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MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

AMPHIPHILIC NANOSTRUCTURES

M. Clara Gonçalves

Summary

Summary

• Introduction

•Amphiphilic Molecules

• Case Studies

1. Mayonnaise, Chocolate Mouse
2. Detergent
3. Cell Membrane
4. Origin of Life

•Amphiphilic Molecules

DLVO theory

Phase Diagrams

Nanostructures

•Further Reading

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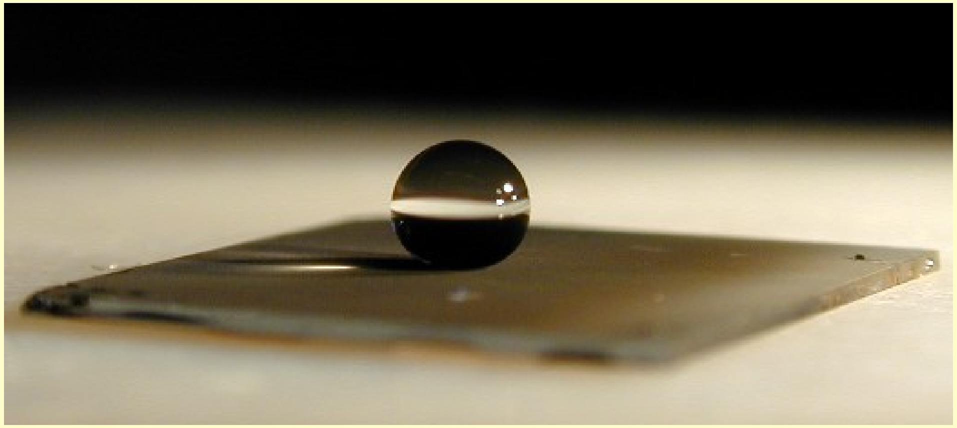
Super Hydrophobic Surfaces,



The combination of an **hydrophobic material** and and **rough surface** can lead to **super hydrophobic** surfaces. A water droplet deposited on such a substrate remains at rest on the tops of the roughness which widely reduces the contact area of the liquid with the solid. The drop is mainly in contact with air and keeps the shape it would have in the air.

Introduction

Bild 8: Seifenblasen 1

Bild 2: Seifenblasen 2

Introduction

Dripping of a jelly liquid,

with Christian Clasen , Gareth McKinley & Vladimir Entov

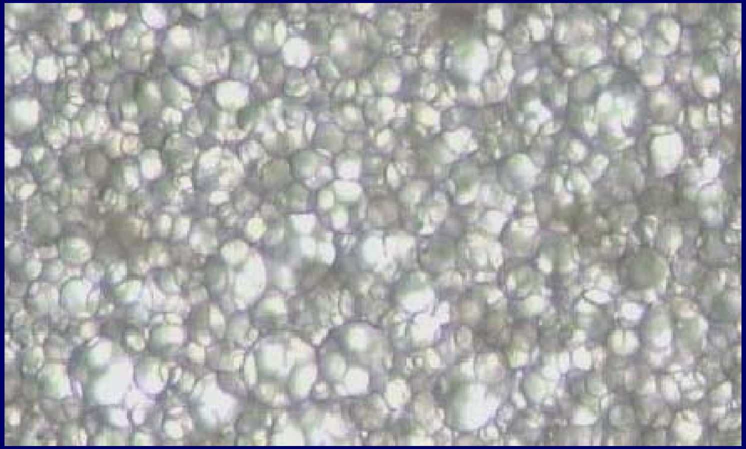
Concentrated **surfactant solutions** eventually exhibit particular molecular structures ("worm like micelles") which lead to a jelly liquid. The material behaves as a soft elastic solid when a light stress is applied but flows as a liquid under higher stresses.

When a droplet of such a liquid drips from a pipette, a long thread connects the droplet to the pipette and progressively **necks** and breaks down when the thread reaches a certain diameter.

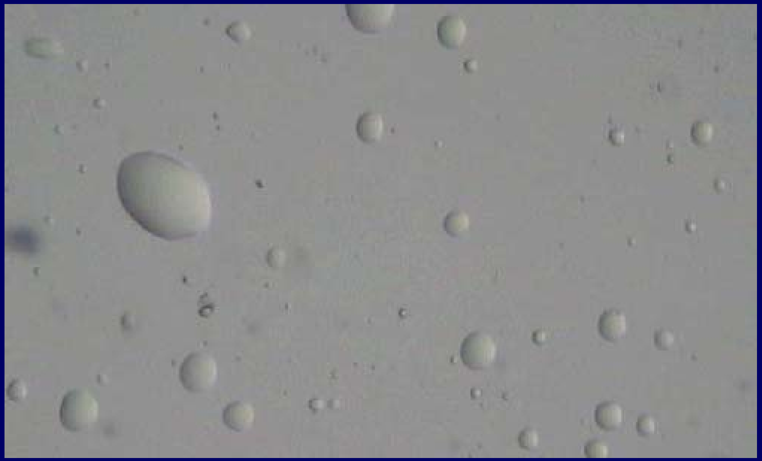
Click on any picture to watch the video (2.2Mo).

Introduction

Mayonnaise
(eggs / cream)

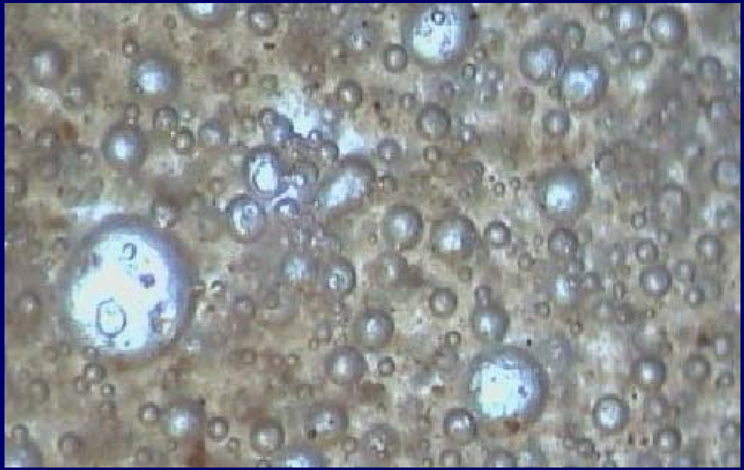


Mayonnaise
(eggs / cream)

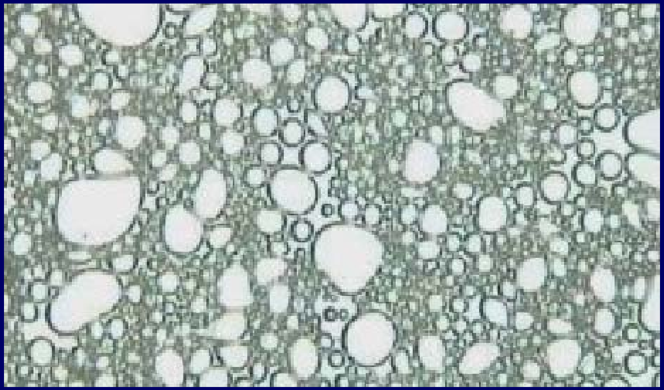


Water / oil

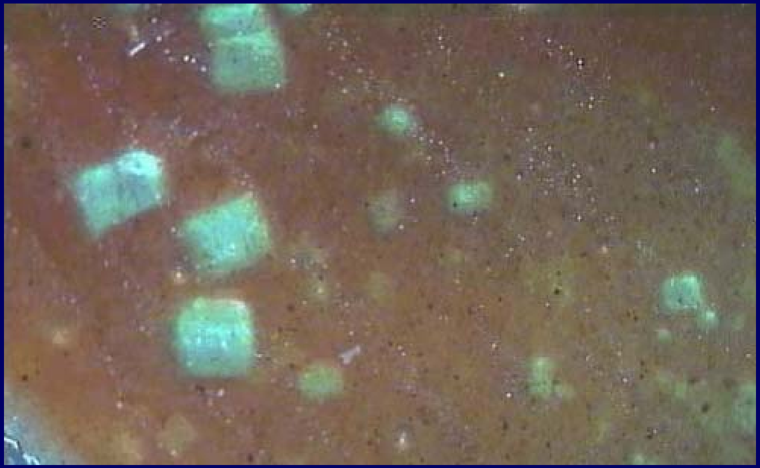
Introduction



Chocolate Mousse
(cacao / cacao butter / eggs / sugar)



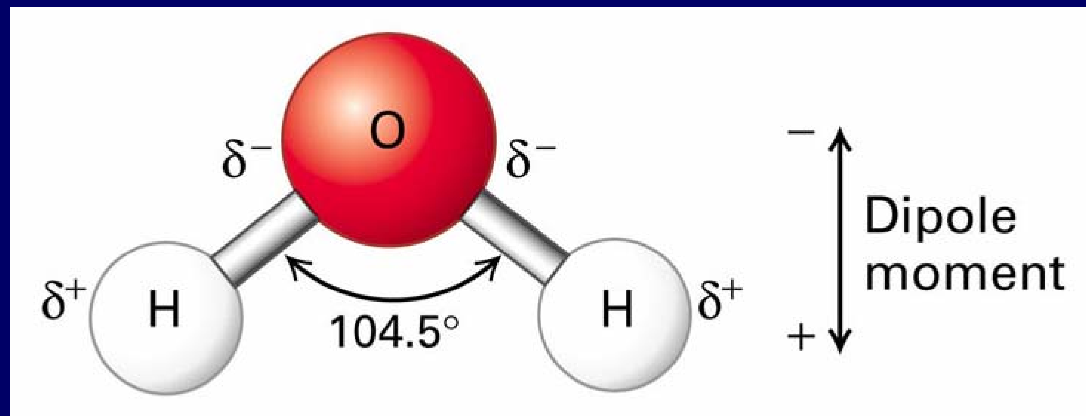
White
(white / air)

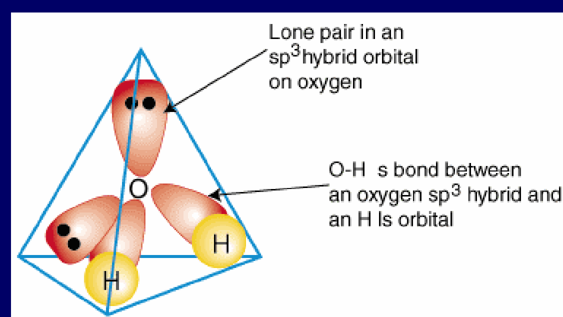


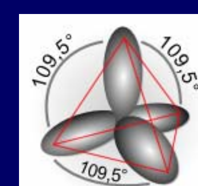
Chocolate Mousse
(cacao / cacao butter / eggs / sugar)

Introduction

• **WATER MOLECULE**







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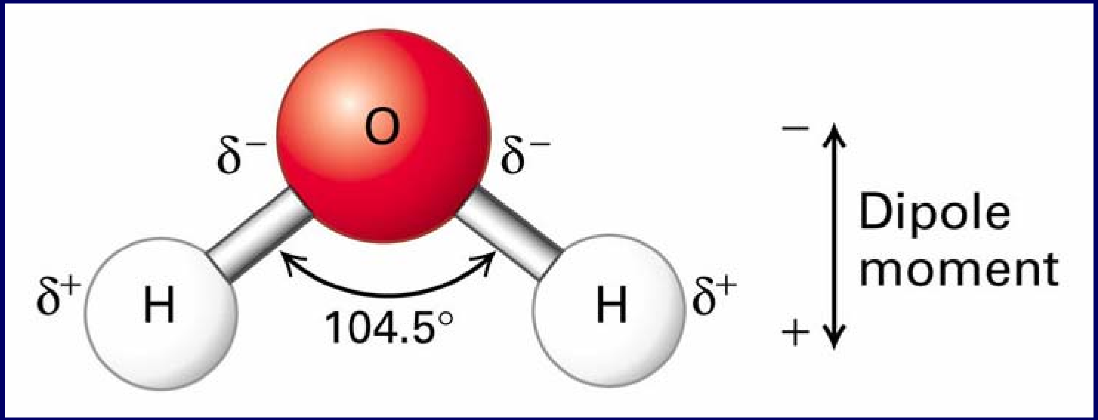
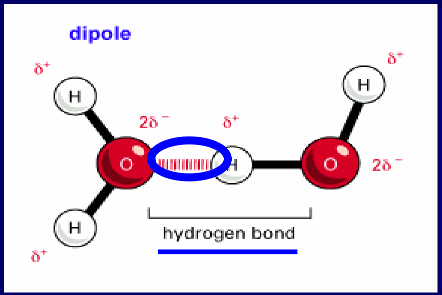
• **WATER MOLECULE**





*My name is **Bond**, **Hydrogen Bond**…*

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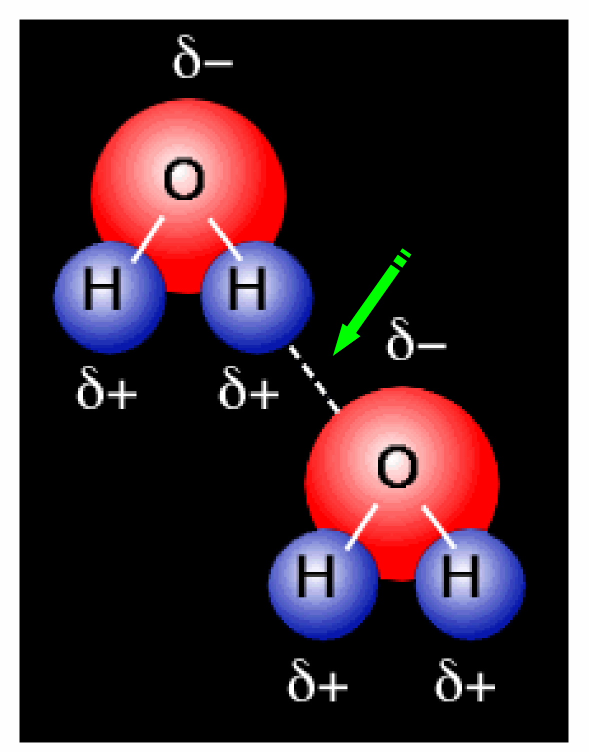
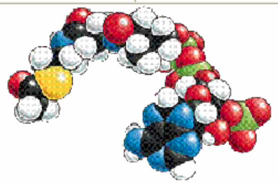
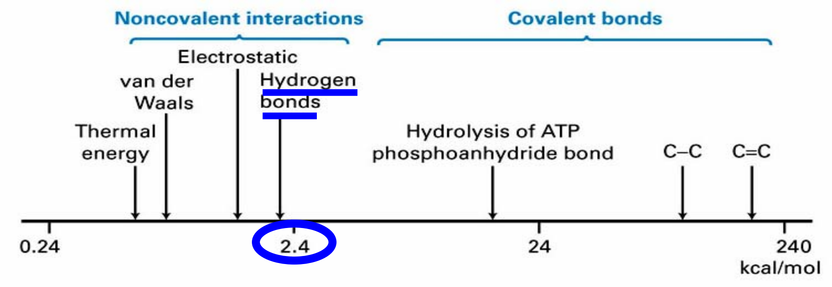
• WATER MOLECULE

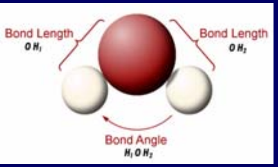


Covalent & Weak Molecular Forces of Life ...

