Lecture 2: Biomaterials Surfaces: Physics

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

<table>
<thead>
<tr>
<th>Surface Properties Influencing Cell Adhesion</th>
<th>Bulk Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wettability</td>
<td>Crystallinity</td>
</tr>
<tr>
<td>Roughness</td>
<td>Composition</td>
</tr>
<tr>
<td>Electrical Charge</td>
<td>Mobility</td>
</tr>
</tbody>
</table>

What’s so special about a surface?

**Surface vs. Bulk**

1. Inherently Small # of Atoms

   1 cm³ material
   \[\sim 10^{23} \text{ atoms}\]

   Requires special characterization tools

2. Enhanced Mobility

   - fewer bonds
   - gradient in density

   \[D = D_0 \exp\left(-\frac{E_a}{kT}\right)\]

   \[D_{\text{surf}} \gg D_{\text{bulk}}\]

   \[\sim 1 \text{ nm}\]

   Facilitates rate-limited processes
   (phase transformations, crystallization, corrosion…)
Example: Devitrification of calcium phosphate glass $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ (44:40:15)

<table>
<thead>
<tr>
<th>$E_{a,cry}$ (kcal/mol)</th>
<th>powder size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>&lt; 44</td>
</tr>
<tr>
<td>108</td>
<td>297-590</td>
</tr>
</tbody>
</table>

Crystallization initiates at surface

3. Higher Energy State

Atoms/molecules with unsatisfied ("dangling") or strained bonds

$\rightarrow$ $\text{High reactivity and susceptibility to adsorbates}$

Quantifying Surface Energy

loss of bonds at a surface $\rightarrow$ attraction towards bulk

$= \text{areal contraction force}$

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

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>( \gamma ) (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon (PTFE)</td>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>Silicone (PDMS)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>PE</td>
<td>20</td>
<td>36</td>
</tr>
<tr>
<td>PMMA</td>
<td>20</td>
<td>41</td>
</tr>
<tr>
<td>PEO</td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td>Water</td>
<td>20</td>
<td>73</td>
</tr>
<tr>
<td>soda-lime-silicate (l)</td>
<td>1350</td>
<td>350</td>
</tr>
<tr>
<td>FeO</td>
<td>1400</td>
<td>580</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1850</td>
<td>950</td>
</tr>
<tr>
<td>TiC</td>
<td>1100</td>
<td>1190</td>
</tr>
<tr>
<td>Ti (l)</td>
<td>1660</td>
<td>1550</td>
</tr>
<tr>
<td>( \delta )-Fe (bcc)</td>
<td>1400</td>
<td>1900</td>
</tr>
</tbody>
</table>

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

\( \gamma \downarrow \text{ w/ } \uparrow T \)

\( \gamma_{sv} \propto \Delta H_{\text{sublim}} \)

\( \gamma_{lv} \propto \Delta H_{\text{vapor}} \)

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### Trends:

**High \( \gamma \) materials:** (>200 dyn/cm) – metals, carbides, oxides

**Low \( \gamma \) materials:** polymers, organics

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### 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

Classes of adsorption:

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

Example: H$_2$O on silica

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

Measured $\gamma$ of metals & oxides ~ 37 dyn/cm
- **physisorption** – adsorbate weakly adherent via secondary (i.e., van der Waals’) interactions \(< 0.25 \text{ eV/surface site}\) 

\[ \text{1 eV/molec} = 96.5 \text{ kJ/mol} \]
\[ kT_{293} \approx 0.025 \text{ eV} \]

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 H₂O 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

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.

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

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

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

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

By analogy, for $\alpha/\beta$ adhesion in aqueous:

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

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

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

Suggests 2 strategies for protein resistance: $W_{12} = 0$
Strategies for Inhibiting Protein Adhesion:

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

Example: PTFE (\( \gamma = 19 \) dyn/cm)

\[ \implies \text{Proteins adsorb but don’t adhere well.} \]

(\textit{the “non-stick pan” principle})

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

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

\[ \implies \text{Surface favors water contacts—proteins don’t adsorb.} \]

BSA adsorption on various polymers at 37°C.
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 \( W_{SL} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \)

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

For multi-component surfaces:

Cassie’s eqn: \( \cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \) \( \text{where } f_i = \text{area fraction of } i \)

### 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 \( \Delta G_S = \text{free energy of segregation per mole of solute} \).
Surface enrichment is given by:

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

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 \( \Delta G_S \) 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:

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

The prefactor is the fraction of atom contacting the 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:

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

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

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}).

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

\[ \approx \text{pure } -\text{CF}_3 \]

\[ \gamma_{\text{CF3}} = 14.5 \text{ dyn/cm} \]

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!

Surface segregation importance to biomaterials applications:

- Toxicity
- Corrosion resistance
- Modified protein/cell adhesivity

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

\[ \text{O} = \text{O}^{2-} \quad \text{(fcc lattice pts)} \]
\[ \text{●} = \text{Mg}^{2+} \quad \text{(octahedral interstices)} \]

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

Miscut surfaces will facet

\{100\} surfaces

Oxides surfaces reconstruct to achieve:

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

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Low Energy Oxide Surfaces

<table>
<thead>
<tr>
<th>Structure</th>
<th>low ( \gamma ) plane</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M}_2\text{O}_3 ) \  \text{corundum}</td>
<td>10(_12)</td>
<td>\text{Ti}_2\text{O}_3, \text{V}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{Cr}_2\text{O}_3 \</td>
</tr>
<tr>
<td>( \text{MO}_2 ) \  \text{rutile}</td>
<td>110</td>
<td>\text{TiO}_2, \text{SnO}_2</td>
</tr>
<tr>
<td>( \text{MO} ) \  \text{rocksalt}</td>
<td>100</td>
<td>\text{MgO, CaO, CoO}</td>
</tr>
</tbody>
</table>
Example 2. Reorientation of polymer chains in water vs. air

PDMS in air

\[ \gamma_{\text{PDMS}} = 20 \text{ dyn/cm} \]

\[ (\gamma_{\text{CH}_3} = 23 \text{ dyn/cm}) \]

PDMS in H\(_2\)O

Chain reorientation can be observed with dynamic contact angle studies:

Advancing: Droplet volume increased (by syringe)

Receding: Droplet volume removed

\[ \theta \]

\[ \theta_a \]

\[ \theta_r \]