

LECTURE 9: QUANTITATIVE ASPECTS INTRA- AND INTERMOLECULAR FORCES

Outline :

LAST LECTURE : INTRODUCTION TO INTRA- and INTERMOLECULAR FORCES.....	2
BRIDGING THE GAP BETWEEN LENGTH SCALES	3
INTRA- AND INTERMOLECULAR POTENTIALS	4-9
<i>Review of General Equations and LJ Potential</i>	4
<i>Forms for Different Interactions</i>	5
<i>History and Perspectives</i>	6
<i>Example : Charge -Dipole Interaction</i>	7
<i>More Complex Potentials and Additivity</i>	8
<i>Binding Strengths and Equilibrium Bond Lengths</i>	9

Objectives: To establish a quantitative framework for intra- and intermolecular forces

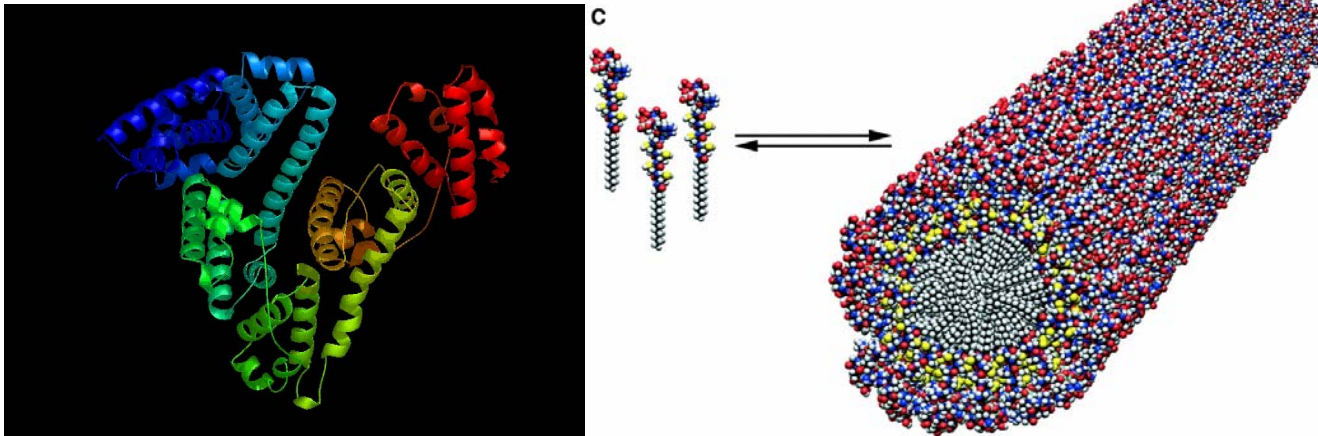
Readings: Course Reader documents 18-20, G. Malescio, "*Intermolecular potentials- past, present, and future*" *Nature Materials* 2, 501 **2003** (posted on Stellar Supplementary Resources)

Multimedia : Heparin Biosensor Podcast; *Monitoring of heparin and its low-molecular-weight analogs by silicon field effect*, Nebojsa M. Milovic, Jonathan R. Behr, Michel Godin, Chih-Sheng Johnson Hou, Kristofor R. Payer, Aarthi Chandrasekaran, Peter R. Russo, Ram Sasisekharan, and Scott R. Manalis *PNAS* **2006**, 103, 36, 13374-13379.

LAST LECTURE : INTRODUCTION TO INTRA- AND INTERMOLECULAR FORCES

(*within* individual molecules) (*between* individual molecules) → no real physical difference