TYPE of BOND	ENERGY (Kc/mol)	TYPE of INTERACTIONS	ENERGY (Kc/mol)
SINGLE COVALENT BONDS		NON-COVALENT BONDS	
O - H	110	IONIC BONDS	1.0 - 5.0
H - H	104	HYDROGEN BONDS	1.0 - 2.0
C - H	99	VANDER WAALS	0.1 - 1.0
C - O	84	HYDROPHOBIC	0.1 - 1.0
C - C	83		
S - H	81		
C - N	70		
C - S	62		
DOUBLE BONDS			
C = O	170		
C = N	147		
C = C	146		







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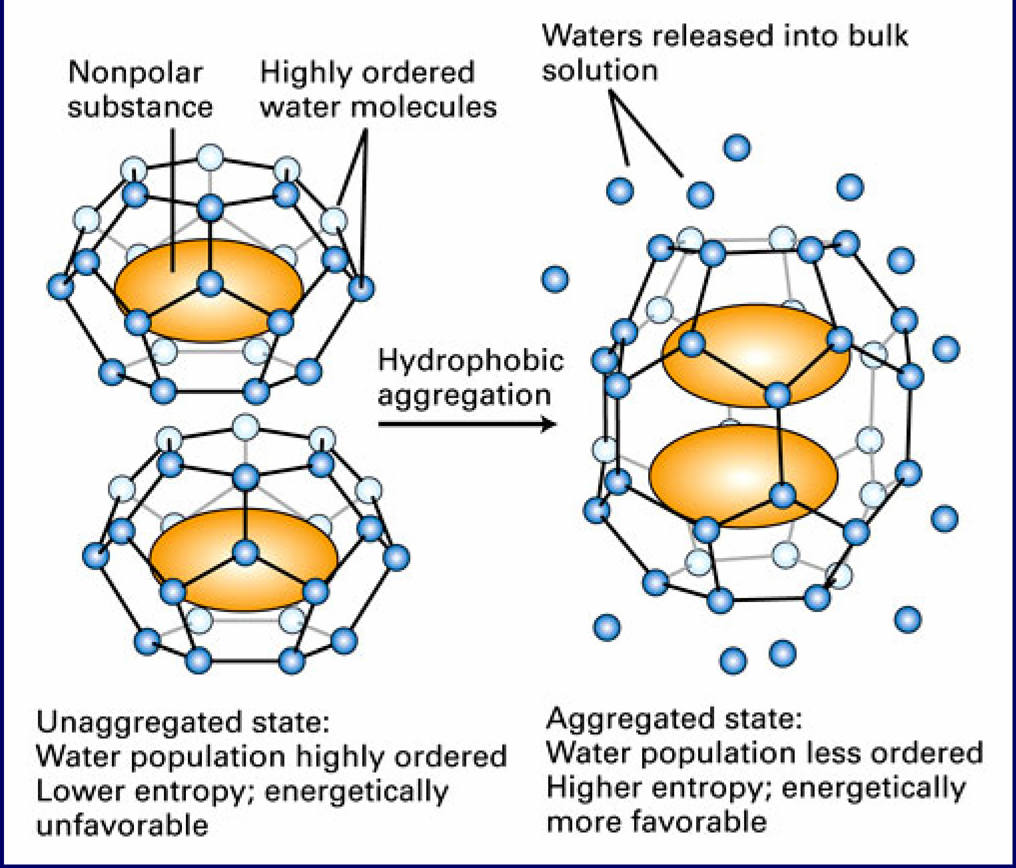
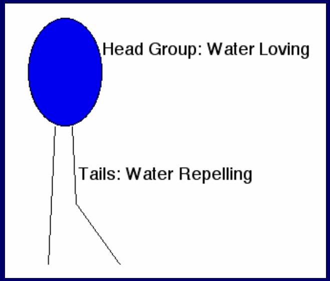
• WATER MOLECULE

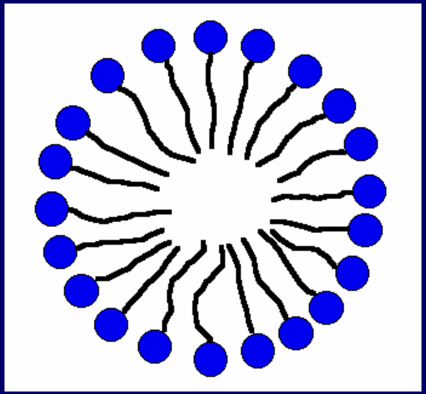


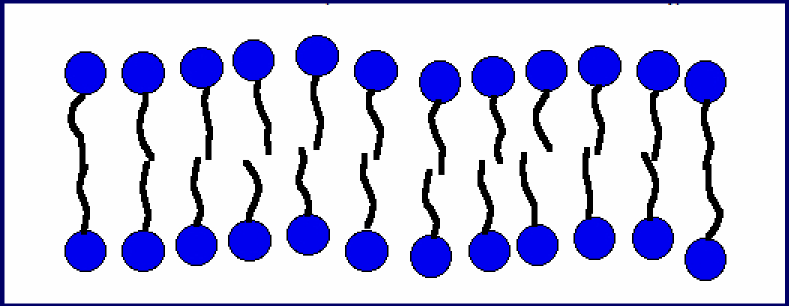
LIQUID ORDERED WATER MOLECULES

Amphiphilic Molecules

- **AMPHIPHILIC MOLECULES**







LIQUID ORDERED AMPHIPHILIC MOLECULES

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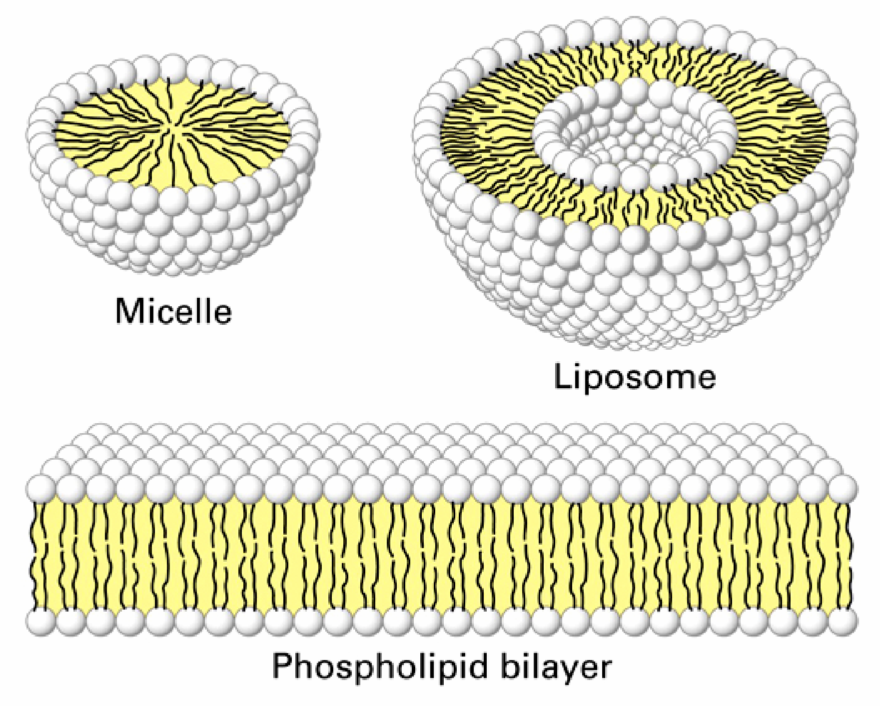
Amphiphilic Molecules

• AMPHIPHILIC MOLECULES



LIQUID ORDERED AMPHIPHILIC MOLECULES

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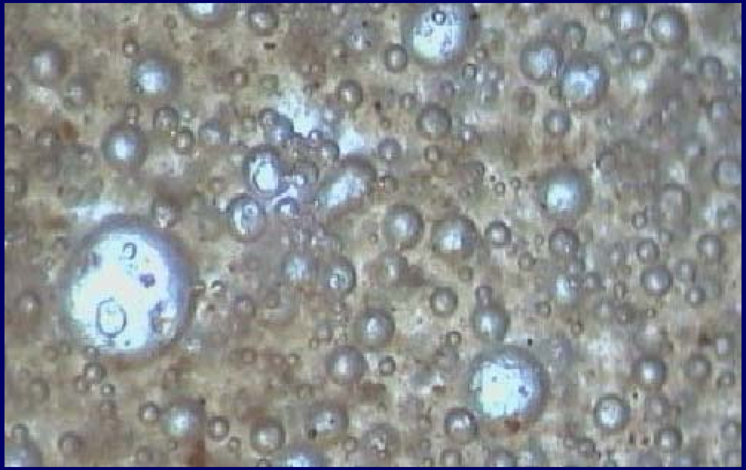
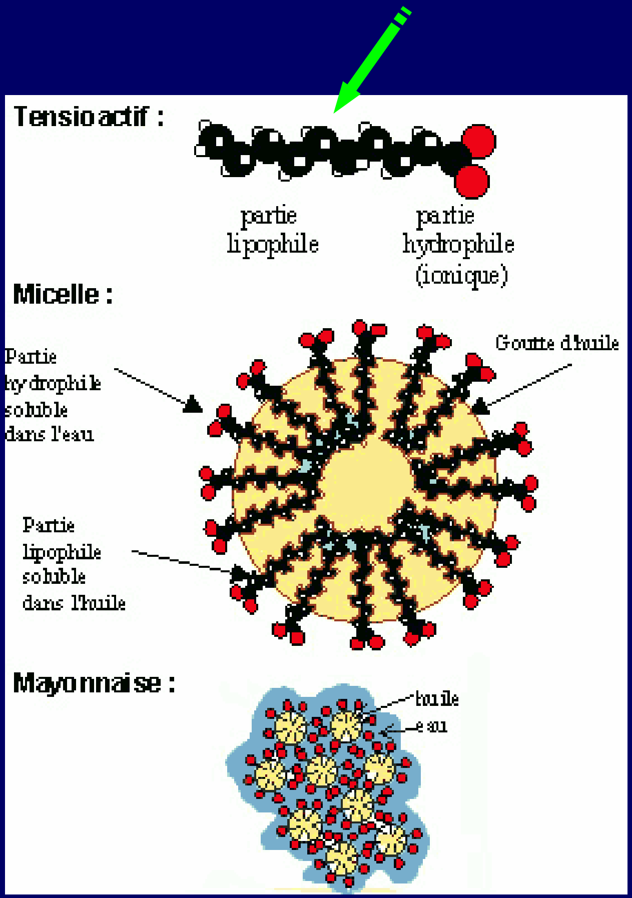
1. MAYONNAISE, CHOCOLATE MOUSSE

Mayonnaise
(eggs / cream)



Mousse Chocolate
(cacao / cacao butter / eggs / sugar)

