanine

Cholesterol benzoate: Rod-like molecule with a chiral C atom;

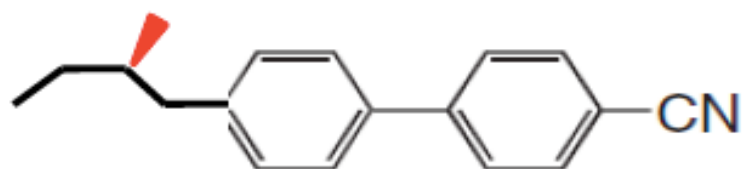
A similar cholesterol derivative was the subject of the first known publication on LCs, reporting double melting point and selective reflection of light, J. Planer, Ann Chem Pharm **118**, 25 (1861)



# Comparative chemistry

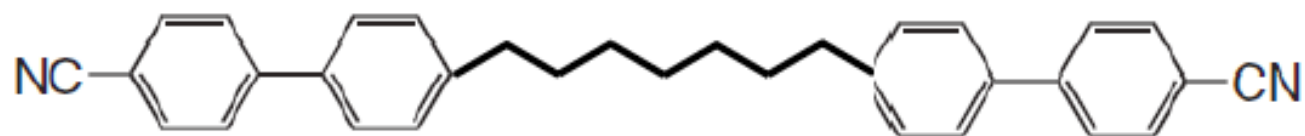


Nematic 5CB molecule

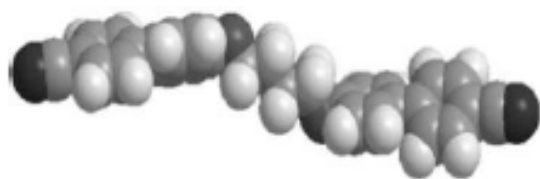


Cholesteric CB15 molecule

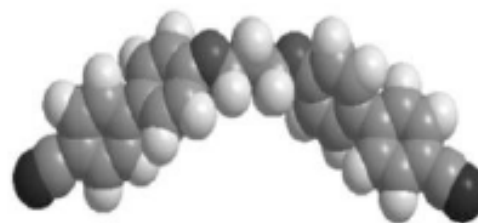
What would happen when two CB molecules are connected by a flexible aliphatic chain and form a “bimesogen” or “dimer”?



Answer: depends on odd-even character of aliphatic chain



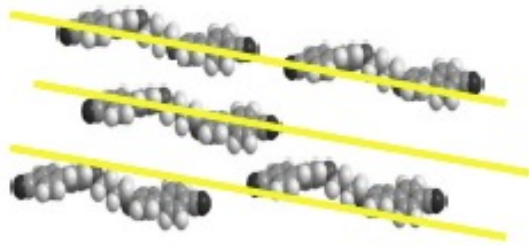
even number  $m$  of CH<sub>2</sub> groups



odd number  $m$  of CH<sub>2</sub> groups

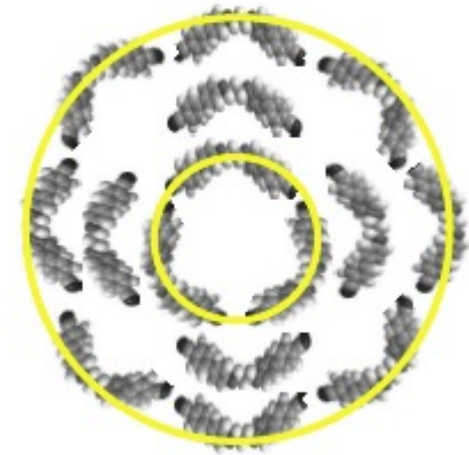
How can we pack these molecules in space?

# Packing bimesogens

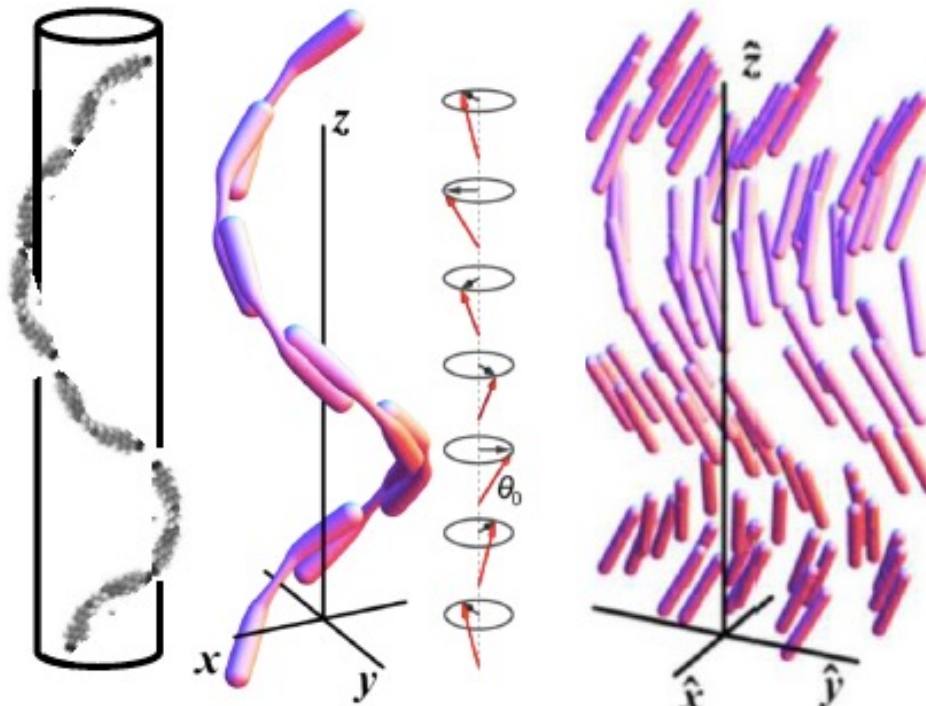


Even  $m$ , rod-like molecules:  
Easy! Nematic!

Odd  $m$ , bent shape:  
Difficult...cannot  
sustain uniform bend in  
2D...



Go to 3D:  
Uniform bend  
is achieved  
through twist!

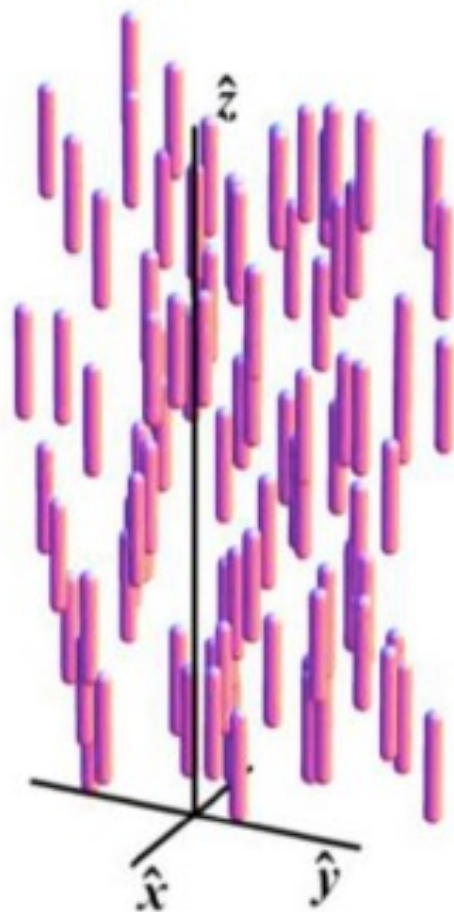


Predictions:

- R.B. Meyer (1973, Les Houches)
- R. Kamien, *J. Phys II* **6**, 461 (1996)
- I. Dozov, *EPL* **56**, 247 (2001)
- J. Selinger et al, *PRE* **87**, 052503 (2013)
- E. Virga, *PRE* **89** 052502 (2014)

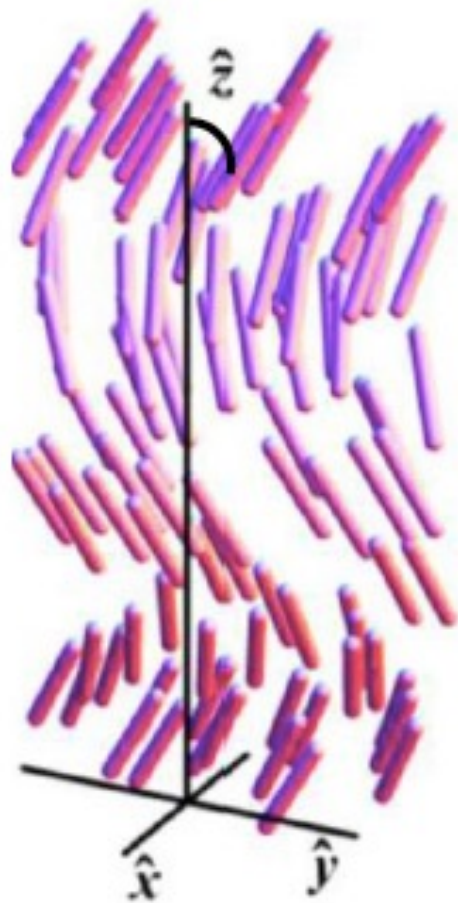
$$\hat{\mathbf{n}} = (\sin \theta_0 \cos tz, \sin \theta_0 \sin tz, \cos \theta_0)$$

$$\theta_0 = 0$$



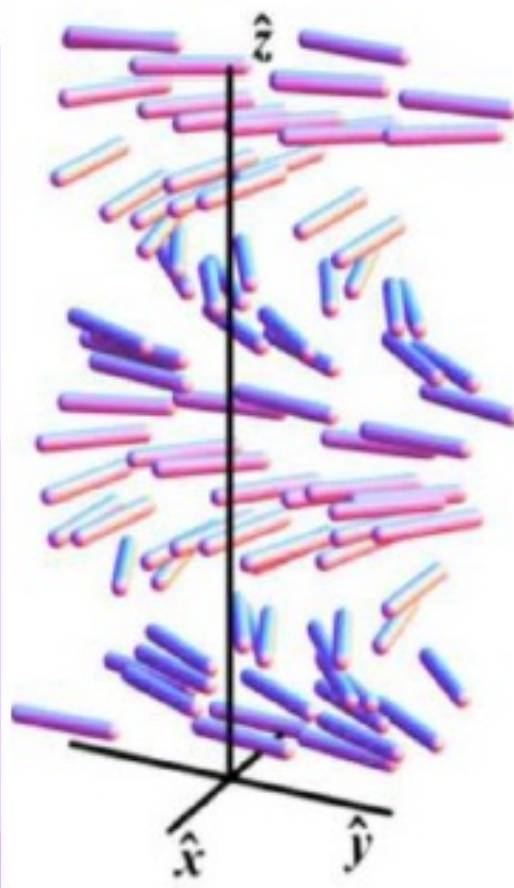
Nematic

$$0 < \theta_0 < \pi/2$$



Twist-bend Nematic

$$\theta_0 = \pi/2$$



Cholesteric

$$\hat{\mathbf{n}} = (\sin \theta_0 \cos \varphi, \sin \theta_0 \sin \varphi, \cos \theta_0)$$

$\theta_0$ : molecular tilt angle

$$\varphi = tz$$

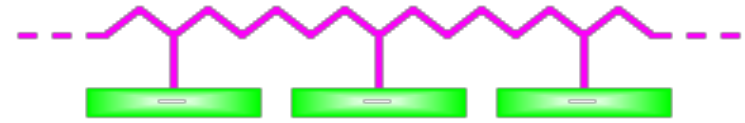
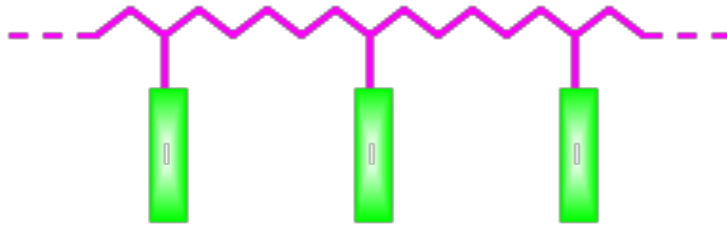
$$t = 2\pi / P$$

# Polymers

MC-PLC



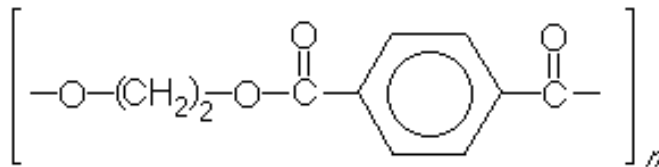
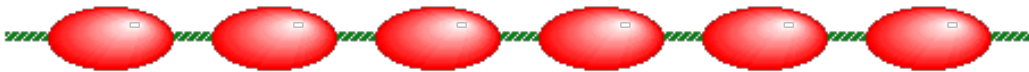
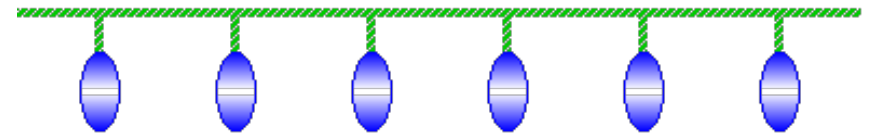
SC-PLCs



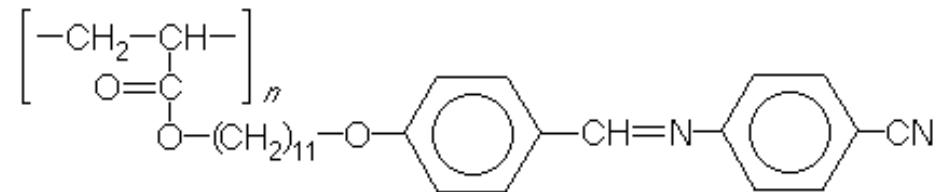
Main-chain PLCs

Side-chain PLCs

Side-Chain PLC



PET poly(p-phenyleneterephthalate)



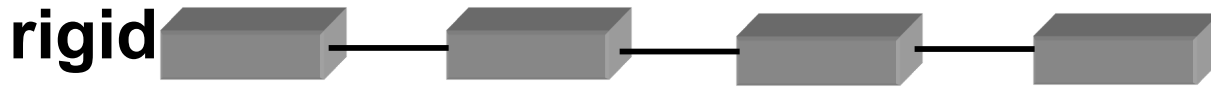
**Polymers (also known as *macromolecules*) are materials consisting of many small molecules (called *monomers*) that are linked together to form long chains. We know them in the form of tars, resins, cotton, oils, wool, rubber, teflon, plastics, and gums. The pictures above show short sections of such chains. A typical polymer may include tens of thousands of monomers (the number of repeated units is given by “n”).**

# Polymeric Liquid Crystals

Combining the properties of liquid crystals and polymers

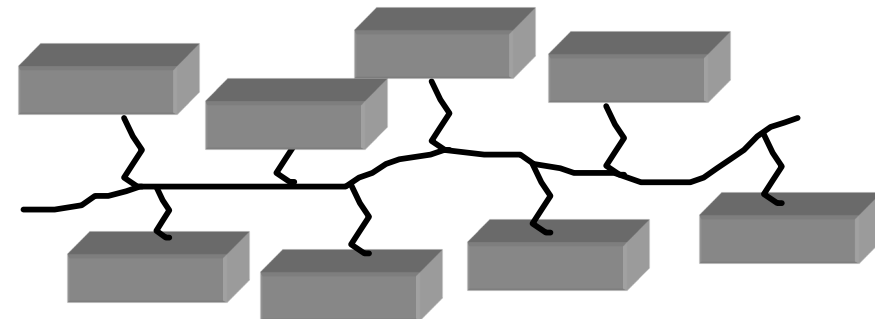
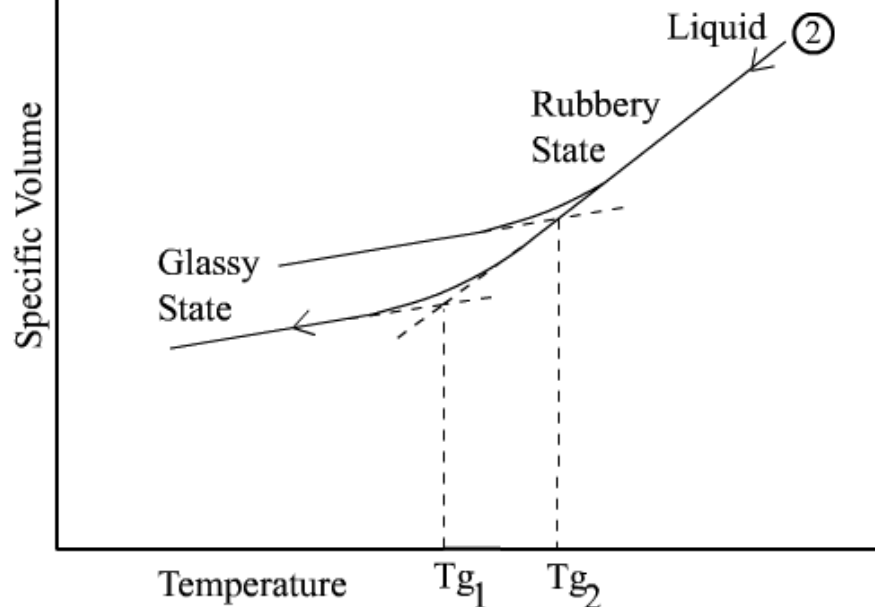
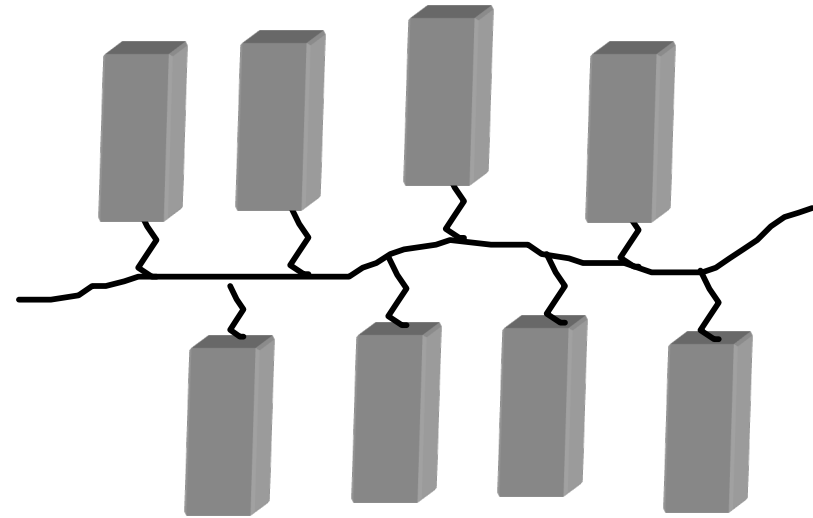
## Main Chain

mesogenic moieties are connected head-to-tail



## Side Chain

mesogenic moieties attached as side chains on the polymer backbone



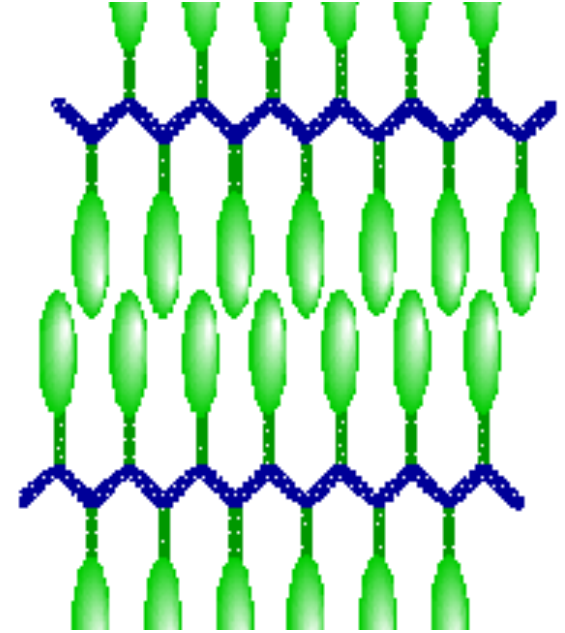
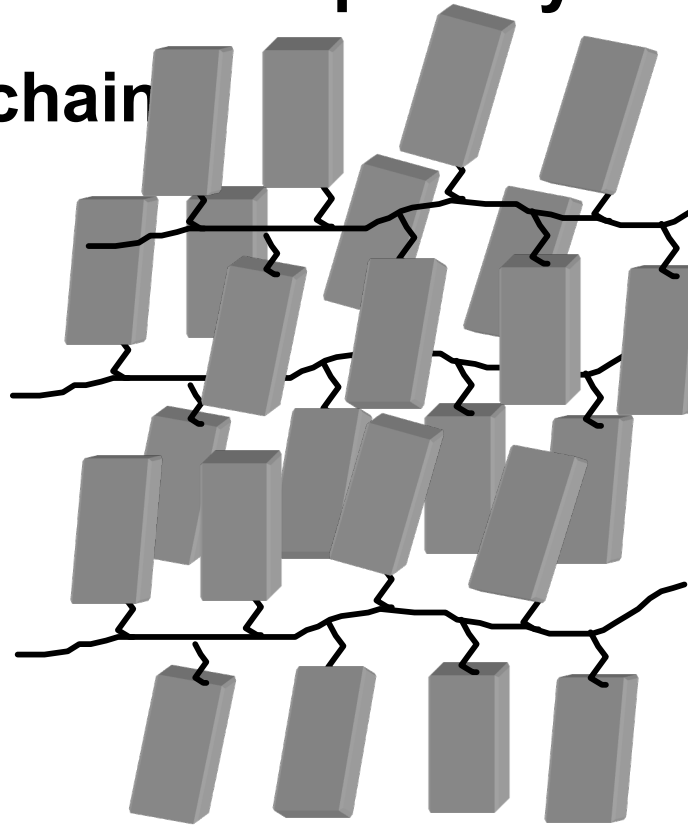
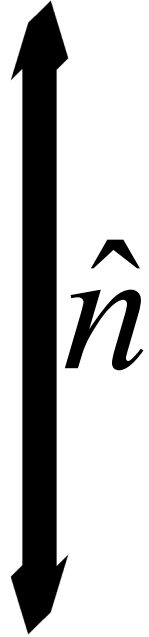
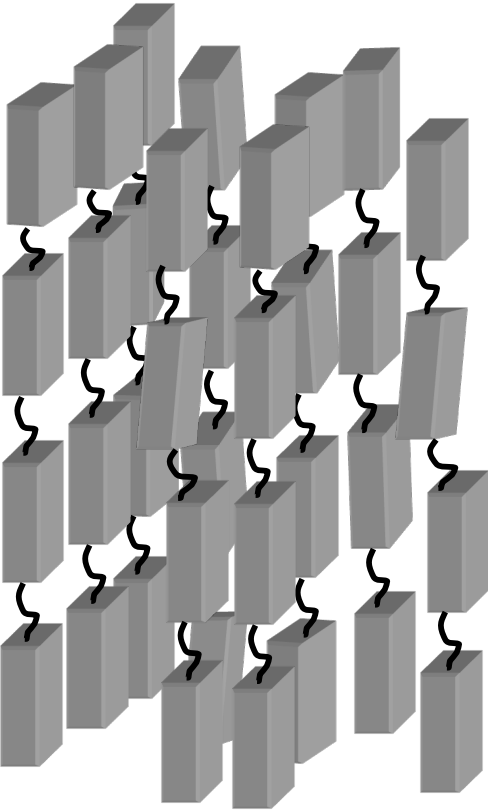
# Polymer Liquid Crystals

main-chain

forming nematic liquid crystal phases

side-chain

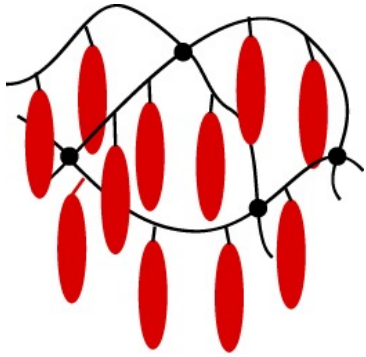
side-chain



***Polymer liquid crystals (PLCs)*** are a class of materials that combine the properties of polymers with those of liquid crystals. These "hybrid" materials can show the same mesophases characteristic of ordinary small-molecule LCs, yet retain many of the useful properties of polymers. The placement of the mesogens determines the type of PLC that is formed. ***Main-chain polymer liquid crystals*** or MC-PLCs are formed when the mesogens are themselves part of the main chain of a polymer. Conversely, ***side chain polymer liquid crystals*** or SC-PLCs are formed when the mesogens are connected as side chains to the polymer by a flexible "bridge"

