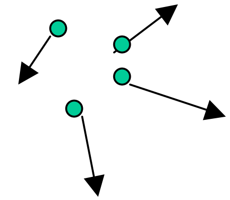
Kinetic Theory of Gases

Kinetic Theory: Theory that deals with prediction of transport (μ, κ, D) and thermodynamic properties of gases based on statistical (average) description of the translational motion of its components (atoms & molecules).

statistical description →



velocity distribution function

Maxwell-Boltzmann speed distribution

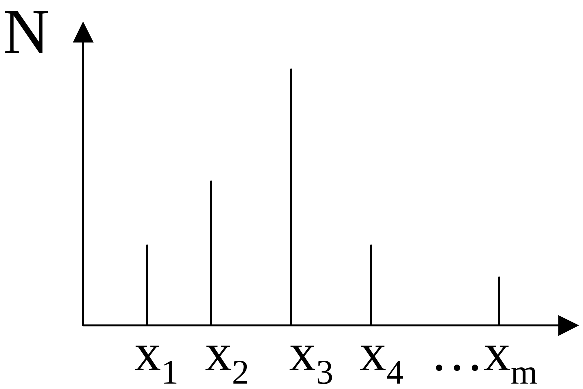
$$F(v) = 4\pi v^2 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}}$$

Probability & Statistics Review

- Suppose we have a series of observation for a value x which can take on a discrete set of values

$$\{x_1, x_2, x_3, \ldots x_m\}$$

- Suppose that in a series of N measurements we observe that



x_1 occurs N_1 times

x_2 occurs N_2 times

: : :

x_m occurs N_m times

- Average value of x

$$< x >= \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \ldots\ldots + N_m x_m}{N} = \sum_{i=1}^{m} \frac{N_i}{N} x_i$$

Probability & Statistics Review

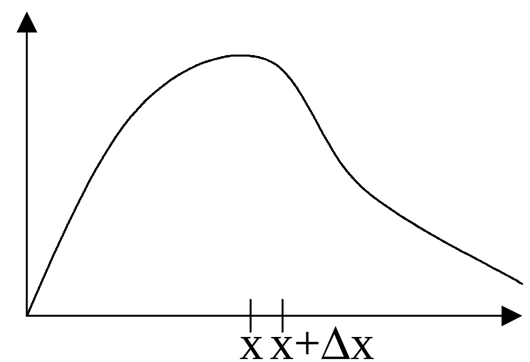
- Define the probability that x_i will be observed as P_i

$$P_i = \frac{N_i}{N} \qquad note \quad \sum_{i=1}^{m} P_i = \frac{1}{N}\sum_{i=1}^{m} N_i = 1$$

- The average value of x becomes

$$< x >= \sum_{i=1}^{m} P_i x_i$$

- Now suppose that x (outcome of an experiment) can take on not discrete but continuous set of values
- Everytime that outcome of the experiment is between x and x+Δx we add 1 to that bin
- N(x) is the number of outcomes out of N total that is between x and x+Δx



Probability & Statistics Review

- Thus, the probability that an experimental outcome will be between x and x+Δx is

$$P(x) = \frac{N(x)}{N}$$

- The value P(x) is proportional to the length of segment Δx. We define probability density function f(x) such that P(x)=f(x)Δx

- The average value of x, <x> is now given by

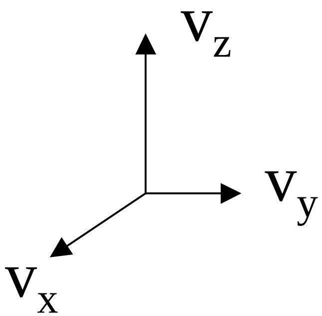
$$< x >= \sum_{all\ segments} xP(x) = \sum_{all\ segments} xf(x)\Delta x$$

