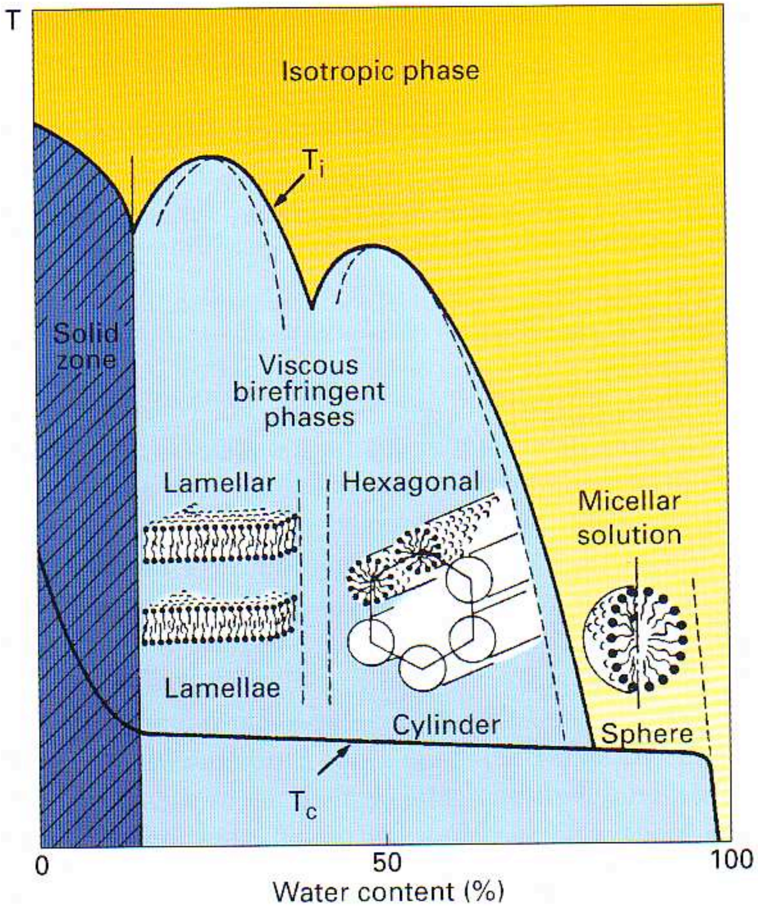
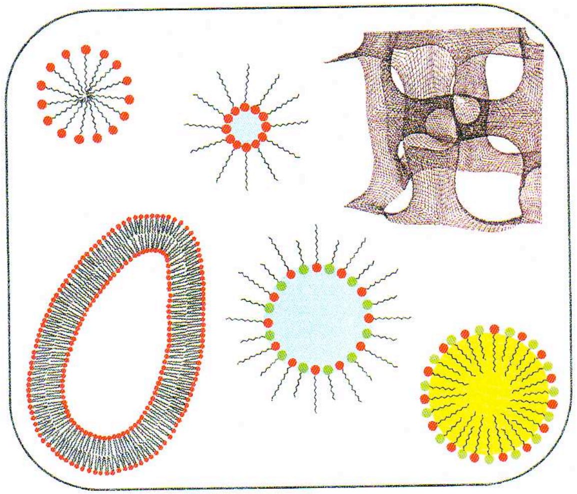
Self assembly & soft matter in nature





Literature

- Jones - chp. 9 - Self Assembly
- Jones - chp. 10 - Soft Matter in nature
- C. A. Angell, *Formation of Glasses from Liquids and Biopolymers,* Science 267, 1924 (31 March 1995)
- Materials Today: March and September issues (2006)
  Templating materials with self assembly

Self-assembly

Characteristics of self-assembly

Self assembly with surfactants & amphiphiles

- *what/types*
- *energies*
- *aggregation geometries & phase behaviour*

Self assembly with polymers

- *phase separation*
- *structures*

4 Characteristics of Soft Matter

i) Length scales:

- Structures of ≈10-1000 nm determine the properties

ii) Time scales: processes from 10^{-12} - 10^{3} s

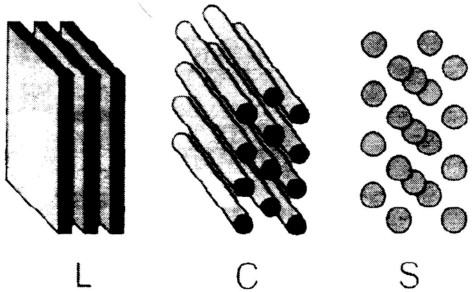
- Dynamics processes over a wide time scales 10^{-12} - 10^{3} s
- Very slow processes in non-equilibrium configurations

iii) Weak interactions

- Interactions ≈ kT

iv) Self assembly

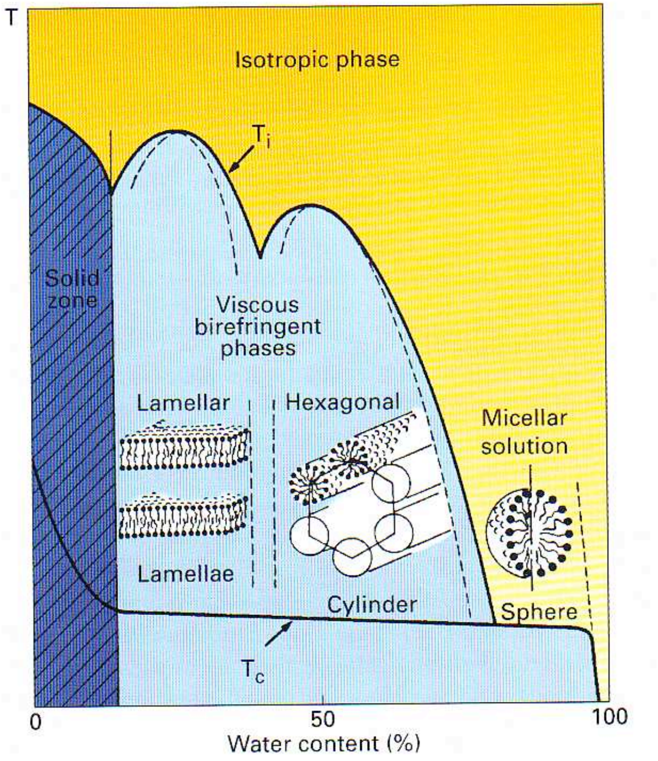
- Hierarchical arrangement of structures



- Competition between interaction energy and entropy

Self-assembly

1. Hierarchical arrangement of structures
2. Competition between interaction energy and entropy
3. Structures of ≈10 to >1000 nm formed and determine the properties of the material



Surfactants and amphiphiles

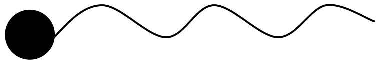
Amphiphilic molecule:
two parts with very different affinities
⇒ *surfactants, bolck co-polymers*

Surfactant:
an amphiphilic molecule with a tendency to adsorb onto free surfaces and interfaces (Swedish - *tensid*)

Surfactants and amphiphiles

Amphiphilic molecule:
two parts with very different affinities

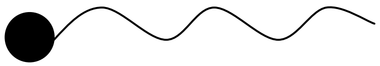
Ex. hydrophilic head and hydrophobic tail



a single molecule is never really comfortable in a solvent
⇒ aggregation to minimize the interfacial energy
⇒ micro-phase separation, thermodynamically stable aggregates - micelles

Surfactants and amphiphiles

Amphiphilic molecule:
two parts with very different affinities
Ex. hydrophilic head and hydrophobic tail



Hydrophobic tail: $CH_3(CH_2)_n$-

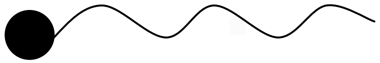
Hydrophilic head:
Anionic (-)
Cationic (+)
non-ionic
block-copolymers

Small molecules $M_W \approx 100\text{-}1000$

Surfactants and amphiphiles

Amphiphilic molecule:
two parts with very different affinities

Ex. hydrophilic head and hydrophobic tail



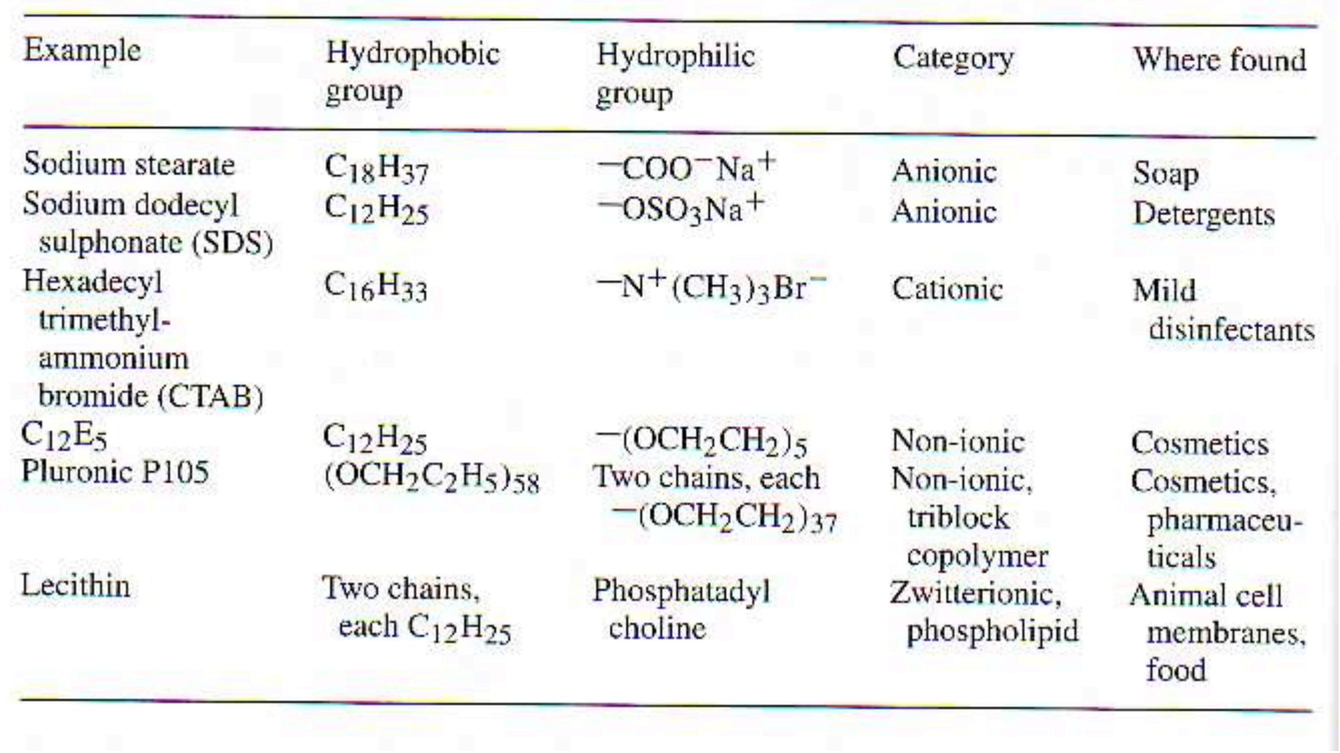


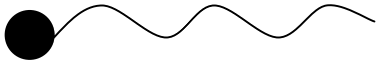
Table 9.1 Examples of common amphiphiles