- Definitions : **Interaction** (more general), **force** (push or pull), **bond** (the attraction between atoms in a molecule or crystalline structure) → all intra- and intermolecular forces are electrostatic in origin → key to life on earth (e.g. water, cell membranes, protein folding, etc.), also materials science (what holds matter together?).
- strength measured relative to the thermal energy (room temperature) : $k_B T = 4.1 \bullet 10^{-21} \text{ J}$: "ruler"
- Classifications; **primary** or chemical, **secondary** or physical, and "**special**"
- Biological systems and bottom-up self-assembly is based on the balance and interplay of intra- and intermolecular forces.
- Noncovalent interactions allow for dynamic systems, i.e. breaking reversible reforming bonds doesn't require much energy)/individually weak, forces are cumulative → stable in parallel.
- Specific types of intra- and intermolecular forces; **ionic**, **polar (e.g. H-bonds)**, **polarization**, **London dispersion**, **hydrophobic** (CR document 17)
- Two examples (biological and synthetic) : noncovalent interactions in folded proteins (human serum albumin) and self-assembling peptide amphiphiles (i.e. how chemical structure was designed)



hierarchical levels of protein structure-"native" and "denatured"

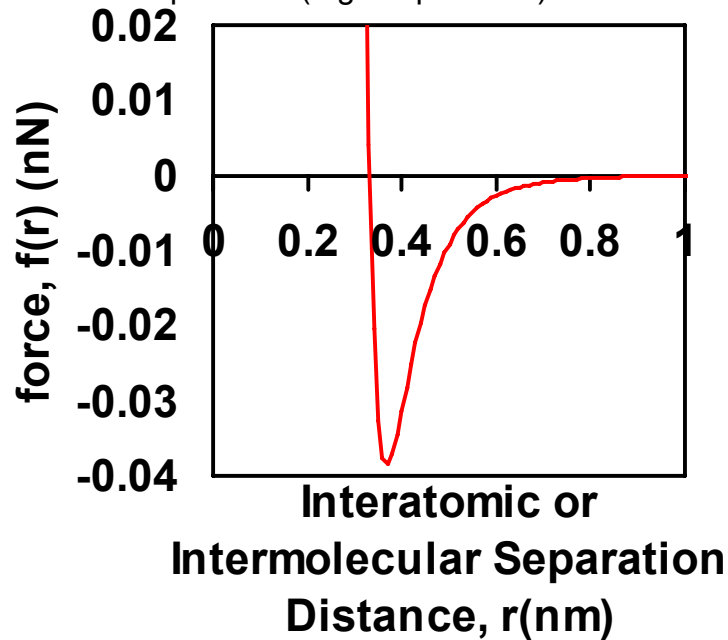
Hartgerink, et al. *Science*, **2001**

Review of Definitions : Supplementary Resources Section of Stellar

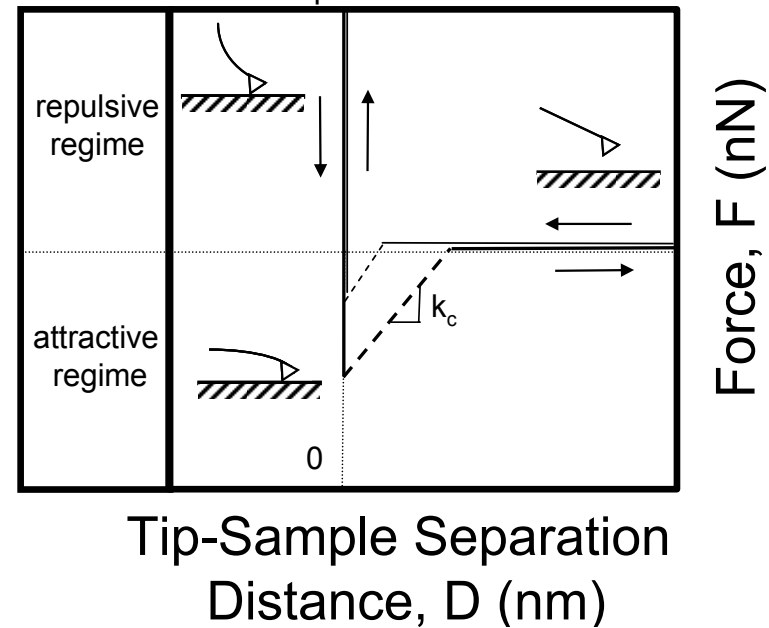
<http://stellar.mit.edu/S/course/3/sp07/3.052/courseMaterial/topics/topic3/resource/intraintermoleculardefinitions/intraintermoleculardefinitions.pdf>

