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Soft Matter: Introduction and Overview

Lecture 25

Glasses and Metastable States

Lecture 26

Soft Matter: Introduction and Overview

Liquid Crystals

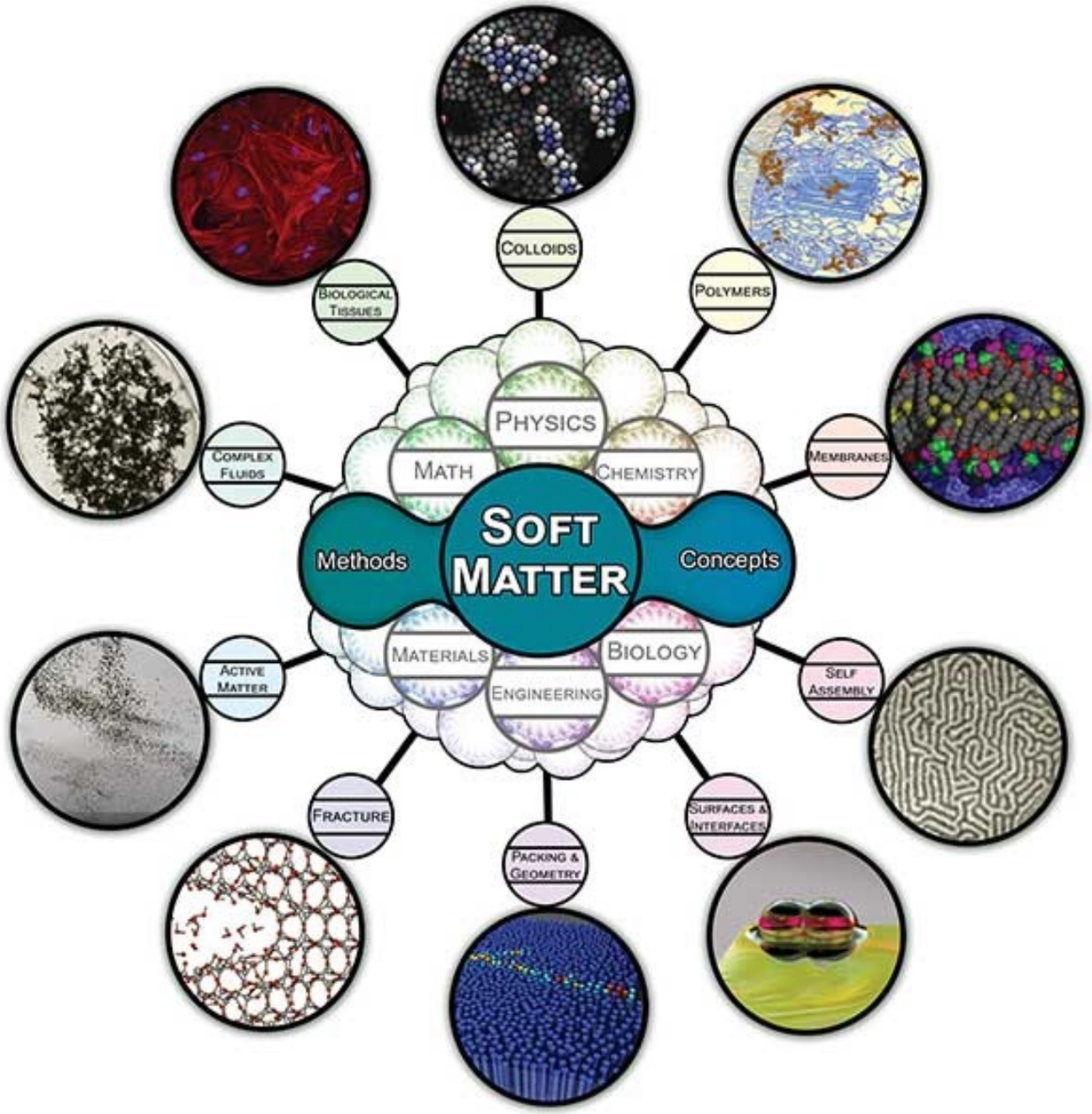
Lecture 27

Soft Matter: Onsager Theory and the Statistical Mechanics of Nematics

How soft is soft?

- When a system can be altered by stresses of the size that might be found in thermal fluctuations, it is called soft matter.

- So how big are thermal fluctuations, and what can they do?



https://www.aps.org/publications/apsnews/201505/backpage.cfm

Thermal energy fluctuations – Boltzmann

Q1

- The Boltzmann Distribution:
  The probability p_i that part of an equilibrium system will be in state i is a function of its energy and the temperature of the system:

$$p_i \propto e^{-\varepsilon_i / kT}$$

where ε_i is the energy of the state (in J),
k is Boltzmann's constant (1.38×10^{-23} J K^{-1}), and
T is the temperature (in K)

- So, if a molecule has two possible states with energies ε_i and ε_j then the ratio of the number of molecules in each of these states is:

$$N_i / N_j = p_i / p_j = e^{-\left(\varepsilon_i - \varepsilon_j / kT\right)}$$

Thermal energy fluctuations – kT

$$N_i/N_j = p_i/p_j = e^{-\left(\varepsilon_i-\varepsilon_j/kT\right)}$$

So, if ε_i-ε_j >> kT, very few molecules are ever thermally excited into the higher state, so very little change/alteration is possible.

$\left(\varepsilon_i-\varepsilon_j/kT\right)$	N_i/N_j
0.0	1.0
0.5	0.607
1.0	0.368
3.0	0.05
10.0	0.000045
50.0	0.000000000000000000000019

So how big is kT?

k =1.38×10^{-23} J K^{-1}

e = 1.6×10^{-19} C

N_A = 6.02×10^{23} mol^{-1}

cal = 4.18 J

T (°C)	T (K)	kT (J)	kT (eV)	kT (J/mol)	kT (kJ/mol)	kT (kcal/mol)
0	273	3.8×10^{-21}	0.024	2300	2.3	0.54
25	298	4.1×10^{-21}	0.026	2500	2.5	0.59
100	373	5.1×10^{-21}	0.032	3100	3.1	0.74

