Interface and Self Assembly

Nick Fang

Course Website: **nanoHUB.org**
Compass.illinois.edu

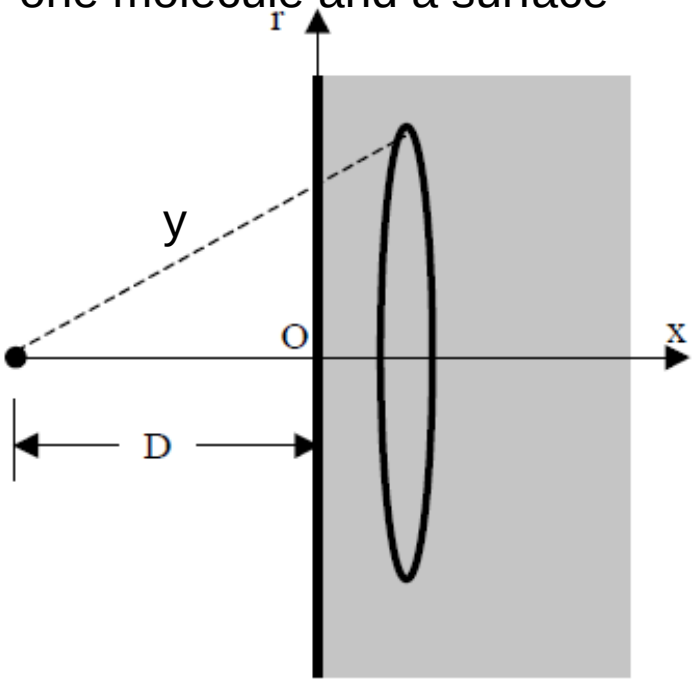
Proposal (Oct 12-16)

- Please send me your intended topic by tomorrow
- Based of similarity of topics you may be asked to work/present as group
- A tentative schedule will be posted on Friday

Origin of Adhesion: VdW Forces

- Van de Waals force: the long range interactions between molecules
- Recall the potential energy: $\phi = -\frac{\alpha}{r^6} + \frac{\beta}{r^n} \quad (n \approx 12)$

Let's find the interaction between one molecule and a surface



At distance x in the wall, consider a circle of radius r:

$$y = \sqrt{(D+x)^2 + r^2}$$

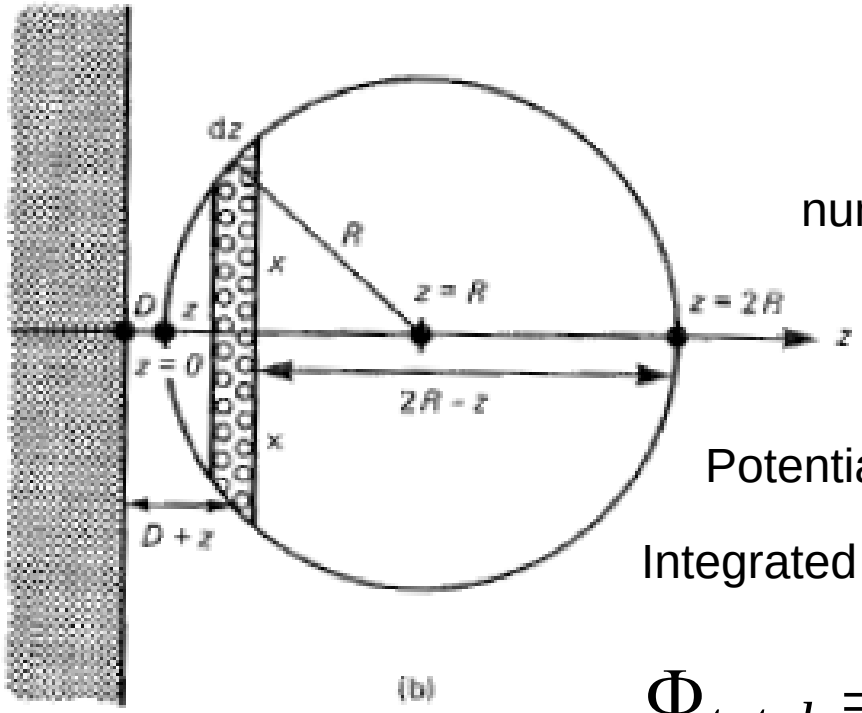
Number density of molecules in wall

$$\Phi(D) = \int_0^\infty \int_0^\infty \rho\phi(y) 2\pi r dr dx$$

$$\Phi(D) = -\frac{\pi\rho\alpha}{6D^3}$$

Example: Sphere to Flat Surface

Consider a thin sheet at location *z* on the sphere:



Radius $x = \sqrt{(2R - z)z}$

number of molecules on this sheet:

$$\rho_2 \pi x^2 dz = \rho_2 \pi (2R - z) z dz$$

Potential energy per molecule: $\Phi(D+z) = -\dfrac{\pi \rho_1 \alpha}{6(D+z)^3}$

Integrated over whole sphere:

$$\Phi_{total} = -\rho_1 \rho_2 \pi^2 \alpha \int_0^{2R} \frac{(2R - z)z}{6(D+z)^3} dz$$

