Classical Mechanics
&
Properties of Gases

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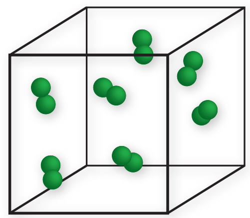
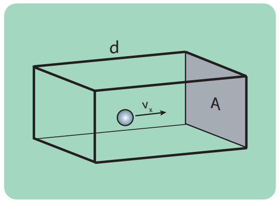
Properties of gases

- Ideal & real gases
- Kinetic theory of gases
- Maxwell-Boltzmann distribution
- Applications of kinetic theory



Kinetic theory of gases

Consider many collisions



Momentum imparted to wall

$$\Delta p = 2mv_x$$

Interval between collisions

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

$$F = ma = \frac{d(p)}{dt} \approx \frac{\Delta p}{\Delta t} \qquad p = \frac{F}{A}$$

$$p = \frac{Nm\left\langle v_x^2\right\rangle}{V}$$

$$pV = \frac{1}{3}Nm\left\langle v^2\right\rangle$$

$$pV = Nk_BT$$

Maxwell-Boltzmann Distribution

$$f(v) = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_BT}\right)$$

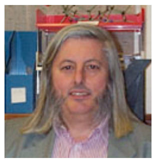
Maxwell-Boltzmann Distribution


$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$





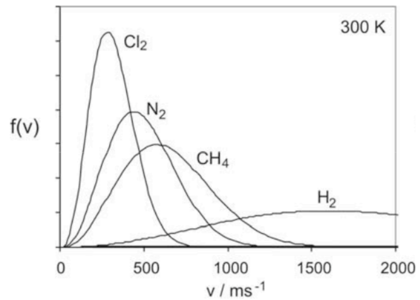



Maxwell Boltzmann Distribution

Mass Dependence

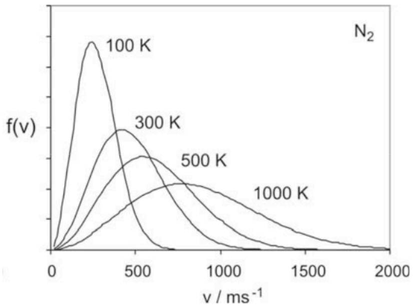
$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$



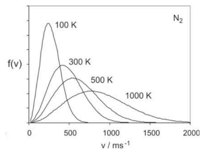
Maxwell Boltzmann Distribution

Temperature Dependence

$$f(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$



Derivation



A Probability Distribution Function

$$f(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$

$$f(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

$$P(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

Derivation

A Probability Distribution Function

$$P(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

- Each velocity component may be treated independently
  - The total probability of finding a particle with components v_x, v_y, v_z is the product of the probabilities for each component

$$P(v_x, v_y, v_z)dv_x dv_y dv_z = P(v_x)dv_x P(v_y)dv_y P(v_z)dv_z$$

- All directions within the gas are equivalent
  - So an alternative to this distribution function is one which depends on the total speed of the particle (v, or even v^2) not on each independent velocity component (v_x, v_y, v_z)

$$P(v_x^2 + v_y^2 + v_z^2) = P(v_x)P(v_y)P(v_z)$$

Derivation

$$\boxed{P(v_x^2 + v_y^2 + v_z^2) = P(v_x)P(v_y)P(v_z)}$$

- A Possible solution $\quad P(v_x) = Ae^{-Bv_x^2}$ $\quad \boxed{e^{x+y+z} = e^x e^y e^z}$

Derivation

- A Possible solution $P(v_x) = Ae^{-Bv_x^2}$
- Normalise $1 = \int_{-\infty}^{\infty} P(v_x)dv_x = \int_{-\infty}^{\infty} Ae^{-Bv_x^2}dv_x \ = A\sqrt{\frac{\pi}{B}}$

$$\int_{-\infty}^{\infty} e^{-x^2}dx = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} e^{-Bv^2}\sqrt{B}dv = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} e^{-Bv^2}dv = \sqrt{\frac{\pi}{B}}$$

$$\begin{aligned} \sqrt{B}v &= x \\ \sqrt{B}dv &= dx \end{aligned}$$

$$1 = A\sqrt{\frac{\pi}{B}}$$

$$A = \sqrt{\frac{B}{\pi}}$$

Derivation

- A Possible solution $P(v_x) = \sqrt{\frac{B}{\pi}}e^{-Bv_x^2}$
- Mean square v_x $\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 P(v_x)dv_x = \sqrt{\frac{B}{\pi}}\int_{-\infty}^{\infty} v_x^2 e^{-Bv_x^2}dv_x$

$$\int_{-\infty}^{\infty} x^2e^{-x^2}dx = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^{\infty} Bv^2e^{-Bv^2}\sqrt{B}dv = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^{\infty} v^2e^{-Bv^2}dv = \frac{\sqrt{\pi}}{2B\sqrt{B}}$$

$$\begin{aligned} \sqrt{B}v &= x \\ \sqrt{B}dv &= dx \end{aligned}$$

$$\langle v_x^2 \rangle = \sqrt{\frac{B}{\pi}}\frac{\sqrt{\pi}}{2B\sqrt{B}} = \frac{1}{2B}$$

