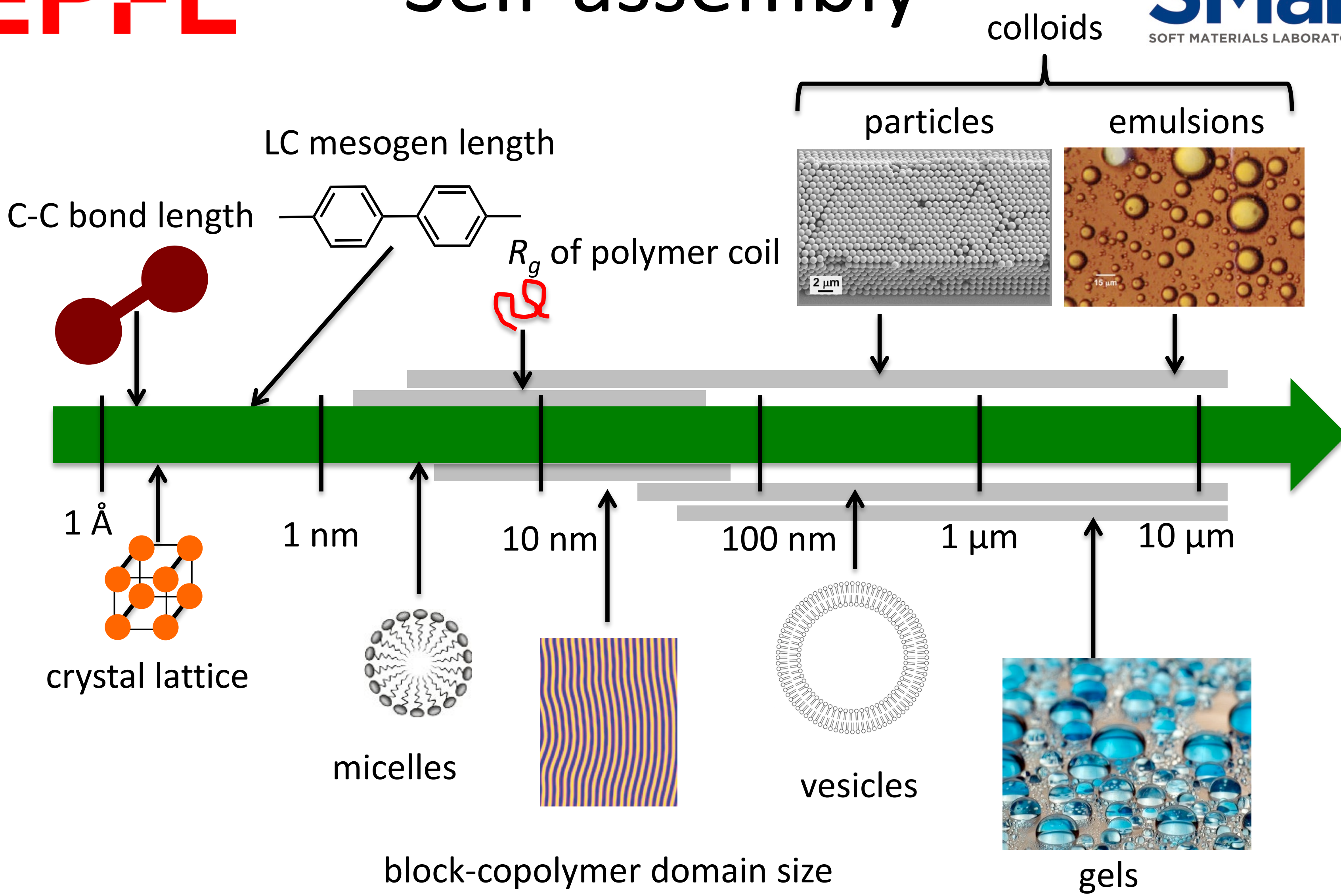
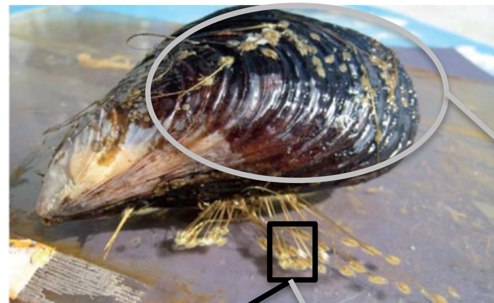
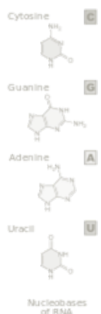
# Self-assembly

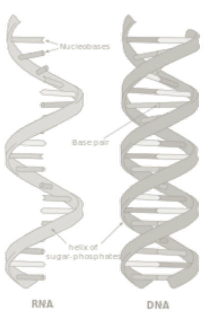


# Course outline



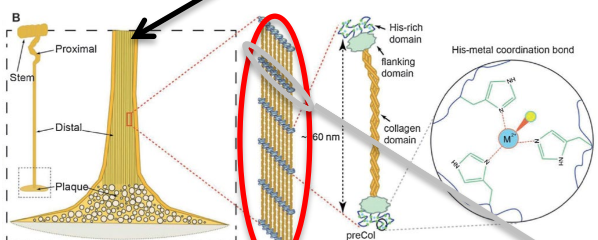
**Introduction**




**Ordered materials**

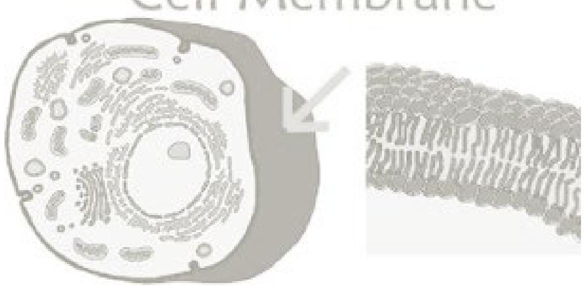
Thermotropic liquid crystals




E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

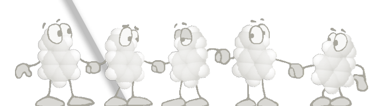
Lyotropic liquid crystals

Cell Membrane



**Disordered materials**

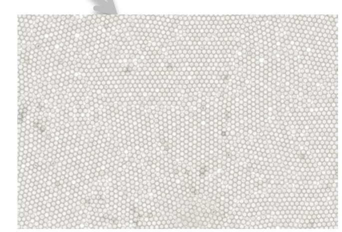
Polymers



Gels

**Colloids**

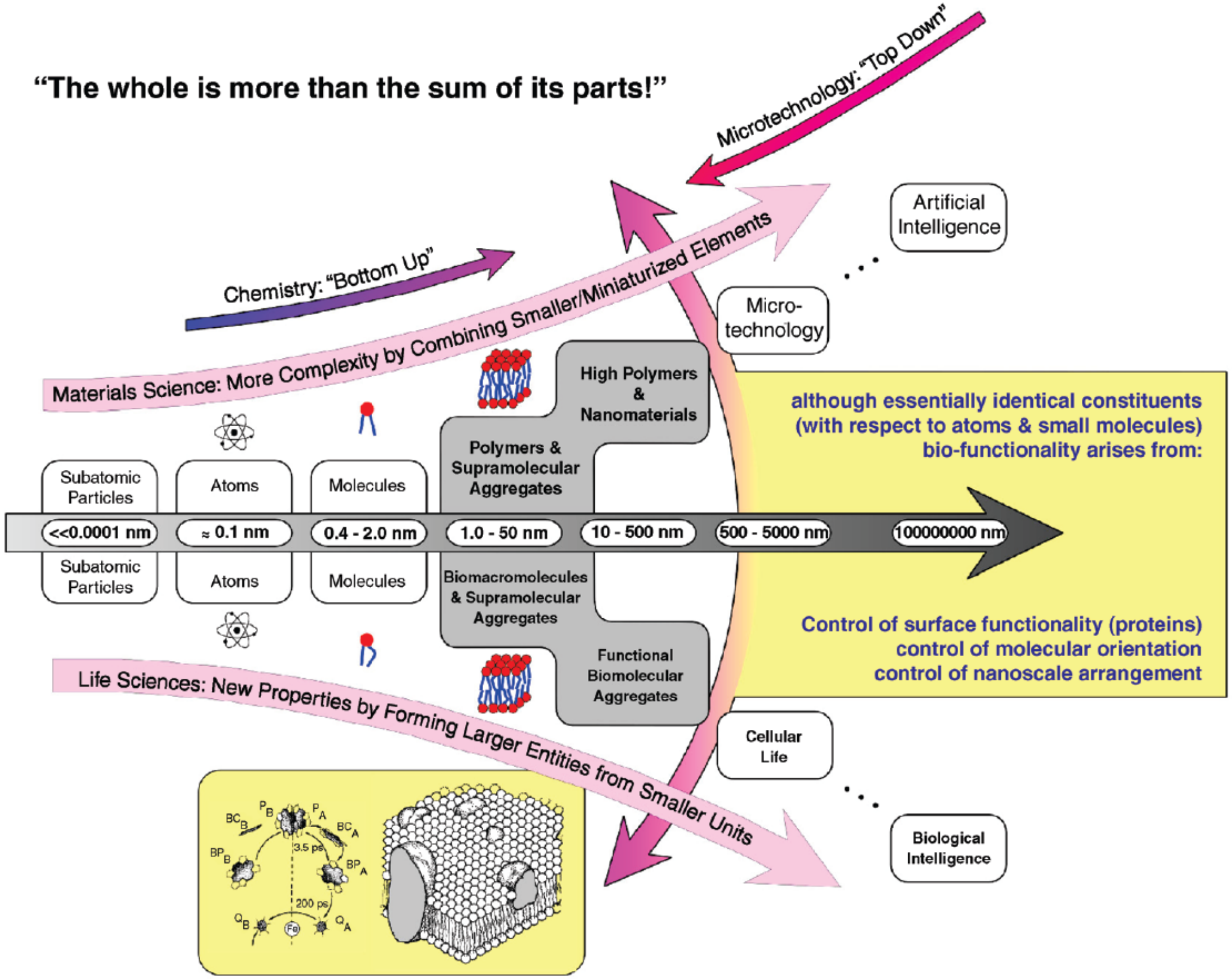
Nanoparticles



Emulsions

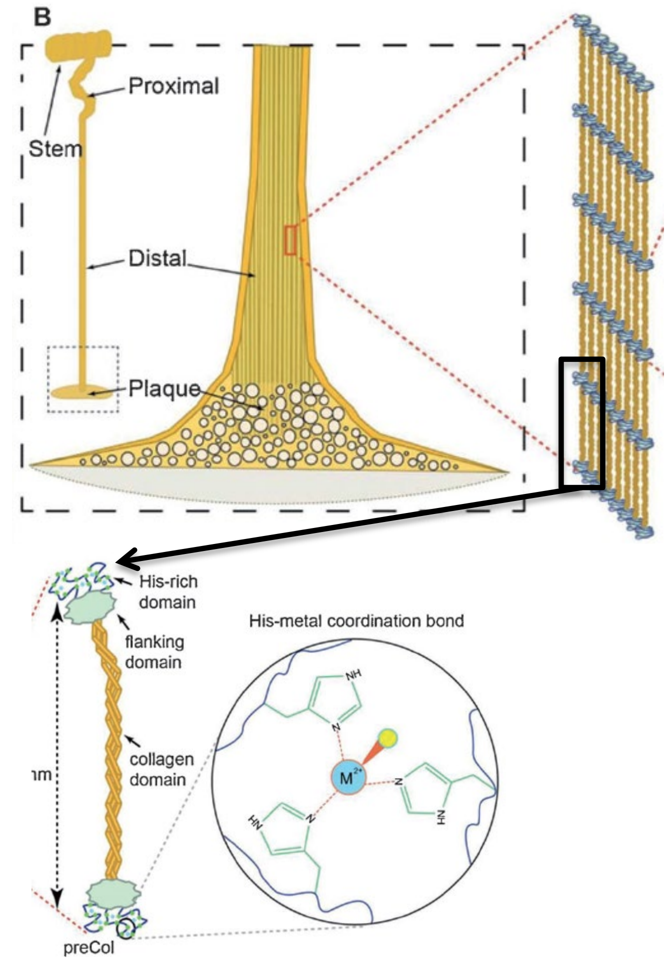
# Self-assembly

Spontaneous arrangement of building blocks into superstructures.




Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials, Second Edition, Edited by Gero Decher and Joseph B. Schlenoff. 2012 Wiley-VCH Verlag GmbH & Co. KGaA. Published 2012 by Wiley-VCH Verlag GmbH & Co. KGaA.

# Self-assembly

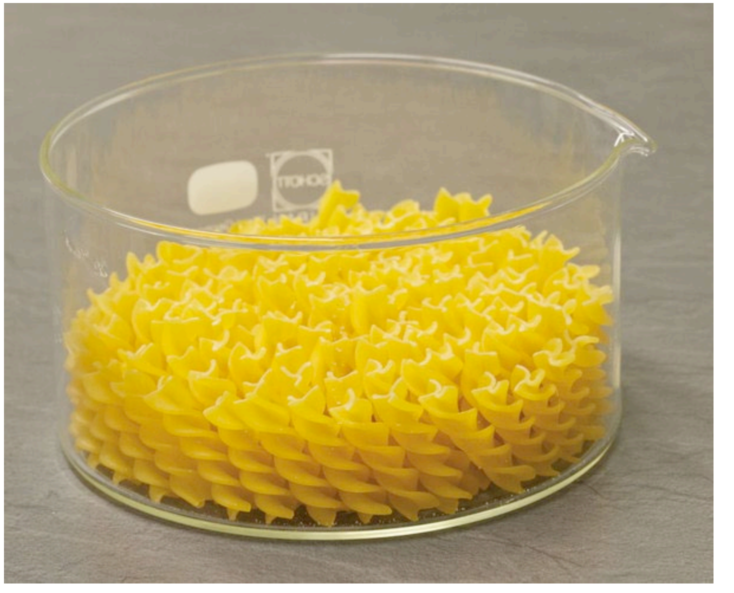




E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

# Self-assembly

**Self-assembly:** Spontaneous molecular ordering resulting from a balance between entropic and intermolecular forces.

Self-assembly occurs in materials with fluid-like or semifluid-like properties



Schaller, V.; Bausch, A. R. *Nature* **2012,** *481* (7381), 268-269.

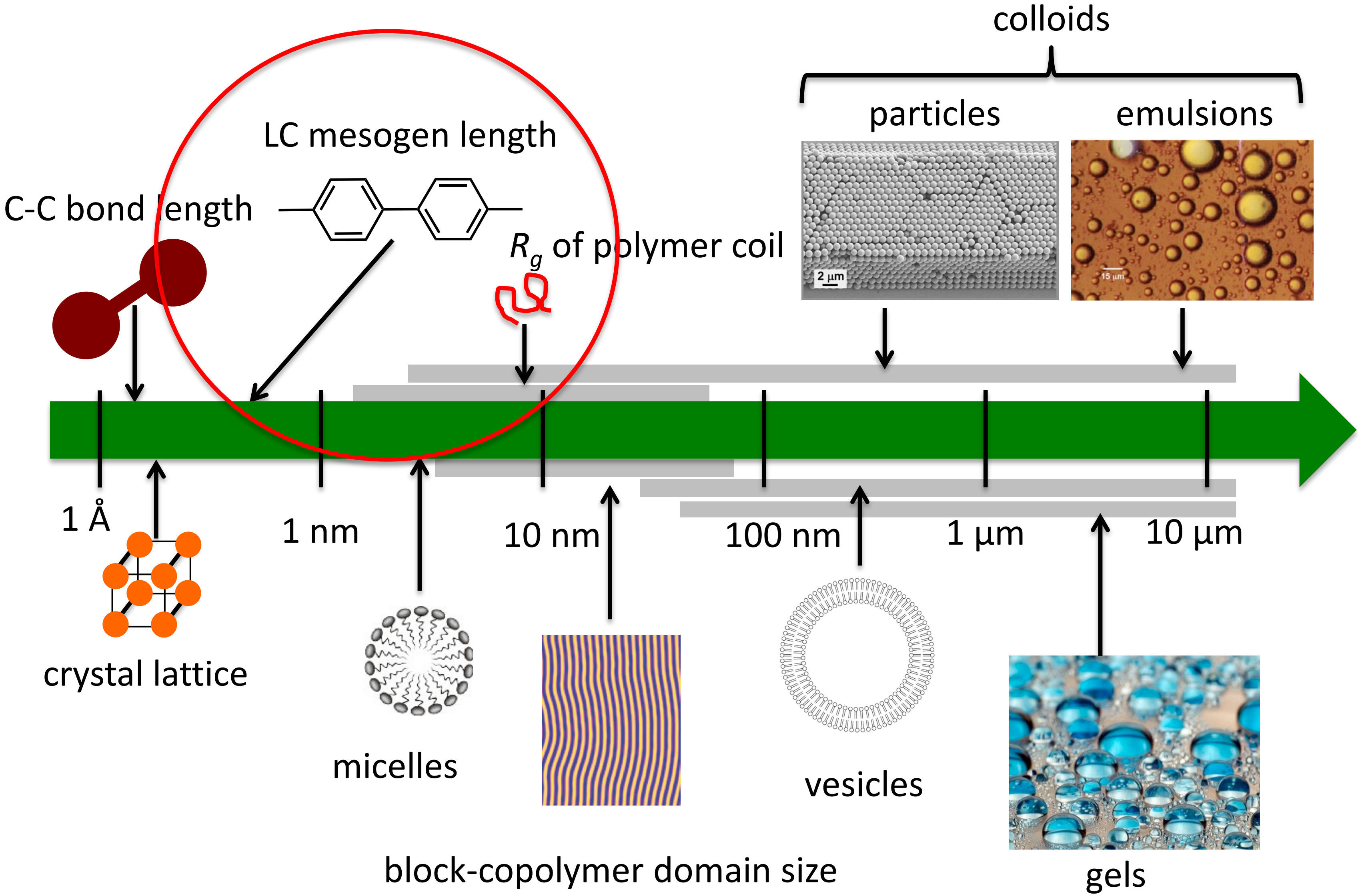
What causes molecules to self-assemble?

Reduction in free energy: $\Delta G = \Delta H - T\Delta S < 0$

The reduction in entropy must be overcompensated by a reduction in enthalpy *e.g.* through an increase in intermolecular forces.

Self-assembly can depend on the environment such as pH, *T*.

# Liquid crystals (LCs)




Reference book: Introduction to liquid crystals, Peter J. Collings and Michael Hird, Taylor and Francis group, 2004

# Liquid crystals

liquid crystal displays

# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

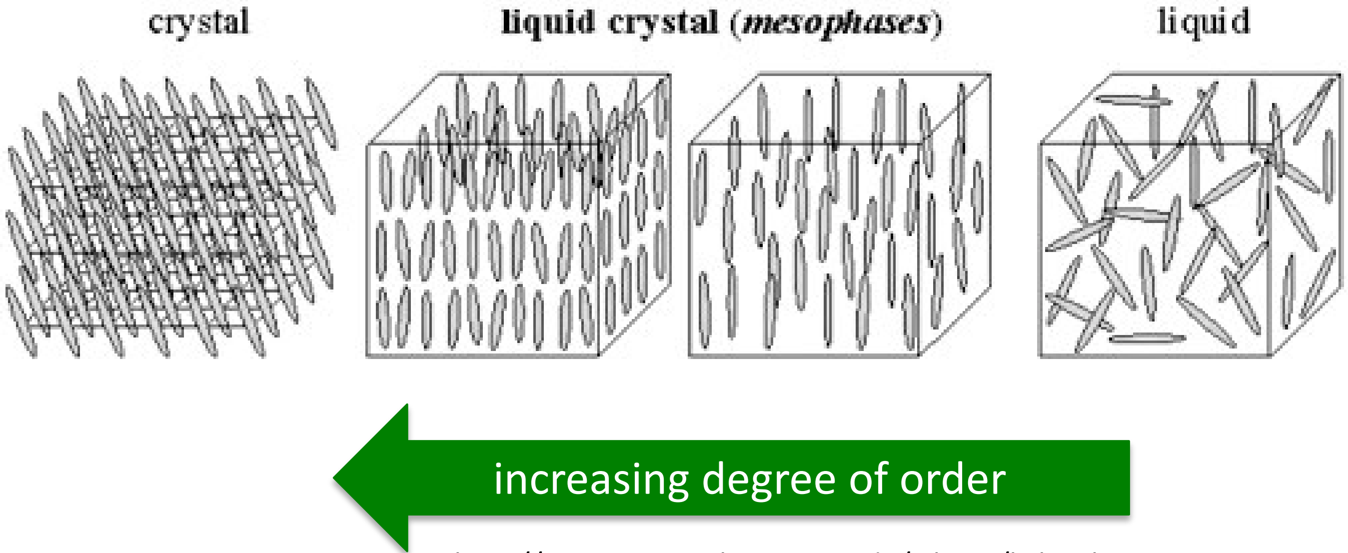
# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

# What are liquid crystals (LCs)?

http://soft-matter.seas.harvard.edu

**Liquid crystals:** A liquid crystal is an ordered fluid phase with some degree of anisotropy.




http://aztec.ms.northwestern.edu/wkung/lc.html

Liquid crystals always have **orientational order**, sometimes they also have positional order.

# Orientational ordering


https://www.bernerzeitung.ch/frequenzrekord-fuer-die-schilthornbahn-339048531103

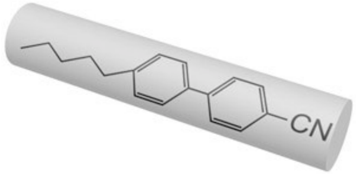
https://de.freepik.com/fotos-kostenlos/rueckansicht-einer-grossen-gruppe-von-musikfans-vor-der-buehne-waehrend-des-musikkonzerts-bei-nacht-kopieren-sie-platz_25567096.htm#query=konzert%20menschenmenge&position=0&from_view=keyword&track=ais

# Mesogens

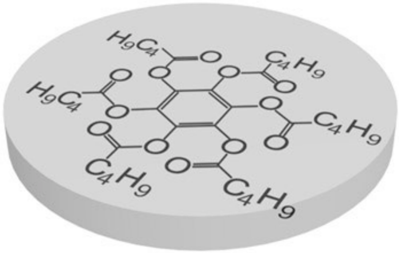
Mesogens are the building blocks of liquid crystals. These are molecules that arrange into liquid crystals.

Mesogens are anisotropic molecules with long range orientational order.

**Calamitic molecules:** Rod-like mesogens made from a rigid core, very often aromatic rings, to which at least one aliphatic chain and very often a terminal group, such as a CN, is attached.

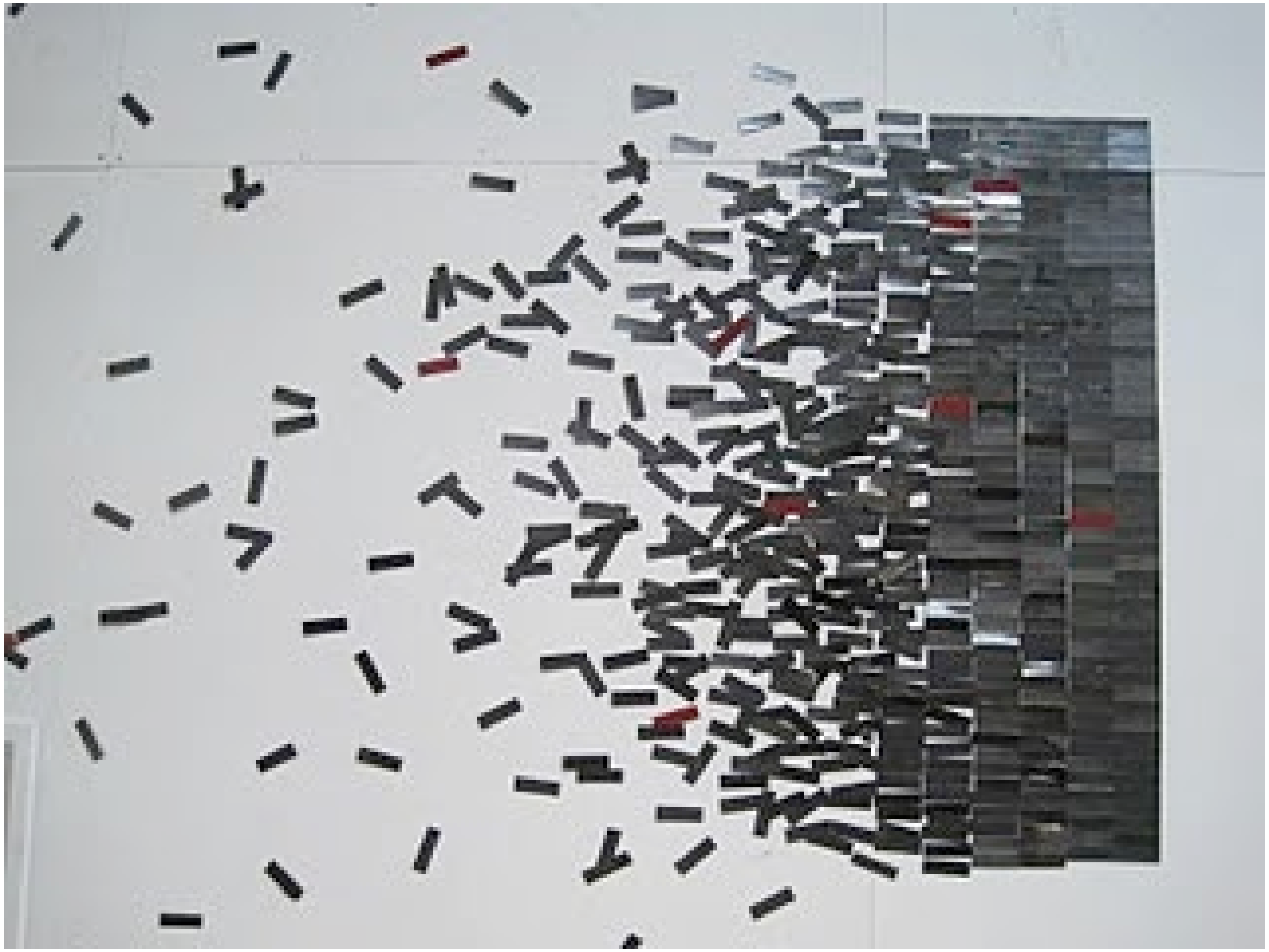



**Discotic molecules:** Disk-like mesogens.




http://www.personal.kent.edu/~bisenyuk/liquidcrystals/maintypes.html

# Order

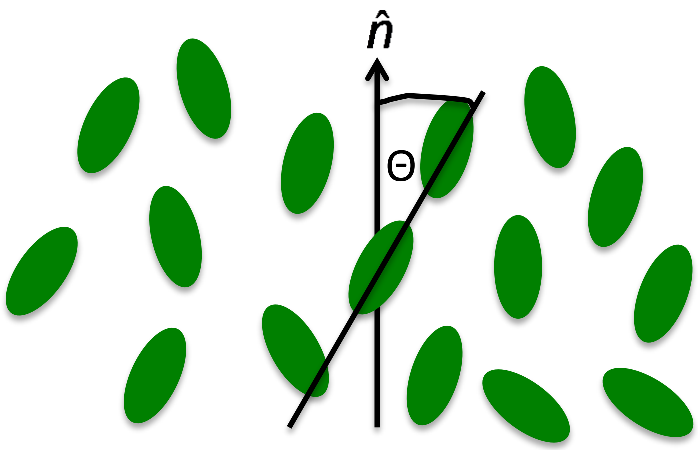


https://www.pinterest.ch/floandstan/chaos-and-order/

# Order parameter

the order parameter:

$$S = \langle P_2(\cos\Theta) \rangle$$




perfectly aligned: S = 1
no orientation: S = 0

The degree of order is small compared to a crystal:
$\Delta H_m$ of a crystal ➔ liquid transition ≈ 250 J/g
$\Delta H_m$ of a liquid crystal ➔ liquid transition ≈ 5 J/g

$\Delta H_m$: latent heat [J/kg]
$P_2(\cos\Theta)$: probability of molecule to be aligned between Θ and Θ+dΘ (2nd Legendre polynom) [-]
$\hat{n}$: director, preferred direction in a volume element [-]

# Why do mesogens spontaneously align?

A. To reduce the entropy of the system
B. To increase the enthalpy of the system
C. Due to intermolecular attraction forces

# Outline: Liquid crystals

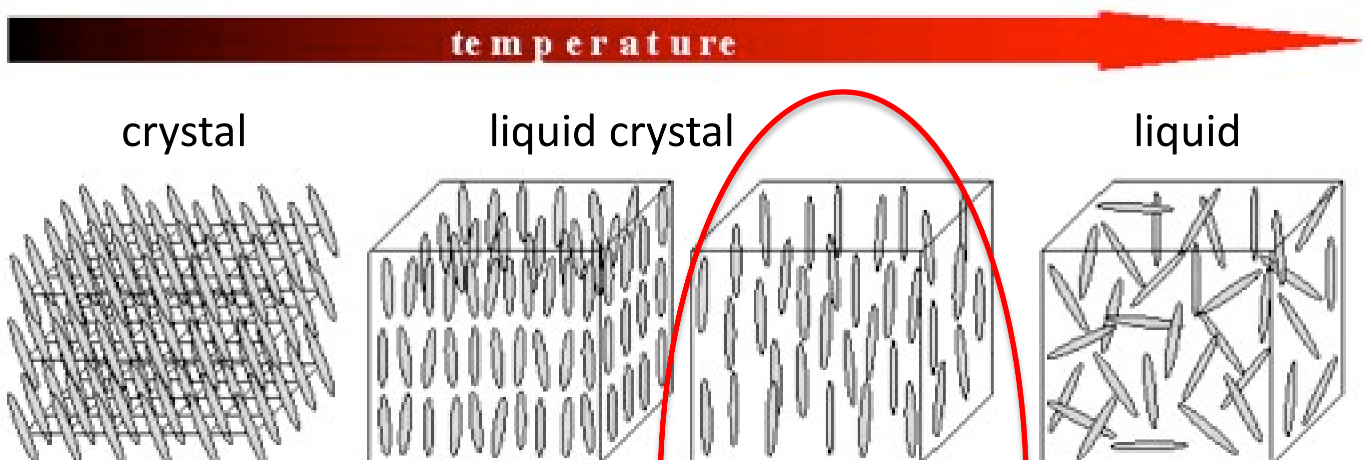
- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

# Thermotropic liquid crystals

**Thermotropic liquid crystals:**

Liquid crystals that are  formed from pure mesogens.

