Synthesis of Organic Nanomaterials

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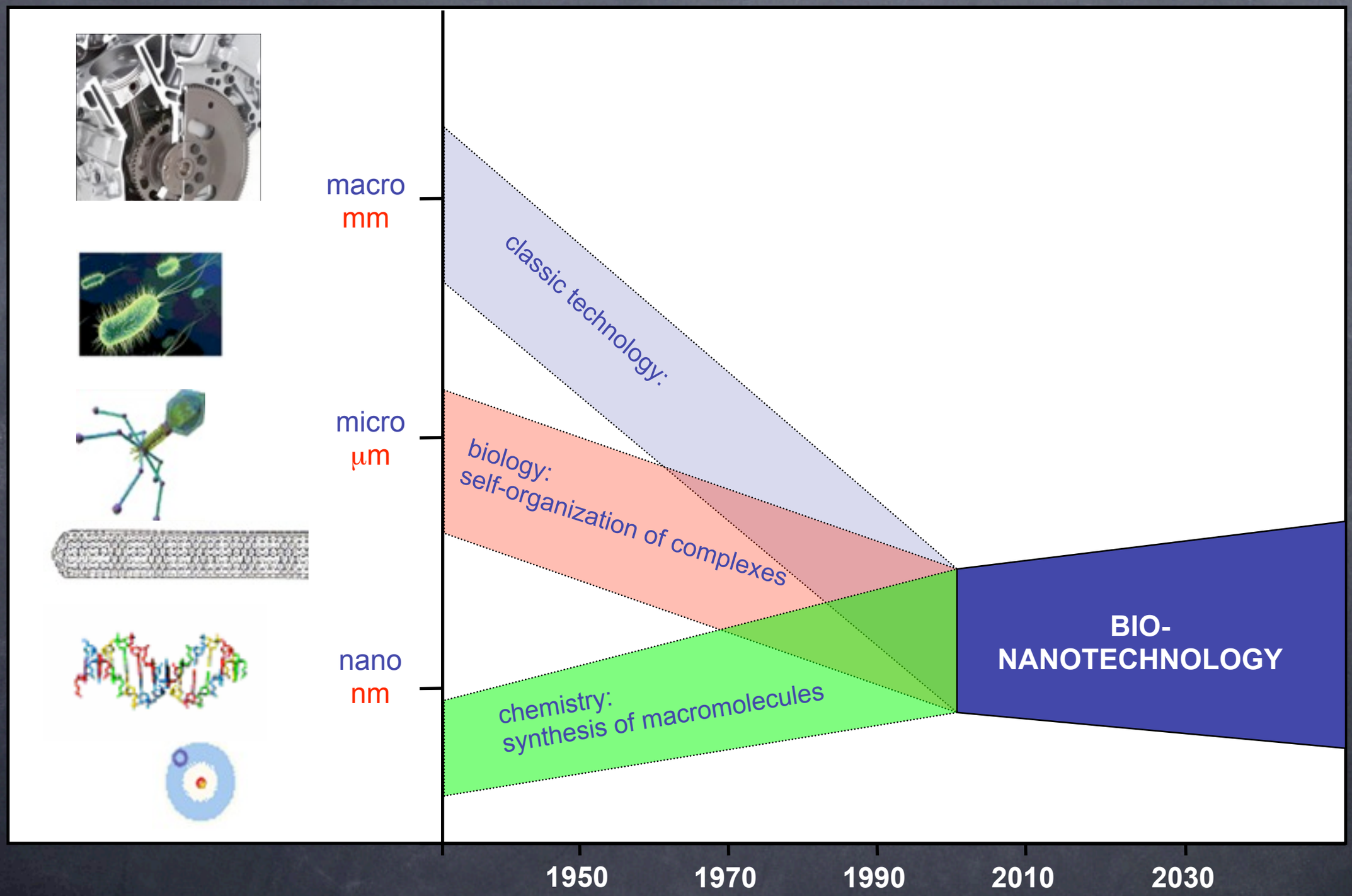
Expectation from the class?

topics:

What will be covered:

* liposomes and micelles
* MOFs
* supramolecular chemistry
* dyes
* liquid crystals
* from oligomers to polymers
* semiconducting organic nanomaterials

Why NANO ?


macro
mm
micro
μm
nano
nm
classic technology:
biology:
self-organization of complexes
chemistry:
synthesis of macromolecules
BIO-
NANOTECHNOLOGY
1950
1970
1990
2010
2030

nanotechnology

TABLE 1.1: Landmarks in the History of Nanotechnology Reproduced with permission from *Modeling MEMS and NEMS*, Pelesko and Bernstein [99].

1940s	Radar drives the development of pure semiconductors.
1959	Richard P. Feynman's famous "There's plenty of room at the bottom" lecture.
1960	Planar batch-fabrication process invented.
1964	H.C. Nathanson and team at Westinghouse produce the resonant gate transistor, the first batch-fabricated MEMS device.
1970	The microprocessor is invented, driving the demand for integrated circuits ever higher.
1979	The first micromachined accelerometer is developed at Stanford University.
1981	K. Eric Drexler's article, *Molecular Engineering: An Approach to the Development of General Capabilities for Molecular Manipulation*, is published in the Proceedings of the National Academy of Sciences. This is arguably the first journal article on molecular nanotechnology to appear.
1982	The scanning tunneling microscope is invented.
1984	The polysilicon surface micromachining process is developed at the University of California, Berkeley. MEMS and integrated circuits can be fabricated together for the first time.
1985	The "Buckyball" is discovered.
1986	The atomic force microscope is invented.
1991	The carbon nanotube is discovered.
1996	Richard Smalley develops a technique for producing carbon nanotubes of uniform diameter.
2000s	The number of MEMS devices and applications continually increases. National attention is focused on funding nanotechnology research and education.

self-assembly

TABLE 1.2: Landmarks in Self-Assembly

1930s	Alan Turing develops the theory of universal computation.
1950s	John von Neumann develops theory of automata replication.
1953	James D. Watson and Francis Crick discover the structure of DNA.
1955	H. Fraenkel-Conrat and R.C. Williams self-assemble the tobacco mosaic virus in a test tube.
1957	Penrose and Penrose construct a simple self-replicating system.
1961	Hao Wang develops "Wang Tiles" demonstrating the equivalence of tiling problems and computation.
1991	Nadrian C. Seeman and Junghuei Chen self-assemble a cube from DNA.
1994	Leonard Adleman launches the field of DNA computation by using DNA to solve a Hamiltonian path problem.
1996	Kazuo Hosokawa's group demonstrates microscale self-assembly using surface tension.
2000	George M. Whitesides's group self-assembles electrical networks from millimeter scale polyhedra.
2004	William Shih adapts the methods of Seeman to self-assemble a DNA octahedron.
2004	Eric Winfree and Paul Rothemund self-assemble a Sierpinski triangle from DNA demonstrating that self-assembly may be used for computation.
2000s	Self-assembly research explodes drawing the interest of researchers from every imaginable field.

definitions of self-assembly

Viruses and bacterial flagella are constructed automatically out of protein subunits. This phenomenon is called self-assembly, which is a powerful technique applicable to microfabrication
To achieve self-assembly, the following conditions must be met: generating bonding forces, bonding selectively, and moving the parts randomly so that they come together by chance.

Spontaneous assembly, often called "self-assembly," refers to aggregation of particles into an organized structure without external assistance.

Self-assembly is the ubiquitous process by which objects autonomously assemble into complexes.

Self-assembly is a process in which small objects autonomously associate with each other to form larger complexes.

what is NOT self-assembly ?

self-assembly

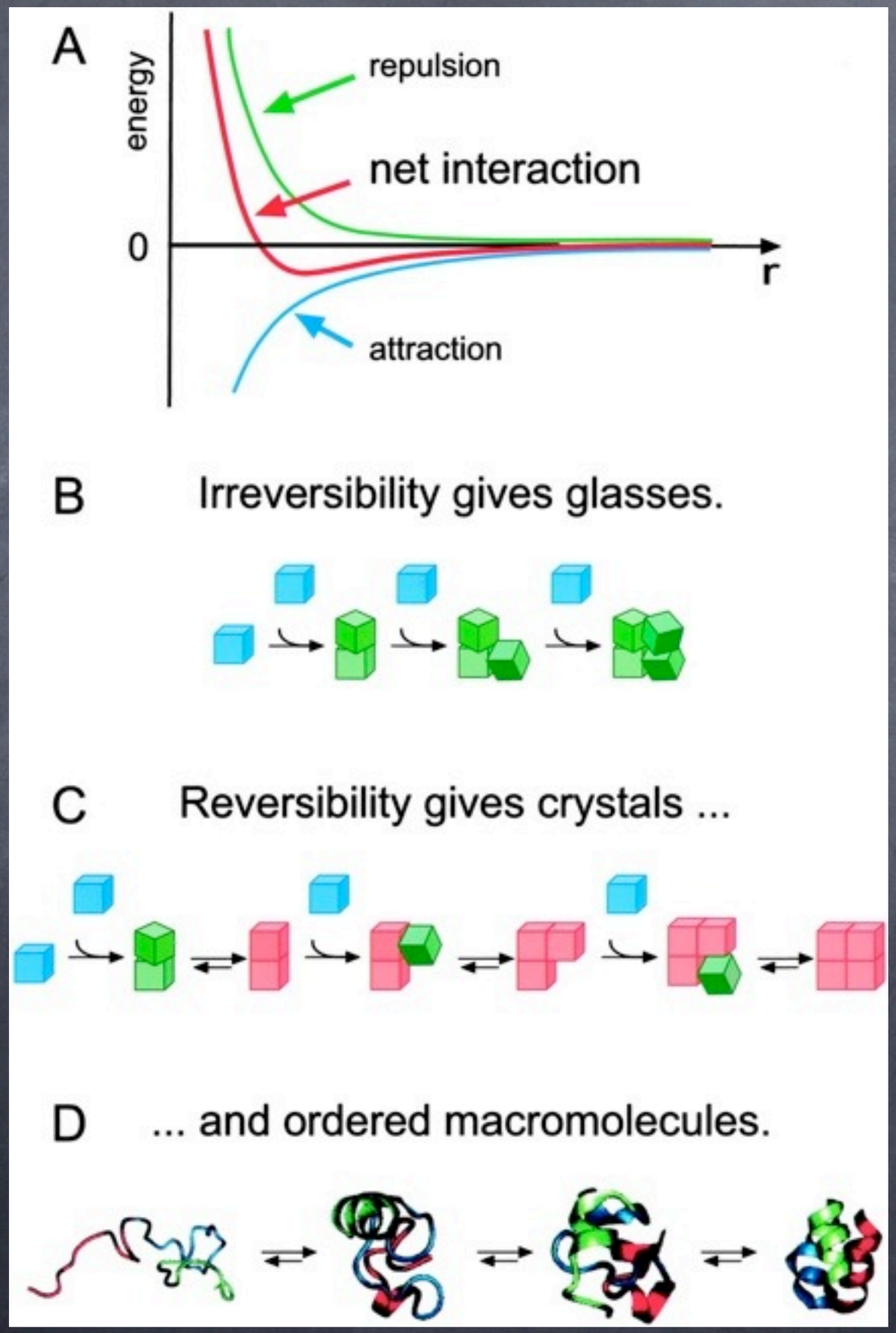
- **Self-assembly** refers to the spontaneous formation of organized structures through a stochastic process that involves pre-existing components, is reversible, and can be controlled by proper design of the components, the environment, and the driving force.

- **Static self-assembly** refers to that subclass of self-assembly processes that leads to structures in local or global equilibrium.

- **Dynamic self-assembly** refers to that subclass of self-assembly processes that leads to stable non-equilibrium structures. These structures persist only so long as the system is dissipating energy.

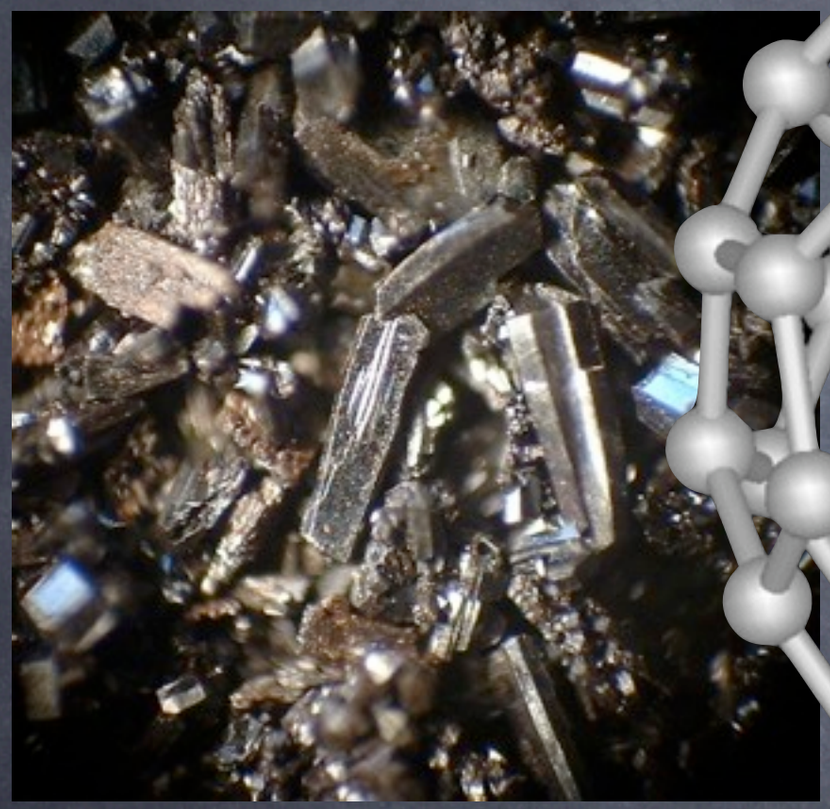
- **Programmed or programmable self-assembly** refers to that subclass of self-assembly processes where the particles of the system carry information about the final desired structure or its function.

