Lecture 11

Solid and Liquid Interfaces

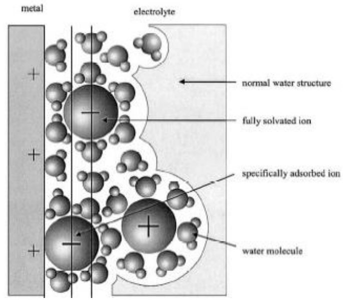
11.1 Structure of Liquid/Solid Interface

- Specific and Non-specific Adsorption
- Stern model

11.2 Surface Tension and Contact Angle

11.3 Langmuir and Langmuir-Blodgett Films

11.4 Self-assembled Monolayers (SAM)

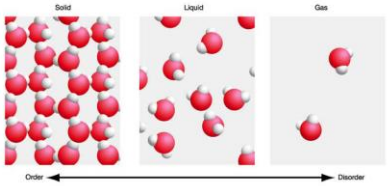


References:

Kolasinski, Chapter 5

11.1 Structure of Liquid/Solid Interface

Important in biological systems, i.e.,H_2O/material



Compare liquid/solid and gas/solid interface:

Solids:

- exhibit long- and short-range order;
- bonding distances, angles, compositions well defined and uniform

Liquid:

- less ordered system;
- only short range order;
- solutes has solvent shell, and liquids with high-κ support stable ionic species

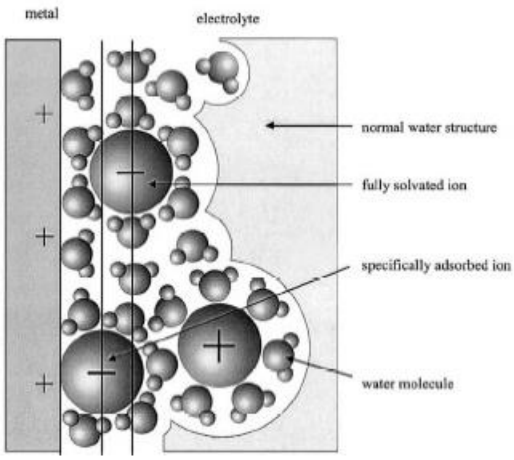
Liquid/solid interface

- nonspecific adsorption

For ionic species – stronger interaction with solvent and solid

- specific adsorption

A Stern model of the liquid/solid interface



The inner Helmholtz layer: a plane that contains a layer of partially solvated ions

The outer Helmholtz layer: a plane of fully solvated ions that reside above the inner layer

Both layers form the **electric double layer.** Depending on the extent to which the charge of the first layer is compensated by excess charge at the solid interface, the outer layer can be composed of (a) like –charged ions (full compensation); (b) counterions (no compensation) or (c) a mixture of two

- Diffuse **Gouy layer** resides on top

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Structure of Liquid/Solid Interface

A model of the liquid/solid interface with examples of specific and non-specific adsorption

(a) The structure of the Helmholtz layer and a pure solvent

(b) Potential drop across the interface in case of nonspecific and specific ion adsorption

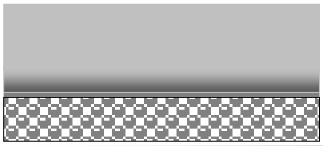
Potentials inside the metal, in the electrolyte, and at the outer Helmholtz plane are shown

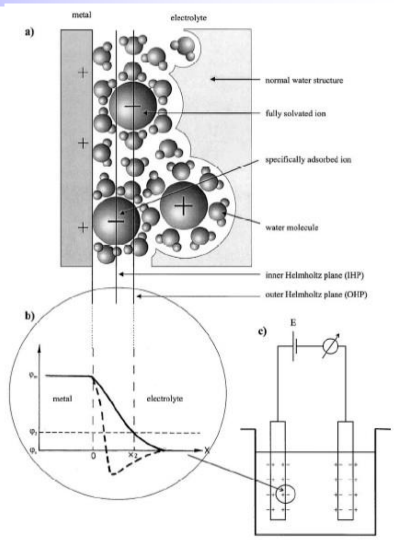
For **<u>nonspecifically adsorbing ions</u>**:

- linear potential drop across the interface

For **<u>specific adsorbing ions:</u>**

- a steeper potential gradient





Kolb D.M., Surf.Sci **500** (2002) 722. 4

Four regions in the liquid/solid system

1. The bulk liquid
2. The bulk solid
3. The surface of the solid along with its adsorbate
4. The region just above the adsorbed layer that is different from the bulk liquid

