LECTURE 10: MOLECULE-SURFACE INTERACTIONS

Outline :

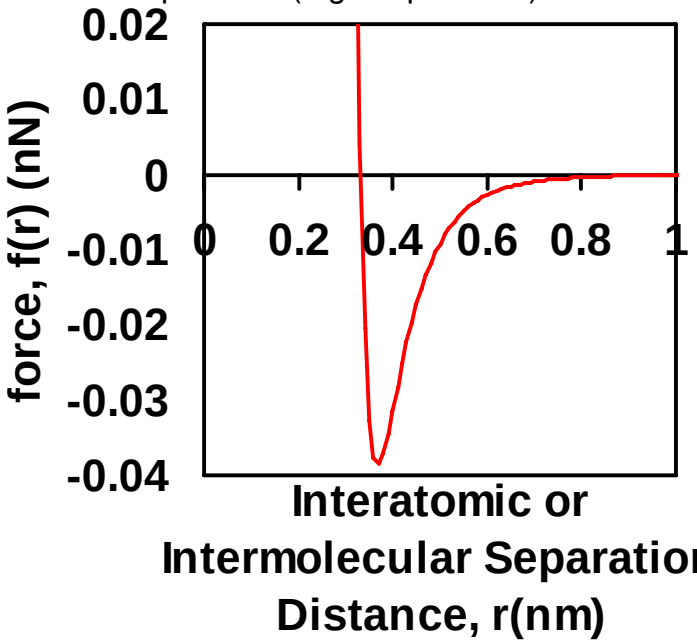
Objectives: To mathematically scale up intermolecular potentials to intersurface and interparticle potentials

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

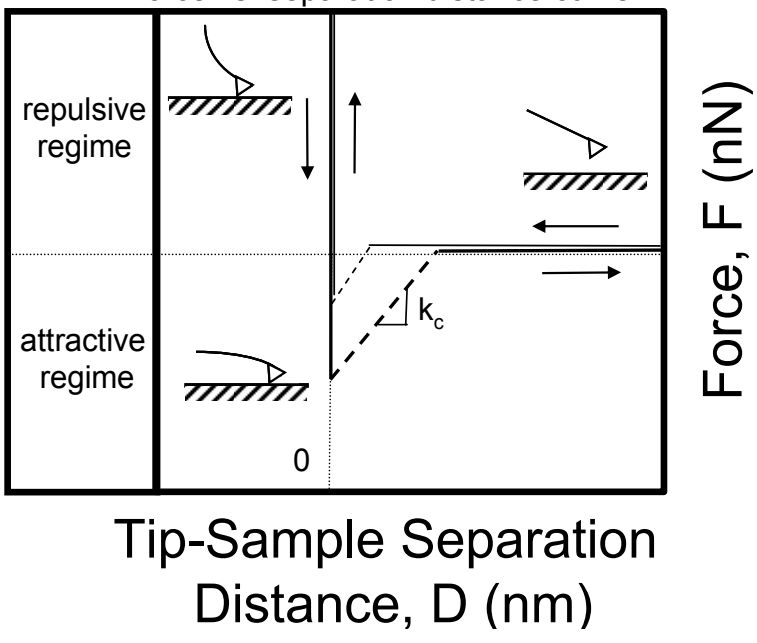
Multimedia : Bonding and Protein Structure Demo (California Lutheran University).

BRIDGING THE GAP BETWEEN LENGTH SCALES

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

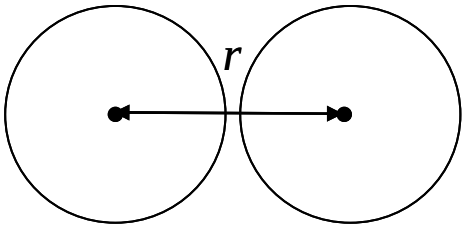


A typical intersurface or interparticle force vs. separation distance curve

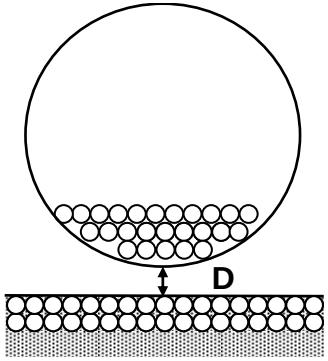


w(r) or U(r) → f(r)
(one atom, ion, or molecule)