- Let Δx→0 and number of segments →∞

$$< x >= \int xf(x)dx$$

- Integral is over the whole domain of x; f(x): distribution function

Maxwell-Boltzmann velocity distribution



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

Gaussian probability distribution

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

Probability that v_x is between v_x and v_x+dv_x

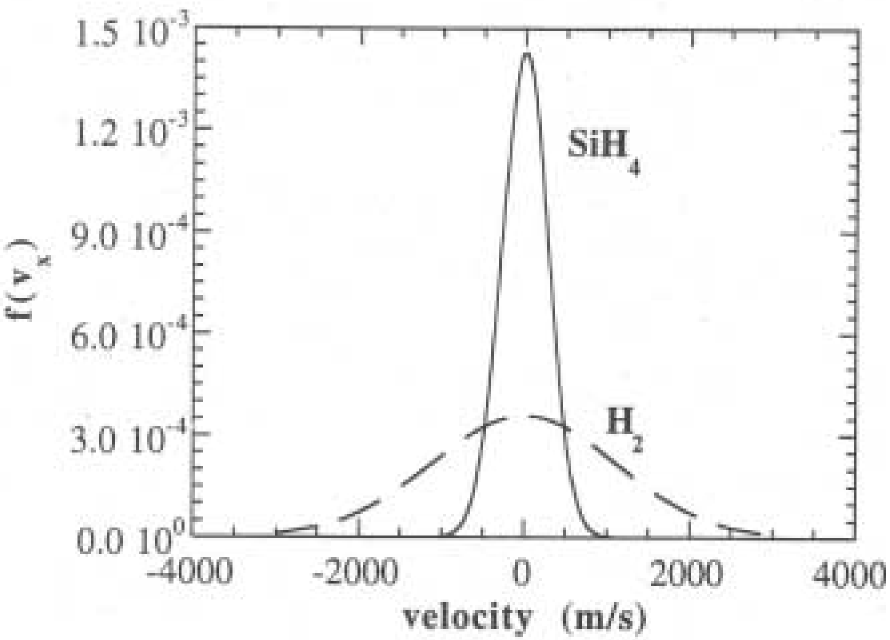
<u>Example</u>

SiH_4 : $m_{SiH4} = 32 \times 1.66 \times 10^{-27}$ kg

H_2 : $m_{H2} = 2 \times 1.66 \times 10^{-27}$ kg

k= 1.38066×10^{-23} J/K

T = 300 K



Maxwell-Boltzmann velocity distribution

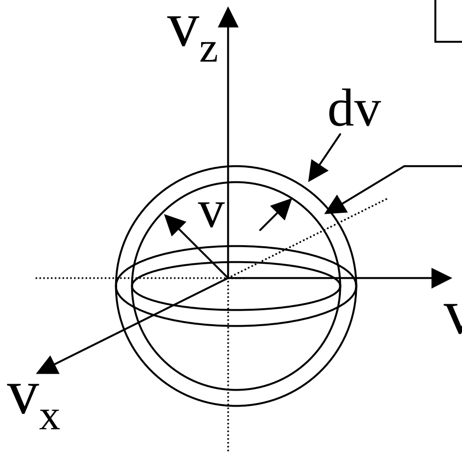
Things to remember/notice

- Gaussian distribution
- Width of the distribution depends on mass; lighter atoms/molecules have wider distribution
- At the same T lighter atoms/molecules are faster
- Higher the T faster the molecules
- On average v_x=0, (makes sense because on average the gas is stationary.)
- Since gas speeds ~1-10 m/s is much smaller than molecular speeds (~500-1000 m/s) we can assume the same distribution even if the gas is flowing.

Maxwell-Boltzmann speed distribution

- The three velocity components are independent of each other

$$f(v_x)\,f(v_y)\,f(v_z)=\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv_x^2}{2kT}} e^{-\frac{mv_y^2}{2kT}} e^{-\frac{mv_z^2}{2kT}}$$



How many molecules are there in a shell with volume $4\pi v^2 dv$?