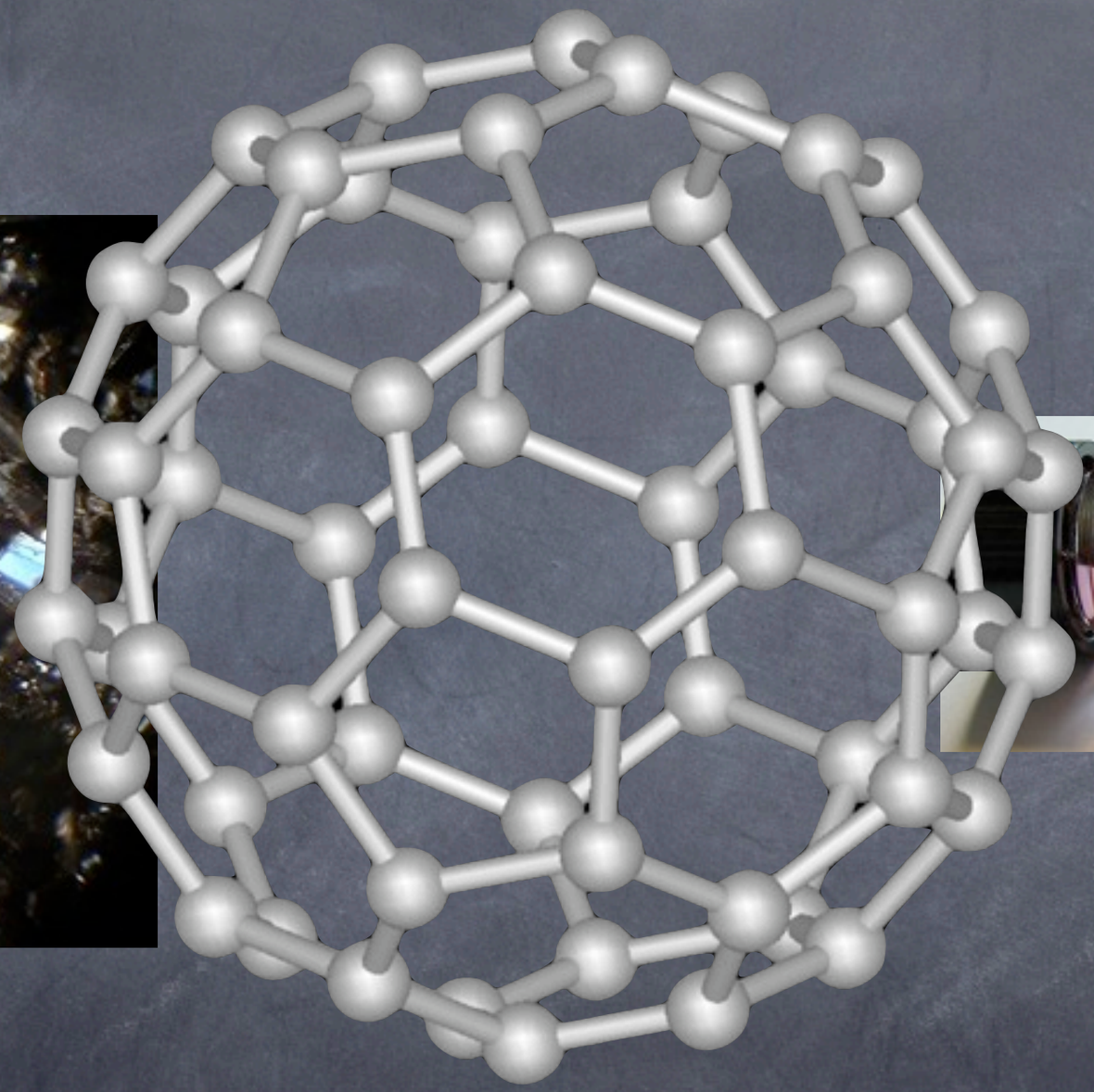
(A) Aggregation occurs when there is a net attraction and an equilibrium separation between the components



Whitesides G M, Boncheva M PNAS 2002;99:4769-4774

THE nanomaterial

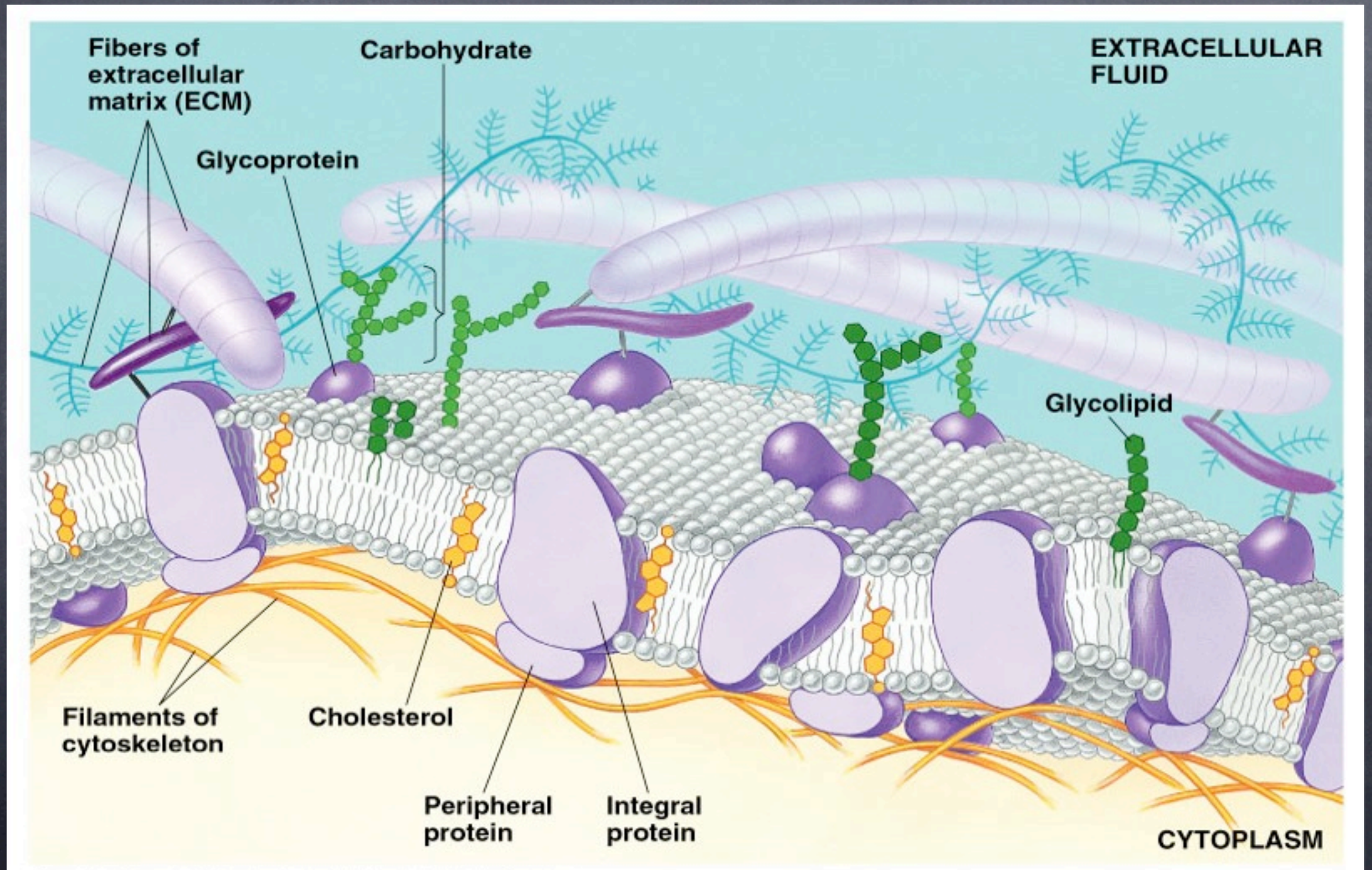




size: 7 Å = 7 • 10^{-10} m = 0.7 nm

cell membrane structure:

The Fluid Mosaic Model



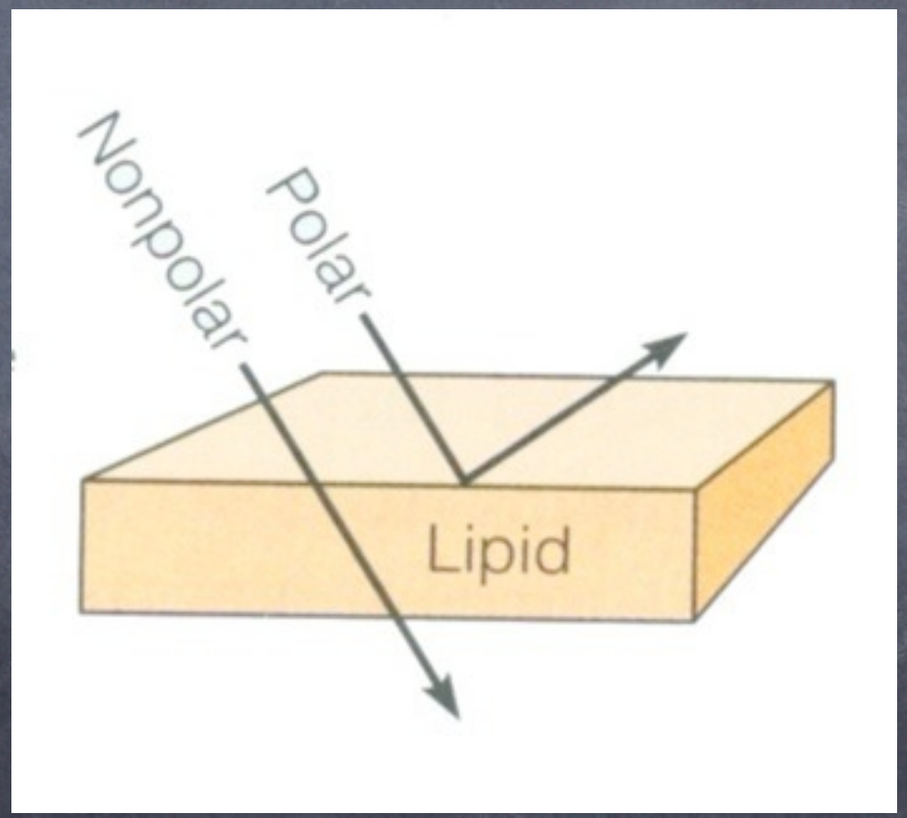
cell membrane

The cell membrane's function is to form a barrier between the cell's inner and outer environment. It is selectively permeable meaning that it allows certain materials to pass through and prevents the movement of other through it.
It is composed of a phospholipid bilayer with protein molecules (intergral proteins) embedded within in the bilayer. Some of these proteins pass completely through both layers of phospholipids. There are also other types of molecules such as cholesterol and carbohydrates that are associated with the cell membrane's outer surface.
The phospholipids and proteins are not in a static state, but have the ability to move from one location to another or change positions within the bilayer. Therefore the molecules which make up the membrane are described as being in a fluid state.
The structure of the membrane as described by cytologist today is called the "fluid-mosaic model." The membrane is literally a mosaic of molecules that have the ability to move from area to area on the surface of the membrane.

cell membrane models

original observation (Charles Overton)- lipid soluble molecules could freely enter and exit cells of plant roots (1890's)

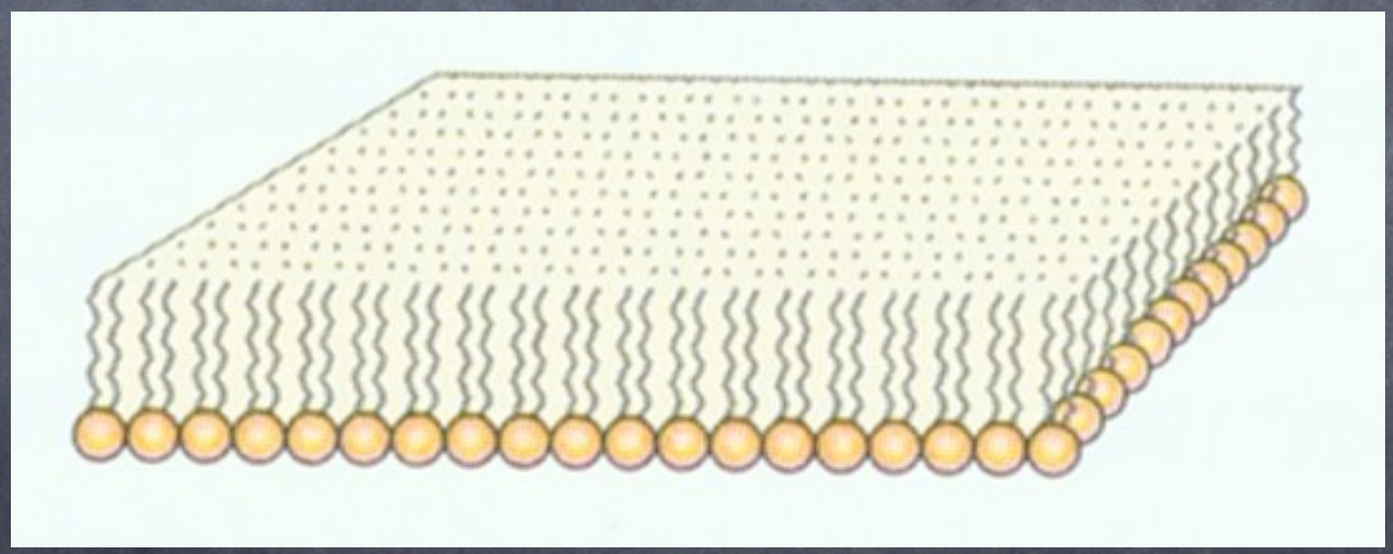
➔ defined lipophilic: lipid loving, able to easily pass cell membranes



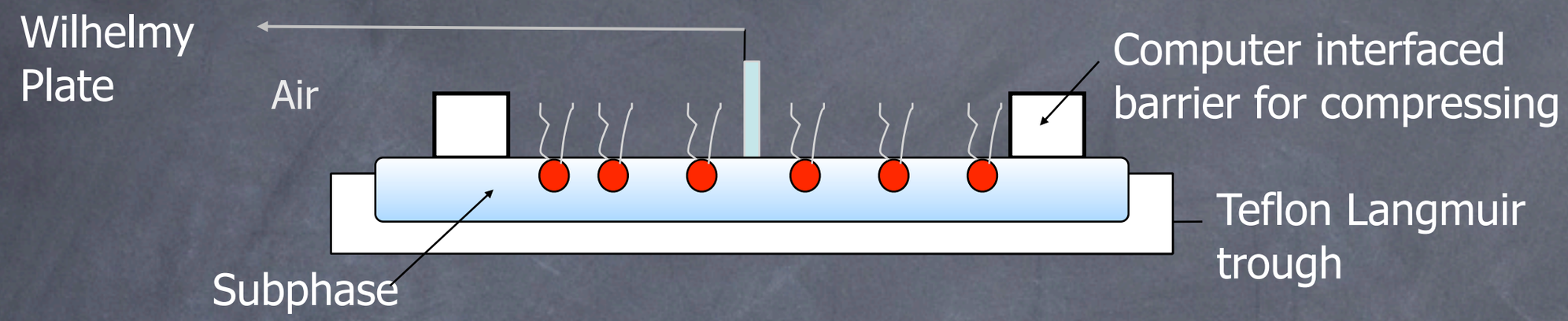
cell membrane models

decade later, Irving Langmuir dissolved phospholipids in benzene and layered the solution on water and waited for benzene to dissolve phospholipids formed a monolayer over the water,