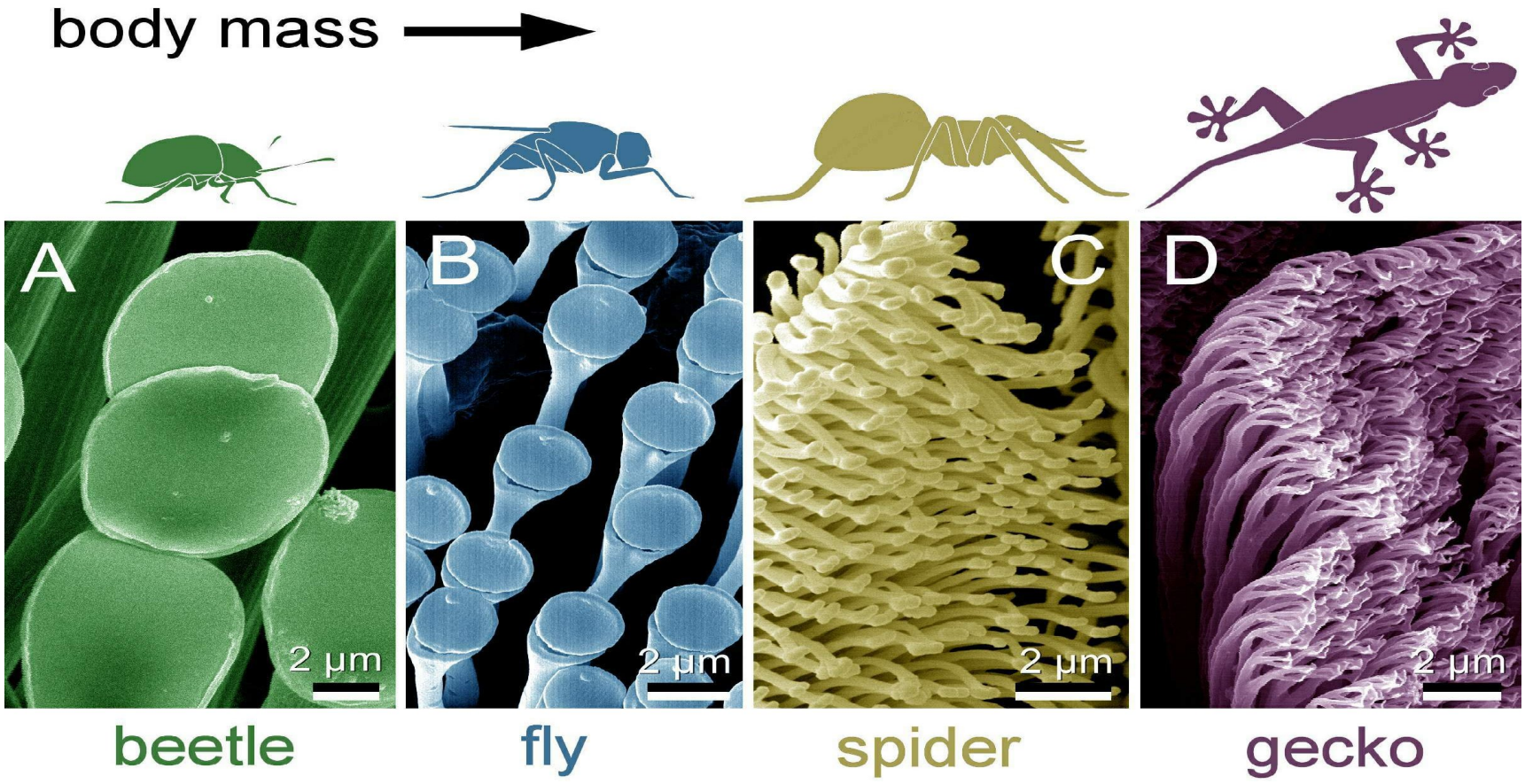
When D<<R, 2R-z ~2R

$$\Phi_{total}(D) \approx -\frac{\rho_1 \rho_2 \alpha \pi^2 R}{6D}$$

← Size of contact

← Distance of contact

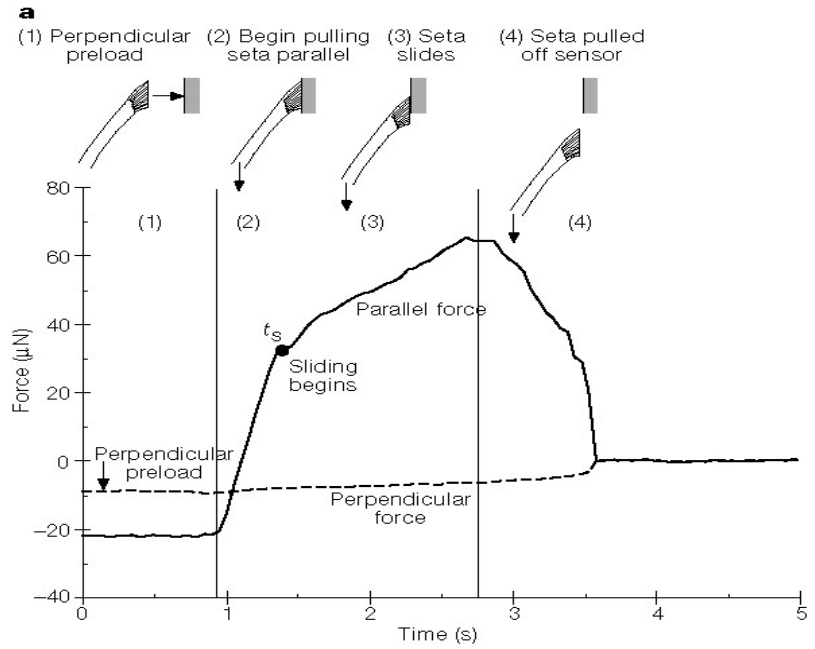
Adhesion Enhancement by Nano-toes

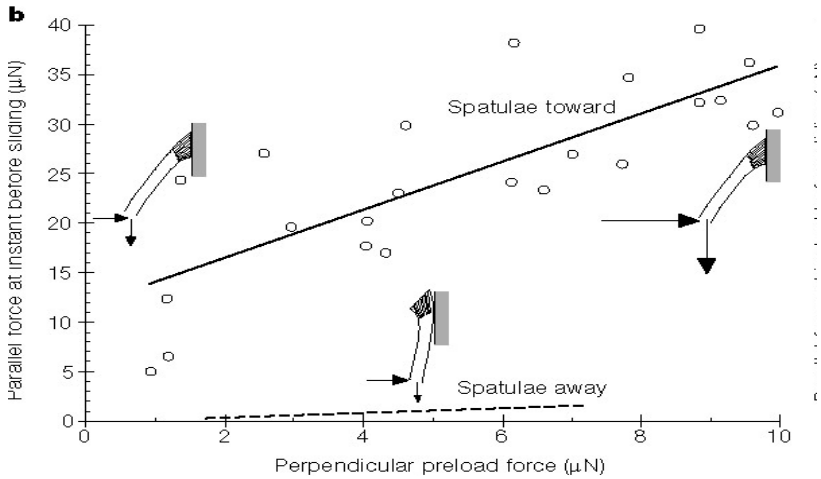


http://shasta.mpi-stuttgart.mpg.de/research/Bio-tribology.htm

$$\Phi_{total}(D) \approx -\frac{\rho_1 \rho_2 \alpha \pi^2 R}{6D}$$

How Can a Gecko Lift Its Foot Off?





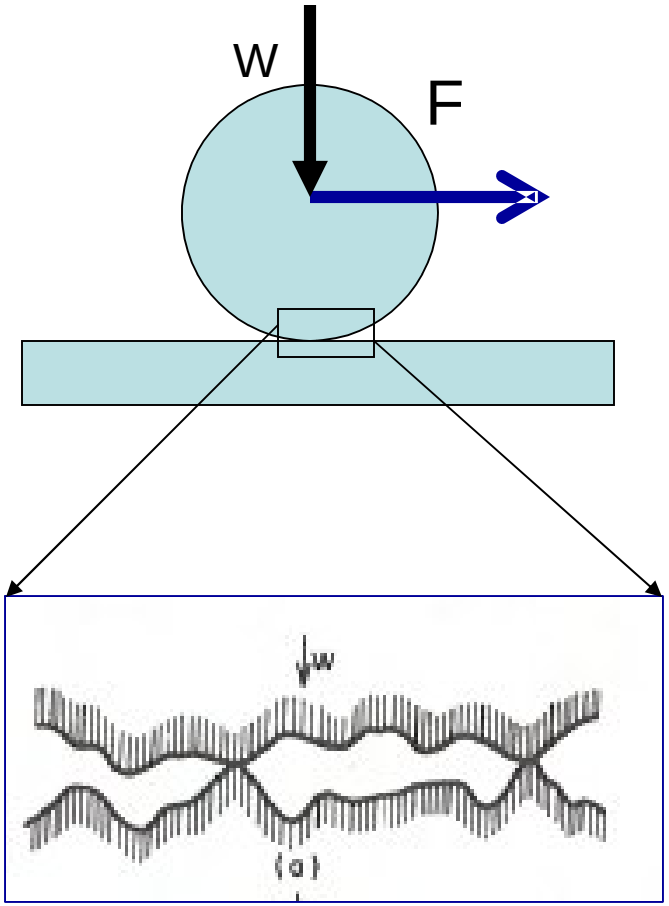
"These lizards uncurl their toes like a paper party favor whistle when putting their feet down;

- and peel the toes back up as if removing a piece of tape when they step away."

