

Find  $C$ : by normalizing the probability

$$1 = \int d^3\vec{v} C e^{-\beta v^2}$$
$$= C \int_{-\infty}^{\infty} dv_x e^{-\beta v_x^2} \int_{-\infty}^{\infty} dv_y e^{-\beta v_y^2} \int_{-\infty}^{\infty} dv_z e^{-\beta v_z^2}$$

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

gives  $C = \left(\frac{\beta}{\pi}\right)^{3/2}$

Find  $B$ : use physics of the ideal gas.

$$\langle v^2 \rangle = \left(\frac{\beta}{\pi}\right)^{3/2} \int d^3\vec{v} v^2 e^{-\beta v^2}$$
$$= - \left(\frac{\beta}{\pi}\right)^{3/2} \frac{d}{d\beta} \int d^3\vec{v} e^{-\beta v^2}$$

$$\langle v^2 \rangle = - \left(\frac{\beta}{\pi}\right)^{3/2} \frac{d}{d\beta} \left(\frac{\pi}{\beta}\right)^{3/2} = \frac{3}{2\beta}$$

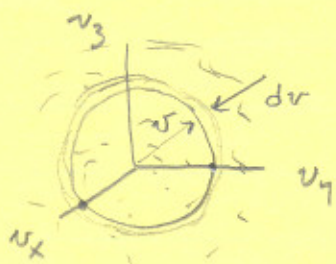
So,

$$\beta = \frac{2}{3} \langle v^2 \rangle = \frac{m}{2kT}$$

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

Maxwell distribution  
of molecular velocities

Speed distribution.  $f(\vec{v})$  is velocity because  $f(\vec{v}) d^3\vec{v}$  is the prob.



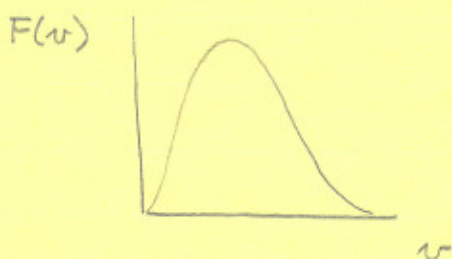
count number of molecules inside a shell of  $dv$  thickness to get speed count.

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$F(v) dv = f(\vec{v}) 4\pi v^2 dv$$

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

the MB speed distribution.



what's the peak?

$$v^*: \quad \frac{dF(v)}{dv} = 0$$

$$4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ 2v e^{-mv^2/2kT} - v^2 \frac{1}{2} \frac{m}{kT} 2v e^{-mv^2/2kT} \right] = 0$$

$$2v - v^3 \frac{m}{kT} = 0 \quad \Rightarrow \quad v=0 \text{ and } v^2 = \frac{2kT}{m}$$

$$v^* = \sqrt{\frac{2kT}{m}}$$

or  $\frac{1}{2} m v^{*2} = kT = \frac{3}{2} kT$  (K)

average?

$$\langle v \rangle = \int v F(v) dv$$

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

class of integrals.

$$I_n = \int_0^{\infty} x^n e^{-ax^2} dx = \frac{[(n-1)/2]!}{2a^{(n+1)/2}} \quad n \text{ odd}$$

$$= \frac{1 \cdot 3 \cdot 5 \cdots (n-1)}{2^{(n/2)+1} a^{n/2}} \sqrt{\frac{\pi}{a}} \quad n \text{ even}$$

$$I_3 = \frac{\left(\frac{3-1}{2}\right)!}{2a^2} = \frac{1}{2a^2}$$

$$\langle v \rangle = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2} \left( \frac{2kT}{m} \right)^2$$

$$= 4\pi \sqrt{\frac{1}{4} \left( \frac{m}{2\pi kT} \right)^3 \left( \frac{2kT}{m} \right)^4}$$

$$= 4\pi \sqrt{\frac{2kT}{m\pi^3}} = \frac{4}{\sqrt{2\pi}} \sqrt{\frac{kT}{m}}$$

$$\frac{\langle v \rangle}{v^*} = \sqrt{\frac{4}{\pi}} \approx 1.13$$

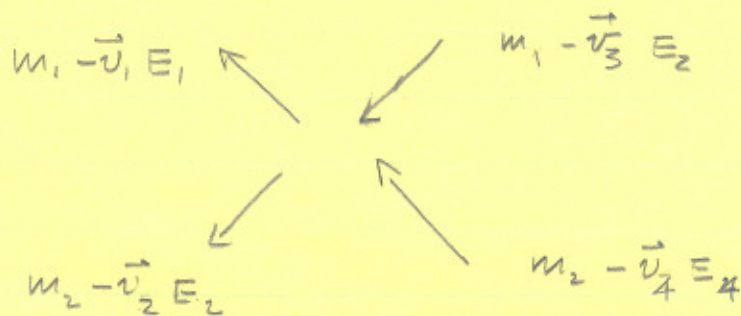
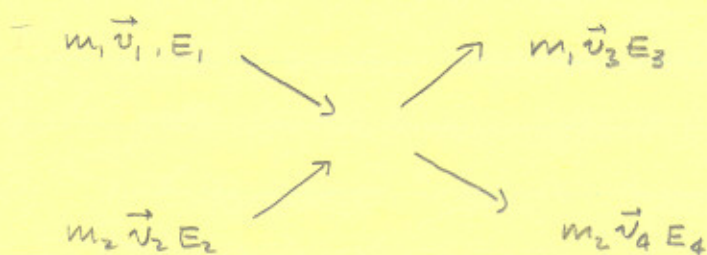
mean above peak  
for any temperature

Standard to remember that the molecules are point-like and non-interacting, so  $E = \frac{1}{2}mv^2$

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

an important quantity

Imagine the collision of two molecules.