→ reasoned the polar head faced the water, hydrophobic end pointed away



LB trough

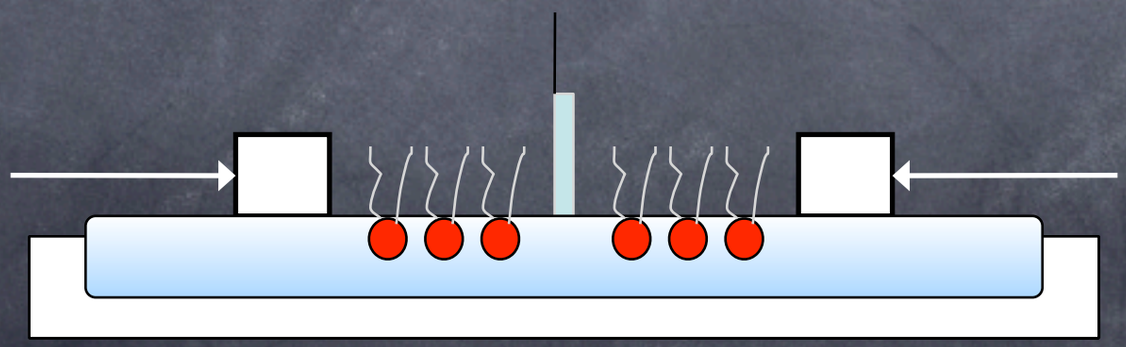


Insoluble (phospholipid ) monolayer is characterized by surface pressure, π

$$\pi = \gamma_o - \gamma$$

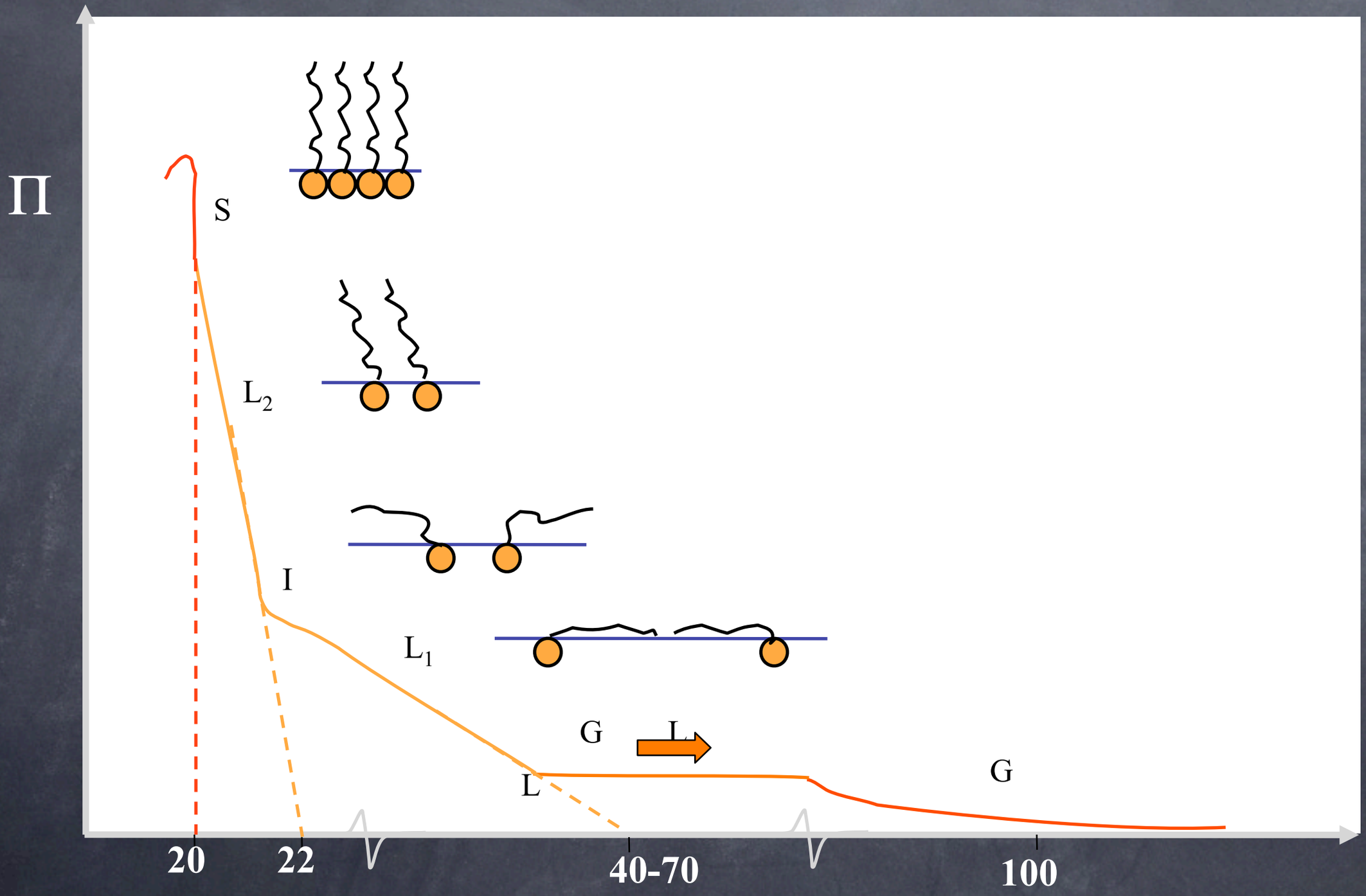
γ_o: clean surface tension

γ : surface tension of surface with adsorbed amphiphiles

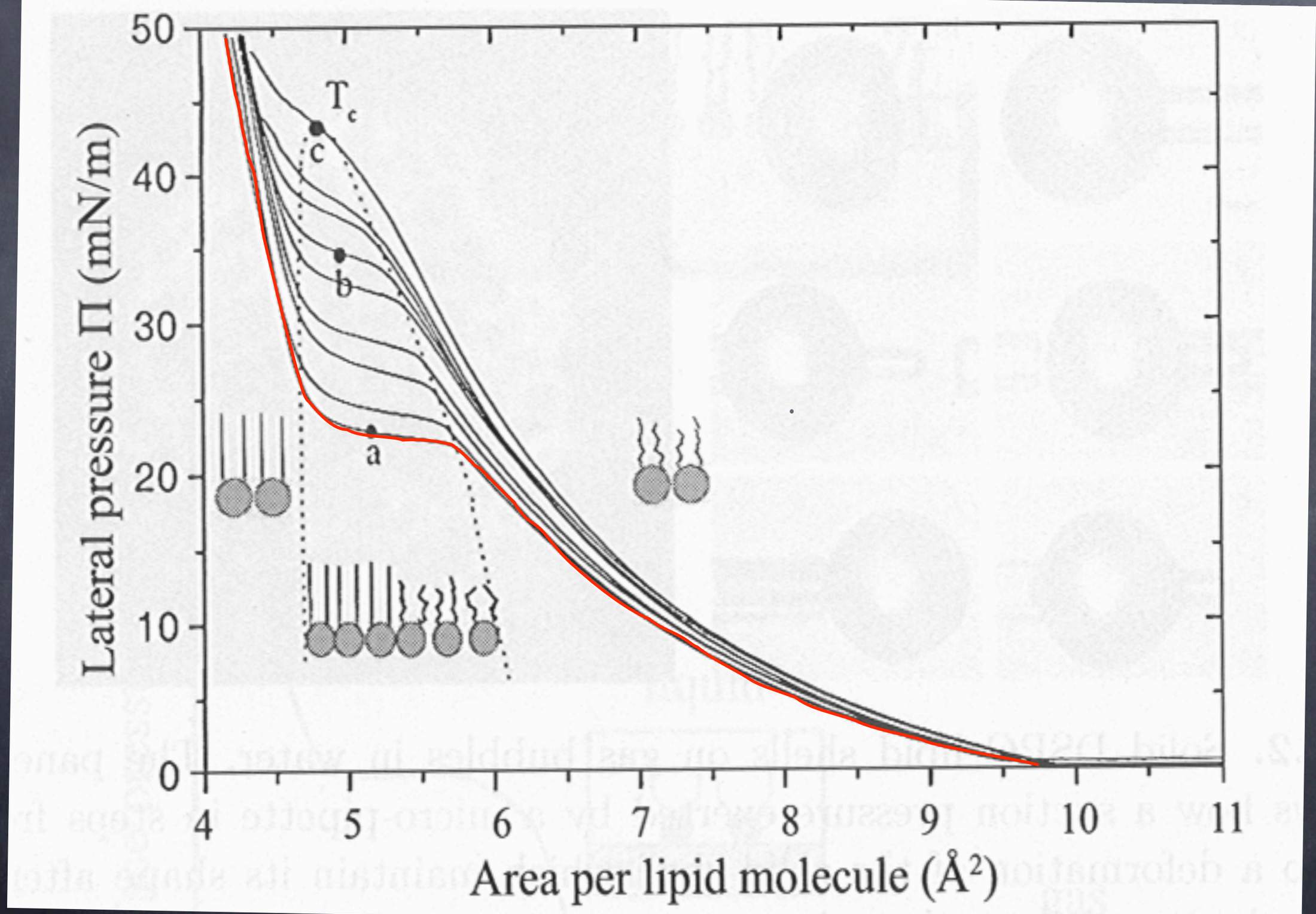


Insoluble monolayers may be compressed by barriers sweeping the interface, allowing p to be easily manipulated

phase transition isotherms

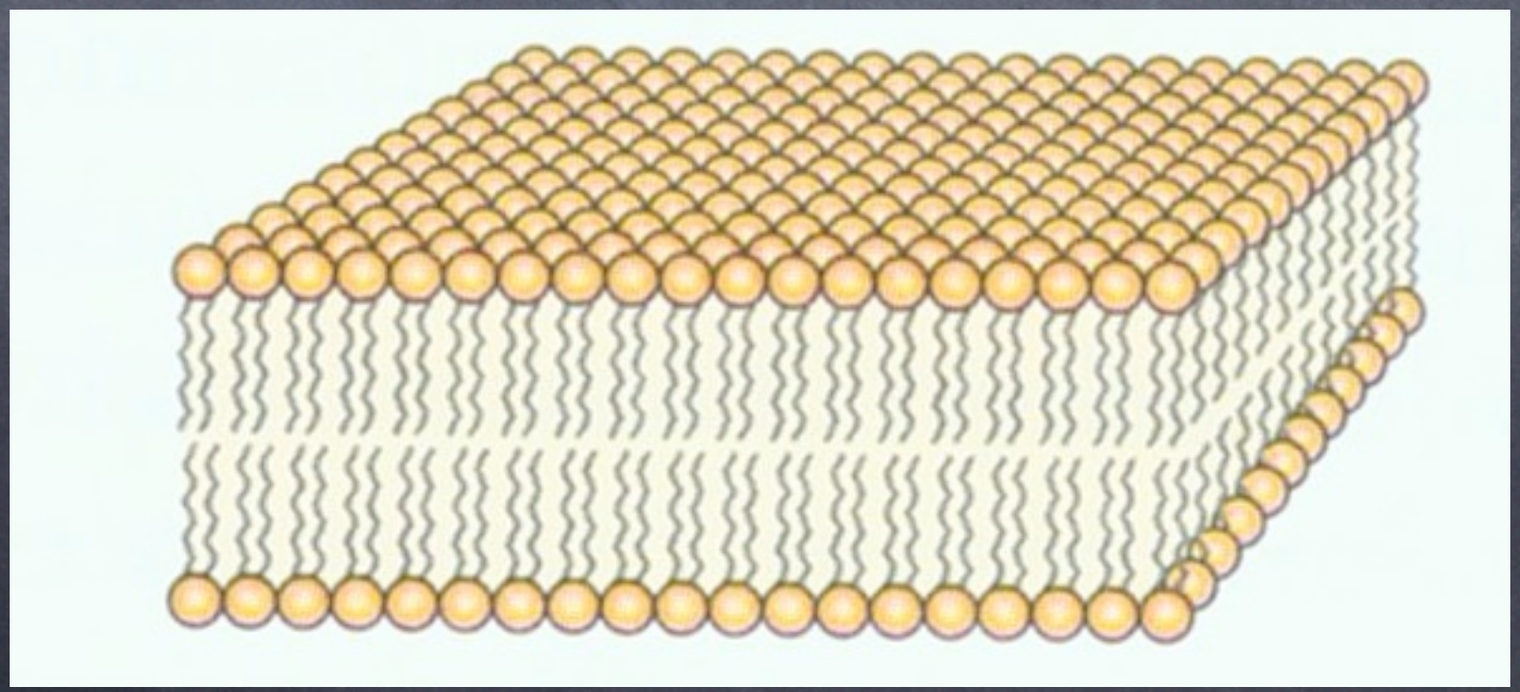


isotherm of DMPC



cell membrane models

1925- Gorter and Grendel lipid bilayer model
interested in red blood cells and figuring out how many lipids are there
took red blood cells and extracted the lipids, then spread them on water
based on size of cells and area of lipid coverage, developed 2 layer idea
(estimated size of lipid layer and cells wrong, errors cancelled out)
→ they suggested the polar headgroups are on both sides, hydrophobic in between to avoid water



cell membrane models

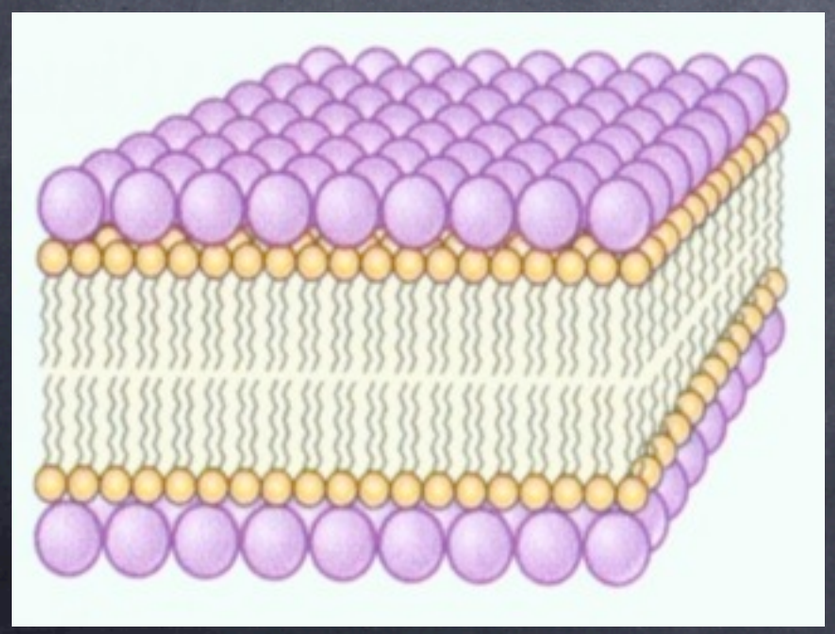
Lipid bilayer model couldn't explain solute permeability of some molecules, nor higher surface tension of purified lipids. K^+ ions pass cell membranes in seconds, artificial membranes in days.

