Chapter Eight

Molecules and Materials
• **Intramolecular forces** determine such molecular properties as molecular geometries and dipole moments.

• **Intermolecular forces** determine the macroscopic physical properties of liquids and solids.

• **Three states of matter: solids, liquids, and gases.**
  – In gases and liquids, motion is mainly translational.
  – In solids, motion is mainly vibrational.
<table>
<thead>
<tr>
<th>Type of interaction</th>
<th>Example</th>
<th>Energy of interaction between molecules or units</th>
</tr>
</thead>
</table>
| Dispersion (Instantaneous dipole–induced dipole) | H$_2$ (bp 20 K)  
CH$_4$ (bp 112 K)  
CCl$_4$ (bp 350 K)  
CF$_4$ (bp 112 K)  
n-C$_{28}$H$_{58}$ (mp 336 K) | ~0.1–5 kJ/mol, or  
~10 (T$_{bp}$ K) J/mol |
| Dipole–induced dipole         | Xe(H$_2$O)$_x$, solvation of noble gases or hydrocarbons (see text)      |                                                   |
| Ion–induced dipole            | Ions in a molecular matrix (see text)                                   |                                                   |
| Dipole–dipole                 | NF$_3$ ─ NF$_3$ (bp 144 K)  
BrF ─ BrF (bp 293 K)                                          | 5–20 kJ/mol, or  
67 kJ/mol (energy per bond) |
| Ion–Dipole                    | K(OH$_2$)$_6^+$  
Ions in aqueous solution and solid hydrates                           |                                                   |
| Hydrogen bond                 | (H$_2$O)$_x$, (HF)$_x$, (NH$_3$)$_x$, alcohols, amines  
HF$^-$                              | 4–50 kJ/mol for neutral molecules |
| Cation–anion                  | NaCl, CaO                                                               | 400–500 kJ/mol of MX “molecules” |
| Covalent bond                 | H$_2$  
F$_2$  
Cl$_2$  
Li$_2$                                             | 432.08 kJ/mol  
154.6 kJ/mol  
239.32 kJ/mol  
100.9 kJ/mol |
States of Matter Compared

Gas

Liquid

Solid

Chapter Eight
Dipole-Dipole Forces

• **Dipole-dipole forces** arise when permanent dipoles align themselves with the positive end of one dipole directed toward the negative ends of neighboring dipoles.

• When molecules come close to one another, repulsions occur between like-charged regions of dipoles.

• A permanent dipole in one molecule can induce a dipole in a neighboring molecule, giving rise to a *dipole-induced dipole force*. 
Dipole-Dipole Interactions

Dipole moment
\[ \mu = \delta \cdot d \]

\[ E = - \frac{2(\mu_1 \cdot \mu_2)}{4\pi \varepsilon r^3} \]
Dispersion Forces

• A **dispersion force** is the force of attraction between an instantaneous dipole and an induced dipole.

• Also called a **London force** after Fritz London who offered a theoretical explanation of these forces in 1928.

• The **polarizability** of an atom or molecule is a measure of the ease with which electron charge density is distorted by an external electrical field.

• The greater the polarizability of molecules, the stronger the intermolecular forces between them.
Dispersion Forces Illustrated

\[ E = - \frac{2(\mu^2 \cdot \alpha)}{r^6} \]

Mean instantaneous dipole

polarizability

\( \mu \)

\( \delta^- \quad \delta^+ \quad \delta^- \quad \delta^+ \)

(a) Unpolarized molecule

(b) Instantaneous dipole

(c) Induced dipole
Predicting Physical Properties of Molecular Substances

- Dispersion forces become stronger with increasing molar mass and elongation of molecules. In comparing nonpolar substances, molar mass and molecular shape are the essential factors.

- Dipole-dipole and dipole-induced dipole forces are found in polar substances. The more polar the substance, the greater the intermolecular force is expected to be.

