

## Lecture 2: Biomaterials Surfaces: Physics

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

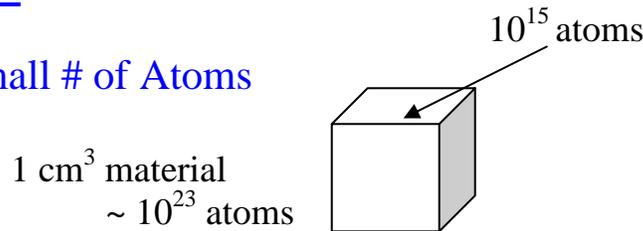
### Surface Properties Influencing Cell Adhesion

Wettability	Crystallinity
Roughness	Composition
Electrical Charge	Mobility

*What's so special about a surface?*

### Surface vs. Bulk

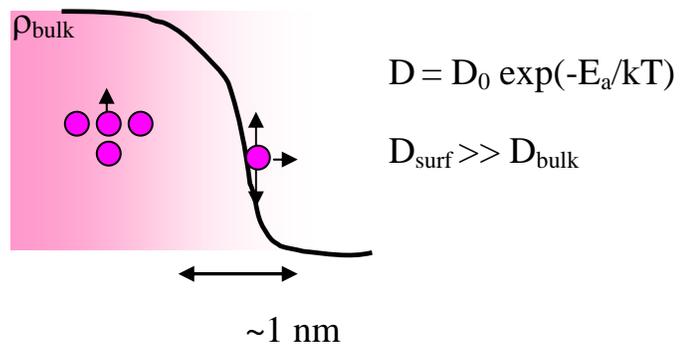
#### 1. Inherently Small # of Atoms



➔ *Requires special characterization tools*

#### 2. Enhanced Mobility

- fewer bonds
- gradient in density



➔ *Facilitates rate-limited processes*  
(phase transformations, crystallization, corrosion...)

Example: Devitrification of calcium phosphate glass CaO-P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> (44:40:15)

Crystallization  
initiates at surface

E <sub>a,cry</sub> (kcal/mol)	powder size (μm)
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



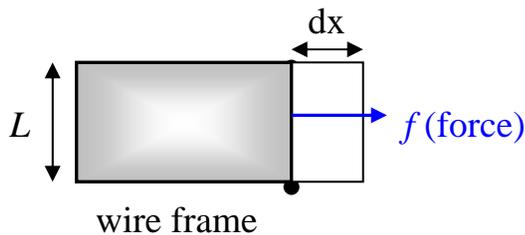
*High reactivity and susceptibility to adsorbates*

### Quantifying Surface Energy

loss of bonds at a surface  $\implies$  attraction towards bulk  
= areal contraction force

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

Consider a simple soap film experiment:



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

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

where G = Gibbs free energy, A = area

↑  
?

*Surface Tensions of Example Materials*

<u>Material</u>	<u>T (°C)</u>	<u><math>\gamma</math> (dyn/cm)</u>
Teflon (PTFE)	20	19
Silicone (PDMS)	20	20
PE	20	36
PMMA	20	41
PEO	20	43
Water	20	73
soda-lime-silicate ( <i>l</i> )	1350	350
FeO	1400	580
Al <sub>2</sub> O <sub>3</sub>	1850	950
TiC	1100	1190
Ti ( <i>l</i> )	1660	1550
$\delta$ -Fe (bcc)	1400	1900

$$1 \text{ dyn/cm} = 1 \text{ mJ/m}^2 \\ = 1 \text{ erg/cm}^2$$

$$\gamma \downarrow \text{ w/ } \uparrow T$$

$$\gamma_{sv} \propto \Delta H_{\text{sublim}}$$

$$\gamma_{lv} \propto \Delta H_{\text{vapor}}$$

*Trends:* high  $\gamma$  materials: (>200 dyn/cm) – metals, carbides, oxides  
 low  $\gamma$  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

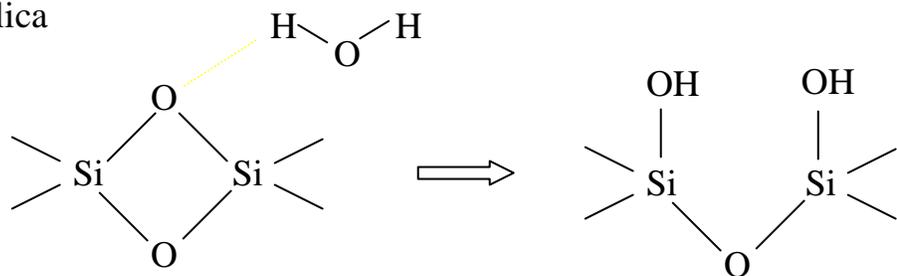
Measured  $\gamma$  of metals & oxides  $\sim 37$  dyn/cm

