Intermolecular Forces (Chapter 13)

Many kinds of bonds play role in chemistry, stability & structure of proteins, melting & vaporization.

Relation between force, $F$, & pot. energy, $V$:

$$F = -\frac{dV}{dr}$$

$r = \text{distance between atoms}$

$r_e = r \text{ at equilibrium}$
Intermolecular Forces (Chapter 13)

We’ll discuss: (1) Ionic bond; (2) Dipole-dipole interaction; (3) Ion-dipole interaction; (4) Induced dipole; (5) Dispersion interactions.

How does $V$ depend on $r$ for these bonds?

(1) Ionic bond: Example is $\text{Na}^+\text{Cl}^-$.

Coulomb’s law: 

$$V = -\frac{q_{\text{Na}^+}q_{\text{Cl}^-}}{4\pi\varepsilon_0 r}$$

$q$ = charge in Coulombs (C).

Attractive contribution to bond.

If ions are close, also repulsive part: $b/r^n$

$b = \text{constant}$ \quad $8 \leq n \leq 12$.

$$V = -\frac{q_{\text{Na}^+}q_{\text{Cl}^-}}{4\pi\varepsilon_0 r} + \frac{b}{r^n}$$

Value of $b$?
Intermolecular Forces (Chapter 13)

(1) Ionic bond: Example is Na\(^+\)Cl\(^-\).

\[
V = -\frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 r} + \frac{b}{r^n}
\]

At \( r = r_e \), \( F = 0 \) and \( V \) is minimum:

\[
F = 0 = -\frac{dV}{dr}\bigg|_{r=r_e} = -\frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 r_e^2} + \frac{nb}{r_e^{n+1}}
\]

Solving for \( b \):

\[
b = \frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 n} r_e^{n-1}
\]

Insert into \( V \) at \( r_e \):

**Binding energy:**

\[
V_0 = V(r_e) = -\frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 r_e} + \frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 nr_e} = -\frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 r_e}\left(1 - \frac{1}{n}\right)
\]
(1) Ionic bond: Example is Na\(^+\)Cl\(^-\).

Binding energy: 
\[ V_0 = V(r_e) = -\frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 r_e} + \frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 nr_e} = -\frac{q_{Na^+}q_{Cl^-}}{4\pi\varepsilon_0 r_e} \left(1 - \frac{1}{n}\right) \]

What is \(V_0\) for NaCl?

\(r_e = 2.36\ \text{Å}\) (measured by rotational spectroscopy)
\(n = 10\) (assume)

\[ V_0 = -\frac{(1.602 \times 10^{-19} \text{C})^2 (6.022 \times 10^{23} \text{ mol}^{-1})}{4\pi (8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(2.36 \times 10^{-10} \text{ m}) \left(1 - \frac{1}{10}\right)} \]

\[ V_0 = -529.7 \ \text{kJ mol}^{-1} \]

(Changing \(n\) changes result by few %.)
(2) Dipole-dipole interaction: Between polar molecules with permanent dipole moment, $\mu$.

$V(r)$ depends on alignment of 2 dipoles, A and B:

\[
V(r) = -\frac{\mu_A \mu_B}{2\pi \varepsilon_0 r^3}
\]

Attractive part of $V$:

\[
V(r) = -\frac{\mu_A \mu_B}{4\pi \varepsilon_0 r^3}
\]

Also attractive:

$\mu$ has dimensions of charge x distance. Units could be $C \times m$; more common to use Debye (D):

1 D = $3.3356 \times 10^{-30} \ C \ m$.  

Example: $\mu_{HCl} = 1.08 \ D$
(2) Dipole-dipole interaction: Between polar molecules with permanent dipole moment, \( \mu \).