$$w(r) = -Ar^{-6}$$

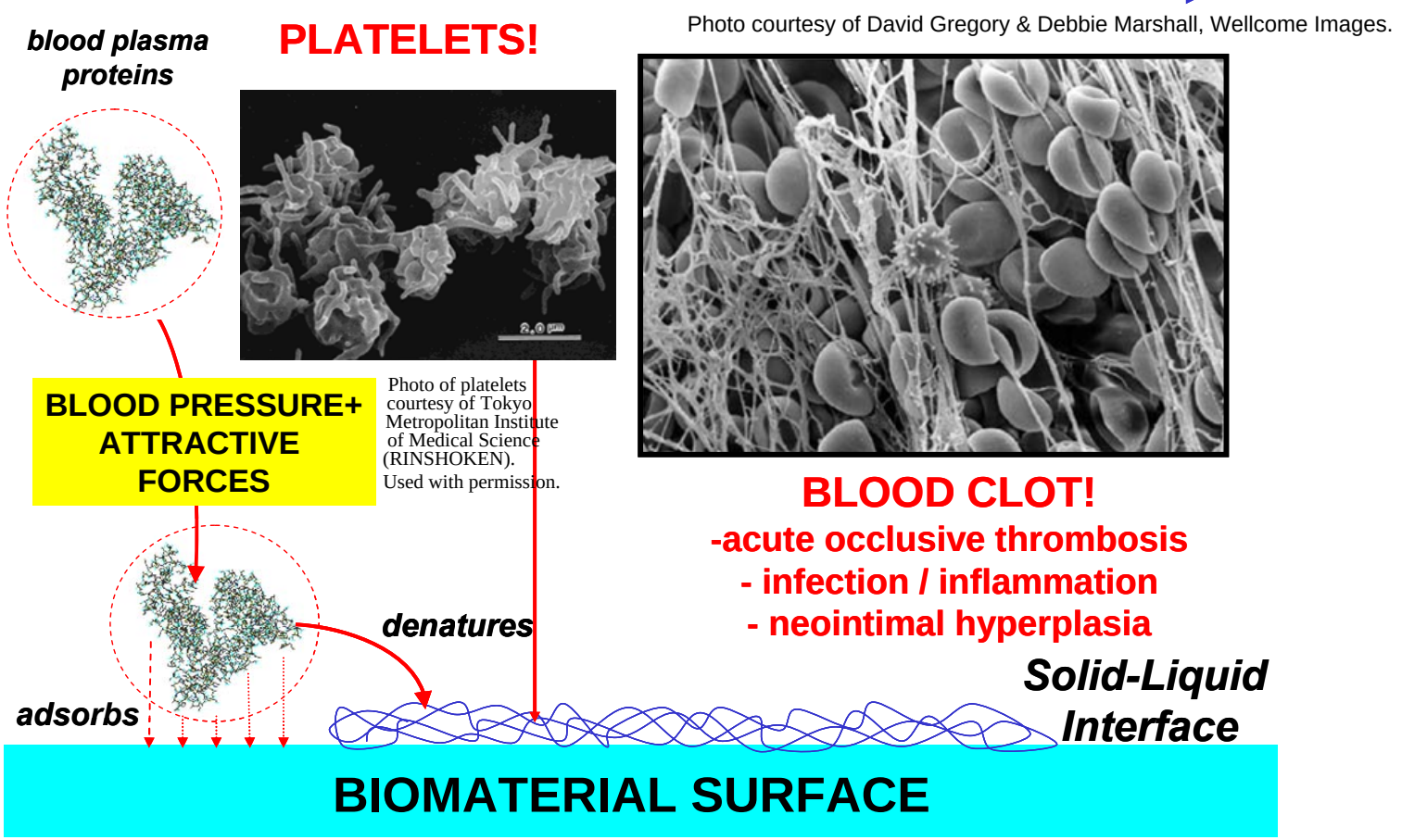


W(D) → F(D)
(net interaction between larger bodies, i.e. assemblies of atoms, ions, or molecules)