# Nematic LC elastomers & their applications

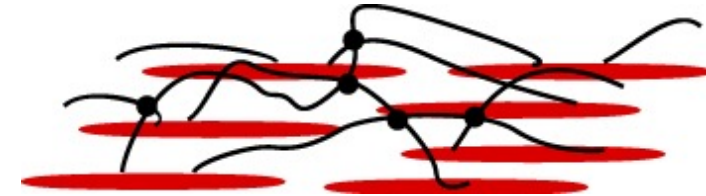
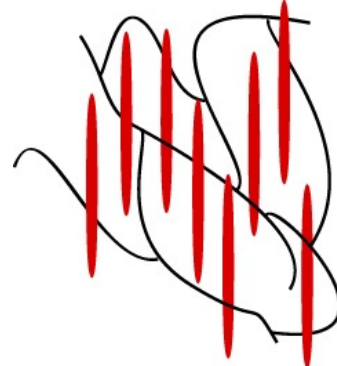
Nematic



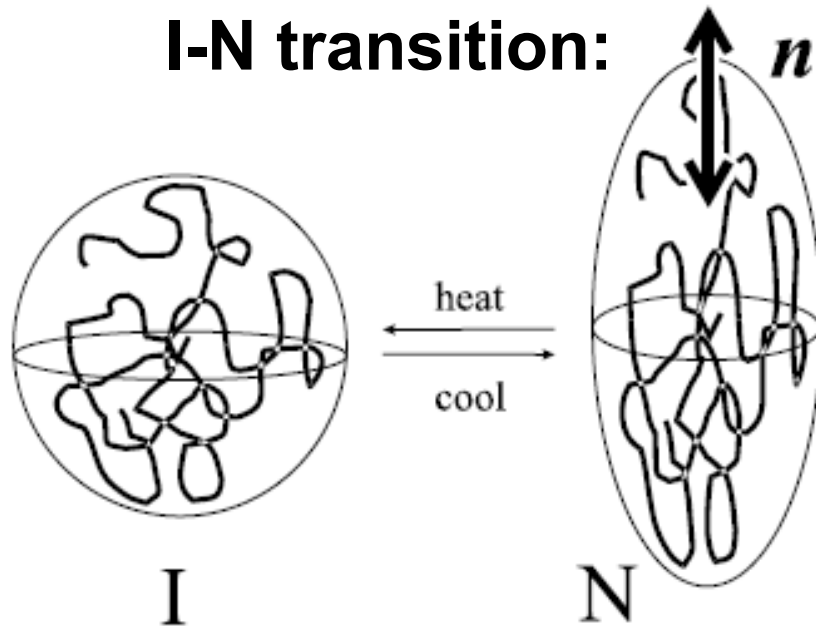
Smectic-C



Gels with rod dispersion



I-N transition:



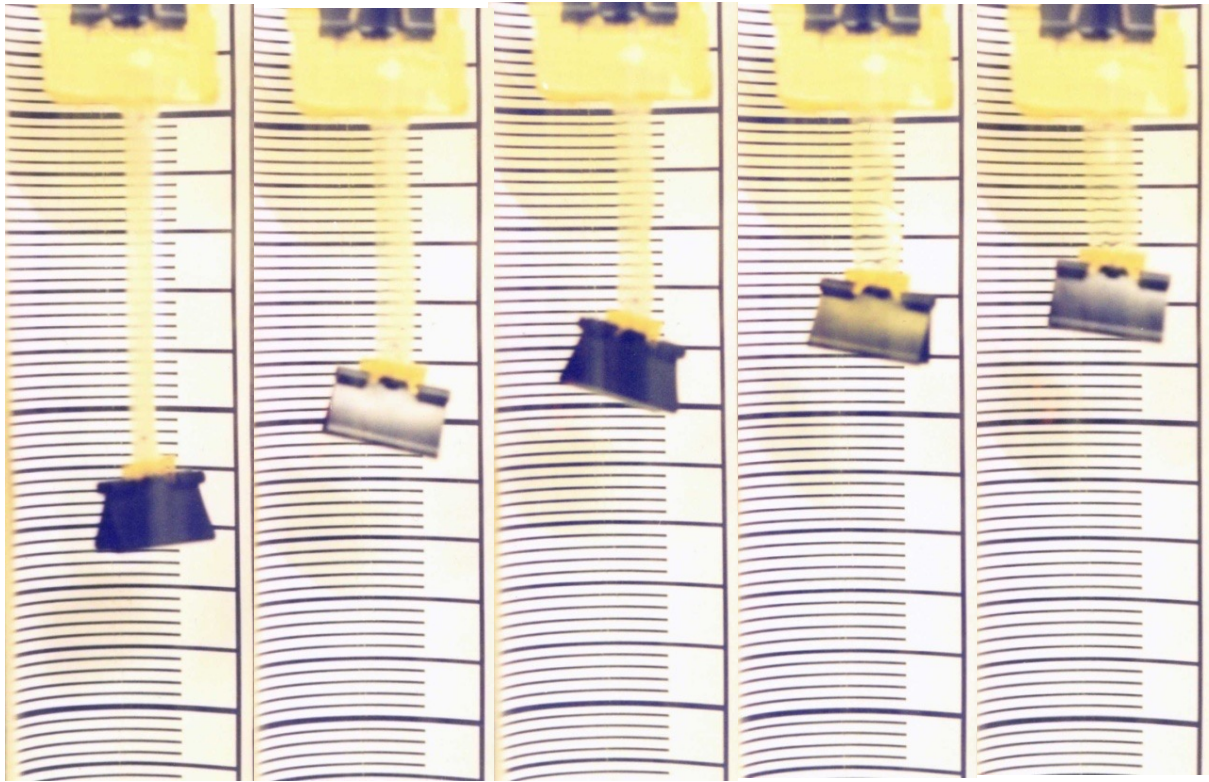
Artificial muscle applications



Liquid-crystal elastomers are rubbers whose constituent molecules are orientationally ordered. Their fascinating feature is strong coupling between the orientational order and mechanical strain. For example, changing the orientational order gives rise to internal stresses, which lead to strains and change the shape of a sample. Orientational order can be affected by changes in externally applied stimuli such as temperature, light, and electric or magnetic fields.

# Large thermoelastic effects

- LCElastomers - Weakly cross-linked LC polymers;
- Large thermally induced strains - artificial muscles



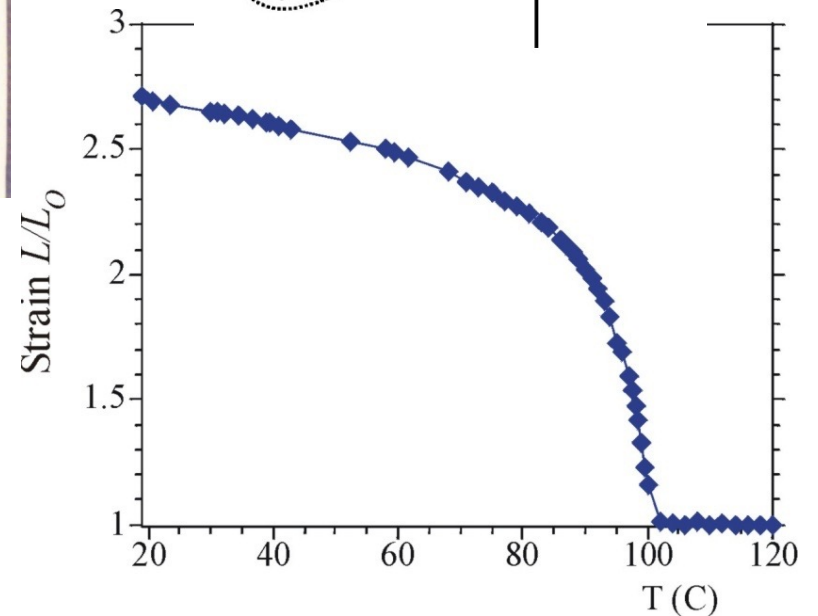
**300% strain**



T  
Isotropic



$T_{IN}$   
Nematic



# **Interactions between LC building blocks**

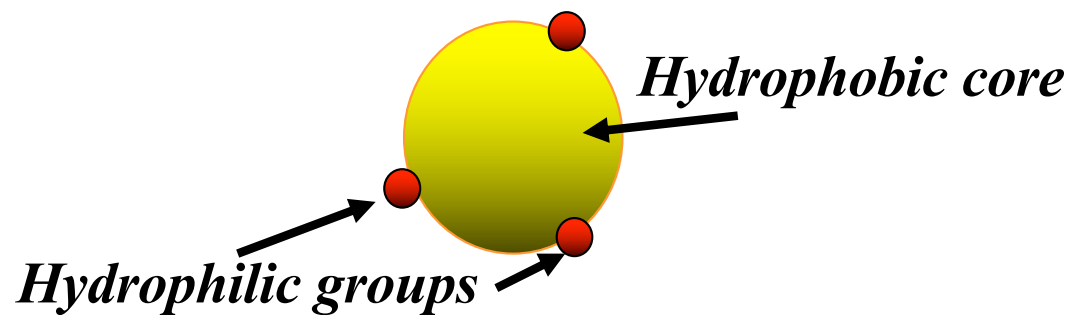
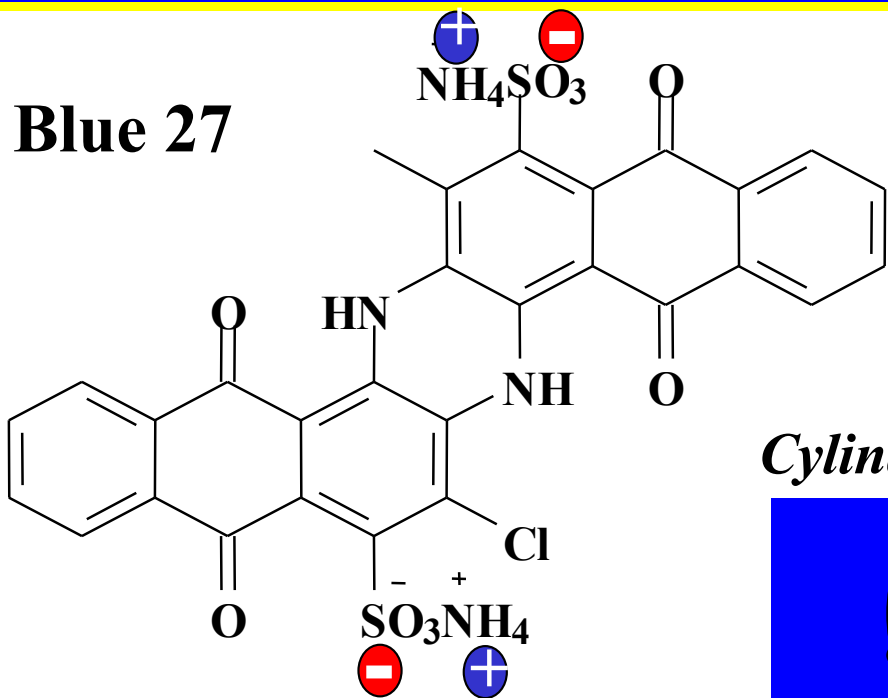
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**Some of the interaction leading to the LC order:**

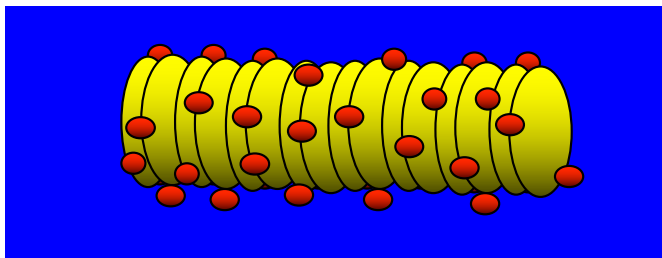
- **Steric interactions (lyotropic LCs of hard rods)**
- **Induced dipole-dipole interactions (thermotropic LCs);**
- **Hydrophobic/hydrophilic interactions (surfactant-based lyotropic LCs, chromonic LCs);**
- **Screened electrostatic (LCs formed by biopolymers and biomolecular complexes)**
- **The interactions are usually weak and comparable in strength to thermal fluctuations.**
- **Will be explored in details for specific LC phases;**

# *Lytotropic chromonic liquid crystals*

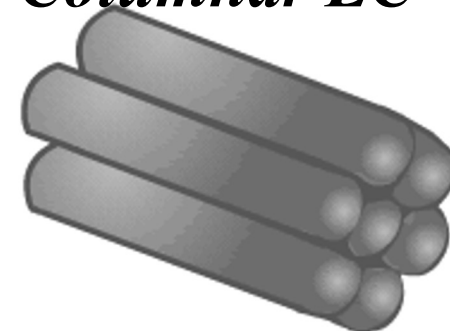
Blue 27



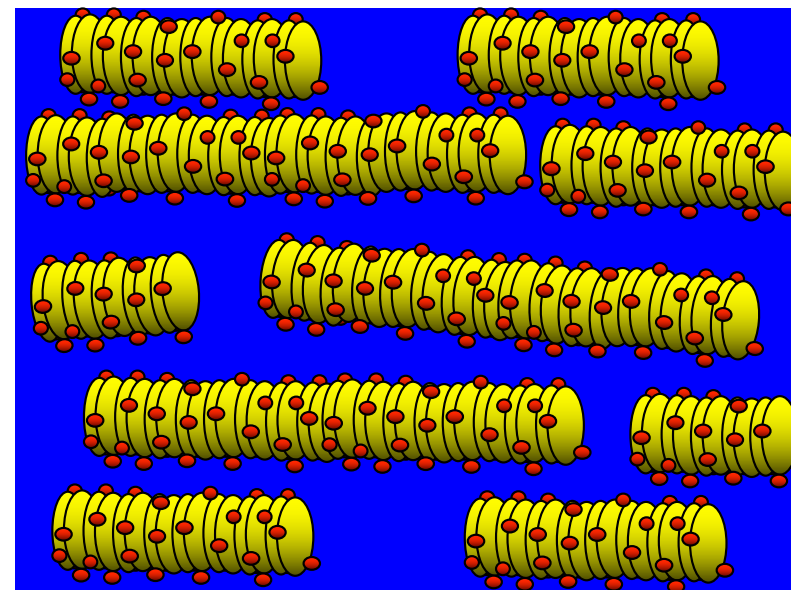
*Cylindrical aggregate in water*



*Columnar LC*



*Nematic phase*



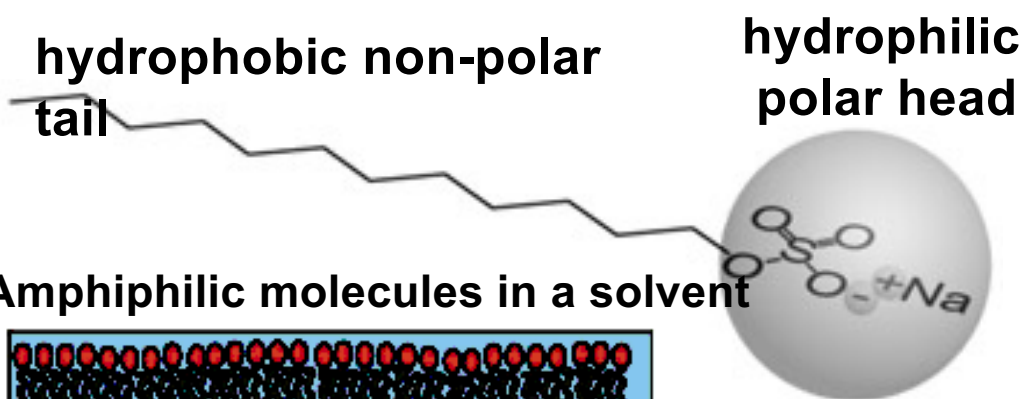
**Usually form nematic and columnar phases**

Building block of lyotropic chromonic liquid crystals is the one-dimensional molecular stack in which the molecules are arranged face-to-face with ionic water-solubility groups at the water-aggregate interface. In the nematic phase, columnar aggregates align parallel to each other but show no long-range positional correlation; molecular planes can adopt different orientations with respect to the axes of the aggregates. Columnar phases have long range orientational order accompanied by 2D positional order in the plane perpendicular to columns. Because of the polyaromatic molecular core, most of the LCLC materials absorb light in the visible spectral range; their absorption is strongly anisotropic as it depends on orientation of the LCLC molecules.

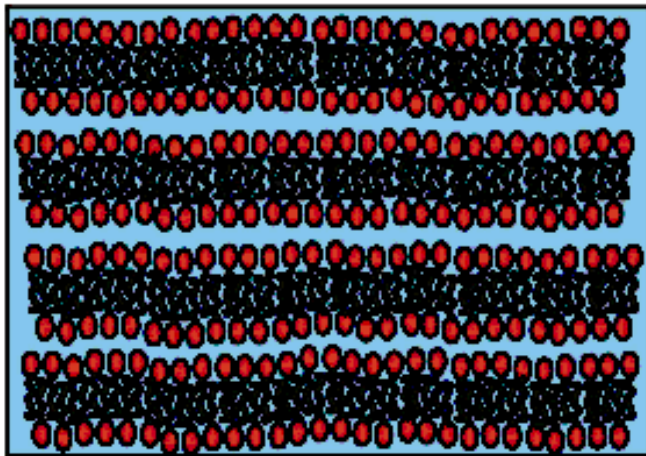
# Classification

## Lyotropic LCs

amphiphilic molecules, polar and non-polar parts form liquid crystal phases over certain concentration ranges when mixed with a solvent

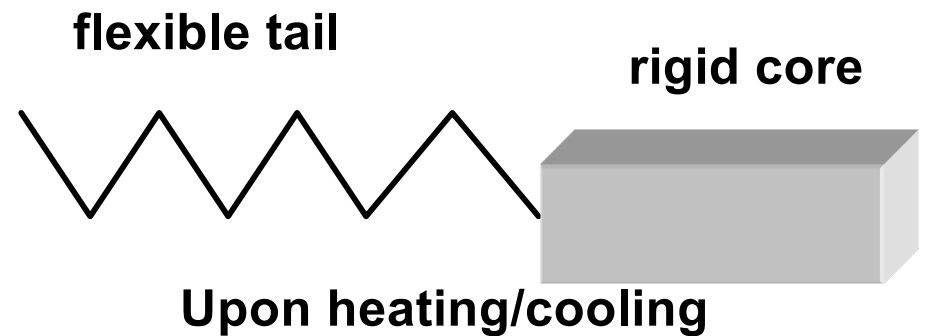


Amphiphilic molecules in a solvent

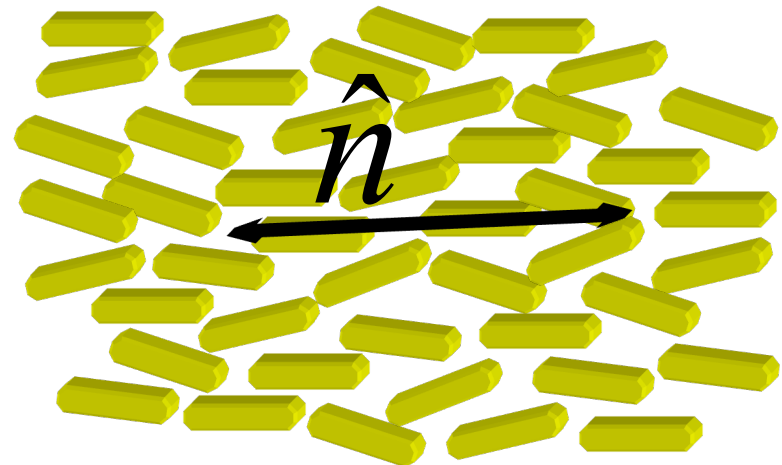


## Thermotropic LCs

molecules consisting of a rigid core and flexible tail(s) form liquid crystal phases over certain temperature ranges.