\( \mu \) has dimensions of charge x distance. Units could be \( \text{C} \times \text{m} \); more common to use Debye (D):

\[
1 \text{ D} = 3.3356 \times 10^{-30} \text{ C m.}
\]

Example: \( \mu_{\text{HCl}} = 1.08 \text{ D} \)

\( V(r) \) depends on orientation; high temp. (T) --> poor alignment of dipoles.

\[
V(r) = -\frac{2 \left( \mu_A \mu_B \right)^2}{3 \cdot 4 \pi \varepsilon_0 r^6} \frac{1}{k_B T}
\]

Trends:

\[
V(r) \propto \frac{1}{T}
\]

\[
V(r) \propto \frac{1}{r^6}
\]

\( k_B \) = Boltzmann’s constant
(3) Ion-dipole interaction: Charge-dipole interaction

\[ V(r) = -\frac{q\mu}{4\pi\varepsilon_0 r^2} \]

(4) Induced dipole:
Neutral, non-polar species has electron density spherically symmetric about nucleus:

Charge or dipole changes charge density:
(4) Induced dipole:

Related to electric field, $E$: $\mu_{\text{ind}} = 4\pi\varepsilon_0 \alpha E$

$\alpha = \text{polarizability}; \text{ ease of distorting electron density by external electric field. (units, } m^3.\text{)}$

Highly polarizable groups: Unsaturated bonds ($C=C$, $C=N$), nitrogroup ($-\text{NO}_2$), phenyl group ($-\text{C}_6\text{H}_5$), base pairs in DNA.

Interactions:

If ion of charge $q$ induces dipole: $V(r) = -\frac{\alpha q^2}{8\pi\varepsilon_0 r^4}$

If permanent dipole, $\mu$, induces dipole: $V(r) = -\frac{\alpha \mu^2}{4\pi\varepsilon_0 r^6}$
Dispersion (London) Interactions: Interactions between atoms, nonpolar molecules.

Instantaneous dipole: If \( \alpha \) is large, instantaneous dipole of molecule A “locks in” with instantaneous dipole of B:

\[
V(r) = -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r^6}
\]

\( I_A \) = first ionization energy of molecule A.

van der Waals interactions: All interactions with \( V(r) \propto \frac{1}{r^6} \)

Van der Waals interactions: dipole-dipole, dipole-induced dipole & dispersion.
Van der Waals Interactions:

Add repulsive term: \( b/r^n \quad 8 \leq n \leq 12. \)

A van der Waals potential:

\[
V(r) = -\frac{a}{r^6} + \frac{b}{r^{12}}
\]

Lennard-Jones potential

Attractive part

Repulsive part

\( a, b = \) constants

Common form:

\[
V(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]

\( \varepsilon = \) depth of potential

\( \sigma = \) separation of molecules at \( V = 0 \)
## Summary of Intermolecular Forces

<table>
<thead>
<tr>
<th>Interaction</th>
<th>r-dependence</th>
<th>Example</th>
<th>Bond strength (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent bond</td>
<td>-</td>
<td>$H_2$</td>
<td>200 - 800</td>
</tr>
<tr>
<td>Ion-Ion</td>
<td>$1/r$</td>
<td>$Na^+Cl^-$</td>
<td>40 - 500</td>
</tr>
<tr>
<td>Ion-Dipole</td>
<td>$1/r^2$</td>
<td>$Na^+H_2O$</td>
<td>5 - 60</td>
</tr>
<tr>
<td>Ion-Induced Dipole</td>
<td>$1/r^4$</td>
<td>$Na^+C_6H_6$</td>
<td>1 - 40</td>
</tr>
<tr>
<td>Dipole-Dipole</td>
<td>$1/r^6$</td>
<td>$HCl - HCl$</td>
<td>1 - 40</td>
</tr>
<tr>
<td>Dipole-Induced Dipole</td>
<td>$1/r^6$</td>
<td>$HCl - C_6H_6$</td>
<td>1 - 40</td>
</tr>
<tr>
<td>Dispersion</td>
<td>$1/r^6$</td>
<td>$CH_4 - CH_4$</td>
<td>1 - 40</td>
</tr>
<tr>
<td>Hydrogen bond</td>
<td>-</td>
<td>$H_2O - H_2O$</td>
<td>1 - 40</td>
</tr>
</tbody>
</table>

Van der Waals: Short-range interactions
Hydrogen Bonding: Forms between polar bond containing H atom (O - H, N - H) and electronegative atom (O, N, F)

A - H ⋮ B A, B are electronegative atoms.

Hydrogen bond

Examples:

Why hydrogen bonds? If H bonds to electronegative atom, its electron moves to σ bond; nucleus is exposed to electronegative atom of different molecule.

Structures can be formed in liquid. For example, HF(liquid):

Hydrogen bonds form nearly linear chains of HF (+/- 30°).
Intramolecular hydrogen bonds: Important for stability, structure of DNA, proteins and can influence melting point of material.