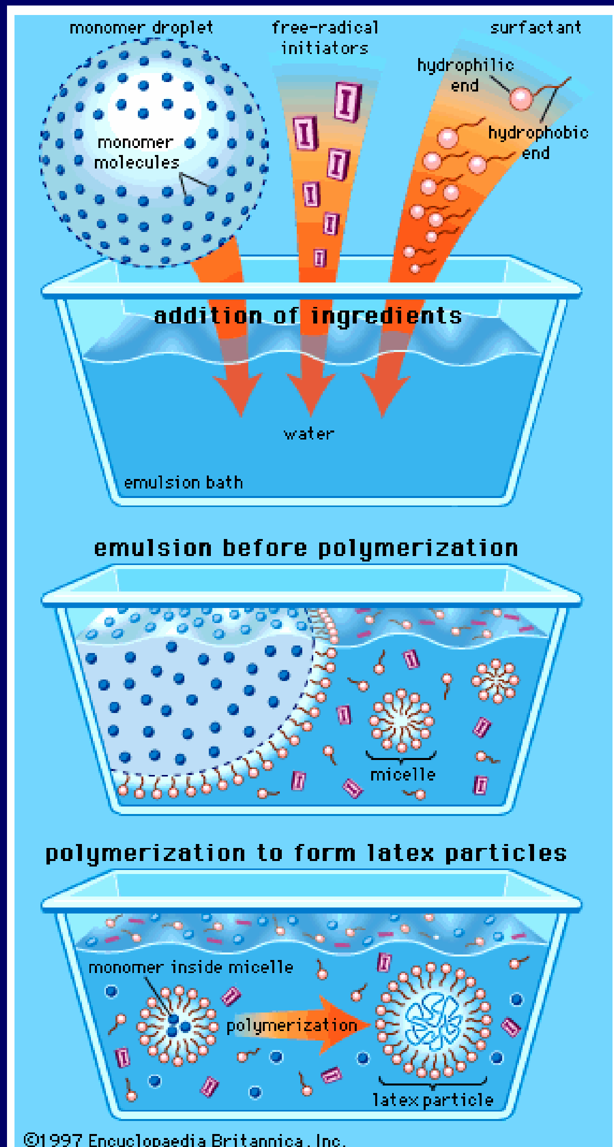
Protein molecules

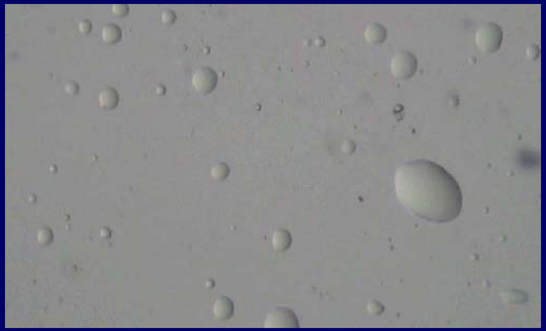


Protein molecules in the interface water / oil

Case Studies

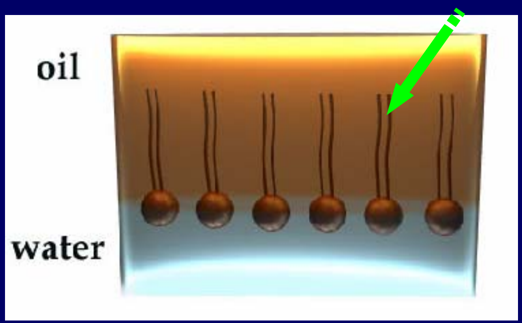
2. DETERGENT





Water / oil

Detergent molecules



Surfactant molecules in the interface water / oil

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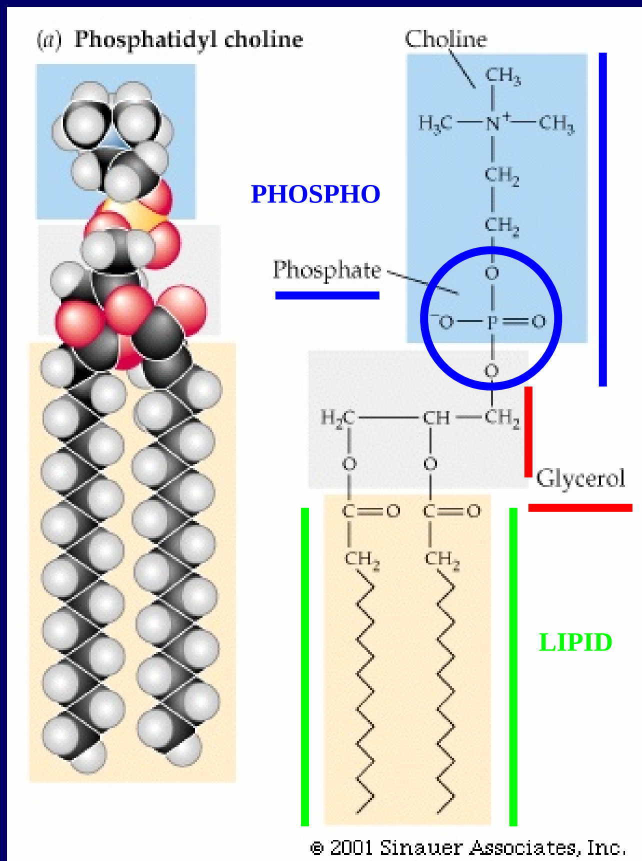
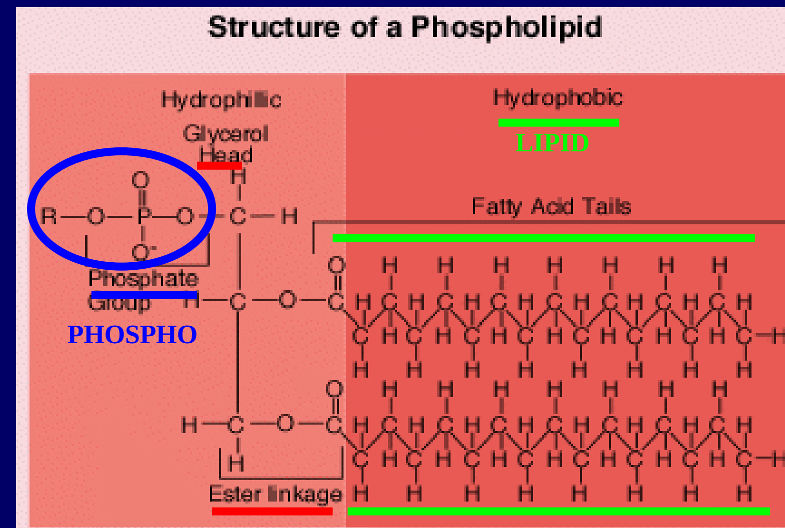
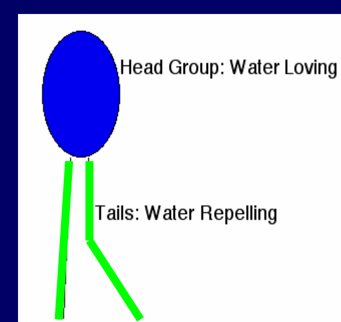
MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

3. CELL MEMBRANE







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3. CELL MEMBRANE

Phospholipids contain only **two fatty acid tails** attached to a **glycerol head**. The **third alcohol group** of the **glycerol** is attached to a **phosphate molecule**. The phosphate group is then attached to other small molecules such as Cl.

The **phosphate group** along with the **glycerol group** make the **head** of the phospholipid **hydrophilic**, whereas the **fatty acid tail** is **hydrophobic**.

Phospholipids are **amphipatic**: water loving and water hating.

When phospholipids are in aqueous solution they will **self-assemble** into **micelles** or **bilayers**, structures that exclude water molecules from the hydrophobic tails while keeping the hydrophilic head in contact with the aqueous solution.

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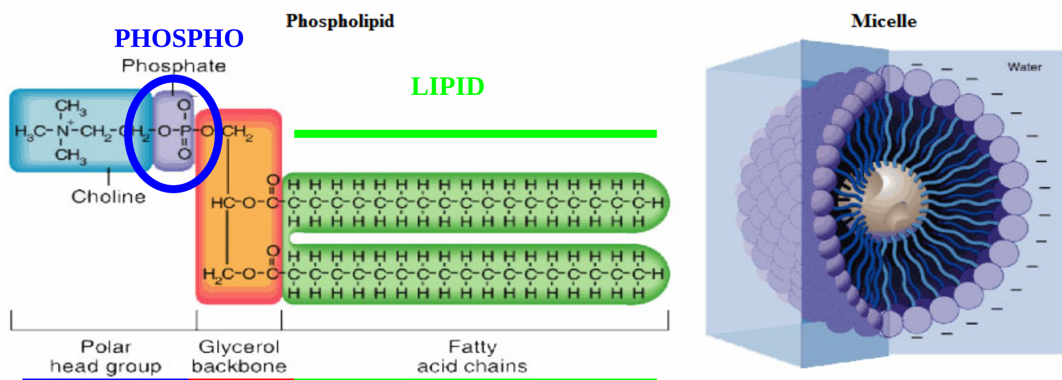
3. CELL MEMBRANE

- **Phospholipids**
  - Phosphate on third -OH group of glycerol
  - Have a polar head
  - Increased hydrophilicity - can form spheroid structures called micelles



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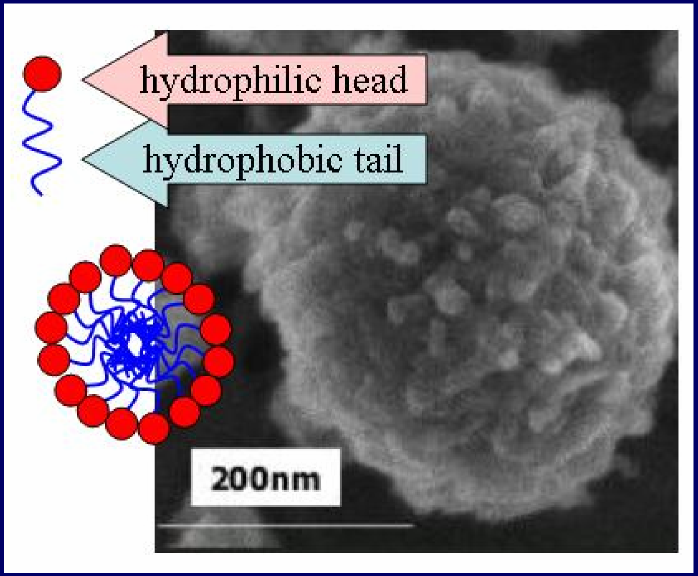
3. CELL MEMBRANE

The common feature of all living cells is a distinct, **lipid-rich barrier**, the **plasma membrane**.

This membrane defines the **boundary** between the **outside** and the **inside** of the cell. The difference between the two is profound. **Outside** is mostly water, with few complex molecules. **Inside** is a concentrated solution of proteins, nucleic acids and smaller molecules – the cytoplasm.

This **bounded system**, or **cell**, has the **properties of life**. **It can reproduce itself by using energy taken from beyond the boundary.**

3. CELL MEMBRANE



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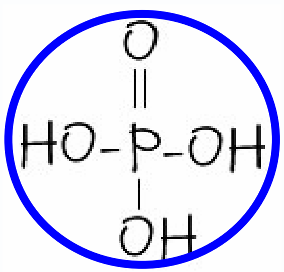
3. CELL MEMBRANE

Building a plasma membrane: The plasma membrane is built on a foundation of lipids. All earthly organisms use lipids built on **glycerol**.

Glycerol has three **hydroxyl** groups.

In the phospholipids, one of these groups is linked to a **phosphate** group.

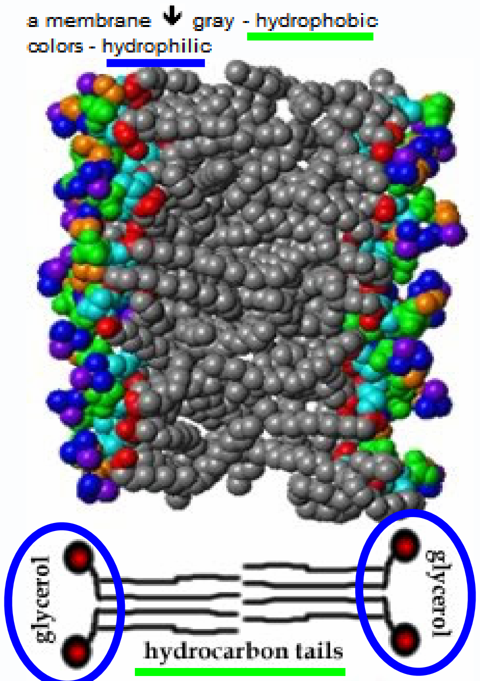


Phosphate is derived from phosphoric acid.

A phosphate group is added to one of glycerol's terminal hydroxyl groups through a condensation reaction.

Phosphoglycerol even hydrophilic than glycerol.

In the bacteria and eukarya, glycerol's two other -OH groups are coupled to **unbranched fatty acid chains** through condensation reactions.



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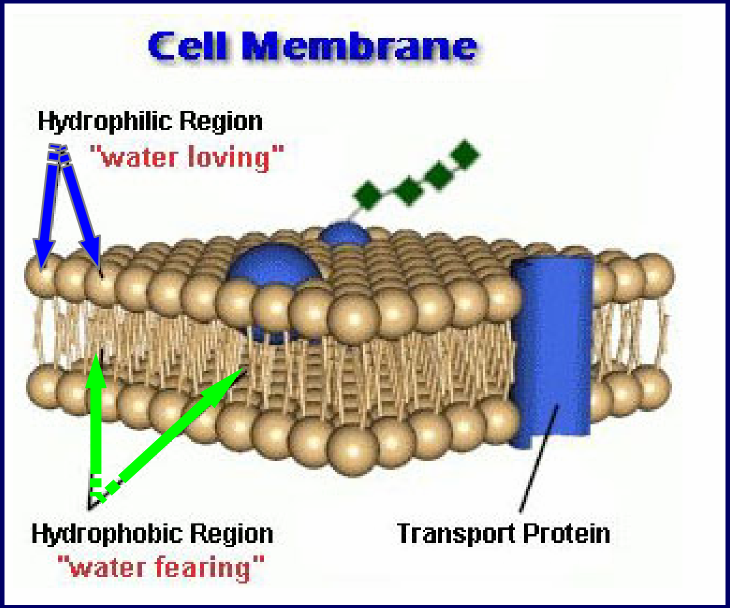
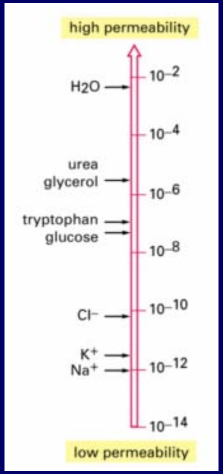
3. CELL MEMBRANE





3. CELL MEMBRANE

Phospholipids serve a major function in the **cells** of all organisms: they form the **phospholipid membranes** that surrounds the cell and intramolecular structures such as mitochondria.

The **cell membrane** is a **fluid**, **semi-permeable bilayer** that separates the cell's contents of from the environment. The membrane is fluid at physiological temperatures and allows cells to change shape due to physical constraints or changing cellular volumes.

