Interface and Self Assembly

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Course Website: nanoHUB.org
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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: \( \phi = -\frac{\alpha}{r^6} + \frac{\beta}{r^n} \) \( (n \approx 12) \)

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

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

\[
\Phi(D) = -\frac{\pi \rho \alpha}{6D^3}
\]
Consider a thin sheet at location $z$ on the sphere:

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

number of molecules on this sheet:

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

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

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 $D \ll R$, $2R - z \approx 2R$

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

Size of contact

Distance of contact
Adhesion Enhancement by Nano-toes

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

\[
\Phi_{\text{total}}(D) \approx \frac{\rho_1 \rho_2 \alpha \pi^2 R}{6D}
\]
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

Microscopic View of Friction

\[ F \approx \frac{A}{D} \left( \gamma_A - \gamma_R \right) \]

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)
“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

hydrated crystals

micelles

monomer

[CMC]

C

T

T_k

T
Micelle Properties

1. Hydrophobic effect
   \[ \Delta G < 0 \]
   \[ \Delta S > 0 \]

2. Head repulsion
   Electrostatic or Steric

3. Packing efficacy (geometric factor)
   \[ N_s = \frac{V}{a_0 l} \]
   - \( N_s = 0.33 \) for \( \text{bilayer} \)
   - \( N_s = 0.5 \)
   - \( N_s = 1.0 \)
Molecular Self Assembly Geometries

Surfactant molecular shape/interactions mainly determines aggregate geometry.

Critical packing factor
\[ \phi = \frac{v}{a_0 l_c} \text{ (unitless)} \]
where:
\[ v = \text{molecular volume of surfactant chain} \]
\[ a_0 = \text{area per surfactant head} \]
\[ l_c = \text{length of surfactant chain} \]

<table>
<thead>
<tr>
<th>Lipid</th>
<th>Critical packing parameter ( \phi = \frac{v}{a_0 l_c} )</th>
<th>Critical packing shape</th>
<th>Structures formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-chained lipids (surfactants) with large head-group areas: SDS in low salt</td>
<td>(&lt; 1/3)</td>
<td>Cone</td>
<td>Spherical micelles</td>
</tr>
<tr>
<td>Single-chained lipids with small head-group areas: SDS and CTAB in high salt, nonionic lipids</td>
<td>(1/3 - 1/2)</td>
<td>Truncated cone</td>
<td>Cylindrical micelles</td>
</tr>
<tr>
<td>Double-chained lipids with large head-group areas, fluid chains: Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG, dihexadeyl phosphate, dialkyl dimethyl ammonium salts</td>
<td>(1/2 - 1)</td>
<td>Truncated cone</td>
<td>Flexible bilayers, vesicles</td>
</tr>
<tr>
<td>Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: phosphatidyl ethanolamine, phosphatidyl serine + Ca(^{2+})</td>
<td>(~1)</td>
<td>Cylinder</td>
<td>Planar bilayers</td>
</tr>
</tbody>
</table>

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
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

\[ \mu_N^0 = \mu_\infty^0 + \frac{\alpha k T}{N_p} \]

\[ \approx \exp\left[ -(\mu_1^0 - \mu_N^0)/kT \right] \]
Size deviation scales as square root of number \((M)\) of monomers required to form the micelle

\[
\sigma^2 \approx \partial \log \langle N \rangle / \partial \log C
\]
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:

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

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


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

- Whitesides Group Website: [http://gmwgroup.harvard.edu/research.html](http://gmwgroup.harvard.edu/research.html)