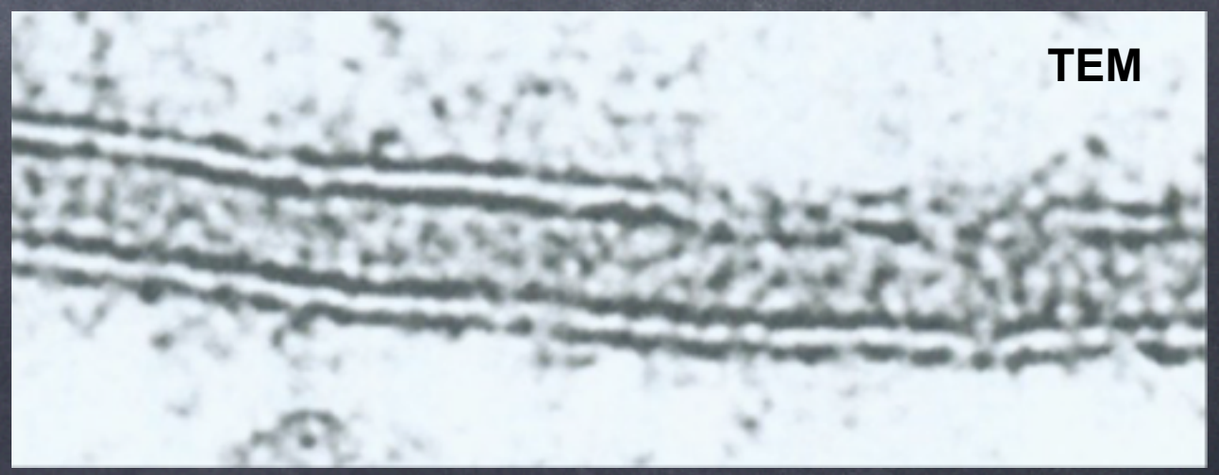
Davson-Danelli Model (1935)- core bilayered lipid membrane with proteins coating both sides-- explained surface tension results

modified in 1950's to suggest some proteins could pass through the membrane and allow ions to pass through to deal with permeability

Robertson-- electron microscopy in 1950's all cell membranes are alike

strong support for the Davson-Danelli model of lipid bilayers





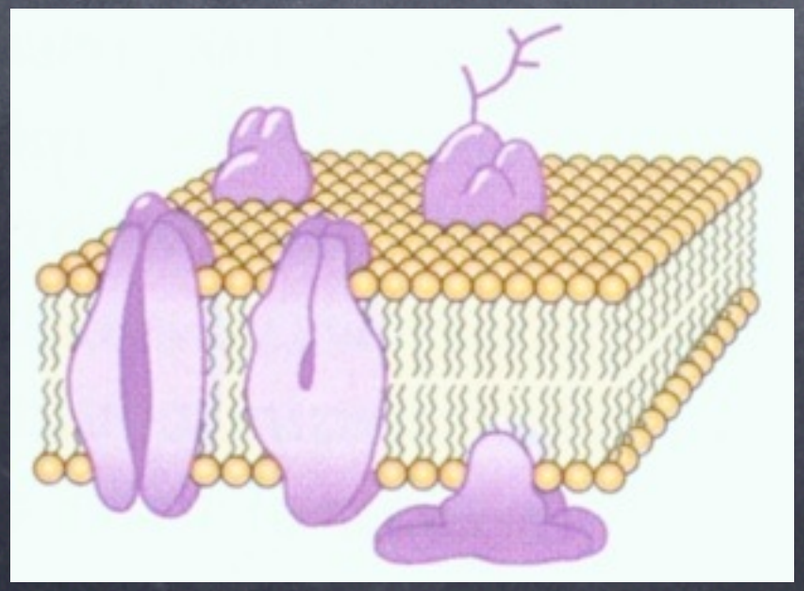
cell membrane models

1972-- Singer and Nicolson-- mosaic of proteins in a fluid lipid bilayer

2 key features of the fluid mosaic model:

1) lipids are fluid -- individual lipids can move around in the plane of the membrane unless they are linked to something (like the cytoskeleton)

2) proteins are embedded individually or as complexes into the membrane itself and are not necessarily evenly distributed, ie. think of buoys in a lake-- floating independent entities unevenly distributed (and having particular functions)



natural membrane lipids

several major classes of lipids in membranes exist:

1) phospholipids
2) glycolipids
3) steroids
4) "strange" lipids

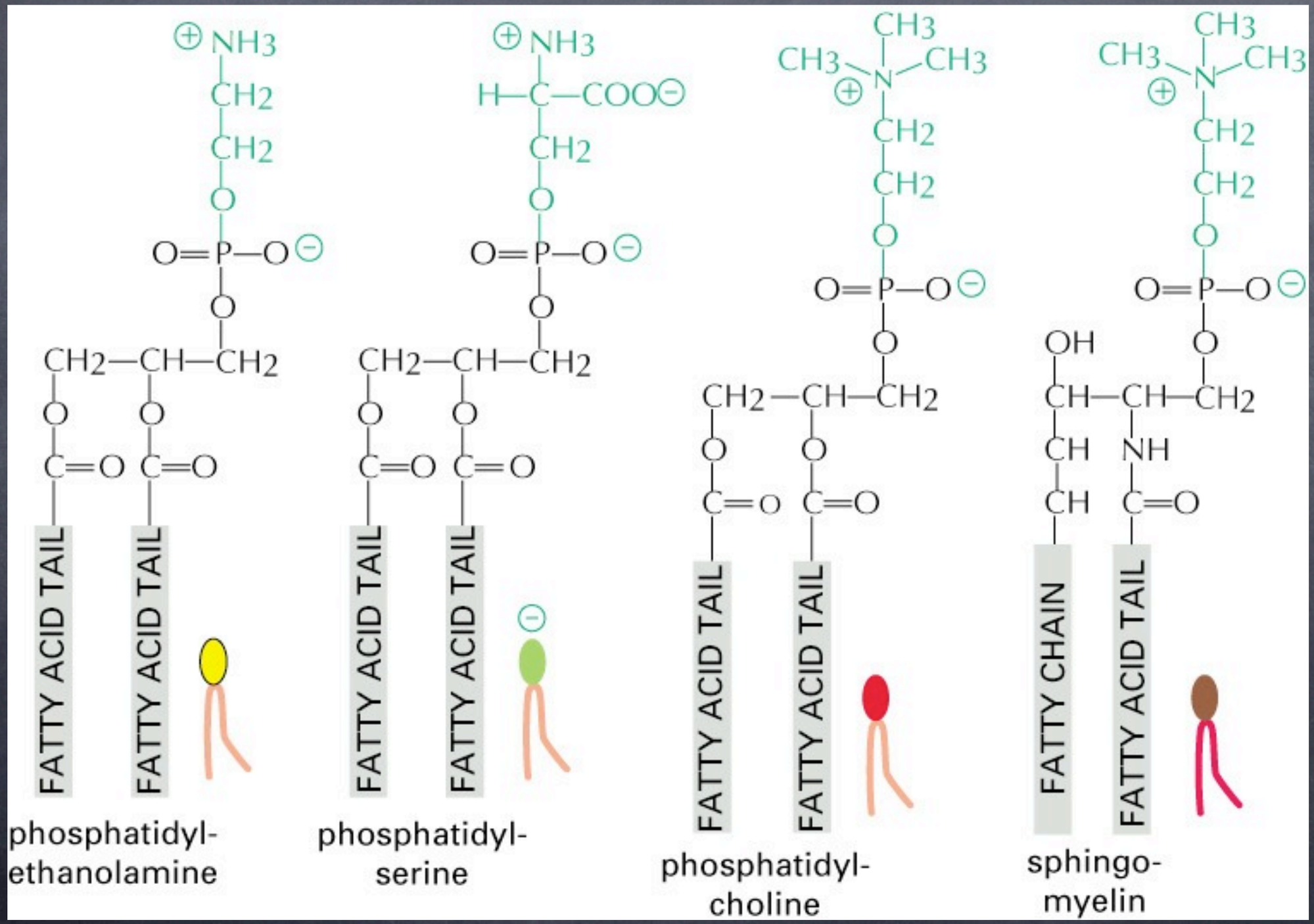
all lipids are based on various fatty acids:

Biologisch relevante Fettsäuren

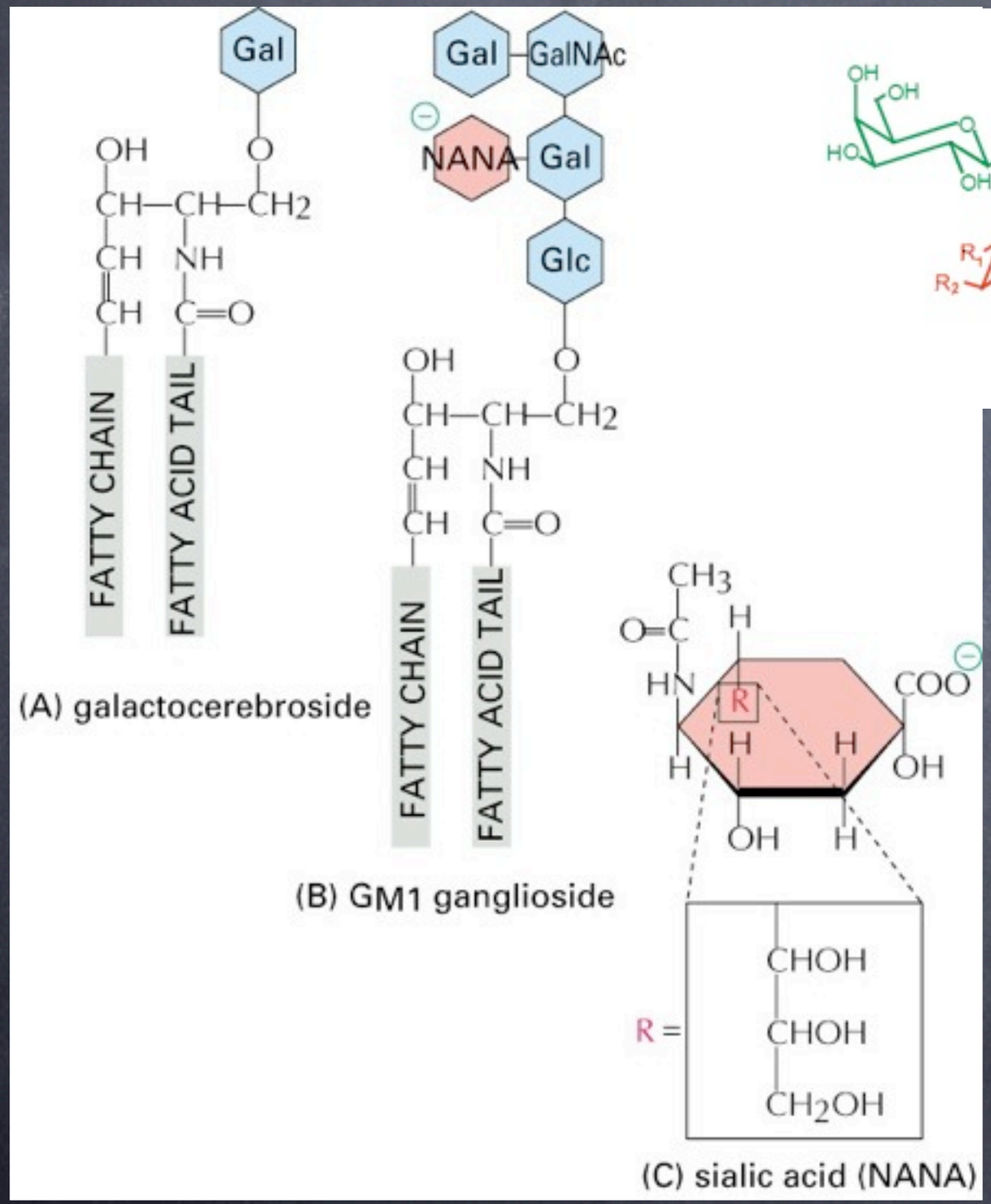
Symbol	Trivialname	Struktur	Schmelzpunkt / °C
Gesättigte Fettsäuren			
12:0	Laurinsäure	$CH_3(CH_2)_{10}COOH$	44.0
14:0	Myristinsäure	$CH_3(CH_2)_{12}COOH$	54.4
16:0	Palmitinsäure	$CH_3(CH_2)_{14}COOH$	62.9
18:0	Stearinsäure	$CH_3(CH_2)_{16}COOH$	69.6
20:0	Arachinsäure	$CH_3(CH_2)_{18}COOH$	75.4
22:0	Behensäure	$CH_3(CH_2)_{20}COOH$	80.0
Ungesättigte Fettsäuren			
16:1, Δ^9	Palmitoleinsäure	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0.5
18:1, Δ^9	Ölsäure	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	13.4
18:2, $\Delta^{9,12}$	Linolsäure	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	- 5
18:3, $\Delta^{9,12,15}$	α-Linolensäure	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	- 11
18:3, $\Delta^{6,9,12}$	γ-Linolensäure	$CH_3(CH_2)_4(CH{=}CHCH_2)_3(CH_2)_3COOH$	- 18
20:4, $\Delta^{5,8,11,14}$	Arachidonsäure	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	- 49.5

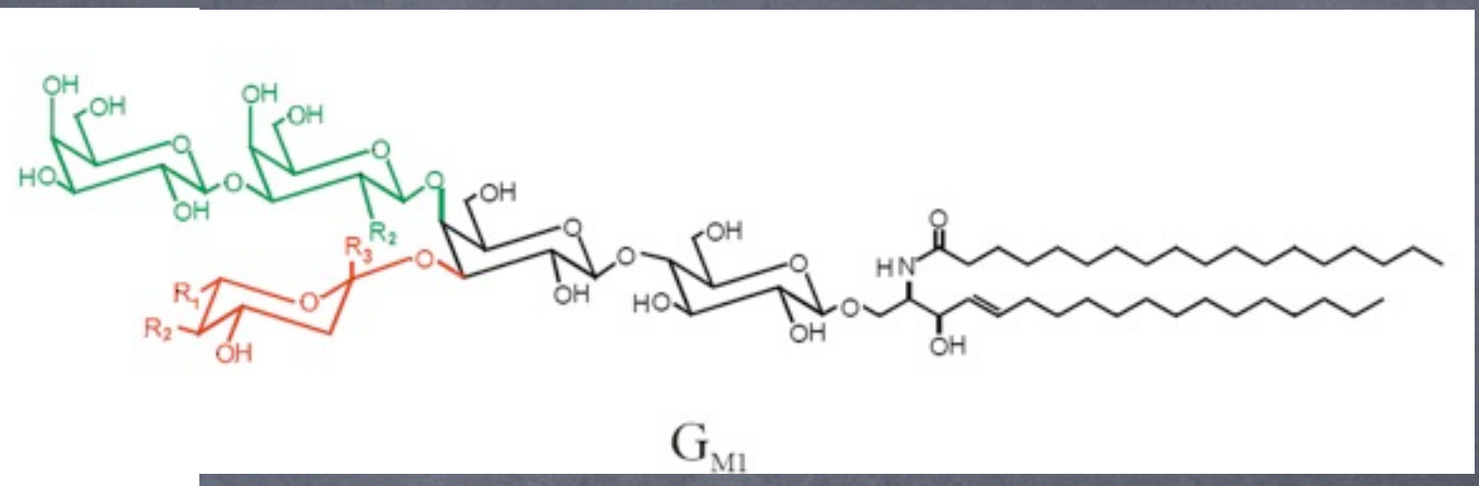
phospholipids

Four major phospholipids are found in mammalian plasma membranes.