They do not require the presence of solvents.




crystal

- 3D lattice
- orientation
- solid

➔ anisotropic

smectic

- 1 or 2 D lattice
- orientation
- fluid

➔ anisotropic

nematic

- no lattice
- orientation
- fluid

➔ anisotropic

liquid

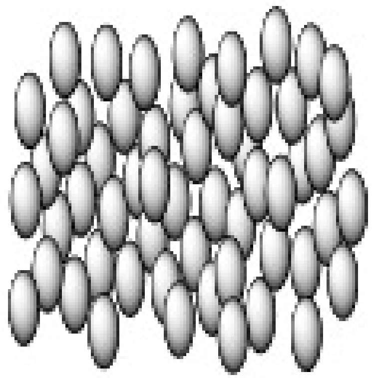
- no lattice
- no orientation
- fluid

➔ isotropic

http://www-g.eng.cam.ac.uk/CMMPE/lcintro1.html

# Nematic liquid crystal displays


https://www.pngegg.com/en/png-yebwp

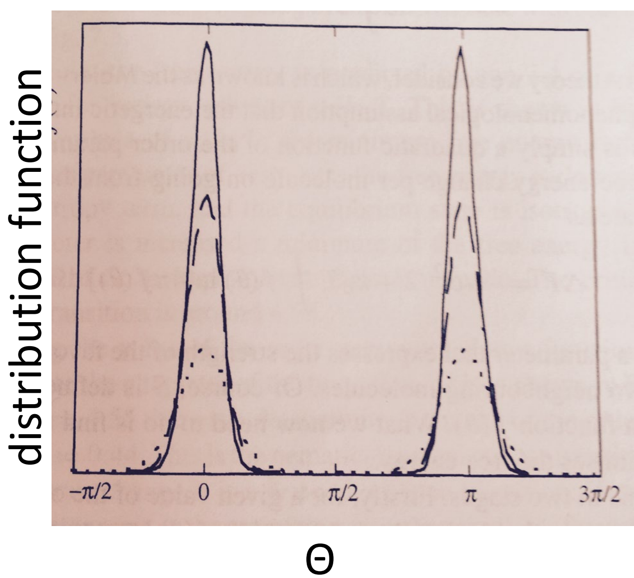


# Nematic phase

$$S = \langle P_2(\cos\Theta)\rangle = \left\langle \frac{3\cos^2\Theta - 1}{2} \right\rangle$$

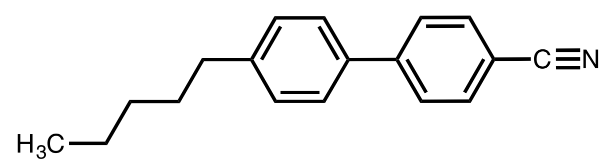
*S*: Order parameter [-]
Θ: Angle between LC molecular axis and the director. [rad]

- Can be formed from calamitic or discotic mesogens.
- Molecules have some long range orientational order.
- Molecules have no long range positional order.




Jones, R. A. L. *Soft Condensed Matter*; Oxford University Press: Oxford, 2002.

The first room temperature nematic material was developed in 1972.




5 CB: (4-cyano-4-n-pentylbiphenyl)

This LC is found in most liquid crystal displays (LCDs).

# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

# Nematic range

Nematic range: The temperature range over which the nematic phase exists.

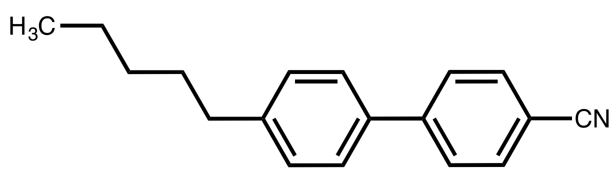
$T_{N\text{-}I}$: Upper temperature limit where the nematic phase transitions into an isotropic phase.

If $T_{N\text{-}I}$ is above $T_m$: Molecules are **enantiotropic.** These molecules exhibit liquid crystalline states if heated above $T_m$ or cooled below $T_{N\text{-}I}$.

If $T_{N\text{-}I}$ is below $T_m$: Molecules are **monotropic.** These molecules exhibit only liquid crystalline state during either cooling or heating but not both.

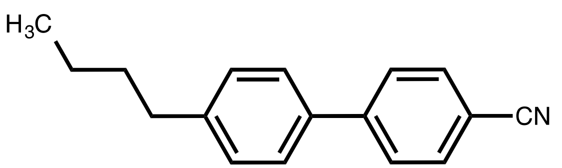
*Examples:*

enantiotropic




$T_m$: 24 °C
$T_{N\text{-}I}$: 35 °C
➔ nematic range 11°C

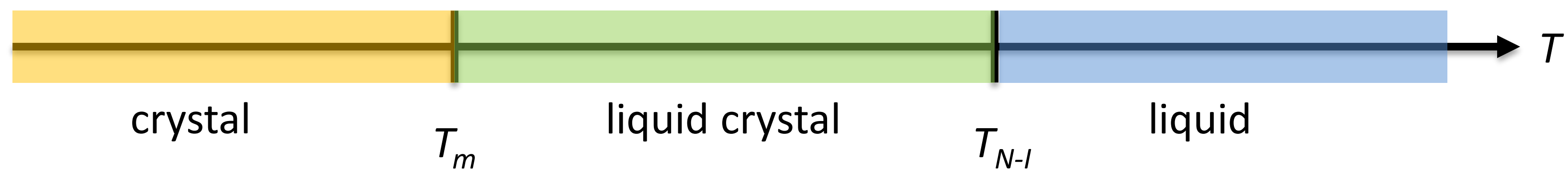
monotropic



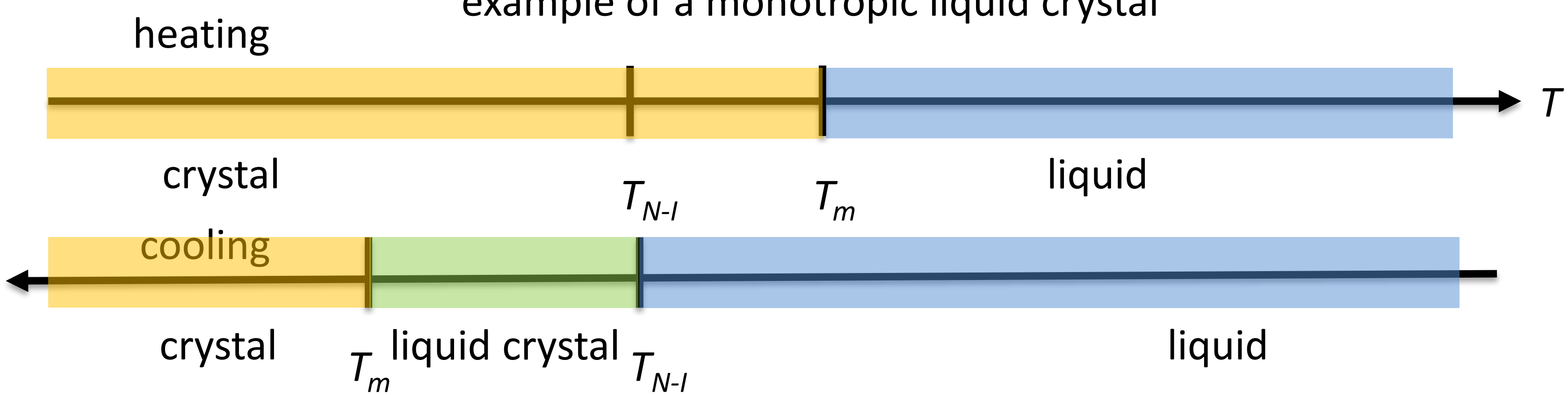

$T_m$: 48 °C
$T_{N\text{-}I}$: 16.5 °C

# Nematic range

enantiotropic liquid crystals

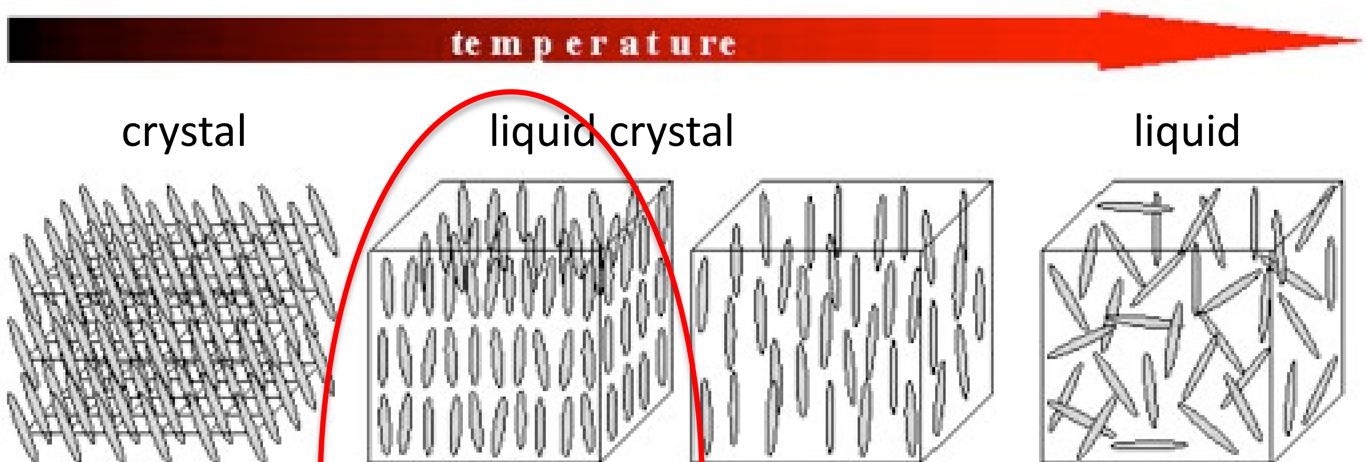



example of a monotropic liquid crystal



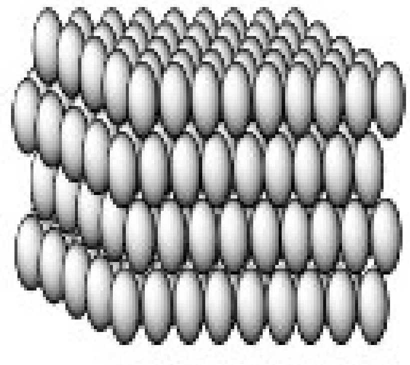
# Thermotropic liquid crystals

**Thermotropic liquid crystals:**
They are formed from pure mesogens. They do not require the presence of solvents.




| | | | |
|---|---|---|---|
| | smectic | nematic | |
| • 3D lattice | • 1 or 2 D lattice | • no lattice | • no lattice |
| • orientation | • orientation | • orientation | • no orientation |
| • solid | • fluid | • fluid | • fluid |
| ➔ anisotropic | ➔ anisotropic | ➔ anisotropic | ➔ isotropic |

http://www-g.eng.cam.ac.uk/CMMPE/lcintro1.html



# Smectic phase

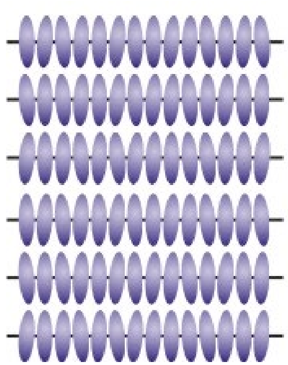
Smectic crystals have a layered structure.

- A smectic liquid crystal is a liquid in two direction (in plane), but behaves elastic in z-direction.
- The smectic phase forms at lower temperatures than the nematic phase.

$$S = \left(\cos\frac{2\Pi z}{d}\right)\left(\frac{3\cos^2\Theta - 1}{2}\right)$$

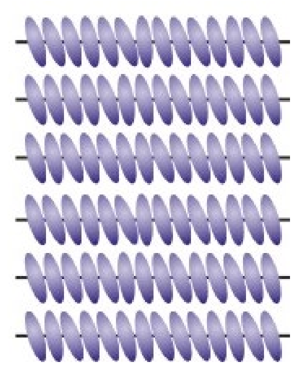
*z*: position of the molecule [m]
*d*: layer spacing [m]
Θ: angle between LC molecular axis and the director [rad]

**Smectic A phase (SmA):**
The molecules are aligned parallel to layer normal.



*z*-direction

**Smectic C phase (SmC):**
The molecules are tilted relative to layer normal.

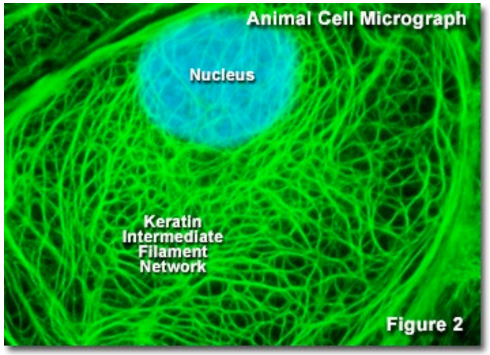


Above a characteristic temperature, the SmC phase transitions into the SmA phase.

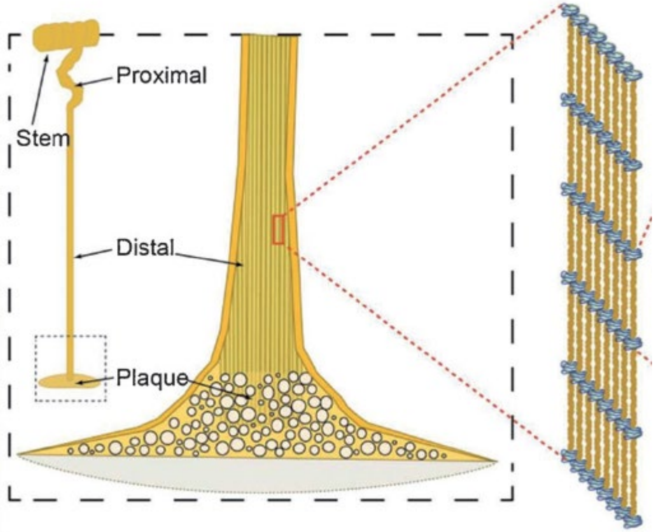
# Smectic LCs in nature

mussel byssus

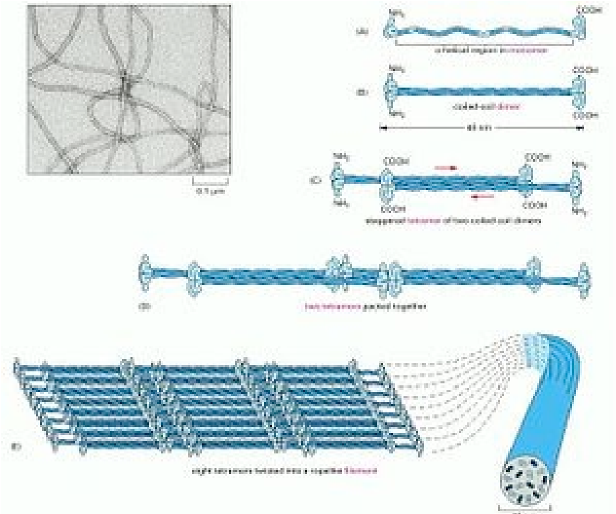
intermediate filaments




https://micro.magnet.fsu.edu/cells/intermediatefilaments/intermediatefilaments.html




E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

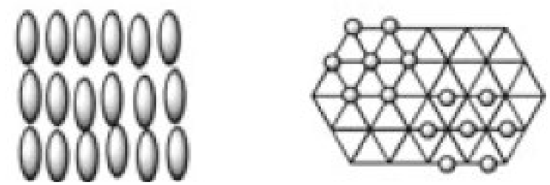


http://www.wikilectures.eu/index.php/Individual_filament_structure_and_function

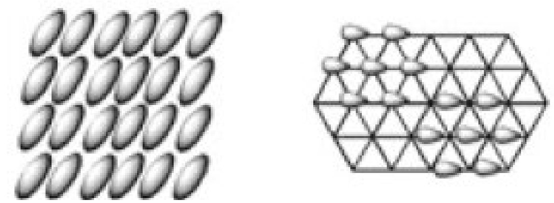
# Soft crystals

Smectic phases with higher degree of order contain layers that are weakly attached to each other.

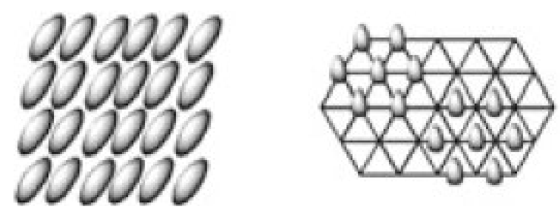
**Smectic B (SmB) phase:**
Resembles the SmA phase but has a long-range hexagonal bond-orientational ordering.



**Smectic I (SmI) phase:**
Tilted version of the SmB phase, where the hexagonal lattice is tilted towards the apex.

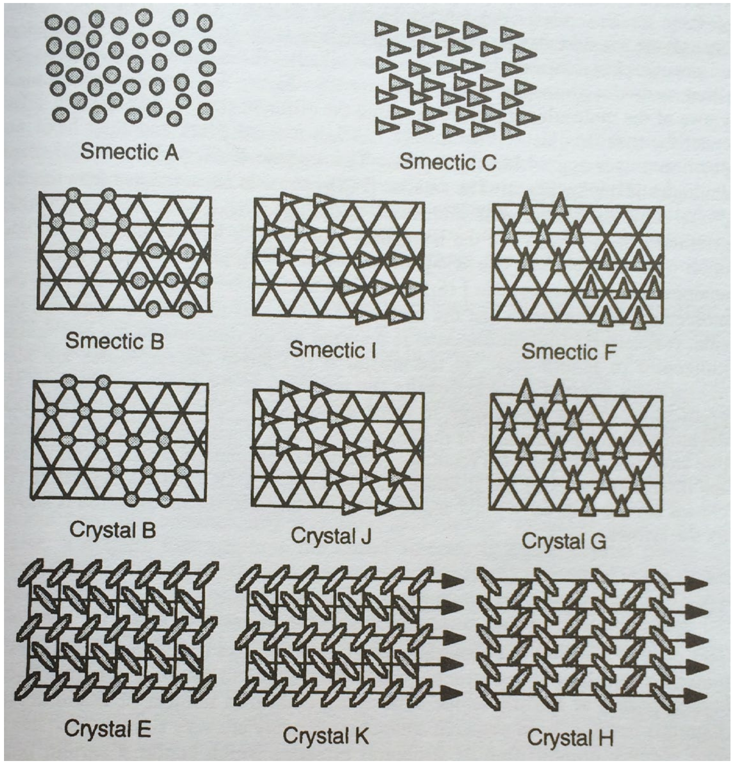


**Smectic F (SmF) phase:**
Tilted version of SmB phase, where the hexagonal lattice is tilted towards the side.



**Crystal B phase:** Molecules are hexagonally ordered like in the SmB phase but over a longer range and in 3D.
**Crystal E phase:** Develops from contracting the hexagonal lattice and resolves in a herringbone-like structure.

# Overview of smectic phases

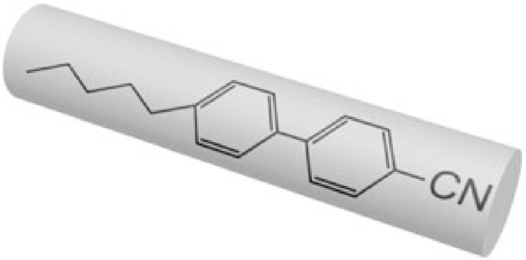



| non-tilted phases | tilted phases | in plane order | molecular rotation |
|---|---|---|---|
| smectic A | smectic C | none | unhindered |
| hexatic B | hexatic F, I | bond order | unhindered |
| crystal B | crystal G, J | positional | unhindered |
| crystal E | crystal H, K | positional | hindered |

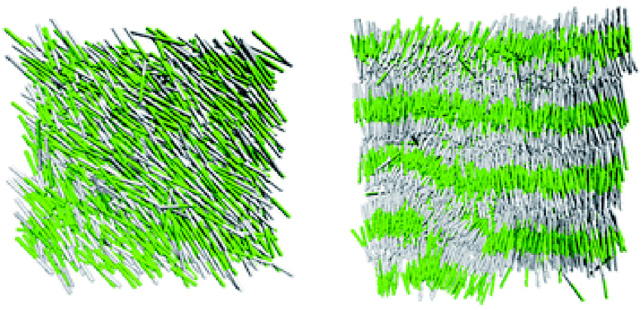


Collings, P. J.; Hird, M. *Introduction to liquid crystals*; Taylor & Francis Ltd.: London, 2004.

# Which molecules can form a smectic phase?




http://www.personal.kent.edu/~bisenyuk/liquidcrystals/maintypes.html



Within a homologous series:
The nematic phase is stable if the alkyl chain is short.
The smectic phase is stable if the alkyl chain is long.

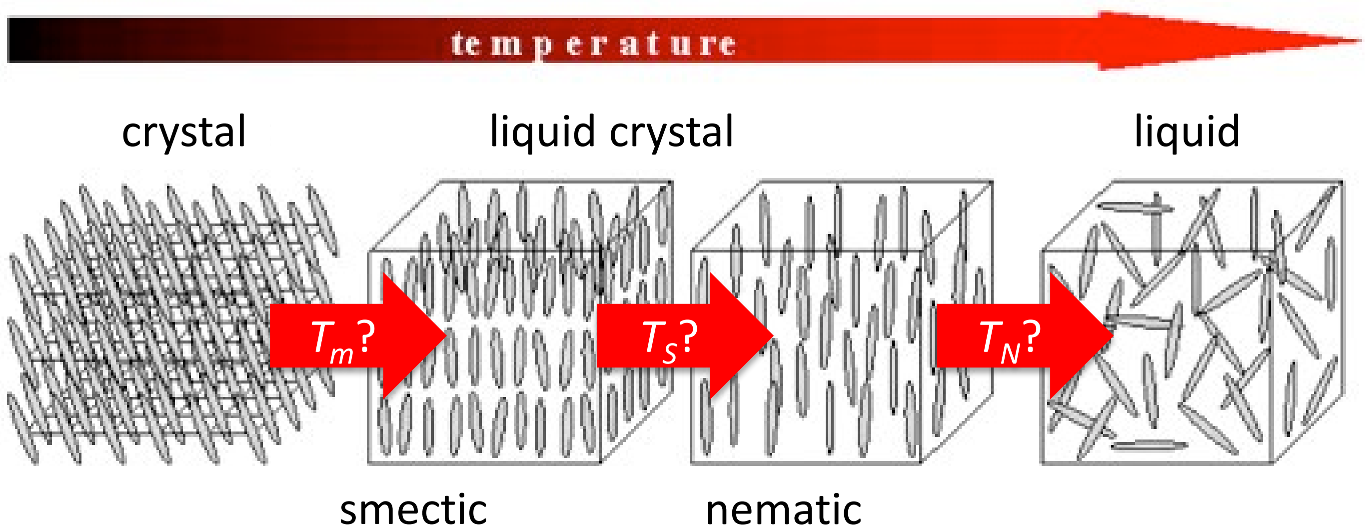
# Which phase is more viscous?

A. smectic
B. nematic

# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

# Influence of mesogen structure on transition temperature

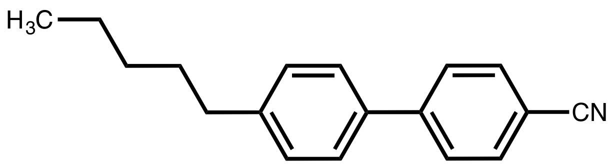



| crystal | smectic | nematic | liquid |
|---|---|---|---|
| • 3D lattice | • 1 or 2 D lattice | • no lattice | • no lattice |
| • orientation | • orientation | • orientation | • no orientation |
| • solid | • fluid | • fluid | • fluid |
| → anisotropic | → anisotropic | → anisotropic | → isotropic |

http://www-g.eng.cam.ac.uk/CMMPE/lcintro1.html

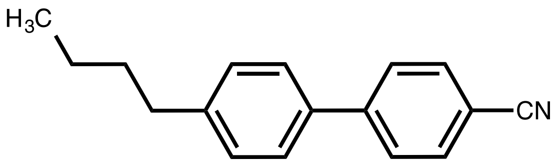
# Influence of mesogen structure on transition temperature

mesogen with 5 C atoms
in aliphatic chain:




$T_m$: 24 °C
$T_{N\text{-}I}$: 35 °C

mesogen with 4 C atoms
in aliphatic chain:




$T_m$: 48 °C
$T_{N\text{-}I}$: 16.5 °C

# Why is $T_m$ of molecule (1) much lower than that of molecule (2)?

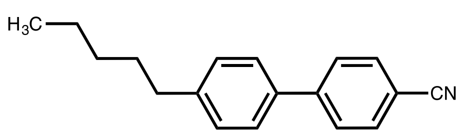
A. molecule (1) forms weaker H-bonds

B. molecule (1) is more difficult to pack into a crystalline structure

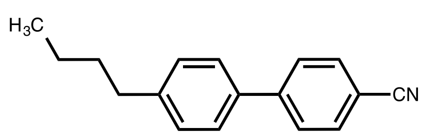
C. molecule (1) forms weaker VdW interactions

D. molecule (1) has a higher mobility

molecule 1




molecule 2



# Why is $T_{N\text{-}I}$ of molecule (1) much higher than that of molecule (2)?

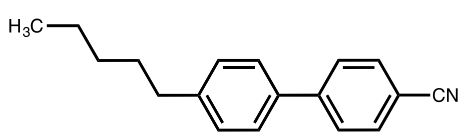
A. molecule (1) forms stronger H-bonding

B. molecule (1) is easier to pack into a crystalline structure

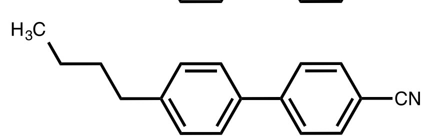
C. molecule (1) forms stronger VdW interactions

D. molecule (1) has a higher mobility

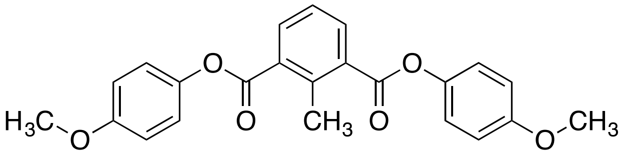
molecule 1



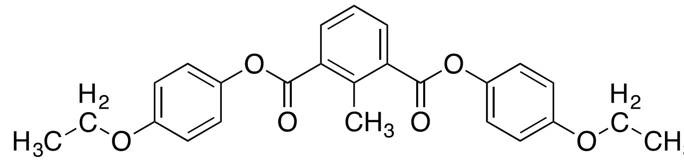

molecule 2



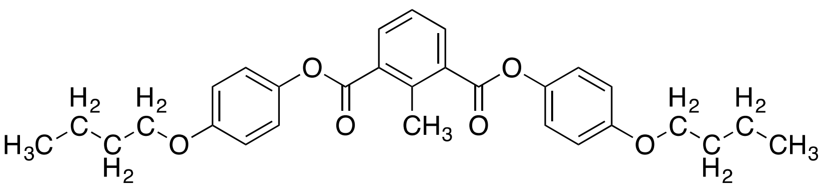
# Influence of aliphatic chain



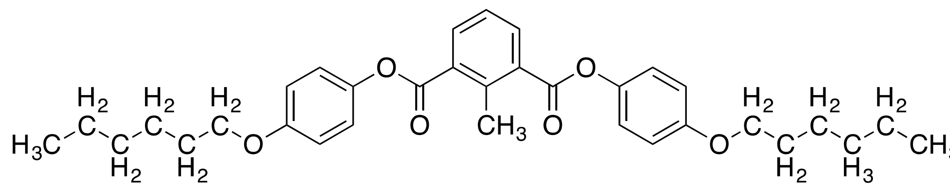
$T_m$ = 134 °C (if heated)
$T_m$ = 38 °C (if cooled)
$T_{N\text{-}I}$ = 85°C



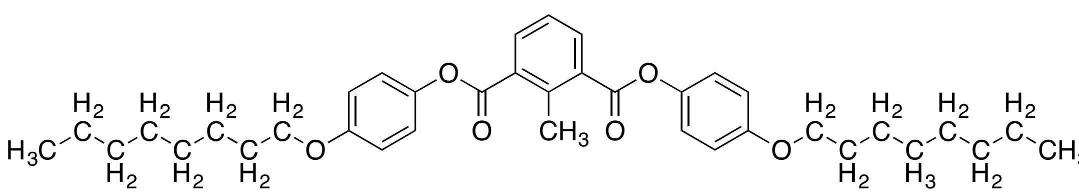
$T_m$ = 120 °C (if heated)
$T_m$ = 38 °C (if cooled)
$T_{N\text{-}I}$ = 103°C



$T_m$ = 100 °C (if heated)
$T_m$ = 44 °C (if cooled)
$T_{N\text{-}I}$ = 83°C



$T_m$ = 80 °C (if heated)
$T_m$ = 59 °C (if cooled)
$T_{N\text{-}I}$ = 71°C

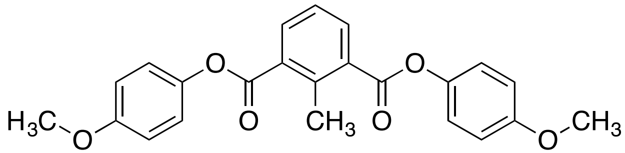


$T_m$ = 74 °C (if heated)
$T_m$ = 55 °C (if cooled)
$T_{N\text{-}I}$ = 72°C

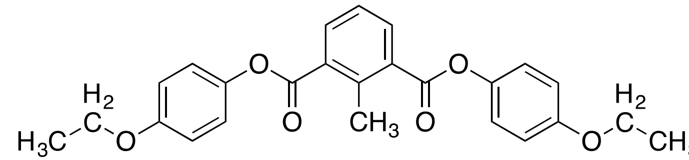


W. Weissflog, *et al.*, *Soft Matter*, 2012, **8**, 2671-2685

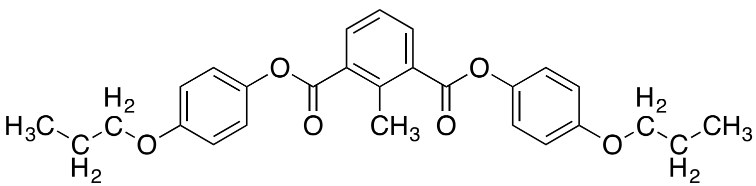
# Influence of aliphatic chain



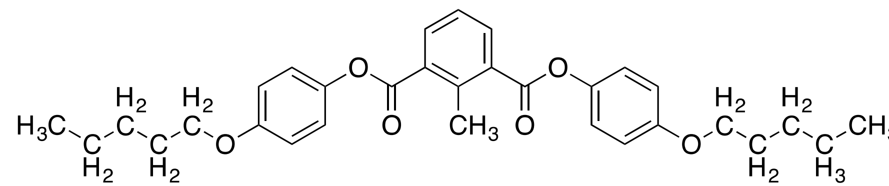
$T_m$ = 134 °C (if heated)
$T_m$ = 38 °C (if cooled)
$T_{N\text{-}I}$ = 85°C