Chemical & Engineering News, 2000

K. Autumn et al, Nature 405, 681-685(2000)

Microscopic View of Friction



$$F \approx \frac{A}{D}(\gamma_A - \gamma_R)$$

Surface energy in Advancing contact

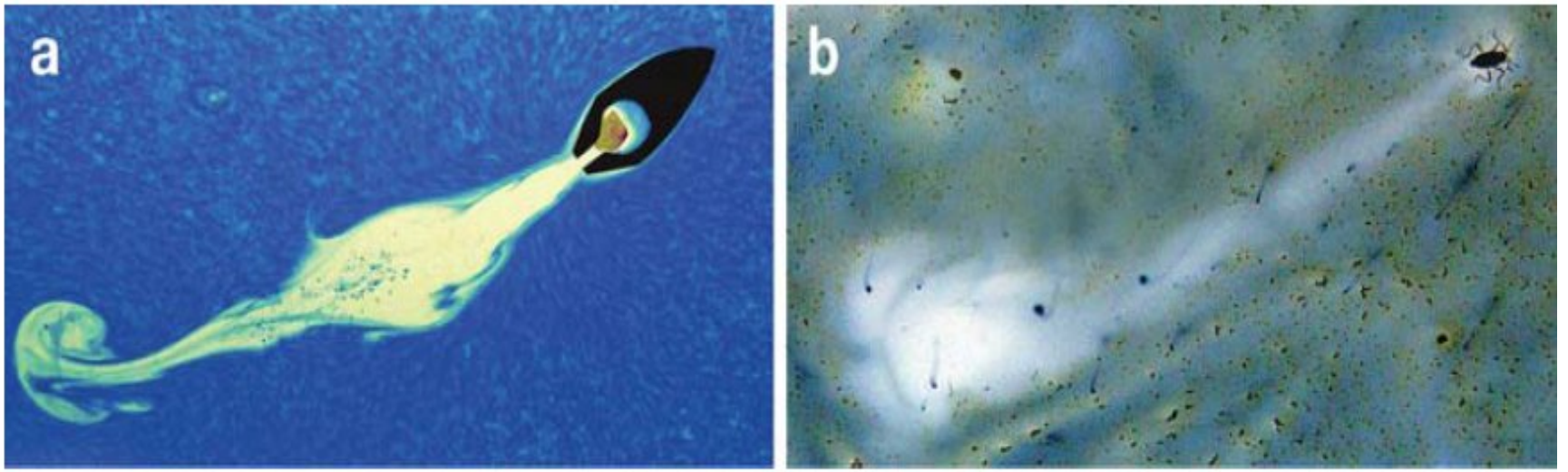
Surface energy in Receding contact

Derjaguin (1957) proposed correction of friction

$$F \approx \mu W + \mu A p_0$$

Due to adhesion energy (no external force needed)

From Surface Forces to Self Assembly



From Bush, J. W. M., and D. L. Hu. “WALKING ON WATER: Biolocomotion at the Interface.” Annu. Rev. Fluid Mech. 2006. 38:339–69

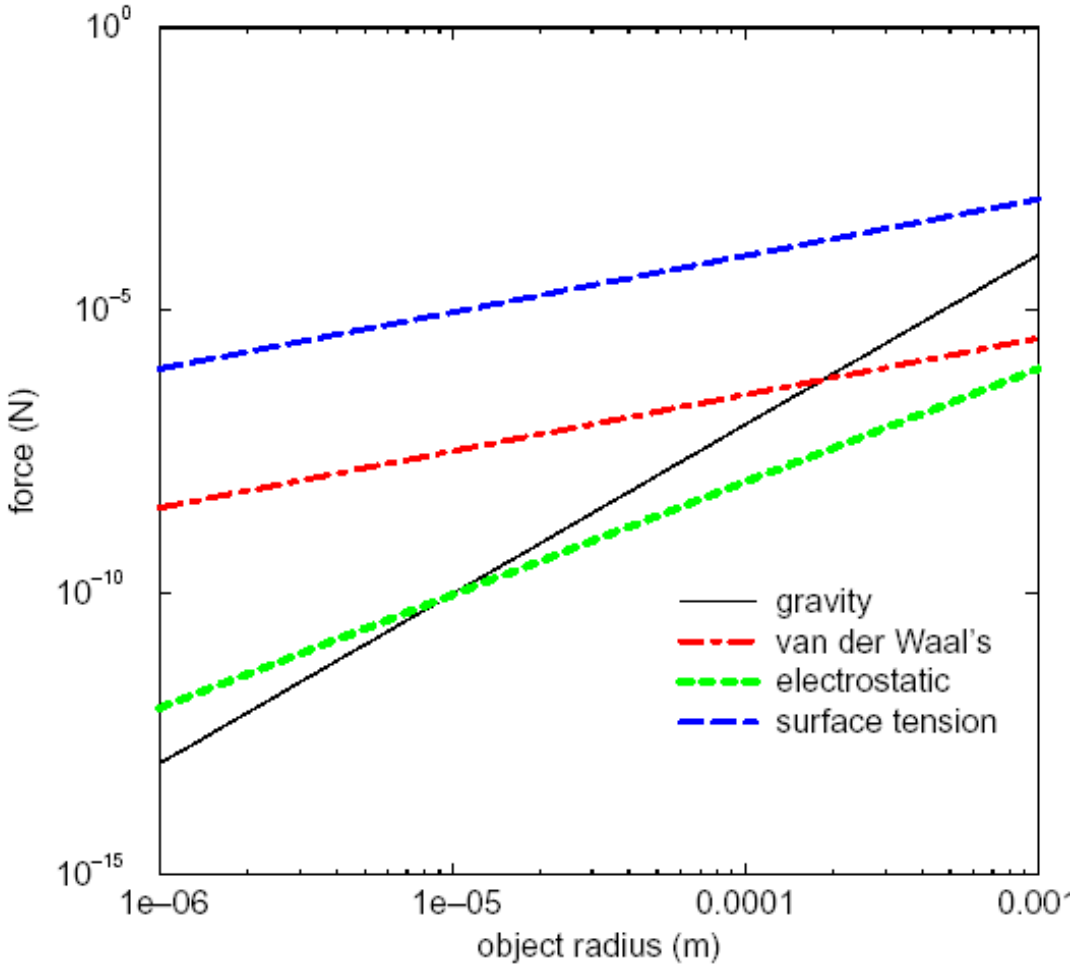
“By releasing a surfactant, water striders and other insects was able to propel itself toward and up the meniscus”

Outline

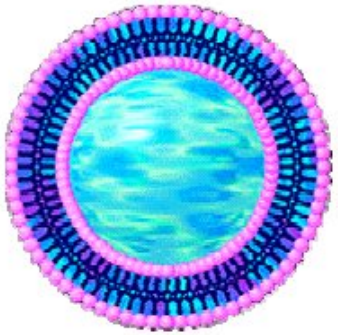
- Self Assembly
  - Thermodynamics of Micelle self assembly
  - Micro/Meso/Macroscale Self Assembly
  - Limitations

