

Soft matter, colloids and self-assembly to create mesoporous materials

February 24, 2020

Soft /Condensed Matter

- The phrase “soft matter” was used by Pierre de Gennes as the title of his 1991 Nobel Prize acceptance speech.
- Refers to condensed matter that exhibits characteristics of both solids and liquids
- Soft matter can flow like liquids (measurable viscosity)
- Soft matter can bear stress (elastic deformation)
- Viscoelastic behaviour = viscous + elastic
- **Examples:** rubbers, gels, pastes, creams, paints, soaps, liquid crystals, proteins, cells

Soft Matter

Soft matter does not exhibit the crystalline order that is characteristic of most hard matter (except amorphous solids). Nevertheless, some order remains. Soft matter lends itself to **self-assembly** which produces a large variety of nanostructures.



Pierre-Gilles de Gennes received the 1991 Physics Nobel Prize for bringing order into soft matter, particularly liquid crystals and polymers.

Phase diagram of water

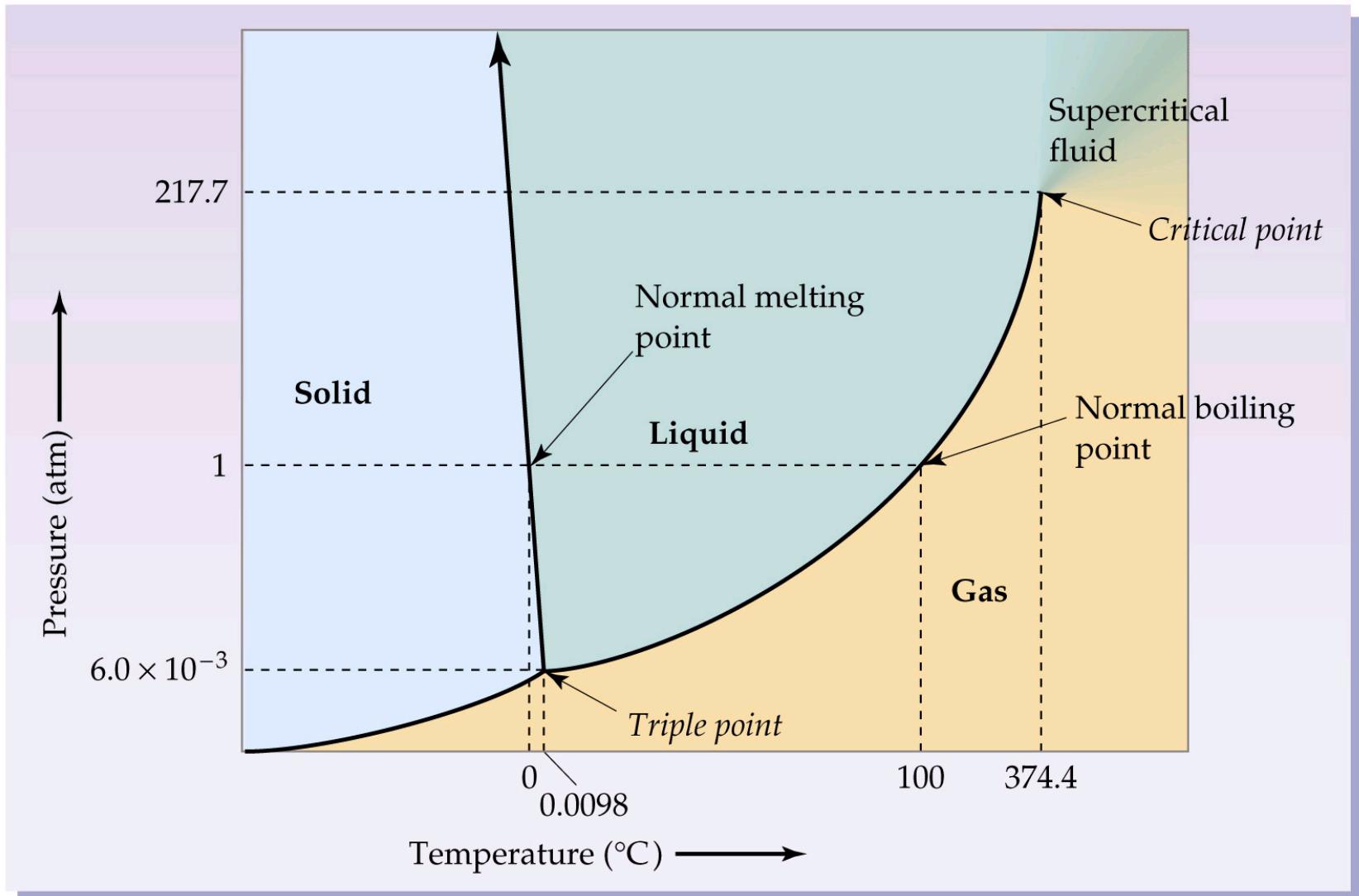


Image: http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_10.html

What is Condensed Matter?

- “Condensed matter” refers to matter that is **not** in the gas phase but is condensed as a liquid or solid. (condensed → denser!)
- Matter condenses when attractive intermolecular bond energies are comparable to or greater than thermal (*i.e.* kinetic) energy $\sim kT$.

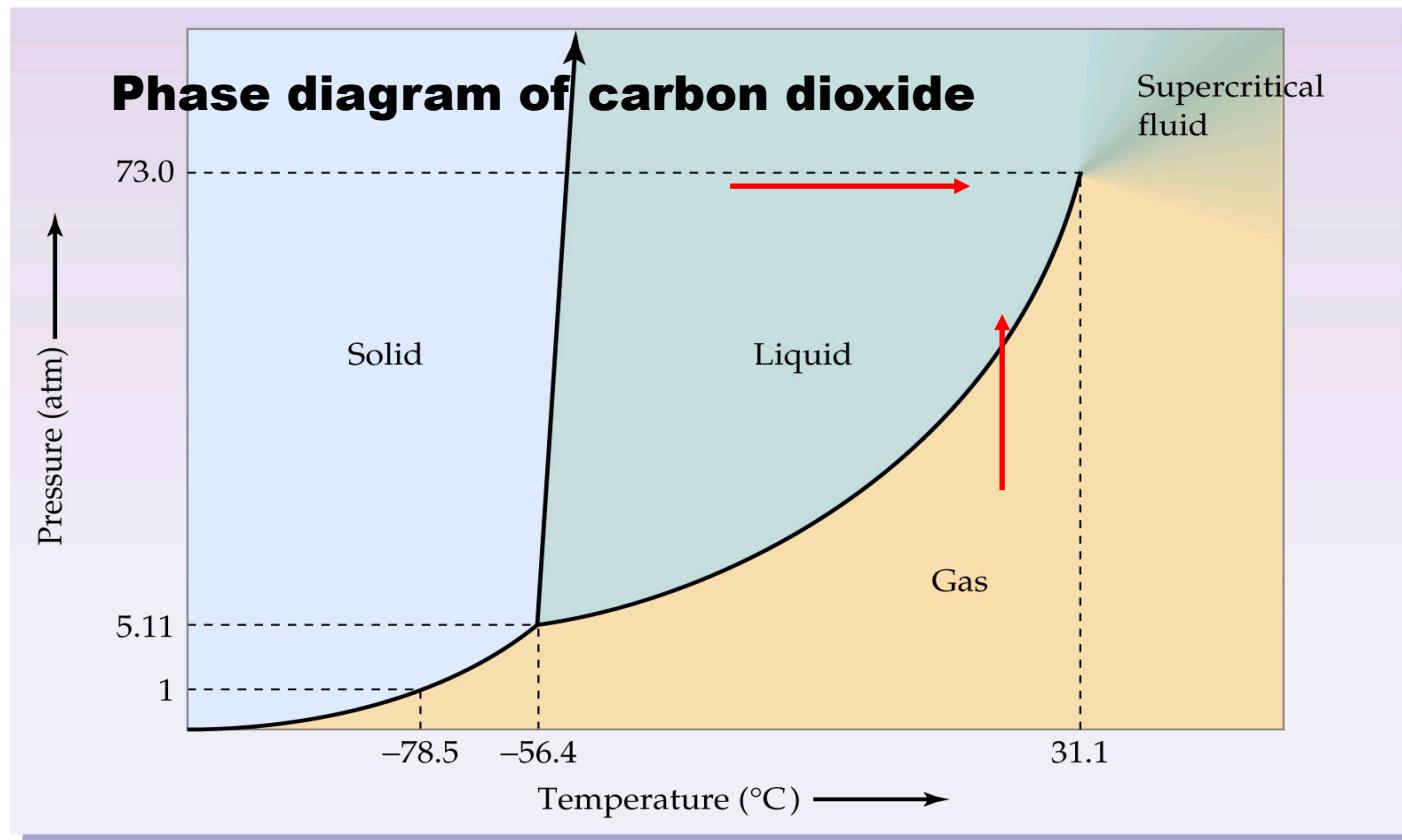
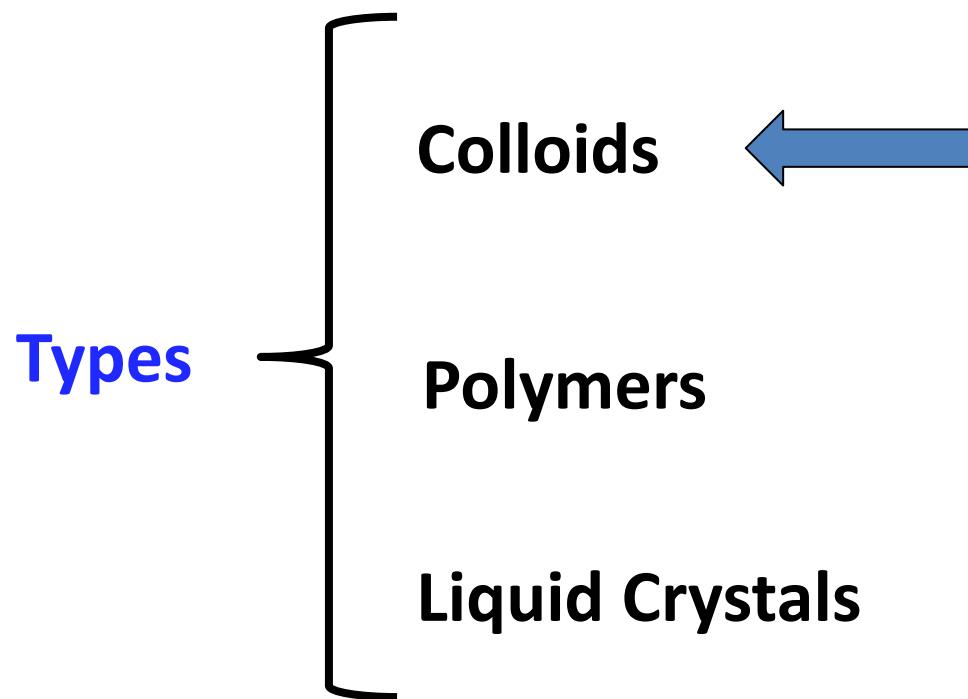


Image: http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_10.html

Soft matter



Four characteristics of Soft Matter

Length scales

- Structures of $\approx 10\text{-}1000$ nm determine the properties

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

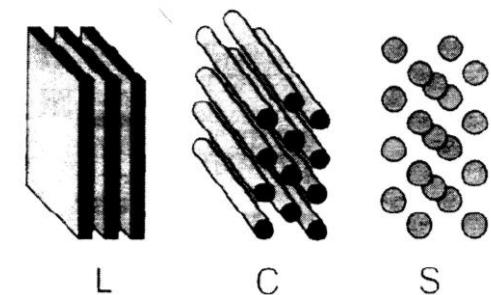
- Dynamics processes over a wide time scales 10^{-12} - 10^3 s
- Very slow processes in non-equilibrium configurations

Weak interactions

- Interactions between molecules and molecular structures $\approx kT$

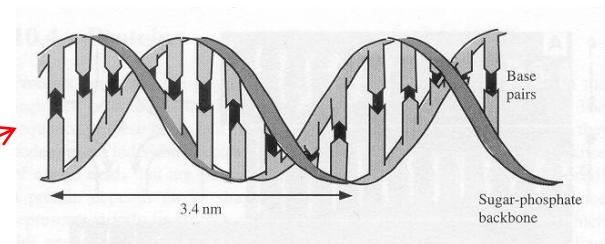
Self assembly

- Hierarchical arrangement of structures
- Competition between interaction energy and entropy



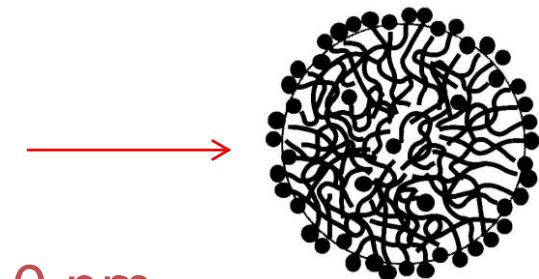
Typical Length Scales

- Atomic spacing: $\sim 0.1 \text{ nm} = 1\text{\AA}^0$



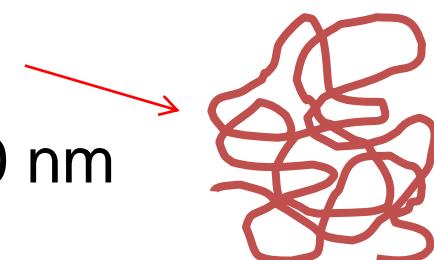
- "Pitch" of a DNA molecule: 3.4 nm

- Diameter of a surfactant micelle: $\sim 6\text{-}7 \text{ nm}$



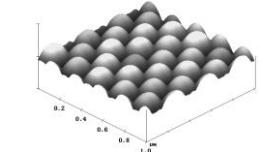
- Gyration radius of a polymer molecule: $\sim 10 \text{ nm}$

- Diam. of a colloidal particle (e.g. in paint): $\sim 200 \text{ nm}$



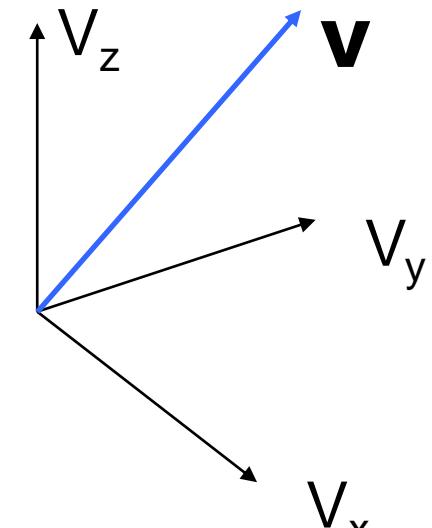
- Bacteria cell: $\sim 2 \mu\text{m}$

- Diameter of a human hair: $\sim 80 \mu\text{m}$



Thermal fluctuations

The kinetic energy for a particle of mass, m , is $1/2 m\mathbf{v}^2 = 3/2 kT$. When m is small, \mathbf{v} becomes significant.



- Soft condensed matter is not static but in constant motion at the level of molecules and particles.
- The “equipartition of energy” means that for each degree of freedom of a particle to move, there is $1/2kT$ of thermal energy.
- For a colloidal particle able to undergo translation in the x, y and z directions, thermal energy is $3/2 kT$.
- $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$, so $kT = 4 \times 10^{-21} \text{ J}$ per molecule at room temperature (300 K).
- kT is a useful “gauge” of bond energy.

Thermal fluctuations of Soft Matter

The importance of thermal fluctuations and Brownian motion

<https://www.youtube.com/watch?v=PzssJDZn9xI>

Brownian motion can be thought of as resulting from a slight imbalance of momentum being transferred between liquid molecules and a colloidal particle.

Colloids

Colloids

- A **colloid** has sub- μm particles (but not single molecules) of one phase dispersed in a continuous phase.
- The size scale of the dispersed phase is between 1 nm and 1 μm .
- The dispersed phase and the continuous phase can consist of either a solid (S), liquid (L), or gas (G)

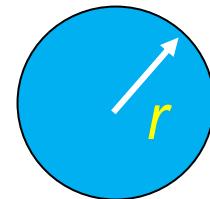
Dispersed Phase	Continuous Phase	Name	Example
L/S	G	aerosol	Fog, hair spray, smoke
G	L/S	foam	Beer froth, shaving foam
L	L/S	emulsion	Mayonnaise, salad dressing
S	L	sol	Latex paint, tooth paste
S	S	solid suspension	Pearl, mineral rocks

There is no “gas-in-gas” colloid, because there is no interfacial tension between gases!

Interfacial Area of Colloids

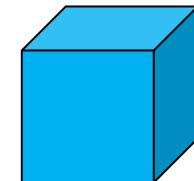
For a spherical particle, the ratio of surface area (A) to volume (V) is:

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} \gg \frac{1}{r}$$



Thus, with smaller particles, the interface becomes more significant. A greater fraction of molecules is near the surface.

Consider a 1 cm^3 phase dispersed in a continuous medium:



No. particles	Particle volume(m^3)	Edge length (m)	Total surface area(m^2)
1	10^{-6}	10^{-2}	0.0006
10^3	10^{-9}	10^{-3}	0.006
10^6	10^{-12}	10^{-4}	0.06
10^9	10^{-15}	10^{-5}	0.6
10^{12}	10^{-18}	10^{-6}	6.0
10^{15}	10^{-21}	10^{-7}	60
10^{18}	10^{-24}	10^{-8}	600

Mesoporous Materials

Outline

1. What are they?
2. What are they useful for?
3. What are some of the theoretical aspects behind these materials?
4. How can we synthesize them?
5. What are the factors affecting their sizes, shapes and their existence ?

What are mesoporous materials?

- Porous materials whose pores are between 2 and 50 nm in diameter.
- The mesoporous materials investigated here have uniformly ordered pores.
- Silica based materials first synthesized by scientists at the Mobil Corporation in 1992.
- Non-silica mesoporous materials first reported at UC Santa Barbara in 1994.

Applications

- Molecular sieves
- High surface area catalysts
- Gas sensors
- Dye sensitized photovoltaic solar cells
- 0-Dimension nano-particles

Mesoporous materials are templated by amphiphilic molecules.



- An amphiphilic molecule has a hydrophilic (water loving) head and a hydrophobic (water loathing) tail.
- *Surfactant* is an amphiphilic molecule with a tendency to adsorb onto free surfaces and interfaces and to aggregate to form micelles
- A micelle is an association of amphiphilic molecules.
- Mesoporous structures are created by the ordered packing of micelles.
- Small molecules $M_w \approx 100-1000$

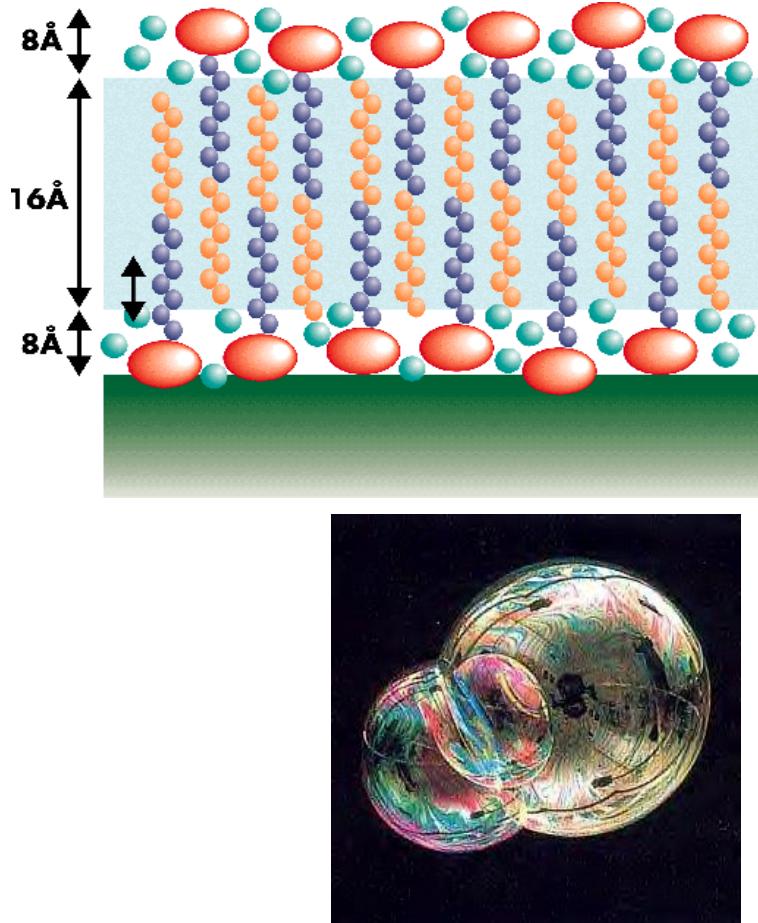
Why do amphiphiles form micelles?

