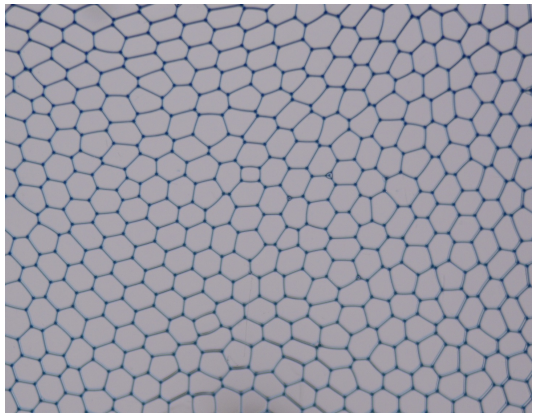
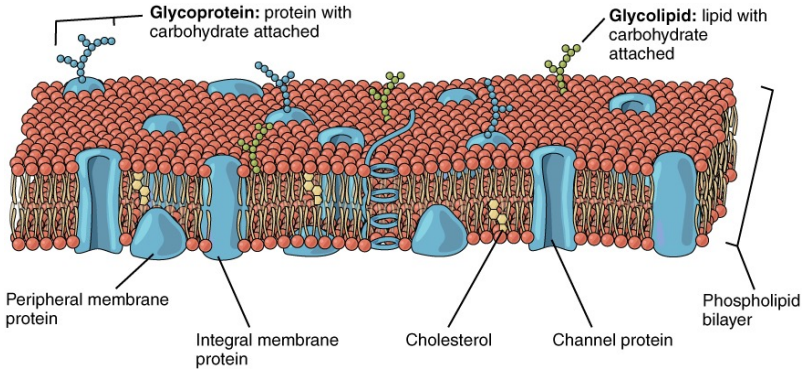
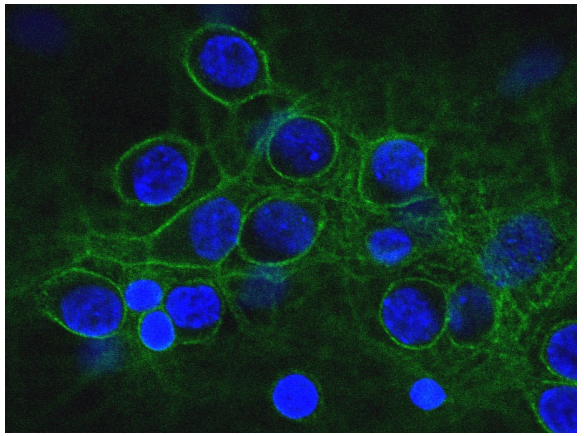
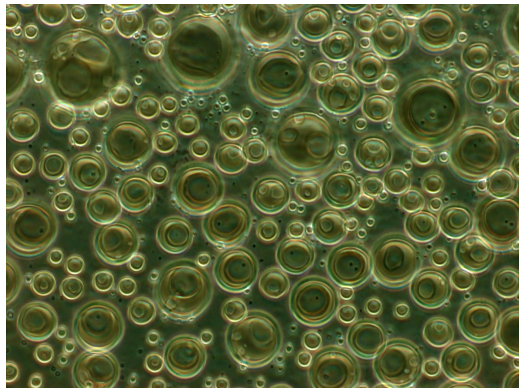
ME470: Mechanics of Soft and Biological Matter
Lecture8: Membrane and Interfaces







