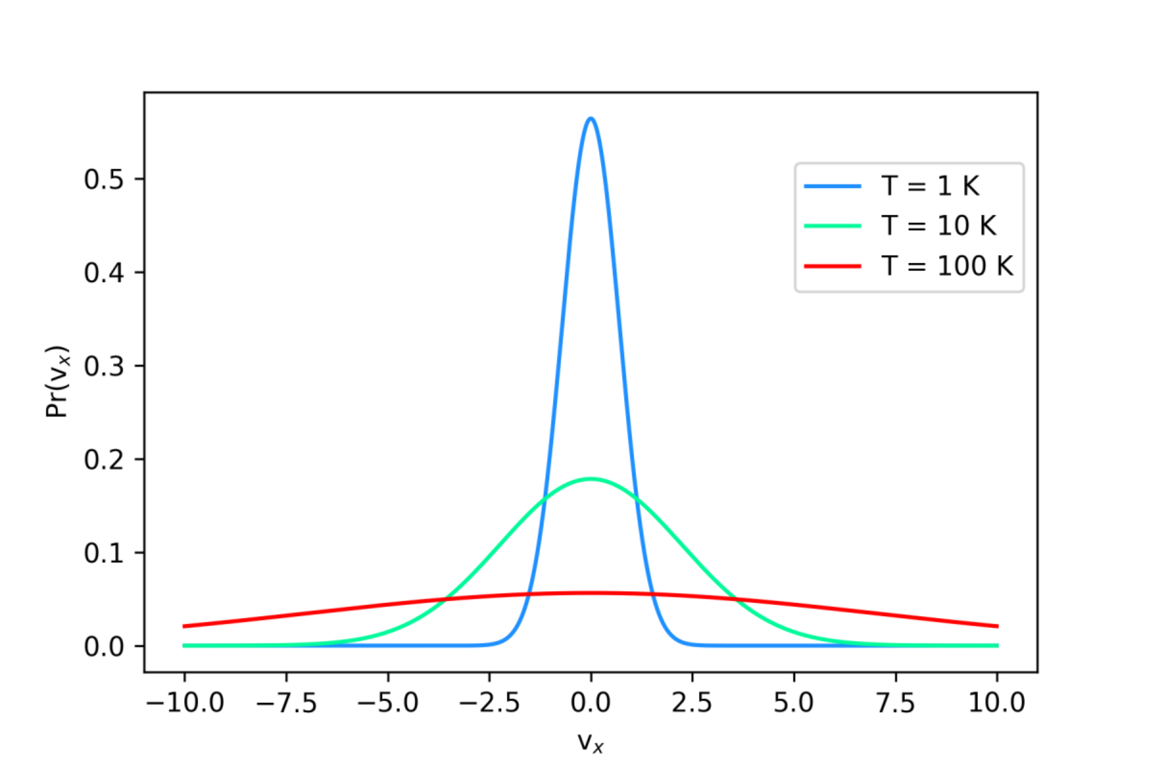
Recap from last time

$$Pr(v_x) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\left(\frac{0.5m(v_x)^2}{k_B T}\right)}$$



No degeneracy in this distribution: only one way to have a specific v_x

A distribution centred around 0 is expected, as velocity can be either positive or negative

As we increase temperature, we increase the chance of occupying higher energy states (higher v_x)

Interesting cases: 1) $T \to 0$: $Pr(E_0) = 1, Pr(E_1) = 0$

2) $T \to \infty$: $Pr(E_0) = 0.5, Pr(E_1)$

Recap from last time

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

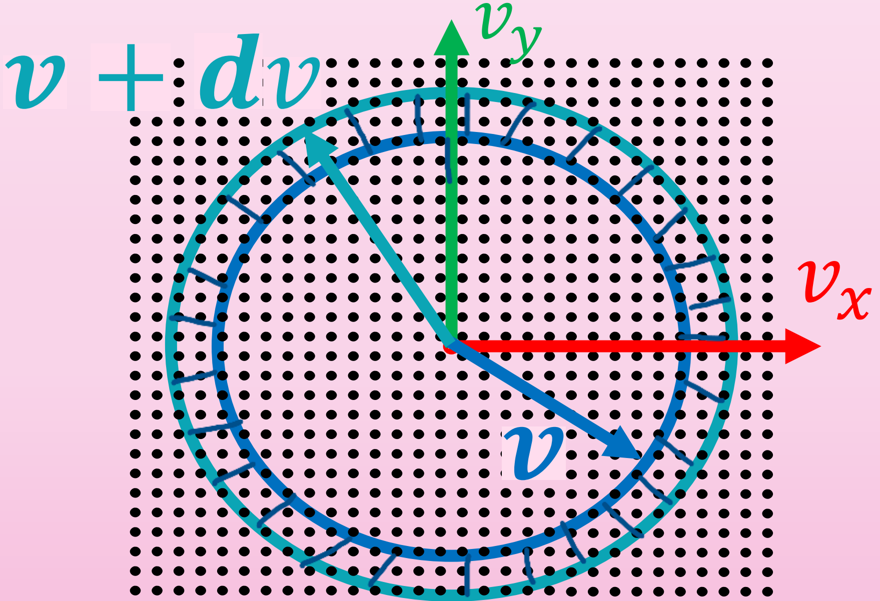
Say that $v^2 = 100$…

$v_x = 10$	$v_x = 0$	$v_x = 0$	$v_x = 5$
$v_y = 0$	$v_y = 10$	$v_y = 0$	$v_y = 8$
$v_z = 0$	$v_z = 0$	$v_z = 10$	$v_z = \sqrt{11}$

