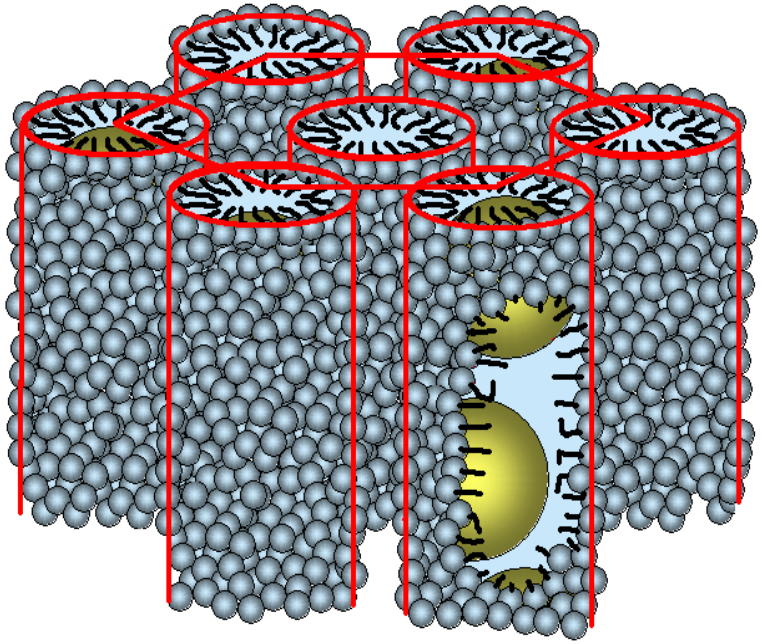
SELF ASSEMBLY
A BOTTOM UP APPROACH



EISER GROUP

La Sapienza, Rome, June 2015

Erika Eiser

OUTLINE

Lecture 1&2

- What do we mean with Self Assembly (SA)?
- What is the difference to aggregation?
- Surfactants – Typical SA materials.
- Thermodynamics
- Molecular geometry determining the SA structures.
- Examples
- Other SA systems

Lecture 3&4 (next week)

- Thermodynamics of DNA hybridization
- Programmable SA using DNA functionalized colloids
- Designing new colloidal materials

WHAT IS SELF ASSEMBLY?

- Self assembly is a type of spontaneous aggregation of (macro)molecules into well-defined mesoscopic structures.
- Examples are micelles, vecicles, lamellae,….
- Also referred to as micro-phase separated systems.
- These are **equilibrium structures** assuming the lowest Gibbs free energy at a given temperature.

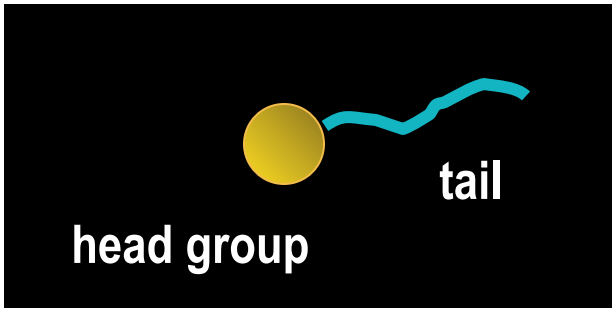
$$\Delta G = \Delta H - T\Delta S$$

- **Aggregation (e.g. flocculation & gelation) are NON-equilibrium structures in terms of thermodynamics!**

Surfactants =

Surface Active Molecules = Amphiphiles

- Surfactants are molecules with **amphiphilic** character.
- This means the molecules consist of a **hydrophobic** (tail) and **hydrophilic** (head group) part.



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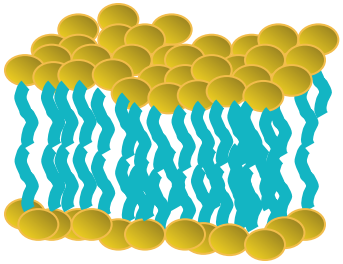
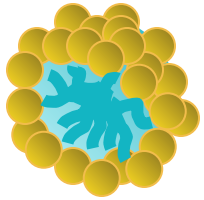
In solution:

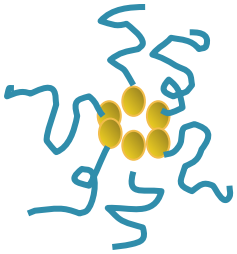
Spontaneous self-aggregation into well defined structures



bilayer membrane

micelle





inverted micelle

… and many other assemblies!

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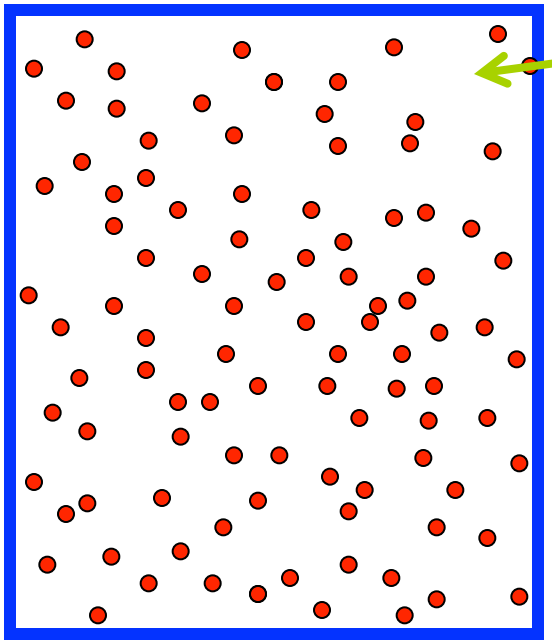
WHAT ARE THE CRITERIA FOR SELF ASSEMBLY?

CHEMICAL POTENTIAL

Consider:



***N* = number of particles**

***V* = volume (= constant)**

T = temperature (= constant)

Gibbs free energy:

$(G = G(T, p, N_1, N_2, \ldots N_\alpha, \ldots))$

$$G = \sum_\alpha \mu_\alpha N_\alpha$$

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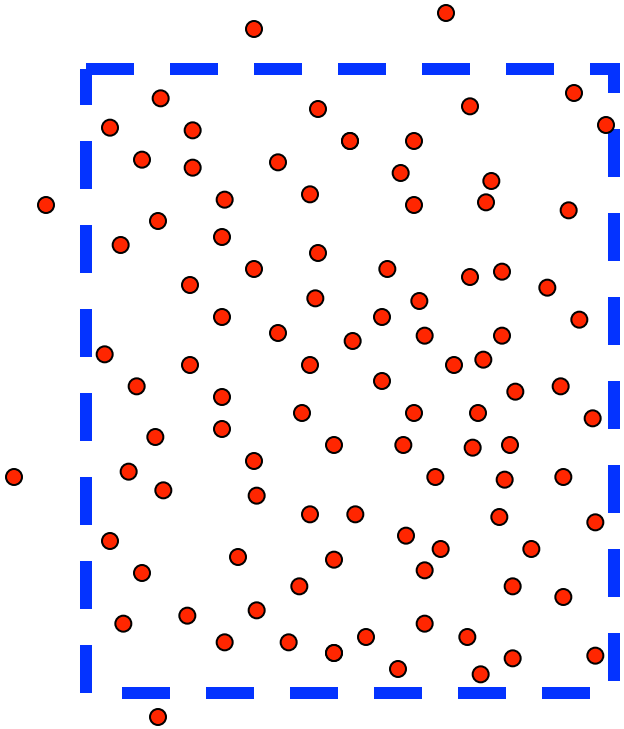
CHEMICAL POTENTIAL



If **V** has permeable walls, such that particles can enter or leave, while **T** & **V** = const.:

$$\mu_\alpha = -T\left(\frac{dS}{dN_\alpha}\right)_{E_{kin}} - \epsilon\left(\frac{dS}{dE_{kin}}\right)_{N_\alpha}$$

ε = internal energy of a particle

N/V = number density

$E_{kin} / N = (3kT)/2$

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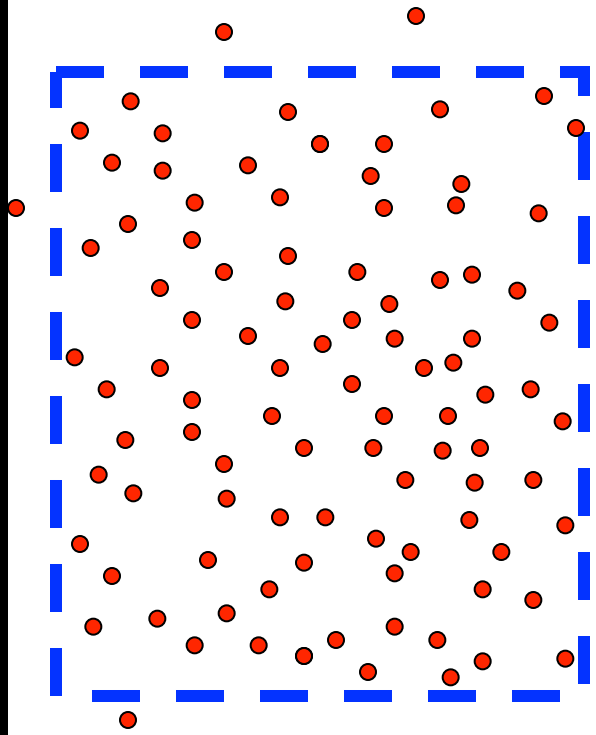
CHEMICAL POTENTIAL



for dilute solutions and gases

$$\mu = kT \ln\left(\frac{c}{c_0}\right) + \mu^0(T)$$

translational entropy

"internal" molecular free energy

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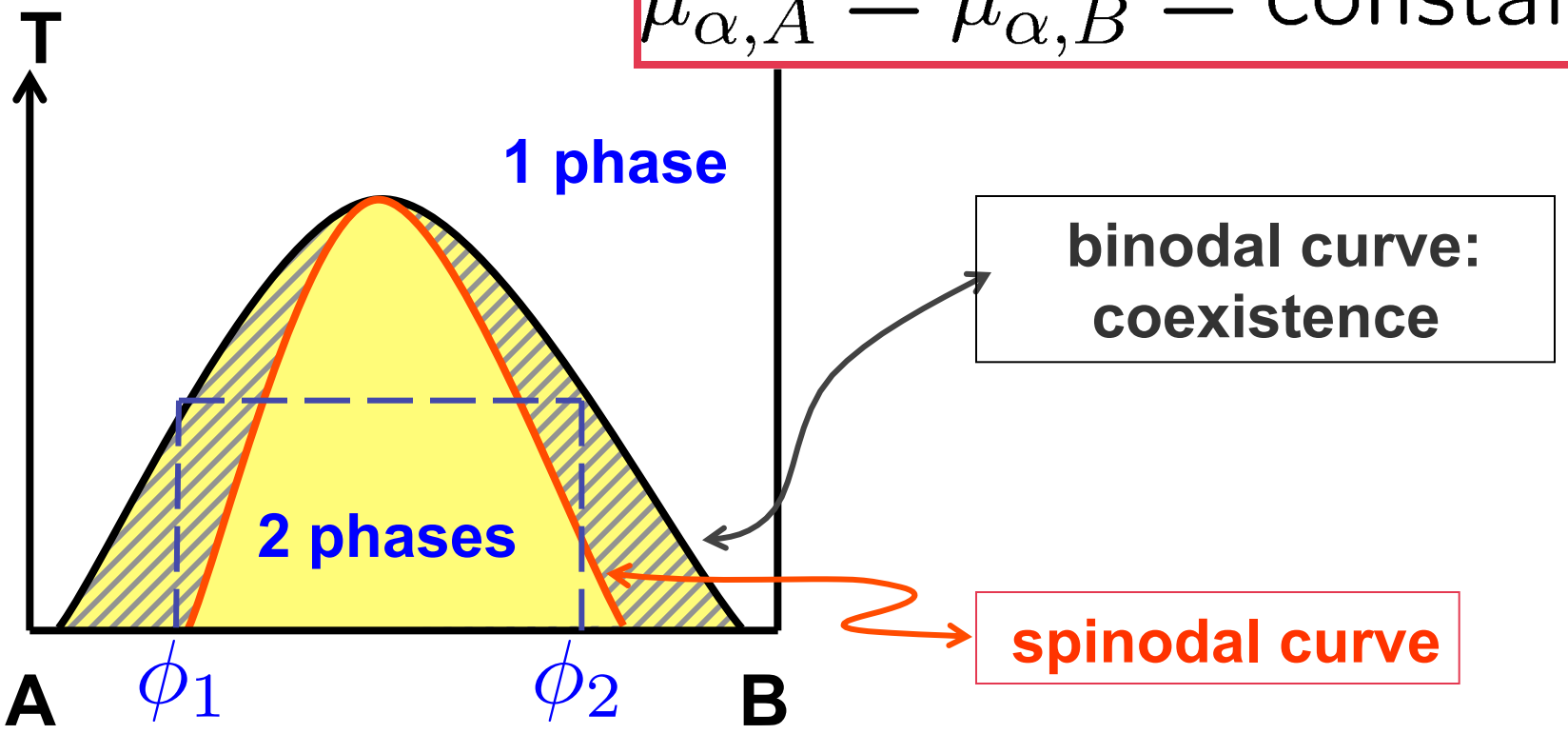
CHEMICAL POTENTIAL

Important: in chemical equilibrium …

$$\mu_{\alpha,A} = \mu_{\alpha,B} = \text{constant}$$



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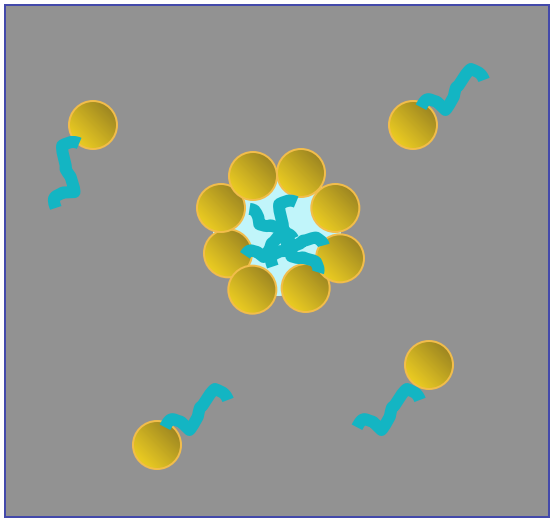
WHAT IS THE CONNECTION TO SELF-ASSEMBLY?