Driving Forces for Self-Assembly

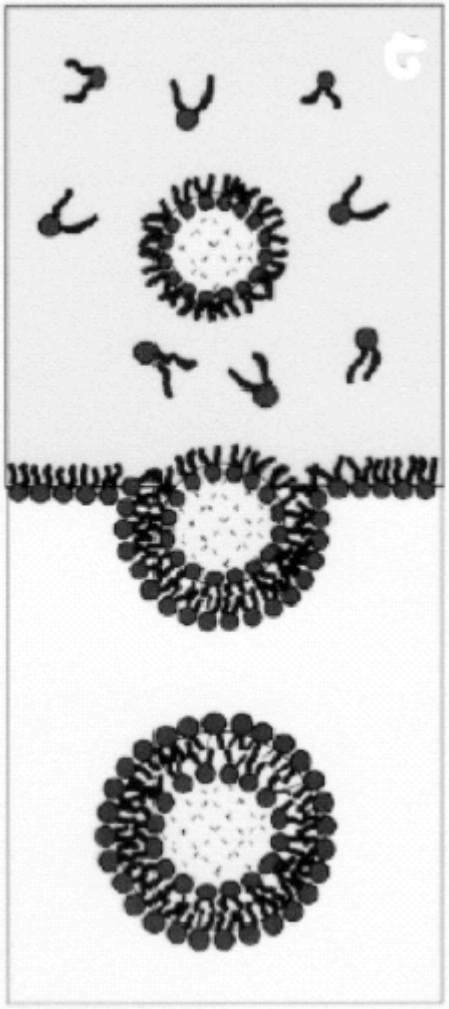
- Molecular Bonding Forces
- Steric Energy
- Capillary Forces
- Electrostatic Forces
- Magnetic Forces