BRIDGING THE GAP BETWEEN LENGTH SCALES

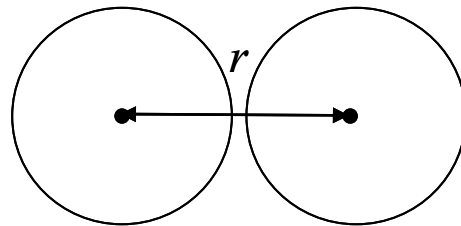
-A typical inter- atomic, ionic, or intamolecular potential (e.g. LJ potential)



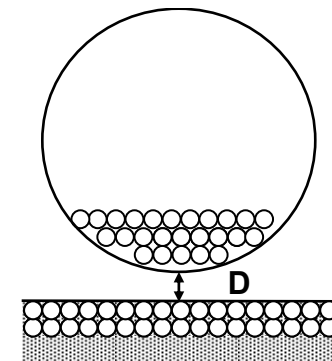
A typical intersurface or interparticle force vs. separation distance curve



$w(r)$ or $U(r) \rightarrow f(r)$
 (one atom, ion, or molecule)
 -1st step is to assume a mathematical form of the potential



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



REVIEW OF GENERAL EQUATIONS AND LENNARD JONES (LJ) POTENTIAL

Interatomic Potential or Bond Energy (J or $k_B T$) :

$$U(r) \text{ or } w(r) = U_{\text{attractive}}(r) + U_{\text{repulsive}}(r) = \frac{-A}{r^m} + \frac{B}{r^n} = -\int F(r) dr \quad (1)$$

$$\text{Interatomic (Bond) Force (nN)} : F(r) = \frac{-dU(r)}{dr} = \int k(r) dr \quad (2)$$

$$\text{Interatomic (Bond) Stiffness (nN/nm)} : k(r) = \frac{-d^2U(r)}{dr^2} = \frac{dF(r)}{dr} \quad (3)$$

r (nm) = interatomic separation distance

A, B, m, n = constants determined by the type of interaction

k_B = Boltzmann's constant = 1.38×10^{-23} J/K

T = absolute temperature (K)

$$U_{LJ}(m=6, n=12) = \frac{-A}{r^6} + \frac{B}{r^{12}} = 4E_B \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (4)$$

$$F_{LJ}(m=6, n=12) = \frac{-6A}{r^7} + \frac{12B}{r^{13}} \quad (5)$$

E_B = "binding energy" or "bond dissociation energy";
or depth of potential well

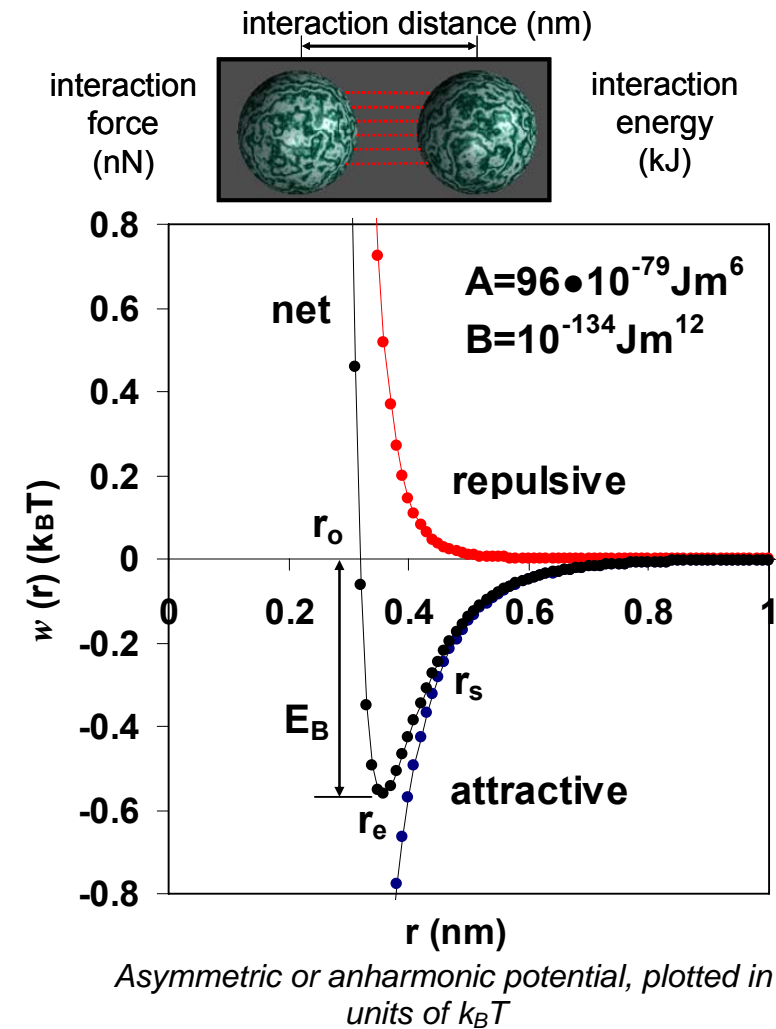
r_s = distance at which $U(r_s)$ exhibits an inflection point,