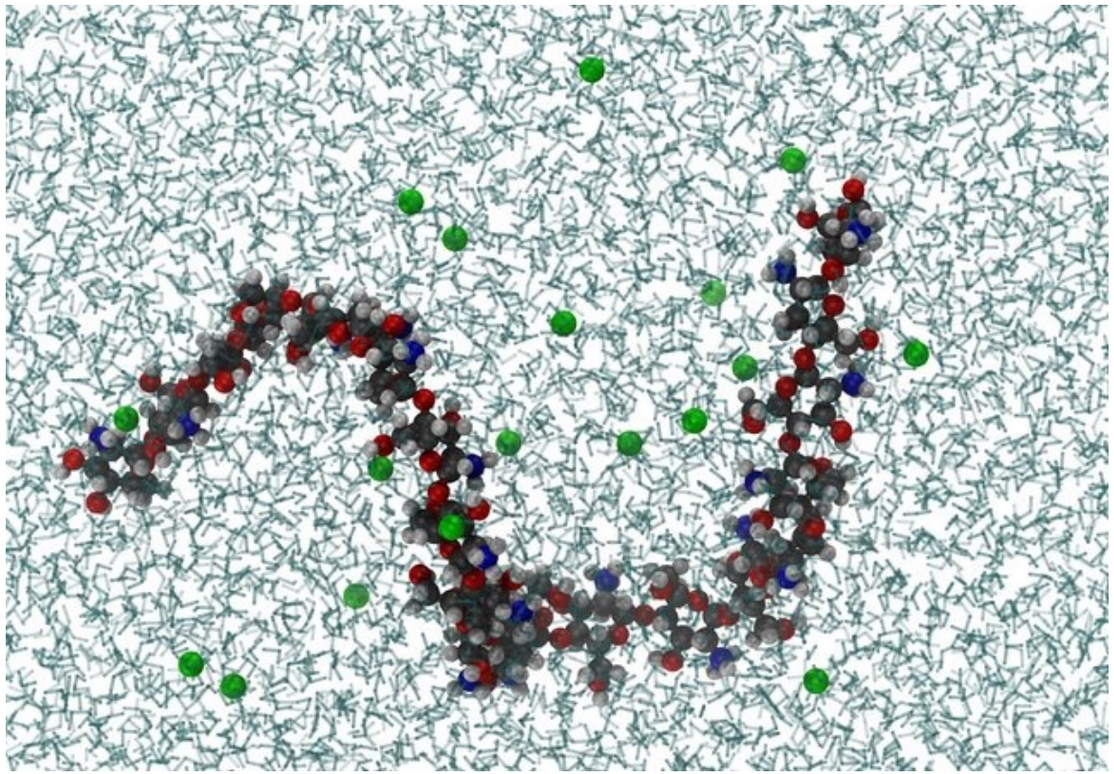
Examples of soft matter - polymers

Q2

C-C bond energy is 348 kJ/mol >> kT

C-C bond torsion is ~12 kJ/mol > kT

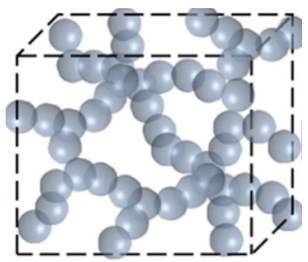
- So polymer chains don't break thermally, but can bend and twist
- Their interactions with solvents or other polymer molecules are at a similar scale, so solubility, swelling, mixing and crystallisation are all possible and can vary with temperature alone, even before chemical modifications.

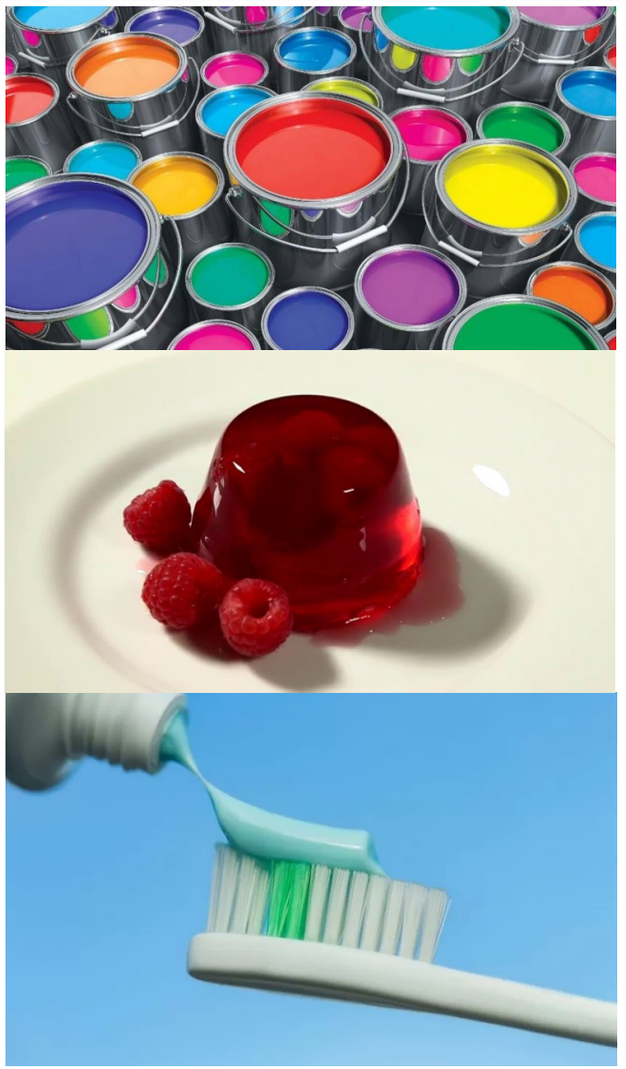


https://pubs.acs.org/doi/10.1021/acs.jpcb.5b11230

Examples of soft matter - colloids

- A colloid is a heterogeneous mixture in which the dispersed particles are between the size of a solution and a suspension.
- The small dispersed particles of a stable colloid do not settle out under gravity if their gravitational potential energy ~ kT.
- For stability, the energy barrier to particles combining and aggregating needs to be >> kT.
- At high volume fractions polymeric colloids can form a gel, and strongly influence the viscosity of the solution.