- Because they occur in all molecular substances, dispersion forces must always be considered. Often they predominate.
Molecular Shape and Polarizability

(a) Octane
CH₃(CH₂)₆CH₃
melting point -56.8 °C
boiling point 125.7 °C

(b) (Isooctane)
2,2,4-Trimethylpentane
CH₃C(CH₃)₂CH₂CH(CH₃)₂
melting point -104.7 °C
boiling point 99.2 °C
### TABLE 11.2  Melting Points of Similar Nonpolar Compounds

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>MELTING POINT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>-182.5</td>
</tr>
<tr>
<td>CF₄</td>
<td>-150.0</td>
</tr>
<tr>
<td>CCl₄</td>
<td>-23.0</td>
</tr>
<tr>
<td>CBr₄</td>
<td>90.0</td>
</tr>
<tr>
<td>CI₄</td>
<td>171.0</td>
</tr>
</tbody>
</table>
## Effect of Molecular Weight & Dipole Moment

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.W.</th>
<th>Dipole (D)</th>
<th>b.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Cl</td>
<td>50.5</td>
<td>1.87</td>
<td>-24.2</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>84.9</td>
<td>1.60</td>
<td>+40</td>
</tr>
<tr>
<td>CHClF$_2$</td>
<td>86.5</td>
<td>1.42</td>
<td>-40.8</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>88.0</td>
<td>0</td>
<td>-129</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>153.8</td>
<td>0</td>
<td>76.5</td>
</tr>
</tbody>
</table>
Hydrogen Bonds

• A **hydrogen bond** is an intermolecular force in which a **hydrogen atom** covalently bonded to a non-metal atom in one molecule is simultaneously attracted to a non-metal atom of a neighboring molecule.

• The strongest hydrogen bonds are formed if the non-metal atoms are small and highly electronegative.

• Usually occurs with **nitrogen, oxygen, and fluorine atoms**.

\[
\begin{align*}
X & \quad \text{H} \quad \cdots \quad Y \\
X, \; Y & = \text{F, O, N, Cl, S} \text{ (highly electronegative elements)}
\end{align*}
\]
Hydrogen Bonds in Water
Hydrogen Bonding in Ice
Solid water is less dense than liquid water due to hydrogen bonding.
9 Hydrogen fluoride, \((\text{HF})_n\)
Hydrogen bonding is also the reason for the unusually high boiling point of $\text{H}_2\text{O}$, $\text{HF}$ and $\text{NH}_3$. 
Intramolecular Hydrogen Bonds

Hydrogen Bonding In Salicylic Acid
The structures of proteins, substances essential to life, are determined partly by hydrogen bonding.

Hydrogen Bonding in Polypeptide Chains

$\alpha$-helix

Secondary Structure
**Intermolecular Hydrogen Bonds**

Hydrogen Bonding between Acetic Acid molecules
Hydrogen Bonding between the base pairs of two strands of a DNA molecule: A-T and C-G
Vaporization and Condensation

- **Vaporization** is the conversion of a liquid to a gas.
- The *enthalpy of vaporization* ($\Delta H_{\text{vapn}}$) is the quantity of heat that must be absorbed to vaporize a given amount of liquid at a constant temperature.
- **Condensation** is the change of a gas to a liquid.

$$\Delta H_{\text{condn}} = - \Delta H_{\text{vapn}}$$
Figure 8.1 This phase diagram for carbon shows which form of the element is most stable as a function of temperature and pressure. Note that pressure is shown in units of thousands of atmospheres. It is clear that graphite is the favored form at all ordinary combinations of $T$ and $P$ and that the formation of diamonds requires extremely high pressure.
In diamond, each carbon atom forms strong covalent bonds to four other carbon atoms.

