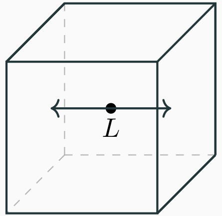
Lecture 31: Kinetics

Kinetic Molecular Theory, Molecular Speeds, Maxwell–Boltzmann

Average Kinetic Energy



Assumptions:

- No intermolecular interactions – ideal gas
- Elastic collisions with wall generate pressure

Change in momentum is:

$$\Delta p = mv_x - (-mv_x) = 2mv_x$$

Time between collisions is:

$$\Delta t = \frac{2L}{v_x}$$

Definition of force:

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

Average Kinetic Energy

Substitute $F = \frac{mv_x^2}{L}$ into definition of pressure:

$$P = \frac{F}{A} = \frac{mv_x^2}{L^3} = \frac{mv_x^2}{V}$$

For N particles:

$$\langle P \rangle = \frac{1}{V} \sum_{i=1}^{N} m \langle v_{x,i} \rangle^2$$

Generalize to 3D using $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$:

$$\langle P \rangle = \frac{1}{3V} \sum_{i=1}^{N} m \langle v_i \rangle^2$$

Average Kinetic Energy

Substitute $\langle KE \rangle = \frac{1}{2}m\langle v^2 \rangle$ into $\langle P \rangle = \dfrac{1}{3V}\displaystyle\sum_{i=1}^{N} m\langle v_i \rangle^2$:

$$\langle P \rangle = \frac{2N}{3V}\langle KE \rangle$$

Substitute $PV = Nk_BT$:

$$\frac{Nk_BT}{V} = \frac{2N}{3V}\langle KE \rangle$$

Rearrange for Equipartition:

$$U = \langle KE \rangle = \frac{3}{2}k_BT$$

Root Mean Squared Speed

Definition:

$$\langle KE\rangle = \langle\frac{1}{2}mv^2\rangle = \frac{1}{2}m\langle v^2\rangle$$

Substitute equipartition $\langle KE\rangle = \frac{3}{2}k_BT$:

$$\langle v^2\rangle = \frac{2\langle KE\rangle}{m} = \frac{2\left(\frac{3}{2}k_BT\right)}{m} = \frac{3k_BT}{m} = \frac{3RT}{M}$$

Take square root:

Root Mean Squared Speed

$$v_{rms} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3RT}{M}}$$

Maxwell Boltzmann Distribution Derivation

Write probability distribution function:

$$h(v) = h(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z)$$

Take natural log:

$$\ln h(v) = \ln f(v_x) + \ln f(v_y) + \ln f(v_z)$$

Take partial derivative with respect to v_x:

$$\frac{\partial \ln h(v)}{\partial v_x} = \frac{d \ln f(v_x)}{d v_x}$$

Maxwell Boltzmann Distribution Derivation

Evaluate with chain rule:

$$\frac{\partial \ln h(v)}{\partial v_x} = \frac{d \ln h(v)}{dv} \left(\frac{\partial v}{\partial v_x} \right) = \frac{d \ln h(v)}{dv} \left(\frac{v_x}{v} \right)$$

Calculate the partial derivative using $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$:

$$\frac{\partial v}{\partial v_x} = \frac{1}{2}(v_x^2 + v_y^2 + v_z^2)^{-1/2} \cdot 2v_x = \frac{v_x}{v}$$

Substitute back in and generalize for all components ($j = x, y, z$):

$$\frac{d \ln h(v)}{v dv} = \frac{d \ln f(v_x)}{v_x dv_x} \implies \frac{d \ln f(v_j)}{v_j dv_j} = -2\gamma$$

Maxwell Boltzmann Distribution Derivation

Integrate both sides for a 1D component:

$$\int d\ln f(v_j) = \int -2\gamma v_j dv_j$$

$$\ln f(v_j) = -\gamma v_j^2 + C$$

$$f(v_j) = Ae^{-\gamma v_j^2}$$

Normalization using Gaussian integral with $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$:

$$A\int_{-\infty}^{\infty} e^{-\gamma v_x^2} dv_x = 1 \implies A = \left(\frac{\gamma}{\pi}\right)^{1/2}$$

$$f(v_x) = \left(\frac{\gamma}{\pi}\right)^{1/2} e^{-\gamma v_x^2}$$

Maxwell Boltzmann Distribution Derivation

Relate to physical constants using average value $\langle v_x^2 \rangle$:

$$\langle v_x^2 \rangle = \frac{RT}{M} = \int_{-\infty}^{\infty} v_x^2 f(v_x) dv_x = \int_{-\infty}^{\infty} v_x^2 \left(\frac{\gamma}{\pi}\right)^{1/2} e^{-\gamma v_x^2} dv_x$$

Evaluate Gaussian with identity $\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{2a^{3/2}}$:

$$\frac{RT}{M} = \left(\frac{\gamma}{\pi}\right)^{1/2} \left(\frac{\sqrt{\pi}}{2\gamma^{3/2}}\right) = \frac{1}{2\gamma} \implies \gamma = \frac{M}{2RT}$$

Substitute $\gamma = \frac{M}{2RT}$ for the 1D Velocity Distribution:

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mv_x^2/2RT}$$

Maxwell Boltzmann Distribution Derivation

Extend to 3D speed distribution (u):

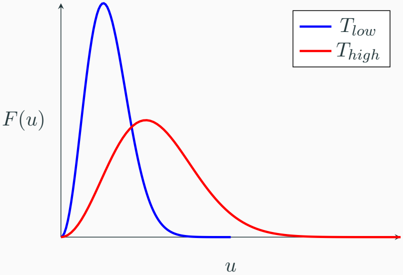
$$\begin{aligned} F(u)du &= f(v_x)f(v_y)f(v_z)dv_xdv_ydv_z \\ &= \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-M(v_x^2+v_y^2+v_z^2)/2RT} dv_xdv_ydv_z \end{aligned}$$

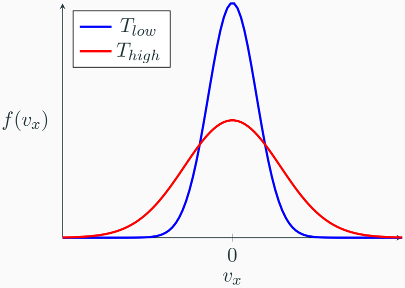
Spherical Jacobian $dv_xdv_ydv_z \to u^2 \sin\theta \, du \, d\theta \, d\phi$:

$$F(u)du = \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \underbrace{\int_0^{\pi} \sin\theta \, d\theta}_{2} \cdot \left[u^2 \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mu^2/2RT}\right] du$$

$$F(u)du = 4\pi u^2 \cdot \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mu^2/2RT} \, du$$

Summary





Speed Distribution (u)

$$F(u) = 4\pi u^2 \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mu^2/2RT}$$

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi M}} \qquad \langle u^2 \rangle = \frac{3RT}{M}$$

Velocity Distribution (v)

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mv_x^2/2RT}$$

$$\langle v_x \rangle = 0 \qquad \langle v_x^2 \rangle = \frac{RT}{M}$$