- Gibb's Free Energy (ΔG) is a thermodynamic quantity which predicts the spontaneity of a reaction. (A decrease in Gibb's Free Energy indicates a spontaneous reaction)
- Water molecules create structure by forming hydrogen bonds with one another.
- The hydrophobic tails of individual amphiphiles placed in solution force water molecules to associate in a particular way. This decreases the entropy (ΔS) of the system.
- When the hydrophobic tails associate to each other (form micelles) in order to minimize their interaction with water molecules they increase the entropy of the system.

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

- An increase in entropy, decreases Gibb's Free Energy of the system therefore the reaction will occur spontaneously.

Examples of Self-Assembly



(a)

(c)

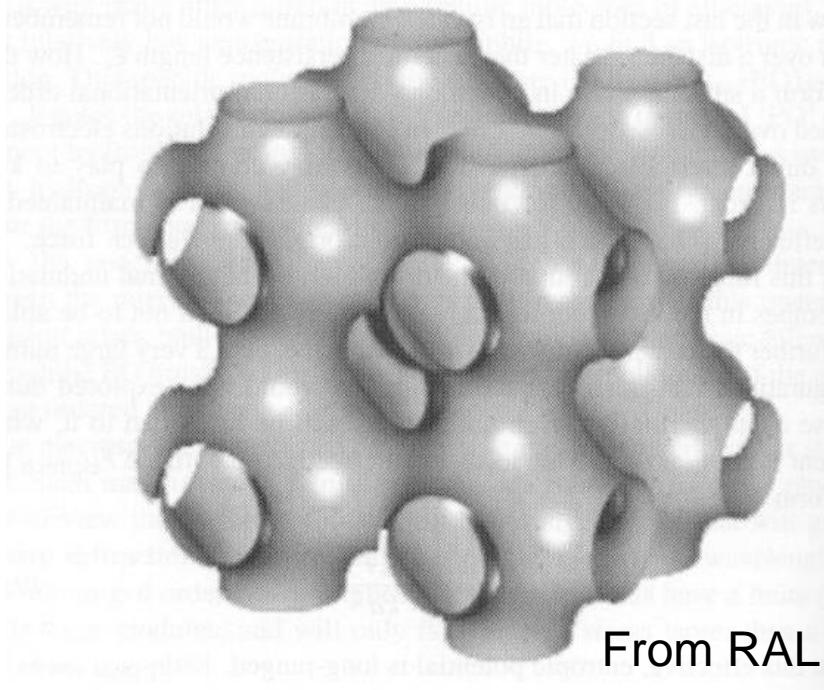
(b)

(d)

From I.W. Hamley, *Introduction to Soft Matter*

Surfactants can assemble into (a) spherical micelles, (b) cylindrical micelles, (c) bi-layers (membranes), or (d) saddle surfaces in bicontinuous structures

Examples of Self-Assembly

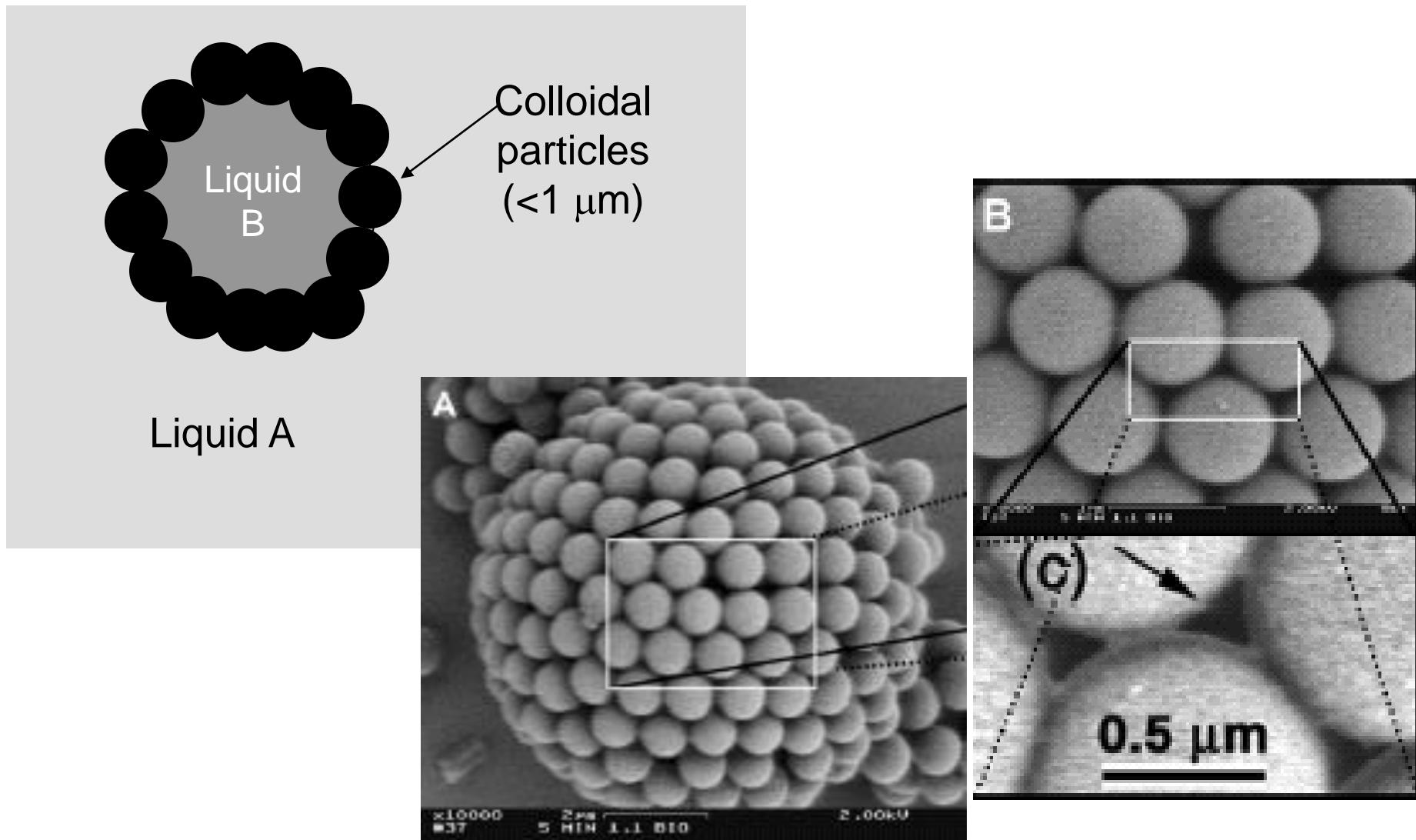


The “plumber’s
nightmare”

From RAL Jones, *Soft Condensed Matter*

- Surfactants can create a bi-continuous surface to separate an oil phase and a water phase.
- The hydrophilic end of the molecule orients itself towards the aqueous phase.
- The oil and water are completely separated but both are **CONTINUOUS** across the system.

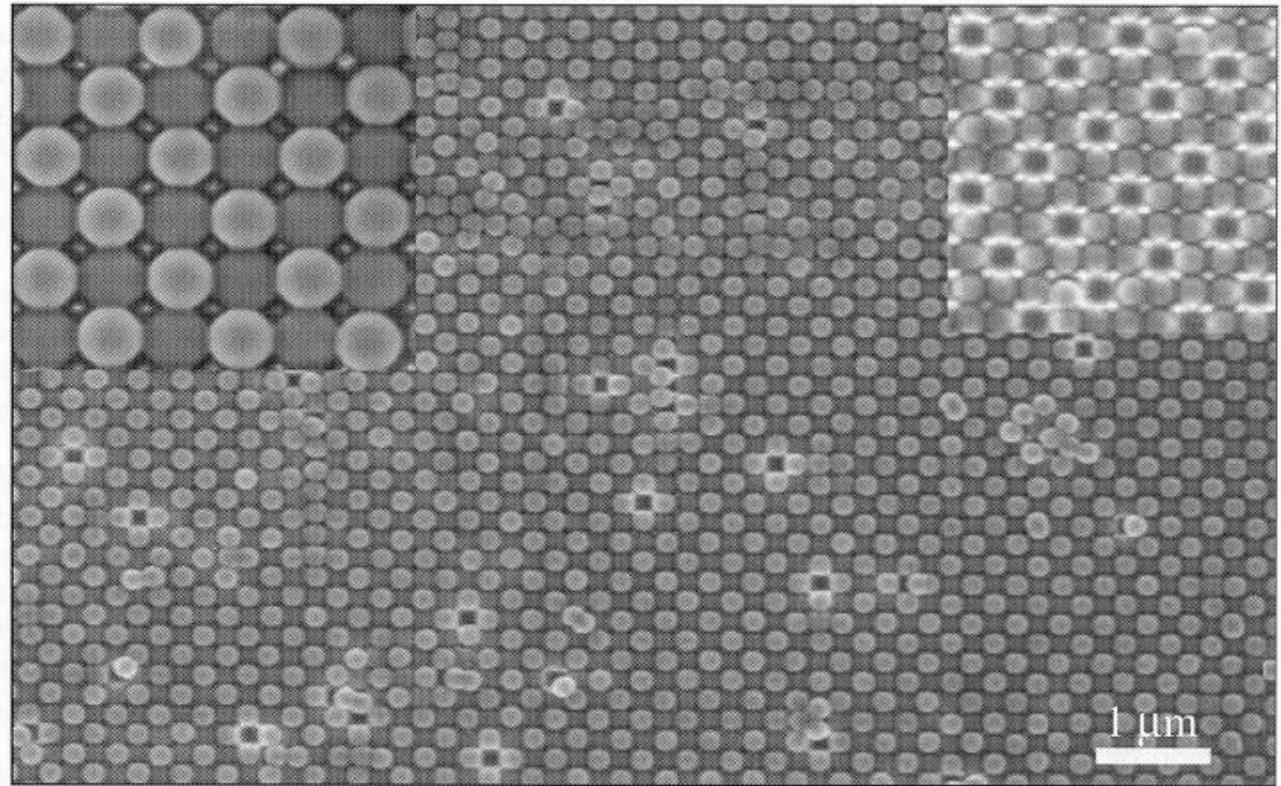
Colloidosomes: Self-assembled colloidal particles



A.D. Dinsmore *et al.*, “Colloidosomes: Selectively Permeable Capsules Composed of Colloidal Particles,” *Science*, **298** (2002) p. 1006.

Colloidal Crystals

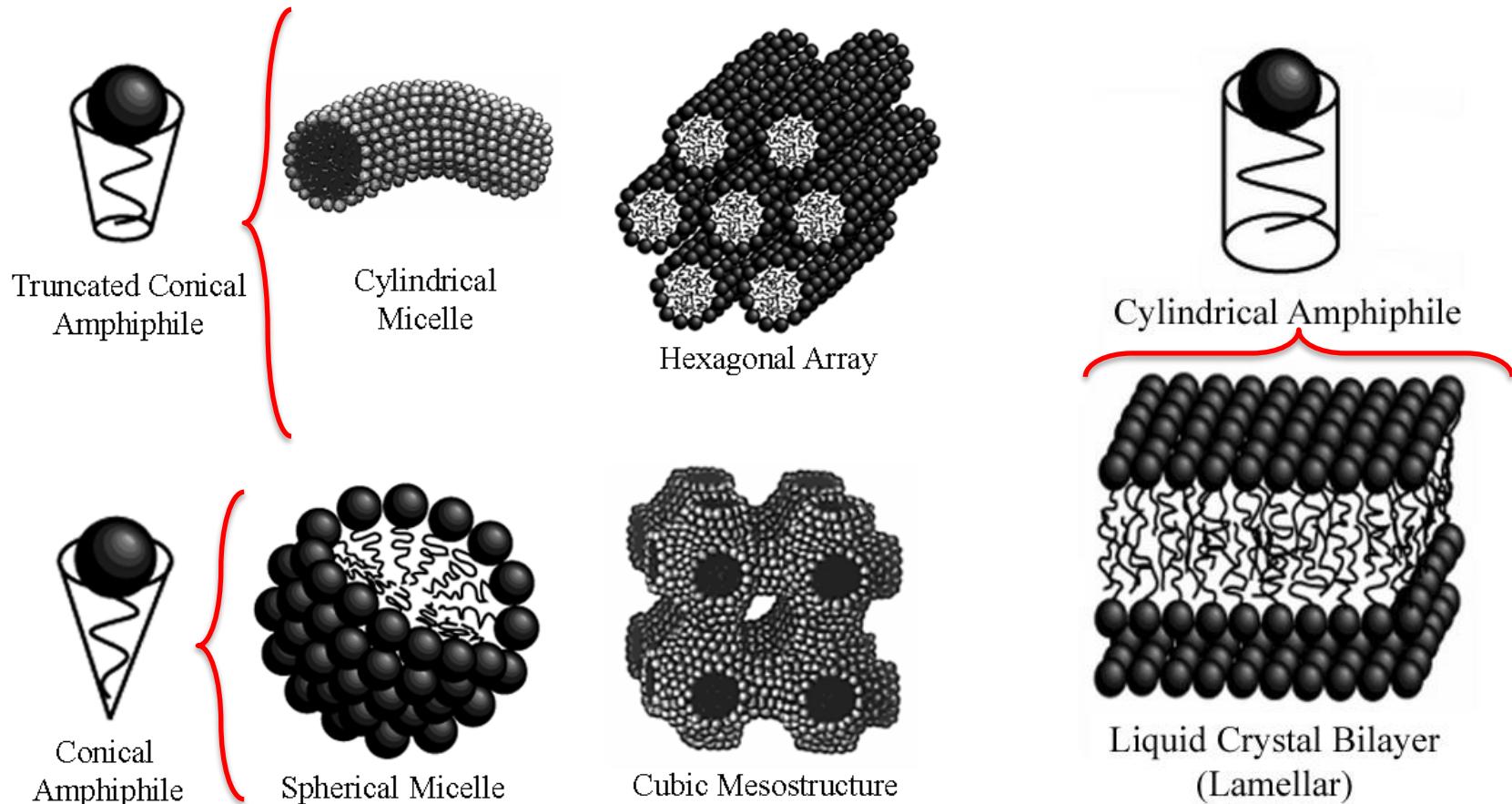
MRS Bulletin,
Feb 2004, p. 86



Colloidal particles can have a +ve or -ve charge.

In direct analogy to salt crystals of +ve and -ve ions, charge attractions can lead to close-packing in ordered arrays.

What determines micelle shape?



Diagrams compiled from work by Brian Eggiman and Soler-Illia et al, "Chemical Strategies To Design Textured Materials: from Microporous and Mesoporous Oxides to Nanonetworks and Hierarchical Structures", Chem. Rev. 2002, 102, 4093-4138.

Transition from dispersed state to condensed state: a universal phenomenon

Beginning of self-assembly of molecules, polymers, or microscopic particles

(a) Gas (dispersed) → Liquid (condensed)

under van der Waals attraction forces

(b) Polymer gels (dispersed) → Collapsed polymer gel (condensed)

under rubber elasticity (entropy change), counter ions osmotic pressure, and electrostatic repulsive forces

(c) Colloidal particles (dispersed) → self-assembled colloidal crystals and super lattice structures

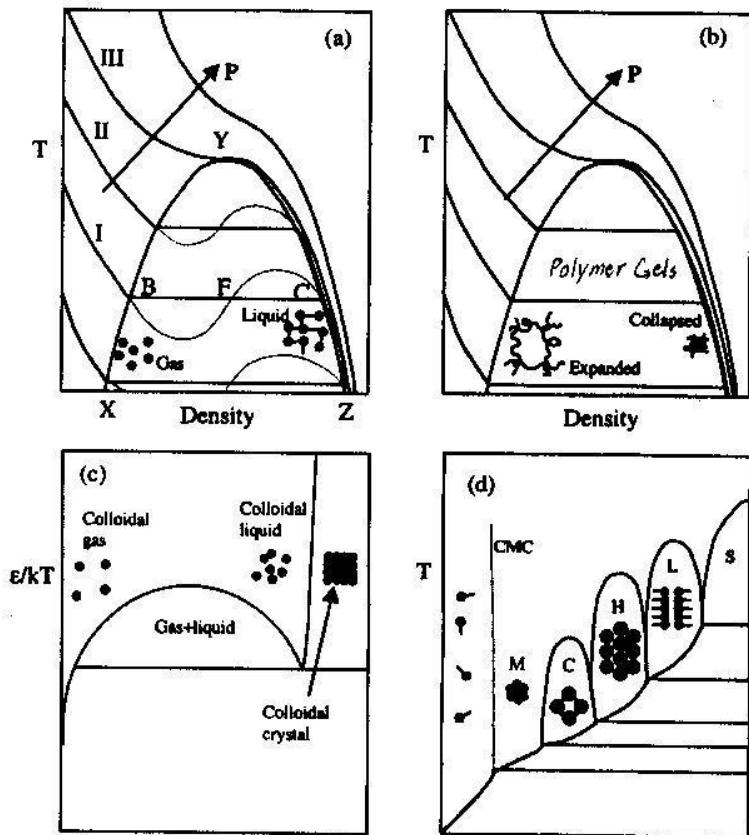


FIGURE 2.4. Phase diagrams of several systems showing the transition from dispersed states to condensed states. (a) Gas-liquid phase transition. (b) Swelling-deswelling in polymer gels. (c) Consolidation of colloidal crystals. (d) Surfactant phase diagrams. In Fig. 2.4(d) M, C, H, L, S represent micelles, cubic phase, hexagonal phase, lamellar phase, and solid phase respectively. Figures 2.4(a) and (b) are redrawn after Refs. 9, 10. Figure 2.4(c) is redrawn after Ref. 13. Figure 2.4(d) is redrawn after Ref. 16.

Surfactants and Amphiphilic Molecules

Surfactant characteristics: Head group charge, chain length, head group size

Cationic:

- long chain amines or ammonium salts are positively charged at pH<7,
- not charged at pH >7, then not active
- quaternary ammonium salts are charged and active at all pH's

Anionic:

- Long chain carboxylic or sulfonic acids, are negatively charged at pH > 7,
- (at pH < 7 not ionized, not active)

Surfactant Activity depends on:

- pH, ionic strength of the solution and by counter ions
- Counter ions neutralize charges on surfactant head groups, and even cause its precipitation.
- Non-ionic surfactants have the advantage in that pH, counter ions, or solvents do not affect their activity.

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 ₃ Na ⁺	Anionic	Detergents
Hexadecyl trimethyl-ammonium bromide (CTAB)	C ₁₆ H ₃₃	—N ⁺ (CH ₃) ₃ Br [—]	Cationic	Mild disinfectants
C ₁₂ E ₅ Pluronic P105	C ₁₂ H ₂₅ (OCH ₂ C ₂ H ₅) ₅₈	—(OCH ₂ CH ₂) ₅ Two chains, each —(OCH ₂ CH ₂) ₃₇	Non-ionic Non-ionic, triblock copolymer	Cosmetics Cosmetics, pharmaceuticals
Lecithin	Two chains, each C ₁₂ H ₂₅	Phosphatidyl choline	Zwitterionic, phospholipid	Animal cell membranes, food

Critical Micelle Concentration

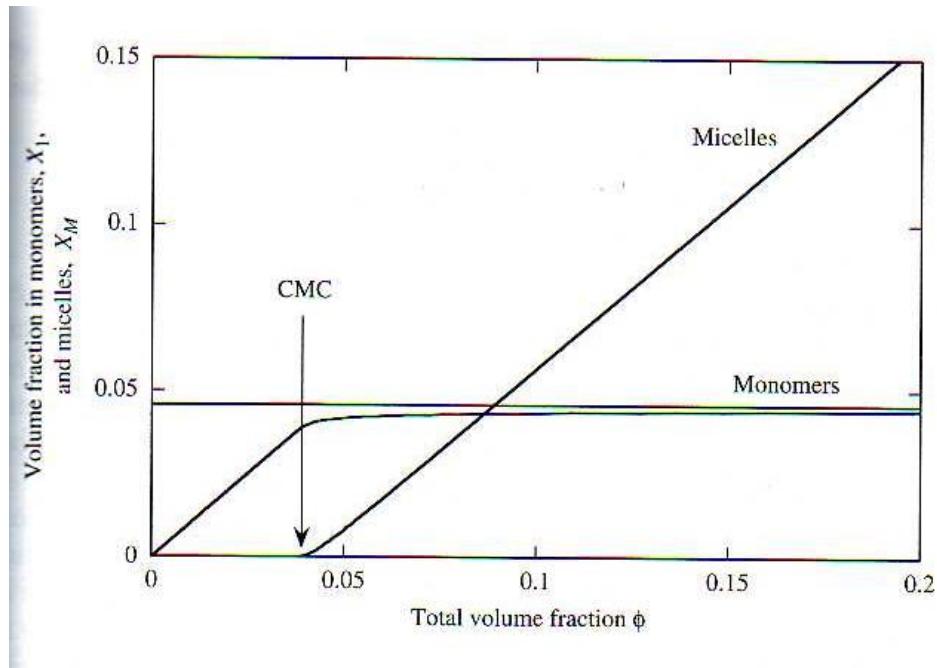
ϕ - volume fraction of amphiphile

$\phi < \phi_c$ - monomers

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

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

$$\phi_c = \exp(-\Delta\varepsilon/k_B T) \quad (\text{CMC})$$



Packing Geometry: Attaining the Desired Self-Assembled Structures

Structure depends on pH, T,
electrolyte concentration

Major driving forces for amphiphiles to form well-defined aggregates are:

- hydrophobic attraction at hydrocarbon-water interfaces and
- hydrophilic ionic or steric repulsion between head groups.