Classes of adsorption:

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

Example: H<sub>2</sub>O on silica

$E_{\text{ads}} = 1.7$  eV



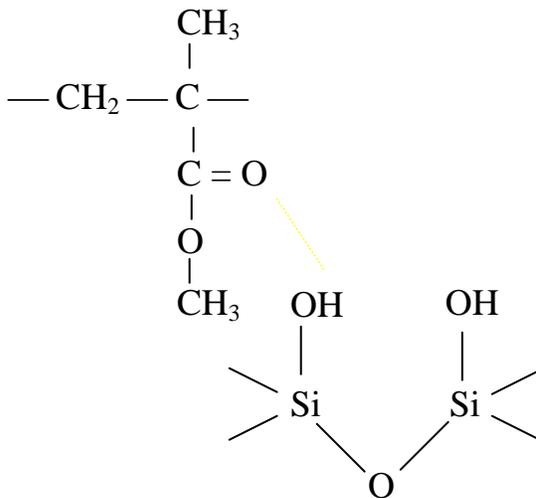
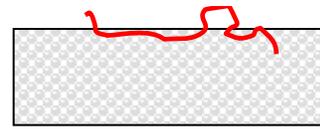
- *physisorption* – adsorbate weakly adherent via secondary (i.e., van der Waals’) interactions ( $< 0.25$  eV/surface site)

$$1 \text{ eV/molec} = 96.5 \text{ kJ/mol}$$

$$kT_{293} \approx 0.025 \text{ eV}$$

Example: PMMA on silica

$$E_{\text{ads}} = 0.1 \text{ eV/mer}$$



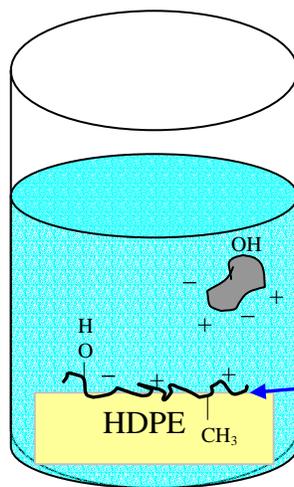
$$N' \text{ mers adsorbed} \times 0.1 \text{ eV/mer} \approx \text{total adsorption energy}$$

$$N' < N \text{ (segments/chain)}$$

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

In H<sub>2</sub>O 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

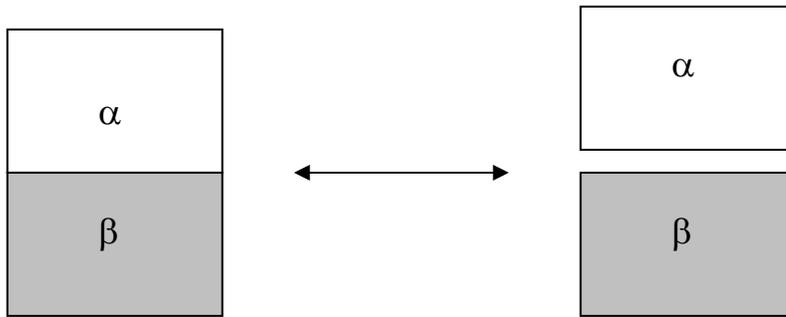


Charged & H-bonding groups orient towards H<sub>2</sub>O; hydrophobic groups orient towards polyethylene

Such adsorption phenomena are examples of “thermodynamic adhesion”

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

**Thermodynamic adhesion** is driven by interfacial forces associated with reversible processes.



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

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

$\gamma_{12} = \alpha/\beta$  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  $\alpha/\beta$  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  $\gamma_1 = \gamma_1^d + \gamma_1^p$

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

*Strategies for Inhibiting Protein Adhesion:*

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

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

Example: PTFE ( $\gamma = 19 \text{ dyn/cm}$ )