$F(r_s)$ = minimum = F_{RUPTURE}

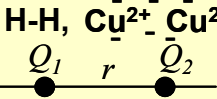
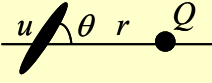
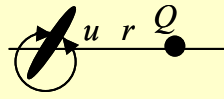
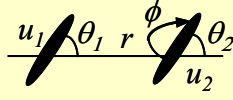
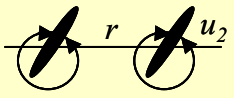
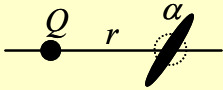
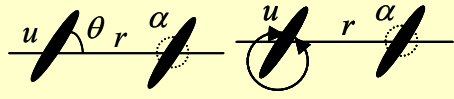
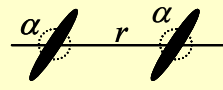
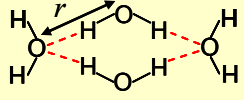
r_e = equilibrium bond length

= distance at which $U(r_e) = \text{minimum}$, $F(r_e) = 0$

$r_o = \sigma$ = distance at which $U(r_o) = 0$, $F(r_o) = \infty$



FORMS OF INTERATOMIC / INTERMOLECULAR POTENTIALS

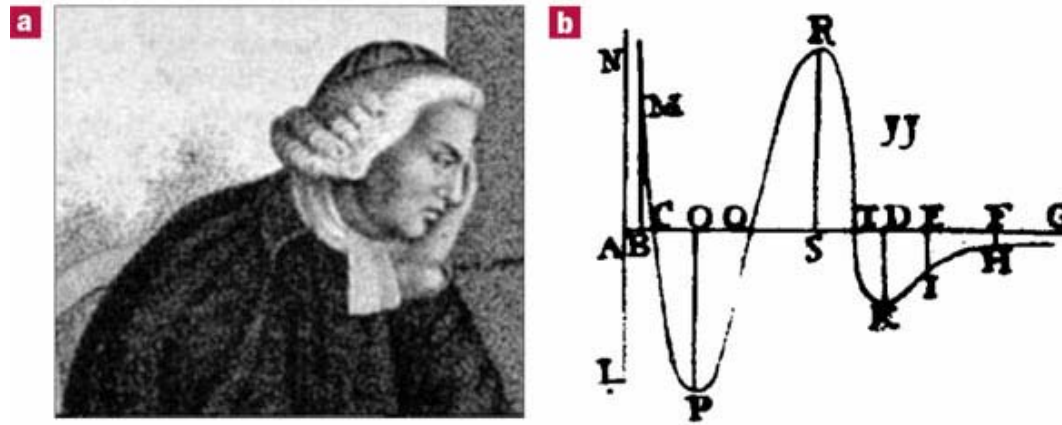
Type of interaction	Schematic	Interaction Energy, $w(r)$
covalent, metallic charge-charge	 <p style="text-align: center;">H-H, Cu^{2+}, Cu^{2+}</p>	Complicated, short range $w(r) = \left(\frac{Q_1 Q_2}{4\pi\epsilon_0} \right) r^{-1} \text{ (Coulomb Energy)}$
charge-dipole	 <p style="text-align: center;"><i>fixed dipole</i></p>  <p style="text-align: center;"><i>freely rotating dipole</i></p>	$w(r) = - \left(\frac{Q u \cos\theta}{4\pi\epsilon_0} \right) r^{-2}$
dipole-dipole	 <p style="text-align: center;"><i>fixed dipole</i></p>  <p style="text-align: center;"><i>freely rotating dipoles</i></p>	$w(r) = - \left(\frac{Q^2 u^2}{6(4\pi\epsilon_0)^2 k_B T} \right) r^{-4}$ $w(r) = - \left(\frac{u_1 u_2 [2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi]}{4\pi\epsilon_0} \right) r^{-3}$
charge-induced dipole		$w(r) = - \left(\frac{Q^2 \alpha}{2(4\pi\epsilon_0)^2} \right) r^{-4}$