Rate is proportional to the densities of projectiles and targets

$$R(12 \rightarrow 34) = C n(E_1) n(E_2)$$

$$R(34 \rightarrow 12) = C' n(E_3) n(E_4)$$

"microscopic reversibility"  $\Rightarrow c = c'$  (no loss)

In equilibrium:  $R(12 \rightarrow 34) = R(34 \rightarrow 12)$

$$\text{so } n(E_1) n(E_2) = n(E_3) n(E_4) \quad (1)$$

$$\text{also: } E_1 + E_2 = E_3 + E_4 \quad (2)$$

Take  $\log$  (1)

$$\ln n(E_1) + \ln n(E_2) = \ln n(E_3) + \ln n(E_4)$$

how can this be compatible with (2)?

only if:  $\ln n(E) = A - \beta E$

$$n(E) = e^{A - \beta E}$$

$$\text{but } e^A = e^{A - \beta(0)}$$

$$\text{so } \ln n(0) = A \Rightarrow e^A = n(0)$$

$$n(E) = n(0) e^{-\beta E}$$

Since this must become the MB distribution  $\beta = 1/kT$

Go back and think about the gas from this perspective

$$n(E) dE = g(E) F_{MB}(E) dE$$

$$= g(E) A e^{-E/kT}$$

need to find density of states  $g(E)$

← proportional to  
the shell volume

Presume uniform  $S(v) dv = C 4\pi v^2 dv$   
distribution

$$\text{where } C = \left( \frac{m}{2\pi kT} \right)^{3/2}$$

each  $v$  corresponds to an  $E$ , so

$$g(E) dE = S(v) dv = C 4\pi v^2 dv$$

so,

$$n(E) dE = g(E) F_{MB}(E) dE = C 4\pi v^2 dv F_{MB}(E)$$

$$= C' 4\pi v^2 dv e^{-E/kT}$$

$$= n(v) dv$$

# particles per unit volume

$$\frac{N}{V} = \int_0^{\infty} n(v) dv = C' \int_0^{\infty} 4\pi v^2 e^{-\frac{mv^2}{2kT}} dv$$

$$= \frac{4\pi C'}{2^2 \left( \frac{m}{2kT} \right)} \sqrt{\frac{\pi 2kT}{m}} = C' \left( \frac{2\pi kT}{m} \right)^{3/2}$$

$$C' = \frac{N}{V} \left( \frac{m}{2\pi\hbar T} \right)^{3/2}$$

so,

$$n(v)dv = 4\pi \frac{N}{V} \left( \frac{m}{2\pi\hbar T} \right)^{3/2} v^2 e^{-mv^2/2\hbar T} dv$$

what we had before

In terms of energy

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

$$E = \frac{1}{2} mv^2$$

$$dE = \frac{2mv}{2} dv = mv dv$$

$$2Em = m^2 v^2 \Rightarrow mv = \sqrt{2Em}$$

$$\frac{dE}{\sqrt{2Em}} = dv$$

and

$$v^2 \frac{dE}{\sqrt{2Em}} = v^2 dv$$

$$\frac{2E}{m} \frac{dE}{\sqrt{2Em}} = \frac{\sqrt{2} \sqrt{E} dE}{(m)^{3/2}}$$

$$F(v)dv \rightarrow 4\pi \left( \frac{m}{2\pi\hbar T} \right)^{3/2} e^{-E/\hbar T} \frac{\sqrt{2} \sqrt{E} dE}{m^{3/2}}$$

$$= \sqrt{\frac{2 \cdot 16\pi^2}{(2\pi\hbar T)^3}} \cdot 2$$

$$F(E) dE = 2\pi \frac{1}{(\pi\hbar T)^{3/2}} E^{1/2} e^{-E/\hbar T} dE$$

This is a famous probability distribution in physics... the Maxwell-Boltzmann Distribution

$$F_{MB} = A e^{-E/kT}$$

\* probability that a single member of a large ensemble at temperature  $T$  has an energy  $E$ . \*

$e^{-E/kT}$  is called the Boltzmann Factor.

$n(E)dE$  the distribution in number of states with energies between  $E$  and  $E+dE$

$$n(E) = g(E) F_{MB}(E) \quad \textcircled{A}$$

where  $g(E)$  is the number of states per unit energy range - called the Density of states.

This can be for continuous situations (Ⓐ) like energies and velocities of molecules in a gas, or DISCRETE situations - like quantum ones!

$$n_i = g_i F_{MB}(E)$$

then  $g_i$  counts the number of states at a given  $E$   
→ The degeneracy factor of QM situations.



This is classical: distinguishable molecules.

What constitutes a point at which classical physics is not right to use?

The thermal energy of the particles  $\frac{3}{2} kT = \frac{1}{2} \frac{p^2}{m}$

So, this  $p$  can also be thought of quantum mechanically.

$$p = \frac{h}{\lambda}, \quad \lambda = \frac{h}{p}$$

If this  $\lambda$  is  $\ll$  average distance between molecules, then classical.

$$\frac{1}{2} \frac{p^2}{m} = \frac{3}{2} kT$$

$$p = \sqrt{3mkT}$$

$$\therefore \lambda = \frac{h}{\sqrt{3mkT}} \ll \sqrt[3]{\frac{V}{N}}$$

So, when

$$\left(\frac{N}{V}\right) \frac{h^3}{(3mkT)^{3/2}} \ll 1 \quad \text{MB statistics okay.}$$

very high  $T$   
very small  $m$