Example	Hydrophobic group	Hydrophilic group	Category	Where found
Sodium stearate	$C_{18}H_{37}$	$-COO^-Na^+$	Anionic	Soap
Sodium dodecyl sulphonate (SDS)	$C_{12}H_{25}$	$-OSO_3Na^+$	Anionic	Detergents
Hexadecyl trimethyl-ammonium bromide (CTAB)	$C_{16}H_{33}$	$-N^+(CH_3)_3Br^-$	Cationic	Mild disinfectants
$C_{12}E_5$	$C_{12}H_{25}$	$-(OCH_2CH_2)_5$	Non-ionic	Cosmetics
Pluronic P105	$(OCH_2C_2H_5)_{58}$	Two chains, each $-(OCH_2CH_2)_{37}$	Non-ionic, triblock copolymer	Cosmetics, pharmaceuticals
Lecithin	Two chains, each $C_{12}H_{25}$	Phosphatadyl choline	Zwitterionic, phospholipid	Animal cell membranes, food

Surfactants and amphiphiles

Amphiphilic molecule:
two parts with very different affinities

Ex. hydrophilic head and hydrophobic tail



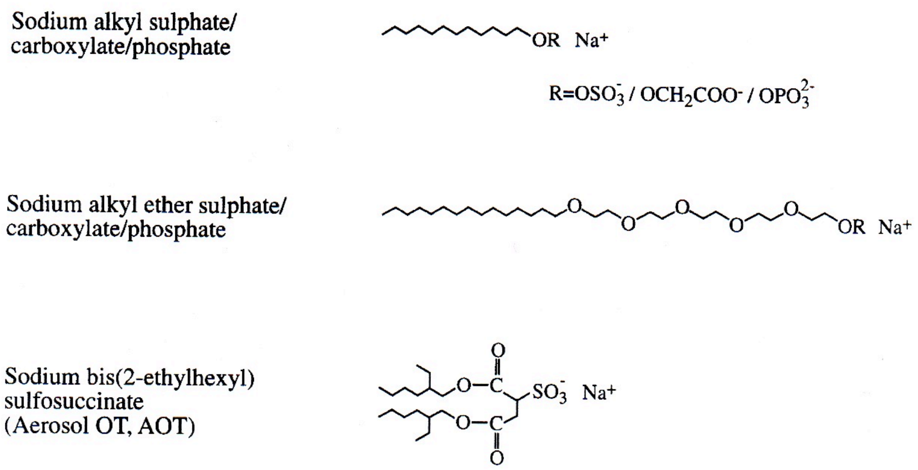


Figure 4.1 Typical anionic surfactants

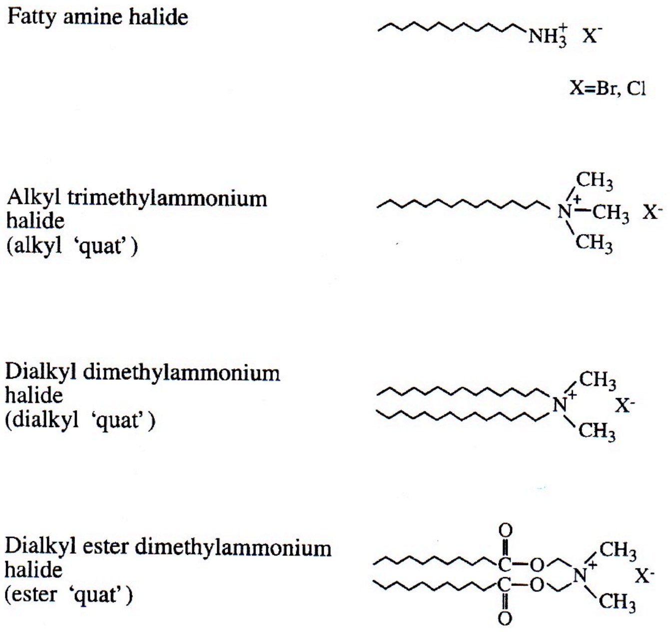
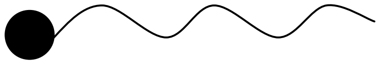


Figure 4.2 Typical cationic surfactants

Surfactants and amphiphiles

Ex. *hydrophilic head and hydrophobic tail*



Self-assembly of molecules in order to minimise free energy
⇒ minimising the contact between water (solvent) and hydrophobic tail while keeping the hydrophilic head in contact with water

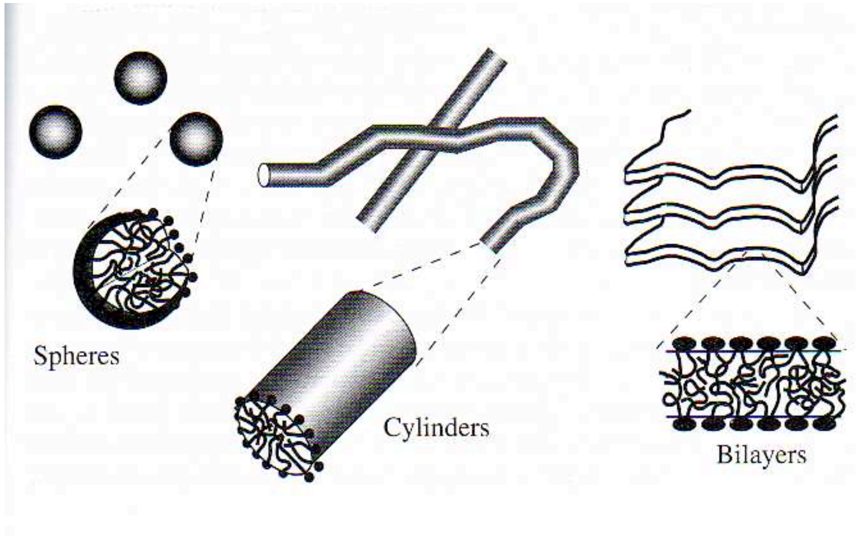


Fig. 9.1 Types of aggregates that are encountered in amphiphile solutions.

Macro vs. micro phase separation

Simple liquids (water & oil):

$\varepsilon_N = \varepsilon_\infty + \frac{\alpha k_B T}{N^{1/3}}$ free energy when a molecule joins an aggregate

N - number of molecules in the aggregate

$\alpha k_B T = 4\pi\gamma\left(3v/4\pi\right)^{2/3}$ γ - interfacial energy, v - molecular volume

ε_N - monotonic decreasing function of N

⇒ infinite aggregates - macroscopic phase separation

Amphiphiles:

⇒ finite size of aggregates - microscopic phase separation

Why?

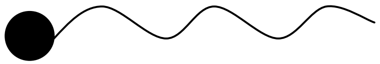
Macro vs. micro phase separation

Amphiphiles:

⇒ micro-phase separation

⇒ finite size of aggregates

entropic considerations more important



Why? Balance between protecting the hydrophobic tail and keeping the head in contact with the water

associating tails vs. repulsion of head groups

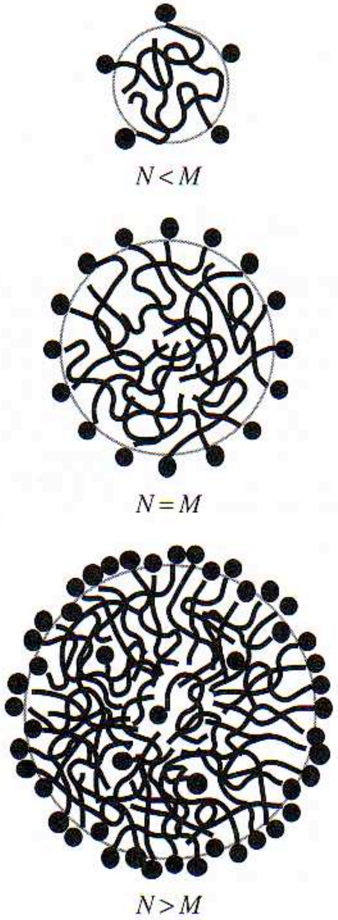


Fig. 9.3 The optimum aggregation number, *M* for a spherical micelle. Micelles containing a smaller number of molecules have too large an area for each head-group, causing unfavourable water/hydrocarbon interactions, while in micelles larger than the optimum number some head-groups are forced inside the hydrophobic core.