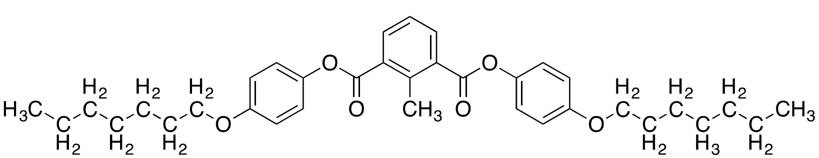
$T_m$ = 120 °C (if heated)
$T_m$ = 38 °C (if cooled)
$T_{N\text{-}I}$ = 103°C



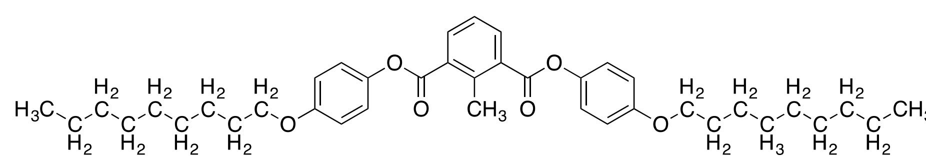
$T_m$ = 132 °C (if heated)
$T_m$ = 45 °C (if cooled)
$T_{N\text{-}I}$ = 68°C



$T_m$ = 82 °C (if heated)
$T_m$ = 54 °C (if cooled)
$T_{N\text{-}I}$ = 67°C



$T_m$ = 83 °C (if heated)
$T_m$ = 49 °C (if cooled)
$T_{N\text{-}I}$ = 66°C



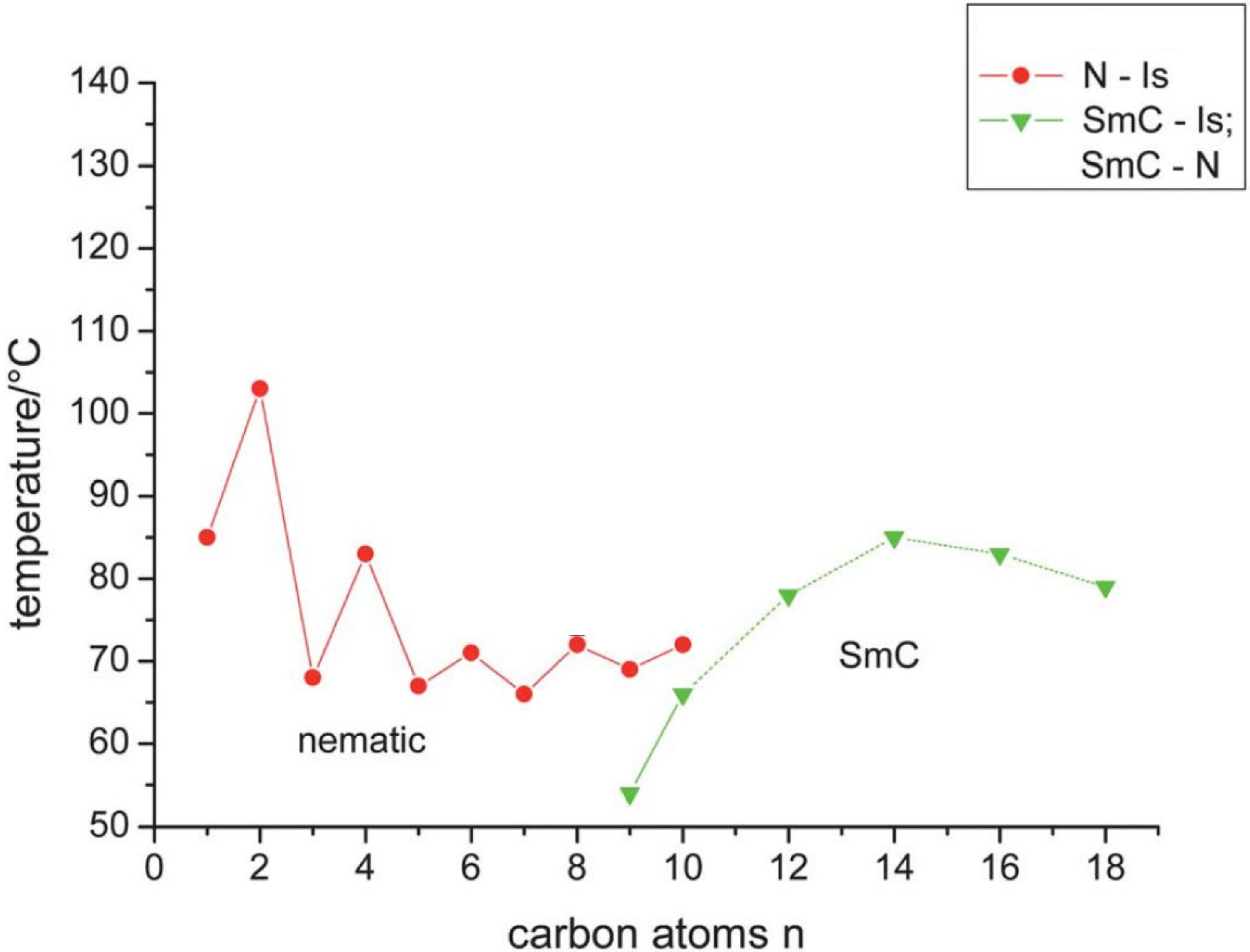
$T_m$ = 81 °C (if heated)
$T_m$ = 73 °C (if cooled)
$T_{N\text{-}I}$ = 69°C

W. Weissflog, *et al.*, *Soft Matter*, 2012, **8**, 2671-2685

# Why does the melting temperature in general decrease for mesogens with increasing length of their aliphatic chain?

A. They form stronger H-bonds.
B. They are more difficult to be packed into a crystal structure because they are already aligned in a smectic phase.
C. They are more rigid and thus more difficult to be packed into a crystal structure.
D. The aliphatic chains are flexible and hence, for steric reasons, make it more difficult to pack mesogens into a crystal structure.
E. They have a higher entropy.

# Influence of aliphatic chain $CH_3(CH_2)_n$



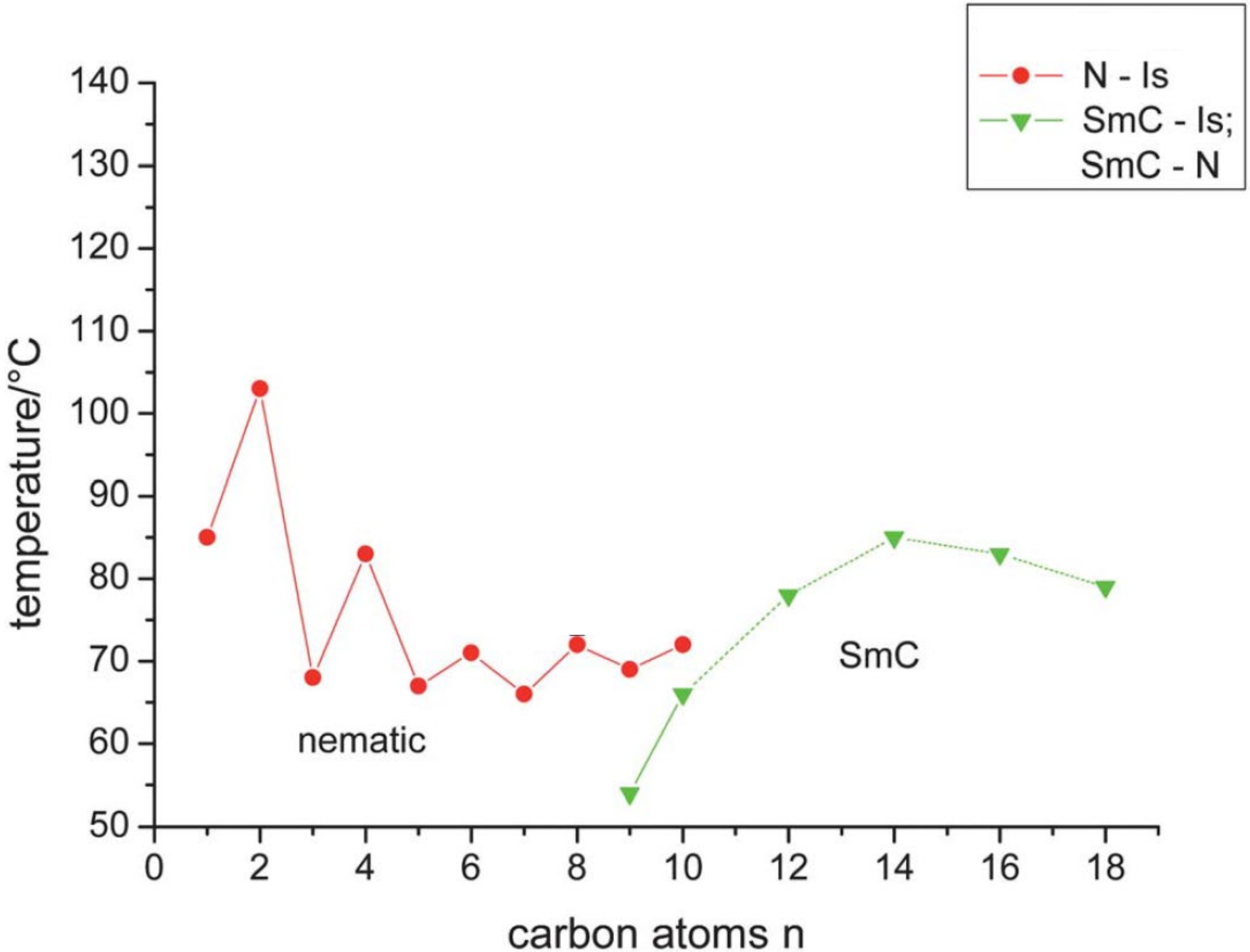



W. Weissflog, *et al.*, *Soft Matter*, 2012, **8**, 2671-2685

# Why does $T_{N\text{-}I}$ in general decrease with increasing aliphatic chain length?

A. They form stronger H-bonds.
B. The intermolecular distances increase such that the VdW forces decrease.
C. They are more difficult to be packed into a crystal structure.
D. They have a higher entropy.

# Influence of aliphatic chain $CH_3(CH_2)_n$




W. Weissflog, *et al.*, *Soft Matter*, 2012, **8**, 2671-2685

# Why does $T_{N-I}$ have a zig-zag shape for mesogens with up to 5 C atoms?

A. Mesogens with an even number of $CH_2$ groups contained in the aliphatic chain have a higher entropy.

B. Mesogens with even number of of $CH_2$ groups contained in the aliphatic chain form weaker intermolecular forces.

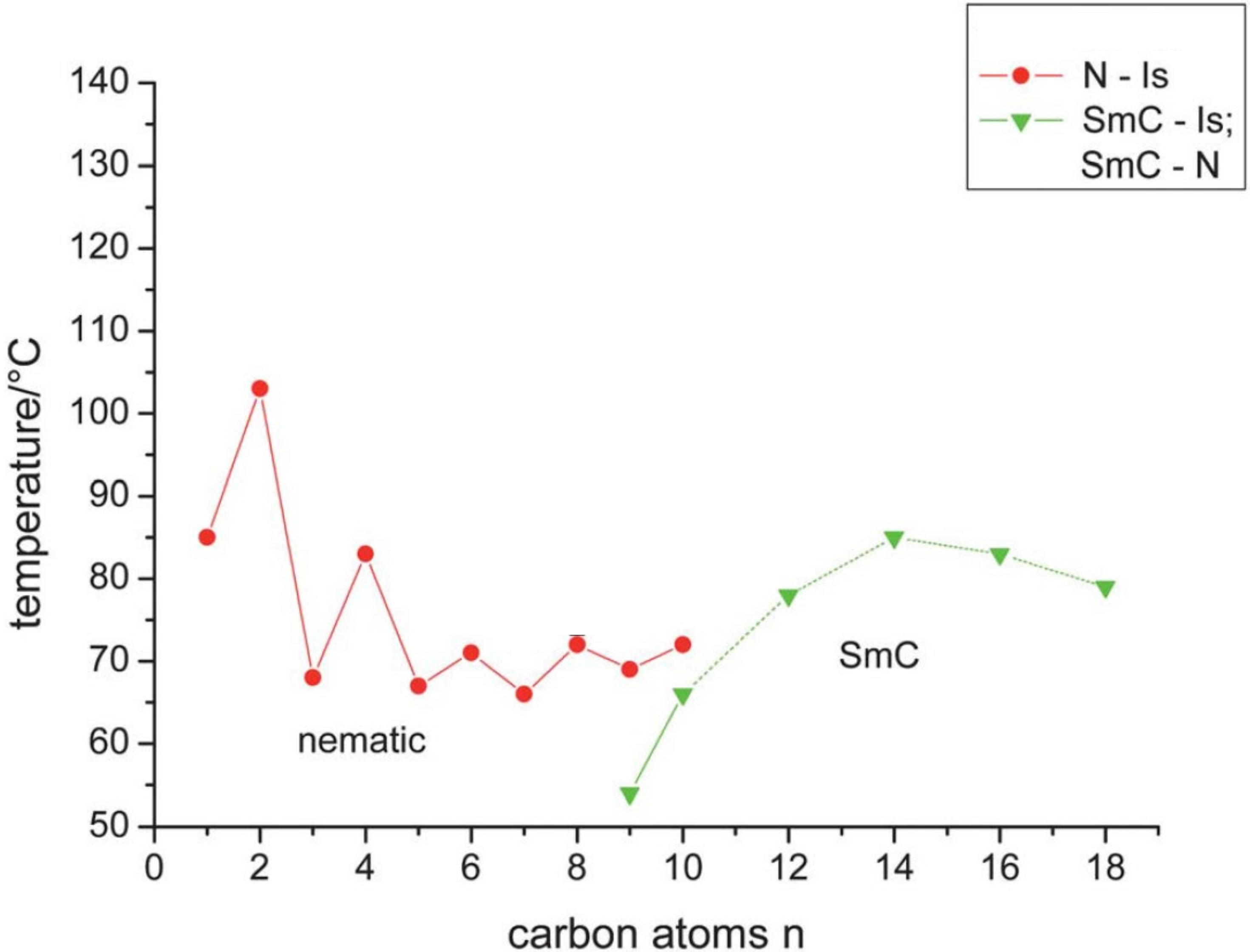
C. For symmetry reasons, mesogens with an even number of $CH_2$ groups in the aliphatic chain are easier to be packed into a crystal structure.

D. Mesogens with even number of of $CH_2$ groups contained in the aliphatic chain coil less and are therefore easier to be packed into a crystal structure.

# Why does $T_{S\text{-}N}$ increase with increasing aliphatic chain length?

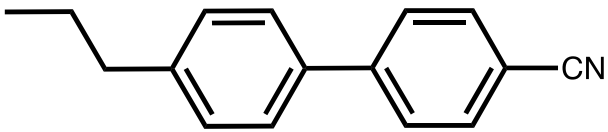
A. The degree of positional order increases with increasing chain length such that intermolecular interactions increase.
B. Because molecules form stronger H-bonds.
C. Because the mobility of the mesogens increases.
D. For steric reasons, it is more difficult to pack them into a crystal structure.

# Influence of aliphatic chain $CH_3(CH_2)_n$

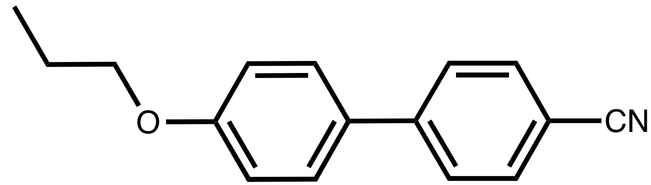



W. Weissflog, *et al.*, *Soft Matter*, 2012, **8**, 2671-2685

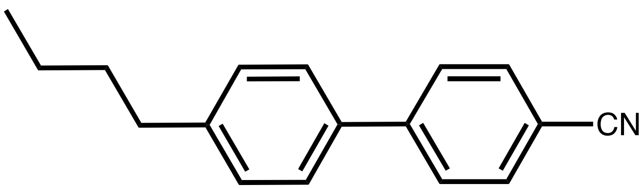
# Influence of terminal groups



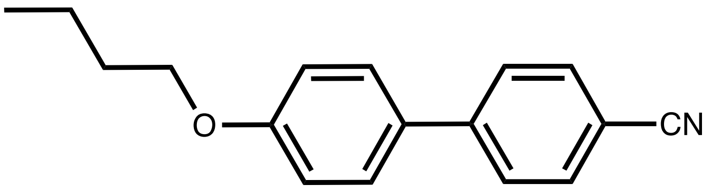

$T_m$: 66 °C
$T_N$: 25 °C




$T_m$: 78 °C
$T_N$: 76 °C

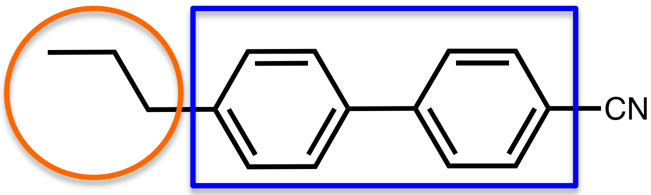



$T_m$: 48 °C
$T_N$: 17 °C

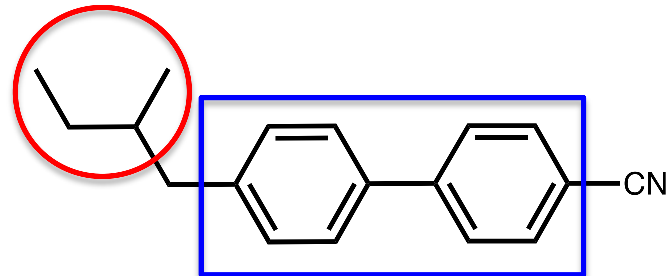



$T_m$: 48 °C
$T_N$: 68 °C

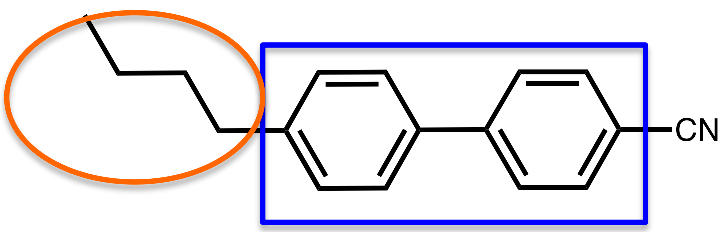
# Branching of terminal groups



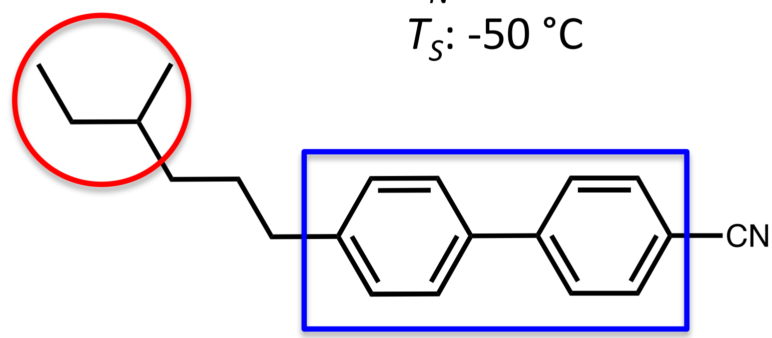

$T_m$: 66 °C
$T_N$: 25 °C




$T_m$: 4 °C
$T_N$: -30 °C
$T_S$: -50 °C




$T_m$: 48 °C
$T_N$: 17 °C



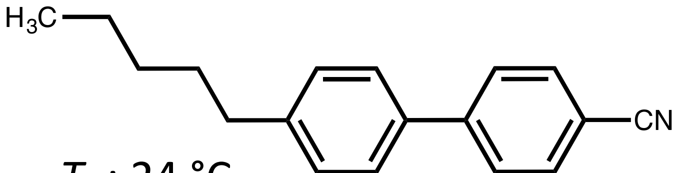

$T_m$: 28 °C
$T_N$: -20 °C
$T_S$: -10 °C

chain branching

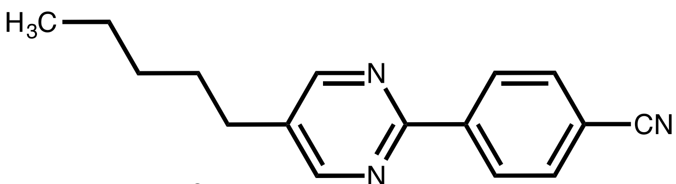
- often lowers $T_m$
- reduces liquid crystal phase stability

$T_N$: transition temperature nematic ➔ isotropic phase
$T_S$: transition temperature smectic ➔nematic phase

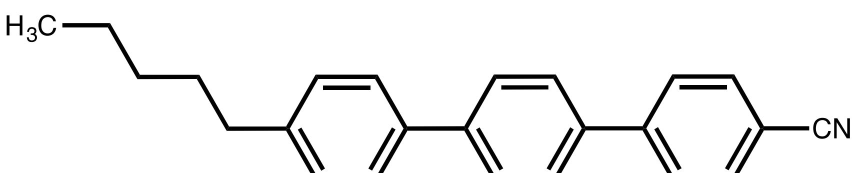
# Influence of structure on transition temperatures



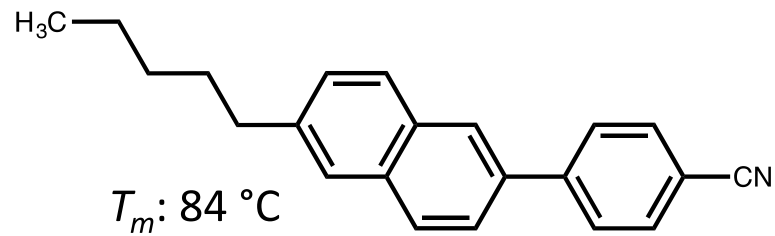

$T_m$: 24 °C
$T_N$: 35 °C



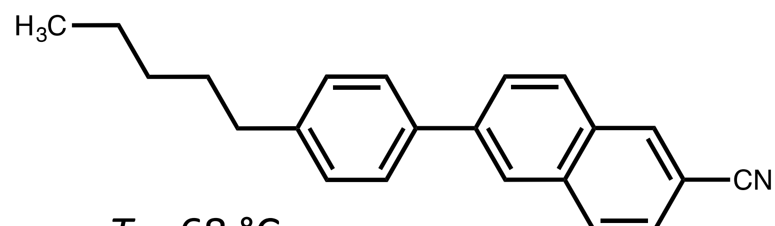

$T_m$: 71 °C
$T_N$: 52 °C




$T_m$: 130 °C
$T_N$: 239 °C




$T_m$: 84 °C
$T_N$: 127 °C

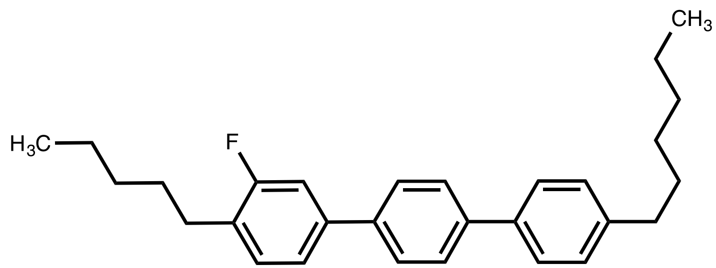



$T_m$: 68 °C
$T_N$: 130 °C

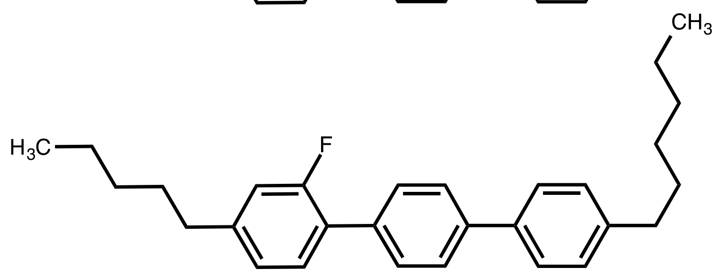


Molecules with long, rigid cores have high order parameters.

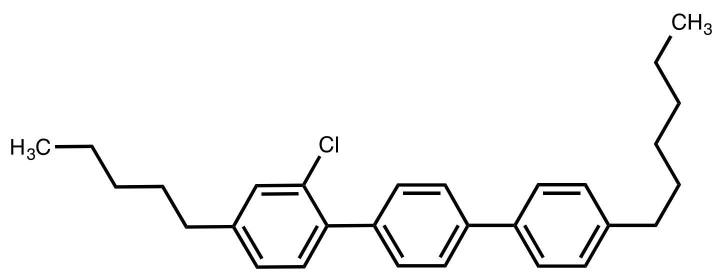
# Effect of substituents




$T_G$: 156 °C
$T_{SA}$: 189 °C




$T_m$: 73 °C
$T_{SC}$: 80 °C
$T_N$: 136 °C




$T_m$: 56 °C
$T_N$: 60 °C

F: small substituents (1.47 Å)

- lower $T_m$
- lower the stability of the smectic phase such that molecules more readily form a nematic phase.

Cl: larger substituents (1.75 Å)

- even lower $T_m$
- further decrease the stability of the liquid crystal phase.

# Why is $T_m$ of molecule (1) much lower than that of molecule (2)?

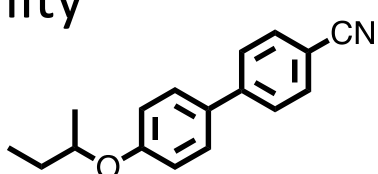
A. molecule (1) forms stronger H-bonds

B. molecule (1) is more difficult to pack into a crystalline structure

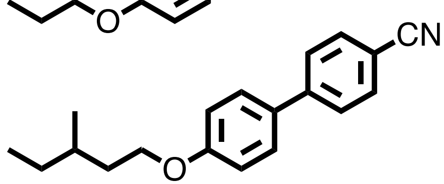
C. molecule (1) forms stronger VdW interactions

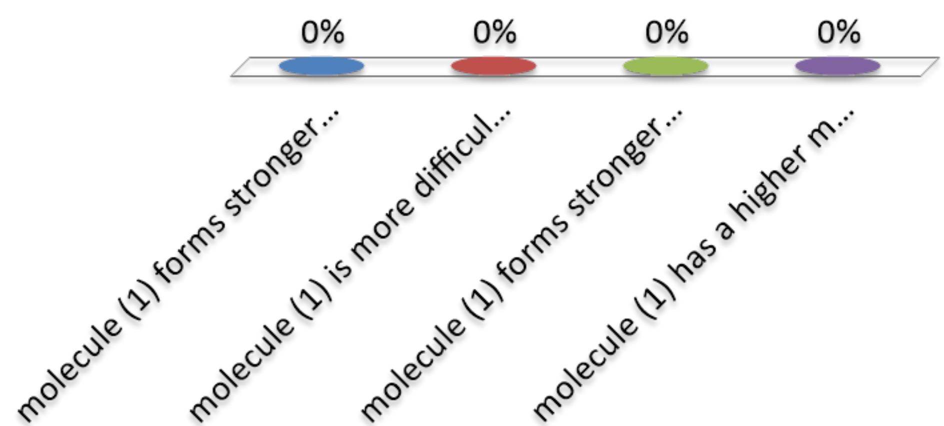
D. molecule (1) has a higher mobility

molecule 1

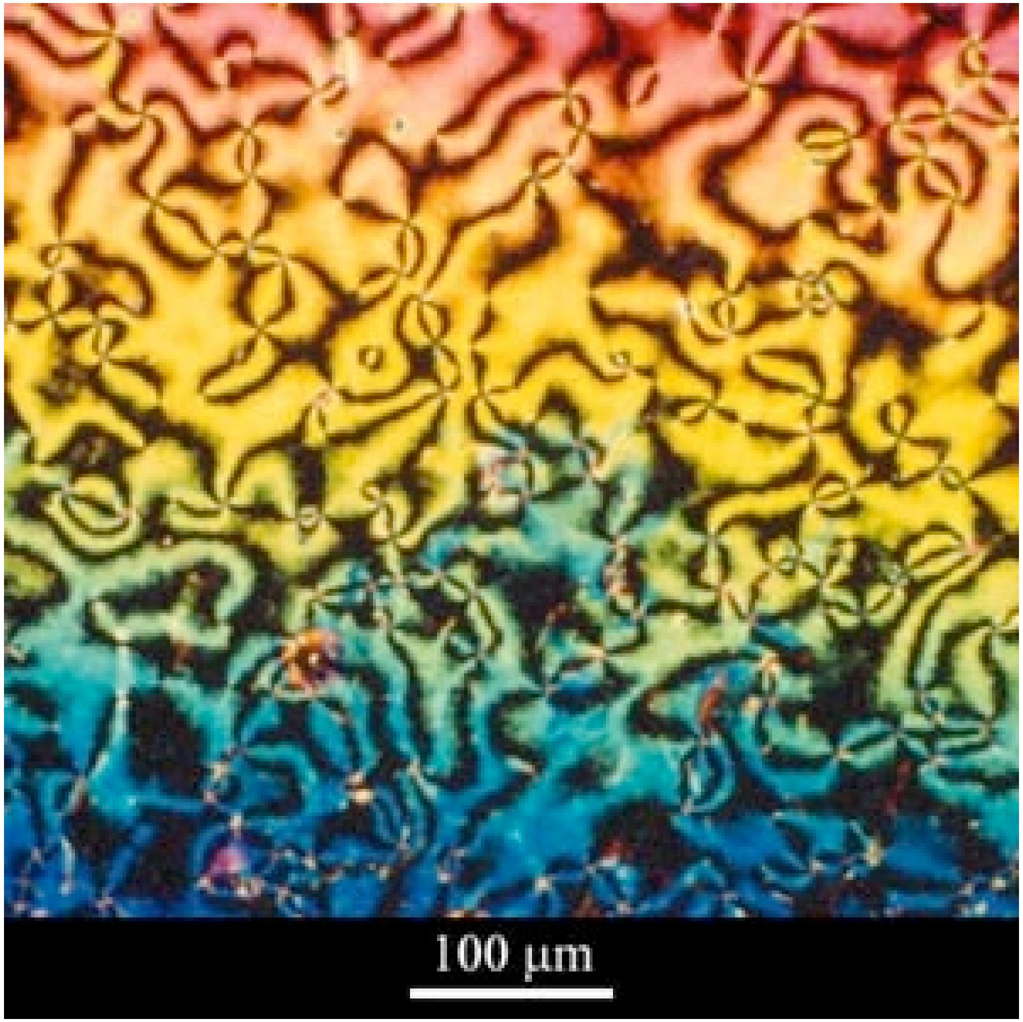



molecule 2



# Nematic liquid crystal

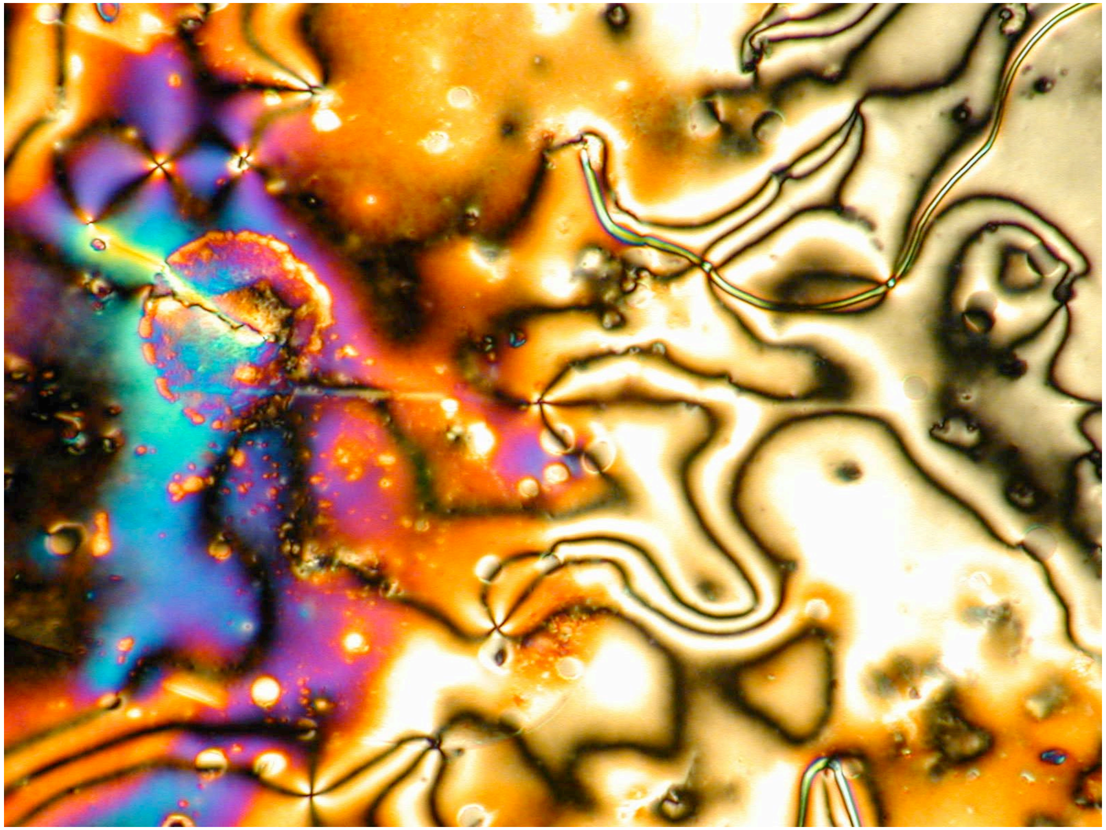



http://www.doitpoms.ac.uk/tlplib/anisotropy/liquidcrystals.php

# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

# How do liquid crystals interact with light?

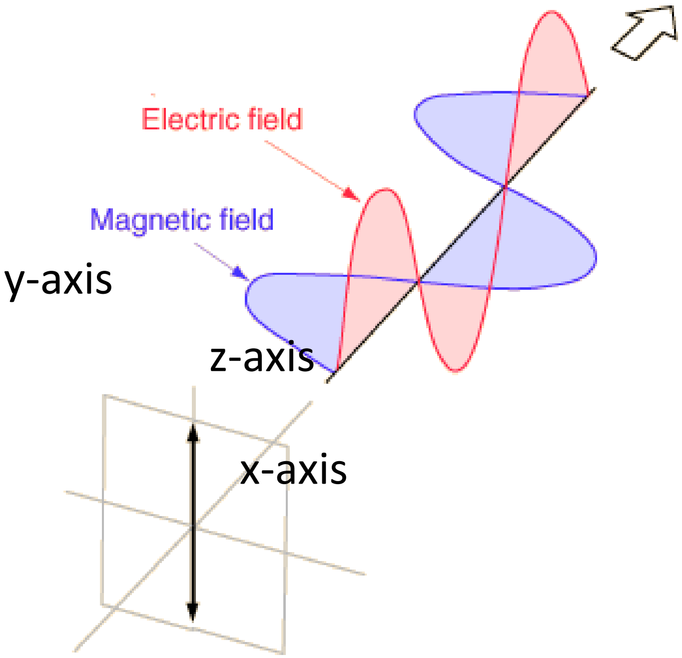


http://www.sfu.ca/chemistry/groups/williams/research/N%20phase%201.jpg

# Light: Polarized electromagnetic waves

- Polarized electromagnetic waves consist of propagating electric and magnetic fields whose vectors are perpendicular to the direction of their propagation.
- The electric field must always be perpendicular to the magnetic field.