Upon heating/cooling



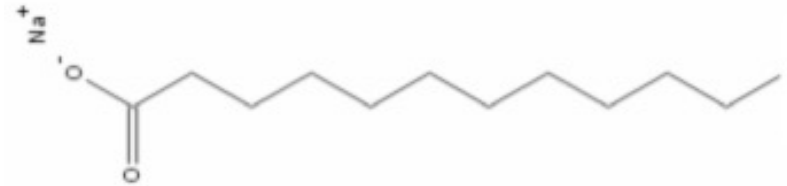
LC phases can be divided into two classes. *Thermotropic* LC phases are formed by organic molecules in a certain temperature range and hence the prefix *thermo-*, referring to phase transitions caused by temperature change. In contrast, *lyotropic* LC phases form a solution, and thus concentration controls the liquid crystallinity (hence *lyo-*, referring to concentration) in addition to temperature.

# Lipid & Surfactant Self-Assembly

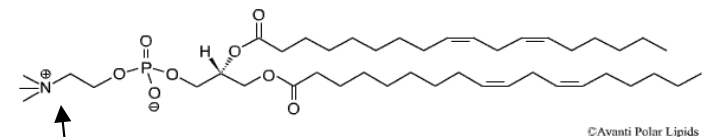
The lyotropic LCs best known to us are soaps and detergents



Sodium laurate

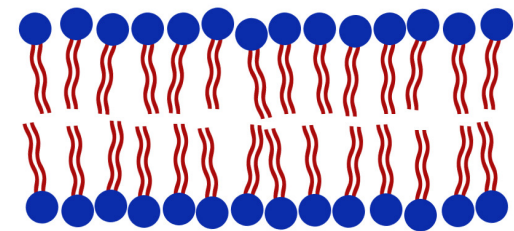


- Lipids are **amphiphilic** and **self-assemble** into different structures in aqueous solution.
- They are **lyotropic Liquid crystals** with a hydrophilic head group and a hydrophobic flexible tail.
- Lipids may form a wide variety of lyotropic phases, micelles, lamellar, hexagonal etc... We are particularly interested in the **lamellar phase** (cell membrane)



Hydrophilic head group

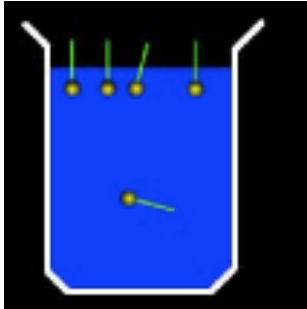
Hydrophobic tail



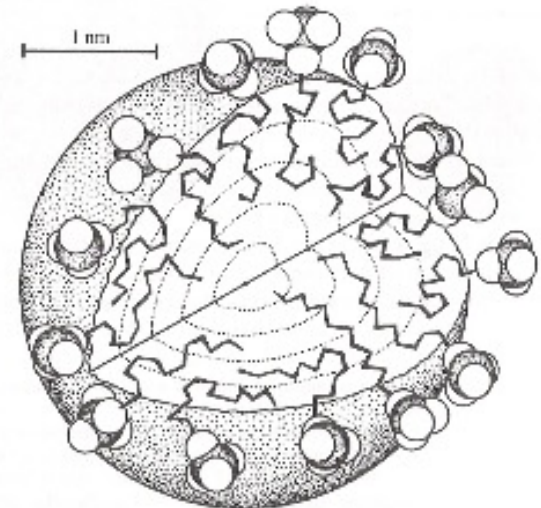
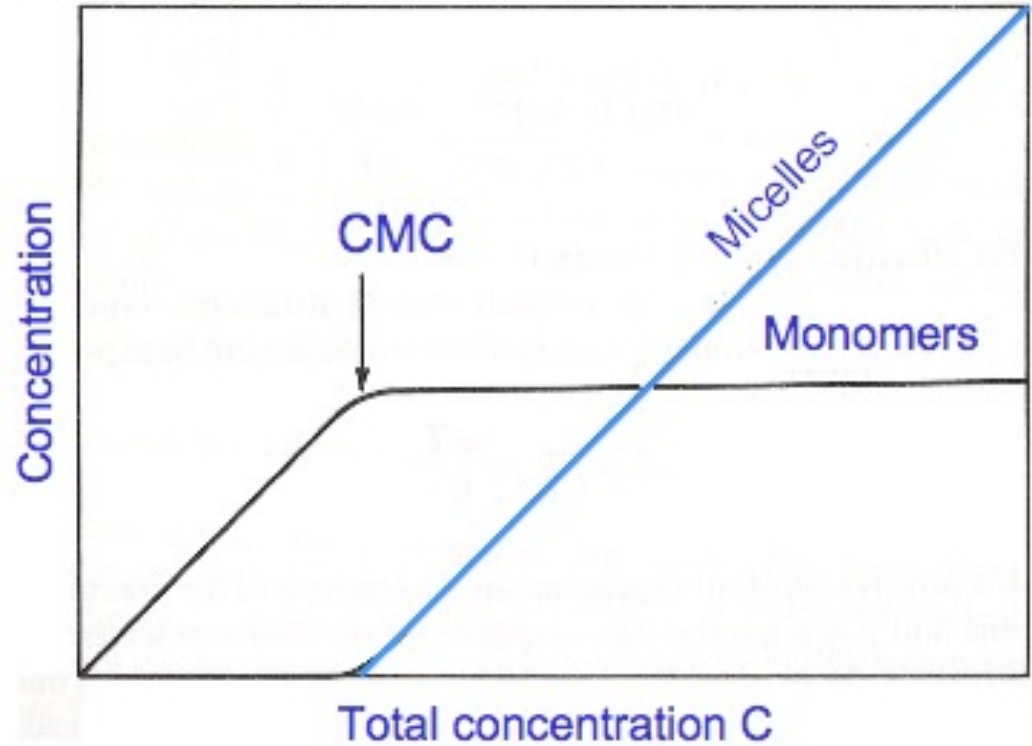
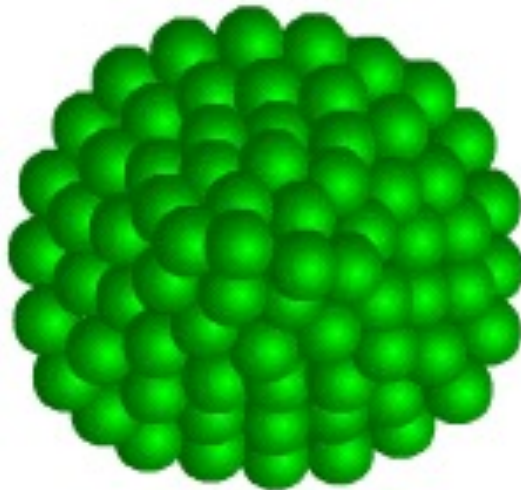
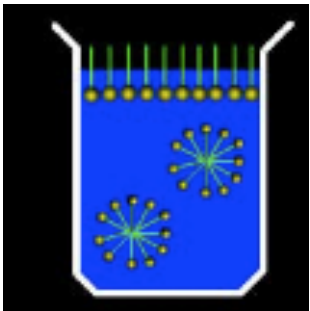
A simple lipid bilayer

# The Critical Micelle Concentration

- Up to a certain concentration surfactants can be stable in the solvent as isolated molecules.



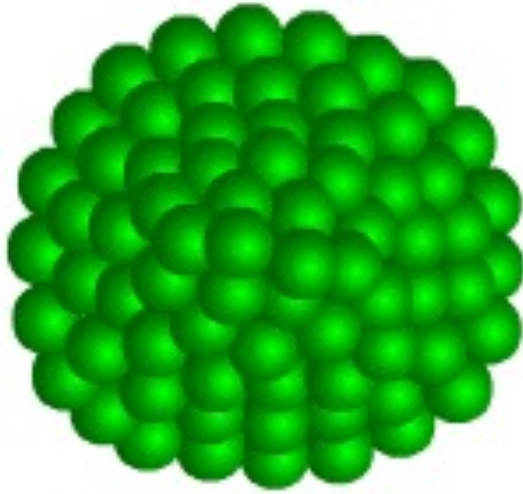
- At the critical micelle concentration (CMC) the surfactant molecules form into micelles



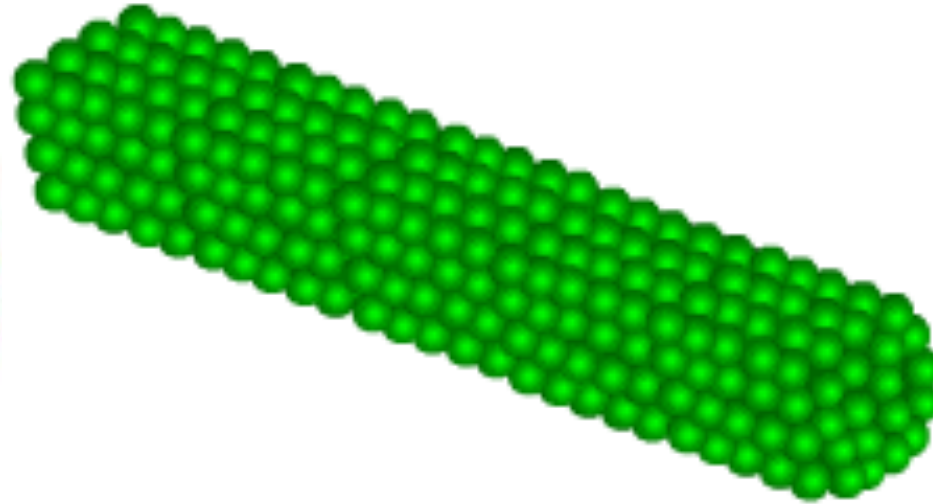
# Micelles, vesicles, and lyotropic LCs

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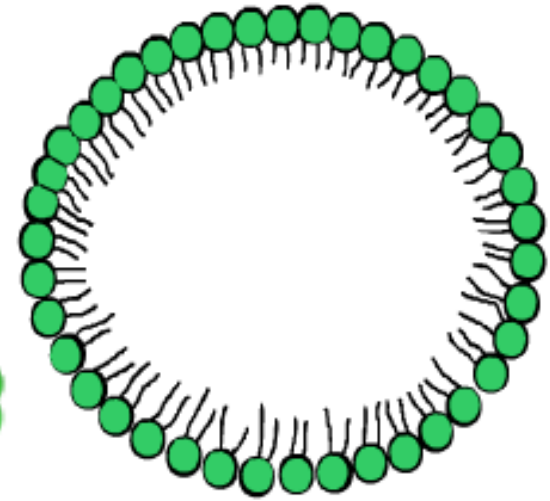
**Spherical micelle**



**Rod-like micelle**

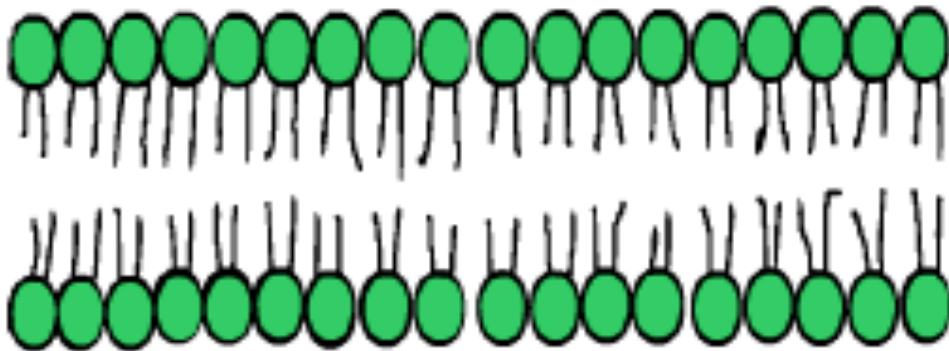


**Cross-section**

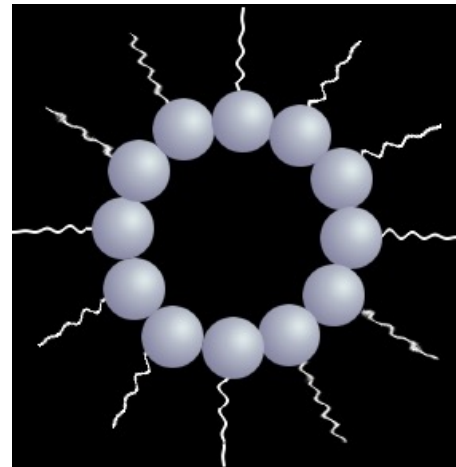


Concentration at which micelles form in solution is called the critical micelle concentration

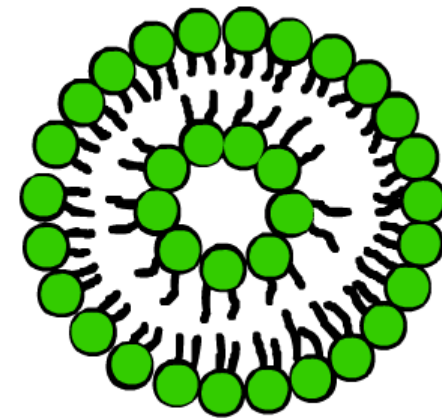
**Bilayer**



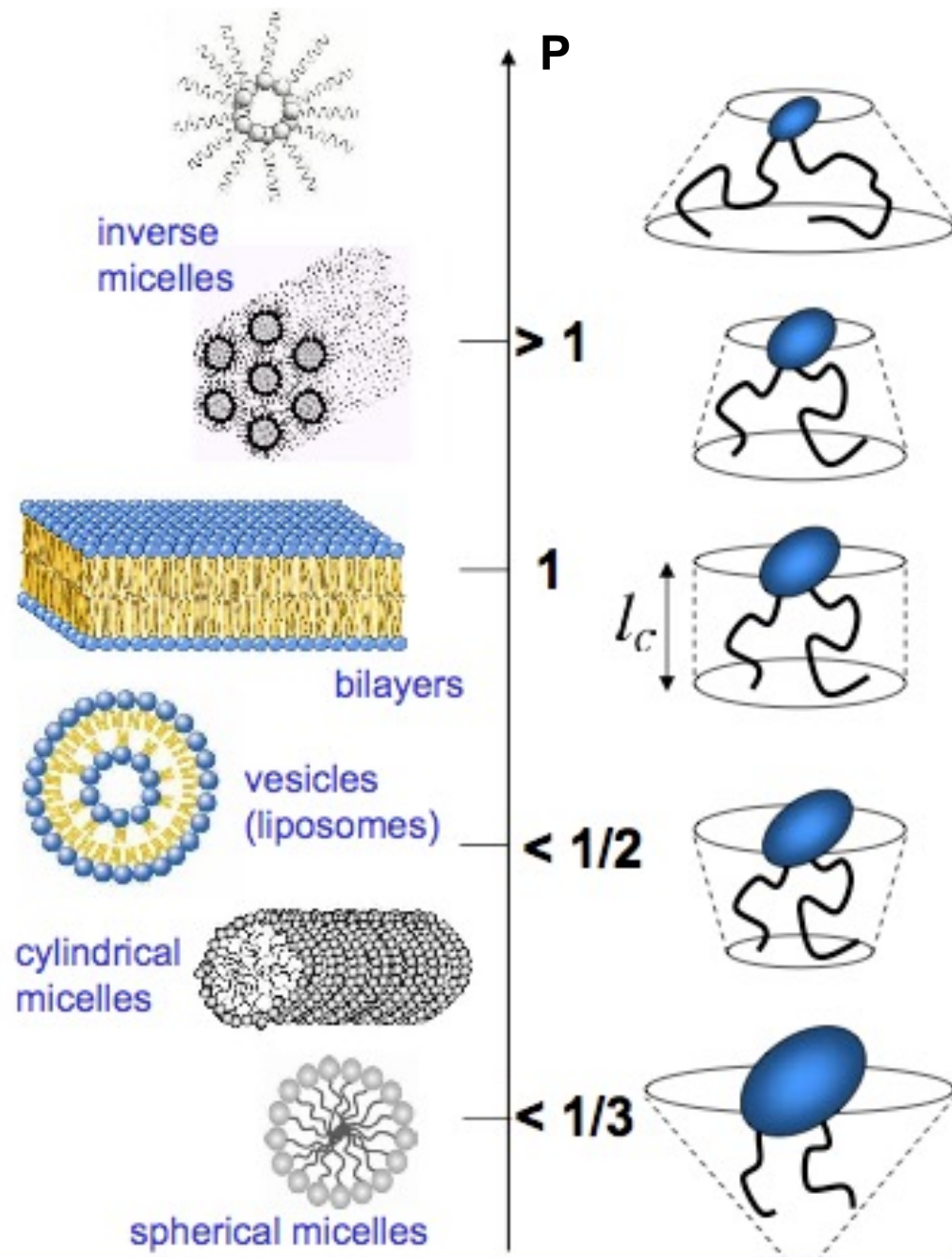
**reverse micelle**



**Vesicle**



# Molecular shape of lipids/surfactants



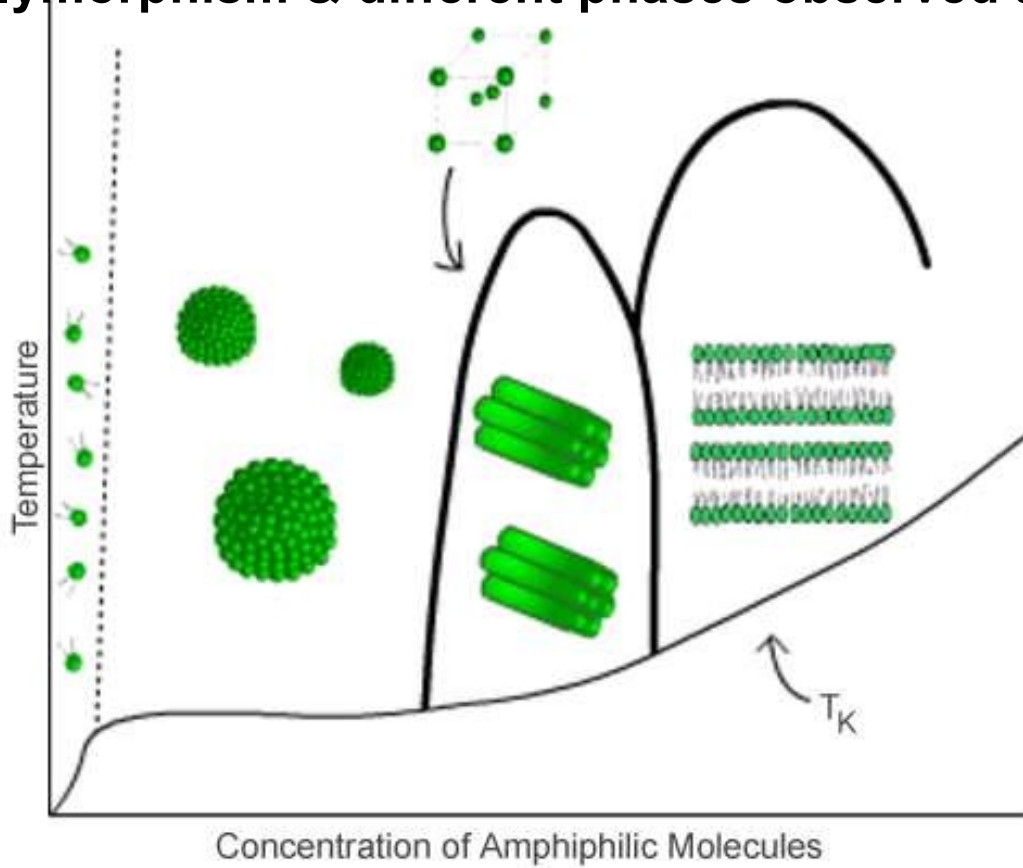
**Molecular shape is also an important factor in phase formation:**

**Lipids can be “cones” “inverted cones” or “cylinders”**

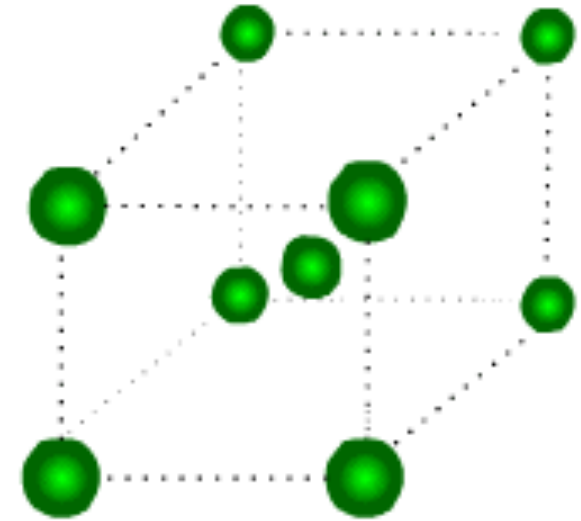
**The “packing parameter”  $P$ , demonstrates this effect.**

