LECTURE 10: MOLECULE-SURFACE INTERACTIONS

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Objectives: To mathematically scale up intermolecular potentials to intersurface and interparticle potentials

Readings: Course Reader documents 22 & 23 and Israelachvili, Chapter 10.

Multimedia: Bonding and Protein Structure Demo (California Lutheran University).
BRIDGING THE GAP BETWEEN LENGTH SCALES

-A typical interatomic, ionic, or intamolecular potential (e.g. LJ potential)

\[ w(r) \text{ or } U(r) \rightarrow f(r) \]
(one atom, ion, or molecule)

\[ w(r) = -A r^{-6} \]

A typical intersurface or interparticle force vs. separation distance curve

**Tip-Sample Separation Distance, \( D \) (nm)**

**Force, \( F \) (nN)**

\[ W(D) \rightarrow F(D) \]
(net interaction between larger bodies, i.e. assemblies of atoms, ions, or molecules)
MOLECULE-SURFACE INTERACTIONS: MOLECULAR ORIGINS OF BIOCOMPATIBILITY

BLOOD FLOW

blood plasma proteins

PLATELETS!

BLOOD PRESSURE+
ATTRACTIVE FORCES

denatures

adsorbs

BLOOD CLOT!
- acute occlusive thrombosis
- infection / inflammation
- neointimal hyperplasia

Solid-Liquid Interface

BIOMATERIAL SURFACE

Photo courtesy of David Gregory & Debbie Marshall, Wellcome Images.

Photo of platelets courtesy of Tokyo Metropolitan Institute of Medical Science (RINSHOKEN). Used with permission.
CALCULATION OF THE NET POTENTIAL FOR INTERACTING BODIES: VOLUME INTEGRATION METHOD: PROCEDURES AND ASSUMPTIONS

1) **Choose the mathematical form** of the interatomic/ionic/molecular potential, $w(r)$ (e.g. in this case we will use an arbitrary power law: $w(r) = -\frac{A}{r^n}$)

2) **Set up the geometry** of the particular interaction being derived (e.g. molecule-surface, particle-surface, particle-particle, etc.)

3) **Assume "pairwise additivity"**: i.e. the net interaction energy of a body is the sum of the individual interatomic/intermolecular interactions of the constituent atoms or molecules which make up that body

4) A solid **continuum** exists: the summation is replaced by an integration over the volumes of the interacting bodies assuming a number density of atoms/molecules/m$^3$, $\rho$

5) **Constant material properties**: $\rho$ and $A$ are constant over the volume of the body

$W(D) = \int \int \int w(r) \bullet \rho \, dV$
INTERACTION POTENTIAL BETWEEN AN ATOM / MOLECULAR AND SURFACE: GEOMETRY

Geometry:

$z =$ direction perpendicular to the sample surface

$D$ (nm) = normal molecule-surface separation distance

$x$ (nm) = direction parallel to sample surface

$= \text{circular ring radius (m)}$

$A = \text{infinitesimal cross-sectional area (m}^2\text{)} = dx \, dz$

$V = \text{ring volume (m}^3\text{)} = 2\pi x \, (dx \, dz)$

$N = \# \text{ of atoms within the ring} = \rho \, (2\pi x) \, dx \, dz$

$\rho = \text{number density of atoms in the material constituting the surface (atoms/m}^3\text{)}$

$r = \text{distance from molecule to differential area}$
INTERACTION POTENTIAL BETWEEN AN ATOM / MOLECULAR AND SURFACE: DERIVATION

\[ w(r) = -\frac{A}{r^n} \quad (1) \]

Substitute (2) into (1): \( r = \sqrt{z^2 + x^2} \) \quad (2)

\[ w(r) = -\frac{A}{\left(z^2 + x^2\right)^{n/2}} \quad (3) \]

Net Interaction Energy:

\[ W(D) = \int \int w(r) \cdot \rho \, dV \]

\[ W(D) = \int \int \frac{w(r)}{\rho} \left(\frac{2\pi x}{dz \, dx}\right) \, dz \, dx \quad (4) \]

Substitute (1) \( \rightarrow \) (2)

\[ W(D) = \int \int -\frac{A}{\left(z^2 + x^2\right)^{n/2}} \cdot \rho \left(\frac{2\pi x}{dz \, dx}\right) \, dz \, dx \quad (5) \]
INTERACTION POTENTIAL BETWEEN AN ATOM / MOLECULAR AND SURFACE: DERIVATION

Pull out constant terms:

\[ W(D) = A \rho 2\pi \int_{Z=D}^{Z=\infty} \int_{x=0}^{x=\infty} \frac{x}{(z^2 + x^2)^{n/2}} \, dx \, dz \]  

\[ W(D) = -A \rho 2\pi \int_{Z=D}^{Z=\infty} \frac{1}{(2-n)z^{n-2}} \, dz \]  

\[ W(D)_{MOL-SFC} = \frac{-2\pi A \rho}{(n-2)(n-3)D^{n-3}} \]  

\( n = \) determined by the type of interaction (see slide 2), related to the range of the interaction

\( A = \) molecular level parameter; related to strength of the interaction

\( \rho = \) atomic density
INTERACTION POTENTIAL BETWEEN AN ATOM / MOLECULAR AND SURFACE: DERIVATION

\[ W(D)_{MOL-SFC} = \frac{-2\pi A \rho}{(n-2)(n-3)D^{n-3}} \]

London Dispersion Interactions \( n = 6 \):

\[ W(D)_{MOL-SFC} = \frac{-\pi A \rho}{6D^3} \]

\[ F(D)_{MOL-SFC} = \frac{\partial W(D)}{\partial D} = \frac{-\pi A \rho}{2D^4} \]