Lecture 2: Biomaterials Surfaces: Physics

The surface of a material strongly dictates its performance *in vivo*.

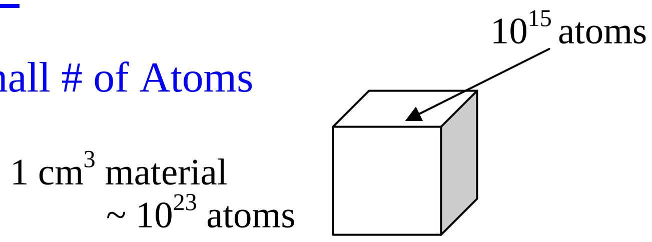
Surface Properties Influencing Cell Adhesion

- Wettability
- Roughness
- Electrical Charge
- Crystallinity
- Composition
- Mobility

What's so special about a surface?

Surface vs. Bulk

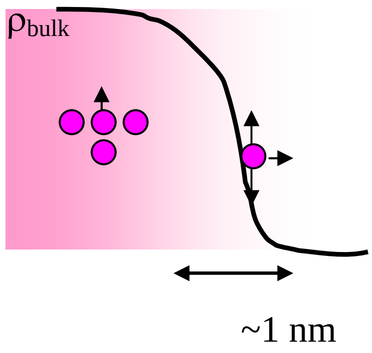
1. Inherently Small # of Atoms



→ *Requires special characterization tools*

2. Enhanced Mobility

- fewer bonds
- gradient in density



$D = D_0 \exp(-E_a/kT)$

$D_{surf} >> D_{bulk}$

→ *Facilitates rate-limited processes*
(phase transformations, crystallization, corrosion…)

Example: Devitrification of calcium phosphate glass $CaO\text{-}P_2O_5\text{-}SiO_2$ (44:40:15)

	$E_{a,cry}$ (kcal/mol)	powder size (μm)
Crystallization initiates at surface	75	< 44
	108	297-590

from J.-S. Lee et al., *J. Thermal Anal. Cal.* **56** (1999) 137.

3. Higher Energy State

Atoms/molecules with unsatisfied (“dangling”) or strained bonds

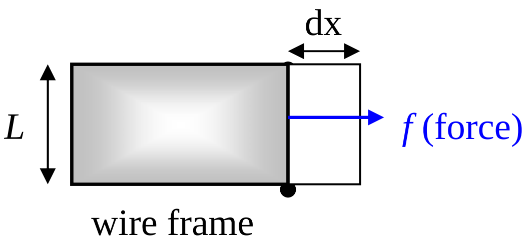
→ *High reactivity and susceptibility to adsorbates*

Quantifying Surface Energy

loss of bonds at a surface ⇒ attraction towards bulk
= areal contraction force

Surface tension, γ, is the *work required to create unit surface area at constant T,P and composition.*

Consider a simple soap film experiment:



$$dG = -SdT + VdP + \gamma dA$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P,n} = \frac{fdx}{2Ldx} = \frac{f}{2L}$$

?

where G = Gibbs free energy, A = area

Surface Tensions of Example Materials

Material	T (°C)	γ (dyn/cm)
Teflon (PTFE)	20	19
Silicone (PDMS)	20	20
PE	20	36
PMMA	20	41
PEO	20	43
Water	20	73
soda-lime-silicate (*l*)	1350	350
FeO	1400	580
Al_2O_3	1850	950
TiC	1100	1190
Ti (*l*)	1660	1550
δ-Fe (bcc)	1400	1900

1 dyn/cm = 1 mJ/m^2
= 1 erg/cm^2

γ↓ w/ ↑T

$\gamma_{sv} \propto \Delta H_{sublim}$
$\gamma_{lv} \propto \Delta H_{vapor}$

Trends: high γ materials: (>200 dyn/cm) – metals, carbides, oxides
low γ materials: polymers, organics

Why? Consider the nature of bonds…

Surface tension is a measure of *degree of cohesion.*

Work of cohesion: $W_C = 2\gamma$

Surface Phenomena

A simple rule: *Surface phenomena are driven primarily by an associated reduction in surface free energy.*

Important examples in biomaterials:

- adsorption of a species from environment
- surface segregation of a species from bulk
- surface reconstructions
- surface reactions

1. Adsorption phenomena

Tenet 1: Higher energy surfaces are quickly coated/contaminated by lower energy species.