MOLECULE-SURFACE INTERACTIONS : MOLECULAR ORIGINS OF BIOCOMPATIBILITY

BLOOD FLOW



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 interacion energy of a body is the sum of the individual interatomic/intermolecular interactions of the constituent atoms or molecules which make up that body

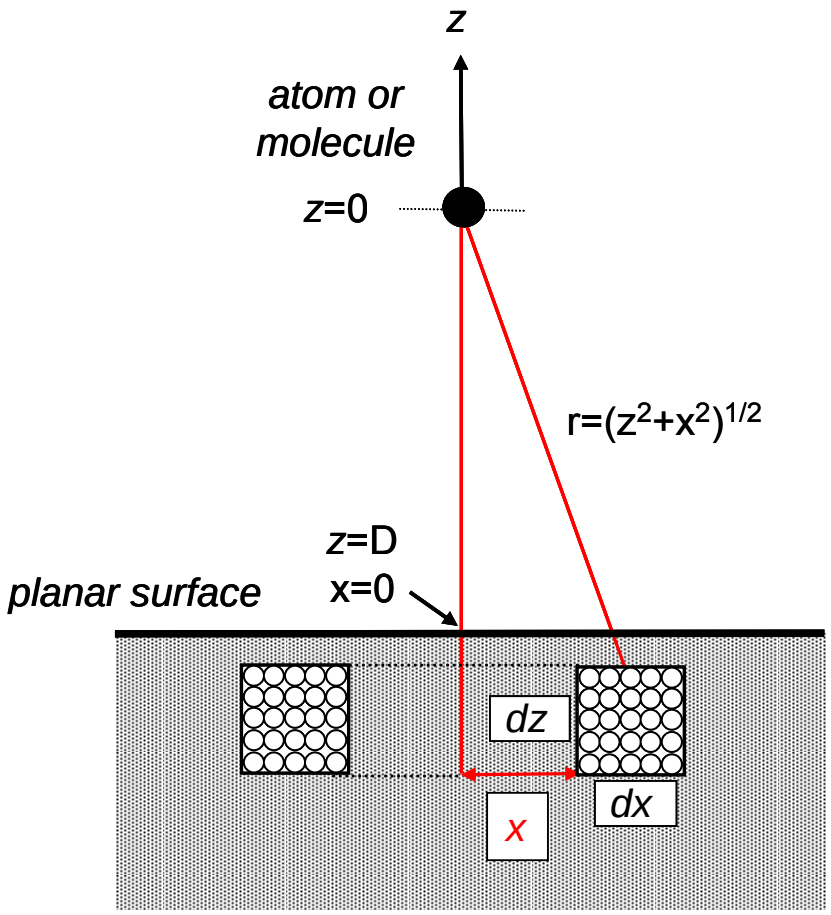
4) A solid **continuum** exists : the summation is replaced by an integration over the volumes of the interacting bodies assuming a number density of atoms/molecules/m^3, ρ

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

↓ volume integration

$$W(D) = \int\int\int w(r) \bullet \rho \, dV$$

\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

= circular ring radius (m)