glycolipids





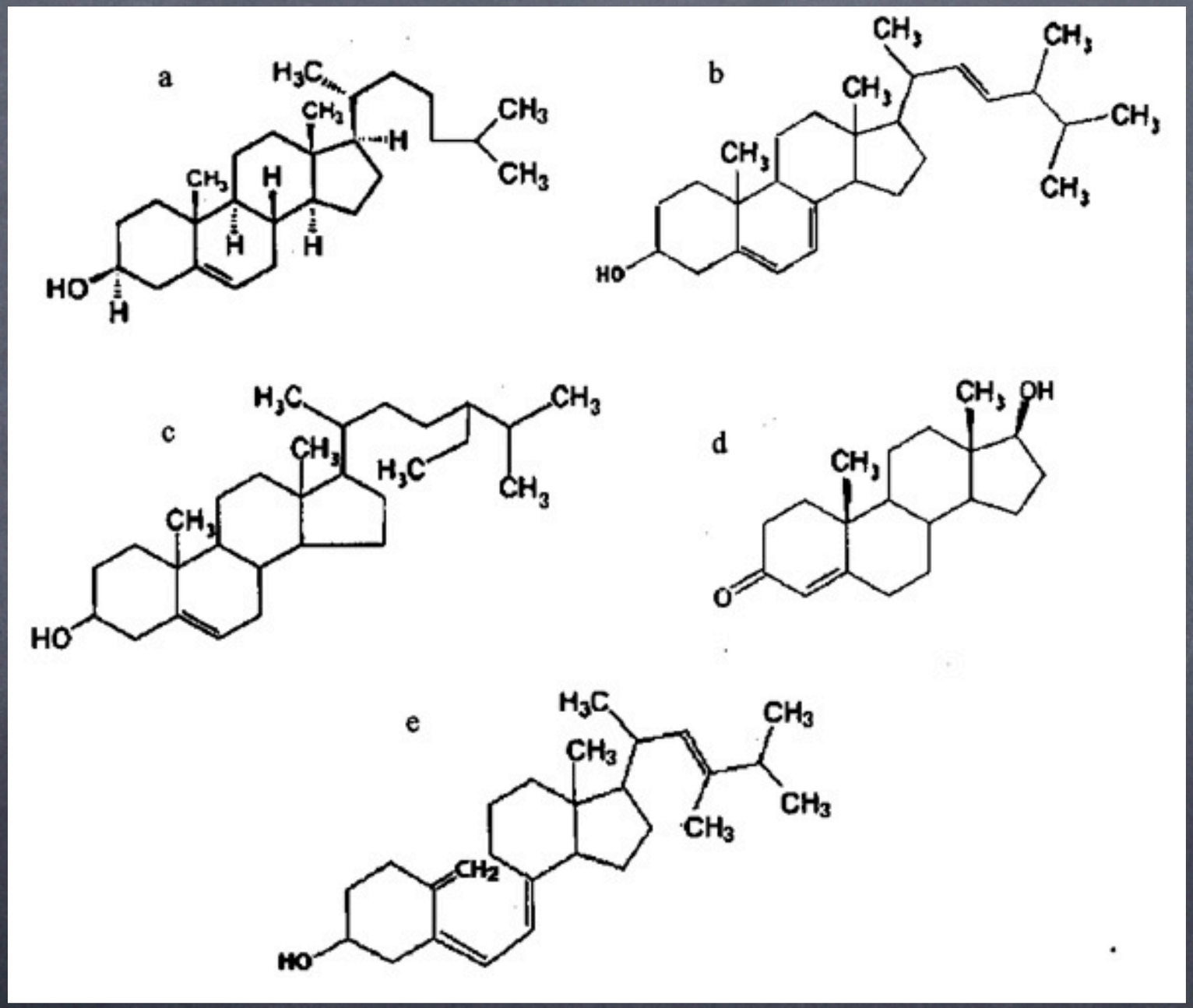
G_{M1}

Animal membranes contain glycolipids. Sugars constitute the polar head group. Gangliosides are common in nerve cells where they influence the electrical properties of cell membranes.

steroids

Cholesterol and derivatives provide stiffness to membrane, mediate fluidity

cholesterol



ergosterol

sitosterol

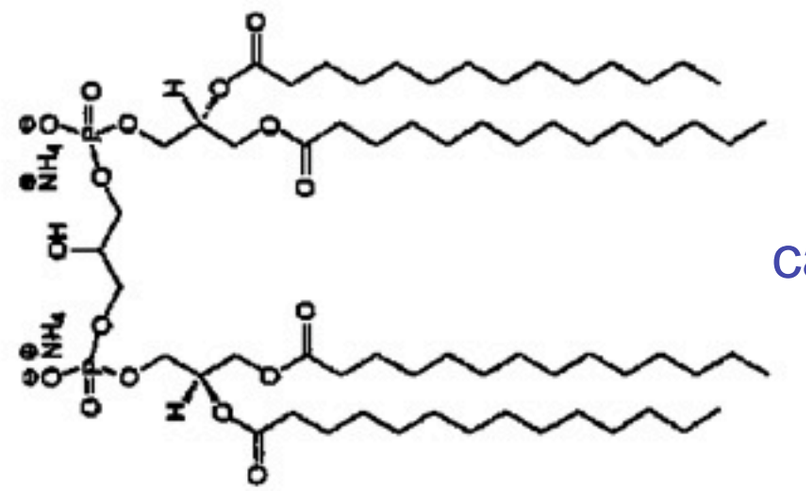
testosterone

vitamin D

"strange" lipids

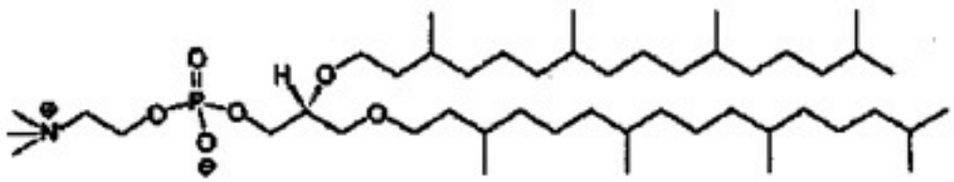
Cholesterol and derivatives provide stiffness to membrane, mediate fluidity

a



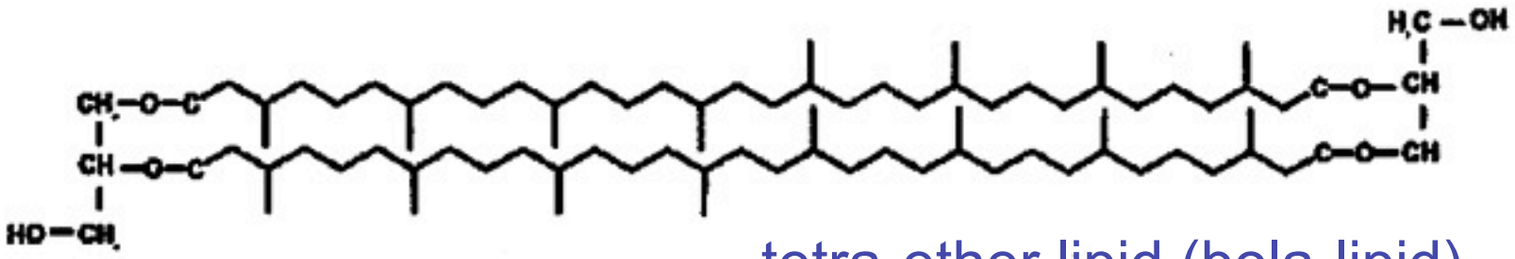
cardiolipin (gemini-lipid)

b



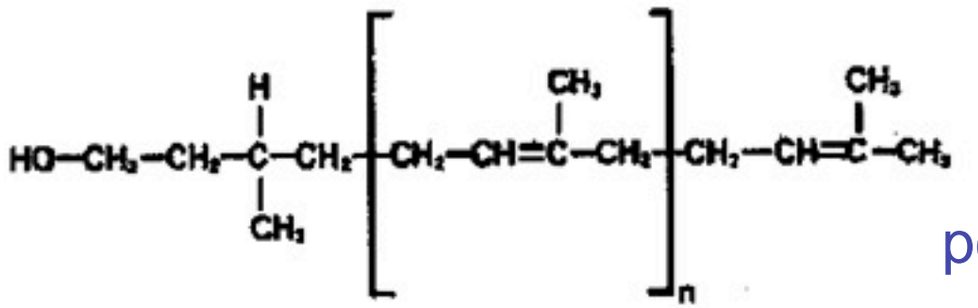
di-ether lipid

c



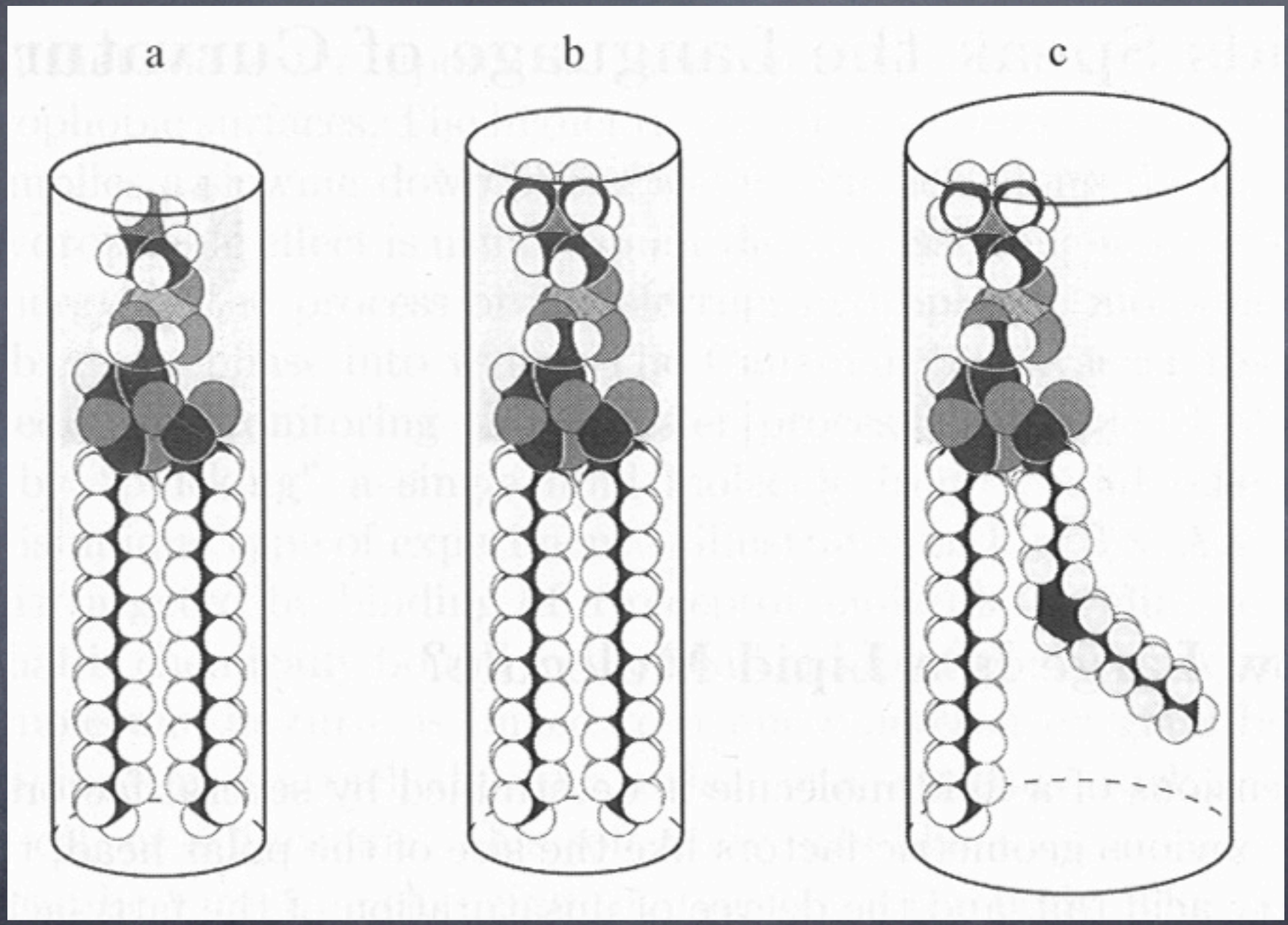
tetra-ether lipid (bola-lipid)