Examples: * Water on glasses, metals or oxides
* Hydrocarbons on inorganic surfaces
* Surfactants at air/water interface

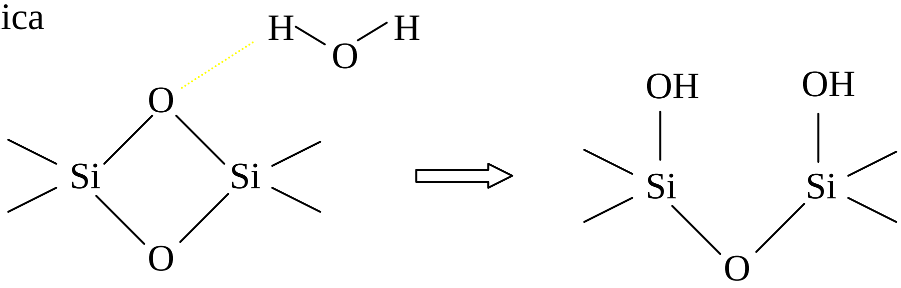
Measured γ of metals & oxides ~ 37 dyn/cm

Classes of adsorption:

- *chemisorption* – strong modifications to electronic structure/electron density of adsorbate molecule (> 0.5 eV/surface site)

Example: H_2O on silica

$E_{ads} = 1.7$ eV

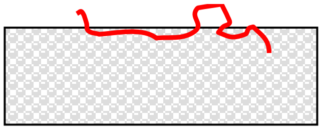


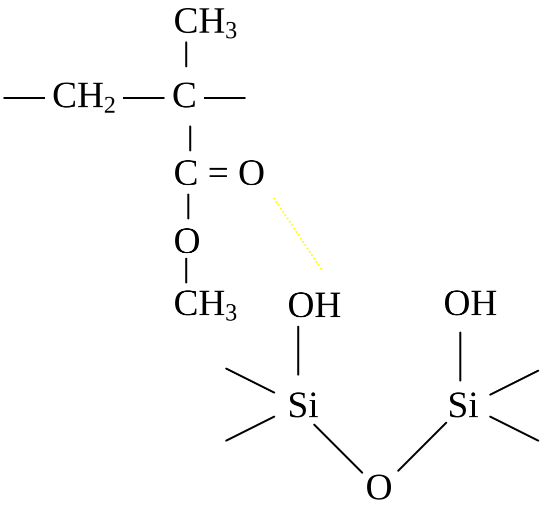
- *physisorption* – adsorbate weakly adherent via secondary (i.e., van der Waals') interactions (< 0.25 eV/surface site)

1 eV/molec = 96.5 kJ/mol
$kT_{293} \approx 0.025$ eV

Example: PMMA on silica

$E_{ads} = 0.1$ eV/mer





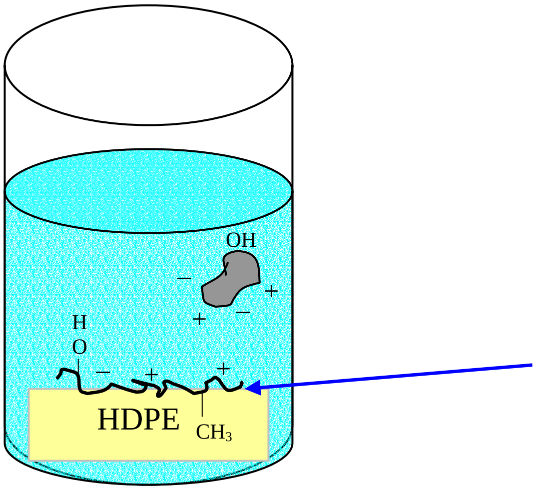
N' mers adsorbed × 0.1 eV/mer
≈ total adsorption energy

N' < N (segments/chain)

Tenet 2: The “high energy surface” of tenet 1 is relative to its surrounding medium.

In H_2O based environments, a hydrophilic material has a *lower interfacial energy* than a hydrophobic one.

Example: Adsorption/denaturing of proteins on hydrophobic surfaces in water-based environments

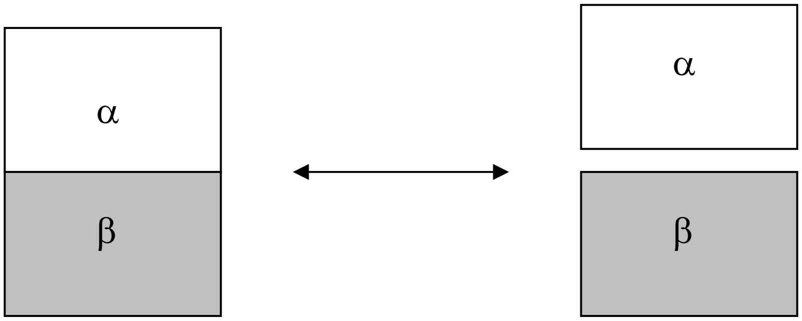


Charged & H-bonding groups orient towards H_2O; hydrophobic groups orient towards polyethylene

Such adsorption phenomena are examples of “thermodynamic adhesion”

Adhesion – state in which 2 dissimilar bodies are held together in intimate contact such that a <u>force can be transferred</u> across the interface.