Thermodynamic equilibrium:

μ of identical molecules must be the same in all possible aggregates.

$$\mu = \mu_1^0 + k_B T \ln X_1 = \mu_2^0 + k_B T \frac{1}{2} \ln \frac{X_2}{2} = \mu_3^0 + k_B T \frac{1}{3} \ln \frac{X_3}{3} = \ldots$$

monomers dimers trimers

Or for an ***n***-mer: $\mu_n = \mu_n^0 + \frac{k_B T}{n} \ln \frac{X_n}{n}$ with ***n*** = 1, 2, 3, …

μ_n = average chem. pot. of a molecule in an aggregate of ***n*** molecules

μ_n^0 = energy needed to bring a molecule from infinity to the system

X_n = volume fraction of molecules in an aggregate of ***n*** molecules

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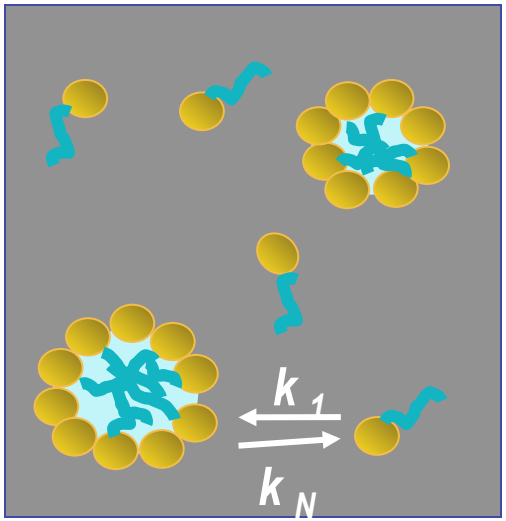
SELF ASSEMBLY



Driving force for aggregation:

difference in cohesive energies between molecules in the aggregated and dispersed state.

$$K_{\mathrm{eq}} = \frac{c}{c_0} = \exp\left[-n\frac{\mu_n^0 - \mu_1^0}{k_B T}\right]$$

$$= \exp\left[-\frac{\Delta G^0}{k_B T}\right]$$

Condition to form large stable aggregates:

$$\mu_1^0 > \mu_n^0$$

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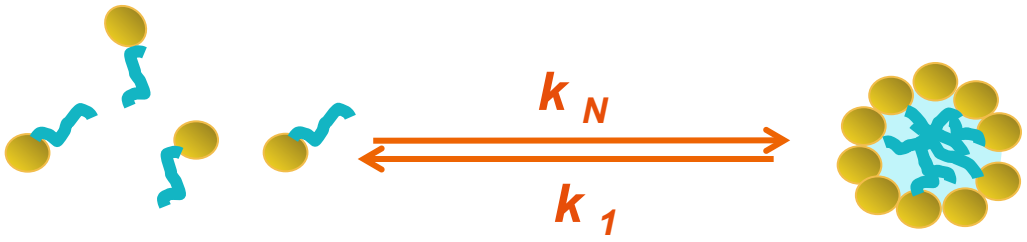
CRITICAL MICELLE CONCENTRATION CMC



Flow in forward direction: $j_F = k_n [c_1]^n$

Flow in backward direction: $j_B = k_1 [c_n]$

equil. $j_F = j_B$

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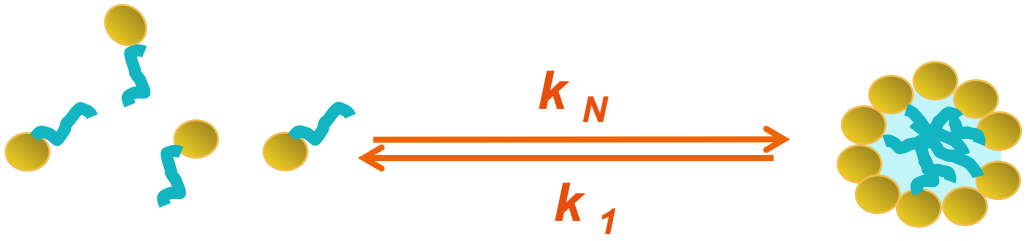
CRITICAL MICELLE CONCENTRATION CMC



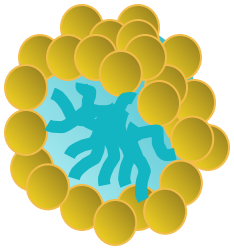
$$j_F = j_B$$

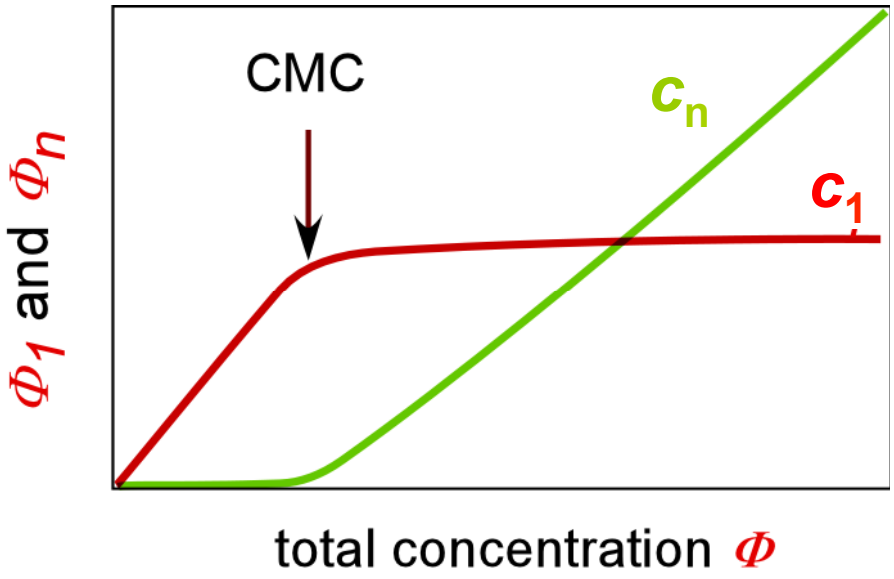
$$k_n[c_1]^n = k_1[c_n]$$

or

$$[c_n] = \frac{k_n}{k_1}[c_1]^n$$

CRITICAL MICELLE CONCENTRATION CMC





$$[c_n] = \frac{k_n}{k_1}[c_1]^n$$

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INFLUENCE OF MOLECULAR GEOMETRY ON THE TYPE OF AGGREGATES

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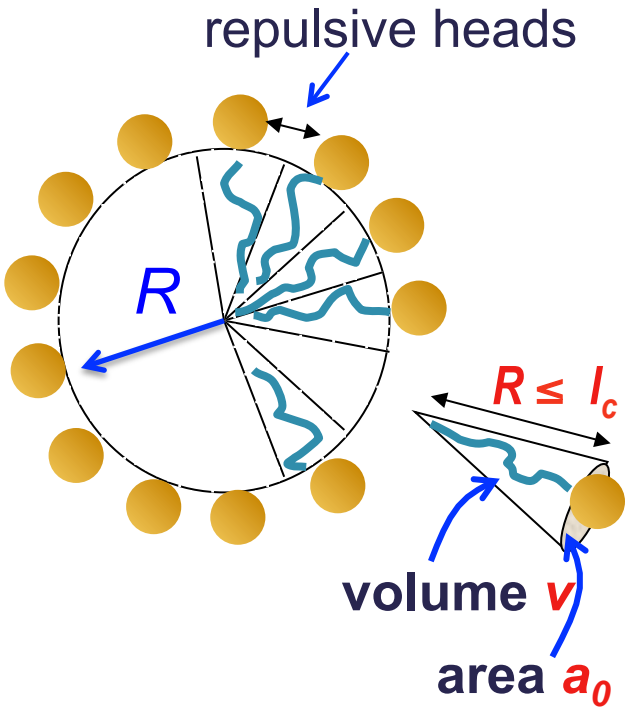
SA STRUCTURE & SPONTANEOUS CURVATURE



Spontaneous curvature 1/*R* depends on:

- the effective head-group size a_0
- the length *l* of the hydrophobic tail.

Note: a_0 can vary strongly with ***T***. In case of aqueous solutions the ***pH*** and ***salinity*** of the solvent also can change a_0.

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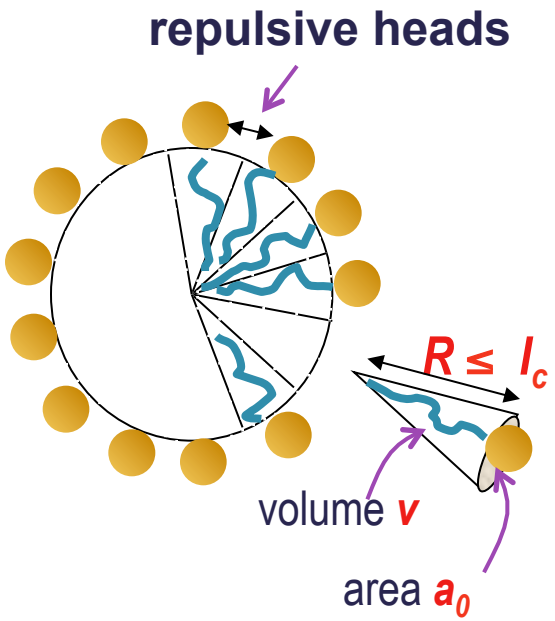
AS-STRUCTURE & SPONTANEOUS CURVATURE



a_0 fixed (constant *T* and *pH*)

the packing geometry is determined by:

v and l_c

parameter $v/(a_0 l_c)$ determines the self-assembled structures :

$\frac{v}{a_0 l_c} < \frac{1}{3}$ spherical micelles	$\frac{1}{2} < \frac{v}{a_0 l_c} < 1$ plane lamellas
$\frac{1}{3} < \frac{v}{a_0 l_c} < \frac{1}{2}$ non-spherical micelles	$1 < \frac{v}{a_0 l_c}$ inverted micelles

