

3.012 Fund of Mat Sci: Structure – Lecture 24

LIQUID CRYSTALS



Source: Wikipedia.

LAST LECTURE !

Last Homework

- Study: Chapter 4 of Allen-Thomas, up to 4.4.3 included

FRI DEC 16 3-5pm 13-S066

MON DEC 19 4-6pm 13-S066

COVERAGE 17-24

Last time:

1. Glass transition, and common glasses
2. Size of linear polymers: random walk $\sqrt{N} \ell$
model (identical to diffusion in a liquid)
3. Packing fraction
4. Solvent – self-avoiding random walk
5. Rouse and reptation diffusion
6. Network glasses: oxides and chalcogenides

Fliessende Krystalle !

A2

Zeitschrift für Physikalische Chemie **4**, 462–72 (1889)

Über fliessende Krystalle.

Von

O. Lehmann.

(Mit Tafel III und 3 Holzschnitten.)

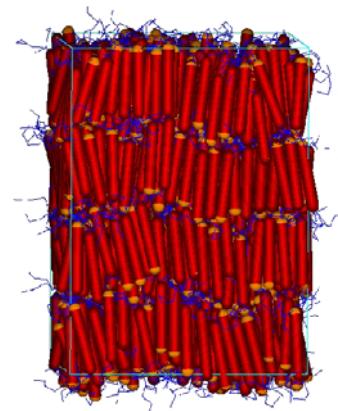
Fliessende Krystalle! Ist dies nicht ein Widerspruch in sich selbst — wird der Leser der Überschrift fragen —, wie könnte denn ein starres, wohlgeordnetes System von Molekülen, als welches wir uns einen Krystall vorstellen, in ähnliche äussere und innere Bewegungszustände geraten, wie wir sie bei Flüssigkeiten als „Fliessen“ bezeichnen und durch mannigfache Verschiebungen und Drehungen der ohnehin schon des Wärmezustandes halber äusserst lebhaft durcheinander wimmelnden Moleküle zu erkären pflegen?

Flowing crystals! Is that not a contradiction in terms? Our image of a crystal is of a rigid well-ordered system of molecules. The reader of the title of this article might well pose the following question: ‘How does such a system reach a state of motion, which, were it in a fluid, we would recognise as flow?’ For flow involves external and internal states of motion, and indeed the very explanation of flow is usually in terms of repeated translations and rotations of swarms of molecules which are both thermally disordered and in rapid motion.

Liquid crystals

- Flow easily: “liquid-like” fluidity, as in isotropic liquids
- Anisotropic material properties, as in crystals

Images of liquid crystal structures removed for copyright reasons.



Reprinted with permission from Van Duijneveldt, J., et al.
Journal of Chemical Physics 112, no. 20 (22 May, 2000).
Copyright 2000, American Institute of Physics
and the University of Bristol, Great Britain.

Movie

Image removed for copyright reasons. See liquid crystal movies at <http://micro.magnet.fsu.edu/movies/crystals/index.html>.

Mesogens

- Molecular-shape anisotropy is key structural requirement for LCs
- Molecules that induce liquid-crystallinity are called *mesogens*
- Typical mesogens are needle-like (large length-to-diameter ratio) or disk-like

Mesogens

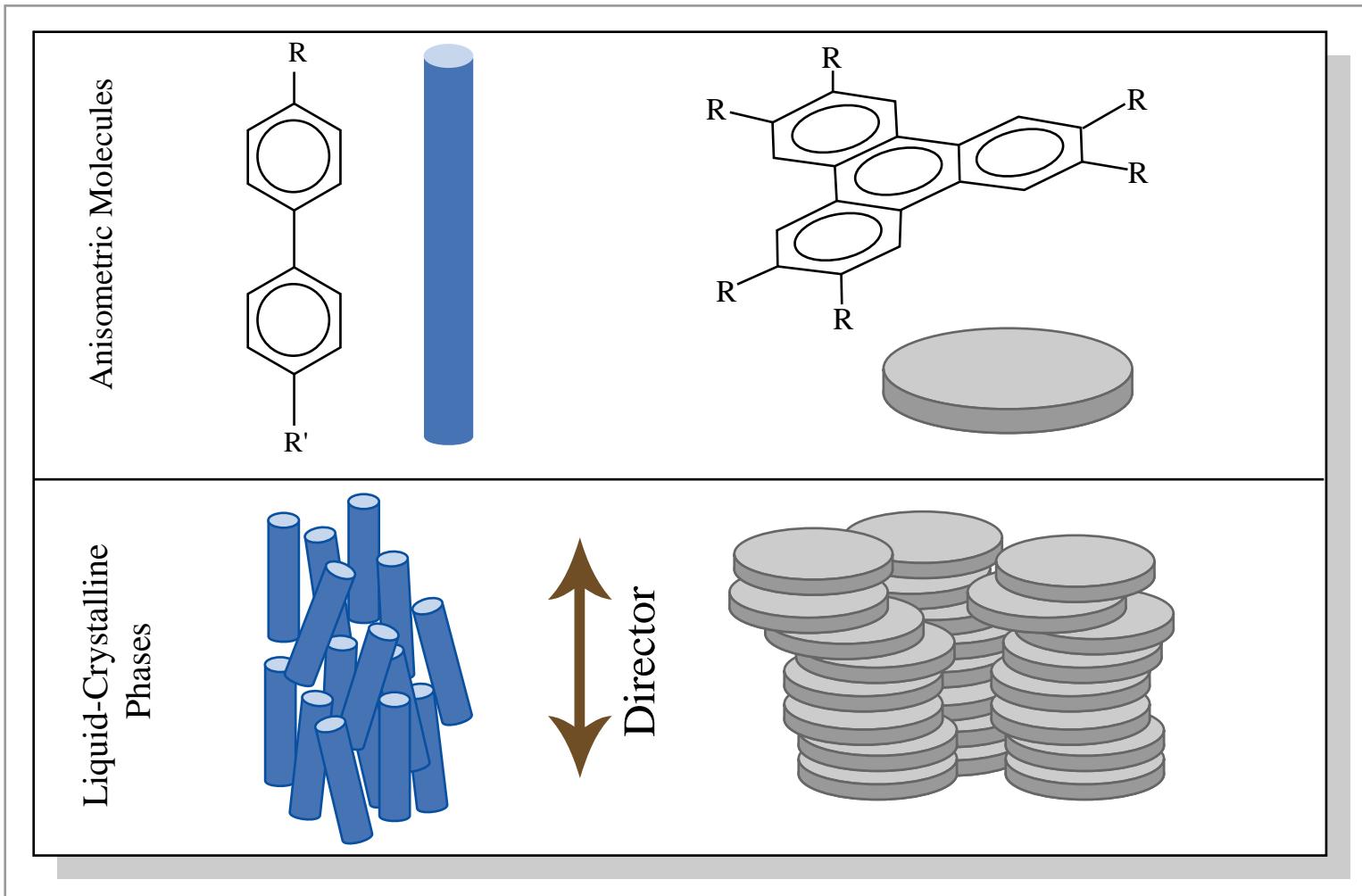
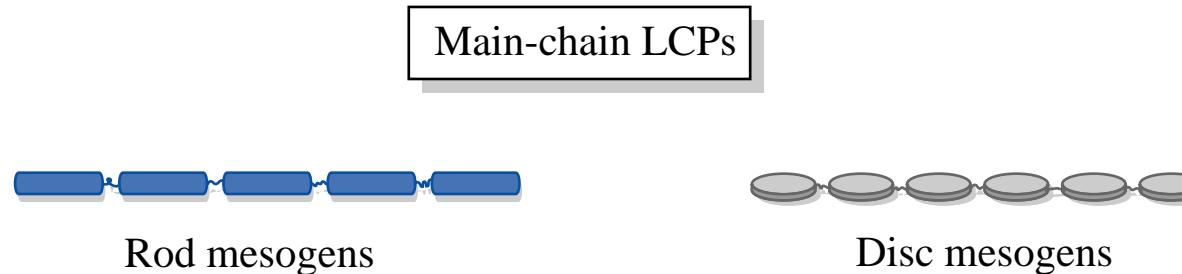