Water/Solid Interface

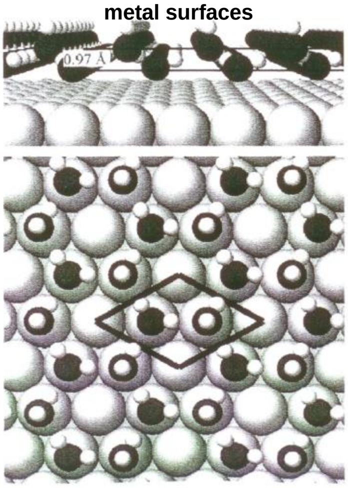
Assume:
- ice layers/solid

Binding energy is comparable to the hydrogen bond strength
$E^{water} = 23 kJ\ mol^{-1}$

- local adsorption sites on the metal
- formation of extended 2D or 3D hydrogen network

On several transition metals (Ir, Rh):
- H_2O binds directly to metal atom through O;
- 2nd layer H_2O forms H-bonds with the layer below

Water bilayer structure on closed packed metal surfaces



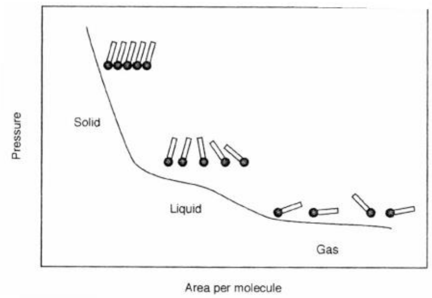
C.Clay, *Curr.Opin.Solid State Mater* 9 (2005) 11.

11.3 Langmuir and Langmuir-Blodgett Films

Amphiphile molecules: molecules with both **polar** (hydrophilic) and **nonpolar** (hydrophobic) ends

e.g., stearic acid, $C_{17}H_{35}CO_2H$; alkanethiols, $CH_3(CH_2)_nSH$

Polar groups: $-CH_2OH$, $-COOH$, $-CN$, $-CH{=}NOH$, $-C_6H_4OH$, $-CONH_2$



Phase diagram of surface pressure *vs* area per molecule (amphiphile) in Langmuir film

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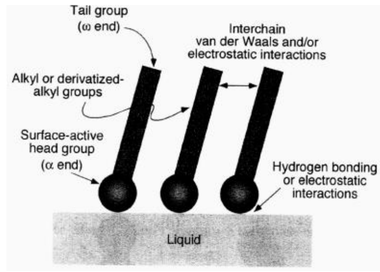
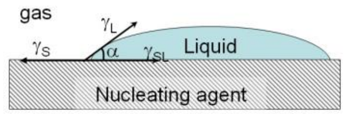


The polar head group of the amphiphile molecule interacts with the liquid through hydrogen bonding or electrostatic interactions; by aligning and tilting, the tail groups maximize their attractive interactions

Young equation



Equilibrium shape and wetting angle of the solid on a nucleating agent

Contact angle

γ_L, γ_S – surface free energy of liquid (solid)

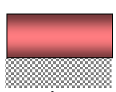
γ_{SL} – interface energy or tension

Surface tension exerts force along surface at line of intersection

At equilibrium: $\gamma_L \cos\alpha = \gamma_S - \gamma_{SL}$ (Young's eq.)

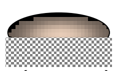
$$\boxed{\cos\alpha = \frac{\gamma_S - \gamma_{SL}}{\gamma_L}}$$

Complete wetting



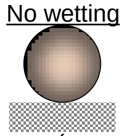
$\gamma_S > (\gamma_L + \gamma_{SL})$

Wetting



$-\gamma_L < (\gamma_S + \gamma_{SL}) < \gamma_L$

No wetting



$\gamma_{SL} > (\gamma_L + \gamma_S)$

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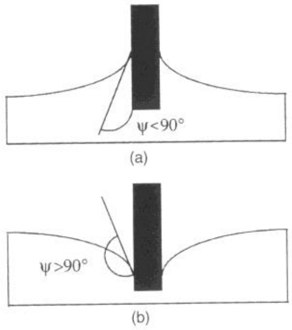
Langmuir – Blodgett Films

• capillary condensation and meniscus formation

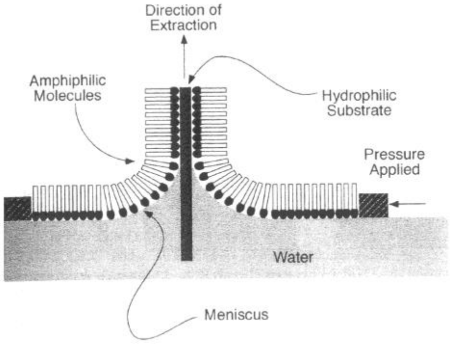


Meniscus formation on a planar substrate:

(a) hydrophilic substrate in water;

(b) hydrophobic substrate in water

Vertical Deposition: transfer of a Langmuir film onto a solid substrate



Substrate is hydrophilic and interacts attractively with the head groups of the amphiphile;