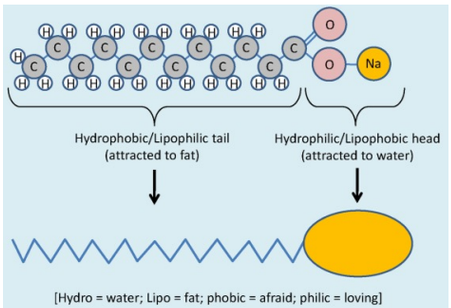




https://www.pinterest.com.au/pin/682506518500394782/
youtube.com/watch?v=ZcyK95phrNQ
dentalcaregroup.com.au/ask-dentist-armadale-how-much-toothpaste-do-you-need/

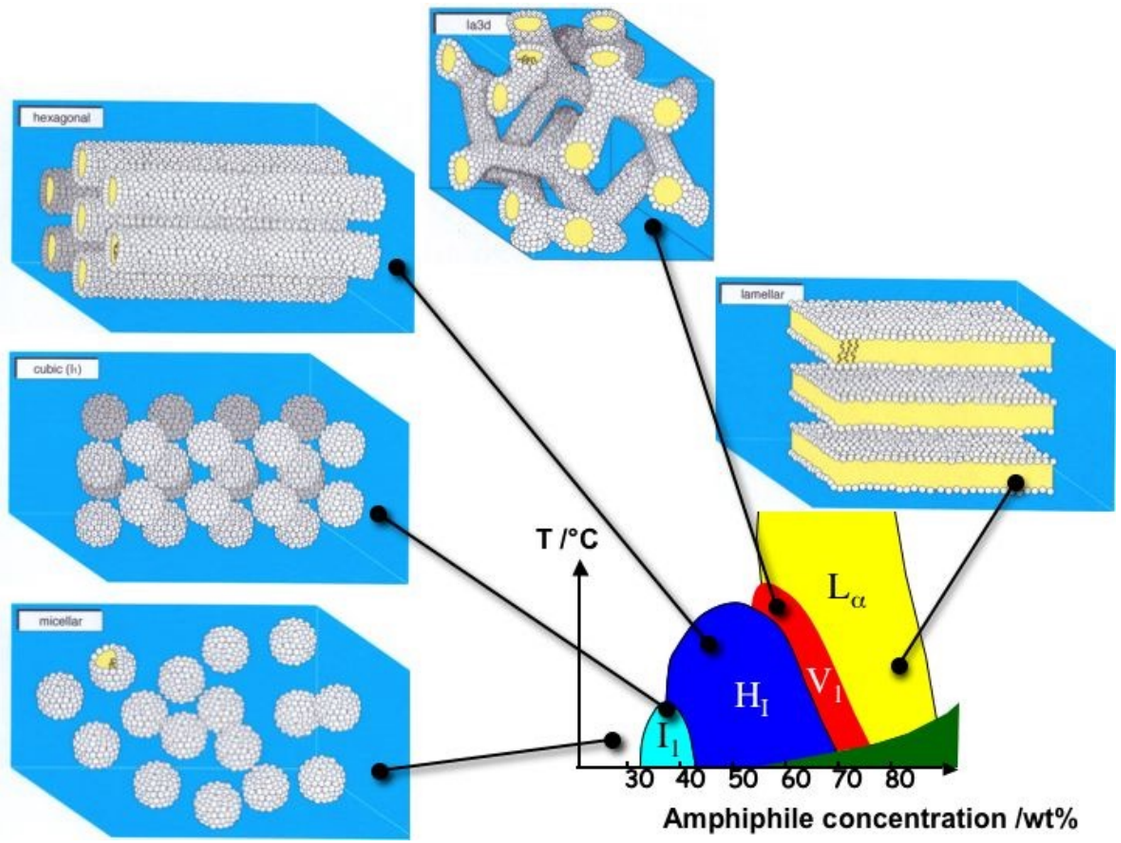
Self-organisation: the mesoscopic scale

- Amphiphiles always have one solvophilic end (here the Na^+ will dissociate leaving a charged head), but also one solvophobic end (here the fatty tail).



- So at high concentrations they will aggregate into 1-d, 2-d, or 3-d structures to reduce exposure of the tail to the solvent.
- Tuning the solvent interactions and relative volumes of head and tail selectively gives a variety of lyotropic liquid crystals.

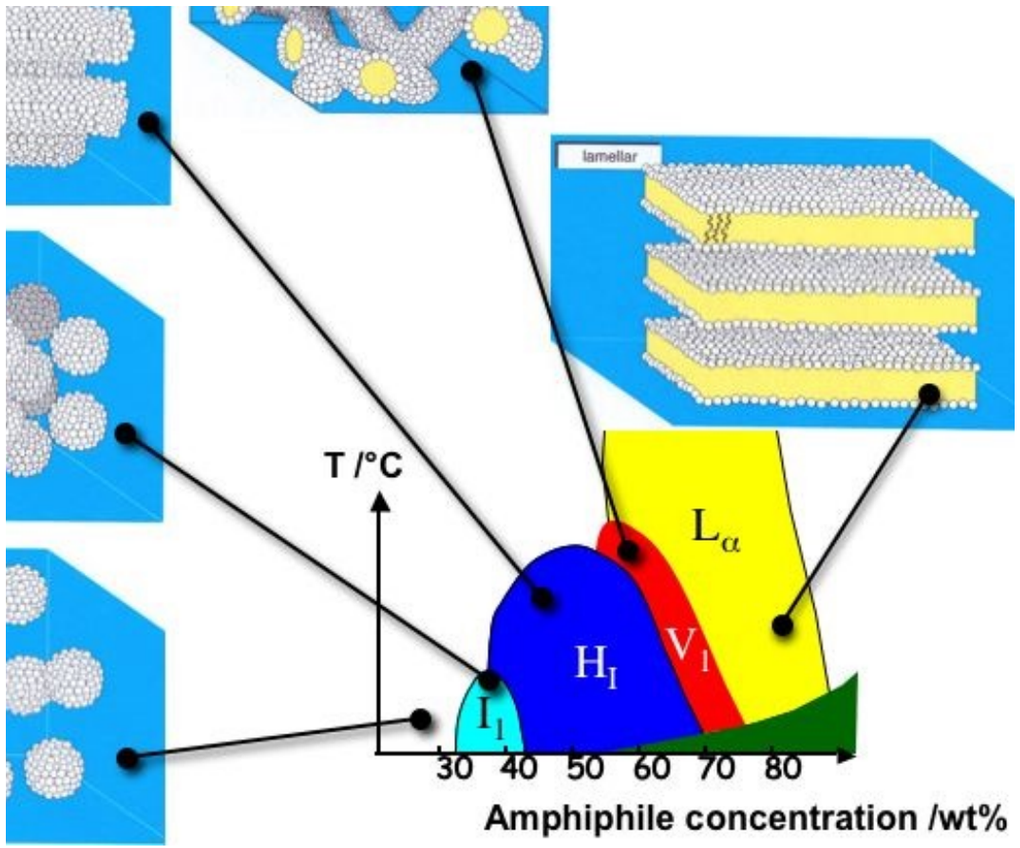
"lyo" = dissolve, "tropic" = change



jenmcintyre.files.wordpress.com/2008/04/howsoapworks_page_4.png

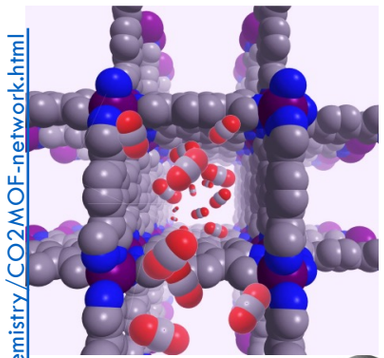
en.wikipedia.org/wiki/File:Lyotropic1.jpg