Which has the higher melting point?:

Weak hydrogen bonds can form between F-H and polarizable (electron rich) group. Example:

Detection of hydrogen bonds: In crystals, X-ray diffraction studies find hydrogen bond shortens distance between A - H & B (A, B electroneg. atoms)

In liquids, hydrogen bonds are detected by NMR or infrared spectroscopy.
Hydrogen bonding in DNA: Double helical structure is result of hydrogen bonds between base pairs. Bonds perpendicular to axis of helix.

Bond energy of each hydrogen bond $\approx 5 \text{ kJ mol}^{-1}$. For CG pairing, $3 \text{ bonds} \times 5 \text{ kJ mol}^{-1} = 15 \text{ kJ mol}^{-1}$. 
Bond energy of each hydrogen bond $\approx 5 \text{ kJ mol}^{-1}$.

For CG pairing, $3 \text{ bonds } \times 5 \text{ kJ mol}^{-1} = 15 \text{ kJ mol}^{-1}$.

**What is relative population of CG bonded to CG non-bonded?**

For 2 populations, $P_1$ & $P_2$, with energies $E_1$ & $E_2$,

Relative populations: $P_2 / P_1 = e^{-(E_2 - E_1)/RT}$ (Boltzmann)

Call: non-bonded CG pair = “free”

bonded CG = “pair”

Then: $P_{CG,\text{free}} / P_{CG,\text{pair}} = e^{-(E_{\text{free}} - E_{\text{pair}})/RT} = e^{-\Delta E / RT}$

$\Delta E = E_{\text{free}} - E_{\text{pair}} = 0 - (-15 \text{ kJ/mol}) = 15,000 \text{ J/mol}$

$P_{CG,\text{free}} / P_{CG,\text{pair}} = e^{-(15,000 \text{ J/mol})/(8.314 \text{ J/mol K})(300K)} = 0.00244$

Then $(0.00244)^{-1} = 409$ pairs of CG’s for each free C & G.
Hydrophobic effect: Important for DNA stability, protein stability: origin is mainly entropy (rather than enthalpy).

Oil & water do not mix. Why?

Water forms structures (clathrate cages) around hydrocarbons of oil.

Clathrate cages are ice-like, low-entropy structures.

For example:

\[ C_6H_6(C_6H_6) \rightarrow C_6H_6(H_2O) \quad \Delta H \approx 0 \text{ kJ mol}^{-1} \]
\[ \Delta S = -57.7 \text{ J K}^{-1} \text{ mol}^{-1} \]

At \( T = 298 \text{K} \):

\[ \Delta G = \Delta H - T\Delta S = (-298 \text{ K})(-57.7 \text{ J K}^{-1} \text{ mol}^{-1}) = 17.2 \text{ kJ mol}^{-1} \]
Hydrophobic interaction: “Bonding” of nonpolar molecules to release some $\text{H}_2\text{O}$ from clathrate cage:

Gain in entropy from hydrophobic interaction.

$\Delta S < 0$
$\Delta G > 0$

$\Delta S > 0$
$\Delta G < 0$
Proteins form from amino acids (peptides):

Amino acids

\[ \text{H}_3\text{N}^+\text{C} \equiv \text{C} \equiv \text{O}^- + \text{H}_3\text{N}^+\text{C} \equiv \text{C} \equiv \text{O}^- \]

Dipeptide

\[ \text{H}_3\text{N}^+\text{C} \equiv \text{C} \equiv \text{N} \equiv \text{C} \equiv \text{O}^- \]

Polypeptide

\[ \text{H}_3\text{N}^+\text{C} \equiv \text{C} \equiv \text{N} \equiv \text{C} \equiv \text{N} \equiv \text{C} \equiv \text{O}^- \]

\( R = \text{side chain} \)

What is effect of moving \( R \) from non-polar solvent (such as \( C_6H_6 \)) to water?
Structure/Stability of Proteins (Chapter 16)

What is effect of moving R from non-polar solvent (such as $C_6H_6$) to water?