dipole-induced dipole	 <p style="text-align: center;"><i>fixed dipole</i> <i>freely rotating dipole</i></p>	$w(r) = - \left(\frac{u^2 \alpha (1 + 3\cos^2\theta)}{2(4\pi\epsilon_0)^2} \right) r^{-6}$
induced dipole-induced dipole		$w(r) = - \left(\frac{u^2 \alpha}{(4\pi\epsilon_0)^2} \right) r^{-6} \text{ (Debye Energy)}$
hydrogen bond		$w(r) = - \left(\frac{3h\nu\alpha^2}{4(4\pi\epsilon_0)^2} \right) r^{-6} \text{ (London Dispersion)}$ <p style="text-align: center;">Complicated, short range, $w(r) \sim -r^{-2}$</p>

$w(r)$ = interaction free energy (J), Q = electric charge (C), u = electric dipole moment (C m), α = electric polarizability ($\text{C}^2 \text{m}^2 \text{J}^{-1}$), r = distance between interacting atoms or molecules (m), k_B = Boltzmann's constant = $1.381 \cdot 10^{-23} \text{ J K}^{-1}$, T = absolute temperature (K), h = Planck's constant = $6.626 \cdot 10^{-34} \text{ J s}$, ν = electronic absorption (ionization) frequency (s^{-1}), ϵ_0 = dielectric permittivity of free space = $8.854 \cdot 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1}$. The force is obtained by differentiating the energy, $w(r)$, with respect to the distance, r . (*Adapted from Israelachvili, *Intermolecular and Surface Forces* 1992)

INTERMOLECULAR POTENTIALS: HISTORY AND PERSPECTIVE

A really interesting article (posted in Supplementary Materials Resources of Stellar) :

"Intermolecular Potentials- past, present, future" Gianpietro Maescio *Nature Materials* **2003**, 2, 501.



-**Isaac Newton** (1704) : Attraction between atoms

-**Roger Joseph Boscovich** (1745) - 1st force-distance curve (qualitative)