The **phospholipid membrane** allows **free diffusion** of some small molecules such as **oxygen**, **carbon dioxide**, and **small hydrocarbons**, but not **water**, **charged ions**, or **other larger molecules** such as **glucose**. This **semi-permeable nature** of the membrane allows **the cell to maintain the composition of the cytosol independent of the external environment.**

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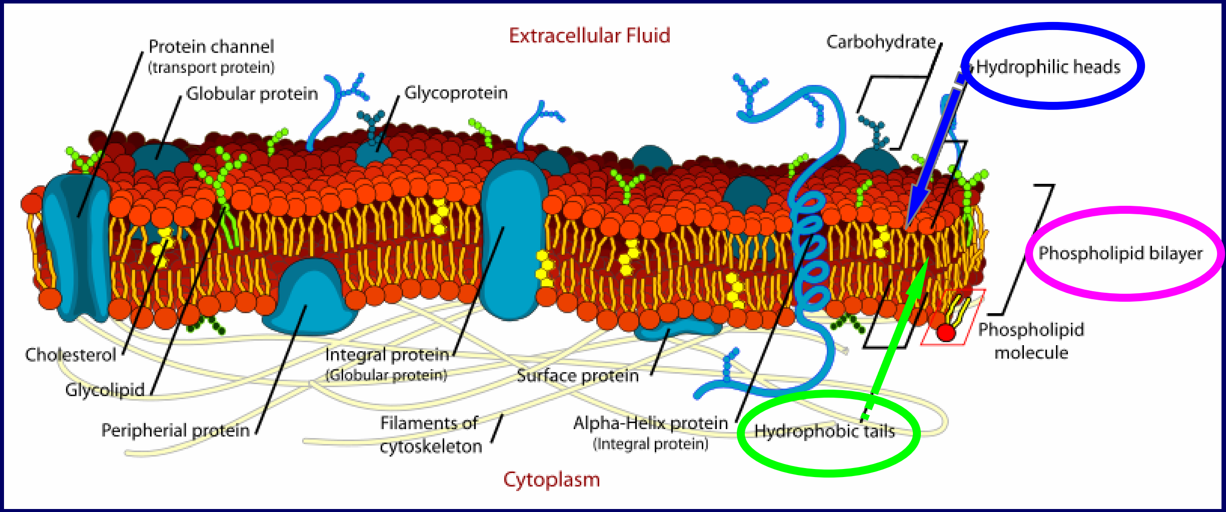
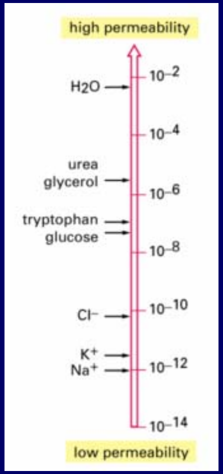
3. CELL MEMBRANE





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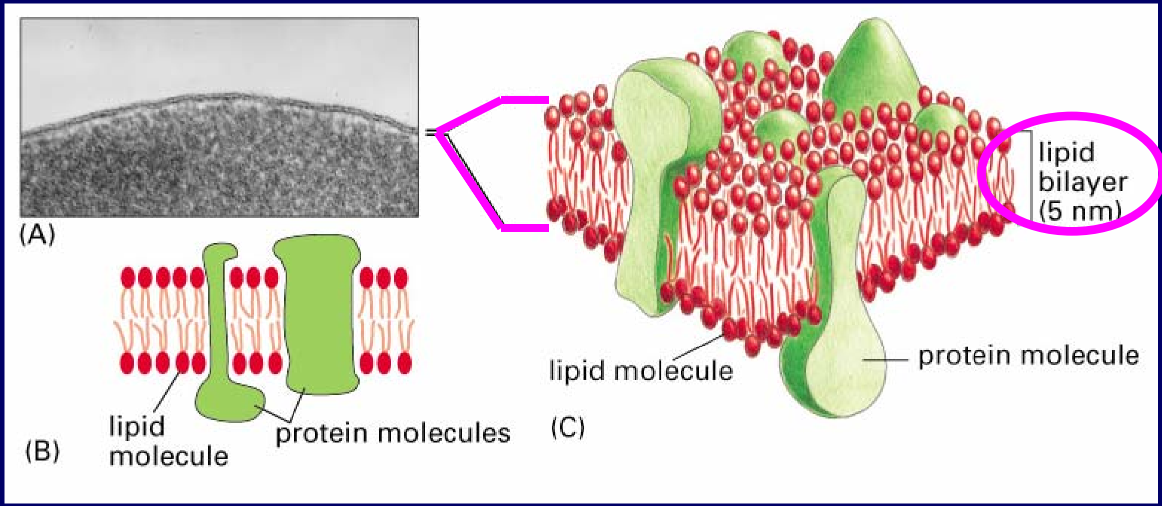
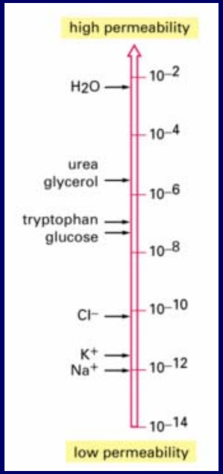
3. CELL MEMBRANE





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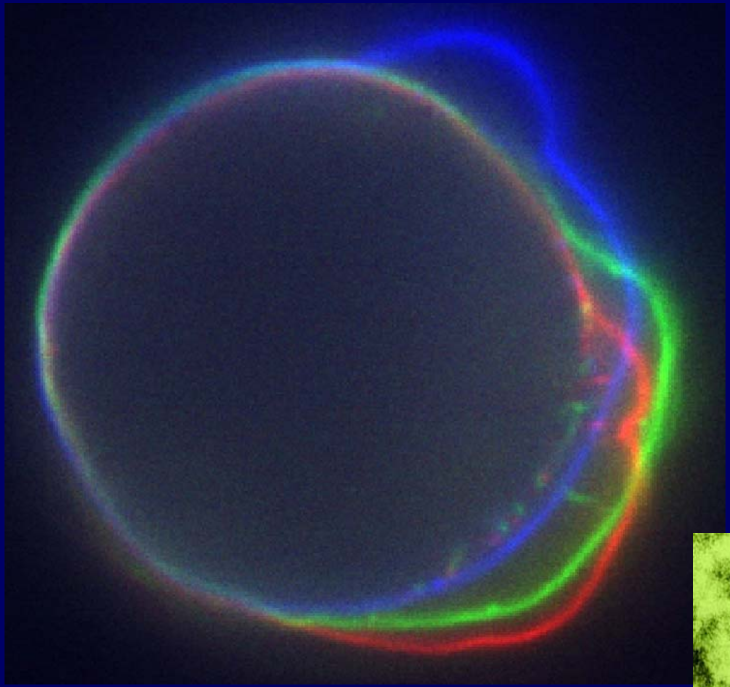
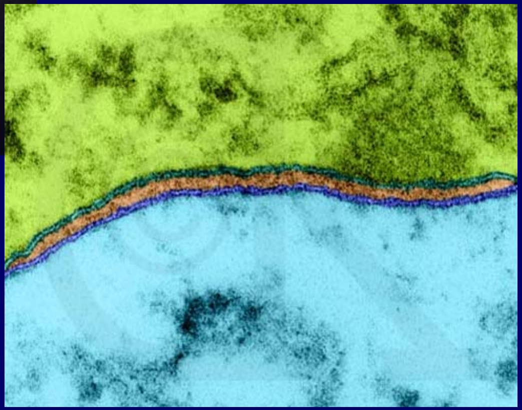
3. CELL MEMBRANE





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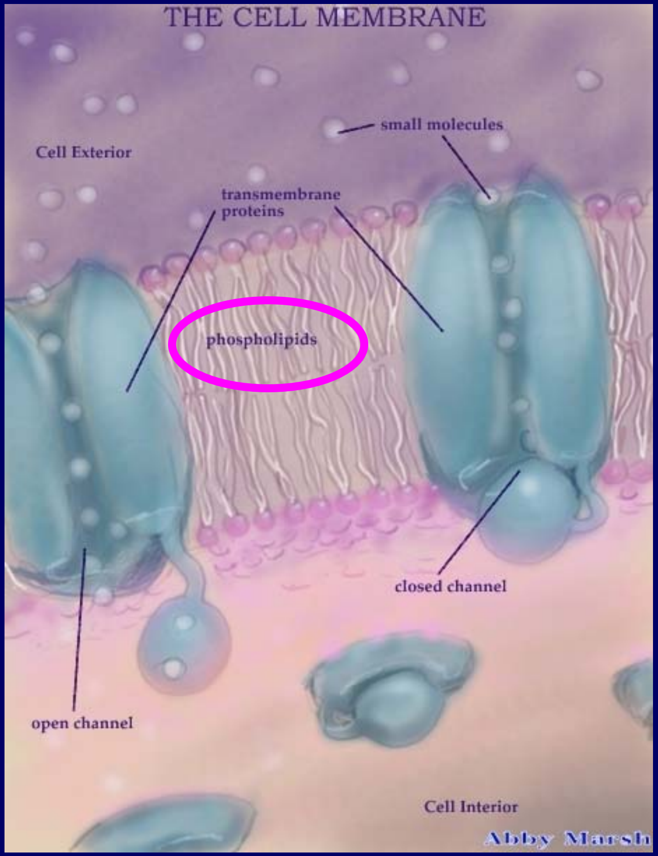
3. CELL MEMBRANE

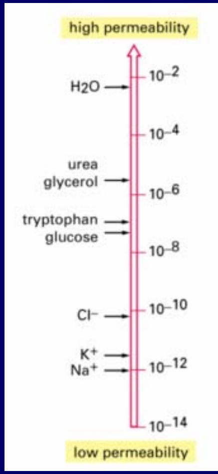
The **cell membrane** must be a **dynamic structure** if the cell is to grow and respond to environmental changes. To keep the **membrane fluid** at **physiological temperatures** the cell alters the composition of the phospholipids. The right **ratio** of **saturated to unsaturated fatty acids** keeps the membrane fluid at any temperature conductive to life.

⇨ For example, winter wheat responds to decreasing temperatures by increasing the amount of unsaturated fatty acids in cell membranes.

⇨ In animal cells cholesterol helps to prevent the packing of fatty acid tails and thus lowers the requirement of unsaturated fatty acids. This helps maintain the fluid nature of the cell membrane without it becoming too liquid at body temperature.

3. CELL MEMBRANE





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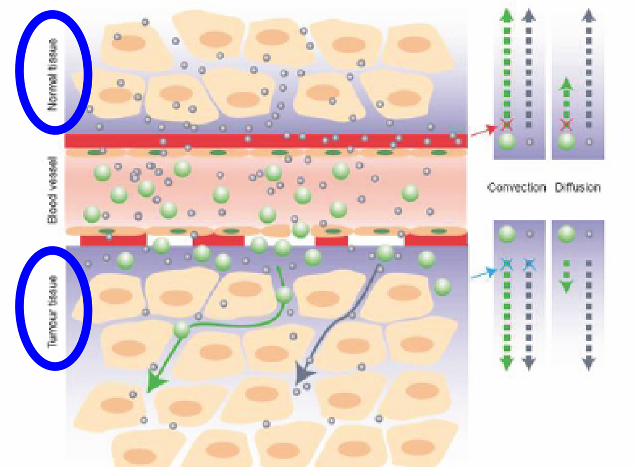
3. CELL MEMBRANE

Identifying Cancer

Cancer cells are malfunctioned cells which reproduce quicker and use more nutrients than normal cells. To keep up with this increased growth, blood vessels for tumors must be made faster than normal. In the process, the blood vessels are not made as well as under normal circumstances, resulting in vessels full of small holes. The micelles utilize their small size to penetrate the holes of tumors rather than relying on traditional absorption through the walls of the vessels.

The resulting effect is if micelles are allowed to circulate in the blood they will flow through the blood until they pass the holes of the vessels and then accumulate inside the tumor. Studies have shown a significant increase in the concentration of the micelles at the site of tumor over traditional drugs.



Enhanced Permeability. Micelles accumulate in higher concentration inside tumors with leaky vessels as opposed to normal vessels.