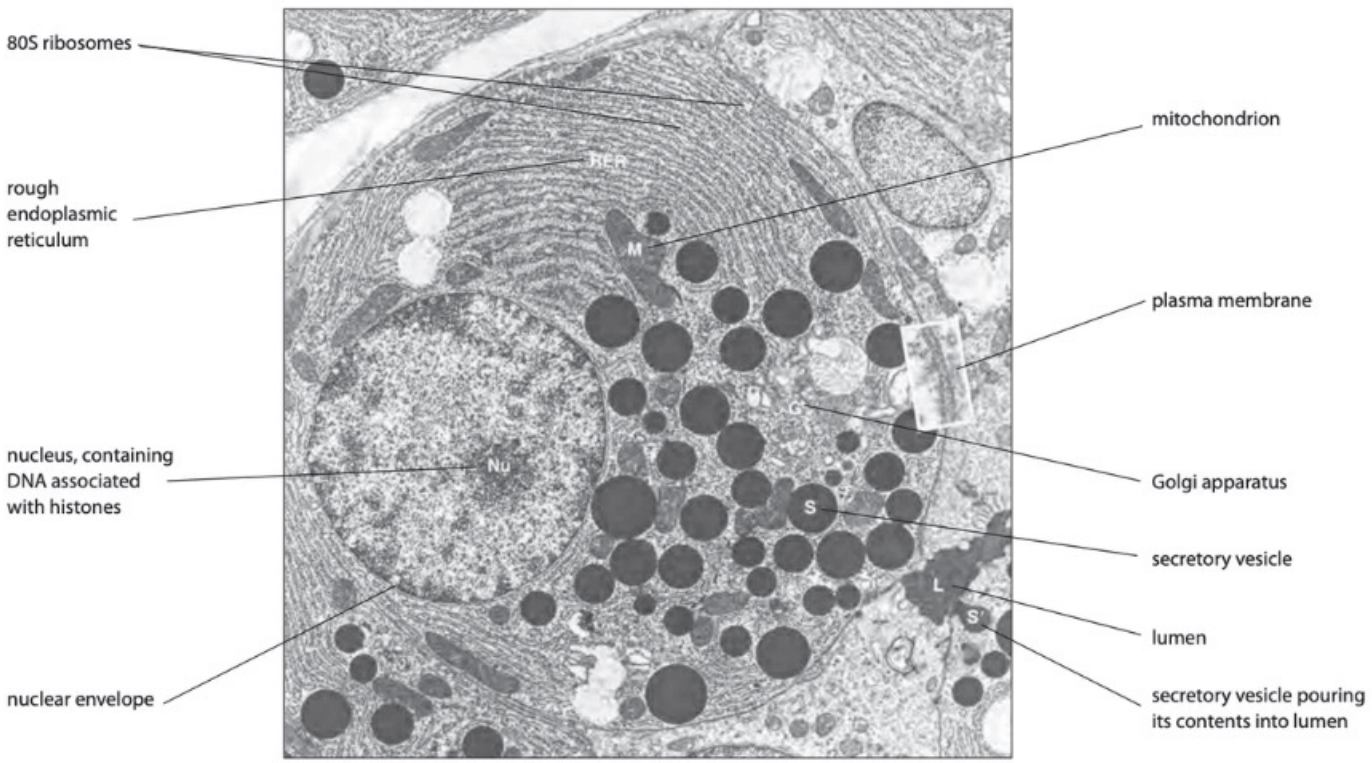


Red Blood Cells

Sangwoo Kim

MESOBIO – IGM – STI – EPFL

Motivation



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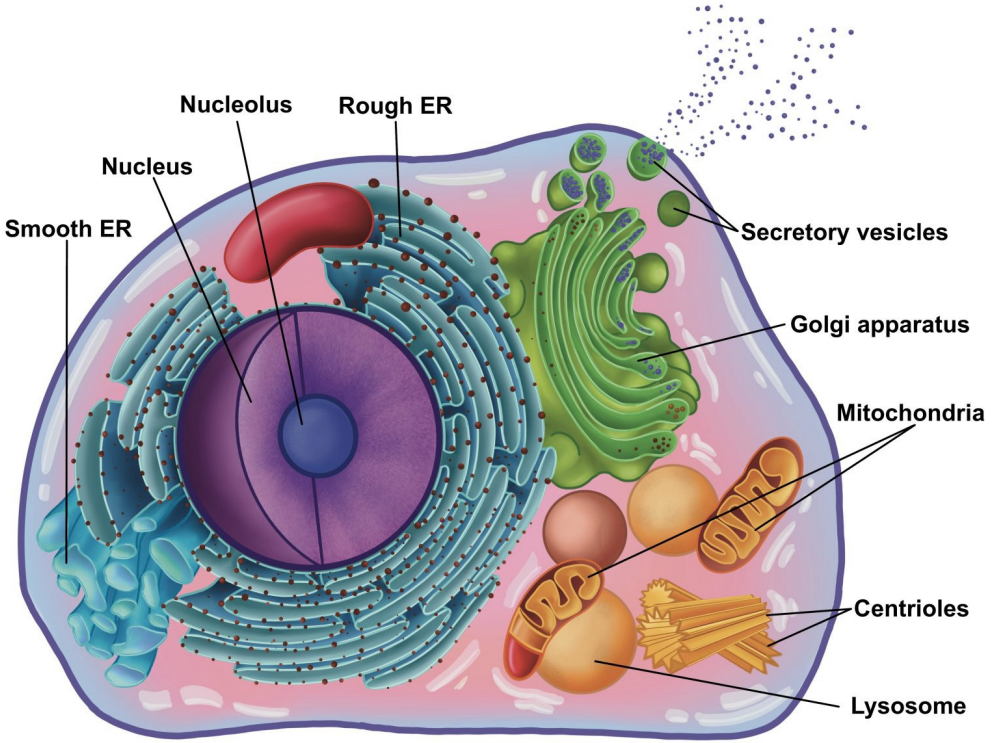

