Maxwell's Distribution

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1 Derivation

Let's first start with an isotropic gas. We are going to try to find the velocity distribution of particles in this gas. If we know that all three directions x, y, z will have velocities independent of each other then the probability of finding a velocity in a certain state is the product of the probabilities of finding a velocity in a certain state in each direction. Mathematically this becomes:

$$f(\vec{v})dv_x dv_y dv_z = \phi(v_x)dv_x \phi(v_y)dv_y \phi(v_z)dv_z$$

$$f(\vec{v}) = \phi(v_x)\phi(v_y)\phi(v_z)$$

We note that it is the same ϕ for x, y, z because there is no reason one direction should have a different distribution then another. Because of our isotropy the probability that we have a certain velocity magnitude shouldn't depend on direction so we can reframe our probability to the probability that we have a certain energy. This will give us:

$$\bar{f}(E)dv_x dv_y dv_z = dv_x dv_y dv_z$$

$$\phi(v_x)\phi(v_y)\phi(v_z) = \bar{\phi}(E_x)\bar{\phi}(E_y)\bar{\phi}(E_z)$$

Where our new bar functions are different from the old but they provide the same probability, you just have to give them energy. Now we shall consider all particles in the gas with the same z energy E_z and the same energy E. This lets us use conservation of energy to say that:

$$E_x + E_y = C$$

Because we have picked up one energy we know that $\bar{f}(E)$ has some constant value, we also know that picking our a specific E_z lets us discard our z probability. All of this lets us say that:

$$\bar{\phi}(E_x)\bar{\phi}(E_y) = const.$$

If we differentiate with respect to E_x we get:

$$\frac{d\bar{\phi}(E_x)}{dE_x}\bar{\phi}(E_y) + \bar{\phi}(E_x)\frac{d\bar{\phi}(E_y)}{dE_x} = 0$$

We can use $E_x + E_y = C$ and consider the differential which gives us the relationship:

$$dE_x + dE_y = 0$$

$$dE_x = -dE_y$$

If we plug into our equation we have:

$$\frac{d\bar{\phi}(E_x)}{dE_x}\bar{\phi}(E_y) - \bar{\phi}(E_x)\frac{d\bar{\phi}(E_y)}{dE_y} = 0$$

Let us now divide by our two phi functions to get:

$$\frac{\frac{d\bar{\phi}(E_x)}{dE_x}}{\bar{\phi}(E_x)} - \frac{\frac{d\bar{\phi}(E_y)}{dE_y}}{\bar{\phi}(E_y)} = 0$$

This is a classic separation of variables situation. We first note that our two equations are independent so they must both be equal to constants for this to be true. And for our specific case this must actually be the same constant so we can say that:

$$\frac{\frac{d\bar{\phi}(E_x)}{dE_x}}{\bar{\phi}(E_x)} = \frac{\frac{d\bar{\phi}(E_y)}{dE_y}}{\bar{\phi}(E_y)} = -\alpha$$

For some constant α. If we solve this equation for either variable we get that:

$$\bar{\phi}(E_x) = Ae^{-\alpha E_x}$$

We note that we just found a universal distribution because we while we fixed E and E_z we did it for arbitrary values of those two values so our solution is still universal. Now we can turn this into a probability distribution in terms of velocity by just substituting in kinetic energy:

$$\phi(v_x) = Ae^{-\frac{\alpha m v_x^2}{2}}$$

Now we apply our normalization condition to find A and we will apply our knowledge of the average velocity to find α. We know two facts:

$$\int_{-\infty}^{\infty} \phi(v_x)dx = 1$$

$$\int_{-\infty}^{\infty} v_x^2\phi(v_x)dx = \langle v_x^2 \rangle = \frac{k_B T}{m}$$

Plugging in we get the two integrals:

$$\int_{-\infty}^{\infty} Ae^{-\frac{\alpha m v_x^2}{2}}dx = 1$$

$$\int_{-\infty}^{\infty} v_x^2 Ae^{-\frac{\alpha m v_x^2}{2}}dx = \frac{k_B T}{m}$$