Teacher

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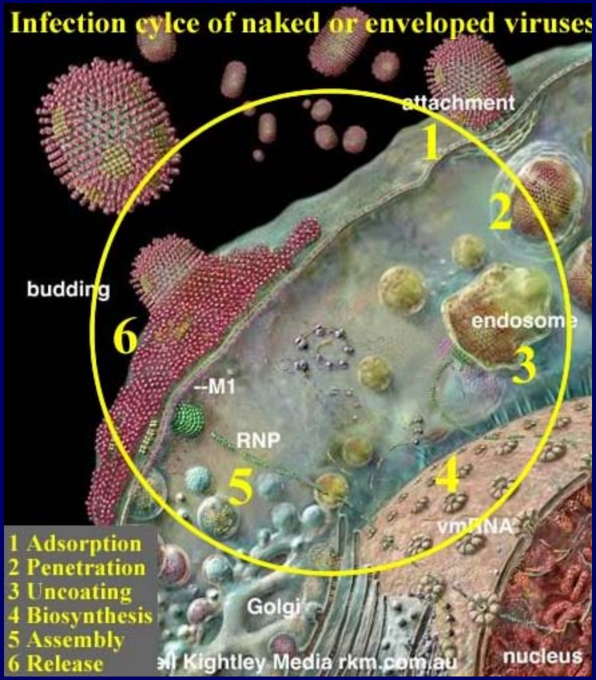
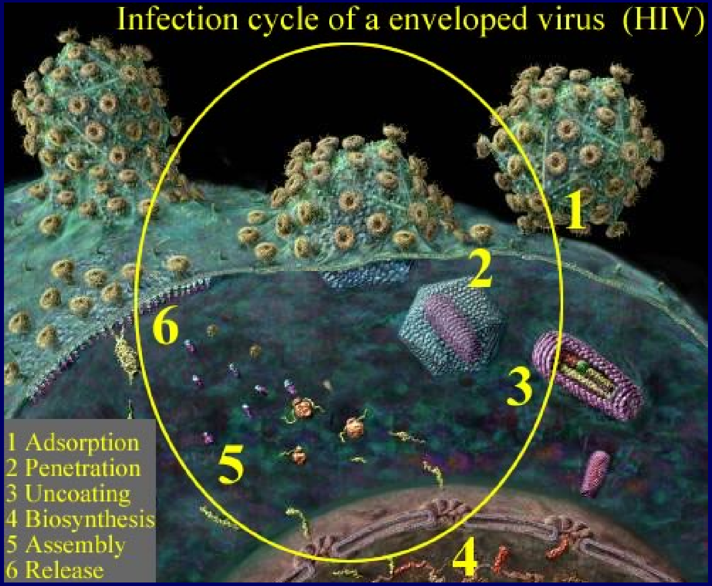
3. CELL MEMBRANE





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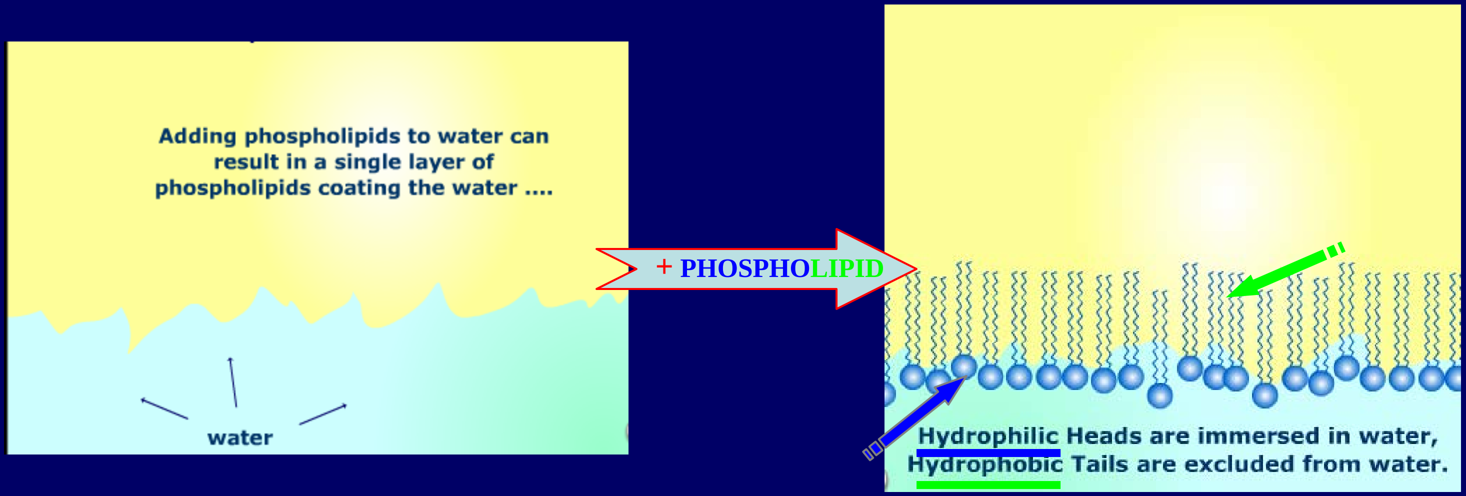
4. ORIGIN OF LIFE



Liposomes are **artificial vesicle membranes**, which form upon hydration of **membranogenic lipids in an aqueous medium**. They are commonly used as model systems, among others, for the study of the physical-chemical attributes of early membrane processes.

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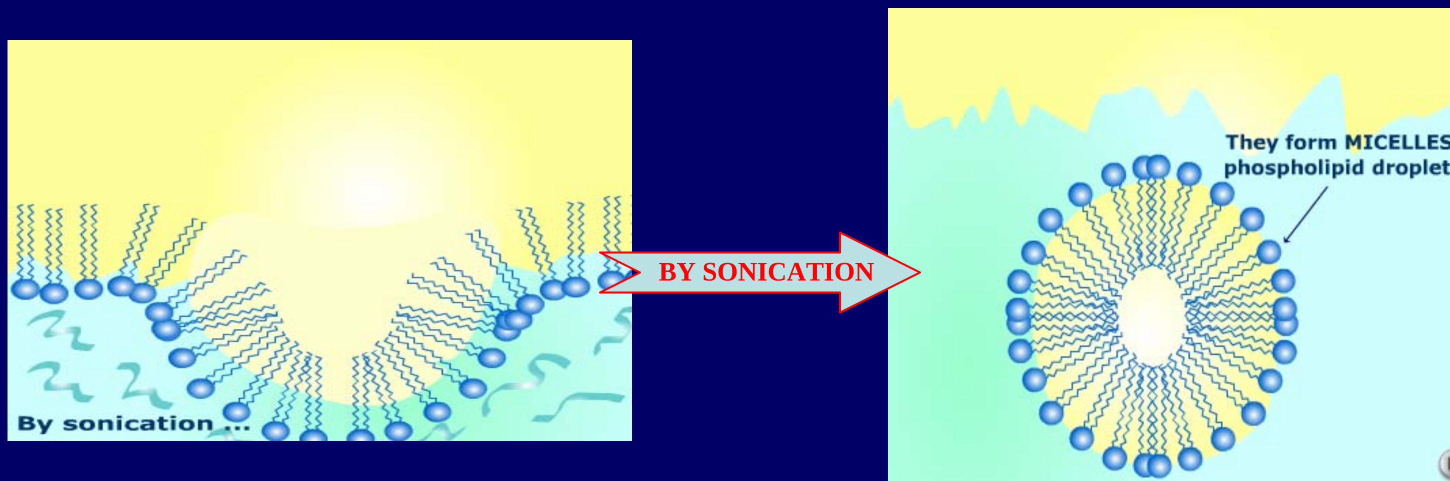
4. ORIGIN OF LIFE



There is good evidence that **membrane vesicles** are the intermediate between prebiotic cells and the first cells capable of growth and division.

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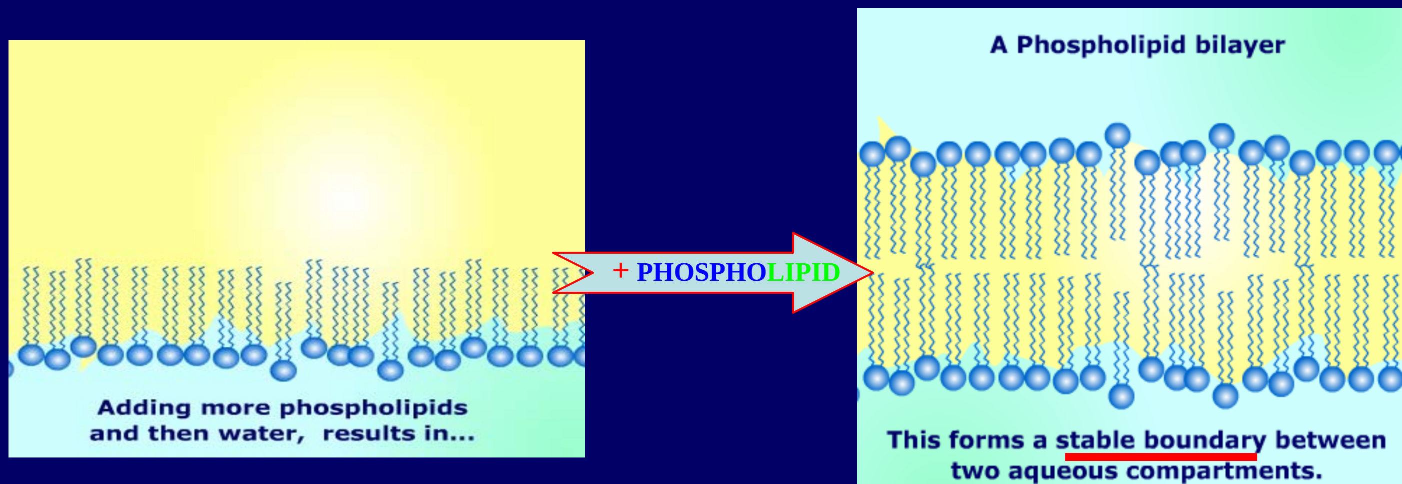
4. ORIGIN OF LIFE

Life emerged through a complex chain of evolutionary events, dictated by the physical-chemical environment on the early Earth.

The **reducing atmosphere**, provided energetic surroundings for the formation of relatively **complex polymers** from organic monomers which were already present on the primitive Earth. Over time, **simple molecules** developed into larger, **more complex biological molecules** and eventually to **cells.** Following further diversification, some cells developed that became metabolically capable of **photosynthesis**.

Assembly of the first cellular life on the prebiotic Earth required the presence of three essential substances: water, a source of free energy and a source of organic compounds.

4. ORIGIN OF LIFE



The **self-aggregation of amphiphilic molecules** would have constituted local high concentrations within the dilute solution of organic compounds.

Held together primarily by **weak non-covalent interactions** driven by hydrophobic forces, the early amphiphilics assemblies would have been **extremely stable over time**.

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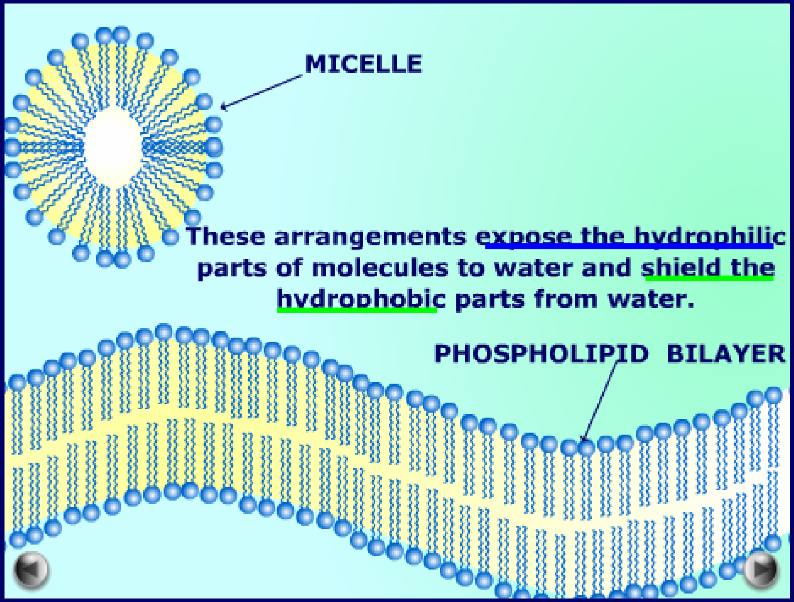
4. ORIGIN OF LIFE

The **earliest forms of life** required **membranes**. **Phospholipids** are the primary components of **modern cell membranes**, but it is improbable that such complex molecules were part of the prebiotic soup. Instead, simpler **membranogenic amphiphilic molecules** probably served as precursors, which then evolved chemically to the varied and complex phospholipid form.

It is speculated that although modern phospholipids were absent, these **amphiphilic molecules** were **abundant** in the prebiotic environment. This components are capable of **spontaneously forming stable membrane vesicles** with defined compositions and organization.

4. ORIGIN OF LIFE



Once formed, **cell membranes** also have the potential to maintain a concentration gradient, providing a source of free energy that can drive transport processes across the membrane boundary.

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4. ORIGIN OF LIFE

When **amphiphilic molecules self-assemble into membranes**, their **vesicular organization** creates an **effective permeability** between interior and the exterior aqueous compartments. The **selective entry** of the early membranes that formed the boundary of primitive cells permitted the **permeation of essential nutrients**.

However, less sophisticated than their modern counterparts, the early membranes would have been impermeable to larger, polymeric molecules, such as the precursors of nucleic acid and protein polymers.

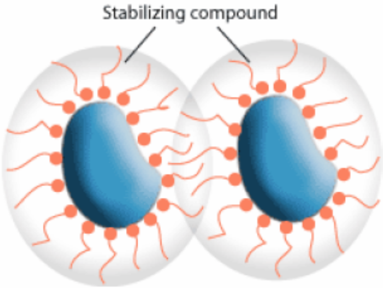
As the composition of the interior compartments became more specific, a population of these bounded molecular systems advanced and increase in metabolic complexity.

The **amphiphilic molecules** on the primitive earth have undeniably undergone considerable evolution as the first forms of life emerged and acquired new catalytic capacities.

Amphiphilic Molecules: DLVO theory

Important factors in colloidal dispersions

- **Brownian motion**
  Constant, random motion of particles due to collisions with the other molecules in the solution. Displacement of particles is given by the Einstein relation.
- **Gravity**
  Density differences between the solute particles and the external phase lead to sedimentation or creaming of the solutes.
- **Steric stabilization (e.g., by polymer grafting)**
  Lyophilic molecules chemically or physically attached to the solute surface prevent aggregation of colloidal particles. Overlap of the stabilizing molecules results in an osmotic pressure in the overlap region and the stabilized solutes are pushed apart.