**Figure 8.7** The carbon atoms in diamond are joined by covalent bonds, and each atom displays the same tetrahedral geometry we saw in Chapter 7 for molecules like methane. Fracturing a diamond crystal requires breaking many covalent bonds, and this explains the inordinately high strength of diamond.
Crystal Structure of Graphite

van der Waals force

Covalent bond
Structure of a Buckyball

Covalent bond
Structure of Carbon Nanotube

SWCNT - single-wall carbon nanotube

MWCNT - multiple-wall carbon nanotube
## Some Enthalpies of Vaporization

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\Delta H_{\text{vapn}}$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon disulfide, CS$_2$</td>
<td>27.4</td>
</tr>
<tr>
<td>Carbon tetrachloride, CCl$_4$</td>
<td>37.0</td>
</tr>
<tr>
<td>Methanol, CH$_3$OH</td>
<td>38.0</td>
</tr>
<tr>
<td>Octane, C$<em>8$H$</em>{18}$</td>
<td>41.5</td>
</tr>
<tr>
<td>Ethanol, CH$_3$CH$_2$OH</td>
<td>43.3</td>
</tr>
<tr>
<td>Water, H$_2$O</td>
<td>44.0</td>
</tr>
<tr>
<td>Aniline, C$_6$H$_5$NH$_2$</td>
<td>52.3</td>
</tr>
</tbody>
</table>

$^a$Δ$H_{\text{vapn}}$ values are somewhat temperature dependent.
Vapor Pressure

- The **vapor pressure** of a liquid is the partial pressure exerted by the vapor when it is in dynamic equilibrium with a liquid at a constant temperature.
- The vapor pressures of liquids increases with temperature.
- A **vapor pressure curve** is a graph of vapor pressure as a function of temperature.
Liquid-Vapor Equilibrium

(a) Vaporization

(b) Vaporization rate > condensation rate

(c) Vaporization rate = condensation rate
Vapor Pressure Curves

a) Carbon disulfide: $\text{CS}_2$

b) Methanol: $\text{CH}_3\text{OH}$

c) Ethanol: $\text{CH}_3\text{CH}_2\text{OH}$

d) Water: $\text{H}_2\text{O}$

e) Aniline: $\text{C}_6\text{H}_5\text{NH}_2$

- The temperature of the line at $P=760$ mmHg with a vapor pressure curve is the normal boiling point.
Table 8.1

Vapor pressures at 295 K and normal boiling points of a variety of substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>Vapor Pressure (torr)</th>
<th>Normal Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>200</td>
<td>56.2</td>
</tr>
<tr>
<td>Br₂</td>
<td>184</td>
<td>58.8</td>
</tr>
<tr>
<td>CClF₃</td>
<td>24,940</td>
<td>-81.1</td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>4448</td>
<td>-29.8</td>
</tr>
<tr>
<td>CCl₃F</td>
<td>717</td>
<td>23.8</td>
</tr>
<tr>
<td>CCl₄</td>
<td>99.0</td>
<td>76.54</td>
</tr>
<tr>
<td>HCN</td>
<td>657</td>
<td>26</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>3525</td>
<td>-21</td>
</tr>
<tr>
<td>Methanol</td>
<td>108</td>
<td>64.96</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>549</td>
<td>36.07</td>
</tr>
<tr>
<td>Neopentane</td>
<td>1365</td>
<td>9.5</td>
</tr>
<tr>
<td>Isobutane</td>
<td>2393</td>
<td>-11</td>
</tr>
<tr>
<td>n-Butane</td>
<td>1658</td>
<td>-0.5</td>
</tr>
<tr>
<td>Propane</td>
<td>6586</td>
<td>-42.07</td>
</tr>
<tr>
<td>Ethane</td>
<td>29,380</td>
<td>-88.63</td>
</tr>
<tr>
<td>Water</td>
<td>23.76</td>
<td>100</td>
</tr>
</tbody>
</table>
## Table 11.2 Vapor Pressure of Water at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Pressure, mmHg</th>
<th>Temperature, °C</th>
<th>Pressure, mmHg</th>
<th>Temperature, °C</th>
<th>Pressure, mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.6</td>
<td>29.0</td>
<td>30.0</td>
<td>93.0</td>
<td>588.6</td>
</tr>
<tr>
<td>10.0</td>
<td>9.2</td>
<td>30.0</td>
<td>31.8</td>
<td>94.0</td>
<td>610.9</td>
</tr>
<tr>
<td>20.0</td>
<td>17.5</td>
<td>40.0</td>
<td>55.3</td>
<td>95.0</td>
<td>633.9</td>
</tr>
<tr>
<td>21.0</td>
<td>18.7</td>
<td>50.0</td>
<td>92.5</td>
<td>96.0</td>
<td>657.6</td>
</tr>
<tr>
<td>22.0</td>
<td>19.8</td>
<td>60.0</td>
<td>149.4</td>
<td>97.0</td>
<td>682.1</td>
</tr>
<tr>
<td>23.0</td>
<td>21.1</td>
<td>70.0</td>
<td>233.7</td>
<td>98.0</td>
<td>707.3</td>
</tr>
<tr>
<td>24.0</td>
<td>22.4</td>
<td>80.0</td>
<td>355.1</td>
<td>99.0</td>
<td>733.2</td>
</tr>
<tr>
<td>25.0</td>
<td>23.8</td>
<td>90.0</td>
<td>525.8</td>
<td>100.0</td>
<td>760.0</td>
</tr>
<tr>
<td>26.0</td>
<td>25.2</td>
<td>91.0</td>
<td>546.0</td>
<td>110.0</td>
<td>1074.6</td>
</tr>
<tr>
<td>27.0</td>
<td>26.7</td>
<td>92.0</td>
<td>567.0</td>
<td>120.0</td>
<td>1489.1</td>
</tr>
<tr>
<td>28.0</td>
<td>28.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Vapor Pressure as a Function of Temperature

