Chapter 10
Liquids & Solids

Representation of the states of matter.

\[ PV = nRT \]

Changes of State
- A change of state or phase transition is a change of a substance from one state to another.

Intermolecular Forces
Forces between (rather than within) molecules.

- Dipole-dipole attraction: molecules with dipoles orient themselves so that “+” and “−” ends of the dipoles are close to each other.
- Hydrogen bonds: dipole-dipole attraction in which hydrogen is bound to a highly electronegative atom. (F, O, N)
Dipole-Dipole Forces

- Polar molecules can attract one another through **dipole-dipole forces**.
  - The **dipole-dipole force** is an attractive intermolecular force resulting from the tendency of polar molecules to align themselves positive end to negative end.

![Figure 11.21](image)

Table 11.4

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Approximate Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermolecular</td>
<td>0.1 to 10</td>
</tr>
<tr>
<td>Van der Waals (dipole–dipole, London)</td>
<td>0.1 to 10</td>
</tr>
<tr>
<td>Hydrogen bonding</td>
<td>10 to 40</td>
</tr>
<tr>
<td>Chemical bonding</td>
<td>100 to 1000</td>
</tr>
<tr>
<td>Ionic</td>
<td>100 to 1000</td>
</tr>
<tr>
<td>Covalent</td>
<td>100 to 1000</td>
</tr>
</tbody>
</table>

Hydrogen Bonding

- **Hydrogen bonding** is a force that exists between a hydrogen atom covalently bonded to a very electronegative atom, X, and a lone pair of electrons on a very electronegative atom, Y.
  - To exhibit hydrogen bonding, one of the following three structures must be present:
    - $\text{H}^\cdots\text{N}$
    - $\text{H}^\cdots\text{O}$
    - $\text{H}^\cdots\text{F}$
  - Only N, O, and F are electronegative enough to leave the hydrogen nucleus exposed.

![Figure 11.23](image)

- A hydrogen atom bonded to an electronegative atom appears to be special.
  - The electrons in the O-H bond are drawn to the O atom, leaving the dense positive charge of the hydrogen nucleus exposed.
  - It’s the strong attraction of this exposed nucleus for the lone pair on an adjacent molecule that accounts for the strong attraction.
  - A similar mechanism explains the attractions in HF and NH$_3$. 

![Figure 11.23](image)
Hydrogen Bonding

- Molecules exhibiting hydrogen bonding have **abnormally high boiling points** compared to molecules with similar van der Waals forces.
  - For example, water has the highest boiling point of the Group VI hydrides. (see Figure 11.24A)
  - Similar trends are seen in the Group V and VII hydrides. (see Figure 11.24B)

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**Figure 11.24:** Boiling point versus molecular weight for hydrides.

**Figure 11.25:** Hydrogen bonding in water.

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**Figure 10.3:** (a) The polar water molecule. (b) Hydrogen bonding among water molecules.

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**Table 10.1**

<table>
<thead>
<tr>
<th>State</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (0°C, 1 atm)</td>
<td>0.9168</td>
</tr>
<tr>
<td>Liquid (25°C, 1 atm)</td>
<td>0.9971</td>
</tr>
<tr>
<td>Gas (900°C, 1 atm)</td>
<td>3.26 × 10⁻⁴</td>
</tr>
</tbody>
</table>
London Dispersion Forces

Relatively weak forces that exist among noble gas atoms and nonpolar molecules. (Ar, C₂H₆)

Caused by instantaneous dipole, in which electron distribution becomes asymmetrical.

The ease with which electron “cloud” of an atom can be distorted is called polarizability. Atoms with larger electron clouds are more “polarizable” and exhibit stronger LD forces.

Table 10.2: The Freezing Points of the Group 8A Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Freezing Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>-269.7</td>
</tr>
<tr>
<td>Neon</td>
<td>-248.6</td>
</tr>
<tr>
<td>Argon</td>
<td>-189.4</td>
</tr>
<tr>
<td>Krypton</td>
<td>-157.3</td>
</tr>
<tr>
<td>Xenon</td>
<td>-111.9</td>
</tr>
</tbody>
</table>

Figure 10.4: The boiling points of the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A.
Properties of Liquids

The particles in the gas phase (whether they are atoms, molecules, or ions) have sufficient kinetic energy to overcome their intermolecular forces and move freely within their container.

Particles in the liquid phase have sufficient kinetic energy to move past one another but lack enough kinetic energy to completely escape from their intermolecular forces.

Some Properties of a Liquid

**Surface Tension**: The resistance to an increase in its surface area (strongest in polar molecules).

**Capillary Action**: Spontaneous rising of a liquid in a narrow tube.

**Viscosity**: Resistance to flow (molecules or atoms with large intermolecular forces). Molecules which can hydrogen-bond tend to be more viscous than those which cannot (exception: Hg - it is highly polarizable.)