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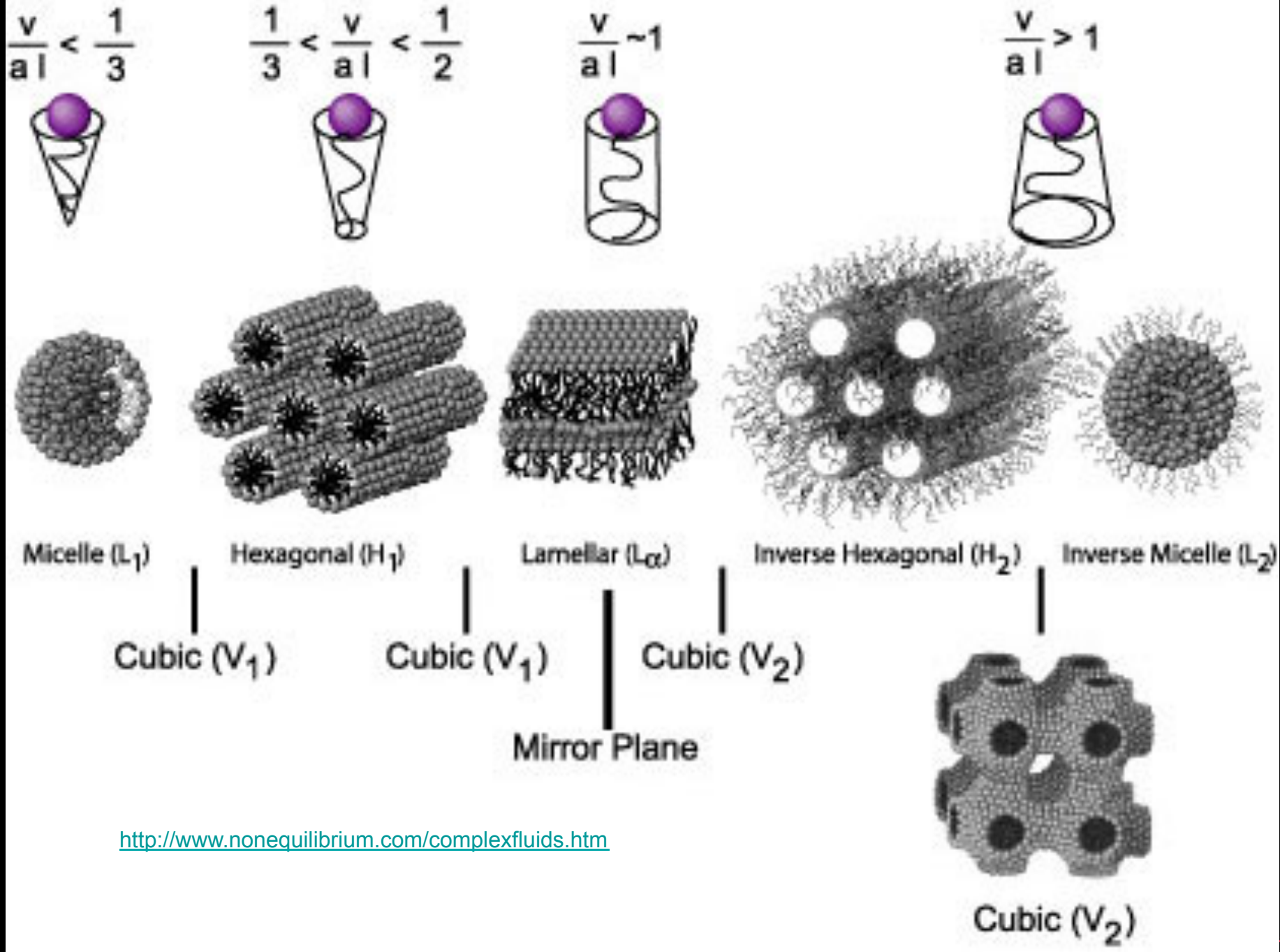
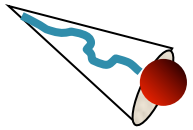


http://www.nonequilibrium.com/complexfluids.htm

A WORD ABOUT DRIVING FORCES

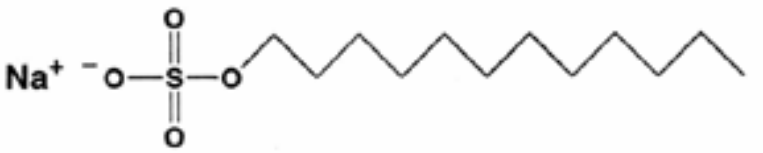
- In many surfactant systems the driving force for spontaneous self-assembly are the 'hydrophobic' effect combined with the Coulomb interactions of a polar or charged head groups.
- These Coulomb interactions are also related to the entropy of water packing around the head group.
- In general we need some net attraction.

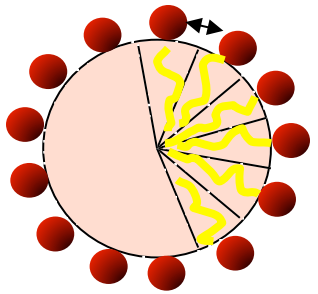


- If the net-attraction is too strong (on the order of 10 $k_B T$) irreversible aggregation takes place – hence, no equilibrium can be found. These systems are often aggregating irreversibly.

HOW TO GO FROM SPHERICAL TO WORMLIKE MICELLES?

Sodium dodecyl sulfate (SDS)





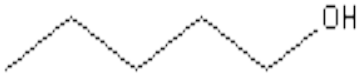
\+ Water

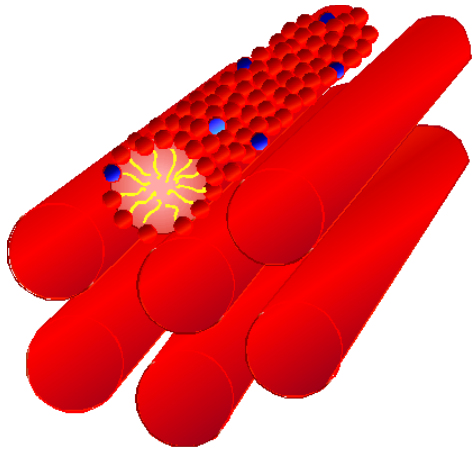
only spherical micelles form

adding a co-surfactant

changes spontaneous curvature

\+ Pentanol





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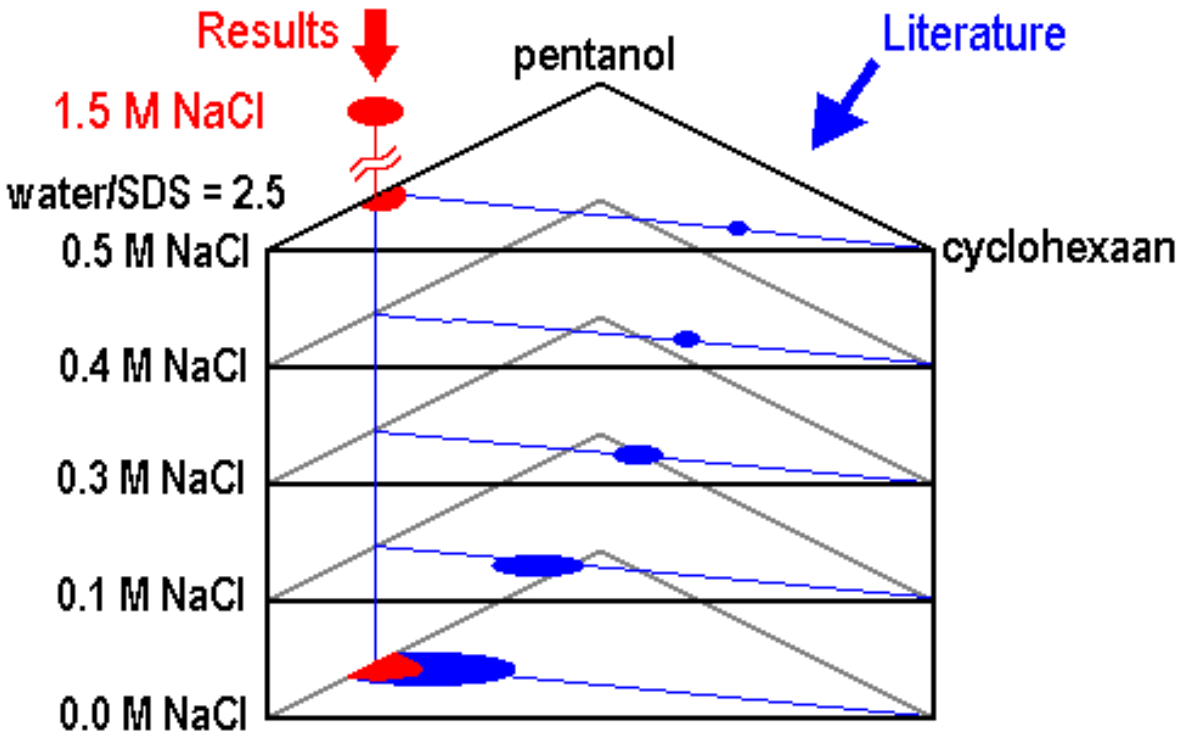
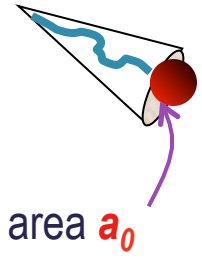
PHASE DIAGRAM



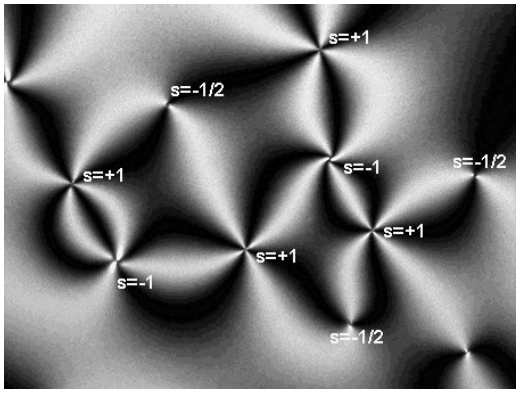
- One can swell the hexagonal phase with organic solvent by further decreasing the spontaneous curvature **1/*R*** by adding salt (which decreases the effective head-group size a_0)



HOW DO WE KNOW WHAT STRUCTURE WE HAVE?

There are simple lab techniques:

- Birefringence
- Microscopy under crossed polarizers – the resulting texture gives indications about the type of liquid crystalline properties
- Flow properties & Shear birefringence



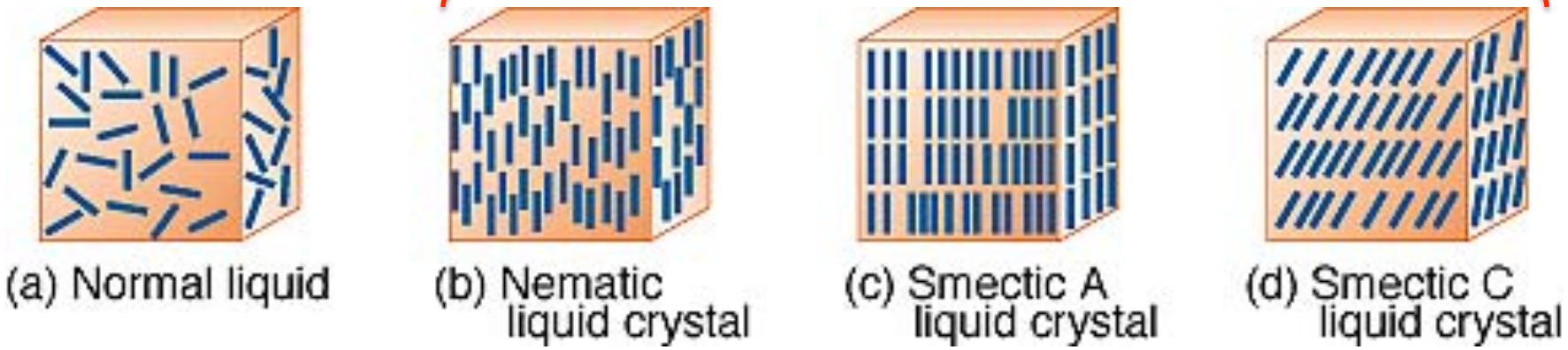
http://www.personal.kent.edu/~bisenyuk/liquidcrystals/textures1.html

For exact structural analysis we need:

- SAXS – Small Angle X-ray Scattering
- SANS – Small Angle Neutron Scattering
- Combination of Rheology & SAXS

LIQUID CRYSTALS

isotropic **non-isotropic**



- Under crossed polarizers **anisotropic** samples allow light passing through
- **Isotropic** samples do not let light pass through when placed between crossed polarizers.