**Clausius-Clapeyron equation:**

\[
\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]

where, \(\Delta H_{\text{vap}}\) = enthalpy of vaporization
Generalized Phase Diagram

- Triple point
- Critical point
- Supercritical fluid
- Fusion curve
- Sublimation curve
- Vapor Pressure curve
- Solid
- Liquid
- Gas

Pressure

Temperature
Phase Diagram For H$_2$O

- **Normal Melting Point**
- **Normal Boiling Point**
Boiling Point

- The **boiling point** of a liquid is the temperature at which its vapor pressure becomes equal to the external pressure.

- The **normal boiling point** is the boiling point at 1 atm.
Critical Point

• The critical temperature, $T_c$, is the highest temperature at which a liquid and vapor can coexist in equilibrium as physically distinct states of matter.
• The critical pressure, $P_c$, is the vapor pressure at the critical temperature.
• The condition corresponding to a temperature of $T_c$ and a pressure of $P_c$ is called the critical point.
# Critical Temperature and Pressure of Various Substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_c$, K</th>
<th>$P_c$, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>33.0</td>
<td>12.8</td>
</tr>
<tr>
<td>N₂</td>
<td>126.3</td>
<td>33.5</td>
</tr>
<tr>
<td>O₂</td>
<td>154.8</td>
<td>50.1</td>
</tr>
<tr>
<td>CH₄</td>
<td>190.6</td>
<td>45.4</td>
</tr>
<tr>
<td>CO₂</td>
<td>304.2</td>
<td>72.9</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>305.4</td>
<td>48.2</td>
</tr>
<tr>
<td>HCl</td>
<td>324.6</td>
<td>81.5</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>369.8</td>
<td>41.9</td>
</tr>
<tr>
<td>NH₃</td>
<td>405.6</td>
<td>111.3</td>
</tr>
<tr>
<td>SO₂</td>
<td>430.6</td>
<td>77.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>647.3</td>
<td>218.3</td>
</tr>
</tbody>
</table>
The Critical Point

Diagram showing the phases of matter at different temperatures and densities:
- **Room temperature:** Liquid
- **Slightly below $T_c$:** Liquid
- **Critical temp, $T_c$:** Supercritical fluid

Legend:
- Vapor
- Liquid
- Supercritical fluid
Phase Changes Involving Solids

- The conversion of a solid to a liquid is called **melting**, or **fusion**, and the temperature at which a solid melts is its **melting point**.

- The **enthalpy of fusion**, $\Delta H_{\text{fusion}}$, is the quantity of heat required to melt a given amount of solid.

- **Sublimation** is the process of a molecules passing directly from the solid to the vapor state.