Density of states, $g(v)\,\mathrm{d}v$, is given by the area of the ring between v and v + dv

In 3 dimensions this is given by

$$g(v)\,\mathrm{d}v = 4\pi v^2\,\mathrm{d}v$$



Recap from last time

The probability of a molecule in an ideal gas having a specific velocity, v, can be described by the Maxwell-Boltzmann distribution:

(mass per molecule, m) $$Pr(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\left(\frac{m(v^2)}{2k_B T}\right)}$$

$$m \times N_A = M$$

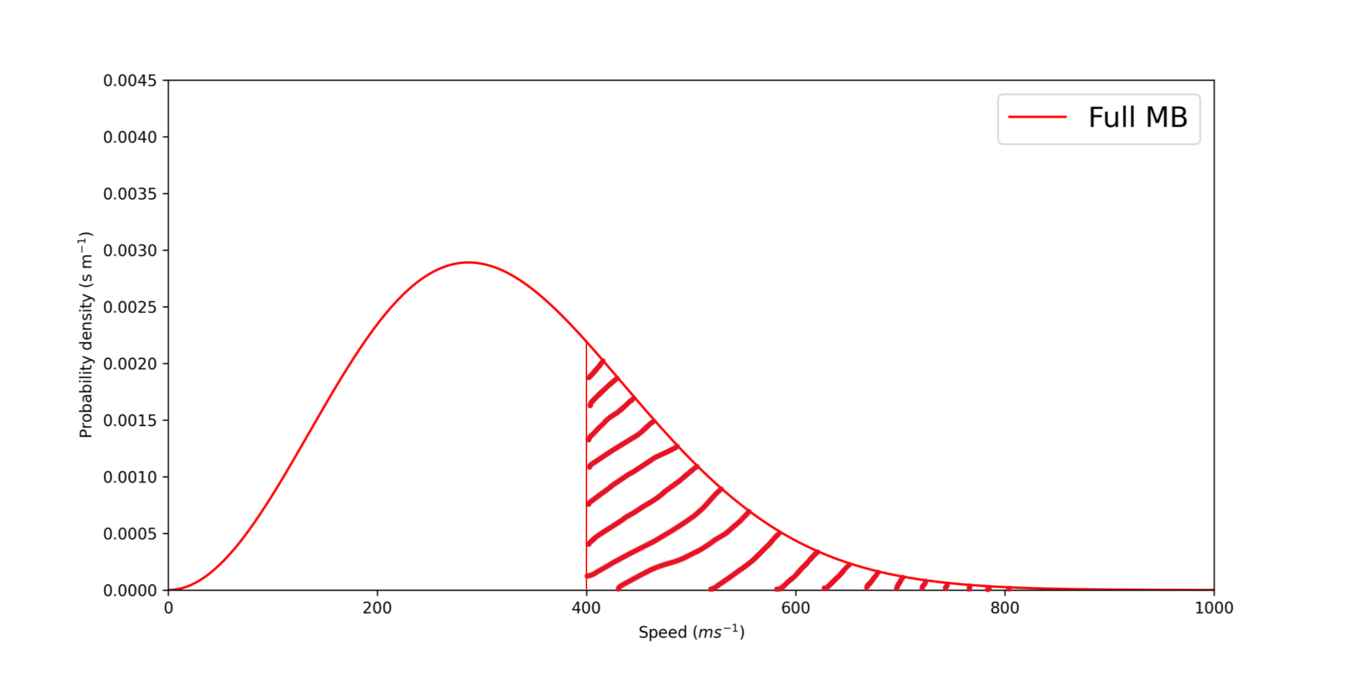
$$k_B \times N_A = R$$

(mass per mole, M) $$Pr(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-\left(\frac{M(v^2)}{2RT}\right)}$$

Using the Maxwell-Boltzmann distribution

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

What is the probability of finding a particle with a speed greater than 400 ms^{-1} ($Pr(v < 400\ m/s)$)?



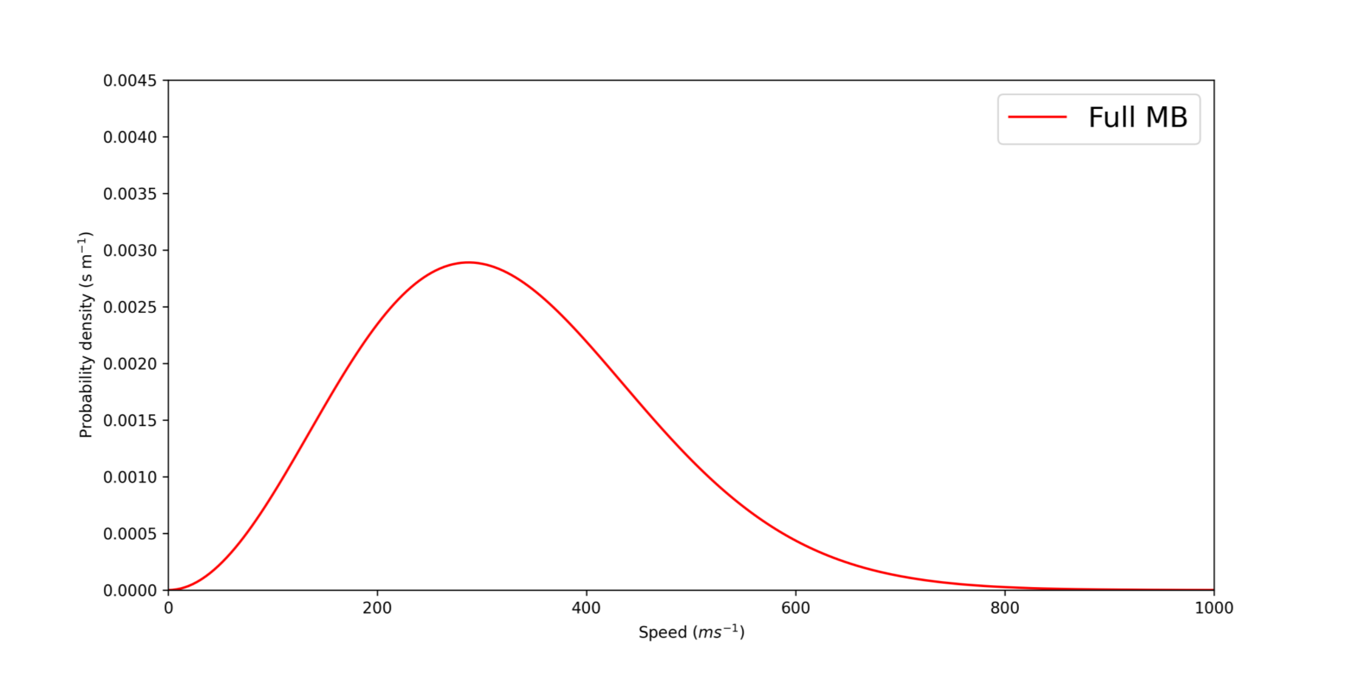
$$Pr(v < 400\ m/s) = \int_{v_0}^{\infty} Pr(v)\,\mathrm{d}v$$