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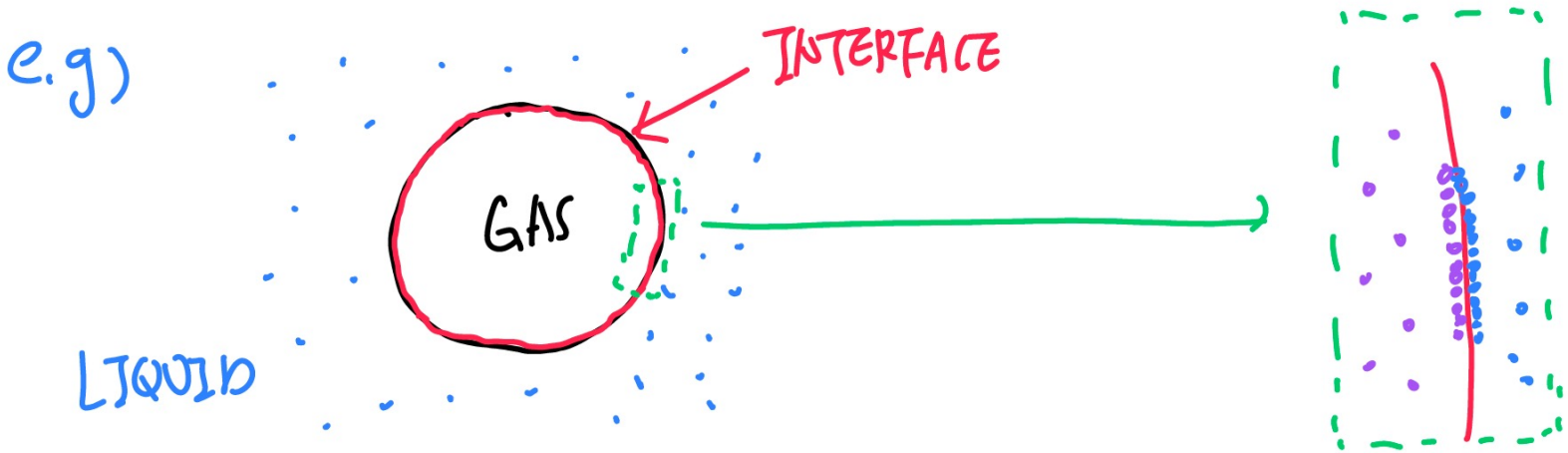
Membrane distinguishes inside and outside

⇨ Mechanics of membrane!!