# Phases of surfactant-based lyotropic Liquid Crystals

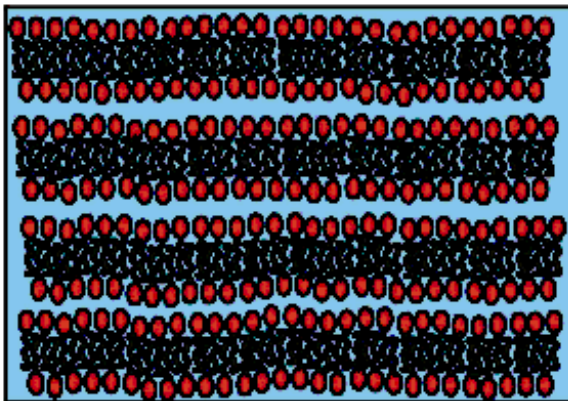
Polymorphism & different phases observed as a function of surfactant concentration



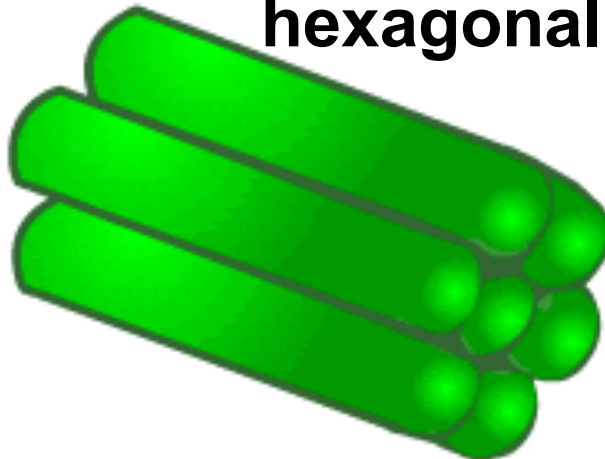
**cubic**



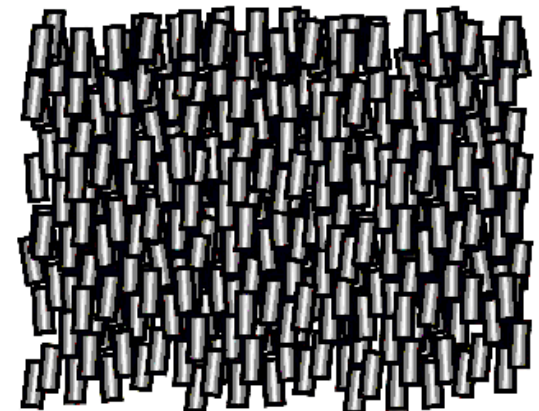
**lamellar**



**hexagonal**



**nematic**

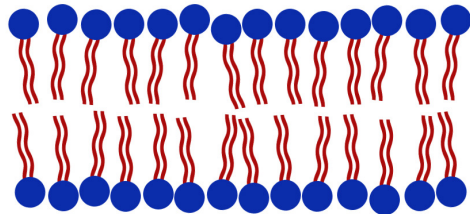


# Lipids as lyotropics and their phases

---

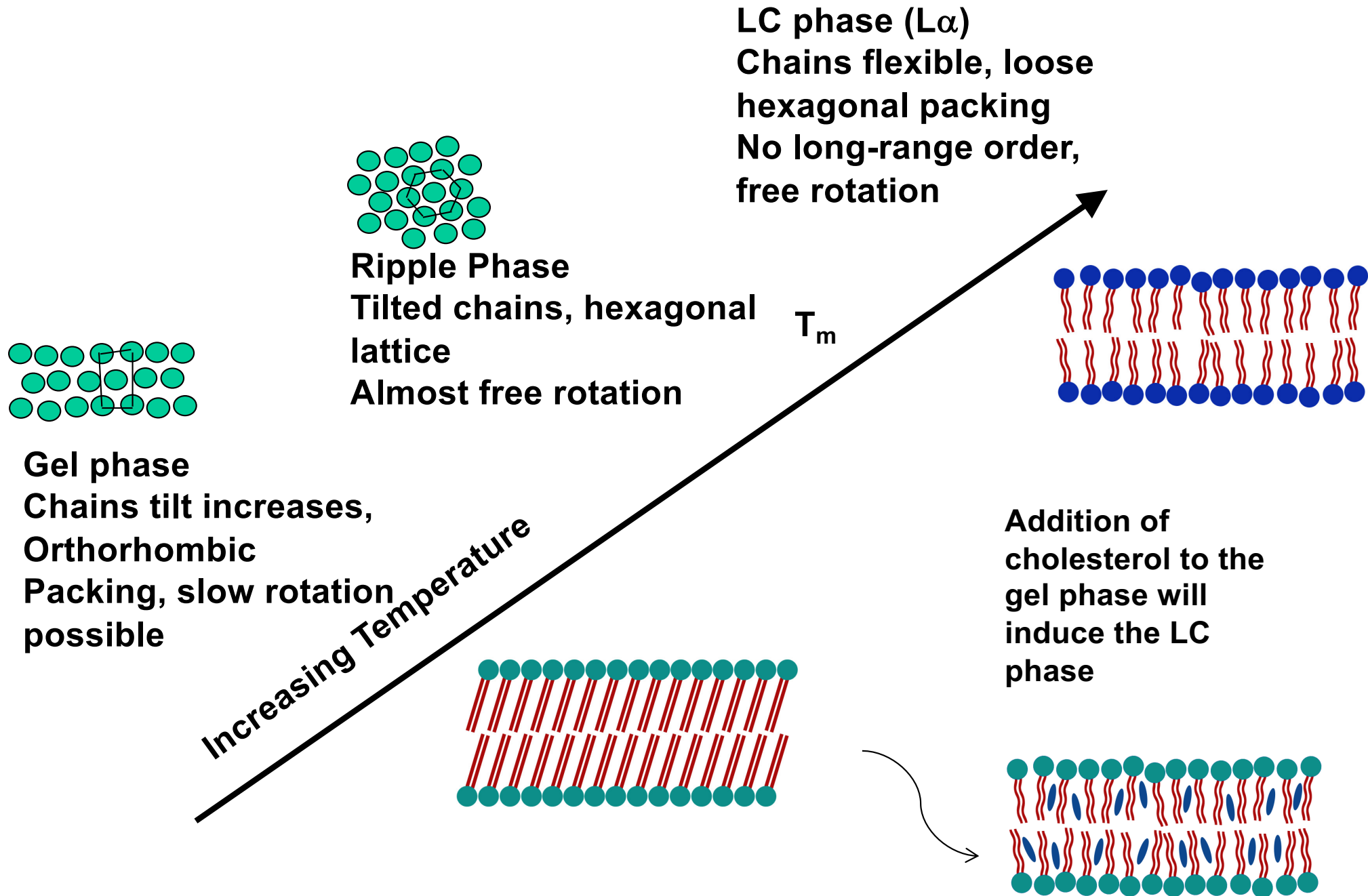
The cell membrane is a flat bilayer

Variants of this phase differ in 'in-plane ordering'



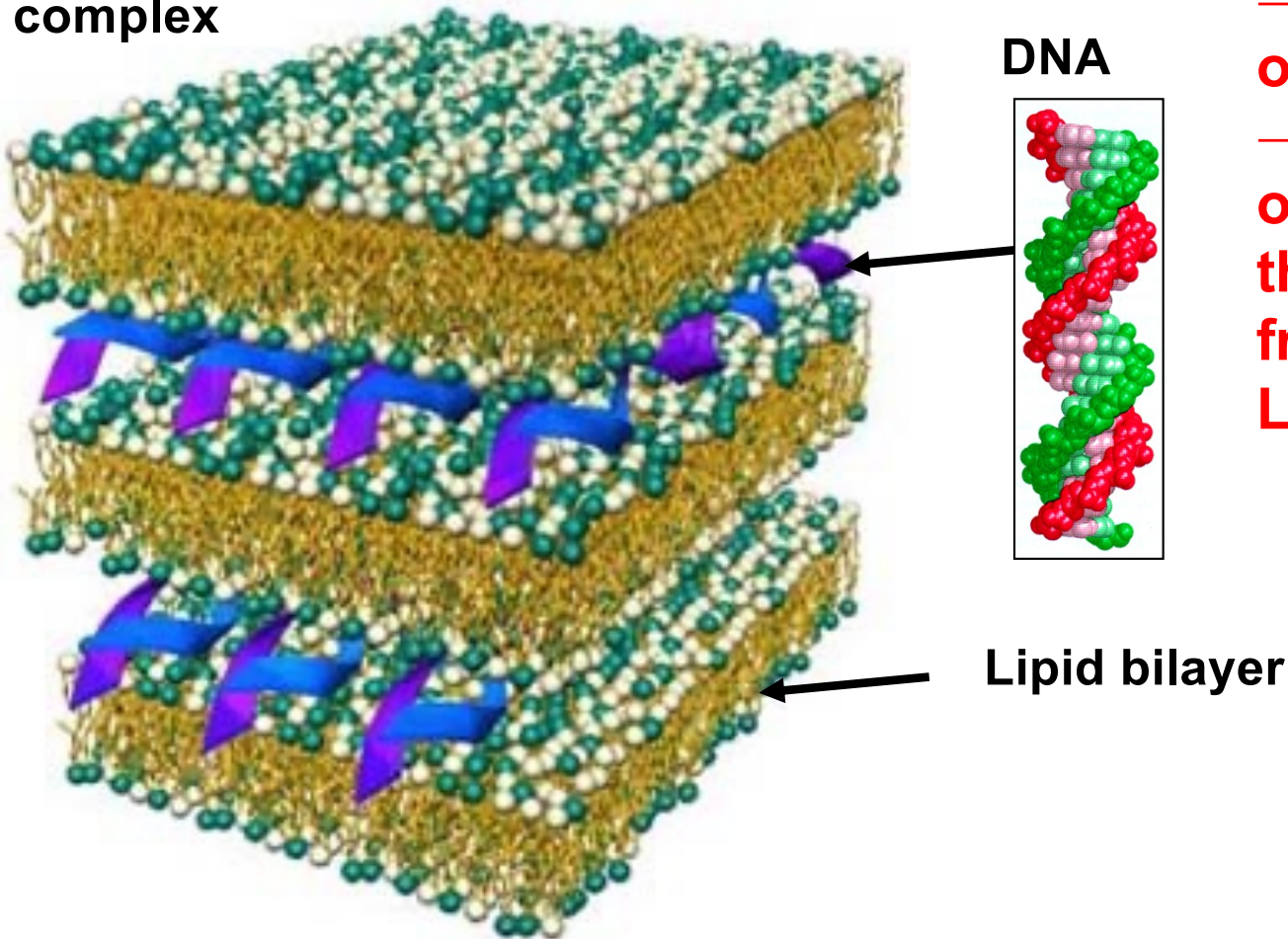
The most commonly known membrane phase is the L $\alpha$  phase (also known as liquid disordered – l $_o$ )

# Membrane (lamellar) phases vs. temperature



# DNA/lipid, DNA/virus, & other LC complexes

Lyotropic LC phase of LC DNA/Lipid complex



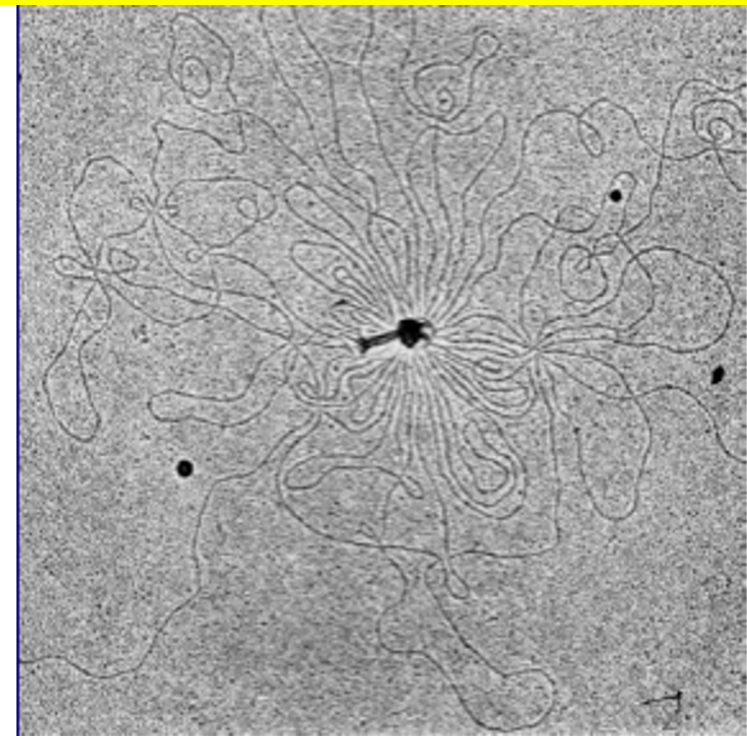
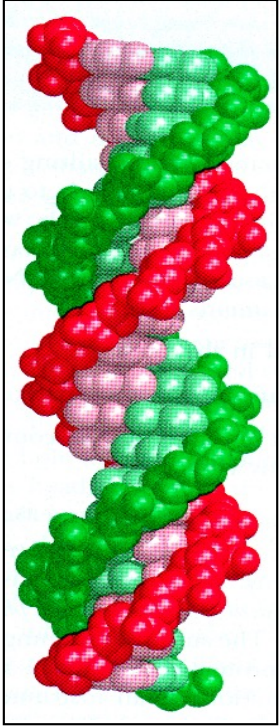
→ **Electrostatic interactions often play an important role;**  
→ **Many phases with exotic organization and symmetry that are distinctly different from that of thermotropic LCs have been observed;**

**Other complexes that have been observed to exhibit LC polymorphism include: (1) F-actin/cationic lipids; (2) virus/membrane; (3) actin/lysozyme; (4) DNA/proteins; (5) DNA/anionic liposome complexes, and many others.**

# *LC phases of DNA Biopolymers*

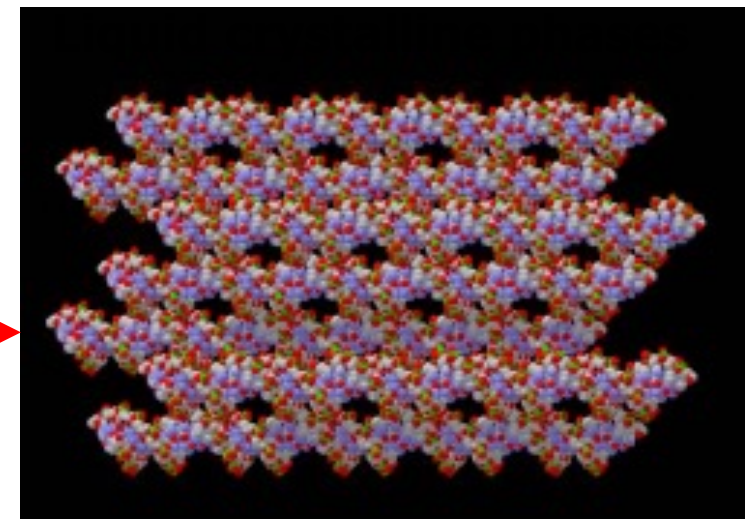
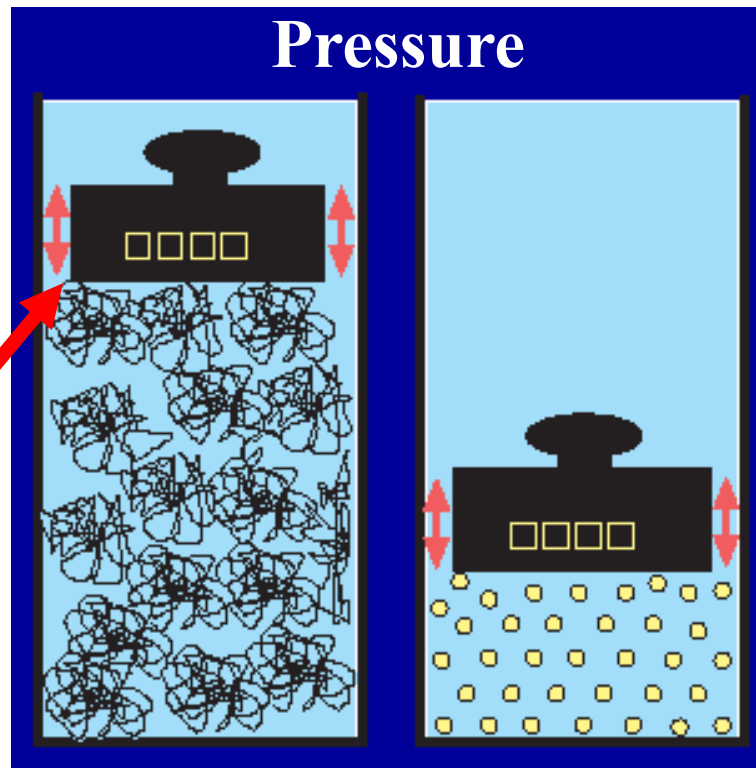
## DNA chains:

- Charge Density:  $e^-/1.7\text{\AA}$
- Diameter:  $D \sim 2\text{nm}$
- Persistence Length:  $\xi_p \sim 50\text{nm}$



(Kleinschmidt et al. (1962))

Water-permeable membrane



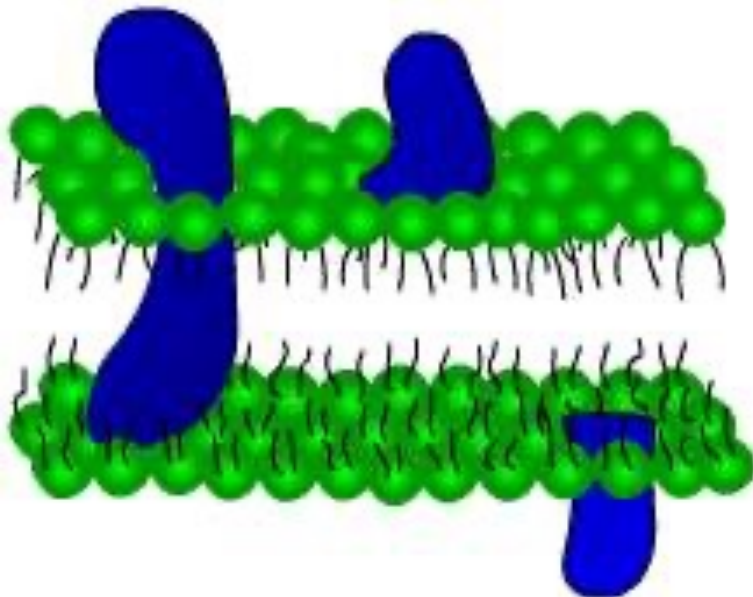
1. H.Strey, V.Parsegian, R.Podgornik, *Phys. Rev. E* 59, 999 (1999).
2. J.V. Selinger & R.F. Bruinsma, *Phys. Rev. A* 43, 2910 (1991).

# Liquid Crystals in Biology

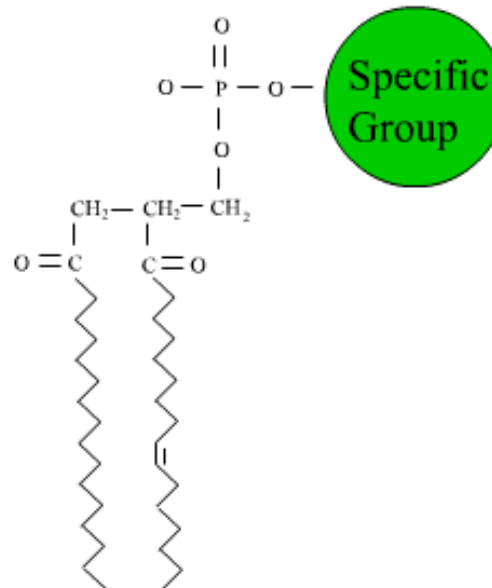
Liquid crystals stand between the isotropic liquid and the strongly organized solid state, life stands between complete disorder, which is death and complete rigidity, which is death again.