http://wps.prenhall.com/wps/media/objects/3082/3156435/blb1201/bl12fg04.jpg

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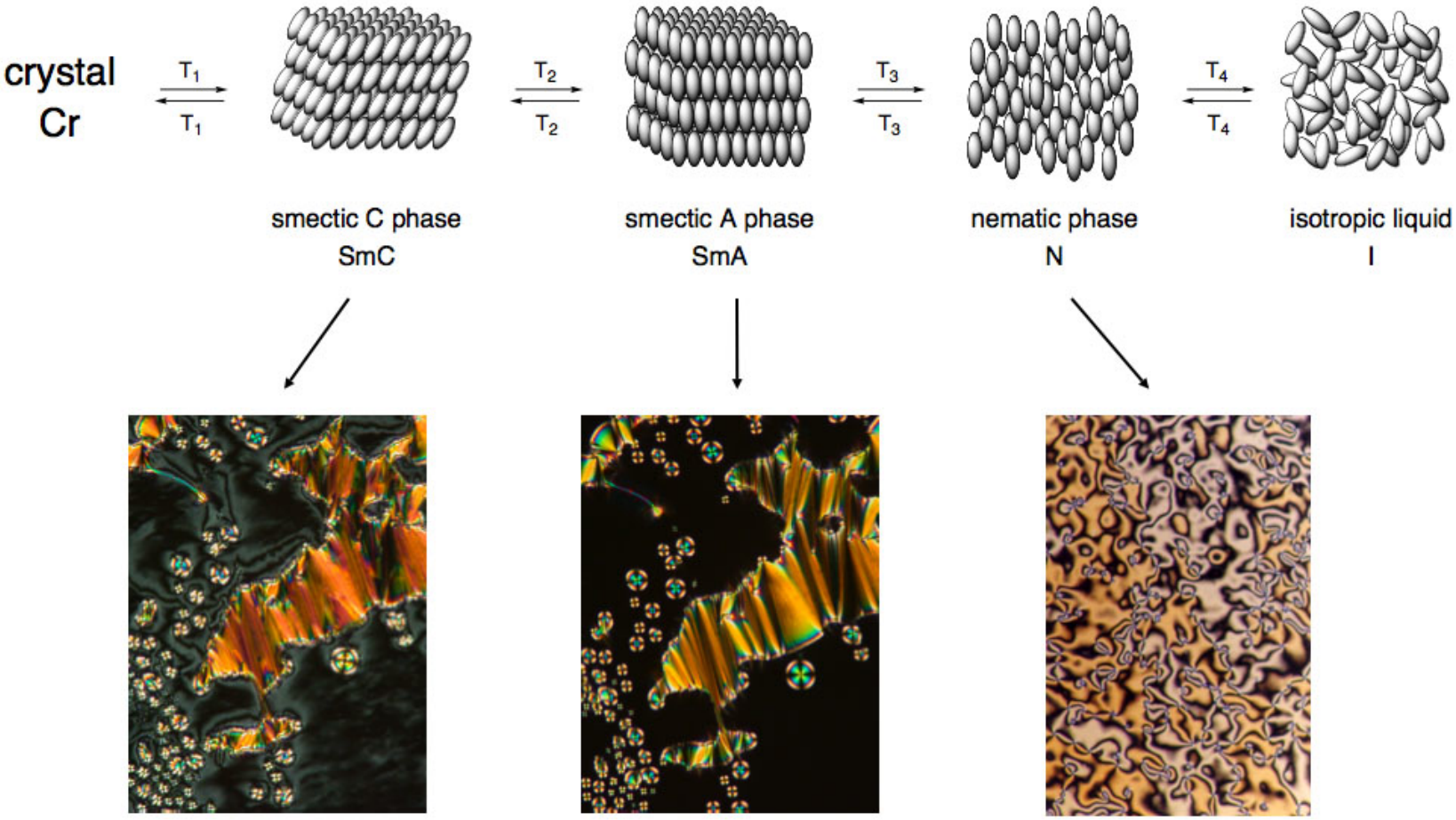
LIQUID CRYSTALS



http://faculty.chem.queensu.ca/people/faculty/lemieux/images/web-Fig.%201.jpg

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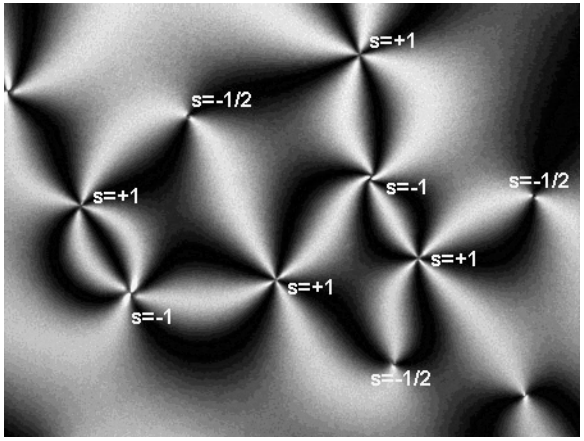
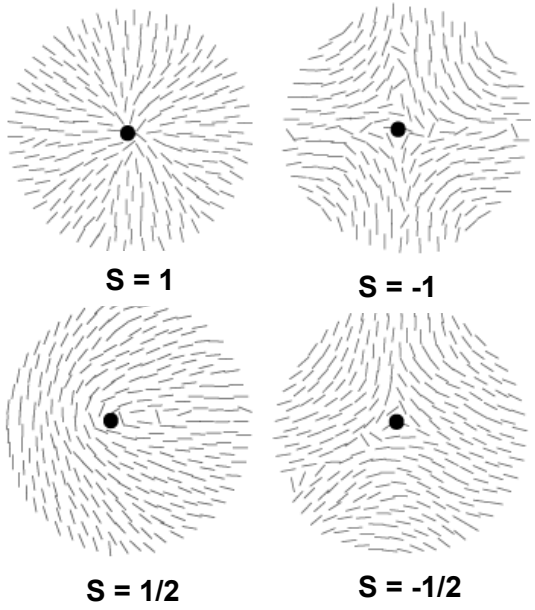
POLARIZED BRIGHT-FIELD MICROSCOPY

In polarized microscopy we cannot see the micelles but we do see defects or disclination lines

- To see birefringence (meaning different axial refractive indices, the sample needs to show **anisotropy**.
- The specific textures can give us a hint to what type of LC texture we have.



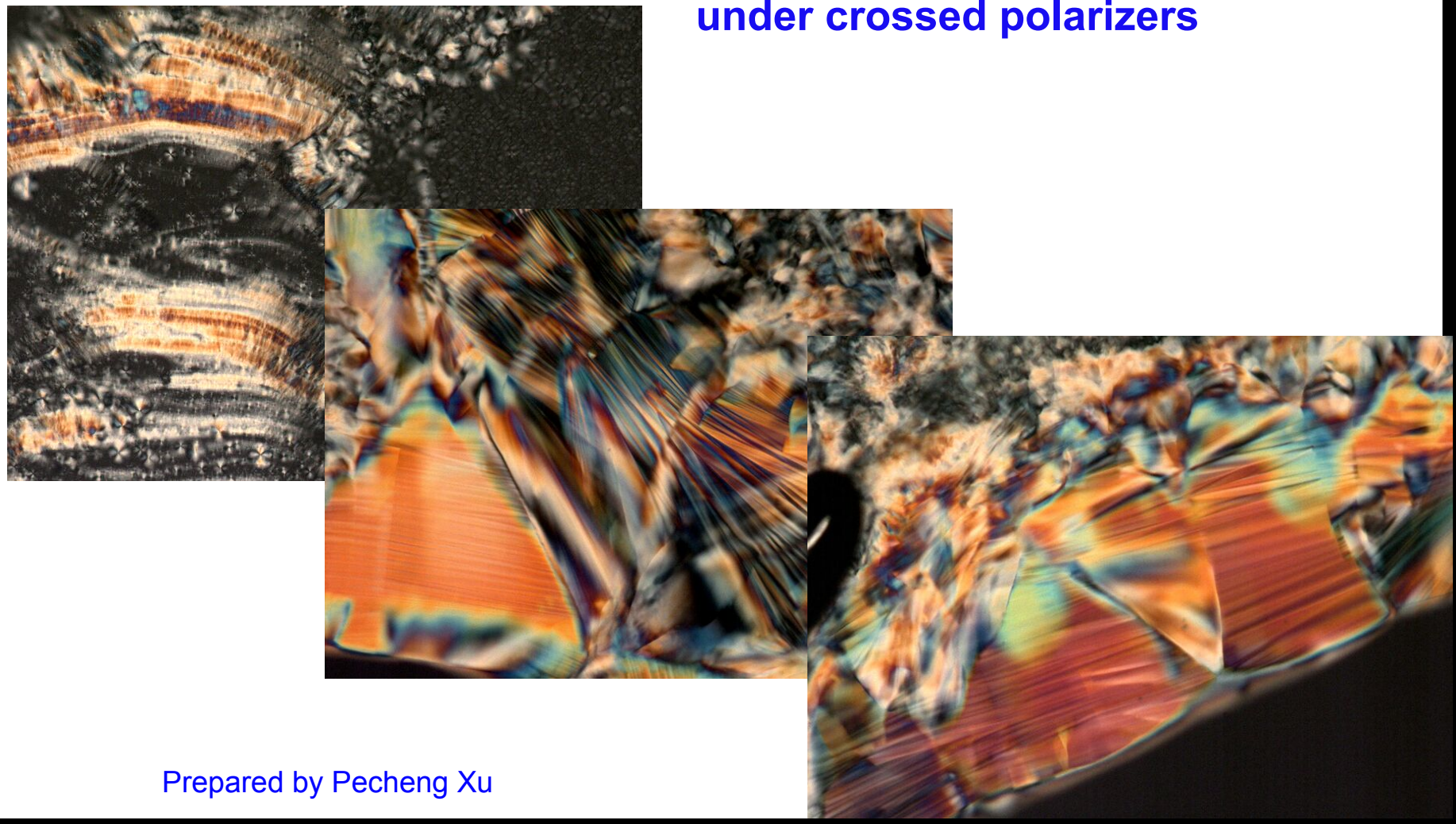
http://www.personal.kent.edu/~bisenyuk/liquidcrystals/textures1.html