Figure by MIT OCW.

Liquid Crystalline Polymers

- A string of mesogens
 - Connect into backbone



- Connect as side chain

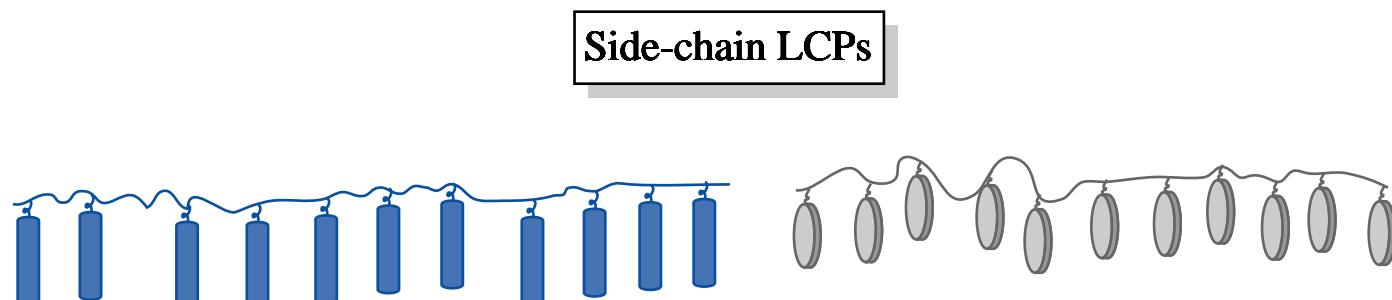


Figure by MIT OCW.

Figure by MIT OCW.

Friedel classification (1922)

- Nematic
- Cholesteric (i.e. twisted nematic)
- Smectic
- Columnar (*discovered later*)

Nematic phases

- Long-range orientational order (uniaxial)
- Short-range translational order

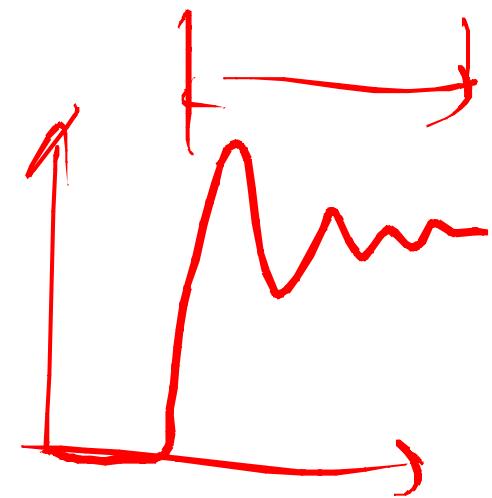
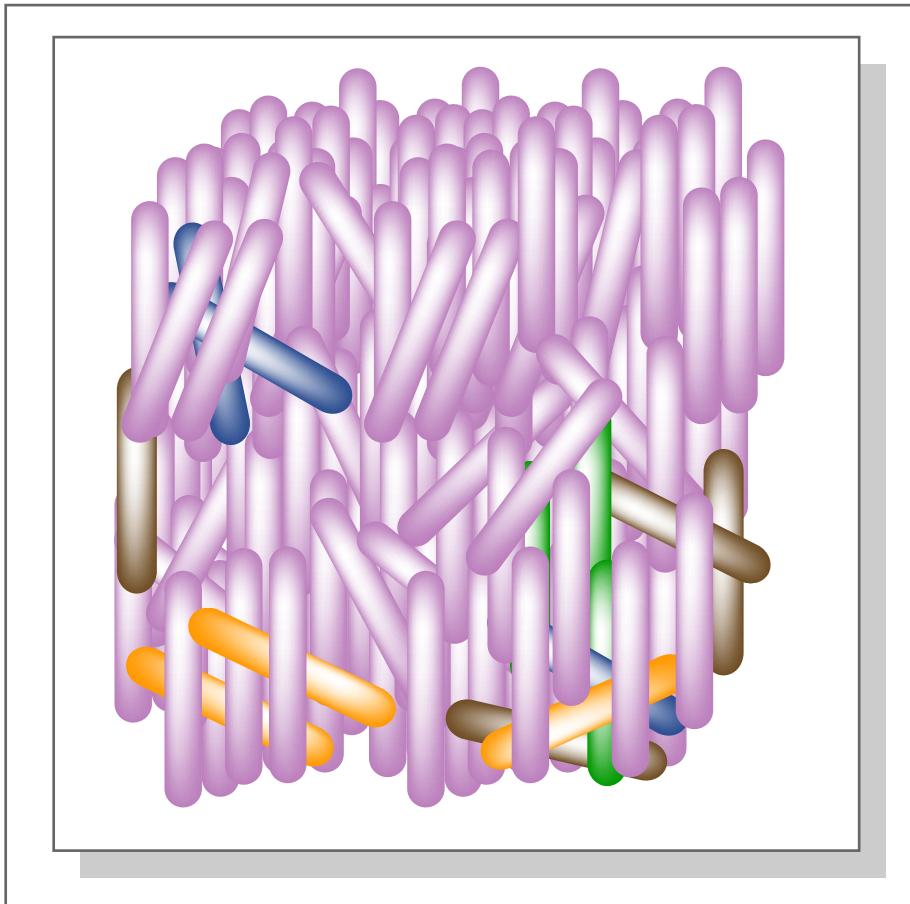