Self-organisation: equilibrium and change



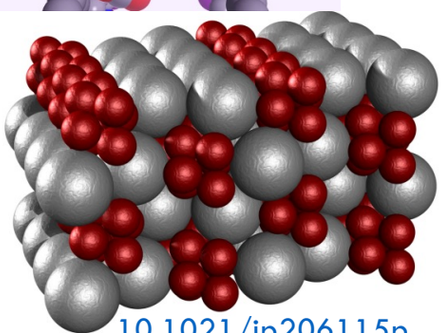
- These are equilibrium phases, so are not gradually aggregating into something else.
- The diagram shows that the equilibrium phase depends on temperature and concentration.
- Even without changing the molecule, the phase diagram can also be adjusted by altering pH or salt concentration.

Self-organisation: self-assembly



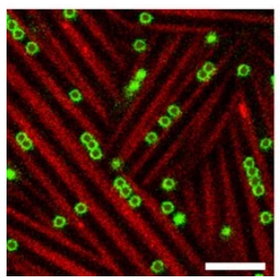
sydney.edu.au/science/our-research/research-areas/chemistry/CO2MOF-network.html

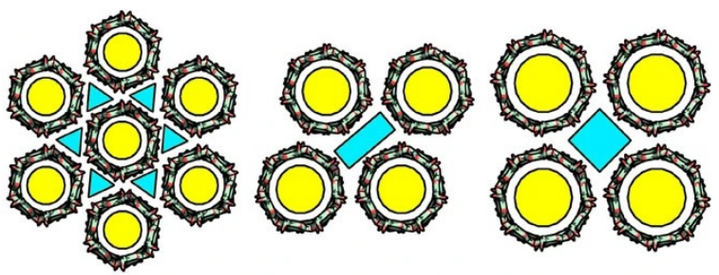
- The same kind of process can occur between multiple components, with specifically designed interactions.



10.1021/jp206115p

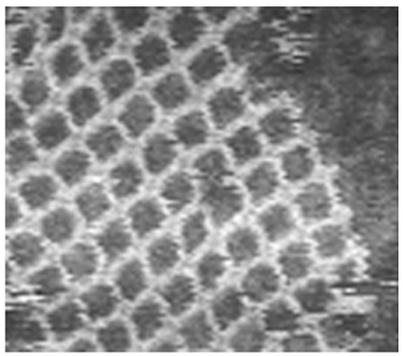
- This gives rise to a lot of chemistry research potential!



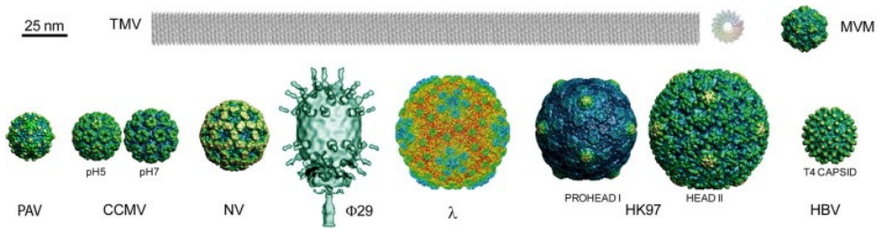


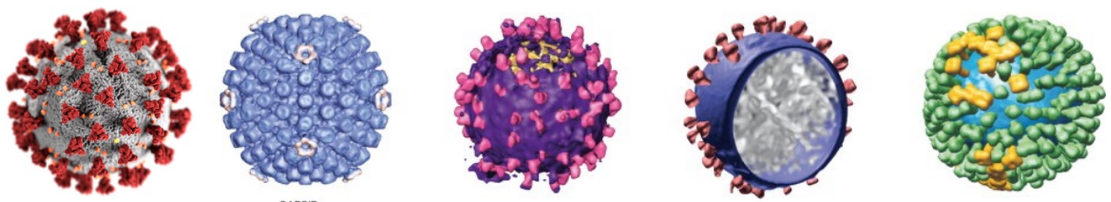
10.1038/ncomms15856





10.1371/journal.pbio.0020073



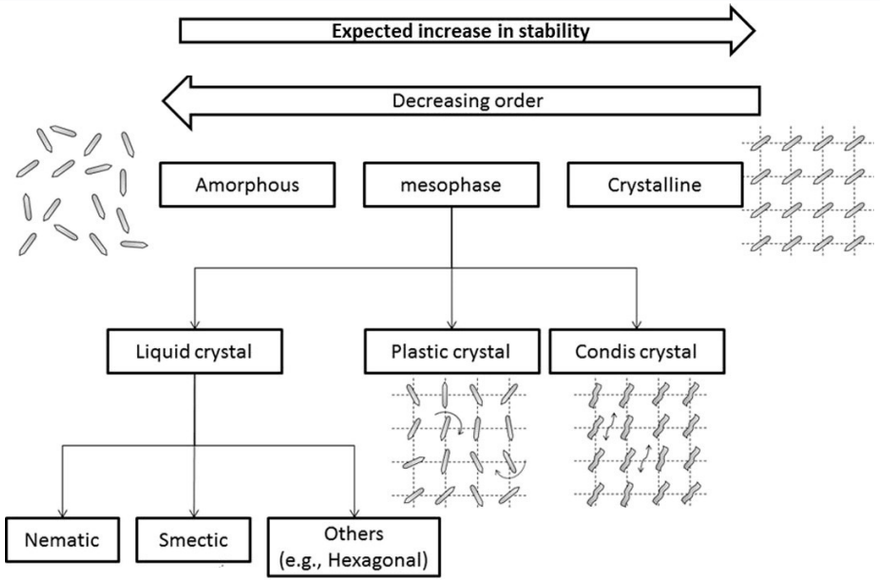


Alissa Eckert, Dan Higgins/CDC

10.1016/j.abb.2012.10.015

Mesophases: in between liquids and crystals

Typical molecular liquid	Typical molecular crystal
Molecules free to diffuse in all 3 directions	Molecules vibrate around a specific site
Molecules free to rotate around all 3 axes	Molecules vibrate around a fixed orientation
Location of molecules has no long-range structure	Long-range translational order in all 3 directions
Orientation of molecules is isotropic	Long-range orientational order in all 3 directions