CROSSED POLARIZER MICROSCOPY

Pure SDS + pentanol in water - hexagonal phase, freshly prepared

under crossed polarizers



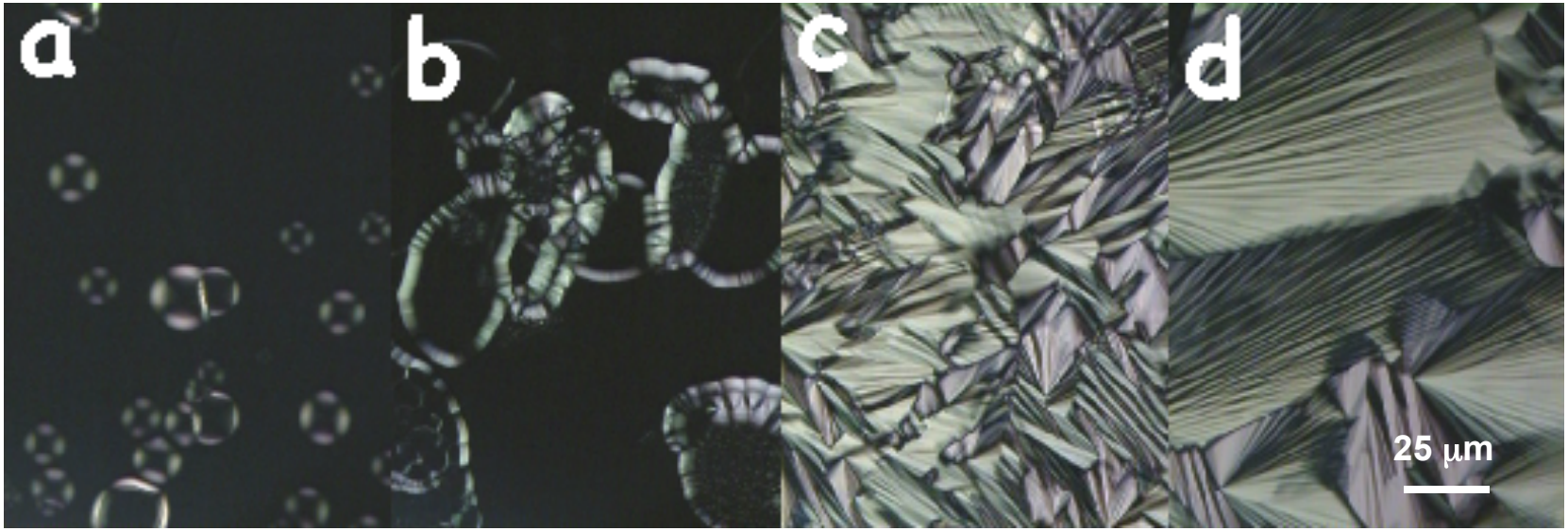
Prepared by Pecheng Xu

Erika Eiser

CROSSED POLARIZER MICROSCOPY

Pure SDS + pentanol in water - hexagonal phase

under crossed polarizers



Freshly prepared | 2 h | 1 day | 2 days

Growth of crystals in time

Because the end-cap energy is high small crystals shrink

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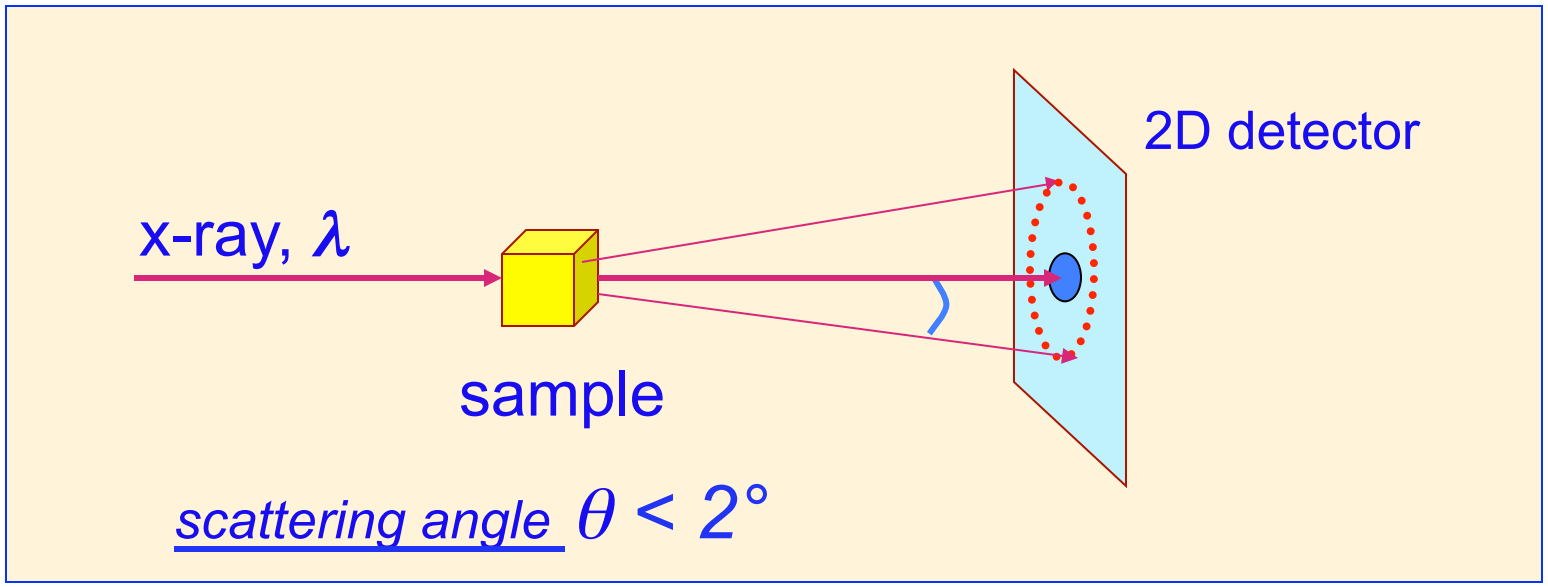
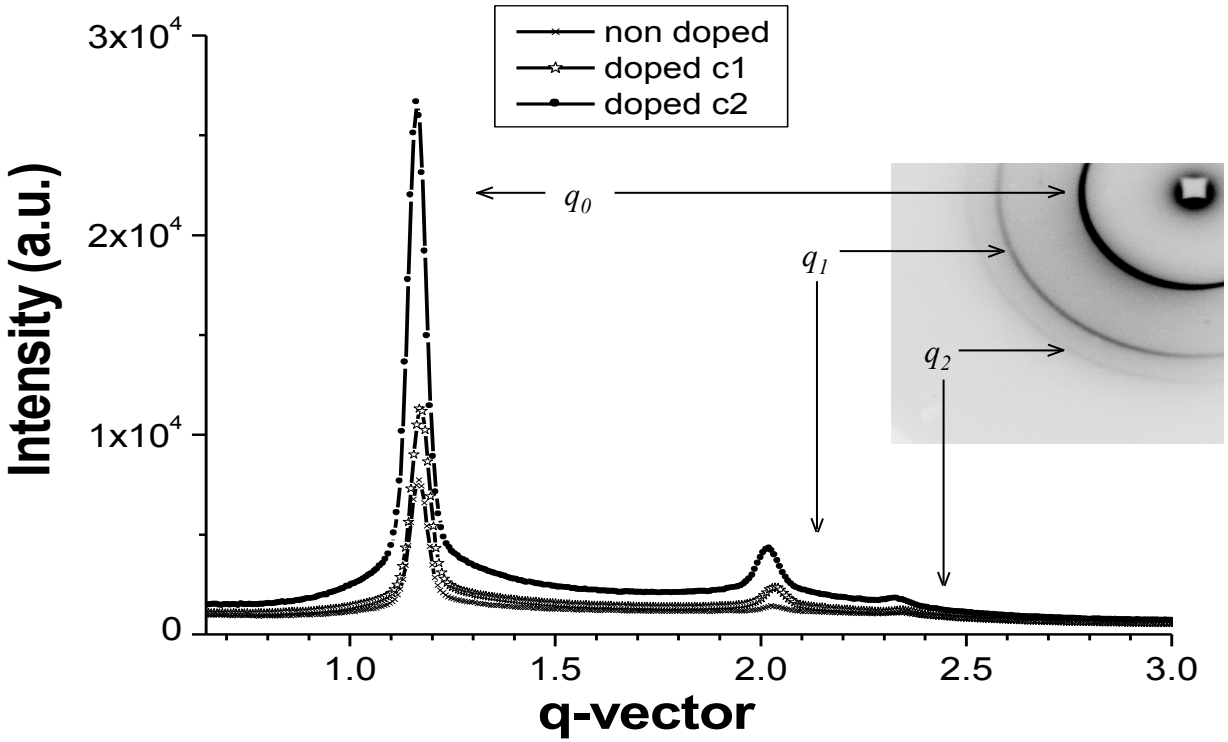
SMALL ANGLE X-RAY SCATTERING



- Home made setup (λ = 1.54 Å)
- Synchrotron ESRF : DUBBLE beam line BM26

  sample-to-detector distance = 4 m

SAXS: SIGNATURE OF A HEXAGONAL PHASE



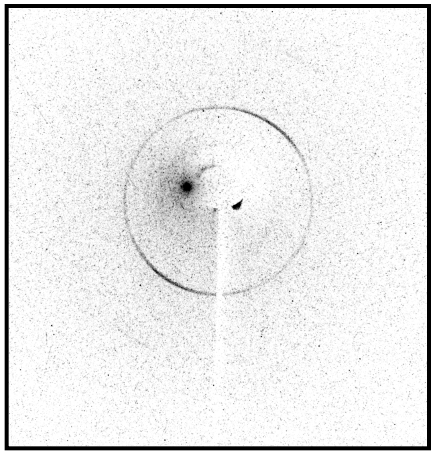
Powder spectrum of a hexagonal phase:

$$\frac{q_i}{q_0} = 1 : \sqrt{3} : 2 : \sqrt{7} : \ldots$$

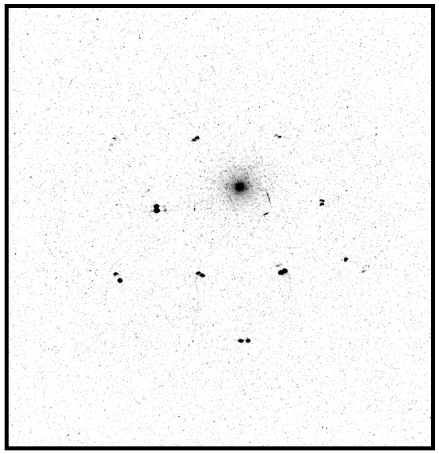
E. Eiser, F. Bouchama, M.B. Thathagar, and G. Rothenberg, "Trapping Metal Nanoclusters in "Soap and Water" Soft Crystals," *Chem. Phys. Chem.*, **4**, 526 (2003).

SAXS: SIGNATURE OF A HEXAGONAL PHASE

Ruthenium nanoclusters in hexagonal phase



a) 2 hours

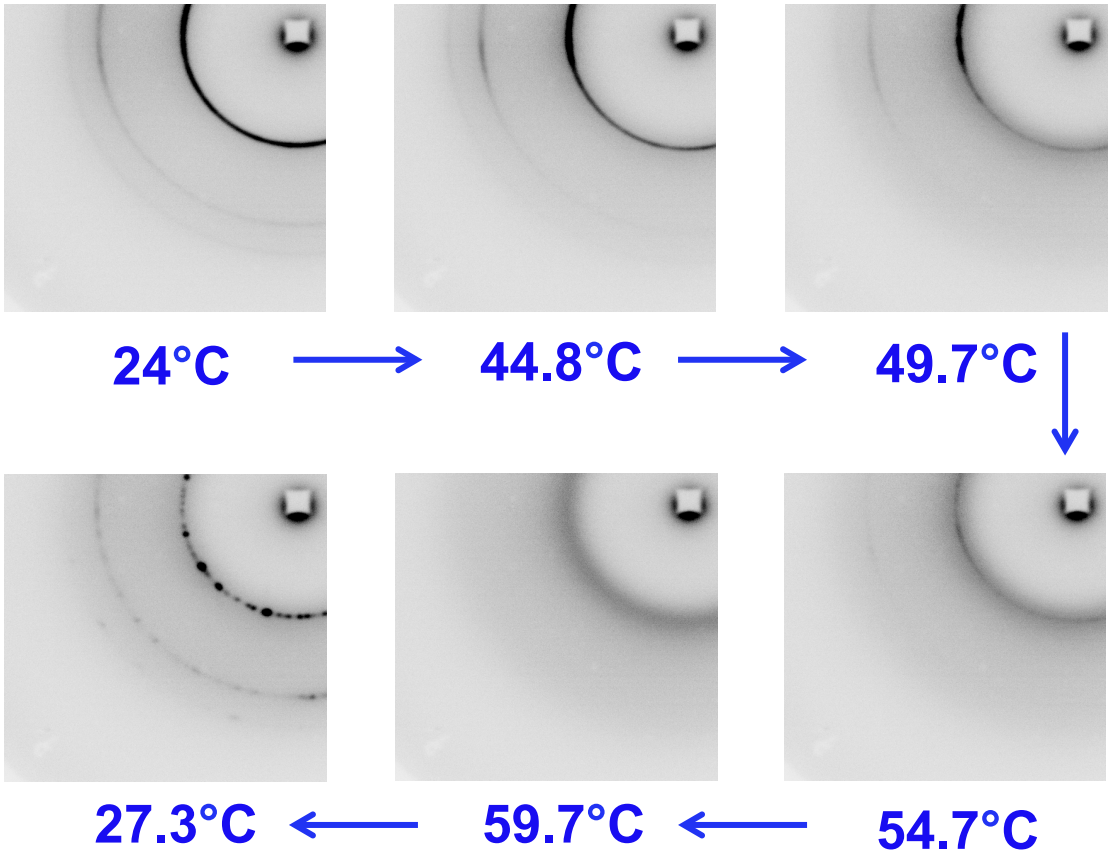


b) 60 days

- Measured with a home made setup (λ = 1.54 Å)
- *After 2h*: rings indicates a powder crystalline sample
- *After 60 days*: small crystals are 'eaten up' leaving a single crystal.

E. Eiser, F. Bouchama, M.B. Thathagar, and G. Rothenberg, "Trapping Metal Nanoclusters in "Soap and Water" Soft Crystals," *Chem. Phys. Chem.*, **4**, 526 (2003).