d



polyisoprenoid lipid

Lipid dimensions



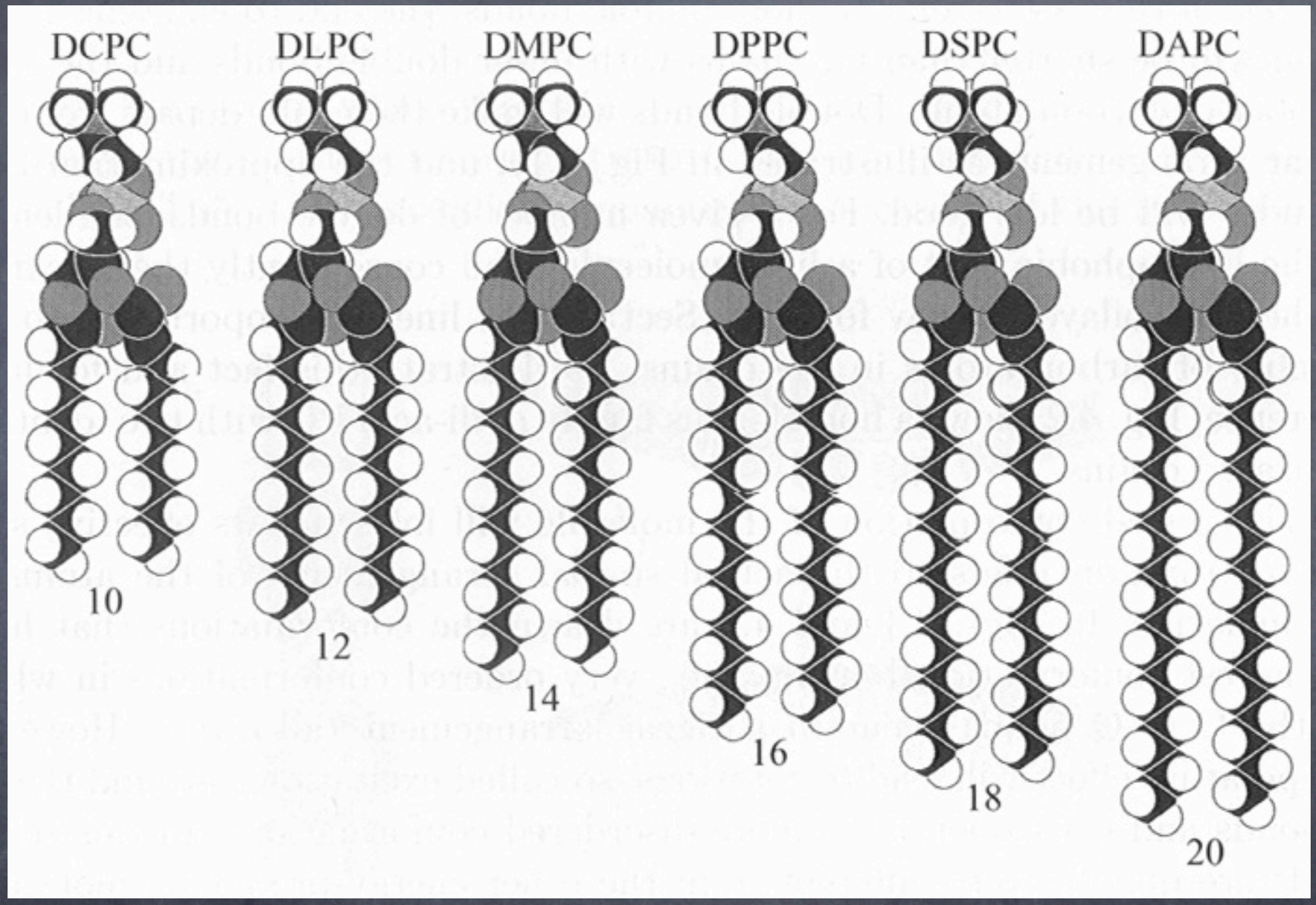
Schematic illustrations of the dimensions of lipid molecules:

a) DSPE

b) DSPC

c) SOPC

lipid dimensions

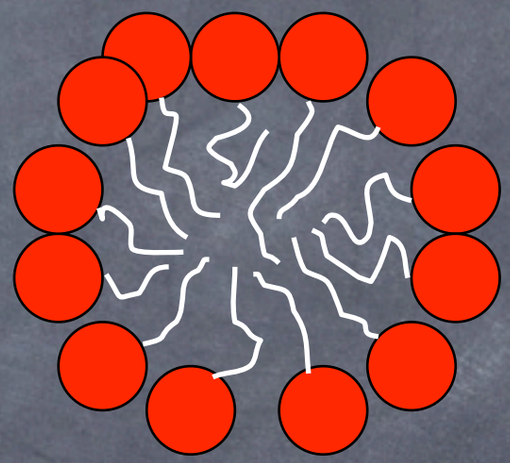


The homologous family of di-acyl PC lipids with two identical saturated chains

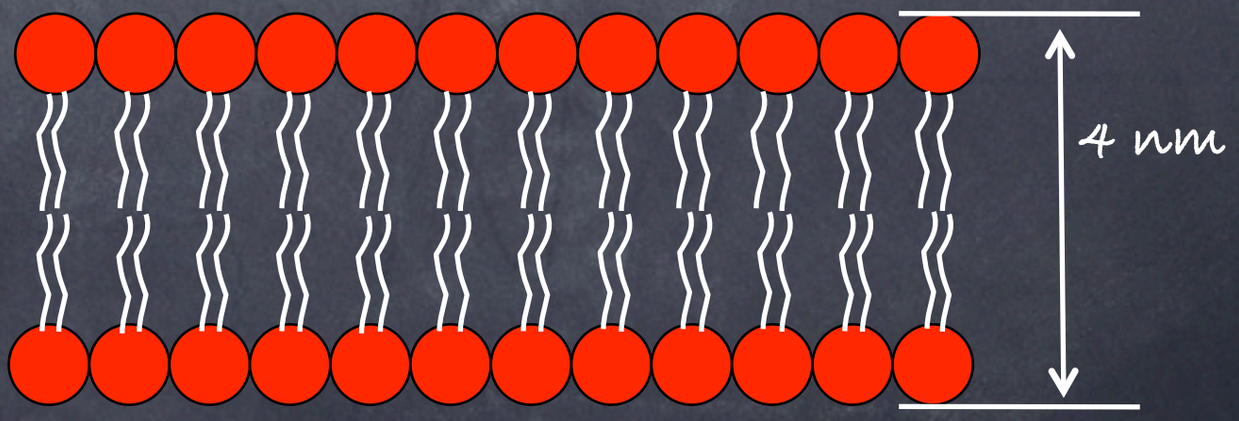
lipids = a class of amphiphilic molecules

the hydrophobic effect determines the structure of amphiphilic molecules in water. Above a critical concentration (crtical micelle concentration, CMC) amphiphilic molecules form aggregates, e.g.

SDS → micelles



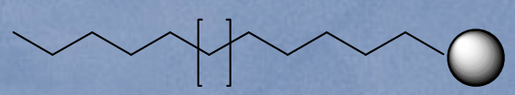
DPPC → lipid bilayers



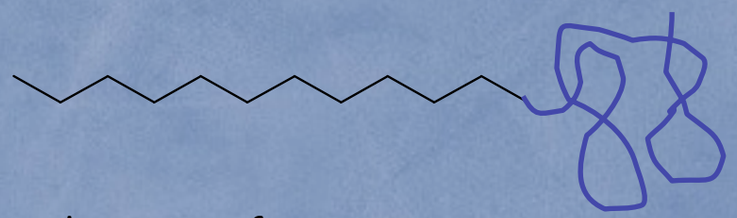
amphiphilic structures

low molecular weight amphiphiles

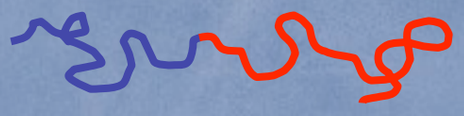
polymeric amphiphiles

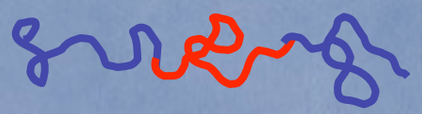


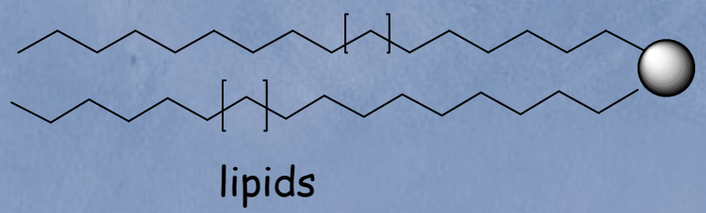
surfactant



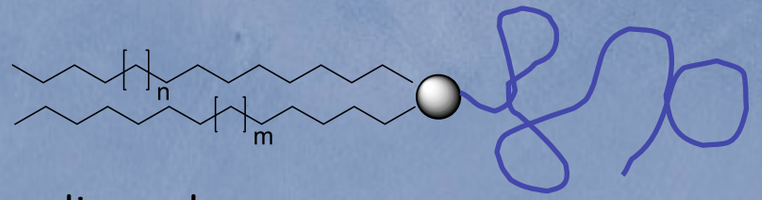
polymer-surfactant



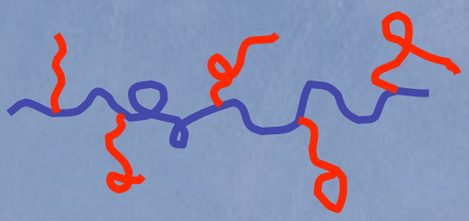


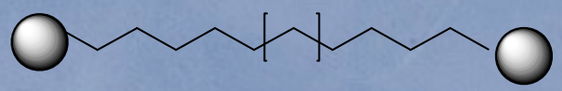


lipids

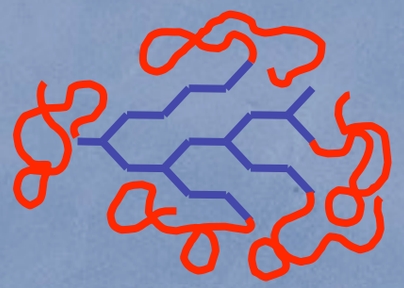


lipo-polymer

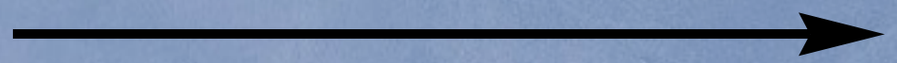




bola-Amphiphile



- structural diversity
- HLB (hydrophilic-lipophilic balance



type of amphiphiles

from Membrane Transport

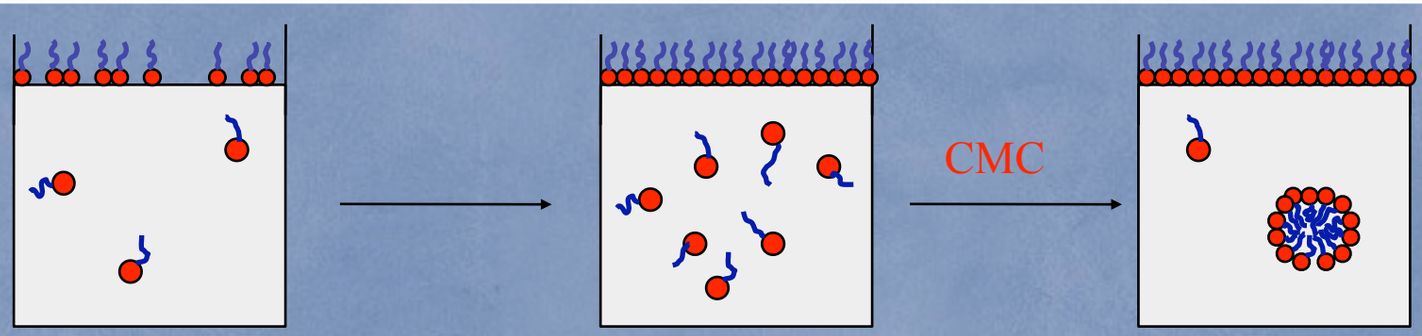
Table 2 Detergents used in the solubilization of membrane proteins

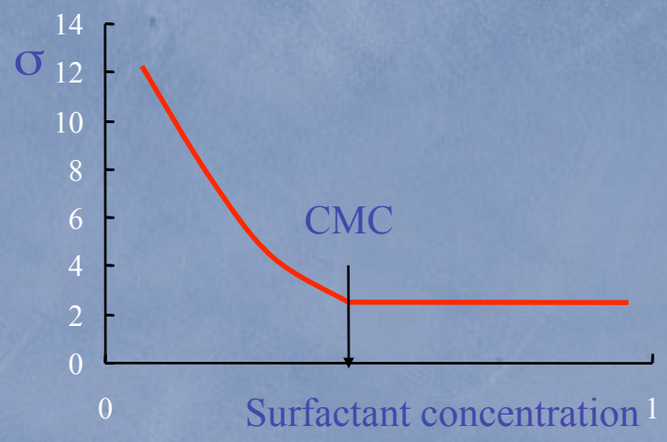
Biological detergent	Formula	Molecular weight (g/mol)	CMC (mM)	Aggregation number
Anionic				
Cholic acid, sodium salt	$C_{24}H_{39}O_5Na$	430.6	9.5 (pH 9.0), 14 (pH 7.5)	2–4
Deoxycholic acid, sodium salt	$C_{24}H_{39}O_4Na$	414.6	5	4–10
Lauryl sulfate, sodium salt (sodium dodecyl sulfate, SDS)	$C_{12}H_{25}NaSO_4$	288.4	2.6 (pH 7.5), 8.27 (H_2O)	60–100
Taurocholic acid, sodium salt	$C_{26}H_{44}NNaO_7S$	537.7	3–11 (0.05 M NaCl)	4
Taurodeoxycholic acid, sodium salt	$C_{26}H_{44}NNaO_6S$	521.7	1–4 (0.05 M NaCl)	6
Cationic				
Cetyltrimethylammonium bromide (CTAB, Hexadecyltrimethylammonium bromide	$C_{19}H_{42}NBr$	364.5	1	169
Dodecyltrimethylammonium bromide	$C_{15}H_{34}NBr$	308.3	14	—
Zwitterionic				
CHAPS	$C_{32}H_{58}N_2O_7S$	614.9	8 (H_2O)	10 (H_2O)
CHAPSO	$C_{32}H_{58}N_2O_8S$	630.9	8 (H_2O)	11 (H_2O)
DHPC (diheptanoylphosphatidylcholine)	$C_{22}H_{44}NO_8P$	481	1	—
LDAO (lauryldimethylamine-*N*-oxide)	$C_{14}H_{31}NO$	229.4	1–2	76
Zwittergent 3-08 (3-(*N*,*N*-dimethyloctylammonio)-propansulfonate)	$C_{13}H_{29}NO_3S$	279.4	330	—
Zwittergent 3-10 (3-decyldimethylammonio)-propansulfonate)	$C_{15}H_{33}NO_3S$	307.5	25–40	41
Zwittergent 3-12 (3-(*N*,*N*-dimethyllaurylammonio)-propansulfonate) (lauryl sulfobetain, SB-12)	$C_{17}H_{37}NO_3S$	335.5	2–4	55
Zwittergent 3-14 (3-(*N*,*N*-dimethylmyristylammonio)-propansulfonate)	$C_{19}H_{41}NO_3S$	363.6	0.1–0.4	83
Zwittergent 3-16 (3-(*N*,*N*-dimethylpalmitylammonio)-propansulfonate)	$C_{21}H_{45}NO_3S$	391.7	0.01–0.06	155