$$f(v_x)\,f(v_y)\,f(v_z)\,dv_x dv_y dv_z = F(v)dv$$

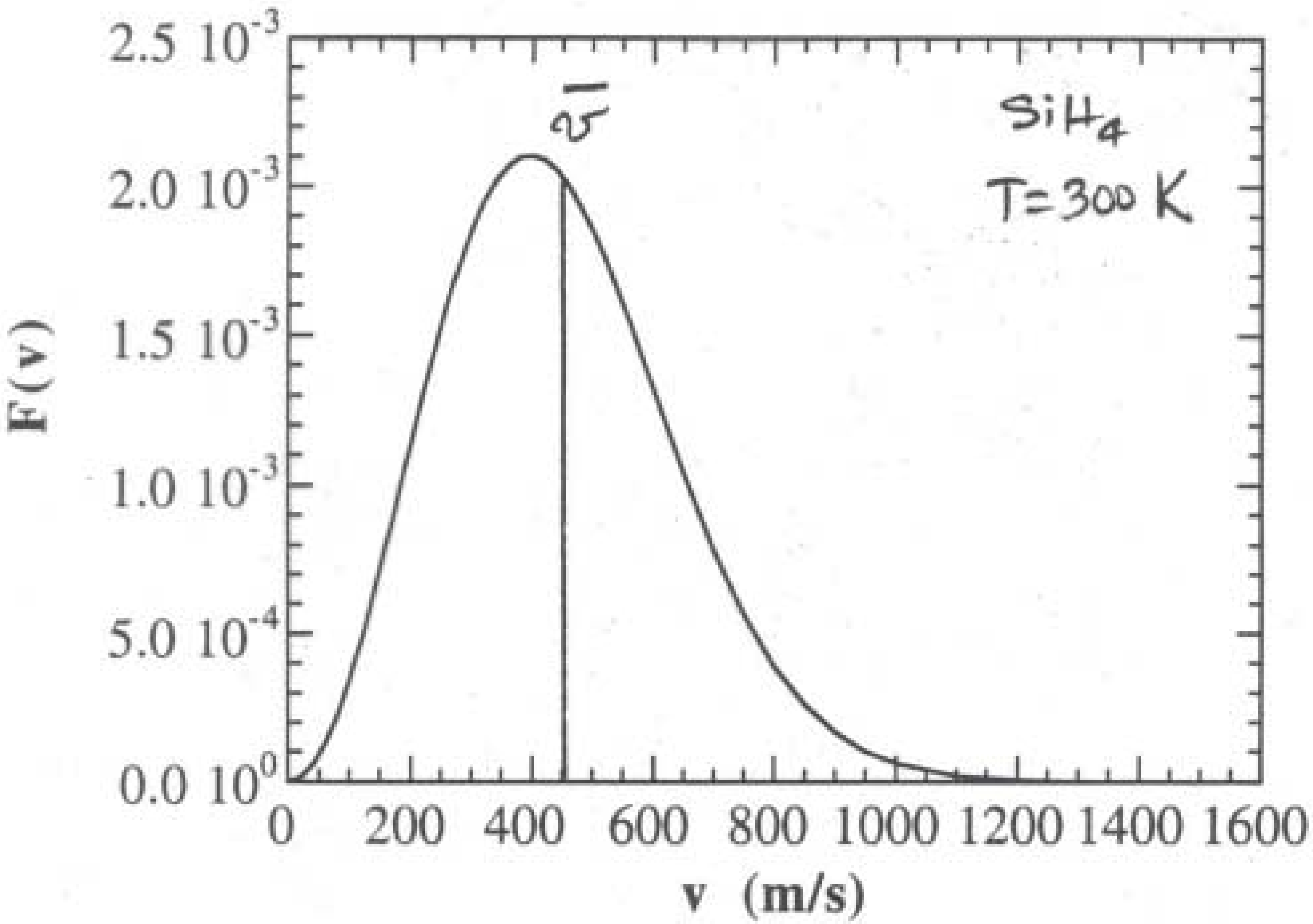
Transform into cylindrical coordinates

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad \longleftarrow \quad \text{speed}$$

Probability of finding a molecule that has speed between v and v+dv

$$F(v)\,dv = 4\pi v^2\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} dv$$

Maxwell-Boltzmann speed distribution



Why is Maxwell-Boltzmann speed distribution useful? How do you use it?

Calculating an average property <ψ>

$$<\psi> \int_0^\infty \psi F(v)\, dv$$

Example: <v>, average speed:

$$<v> = \int_0^\infty vF(v)\, dv = \int_0^\infty 4\pi v^3 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}}\, dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}}\, dv$$

$$<v>_{He} = 1256\, m/s$$

$$<v>_{H2} = 1770\, m/s$$

$$<v>_{Ar} = 398\, m/s$$

$$<v>_{O2} = 444\, m/s$$

$$<v> \approx 500\, m/s$$

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

using $\int_0^\infty x^3 e^{-ax^2}\, dx = \frac{1}{2a^2}$

Why is Maxwell-Boltzmann speed distribution useful? How do you use it?