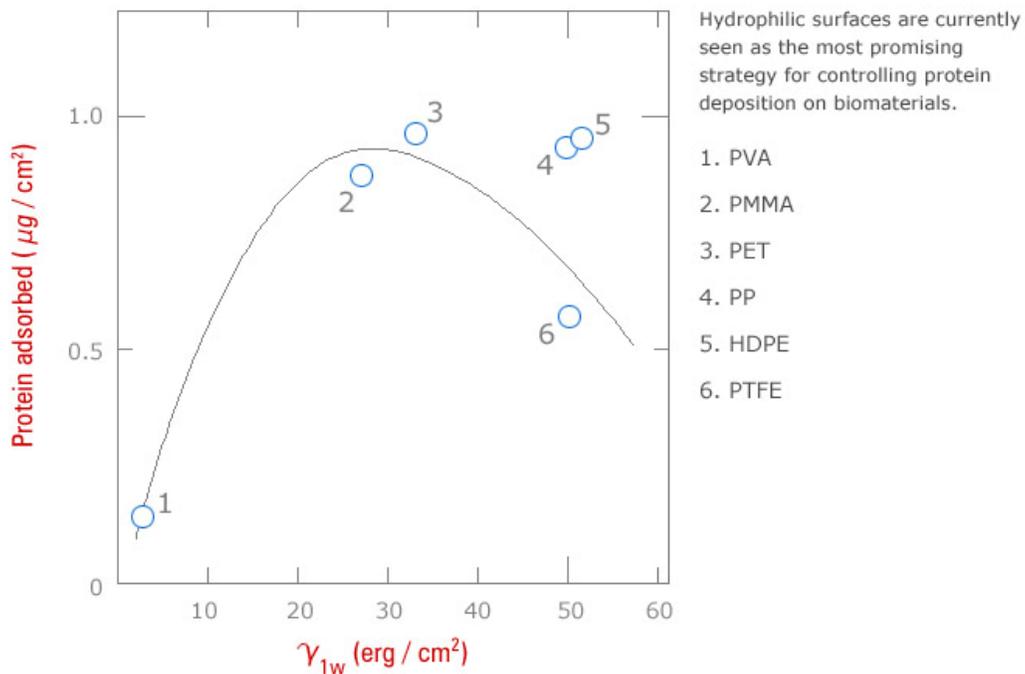
$\Rightarrow$  Proteins adsorb but don't adhere well.  
 (the "non-stick pan" principle)

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.

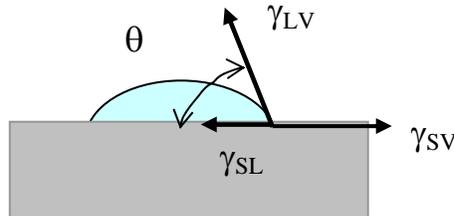
BSA adsorption on various polymers at 37°C.



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

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

$\theta$	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  $\Delta G_S$  = free energy of segregation per mole of solute.

**Surface enrichment** is given by:

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

$$\begin{aligned} \ln X &= 2.3 \log_{10} X \\ R &= 8.314 \text{ J/mol-K} \end{aligned}$$

The predicted behavior is more transparent by expanding the exponential...

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

The Langmuir-McLean relation indicates:

- Surface enrichment occurs when  $\Delta G_S$  is negative
- Surface coverage increases with bulk solute content
- Surface enrichment decreases with increasing T

$\Delta G_S$  can be estimated from the Miedema eqn:

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

↑  
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:

$$\gamma_{B,SV} = \frac{\Delta H_{sub}}{6N_{Av}^{1/3} V_{m,B}^{2/3}}$$

↙  
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<sub>45</sub>O<sub>18</sub>F<sub>59</sub>H<sub>31</sub>).

$\gamma_{PVC} = 41 \text{ dyn/cm}$  vs.  $\gamma_{blend} = 17.3 \text{ dyn/cm}$

$\approx \text{pure } -CF_3$   
 $\gamma_{CF_3} = 14.5 \text{ dyn/cm}$

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

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

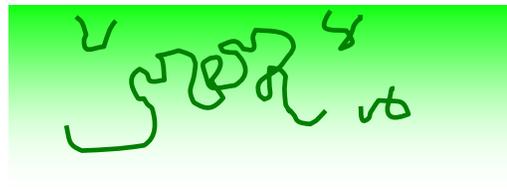
⇒ **Less chain configurations!**



Chain ends surface segregate to decrease entropic penalty



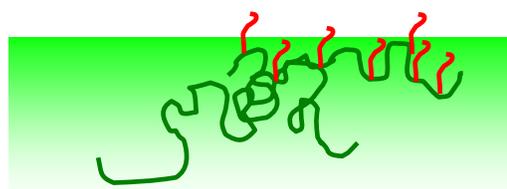
Short chains surface segregate when mixed with long chains



Surface segregation importance to biomaterials applications:

- Toxicity
- Corrosion resistance
- Modified protein/cell adhesivity

Surface modification with a comb polymer additive



But...also a strategy for surface modification!