- **Enthalpy of sublimation**, $\Delta H_{\text{subln}}$, is the sum of the enthalpies of fusion and vaporization.

- The **triple point** is the point at which the vapor pressure curve and the sublimation curve meet.
Phase Diagram For CO₂

Sublimation of dry ice

Temperature (not to scale)

Pressure (not to scale)

CO₂ (s)
CO₂ (l)
CO₂ (g)

72.9 atm
5.1 atm
1 atm

-78.5 °C
-56.7 °C
31 °C

SCF
Phase Diagram For HgI₂
Liquid crystal
**FIGURE 11.15** The liquid crystalline state

(a) Orientation of molecules in liquid

Nematic liquid crystal

Smectic C liquid crystal

Smectic A liquid crystal

Cholesteric liquid crystal

(b) Orientation of molecules in liquid crystals
Figure 12.5 Structures and liquid crystal temperature intervals of some typical liquid-crystalline materials.
A forehead thermometer, made of cholesteric liquid crystals, provides a fast, accurate, noninvasive way to measure body temperature. For example, forehead thermometers are used by medical professionals monitoring the temperature of patients during surgery.
## Some Enthalpies of Fusion

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point, °C</th>
<th>$\Delta H_{\text{fusion}}$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury, Hg</td>
<td>−38.9</td>
<td>2.30</td>
</tr>
<tr>
<td>Ethanol, CH$_3$CH$_2$OH</td>
<td>−114</td>
<td>5.01</td>
</tr>
<tr>
<td>Water, H$_2$O</td>
<td>0.0</td>
<td>6.01</td>
</tr>
<tr>
<td>Benzene, C$_6$H$_6$</td>
<td>5.5</td>
<td>9.87</td>
</tr>
<tr>
<td>Silver, Ag</td>
<td>960.2</td>
<td>11.95</td>
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<tr>
<td>Iron, Fe</td>
<td>1537</td>
<td>15.19</td>
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</table>
## Crystal Structure of Solid Elements

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
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<td>Li</td>
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<td>Te</td>
<td>I</td>
<td>Xe</td>
</tr>
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<td>Ta</td>
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<td>Rf</td>
<td>Ha</td>
<td>Sg</td>
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<td>Hs</td>
<td>Mt</td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

- Simple cubic (s.c.)
- Body-centered cubic (b.c.c.)
- Face-centered cubic (f.c.c.)
- Orthorhombic (ortho)
- Hexagonal close-packed (h.c.p.)
- Rhombohedral (rhomb)
- Tetragonal (tetrag)
- Monoclinic (mono)
Unit Cells In Cubic Crystal Structures

- simple cubic (primitive cubic)
- bcc
- fcc

Chapter Eight
**Figure 11.22** The relationship between the edge length \(a\) and radius \(r\) of atoms in the simple cubic cell, body-centered cubic cell, and face-centered cubic cell.

- **Primitive cubic**
  \[ a = 2r \]

- **Body-centered cubic**
  \[
  \begin{align*}
  b^2 &= a^2 + a^2 \\
  c^2 &= a^2 + b^2 \\
  c &= \sqrt{3}a = 4r \\
  a &= \frac{4r}{\sqrt{3}}
  \end{align*}
  \]

- **Face-centered cubic**
  \[
  \begin{align*}
  b &= 4r \\
  b^2 &= a^2 + a^2 \\
  16r^2 &= 2a^2 \\
  a &= \sqrt{8}r
  \end{align*}
  \]
Occupancies per Unit Cells

**Primitive cubic:** \( a = 2r \)
- 1 atom/unit cell
- Occupancy = \( \frac{4/3(\pi r^3)}{a^3} = \frac{4/3(\pi r^3)}{(2r)^3} \)
  \( = \frac{4}{27} \times \frac{\pi}{r^3} \times \frac{r^3}{r^3} = 0.52 \approx 52\% \)