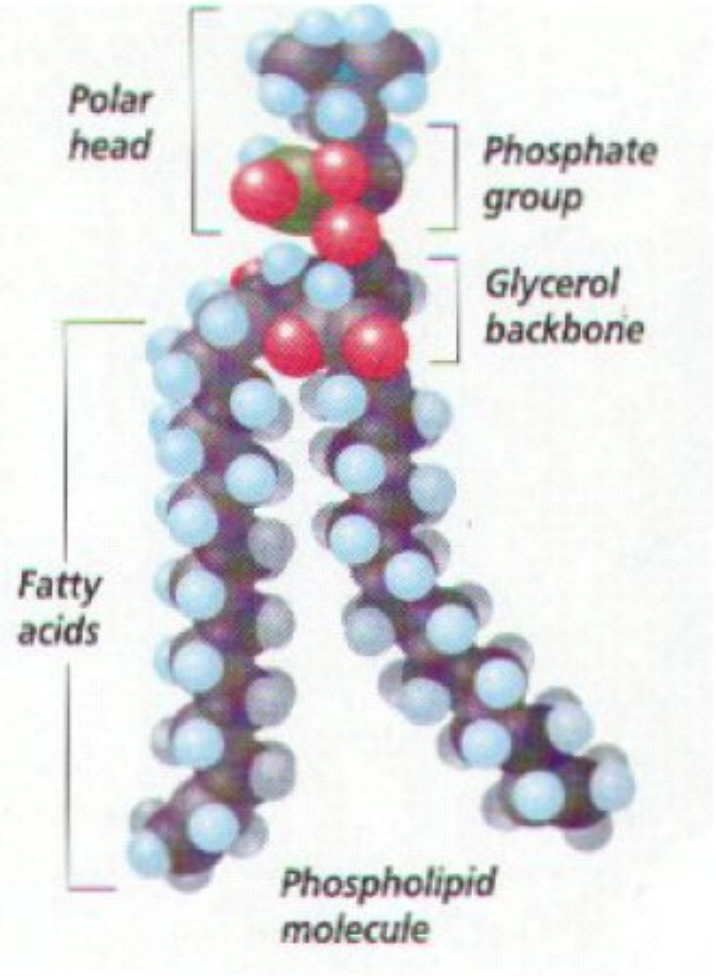


Assembly by Surface Energy



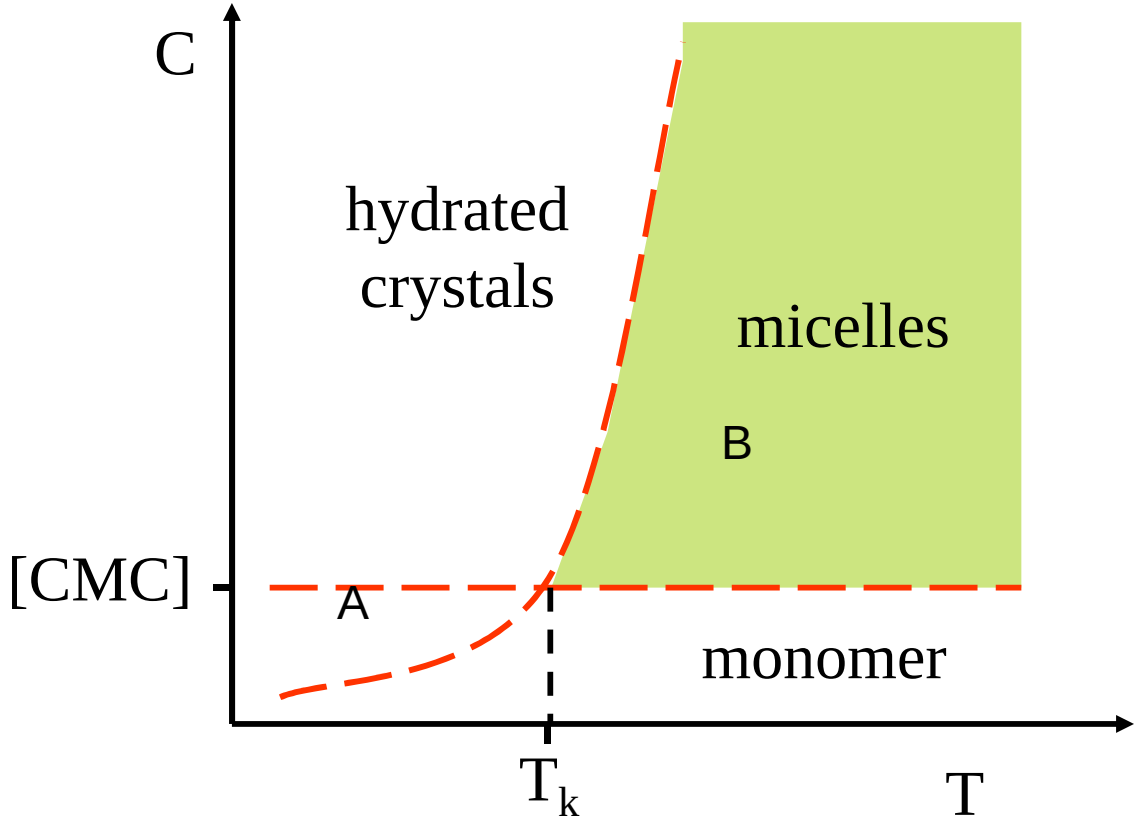
Vesicles of bilayer membranes





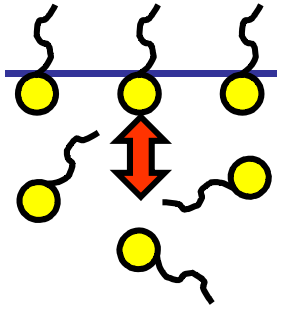
Surfactant molecule: amphiphilic

Phase Diagram of Micelles

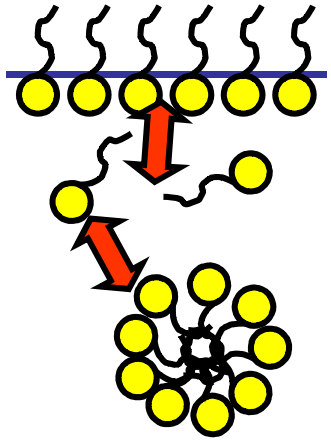


Phase diagram

Situation A

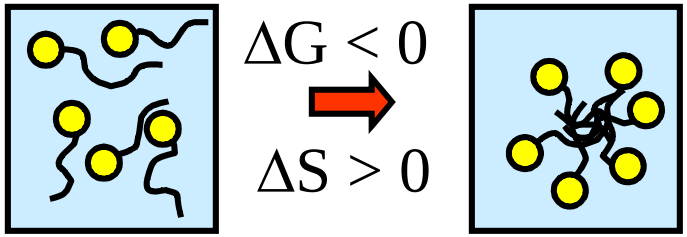


Situation B



Micelle Properties

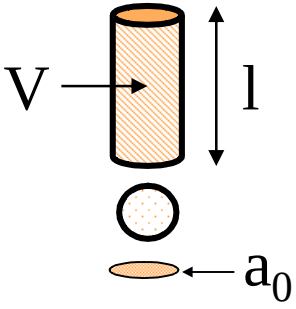
1. Hydrophobic effect



2. Head repulsion

Electrostatic or Steric

3. Packing efficacy (geometric factor)

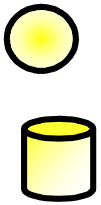


$$Ns = \frac{V}{a_0 l}$$

Ns = 0.33

Ns = 0.5

Ns = 1.0



bilayer

Molecular Self Assembly Geometries

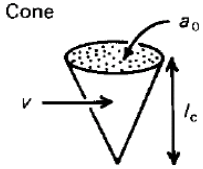
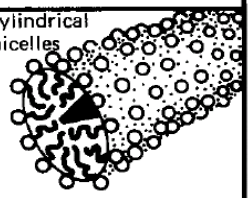
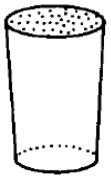
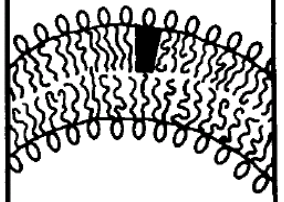
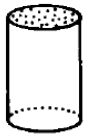
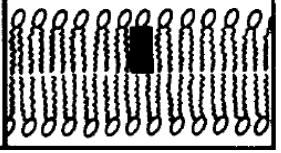
Surfactant molecular shape/interactions mainly determines aggregate geometry.

Critical packing factor = $v/a_o l_c$ (unitless), where:

v = molecular volume of surfactant chain

a_o = area per surfactant head

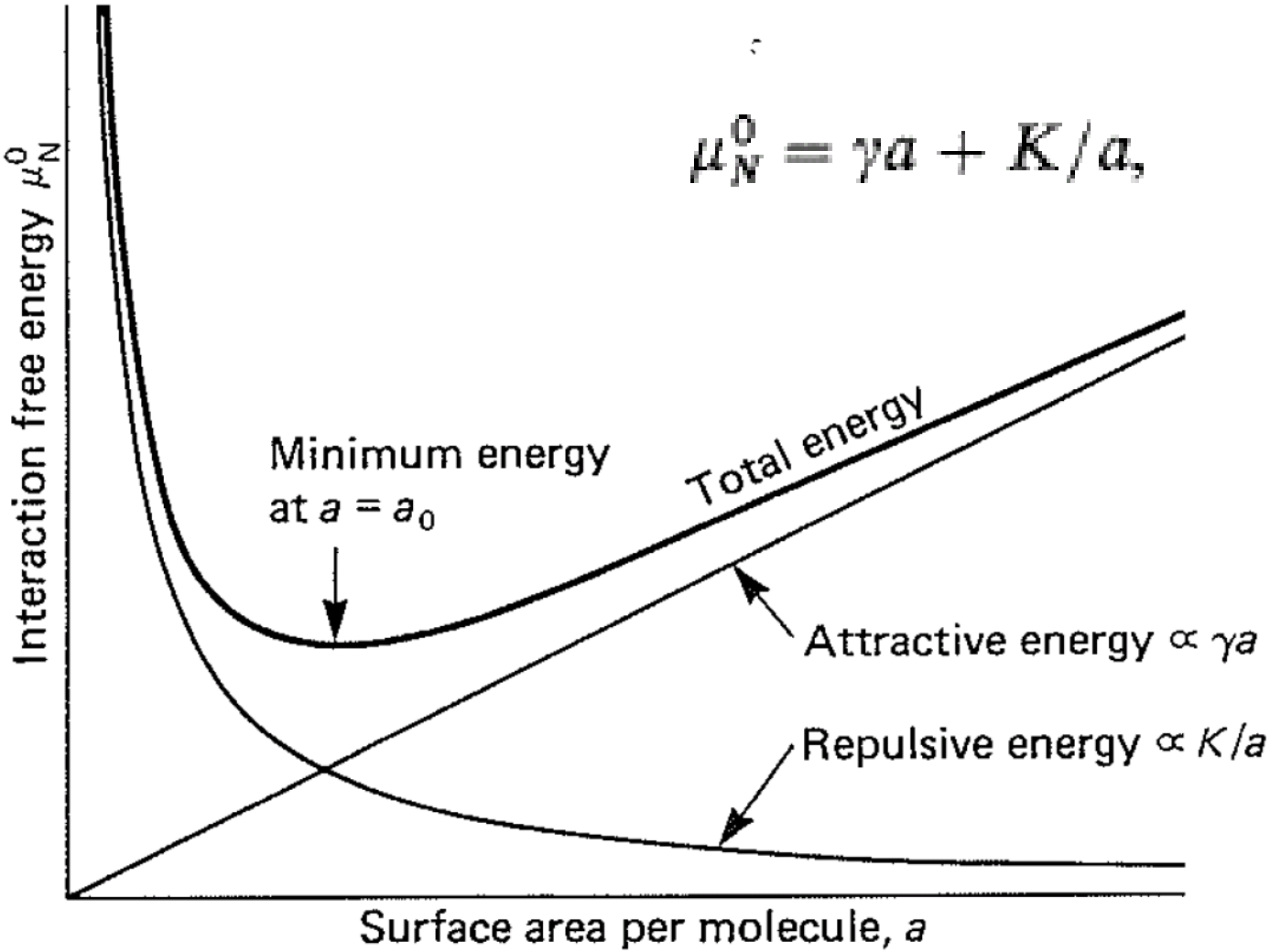
l_c = length of surfactant chain

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 

From Israelachvili, Chap 16

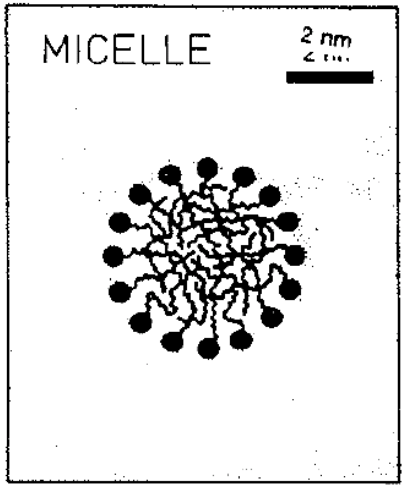
Critical Size of Self Assembled Micelles

