Deriving the Maxwell-Boltzmann distribution

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Maxwell's symmetry argument

We wish to derive the fraction of particles in an ideal gas with speed between v and $v + \mathrm{d}v$.

Let v_x, v_y and v_z be the components of the velocity of each particle in three perpendicular directions. If $\rho(v_x)$ is the probability density function of v_x, then the fraction of particles for which this velocity lies between v_x and $v_x + \mathrm{d}v_x$ is $\rho(v_x)\,\mathrm{d}v_x$. The x-direction is special in no way and therefore the same function applies to v_y and v_z also.

These three velocities must not affect each other in any way because they are at right angles and statistically independent, and so the fraction of particles with velocities between v_x and $v_x+\mathrm{d}v_x$, and between v_y and $v_y + \mathrm{d}v_y$, and between v_z and $v_z + \mathrm{d}v_z$, is $\rho(v_x)\,\mathrm{d}v_x\rho(v_y)\,\mathrm{d}v_y\rho(v_z)\,\mathrm{d}v_z = \rho(v_x)\rho(v_y)\rho(v_z)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$.

However, the choice of direction of the axes we're using is purely arbitrary, and so this fraction must depend only on the speed of the particle $v^2 = v_x^2 + v_y^2 + v_z^2$. Therefore,

$$\rho(v_x)\rho(v_y)\rho(v_z)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z = \phi(v_x^2 + v_y^2 + v_z^2)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$$

for some function ϕ.

We note that a product appears on the left and a sum on the right; thus, the solution to this *must* be an exponential. We let $\rho(x) = A\mathrm{e}^{-Bx^2}$ for some positive constants A and B so that $\phi(v^2) = A^3\mathrm{e}^{-Bv^2}$. We add the negative sign to B since the number of particles with velocities of increasing size must decrease.

So, the fraction of particles with velocity vector in the 'box' of volume $\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$ with its innermost vertex a distance v from the origin is $A^3\mathrm{e}^{-Bv^2}\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$. A particle with speed between v and $v + \mathrm{d}v$ will have its velocity vector in the space occupied by the sphere of radius $v + \mathrm{d}v$ with its centre at the origin, and *not* by the similar sphere of radius v. The volume of this space, due to the smallness of $\mathrm{d}v$, is $4\pi v^2\,\mathrm{d}v$ and so, replacing $\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$, the fraction of particles with speed between v and $v+\mathrm{d}v$ is $4\pi A^3v^2\mathrm{e}^{-Bv^2}\,\mathrm{d}v$. If the probability density function for particle speed is $f(v)$ then it follows that

$$f(v) = 4\pi A^3v^2\mathrm{e}^{-Bv^2}.$$

As this must be normalised,

$$4\pi A^3\int_0^\infty v^2\mathrm{e}^{-Bv^2}\,\mathrm{d}v = 1$$

which implies that since $\int_0^\infty x^2 e^{-x^2}\,\mathrm{d}x = \frac{\sqrt{\pi}}{4}$,

$$\begin{aligned} 4\pi A^3 \frac{\sqrt{\pi}}{4B^{3/2}} &= 1 \\ \implies A &= \sqrt{\frac{B}{\pi}} \end{aligned}$$

and thus $f(v) = 4\pi \left(\frac{B}{\pi}\right)^{3/2} v^2 \mathrm{e}^{-Bv^2}$.

The mean square speed is given by

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v)\,\mathrm{d}v = 4\pi \left(\frac{B}{\pi}\right)^{3/2} \int_0^\infty v^4 \mathrm{e}^{-Bv^2}\,\mathrm{d}v$$

and so as $\int_0^\infty x^4 \mathrm{e}^{-x^2}\,\mathrm{d}x = \frac{3\sqrt{\pi}}{8}$, we come to $\langle v^2 \rangle = 4\pi \left(\frac{B}{\pi}\right)^{3/2} \frac{3\sqrt{\pi}}{8B^{5/2}} = \frac{3}{2B}$.

However, from kinetic theory we know that

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

where m is the mass of each particle, T is the thermodynamic temperature of the gas and k_B is Boltzmann's constant. Therefore,

$$\begin{aligned} \frac{1}{2} m \frac{3}{2B} &= \frac{3}{2} k_B T \\ \implies B &= \frac{m}{2k_B T}. \end{aligned}$$

This leads us to our final expression for the Maxwell-Boltzmann distribution,

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