linearly polarized light




$$k_0 = \left|\vec{k_0}\right| = \frac{2\Pi}{\lambda}$$

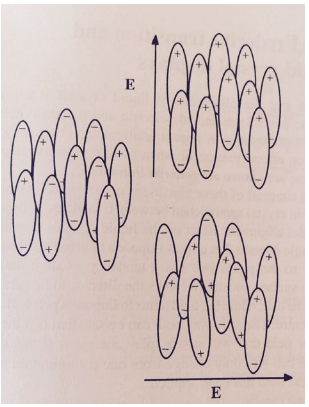
$$c = \frac{\omega}{k_0} = \frac{\lambda}{T}$$

$$\omega = \frac{2\Pi}{T}$$

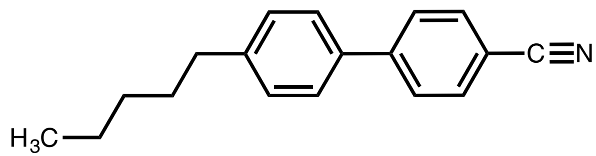
$k_0$: wave vector [$m^{-1}$]
$\lambda$: wavelength [m]
$T$: period of wave [s]
$c$: speed of electromagnetic waves in vacuum = $3\times10^8$ m/s

# Polarization

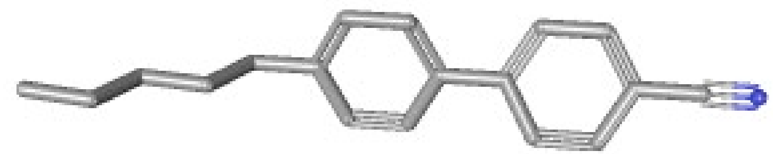
Nematic liquid crystals:




R. A. L. Jones, *Soft Condensed Matter*.
(Oxford University Press, Oxford, 2002)




5 CB: (4-cyano-4-n-pentylbiphenyl)



http://pubchem.ncbi.nlm.nih.gov

dipole moment per unit volume

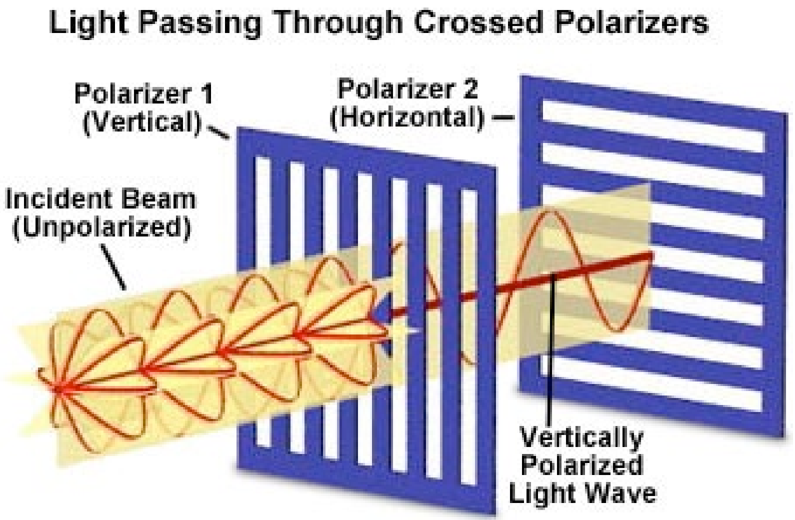
$$\vec{P} = \varepsilon_0 \chi \vec{E} V$$

with $\chi_e = \varepsilon_r - 1$

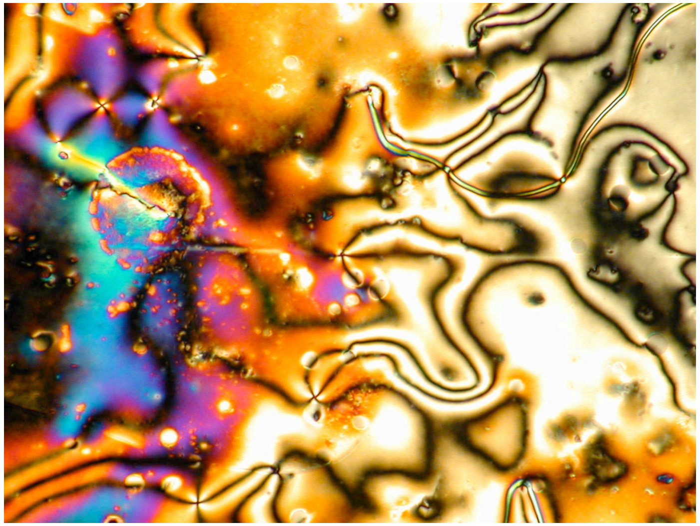
$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \varepsilon_0 \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_{//} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} V \qquad \vec{P} = \varepsilon_0 \underline{\underline{\chi}} \vec{E} V$$

*P*: dipole moment [Cm]
$\varepsilon_0$: permittivity of vacuum [F/m]
$\chi$: electric susceptibility [-]
*E*: electric field [V/m]
$\underline{\underline{\chi}}$: susceptibility tensor [-]
V: volume [$m^3$]

# How do liquid crystals interact with light?




http://www.olympusmicro.com/primer/lightandcolor/polarization.html

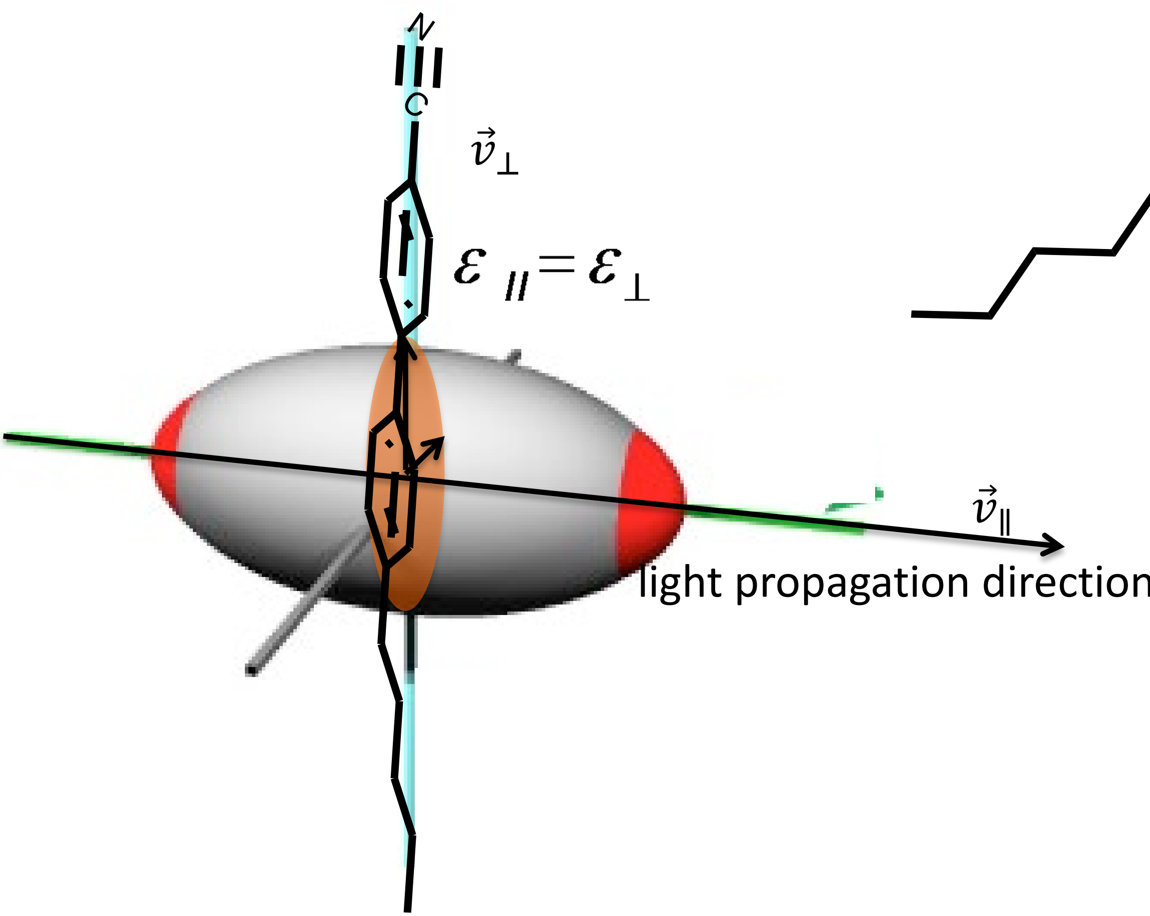


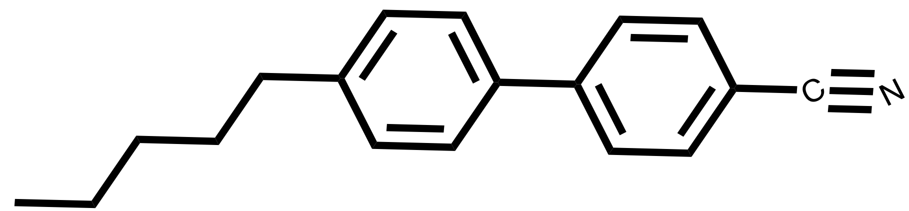
http://www.sfu.ca/chemistry/groups/williams/research/N%20phase%201.jpg

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \varepsilon_0 \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_{II} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} V$$

# Interaction of light with liquid crystals

**Uniaxial materials:** Materials whose elastic or electromagnetic properties are identical in two of the three directions.
*Example:* The nematic phase of a liquid crystal, the smectic A phase of a liquid crystal

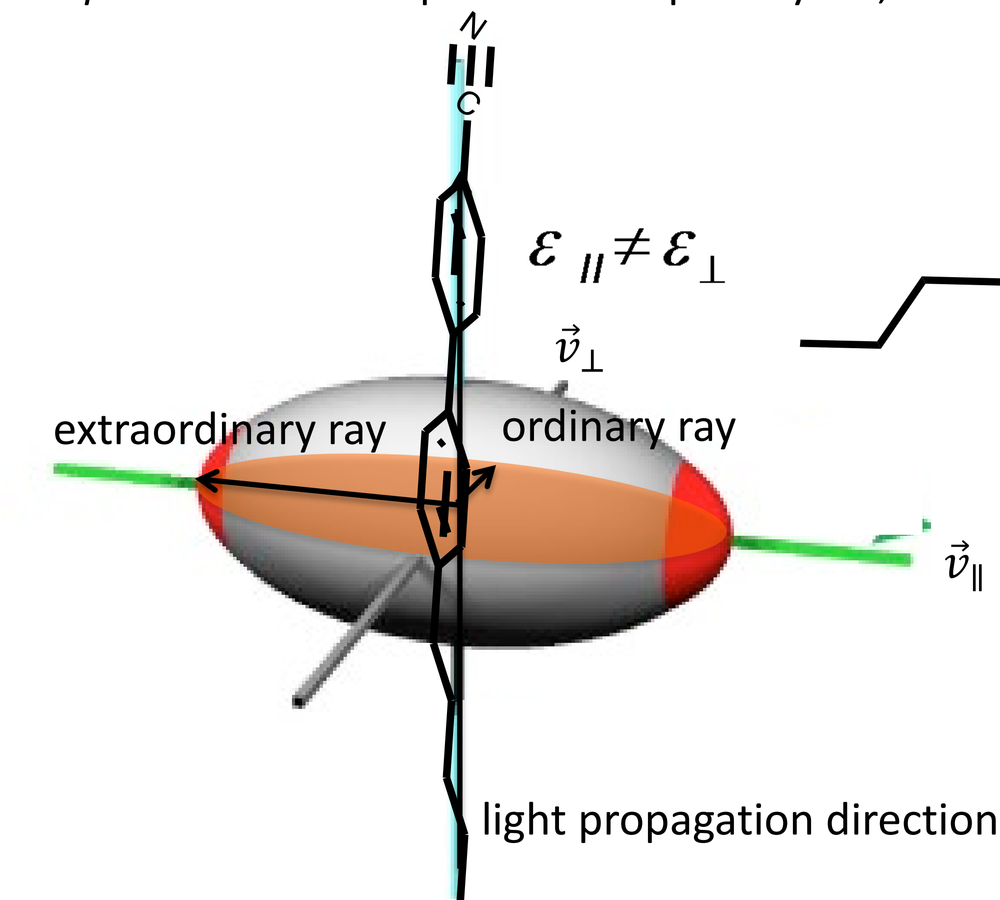


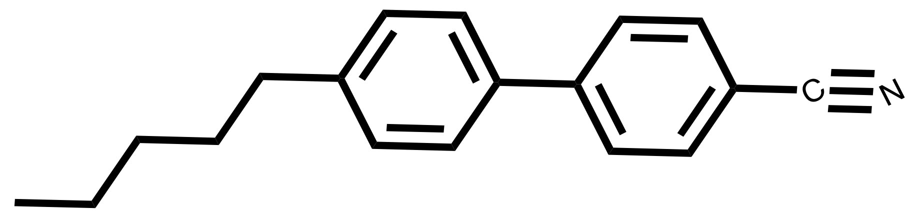




$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \varepsilon_0 \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_{II} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} V$$

# Interaction of light with liquid crystals

**Uniaxial materials:** Materials whose elastic or electromagnetic properties are identical in two of the three directions.
*Example:* The nematic phase of a liquid crystal, the smectic A phase of a liquid crystal.

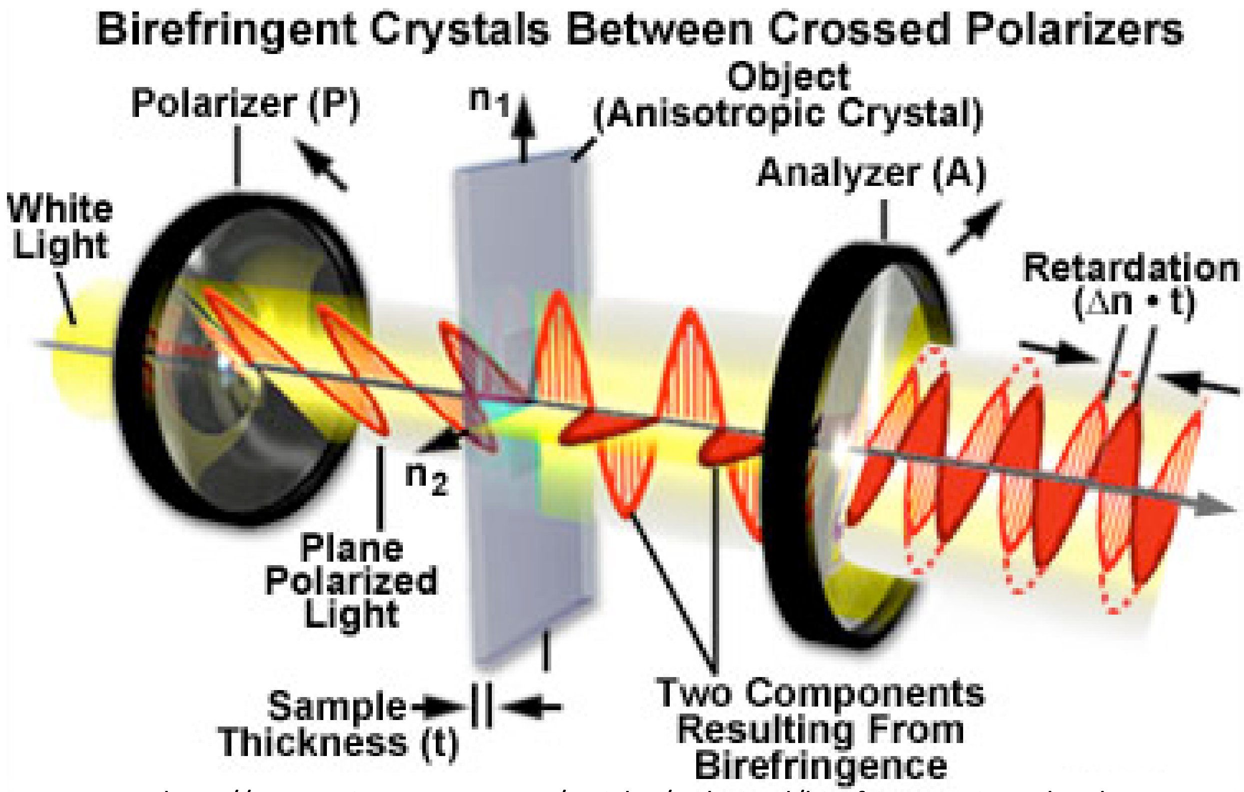



$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \varepsilon_0 \begin{pmatrix} \chi_{\perp} & 0 & 0 \\ 0 & \chi_{\perp} & 0 \\ 0 & 0 & \chi_{\parallel} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} V$$

# Polarized light microscopy

Can be used to identify the liquid crystal structure.




http://www.microscopyu.com/articles/polarized/birefringenceintro.html

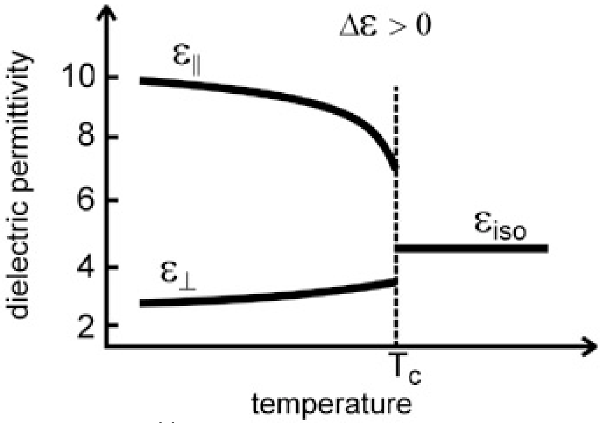
Cross-polarizers are usually oriented 90° to each other.

# Dielectric anisotropy, $\Delta\varepsilon$

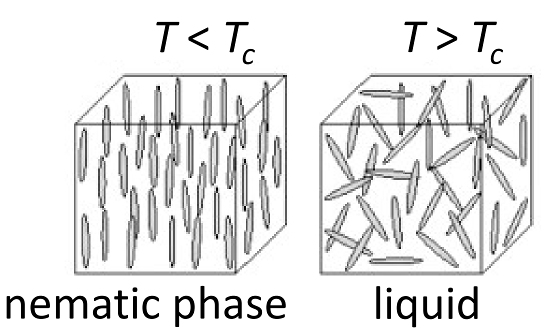
$$\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$$

The dielectric anisotropy depends on the polarizability of the molecules and the orientation of the dipoles

*Example:* Molecules with terminal cyano groups often have high values of $\Delta\varepsilon$.




http://www.personal.kent.edu



# Optical anisotropy, Δ*n*

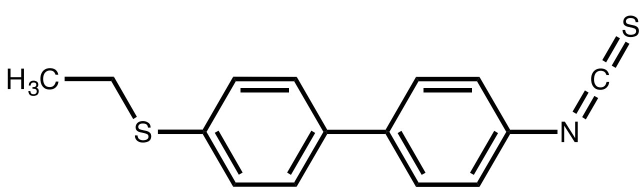
for non-magnetic materials: $n = \sqrt{\varepsilon_r}$ with $\varepsilon = \varepsilon_r \varepsilon_0$

$$\Delta n = n_{II} - n_{\perp}$$

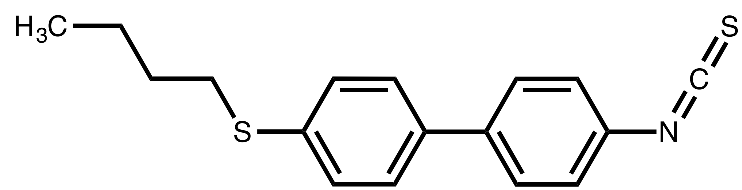
Δn depends on

- the polarizability of molecules
- the ordering of molecules

*Example:* Molecules with aromatic rings that are rigidly linked to the core and have thiocyanate end-groups have a high birefringence.




Δ*n*: 0.396

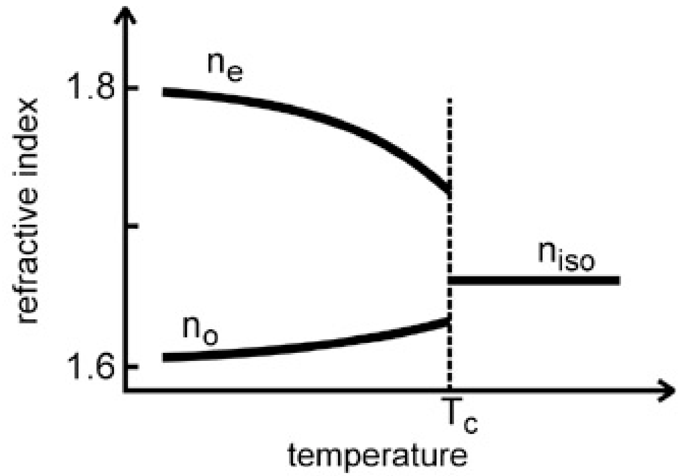



Δ*n*: 0.352

Optical anisotropy is important if LCs are used as optical displays.

# Birefringence

The optical property of a material whose refractive index depends on the polarization and propagation direction of the light.



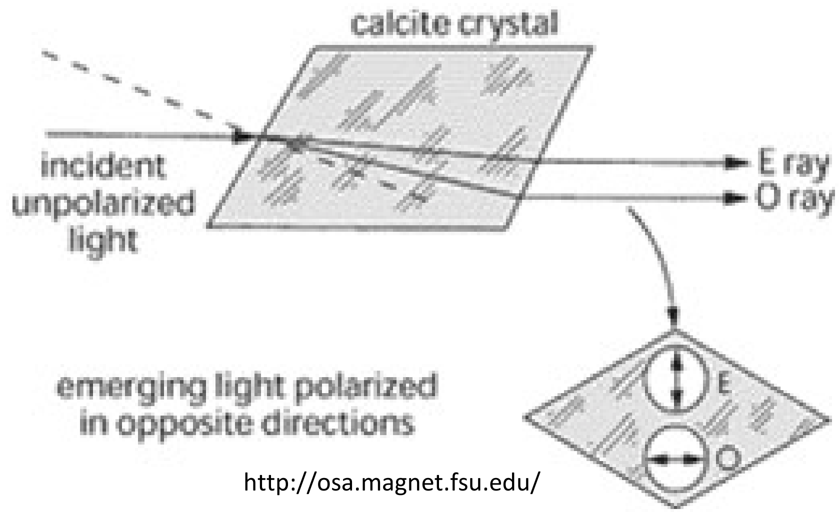

http://www.personal.kent.edu/~bisenyuk/liquidcrystals/maintypes3.html

$$n_\perp \neq n_{//}$$

$\lambda_0$: wavelength in vacuum [m]
$k_0$: wave vector in vacuum [$m^{-1}$]

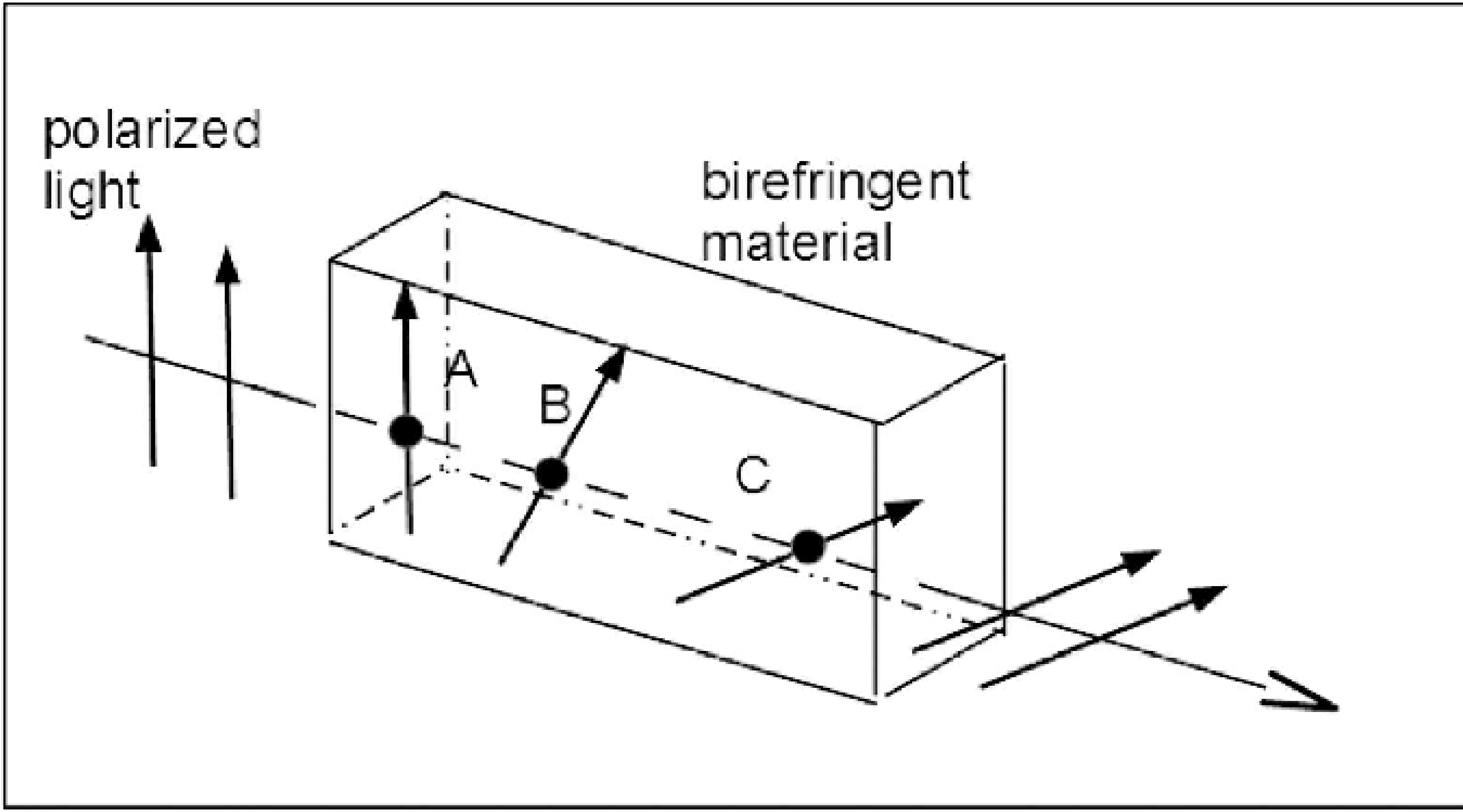
$$v = \frac{c}{n} \qquad \lambda = \frac{\lambda_0}{n}$$

$$k = \frac{2\Pi}{\lambda} = \frac{2\Pi n}{\lambda_0} = nk_0$$




http://osa.magnet.fsu.edu/

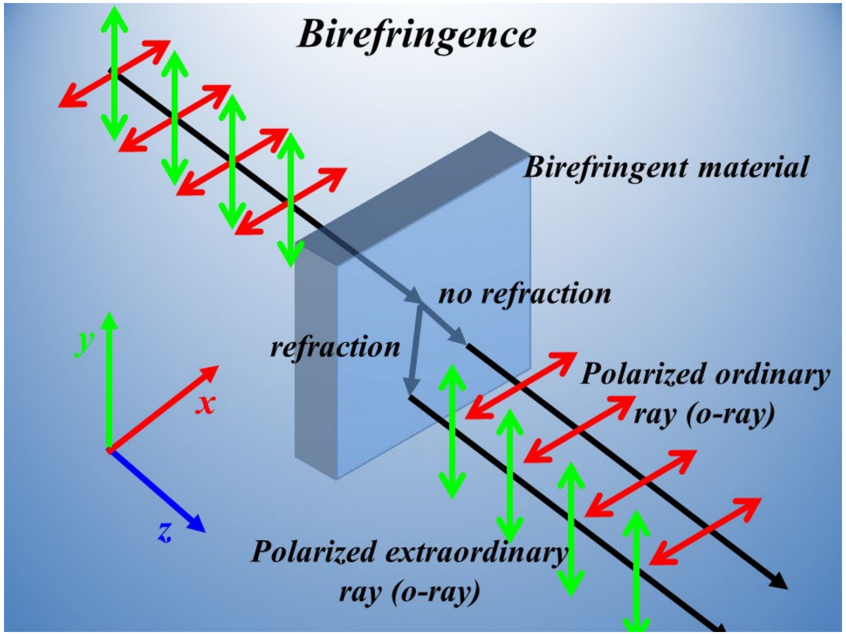
# Birefringent materials



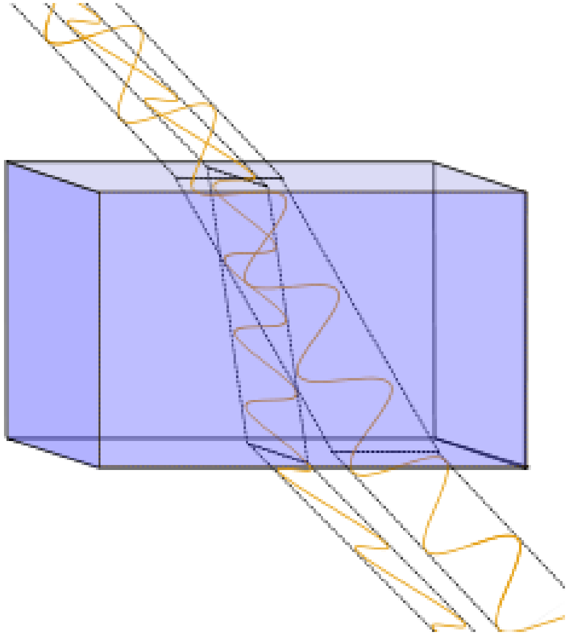

D. Soga, D.M. Faes, and M. Muramatsu, Rev. Bras. Ensino Fís. **41**, (2018).

Birefringent materials change the direction of the polarized light that passes through them.