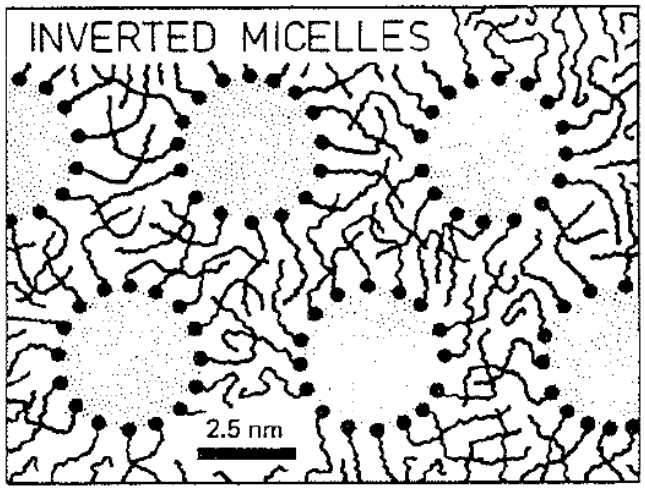
$$\mu_N^0 = \gamma a + K/a,$$

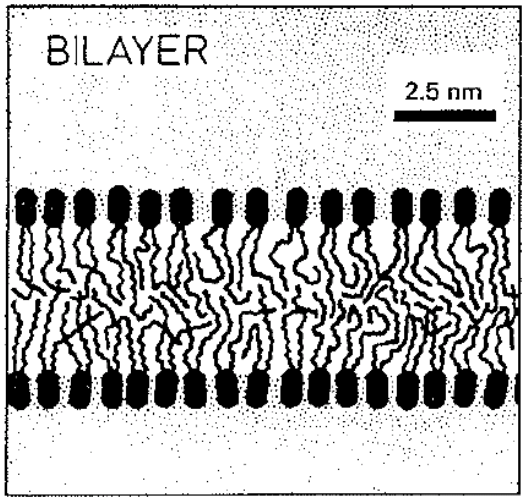


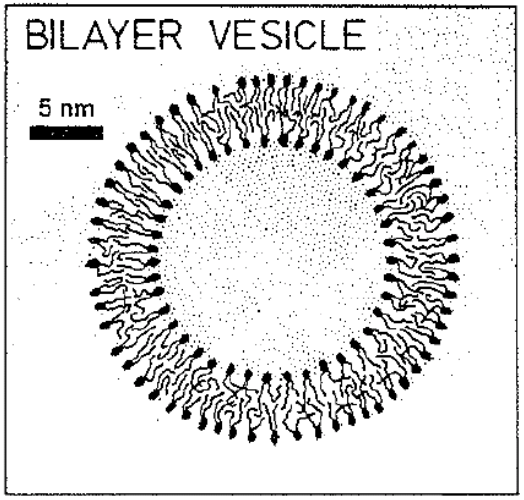
From Israelachvili, Chap 17

Possible Phase Transformation of SAMs









From Israelachvili, Chap 16

Thermodynamic Balance of SAM

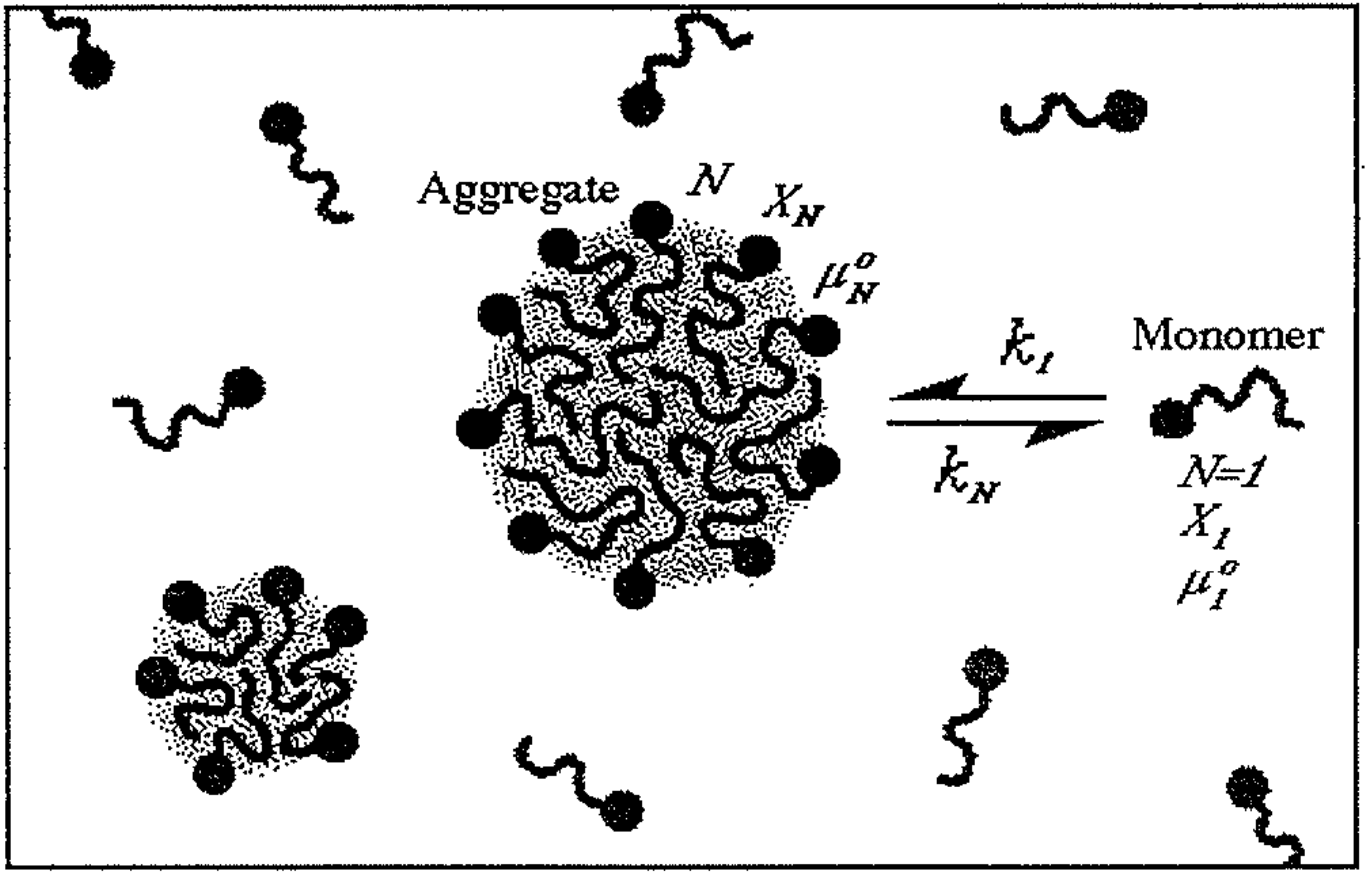
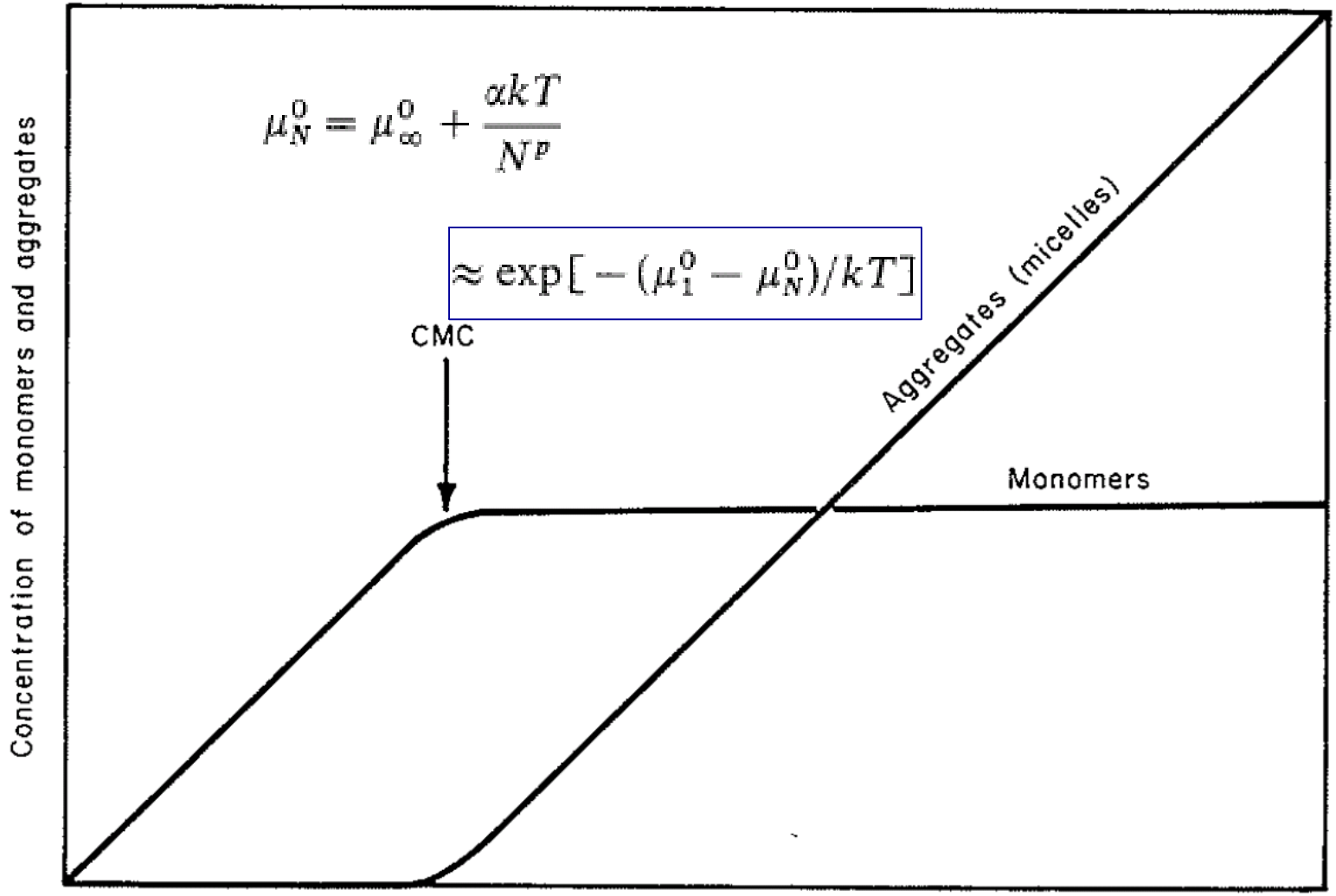