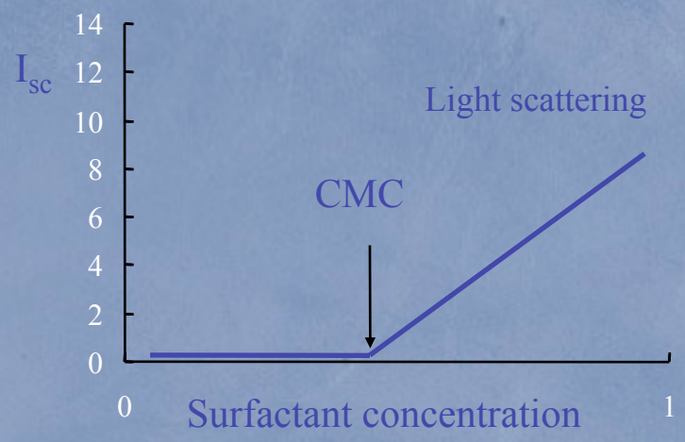
type of amphiphiles

Biological detergent	Formula	Molecular weight (g/mol)	CMC (mM)	Aggregation number
Non-Ionic				
BIGCHAP	$C_{42}H_{75}N_3O_{16}$	878.1	3.4	10
Deoxy-BIGCHAP	$C_{42}H_{75}N_3O_{15}$	862.1	1.1–1.4	8–16
Brij 35 (polyethyleneglycol-dodecylether, $C_{12}E_{23}$)	—	—	0.05–0.1	40
Digitonin	$C_{56}H_{92}O_{29}$	1229.3	—	5–6
n-Decyl-β-D-glucopyranoside	$C_{16}H_{32}O_6$	320.4	2.2 (H_2O), 2.3 (0.01 M PBS)	—
n-Decyl-hexaethyleneglycolether ($C_{10}E_6$)	$C_{22}H_{46}O_7$	422.6	0.9 (0.05 M NaCl)	—
n-Decyl-β-D-maltopyranoside (DM)	$C_{22}H_{42}O_{11}$	482.6	1.8 (0.15 M NaCl)	—
n-Dodecyl-nonaethyleneglycolether ($C_{12}E_9$)	$C_{30}H_{62}O_{10}$	582.8	0.046 (0.01–0.2 M NaCl)	—
n-Dodecyl-β-D-glucopyranoside	$C_{18}H_{36}O_6$	348.5	0.19 (H_2O), 0.13 (0.05 M NaCl)	—
n-Dodecyl-hexaethyleneglycolether ($C_{12}E_6$)	$C_{24}H_{50}O_7$	450.6	0.087 (0.05 M NaCl)	—
n-Dodecyl-octaethyleneglycolether ($C_{12}E_8$)	$C_{28}H_{58}O_9$	538.8	0.05–0.1 (0.1–0.2 M NaCl)	120–127
n-Dodecyl-β-D-maltopyranoside (lauryl maltoside, DDM)	$C_{24}H_{46}O_{11}$	510.6	0.17 (H_2O)	98
HECAMEG (methyl-6-O-(*N*-heptyl-carbamoyl)-α-D-glucopyranoside	$C_{15}H_{29}NO_7$	335.4	19.5	—
n-Heptyl-β-D-glucopyranoside	$C_{13}H_{26}O_6$	278.3	79	—
n-Heptyl-β-D-thioglucopyranoside (HTG)	$C_{13}H_{26}O_5S$	294.4	30	—
Lubrol ($C_{12}E_{9-10}$)	—	582	0.1 (0–0.05 M NaCl)	110 (0–0.1 M NaCl)
Mega-8 (*N*-octanoyl-*N*-methylglucamine)	$C_{15}H_{31}NO_6$	321.4	79 (H_2O). 58 (0.05 M NaCl)	—
Mega-9 (*N*-nonanoyl-*N*-methylglucamine)	$C_{16}H_{33}NO_6$	335.5	25 (H_2O)	—
Mega-10 (*N*-decanoyl-*N*-methylglucamine)	$C_{17}H_{35}NO_6$	349.5	6–7 (H_2O)	—
n-Nonyl-β-D-glucopyranoside (NG)	$C_{15}H_{30}O_6$	306.4	6.2–6.5 (0.15 M NaCl), 3.5 (1 M NaClO	—
Nonidet P-40 (NP-40) (Octylphenoxypolyethoxyethanol)	—	603.0	0.05–0.3	—
n-Octyl-β-D-glucopyranoside (OG)	$C_{14}H_{28}O_6$	292.4	24.4 (H_2O), 23.4 (0.1 M NaCl)	—
n-Octyl-β-D-thioglucopyranoside (OTG)	$C_{14}H_{28}O_6S$	308.4	9 (H_2O)	—
Octyl polydisperse oligooxyethylene (8-POE) ($C_8E_{3-11,\ mean\ n=5}$)	—	—	6.6	—
Octyl tetraoxyethylene (C_8E_4)	$C_{16}H_{34}O_5$	306.45	6	—
Tween-20 (polyoxyethylene (20) sorbitan monolaurate	—	1227.54	0.059	—
Tween-80 (polyoxyethylene (80) sorbitan monolaurate	—	1309.68	0.012	—
Triton X-100 (polyethylene glyco-*p*-isooctylphenyl ether)	—	625	0.3 (H_2O), 0.29 (0.1 M NaCl)	100–155
Triton X-100 hydrogenated	—	631	0.25 (0.05 M NaCl)	—
Triton X-114 (cloud point 22°C)	—	537	0.2	—

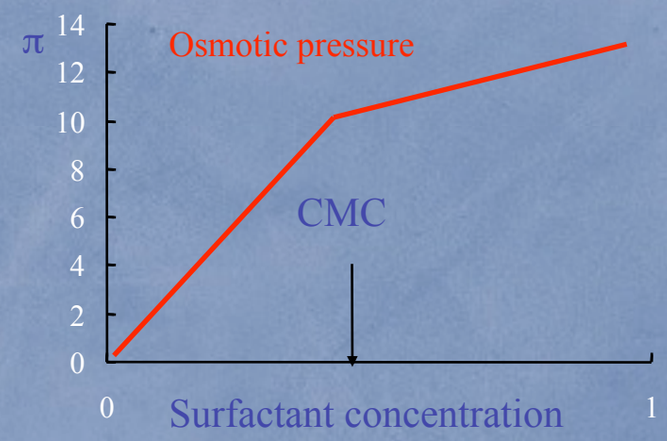
Critical micelle concentration (CMC)

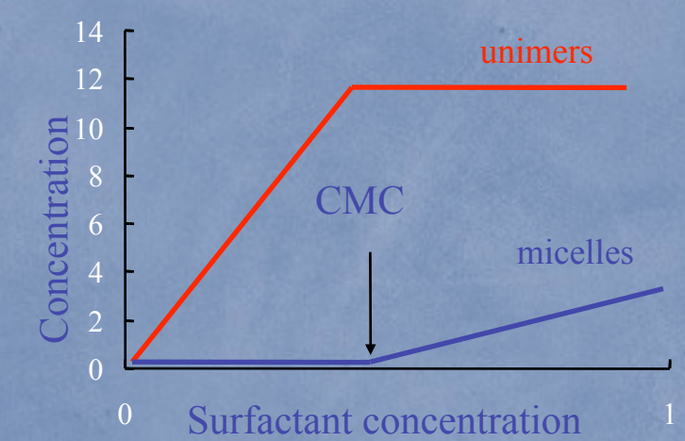




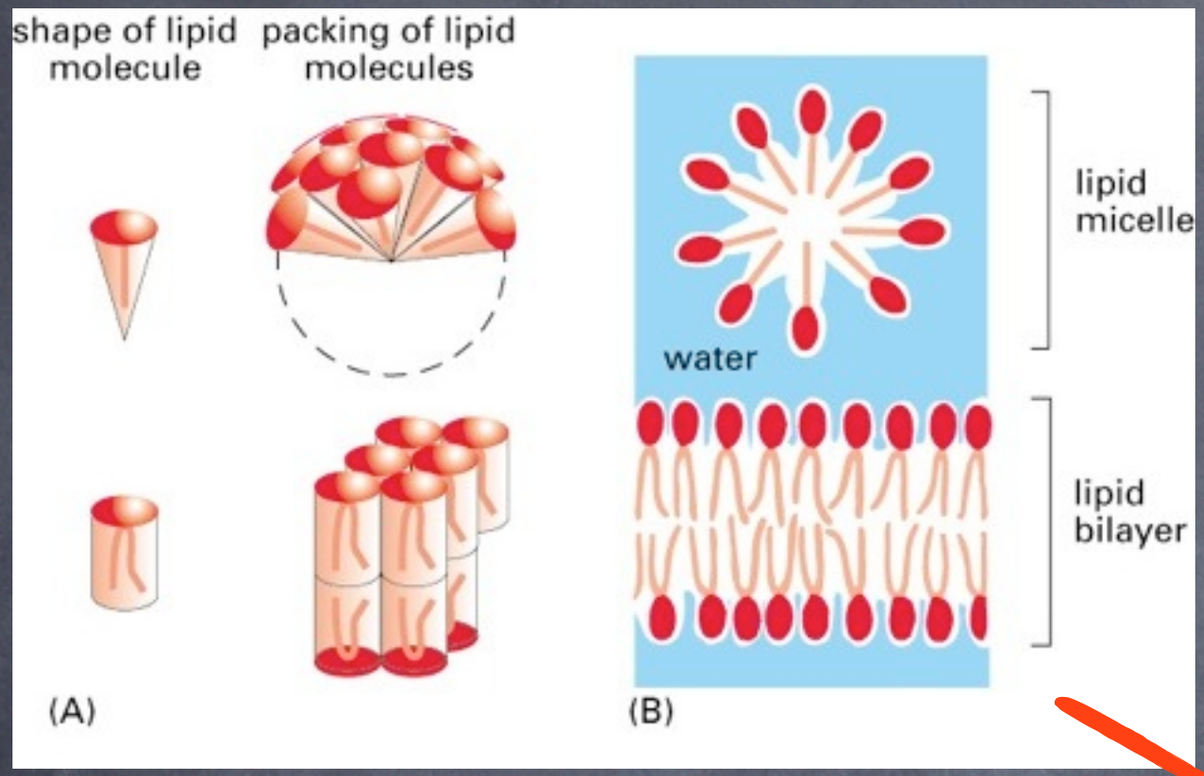


- Below CMC only unimers are present
- Above CMC there are micelles in equilibrium with unimers

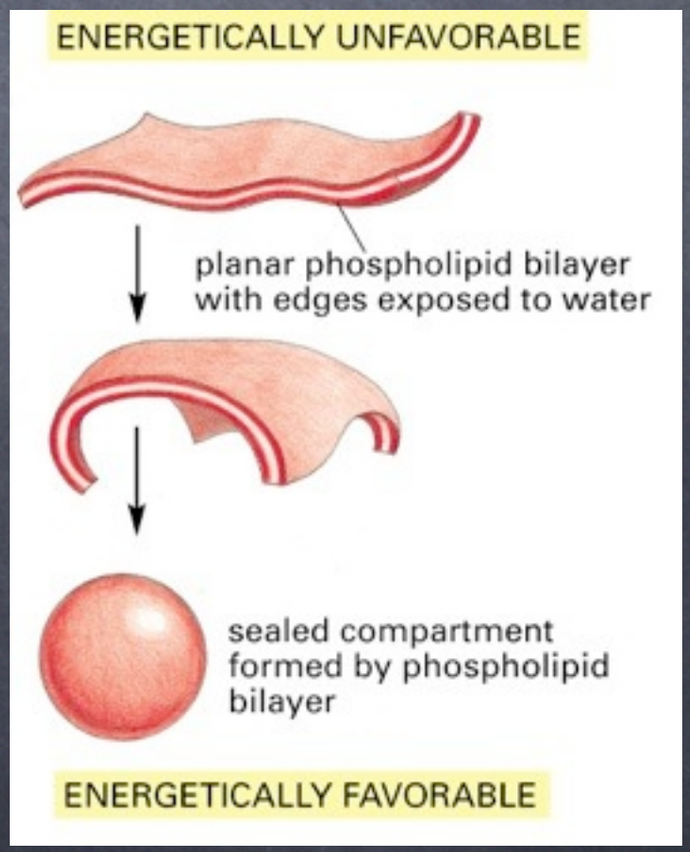




lipids



Amphipilic molecules pack so as to minimize the interaction between water and the nonpolar part of the molecule. The two hydrocarbon tails give phospholipids a cylindrical shape that causes the molecules to pack as a bilayer in water.



Minimum contact between water and the hydrocarbon chains is achieved by forming the bilayer into a closed compartment.

surfactant packing parameter

association number: ratio of micelle volume to volume per molecule V

$$p = \frac{\frac{4}{3}\pi R_{mic}^3}{V}$$

R_{mic}: micelle radius

association number: ratio of micellar area to cross-sectional area per molecule a

$$p = \frac{4\pi R_{mic}^2}{a}$$

$$\Rightarrow \qquad \frac{V}{aR_{mic}} = \frac{1}{3}$$

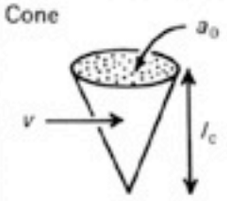
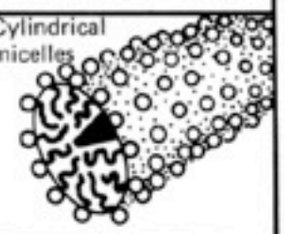
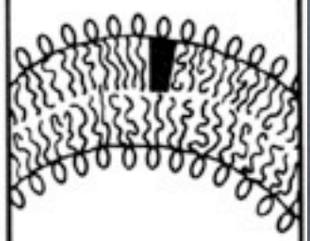
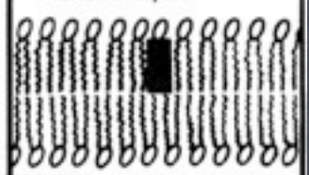
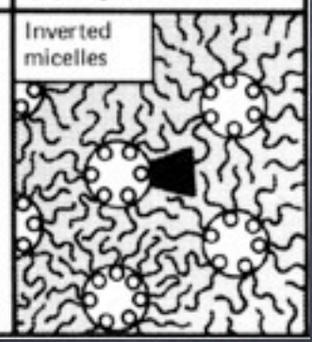
R_{mic} cannot exceed length of fully extended chain l

$$\frac{V}{al} \leq \frac{1}{3}$$

$$\Rightarrow \qquad N_s = \frac{V}{al}$$

N_s: surfactant (critical) packing parameter

prediction of assembly

Lipid	Critical packing parameter $v/a_o l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	< 1/3	Cone 	Spherical micelles 
Single-chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionic lipids*	1/3-1/2	Truncated cone 	Cylindrical micelles 
Double-chained lipids with large head-group areas, fluid chains: *Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG[a], dihexadecyl phosphate, dialkyl dimethyl ammonium salts*	1/2-1	Truncated cone 	Flexible bilayers, vesicles 
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: *phosphatidyl ethanolamine, phosphatidyl serine + Ca^{2+}*	~1	Cylinder 	Planar bilayers 
Double-chained lipids with small head-group areas, nonionic lipids, poly *(cis)* unsaturated chains, high *T*: *unsat. phosphatidyl ethanolamine, cardiolipin + Ca^{2+} phosphatidic acid + Ca^{2+} cholesterol, MGDG[b]*	> 1	Inverted truncated cone or wedge 	Inverted micelles 

"critical packing parameter"