Thermodynamic adhesion is driven by interfacial forces associated with <u>reversible</u> processes.



Work of Adhesion (W_{12}): the work required to separate a unit area of interface between 2 phases.

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad W_{12} > 0 \Rightarrow \text{adhesion}$$

γ_{12} = α/β interfacial tension

(for $\alpha = \beta$, $W_{12} = W_C = 2\gamma_1$)

We can approximate W_{12} with a geometric mean:

$$W_{12} \approx (W_{C,1}\, W_{C,2})^{1/2} = 2(\gamma_1\, \gamma_2)^{1/2}$$

By analogy, for α/β adhesion in aqueous:

$$W_{12,w} = \gamma_{1w} + \gamma_{2w} - \gamma_{12,w} \approx 2(\gamma_{1w}\, \gamma_{2w})^{1/2}$$

Suggests 2 strategies for protein resistance: $W_{12} = 0$

Or for $\gamma_1 = \gamma_1^{d} + \gamma_1^{p}$

$$W_{12} = 2(\gamma_1^{d}\, \gamma_2^{d})^{1/2} + 2(\gamma_1^{p}\, \gamma_2^{p})^{1/2}$$

For $W_{1W} = 2(\gamma_1\gamma_W)^{1/2}$

$\Rightarrow \gamma_{1W} = (\gamma_1^{1/2} - \gamma_W^{1/2})^2$

Strategies for Inhibiting Protein Adhesion:

a) Ultra-hydrophobic systems $\gamma_1 = 0 \Rightarrow \gamma_{1W} \approx \gamma_W$

Example: PTFE (γ= 19 dyn/cm)

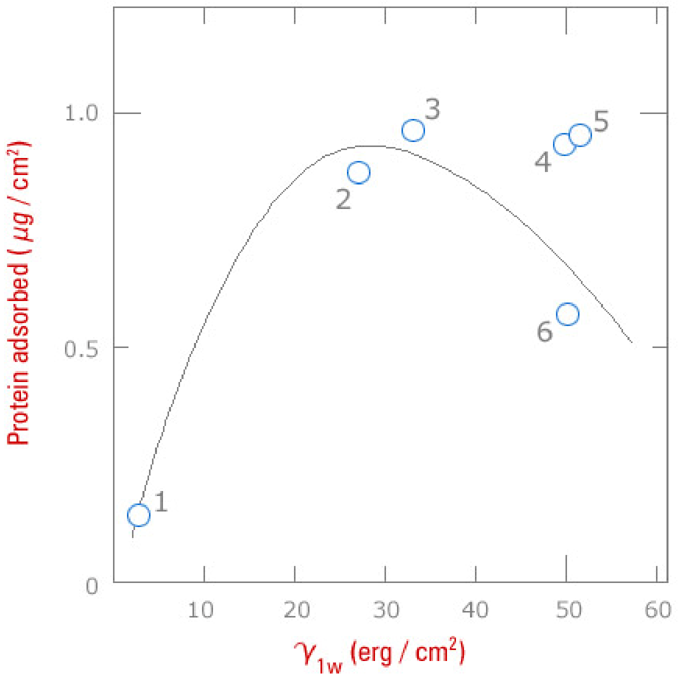
$\Rightarrow$ Proteins adsorb but don't adhere well. (*the "non-stick pan" principle*)

b) Ultra-hydrophilic systems $\gamma_{1W} = 0 \Rightarrow \gamma_1 \approx \gamma_W$

Example: PEO ($\gamma_{1W} \approx 0$)

$\Rightarrow$ Surface favors water contacts—proteins don't adsorb.

BSA adsorption on various polymers at 37°C.



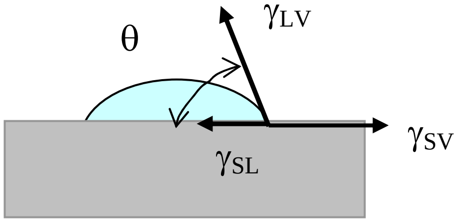
Hydrophilic surfaces are currently seen as the most promising strategy for controlling protein deposition on biomaterials.