Dervichian, D. G., 1997,

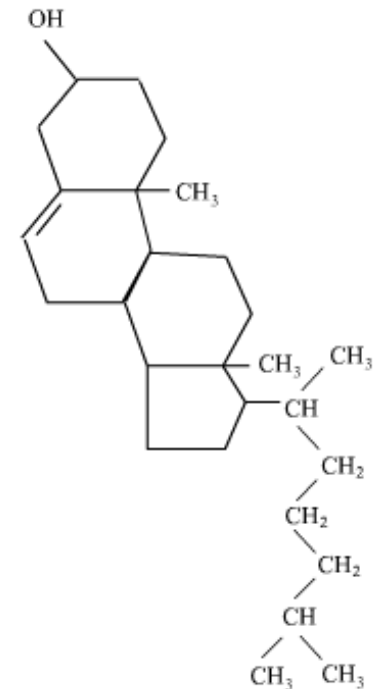
Biological membrane



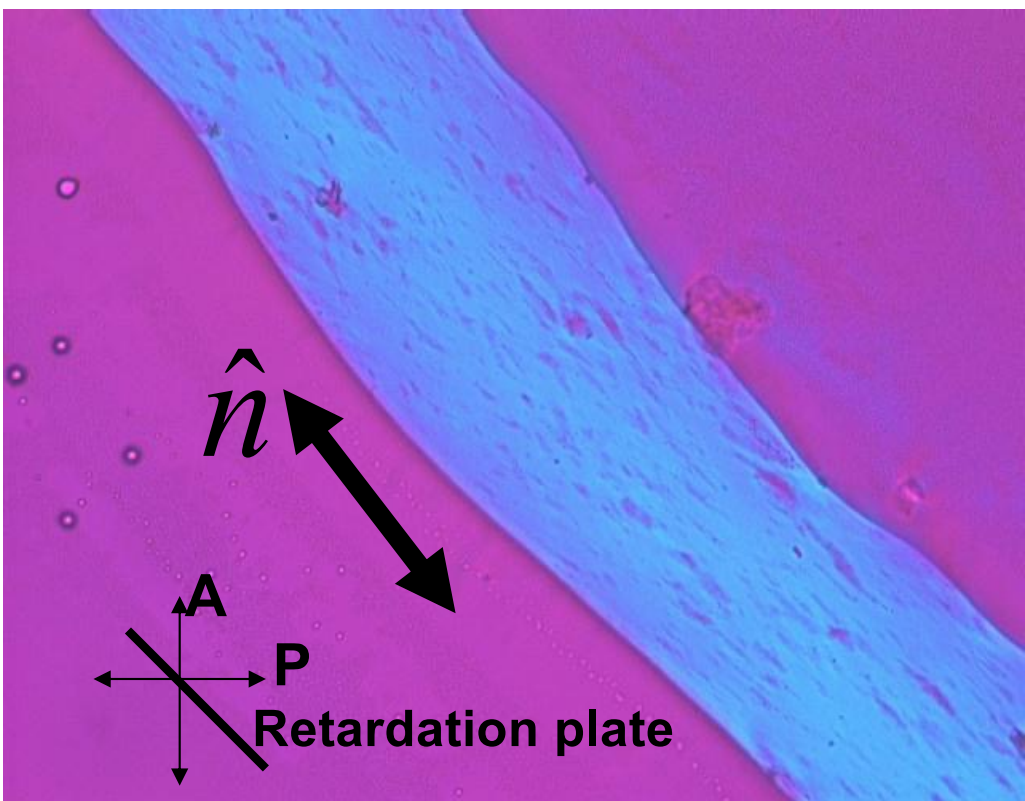
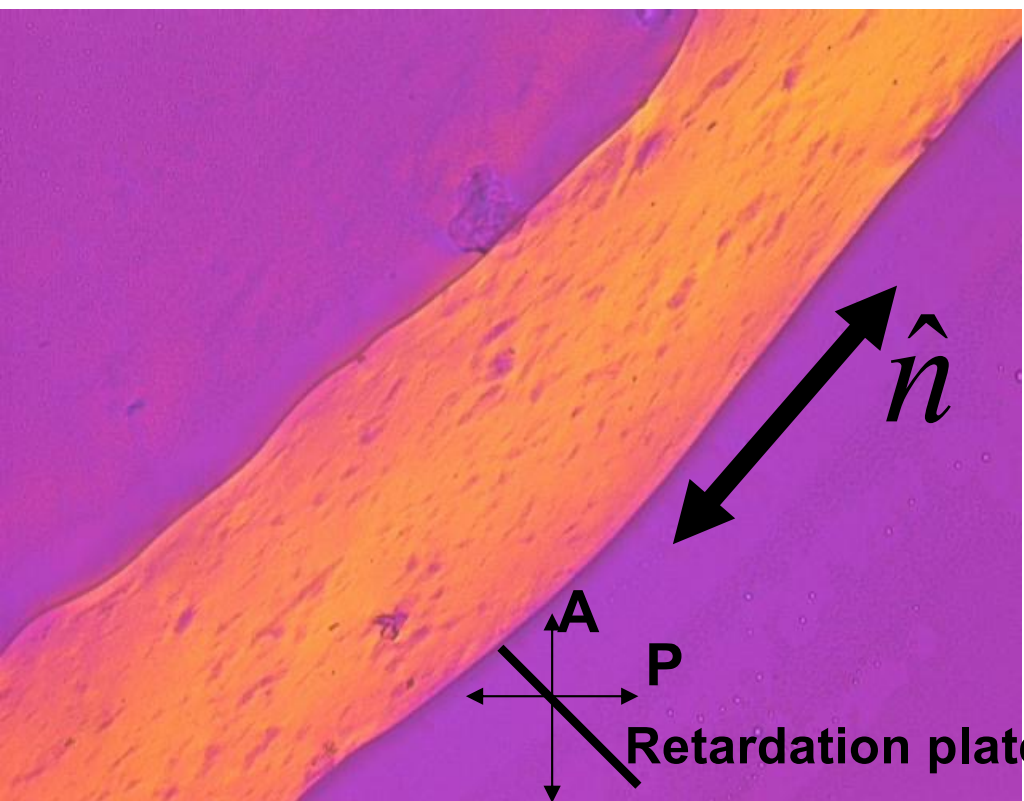
phospholipid structure



cholesterol structure



# Aligned liquid crystal states of biological rods



**DNA**

**Length: 50nm-1m**  
**Diameter: 2nm**  
**Persistence Length:**

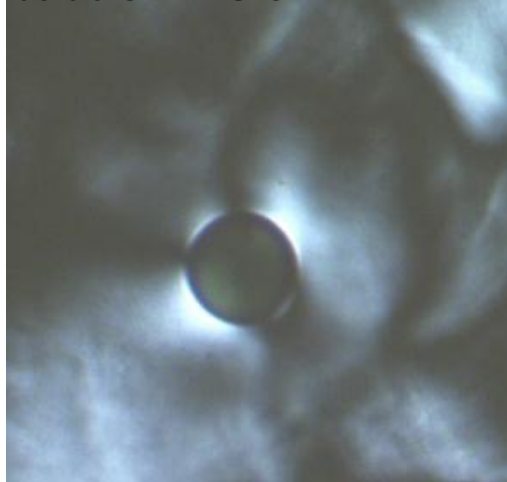


**fd virus**

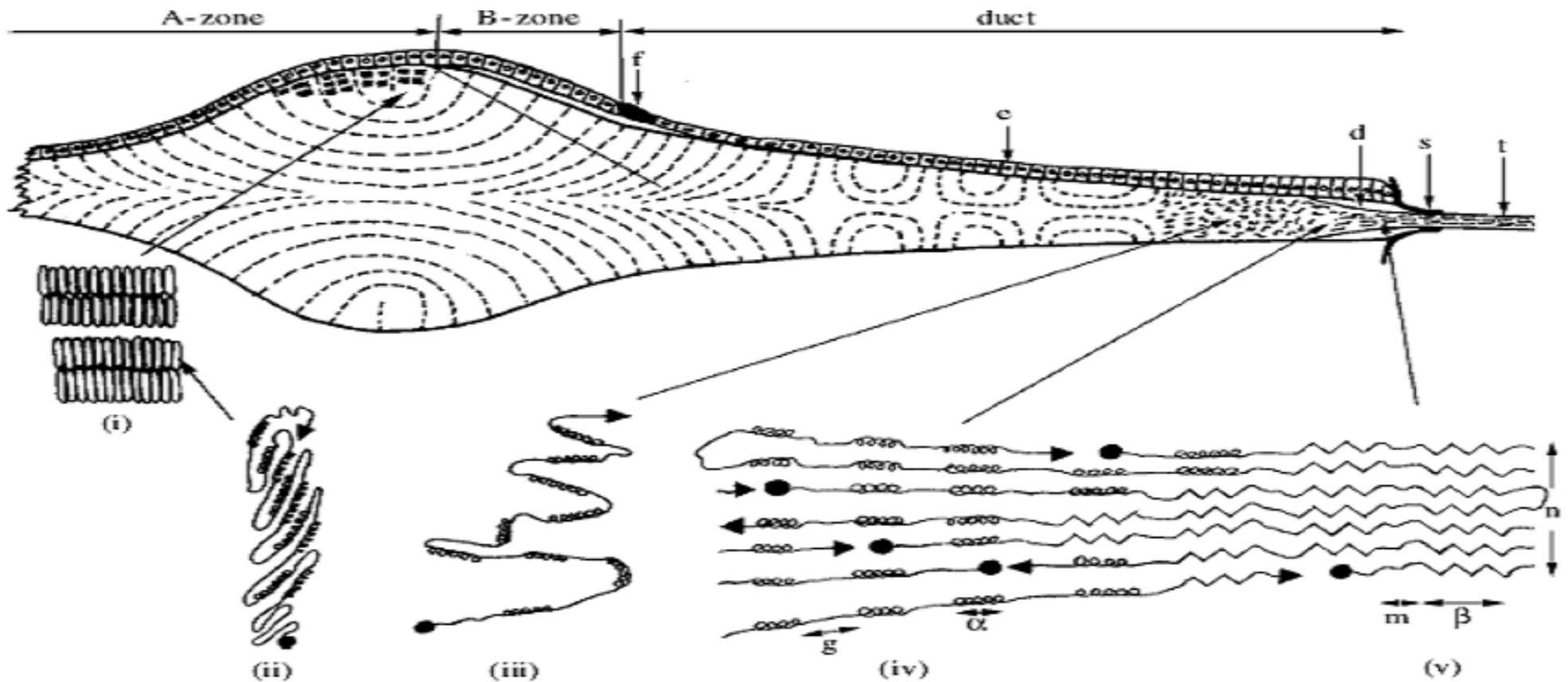
**Length: 880 nm**  
**Diameter : 6.6 nm**  
**Persistence length : 2.8 μm**



**Texture around an air bubble in LC of DNA**



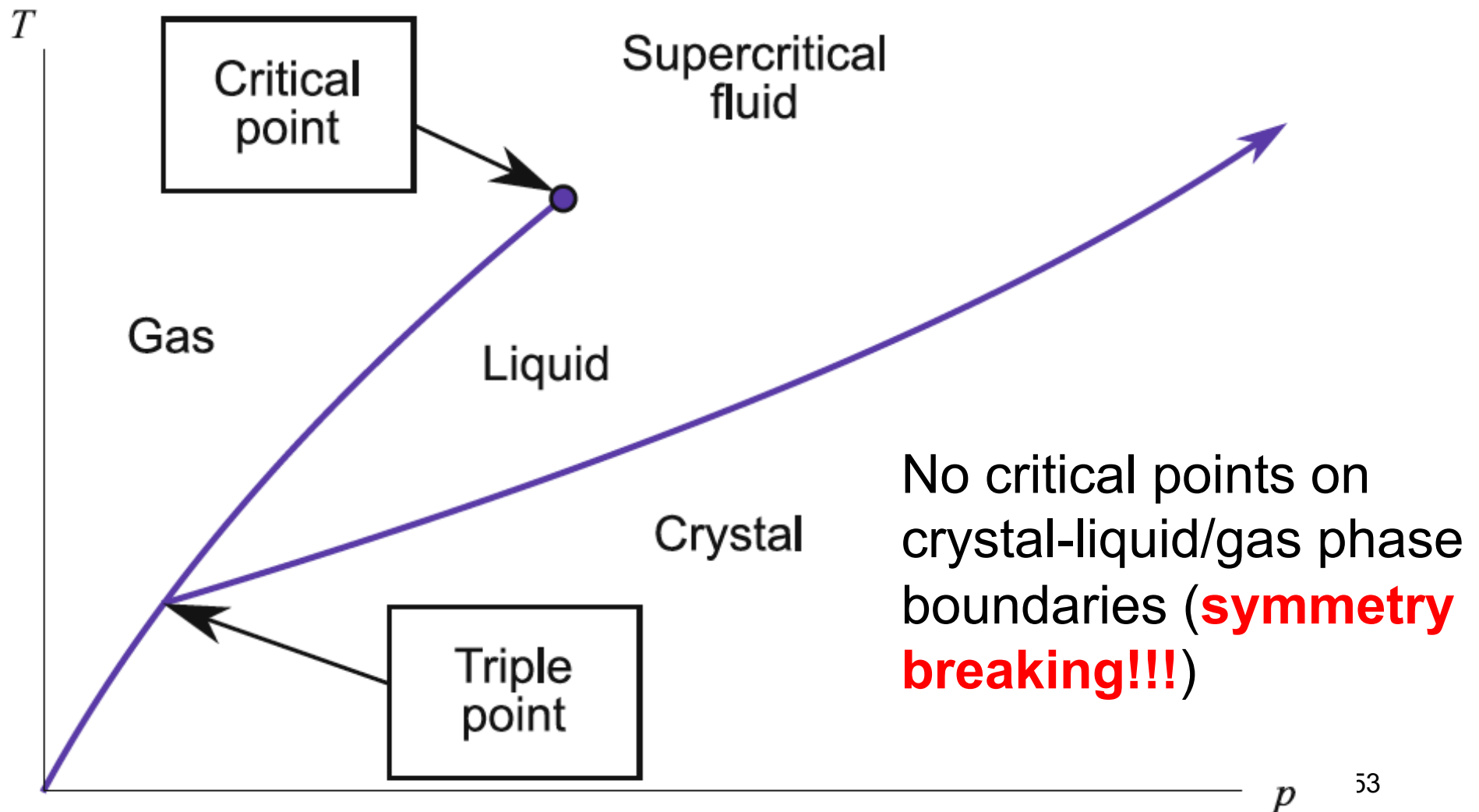
# Liquid crystal states in spider Silk



Liquid crystalline organization is very important for unique mechanical properties of spider silk. Liquid crystals can be also found in high strength plastics, snail slime, and fibers such as silk and Kevlar.

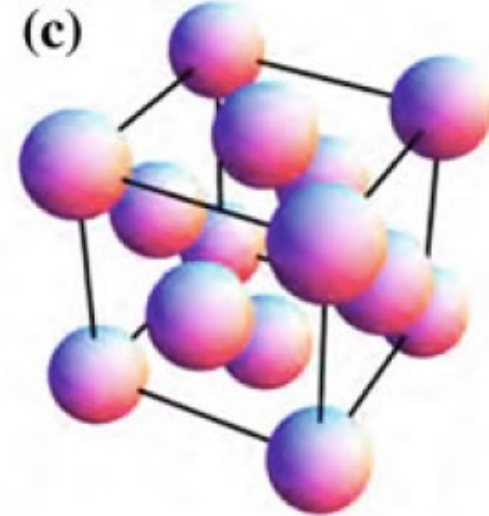
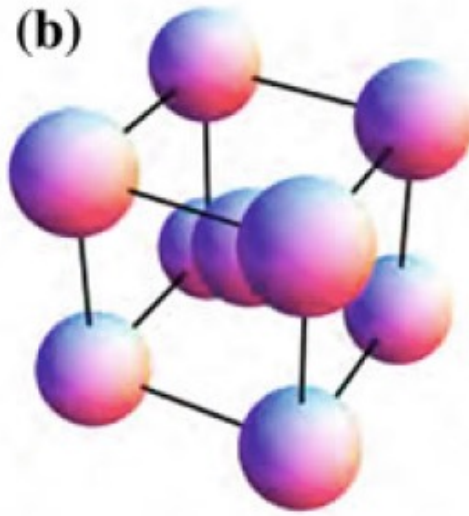
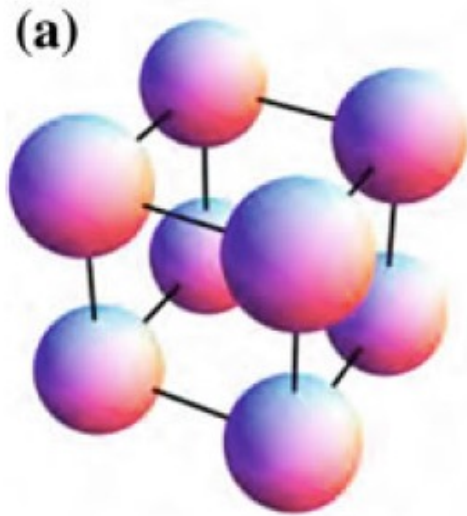
# Phase diagram

- No single simple model (like for a fluid-gas transition)
- Models depend on the type of crystal & the origin of interaction forces leading to the crystal formation



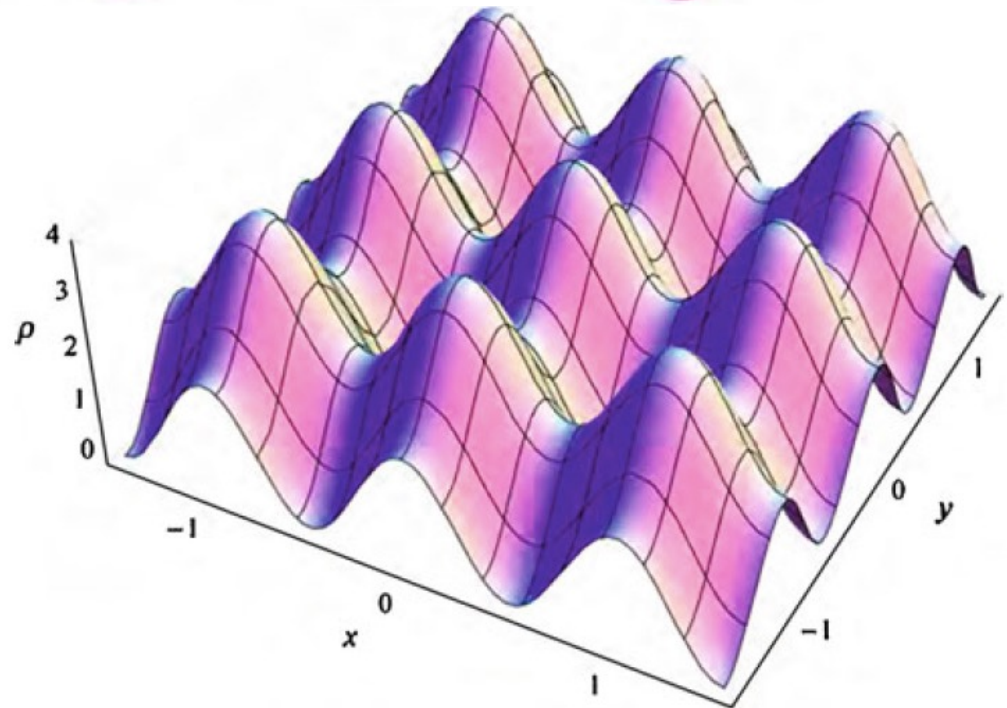
# 3D Crystal Examples?

- Cubic crystals
- Simple cubic, body-centered cubic and face-centered cubic...



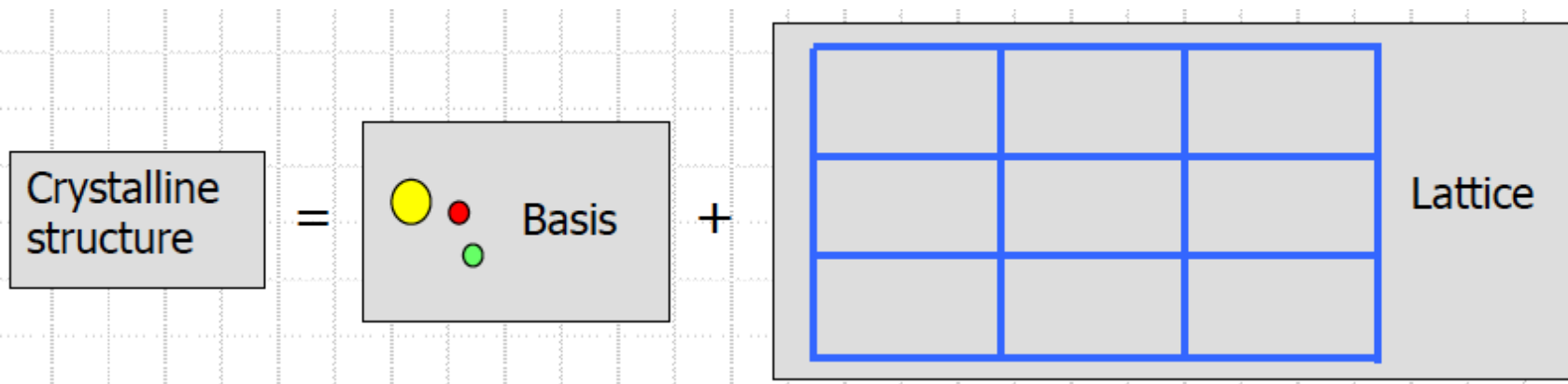
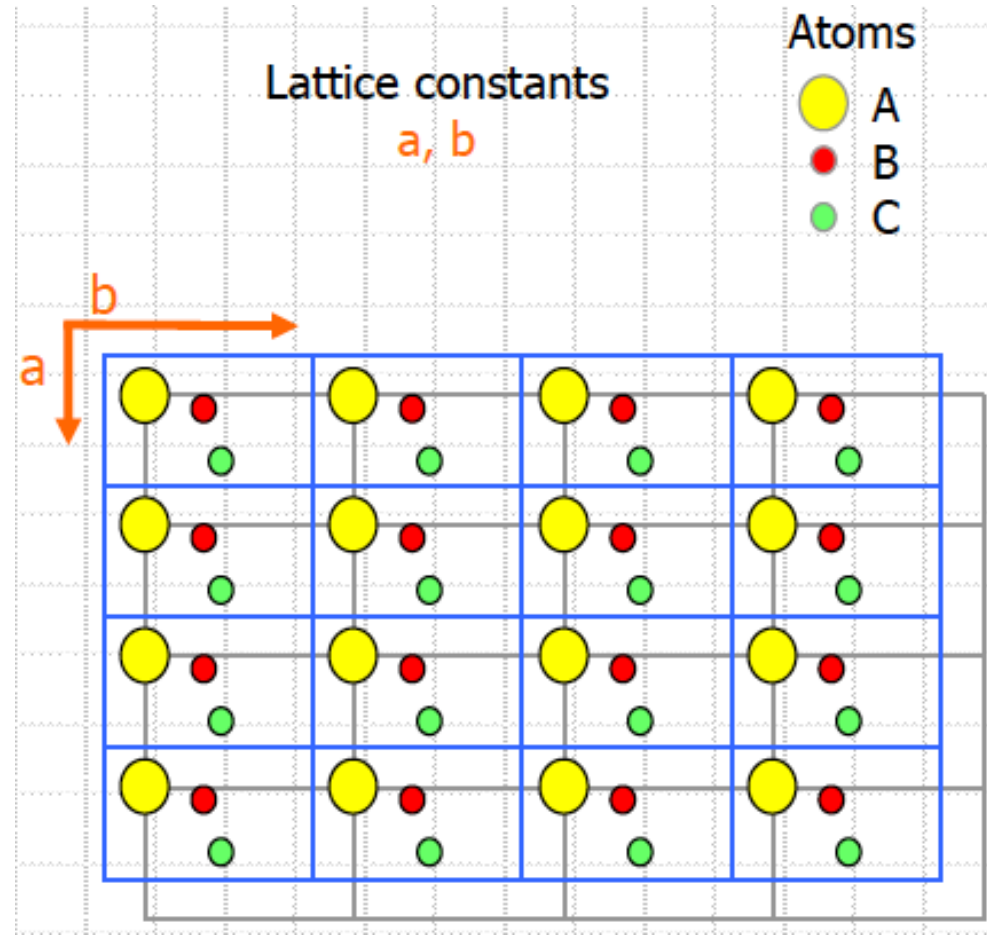
$$\rho_{\text{crystal}}(\mathbf{r}) = \rho_0 + \sum_{\mathbf{q}} \rho_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}$$

In each crystallographic plane, density is a function of position

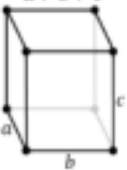
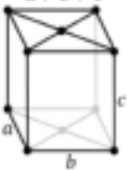
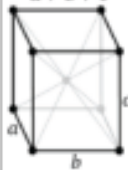
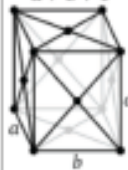


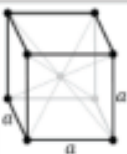
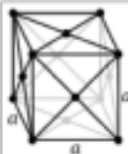


# Crystal order & symmetry: brief overview

Not only atom, ion or molecule positions are repetitious –there have well defined symmetry relations in their arrangement.