Shape of aggregates

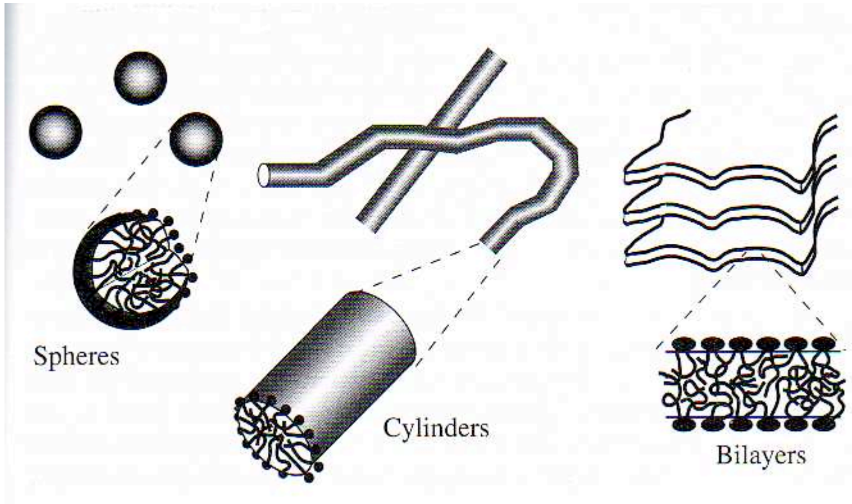
Basic shapes:

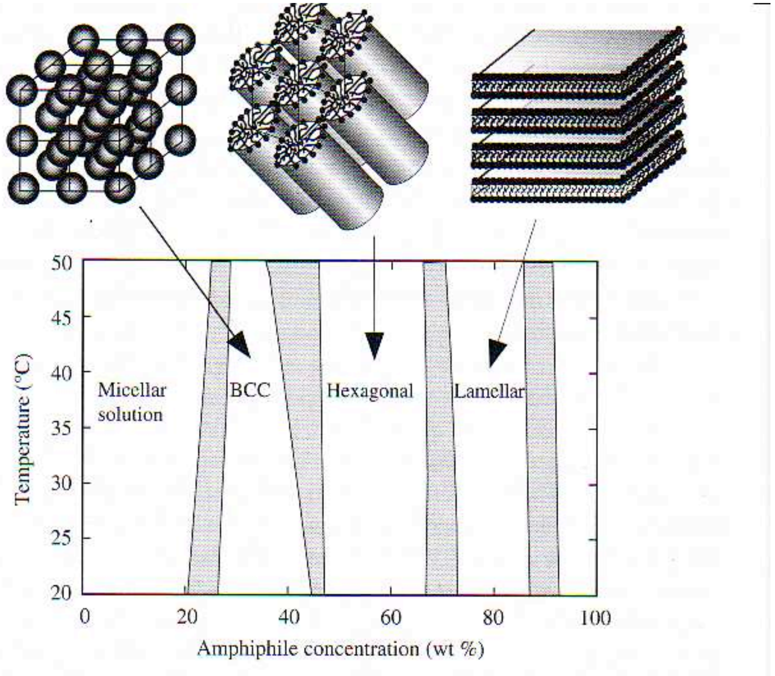
- spheres
- cylinders
- bilayers
- vesicles

micelles

Superstructures:

- micellar crystals
- lamellar phases
- bicontinuous networks
- …

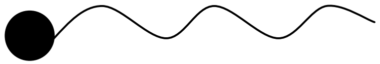




Shape of aggregates

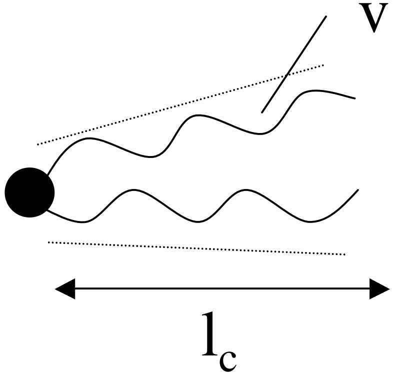
Factors determining the shape

i) Optimum head group are, a_0
ii) Critical chain length, l_c
iii) Hydrocarbon volume, v

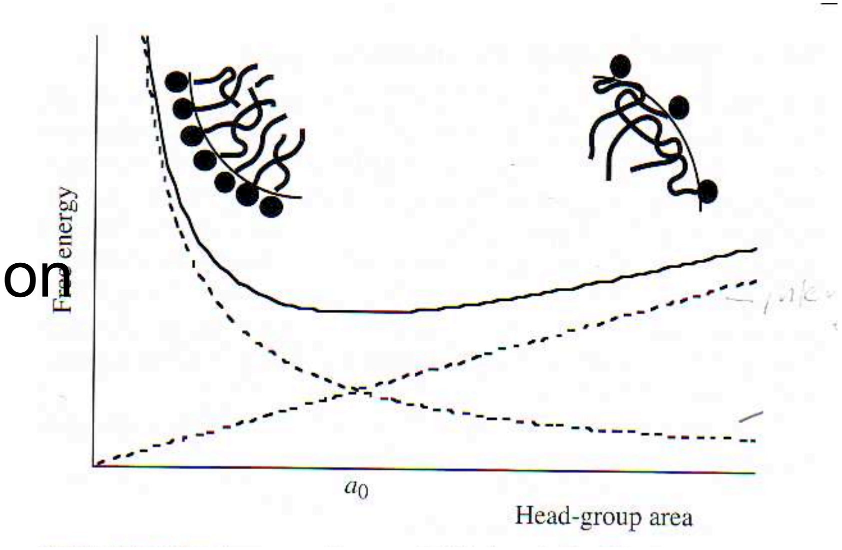


l_c - length of fully extended tail

v - volume of the tail
\# of tails, side groups, …



Optimum head group area, a_0



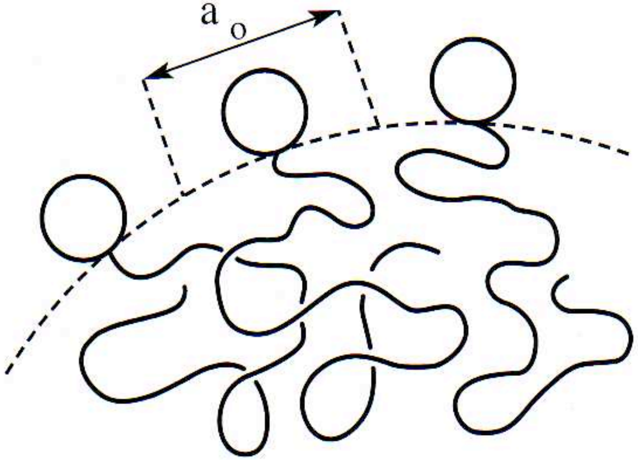
a_0 controlled by

repulsive forces:

electrostatic or steric repulsion
(can be altered by e.g
salt concentration)

attractive forces:

protecting the tail



Shape of aggregates

Spheres - smallest area/volume

Volume:
$4\pi r^3/3=Nv$
(N - # of molecules in aggregate)

Surface area:
$4\pi r^2=Na_0$

$\Rightarrow r=3v/a_0$ but $r_{max} \leq l_c$

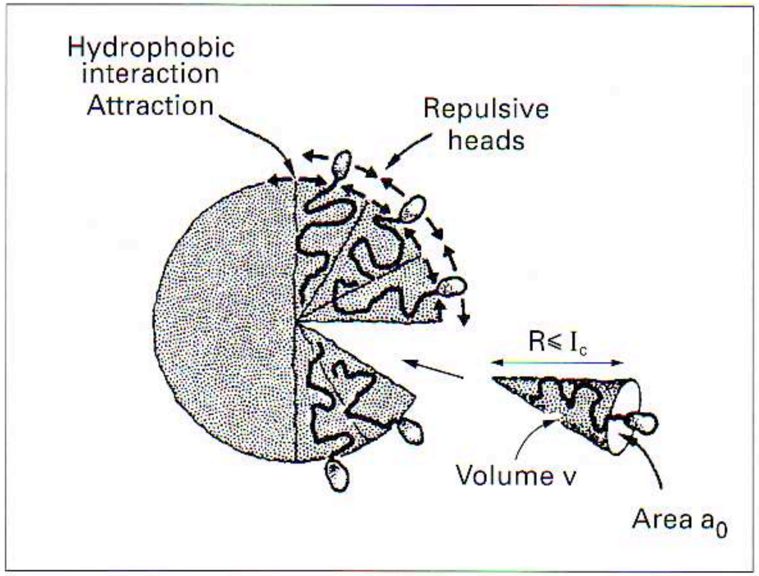


Fig. 4.4. Schematic diagram of a micelle

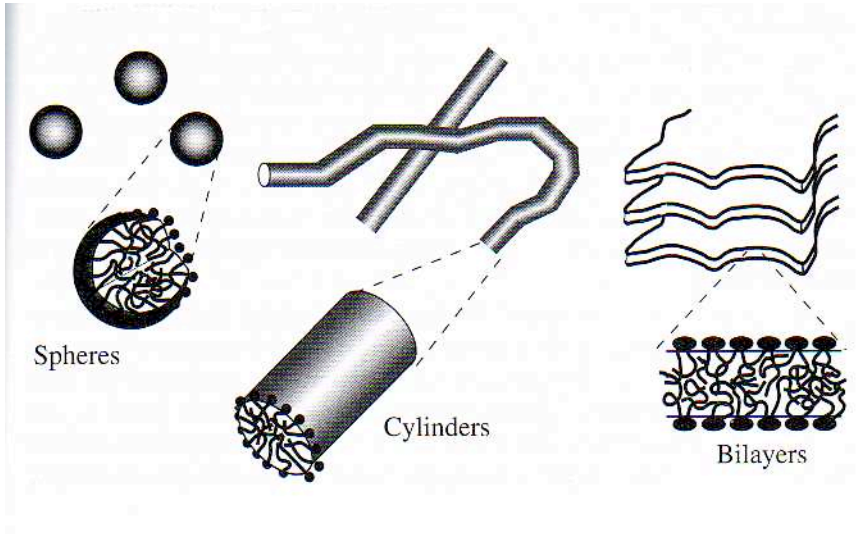
$\boxed{v/l_c a_0 \leq 1/3 \text{ for spherical micells}}$

Shape of aggregates

Spheres:
$v/l_c a_0 \leq 1/3$

Cylinders:
$1/3 \leq v/l_c a_0 \leq 1/2$

Bilayer:
$v/l_c a_0 > 1/2$



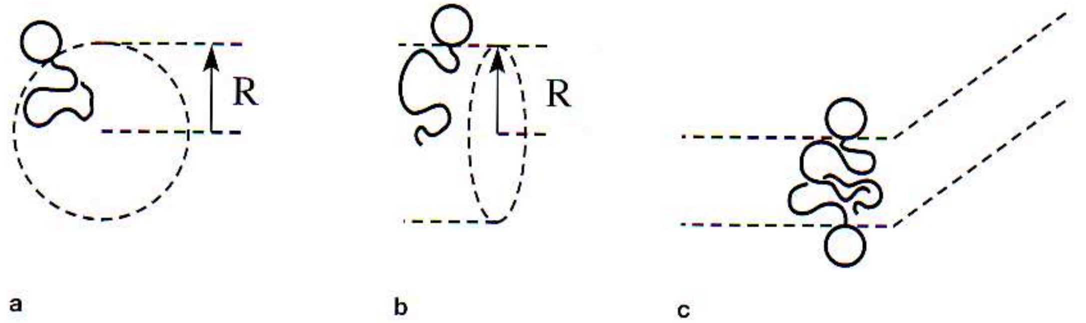


Fig. 5.4. Three possible morphologies, with their curvature. (**a**) Sphere, curvature $1/R+1/R = 2/R$. (**b**) Cylinder, curvature $1/R + 0 = 1/R$. (**c**) Bilayer, zero curvature