- **Depletion interactions**
  Depletion of other solutes (intermediate in size with respect the colloidal particles and the solvent molecules) in a region between two colloidal particles results in an (osmotic) pressure difference. The pressure difference in the depletion region and bulk solvent results in an effective attraction between the colloidal particles.
- **Electrostatics**
- **van der Waals interactions**

} **Electrostatic Stabilization — DLVO theory**

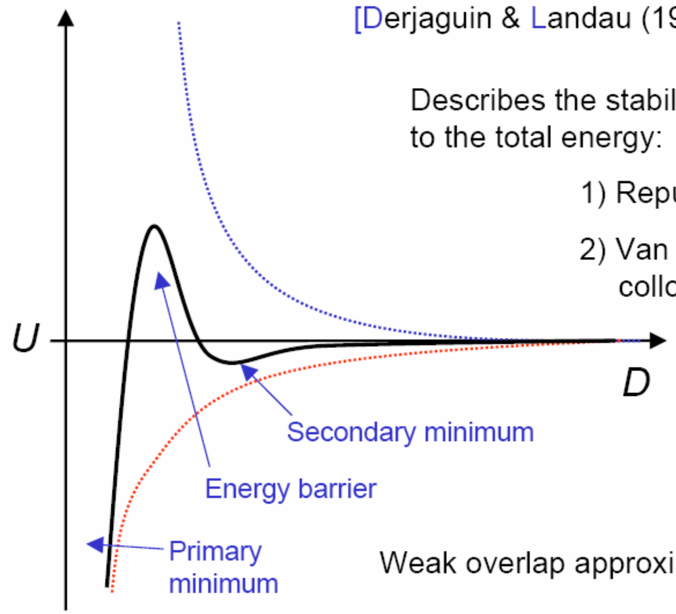
Amphiphilic Molecules: DLVO theory

COLOIDAL STABILITY: DLVO theory

i) ATRACTIVE INTERACTIONS + **ii) REPULSIVE INTERACTIONS**

DLVO theory

[Derjaguin & Landau (1941) / Verwey & Overbeerk (1948)]



Describes the stability of colloids with two contributions to the total energy:

1) Repulsion of the ionic double layers U_R
2) Van der Waals attraction between the colloidal particles U_A

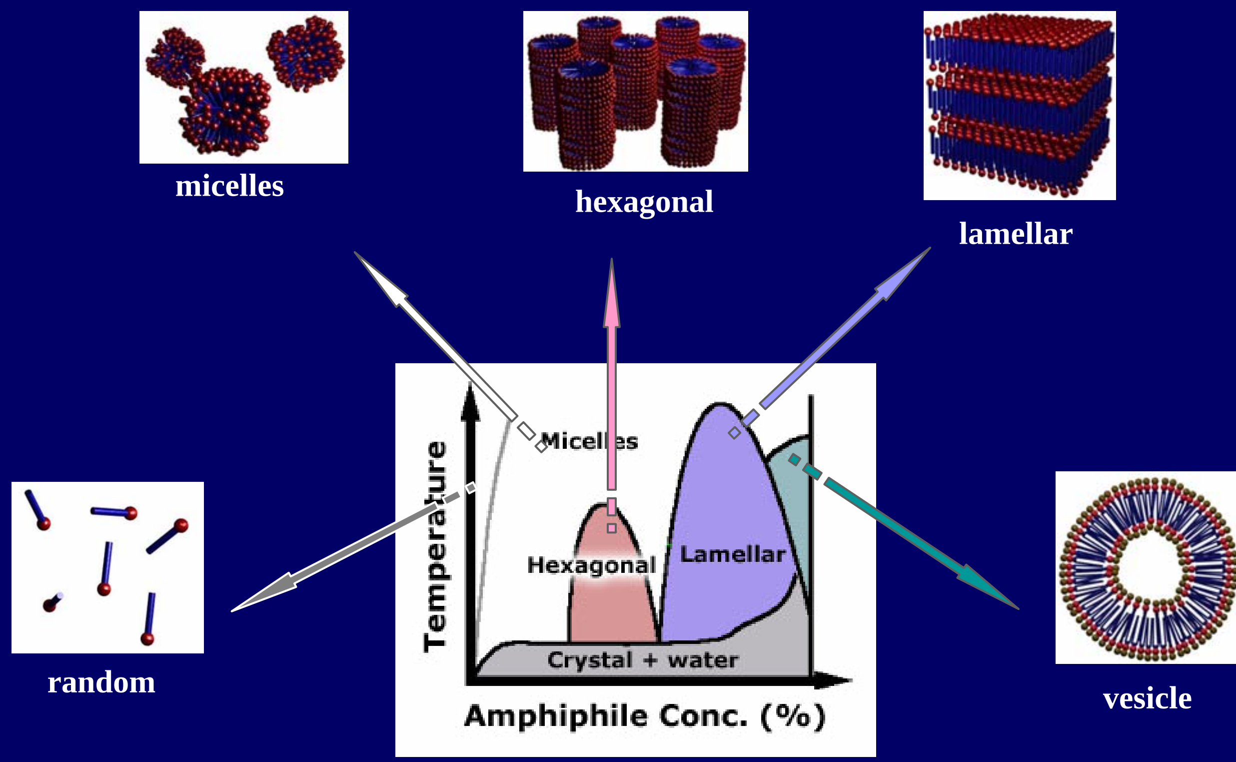
Weak overlap approximation:

$$U_{DLVO} = U_R + U_A = (64\pi k_B T R c_0 \Gamma_0^2/\kappa^2) e^{-\kappa D} - AR/12D$$

[J. Israelachvili, *Intermolecular & Surface Forces* (Academic Press, 1992)]

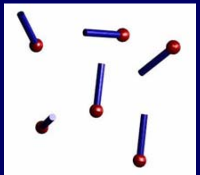
Amphiphilic Molecules: Phase Diagrams

- **AMPHIPHILIC MOLECULE: PHASE DIAGRAMS**



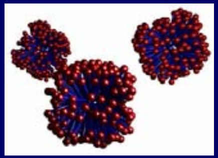
Amphiphilic Molecules: Phase Diagrams

• AMPHIPHILIC MOLECULE: PHASE DIAGRAMS



random

In **dilute solution**, the surfactants **do not form** any particular **structure**. As the concentration is increased, however, the amphiphiles condense into well defined structures.

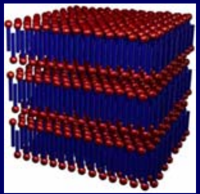


micelles

The most readily formed structure is **micelles**, where the surfactants **hide the hydrophobic tails inside a sphere**, leaving only the water-soluble ionic **heads exposed to solution**.

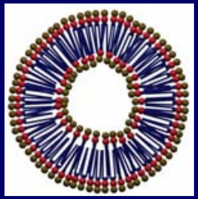
hexagonal

At higher concentrations, surfactants can also form elongated columns that pack into **hexagonal** arrays. The **columns** have **hydrophobic cores** and **hydrophilic surfaces**. The columns are separated from one another by water.



lamellar

At extremely high concentration (neat soap), surfactants crystallize into a **lamellar** structure, with elongated sheets separated by thin water layers. The structure is very reminiscent of the lipid bilayers seen in biological systems.



vesicle

Phospholipids spontaneously form **vesicles** in water, encapsulating a small water droplet in a spherical shell of phospholipid molecules. Both the **inner** and the **outer wall** of the shell are composed of **hydrophilic heads**, whereas the **inside of the vesicle** shell is the **alkane tails.**

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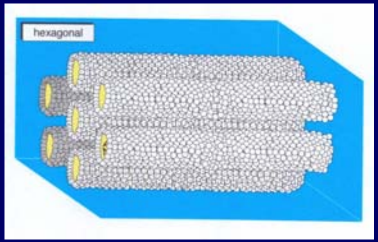
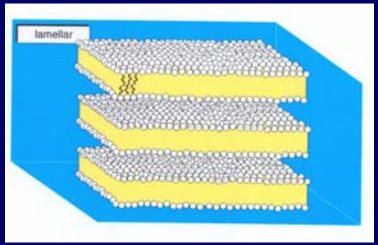
Amphiphilic Molecules: Phase Diagrams

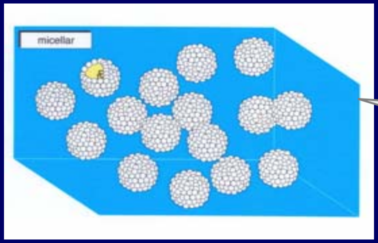
- **AMPHIPHILIC MOLECULE: PHASE DIAGRAMS**



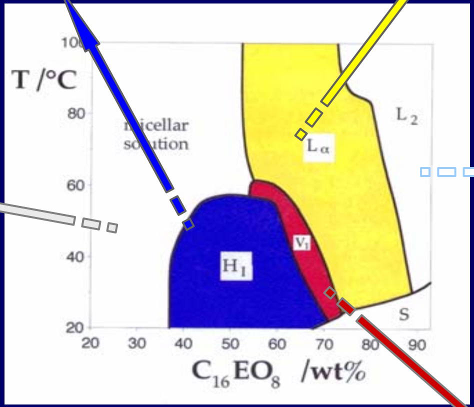
hexagonal

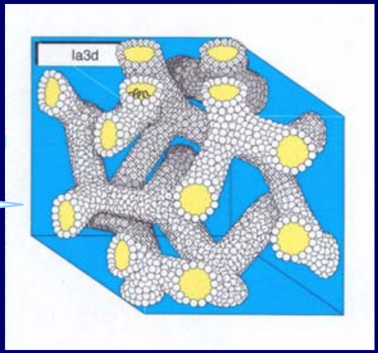


lamellar



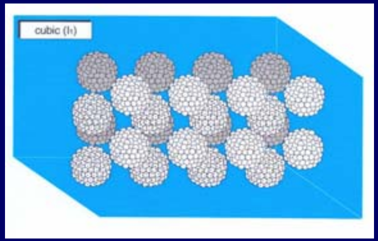
micelles





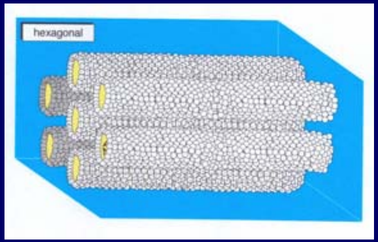
cubic

micelles cubic

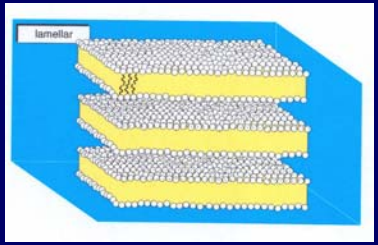


Amphiphilic Molecules: Phase Diagrams

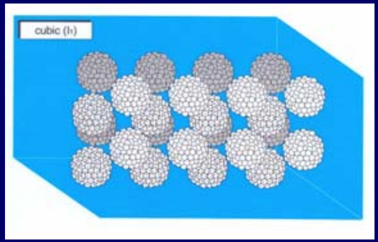
- **AMPHIPHILIC MOLECULE: PHASE DIAGRAMS**



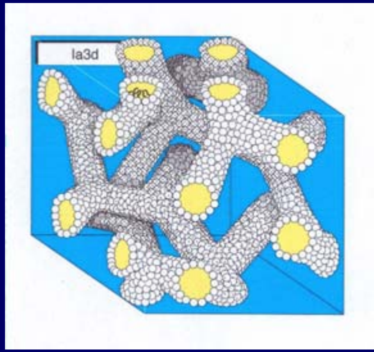
hexagonal



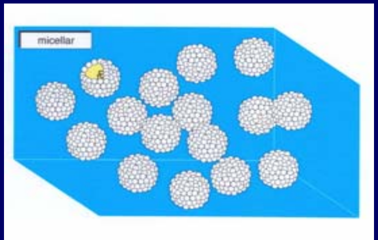
lamellar



micelles cubic

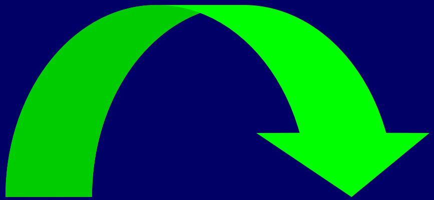


cubic



micelles

Transfer of structure from Brij56 surfactant aggregates to

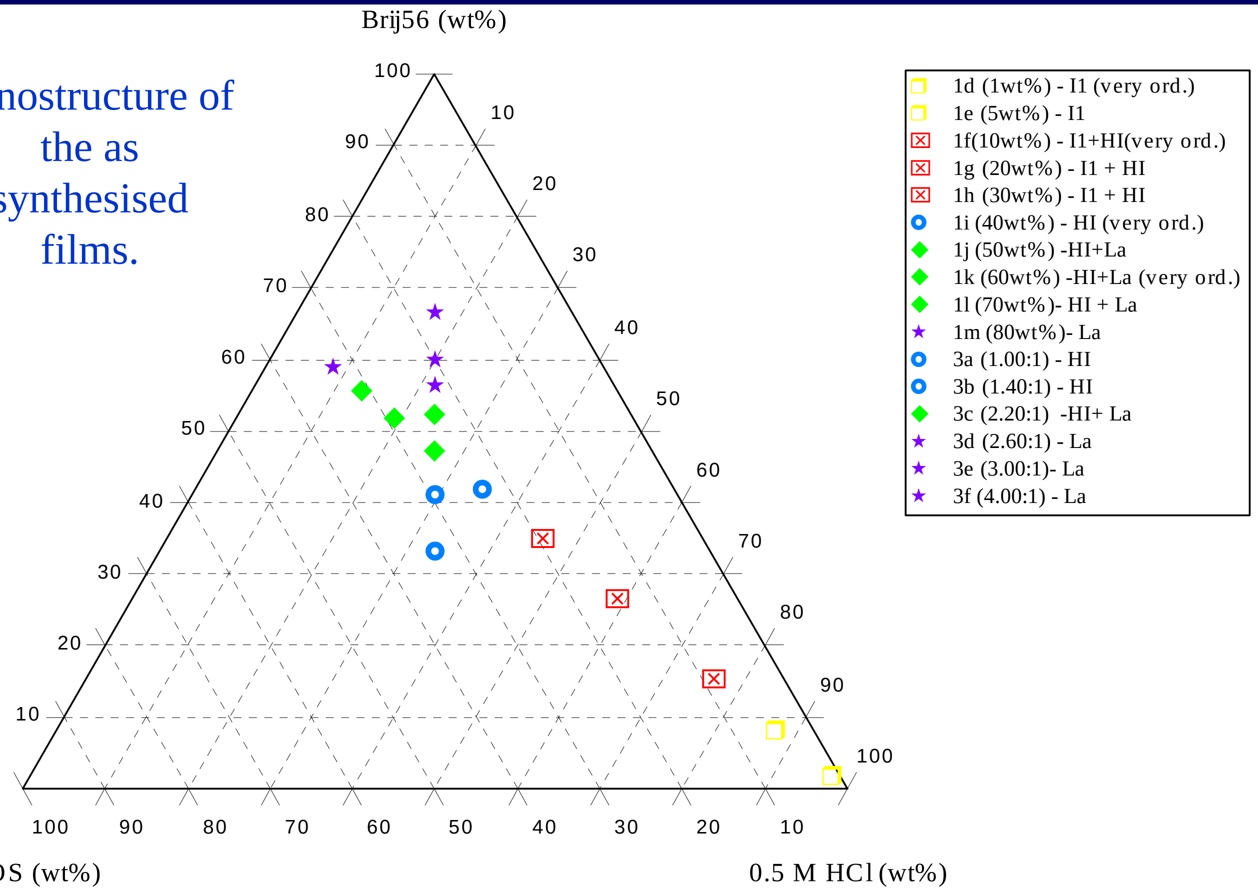


a-SiO_2 inorganic films.