-**Giuseppe Belli** (1814) : from experimental data concluded $\sim 1/r^n$

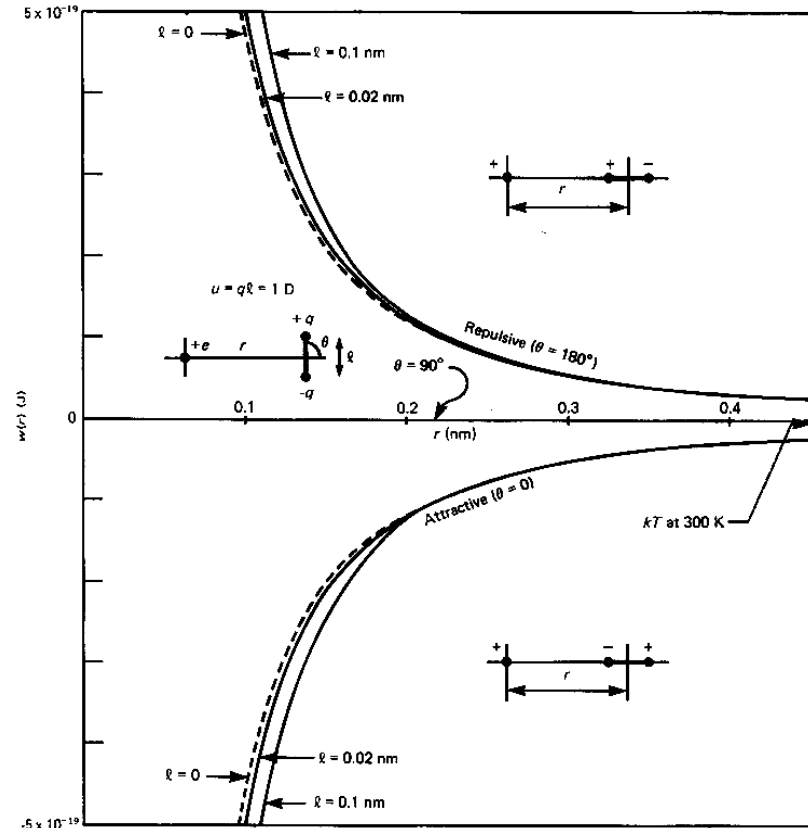
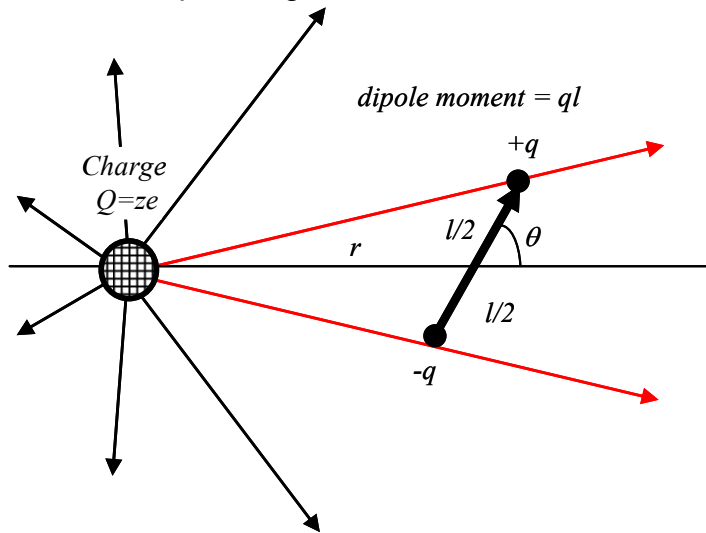
-**Maxwell, Van der Waals, Debye, London** :

- quantum mechanics/ correspondence with classical electrostatics, interactions between the electrons and nuclei forming the molecules \rightarrow calculation requires solving the Schrödinger equation for a system of interacting particles. The energy associated with the electronic motion is the potential energy for the motion of the nuclei, and can be regarded as the intermolecular (effective) interaction potential.

SAMPLE POTENTIAL : CHARGE - FIXED DIPOLE INTERACTION

$$w(r) = - \left(\frac{Qucos\theta}{4\pi\epsilon_0} \right) r^{-2} \quad (1)$$

- r = charge-dipole separation distance (nm)
- u = electric dipole moment = ql (Cm)
- q = charge of dipole (C)
- l = separation distance between dipole charges (m)
- Q = charge of the ion (C)
- θ = dipole angle relative to horizontal



(*From Israelachvili, Intermolecular and Surface Forces 1992)

MORE COMPLEX POTENTIALS : ADDITIVITY

$$w(r)_{VDW} = w(r)_{orient} + w(r)_{induced} + w(r)_{dispersion} \quad (1)$$

Keesom Energy : Freely rotating dipole-freely rotating dipole interaction : $w(r)_{orient} = \left(\frac{-u^2 \alpha}{3kT(4\pi\epsilon_0)^2} \right) r^{-6} = C_{orient} r^{-6} \quad (2)$