Spherical micelles

Spheres formed when:
$v/l_c a_0 \leq 1/3$

Size of micelles finite $\Rightarrow$
ε_N has a minimum value at an optimum number M

$$\varepsilon_N = \varepsilon_M + \Lambda(N-M)^2$$

$$X_N = N\left[\frac{X_M}{M}\exp\left(\frac{-M\Lambda(M-N)^2}{k_B T}\right)\right]^{N/M}$$

$$\left\langle |N-M|^2 \right\rangle = \frac{k_B T}{2M\Lambda}$$

size distribution

X_N - volume fraction of micelles with N molecules

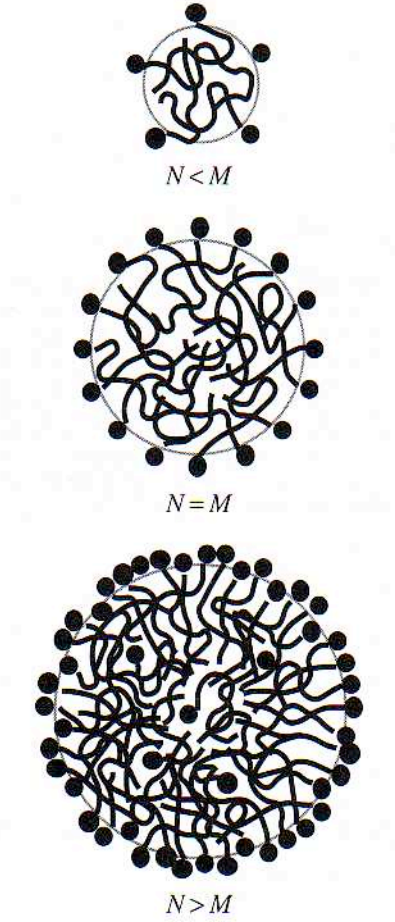


Fig. 9.3 The optimum aggregation number, M for a spherical micelle. Micelles containing a smaller number of molecules have too large an area for each head-group, causing unfavourable water/hydrocarbon interactions, while in micelles larger than the optimum number some head-groups are forced inside the hydrophobic core.

Critical Micelle Concentration

$$X_N = N\left[\frac{X_M}{M}\exp\left(\frac{-M\Lambda(M-N)^2}{k_BT}\right)\right]^{N/M}$$

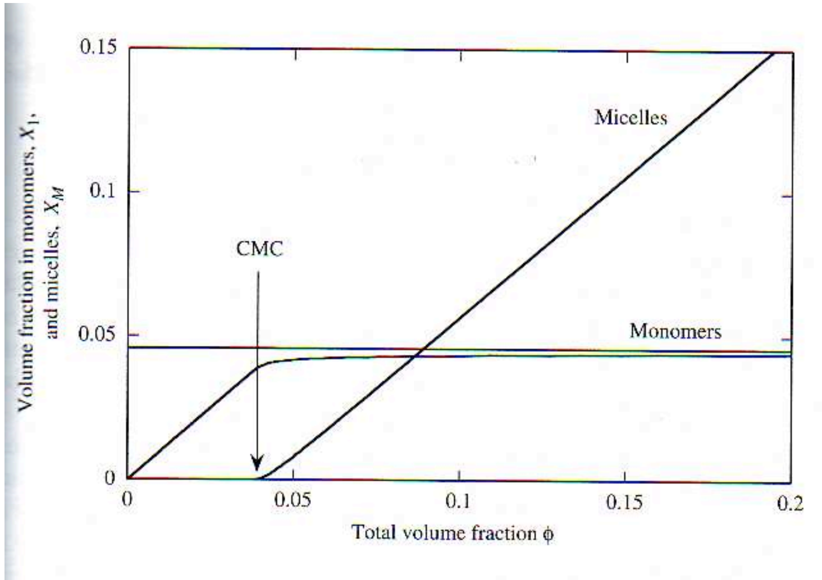
Monomers vs. micelles

ϕ - volume fraction of amphiphile

$\phi < \phi_c$ - *monomers*

$\phi > \phi_c$ - *micelles of average size M*

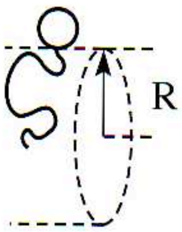
$$X_M = M\left[X_1\exp\left(\frac{\Delta\varepsilon}{k_BT}\right)\right]^M \qquad \Delta\varepsilon = \varepsilon_1 - \varepsilon_M$$



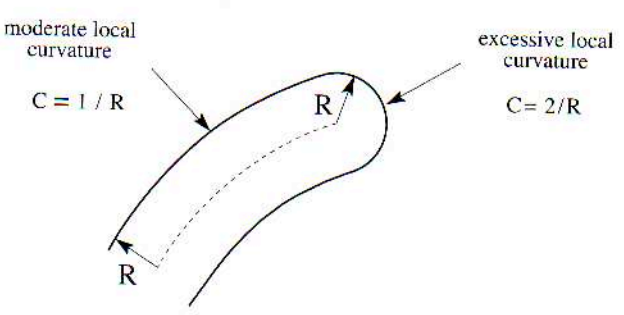
$\phi_c = \exp(-\Delta\varepsilon/k_BT)$ - *CMC*

Cylindrical micelles

Cylinders formed when:
$1/3 < v/l_c a_0 \leq 1/2$



Size of micelles finite but ε_N has a no minimum - energy of a molecule in the cylinder is independent of the size ⇒ only $2\Delta E_{end}$



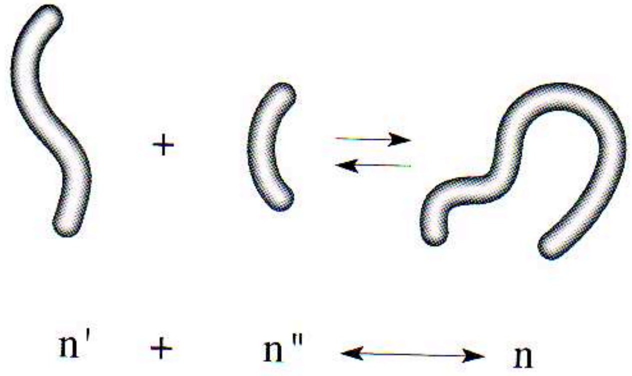
$$\varepsilon_N = \varepsilon_\infty + \frac{\alpha k_B T}{N} \quad , \quad \frac{\alpha k_B T}{N} = \frac{2\Delta E_{end}}{N}$$

⇒ forming larger micelles leads to energy gain, but a loss in entropy

Cylindrical micelles

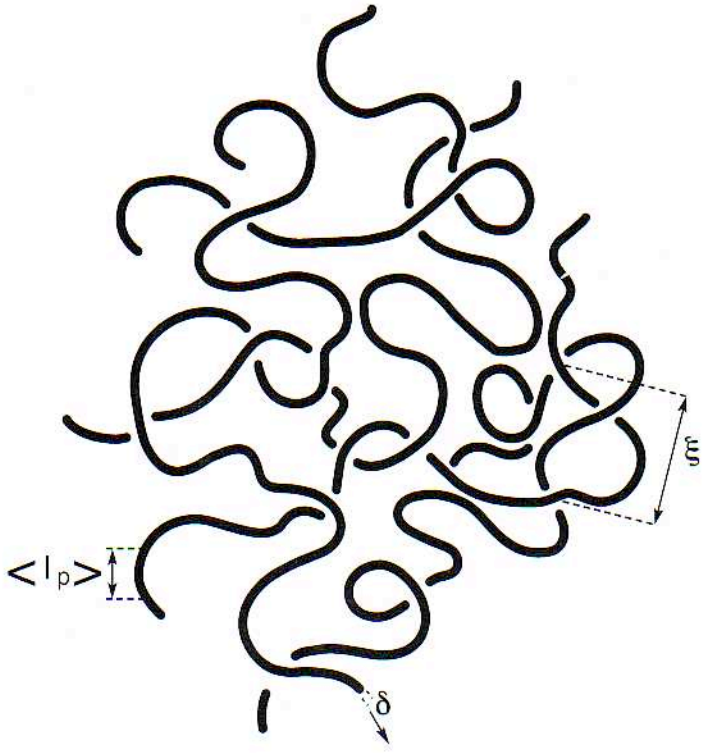
If ΔE_{end} is large $\Rightarrow$ very long cylinder > µm

$$\langle L \rangle \propto \sqrt{\phi \exp \frac{2\Delta E_{end}}{k_B T}}$$

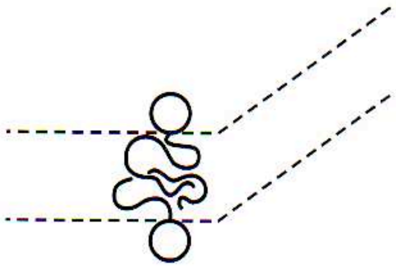


Polymer-like system but:

i) Polymer length fixed
ii) Micelles form and break
iii) Micellar size varies with external conditions
iv) Change in dynamic properties

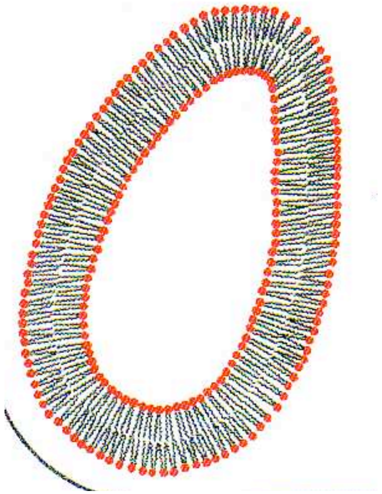


Bilayers



Bilayers formed when:
$v/l_c a_0 > 1/2$

$\Delta E_{edge}(A) \propto A^{1/2}$ *(A - area of a layer)*
dependent on the size of the bilayer
⇒ formation of infinite layers