A = infinitesimal cross-sectional area (m^2) = dx dz

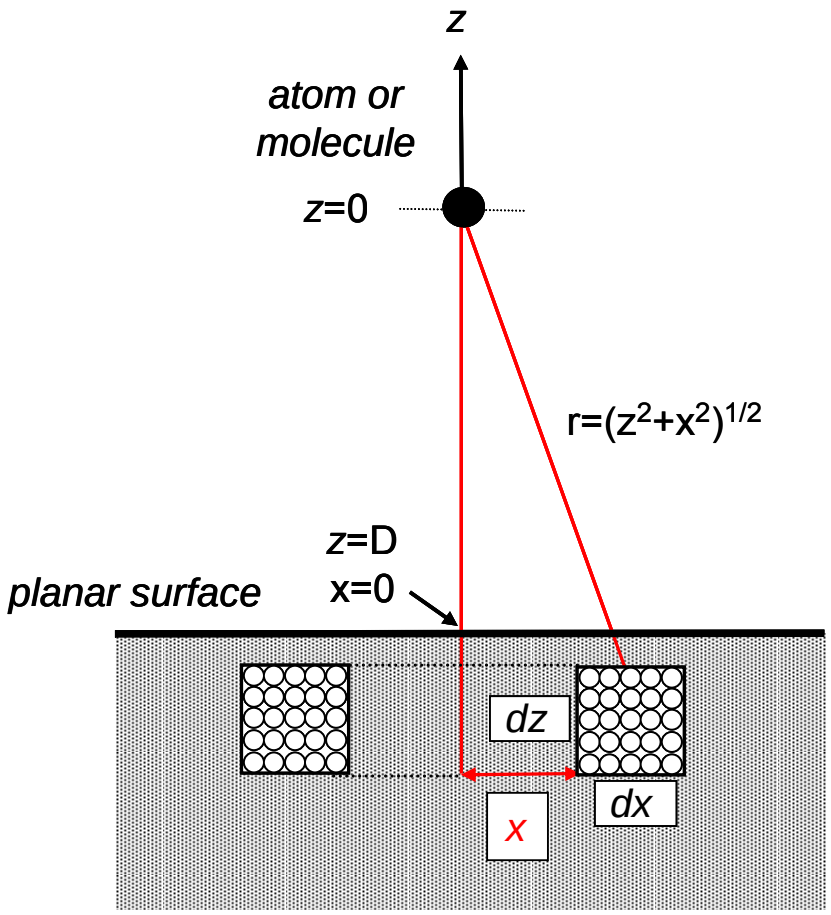
V = ring volume (m^3)= $2\pi x$ (dxdz)

N = # of atoms within the ring = ρ ($2\pi x$) dx dz

ρ = number density of atoms in the material constituting the surface ($atoms/m^3$)

r = 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)* : $r = \sqrt{z^2 + x^2}$ *(2)*

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

Net Interaction Energy :

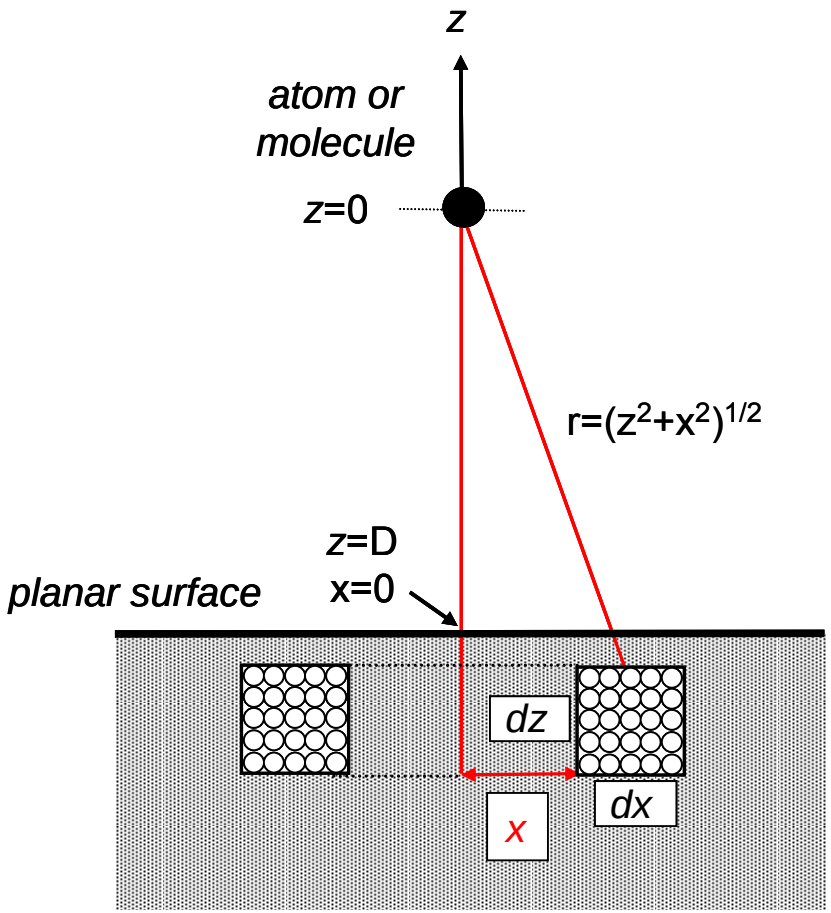
$$W(D) = \iiint w(r) \bullet \rho \, dV$$