# Why does the direction of polarized light change when it passes through birefringent materials?



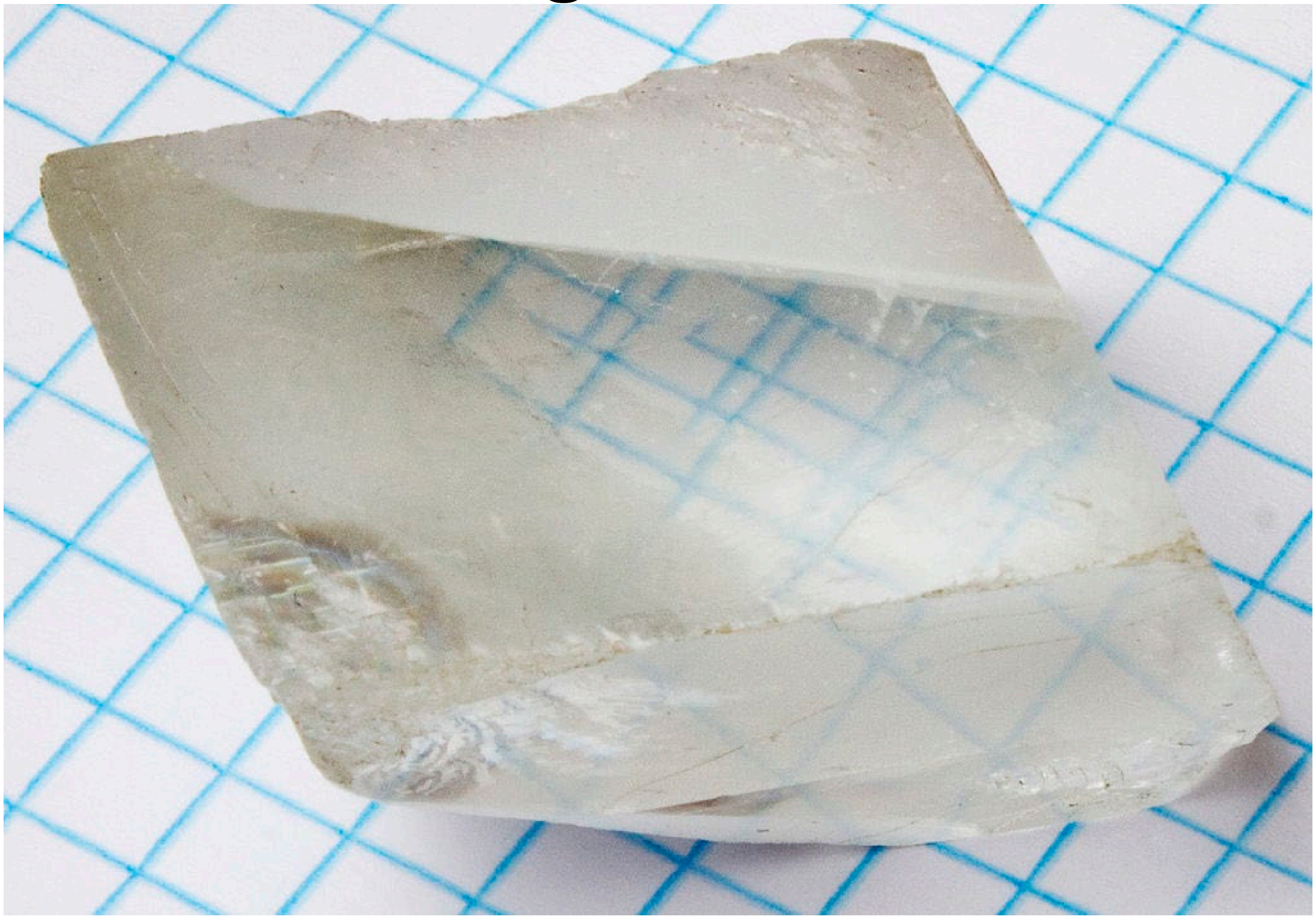

https://www.asrmeta.com/birefringence-and-birefringent-materials/?utm_source=rss&utm_medium=rss&utm_campaign=birefringence-and-birefringent-materials



https://en-academic.com/dic.nsf/enwiki/117527

Because the ordinary and extraordinary rays travel through birefringent materials at different speeds, they experience different refractive indices.

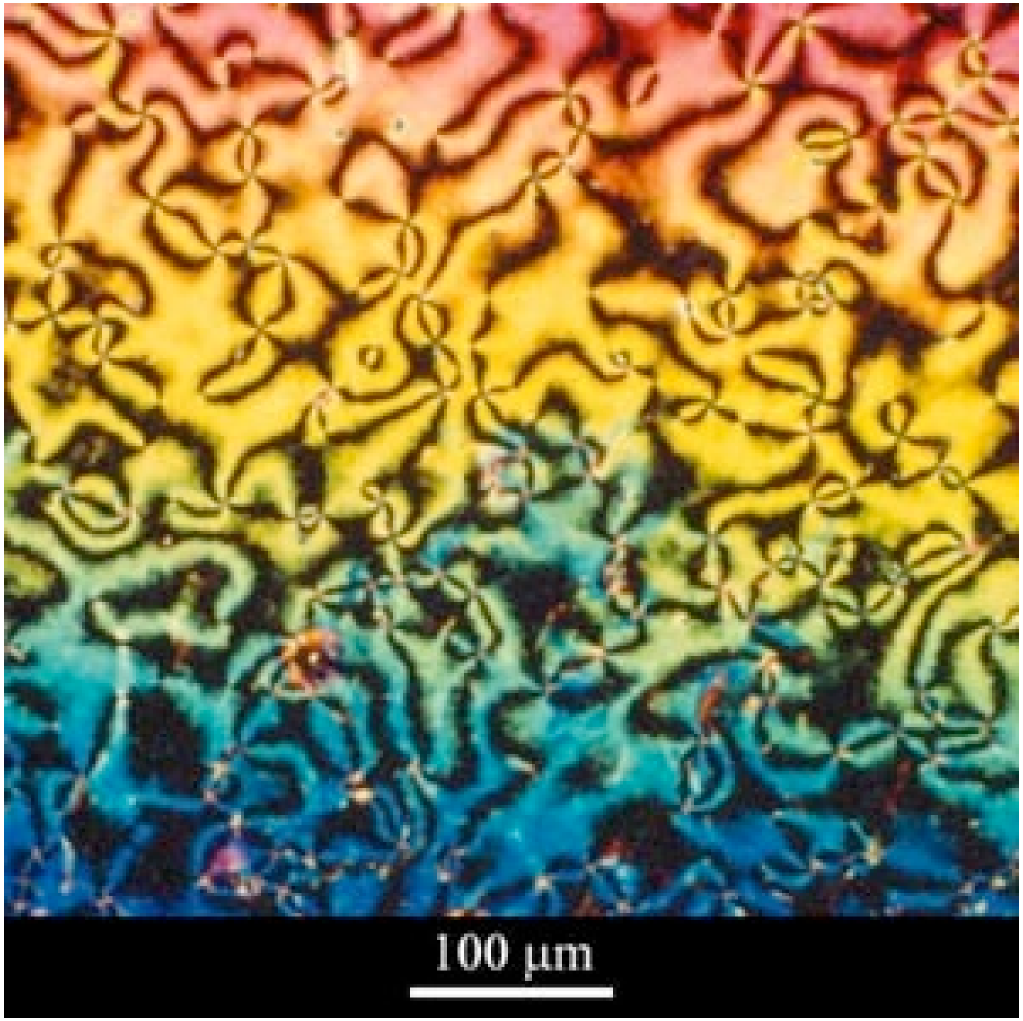
# Typical example of a birefringent material





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

# Where do the patterns come from?




http://www.doitpoms.ac.uk/tlplib/anisotropy/liquidcrystals.php

# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotrophic liquid crystals

# Defects

### Point defects

Point defects occur in restricted geometries at the surface.

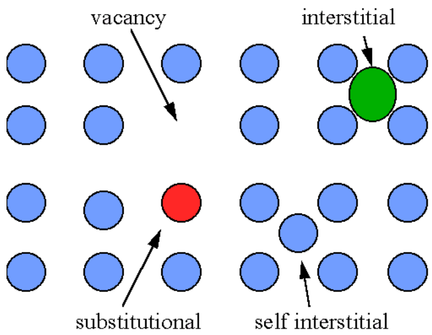
### Line defects

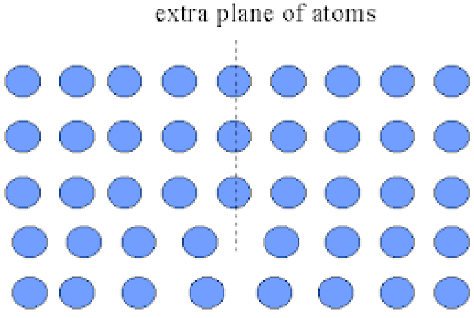
Line defects are discontinuities of the director orientation. They are the most often seen defects in liquid crystals.

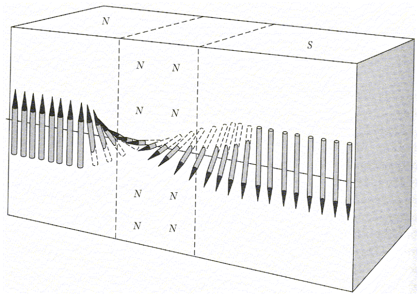
### Wall defects

Wall defects are continuous changes in the director over some distance.

*analogy to metals*



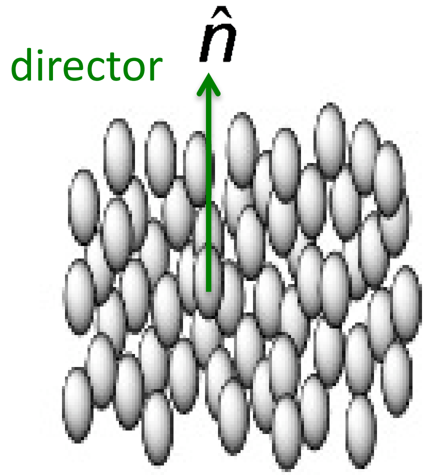



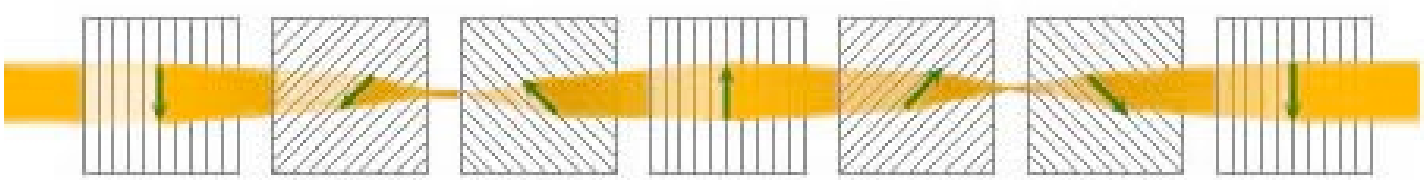
# Disclinations

**Disclination:** Defects in the orientation of the director.

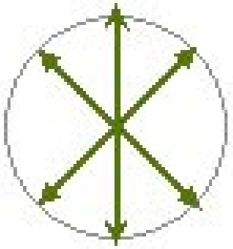
**Director:** Vector, along the average direction of the alignment of mesogens.




*Example of a disclination:*

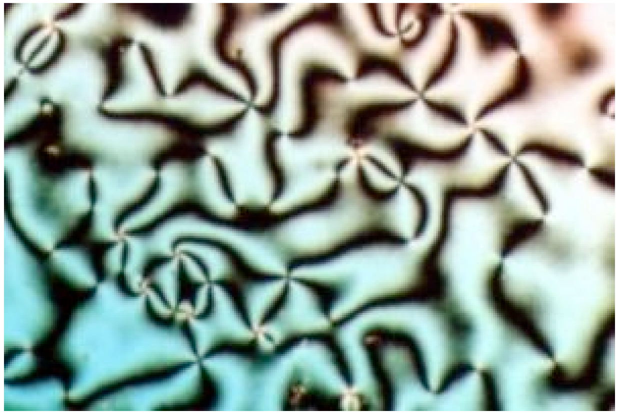


http://plc.cwru.edu/tutorial/enhanced/files/lc/phase/phase.htm



# Disclinations

Disclinations are responsible for these patterns.



They are described by their strength, *s*:

$$s = \pm\frac{1}{2}, \pm 1, \pm\frac{3}{2}, \ldots$$

*Convention:*
*s* is positive if the sample is rotated and the liquid crystal patterns (*e.g.* brushes) rotate in the same direction.

# Nematic phase

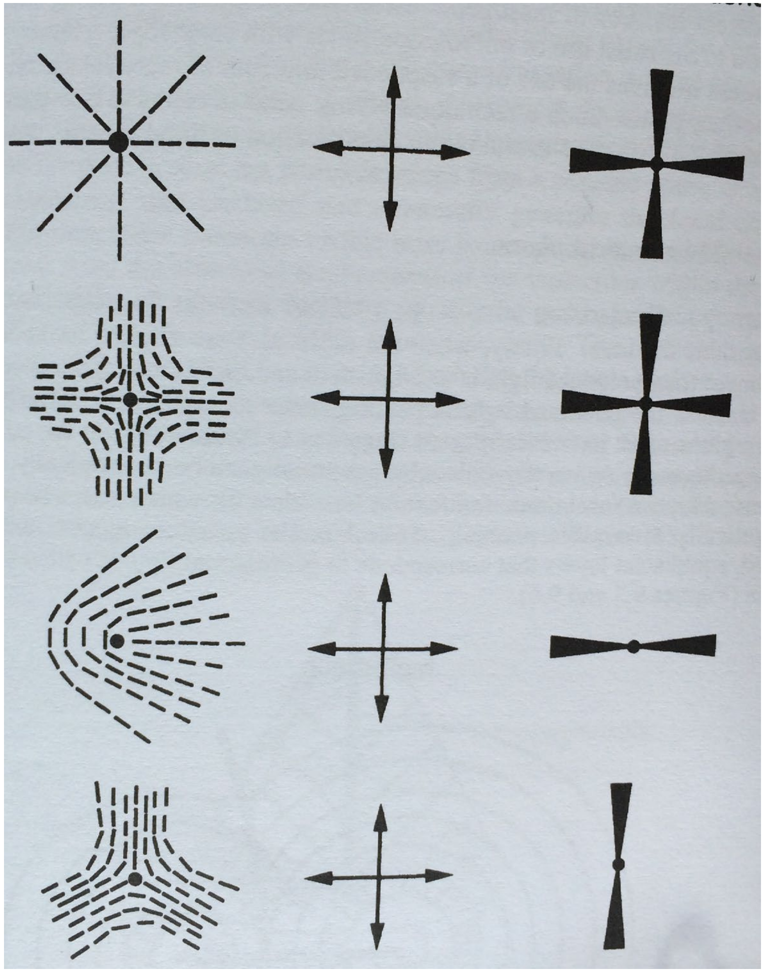
| | arrangement of nematic molecules | crossed polarizers | appearance of Schlieren brushes |
|---|---|---|---|
| | | | |

*s* = 1

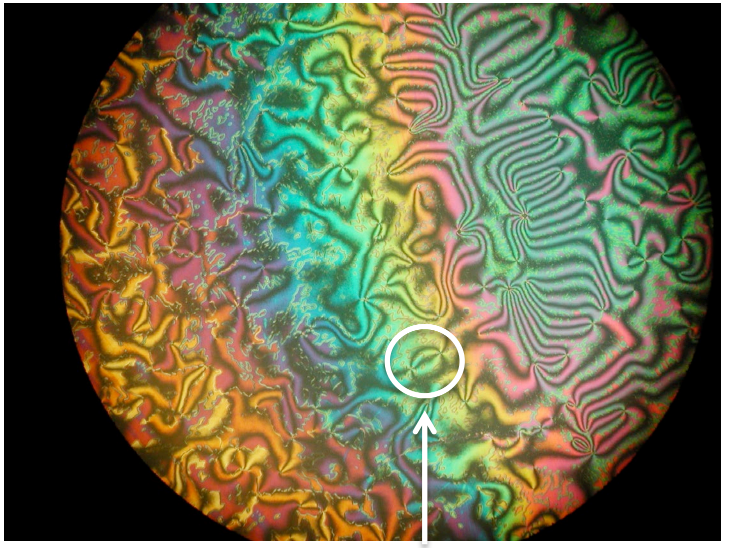
*s* = -1

*s* = +1/2

*s* = -1/2



nematic phase

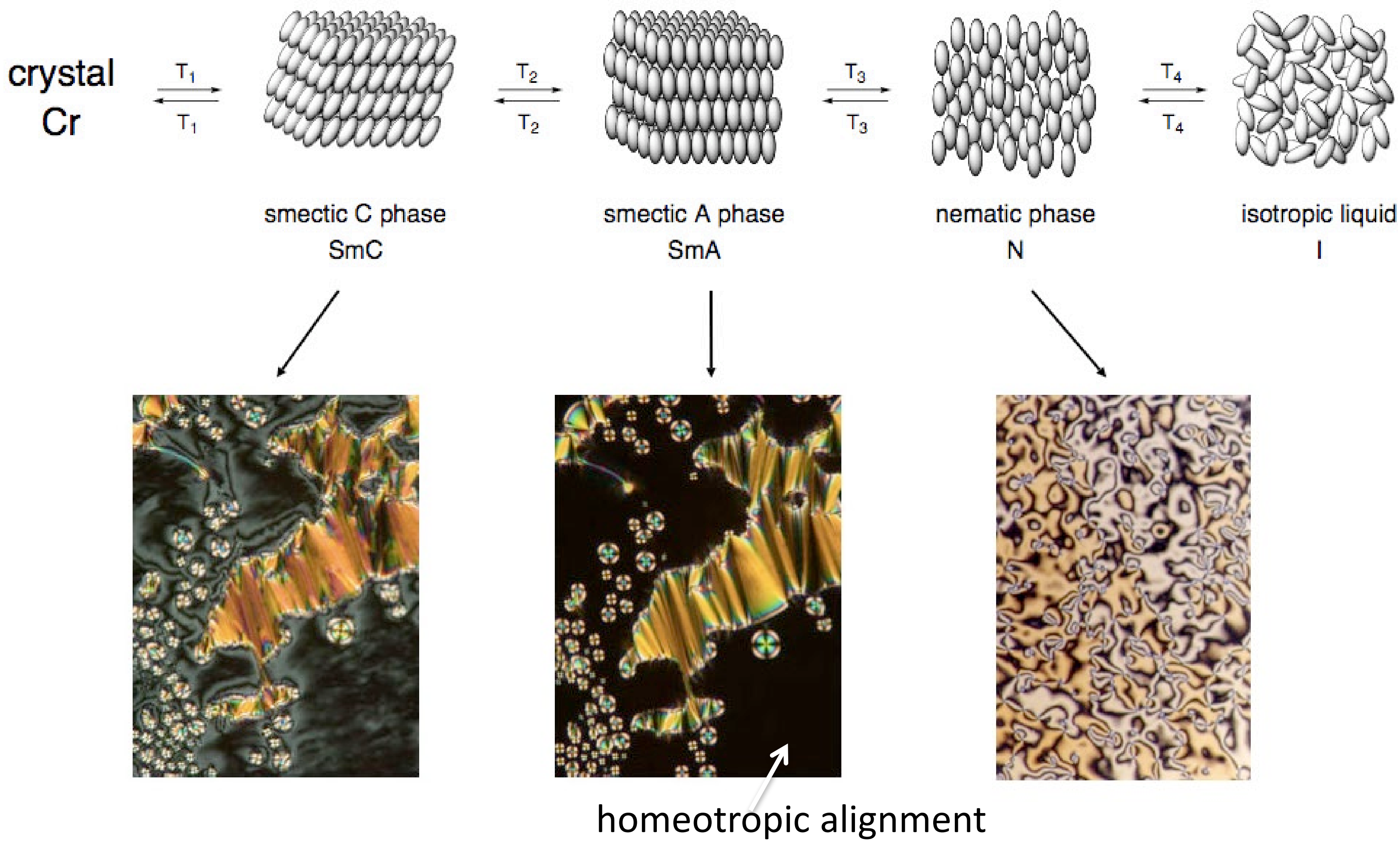


http://liq-xtal.case.edu/

two-brush Schlieren texture

Collings, P. J.; Hird, M. *Introduction to liquid crystals*; Taylor & Francis Ltd.: London, 2004.

# Characterization of liquid crystals with polarized optical microscopy




http://faculty.chem.queensu.ca/people/faculty/lemieux/Research.asp

# Can a nematic phase result in birefringence?

A. Yes
B. No
C. It depends

# Can an isotropic phase result in birefringence?

A. Yes
B. No
C. It depends

# Can a smectic A phase result in birefringence?

A. Yes
B. No
C. It depends

# Outline: Liquid crystals

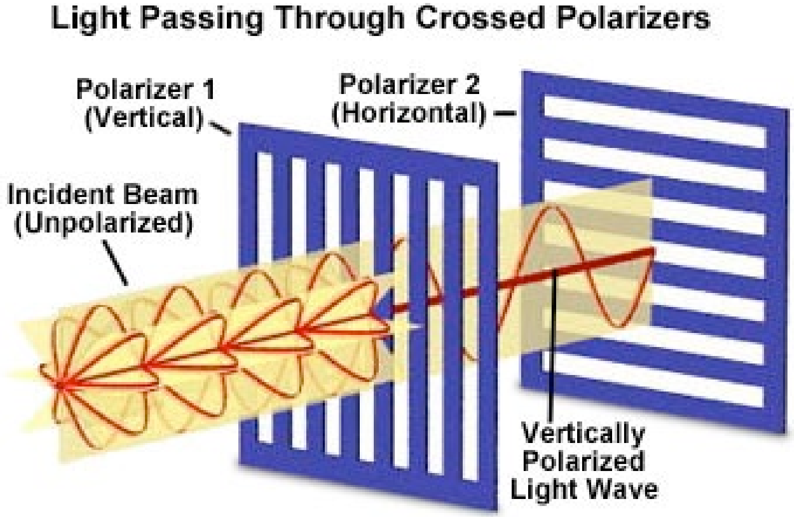
- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

# Where can nematic liquid crystals be used?

Displays

*Example:* twisted nematic liquid crystal

http://www.pacificdisplay.com/products.htm




http://www.olympusmicro.com/primer/lightandcolor/polarization.html

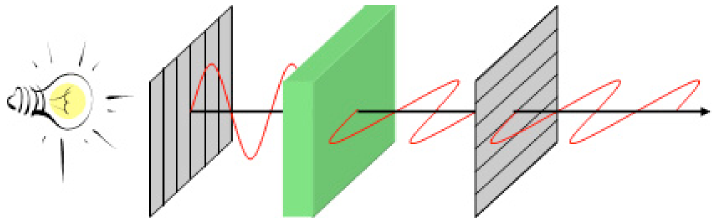
# Nematic crystals

Nematic crystals have uniaxial anisotropy. The refractive index in one direction is different from that in the other two directions.

$\delta$: angle by which polarization of light changes [rad]
$d$: thickness of material [m]
$\Delta n$: birefringence [-]

Extraordinary refractive index: $n_e = n_{//}$
Ordinary refractive index: $n_o = n_\perp$

$$E_x(z,t) = E_0 cos(n_\perp kd - \omega t)$$
$$E_y(z,t) = E_0 cos(n_\parallel kd - \omega t)$$
$$E_y(z,t) = E_0 cos(n_\perp kd - \omega t - \Delta nkd)$$



http://lcp.elis.ugent.be/tutorials/lc/lc2

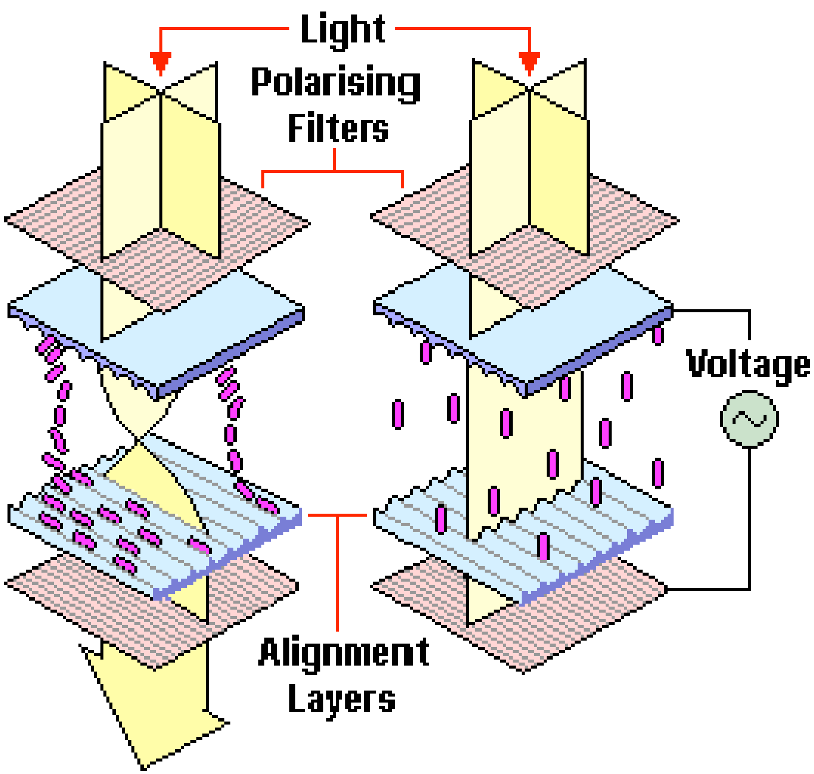
➔ $\delta = \Delta nkd = (n_\perp - n_{//})kd = \frac{2\Pi}{\lambda}(n_\perp - n_{//})d$

Birefringent materials change the polarization of light. Quarter wavelength plate: δ = 90°



https://www.youtube.com/watch?v=BiRiUOwNdEs

# Twisted nematic liquid crystal displays




http://www.longtech-display.com

Passive displays: No light is generated by the display.

- This display produces black numbers or letters on a silver background.
- This display consumes very little power.