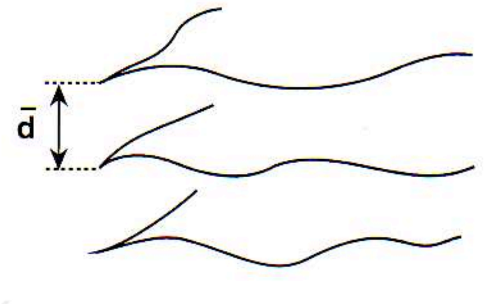
Vesicles - closed surface by a bilayer
- ⇒ model for cell membranes
- ⇒ drug delivery systems
- ⇒ colloidal behaviour

Bilayers

Bilayers are not flat - highly crumpled

Persistence length:

$$\xi_k = a \exp\left(\frac{4\pi k}{\alpha k_B T}\right)$$

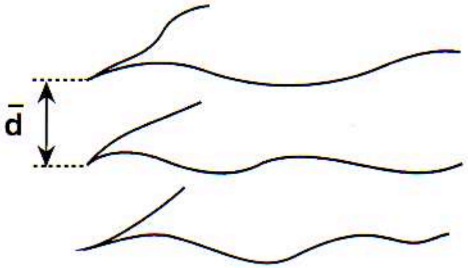


k - bending modulus of membrane
For *r* > ξ direction in membrane is lost

Lamellar phases can anyway be obtained with very large d ⇒ confinement between two adjacent planes leads to loss in entropy

Bilayers

Lamellar phase can be distorted by fluctuations forming complex geometries



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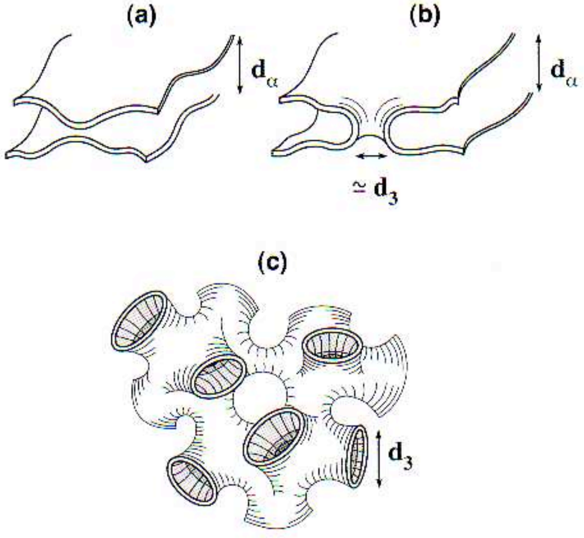


Fig. 5.21. Structure of the sponge phase. **(a)** Two bilayers in the lamellar phase. **(b)** Formation of an elementary passage. **(c)** Proliferation of passages, leading to the sponge phase L_3

Phase behaviour

Self assembled structures
are rich in phases

⇒ response by changing size and shape and arrangement of micelles

⇒ dramatic change in properties

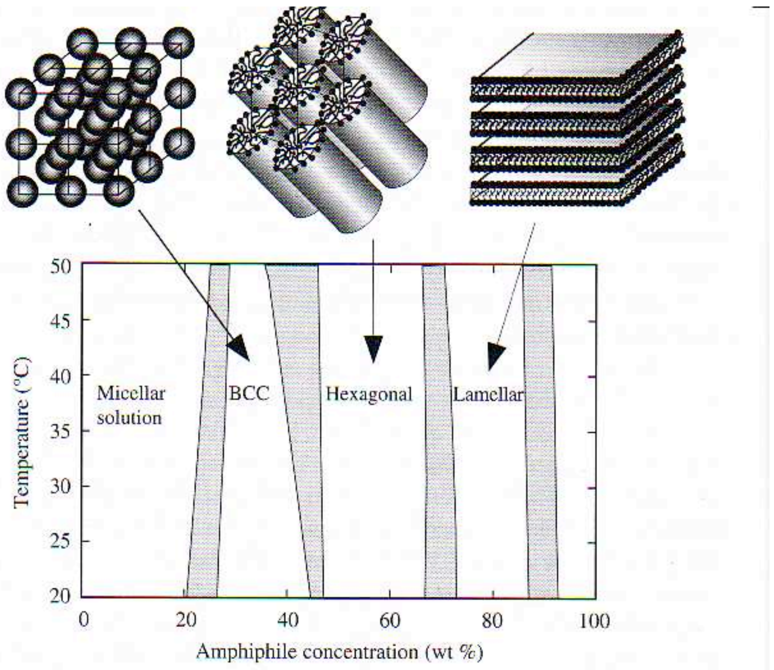
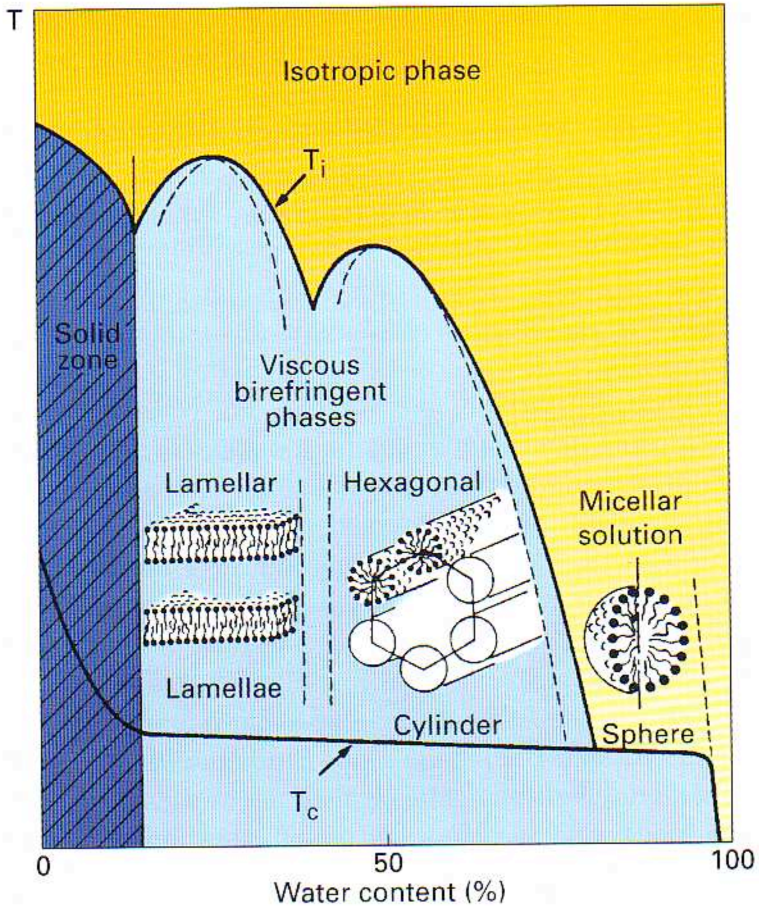
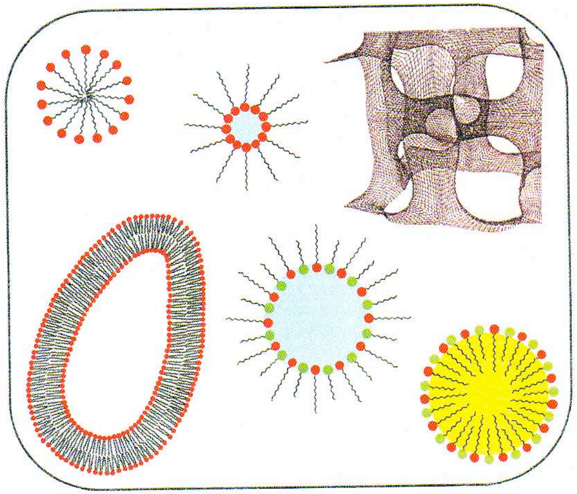


Fig. 9.7 The phase diagram of an amphiphilic copolymer in water, showing schematically the structures of the ordered phase. The material is a short triblock copolymer of ethylene oxide (EO) and propylene oxide (PO), with the structure $(EO)_{37}(PO)_{58}(EO)_{37}$. Data from P. Alexandris, D. Zhou, and A. Khan, *Langmuir*, **12**, 2690 (1996).

Self-assembly





More complexity from:

- several types of amphiphiles
- mixed solvents
- changing pH, temperature, …

Self assembly in polymers

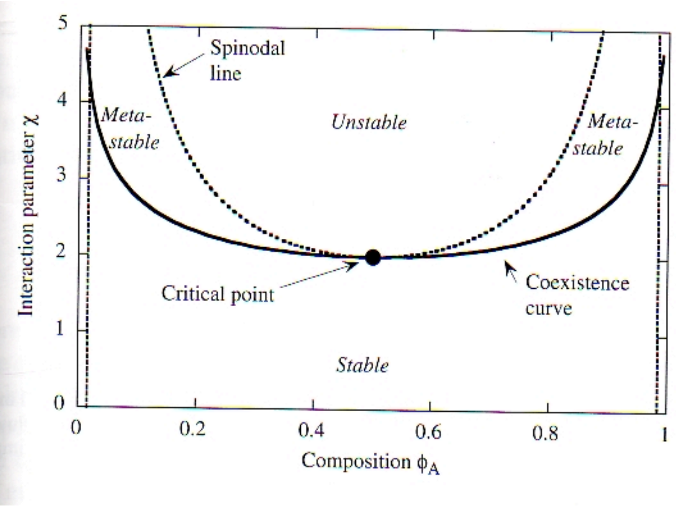
Mixing polymers

Generally polymers don’t mix - why?

Free energy of mixing:
(two molecular liquids)

$$\frac{F}{k_B T} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi \phi_A \phi_B$$

entropic *interaction energy*



regular solution model

Interaction parameter χ:

χ < 2 always single phase

χ > 2 phase separation

Mixing polymers

Generally polymers don’t mix - why?