Figure by MIT OCW.

Birefringence

- Different refraction index $n=c/v$ depending on direction
- Schlieren pictures between cross polarizers highlight refraction-index texture

Images removed for copyright reasons.

Twisted nematic (cholesteric)

Nematic alignment with slight preference for a twist

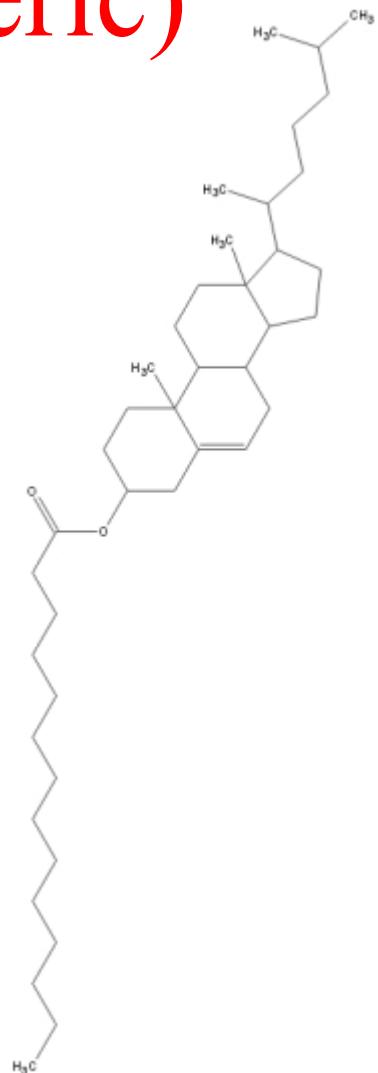
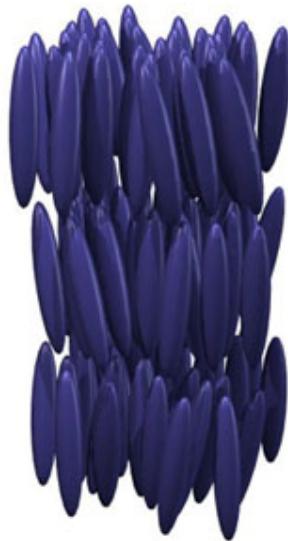


Image courtesy of Kevin Yager and the Barrett Research Group. Used with permission.

Smectic phases

- Long-range one-dimensional translational order
- Long-range orientational order

Smectic A



Smectic C



Smectic C^{*}

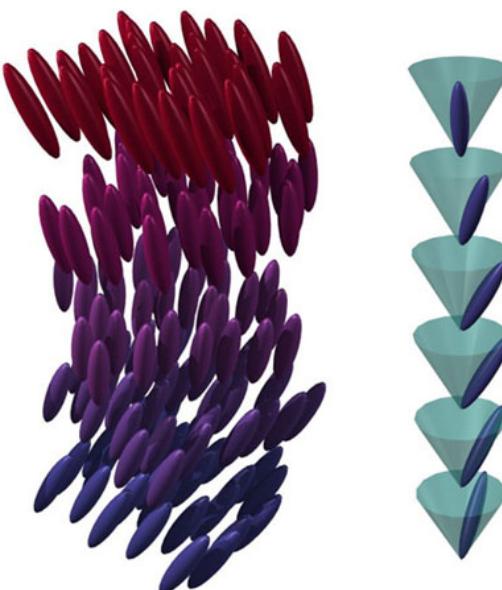


Image courtesy of Kevin Yager and the Barrett Research Group. Used with permission.