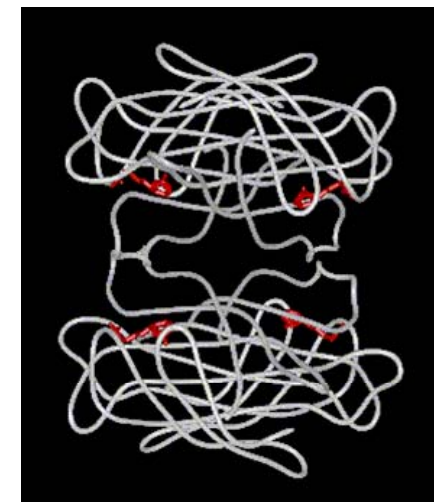
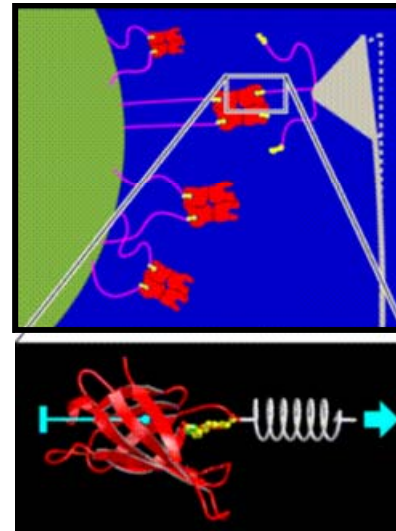
Debye Energy : Freely rotating dipole- nonpolar (induced dipole) interaction : $w(r)_{induced} = \left(\frac{-u^2 \alpha}{(4\pi\epsilon_0)^2} \right) r^{-6} = C_{induced} r^{-6} \quad (3)$

Dispersion Energy : Induced dipole-induced dipole : $w(r)_{dispersion} = \left(\frac{-3h\nu\alpha^2}{4(4\pi\epsilon_0)^2} \right) r^{-6} = C_{dispersion} r^{-6} \quad (4)$

Biomolecular Adhesion :

-controlled by bonds between molecular “ligands” and cell surface “receptors” which exhibit the “lock-n-key principle” (e.g. biotin-streptavidin)

- **complex, multiatomic, relatively weak**
- **formed by an assembly of multiple, weak non-covalent interactions**
(e.g. H-bonding, coulombic, van der Waals, hydrophilic / hydrophobic, electrostatic)
- **complementary, sterically-constrained geometric considerations**
- **specificity**



Grubmüller, et al, Science 1996 (*<http://www.mpibpc.gwdg.de/abteilungen/071/strept.html>)
(*<http://www.amber.ucsf.edu/amber/tutorial/streptavidin/index.html>)

BINDING STRENGTH AND EQUILIBRIUM BOND LENGTHS

Interaction	Strength, kJ/mol	Strength, $k_B T$
dispersion	0.05-40	0.02-16
hydrophobic	0.4	0.17
dipole-induced dipole	2-10	0.8-4
THERMAL ENERGY	2.5	1
dipole-dipole	5	2
ion-ion	13	5
H-bond	10-40	4-16
lipid in bilayer (hydrophobic)	25	10
carbohydrate-L-selection	62	25
biotin-avidin	125	50
single covalent, C-C	380	150
double covalent, C=C	630	250
triple covalent, C≡C	840	340

Interaction	Interaction Distance (nm)
dispersion	0.35
hydrophobic	0.35
H-bonding	0.3
ion-ion	0.25
covalent	0.1-0.2

Material	Interaction
metals	metallic
ceramics and glasses	covalent / ionic
semiconductors	covalent / ionic
diamond	covalent
water	covalent, H-bonding
inert gases	dispersion
solid salt crystals	ionic
alkanes, hydrocarbons, flourocarbons, amphiphiles in water	hydrophobic
polymers/proteins	potentially all-depending on chemical structure