INTERATOMIC/INTERMOLECULAR INTERACTIONS:

Repulsive Interaction

Attractive Interaction

Graph showing the interaction as a function of $R_{AB}$.
# Intermolecular Interactions

## Electrostatic Interactions

<table>
<thead>
<tr>
<th>Type</th>
<th>Distance Dependence</th>
<th>Energy</th>
<th>$kJ$/mole Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>$r^{-1}$</td>
<td>$\frac{8a_1 8b}{\varepsilon r}$</td>
<td>40 - 400</td>
</tr>
<tr>
<td>Ion-Dipole</td>
<td>$r^{-2}$</td>
<td>$-\frac{18a_1 \mu b}{\varepsilon r^2}$</td>
<td>4 - 40</td>
</tr>
<tr>
<td>Dipole-Dipole</td>
<td>$r^{-3}$ $r^{\frac{8}{6}}$</td>
<td>$-\frac{k \mu a \mu b}{\varepsilon r^3}$</td>
<td>0.4 - 4</td>
</tr>
<tr>
<td>Ion-Induced Dipole</td>
<td>$r^{-4}$</td>
<td>$-\frac{1}{2} \frac{\alpha b^2}{\varepsilon r^4}$</td>
<td>0.4 - 4</td>
</tr>
<tr>
<td>Dipole-Induced Dipole</td>
<td>$r^{-6}$</td>
<td>$-\frac{2 \alpha a_1 \mu^2}{\varepsilon r^6}$</td>
<td>0.4 - 4</td>
</tr>
<tr>
<td>Dispersion</td>
<td>$r^{-6}$</td>
<td>$-\frac{3}{2} C \frac{\alpha a_1 \alpha b}{r^6}$</td>
<td>0.04 - 40</td>
</tr>
</tbody>
</table>

**Van der Waals Forces**

- Hydrogen Bond
- Covalent Bond
1. Ionic Interactions

\[ \frac{1}{r} \]

Long range interaction
Proportional to product of charges

2. Ion-Dipole Interactions

\[ \frac{1}{r^2} \]

Repulsive
Attractive
Orientation dependent

3. Dipole-Dipole Interactions

\[ k = 2 \]

\[ k = 1 \]

\[ E = -\frac{x m_A m_B}{\varepsilon r^3} \]

\( k \) is a geometry dependent factor

In a liquid - "Randomly oriented"

\[ \langle E \rangle = -\frac{2}{3} \frac{m_A^2 m_B^2}{\varepsilon \mu^2} \left( \frac{1}{kT} \right) \]

High temp ⇒ less tendency to align
4. Ion-Induced Dipole Interaction

The presence of an ion can induce formation of a dipole.

* \( \alpha = \text{polarizability} \times (\text{length})^3 \)

"The ability of an electron distribution to be polarized by an external charge distribution, or electric field."

\[
\mu_{\text{ind}} = \alpha \overline{E} \quad \text{Electric field} \quad \left( \frac{Q}{F^2} \right)
\]

Induced dipole

\[
E = -\frac{1}{2} \frac{\alpha Q^2}{F^4}
\]

Polarizability is related to the volume of the electron cloud.

\( \alpha_{\text{Ne}} < \alpha_{\text{Ar}} < \alpha_{\text{Kr}} < \alpha_{\text{Xe}} \)
5. DIPOLE - INDUCED DIPOLE INTERACTIONS

The presence of a dipole will induce formation of a dipole.

\[
E = -\frac{2\alpha \mu^2}{\varepsilon r^6}
\]

Depends on polarizability.

Note: Induced dipoles are always in an attractive orientation.

Very short range interaction.

\[\gamma \approx \gamma_0 \text{ for large } \gamma!\]

Doesn't drop off quite as fast.
6. LONDON DISPERSION INTERACTION

Electrons moving "randomly" in atom or molecule.

Instantaneous dipole may induce a dipole moment in neighboring atoms or molecules.

Dipole-induced dipole \( \propto \frac{1}{r^6} \)

\[ E = -k \alpha_a^2 \frac{1}{\varepsilon r^6} \quad \text{or} \quad -k \alpha_a \alpha_B \frac{\alpha_a \alpha_B}{\varepsilon r^6} \]

\( k \) is \( \alpha_a \) or \( \alpha_B = "\text{probability of instantaneous dipoles being formed}" \)
**REPUlSIVE INTERACTIONS**

Clearly atoms or molecules can only get so close before repulsive interactions become dominant.

Molecules/atoms cannot occupy the same space.

But interaction is not "hard sphere" because electron clouds can deform.

Extremely short range $\frac{1}{r^9} \rightarrow \frac{1}{r^{12}}$

"Tennis ball" like $\rightarrow$ "Billiard ball" like
LENNAARD - JONES 6-12 POTENTIAL

\[ E = -\frac{A}{r^6} + \frac{B}{r^{12}} \]

**ATTRACTION**  \[\underline{\text{REPELLENT}}\]

DIPOLE - DIPOLE
DIPOLE - INDUCED DIPOLE
DISPERSION

THEORETICAL SIMULATIONS ARE OFTEN PERFORMED ON LENNARD-JONESIUM, A REALISTIC BUT STILL ANALYTIC POTENTIAL

\[ V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \]
HYDROGEN BONDS:

\[ \delta^- - \delta^+ \]

\[ \text{A-H bond} \]

- Substantial charge separation

\[ \Rightarrow \text{Large bond moment} \]

- \[HF\] \( \mu = 1.91 \text{ Debye}\n\]
- \[HCl\] \( \mu = 1.08 \text{ D}\n\]
- \[HO\] \( \mu = 1.5 \text{ D}\n\]
- \[HN\] \( \mu = 1.3 \text{ D}\n\]

HYDROGEN PROTON IS LEFT RELATIVELY UNSHIELDED!

"BARE PROTON!"
Hydrogen Bonds in Biology:

Responsible for DNA Double Helix:

\[
\text{A} \quad \text{T} \\
\text{C} \quad \text{G}
\]

The hydrogen bonds are base specific

Cytosine and Guanine fit

Adenine and Thymine fit

All other combinations do not allow formation of the full complement of hydrogen bonds.
Hydrogen bonds and protein secondary structure:

Alpha-helix

Held together by hydrogen bonds.

Beta-sheet is also held together by hydrogen bonds.
(6) WATER AND ICE

DENSITY OF ICE