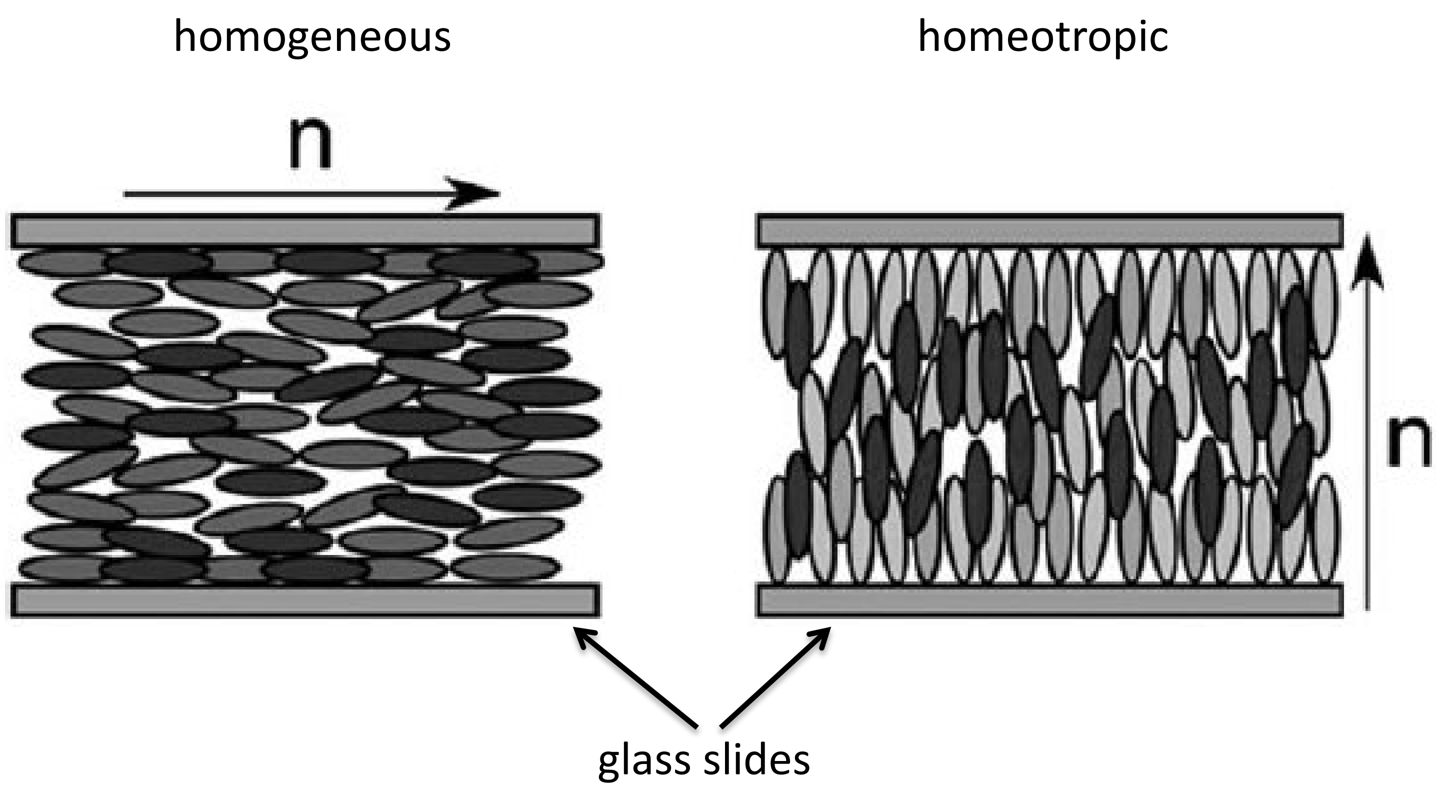
The electric field is applied normal to glass and used to re-orient unpinned molecules.

The twist angle between the two polarizers is 90°.
The typical switching speed is 20-50 ms.



https://www.youtube.com/watch?v=jiejNAUwcQ8

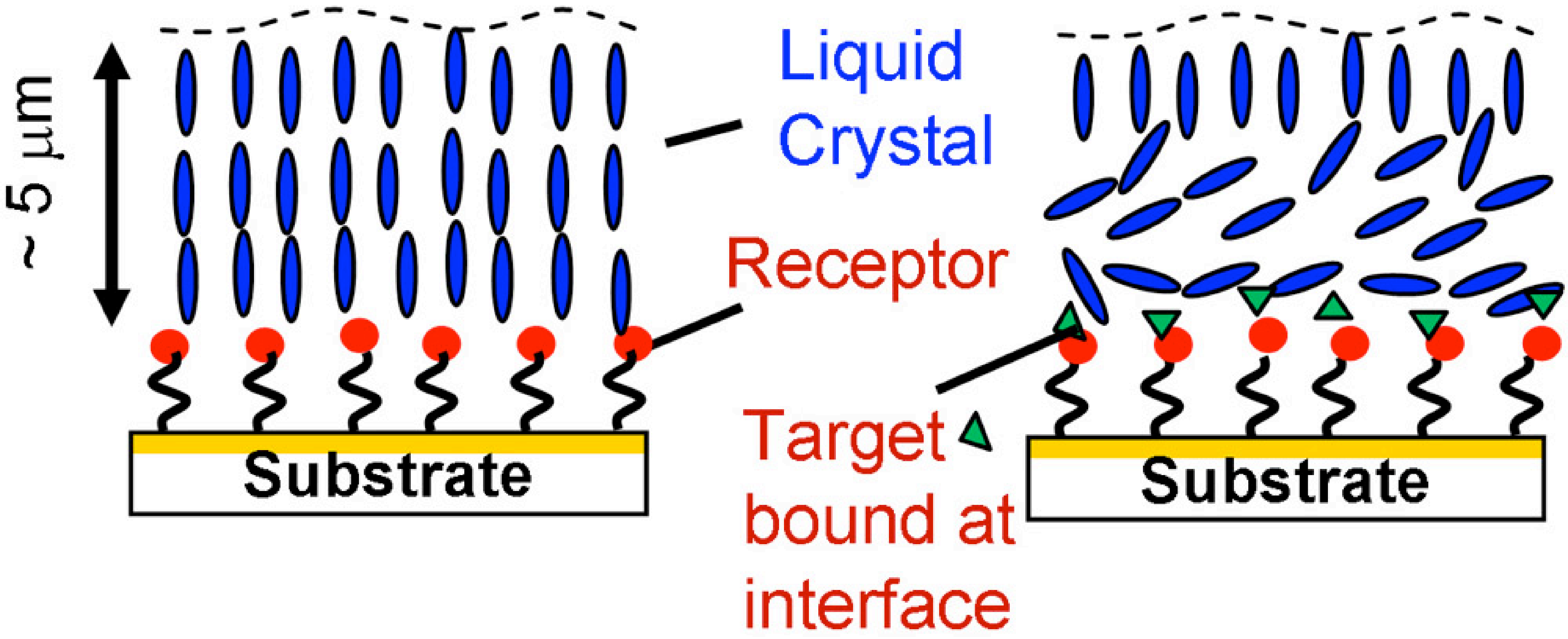
# Alignment of molecules



# How can you control the orientation of nematic liquid crystals close to the surface? By…

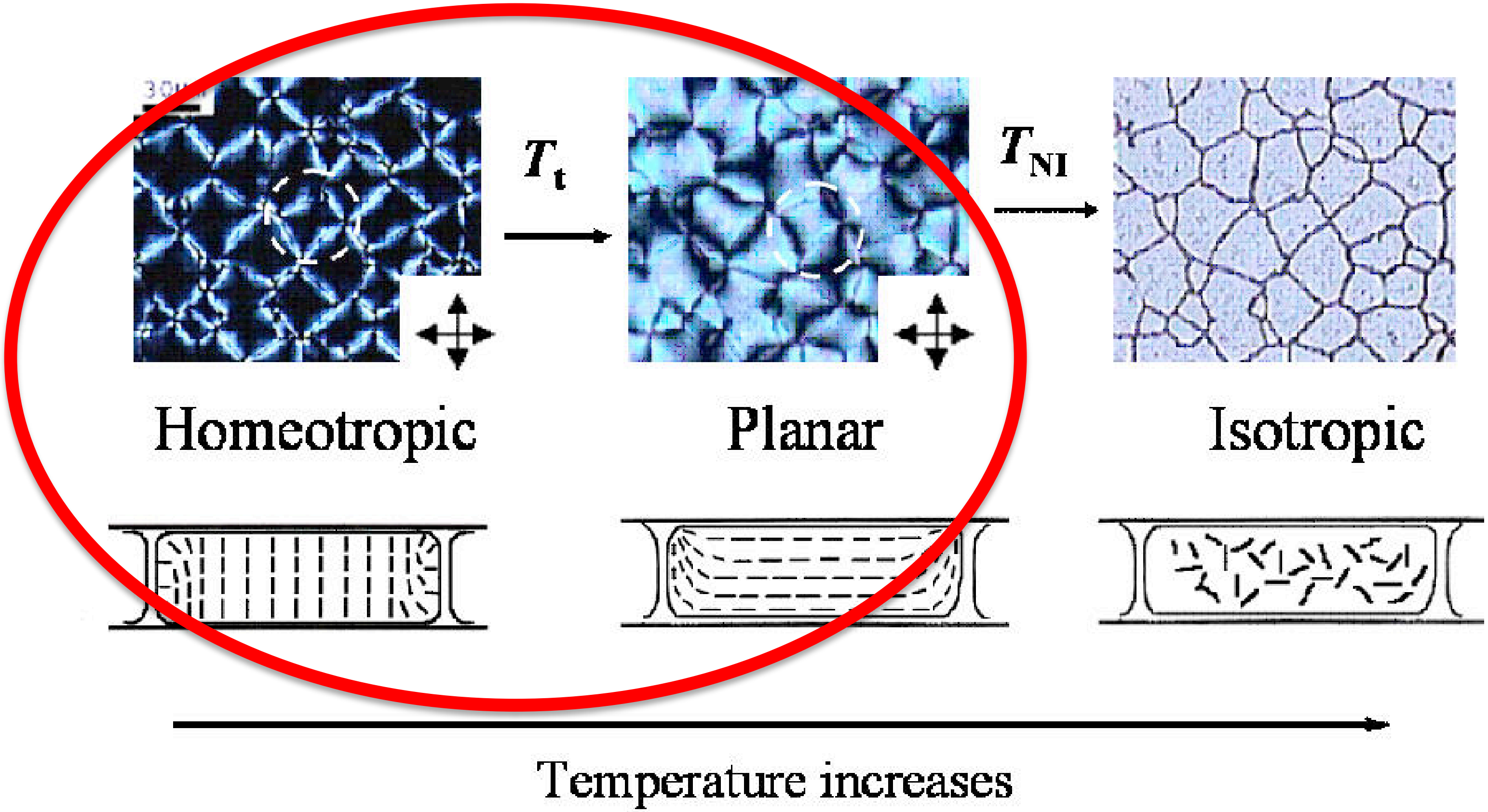
A. tuning the surface chemistry of the two parallel plates
B. controlling the surface roughness of the polarizers
C. controlling the thickness of the liquid crystal layer
D. controlling the intensity of the light
E. controlling the temperature

# Controlling the arrangement of liquid crystals




B. R. Acharya, Defense and Security, 2011

# How can we tune the alignment of liquid crystals without using an external field?




http://mohan.mse.gatech.edu/Research/pdlc/pdlc.htm

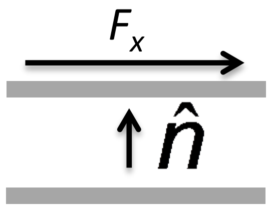
The alignment of molecules can be tuned for example by:

- controlling the chemistry of the liquid crystals.
- controlling the surface chemistry.

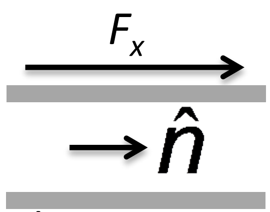
# How can you tune the viscosity of liquid crystals contained in a twisted nematic phase?

A. With the surface treatment of glass substrates
B. With the structure and composition of liquid crystal molecules
C. With the thickness of the liquid crystal layer
D. With the applied electric field

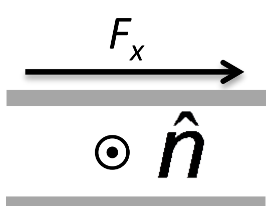
# Viscosity of liquid crystals



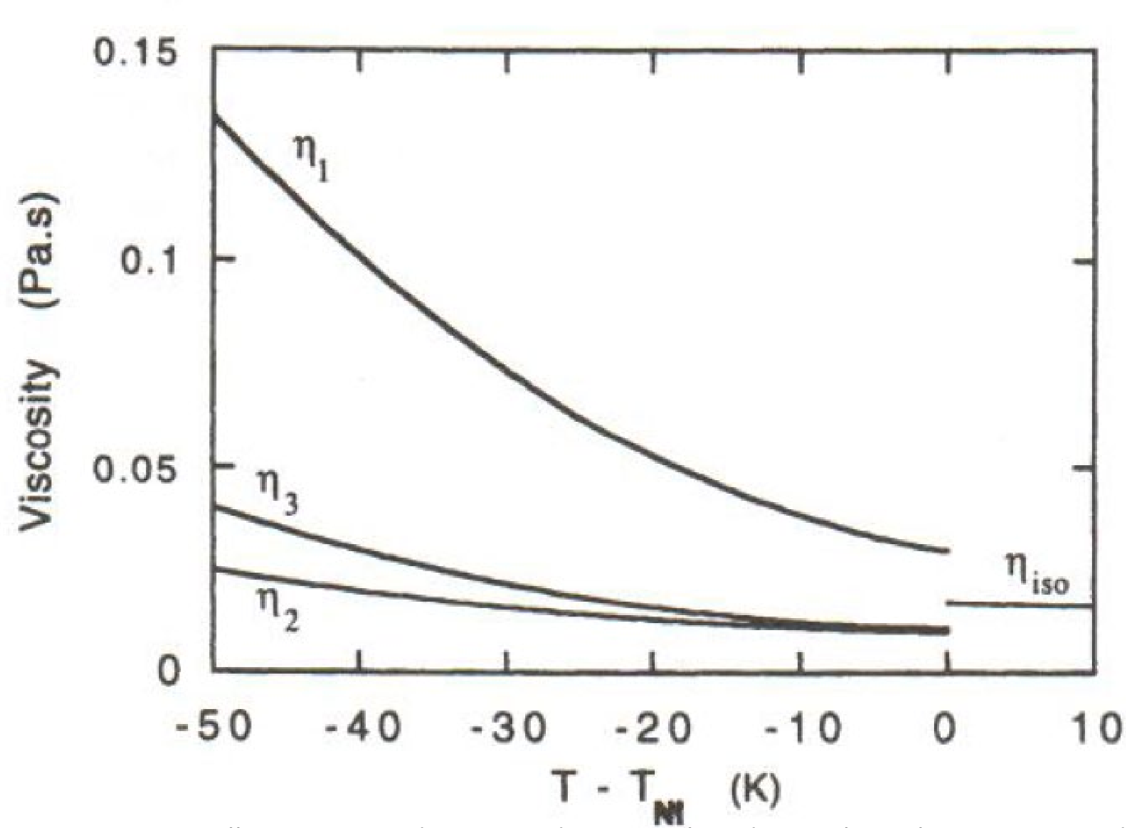

$\eta_1$: director normal to flow and parallel to velocity gradient




$\eta_2$: director parallel to flow




$\eta_3$: director normal to flow and normal to velocity gradient

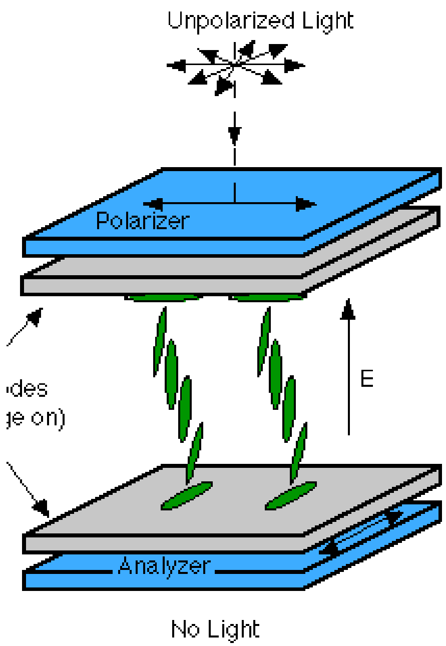



Collings, P. J.; Hird, M. *Introduction to liquid crystals*; Taylor & Francis Ltd.: London, 2004

$T_{NI}$: temperature of the nemantic –isotropic phase transition [K]
To allow fast switching of optical devices $\eta$ must be low.

# Liquid crystal display

How strong does the E-field have to be to orient the mesogens?




$$F_{tot} = F_{elastic} + F_{field}$$

$$F_{tot} = \frac{1}{2}K_1\left(\frac{\partial \delta n(z)}{\partial z}\right)^2 - \frac{\Delta\varepsilon E^2}{8\pi}\partial\delta n(z)^2$$

$$\int_0^d F_{tot}\,dz = \delta n^2\left[\left(\frac{K_1\pi^2}{4d}\right) - \left(\frac{\Delta\varepsilon E^2 d}{16\pi}\right)\right]$$

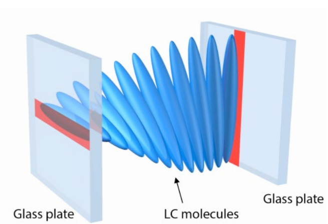
$$E_{crit} = \frac{2\pi}{d}\sqrt{\frac{\pi K_1}{\Delta\varepsilon}}$$

assumption:

$$\delta n(z) = \delta n \sin\left(\frac{\pi z}{d}\right)$$

for twisted nematic liquid crystals:

$$E_{crit} = \frac{2\pi}{d}\sqrt{\frac{\pi}{\Delta\varepsilon}}\left[K_1 + \frac{1}{4}(K_3 - 2K_2)\right]^{\frac{1}{2}}$$

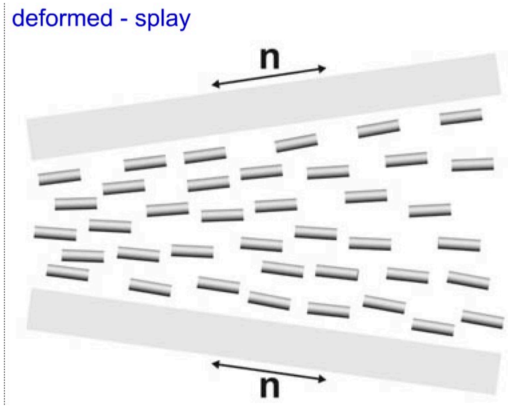



With $n = \sqrt{\frac{\varepsilon}{\varepsilon_0}}$

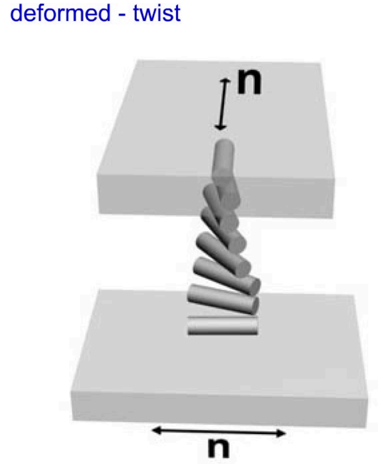
$F$: force per unit area [N/m$^2$]
$K_1$: splay elastic modulus [N]
$n_0$: director [-]
$\delta n(z)$: vector perpendicular to plates [-]
$E$: electric field [V/m]
$d$: thickness of cell [m]

# Elastic constants

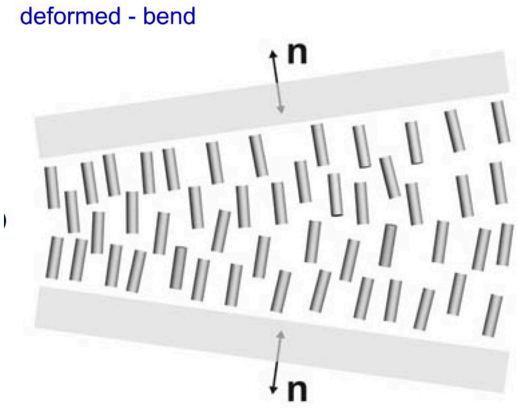
$K_1$: splay constant




$K_2$: twist constant




$K_3$: bend constant




http://www.personal.kent.edu/~bisenyuk/liquidcrystals/nematics1.html

# Nematic liquid crystal display

nematic
liquid crystal display

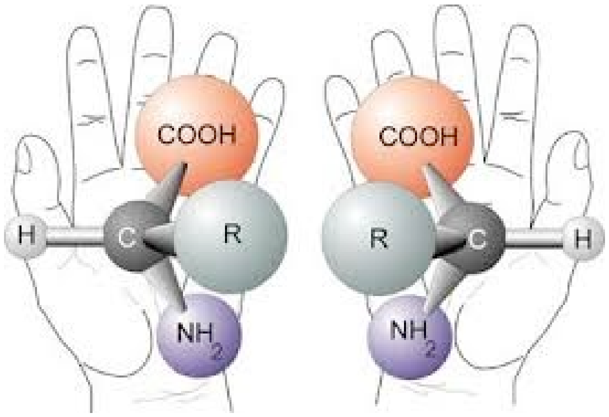
https://seminarlinks.blogspot.ch/2014/04/ferroelectric-liquid-crystal-display.html

# Outline: Liquid crystals

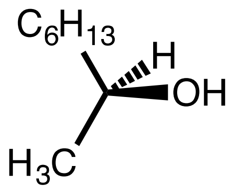
- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Lyotropic liquid crystals

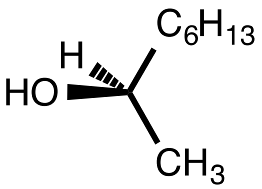
# Chiral phases

**Chiral object:** An object whose mirror image is not superimposable.




2-octanol has two enantiomers:




**Chiral molecules:** Only the spatial arrangement of their atoms differs.

(S)-2-octanol (R)-2-octanol

Chiral molecules are optically active.

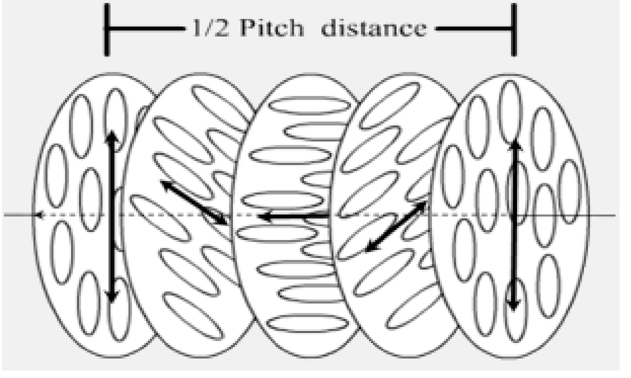
A 1:1 mixture of the two enantiomers is called racemic; it is not optically active.

# Chiral nematic phase (Cholesteric phase)

A nematic phase formed with chiral molecules has **chirality**, it has **no long-range translational order** and a **low viscosity.**

http://barrett-group.mcgill.ca

**Pitch:** The average orientation of molecules in a plane twists around the main axis as a helix



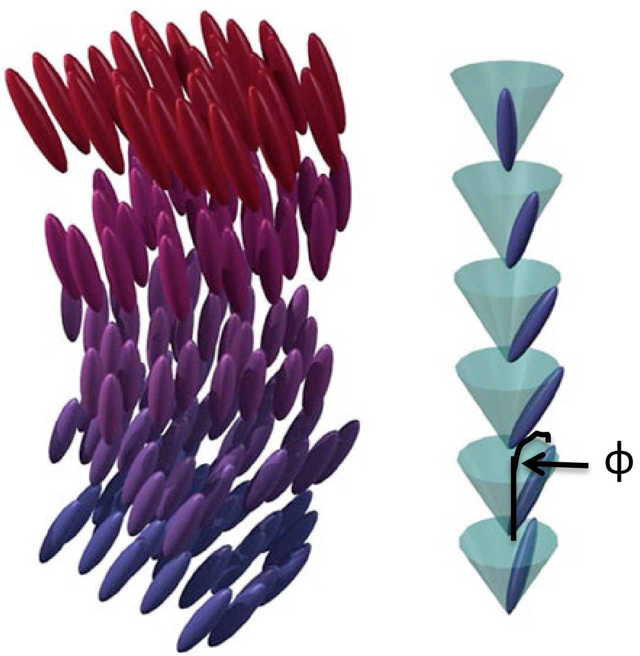

Ferrarini, A.; Pieraccini, S.; Masiero, S.; Spada, G. P. *Beilstein Journal of Organic Chemistry* **2009**, *5*.

**Pitch:** The length of a chiral nematic phase over which the director rotates by 360°.

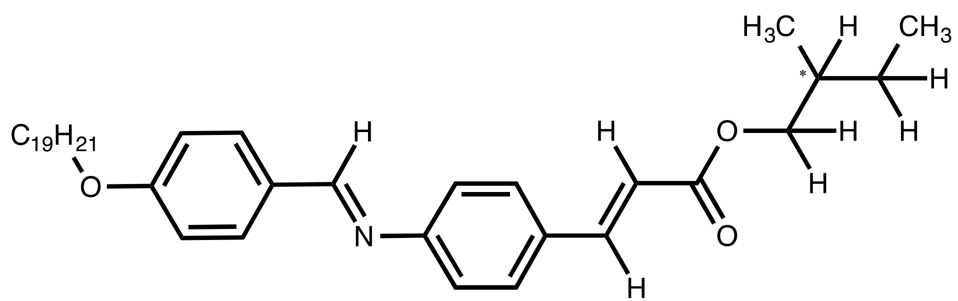
# Chiral smectic phase

Chiral moieties are typically the terminal groups of liquid crystals because end-functionalized mesogens are easier to synthesize than mesogens with chiral groups in their center.

Molecules are aligned in a layered structure with a tilt angle θ with respect to the layer normal.
The molecules precess around the direction of the director.



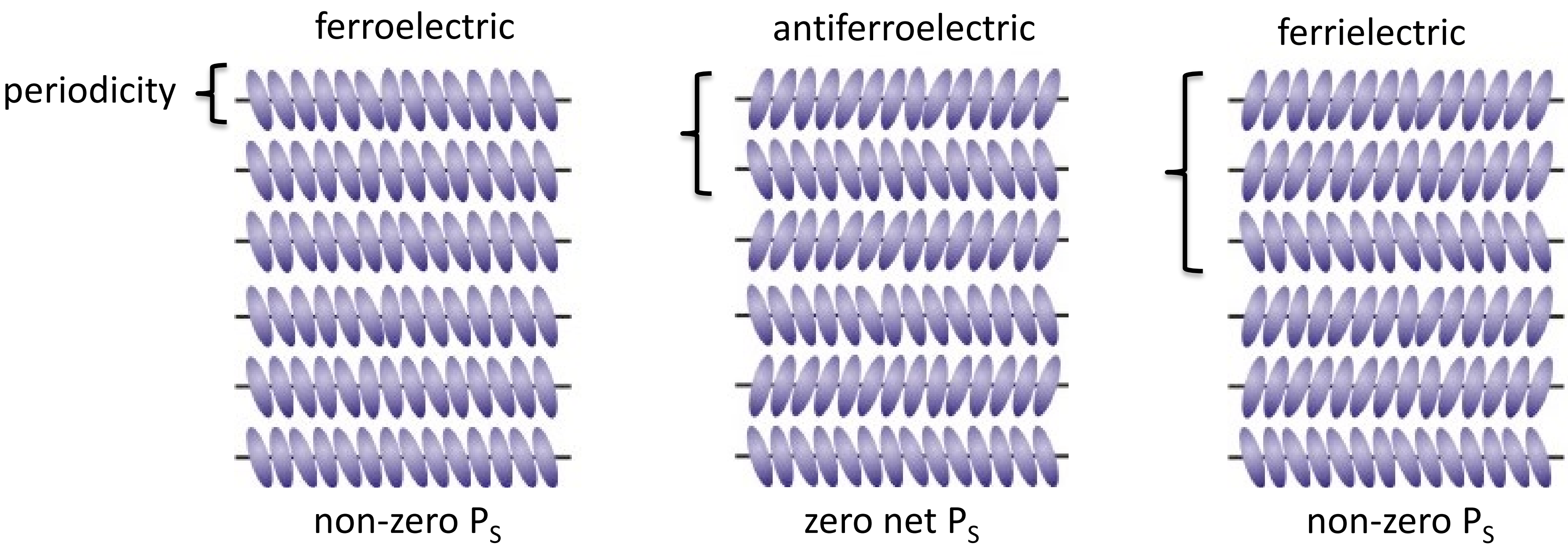

http://barrett-group.mcgill.ca




P-(m-decyloxybenzylindene)-p-amino-(2-methyl-butyl) cinnamate (DOBAMBC)

If chiral mesogens display a net polarization, they are ferroelectric.

# Chiral smectic C phases




The antiferrielectric smectic C phase has an alternating tilting structure but the structure is not symmetrical the phase has a non-zero $P_S$.

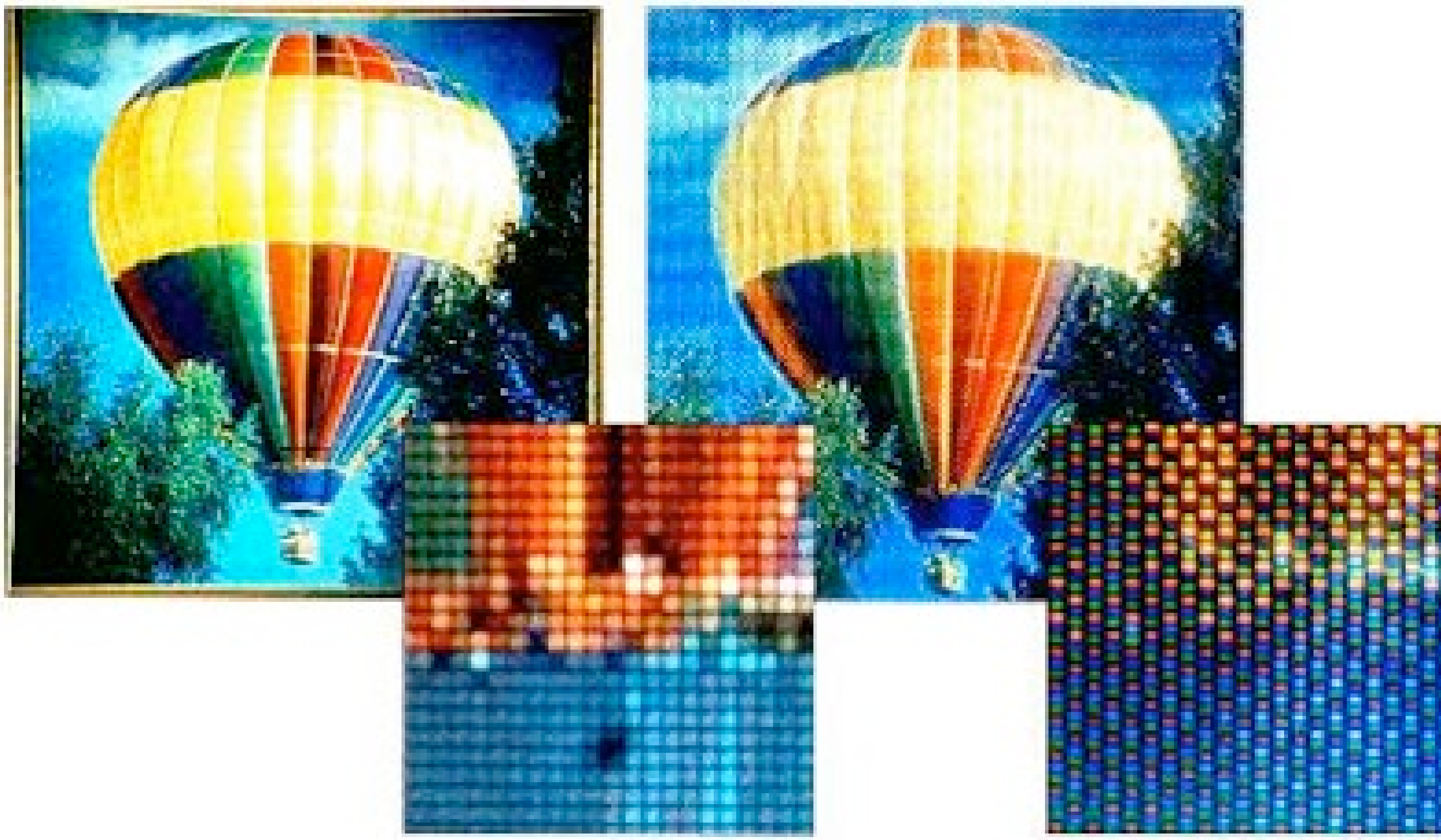


http://www-g.eng.cam.ac.uk/CMMPE/lcintro2.html

# Ferroelectric liquid crystals

ferroelectric
liquid crystal display

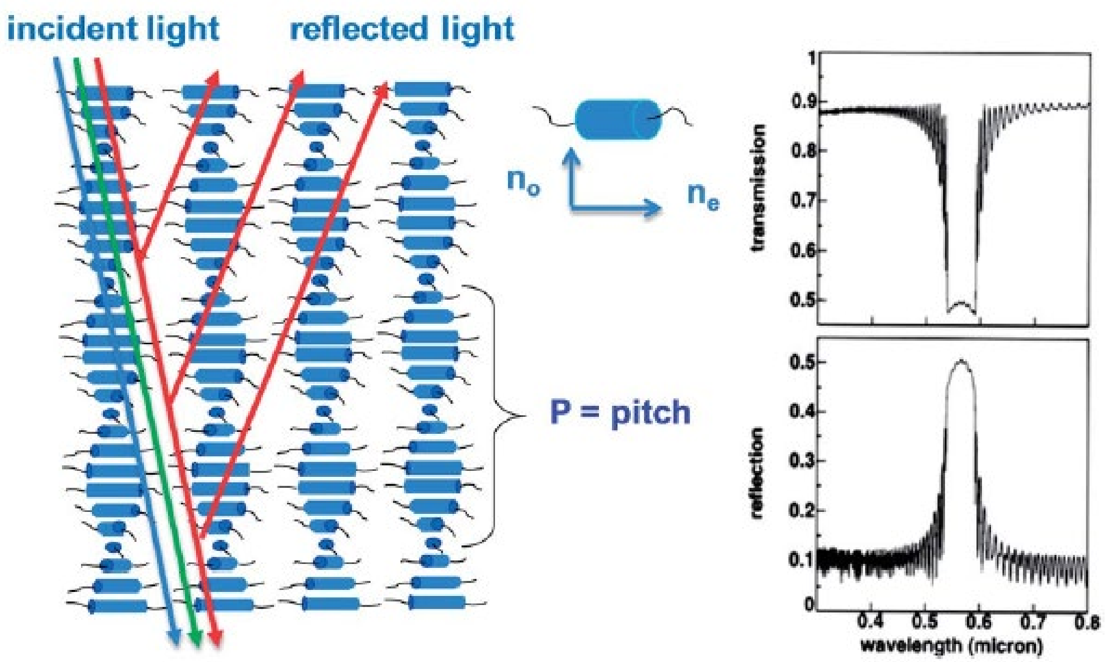
nematic
liquid crystal display



https://seminarlinks.blogspot.ch/2014/04/ferroelectric-liquid-crystal-display.html

# Chiral nematic phase

**Helical structure:** This structure can reflect light if the helical axis is parallel to the light propagation direction.
If the pitch length is similar to the wavelength of light, only certain wavelengths constructively interfere.