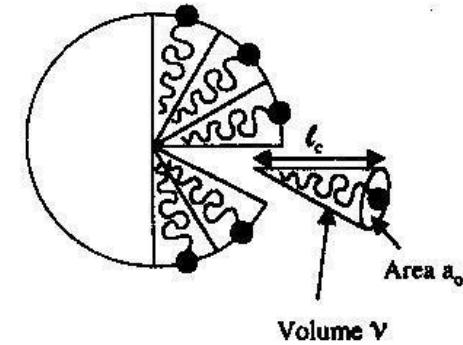
**Geometric packing parameter
(shape factor)**

$$R = \frac{v}{a_0 l_c}$$

v = hydrocarbon chain volume
 a_0 = optimal head group area
 l_c = critical chain length

R	< 0.5	> 0.5	> 1
structure	spherical-cylindrical	bilayers	inverse micelle

Critical packing parameter $v/a_0 l_c$	Critical packing shape	Structures formed
< 1/3	Cone	Spherical micelles
1/3-1/2	Truncated cone	Cylindrical micelles
1/2-1	Truncated cone	Flexible bilayers, vesicles
~1	Cylinder	Planar bilayers
> 1	Inverted truncated cone or wedge	Inverted micelles



Critical packing parameter
 $R = v/a_0 l_c$

FIGURE 2.5. Relationship between the bilayer structures and the packing parameters (shape factors) (reproduced and adapted from Ref. 17 with permission from Academic Press).

Packing Geometry: Attaining the Desired Self-Assembled Structures at Constant Temperature

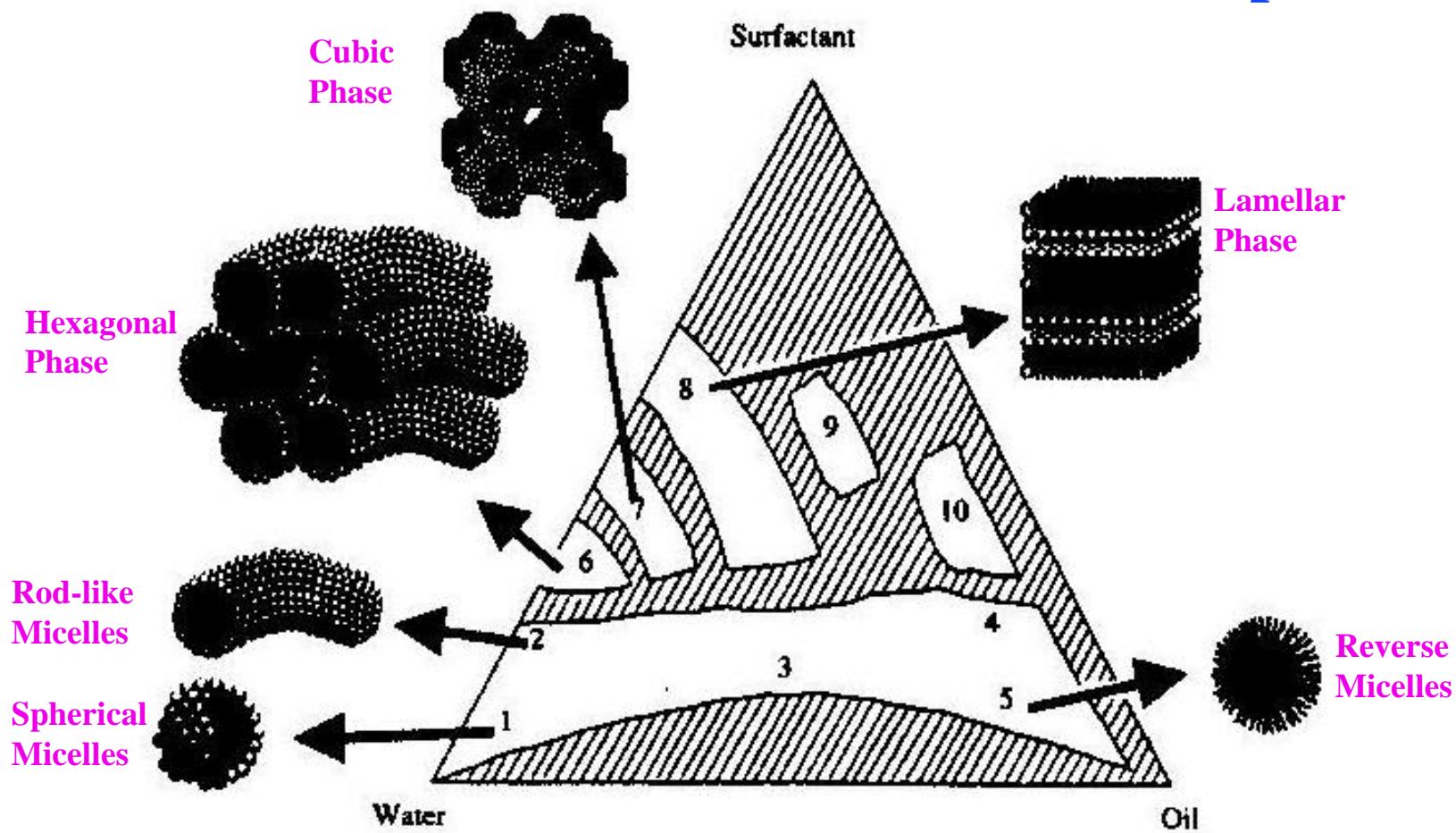
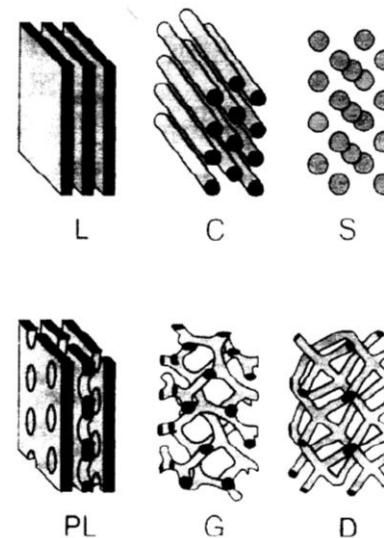
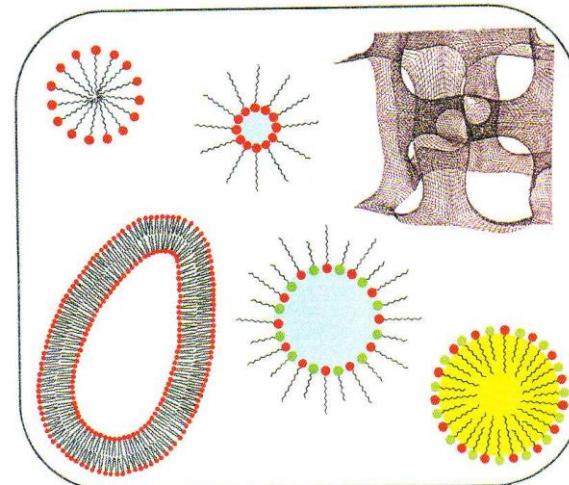
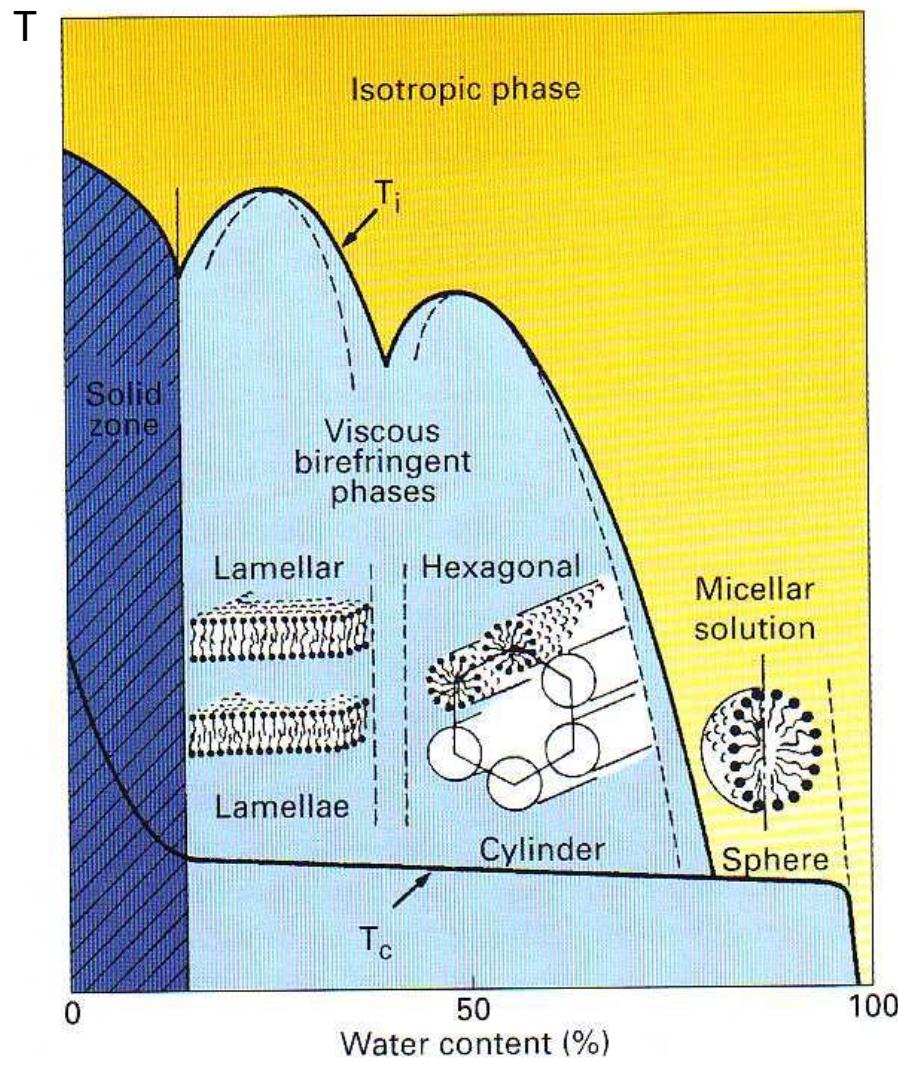


FIGURE 2.6. Schematic phase diagrams of surfactant-water-oil systems. 1. Spherical micelles. 2. Rod-like micelles. 3. Irregular bicontinuous phase. 4. Reverse cylindrical micelles. 5. Reverse micelles. 6. Hexagonal phase. 7. Cubic phase. 8. Lamellar phase. 9. Reverse cubic phase. 10. Reverse hexagonal phase (Derived from Refs. 18 and 19 with permissions from the publishers).

Increase Surfactant Conc.: spherical micelles → rod-like micelles → cubic → lamellar

Packing Geometry: Attaining the Desired Self-Assembled Structures vs. Temperature



Packing Geometry: Attaining the Desired Self-Assembled Structures considering Physico-Chemical aspects

- **Effect of surfactant concentration**

Surfactant conc \uparrow : lower hydration of head groups \rightarrow $R = \frac{v}{a_0 l_c}$
lower $a_0 \rightarrow$ higher R \rightarrow lamellar structure

- **Effect of surfactant chain length**

If l_c increases, v increases, however if R increases too much, spherical \rightarrow lamellar

- **Effect of co-solvent**

- Polar solvents, like alcohols, tend to associate with head groups and reduce the tendency for the surfactant molecules to associate; CM may disappear,
- Non-polar solvents associate with hydrophobic chains of the surfactant increase v \rightarrow increase R \rightarrow less curved structures

- **Effect of salts and ionic species**

- On ionic surfactants, reduces repulsive energy between head groups, reducing $a_0 \rightarrow$ larger R \rightarrow less curved structures

Shape of aggregates

Self assembled structures are rich in phases:

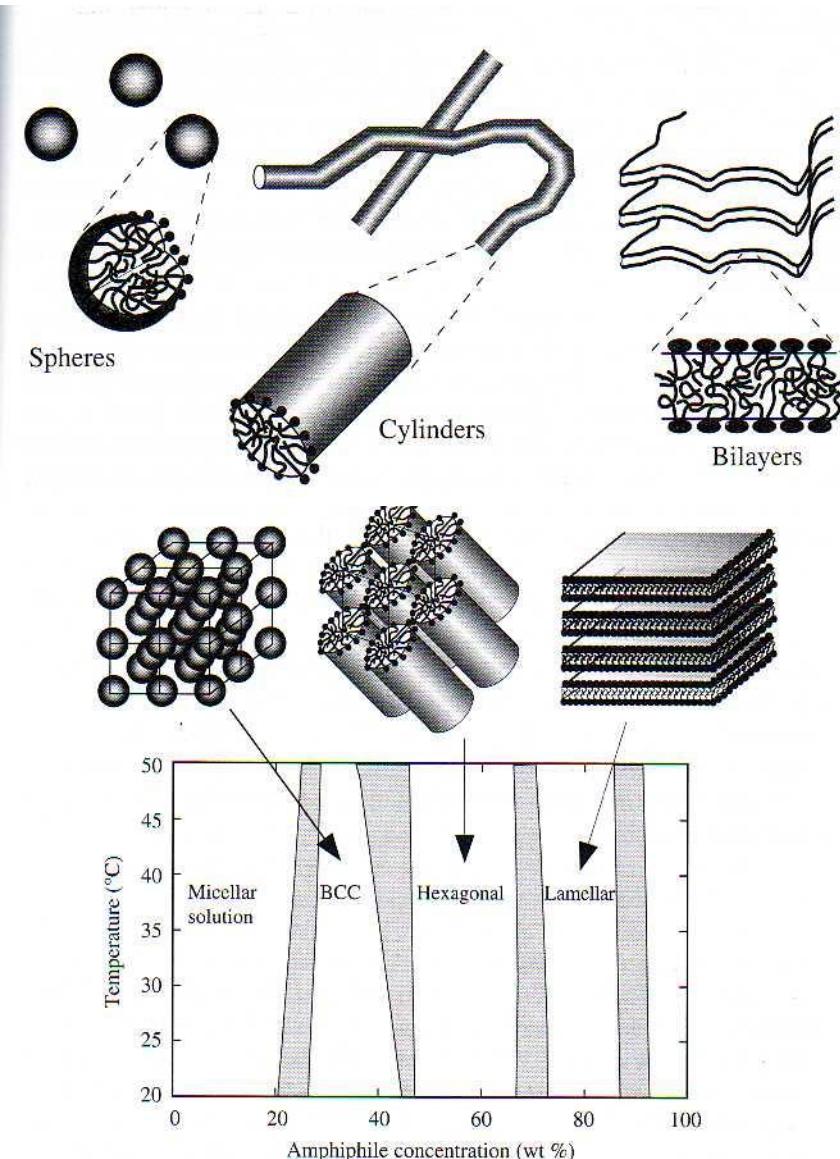
- response by changing size and shape and arrangement of micelles
- dramatic change in properties

Basic shapes:

- spheres
- cylinders
- bilayers
- vesicles

Superstructures:

- micellar crystals
- lamellar phases
- bicontinuous networks



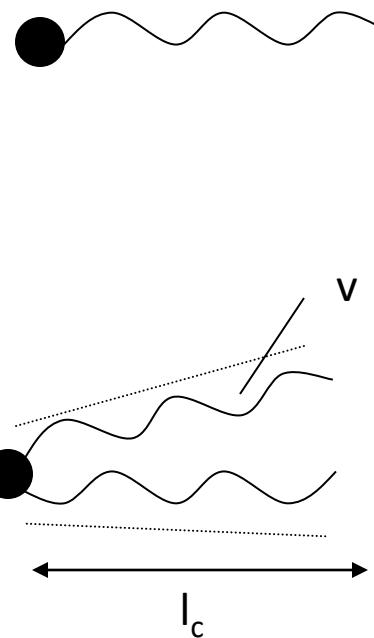
Shape of aggregates

Factors determining the shape

- i) Optimum head group area, 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, ...

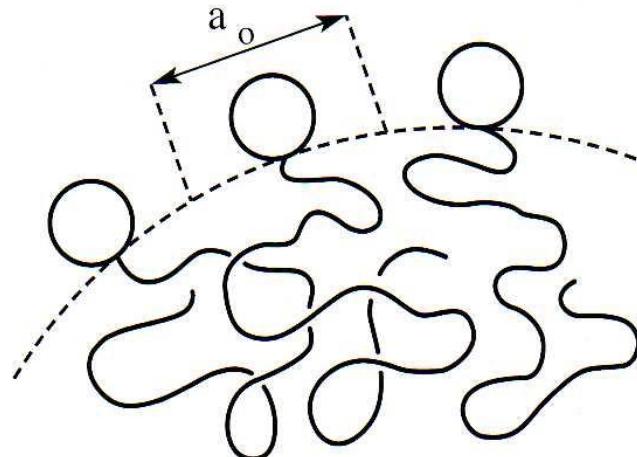
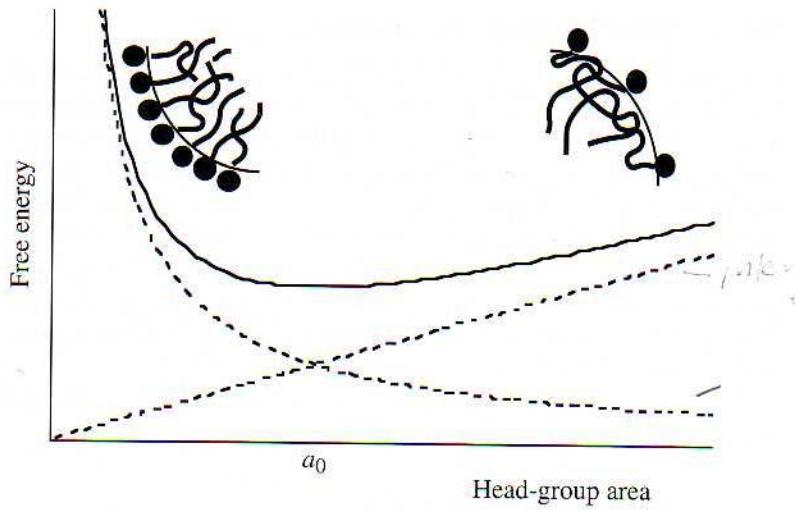


Optimum head group area, a_0

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 is the # of molecules in aggregate)

Surface area:

$$4\pi r^2 = Na_0$$

$$\rightarrow r = 3v/a_0$$

but $r_{\max} \leq l_c$

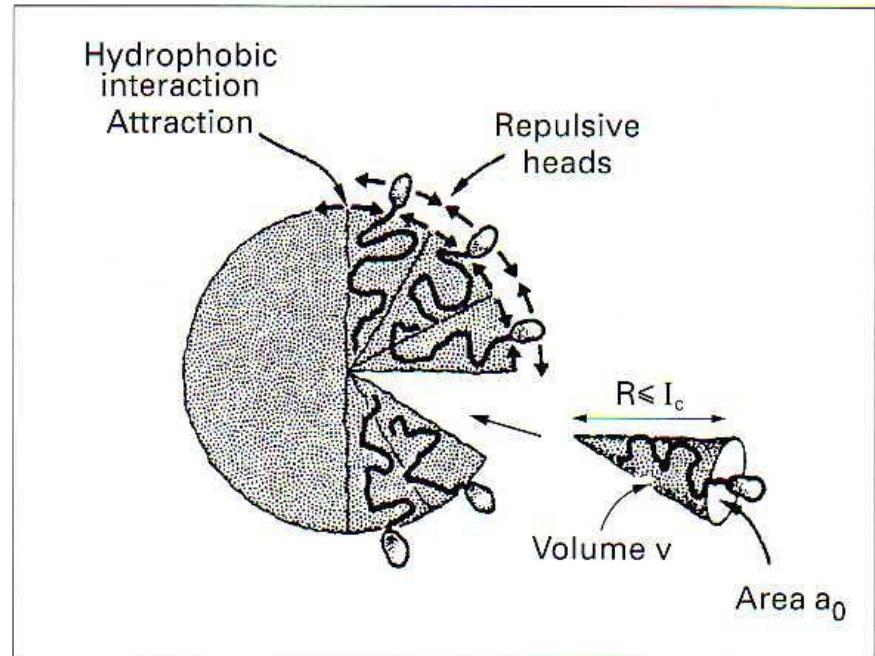


Fig. 4.4. Schematic diagram of a micelle

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

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:

