

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, $R = 8.314\text{J/mol.K}$

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, r_0 , 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 (N_A):** 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 by the equation $M = N_A m$.

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** ($1.381 \times 10^{-23} \text{J/K}$).

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

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

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.

- **Mean Collision Time** (t_{mean}): Related to the mean free path is the **mean collision time**, which is the average time a molecule travels between collisions. It can be found by dividing the mean free path by the average speed of the molecules.

$$t_{mean} = \frac{\lambda}{v_{av}}$$

Alternatively, by substituting the ideal gas law into the equation for the mean free path, we can express the mean collision time more directly in terms of the number of molecules (N) and volume (V):

$$t_{mean} = \frac{V}{4\pi\sqrt{2}r^2 N v_{av}}$$

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 $\frac{1}{2}kT$ 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

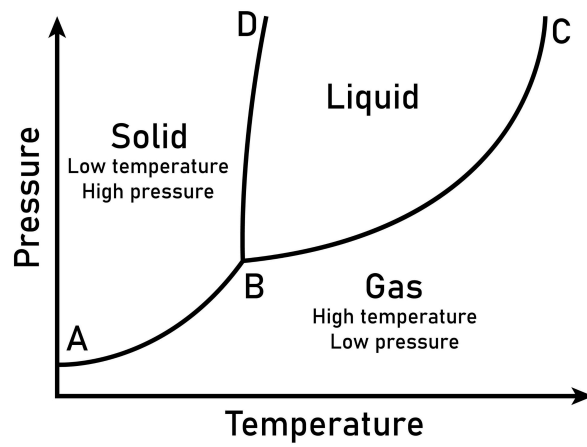
Not all molecules in a gas travel at the same speed. The **Maxwell-Boltzmann distribution** is a function that describes this range of speeds.

- **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 (v_{av}):** The average of all the speeds.
$$v_{av} = \sqrt{\frac{8kT}{\pi m}}$$
 - **RMS speed (v_{rms}):** 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.