Using the Maxwell-Boltzmann distribution

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

What is the probability of finding a particle a speed of the speed of light?

$$Pr(v = 3 \times 10^8\ m/s)$$



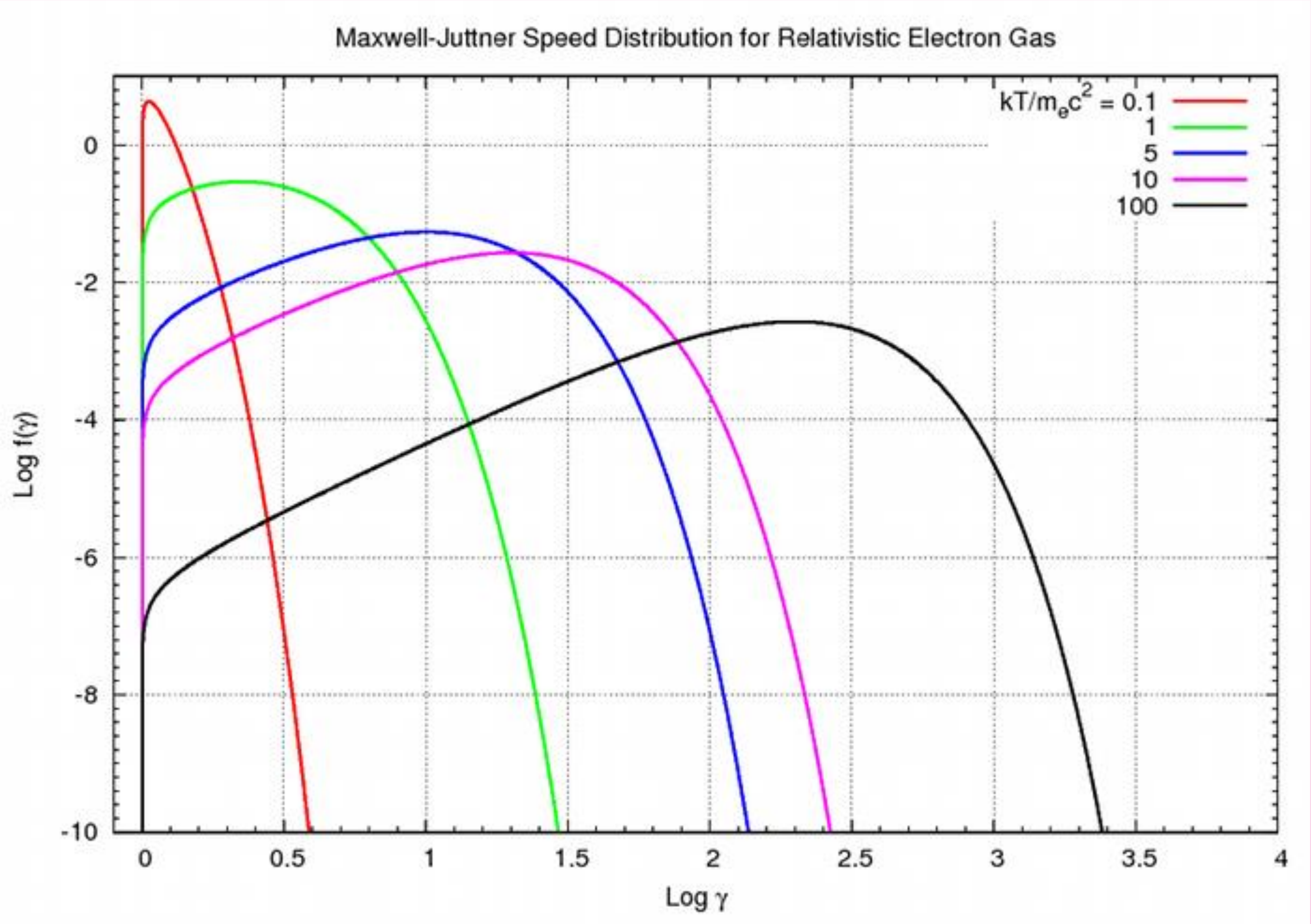
… non-zero (big yikes)