http://www.barrett-group.mcgill.ca/teaching/liquid_crystal/LC01.htm

Columnar phases

- Typically generated by discotic mesogens



Discotic Nematic

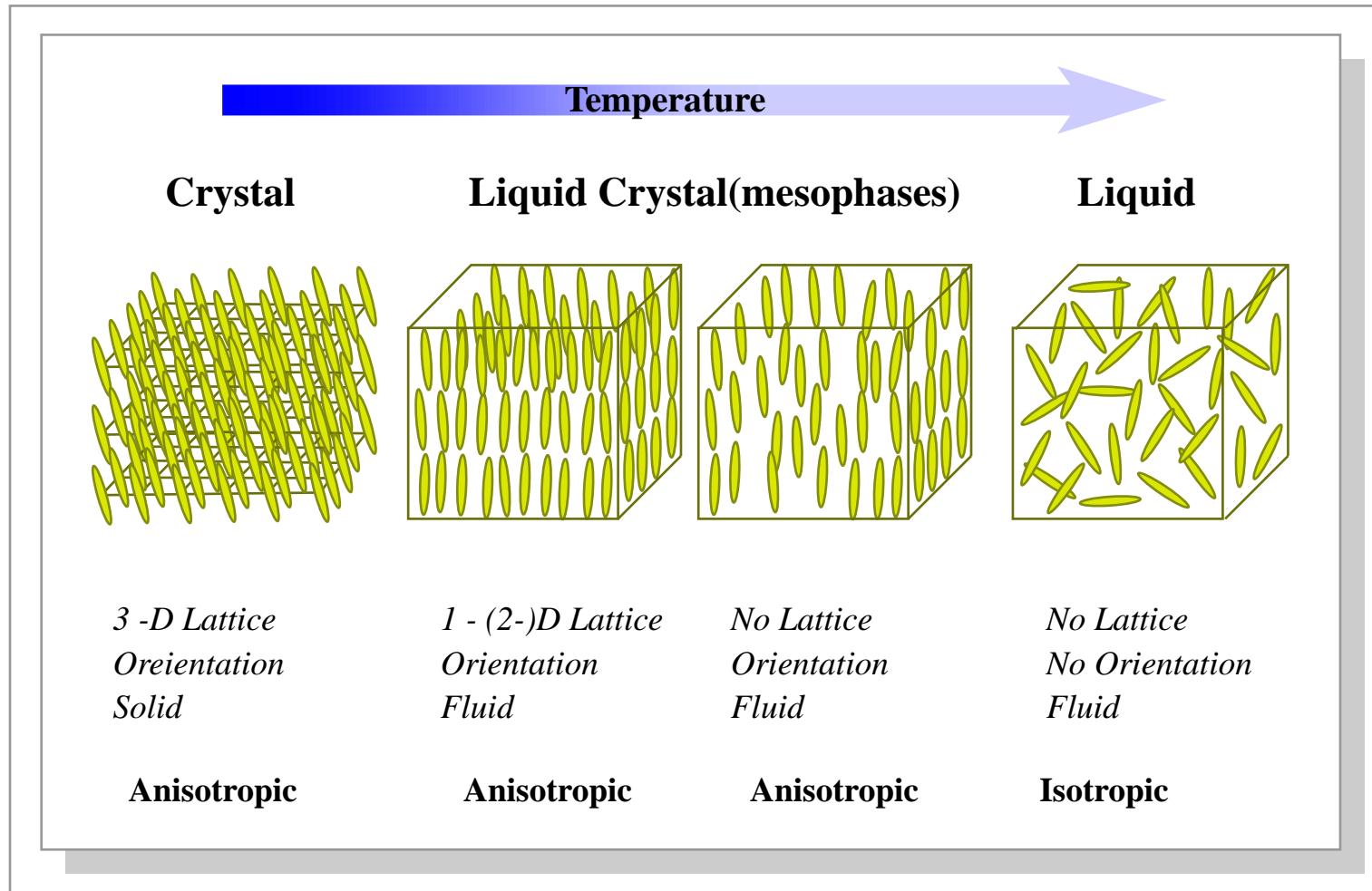


Discotic Columnar

Image courtesy of Kevin Yager and the Barrett Research Group. Used with permission.