$\lambda_B$: Bragg reflection wavelength [m]
$\bar{n}$: average refractive index [-]
*P*: pitch length [m]
Θ: angle between incident light and helix [rad]

$$\lambda_B = \bar{n} P \cos\Theta$$

$$\bar{n} = \frac{n_e + n_o}{2}$$

Mulder, D. J.; Schenning, A. P. H. J.; Bastiaansen, C. W. M. *Journal of Materials Chemistry C* **2014**, *2*, 6695

The pitch length is temperature dependent.
At high temperatures: The angle at which the director changes is large ➔ the pitch is small.
At low temperatures: The angle at which the director changes is smaller ➔ the pitch is longer.

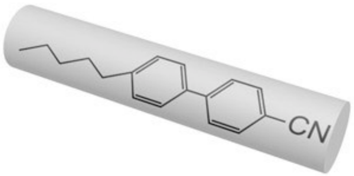
# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

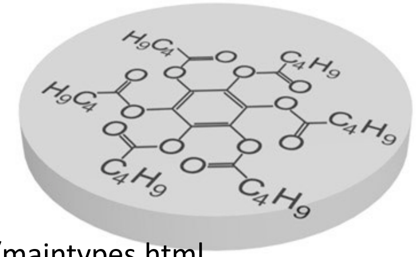
# Mesogens

Molecules that form liquid crystals; these are anisotropic molecules with long range orientational order.

**Calamitic molecules:** Rod-like mesogens made from a rigid aromatic core to which at least one aliphatic chain is attached.




**Discotic molecules:** Disk-like mesogens



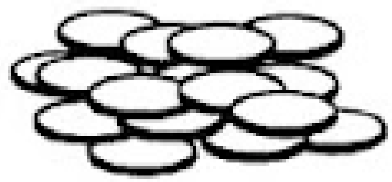

http://www.personal.kent.edu/~bisenyuk/liquidcrystals/maintypes.html

The ordering within columns is fluid-like.
The columns order into a lattice.

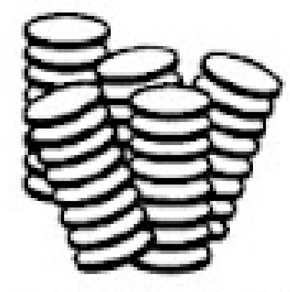
Within a homologous series:

The nemantic phase is stable if alkyl chain is short.
The smectic phase is stable if alkyl chain is long.

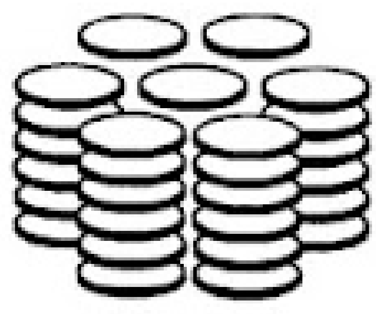
# Discotic mesogens



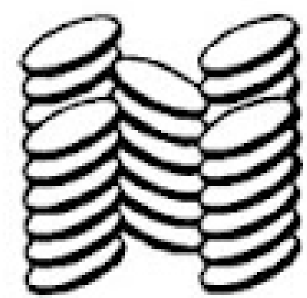
nematic-discotic ($N_D$)



nematic-columnar ($N_{Col}$)



columnar-hexagonal ($Col_h$)



columnar-rectangular ($Col_r$)

# Classification of columnar mesophases

symmetry group

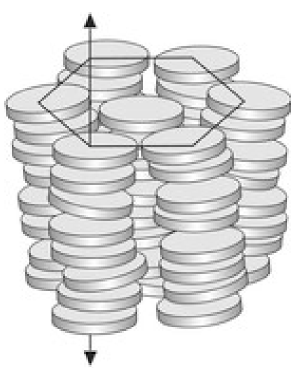
- hexagonal
- rectangular
- oblique

molecular arrangement within columns

- ordered
- disordered

designation

$D_{ho}$ $D_{hd}$ $D_{rd}$ $D_{ob.d}$

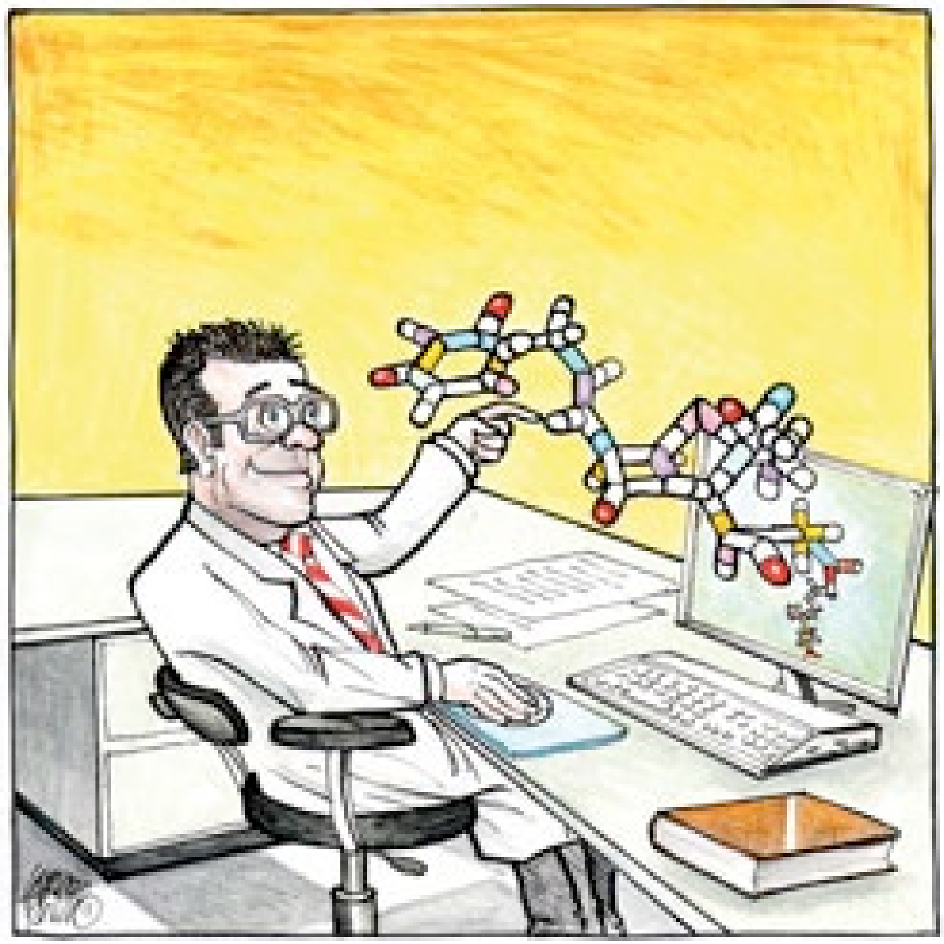


$D_{hd}$

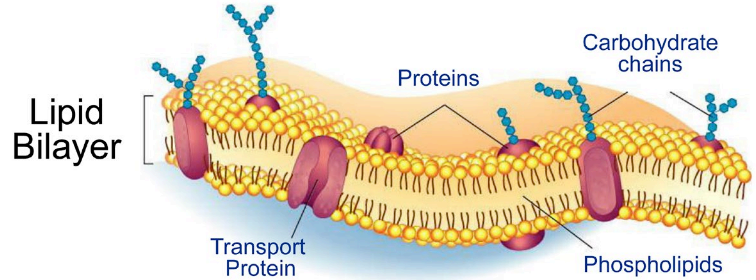
# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Lyotropic liquid crystals

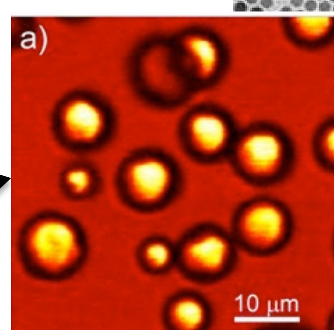
# Characterization of liquid crystals

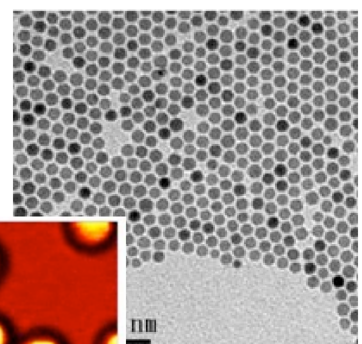


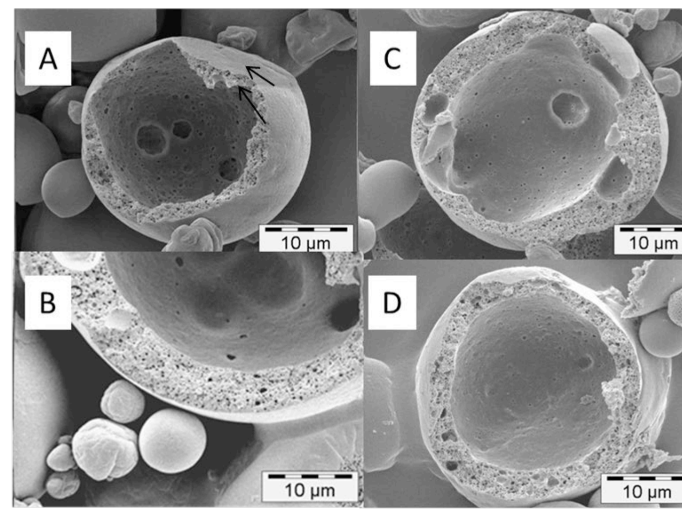
# How would you visualize these samples?





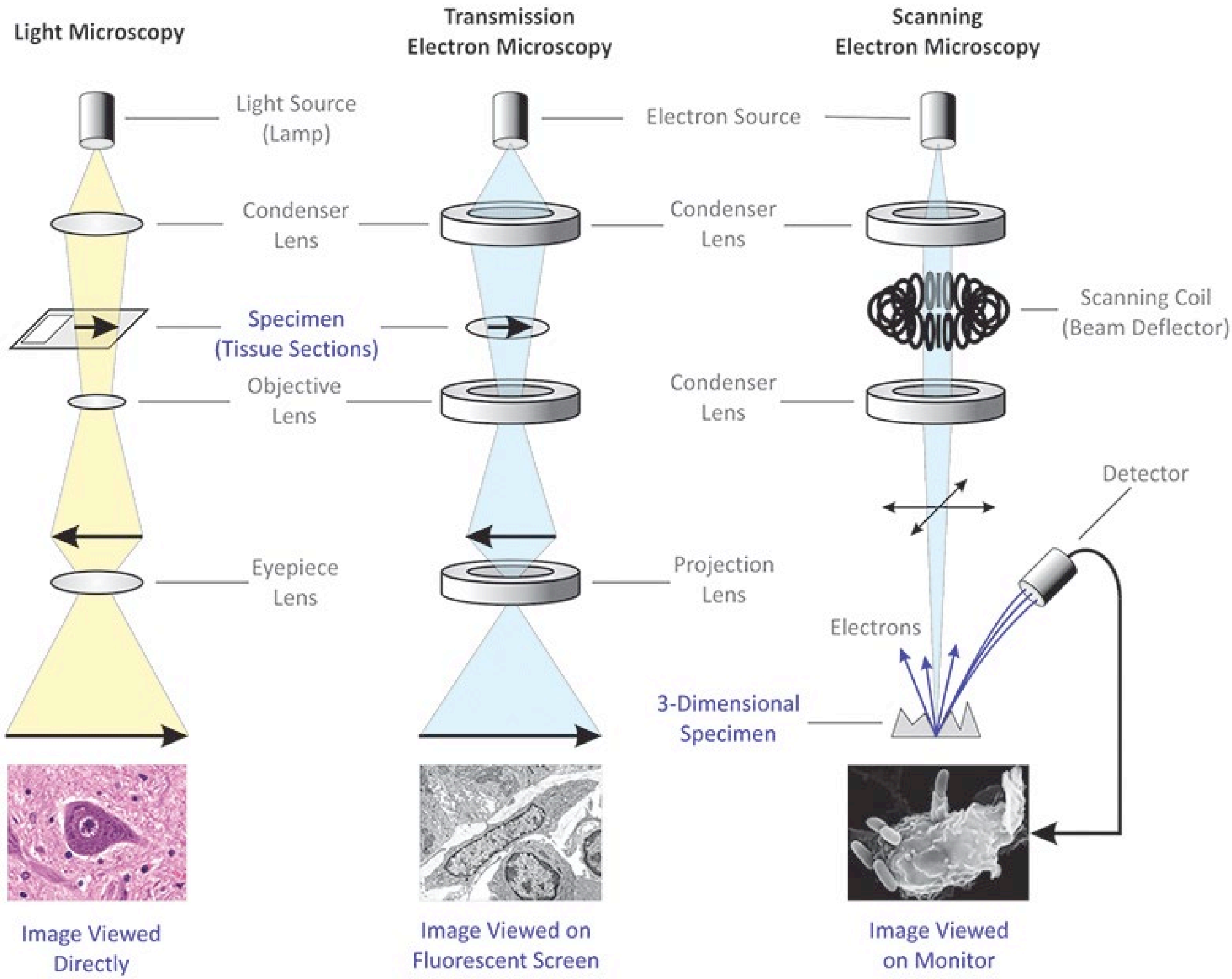





L. Frenkel, Y. Rosenberg and M. Rosenberg, *AIMS Agriculture and Food*, 2016, **1**, 33-51

# Microscopy



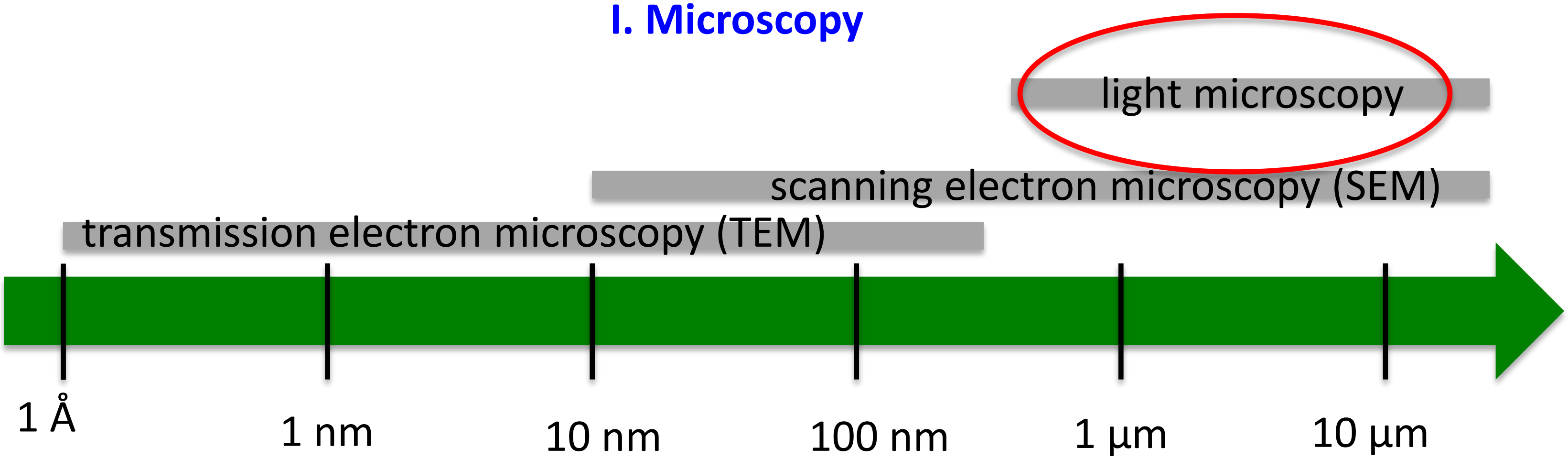

Resolution limit: ≈ 200 nm (for standard optical microscopes) | 0.1 nm | 1-10 nm



http://www.histologyguide.org/01_Introduction/Microscopes.html

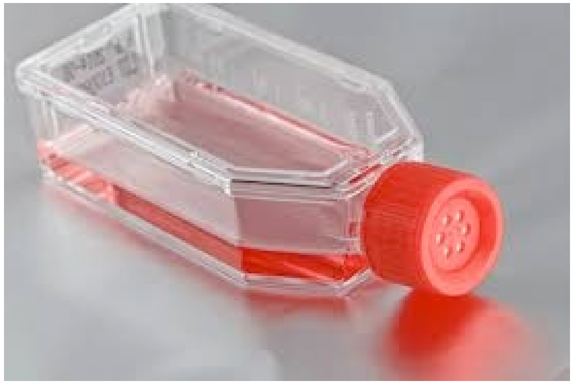
# Characterization of soft materials

**I. Microscopy**

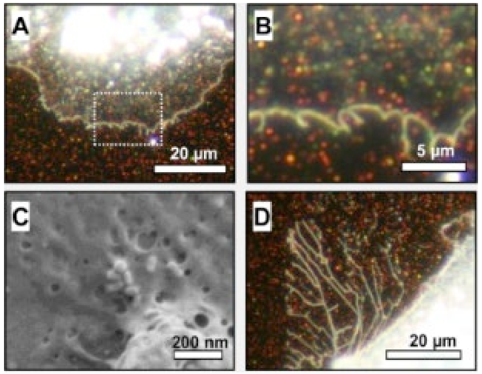


# Light microscopy

Cell cultures

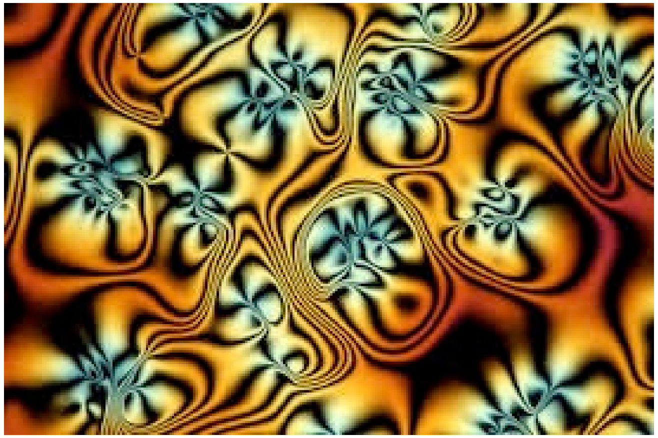


Localization of gold nanorods




C. Rosman *et al.*, *Beilstein Journal of Nanotechnology* **5**, 2479 (2014)

Liquid crystals

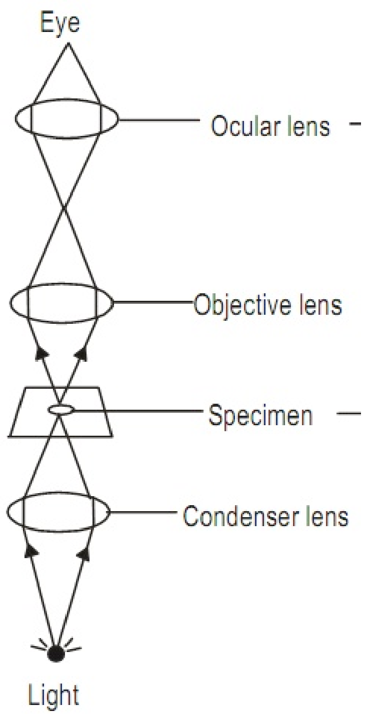


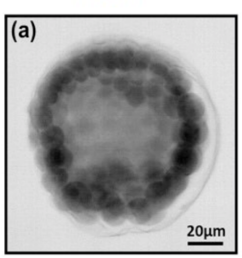
http://www.nsf.gov/news/mmg/mmg_disp.jsp?med_id=68655

# Light microscopy

**Modes of operation:**

Bright field



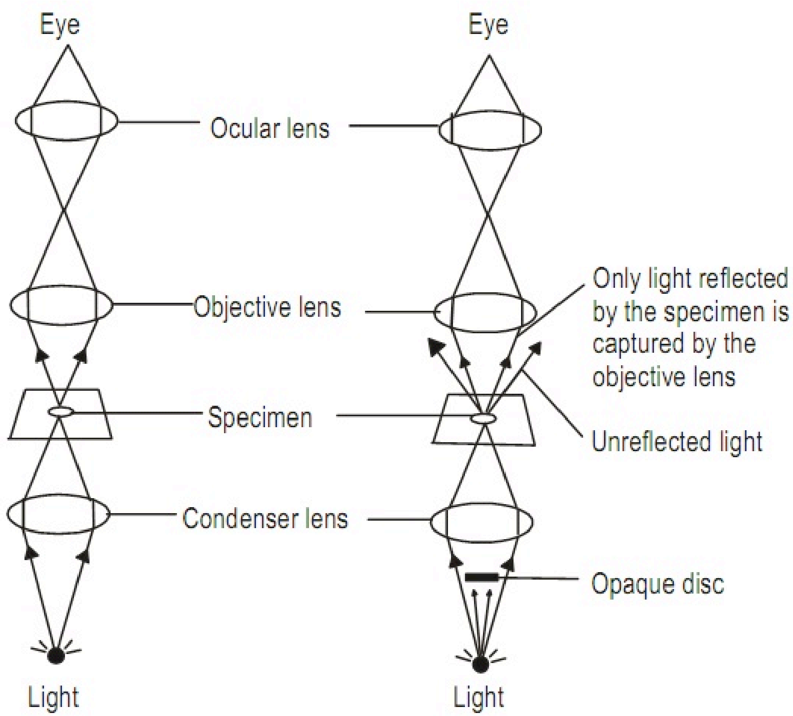


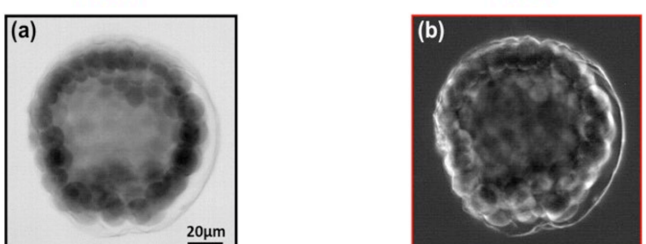

http://www.opticsinfobase.org/ol/fulltext.cfm?uri=ol-36-20-3987&id=222960

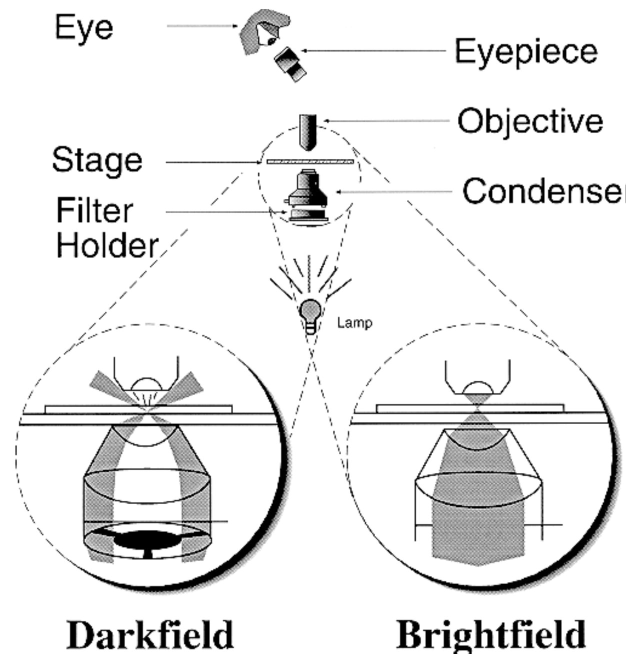
# Light microscopy

**Modes of operation:**

Bright field Dark field




http://public.wsu.edu/~omoto/papers/Fig1.html

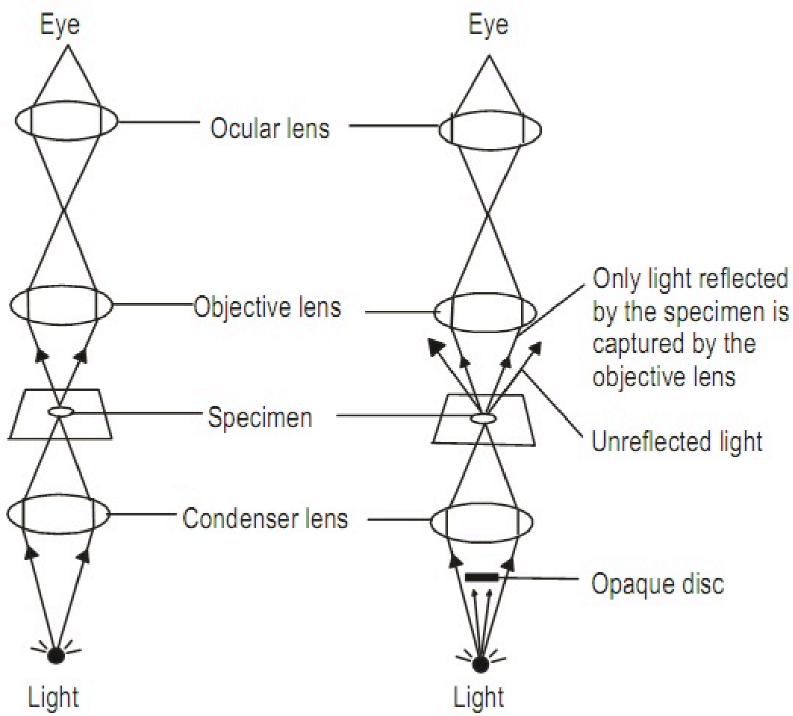


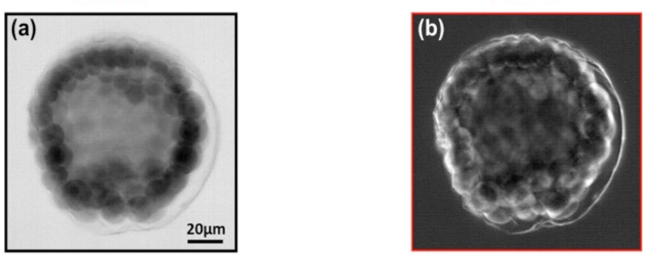
http://www.opticsinfobase.org/ol/fulltext.cfm?uri=ol-36-20-3987&id=222960

# Light microscopy

**Modes of operation:**

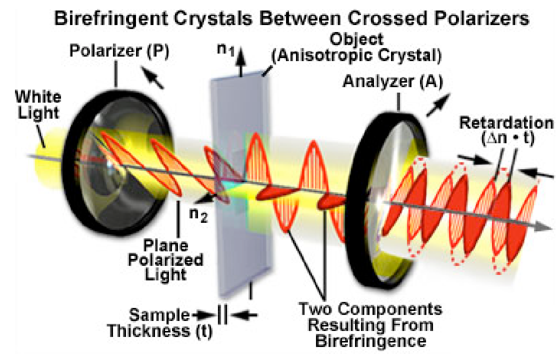
Bright field　　Dark field




http://www.opticsinfobase.org/ol/fulltext.cfm?uri=ol-36-20-3987&id=222960

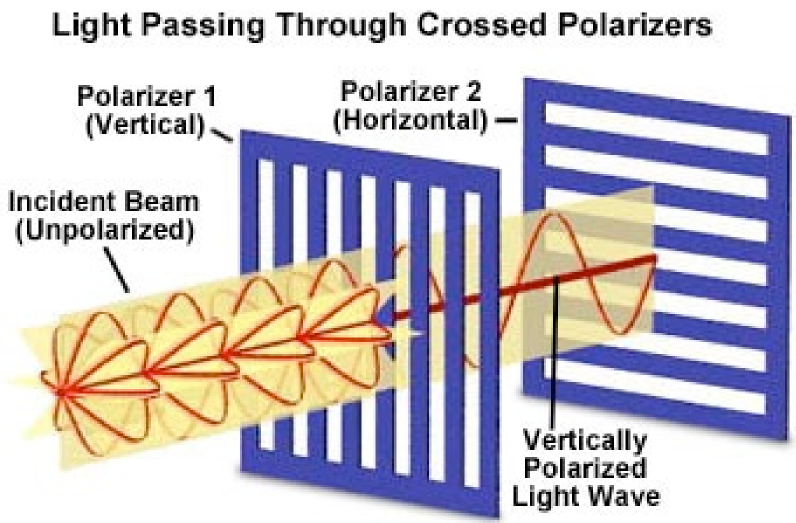
Polarized light can be used for the analysis of birefringence (e.g. for liquid crystals)