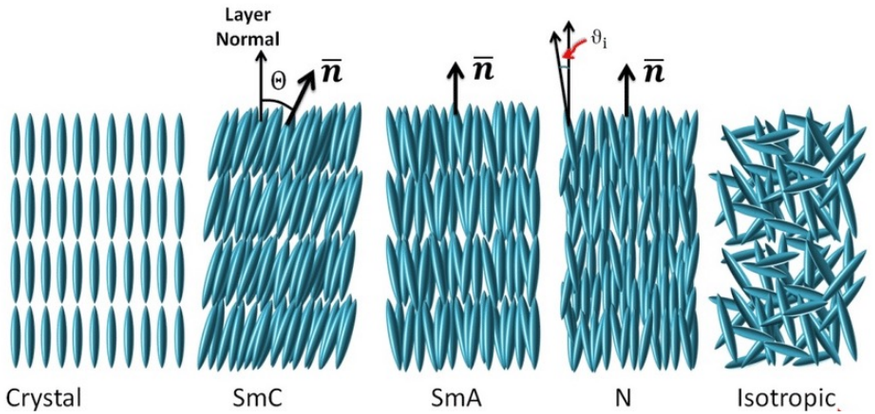


10.1016/j.addr.2016.04.002

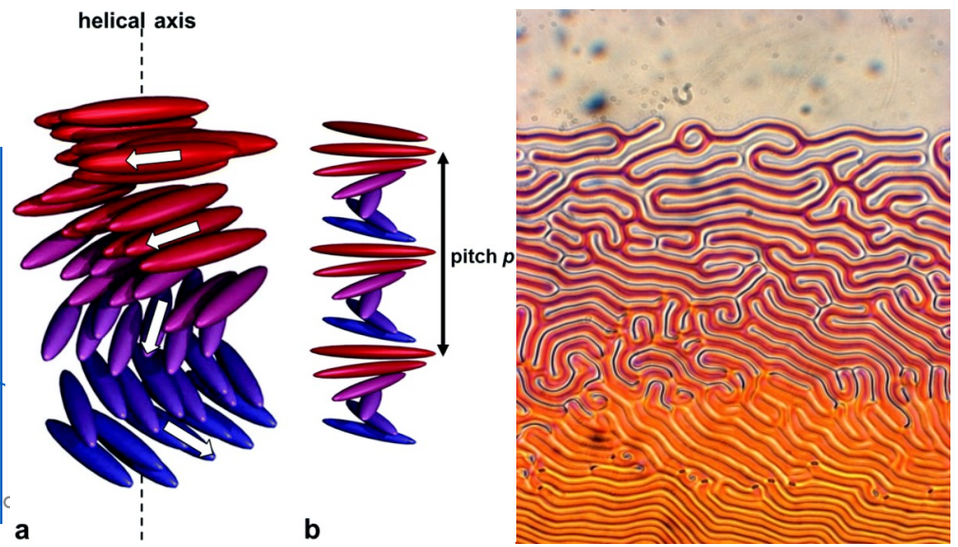
- The microscopic structural and dynamic properties of liquids and solids dictate many of their macroscopic properties:
  - Fluidity (response to shear)
  - Optical isotropy
  - Interaction with electric fields

- Mesophases are equilibrium phases which match some properties of liquids and other properties of crystals.
- Molecules capable of forming these phases are sometimes called Mesogens.
- They don't have to be lyotropic/amphiphilic in a solvent, instead forming in single-component system. (From here on we will see how this can happen due to molecular shape alone.)

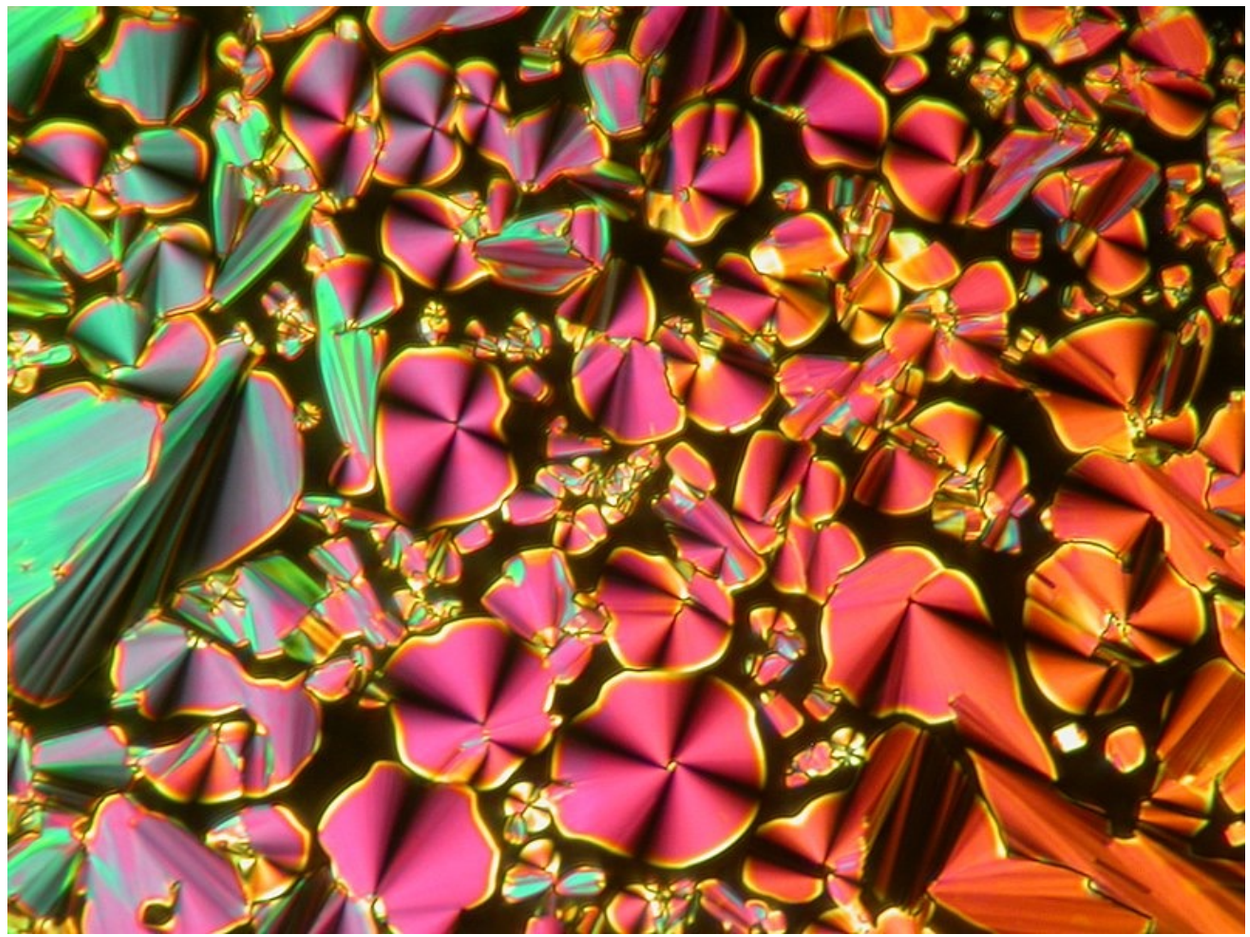
Thermotropic mesophases: micro/macro scales