Simple Interface



Energetically unfavorable to be neighbors to unlike molecules

⇨ Energy penalty $\propto A$

⇨ Change in free energy

$$dF = -SdT + \int \sigma_{ij} d\varepsilon_{ij}\, dV + \gamma dA$$

$-PdV$

Energy per area: interfacial tension

For isotropic stress (bubble)

Simple Interface

Consider a system of bubble + liquid

$$dV_{gas} = -dV_{liq} = dV \qquad \text{at constant T}$$

$$dF = -P_g dV + P_l dV + \gamma dA = 0$$

$$\Delta P = P_g - P_l = \gamma \frac{dA}{dV}$$

Young-Laplace law

For spherical bubble:

$$\Delta P = \frac{2\gamma}{R}$$

Note: looks like free enthalpy, $G = F_0 - \tau A$, where $\tau = \gamma$

Note: soap bubble in air, $\Delta P = 4\gamma/R$ (2 interfaces)

Note: such interface is NOT elastic.

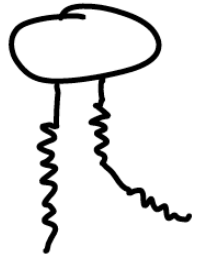
Surfactants

Detergent (e.g. SDS)

Hydrophilic head

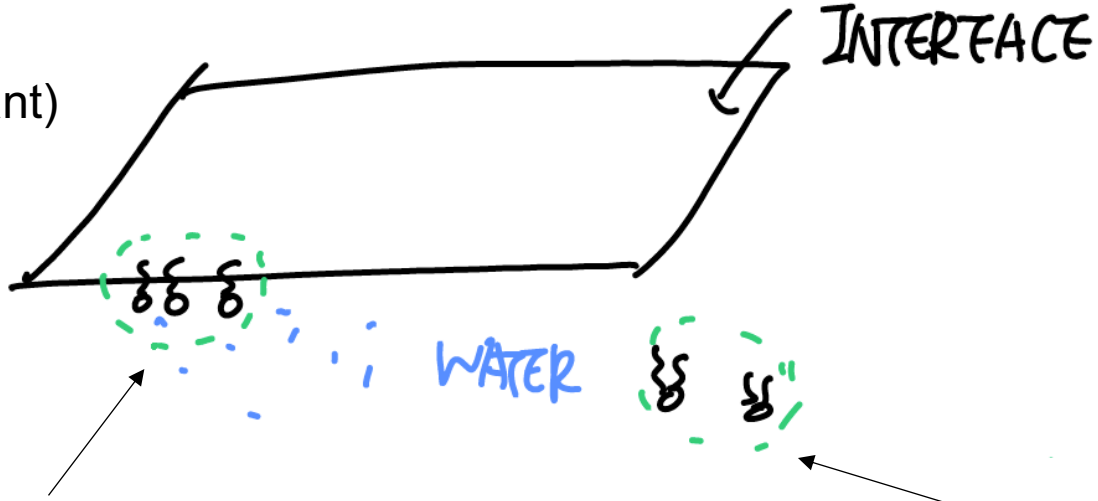
Hydrophobic tail

Phospholipids (e.g. DOPC)



2 ~ 2.5 nm

(T=Constant)



Micelle

At interface state (2):
Lower energy per molecule

In bulk state (1):
Higher entropy

Surfactants

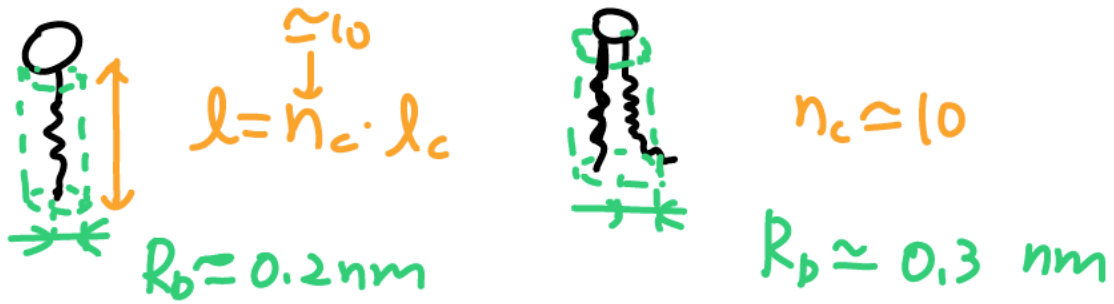
⇨ Minimize free energy: $\Delta F = F_1 - F_2 = \Delta U - T\Delta S$