Amphiphilic Molecules: Phase Diagrams

• AMPHIPHILIC MOLECULE: PHASE DIAGRAMS

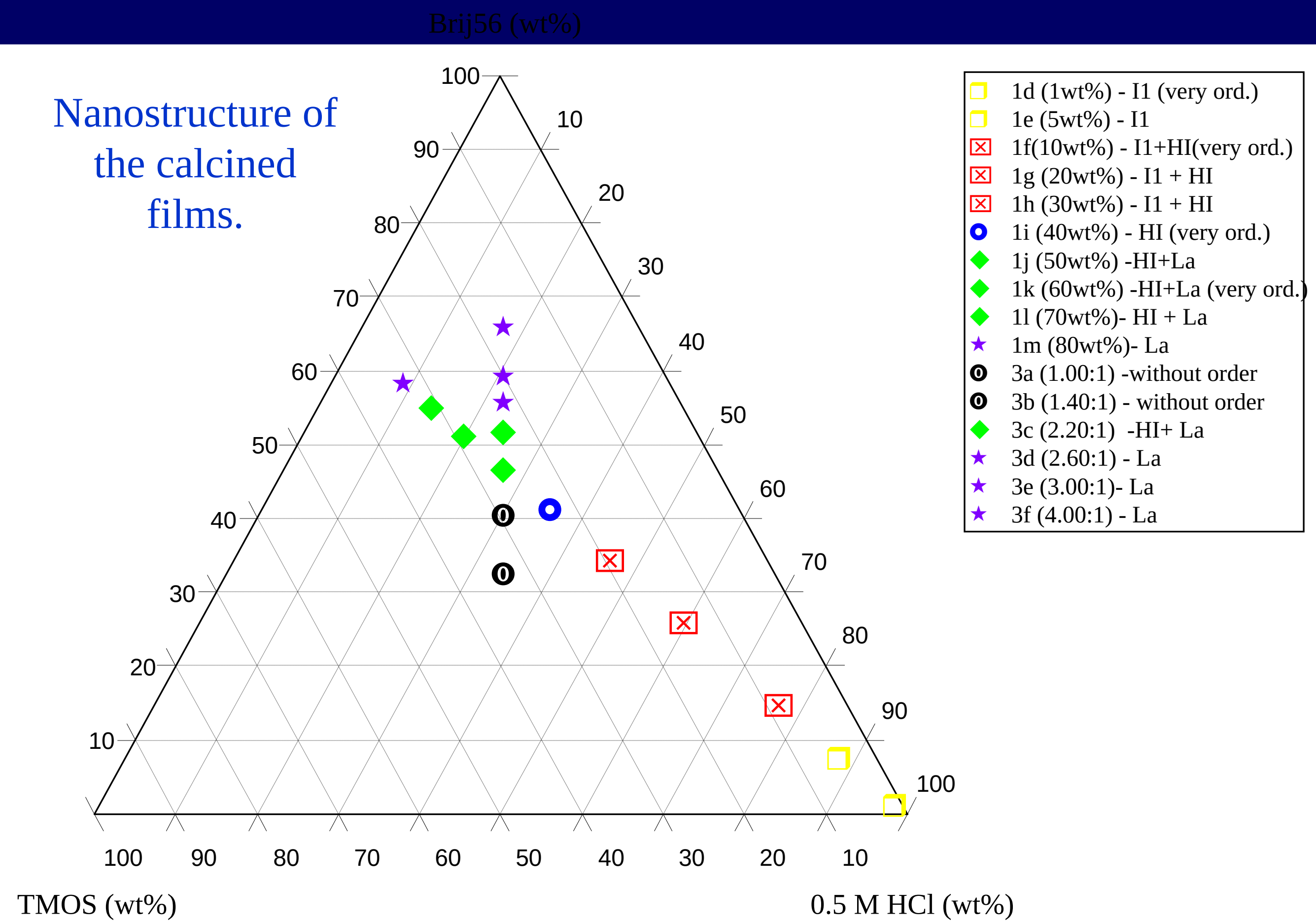
Nanostructure of the as synthesised films.



Amphiphilic Molecules: Phase Diagrams

- **AMPHIPHILIC MOLECULE: PHASE DIAGRAMS**

Nanostructure of the calcined films.



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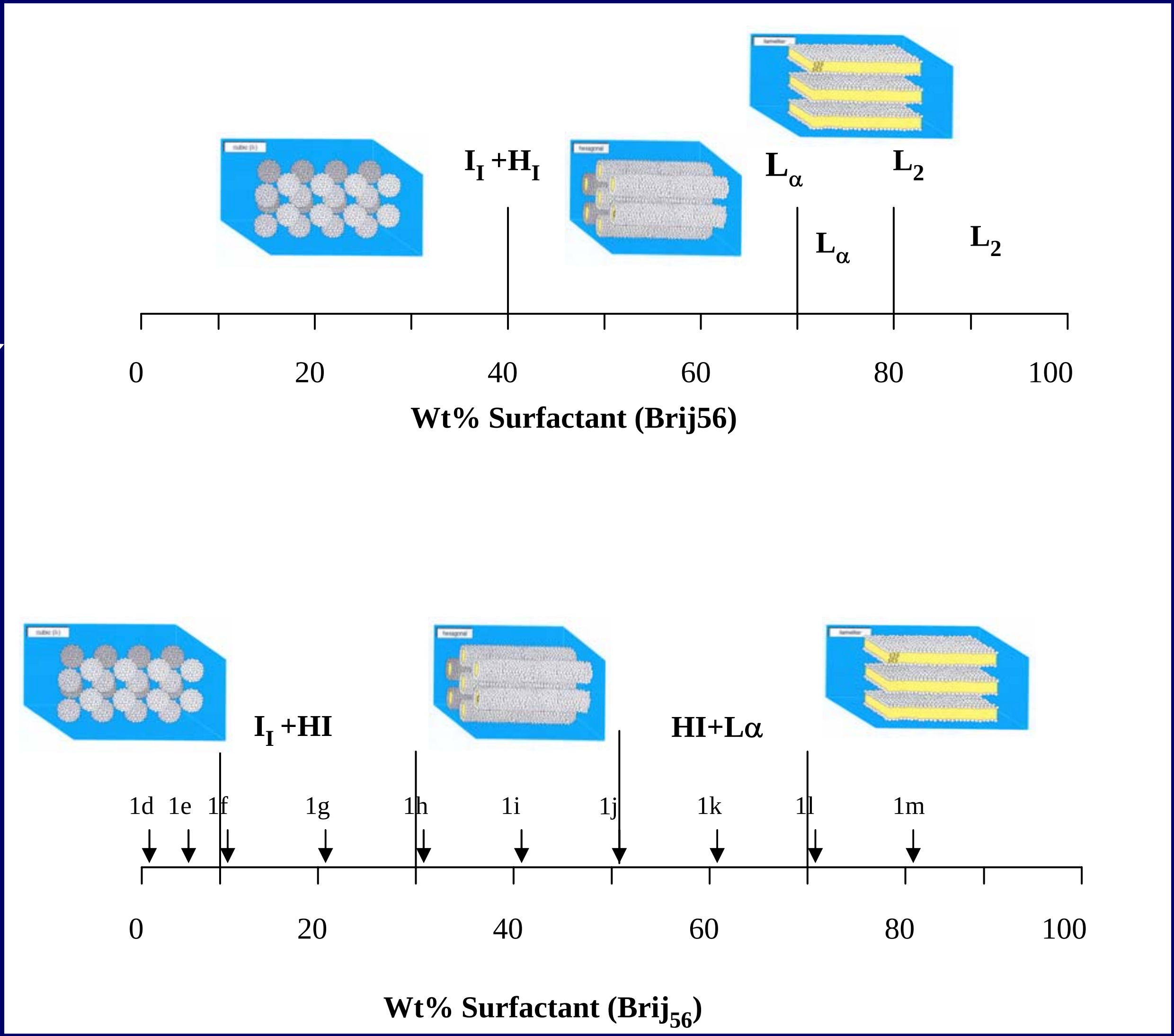
• AMPHIPHILIC MOLECULE: PHASE DIAGRAMS