Maxwell-Jüttner distribution (just for interest)

For particles in an ideal gas in which the thermal energy $k_B T$ is comparable to (or larger than) its mass (in units of energy)

Distribution is given in terms of $\gamma = \frac{1}{\sqrt{1 - v^2/c^2}}$

rather than just v



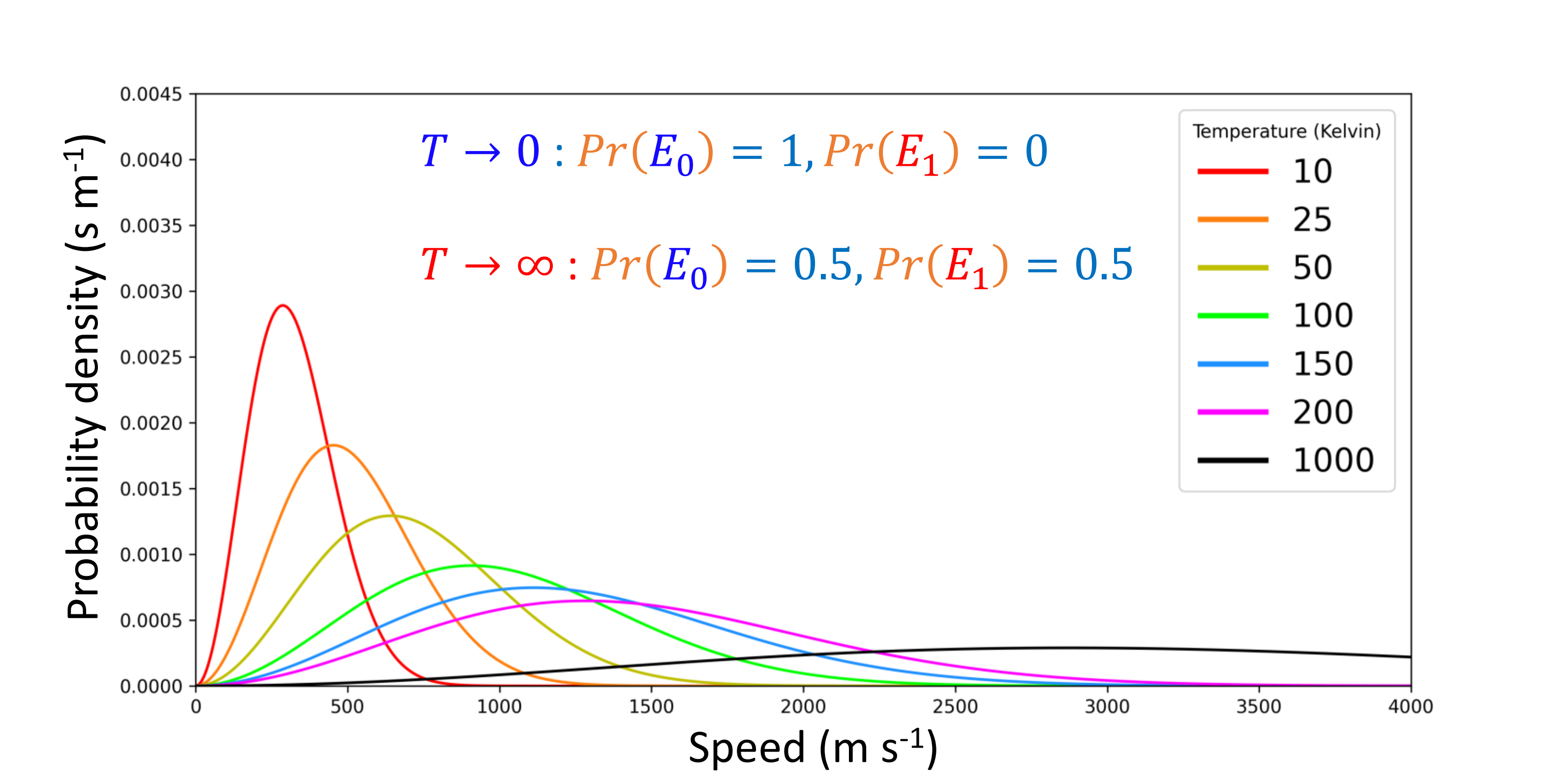
https://en.wikipedia.org/wiki/Maxwell%E2%80%93J%C3%BCttner_distribution