Fig. 16.3. Association of N monomers into an aggregate (e.g., a micelle). The mean lifetime of an amphiphilic molecule in a small micelle is very short, typically 10^{-5}–10^{-3} s.

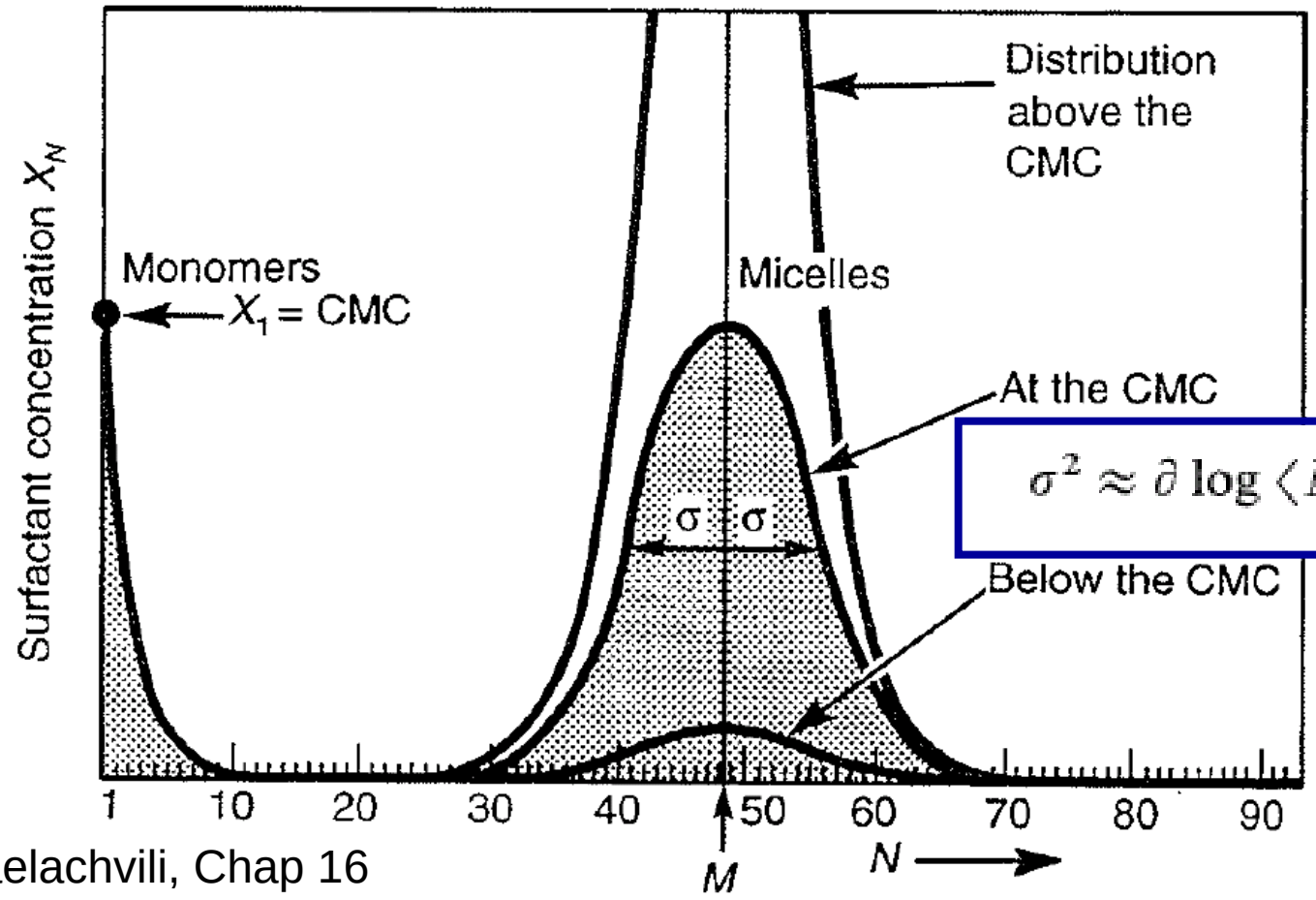
From Israelachvili, Chap 16

Critical Micelle Concentration (CMC)