10.3390/nanoZ100305



10.1039/C7SM00384F



commons.wikimedia.org/wiki/File:Liquid_crystal_textures_2.jpg

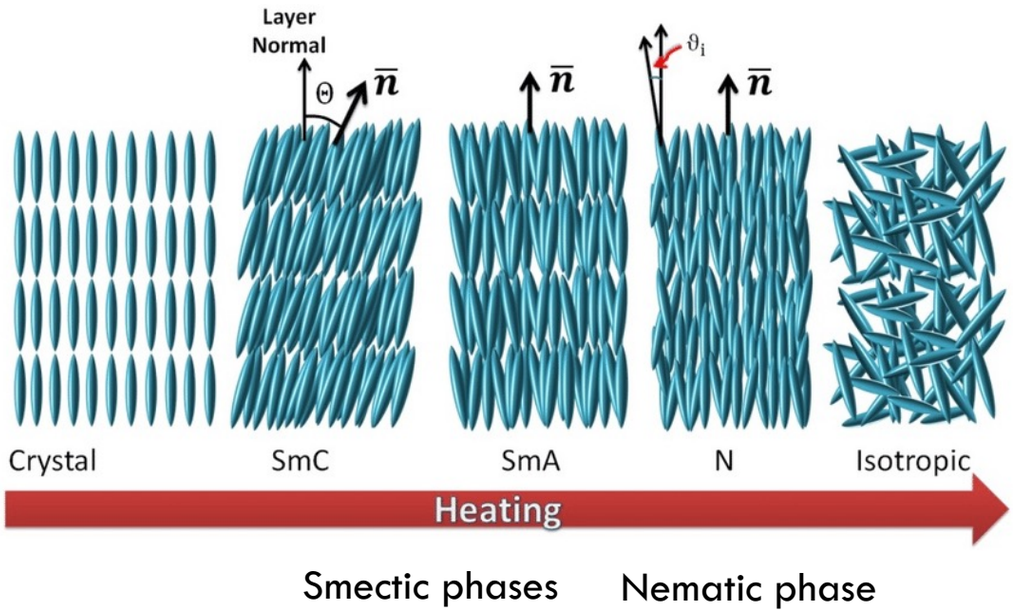
flickr.com/photos/benjaminoutram/11380005443/

Mesophases: nematic, smectic, columnar

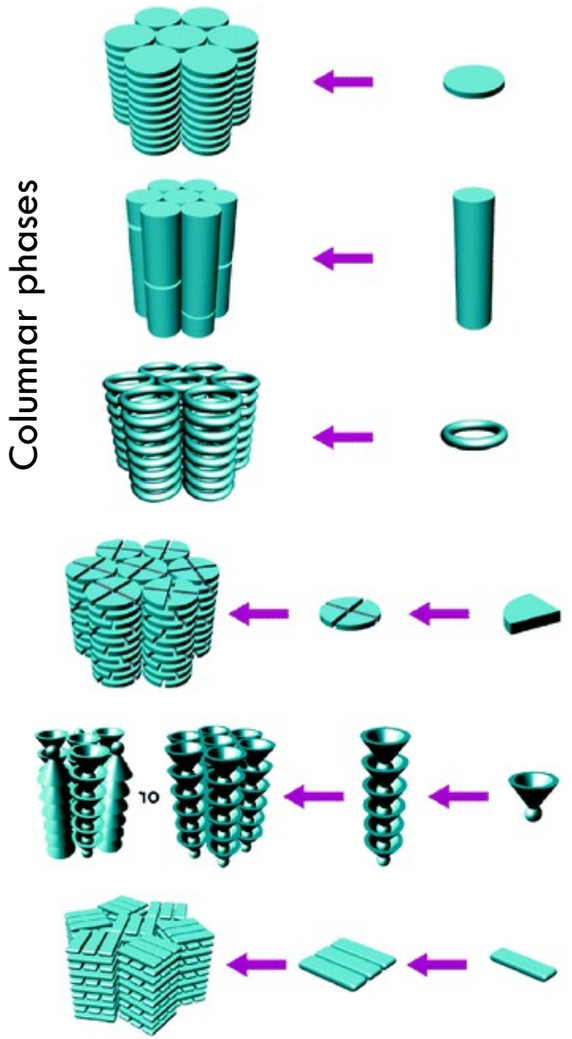
Q3

- The shape of a molecule and the temperature determine whether or how it will act as a mesogen.