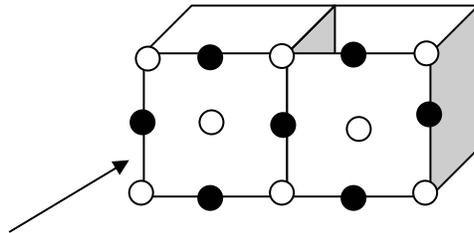
### 3. Surface Reconstruction

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

#### Example 1: Faceting in MgO

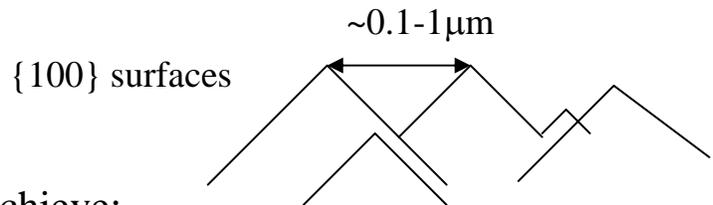
Rocksalt structure

○ = O<sup>2-</sup> (fcc lattice pts)  
● = Mg<sup>2+</sup> (octahedral interstices)



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

Miscut surfaces will facet



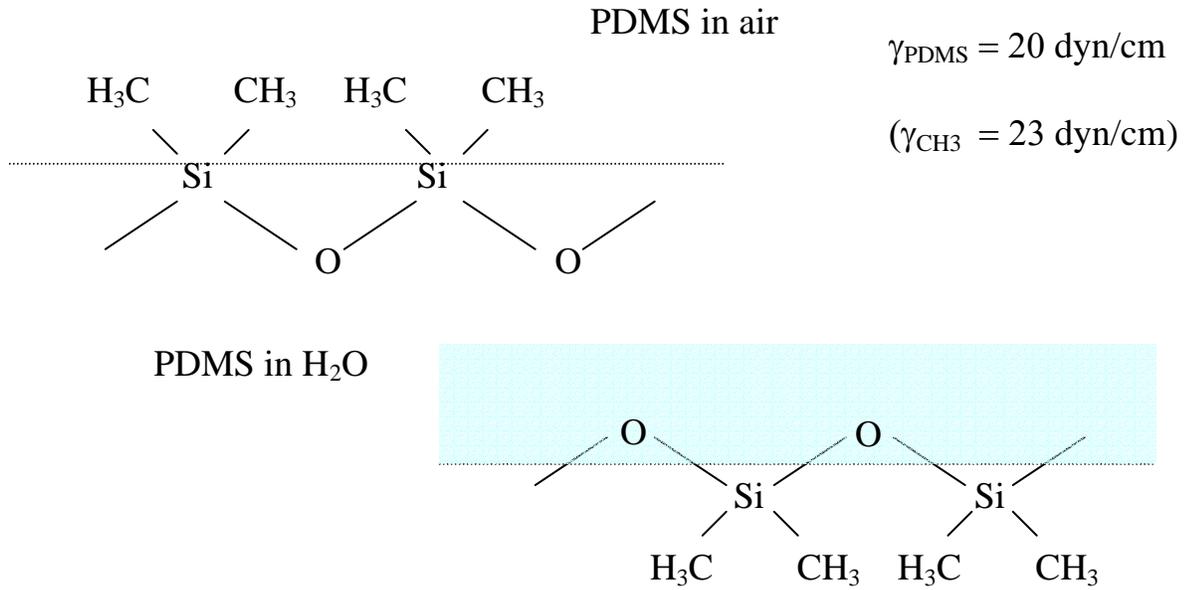
Oxides surfaces reconstruct to achieve:

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

#### Low Energy Oxide Surfaces

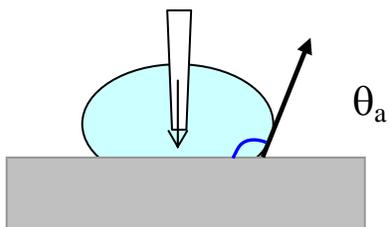
Structure	low $\gamma$ plane	Examples
M <sub>2</sub> O <sub>3</sub> corundum	10 $\bar{1}$ 2	Ti <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub>
MO <sub>2</sub> rutile	110	TiO <sub>2</sub> , SnO <sub>2</sub>
MO rocksalt	100	MgO, CaO, CoO

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



Chain reorientation can be observed with dynamic contact angle studies:

Advancing: Droplet volume increased (by syringe)



Receding: Droplet volume removed