Maxwell-Boltzmann distribution for fixed temp

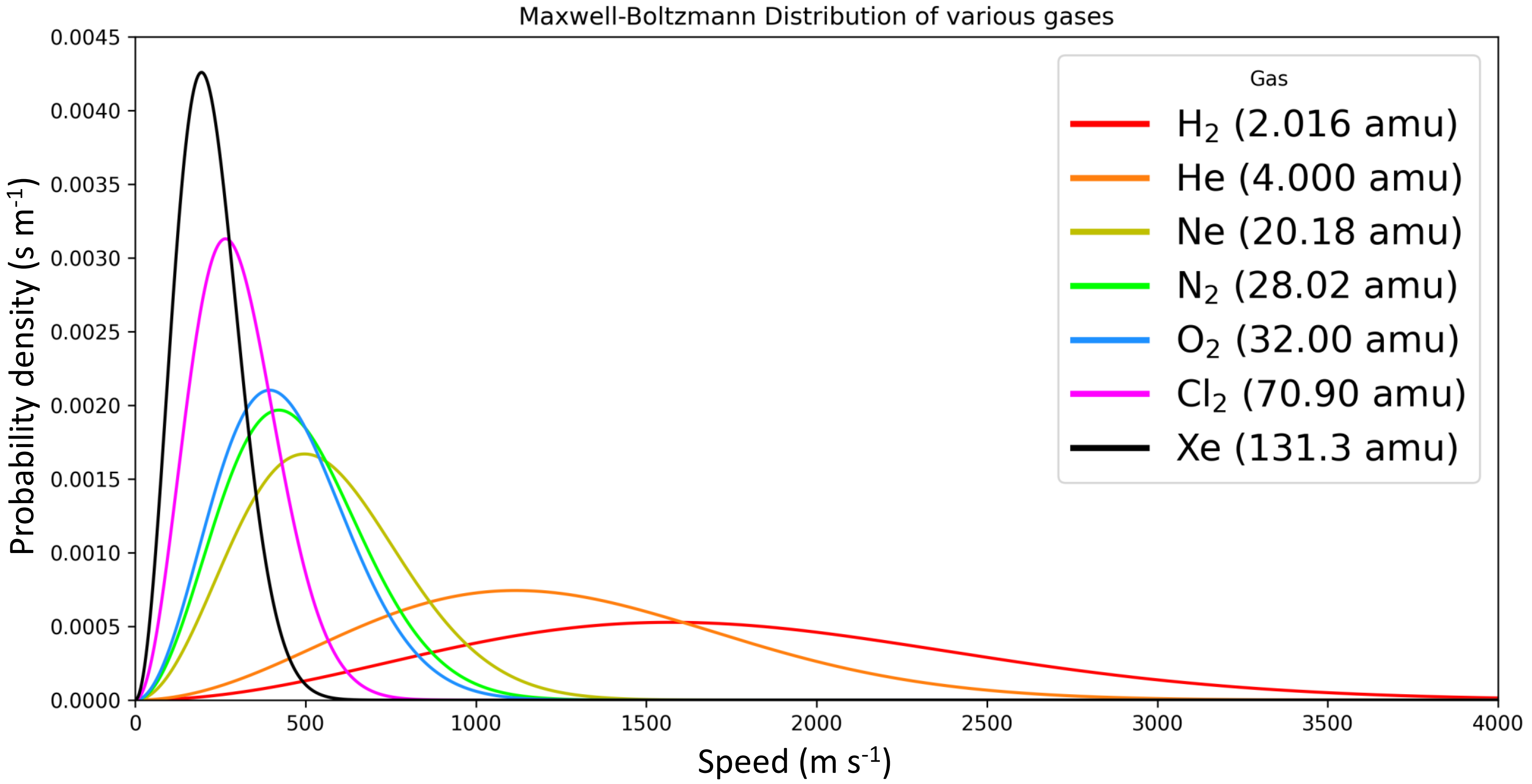
As temperature, T, increases, distribution shifts to the right and “peak” decreases in height…