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Side Chain</th>
<th>$\Delta G$ (kJ mol$^{-1}$) at 275 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanine</td>
<td>-CH$_3$</td>
<td>3.0</td>
</tr>
<tr>
<td>Valine</td>
<td>-CH(CH$_3$)$_2$</td>
<td>7.0</td>
</tr>
<tr>
<td>Leucine</td>
<td>-CH$_2$-CH(CH$_3$)$_2$</td>
<td>10.0</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>-CH$_2$-C$_6$H$_5$</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Hydrophobic effect: entropic; these side chains cluster together rather than “dissolve” in H$_2$O, just like benzene: $C_6H_6(C_6H_6) \rightarrow C_6H_6(H_2O)$ \[\Delta S = -57.7 \text{ J mol}^{-1} \text{ K}^{-1}\]
Hydrophobic effect: entropic; these side chains cluster together rather than “dissolve” in $H_2O$, just like benzene:

$C_6H_6(C_6H_6) \rightarrow C_6H_6(H_2O) \quad \Delta S = -57.7 \text{ J mol}^{-1} \text{ K}^{-1}$

Nonpolar side chains cluster to form hydrophobic core, preventing $H_2O$ from forming clathrate cages.

“Hydrophobic” bonds key to protein stability.

Polar side chains lie near surface in contact with $H_2O$. 
Protein Structure

Order of 20 amino acids determine structure. Only small fraction of amino acid sequences fold to a functional protein.

How many possible sequences? Consider 50 amino acids (small polypeptide). With 20 naturally occurring amino acids:

$$20^{50} \approx 10^{65}$$
different possible polypeptide sequences!

Almost none exist in nature & tiny fraction folds to functional protein structure (such as insulin, which has \(\approx\) 50 amino acids).
Rules Governing Protein Structure

From X-ray diffraction studies (Pauling & Corey):

1. Amide group essentially planar due to structural resonance:

   \[ \text{C-N bond has 30 - 40\% double bond character. Barrier to rotation is high: } \approx 60 \text{ kJ mol}^{-1} \]

2. Trans more stable than cis due to steric interaction of R's in cis conformer.

3. Hydrogen bonds between amide groups play essential role in stabilizing polypeptide chain conformation. Most stable:

   \[ \text{Collinear bonding between 2 amide groups.} \]
Rules Governing Protein Structure

Structure that maximizes hydrogen bonding is $\alpha$-helix:

- 3.6 amino acids/turn
- Each turn is 5.4 Å

Hemoglobin (& many other proteins) are very helical:

Hydrogen bonds between $>\text{N-H} \cdots \text{O=C}<$ are 3 amino acids away.
Ice: 11 known structures, most stable at high pressure. Complex structures: $H_2O$ has as many lone electron pairs (2) as H atoms.

Other hydrogen-bonding molecules (HF, NH$_3$) only form chains; have only one H or one lone pair.

Hexagonal ice (forms at 0 °C and 1 atm)
At 0 °C, ice is less dense than water. Ice found at the top of a pond: protective layer for organisms.

Maximum density at 4 °C (at 1 atm).
Probability of finding molecule in spherical shell of width $dr$ a distance $r + dr$ from center of another molecule:

$$\text{Probability} = 4\pi r^2 g(r) dr$$

Radial distribution function, $g(r)$, is defined such that:

Structure of liquid water: Short-range order given by radial distribution function, $g(r)$. 

Crystalline solid: 

Liquid water at 4 °C:
Liquid water at 4 °C:

Structure of liquid water: Short-range order given by radial distribution function, $g(r)$.

Peaks at 2.9 Å, 4.5 Å & 7 Å all seen for ice.

Peak at 3.5 Å not seen for ice: corresponds to H$_2$O molecule filling in open spaces of tetrahedral ice structure.
Properties of Water


2. High heat capacity, $C_p$: Since $\Delta T = \Delta H/C_p$, if $C_p$ is large, lots of heat needed to raise $T$ by 1 K.

3. High thermal conductivity: Following chemical reaction in cell, water carries heat away efficiently: regulates $T$ in living organisms.

4. High molar heat of vaporization (41 kJ mol$^{-1}$); body temperature regulated by sweating. For example, heat from metabolism $\approx 10^7$ J/day.

$$\rightarrow 10^7 \text{ J day}^{-1}/41,000 \text{ J mol}^{-1} = 244 \text{ mol} = 4.4 \text{ liters H}_2\text{O sweated per day.}$$