10.2: The Boltzmann Distribution

Nature has a formula for the probability density of energy, which represents how nature doles out energy to molecules. Unfortunately, the derivation is difficult, so we will instead just discuss the logic of the Boltzmann Distribution . Let's think back to the flip of a coin, where we ask about the occurrence we are investigating divided by all possible results. When applied to energy we might believe that the probability of having energy E_i is: $\frac{E_i}{\sum_i E_i}$. While sensible, this actually doesn't work because this expression would not conserve mass and energy. Instead, Boltzmann figured out that nature uses a similar expression but with exponentials: \(\frac{e^

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{\sum_i{}e^{-E_i}}\). However, there is one last problem which is that the argument of an exponential cannot have units. The answer is to divide E_i by k_BT, which gives us the proper expression for Boltzmann's formula:

\[P_{dens}\left(E_i\right)=\frac{e^{\frac

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}{\sum_i{}e^{\frac{-E_i}{k_BT}}} \nonumber \]

Recall that the Boltzmann constant k_B is simply the S.I. gas constant R = 8.314 J/K/mol divided by Avogadro's number: $k_B = \frac{R}{N_A} = 1.38 \times 10^{-23}\ J/K$. It's like the gas constant for a single molecule.

Now this expression is like a gas engine- powerful, but towards what purpose do we apply it? For our purposes here we will apply it towards calculating the velocities of gas molecules. In the process we will be able to demonstrate some interesting facts about gases, as well as derive the Equipartition Theorem all the way back from Chapter 2. Regardless, as it applies to velocity we will use kinetic energy, i.e. $E_i = \frac{1}{2}mv^2$. Therefore:

$$P_{dens}\left(v\right) = \frac{e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}}{\sum e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}}$$

A clever thing about the above is that we transformed the probability density for energy into the same for velocity simply by inserting the correct expression for energy as a function of velocity.

In the present form the probability density is too difficult to do anything with, so we will simplify it piece-by-piece. We will start with the denominator, which is the part of the expression that normalizes the probability density. First, we have to apply the fact that the Universe is three-dimensional which means $v^2 = v_x^2 + v_y^2 + v_z^2$. The identity $e^{a+b+c} = e^a \cdot e^b \cdot e^c$ helps us show that:

$$\sum e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} = \sum_{v_x=-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}} \cdot \sum_{v_y=-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}} \cdot \sum_{v_z=-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}$$

The summation is performed over negative to positive velocities, which is because gas molecules can move either forward (positive velocity) or backward (negative velocity). This is different that the net velocity: $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, which cannot be negative. But what's with the sum in the denominator? How do you sum over a variable like velocity that is continuous? The answer is you can't, so we have to replace the summation with an integral. This can be done with an identity called a Riemann sum: $\sum_1^n f\left(x\right) cdot \left(\frac{b-a}{n}\right) = \int_a^b f\left(x\right)\cdot\partial x$. Based on this identity it's important that we have a factor like $\left(\frac{b-a}{n}\right)$ in our sum, which is the origin for ∂x for the integral. When we examine a denominator term such as: $\sum_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}$, it appears there is no such factor. And as usual, there is a clever answer, which is to multiply and divide the denominator by ∂v_x (and ∂v_y and ∂v_z) which then allows us to transform the triple sum into a triple integral (bold for emphasis):

$$\frac{e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}}{\sum_{v_x=-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\sum_{v_y=-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\sum_{v_z=-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}} = \frac{e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\partial v_y\cdot\partial v_z}{\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\partial v_y\cdot\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}\cdot\partial v_z}$$

First we will solve the denominator:

$$\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\partial v_y\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}\cdot\partial v_z\right)$$

While this looks absolutely horrible, in reality there is just one calculus expression because there is no reason why the integral along x will be different that y or z. As a result, we can just solve $\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x$ and then cube the result. We can look up a standard Gaussian-type integral:

$$int_{-\infty}^{\infty} e^{-a\cdot x^2}\cdot\partial x = \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