SAXS: MELTING OF THE HEXAGONAL PHASE



Bouchama, Thathagar, Rothenberg, Turkenburg, Eiser, "Self-Assembly of a Hexagonal Phase of Wormlike Micelles Containing Metal Nanoclusters," Langmuir, 20, 477 (2004)

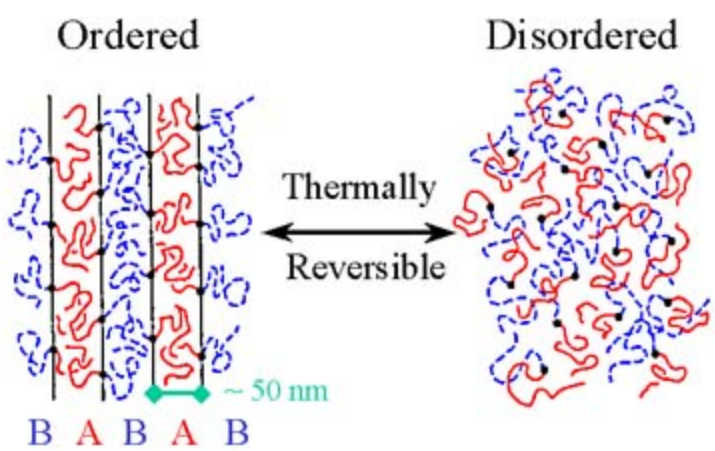
NOTE: THERE ARE MANY OTHER SELF-ASSEMBLING SYSTEMS

- Block-copolymers – melts & solutions
- Biological surfactants and macromolecules

- 2D self-assembly at interfaces

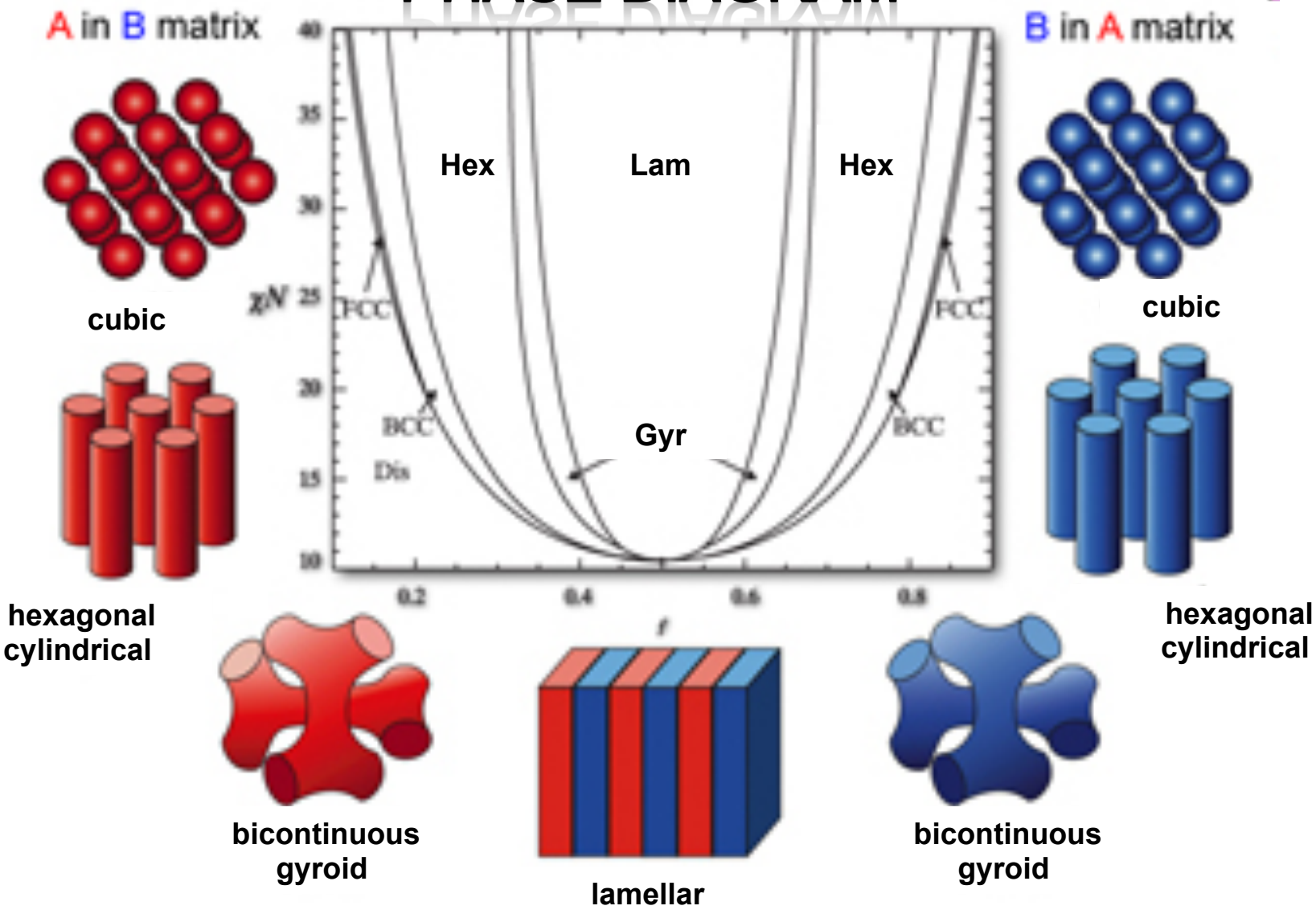
- And we need to consider the different driving energies: hydrophobic effect, π-π interactions, H-bonds, …

POLYMERIC SURFACTANTS



http://www.princeton.edu/~polymer/block.html

PHASE DIAGRAM



http://www.physics.nyu.edu/pine/research/nanocopoly/CopolyPhases.jpg

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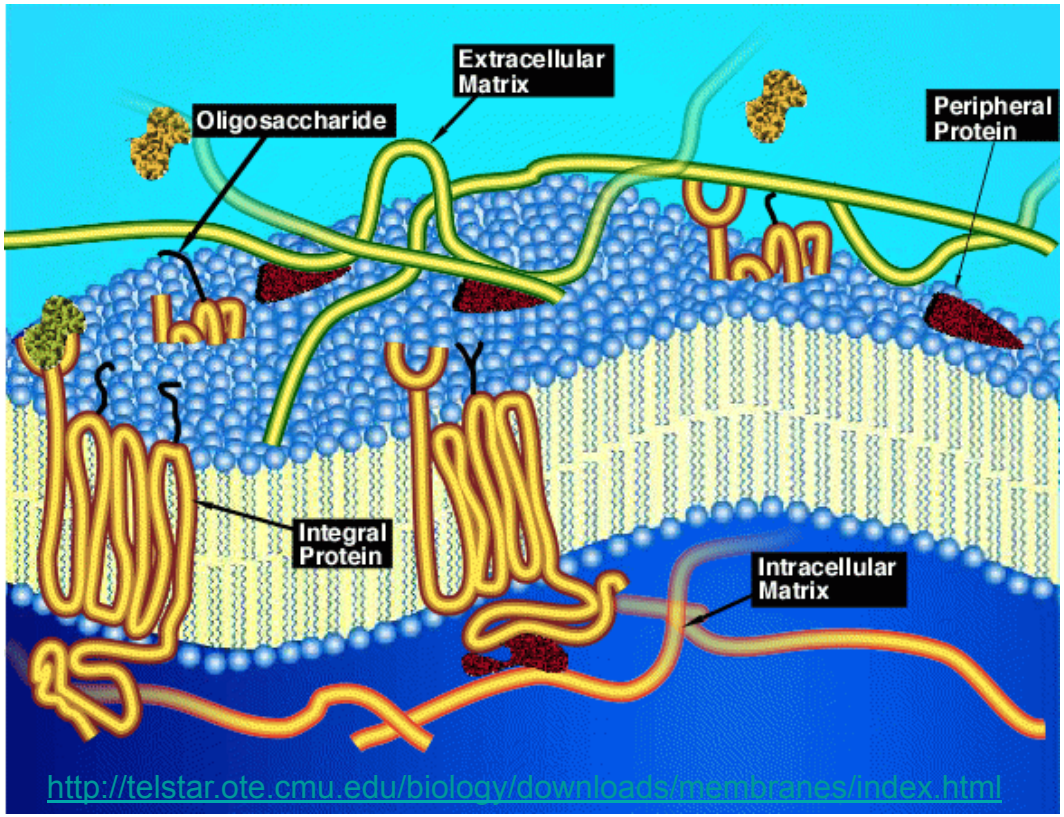
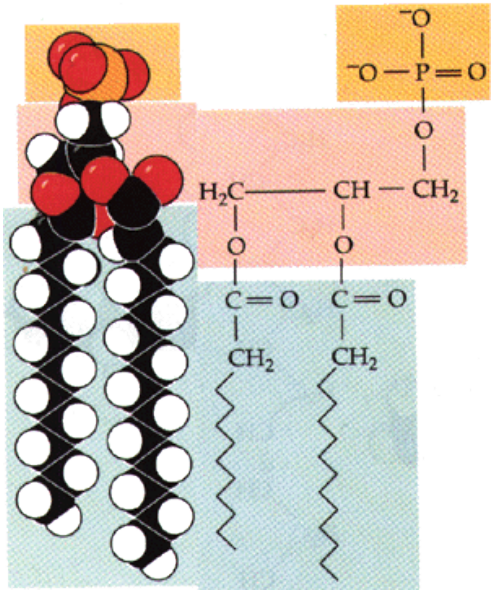
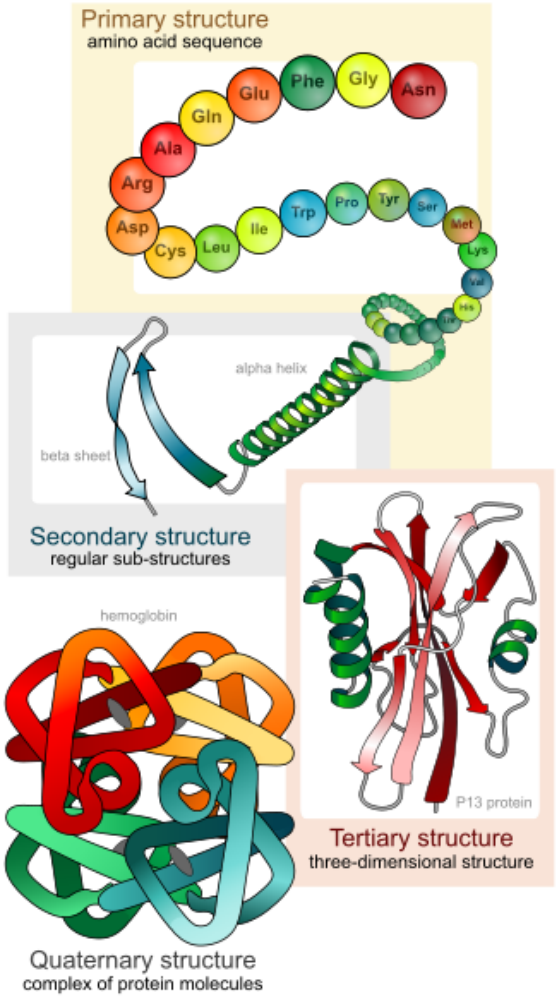
BIOLOGICAL EXAMPLES



CELL MEMBRANES & PROTEINS



phospholipids



http://en.wikipedia.org/wiki/Amyloid

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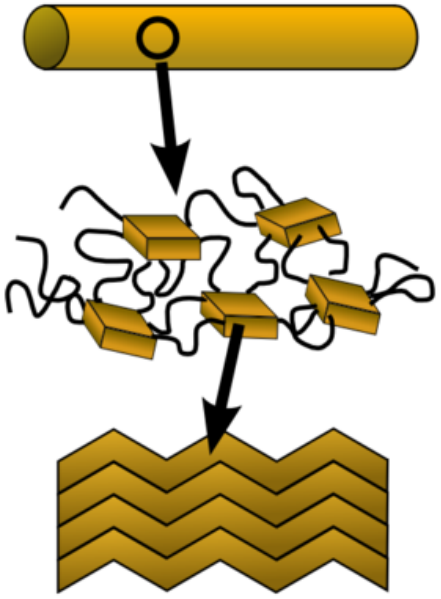
PROTEIN FOAMS

NON-DISEASED AMYLOID



Structure of spider silk: crystalline regions (beta-sheets) are separated by amorphous linkages.