# Bravais Lattices in 3D

<u>triclinic</u>	P	P		C
	$\alpha, \beta, \gamma \neq 90^\circ$	$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$		$\alpha \neq 90^\circ$ $\beta, \gamma = 90^\circ$
<u>orthorhombic</u>	P	C	I	F
	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$
				
	$a$ $b$ $c$	$a$ $b$ $c$	$a$ $b$ $c$	$a$ $b$ $c$
<u>tetragonal</u>	P	I		
	$a \neq c$	$a \neq c$		
<u>rhombohedral</u>	P			
	$\alpha = \beta = \gamma \neq 90^\circ$			
<u>hexagonal</u>	P			
				
<u>cubic</u>	P (bcc)	I (bcc)	F (fcc)	
	$a$	$a$	$a$	
				

14 conventional Bravais lattices

7 distinct types + centering (face and body): total: 14 types

Hexagonal, FCC and BCC especially important because they are most common for simple materials

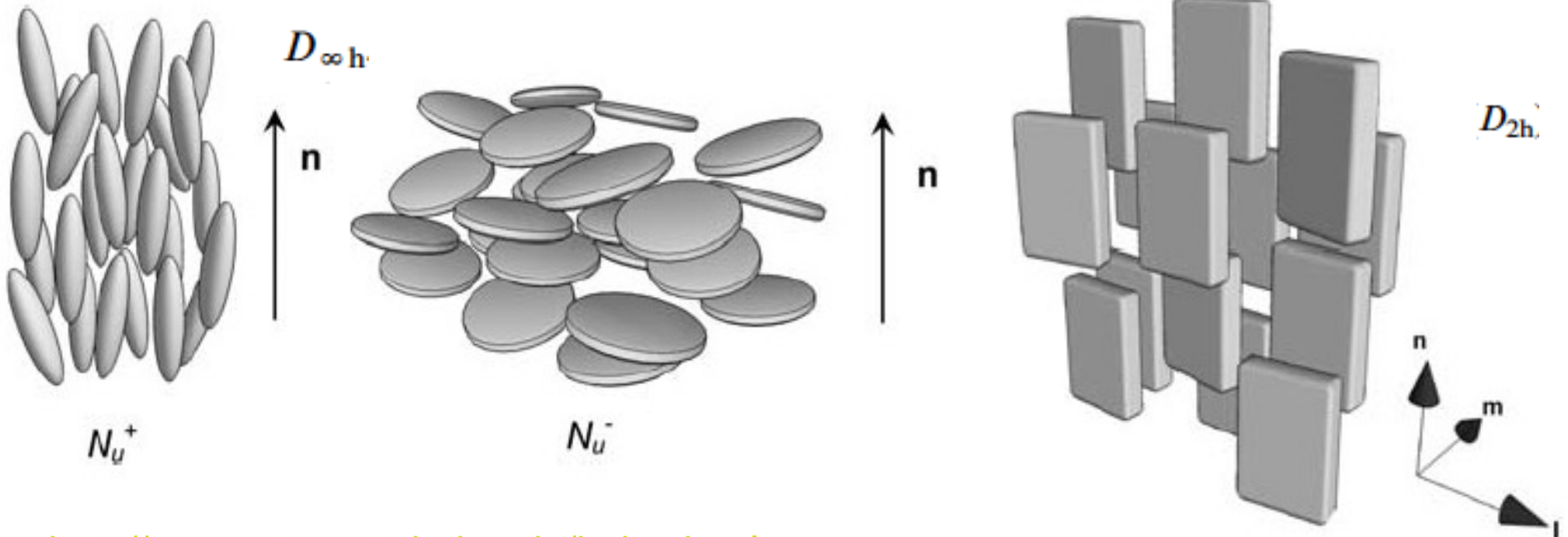
230 space groups

Useful web page with demonstrations:

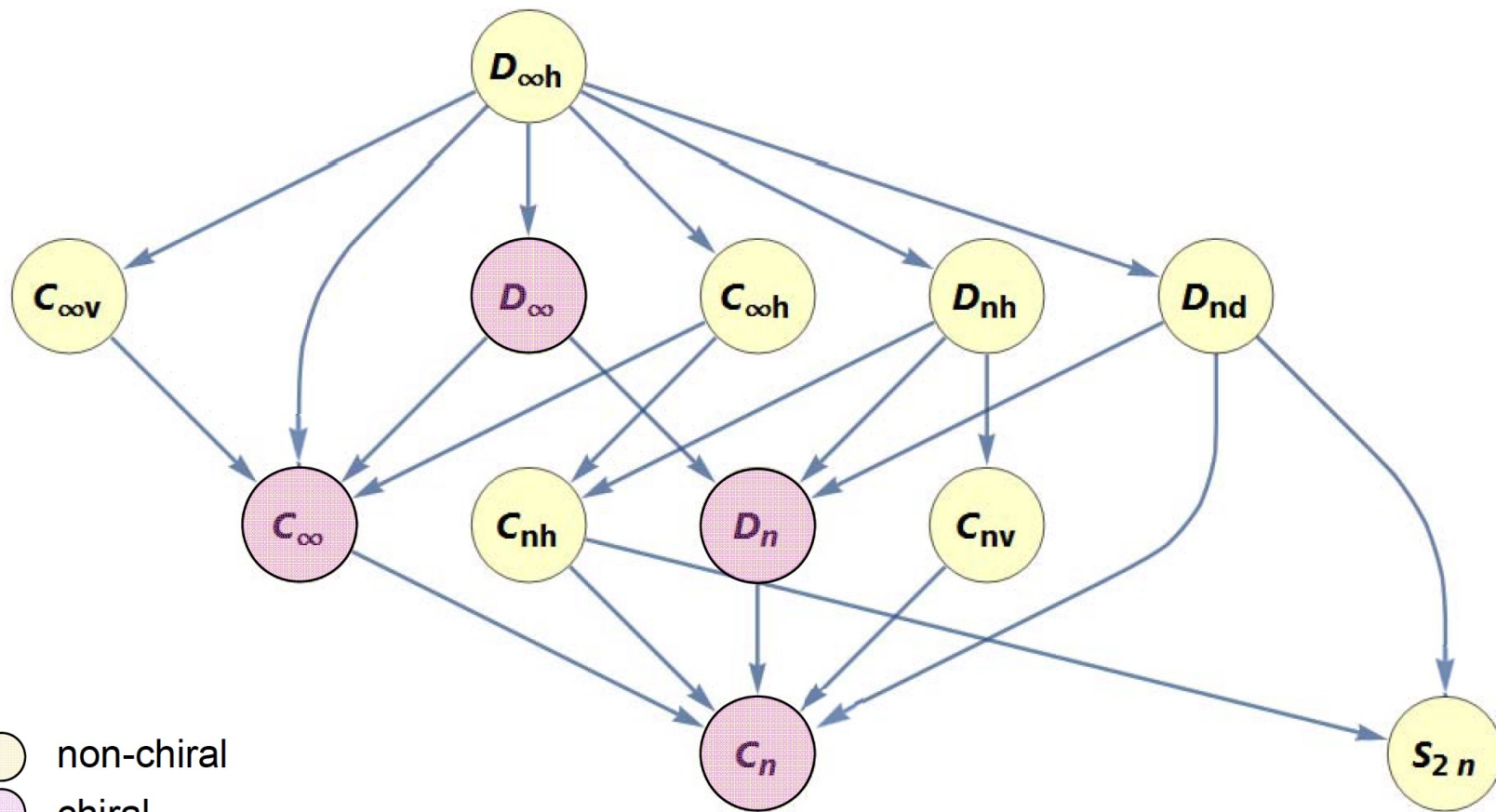
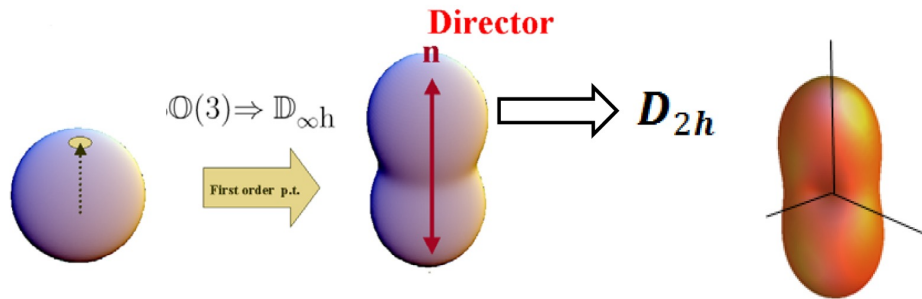
<http://www.materials.ac.uk/elearning/matter/crystallography/3dcystallography/7crystalsystems.html>

# How about symmetries of LCs?

- Simplest – nematic LC (no positional order)
- Uniaxial nematic - point symmetry group  $D_{\infty h}$
- Biaxial nematic –  $D_{2h}$

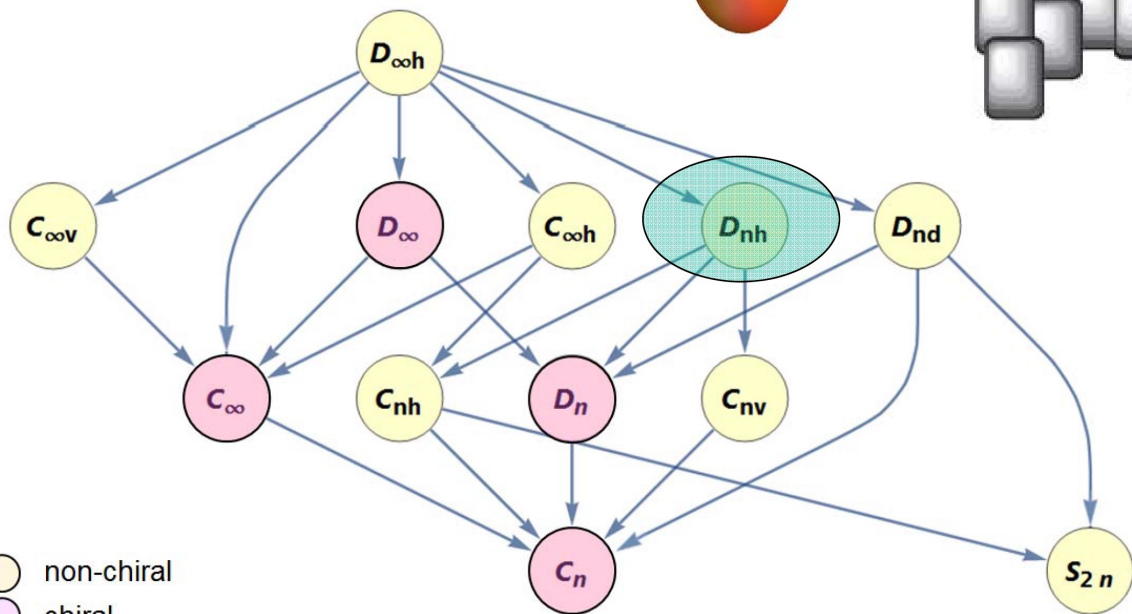
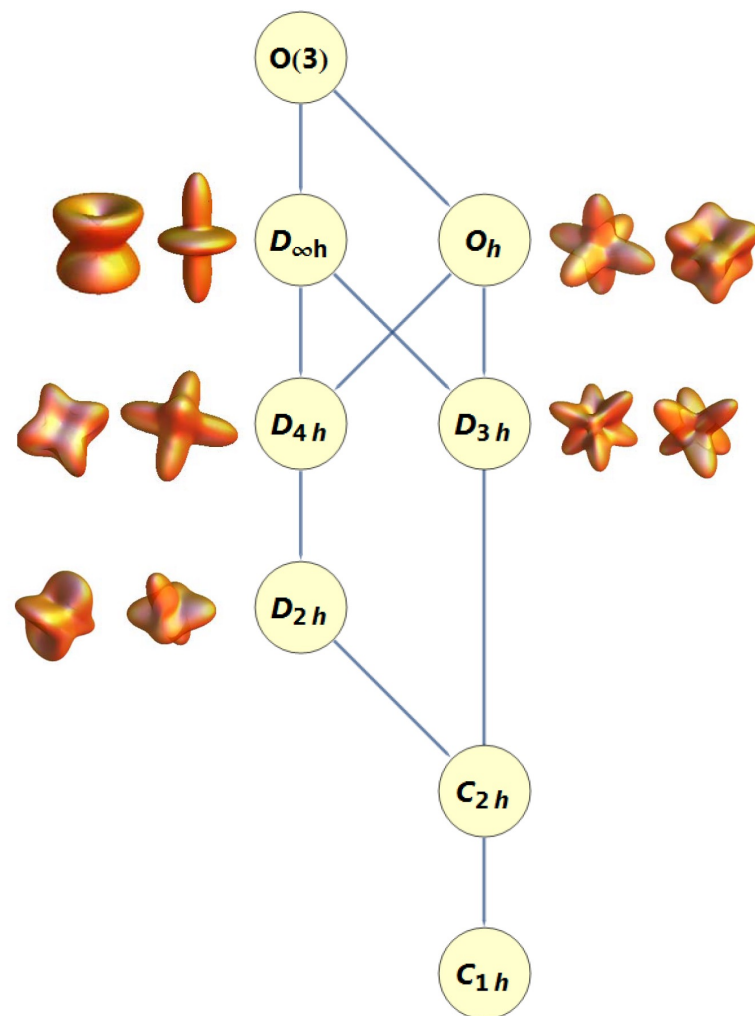
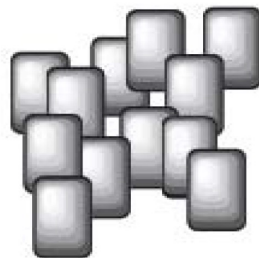
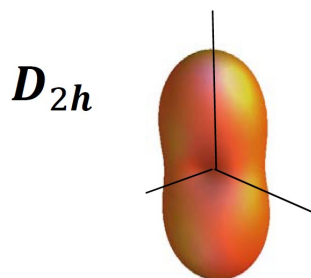


# Examples: the nematic phases



- non-chiral
- chiral

# Low-symmetry nematic liquid crystals



● non-chiral  
● chiral

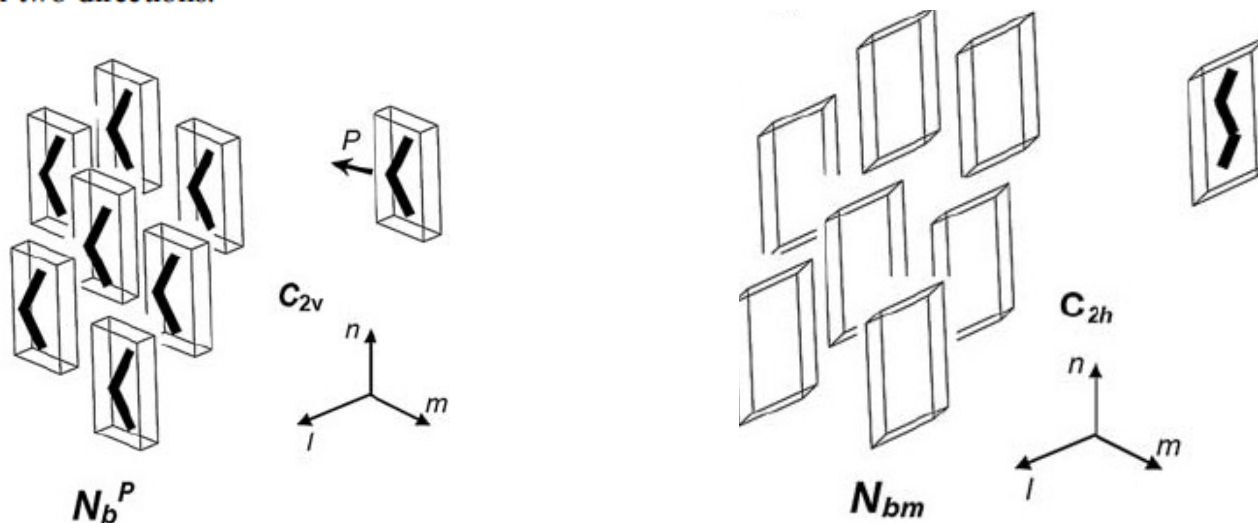
Most remain to be discovered

# Nematic phases with other symmetries?

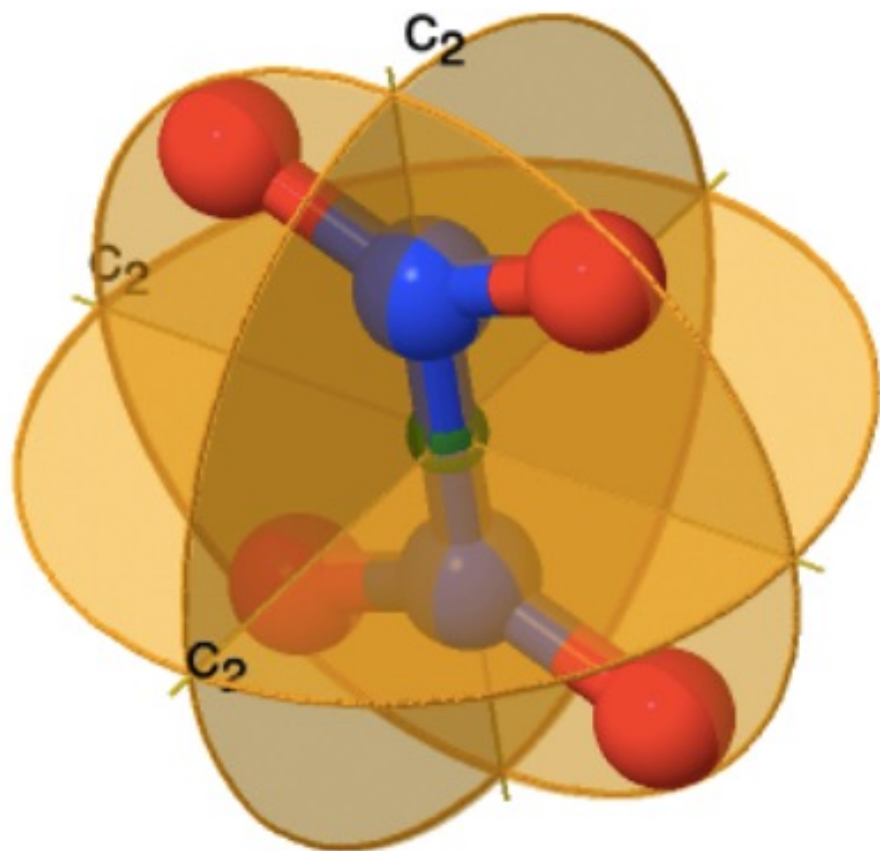
**Table 1** Summary of the abbreviations used for the assignment of the different types of nematic phases and their symmetries<sup>a</sup>

Detailed structural notation	Generic cluster-model notation	Nature of biaxiality <sup>a</sup>	Tilt <sup>b</sup>	Polarity	Point symmetry group
$N_u$	$N_u$	—	—	—	$D_{\infty h}$
$N_{uCybA}$	$N_u$	—	—	—	$D_{\infty h}$
$N_{ulCybAb}$	$N_{ul}$	Local	—	—	$D_{\infty h}$
$N_{bCybAb}$	$N_{bo}$	Phase; HR	—	—	$D_{2h}$
$N_{ulCybAP}$	$N_{ul}$	Local	—	Local	$D_{\infty h}$
$N_{bCybAP}^P$	$N_b^P$	Phase; HR	—	Phase	$C_{2v}$
$N_{uCybC}$	$N_u$	Local, weak; tilt only	+	—	$D_{\infty h}$
$N_{ulCybC}$	$N_{ul}$	Local, strong; tilt only	+	—	$D_{\infty h}$
$N_{bCybC}$	$N_{bm}$	Phase; tilt only	+	—	$C_{2h}$
$N_{ulCybCb}$	$N_{ul}$	Local; tilt + HR	+	—	$D_{\infty h}$
$N_{bCybCb}$	$N_{bm}$	Phase; tilt + HR	+	—	$C_{2h}$
$N_{ulCybCP}$	$N_{ul}$	Local; tilt + HR	+	Local	$D_{\infty h}$
$N_{bCybCP}^P$	$N_b^P$	Phase; tilt + HR	+	Phase	$C_2$
$N_{ulCybCg}$	$N_{ul}$	Local; tilt + HR	++	—	$D_{\infty h}$
$N_{bCybCg}$	$N_{bt}$	Phase; tilt + HR	++	—	$C_i$
$N_{ulCybCg}^P$	$N_{ul}$	Phase; tilt + HR	++	Local	$D_{\infty h}$
$N_{bCybCg}^P$	$N_b^P$	Phase; tilt + HR	++	Phase	$C_1$

<sup>a</sup> Abbreviations: HR = hindered rotation (rotational freeze out) about the long molecular axis; g = general phase, for an explanation see refs. 52,149 and references therein. <sup>b</sup> ++ = tilt in two directions.



