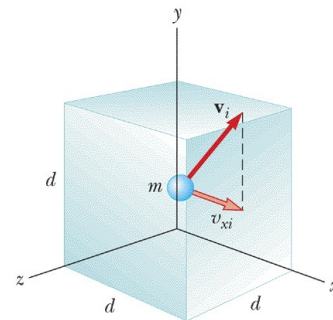


Lecture 21 The Kinetic Theory of Gases

21.1 Molecular Model of an Ideal Gas

1. The number of molecules in the gas is large, and the average separation between them is large compared with their dimensions.
2. The molecules obey Newton's law of motion, but as a whole they move randomly.
3. The molecules interact only by short-range force during elastic collisions.
4. The molecules make elastic collisions with the walls
5. The gas under consideration is a pure substance; that is, all molecules are identical.

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Figure 16.12



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$$\Delta t = \frac{2d}{v_{xi}}, \quad F\Delta t = 2mv_{xi}, \quad F_{i,on_wall} = \frac{2mv_{xi}}{\Delta t} = \frac{mv_{xi}^2}{d}$$

$$F = \sum_{i=1}^N \frac{mv_{xi}^2}{d} = \frac{m}{d} \sum_{i=1}^N v_{xi}^2, \quad \sum v_{xi}^2 = N \langle v_x^2 \rangle, \quad \langle v^2 \rangle = 3 \langle v_x^2 \rangle$$

$$F = \frac{m}{d} N \frac{1}{3} \langle v^2 \rangle, \quad P = \frac{F}{A} = \frac{F}{d^2} = \frac{N}{3d^3} m \langle v^2 \rangle = \frac{N}{V} \frac{1}{3} \langle mv^2 \rangle$$

Molecular Interpretation of Temperature

$$PV = Nk_B T, \quad k_B T = \frac{1}{3} \langle mv^2 \rangle, \quad \langle \frac{1}{2} mv^2 \rangle = \frac{3}{2} k_B T$$

→ $T = \frac{2}{3k_B} \left\langle \frac{1}{2} mv^2 \right\rangle$ The temperature is a direct measure of average molecular kinetic energy.

Theorem of equipartition of energy:

$$\langle \frac{1}{2} mv_x^2 \rangle = \frac{1}{2} k_B T \quad \text{one degree of freedom}$$

$$\langle \frac{1}{2} mv^2 \rangle = \frac{3}{2} k_B T \quad \text{three degrees of freedom}$$

Total translational kinetic energy: $E_k = N \cdot \langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}Nk_B T = \frac{3}{2}nRT$

Root mean square speed: $v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$

For hydrogen, at room temperature, $v_{rms} = \sqrt{\frac{3 \cdot 8.315 \cdot 300}{2 \times 10^{-3}}} = 1.9 \times 10^3 \text{ m/s}$

Example: A Tank of Helium

A tank of volume 0.3 m^3 contains 2 mole of helium gas at 20°C . Assuming the helium behaves like an ideal gas, (a) find the total internal energy of gas. (b) What is the rms speed of the atoms?

$E = \frac{3}{2}nRT = 7.3 \times 10^3 \text{ J}$, $v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \cdot 8.31 \cdot 293}{4 \times 10^{-3}}} = 1.35 \cdot 10^3 \text{ m/s}$

21.2 Molar Specific Heat of an Ideal Gas

Energy Conservation: $dE = dQ + dW$

Ideal Gas: $E_{int} = \frac{3}{2}nRT$, $R = 8.31 \text{ J/mol K}$, $PV = nRT$

Constant volume: $Q = nC_v \Delta T$

$E_{int} = \frac{3}{2}nRT$

$dW = PdV = 0$, $dE = dQ$, $C_v = \frac{1}{n} \frac{dQ}{dT} = \frac{1}{n} \frac{dE}{dT} = \frac{3}{2}R = 12.5 \frac{\text{J}}{\text{mol} \cdot \text{K}}$

	C_p	C_v	$C_p - C_v$	C_p / C_v
He	20.8	12.5	8.33	1.67
H ₂	28.8	20.4	8.33	1.41
CO ₂	37	28.5	8.5	1.31

Constant pressure: $Q = nC_p \Delta T$

$dE = dQ + dW$, $nC_v dT = nC_p dT - PdV$, $PdV = nRdT$

$nC_v dT = nC_p dT - nRdT$

$C_p = C_v + R \rightarrow \text{ideal gas } C_p = \frac{5}{2}R$

$\gamma = \frac{C_p}{C_v} = \frac{5R/2}{3R/2} = 1.67$

Example: A cylinder contains 3.00 mol of helium gas at a temperature of 300 K.

- (a) If the gas is heated at constant volume, how much energy must be transferred by heat to the gas for its temperature to increase to 500 K?
 (b) How much energy must be transferred by heat to the gas at constant pressure to raise the temperature to 500 K?