For two polymer with N monomers

$$\frac{F^{pol}}{k_B T} = \phi_A \ln\phi_A + \phi_B \ln\phi_B + N\chi\phi_A\phi_B$$

$$\frac{F^{mon}}{k_B T} = \frac{\phi_A}{N}\ln\phi_A + \frac{\phi_B}{N}\ln\phi_B + \chi\phi_A\phi_B$$

(Flory-Huggins free energy)

Interaction parameter χ:

$\chi < 2/N$ always single phase

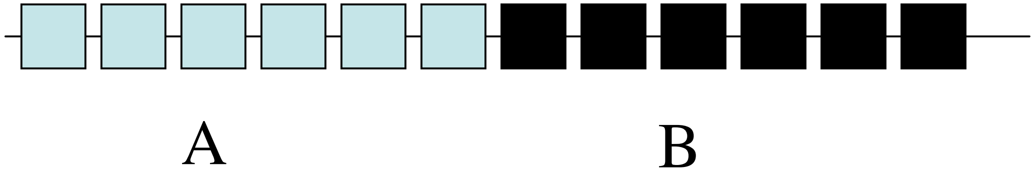
$\chi > 2/N$ phase separation

N is usually ≈ 10^3-10^6

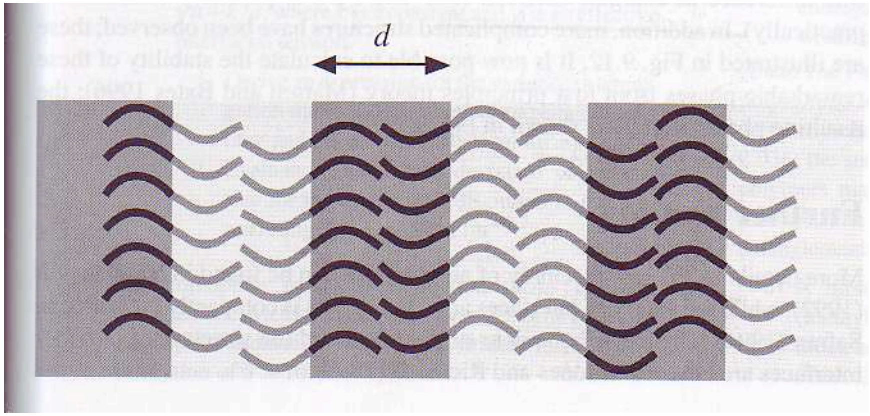
⇒ even for small χ we get macro-phase separation

Block copolymers

Blocks of different polymers covalently linked together

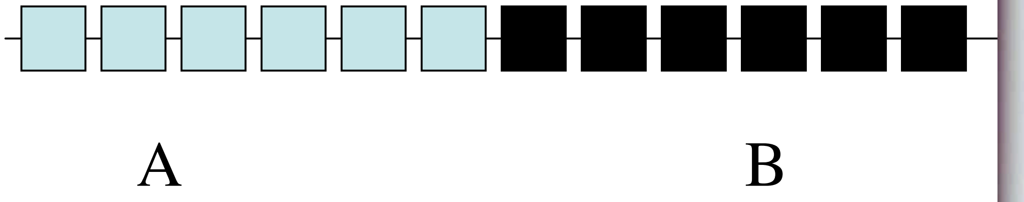


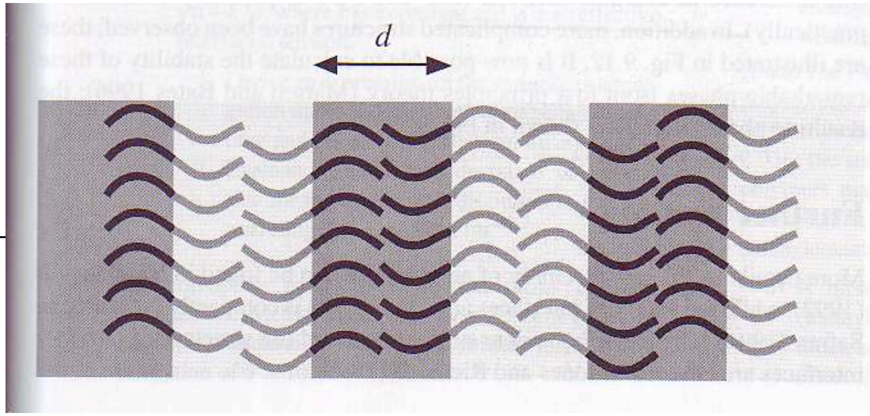
Even if $\chi < 2/N$ the system cannot macro-phase separate (similar to amphiphiles)



Block copolymers

Symmetric block copolymers
⇒ lamellar structures





Asymmetric structures
⇒ more complex morphology

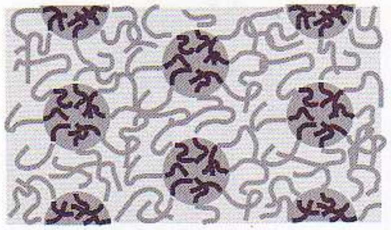


Fig. 9.11 A lamellar morphology (top) is less favoured for an asymmetric diblock copolymer, as it requires the two blocks to be stretched to different degrees. Instead, a morphology with curved interfaces (bottom) is favoured.

Templating with block copolymers

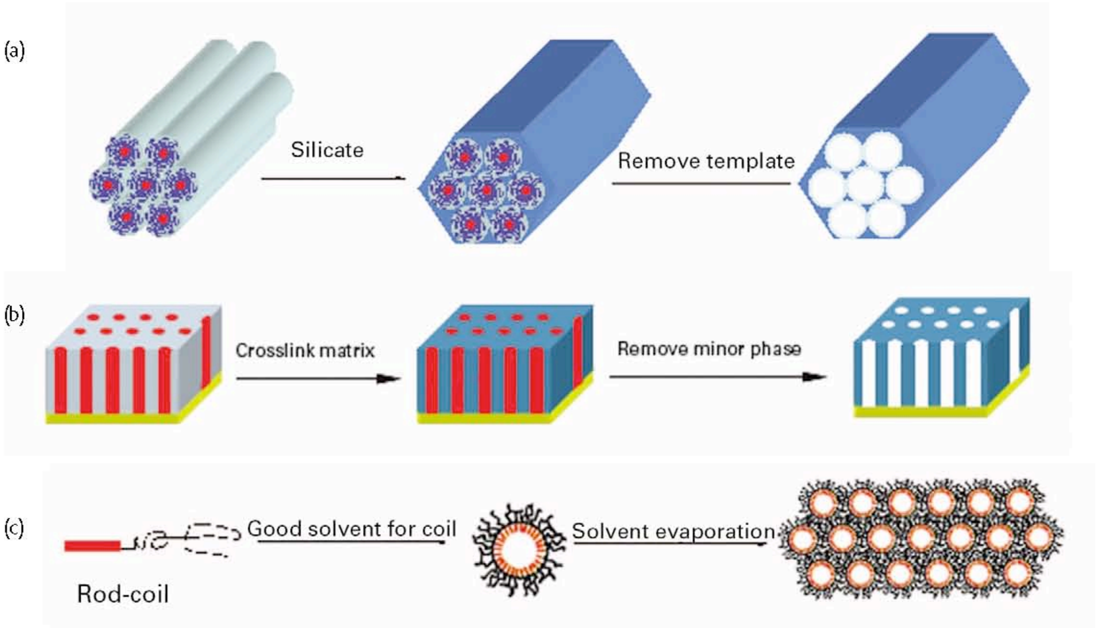


Fig. 6 Schematic of three approaches to generate nanoporous and mesoporous materials with block copolymers. (a) Block copolymer micelle templating for mesoporous inorganic materials. Block copolymer micelles form a hexagonal array, silicate species (in blue) then occupy the spaces between the cylinders. The removal of the micelle template leaves hollow cylinders. (b) Block copolymer matrix for nanoporous materials. Block copolymers form a hexagonal cylinder phase in a bulk or thin film state. Subsequent crosslinking fixes the matrix. Hollow channels are generated by removing the minor phase. (c) Rod-coil block copolymer for microporous materials. Solution-cast micellar films consist of multilayers of hexagonally ordered arrays of spherical holes. (Adapted from[85] and reprinted with permission. © 1999 American Association for the Advancement of Science.)

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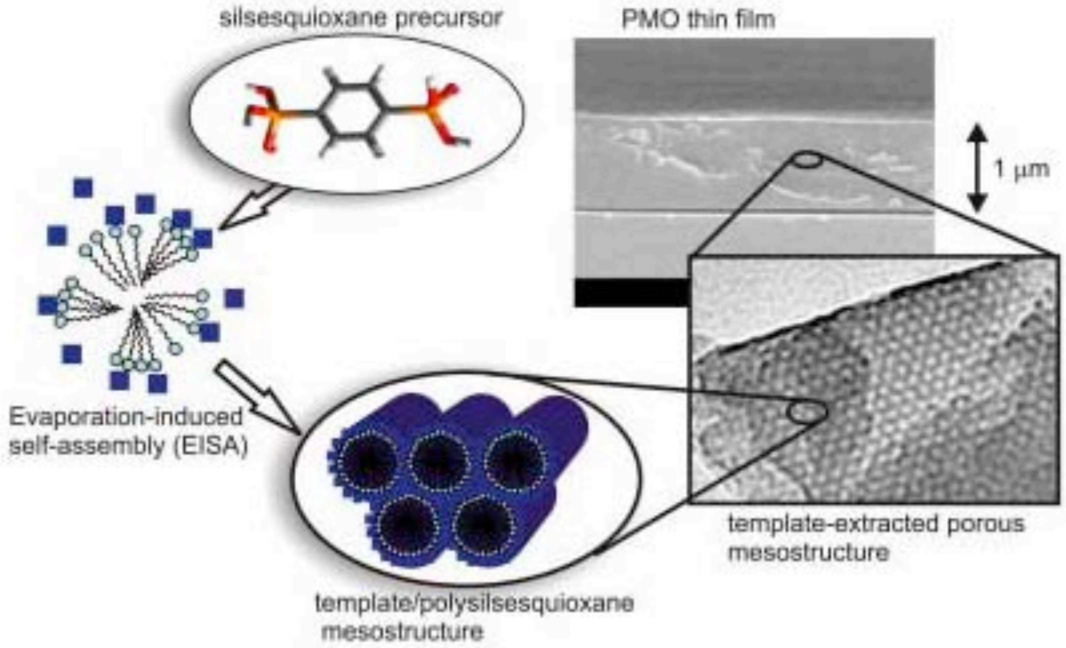

Fig. 6 Schematic illustration of the synthesis and structure of PMO thin films.