From Israelachvili, Chap 16

Size Distribution of SAMs



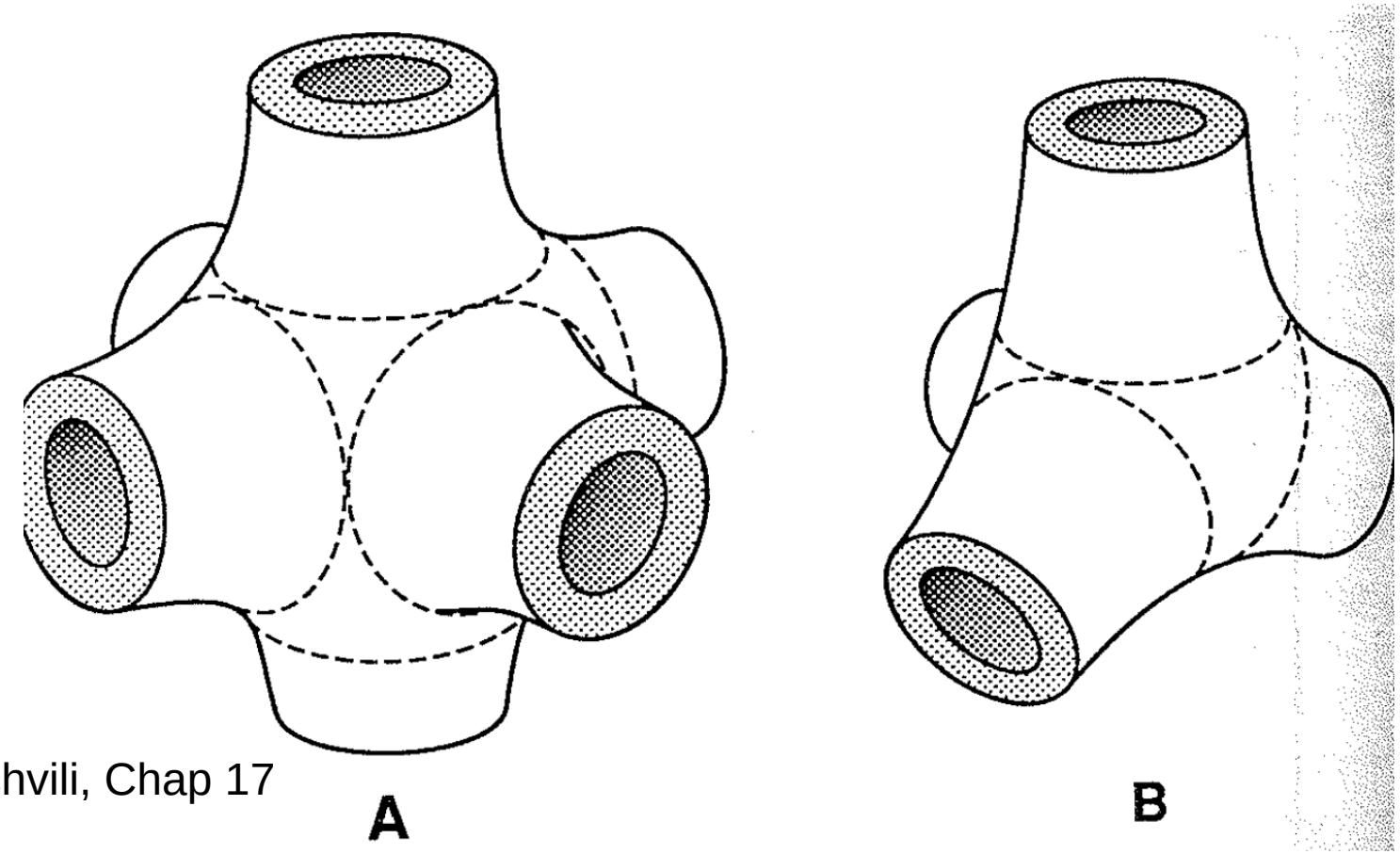
$$\sigma^2 \approx \partial \log \langle N \rangle / \partial \log C$$

From Israelachvili, Chap 16

Size deviation scales as square root of number (M) of monomers required to form the micelle

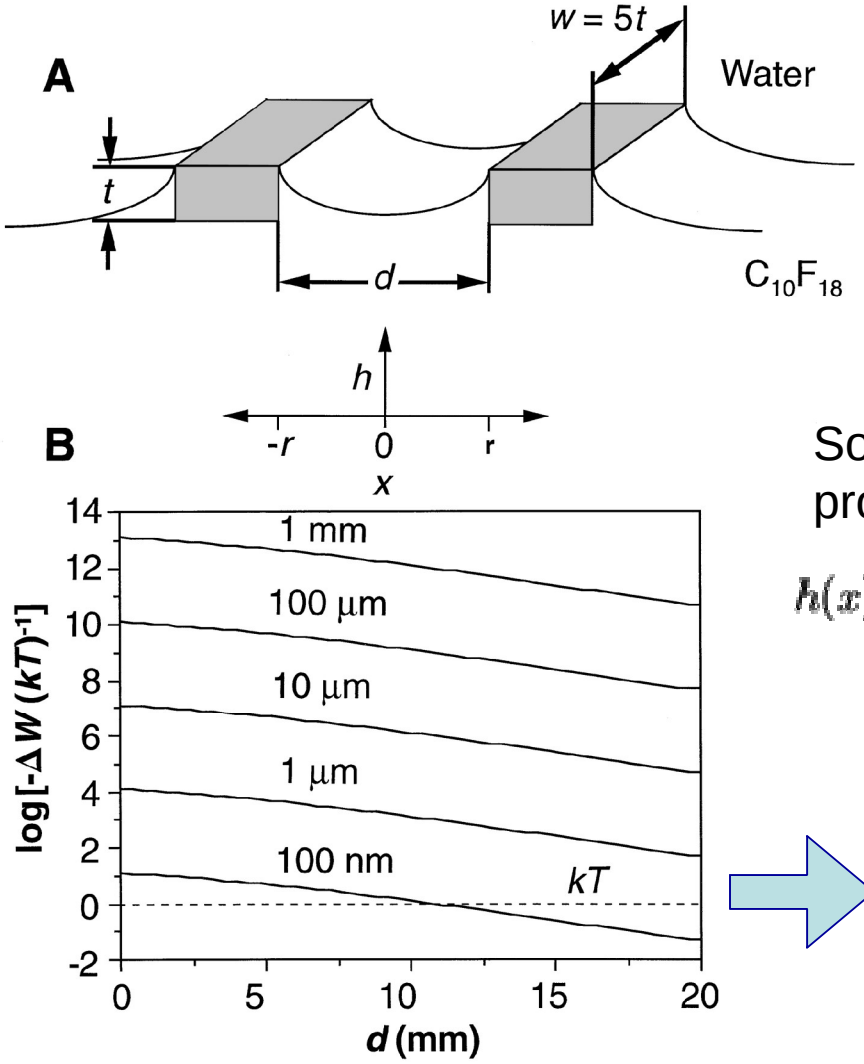
More Complex Shapes

- Need to consider the curvature elasticity of membranes/microphases



From Israelachvili, Chap 17

Self Assembly Driven by Capillary Forces



The height of the meniscus is given by Laplace Equation:

$$\frac{\partial^2 h}{\partial x^2} = \frac{1}{\gamma}(\Delta\rho g h - \Delta P_0)$$

Solution of the above gives the surface profile due to capillary force and gravity:

$$h(x) = t\left[\frac{2}{1 - e^{(d/x_c)}} + \frac{e^{(-x/x_c)} + e^{(x/x_c)}}{e^{(d/2x_c)} - e^{(-d/2x_c)}}\right]$$

self-assembly are favorable for objects with t as small as 100 nm

WHITESIDES et al, Science 1997

Additional Readings

- Jacob N. Israelachvili, “Intermolecular and Surface Forces”, Chapter 16, 17, Academic Press, 2nd Edition, 1992

- MRS Bulletin, Focused Issue on “Self Assembly in Materials Synthesis”, 2005

- Whitesides Group Website: *http://gmwgroup.harvard.edu/research.html*