Thermotropic liquid crystal

- Hierarchy of temperature-driven phase transitions



Lyotropic liquid crystals

- Phase transitions are mostly driven by changes in concentration

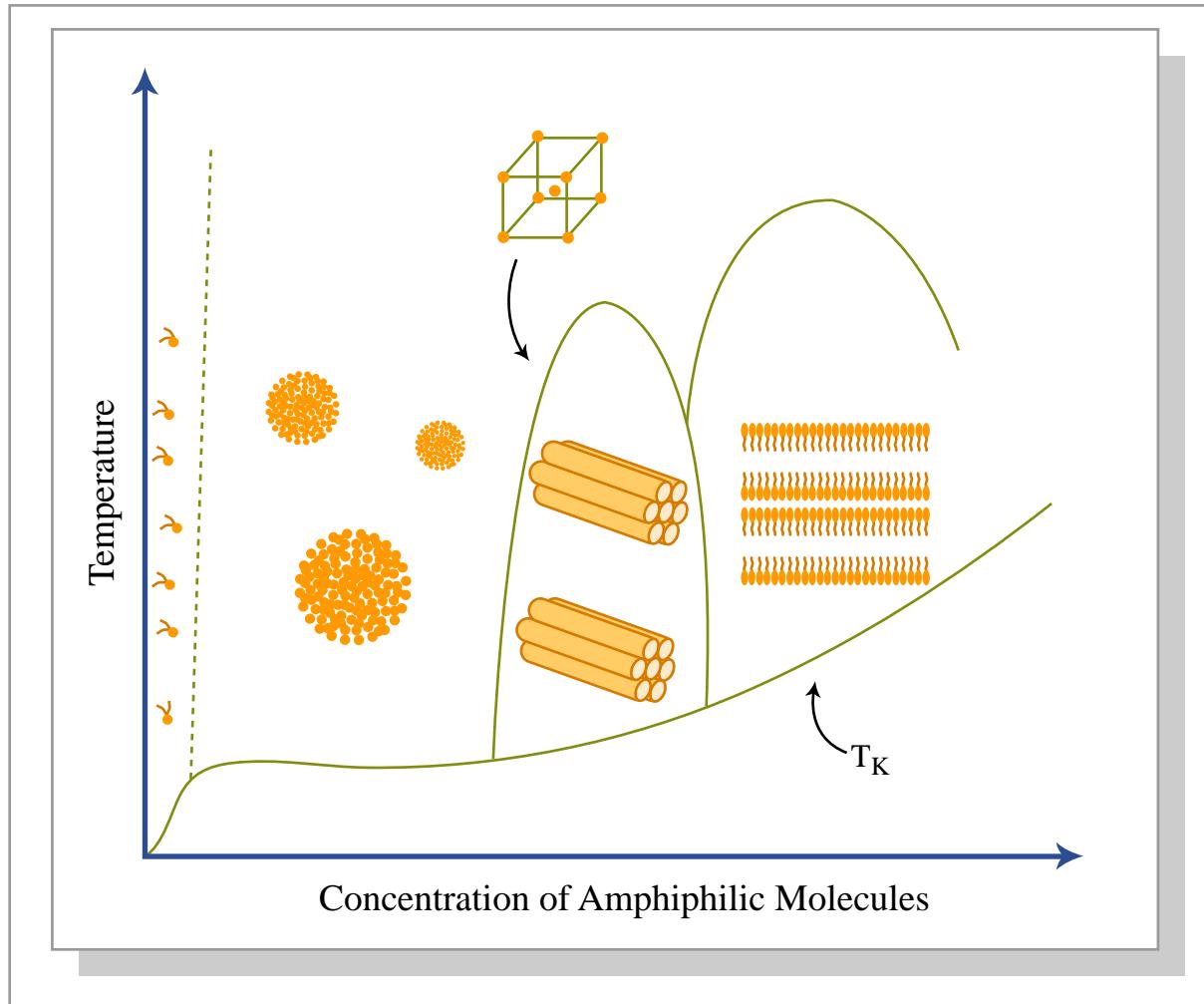


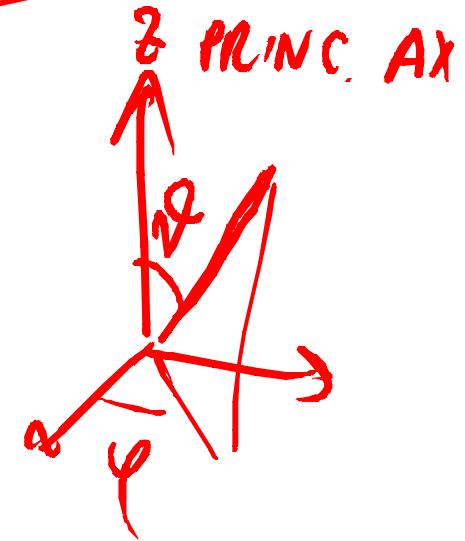
Figure by MIT OCW.

Descriptors: orientational order

- Director (“a vector with no arrow”)



- Director field: $P(\theta, \varphi)$



- Scalar orientational order parameter:

$$S = \frac{3\langle \cos^2 \theta \rangle - 1}{2}$$

ENSEMBLE AVERAGES

I PERFECT ORDER

$\int_0^\pi d\vartheta \int_0^{2\pi} d\varphi \cos^2 \vartheta \sin \vartheta$

Satisfy unit

A mathematical equation for the scalar orientational order parameter S is shown. The equation is $S = \frac{3\langle \cos^2 \theta \rangle - 1}{2}$. A red arrow points from the term $\langle \cos^2 \theta \rangle$ to the text "ENSEMBLE AVERAGES". Another red arrow points from the integral part to the text "I PERFECT ORDER". A red bracket under the integral part is labeled "Satisfy unit".

Descriptors: translational order

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

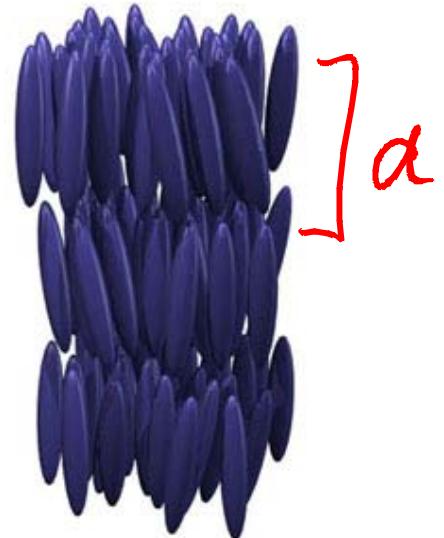


Image courtesy of Kevin Yager and the Barrett Research Group. Used with permission.

Graph removed for copyright reasons. See: p. 231, Figure 4.15 in Allen, S. M., and E.L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.