Estimate ΔU: classical approximation

Using surface tension of the hydrocarbon chain w.r.t water

$$\gamma_D \approx \gamma_P \approx 0.05 N/m$$

Approximate geometry:
$l_c = 0.126nm$



$$\Delta U \approx 2\pi\gamma R n_c l_c \quad \Rightarrow \quad \Delta U_D \approx 20 k_B T \qquad \Delta U_P \approx 30 k_B T$$

Surfactants

⇨ Entropy: $\Delta S = S_1 - S_2 \approx S_1$

Model as ideal gas (non-interacting molecules):

$$S_1 = k_B \left[\frac{5}{2} - \ln\left(\frac{nh^3}{(2\pi m k_B T)^{3/2}} \right) \right]$$ Per molecules

n = volume density

m = molecular mass

$h = 6.626 \times 10^{-34} J \cdot s$ = Planck constant

Masses: $m_D \approx 400Da$, $m_P \approx 570Da$ $\quad (1Da \approx 1.66 \times 10^{-27} kg)$

ΔF can be either positive or negative depending on n

⇨ Critical concentration n_{agg}, where interface gets preferentially populated!

Surfactants

$\Delta F = 0$ ⇨

$$n_{agg} = \frac{(2\pi m k_B T)^{3/2}}{h^3} e^{5/2 - \Delta U / k_B T}$$

$n_{agg}^{(D)} \approx 0.3M$ (large concentration)

$n_{agg}^{(P)} \approx 2\times10^{-5}M$ (very small concentration)

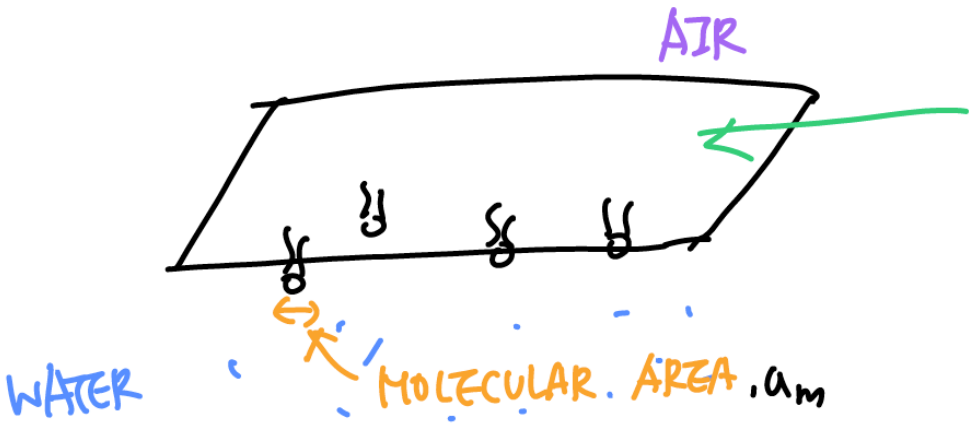
⇨ Phospholipids aggregate rarely leave interface (insoluble surfactants) while detergents are very soluble

⇨ Tightly packed phospholipids at the surface : MEMBRANE!

Note: $n_{agg} = n_{micelle}$ (same energetic argument)