Probability of populating a high v state in some way increases with increasing T

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



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

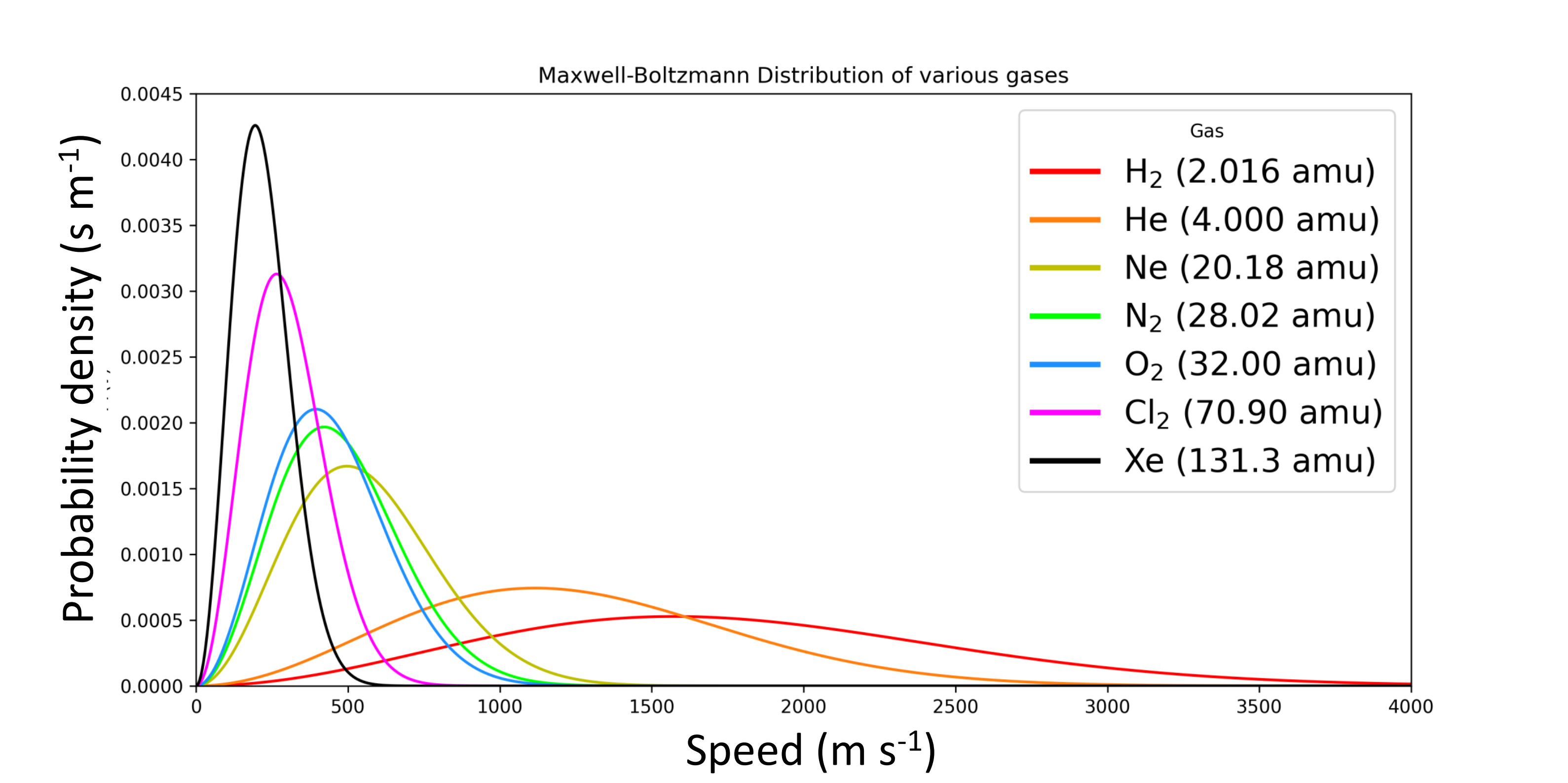


Maxwell-Boltzmann distribution for fixed mass

As mass, m, increases, distribution shifts to the left and "peak" increases in height…

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

Probability of populating a high v state in some way decreases with increasing m



As $v \rightarrow 0$, $v^2 \rightarrow 0$, $e^{-\left(\frac{m(v^2)}{2k_B T}\right)} \rightarrow \infty$

As $v \rightarrow \infty$, $v^2 \rightarrow \infty$, $e^{-\left(\frac{m(v^2)}{2k_B T}\right)} \rightarrow 0$

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

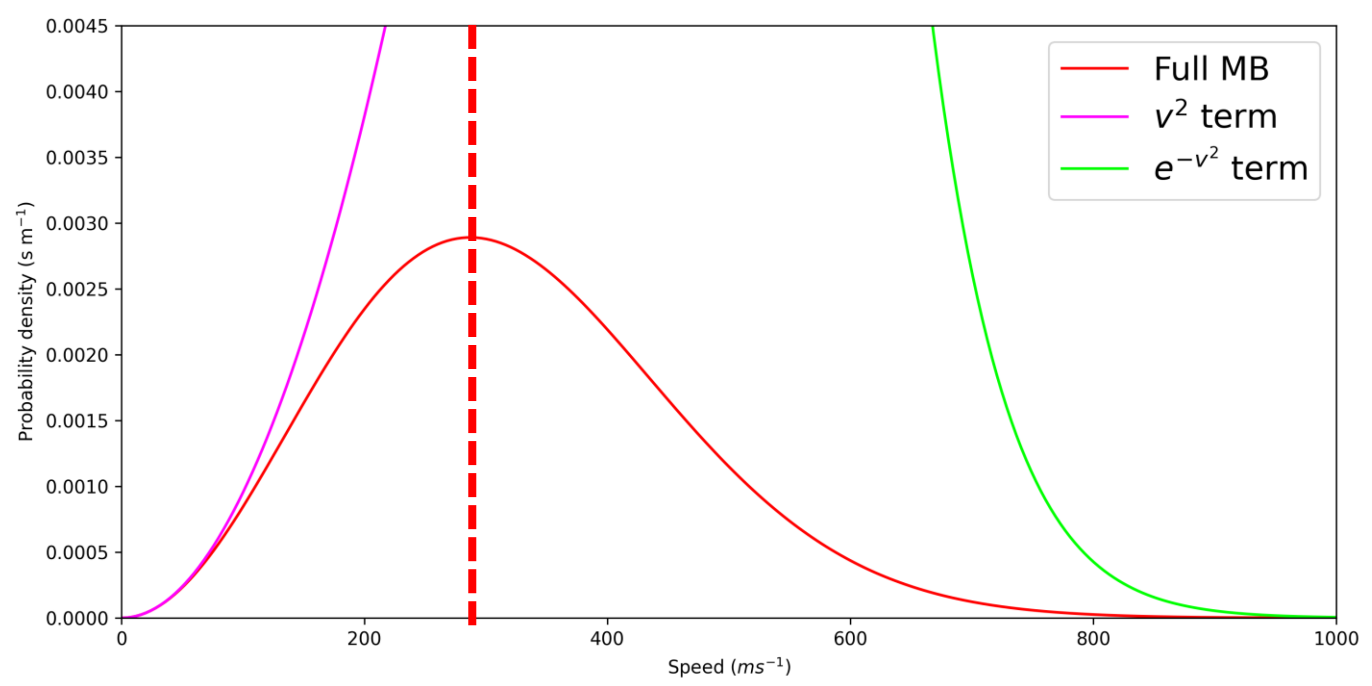
Shape of distribution depends on $\frac{m}{T}$ ratio

Hence, as $Pr(v)$ is given by the product of these two terms:

