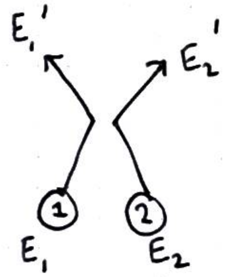
Maxwell Boltzman Distribution

With molecules moving randomly in a system in thermal equilibrium, it would be futile to try and measure the exact velocity of a molecule at a given time. A more appropriate question is what is the probability that a molecule is in a given state - i.e that it has a particular velocity or, more generally, a given energy?

To solve this, consider two particles with energies E_1 and E_2 colliding in <u>thermal equilibrium</u>.



After collision, they have energies E_1' and E_2'

Since energy is conserved, we can say:

$$E_1 + E_2 = E_1' + E_2'$$

Now for the statistics!

The probability of one particle having energy E_1 <u>and</u> the other having energy E_2 is $P(E_1)P(E_2)$ where $P(E)$ is the probability of a particle having energy E. Equally, after the collision, the probability of the two particles having those energies is $P(E_1')P(E_2')$.

The key argument here is called detailed balance:

$$P(E_1)P(E_2) = P(E_1')P(E_2')$$

This is because the probalities of particles having the energy after must be the same as the energy before, otherwise the particles in the gas would have a "preference" as to their energy and all the particles in the gas would speed up or slow down which isn't possible in thermal equilibrium!

Taking logs both sides:

$$\ln(P(E_1)P(E_2)) = \ln(P(E_1')P(E_2'))$$

$$\ln(P(E_1)) + \ln(P(E_2)) = \ln(P(E_1')) + \ln(P(E_2'))$$

This equation has only one solution in the form:

$$\ln(P(E)) = \alpha - \beta E \Rightarrow P(E) = Ae^{-\beta E}$$

If we use the kinetic energy for E: $E = \frac{1}{2} m v_x^2$

P(E) becomes the probability function for v_x:

$$P(E) \rightarrow \underbrace{\rho(v_x) = Ae^{-\frac{\beta m}{2} v_x^2}}_{}$$

This is in the form of a normal distribution!

A note on the normal distribution

Normal distributions have the form:

$$\rho_N(x) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-\frac{x^2}{2\sigma^2}}$$

$\langle x \rangle$ is always 0 since the function is symmetric about 0

$\langle x^2 \rangle = \sigma^2$ $\quad \sigma$ is often called the standard deviation and σ^2 is the variance.

The full width at half-maximum is found to be:

$\sqrt{8\ln 2}\,\sigma \approx 2.35\sigma$

Back to the topic

So the solution to the equation:

$$\rho(v_x) = Ae^{-\frac{\beta m}{2} v_x^2}$$

Comparing this with the general normal distribution, we can obtain some values for the unknown parameters.

$$\rho(v_x) = Ae^{-\frac{\beta M}{2} v_x^2}$$ Solution to Equation

$$\rho_N(x) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-\frac{1}{2\sigma^2} x^2}$$ General Normal Distribution Function

$$\therefore \quad \frac{1}{2\sigma^2} = \frac{\beta M}{2} \Rightarrow \langle v_x^2 \rangle = \sigma^2 = \frac{1}{\beta M}$$

but we know $\frac{1}{2} M \langle v^2 \rangle = \frac{3}{2} k_B T \Rightarrow 3\left(\frac{1}{2} M \langle v_x^2 \rangle\right) = \frac{3}{2} k_B T$

$\frac{1}{2} M \langle v_x^2 \rangle = \frac{1}{2} k_B T$ so : $\langle v_x^2 \rangle = \frac{k_B T}{M}$ subbing this into equation for variance

so: $\frac{k_B T}{M} = \frac{1}{\beta M}$ $\quad \underline{\underline{\beta = \frac{1}{k_B T}}}$

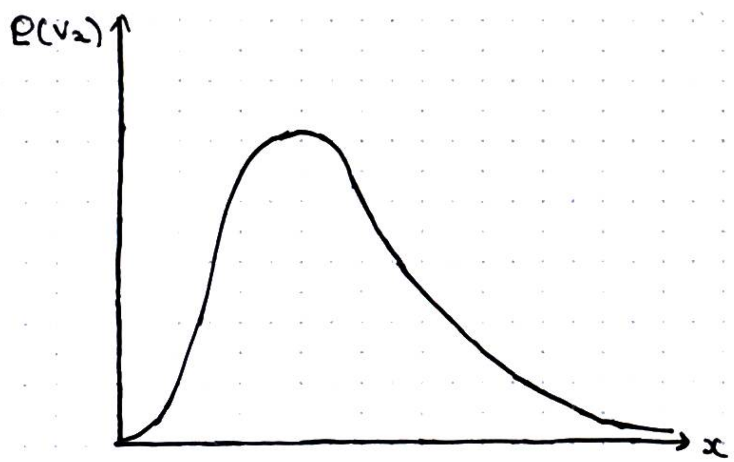
$$A = \frac{1}{\sqrt{2\pi}\,\sigma} = \frac{\sqrt{\beta M}}{\sqrt{2\pi}} = \sqrt{\frac{M}{2\pi k_B T}}$$

This gives the final solution to be:

$$\boxed{\rho(v_x) = \sqrt{\frac{M}{2\pi k_B T}}\, e^{-\frac{M v_x^2}{2 k_B T}}}$$

This is the distribution of velocities a gas in thermal equilibrium must have.

This result is called the Maxwell-Boltzmann Distribution and looks like:



Mean Energy

To compute the mean energy, $\langle E \rangle$:

$$\langle E \rangle = \langle \tfrac{1}{2} m v^2 \rangle = \tfrac{1}{2} m \langle v^2 \rangle$$ as we've seen before

$$= \tfrac{1}{2} m \int v^2 \rho(\underline{v})\, dv_x\, dv_y\, dv_z$$

Using the proper change of variables, we find

$$\langle E \rangle = \tfrac{3}{2} k_B T$$

$$\therefore \underline{\underline{U = \tfrac{3}{2} k_B T}}$$