Note: some surfactants make inverted micelles in oil if the geometry is right

Monolayers



Area per molecule @ interface: a

⇨ $(a - a_m)$: surface exposed to air molecule

⇨ Surface energy cost: $U_I = \gamma(a - a_m)$

⇨ Repulsive interaction between molecules:

$$U_p = \alpha \frac{1}{a^k}$$

α, k: constant

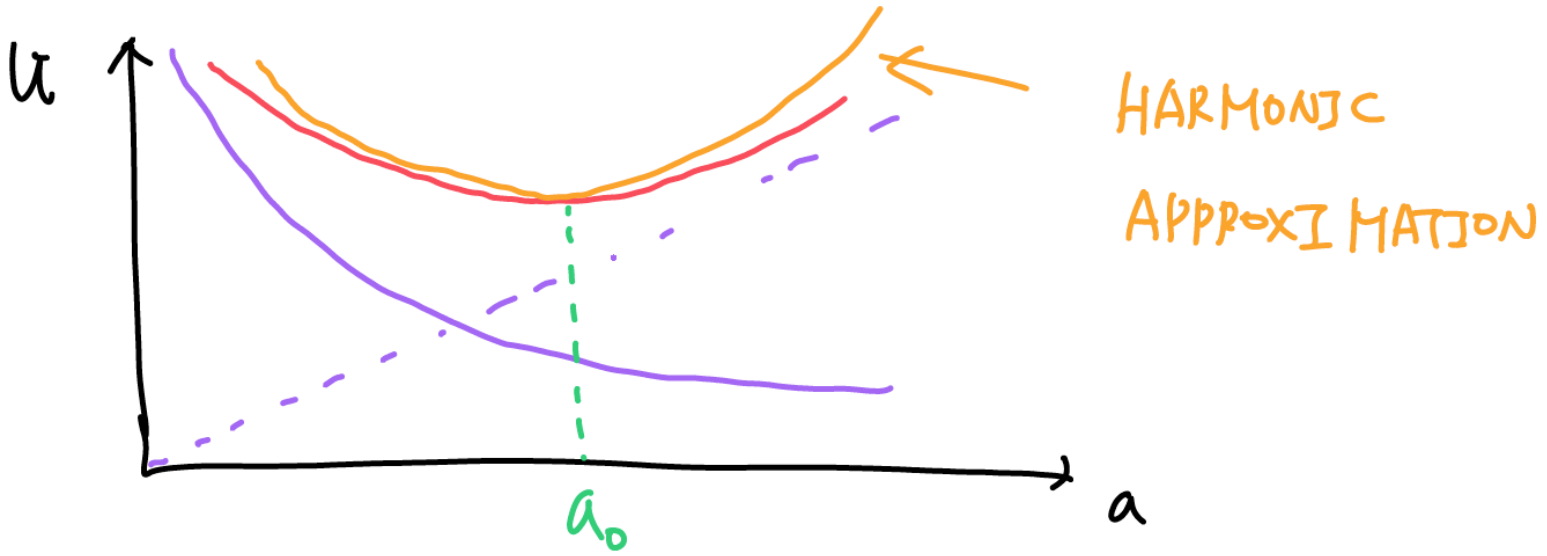
Theory: $k = 1$: Coulomb

$k = 2$: Steric repulsion

Monolayers

constant

$$U(a) = U_I + U_p = \gamma a + \frac{\alpha}{a^k} - \gamma a_m$$



$$\frac{\partial U}{\partial a} = 0 \quad \Rightarrow \quad a_0 = \left(\frac{k\alpha}{\gamma}\right)^{1/(k+1)}$$

Taylor expansion (exercise):

$$U - U(a_0) = \frac{k+1}{2}\gamma \cdot \frac{(a-a_0)^2}{a_0} + H.O.T$$

Monolayers

Compare to 2D continuum material:

$$u_A = \frac{U - U(a_0)}{\partial a} = \frac{k+1}{2}\gamma \cdot \left(\frac{a - a_0}{a_0}\right)^2 = \frac{1}{2} K_A \varepsilon_{ll}^2$$

$$\Rightarrow \quad \boxed{K_A = (k+1)\gamma}$$

Langmuir trough measurements: often presented as effective surface pressure

$$\Pi_{eff} = -\frac{\partial U}{\partial a} = \frac{k\alpha}{a^{k+1}} - \gamma$$

Micelles, Bilayers, Membrane Mechanics

Q: what will happen if we force PL molecules in bulk water?

PL bilayers ⟺ Cell membrane

Goal: describe bilayer mechanics as 2D continuum

1. Extension/compression
2. Shear
3. Bending (not independent)