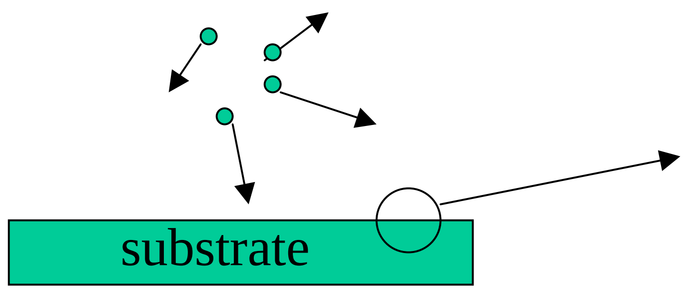
Example: average kinetic energy and C_v:

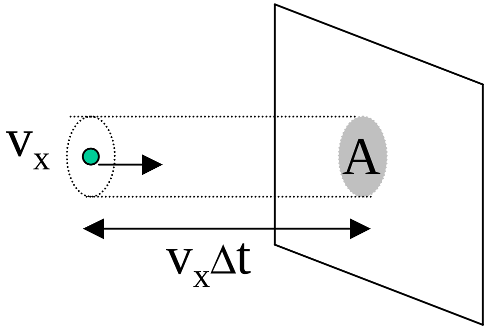
$$\bar{\varepsilon}_K = \frac{1}{2} m < v^2 > = \frac{3}{2} kT$$

$$< v^2 > = \int_0^\infty v^2 F(v)\, dv = 3\frac{kT}{m}$$

$$\bar{E}_K = \frac{3}{2} N_{Av} kT = \frac{3}{2} RT = U \quad \Rightarrow \quad C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{3}{2} R$$

Example: average flux to a plane

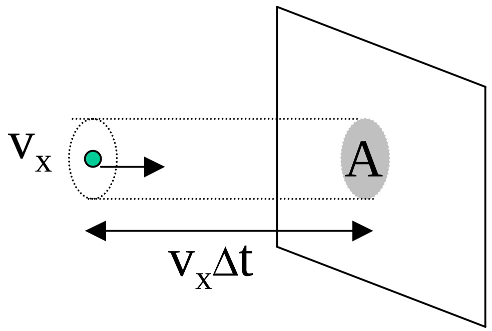




If a particle has velocity v_x it will strike A if it is $v_x\Delta t$ away

Random flux to a surface

of collisions = gas density × cylinder volume = $NAv_x\Delta t$



Total # of collisions = $NA\Delta t \int_0^\infty f(v_x)v_x dv_x$

$$Flux = F = \frac{Z_w}{A\Delta t} = N\int_0^\infty \left(\frac{m}{2\pi kT}\right)^{1/2} v_x e^{-\frac{mv_x^2}{2kT}} dv_x$$

$$\int_0^\infty e^{-ax^2}dx = \frac{1}{2a}$$

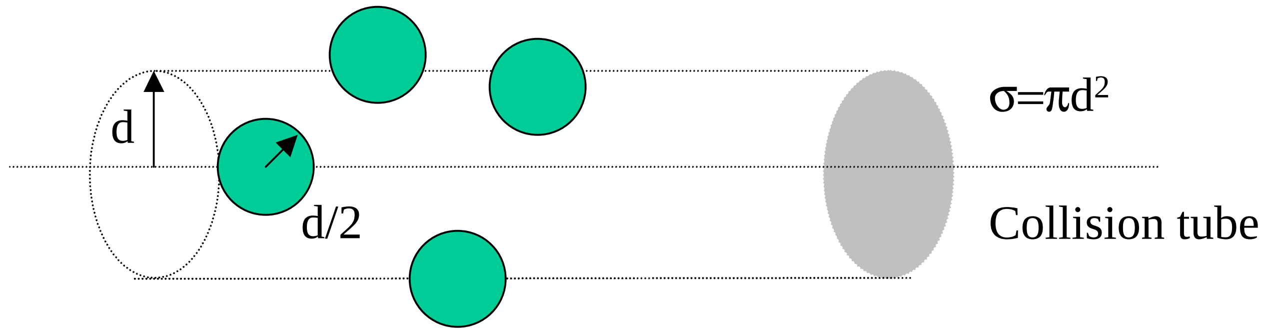
$$F = N\left(\frac{m}{2\pi kT}\right)^{1/2} \frac{1}{2}\frac{2kT}{m} = \frac{N}{4}\sqrt{\frac{8kT}{\pi m}}$$