**Body-centered cubic:** \( a = \frac{4r}{(3)^{1/2}} \)
- 2 atom/unit cell
- Occupancy = \( 2 \times \frac{4/3(\pi r^3)}{a^3} \)
  \( = 2 \times \frac{4/3(\pi r^3)}{[\frac{4r}{(3)^{1/2}}]^3} \)
  \( = 0.68 \approx 68\% \)

**Face-centered cubic:** \( a = (8)^{1/2} r \)
- 4 atom/unit cell
- Occupancy = \( 4 \times \frac{4/3(\pi r^3)}{a^3} \)
  \( = 4 \times \frac{4/3(\pi r^3)}{[(8)^{1/2} r]^3} \)
  \( = 0.74 \approx 74\% \)

Closest packed
The atomic radius of copper is 128 pm, mass number is 63.54, and the density of copper is 8.93g/cm³. Is copper metal close packed?

Density = \( \frac{M}{V} \), \( V = \frac{M}{D} \)

The volume of a Cu atom occupied in the lattice

\[
= \frac{63.54 \text{g/mol}}{8.93 \text{g/cm}^3} \div 6.02 \times 10^{23} \text{atom/mol}
\]

\[
= 1.18 \times 10^{-23} \text{cm}^3/\text{atom} = 1.18 \times 10^7 \text{pm}^3/\text{atom}
\]

Occupancy = \( \frac{\left[ \frac{4}{3} \pi r^3 \right]}{\left[ 1.18 \times 10^7 \right]} \)

\[
= \frac{4}{3} \pi \left( 128^3 \right) / [1.18 \times 10^7]
\]

\[
= 0.744 = 74.4\% \quad \text{Close-packed structure}
\]
Closest packed

unoccupied holes
Hexagonal close-packed structure

Cubic close-packed structure
= Face-centered cubic
Close-packing of Spheres in Three Dimensions

Top view of close-packed spheres

Tetrahedral holes (γ)
Octahedral holes (δ)

Side view
Cover tetrahedral holes in layer B
Hexagonal close-packed

Side view
Cover octahedral holes in layer B
Cubic close-packed
Close Packed Structures

- **Hexagonal close-packed (hcp)** arrangements occur when the third layer covers the tetrahedral holes. These produce two-layer repeating units. ABABAB.....

- **Cubic close-packed (ccp)** arrangements occur when the third layer covers the octahedral holes. These produce three-layer repeating units. ABCABC....
Holes in Close Packed Structures

- *Tetrahedral holes* are located above a sphere in the bottom layer.
- *Octahedral holes* are located above a void in the bottom layer.
Tetrahedral holes

Octahedral holes

Cubic holes

Close packed structure
<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Radius ratio</th>
<th>Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>&gt;0.7</td>
<td><img src="image1.png" alt="Diagram" /></td>
</tr>
<tr>
<td>6</td>
<td>0.4–0.7</td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>4</td>
<td>0.2–0.4</td>
<td><img src="image3.png" alt="Diagram" /></td>
</tr>
<tr>
<td>3</td>
<td>0.1–0.2</td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

\[ \frac{r_h}{r} = 0.156 \]

\[ \frac{r_h}{r} = 0.225 \]

\[ \frac{r_h}{r} = 0.414 \]
Table 5.4  Radius ratios for arrangements of rigid spheres

<table>
<thead>
<tr>
<th>Coordination number of M</th>
<th>Arrangement of X</th>
<th>Radius ratios ( \rho = r_M/r_X )</th>
<th>Radius ratios ( \rho' = r_X/r_M )</th>
<th>Crystal structure corresponding to cation C.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Triangular</td>
<td>0.150–0.225</td>
<td>4.44–5.67</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>0.225–0.414</td>
<td>2.42–4.44</td>
<td>Antifluorite, ZnS</td>
</tr>
<tr>
<td>4</td>
<td>Planar</td>
<td>0.414–0.732</td>
<td>1.37–2.42</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>0.414–0.732</td>
<td>1.37–2.42</td>
<td>NaCl, TiO₂, CdCl₂</td>
</tr>
<tr>
<td>8</td>
<td>Cubic</td>
<td>0.732–1.00</td>
<td>1.00–1.37</td>
<td>CsCl, CaF₂</td>
</tr>
</tbody>
</table>
Metallic bond