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

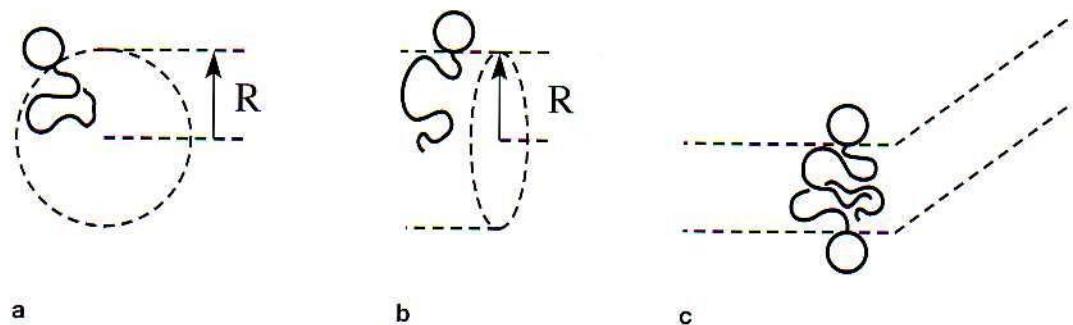
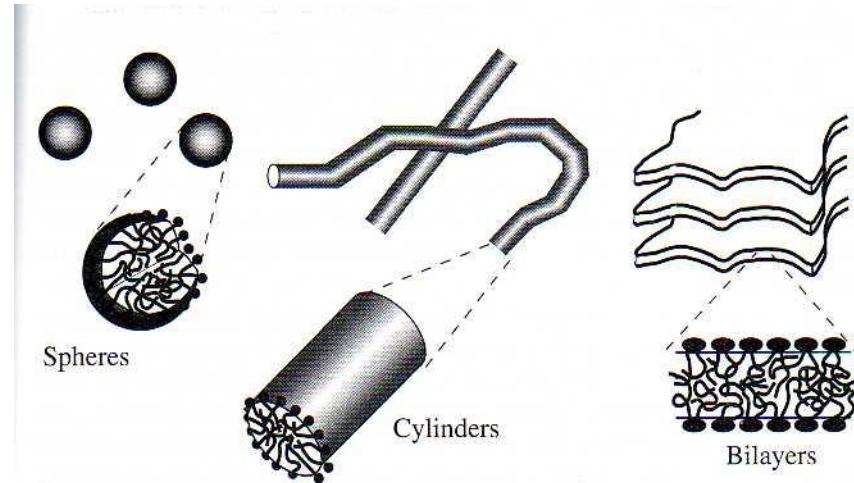


Fig. 5.4. Three possible morphologies, with their curvature. (a) Sphere, curvature $1/R + 1/R = 2/R$. (b) Cylinder, curvature $1/R + 0 = 1/R$. (c) Bilayer, zero curvature

Spherical micelles

Spheres formed when:

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

Size of micelles finite ->

ε_N has a minimum value at an optimum number M

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

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

X_N - volume fraction of micelles
with N molecules

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

↑
size distribution

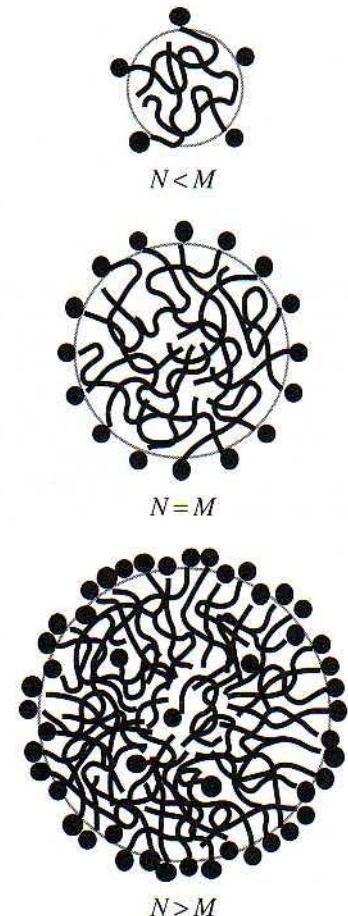


Fig. 9.3 The optimum aggregation number, M for a spherical micelle. Micelles containing a smaller number of molecules have too large an area for each head-group, causing unfavourable water/hydrocarbon interactions, while in micelles larger than the optimum number some head-groups are forced inside the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

Packing Geometry: Attaining the Desired Self-Assembled Structures

$$R = \frac{v}{a_0 l_c}$$

Increasing surfactant concentration, surfactant chain length,
added high concentration salts and nonpolar solvent.

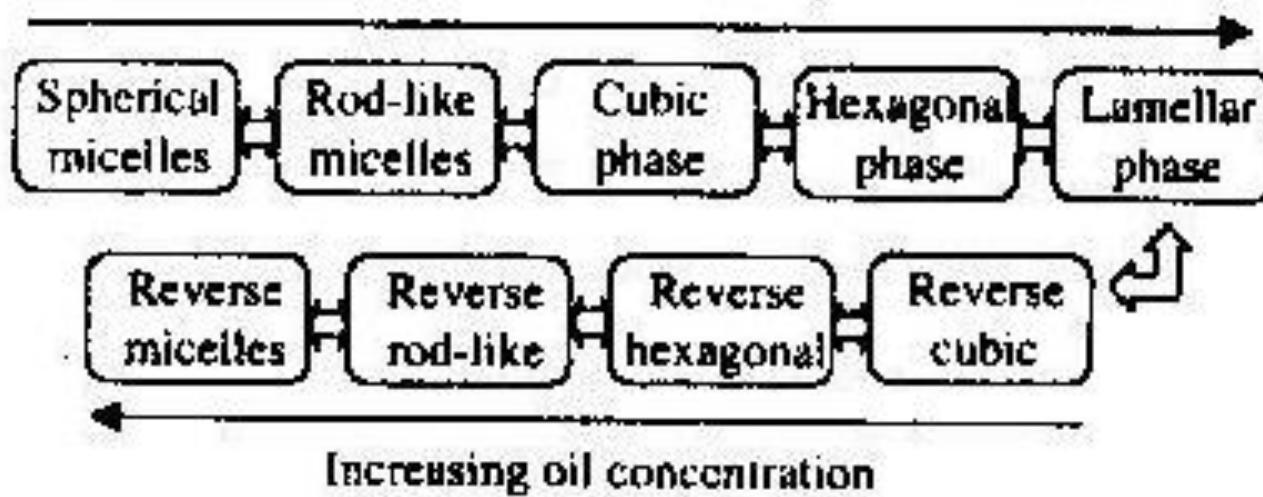


FIGURE 2.7. Phase structures as a function of external conditions.

Macro vs. micro phase separation

Simple liquids (water & oil):

$$\varepsilon_N = \varepsilon_\infty + \frac{\alpha k_B T}{N^{1/3}}$$

$$\alpha k_B T = 4\pi\gamma(3v/4\pi)^{2/3}$$

free energy when a molecule joins an aggregate
 N - number of molecules in the aggregate
 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

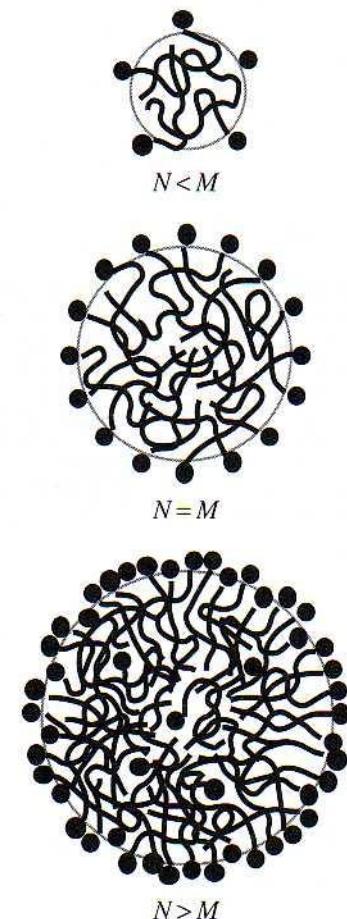


Fig. 9.3 The optimum aggregation number, M for a spherical micelle. Micelles containing a smaller number of molecules have too large an area for each head-group, causing unfavourable water/hydrocarbon interactions, while in micelles larger than the optimum number some head-groups are forced inside the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

Cylindrical micelles

Spheres 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 $2\Delta E_{end}$

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

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

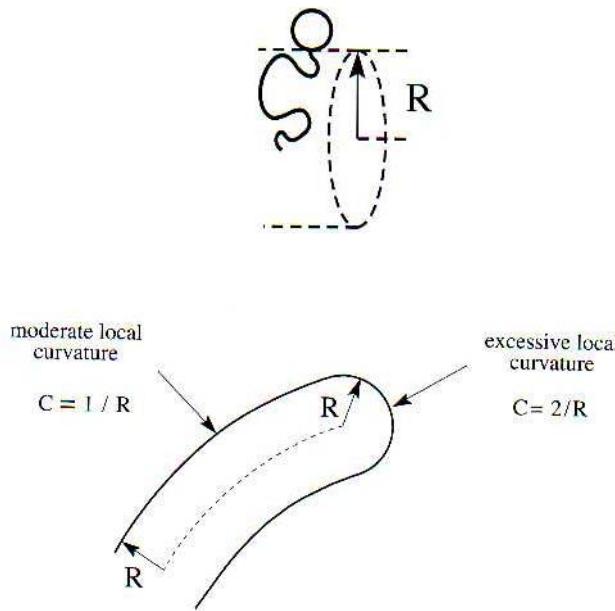


Fig. 5.11. To isolate its hydrophobic interior from water, a more or less hemispherical surface must form at the two ends of a giant cylindrical micelle

Bi-layers

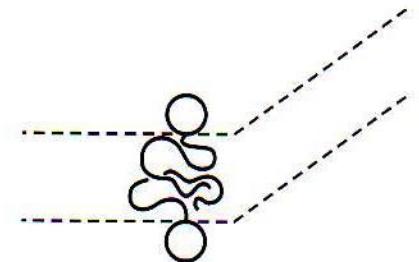
Bilayers

Bilayers formed when:

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

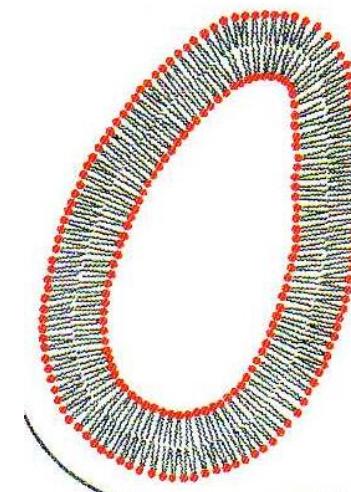
$$\Delta E_{\text{edge}}(A) \propto A^{1/2} \quad (\text{A - area of a layer})$$

dependent on the size of the bilayer
-> formation of infinite layers



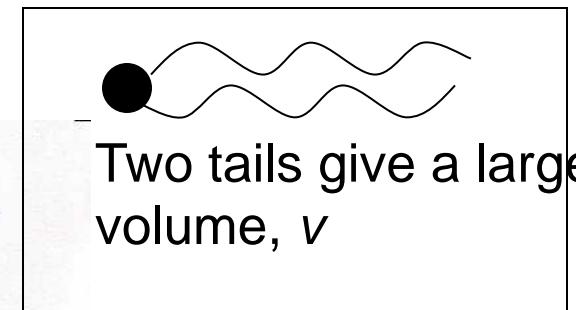
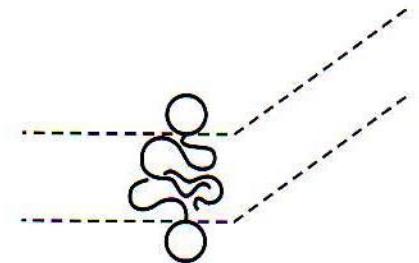
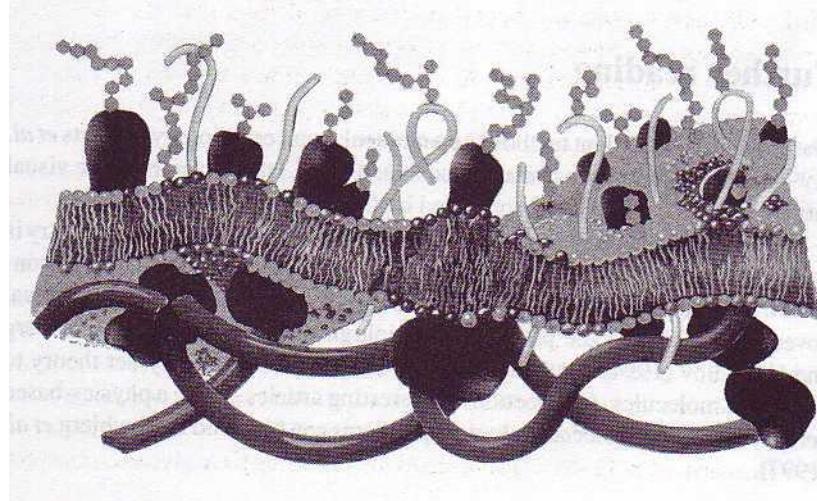
Vesicles - closed surface by a bilayer

- > model for cell membranes
- > drug delivery systems
- > colloidal behaviour



Bilayers

Cell membranes - phospholipid bilayers



Two tails give a large volume, v

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

Fig. 10.11 A schematic diagram of the cell membrane of a eukaryotic cell. The basic structural element is a lipid bilayer; the bilayer is decorated by a number of protein molecules. On the inside of the membrane (below) a network of actin filaments is anchored by protein molecules, while the outside of the membrane is decorated by carbohydrate chains. Reproduced with permission from Mouritsen and Andersen (1998).

Bilayers

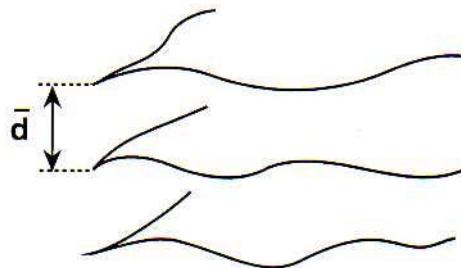
Bilayers are not flat - highly crumpled

Persistence length:

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

k - bending modulus of membrane

For $r > \xi$ direction in membrane is lost



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

Bilayers

Lamellar phase can be distorted by fluctuations forming complex geometries

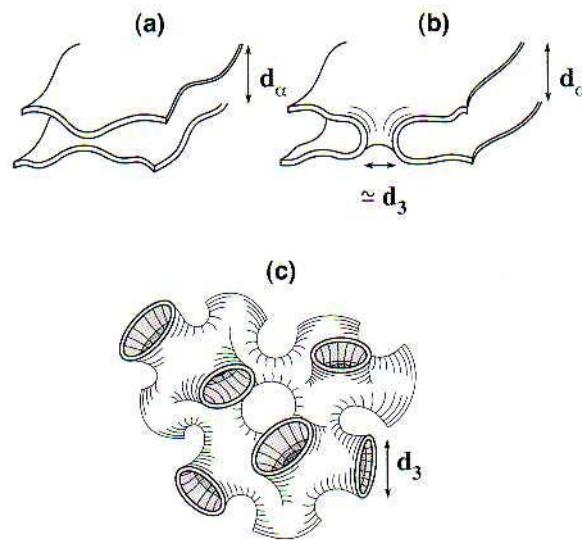
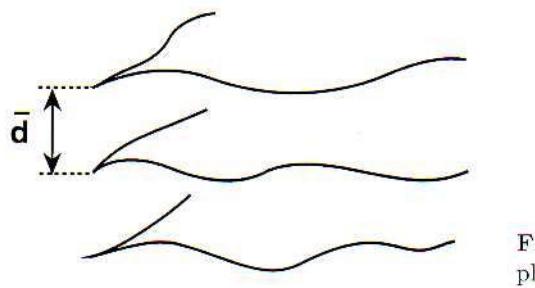


Fig. 5.21. Structure of the sponge phase.
(a) Two bilayers in the lamellar phase.
(b) Formation of an elementary passage.
(c) Proliferation of passages, leading to the sponge phase L_3

Phase behaviour

Self assembled structures are rich in phases
-> response by changing size and shape and arrangement of micelles
-> dramatic change in properties

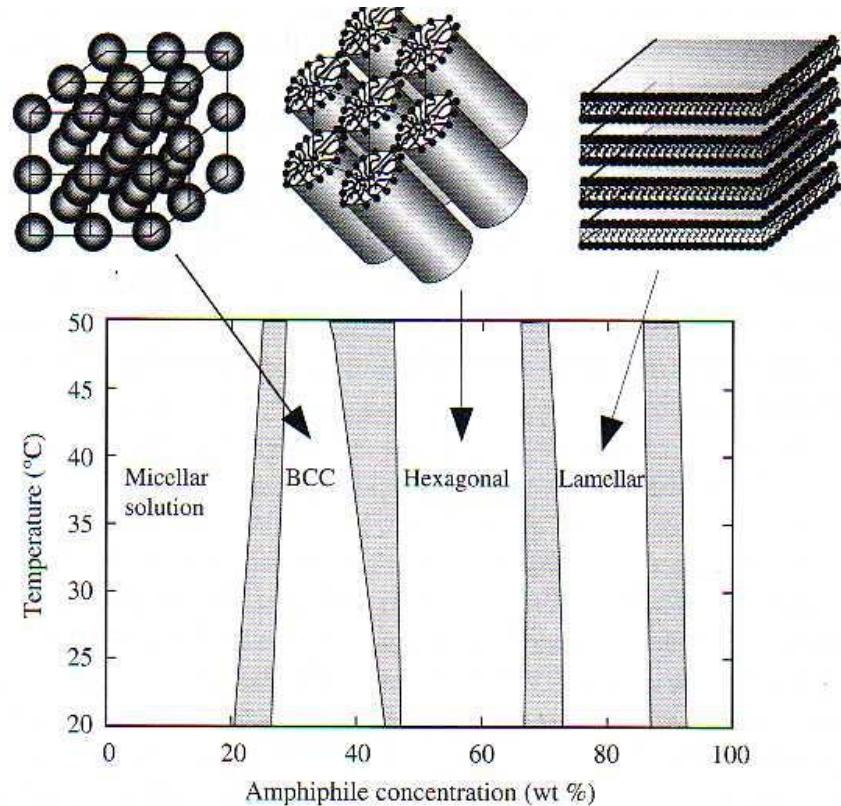


Fig. 9.7 The phase diagram of an amphiphilic copolymer in water, showing schematically the structures of the ordered phase. The material is a short triblock copolymer of ethylene oxide (EO) and propylene oxide (PO), with the structure $(EO)_{37}(PO)_{58}(EO)_{37}$. Data from P. Alexandris, D. Zhou, and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

Phase behaviour

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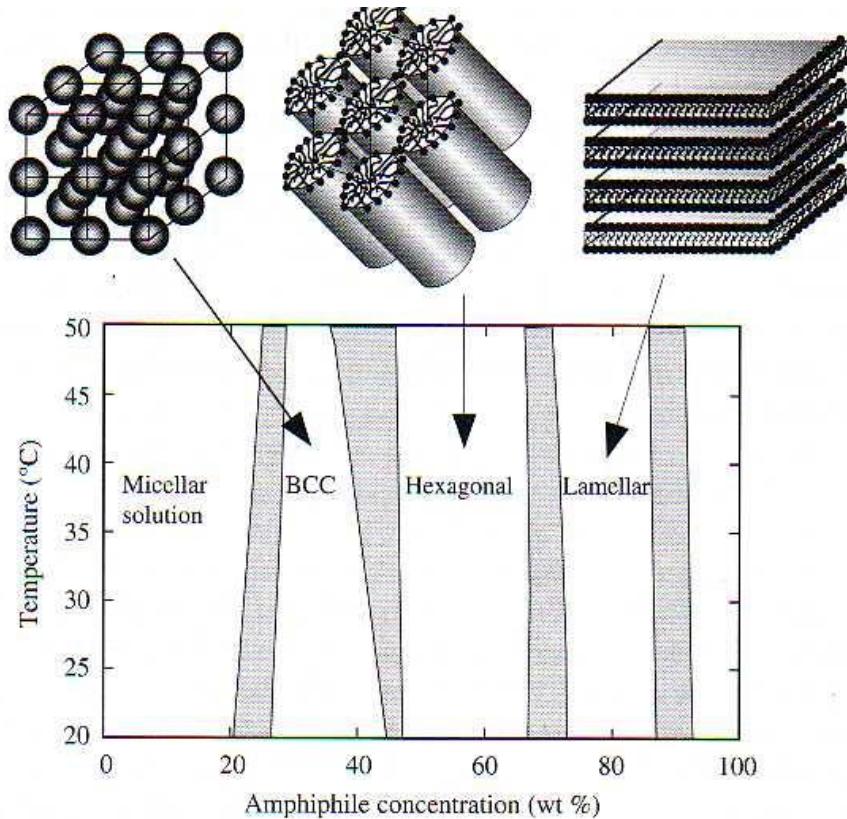
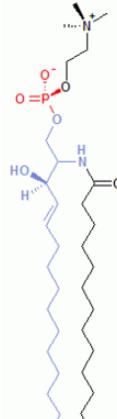


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Micelles and Inverse Micelles