$Pr(0) \rightarrow 0$

$Pr(\infty) \rightarrow 0$

Results in a peak of most likely probability

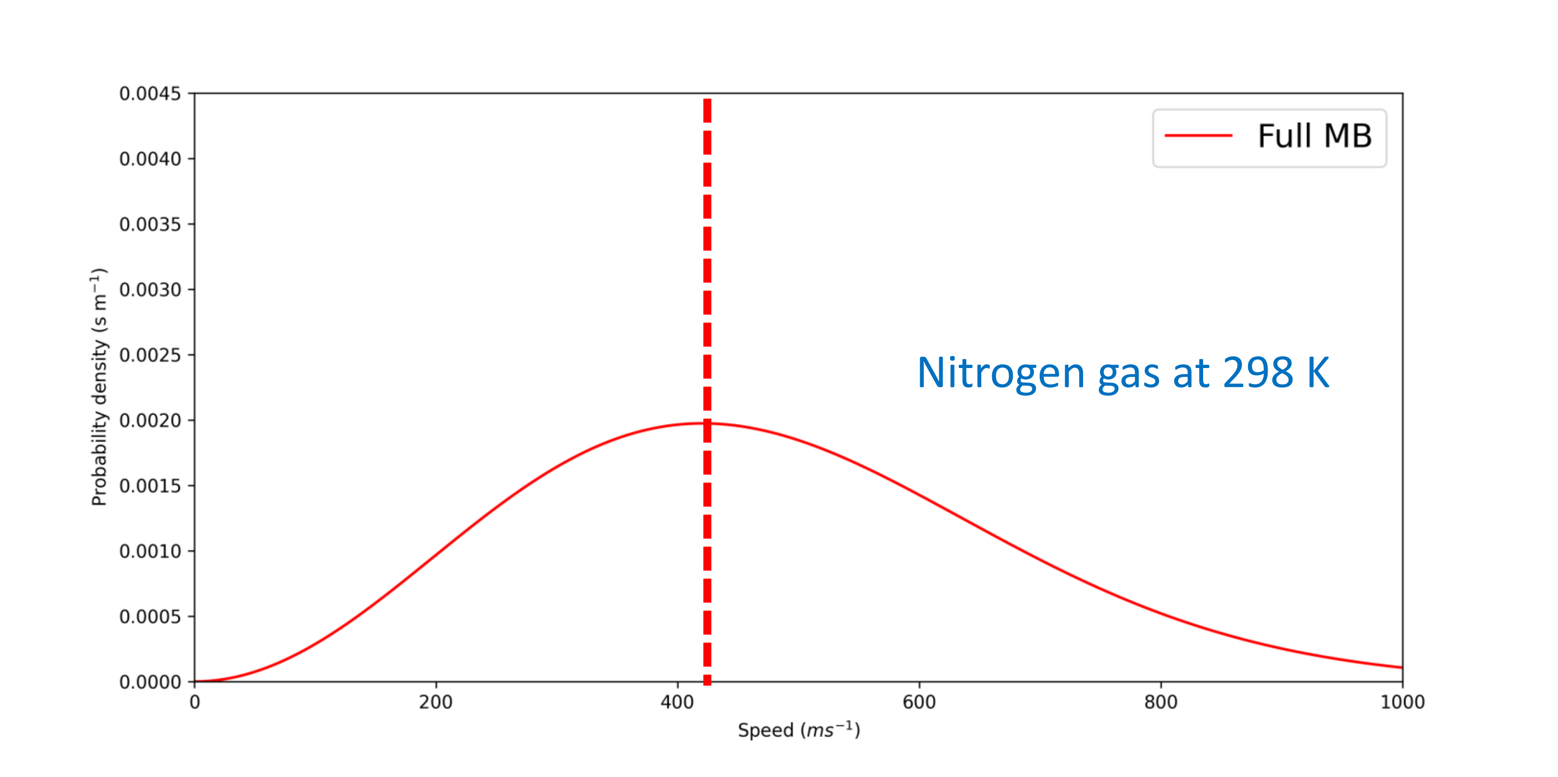


Finding the peak

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

How do we go about finding the most probable speed in the MB distribution?

$$\frac{\mathrm{d}Pr(v)}{\mathrm{d}v} = 0$$



Most probable speed:

$$v_m = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 298}{1.66 \times 10^{-27} \times 28.02}} = 421\ \mathrm{ms^{-1}}$$