For both of these integrals we make the u-substitution:

$$u = \sqrt{\frac{\alpha m}{2}} v_x$$

$$du = \sqrt{\frac{\alpha m}{2}}$$

This turns our integrals into:

$$\sqrt{\frac{2}{\alpha m}} A \int_{-\infty}^{\infty} e^{-u^2} du = 1$$

$$A \left(\frac{2}{\alpha m} \right)^{3/2} \int_{-\infty}^{\infty} u^2 e^{-u^2} du = \frac{k_B T}{m}$$

Doing our first integral we get the equation:

$$A \sqrt{\frac{2\pi}{\alpha m}} = 1$$

$$A = \sqrt{\frac{\alpha m}{2\pi}}$$

If we plug into our second integral we get

$$\left(\frac{2}{\alpha m \sqrt{\pi}} \right) \frac{\sqrt{\pi}}{2} = \frac{k_B T}{m}$$

$$\frac{1}{\alpha m} = \frac{k_B T}{m}$$

$$\alpha = \frac{1}{k_B T}$$

This gives the final expression of:

$$\phi(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m v_x^2}{2 k_B T}}$$

If we multiply the distributions for x, y, z we get the total velocity distribution of:

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

We first note that this is not a distribution of speed (as can evidently be seen in the fact that it is symmetric about 0). But we can actually get a distribution of speed. To do this we relate the probability that a particle has a certain velocity to the probability a particle has a certain speed. To do this we consider the x, y, z phase space for velocity. We note that to the probability that you have a certain speed for a given shell in this space is constant. So we now consider an arbitrary spherical shell of infinitesimal thickness which will have volume:

$$4\pi v^2 dv$$

The integral of this multiplied by our probability over any velocity magnitude range should give the probability that you have a speed in that velocity range. Thus we can say that if we have our speed function $F(v)$:

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

This means that our speed function is:

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

This is the Maxwell-Boltzmann distribution for the speed of a particle and it is one of the landmark results in statistical physics.

2 A Note on the Gaussian

Let's talk about those integrals we solved earlier. We made the u-substitution to obtain a common form which we already knew, let's talk about how you derive that form. We start first with the classic Gaussian:

$$I_o = \int_{-\infty}^{\infty} e^{-x^2} dx$$

We can multiply this by another integral of the same type but just let x become y arbitrarily to get:

$$I_o^2 = \int_{-\infty}^{\infty} \int_{\infty}^{-\infty} e^{-(x^2+y^2)} dx dy$$

If we switch to cylindrical coordinates then we get:

$$I_o^2 = \int_0^{\infty} \int_0^{2\pi} e^{-r^2} r d\theta dr$$

We can then do a u-substitution letting $u = r^2$ to get:

$$I_o^2 = \pi \int_0^{\infty} e^{-u} du$$

$$I_o^2 = -\pi e^{-u} \Big|_{u=0}^{u=\infty}$$

$$I_o^2 = \pi$$

$$I_o = \sqrt{\pi}$$

We have now obtained a solution for the first Gaussian integral. Now consider integrals more generally of the form:

$$I_n = \int_{-\infty}^{\infty} x^n e^{-\lambda x^2} dx$$

Now consider taking the derivative of this with respect to λ:

$$\frac{dI_n}{d\lambda} = \frac{d}{d\lambda} \int_{-\infty}^{\infty} x^n e^{-\lambda x^2} dx$$

$$\frac{dI_n}{d\lambda} = -\int_{-\infty}^{\infty} x^{n+2} e^{-\lambda x^2} dx$$

We can recognize the form on the right side and say that:

$$\frac{dI_n}{d\lambda} = -I_{n+2}$$

Now this lets us get I_2 in terms of I_0 which we know, but we don't have a λ in our expression. Well if we recognize that the λ will stay up until we do the final integral, at that point we will get:

$$I_o^2 = \frac{\pi}{\lambda}$$

$$I_o = \sqrt{\frac{\pi}{\lambda}}$$

If we take the λ derivative of this and then plug in $\lambda = 1$ we get:

$$I_{n+2} = \frac{\sqrt{\pi}}{2}$$