(a) $Q = nC_V\Delta T$, $C_V = \frac{3}{2}R$

(b) $Q = nC_P\Delta T$, $C_P = \frac{5}{2}R$

21.3 Adiabatic Processes for an Ideal Gas

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 Figure 17.14

Energy Conservation: $dE = dQ + dW$

Ideal Gas: $E_{\text{int}} = \frac{3}{2}nRT$, $R = 8.31 \text{ J/mol K}$, $PV = nRT$

$$P_1V_1 = nRT_1 \neq P_2V_2 = nRT_2$$

$$dE = dW$$

$$nC_v dT = -PdV \quad \text{-- (1)}$$

$$PV = nRT$$

$$PdV + VdP = nRdT \quad \text{-- (2)}$$

$$PdV + VdP = -\frac{R}{C_v} PdV$$

$$\frac{dV}{V} + \frac{dP}{P} = -\frac{R}{C_v} \frac{dV}{V} = -\frac{C_p - C_v}{C_v} \frac{dV}{V} = \left(-\frac{C_p}{C_v} + 1\right) \frac{dV}{V}$$

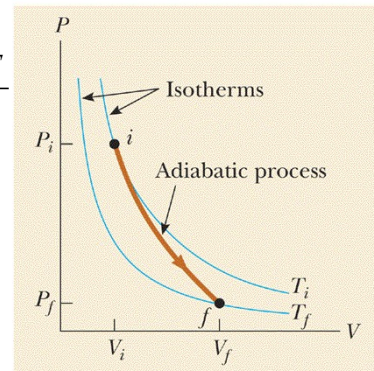
$$\frac{dP}{P} = -\frac{C_p}{C_v} \frac{dV}{V} = -\gamma \frac{dV}{V}, \quad \frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

$$\ln P + \gamma \ln V = \text{const}, \quad PV^\gamma = \text{const}$$

$$\text{since } PV = nRT, \quad TV^{\gamma-1} = \text{const}$$

Example: A Diesel Engine Cylinder

The fuel-air mixture in the cylinder of a diesel engine at 20.0°C is compressed from an initial pressure of 1 atm and volume of 800 cm³ to a volume of 60 cm³. Assuming



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that the mixture behave as an ideal gas with $\gamma = 1.4$ and that the compression is adiabatic, find the final pressure and temperature of the mixture.

$$P_f = P_i \left(\frac{V_i}{V_f} \right)^\gamma = 1 \cdot \left(\frac{800}{60} \right)^{1.4} = 37.6 \text{ atm}, \quad T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1} = 293.15 \left(\frac{800}{60} \right)^{0.4} = 826 \text{ K}$$

21.4 The Equipartition of Energy

The theorem of equipartition of energy: at equilibrium, each degree of freedom contributes, on the average, $\frac{1}{2} k_B T$ of energy per molecule

Monatomic gas: three degrees of freedom
more complex molecules, the vibrational and rotational motions contribute to the internal energy

Diatomic gas:

including rotational energy: $E = 5 \frac{1}{2} N k_B T$

$$C_V = \frac{5}{2} R, \quad C_V = \frac{7}{2} R$$

including vibrational energy: $E = 7 \frac{1}{2} N k_B T$

$$C_V = \frac{7}{2} R, \quad C_V = \frac{9}{2} R$$

Agrees with equipartition theorem at high temperature \rightarrow classical limit, Boltzmann statistics

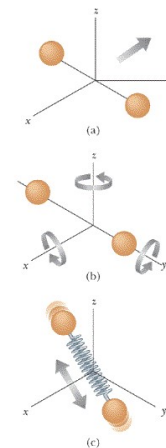
A Hint of Energy Quantization:

classical statistics
or quantum statistics

energy level splitting:

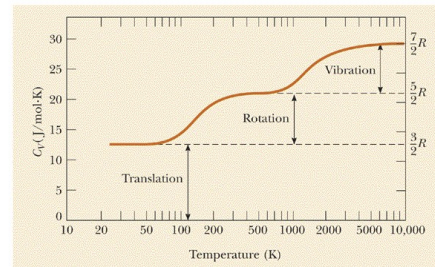
$$\Delta E_{\text{translation}} < \Delta E_{\text{rotation}} < \Delta E_{\text{vibration}}$$

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Figure 17.15



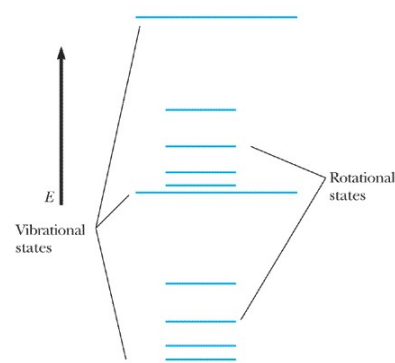
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Figure 17.17



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21.5 Distribution of Molecular Speeds

Distribution functions (number of occurrence times): $f_i = \frac{n_i}{N} \rightarrow$ value s_i

$$\sum_i f_i = 1 \text{ since } \sum_i n_i = N$$

The average value will be $s_{av} = \sum_i s_i f_i$.