It took more than one million spiders, five years and £300,000 to create the world's largest and rarest shawl made entirely from spider silk

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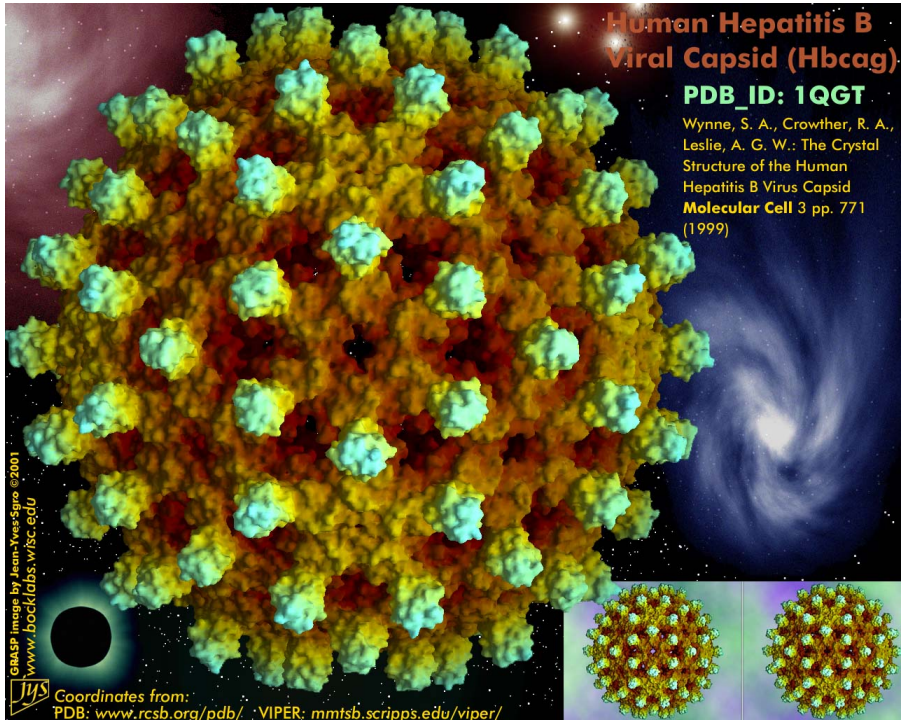
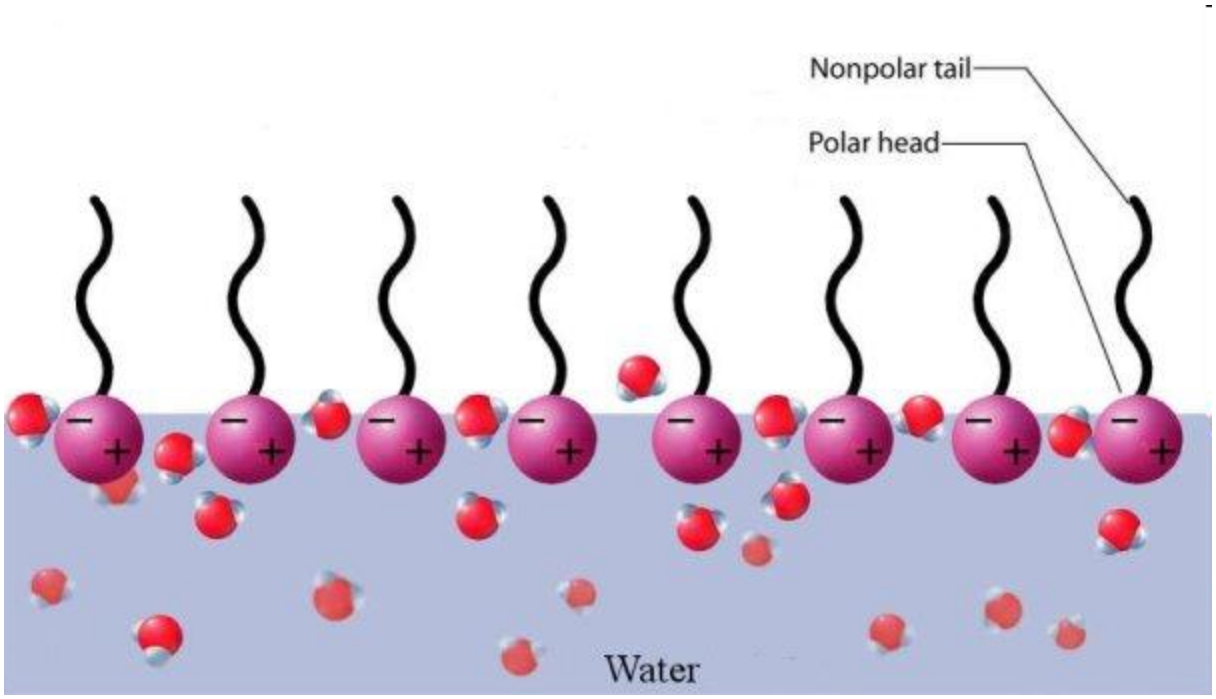
VIRUS CAPSIDS



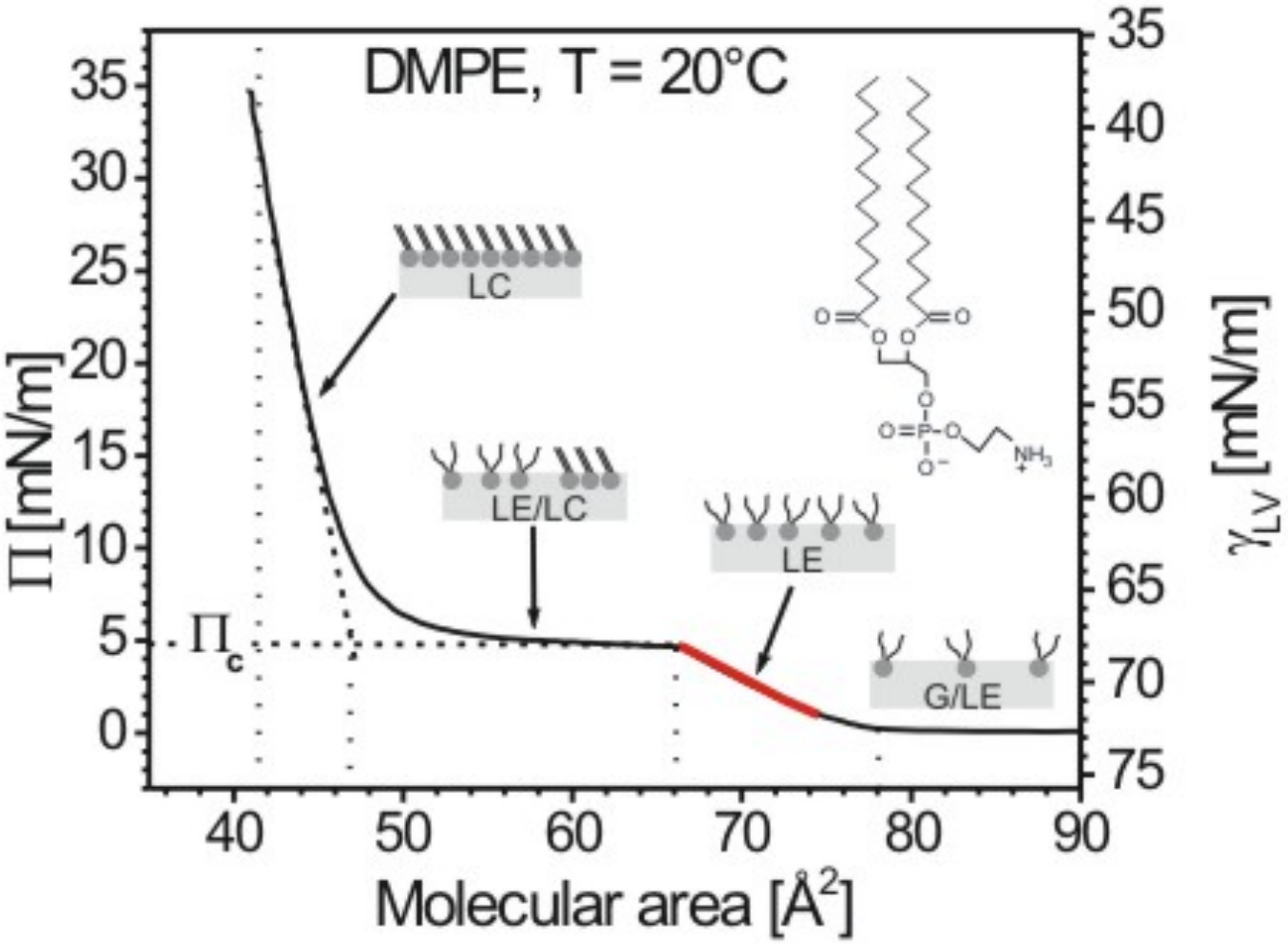
MEMBRANES AT THE AIR-WATER INTERFACE



http://www.answers.com/topic/langmuir-blodgett-film

LANGMUIR-BLODGETT FILMS

lipid DMPE (1,2-Dimyristoyl-*sn*-glycero-phosphoethanol- amine)



http://www.mpip-mainz.mpg.de/~grafk/Monolayer_LB.html

LANGMUIR-BLODGETT FILMS

Surface pressure – area isotherms…

…are the best method to study monolayers.

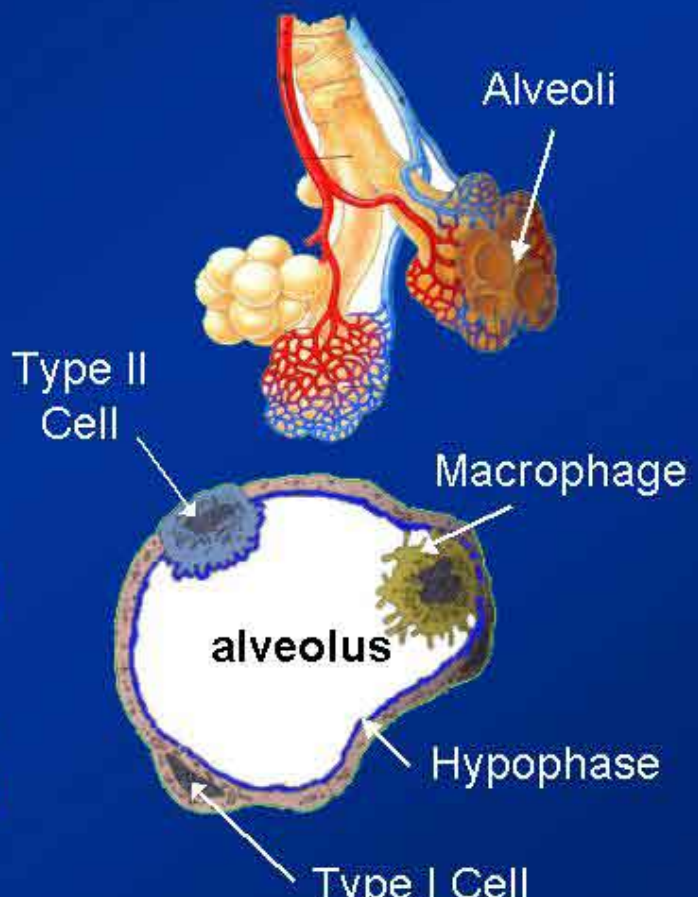
$$\pi = \gamma_0 - \gamma$$

= pressure that opposes the normal contracting tension of the surfactant free interface.

LUNG SURFACTANTS

The Alveolus

- Alveoli are lined with an aqueous hypophase
- The hypophase generates a high surface tension, which threatens lung function
- Type II cells produce pulmonary surfactant



http://www.science.org.au/events/frontiers2003/orgeig.htm

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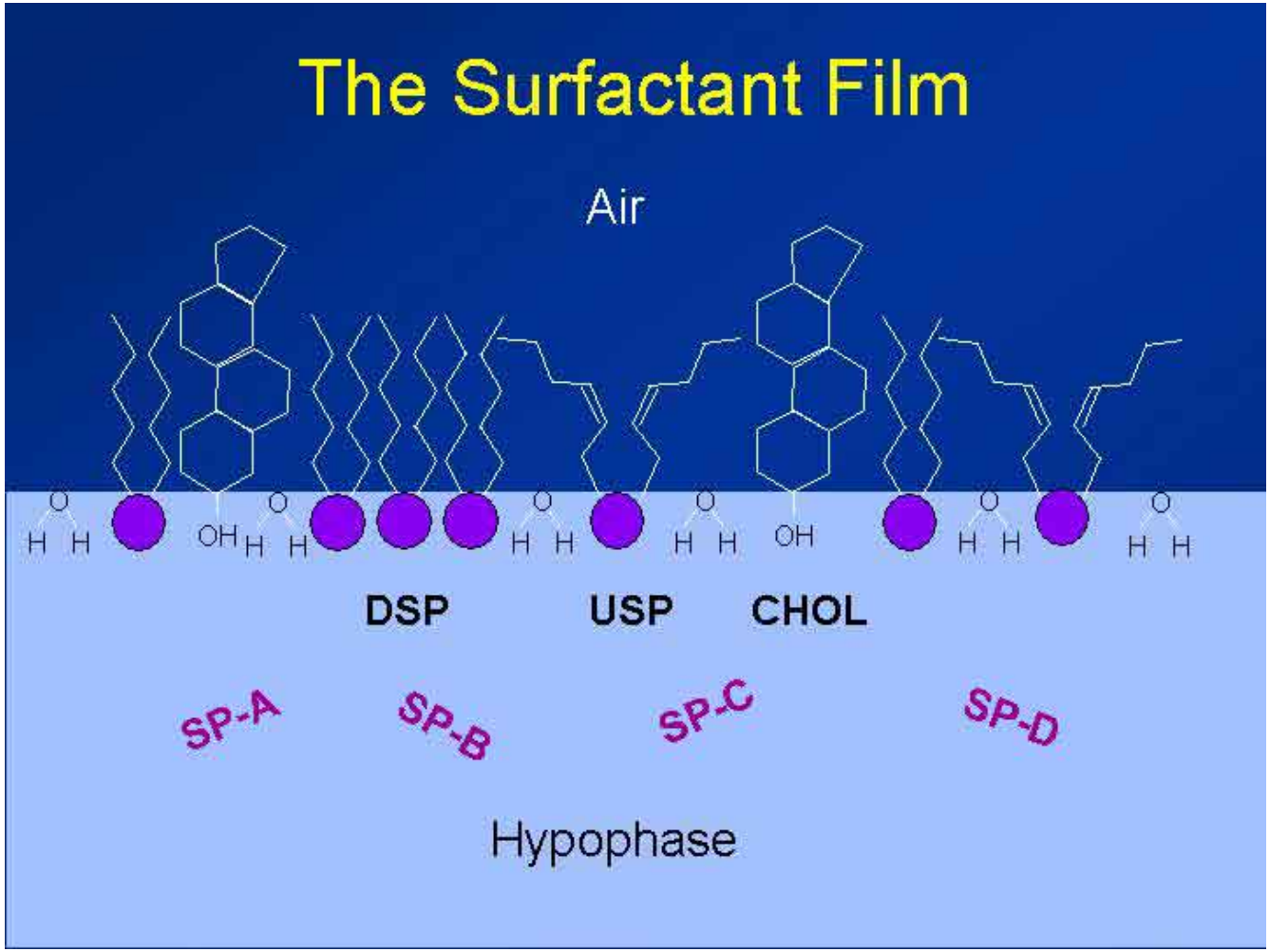
LUNG SURFACTANTS