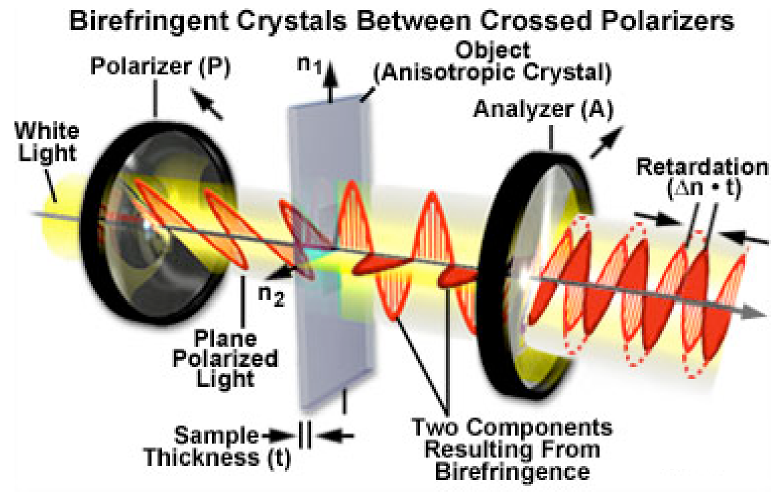

http://www.microscopyu.com/articles/polarized/birefringenceintro.html

http://www.intercomet.com/liquid_crystal.html

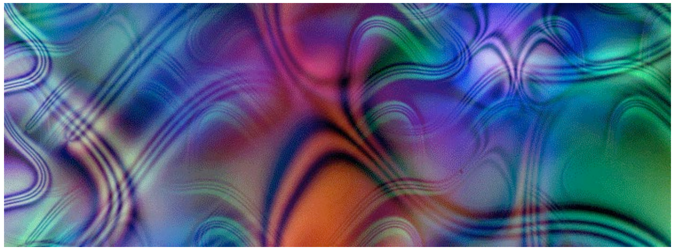
# Polarized light microscopy




http://www.olympusmicro.com/primer/lightandcolor/polarization.html



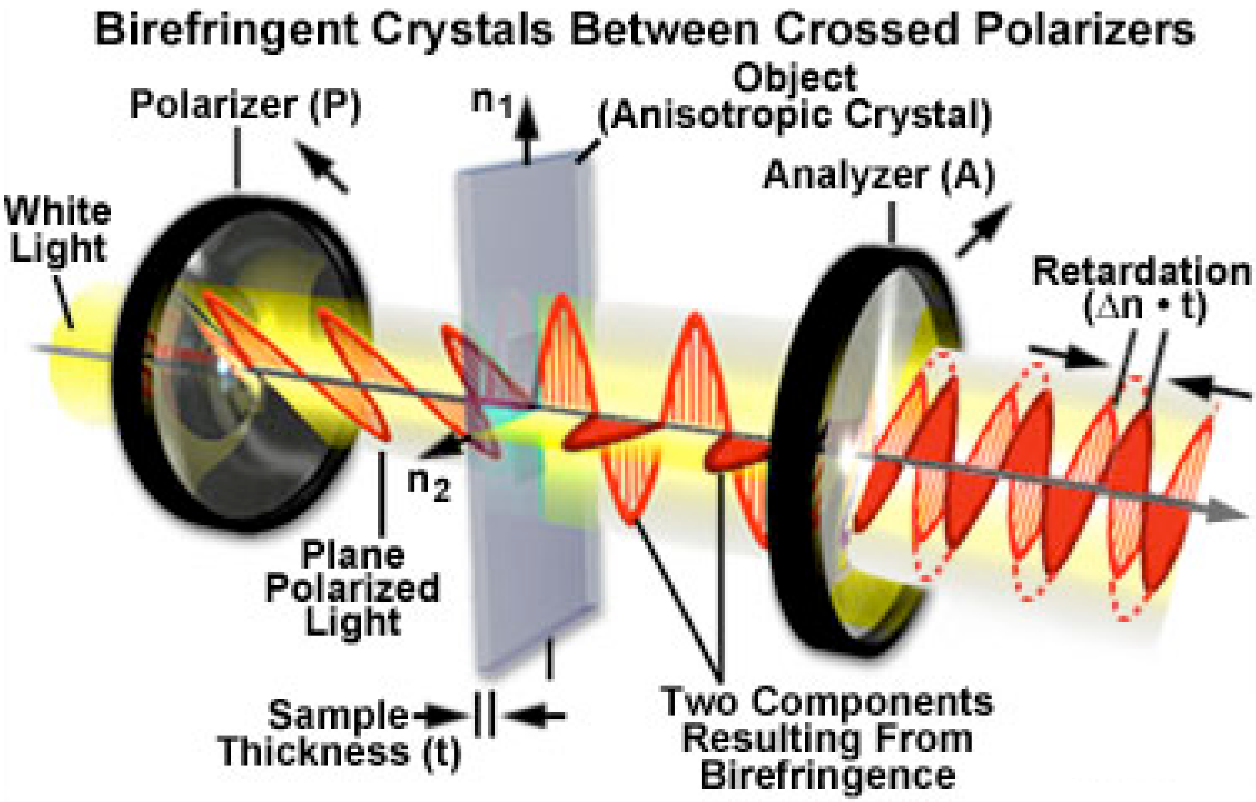

http://www.microscopyu.com/articles/polarized/birefringenceintro.html



http://www.intercomet.com/liquid_crystal.html

# Polarized light microscopy

identification of type of liquid crystal

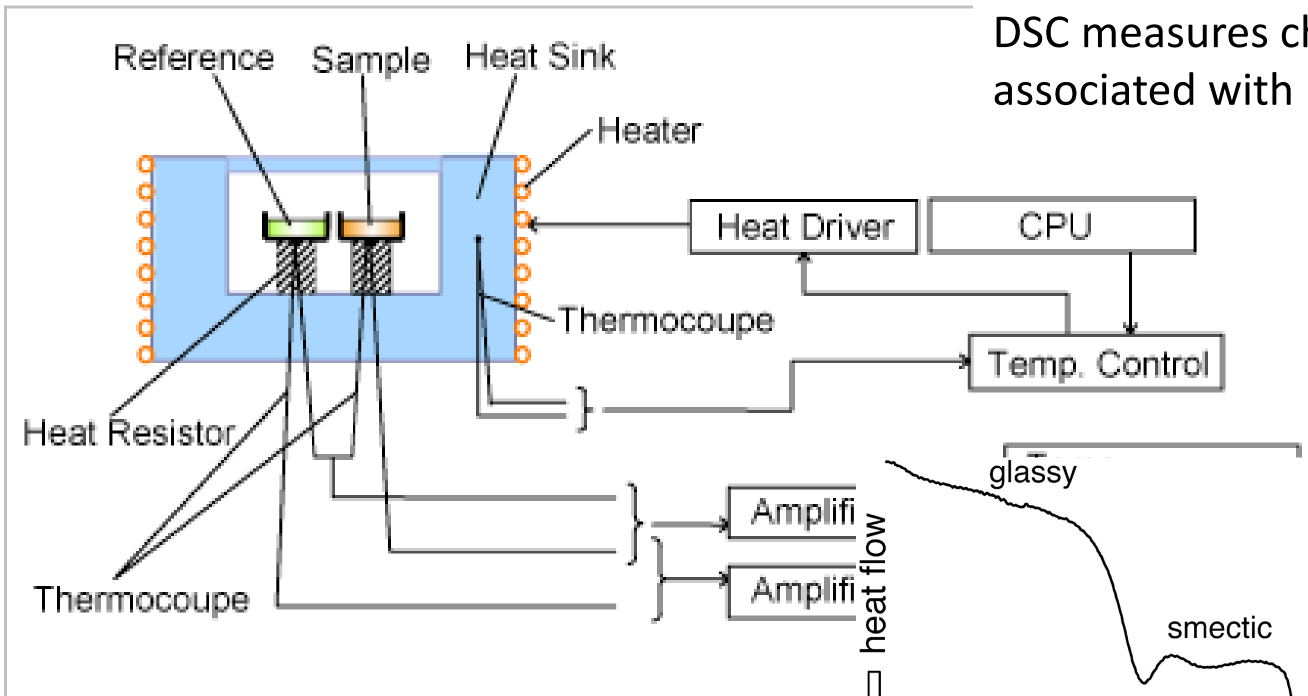



http://www.microscopyu.com/articles/polarized/birefringenceintro.html

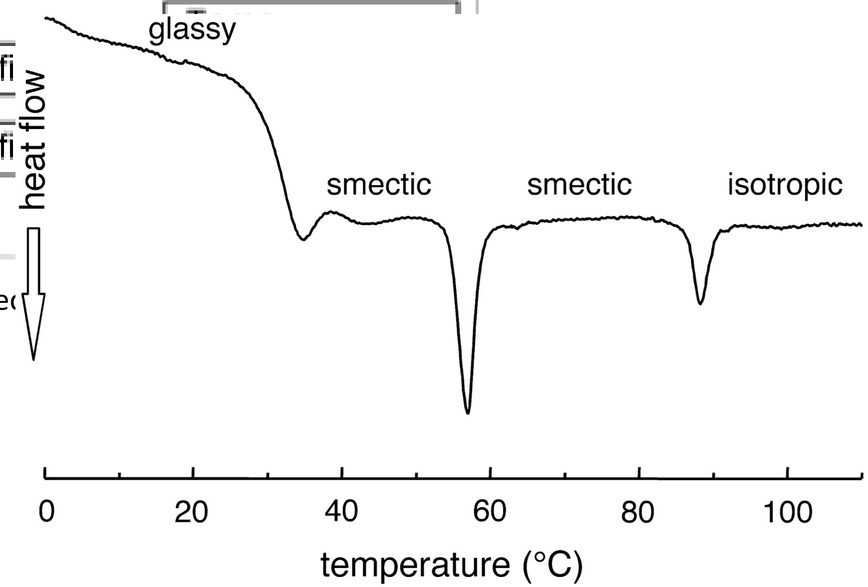
Most commonly, cross-polarizers are oriented 90° to each other.

# Differential scanning calorimetry (DSC)

DSC measures changes in enthalpy associated with phase transitions.




http://www.hitachi-hitec-science.com/en/products/thermal/tec




Hwang, J. J.; Iyer, S. N.; Li, L.-S.; Claussen, R.; Harrington, D. A.; Stupp, S. I. *Proceedings of the National Academy of Sciences* **2002**, *99*, 9662

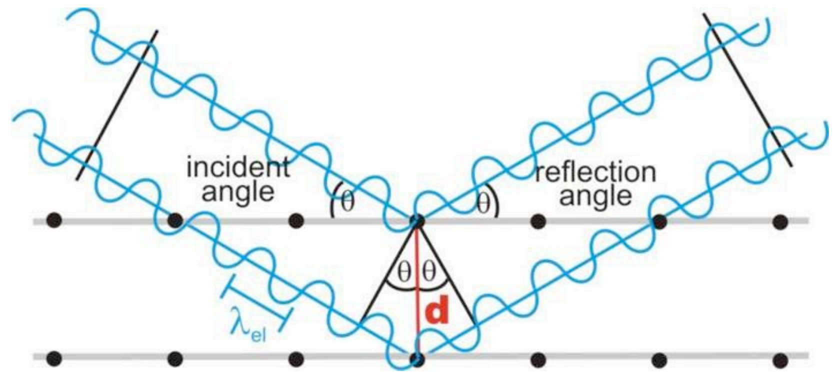
# X-ray diffraction (XRD)

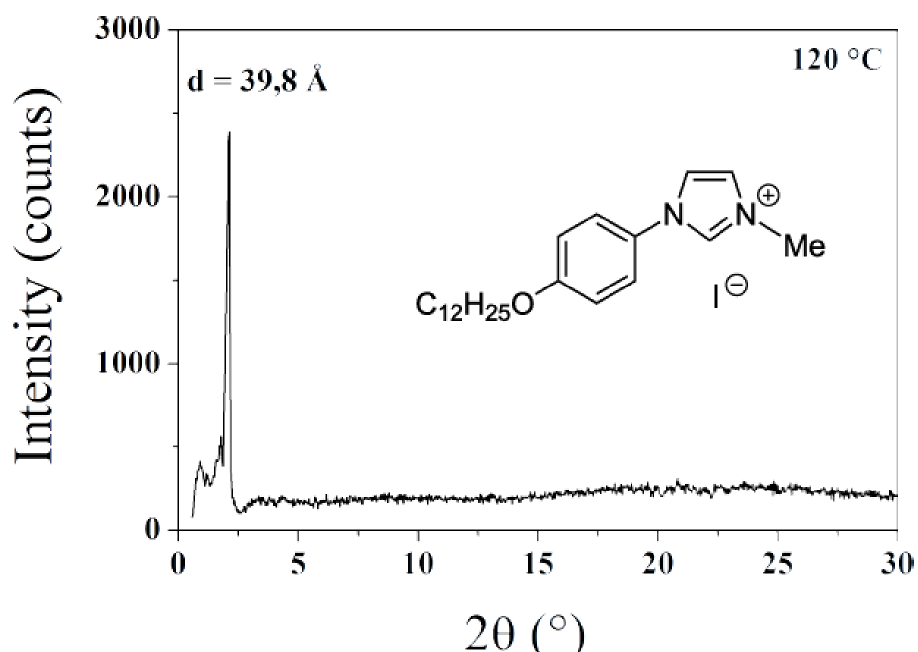
Bragg reflection:

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

$$q = \frac{4\Pi}{\lambda}\sin\theta$$

$\lambda \approx 1.5$ Å



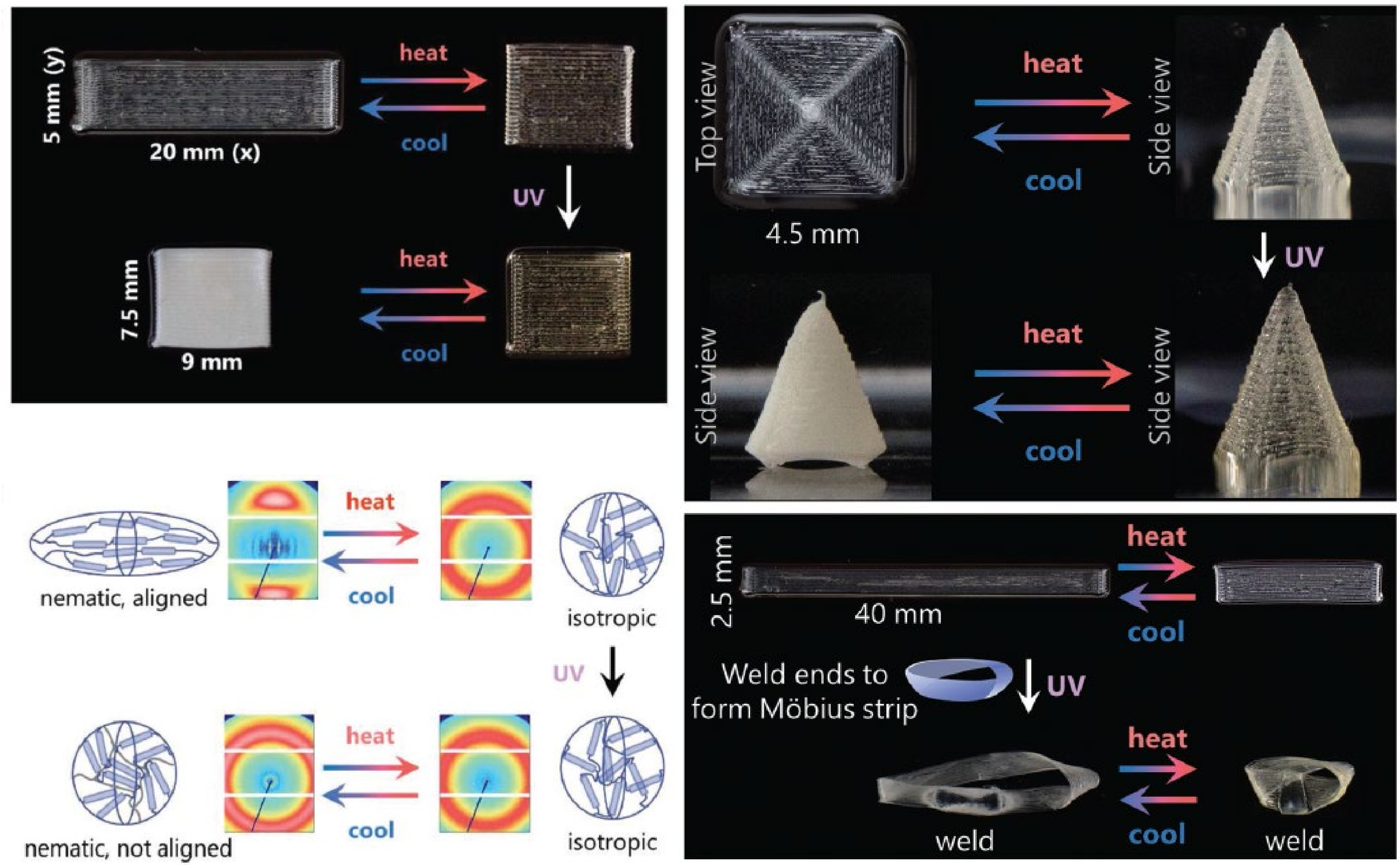




Fouchet, J.; et al. *Beilstein Journal of Organic Chemistry* **2009**, *5*.

# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Example
- Lyotropic liquid crystals

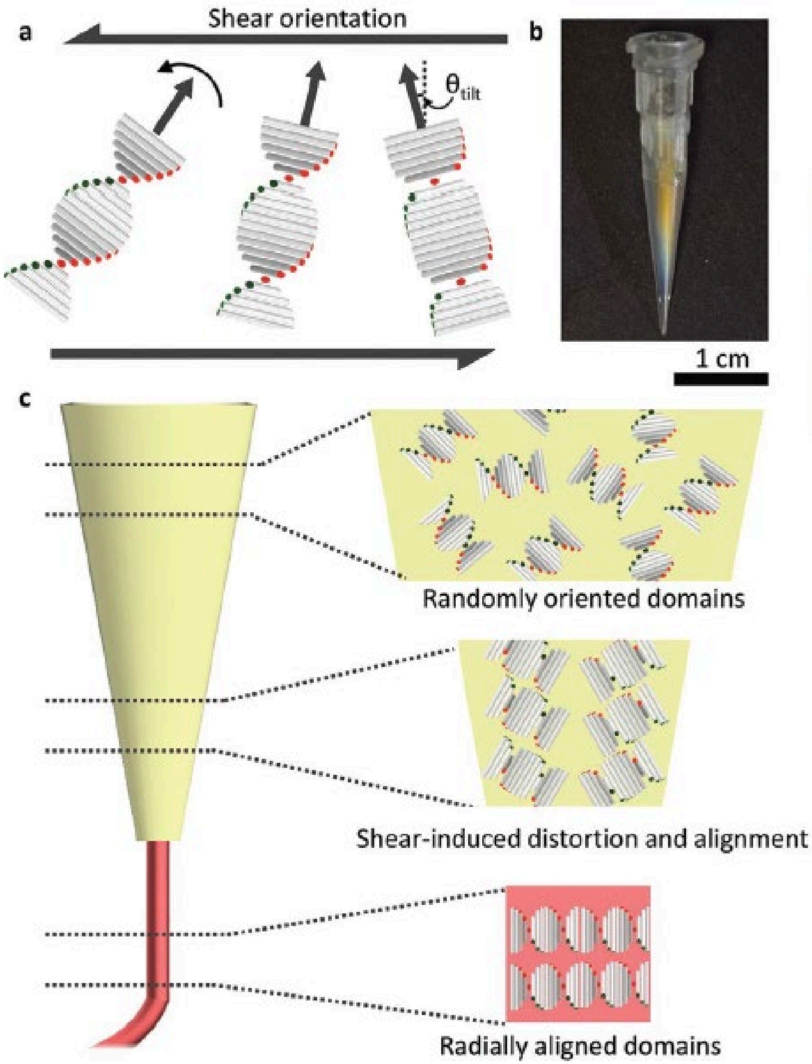
# Example: 3D printing of liquid crystal elastomers

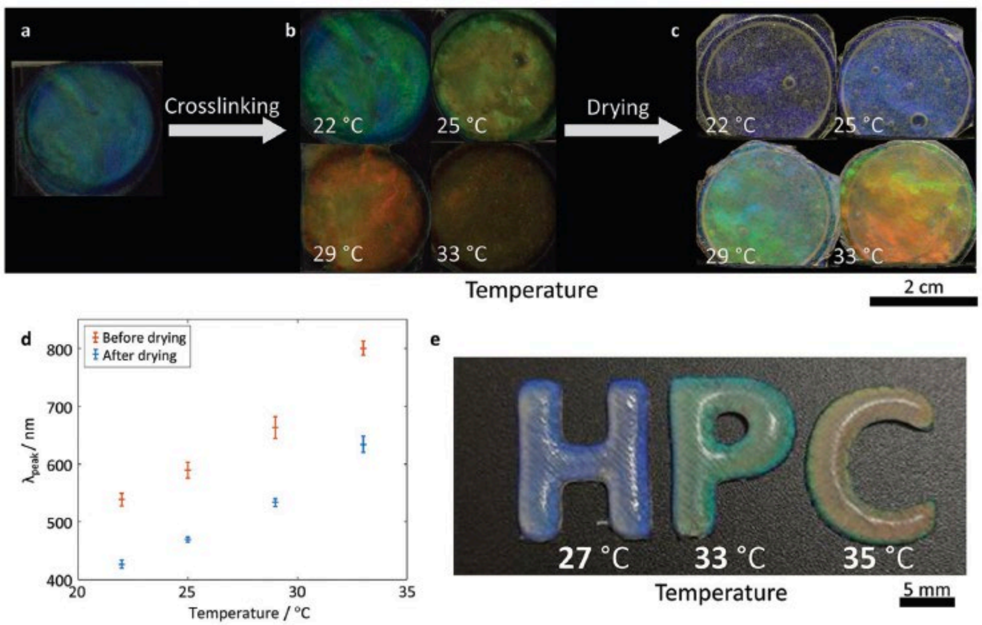





Davidson, E. C.; et al. *Advanced Materials* **2020**, *32* (1), 1905682. https://doi.org/10.1002/adma.201905682

# Example: 3D printing of cholesteric liquid crystals



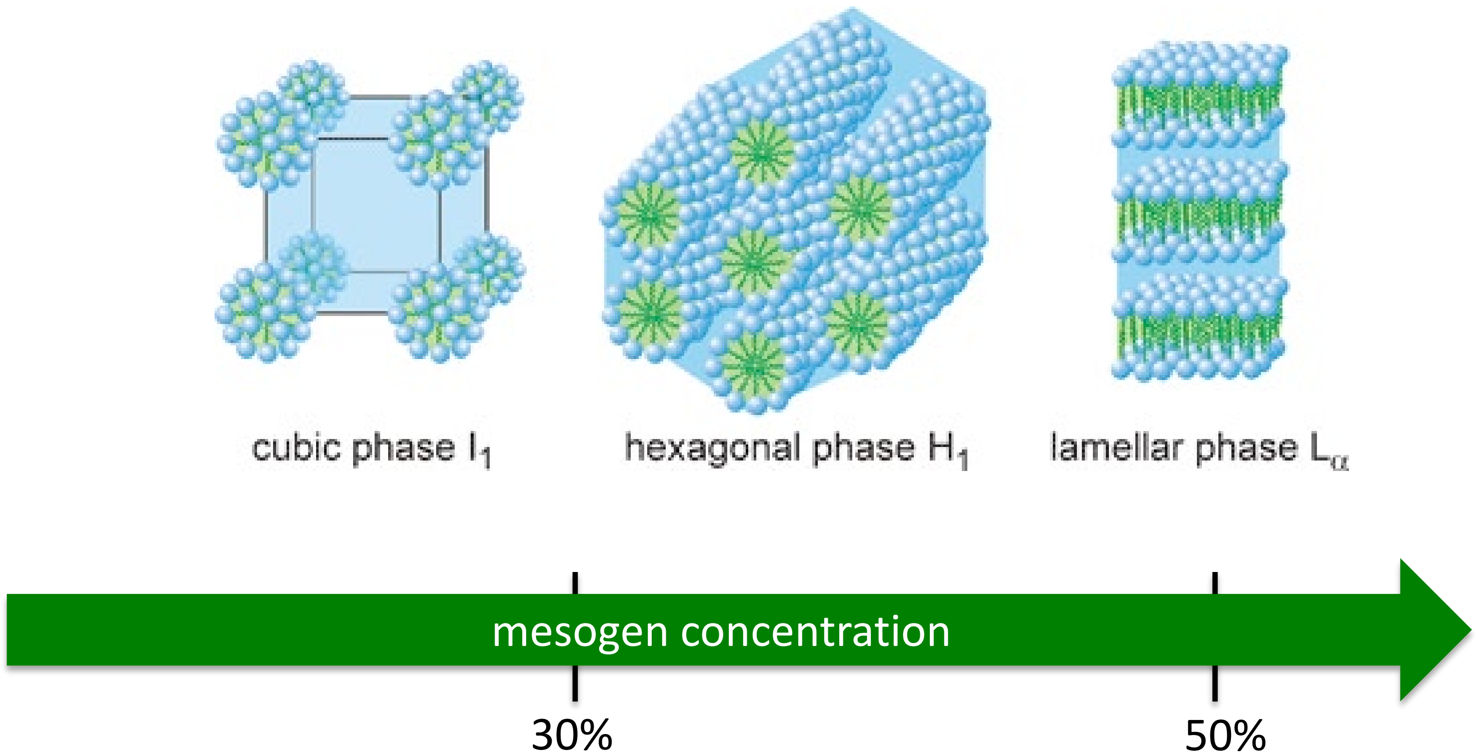

C. L. C. Chan, et al, *Advanced Functional Materials* **2022**, 2108566

# Outline: Liquid crystals

- Introduction
- Thermotropic liquid crystals
  - Calamitic mesogens
    - Influence of structure on transition temperature
    - Interactions with light
    - Defects
    - Liquid crystal displays
    - Chiral liquid crystals
  - Discotic mesogens
- Characterization of liquid crystals
- Lyotropic liquid crystals

# Lyotropic liquid crystals

Lyotropic liquid crystals form in solution. Liquid crystals form if the solute concentration exceeds some values.

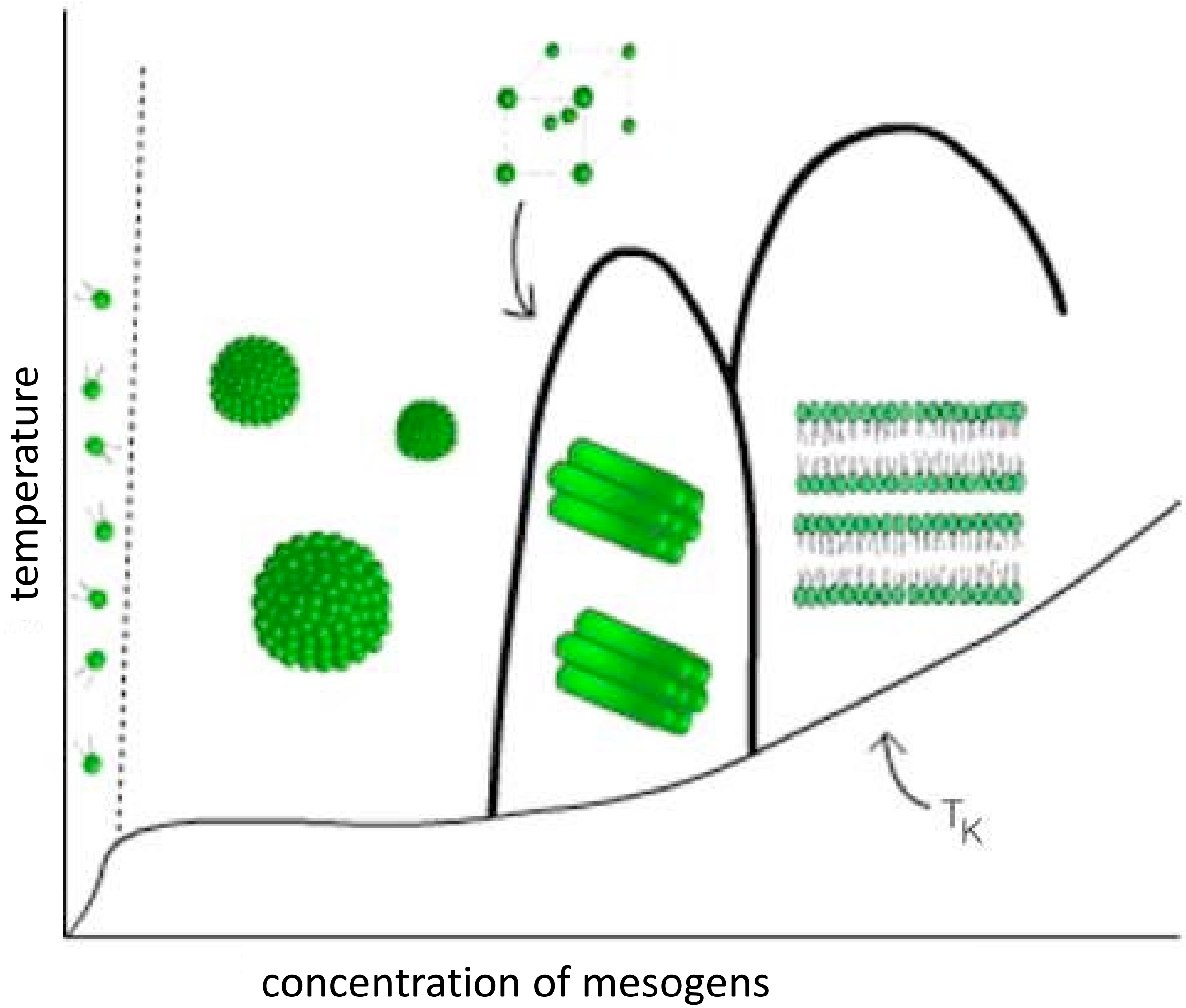



*Examples:* Amphiphilic molecules with a hydrophilic head and a hydrophobic chain such as phospholipids, surfactants.



Blunk, D.; Bierganns, P.; Bongartz, N.; Tessendorf, R.; Stubenrauch, C. *New Journal of Chemistry* **2006**, *30*, 1705.

# Lyotropic liquid crystals




http://plc.cwru.edu/tutorial/enhanced/files/llc/phase/phase.htm