*Sea of Electrons* surrounding a giant lattice of positive ions
Band Theory

- This is a *quantum-mechanical* treatment of *bonding* in metals.
- The spacing between energy levels is so minute in metals that the levels essentially merge into a *band*.
- When the band is occupied by valence electrons, it is called a *valence band*.
- A partially filled or low lying empty band of energy levels, which is required for electrical conductivity, is a *conduction band*.
- Band theory provides a good explanation of metallic luster and metallic colors.
The 2s Band in Lithium Metal

\[ \frac{1}{2s} \quad \frac{1}{2s} \quad \ldots \]

- Valence band
- Conduction band
- Anti-bonding
- Bonding

\[ \text{Li}_n \]
Band Overlap in Magnesium

Valence band

Conduction band

Chapter Eight
Alloy

• An alloy is a combination, either in solution or compound, of two or more elements, at least one of which is a metal, and where the resulting material has metallic properties.

• Alloys are usually designed to have properties that are more desirable than those of their components. For instance, steel is stronger than iron, one of its main elements.
Shape memory alloy (SMA)

• A shape memory alloy (SMA) (also known as memory metal or smart wire) is a metal that remembers its geometry.

• After it is deformed, it regains its original geometry by itself during heating (one-way effect), at higher ambient temperatures, or simply during unloading (pseudo-elasticity).

• These extraordinary properties are due to a temperature-dependent martensitic phase transformation from a low-symmetry to a highly symmetric crystallographic structure.

• Three main types of SMA are the Cu-Zn-Al, Cu-Al-Ni, and Ni-Ti alloys.
starting from martensite (a), adding a reversible deformation for the one-way effect or severe deformation with an irreversible amount for the two-way (b), heating the sample (c) and cooling it again (d).
Shape memory alloy (SMA)

\[ \xi \] (\( \xi \)) represents the martensite fraction.

\( M_s \): temperature at which the structure *starts* to change from *austenite* to *martensite* upon cooling

\( M_f \): temperature at which the transition is *finished*. 
**Austenite**
- High temperature phase
- Cubic Crystal Structure

**Martensite**
- Low temperature phase
- Monoclinic Crystal Structure

Twinned Martensite

Detwinned Martensite

**Figure 1. Different phases of an SMA.**
Figure 2. Temperature-induced phase transformation of an SMA without mechanical loading.
Band Structure of Insulators and Semiconductors

The diagram illustrates the energy bands for both insulators and semiconductors. The conduction band is separated from the valence band by an energy gap $E_g$. Insulators have a large energy gap, while semiconductors have a smaller one, allowing for the possibility of electron movement under external forces.
Intrinsic and Extrinsic Semiconductors

**n-type**

Donor electrons are promoted easily into conduction band.

Valence band is full in pure Si.

**p-type**

Acceptor energy level from dopant

Valence electrons are promoted easily into acceptor level.

Valence band is full in pure Si.
p-type \hspace{1cm} n-type

(a) Applied voltage drives electrons and holes across junction, and current flows.

(b) With polarity of applied voltage reversed, no current flows across junction.

(c) 

p-n junction

Chapter Eight
Type of Polymers
- based on synthesis

Addition polymers
Condensation polymers
Condensation Polymerization

Polyamide

\[ \text{adipoyl chloride} + \text{hexamethylenediamine} \rightarrow \text{amide link in nylon-66, a polyamide} \]
Polyester

Ethylene glycol + Terephthalic acid →

Ester linkage

Polyethylene terephthalate (PET), a polyester

Dacron
Kevlar

©George V. Kelvin

Nylon-6,6.
Addition Polymerization

Initiation

\[ R\text{--}\ddot{O}\text{--}\ddot{O}\text{--}R \rightarrow R\text{--}\ddot{O}\cdot + \ddot{O}\text{--}R \]