Derivation

$$\langle v_x^2 \rangle = \frac{1}{2B}$$

- Use Classical Equipartition once more

$$\frac{1}{2}k_BT = \frac{1}{2}m\langle v_x^2 \rangle$$

$$\langle v_x^2 \rangle = \frac{k_BT}{m}$$

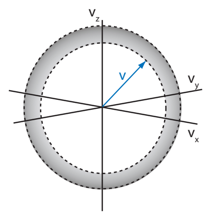
$$B = \frac{m}{2k_BT}$$

$$P(v_x) = \sqrt{\frac{B}{\pi}}e^{-Bv_x^2}$$

$$P(v_x)dv_x = \left(\frac{m}{2\pi k_BT}\right)^{1/2} e^{-\frac{mv_x^2}{2k_BT}}dv_x$$

Derivation

$$\begin{aligned} P(v_x, v_y, v_z)dv_xdv_ydv_z &= P(v_x)^3dv_xdv_ydv_z \\ &= \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp -\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}dv_xdv_ydv_z \\ &= \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp -\frac{mv^2}{2k_BT}dv_xdv_ydv_z \end{aligned}$$

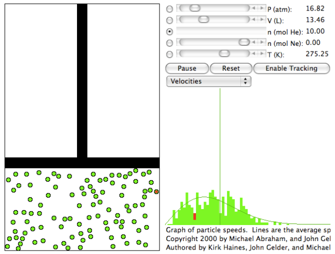


$$dv_xdv_ydv_z = 4\pi v^2dv$$

$$P(v)dv = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 \exp -\frac{mv^2}{2k_BT}dv$$

An example

Simulation of Velocity Distribution



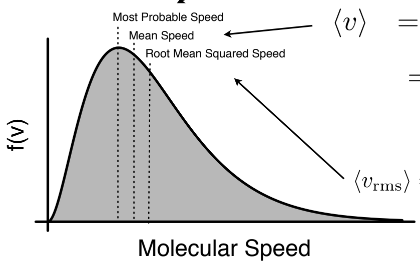
- http://intro.chem.okstate.edu/1314F00/Laboratory/GLP.htm

Speeds

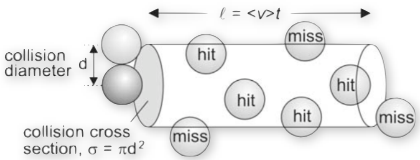
$$\langle v_{\text{mode}} \rangle = \left(\frac{2k_B T}{m} \right)^{1/2}$$

$$\langle v \rangle = \int_0^\infty v f(v) dv = \left(\frac{8k_B T}{\pi m} \right)^{1/2}$$

$$\langle v_{\text{rms}} \rangle = \left(\frac{3k_B T}{m} \right)^{1/2}$$



Collision Frequency



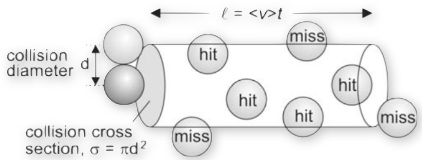
- Volume swept-out by a single particle

$$\pi d^2 < v_{rel} > t$$

- Number of collisions for one particle = volume × number density
- Collision frequency for one particle = number of collisions in unit time

$$z = \sigma \langle v_{\text{rel}} \rangle \frac{N}{V} = \sigma \langle v_{\text{rel}} \rangle \frac{p}{k_B T}$$

Collision Density



- Collision density is the total number of collisions occurring per unit volume

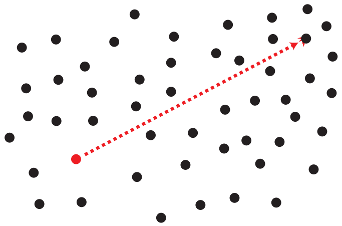
$$Z = \frac{1}{2} \sigma \langle v_{\text{rel}} \rangle \left(\frac{N}{V} \right)^2$$

$$z = \sigma \langle v_{\text{rel}} \rangle \frac{N}{V}$$

$$Z = \frac{1}{2} \sigma \sqrt{2} \sqrt{\frac{8k_B T}{\pi m}} \left(\frac{N}{V} \right)^2$$

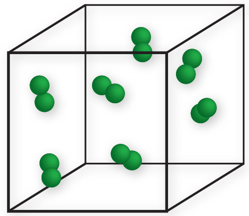
Mean free path

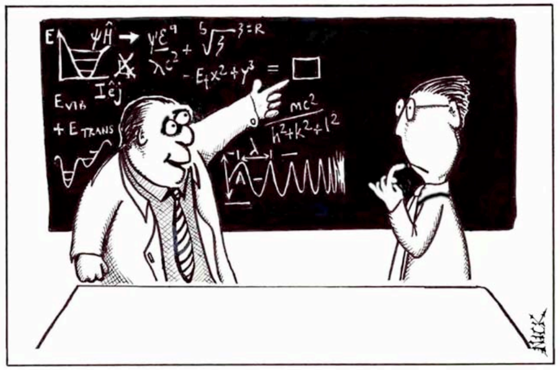
$$\lambda = \frac{\langle v \rangle}{z}$$



Lecture Summary

- Maxwell Boltzmann distribution
    - Variation with m and T
    - Derivation
    - Speeds
- Collision frequency
- Mean free path





"If my calculations are correct, not only must we always wear white lab coats, but the boundaries of our existence are defined solely by what is allowed to occur within the confines of a small two-dimensional box..!"