$\bar{n}$, the "director", is the average direction of the particle axis



10.3390/nano7100305

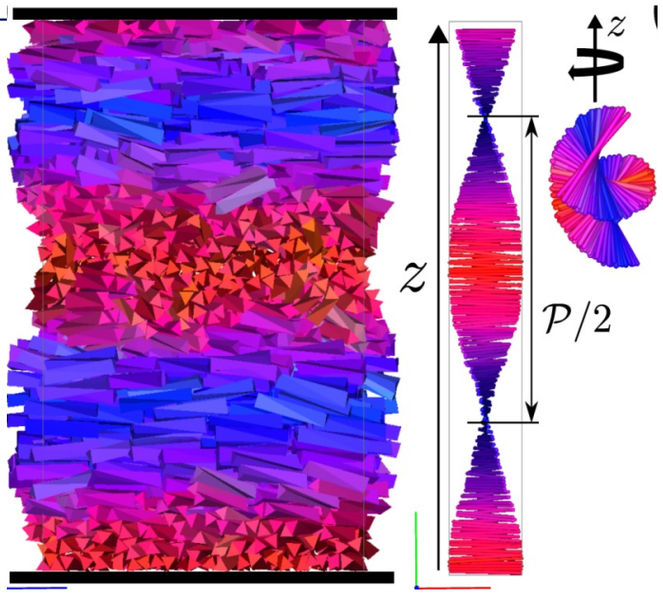


10.1039/B816624B

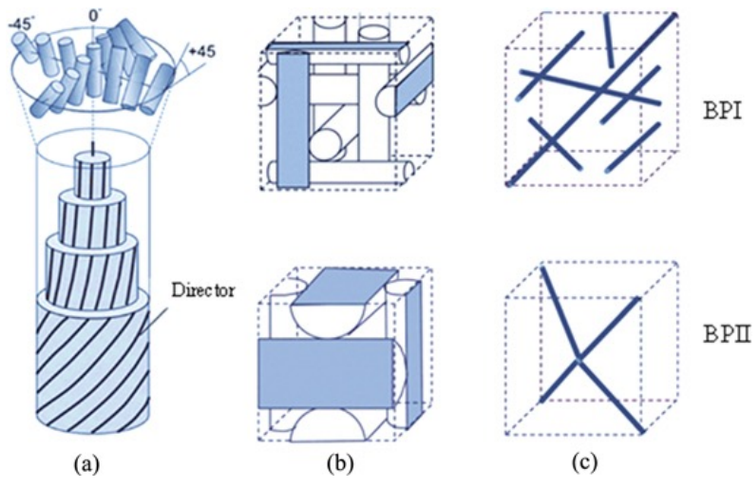
- Wikipedia has a good discussion of liquid crystals

Mesophases: cholesteric - the chiral nematic phase

- If the mesogen is chiral, what looks like a nematic on the small scale, may actually show a gradual rotation of the nematic director on a longer scale.
- The "pitch" of this cholesteric phase is the distance to rotate a full turn.
- Even when the particles are small molecules, this pitch can be on scales long enough to match the wavelength of light, and therefore cause optical effects.
- In a very small temperature range, double-twist cholesteric cylinders pack to form a "blue phase"which can selectively reflect a colour.



colloid.nl/people/simone-dussi

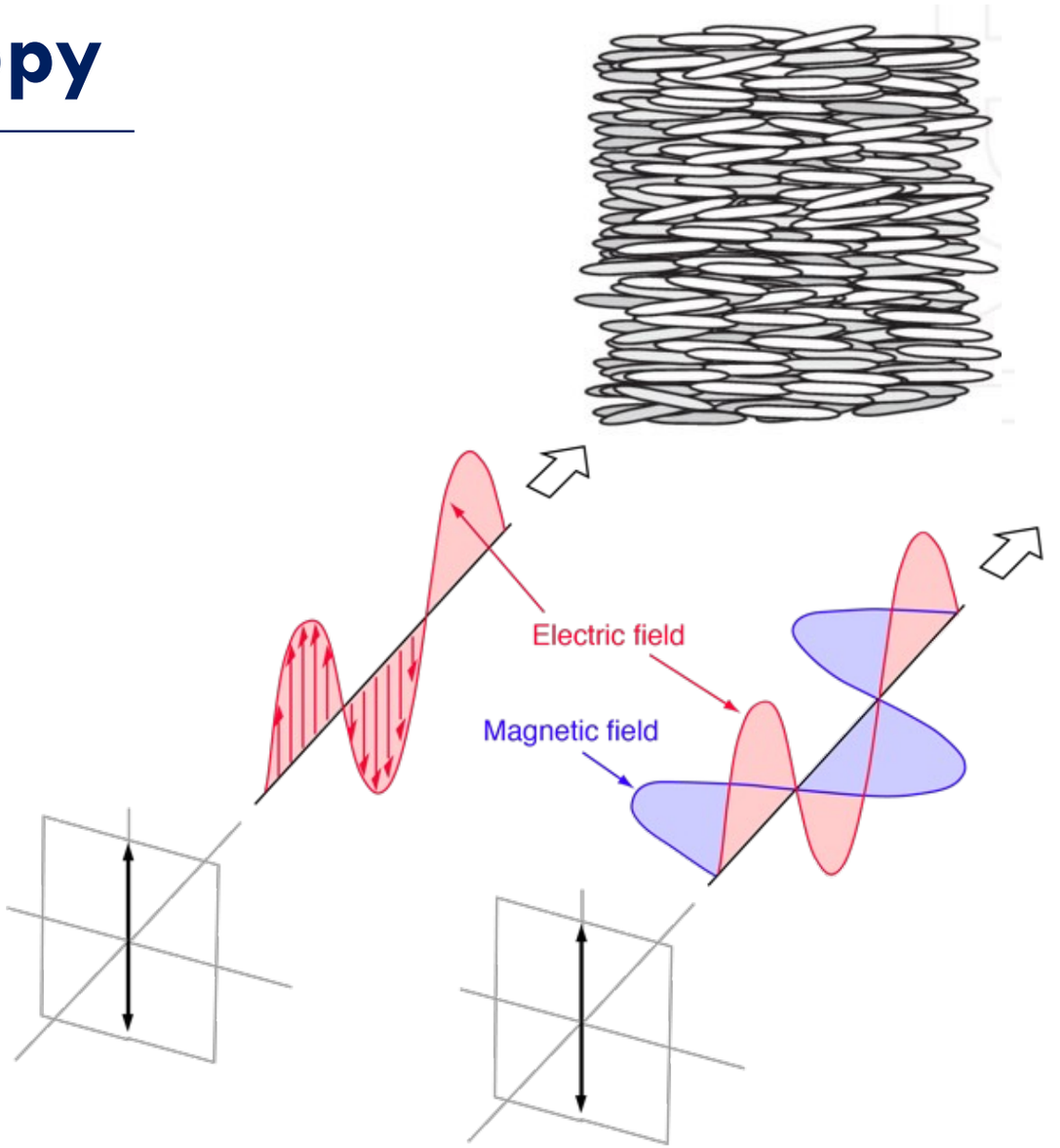


Kikuchi H 2008 Liquid crystalline blue phases *Liquid Crystalline Functional Assemblies and Their Supramolecular Structures* ed T Kato, p99–117 vol 128

Mesophases: anisotropy

Q4

- Many of these phases have one two or three different axes of symmetry over macroscopic distances. This is called anisotropy.
- As a consequence, physical and mechanical properties (e.g. electrical and thermal conductivity, light polarisation) can also depend on the direction in which they are measured.