Notation for averages

Average value of x can be written as

$$\langle x \rangle, \qquad \bar{x}, \qquad E\{x\}$$

$$\langle x \rangle = \frac{1}{N}\sum_i^N N_i x_i = \sum_i^N Pr_i(x_i)x_i$$

If we have infinite bins, so the width of each bin → 0…

$$\langle f(x) \rangle = \int_0^\infty Pr(x) f(x)\, \mathrm{d}x$$

General form for a distribution $f(x)$

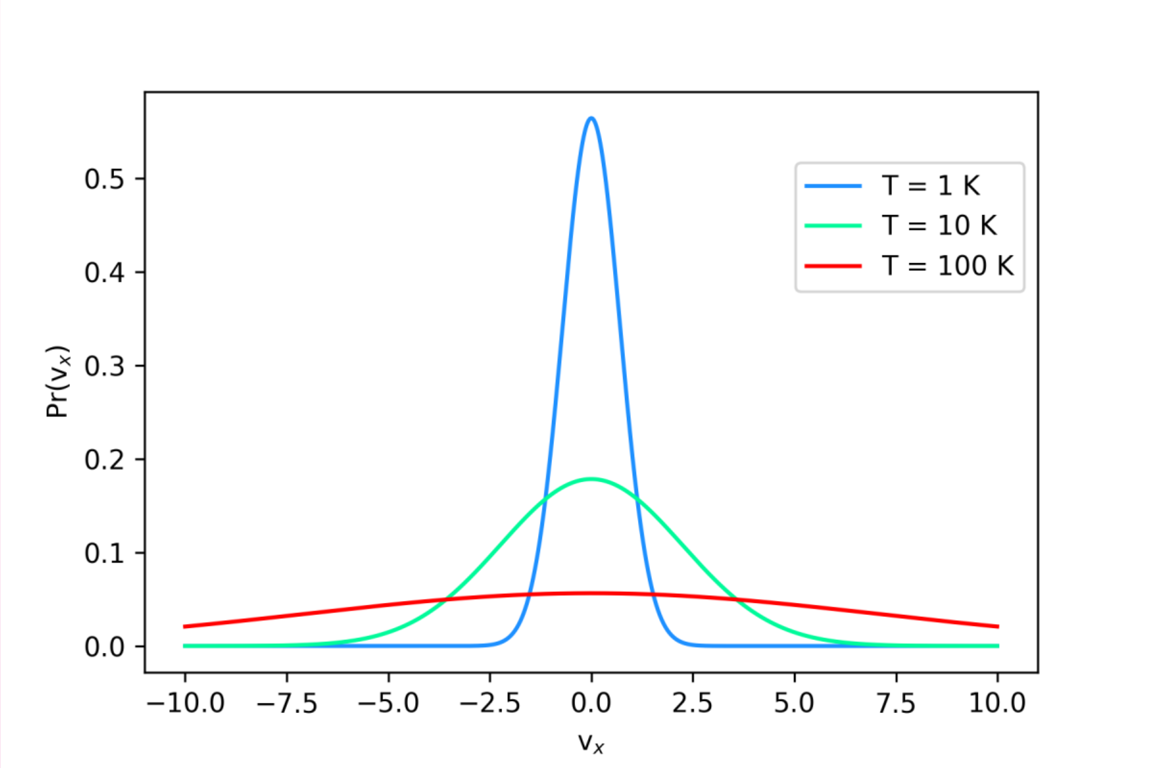
Average velocity of the distribution

Velocity of our particles can vary between $-\infty$ and ∞:

Velocity should be symmetric about 0, so we expect average velocity to be 0

Can also justify via

$$\langle \vec{v}_x \rangle = \int_{-\infty}^{\infty} \overrightarrow{v_x} Pr(v_x)\, \mathrm{d}\overrightarrow{v_x} = 0$$



Odd functions (odd x even = odd) between symmetric limits always equal 0

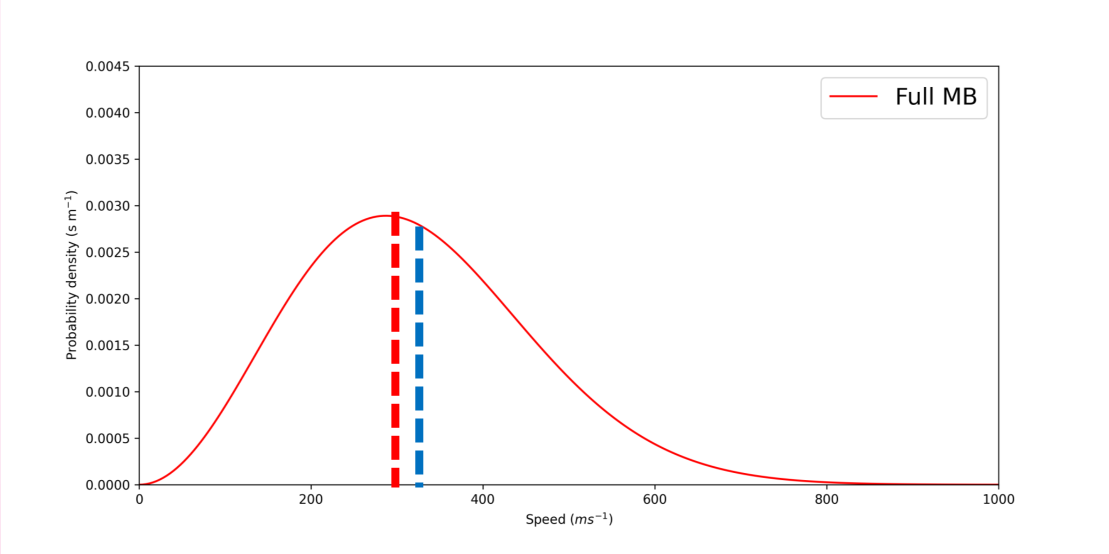
Average speed of the distribution

As the MB distribution is asymmetric, average speed is not equal to most probable speed

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

$$\langle\vec{v}\rangle = \int_0^\infty \vec{v}Pr(\vec{v})\,\mathrm{d}\vec{v}$$

$$\langle\vec{v}\rangle = \sqrt{\frac{8k_BT}{\pi m}} = \frac{2}{\sqrt{\pi}}\sqrt{\frac{2k_BT}{m}} = \frac{2}{\sqrt{\pi}}v_m$$



Average KE of the distribution

$\langle KE\rangle = \frac{1}{2}mv^2$ so we expect that $\langle KE\rangle = \frac{1}{2}m\langle v^2\rangle$

$$\langle f(x)\rangle = \int_0^\infty Pr(x)f(x)\,\mathrm{d}x \qquad \langle v^2\rangle = \int_0^\infty Pr(v)v^2\,\mathrm{d}v$$

We can use Feynman's trick, $\int_0^\infty \mathrm{e}^{-\alpha x^2}x^{2\mathrm{n}}\,\mathrm{d}x = \frac{1}{2}\left(-\frac{\partial}{\partial\alpha}\right)^n\sqrt{\frac{\pi}{\alpha}}$

To show $\langle KE\rangle = \frac{3}{2}k_BT$ and $\langle v^2\rangle = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3}{2}}v_m$

Summary

$$v_m = \sqrt{\frac{2k_BT}{m}}$$

$$\langle \vec{v} \rangle = \sqrt{\frac{8k_BT}{\pi m}} = \frac{2}{\sqrt{\pi}} v_m$$

$$\langle v^2 \rangle = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3}{2}} v_m$$