$$F = \frac{N<v>}{4}$$

← The random flux

Mean Free Path, λ_{mf}

Consider a hard sphere traveling at <v> for a time Δt on a straight path



Atom will sweep out a collision tube whose cross section is $\sigma = \pi d^2$

Distance traveled in Δt is = $<v>\Delta t$

# of molecules inside the tube = $\sigma <v> \Delta t\, N$ = # of hits

# of hits/unit time = $\sigma <v> N$

Z = collision frequency = $\sigma <v> N$

But we should take into account that other molecules are moving. When this is considered <v> should be replaced by $\sqrt{2} <v>$. Also we should not double count.

$$Z = \frac{\sqrt{2} N\sigma <v>}{2} \quad \Rightarrow \quad Z = \frac{N\sigma <v>}{\sqrt{2}} \qquad \lambda_{mf} = \frac{<v>}{Z} \quad \Rightarrow \quad \boxed{\lambda_{mf} = \frac{1}{\sqrt{2} N\sigma}}$$

Mean free path & Gas phase collision rates

Molecule	σ (cm^2)	λ_{MF} (cm)
He	2.1×10^{-15}	10
H_2	2.7×10^{-15}	8
Ar	3.6×10^{-15}	6

Example: Reaction rates of gas phase reactions that proceed at gas phase collision frequencies.

Consider for example the following gas phase reaction

$$SiH_4 + O_2 \xrightarrow{k} SiH_3 + OH$$

What is the upper limit for k?

Equal if they react everytime they colide

$$Z_{AB} = \sigma_{AB} < v_{AB} > N_A N_B = k N_A N_B$$

Gas phase collision rates & transport coefficients

$$< v_{AB} > = \sqrt{\frac{8kT}{\pi\mu}} \qquad with \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

$$\sigma_{AB} = \frac{1}{2}(d_A + d_B) \quad k_{max} = \sigma_{AB} < v_{AB} >$$

$$\sigma_{AB} \sim 3\times10^{-15} cm^2 \quad < v_{AB} > \sim 50{,}000\, cm/s$$

$$\therefore k_{max} = 1.5\times10^{-10}\ cm^3/s$$

$$\lambda_{mf} = \frac{1}{\sqrt{2}N\sigma}$$

$$D = \frac{1}{3}\lambda_{mf} < v >$$

$$D \sim \frac{T^{3/2}}{P}$$

$$\kappa = \frac{1}{3}\lambda_{mf} < v > C_V N$$

Classic Example: "Monolayer formation time"- Why we use UHV for fundamental surface science studies

Example: there are about ~ 10^{15} cm^{-2} surface sites on a surface. How much time is required to form a monolayer if all molecules hitting the surface stick to the surface at 300 K and 1 mTorr. (e.g, H_2O)

$$<v> = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8\times 1.38\times 10^{-23}\ J/K \times 300\ K}{\pi \times 1.66\times 10^{-27}\ kg \times 18}} = 594\ m/s$$

$$N = \frac{P}{kT} = \frac{0.001\ Torr}{1.38\times 10^{-23}\ J/K \times 300\ K}\ \frac{1.013\times 10^{5}\ N/m^{2}}{760\ Torr} = 3.219\times 10^{19}\ m^{-3} = 3.219\times 10^{13}\ cm^{-3}$$

$$F = \frac{N<v>}{4} = \frac{3.219\times 10^{13}\ cm^{-3} \times 59{,}400 cm/s}{4} = 4.78\times 10^{17}\ cm^{-2} s^{-1}$$

$$\tau_{ML} = \frac{surface\ site\ density}{Flux} = \frac{10^{15}\ cm^{-2}}{4.78\times 10^{17}\ cm^{-2} s^{-1}} = 0.002\ s = 2\ ms$$

Vacuum	P (Torr)	τ_{ML} (seconds)
High	10^{-6}	2
Very High	10^{-8}	200
UHV	10^{-10}	20,000