Properties of Liquids; Surface Tension and Viscosity

- **Surface tension** is the energy required to increase the surface area of a liquid by a unit amount.
  - This explains why falling raindrops are nearly spherical, minimizing surface area.
  - In comparisons of substances, as intermolecular forces between molecules increase, the apparent surface tension also increases.

![Figure 11.18: A steel pin floating on the surface of water. Photo courtesy of American Color.](image)

![Figure 10.6: A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by molecules below it and on each side.](image)

![Figure 11.18: The water surface is depressed and stretched by the pin.](image)
Intermolecular Forces; Explaining Liquid Properties

- **Viscosity** is the resistance to flow exhibited by all liquids and gases.
- Viscosity can be illustrated by measuring the time required for a steel ball to fall through a column of the liquid. (see Figures 11.19 and 11.20)
- Even without such measurements, you know that syrup has a greater viscosity than water.
- In comparisons of substances, as intermolecular forces increase, viscosity usually increases.

Van der Waals Forces and the Properties of Liquids

- The **normal boiling point** is related to vapor pressure and is lowest for liquids with the weakest intermolecular forces. The same is true of melting point - lower melting points are found for liquids with weak intermolecular forces.

Bonding in Solids

Bonding in solids may be described as “bands” of molecular orbitals
- In metals – conduction “bands” are partially vacant orbitals which allow electrons to flow
- In insulators – the valence orbitals or bands are “full” there is a large energy difference (gap) between the valence band and lowest band of empty orbitals (conduction band)
- In semiconductors – there is a small gap between between the valence band and conduction band

Van der Waals Forces and the Properties of Liquids

- Viscosity increases with increasing intermolecular forces because increasing these forces increases the resistance to flow.
- Other factors, such as the possibility of molecules tangling together, affect viscosity.
- Liquids with long molecules that tangle together are expected to have high viscosities.
Types of Solids

Crystalline Solids: highly regular arrangement of their components [table salt (NaCl), pyrite (FeS₂)].

Amorphous solids: considerable disorder in their structures (glass).

Representation of Components in a Crystalline Solid

Lattice: A 3-dimensional system of points designating the centers of components (atoms, ions, or molecules) that make up the substance.

Unit Cell: The smallest repeating unit of the lattice.
- simple cubic
- body-centered cubic
- face-centered cubic

Bragg Equation

Used for analysis of crystal structures.

\[ n\lambda = 2d \sin \theta \]

\( d \) = distance between atoms
\( n \) = an integer
\( \lambda \) = wavelength of the x-rays

Types of Crystalline Solids

Ionic Solid: contains ions at the points of the lattice that describe the structure of the solid (NaCl).

Molecular Solid: discrete covalently bonded molecules at each of its lattice points (sucrose, ice).

Atomic Solid: atoms occupy lattice points (carbon, metal) of the solid
Packing in Metals

Model: Packing uniform, hard spheres to best use available space. This is called closest packing. Each atom has 12 nearest neighbors.

- hexagonal closest packed ("aba")
- cubic closest packed ("abc")
Figure 10.17: The net number of spheres in a face-centered cubic unit cell.

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Figure 11.33: Space-filling representation of cubic unit cells.

Figure 11.40: Crystal structures of metals.

Basic Equation for Unit Cell Calculations

Density (g/cm³) =
(Molar mass of substance, g/mol)(# atoms/unit cell)
(Unit cell volume, cm³)(6.02 x 10²³ atoms/mol)

Unit cell volume = (edge, cm)³
By definition: 1 mL = 1 cm³
1.00 pm³ (1.00 x 10⁻¹⁰ cm/pm)³ = 1.00 x 10⁻³⁰ cm³

Bonding Models for Metals

Electron Sea Model: A regular array of metals in a “sea” of electrons.

Band (Molecular Orbital) Model: Electrons assumed to travel around metal crystal in MOs formed from valence atomic orbitals of metal atoms.

Figure 10.18: The electron sea model for metals postulates a regular array of cations in a "sea" of valence electrons. (a) Representation of an alkali metal (Group 1A) with one valence electron. (b) Representation of an alkaline earth metal (Group 2A) with two valence electrons.
Figure 10.20: (left) A representation of the energy levels (bands) in a magnesium crystal. (right) Crystals of magnesium grown from a vapor.

Figure 10.21: Two types of alloys.

Metal Alloys
Substances that have a mixture of elements and metallic properties.

1. **Substitutional Alloy**: some metal atoms replaced by others of similar size.
   
   brass = Cu/Zn

2. **Interstitial Alloy**: Interstices (holes) in closest packed metal structure are occupied by small atoms.
   
   steel = iron + carbon

3. **Both types**: Alloy steels contain a mix of substitutional (carbon) and interstitial (Cr, Mo) alloys.

Network Solids
Composed of strong directional covalent bonds that are best viewed as a “giant molecule”.

- brittle
- do not conduct heat or electricity
- carbon, silicon-based

graphite, diamond, ceramics, glass

Figure 10.22: The structures of diamond and graphite. In each case only a small part of the entire structure is shown.