$$W(D) = \int_{Z=D}^{Z=\infty} \int_{x=0}^{x=\infty} \underbrace{w(r)}_{\text{potential of each molecule}} \underbrace{\rho\left(2\pi x\right) dz\, dx}_{\text{number of molecules}} \quad (4)$$

substitute (1) → (2)

$$W(D) = \int_{Z=D}^{Z=\infty} \int_{x=0}^{x=\infty} -\frac{A}{\left(z^2 + x^2\right)^{n/2}} \rho\left(2\pi x\right) dz dx \quad (5)$$

INTERACTION POTENTIAL BETWEEN AN ATOM / MOLECULAR AND SURFACE: DERIVATION



Pull out constant terms :

$$W(D) = A\rho 2\pi \int_{Z=D}^{Z=\infty} dz \underbrace{\int_{x=0}^{x=\infty} -\frac{x}{\left(z^2+x^2\right)^{n/2}}\,dx}_{\text{Integral 1}} \quad (6)$$

$$W(D) = -A\rho 2\pi \underbrace{\int_{Z=D}^{Z=\infty} \frac{1}{(2-n)\,z^{n-2}}dz}_{\text{Integral 2}} \quad (7)$$

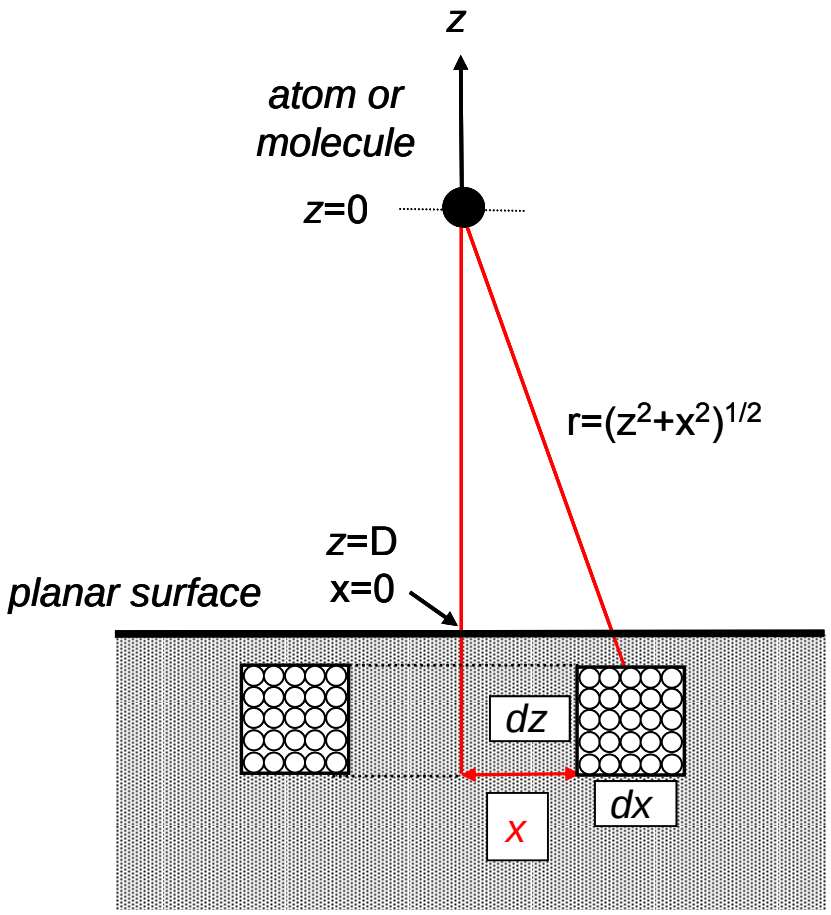
$$W(D)_{MOL\text{-}SFC} = \frac{-2\pi A\rho}{(n-2)(n-3)D^{n-3}} \quad (8)$$

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

ρ = atomic density

INTERACTION POTENTIAL BETWEEN AN ATOM / MOLECULAR AND SURFACE: DERIVATION



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

London Dispersion Interactions n = 6 ;

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

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