# What symmetry operations are allowed for $D_{2h}$ ?



**Element Operation**

$C_2$  axis

$C_2$  axis

$C_2$  axis

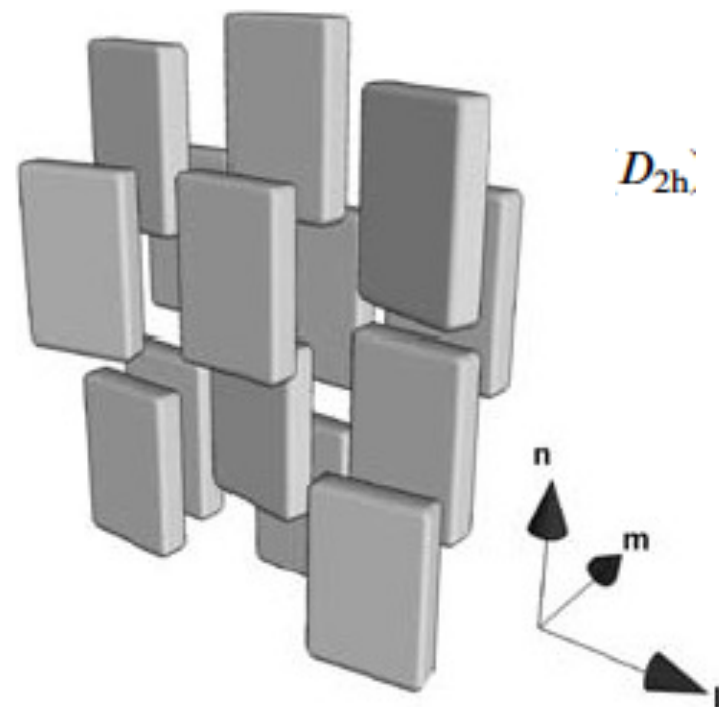
**Element Operation**

inv ctr

plane ( $\sigma_{xy}$ )

plane ( $\sigma_{xz}$ )

plane ( $\sigma_{yz}$ )

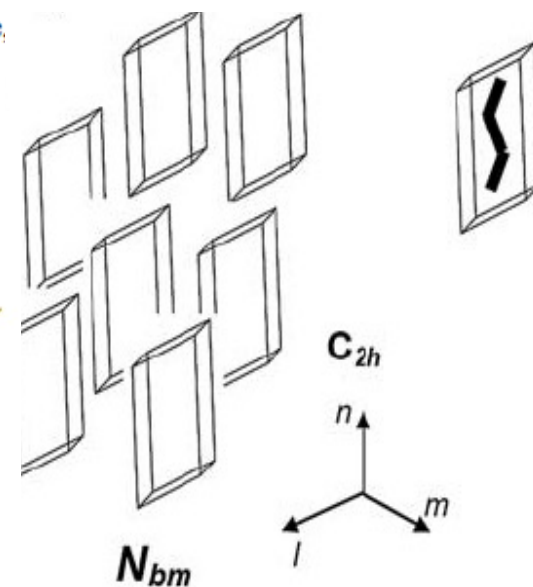
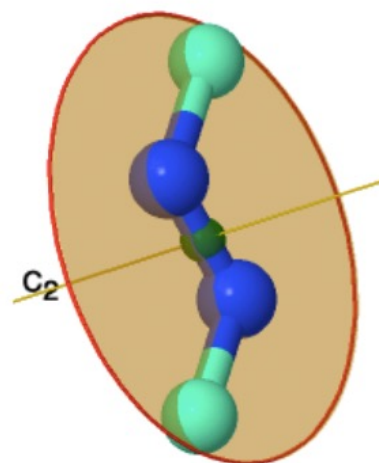
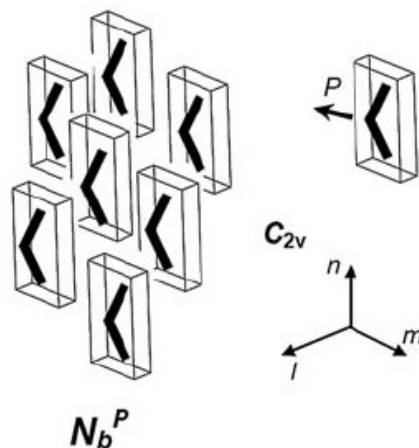
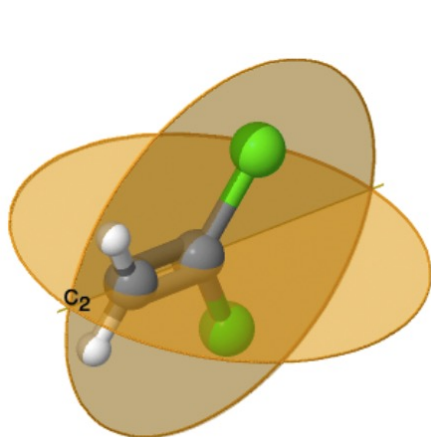


# Nematic phases with other symmetries?

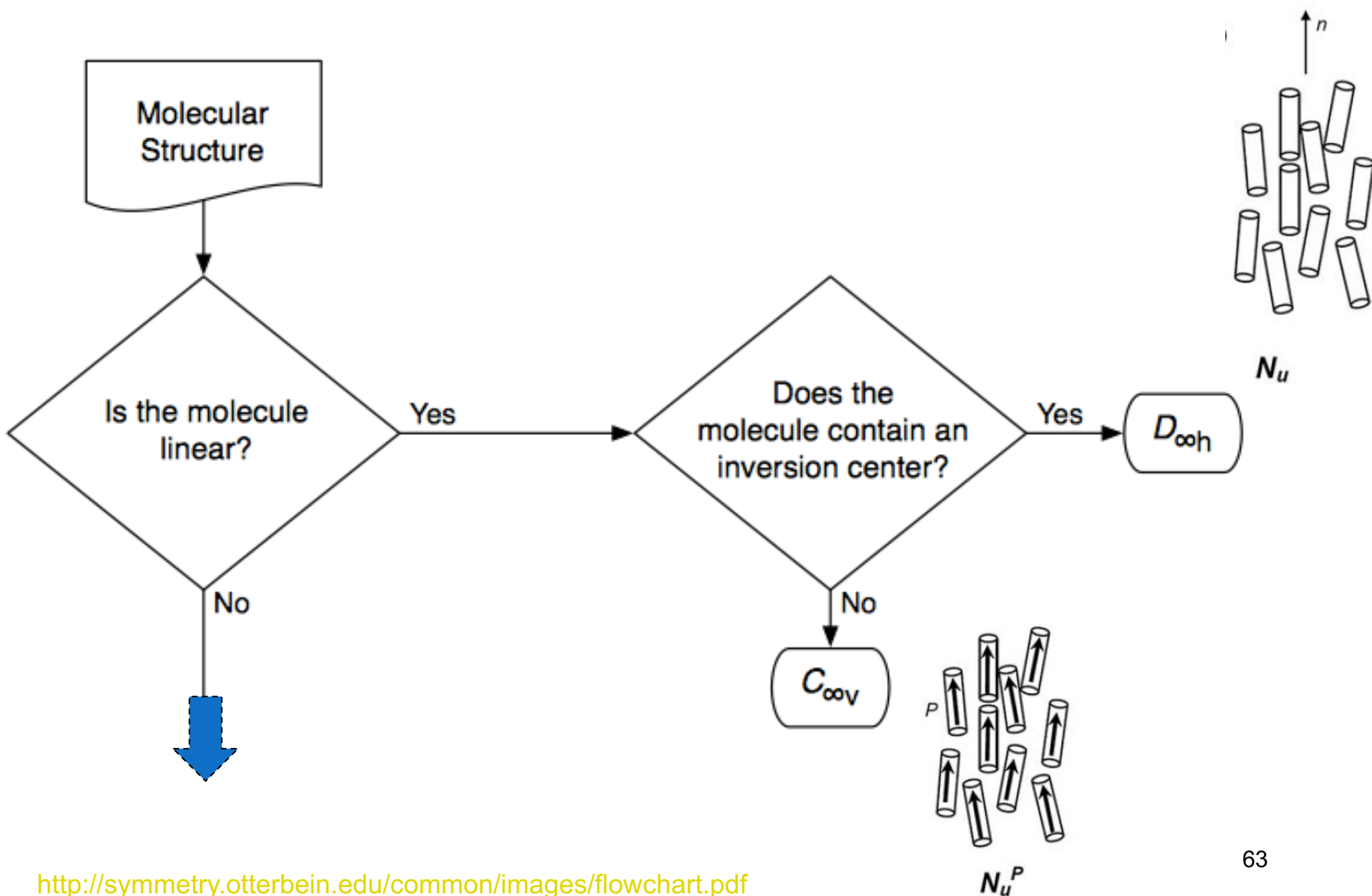
**Table 1** Summary of the abbreviations used for the assignment of the different types of nematic phases and their symmetries<sup>a</sup>

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$N_{uCybA}$	$N_u$	—	—	—	$D_{\infty h}$
$N_{ul\ CybAb}$	$N_{ul}$	Local	—	—	$D_{\infty h}$
$N_{bCybAb}$	$N_{bo}$	Phase; HR	—	—	$D_{2h}$
$N_{ul\ CybAP}$	$N_{ul}$	Local	—	Local	$D_{\infty h}$
$N_{bCybAP}^P$	$N_b^P$	Phase; HR	—	Phase	$C_{2v}$
$N_{uCybC}$	$N_u$	Local, weak; tilt only	+	—	$D_{\infty h}$
$N_{ul\ CybC}$	$N_{ul}$	Local, strong; tilt only	+	—	$D_{\infty h}$
$N_{bCybC}$	$N_{bm}$	Phase; tilt only	+	—	$C_{2h}$
$N_{ul\ CybCb}$	$N_{ul}$	Local; tilt + HR	+	—	$D_{\infty h}$
$N_{bCybCb}$	$N_{bm}$	Phase; tilt + HR	+	—	$C_{2h}$
$N_{ul\ CybCP}$	$N_{ul}$	Local; tilt + HR	+	Local	$D_{\infty h}$
$N_{bCybCP}^P$	$N_b^P$	Phase; tilt + HR	+	Phase	$C_2$
$N_{ul\ CybCg}$	$N_{ul}$	Local; tilt + HR	++	—	$D_{\infty h}$
$N_{bCybCg}$	$N_{bt}$	Phase; tilt + HR	++	—	$C_i$
$N_{ul\ CybCg}^P$	$N_{ul}$	Phase; tilt + HR	++	Local	$D_{\infty h}$
$N_{bCybCg}^P$	$N_b^P$	Phase; tilt + HR	++	Phase	$C_1$

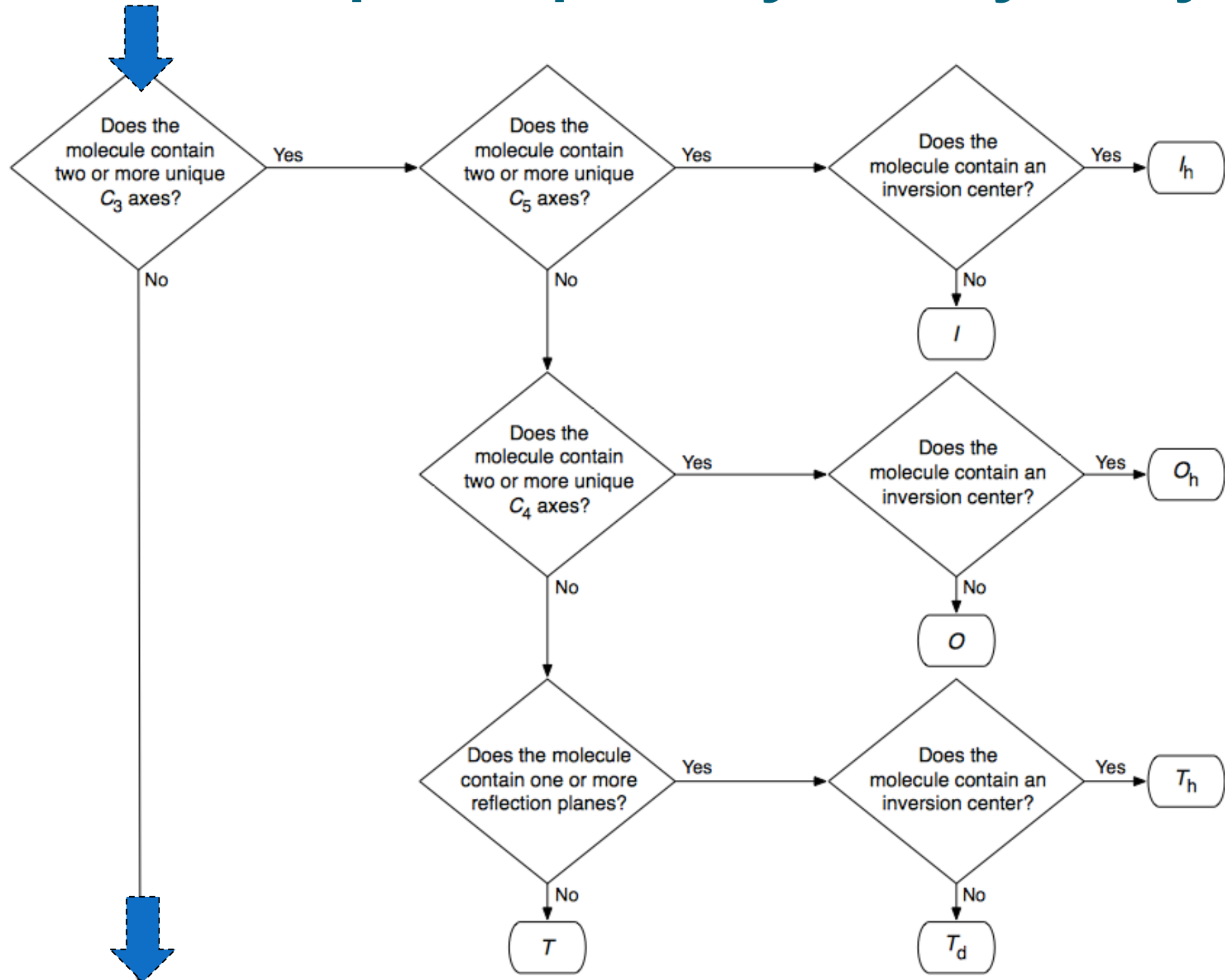
<sup>a</sup> Abbreviations: HR = hindered rotation (rotational freeze out) about the long molecular axis; g = general phase, references therein. <sup>b</sup> ++ = tilt in two directions.



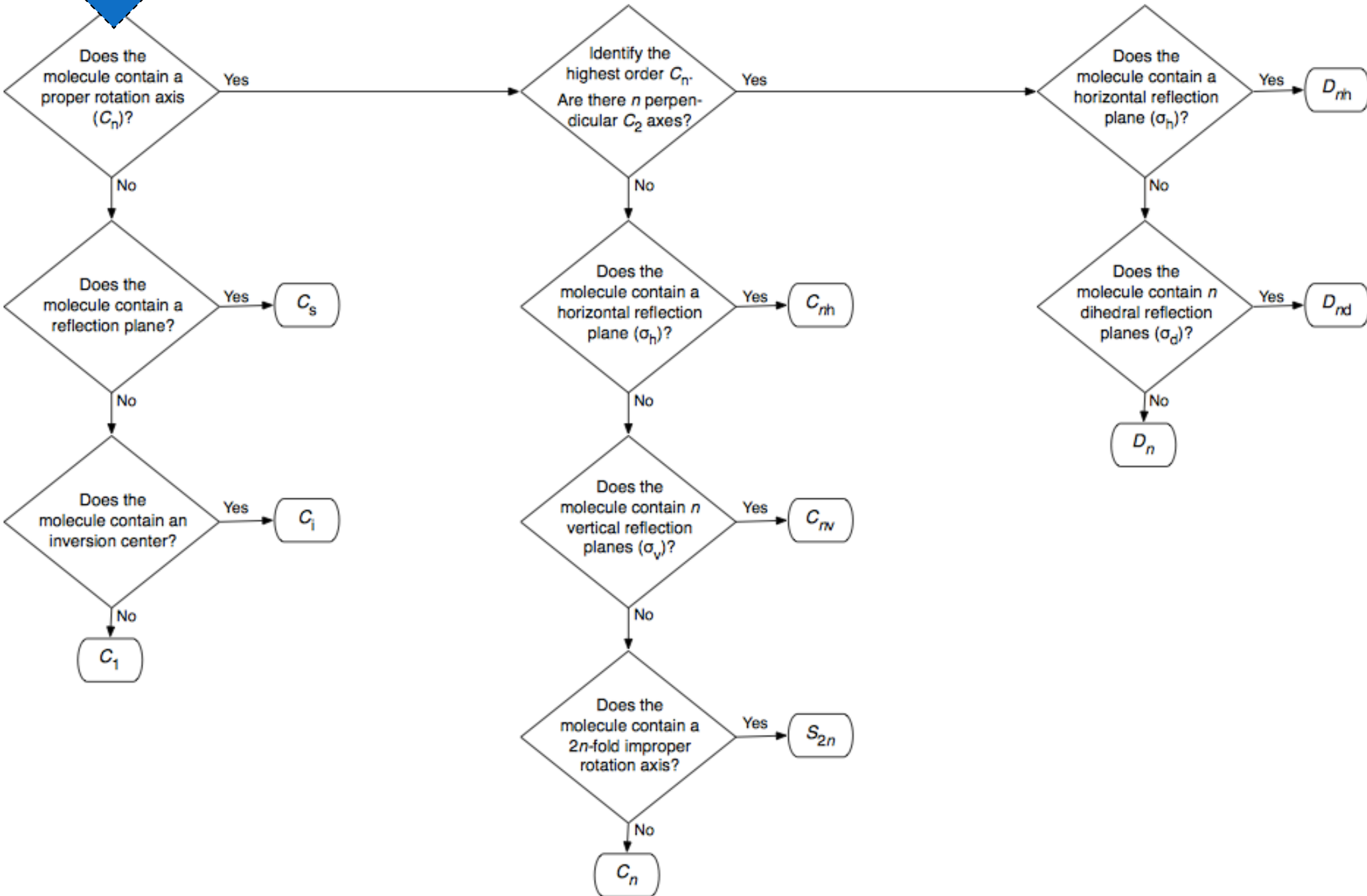
# Molecule & phase point symmetry analysis



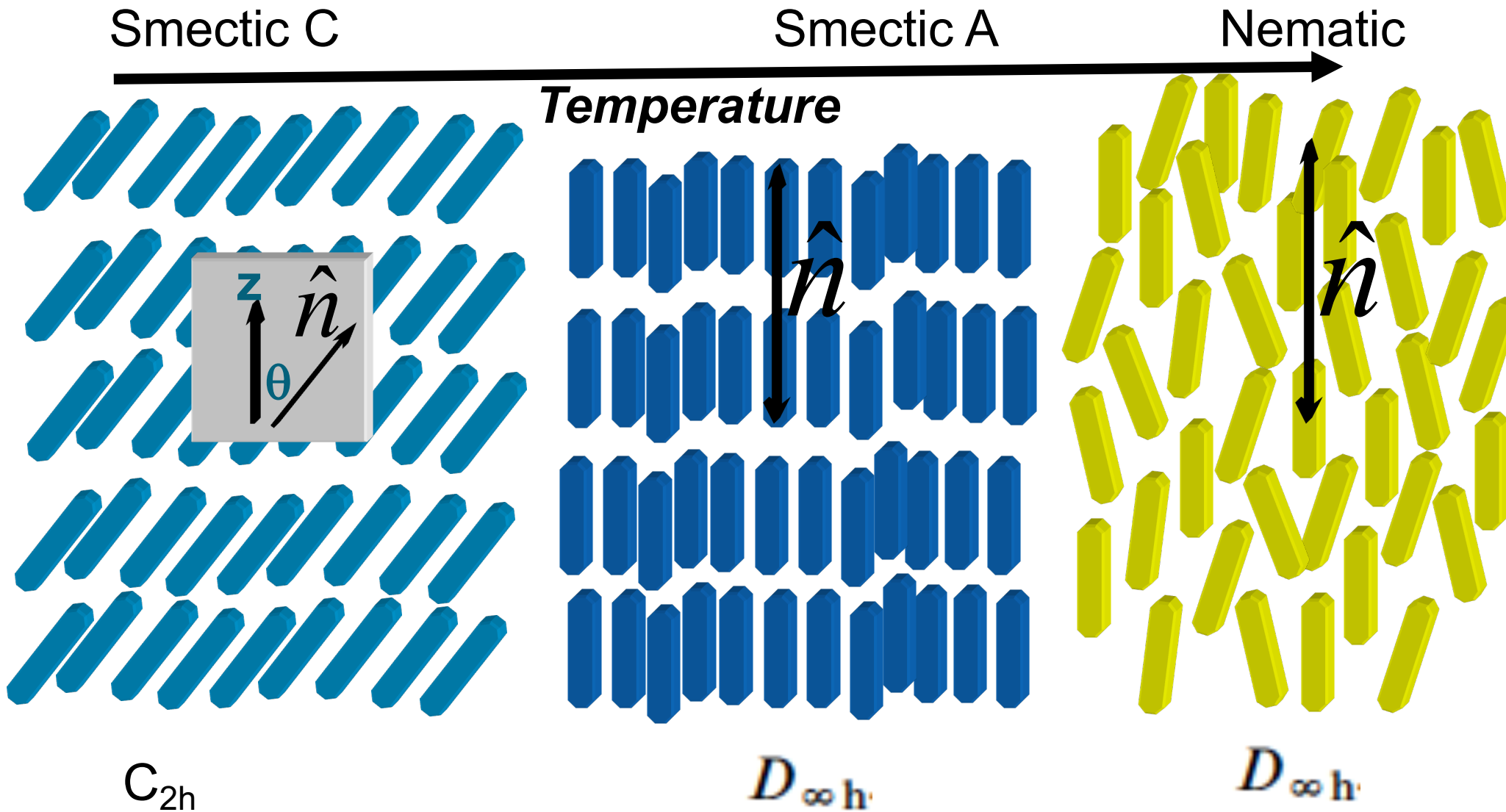
# Molecule & phase point symmetry analysis



# Molecule & phase point symmetry analysis



# 1D solids: Smectic A & smectic C



Molecules in the smectic phases show a degree of *translational order* not present in the nematic. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted to within these planes, and separate planes are observed to flow past each other.