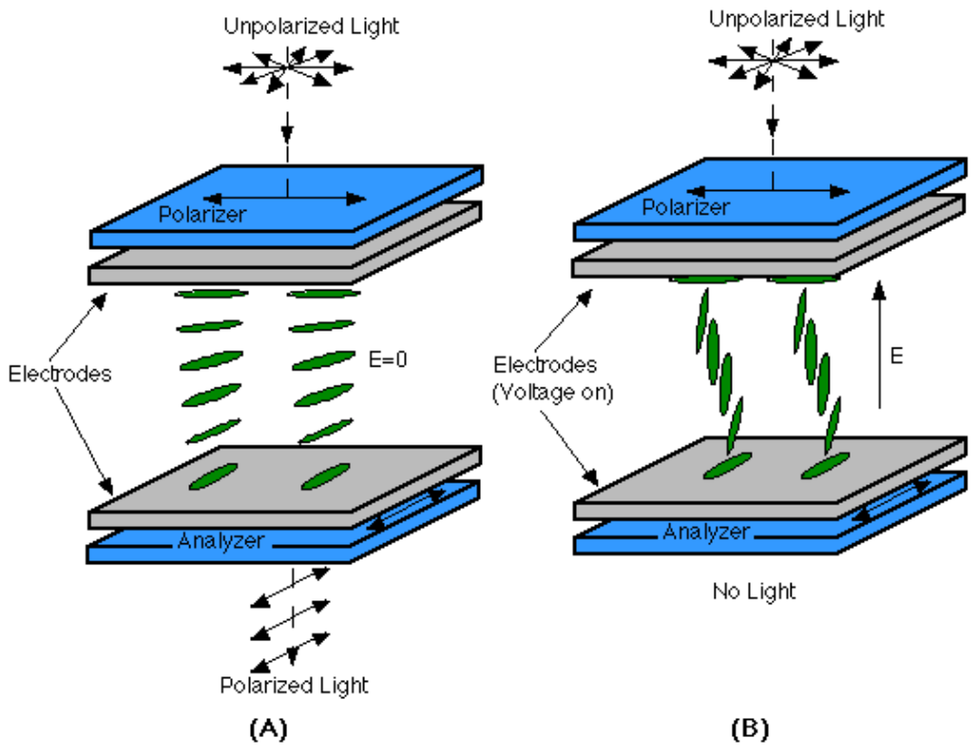


10.5772/60776

hyperphysics.phy-astr.gsu.edu/hbase/phyopt/polclas.html

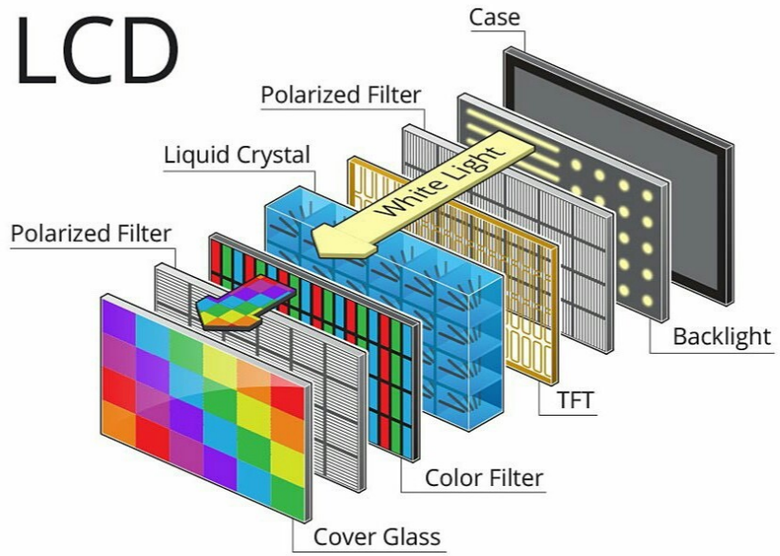
Mesophases: interaction with electric fields

- The charge distribution or polarisability of the molecules means that the structure of mesophases can be altered by the application of an external electric field.
- The new equilibrium can be established very quickly (although the kinetics depend on the temperature and molecular interactions).
- Together with polarised light, this allows for switchable transmission.



bly.colorado.edu/lcphysics/lcintro/tnlc.html

Mesophases: applications



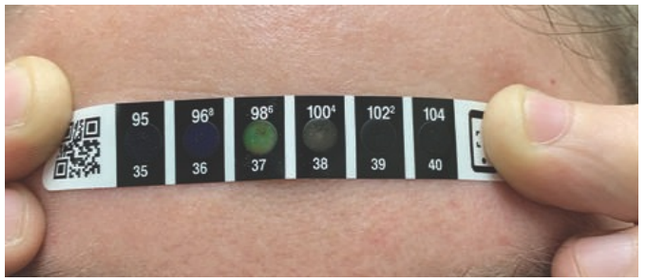
mygacorner.blogspot.com/2017/01/liquid-crystal-display.html





commons.wikimedia.org/wiki/File:Banana_Slug-1.jpg







ebay.com.au/i/114242157526

Learning outcomes

After this lecture you should be able to

- Describe the energetic scale at which soft matter phenomena occur
- Describe the role of thermal fluctuations in soft matter systems
- Provide examples of soft matter systems and phenomena
- Describe the spatial scale at which mesophases occur
- Explain anisotropy and its role in the applications of mesophases
- Appreciate the technological importance of soft matter phenomena

Further reading

- D. Fennel Evans, H. Wennerström. *The Colloidal Domain: Where physics, chemistry and biology meet*. Wiley, 1999.
- https://chem.libretexts.org/Courses/University_of_Kentucky/UK%3A_CHE_103_-_Chemistry_for_Allied_Health_(Soult)/Chapters/Chapter_7%3A_Solids,_Liquids,_and_Gases/7.6%3A_Colloids_and_Suspensions
- Banana slugs, secret of the slime
- https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book%3A_Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/07%3A_Molecular_and_Solid_State_Structure/7.09%3A_The_Analysis_of_Liquid_Crystal_Phases_using_Polarized_Optical_Microscopy