1. PVA
2. PMMA
3. PET
4. PP
5. HDPE
6. PTFE

(after Y. Ikada et al., *Polymers as Biomaterials*, Plenum Press, NY 1984)

Figure by MIT OCW.

The *hydrophilicity* of a surface can be gauged by measuring the *contact angle* of a droplet of water on the surface. The balance of interfacial forces is described by *Young's Equation*:



$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$$

Since $W_{SL} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$

$$\Longrightarrow W_{SL} = \gamma_{LV}(1+\cos\theta)$$

θ	Wettability
0	Complete
<90	Partial
>90	Non wetting

For multi-component surfaces:

Cassie's eqn: $\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2$ where f_i =area fraction of i

2. Surface Segregation

An interfacial adsorption phenomenon involving a bulk component of a multi-component material.

Example 1: Surface segregation of a dilute solute (B) in a binary AB alloy

Surface fraction of B ($X_{B,S}$) can be described using the Langmuir-McLean relation:

$$\frac{X_{B,S}}{1-X_{B,S}} = \frac{X_B}{1-X_B}\exp\left[\frac{-\Delta G_S}{RT}\right]$$

where ΔG_S = free energy of segregation per mole of solute.

Surface enrichment is given by:

$$\frac{X_{B,S}}{X_B} \approx \exp\left[\frac{-\Delta G_S}{RT}\right]$$

ln X = 2.3 $\log_{10}$X
R = 8.314 J/mol-K

The predicted behavior is more transparent by expanding the exponential…

$$\frac{X_{B,S}}{X_B} \approx 1 - \frac{\Delta G_S}{RT} + \ldots$$

The Langmuir-McLean relation indicates:

- Surface enrichment occurs when ΔG_S is negative
- Surface coverage increases with bulk solute content
- Surface enrichment decreases with increasing T

ΔG_S can be estimated from the Miedema eqn:

$$\Delta G_S = \underset{\uparrow}{-0.24}\left[\Delta H_{mix} + (\gamma_{A,SV} - \gamma_{B,SV})6N_{Av}^{1/3}V_{m,B}^{2/3}\right]$$

prefactor is fraction of
atom contacting vacuum

$\Delta G_S > 0$ no surface
enrichment of B

$\Delta G_S < 0$ surface
enrichment of B

Metal surface tensions can be estimated from: $\gamma_{B,SV} = \dfrac{\Delta H_{sub}}{6N_{Av}^{1/3}V_{m,B}^{2/3}}$

↖ molar volume

The Miedema model is ~90% accurate in
predicting segregation in AB alloys.

Source: *Interfaces in Materials*, J.M. Howe, John Wiley
&Sons: NY (1997) pp. 156-168.

Surface segregation also occurs commonly in organic materials…

Example 2: PVC blended w/ 0.25 wt% short fluorocarbon ($C_{45}O_{18}F_{59}H_{31}$).

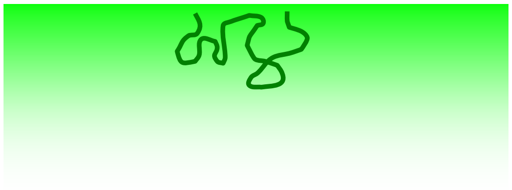
γ_{PVC} = 41 dyn/cm vs. γ_{blend} = 17.3 dyn/cm ←

≈ pure -CF_3
γ_{CF3} = 14.5 dyn/cm

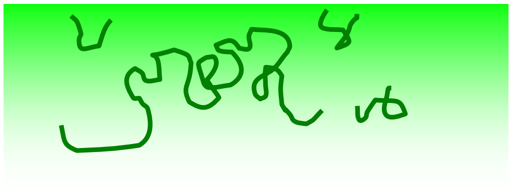
In polymers, ENTROPY can play a significant role in surface segregation.

Polymer "random coil" conformations are restricted by the presence of a surface

⇒ Less chain configurations!



Chain ends surface segregate to decrease entropic penalty

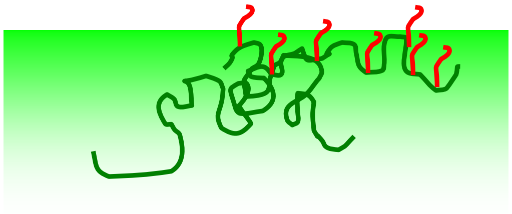


Short chains surface segregate when mixed with long chains

Surface segregation importance to biomaterials applications:

- Toxicity
- Corrosion resistance
- Modified protein/cell adhesivity

But…also *a strategy* for surface modification!