**No change of point symmetry at nematic - Smectic A transition**

# Diversity of point symmetries, possible smectics: Smectic A phases

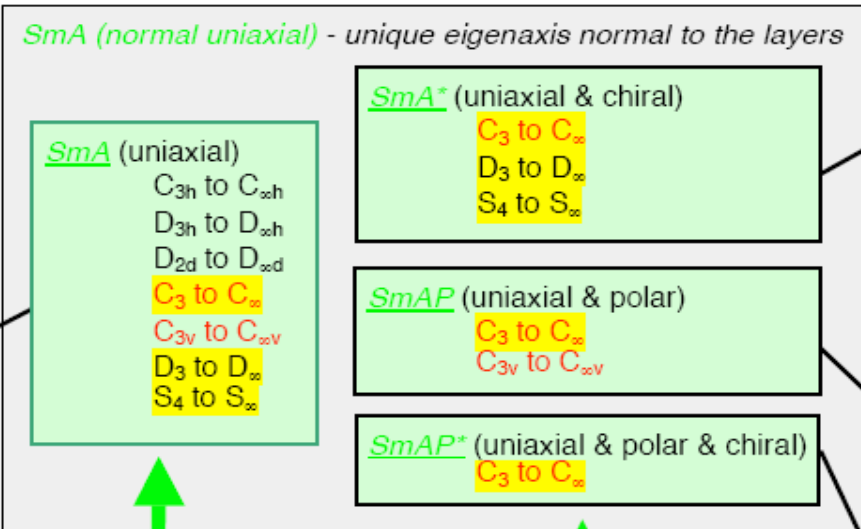
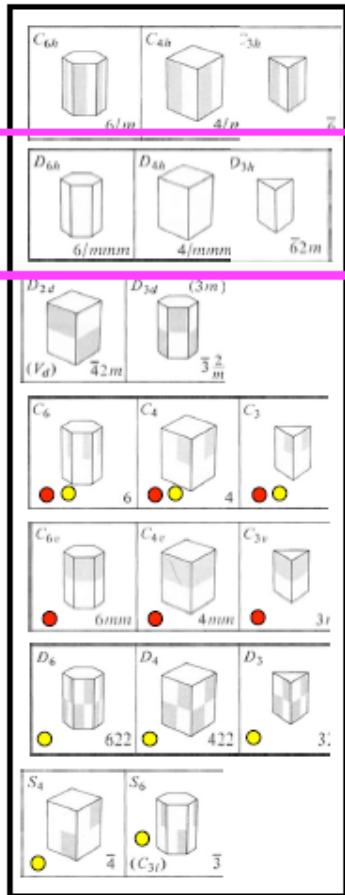
## LEGAND

neither chiral nor polar

● \*, chiral but not polar

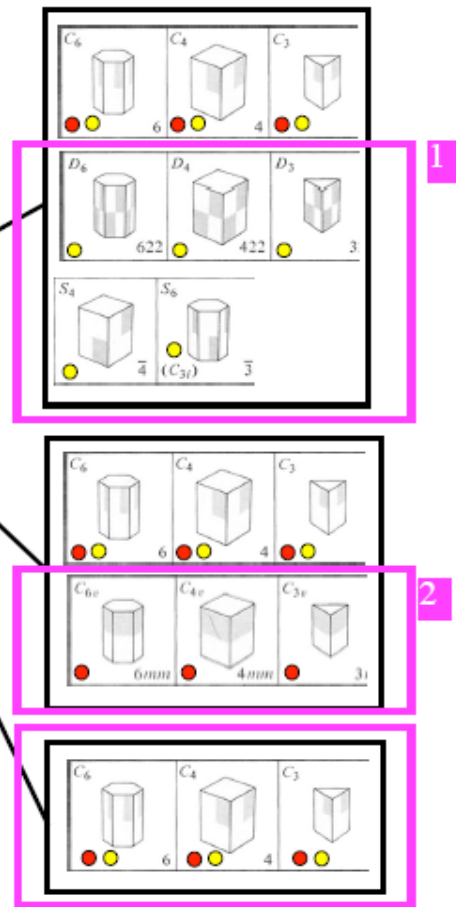
● polar but not chiral

●● both chiral and polar



Identifiable as SMA, but not distinguishable by birefringence or other second order measurement

further distinctions that can be made by additional first order measurement(s)



# Diversity of point symmetries of 1D solids: Smectic B phases

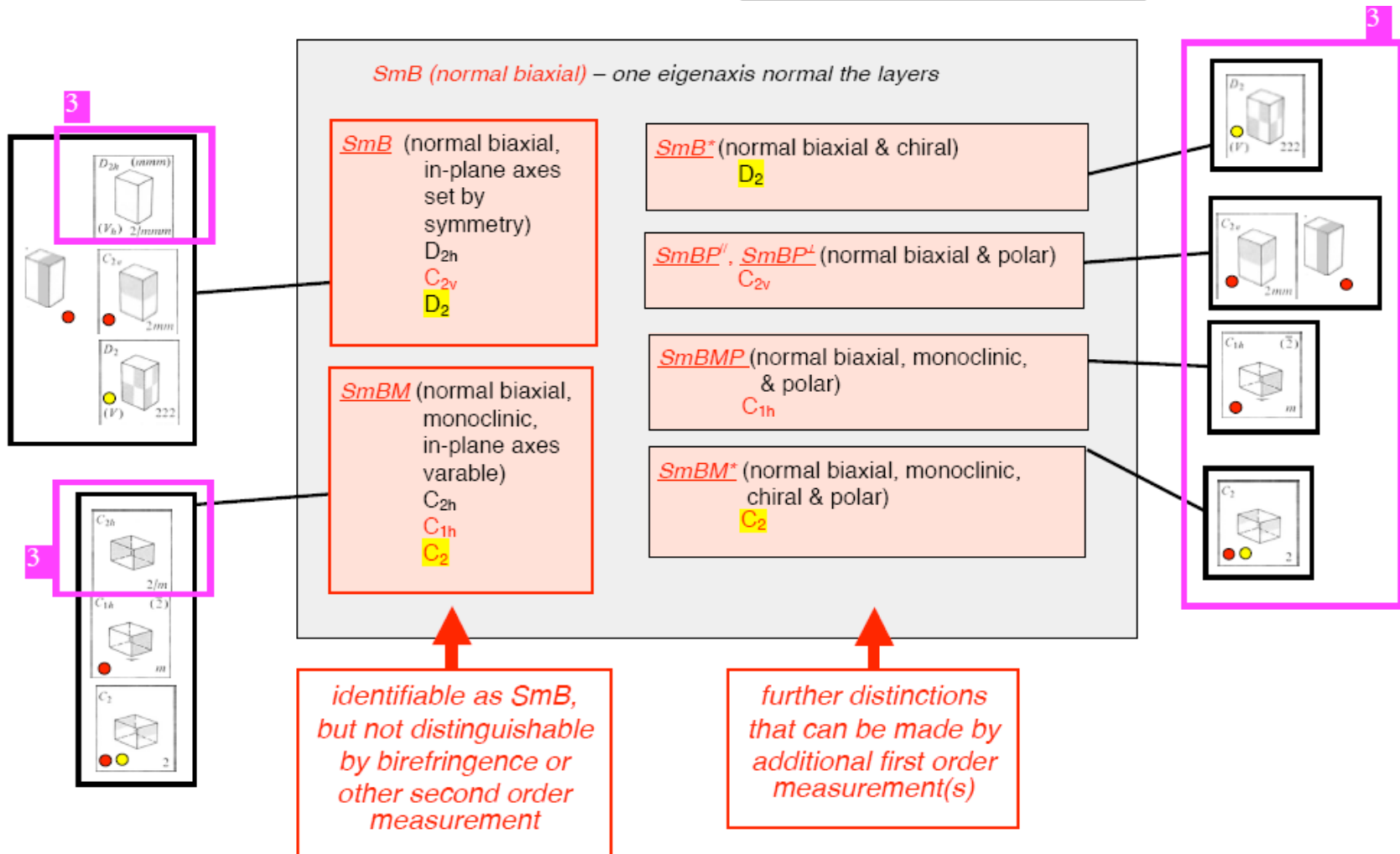
## LEGAND

neither chiral nor polar

○\*, chiral but not polar

● polar but not chiral

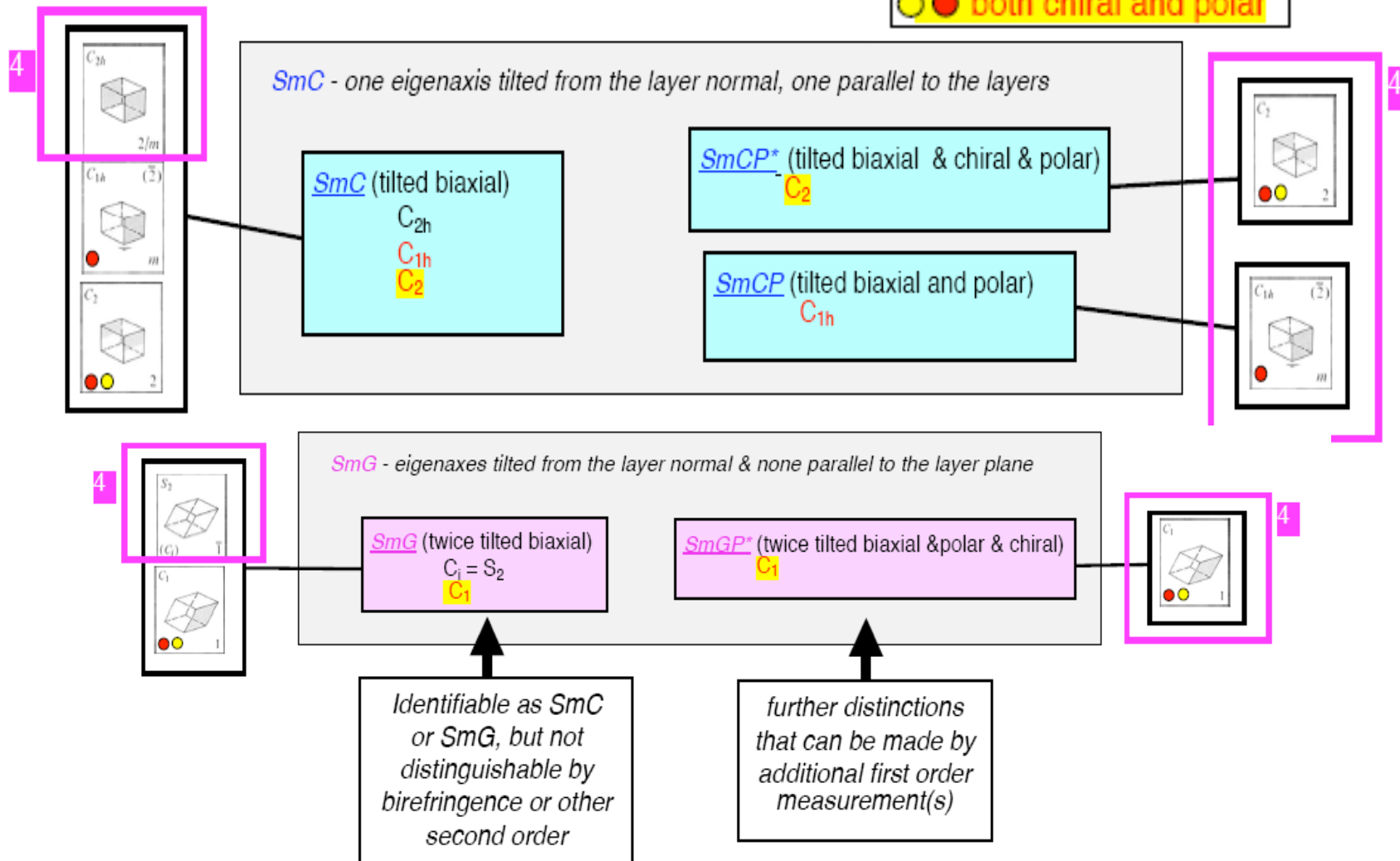
○● both chiral and polar



# Diversity of point symmetries of 1D solids: Smectic C & G phases

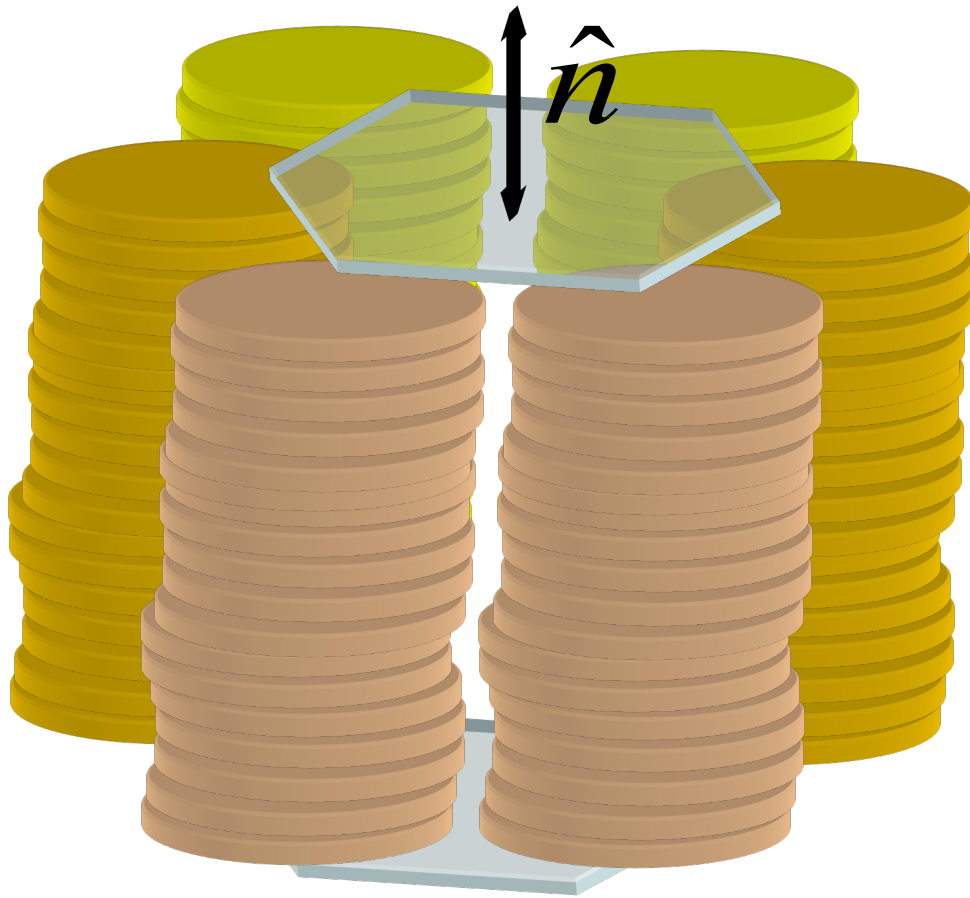
## LEGAND

- neither chiral nor polar
- <sup>\*</sup>, chiral but not polar
- , polar but not chiral
- , both chiral and polar

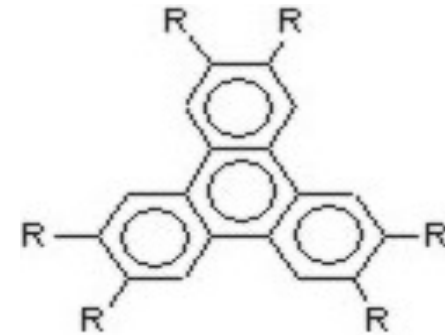
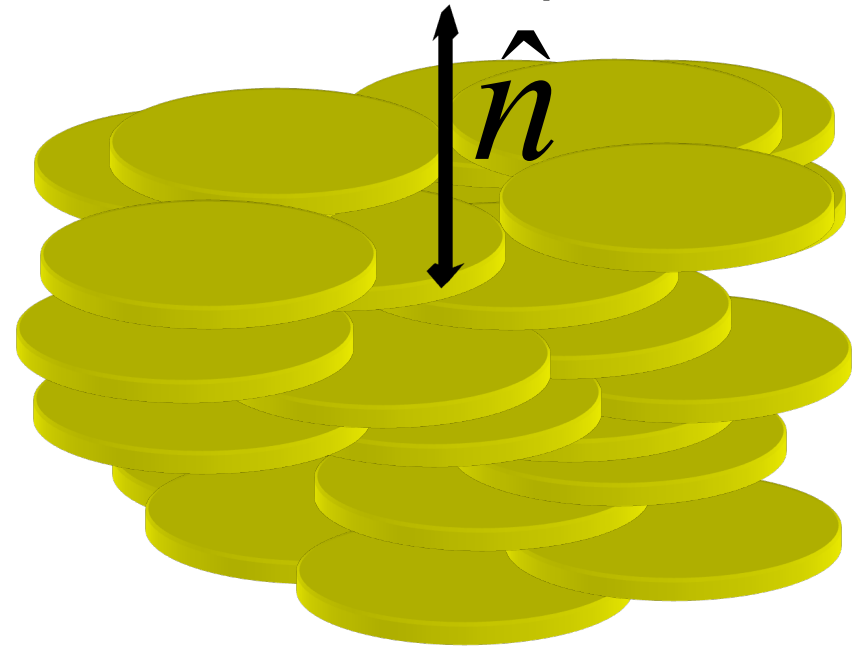


# Discotic LCs as 2D solids

Columnar: columns of molecules  
in hexagonal lattice



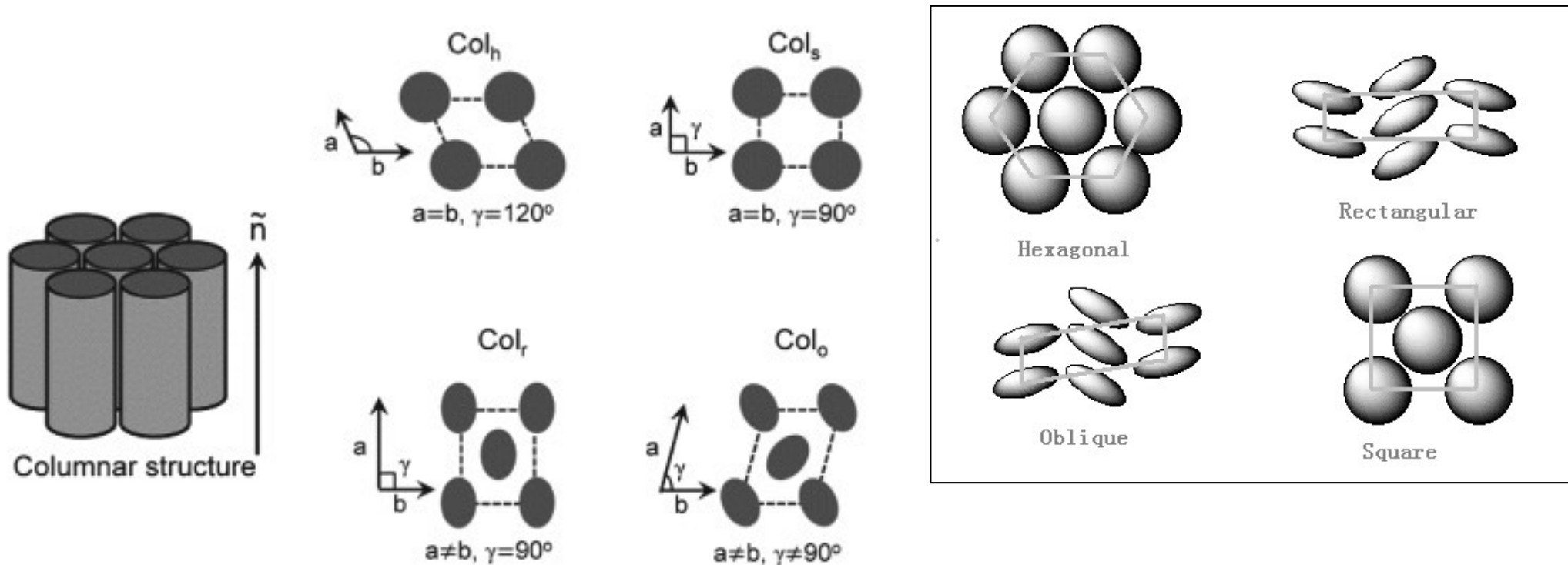
Nematic discotic phase



Typical  
molec  
ule

Columnar liquid crystal molecules are shaped like disks instead of long rods. The columnar mesophase is characterized by stacked columns of molecules. The columns are packed together to form a two-dimensional crystalline array. Existence of long-range orientational and 2D translational order is characteristic for columnar mesophases. The arrangement of the molecules within the columns and the arrangement of the columns themselves leads to new mesophases.

# Diversity of symmetries of columnar LC phases: on a basis of 2D crystal lattice & point symmetry



- 2D long-range crystal order, 1D fluidity;
- Not all point symmetries are compatible with the 2D crystal lattices

# Topological defect mediated phase transitions

- Kosterlitz & Thouless Nobel Prize
- Un-binding of defects by thermal energy
- A different type of phase transition!