Surfactant: Hydrophilic Head
+ Hydrophobic Tail

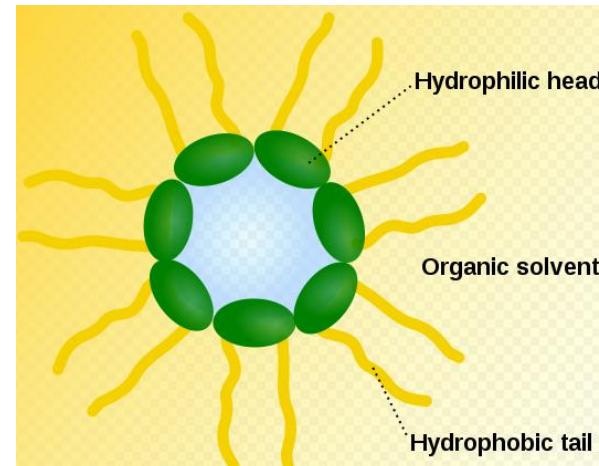
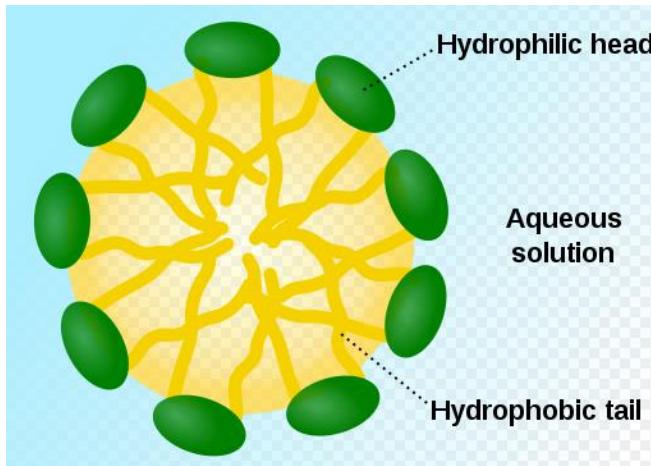


le: Phospholipid

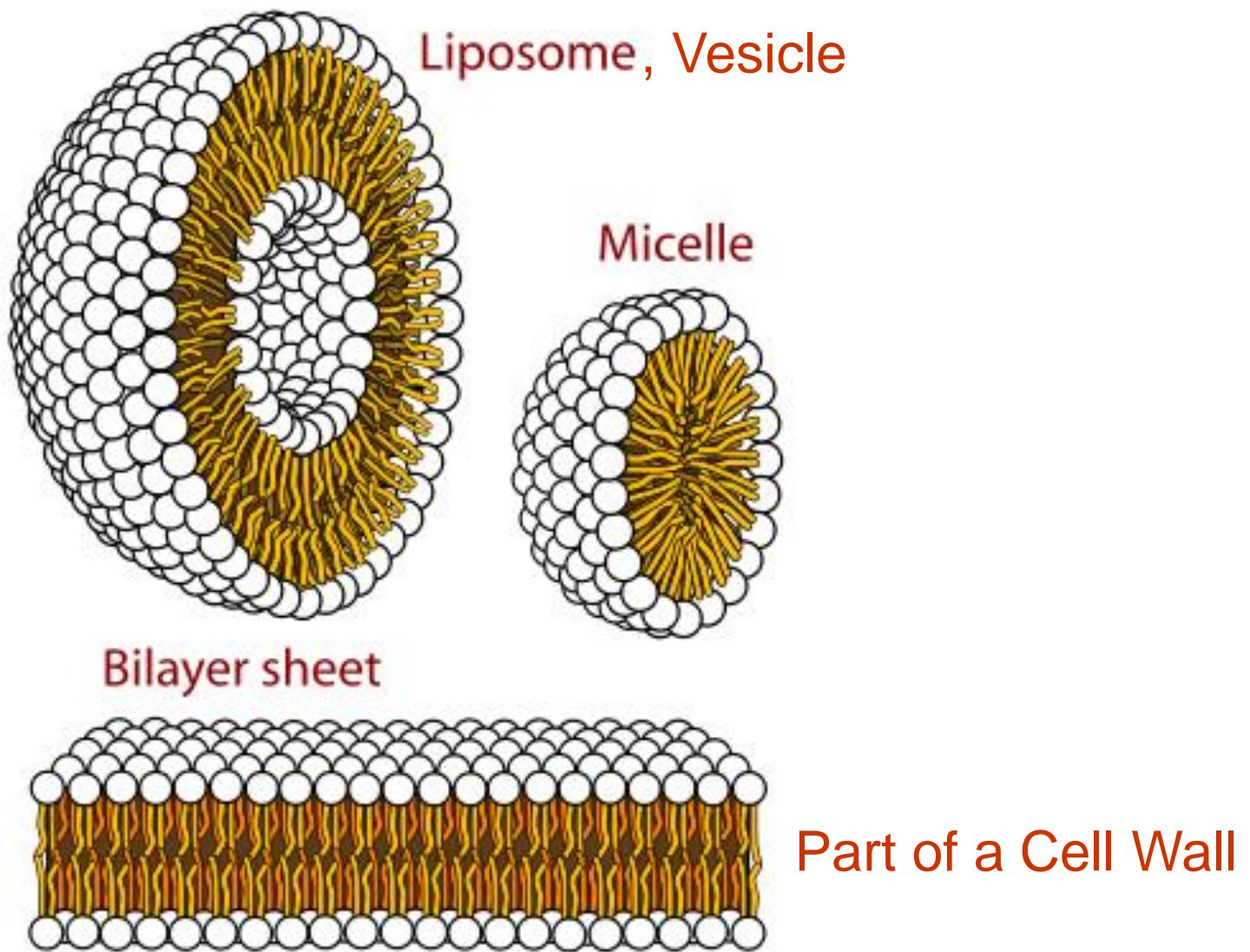
Micelle:

Inverse Micelle:

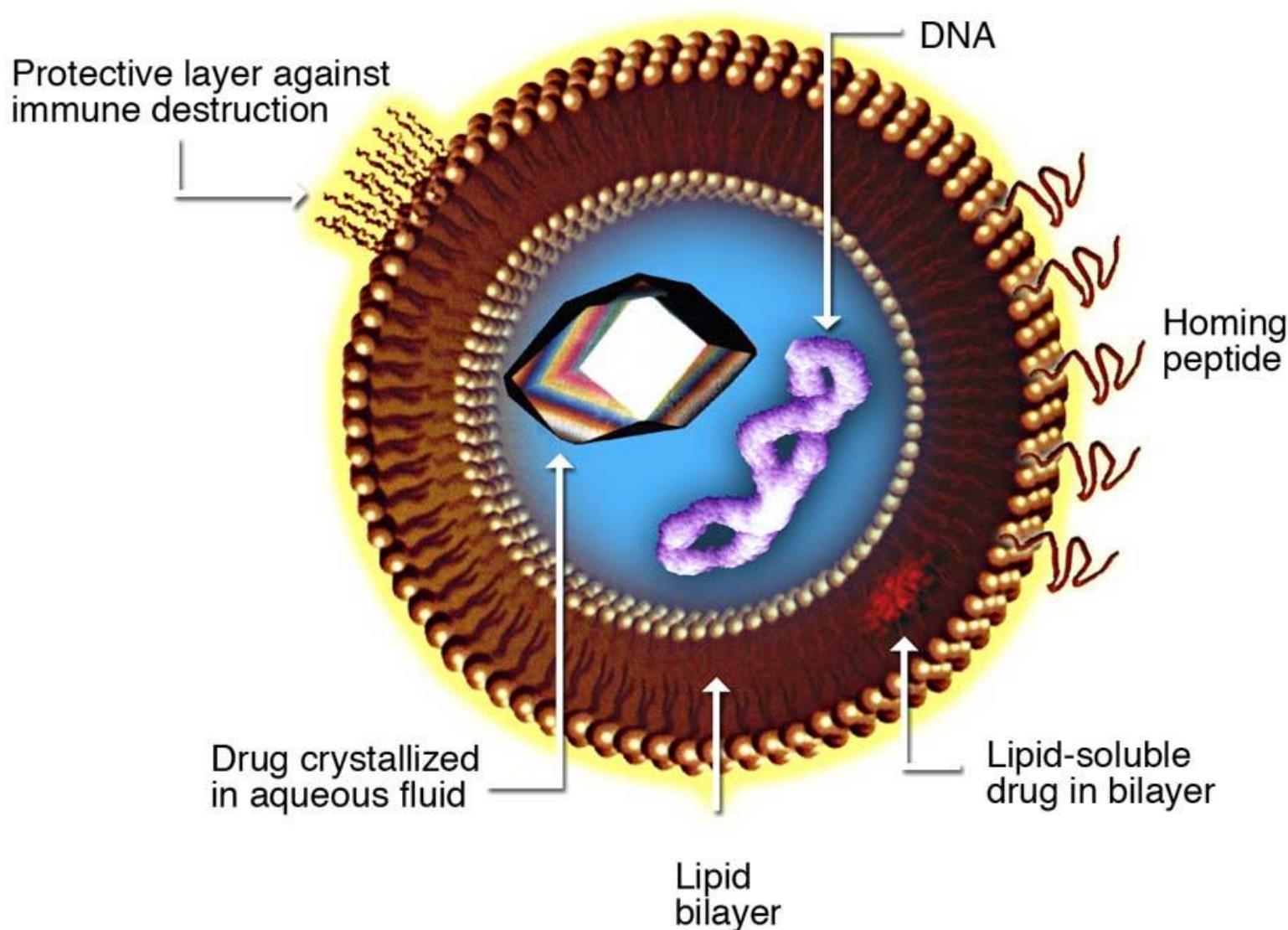
Heads outside, Water outside Heads inside, Water inside



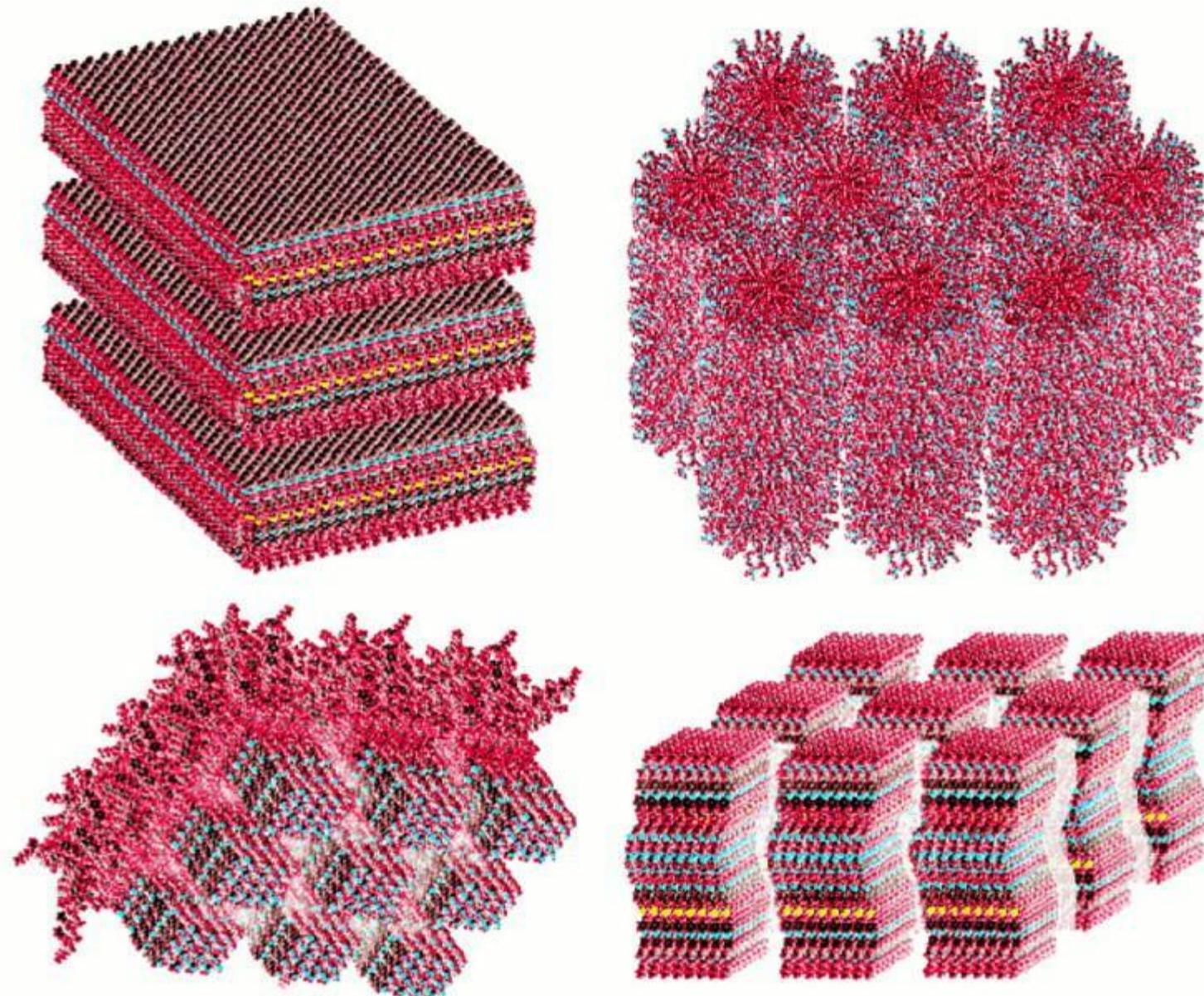
Bilayer Structures

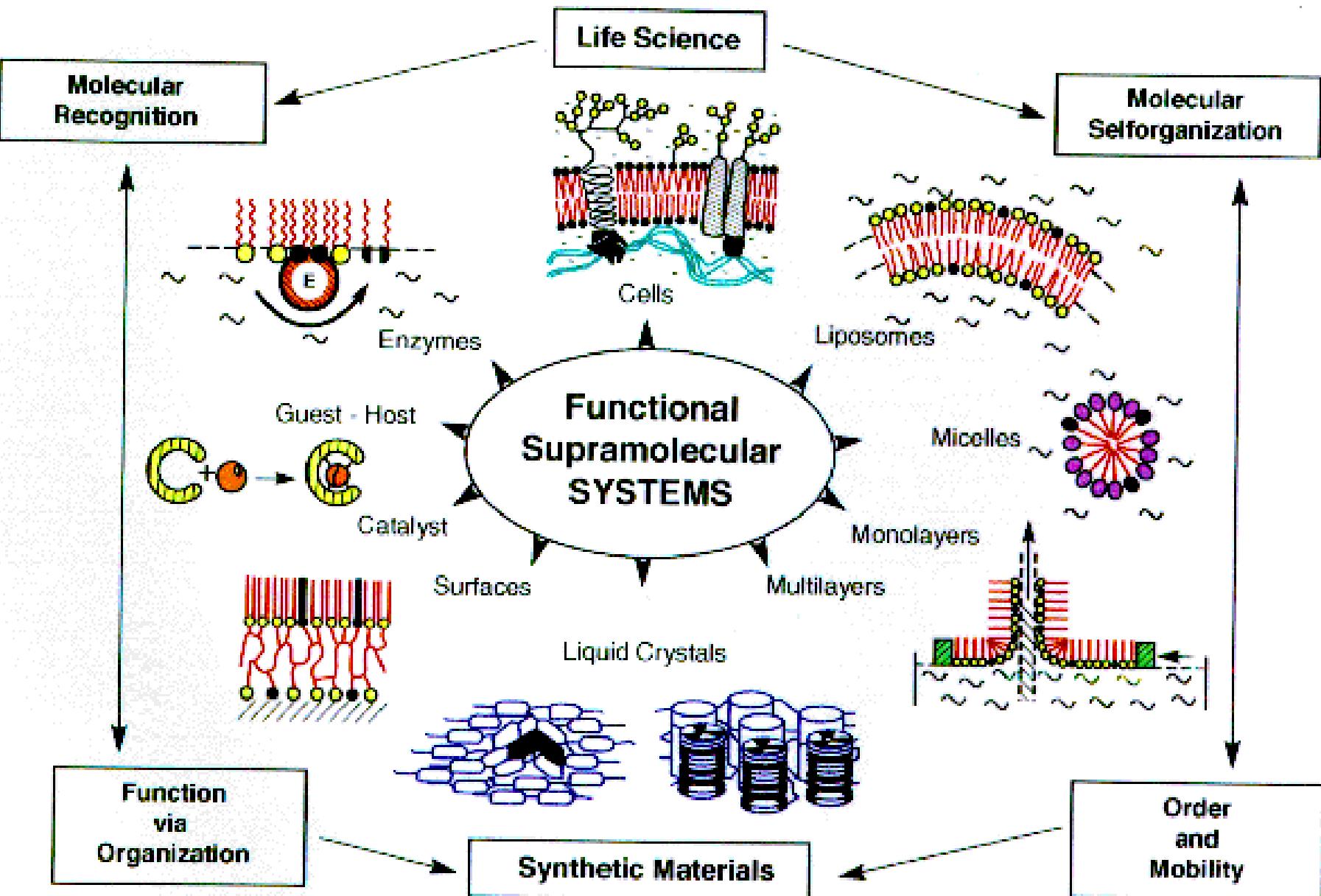


Drug Delivery via Liposomes



Supramolecular Assemblies





Competitions on Self-Assembly

Competitions in Self-Assembly

- Molecules often segregate at an interface to LOWER the interfacial energy - leading to an ordering of the system.
- This self-assembly is opposed by thermal motion that disrupts the ordering.
- Self-assembly usually DECREASES the entropy, which is not favoured by thermodynamics.
- But there are **attractive** and **repulsive** interactions between molecules that dominate.

If free energy decreases ($\Delta F < 0$), then the process is *spontaneous*.

$$\Delta F = \Delta U - T\Delta S$$

Internal Energy (U)
decrease is favourable

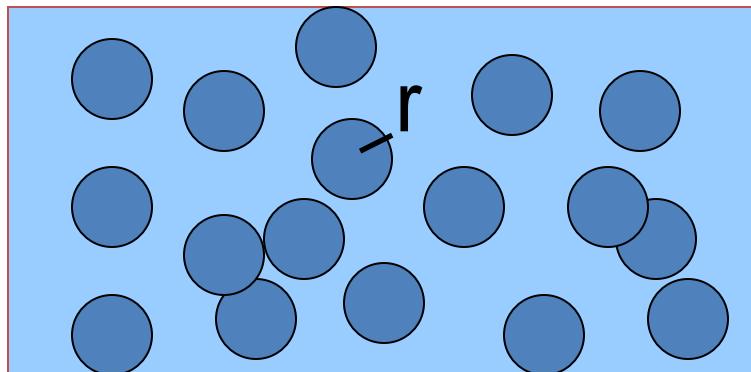
Entropy (S) increase is
favourable

Importance of Interfaces

- Free energy change: $dF = \gamma dA$
- An increase in area raises the system's free energy, which is not thermodynamically favourable.
- So, sometimes interfacial tension opposes and destroys self-assembly.
- An example is coalescence in emulsions.