The average of the square of the value will be $(s^2)_{av} = \langle s^2 \rangle = \sum_i s_i^2 f_i$.

The root mean square value will be $s_{rms} = \sqrt{\langle s^2 \rangle}$.

The standard deviation will be $\sigma^2 = \langle (s_i - s_{av})^2 \rangle = \langle s^2 \rangle - s_{av}^2$

Change to the scheme of continuous distribution:

$$f_i = \frac{n_i}{N} \rightarrow f(x)$$

$$\sum_i f_i = 1 \rightarrow \int f dx = 1; \quad \sum_i s_i f_i \rightarrow \int s(x) f(x) dx$$

$$(s^2)_{av} = \langle s^2 \rangle = \sum_i s_i^2 f_i \rightarrow \int [s(x)]^2 f(x) dx$$

Maxwell-Boltzmann distribution function: $P(E) \propto e^{-\frac{E}{kT}}$

Go into the k space (or velocity space) \rightarrow

Number of atoms with speed v: $N(v) = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$

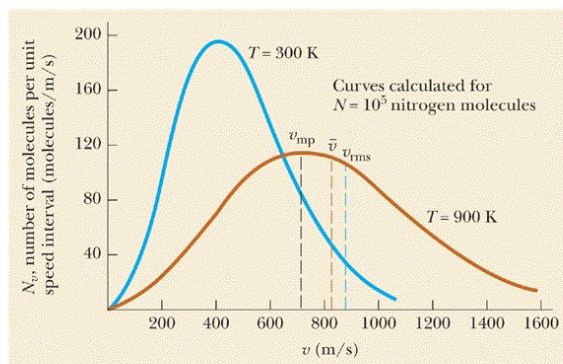
$$v_{rms} = 1.73 \sqrt{\frac{kT}{m}}$$

$$v_{mp} = \sqrt{\frac{2kT}{m}} = 1.4 \sqrt{\frac{kT}{m}}$$

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

$$I = \int_0^{\infty} e^{-Av^2} dv, \quad -\frac{d}{dA} I = \int_0^{\infty} v^2 e^{-Av^2} dv$$

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Figure 16.15



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$$I^2 = \frac{1}{4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-A(x^2+y^2)} dx dy = \frac{\pi}{4A}, \quad I = \frac{1}{2} \sqrt{\frac{\pi}{A}}, \quad \int_0^{\infty} v^2 e^{-Av^2} dv = \frac{\sqrt{\pi}}{4} A^{-\frac{3}{2}}$$

$$\int_0^{\infty} N_v dv = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{\infty} v^2 e^{-\frac{m}{2kT}v^2} dv = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{\sqrt{\pi}}{4} \left(\frac{2kT}{m}\right)^{\frac{3}{2}} = N$$

$$\bar{v} = \frac{\int_0^{\infty} v N_v dv}{N} = ?, \quad \int_0^{\infty} v^3 e^{-Av^2} dv = -\int_0^{\infty} \frac{v^2}{2A} d(e^{-Av^2}) = \frac{1}{A} \int_0^{\infty} e^{-Av^2} v dv = \frac{1}{2A^2}$$

$$\bar{v} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{\infty} v^3 e^{-Av^2} dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m}\right)^2 = \sqrt{\frac{8kT}{\pi m}}$$

$$\langle v^2 \rangle = \frac{\int_0^{\infty} v^2 N_v dv}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^{\infty} v^4 e^{-Av^2} dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{3}{2} \frac{\sqrt{\pi}}{4} \left(\frac{2kT}{m}\right)^{5/2} = \frac{3kT}{m}$$

$$\text{Because } \int_0^{\infty} v^4 e^{-Av^2} dv = -\int_0^{\infty} \frac{v^3}{2A} d(e^{-Av^2}) = -\left[\frac{v^3}{2A} e^{-Av^2}\right]_0^{\infty} + \frac{3}{2} \frac{1}{A} \int_0^{\infty} v^2 e^{-Av^2} dv = \frac{3}{2} \frac{\sqrt{\pi}}{4} A^{-\frac{5}{2}}$$

$$\frac{m}{2} \langle v^2 \rangle = \frac{3kT}{2} \rightarrow \text{Equipartition Theory}$$

Example: A System of Nine Particles

Nine particles have speeds of 5, 8, 12, 12, 12, 14, 14, 17, and 20 m/s. (a) Find the average speed.

$$\bar{v} = 12.7 \text{ m/s}$$

(b) What is the rms speed?

$$v_{rms} = \sqrt{\langle v^2 \rangle} = 13.3 \text{ m/s}$$

(c) What is the most probable speed of the particles?

12m/s