http://www.science.org.au/events/frontiers2003/orgeig.htm

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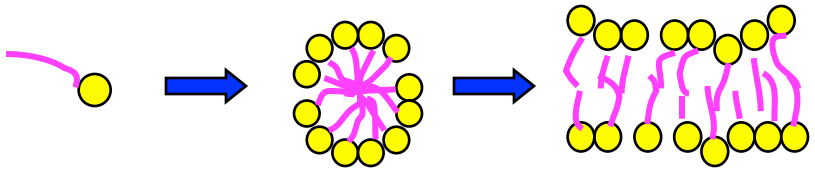
OTHER TYPES OF SELF ASSEMBLY

VARIOUS TYPES OF SA IN SOLVENTS

I. **hydrophobic effect** → surfactant molecules



→ Protein aggregation

II. **attractive π-π interactions** → typically aromatic rings with delocalized π -orbitals

III. **H-bridges in DNA**

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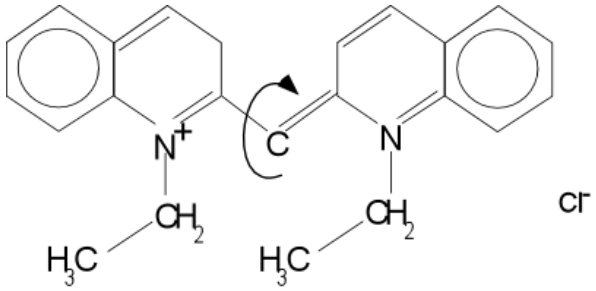
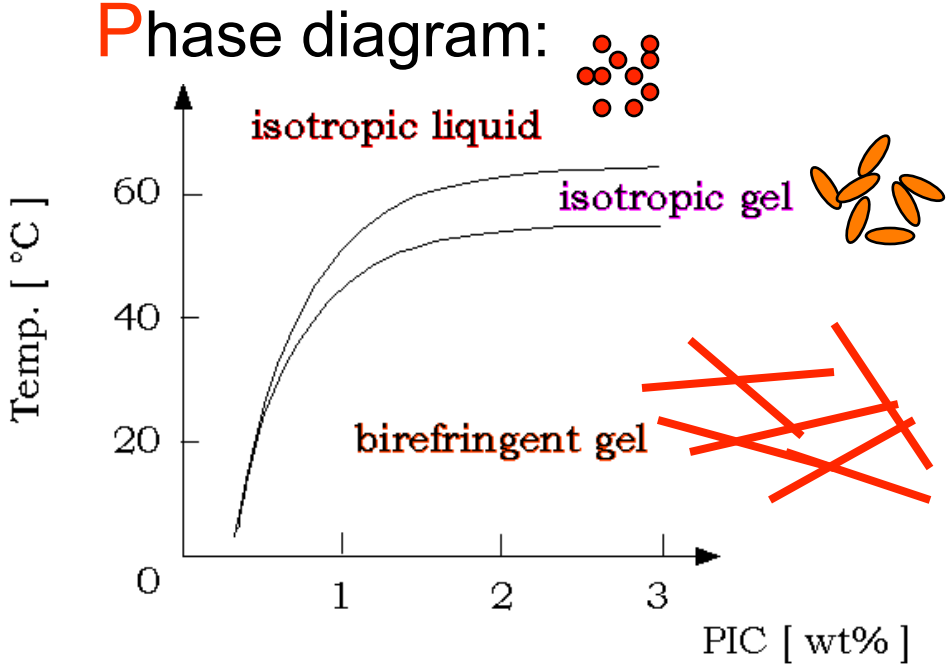
ATTRACTIVE Π-Π INTERACTIONS

- **PIC** pseudoisocyanine chloride

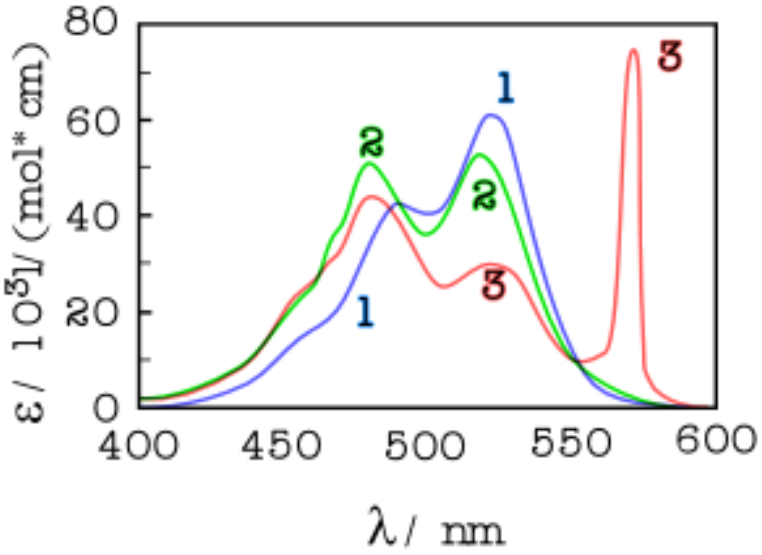


Phase diagram:



J AGGREGATES

- shift the adsorption band towards longer λ (H-aggregates → shift to smaller wavelengths)



UV/Vis-spectrometry:

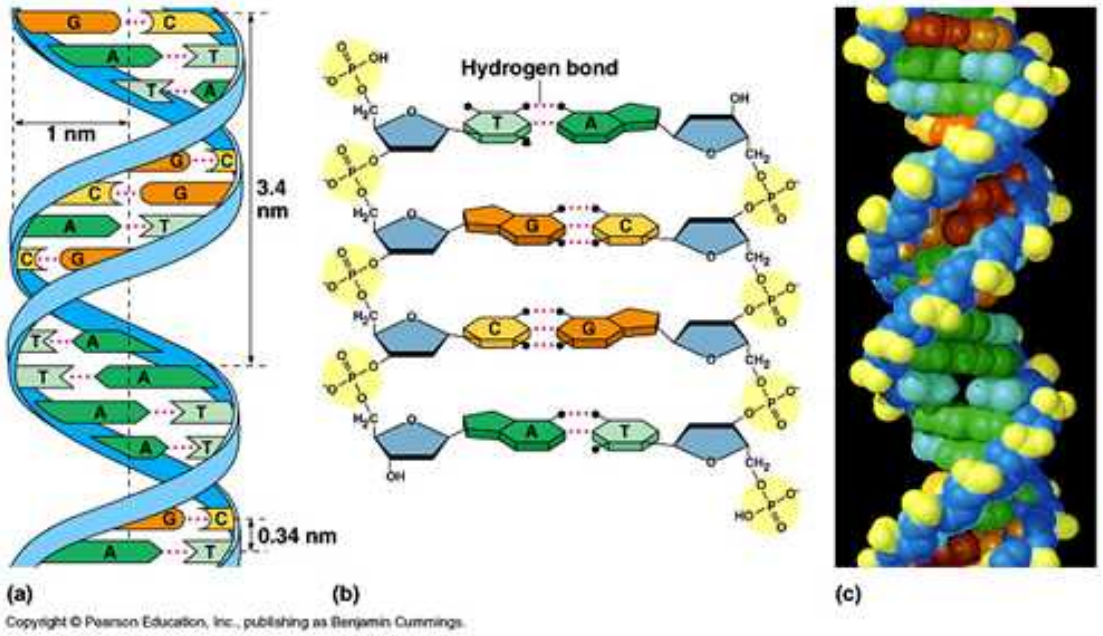
1. 8.6×10^{-6} mol/l, 25°C → monomers
2. 8.6×10^{-4} mol/l, 25°C → mono + dimers
3. 1.08×10^{-2} mol/l, 31°C → dimers + J-aggregates

Light harvesting complex II viewed from above, showing chlorophyll and carotenoid pigments

http://www.steve.gb.com/science/photosynthesis.html

Next time

DNA
A SELECTIVE & REVERSIBLE GLUE



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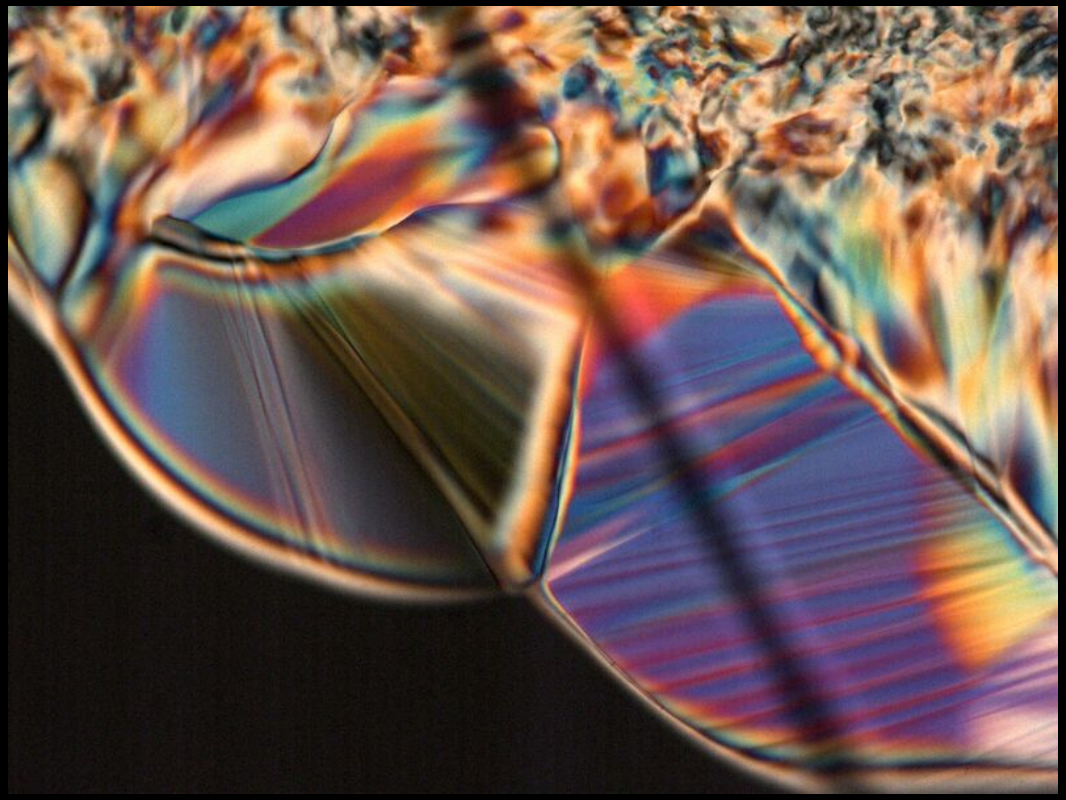
Questions?



MEISER GROUP