To apply it to our expression we see: $a = \frac{m}{2\cdot k_B\cdot T}$, which makes the solution to the v_x integral:

$$\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x = \left(\frac{\pi}{\frac{m}{2\cdot k_B\cdot T}}\right)^{\frac{1}{2}} = \left(\frac{2\pi\cdot k_B\cdot T}{m}\right)^{\frac{1}{2}}$$

And the triple integral can be evaluated: $\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\partial v_y\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}\cdot\partial v_z\right) = \left(\frac{2\pi\cdot k_B\cdot T}{m}\right)^{\frac{3}{2}}$

This leaves the Boltzmann probability density in the form:

$$\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\partial v_y\cdot\partial v_z$$

There is one last problem- the argument of the exponential has net velocity squared (v^2) but the partials are directional vectors. Can we just substitute ∂v for $\partial v_x\cdot\partial v_y\cdot\partial v_z$ and hope that is ok? The answer is **no**.

10.1.1 Transformation of Variables. How do we legitimately make the substitution: $\partial v_x\cdot\partial v_y\cdot\partial v_z\rightarrow\partial v$? The first thing to note is that since we start with an expression with a set of three partials, each in an orthogonal dimension (x, y and z), then we must transform into another set of three orthogonal partials. This is a stipulation in information science- you can't just substitute something in 3D ($\partial v_x\cdot\partial v_y\cdot\partial v_z$) for 1D (∂v). If you do so information is lost and any subsequent analyses will be wrong. A simple answer is that we can transform the standard Cartesian velocity coordinates v_x, v_y, and v_z into spherical coordinates v, ϕ, and θ, where the net velocity is just like the radius of a sphere. Such a transformation also replaces the partials. Next, we can integrate ϕ and θ out of existence leaving the probability density with only the partial of net velocity ∂v left. This uses the mathematics of "Jacobians", and is shown for you in the Appendix.

Rather than take a brute force mathematical derivation, here we demonstrate a visual approach to the transformation of Cartesian to spherical coordinates as it applies to partials. First, let's look more closely at integrals and discuss the job of a partial. As shown in Figure 10.3A, a partial moves along the independent (x) direction from the lower limit to upper limit. As it does so, an area is created from the product of the partial's length and the function's height: $f(x)\cdot\partial x$. The integral is the sum of these areas. For a 2-dimensional integral, the two partials ($\partial x\cdot\partial y$) generate an area in the x-y plane as shown in Figure 10.3B. That area is multiplied by the function's height to create volume, and the integral is the sum of these volumes.

Unfortunately, we cannot graph a 3-dimensional partial with a corresponding function, so instead we just draw the partials as shown in Figure 10.4A. Clearly the product of three partials creates a volume element. As we add up more volume elements (up, down, left, right, forward and backwards) we see that essentially the partials grow like a sphere. The solution has now presented itself- as the radius of a sphere grows by ∂r, the increase in volume is that of a shell which is the sphere's surface area ($4\pi\cdot r^2$) times ∂r. When we use the notation appropriate to velocities, the transformation is:

$$\partial v_x\cdot\partial v_y\cdot\partial v_z\rightarrow 4\pi\cdot v^2\cdot\partial v$$

as the net velocity is the same as the radius. Applied to the probability distribution:

$$\left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v_x \cdot \partial v_y \cdot \partial v_z$$

we now have the Maxwell-Boltzmann equation:

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

The distribution is plotted in Figure 10.5A for O_2 gas as a function of temperature and in 10.5B for He, O_2, and XeF_6 gases at room temperature. The most important feature is that the curve is *almost* bell-shaped, but now quite due to the v^2 skew. The effect of this is to drag the distribution to higher speeds. It is also interesting to see that O_2 can easily reach velocities far in exceed the speed of sound (343 m/s), a very counter-intuitive observation. Heating widens the distribution, but the most significant change occurs with mass. Light elements such as helium have shockingly high velocities; in fact a significant portion of He gas can move faster than escape velocity 11,200 m/s. Does this explain why the Earth is losing helium? Yes, it does, the gas is escaping into outer space. Last, the skew causes the most probable and average velocities to no longer coincide; to demonstrate let's derive them.