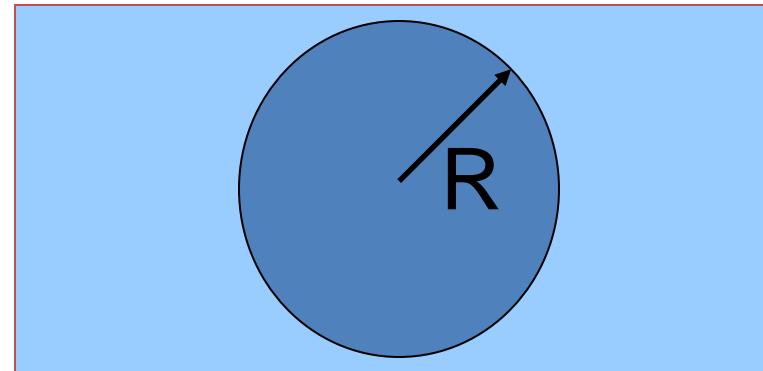
Coalescence in Emulsions

Liquid droplet volume **before** and **after** coalescence:



Surface area of **N** particles:

$$4 N \pi r^2$$



Surface area of droplet made from **coalesced** droplets: $4 \pi R^2$

$$\text{Change in area, } \Delta A = - 4\pi r^2(N - N^{2/3})$$

In 1 L of emulsion (50% dispersed phase), with a droplet diameter of 200 nm, N is $\sim 10^{17}$ particles. Then $\Delta A = -1.3 \times 10^4 \text{ m}^2$

$$\text{With } \Gamma = 3 \times 10^{-2} \text{ J m}^{-2}, \quad \Delta F = \Gamma \Delta A = - 390 \text{ J.}$$

Hydrophilically-driven self-assembly of particles

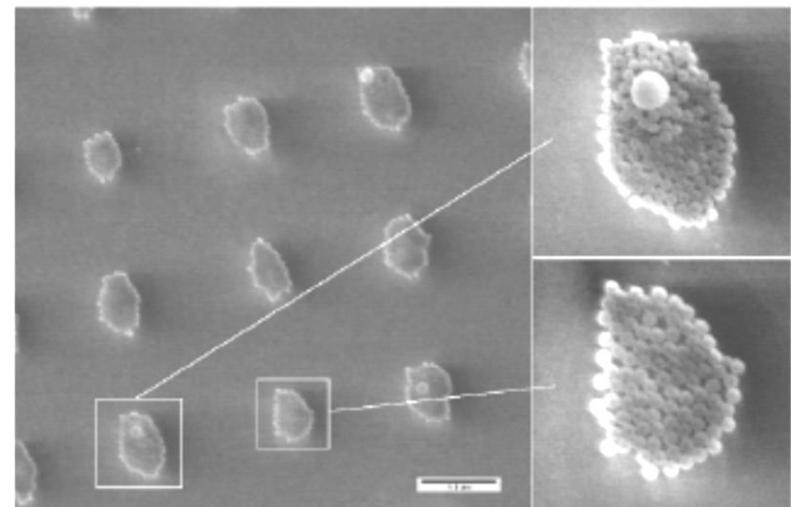
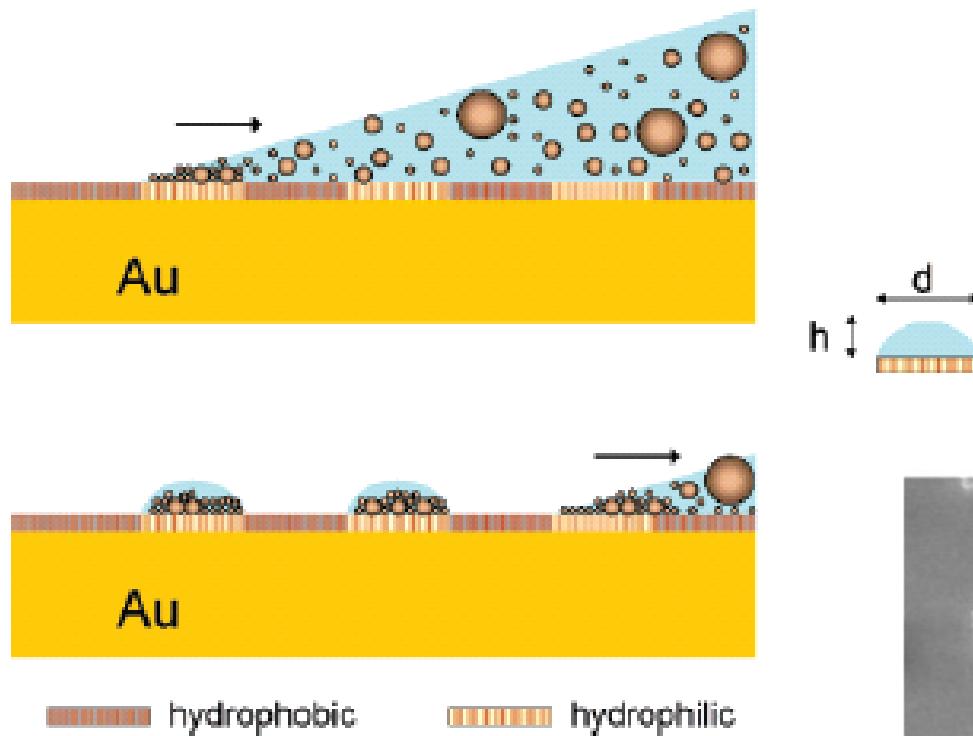
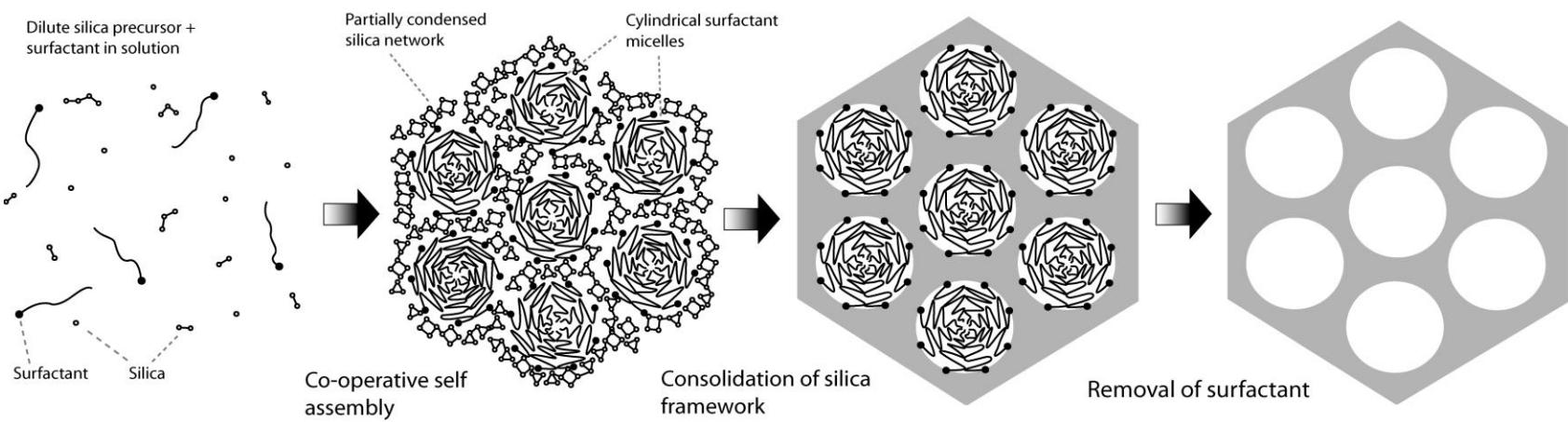


Figure 4. SEM picture of a mixture of PS spheres deposited on a microcontact-printed Au substrate. The mixture contains 3 μm , 800 nm, and 250 nm particles. Hydrophilic regions are $7 \times 4.5 \mu\text{m}$. The bar is 5 μm .

Synthesis of Mesoporous Materials

How do we use micelles to form mesoporous metal oxides?



Courtesy of Brian Eggiman

Self-assembled Block Copolymer Nanostructures

Block copolymers are amphiphilic molecules containing distinctively different polymer segments (blocks):

polystyrene ($\text{H}(\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH})-$) + poly isoprene ($-\text{CH}_2 - \text{H}_3(\text{CH}=\text{CH}_2)\text{C}-$) block

polystyrene and poly butadiene ($-\text{CH-CH=CH-CH}-$) block copolymer

($-\text{CH}_2-\text{CH}_2-$) polyethylene and poly propylene ($-(\text{CH}_2-\text{CH}_3\text{CH})-$) block copolymer

polyUrethane ($-(\text{CH}_2-\text{CH}_2-\text{O}_2\text{C-NH-C}_6\text{H}_{10}\text{CH}_2-\text{C}_6\text{H}_{10}\text{-NH-OC})-$) + polyUrethane block copolymer

Different blocks in a single polymer chain are covalently bonded.

The phase separation occurs on the nanometer scale, as determined by the dimension of the blocks.

Factors: monomer type, composition and molecular size, and molecular configuration.

2.5 Self-assembled Block Copolymer Nanostructures

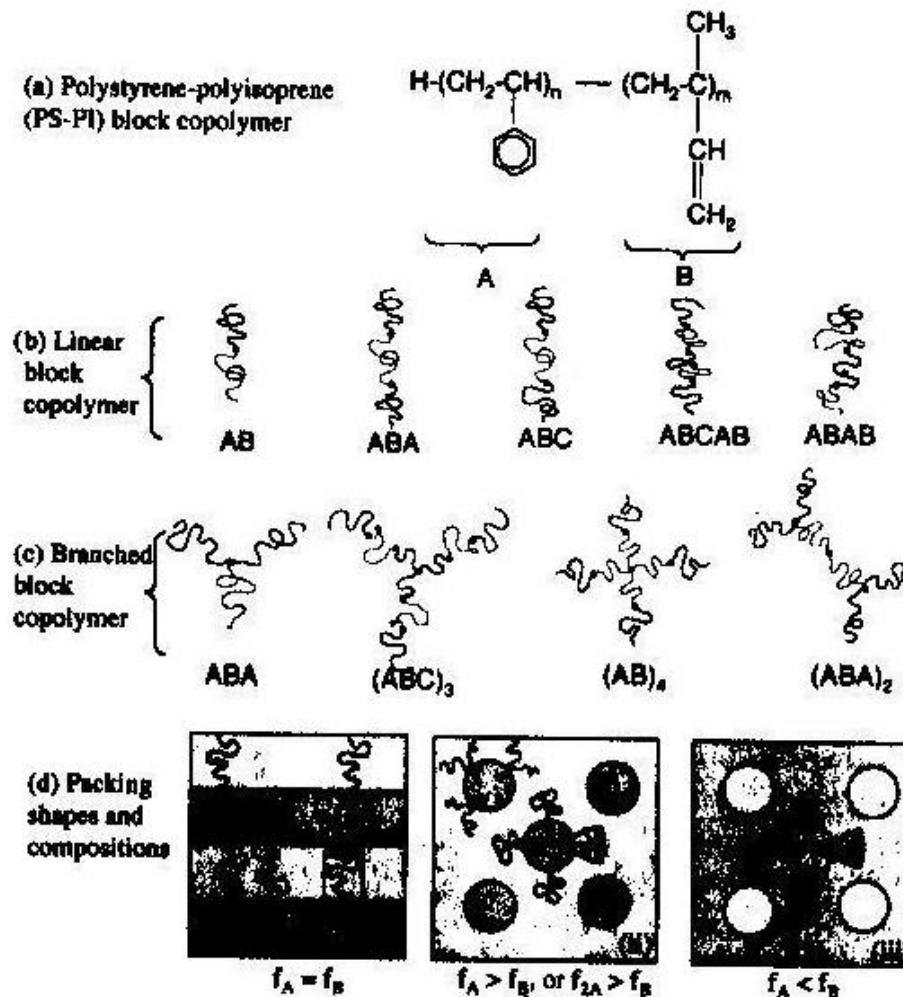


FIGURE 2.8. Variations of block copolymer configurations and the consequences on the packing geometry of the nanostructural ordering. (a) A common block copolymer, polystyrene-polyisoprene (PS-PI). (b) Linear block copolymers. (c) Branched block copolymers. (d) Packing shapes as a function of the compositions or molecular compositions (redrawn from Ref. 22).

2.5 Self-assembled Block Copolymer Nanostructures

Flory-Huggins segment-segment interaction parameter X:

$$\chi = \frac{E_{AB} - 1/2(E_{AA} + E_{BB})}{k_B T} \quad \chi > 0$$

phase separation is favored

E: Interaction Energy

f = volume fraction

$f_A = f_B \rightarrow$ straight cylinder \rightarrow lamellar phase

$f_A > f_B \rightarrow$ cone structure \rightarrow B phase dispersed in A phase as spherical micelles

$f_B > f_A \rightarrow$ cone structure \rightarrow A phase dispersed in B phase as spherical micelles

2.6 Co-Assembly of Liquid Structures and Inorganic Materials

Self-assembled liquid crystals from surfactants act as a **template** to support the growth of ceramic materials. These ordered structures are cross-linked together through the condensation of the aluminosilicate ions. Subsequently, the surfactant molecules can be removed by thermal or chemical treatment without collapsing the ordered structure (2-50 nm tunable).

Self-assembled periodic structures can be further used as a structural frame work to develop new materials:

1. by incorporating functional molecules and active sites into the porous channels (e.g. nanoporous silica)
2. by using the periodic nanoporous structures as a template (e.g. for carbon or metals)
3. by physically confining a new material in the organized nanostructures.

Co-Assembly of Liquid Structures and Inorganic Materials

Interactions between cationic surfactants and Anionic Silicates

Mesoporous materials: mixing aluminosilicate precursors (e.g. sodium aluminate, tetramethyl ammonium silicate, and silica) in a surfactant solution (e.g. ≥ 1 wt% cetyltrimethyl ammonium bromide (CTAB))

Inorganic ions play an important role in the self assembly process

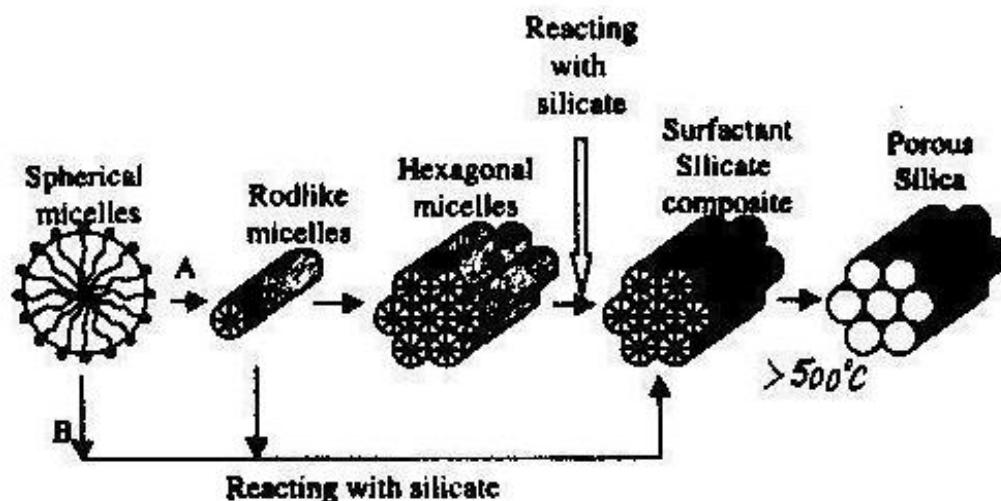
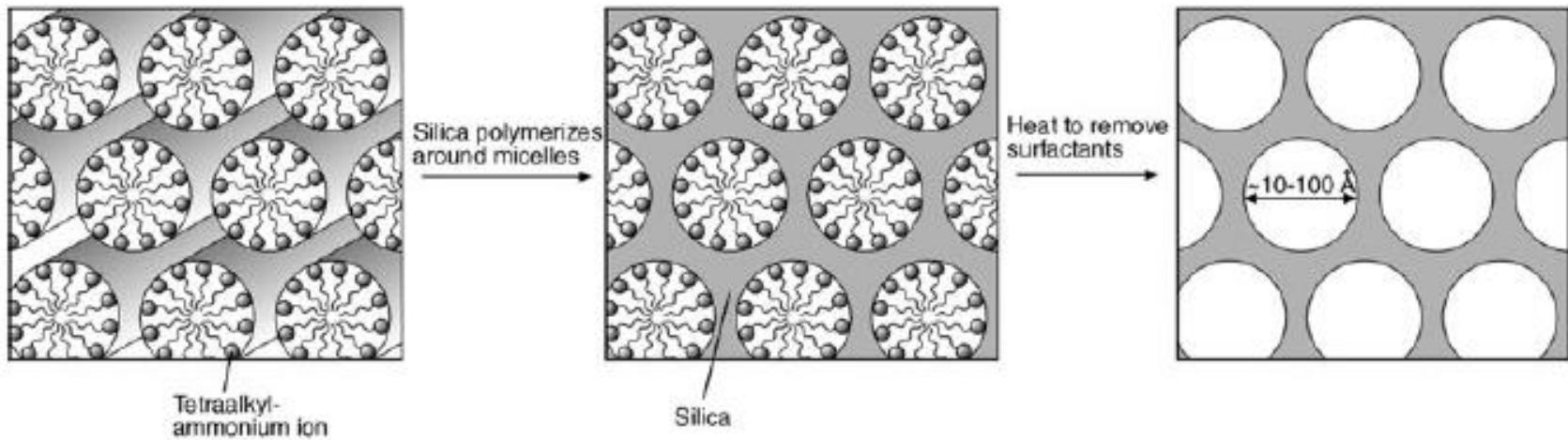


FIGURE 2.11. Liquid crystalline templating mechanisms initially suggested for the formation of ordered nanoscale materials (redrawn after Ref. 23).

Materials with controlled structure obtained through self-assembly



Micelles are packed together

SiO_2 (silica) is grown around the micelles

Micelles are removed to leave ~ 10 nm spherical holes. Structure has low refractive index. Can be used as a membrane.

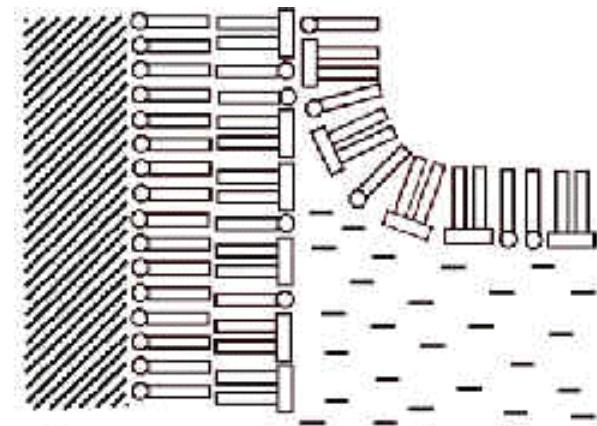
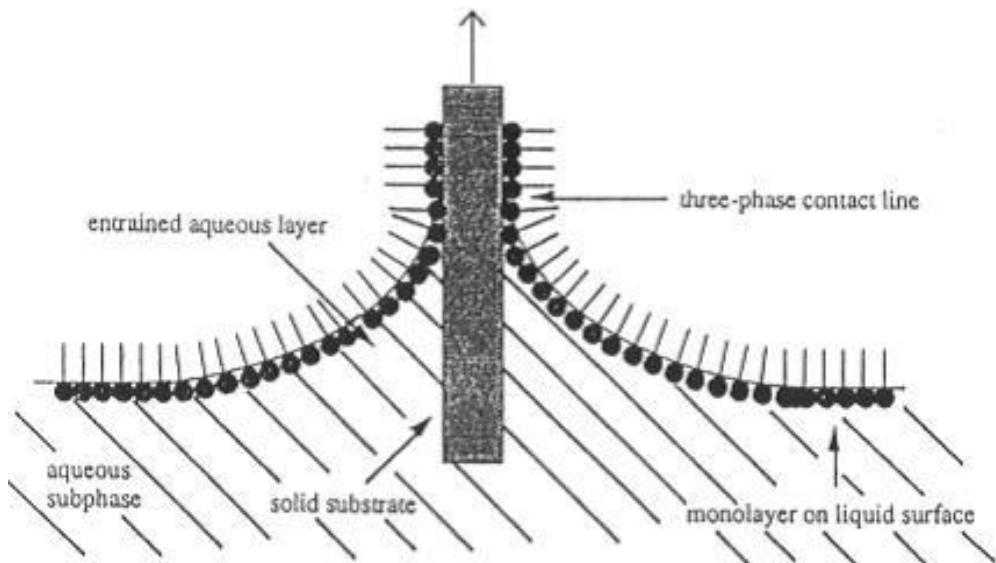
Langmuir-Blodgett Films

- Definition of LB films
 - History and development
- Construction with LB films
- Building simple LB SAMs
- Nano applications of LB films
 - Surface derivatized nanoparticles
 - Functionalized coatings in LB films

Langmuir-Blodgett Films

- A **Langmuir-Blodgett film** contains of one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing (or emersing) the solid substrate into (or from) the liquid. A monolayer is added with each immersion or emersion step, thus films with very accurate thickness can be formed. Langmuir Blodgett films are named after Irving Langmuir and Katherine Blodgett, who invented this technique. An alternative technique of creating single monolayers on surfaces is that of self-assembled monolayers. Retrieved from "http://en.wikipedia.org/wiki/Langmuir-Blodgett_film"

Langmuir-Blodgett Films



http://www.bio21.bas.bg/ibf/PhysChem_dept.html

http://www.ksvlt.com/pix/keywords_html_m4b17b42d.jpg

Deposition of Langmuir-Blodgett molecular assemblies of lipids on solid substrates.