Propagation
Termination

\[
\text{R} \quad (\text{CH}_2\text{-CH}_2)_n \quad \text{CH}_2\text{CH}_2\cdot + \quad \text{R} \quad (\text{CH}_2\text{-CH}_2)_m \quad \text{CH}_2\text{CH}_2\cdot \quad \longrightarrow
\]

\[
\text{R} \quad (\text{CH}_2\text{-CH}_2)_n \quad \text{CH}_2\text{CH}_2\text{-CH}_2\text{CH}_2(\text{CH}_2\text{-CH}_2)_m \quad \text{R}
\]
Molecular Models of a Segment of a Polyethylene Molecule

Ball-and-stick model

Space-filling model
2-methyl-1,3-butadiene

isoprene

poly-cis-isoprene

and/or

poly-trans-isoprene
Conducting Polymers

$\text{nHC} \equiv \text{CH}$

\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}

\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\end{align*}

Chapter Eight
Physical Properties Of Polymers

- A **thermoplastic polymer** is one that can be softened by heating and then formed into desired shapes by applying pressure.
- **Thermosetting polymers** become permanently hard at elevated temperatures and pressures.
- **High-density polyethylene (HDPE)** consists primarily of linear molecules and has a higher density, greater rigidity, greater strength, and a higher melting point.
- **Low-density polyethylene (LDPE)** has branched chains and is a waxy, semi-rigid, translucent material with a low melting point.
In a **thermoplastic** polymer, chains interact only through intermolecular forces.

In **thermosetting** polymers, chains are tied together by actual chemical bonds.
Organization of Polymer Molecules

LDPE

HDPE

(a)

(b)

Chapter Eight

Slide 90 of 99
Figure 1.54  An example of polymer stereoisomers.
Figure 1.56  An example of an asymmetric carbon atom.
Tacticity

(a) isotactic

(b) syndiotactic

(c) atactic
Elastomers

- **Elastomers** are flexible, elastic materials.
- **Natural rubber** is soft and tacky when hot. It can be made harder in a reaction with sulfur, called **vulcanization**.
- Several kinds of synthetic rubber were developed during and after World War II. **Neoprene** (polychloroprene) is one example of this.
- **Copolymerization** is a process in which a mixture of two different monomers forms a product in which the chain contains both monomers as building blocks.
Rubber

- Natural rubber was first introduced to Europe in the mid. 18th century - and is an example of an elastomer - an elastic polymer.
- A problem was that natural rubber is a very weak, soft thermoplastic when heated - but very brittle when cold.
- A process, vulcanization, was invented by Goodyear, where rubber heated with sulphur produces a harder, less tacky elastic material.
### Extent of Cross-linking in Rubber Products

<table>
<thead>
<tr>
<th>Product</th>
<th>Monomer Units Between Cross-links</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surgical gloves</td>
<td>100–150</td>
</tr>
<tr>
<td>Kitchen gloves</td>
<td>50–80</td>
</tr>
<tr>
<td>Artificial heart membrane</td>
<td>30–40</td>
</tr>
<tr>
<td>Bicycle inner tube</td>
<td>20–30</td>
</tr>
<tr>
<td>Bicycle tire</td>
<td>10–20</td>
</tr>
</tbody>
</table>
Copolymers

Copolymers are polymers made by polymerizing a mixture of two or more monomers.

Alternating

Block

Random

Graft
Copolymers

An example is styrene-butadiene rubber (SBR) - which is a copolymer of butadiene and styrene. Most is vulcanized and used in tire production - though some is used for bubble-gum (unvulcanised form).
ABS - Poly(Acrylonitrile, Butadiene, Styrene)

• ABS is a copolymer of Acrylonitrile, Butadiene, and Styrene.
• ABS is often used as the cost and performance dividing line between standard plastics (PVC, polyethylene, polystyrene, etc.) and engineering plastics (acrylic, nylon, acetal, etc.).
• ABS polymers can be given a range of properties, depending on the ratio of the monomeric constituents and the molecular level connectivity. Typically, a styrene-acrylonitrile glassy phase is toughened by an amorphous butadiene/butadiene-acrylonitrile rubber phase.