Series 1

bulks

films



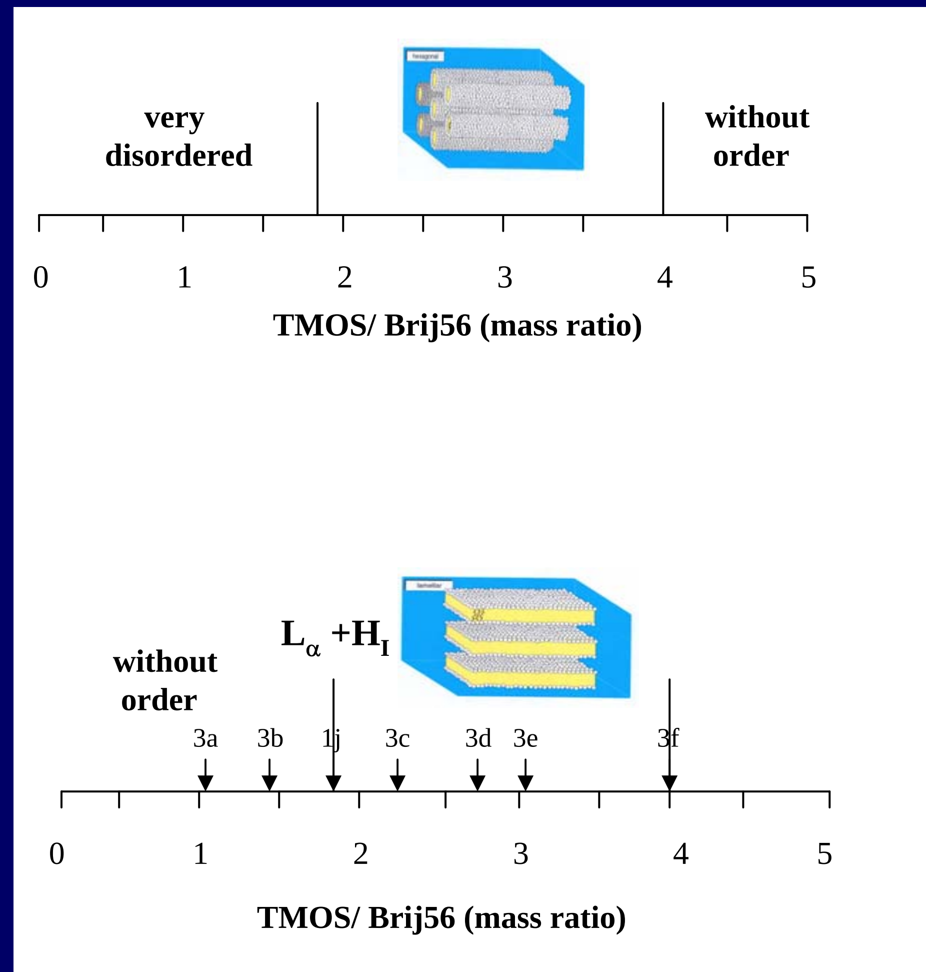
Amphiphilic Molecules: Phase Diagrams

• AMPHIPHILIC MOLECULE: PHASE DIAGRAMS

bulks

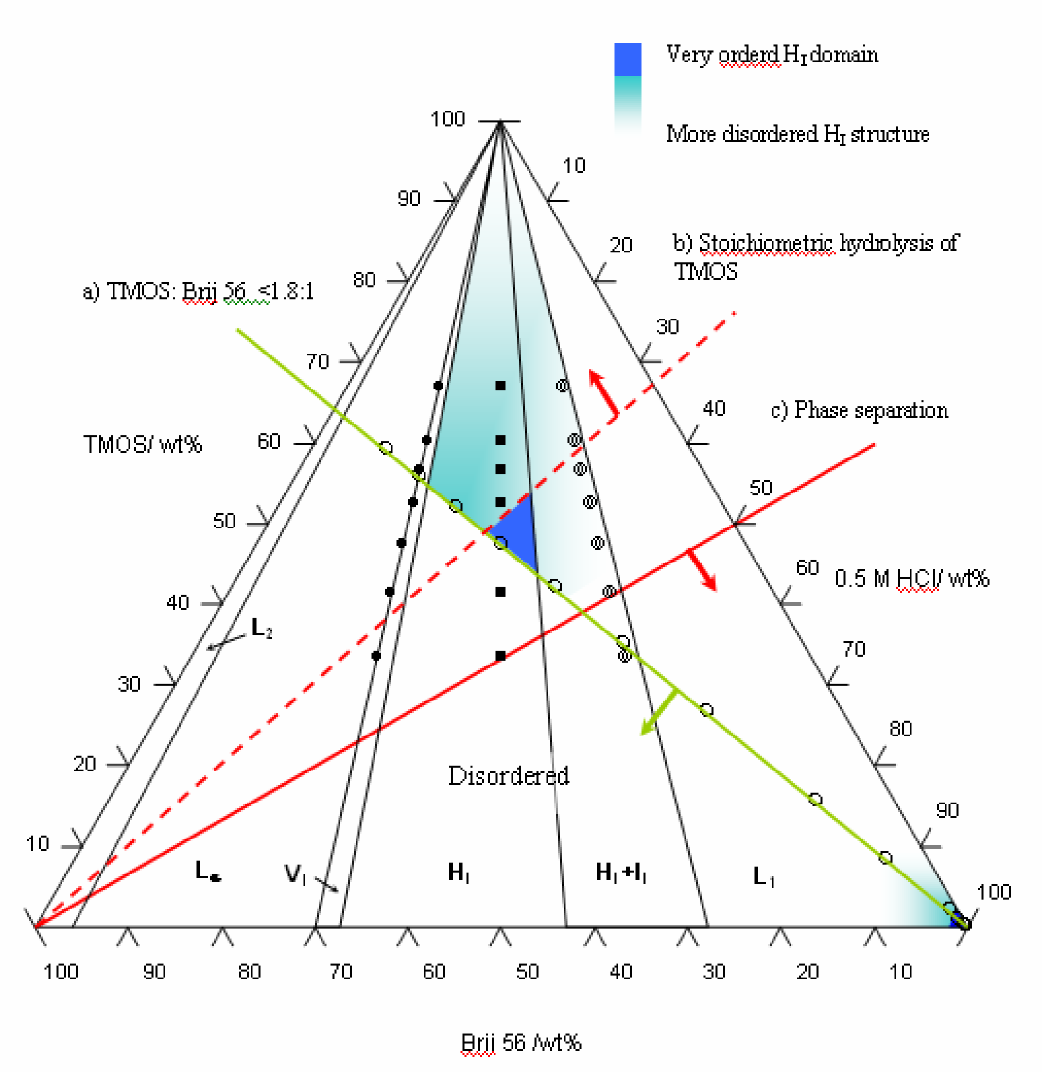
Series 3

films



Amphiphilic Molecules: Phase Diagrams

• AMPHIPHILIC MOLECULE: PHASE DIAGRAMS



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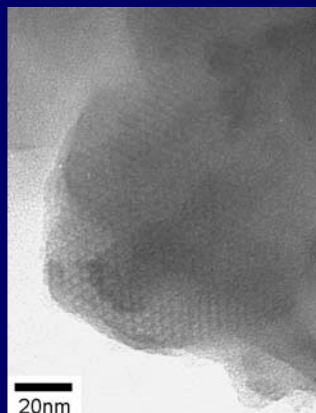
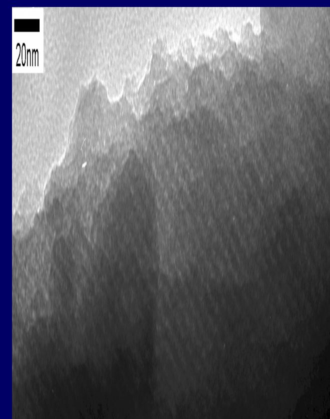
Amphiphilic Molecules: Microstructures

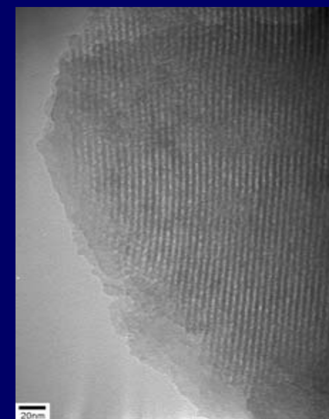
• **AMPHIPHILIC MOLECULE: MICROSTRUCTURES**



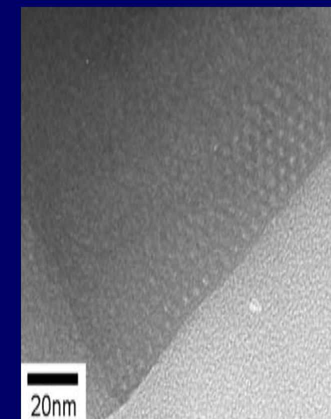
1e - 5.0 wt% BRIJ56



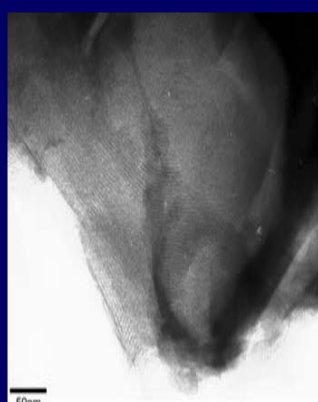
1f - 10 wt% BRIJ56



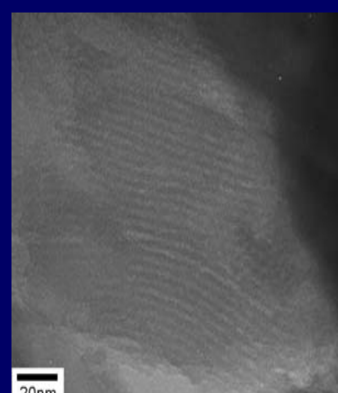
1g - 20 wt% BRIJ56



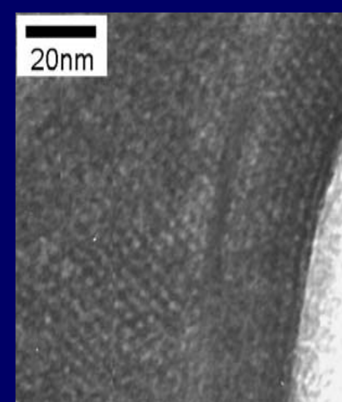
1h - 30 wt% BRIJ56



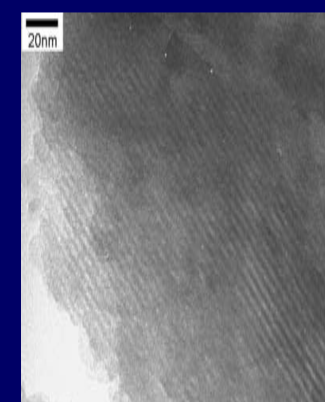
1i - 40 wt% BRIJ56



1j - 50 wt% BRIJ56



1k - 60 wt% BRIJ56



1l - 70 wt% BRIJ56

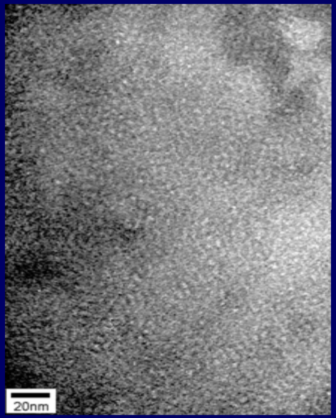
Amphiphilic Molecules: Microstructures

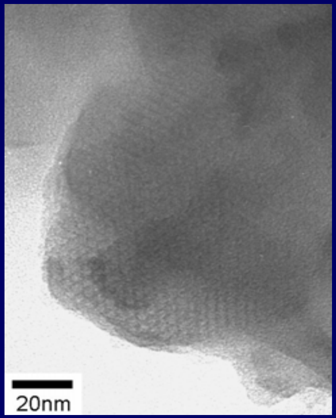
• AMPHIPHILIC MOLECULE: MICROSTRUCTURES

Series 1 and 3 (1 d, 1 e)

Cubic domain

TEM





1e - 5.0 wt% BRIJ56

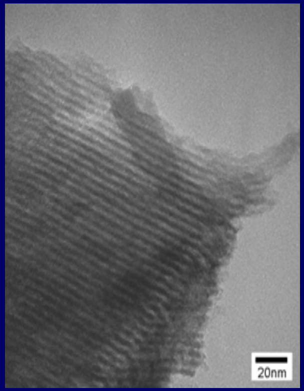
Amphiphilic Molecules: Microstructures

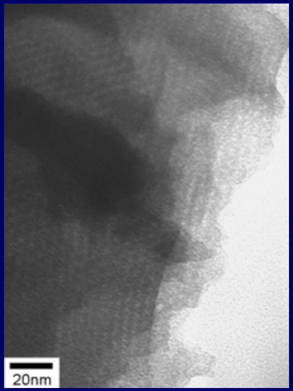
• AMPHIPHILIC MOLECULE: MICROSTRUCTURES

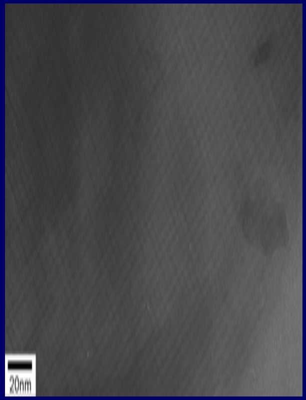
Series 1 and 3 (1m, 3c, 3d, 3e, 3f)

Lamellar domain

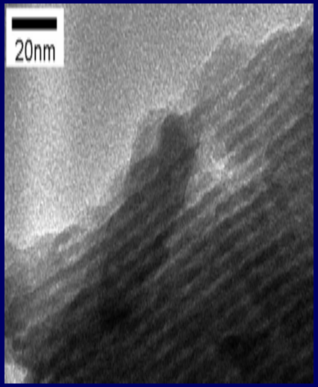
Lα

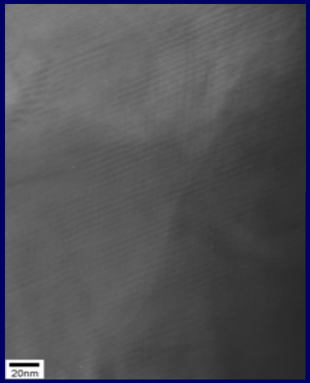


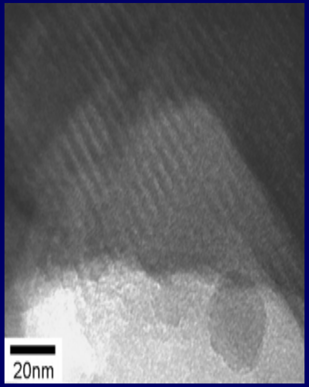


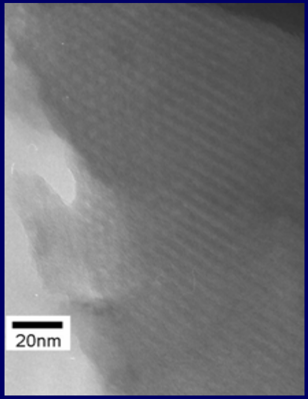


1m - 80 wt% BRIJ56 | **3c - 2.20:1** | **3d - 2.60:1** | **3e - 3.30:1** | **3f - 4.00:1**









Applications

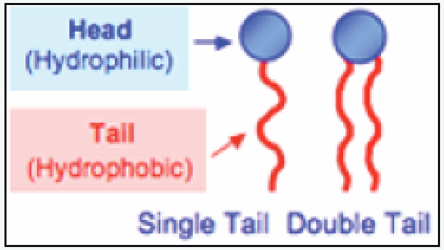


Figure 1. Amphiphilic molecule (Surfactant)

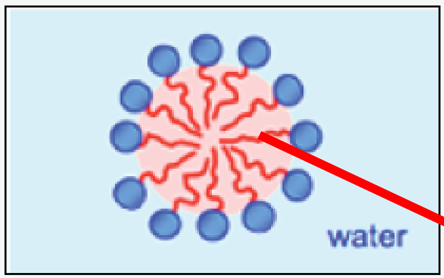


Figure 2. Micelle

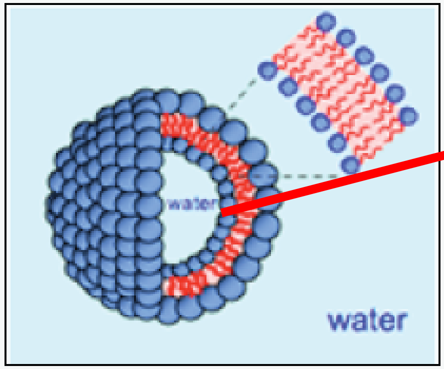


Figure 3. Vesicle

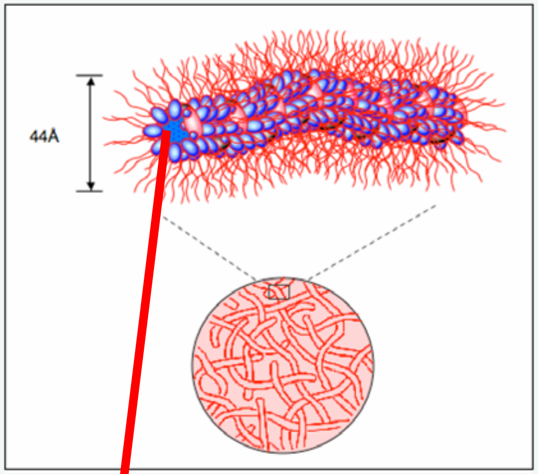


Figure 7. Reverse wormlike micelles and their entangled network

The synthesis of nanoparticles can be achieved by confining the reaction in a restricted space.

Vesicles can be **nano-reactors**.

Further Reading

• Nanostructures and Nanomaterials. Synthesis, Properties & Applications, G. Cao, ICP Imperial College Press, 2007 (ISBN 1-86094-480-9).

•The Colloidal Domain. Where Physics, Chemistry, Biology, and Technology Meet, D. Fennell Evans and H. Wennerström, Wiley-VCH, 1999, ISBN 0-471-24247-0