Self Assembly

- **Self-assembly** is the fundamental principle which generates structural organization on all scales from molecules to galaxies. It is defined as reversible processes in which pre-existing parts or disordered components of a preexisting system form structures of patterns. Self-assembly can be classified as either static or dynamic.
- <http://en.wikipedia.org/wiki/Self-assembly>

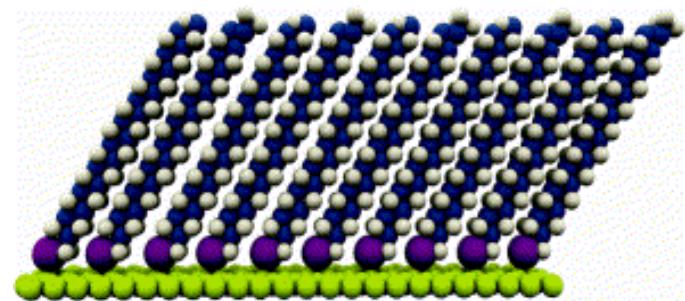
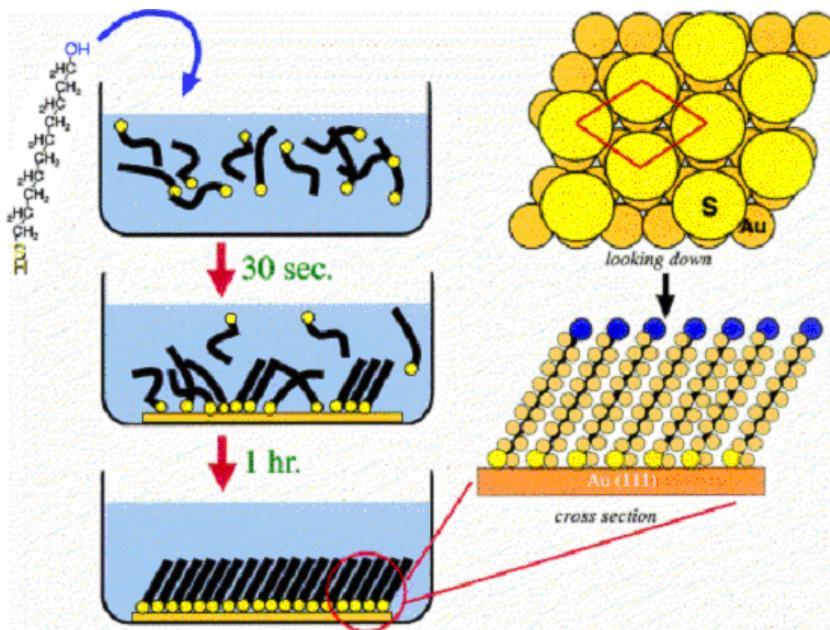
Molecular Self-Assembly

- Molecular self-assembly is the assembly of molecules without guidance or management from an outside source. There are two types of self-assembly, **intramolecular** self-assembly and **intermolecular** self-assembly, although in some books and articles the term self-assembly refers only to intermolecular self-assembly. Intramolecular self-assembling molecules are often complex polymers with the ability to assemble from the random coil conformation into a well-defined stable structure (secondary and tertiary structure). An example of intramolecular self-assembly is protein folding. Intermolecular self-assembly is the ability of molecules to form supramolecular assemblies (quaternary structure). A simple example is the formation of a micelle by surfactant molecules in solution.
- <http://en.wikipedia.org/wiki/Self-assembly>

Self Assembled Monolayers

- **SAMs – Self Assembled Monolayers**
- Alkane Thiol complexes on gold
 - C10 or longer, functionalized end groups
- Can build **multilayer** / complex structures
- Used for creating biosensors
 - Link bioactive molecules into a scaffold
- The first cells on earth formed from **SAMs**

The Self-Assembly Process

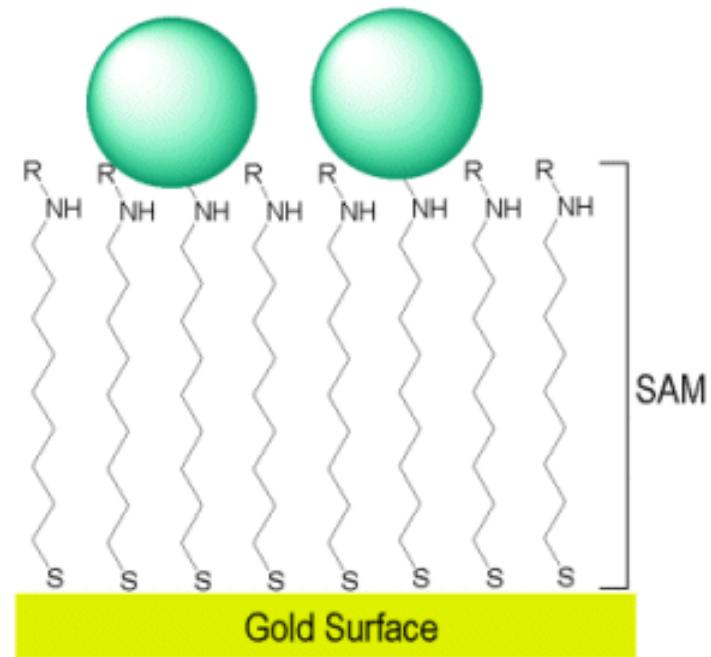


A schematic of SAM (*n*-alkanethiol $\text{CH}_3(\text{CH}_2)_n\text{SH}$ molecules) formation on a Au(111) sample.

The self-assembly process. An *n*-alkane thiol is added to an ethanol solution (0.001 M). A gold (111) surface is immersed in the solution and the self-assembled structure rapidly evolves. A properly assembled monolayer on gold (111) typically exhibits a lattice.

SAM Technology *Platform*

- SAM reagents are used for electrochemical, optical and other detection systems. Self-Assembled Monolayers (SAMs) are unidirectional layers formed on a solid surface by spontaneous organization of molecules.
- Using functionally derivatized C10 monolayer, surfaces can be prepared with active chemistry for binding analytes.



<http://www.dojindo.com/sam/SAM.html>

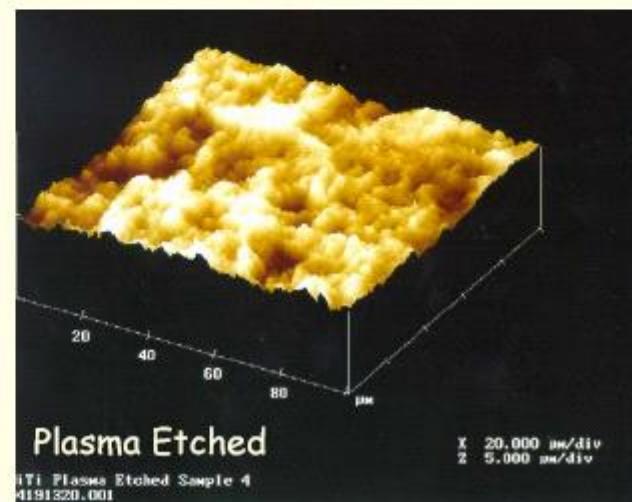
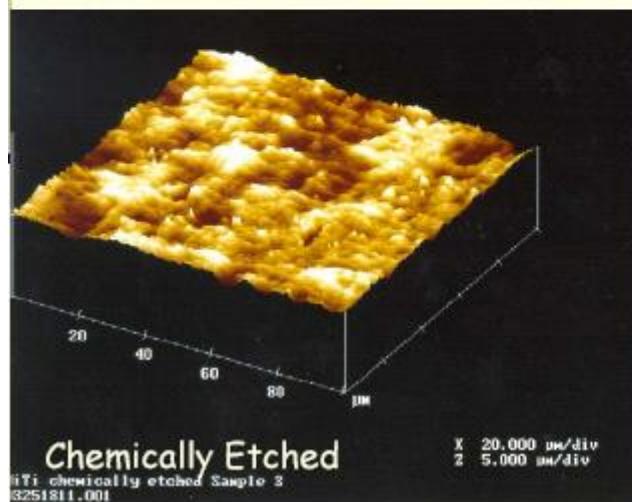
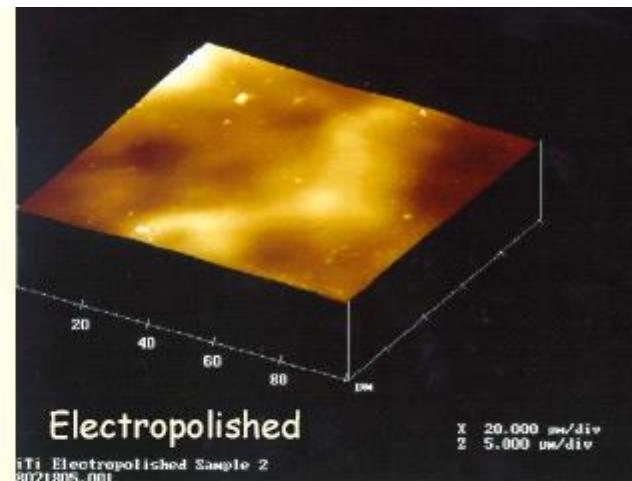
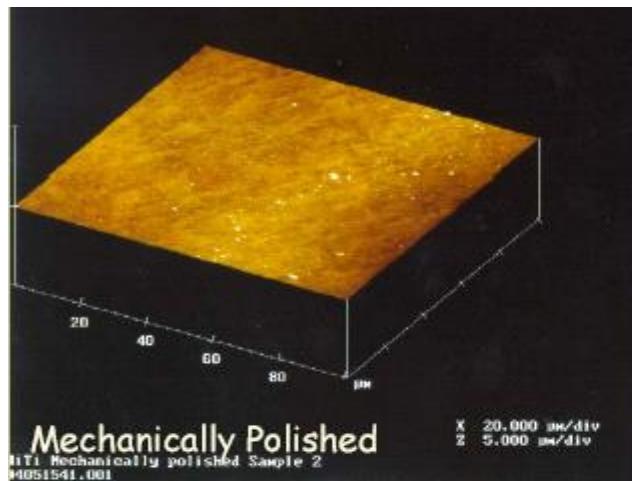
Surface *Contamination*

- ***All surfaces become contaminated!***
- It is a form of '***passivation***'
 - Oxidation of metals
 - Adventitious hydrocarbons
 - Chemisorption of ions
- It can happen very ***rapidly***
- And be ***very difficult to remove***

Surface Treatments

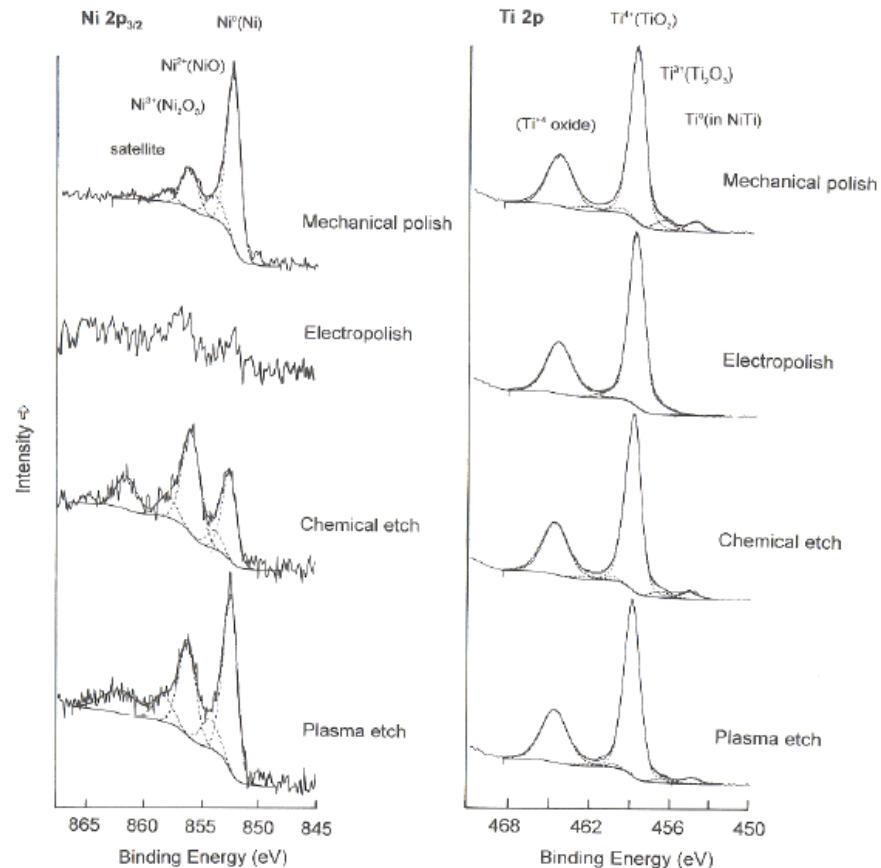
- Control friction, lubrication, and wear
- Improve corrosion resistance (passivation)
- Change physical property, e.g., conductivity, resistivity, and reflection
- Alter dimension (flatten, smooth, etc.)
- Vary appearance, e.g., color and roughness
- Reduce cost (replace bulk material)

Surface Treatment of NiTi



Surface Treatment of NiTi

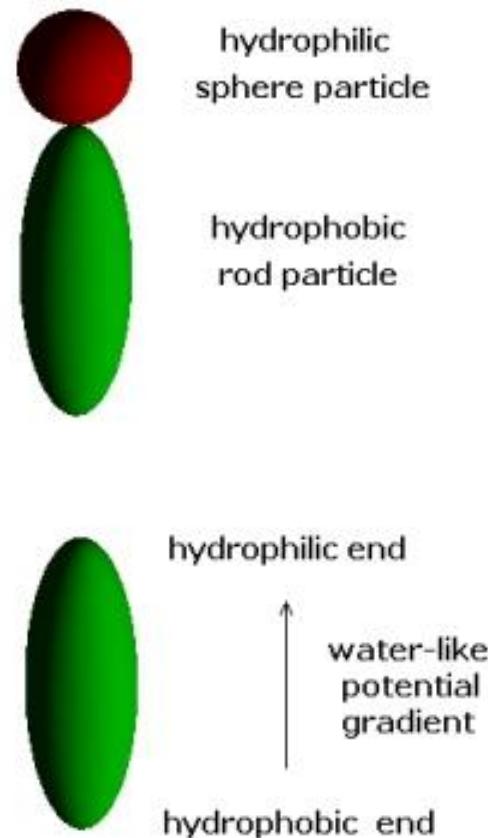
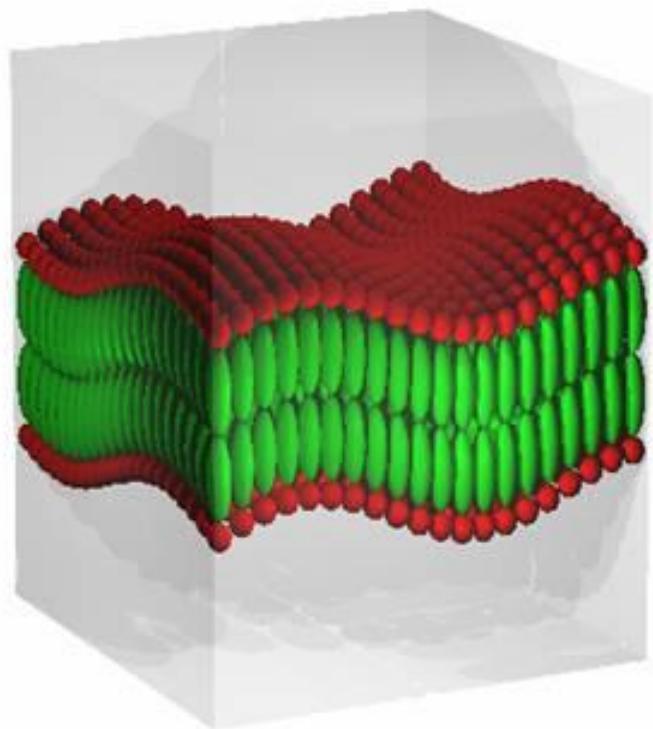
- XPS spectra of the Ni(2p) and Ti(2p) signals from Nitinol undergoing surface treatments show removal of surface Ni from electropolish, and oxidation of Ni from chemical and plasma etch. Mechanical etch enhances surface Ni.



Surfaces in Nature

- Cell membranes
 - Self-assembled phospholipid bilayers
 - Proteins add functionality to the membrane
- Skin (ectoderm)
- Lungs
 - Exchange of O₂, CO₂, and water vapor
- Cell surface recognition (m-proteins)
 - Major histocompatibility complex

Molecular Self Assembly

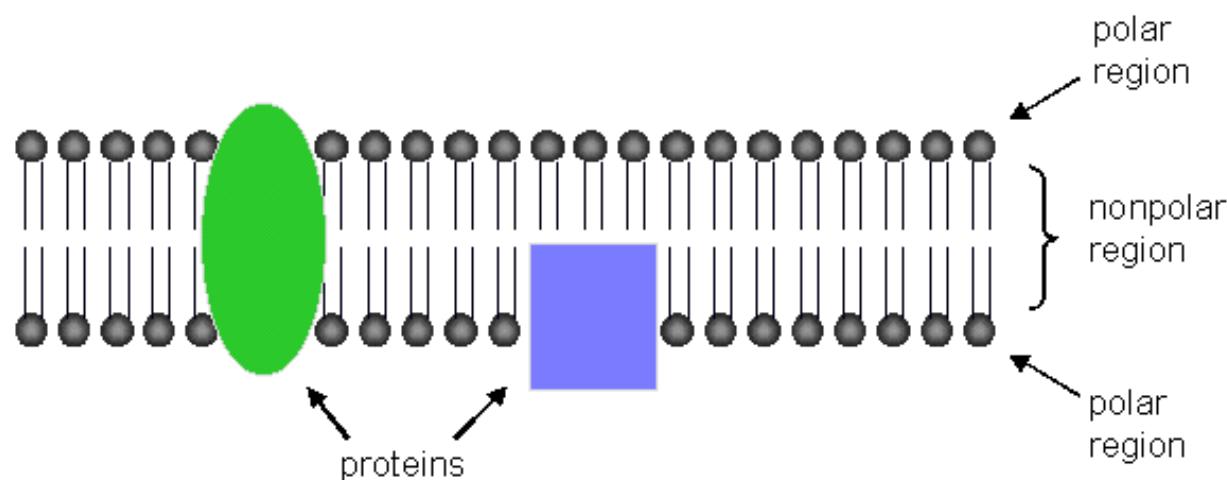
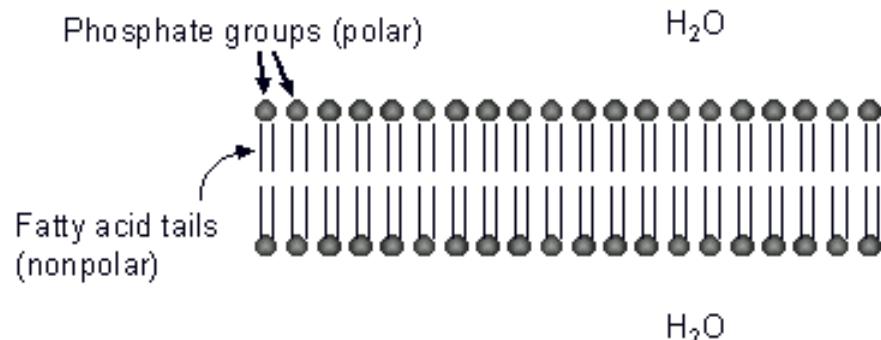
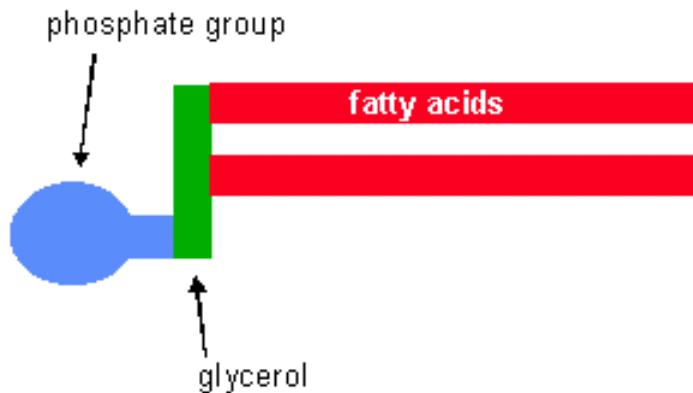


3D diagram of a lipid bilayer membrane - water molecules not represented for clarity

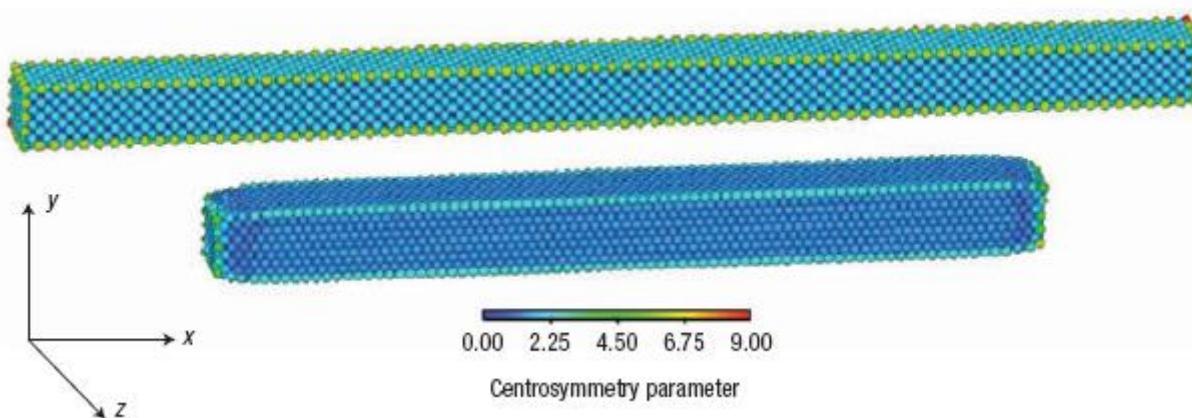
<http://www.shu.ac.uk/schools/research/mri/model/micelles/micelles.htm>

Different lipid model
-top : multi-particles lipid molecule
-bottom: single-particle lipid molecule

Cell Membranes



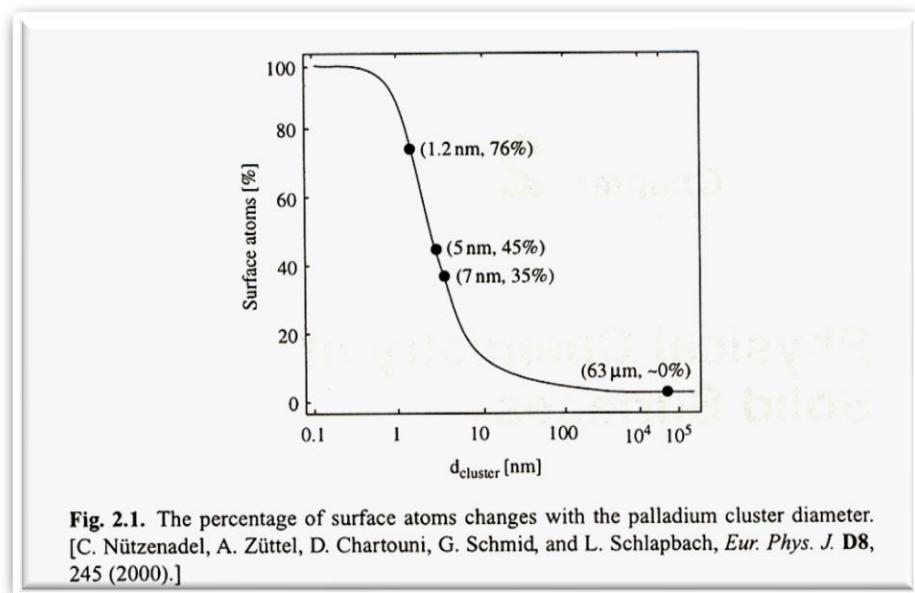
Physical chemistry of solid surfaces



Surface

- Nanostructures and nanomaterials possess a large fraction of surface atoms per unit volume.
 - For a cube of iron of 1 cm^3 the % of surface atoms would be only $10^{-5}\%$.
 - For a cube of iron of 1000 nm^3 the surface atoms would increase to 10%.