Homogeneous vs homeotropic

- Surface boundary conditions

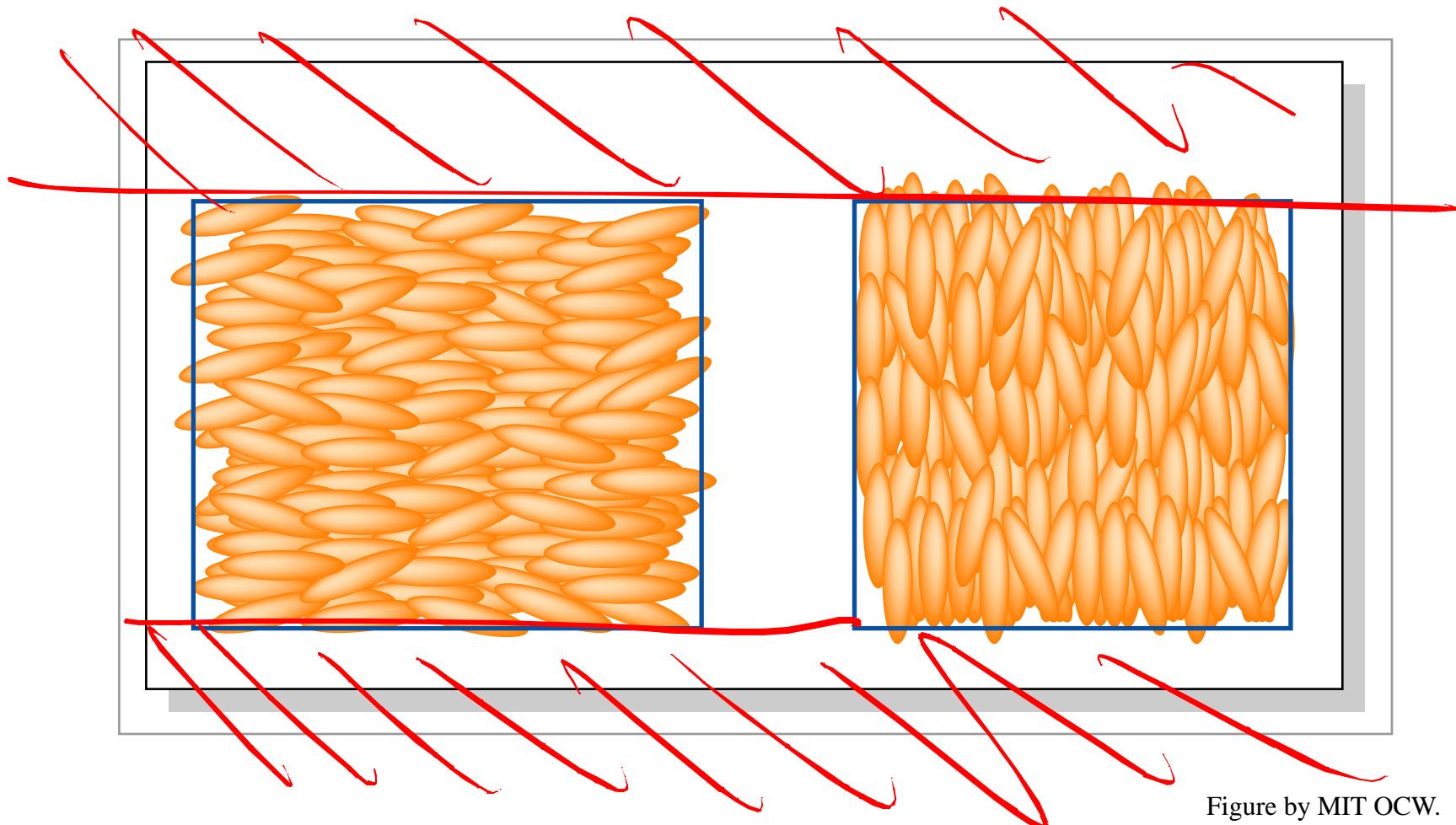


Figure by MIT OCW.

Homogeneous vs homeotropic

- Surface boundary conditions

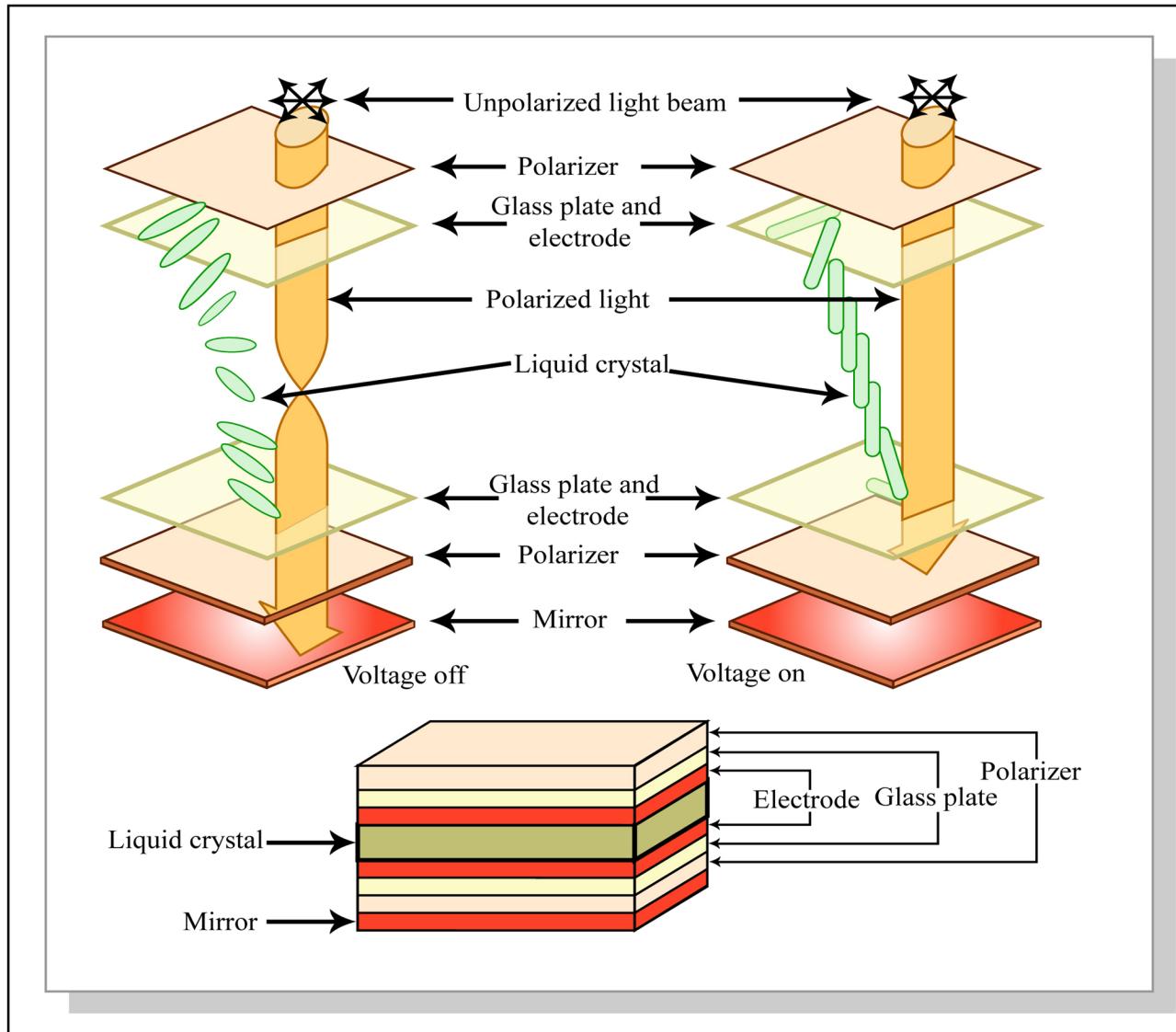


Figure by MIT OCW.