Surface modification with a comb polymer additive

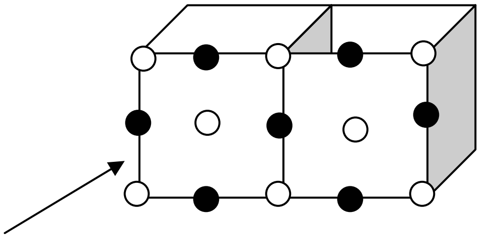
3. Surface Reconstruction

Atomic or molecular rearrangement at surface to reduce surface/ interfacial tension.

Example 1: Faceting in MgO

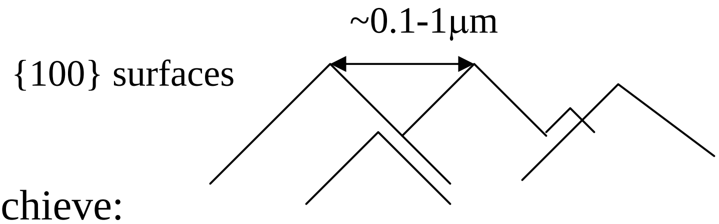
Rocksalt structure

○ = O^{2-} (fcc lattice pts)
● = Mg^{2+} (octahedral interstices)



(100) is preferred plane of cleavage (charge neutral!)

Miscut surfaces will facet



Oxides surfaces reconstruct to achieve:

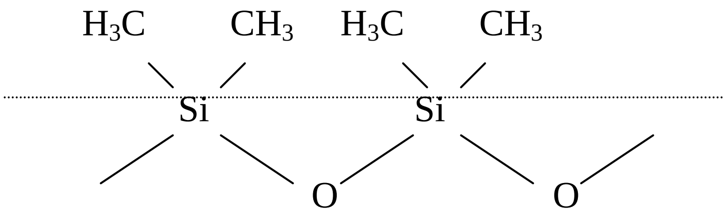
1) no net dipole moment
2) minimial loss of nearest neighbor ligand coordination

Low Energy Oxide Surfaces

Structure	low γ plane	Examples
M_2O_3 corundum	$10\underline{1}2$	Ti_2O_3, V_2O_3, Fe_2O_3, Al_2O_3, Cr_2O_3
MO_2 rutile	110	TiO_2, SnO_2
MO rocksalt	100	MgO, CaO, CoO

Example 2. Reorientation of polymer chains in water vs. air

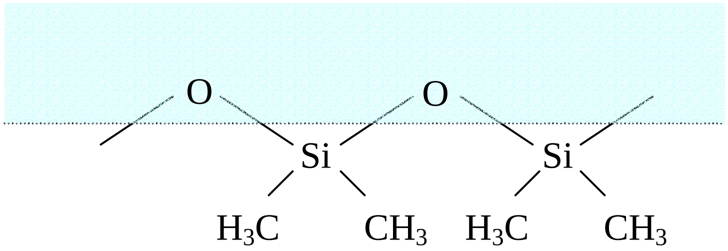
PDMS in air



γ_{PDMS} = 20 dyn/cm

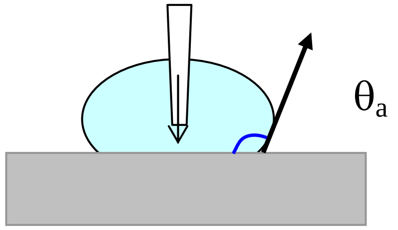
(γ_{CH3} = 23 dyn/cm)

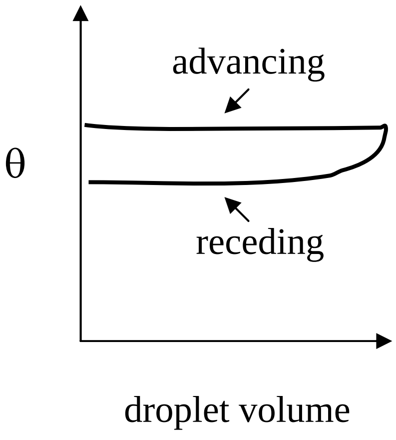
PDMS in H_2O



Chain reorientation can be observed with dynamic contact angle studies:

Advancing: Droplet volume increased (by syringe)





Receding: Droplet volume removed