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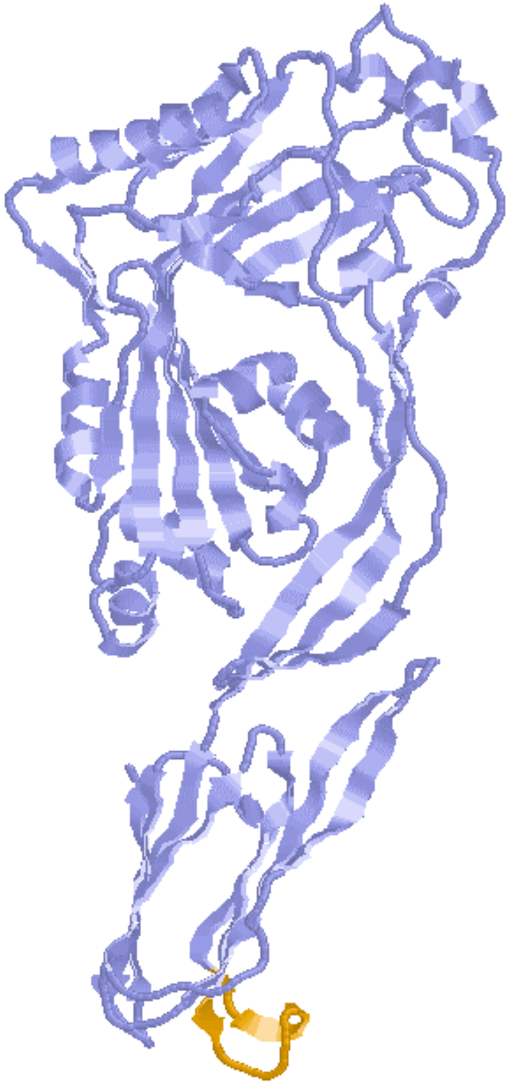
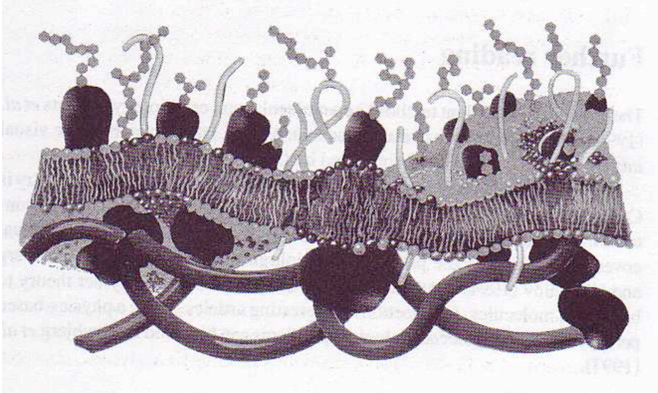
Soft matter in nature

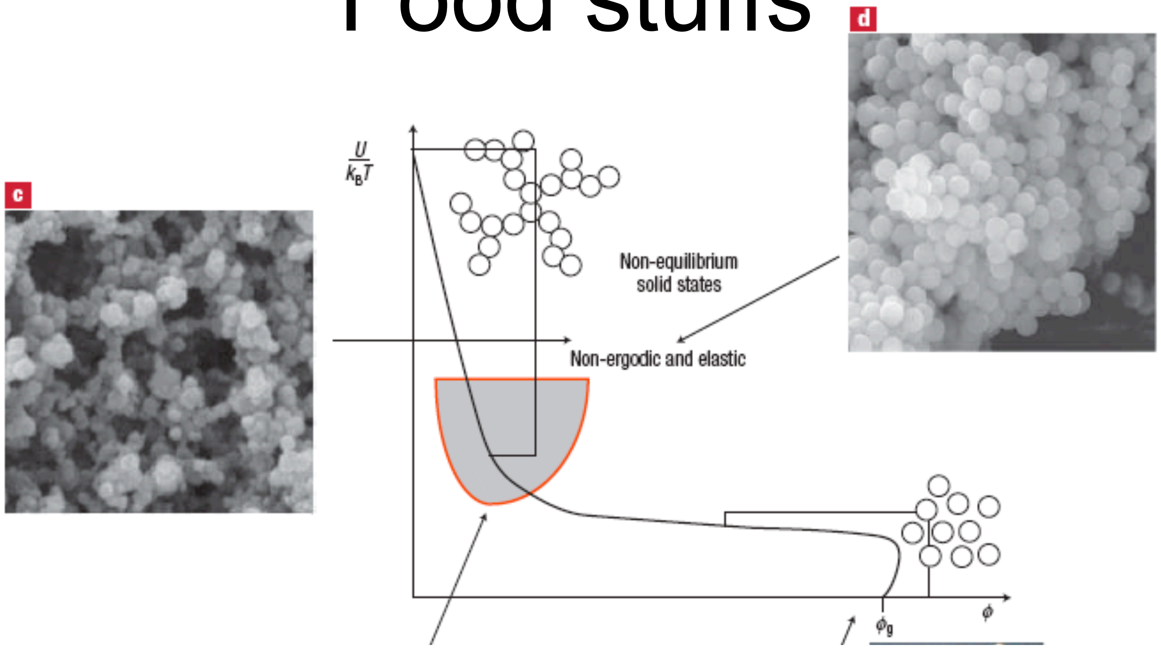


- Biopolymers
    - DNA
    - Proteins, protein folding
    - Polysaccharides

- Biomembranes



Food stuffs



- Colloids (micelles,emulsions, foams…)
- Bio-polymers (proteins, sugars,..)
- Gels (gelatin)
- Amphiphiles (lipids)
- Glass phases
- Liquid crystal phases