Movable barriers to maintain a contact surface pressure in the film to insure uniform deposition

Multilayered structures

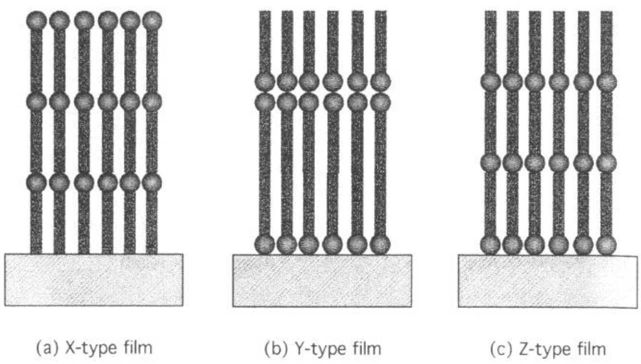


Figure 5.10 X, Y and Z multilayer Langmuir-Blodgett (LB) films. Y-type films are deposited successively on upstrokes and downstrokes. X-type films deposit only on downstrokes. Z-type films deposit only on upstrokes. Downstroke, insertion of the substrate into the LB trough; upstroke, retraction of the substrate from the LB trough.

Horizontal Lifting (Shaefer's method): pressing substrate into a Langmuir film

Sticking coefficient in solution

- Similar to gas/solid case, the sticking coefficient is defined as: $s = \frac{r_{ads}}{Z_W}$

The collision frequency in solution is given by $Z_W = C_{sol}\left(\frac{k_B T}{2\pi m}\right)^{2}$, where c_{sol} is the concentration in molecules per m^3.

Q: The initial sticking coefficient of $CH_3(CH_2)_7SH$ on a gold film is 9×10^{-8}. Assuming a constant sticking coefficient, estimate the time required to achieve a coverage of 0.01ML for adsorption from a 5×10^{-3} mol/l solution. Take the surface density of atoms to be 1×10^{19} m^{-2}.

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11.4 Self-Assemled Monolayers (SAMs)

- Alkanethiols on Au, Ag, GaAs
- Dialkyl sulfides and disulfides on Au
- Organosilanes ($RSiCl_3$) on SiO_2, glass,

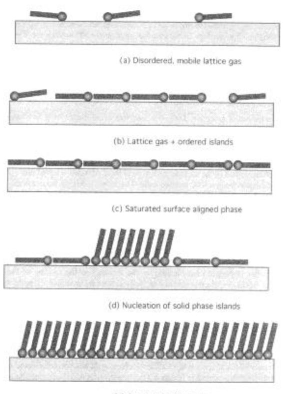


Figure 5.11 Mechanism of self-assembly: (a) disordered, mobile lattice gas; (b) lattice gas plus ordered islands; (c) saturated surface-aligned phase; (d) nucleation of solid-phase islands; (e) saturated solid phase. Self-assembly progresses in stages, as long as a sufficient supply of adsorbates is available, until the thermodynamically most favoured final state is reached. Not depicted in the figure is a reconstruction of the surface, which often accompanies the process.

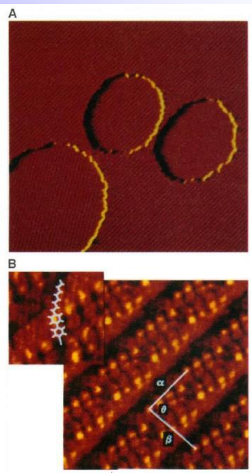
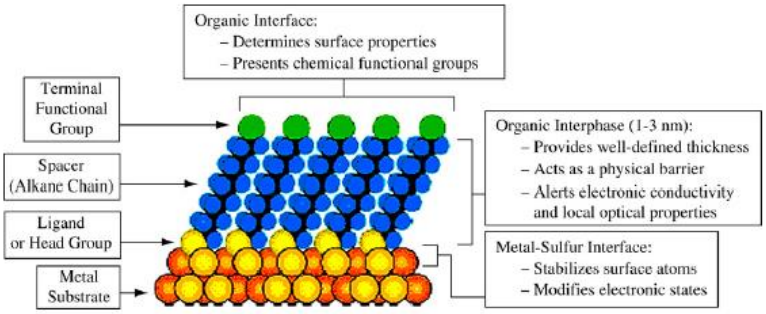


Fig. 1. Self-assembled molecular rows in corrals on graphite. **(A)** A 3000 Å by 3000 Å constant-height STM image of an ordered molecular monolayer of 8CB grown on an HOPG

Lecture 11 Patrick D.L., et al, *Science* **265** (1994) 231.

The SAMs on metals

Factors:
- Surface pretreatment
- Immobilization technique
- Surfactants and solvents
- Temperature



Surface Science Reports 61 (2006) 445–463