Amphiphilic mesogens

- Last (5th) class of mesogens: amphiphilic molecules (they self-assemble in micelles, columns, layers, and higher-order structures that then form mesophases).

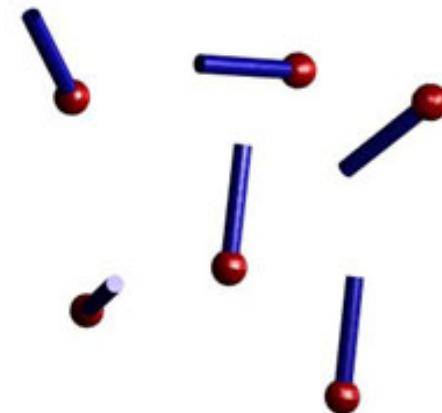
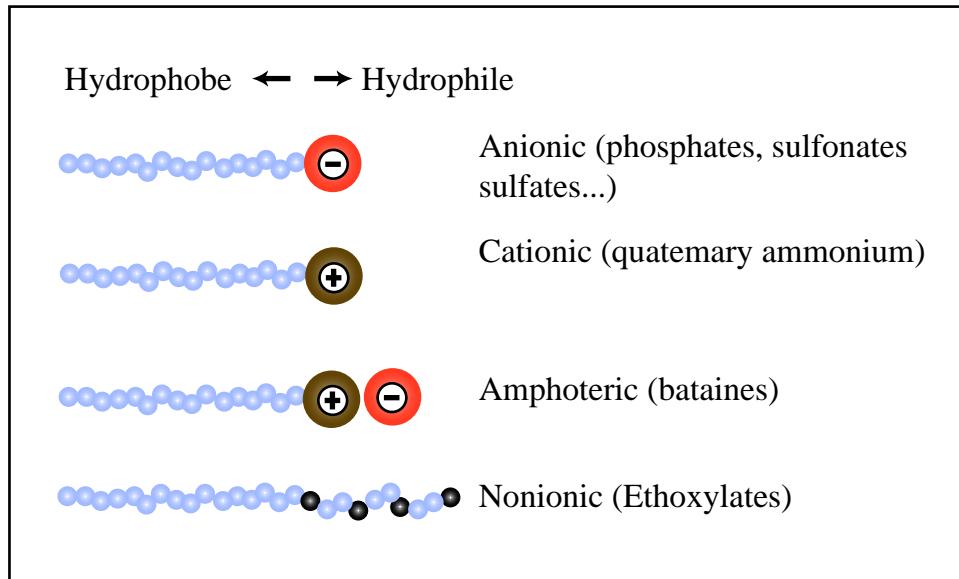
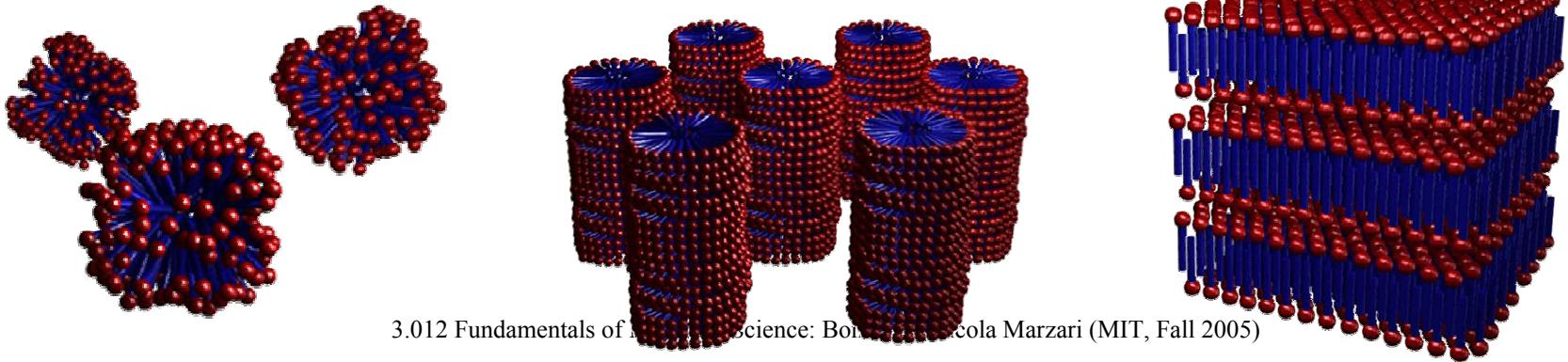


Figure by MIT OCW.

Image courtesy of Kevin Yager and the Barrett Research Group. Used with permission.