Biopolymers

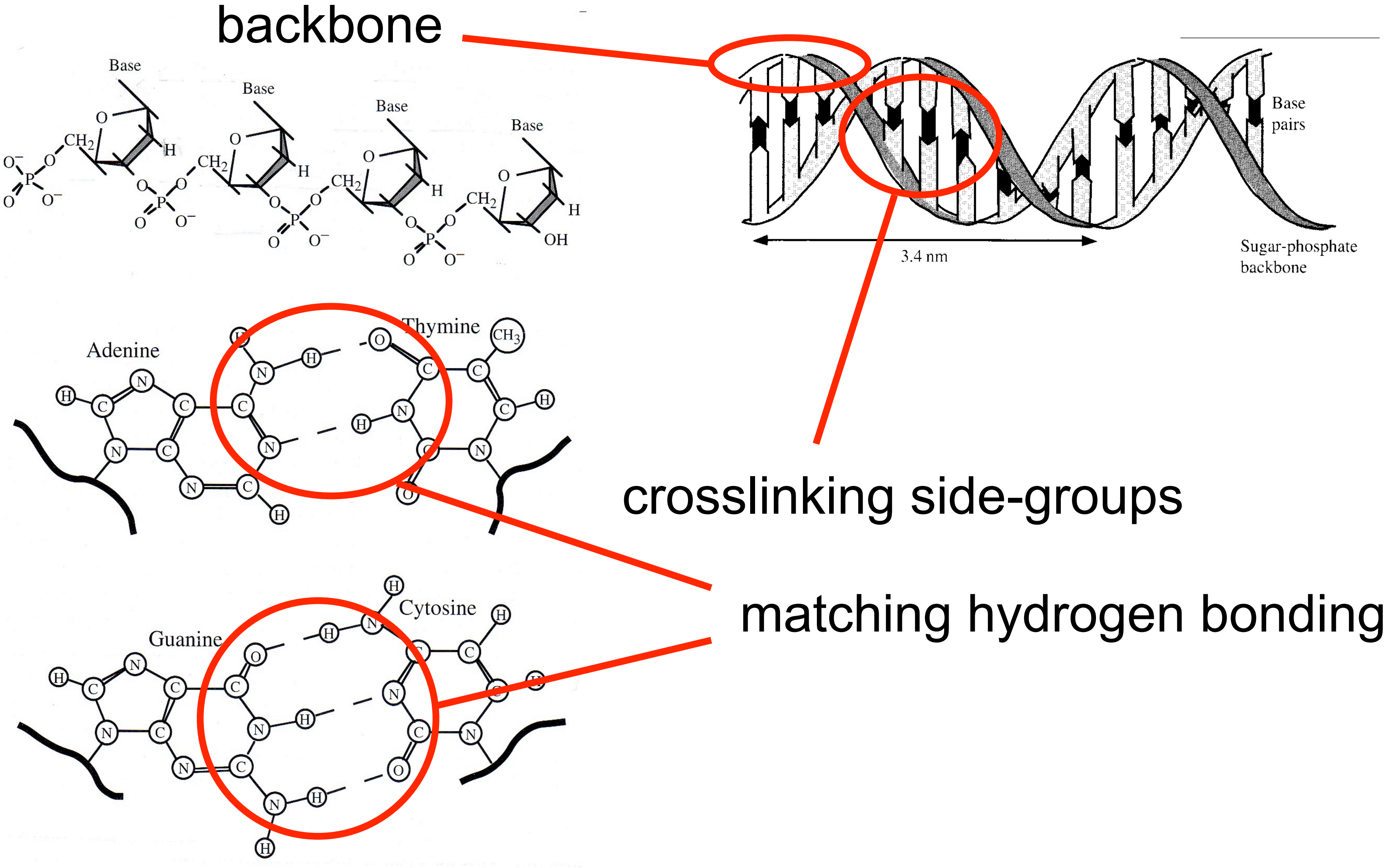
Biopolymers - sequenced copolymers

- Nucleic acids - sequenced copolymers
  ex. DNA, RNA

- Proteins - ordered sequence of amino acids
  ex. enzymes, structural elements

- Polysaccharides - random copolymers
  ex. cellulose, starch

DNA

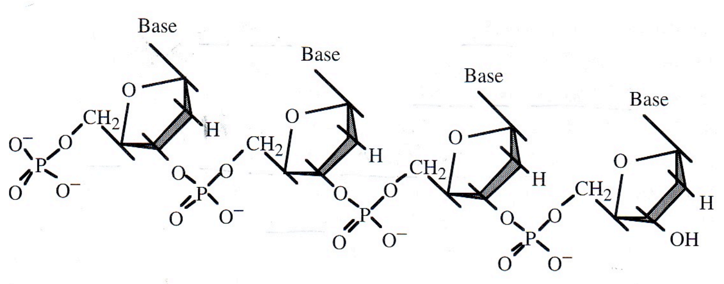


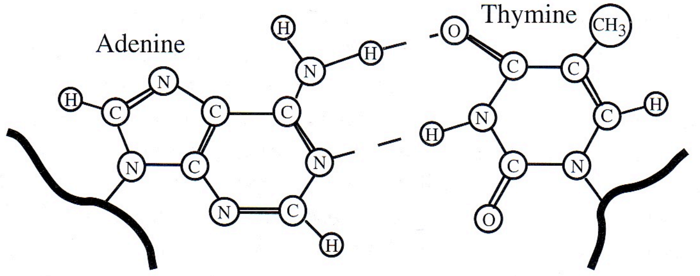
backbone

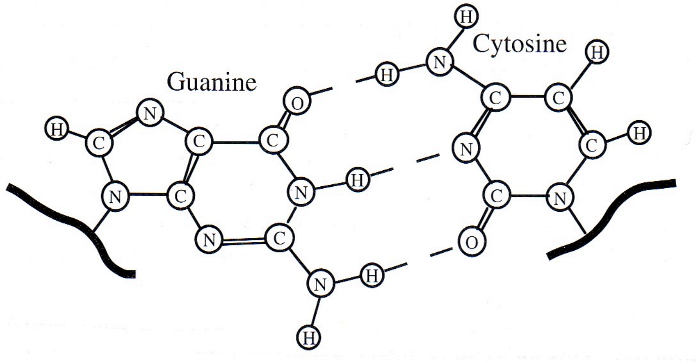
crosslinking side-groups

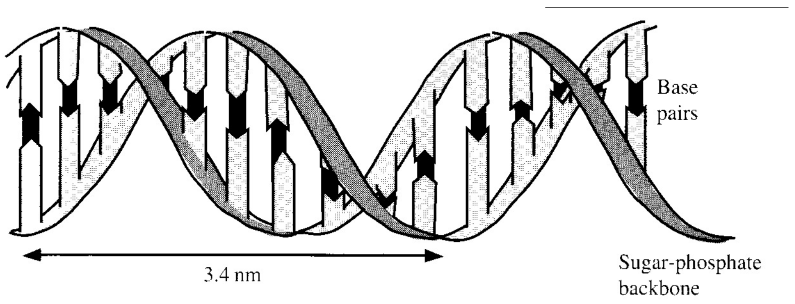
matching hydrogen bonding

DNA









very stiff:

    $l_p \approx 200\text{-}300$ units

long polymer:

    > 10^6 monomers

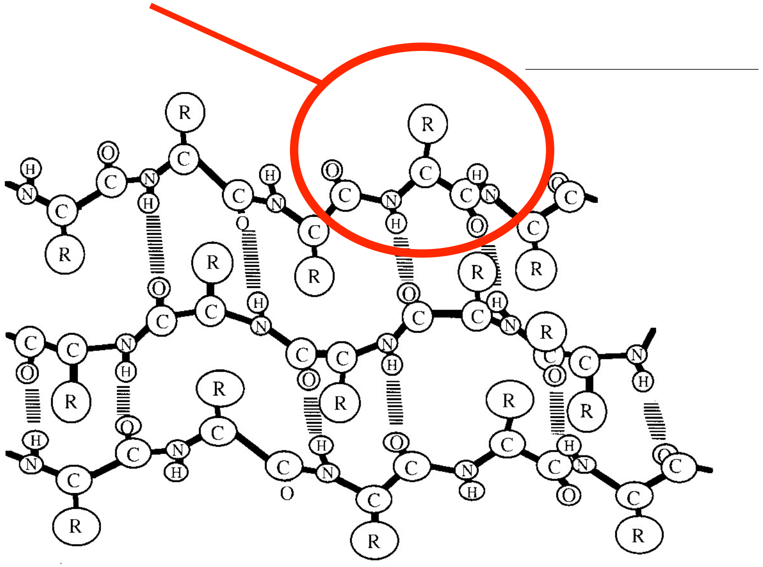
    contour length µm - mm

    end-to-end 200nm - 75µm

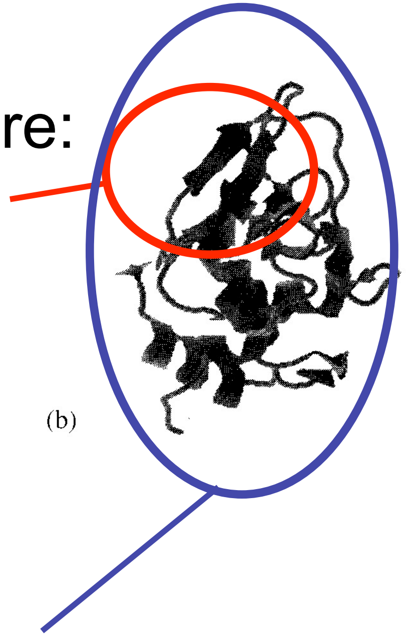
Proteins

Proteins self-assemble and
form hierarchical structures

Primary structure:
Backbone sequence of
amino acids



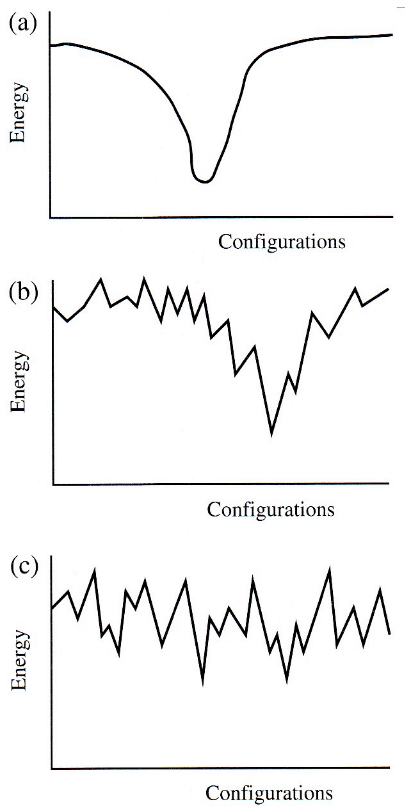
Secondary structure:
- α-helix
- β-sheets

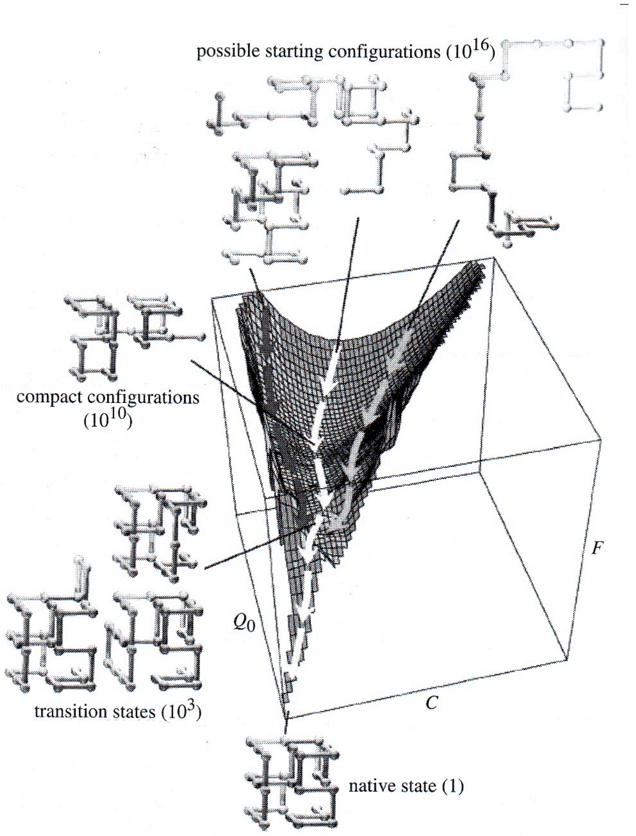


Tertiary structures:
Full 3-D arrangement
Only one configuration
provides the function

Protein folding

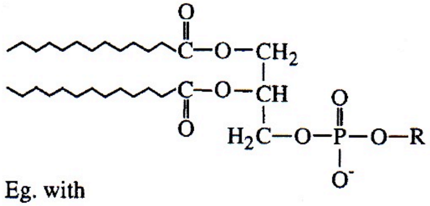
Not a random exploration of the energy landscape in the folding process (ms)





Membranes

Phospholipids

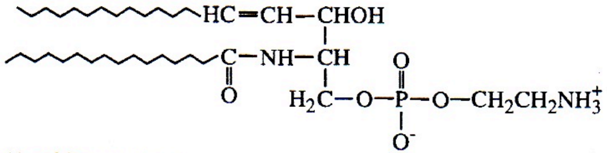


Eg. with

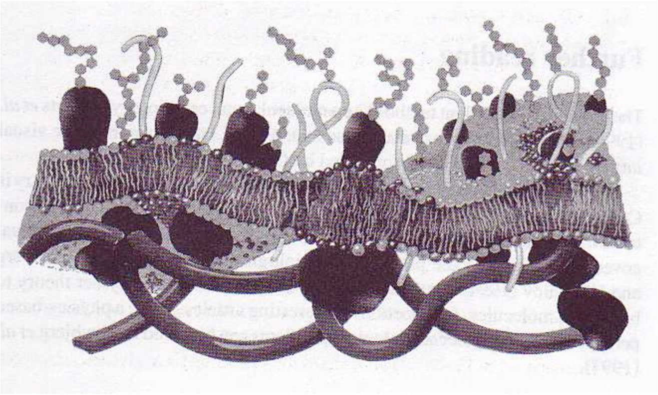
R = $CH_2CH_2NH_3^+$: Phosphatidylethanolamine

R = $CH_2CH_2N(CH_3)_3^+$: Phosphatidylcholine (lecithin)

Sphingolipid



(A sphingomyelin)



Phospholipids from bilayers:
2 chains gives large v
$\Rightarrow v/l_c a_0 > 1/2$

Real cell membrane:
- *several amphiphiles*
- *phase separated regions*
- *membrane proteins*
- *modifying molecules*
- in-plane motions