Lecture 30: Thermal Behavior of Matter
Recap: temperature and heat

- **Thermodynamic equilibrium** is the state reached when macroscopic properties of a system or systems don’t change.

- Systems in thermodynamic equilibrium are at the same **temperature**.
  - The **kelvin** (K) is the SI unit of temperature.

- **Heat** is energy in transit because of a temperature difference alone.
  - The heat required to heat an object by an amount $\Delta T$ depends on its mass and its **specific heat**, $c$: $\Delta Q = mc \Delta T$.
  - Heat transfer mechanisms include conduction, convection, and radiation.

- **Thermal energy balance** is a state in which the rate at which energy is delivered to a system is equal to the rate at which the system loses energy. A system in energy balance maintains a constant temperature.
The ideal gas law

- Experiment shows that a gas of $N$ molecules in a closed container obeys a simple relation between pressure $p$, volume $V$, and temperature $T$:

$$pV = NkT$$

- This is the **ideal gas law**, and the behavior of most real gases closely approximates this ideal.

- Here $k$ is **Boltzmann’s constant**; $k = 1.38 \times 10^{-23}$ J/K.

- The ideal gas law may also be written $pV = nRT$, where $n$ is the number of moles of gas, and $R = 8.314$ J/K·mol.
Kinetic theory of the ideal gas

- The ideal gas law follows by considering a gas to consist of particles that obey Newton’s laws.
- Gas pressure arises from the average force the particles exert when they collide with the container walls.
- The temperature of the gas is a measure of the average kinetic energy of the gas molecules:

\[
\frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT
\]
The Maxwell-Boltzmann distribution

- Molecules in a gas exhibit a range of speeds that result from random collisions among the molecules.

  - This is the Maxwell-Boltzmann distribution.

  - At high temperatures the distribution is broader and peaks at a higher speed.

  - The mean thermal speed is

    \[ v_{th} = \sqrt{\frac{3kT}{m}} \]

    where \( m \) is the molecular mass.
question

• If you double the kelvin temperature of a gas, what happens to the thermal speed of the gas molecules?
A. It doubles.
B. It is halved.
C. It changes by a factor of \( \sqrt{2} \).
D. It changes by a factor of \( \frac{1}{\sqrt{2}} \).
Phase changes

- Most substances occur in three **phases**—solid, liquid, gas.
  - It takes energy, called the **heat of transformation**, $L$, to effect phase changes from solid to liquid and liquid to gas.
    - Heat of transformation measures the energy $Q$ required to change the phase of a mass $m$: $Q = mL$.
    - Energy must be removed to go the other way.
    - The solid-liquid transition involves the **heat of fusion**, $L_f$.
    - The liquid-gas transition involves the **heat of vaporization**, $L_v$.
    - The direct transition from solid to gas involves the **heat of sublimation**, $L_s$.
  - During a phase change, temperature remains constant as energy goes into breaking molecular bonds.
Phase diagrams

- The phases of a substance can be displayed on a plot of pressure versus temperature.
- Curves separate regions characterizing the different phases.
  - The curves meet at the **triple point**, where all three phases coexist in equilibrium.
  - The liquid-gas curve ends at the **critical point**, where the sharp distinction between liquid and gas disappears.
- Different paths in the phase diagram take the material through different phase sequences:
  - Path **CD** shows the familiar solid-liquid-gas.
  - Path **AB** goes directly from solid to gas.
  - Path **GH** shows that changing pressure can result in phase changes.
Thermal expansion

- Most materials expand when heated.
  - Liquids and solids are best characterized by the coefficient of volume expansion, $\beta$.
  - Solids are best characterized by the coefficient of linear expansion, $\alpha$.
- The coefficients are defined as the fractional change in volume over length, per unit temperature change:
  
  \[ \beta = \frac{\Delta V/V}{\Delta T} \quad \text{Typical } \beta \approx 10^{-3} \]
  
  \[ \alpha = \frac{\Delta L/L}{\Delta T} \quad \text{Typical } \alpha \approx 10^{-5} \]
- An unconfined substance expands equally in all its dimensions.
The anomalous behavior of water

- Between 0°C and 4°C, water contracts on heating.
  - This is a residual effect of the hydrogen bonds that form ice crystals.
  - The open structure of the ice crystal makes ice less dense than liquid water.
  - Hence solid water, unlike most substances, floats in its liquid phase.
  - This fact has enormous consequences for aquatic life.
Summary

- The **ideal gas law** relates pressure, temperature, and volume: $PV = NkT$.
  - Derivation of the ideal gas law from Newtonian mechanics shows that temperature measures the average kinetic energy of the gas molecules.

- **Phase changes** take substances between solid and liquid, liquid and gas, solid and gas.
  - Phase diagrams require energy, described by the **heats of transformation**.
  - The phase structure of a substance is described in its **phase diagram**.

- **Thermal expansion** occurs as most substances are heated.
  - An exception is water in the range from 0°C to 4°C.