Lyotropic phase diagram

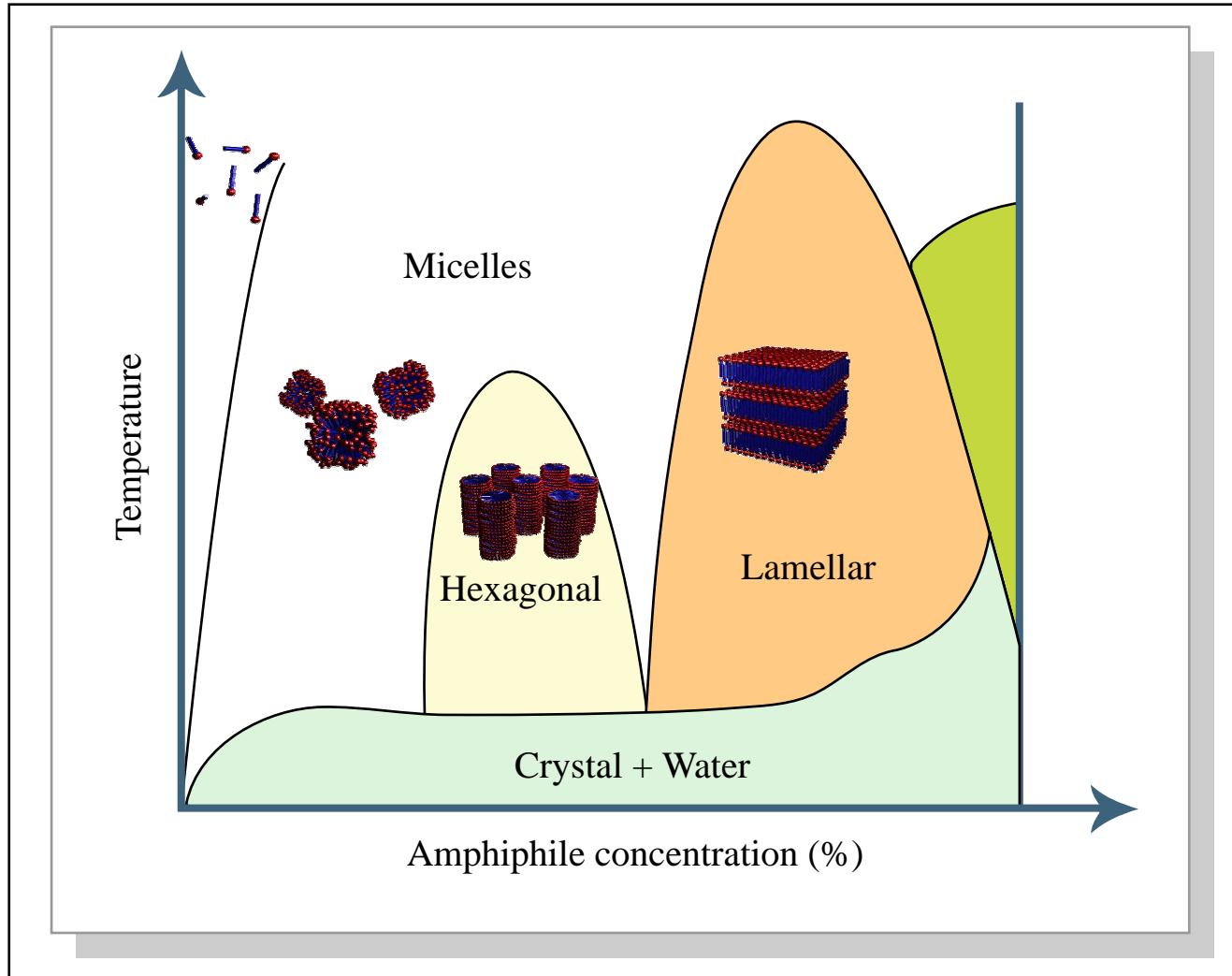


Figure by MIT OCW. Images courtesy of Kevin Yager and the Barrett Research Group. Used with permission.

Surfactants and phospholipids

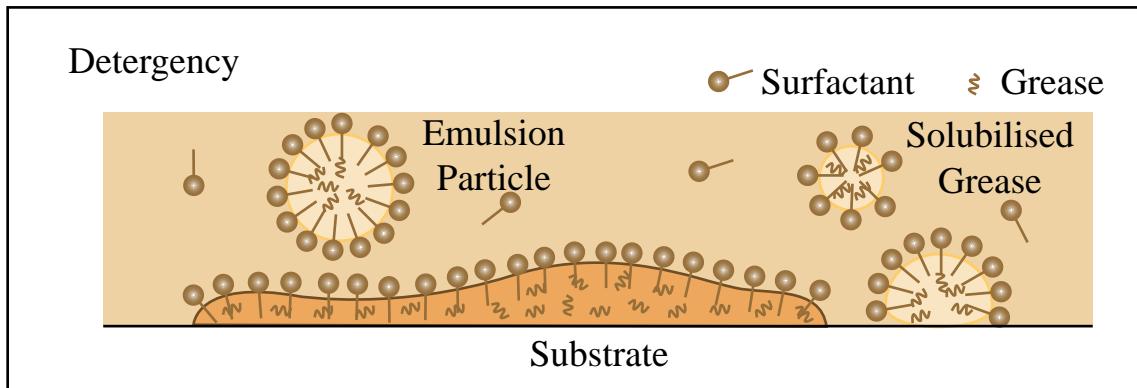


Figure by MIT OCW.

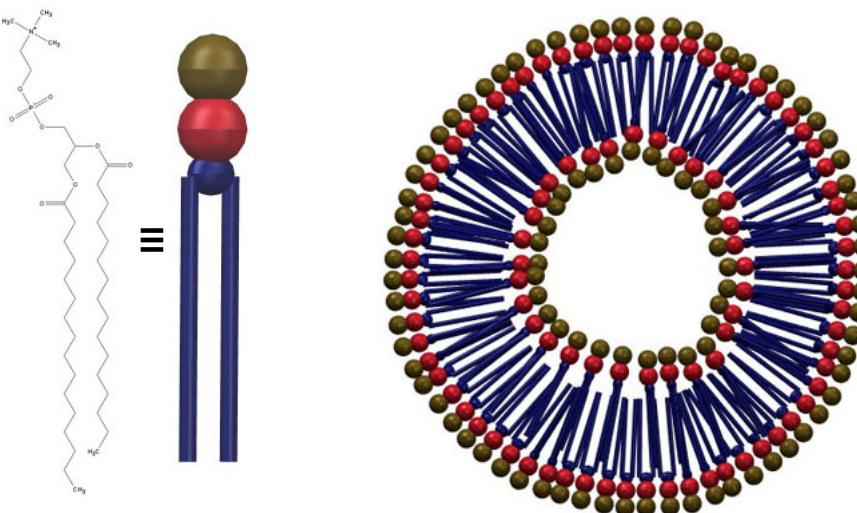


Image courtesy of Kevin Yager and the Barrett Research Group. Used with permission.