$v / a_o l_c$

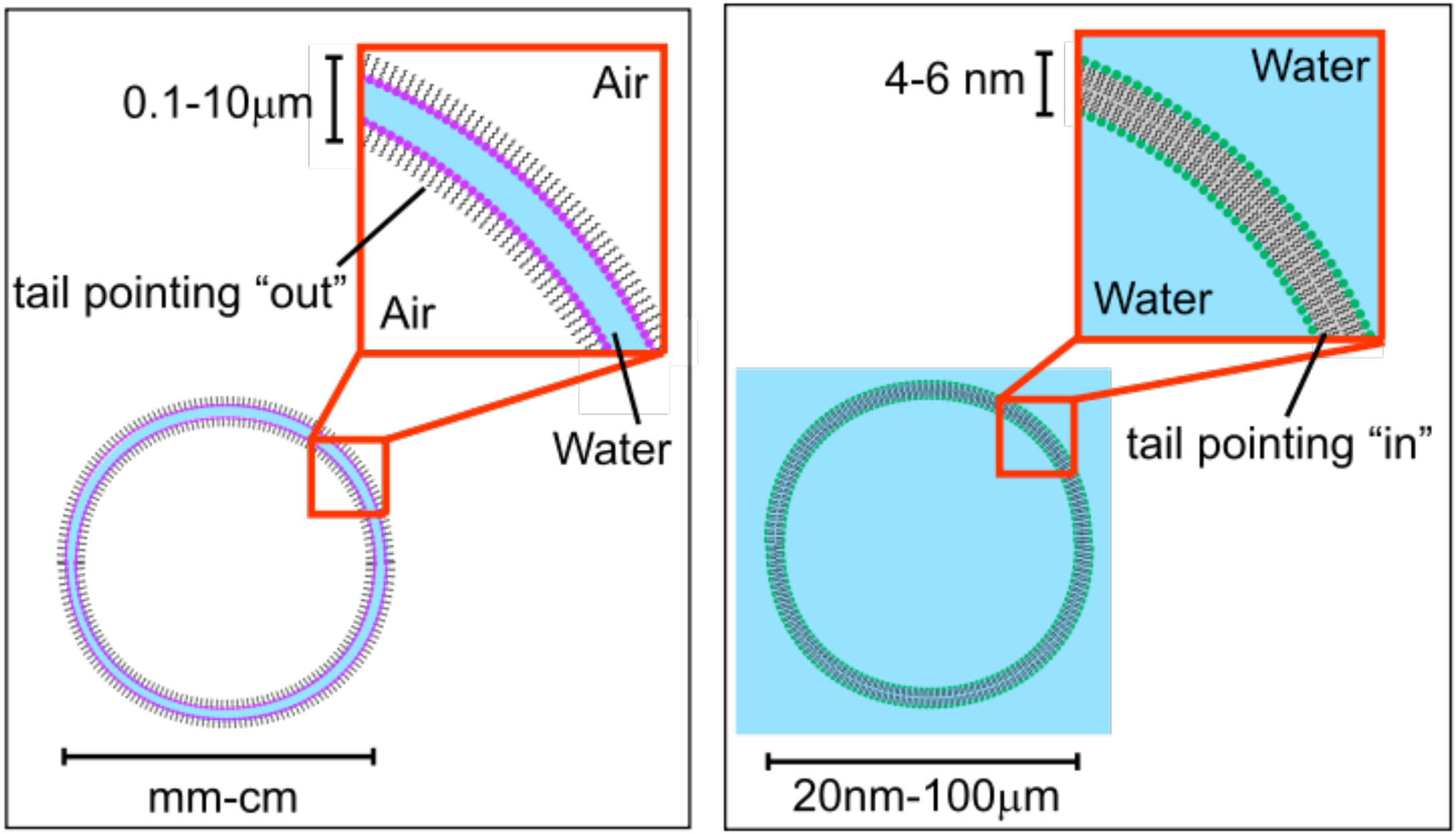
v = volume of amphiphile

a_o = area of head group

l_c = length of head group

can be approximated as the angle of the amphiphile cone or inverse cone

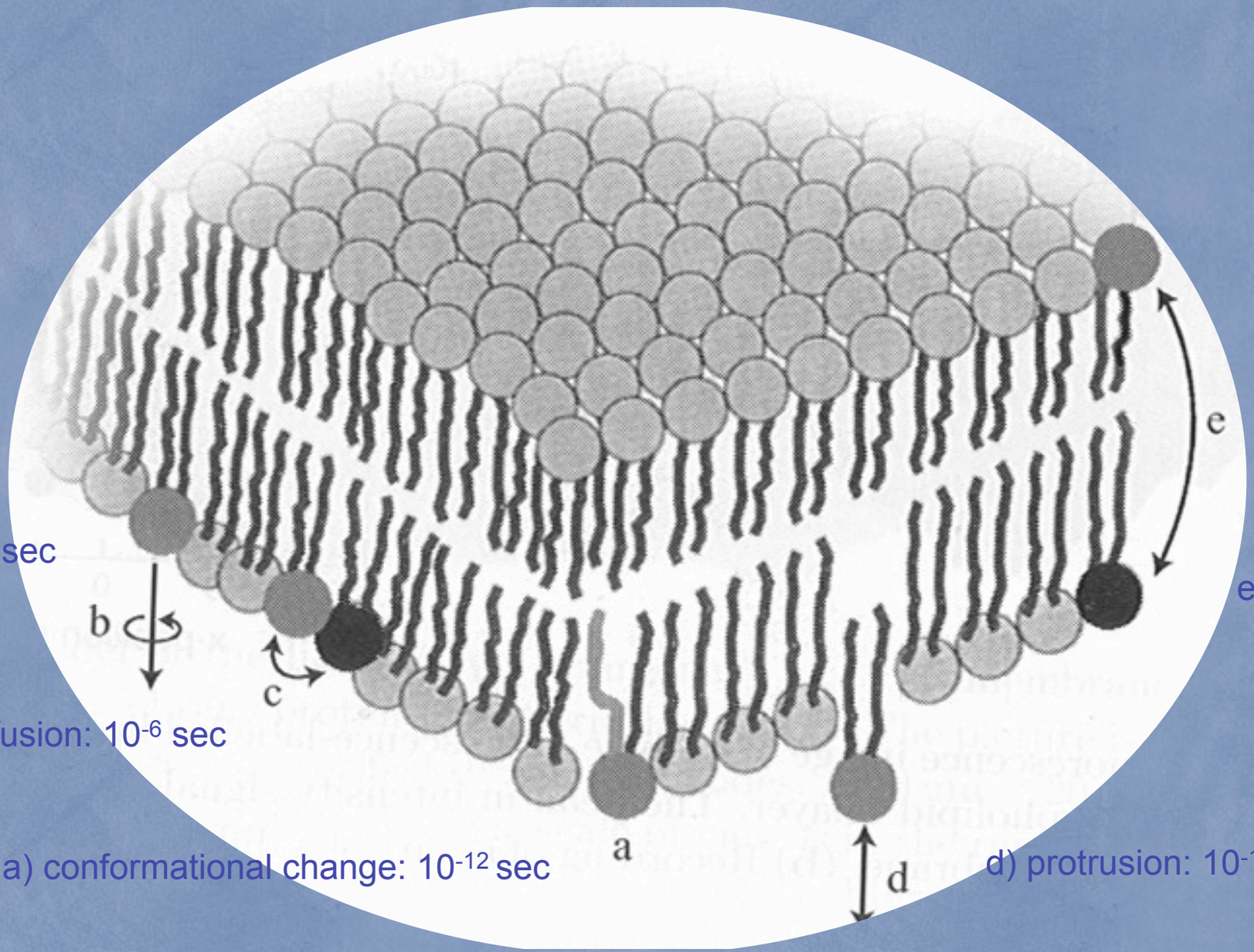
vesicle vs. soap bubble



Soap Bubble

Lipid Vesicle

"lipids on the move"



b) rotation: 10^{-9} sec

e) flip-flop: 10^{5} sec

c) lateral diffusion: 10^{-6} sec

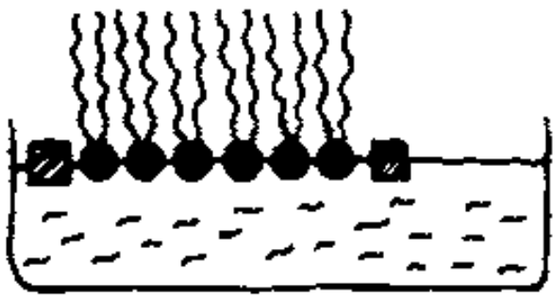
a) conformational change: 10^{-12} sec

d) protrusion: 10^{-12} sec

models of biomembranes

models of biomembranes

Langmuir films

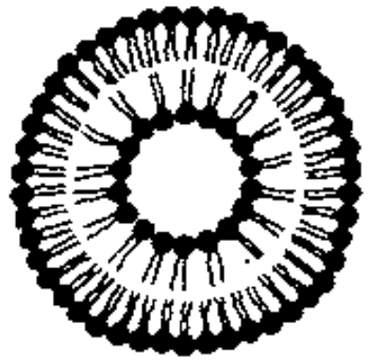


monolayer

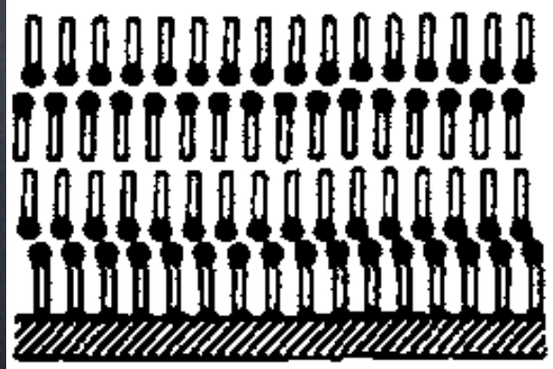
planar lipid membranes

free-standing bilayer (BLM)

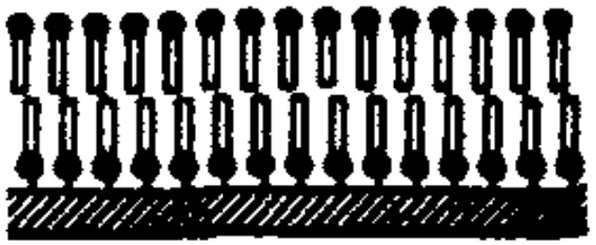
liposomes



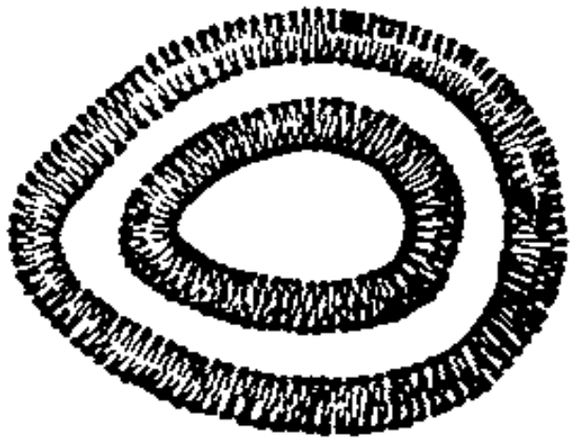
unilamellar



LB multilayer

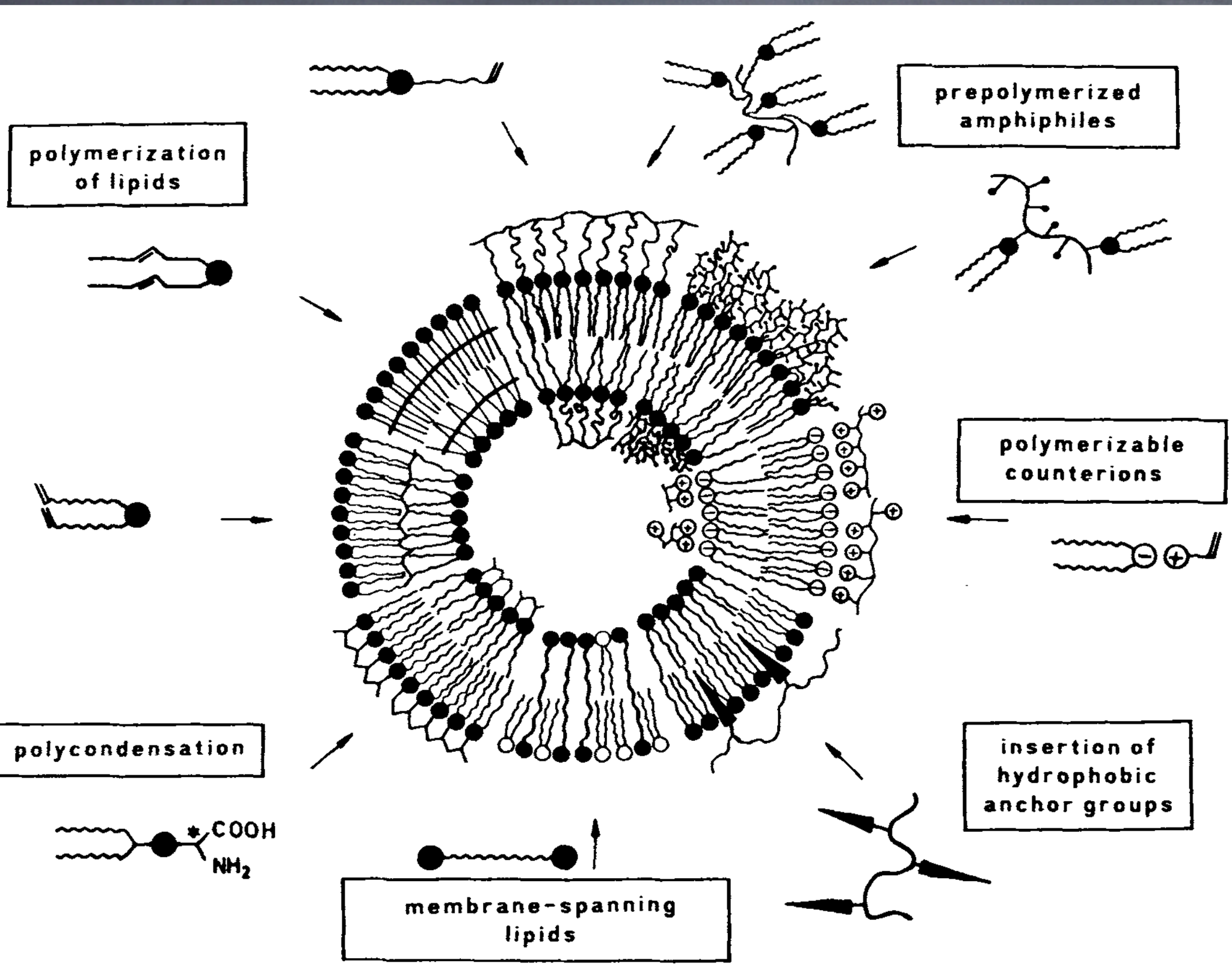


supported bilayer



multilamellar

membrane stabilization



membrane stabilization