This explain why changes in the size range of nanometers are expected to lead to great changes in the physical and chemical properties of the materials.



The total surface energy increases with the overall surface area

Table 2.1. Variation of surface energy with particle size.²²

<i>Side</i> (cm)	<i>Total surface area</i> (cm ²)	<i>Total edge</i> (cm)	<i>Surface energy</i> (J/g)	<i>Edge energy</i> (J/g)
0.77	3.6	9.3	7.2×10^{-5}	2.8×10^{-12}
0.1	28	550	5.6×10^{-4}	1.7×10^{-10}
0.01	280	5.5×10^4	5.6×10^{-3}	1.7×10^{-8}
0.001	2.8×10^3	5.5×10^6	5.6×10^{-2}	1.7×10^{-6}
10^{-4} (1 μm)	2.8×10^4	5.5×10^8	0.56	1.7×10^{-4}
10^{-7} (1 nm)	2.8×10^7	5.5×10^{14}	560	170

For 1gr of NaCl

When the particles change from centimeter size to nanometer size, the surface area and the surface energy increases seven orders of magnitude

Important

- All nanostructured materials possess a huge surface energy.
- They are thermodynamically unstable or metastable.
- It is necessary to overcome the surface energy, and to prevent the nanostructures or nanomaterials from growth in size, driven by the reduction of overall surface energy.

Surface energy

- Origin
 - Atoms or molecules on a solid surface possess fewer nearest neighbors or coordination numbers, thus have unsatisfied bonds exposed to the surface.
 - The lattice constants of the entire solid particles show an appreciable reduction.

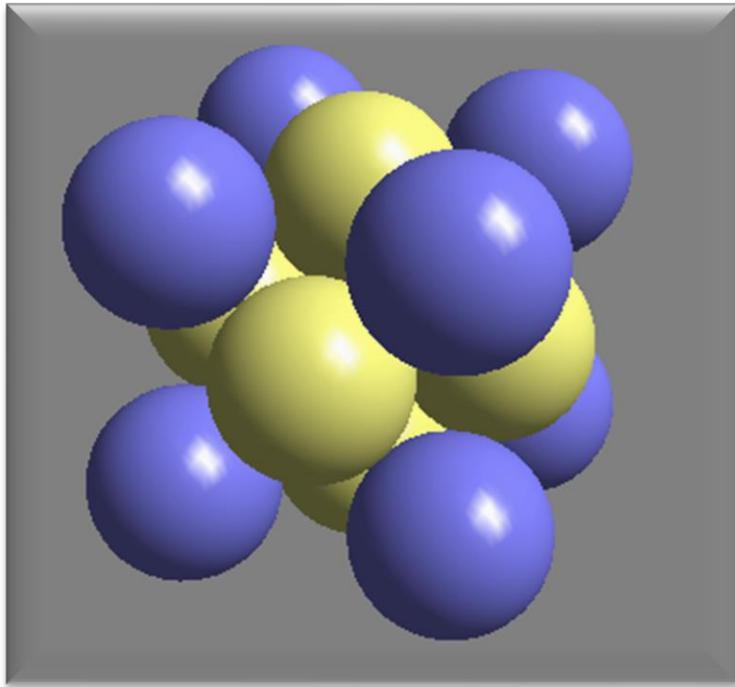
- Definition
 - It is the energy required to create a unit area of “new” surface

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{n_i, T, P} \approx N_b \rho_a \frac{1}{2} \varepsilon$$

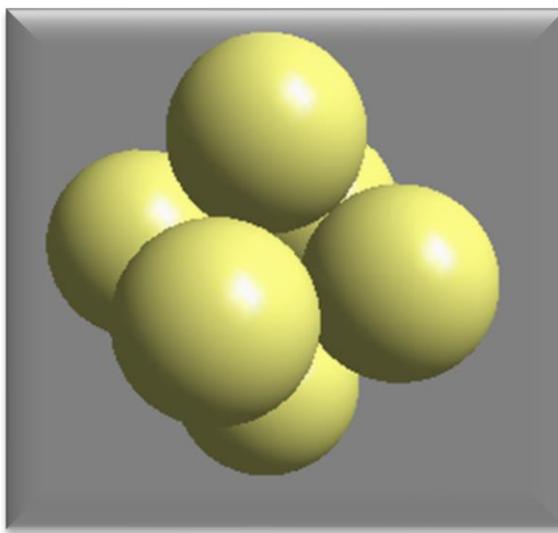
number of broken bonds
 ↓
 Number of atoms/unit area
 ↓
 half of the bond strength

when break into two pieces

When there is an appreciable surface relaxation such as the surface atoms moving inwardly, or there is a surface restructuration, surface energy will be lower than that estimated by this equation.



$$\gamma_{\{100\}} = \frac{1}{2} \frac{2}{a^2} \cdot 4 \cdot \epsilon$$



$$\gamma_{\{100\}} = \frac{4 \cdot \epsilon}{a^2}$$

There is a strong tendency to minimize the total surface energy

- Surface relaxation. The surface atoms or ions shift inwardly which occur more readily in liquid phase than in solid surface due to rigid structure in solids. This would result in a reduction of the surface energy.

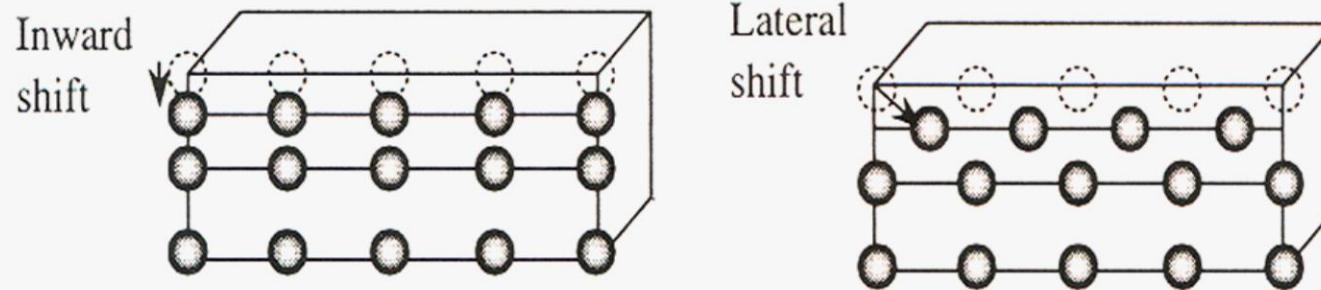
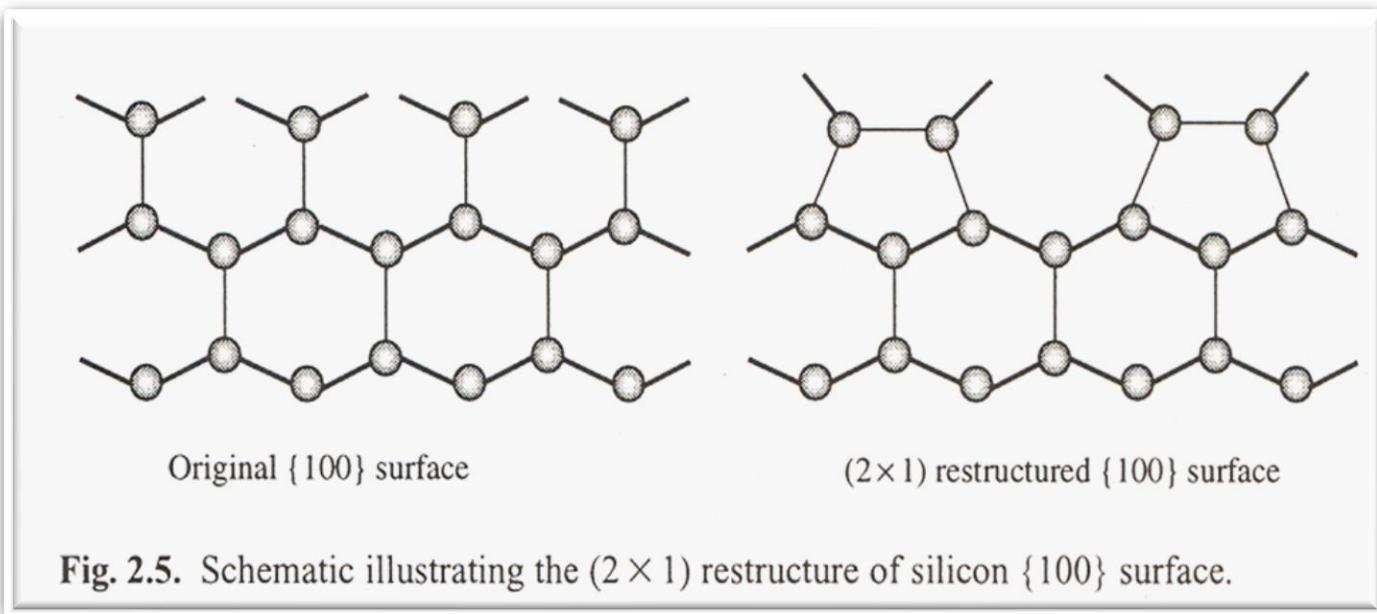


Fig. 2.4. Schematic showing surface atoms shifting either inwardly or laterally so as to reduce the surface energy.

Mechanisms to minimize the total surface energy

- Surface restructuring through combining surface dangling bonds into strained **new chemical bonds**.



- Surface energy of (100) faces in diamond and silicon crystals before restructuring is higher than both (111) and (110) faces.
- However, restructured (100) faces have the lowest surface energy among three low indices faces, and such surface restructuring can have a significant impact on the crystal growth.

Mechanisms to minimize the total surface energy

- Through **chemical or physical adsorption** of terminal chemical species onto the surface by forming chemical bonds or weak attraction forces such as electrostatic or van der Waals forces

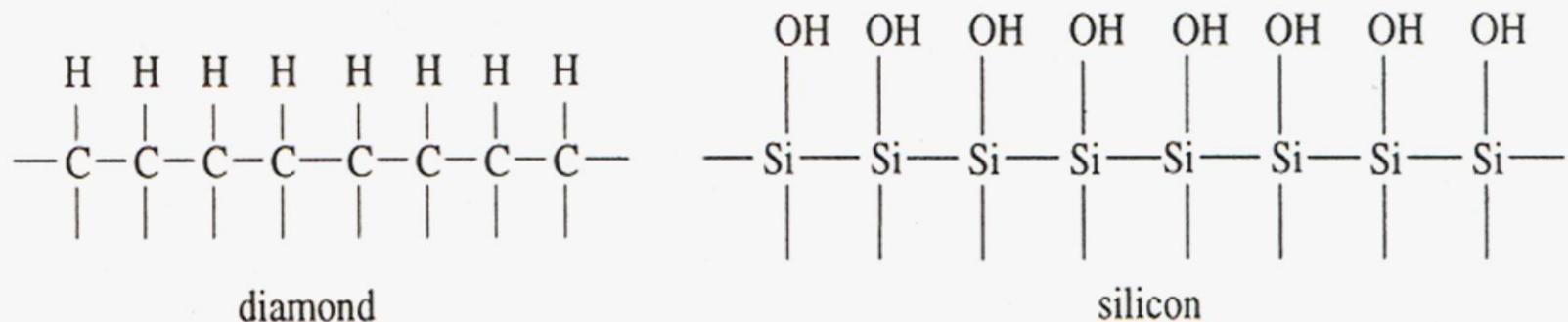


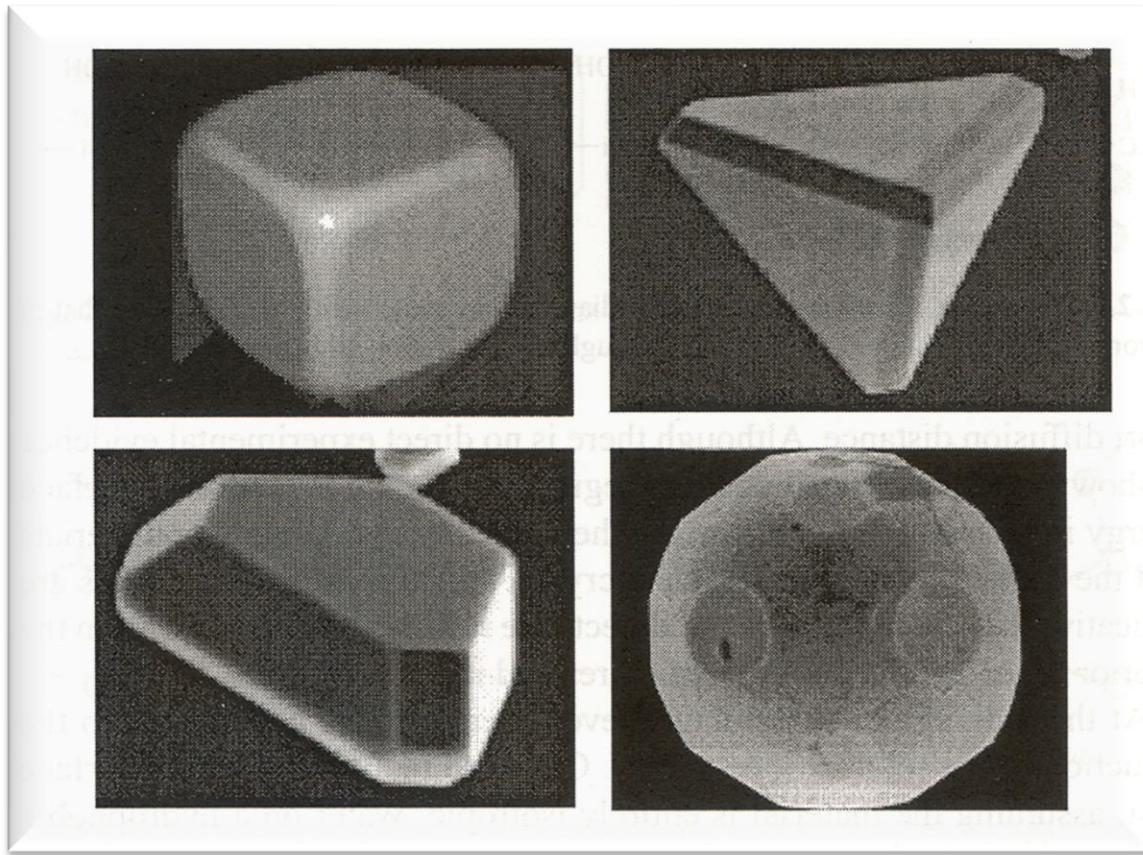
Fig. 2.6. Schematic showing the surface of diamond is covered with hydrogen and that of silicon is covered with hydroxyl groups through chemisorption before restructuring.

Mechanisms to minimize the total surface energy

- Composition **segregation** or enrichment of **impurity** on the **surface** through solid-state diffusion.
- In nanostructures and nanomaterials **phase segregation** may play a significant role in the reduction of surface energy, considering the great impact of surface energy and the **short diffusion distance**.

At the individual nanostructure level, there are two approaches to the reduction of the total surface energy

- Reduce the overall surface.
 - For liquid and amorphous solids, **spherical shape**
 - Water on a hydrophobic surface
 - Hot glass
 - For a crystalline solid different crystals facets possess different surface energy.
 - A crystalline particle normally **forms facets**
 - There is a minimal surface energy when a group of surfaces is **combined in a certain pattern.**



Examples of single crystals with thermodynamic equilibrium shape. (Top-left) Sodium chloride,(top-right) silver, (bottom left) silver, and (bottom-right)gold.

Morphology

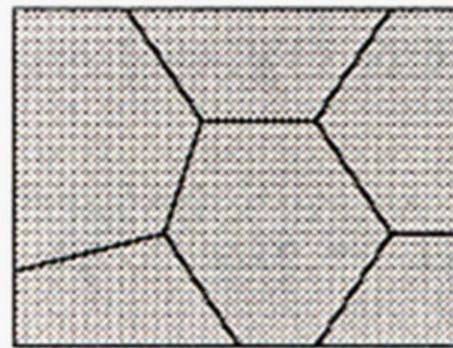
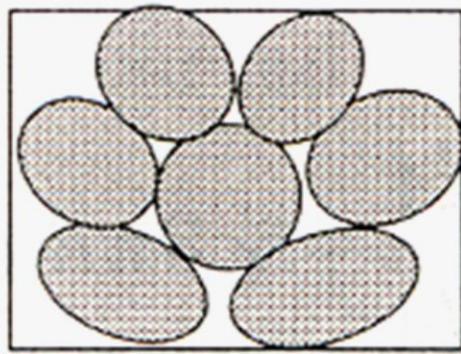
- Kinetic factors, which are dependent on the processing or crystal growth conditions.
- Non equilibrium conditions.
- Below certain temperature the crystal is faceted.
- Most nanoparticles grown by solution methods at elevated temperatures are spherical in shape and do not form any facets.

At the overall system level, mechanisms for

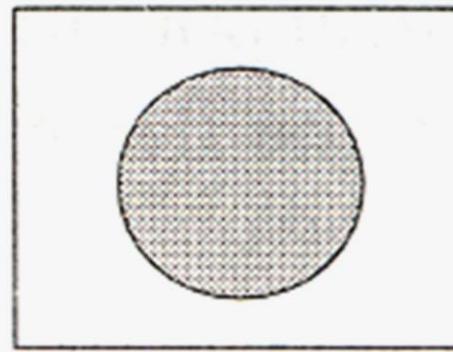
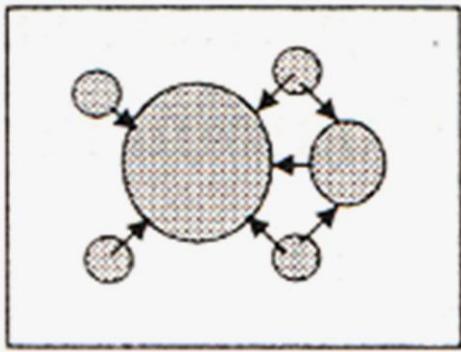
- ~~Combining individual nanostructures together include:~~ reduce the surface
 - Sintering, in which individual structures merge together, $0.7T_m$. (must be avoided)
 - Ostwald ripening, in which relatively large structures grow at the expense of smaller ones.
- Agglomeration of individual nanostructures without altering the individual nanostructures (should be prevented)

Sintering & Ostwald ripening

(a)



(b)



Measuring Surfaces

- AFM – Atomic Force Microscopy (1)
- SEM – Scanning Electron Microscopy (2)
- XPS (ESCA) – X-Ray Photoelectron Spectroscopy (3)
- AES – Auger Electron Spectroscopy (3)
- SSIMS – Static Secondary Ion Mass Spectroscopy (4)
- Laser interferometry/Profilometry (5)

Summary

- Surfaces are ***discontinuities***
- Surface ***area*** creates ***energy***
- Dangling bonds lead to ***passivation***
- ***Interfaces*** are critical to ‘bonding’
- Surfaces can be ***modified / derivatized***
- Surfaces are ***critical to life***
 - ***All important things happen at a surface!***