Chapter 18

Summary: Thermodynamics II - Thermal Properties of Matter (Ch. 18)

This lecture explores the connection between the macroscopic properties of matter (like pressure, volume, and temperature) and its microscopic molecular properties.

18-1: Equations of State

An **equation of state** is a mathematical relationship between the **state variables** that describe a material's condition: pressure (p), volume (V), temperature (T), and amount of substance (n).

- **Ideal Gas:** For a low-density gas, the relationship is simplified into the **ideal gas equation**.

$$pV = nRT$$

  Where:

  - n is the number of moles.
  - R is the universal gas constant, $R = 8.314 \mathrm{J/mol.K}$
    This equation shows that pressure is inversely proportional to volume and directly proportional to temperature.

- **Real Gases:** Real gases deviate from ideal behavior because their molecules have volume and exert attractive forces on each other. The **Van der Waals equation** is a more accurate model for real gases:

  Here, 'a' accounts for intermolecular attraction and 'b' accounts for molecular volume.

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- **pV Diagrams:** These graphs show the relationship between pressure and volume at a constant temperature. Each curve is called an **isotherm**.

18-2: Molecular Properties of Matter

This section looks at matter on a molecular level.

- **Intermolecular Forces:** Molecules exert forces on each other.
  - They **repel** at very close distances.
  - They **attract** at intermediate distances.
    The force is zero at an equilibrium separation distance, r0, where the potential energy is at a minimum.
- **States of Matter:**
  - **Solids:** Molecules vibrate about fixed positions in a crystal lattice.
  - **Liquids:** Molecules are still close but can move around more freely.
  - **Gases:** Molecules are far apart and have very weak attractive forces. In an ideal gas, these forces are considered to be zero.
- **Avogadro's Number (**NA**):** This is the number of constituent particles (atoms or molecules) per mole of a substance.

$$N_A = 6.022 \times 10^{23} \text{molecules/mol}$$

The molar mass (M) of a substance is related to the mass of a single molecule $M = N_A m$.

18-3: Kinetic-Molecular Model of an Ideal Gas

This model explains the macroscopic properties of an ideal gas based on the motion of its molecules.

- **Key Idea:** The pressure exerted by a gas is due to the collisions of its molecules with the container walls.

- **Temperature and Kinetic Energy:** The absolute temperature of an ideal gas is a direct measure of the average translational kinetic energy of its molecules.
    - For **n moles** of gas, the total translational kinetic energy (K_{tr}) is:

$$K_{tr} = \frac{3}{2}nRT$$

    - For a **single molecule**, the average translational kinetic energy is:

$$\frac{1}{2}m(v^2)_{av} = \frac{3}{2}kT$$

  Where $k = \frac{R}{N_A}$ is the **Boltzmann constant** (1.381×10−23J/K).

- **Root-Mean-Square (RMS) Speed:** This is a measure of the typical speed of gas molecules.

$$v_{rms} = \sqrt{(v_{av}^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

This shows that lighter molecules (smaller M) move faster at the same temperature.

- **Mean Free Path** (λ): While the ideal gas model often ignores collisions between molecules, in a real gas these collisions are constant. The **mean free path** is the average distance a molecule travels between collisions.

This distance depends on the size of the molecules and how densely they are packed. The formula is:

$$\lambda = \frac{kT}{4\pi\sqrt{2}r^2p}$$

Where:

- r is the radius of a molecule.
- p is the pressure.
  A shorter mean free path implies more frequent collisions.

18-4: Heat Capacities

- **Degrees of Freedom:** This refers to the number of independent ways a molecule can move and store energy (translation, rotation, vibration).
- **Equipartition of Energy:** This principle states that for a system in thermal equilibrium, the total energy is shared equally among all of its degrees of freedom. Each degree of freedom contributes 21kT of energy per molecule.
- **Molar Heat Capacity at Constant Volume C_V:**
  - **Monatomic Gas:** (3 translational degrees of freedom)
    $C_V = \frac{3}{2}R$
  - **Diatomic Gas:** (3 translational + 2 rotational degrees of freedom)
    $C_V = \frac{5}{2}R$
  - **Solids:** (3 kinetic + 3 potential degrees of freedom)
    $C_V = 3R$

    Note: Vibrational modes in molecules become active only at very high temperatures, which further increases the heat capacity.

18-5: Molecular Speeds

Not all molecules in a gas travel at the same speed. The **Maxwell-Boltzmann distribution** is a function that describes this range of speeds.

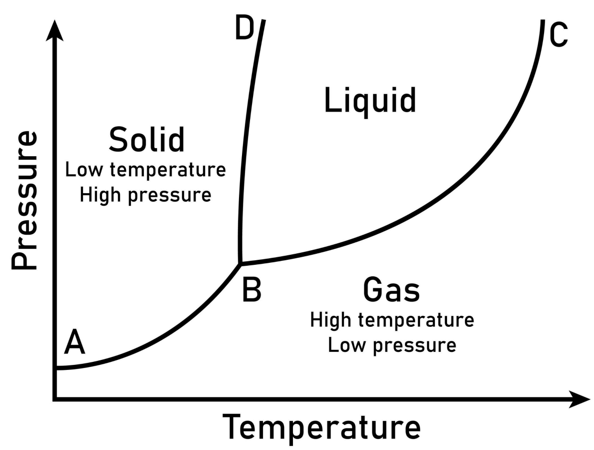
- **Distribution Curve:** The shape of the curve depends on temperature. As temperature increases, the curve flattens out and the peak shifts to higher speeds.
- **Characteristic Speeds:**
  - **Most probable speed (v_{mp}):** The speed at the peak of the distribution.
    $v_{mp} = \sqrt{\frac{2kT}{m}}$
  - **Average speed (**vav**):** The average of all the speeds.
    $v_{av} = \sqrt{\frac{3kT}{m}}$

- **RMS speed (**vrms**):** The square root of the average of the squared speeds. $v_{rms} = \sqrt{\frac{3kT}{m}}$

18-6: Phases of Matter

A **phase diagram** is a graph that shows the conditions of temperature and pressure under which a substance exists as a solid, liquid, or gas.

- **Key Features:**
  - **Phase Boundaries:** Lines on the diagram where two phases can coexist in equilibrium (e.g., melting, boiling). These are the fusion, vaporization, and sublimation curves.
  - **Triple Point:** The unique point where all three phases (solid, liquid, and vapor) coexist in equilibrium.
  - **Critical Point:** The point at which the liquid and vapor phases become indistinguishable. Beyond this point, there is no clear phase transition.



- **pVT-Surfaces:** These are 3D graphs that represent the equation of state by plotting pressure, volume, and temperature for a substance, providing a complete picture of its phases.