Note on Maxwell-Boltzmann Distribution

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The goal of this note is to derive at a more rigorous, albeit not fully motivated, level the Maxwell-Boltzmann distribution velocities. The result is cited immediately for convenience:

$$f(u) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2k_B T} \right) \tag{1}$$

This equation has the following meaning. For a gas satisfying the assumptions of the kinetic theory, with mass per molecule m and at a temperature T, the probability that a particle has velocity of **magnitude** u is given by $f(u)du$. With a little careful integration, you can check that $\int_0^\infty f(u)du = 1$, as a probability density function should.

This note is purely to explain in more detail how to derive the Maxwell-Boltzmann distribution of velocities and how the assumptions of the kinetic theory of ideal gases are used mathematically. You will not be held responsible for reproducing results like this or mastering the mathematics used in this derivation.

1 Probability of finding a particular state

Here we state a more fundamental postulate for our treatment of this topic. Its justification will be deferred to a separate note. Suppose we have a system S in contact with a much larger (really, infinitely larger) system, termed the "bath", and the two are in thermal equilibrium so that the temperature of the system and the temperature of the bath are equal. Call that temperature T. In this setup, the system can exchange energy with the bath, so the energy of the system S will fluctuate as the system evolves in time. Here is the postulate:

Postulate 1. The probability P that the system S is in a particular state X which has an energy $E(X)$ is given by $P(S) = c(T)\exp(-E(S)/k_B T)$ where $c(T)$ is a factor that depends on the system's temperature but does not depend on the state S of the system.

The unspecified factor $c(T)$ (the same factor is used for all states X_i) such that the probabilities sum to 1. This is made clearer in the example below:

Example 1.1 (Two-level system). Suppose a system S at temperature T has only two possible states, X_1 and X_2 with energies $E_1 = E$ and $E_2 = -E$, respectively. What is the probability of finding the system in each state? That is, what is $P(X_1)$ and what is $P(X_2)$? Postulate 1 says that

$$P(X_1) = c(T)e^{-\frac{E}{k_B T}} \tag{2}$$

and

$$P(X_2) = c(T)e^{-\frac{-E}{k_B T}} = c(T)e^{\frac{E}{k_B T}} \tag{3}$$

But we know that the probabilities must sum to 1. So

$$P(X_1) + P(X_2) = c(T)e^{-\frac{E}{k_B T}} + c(T)e^{\frac{E}{k_B T}} = 1 \tag{4}$$

$$c(T)(e^{-\frac{E}{k_B T}} + e^{-\frac{-E}{k_B T}}) = 1 \tag{5}$$

$$c(T) = \frac{1}{e^{-\frac{E}{k_B T}} + e^{\frac{E}{k_B T}}} \tag{6}$$

So the probabilities are:

$$P(X_1) = \frac{e^{-\frac{E}{k_B T}}}{e^{-\frac{E}{k_B T}} + e^{\frac{E}{k_B T}}} = \frac{1}{1 + e^{\frac{2E}{k_B T}}} \tag{7}$$

$$P(X_2) = \frac{e^{\frac{E}{k_B T}}}{e^{-\frac{E}{k_B T}} + e^{\frac{E}{k_B T}}} = \frac{1}{1 + e^{-\frac{2E}{k_B T}}} \tag{8}$$

To summarize, the postulate says that the more energetic a particular state X is, the less likely it is to occur–in fact, exponentially so.

2   Applying this in the Kinetic Theory

In the kinetic theory of gases, the gas is made up of N molecules of equal mass m and the only type of energy they carry is kinetic energy. Recall that the kinetic energy of a molecule of mass m moving at a velocity $\vec{v}$ with magnitude $|\vec{v}|$ is given by

$$E_K = \frac{1}{2} m |\vec{v}|^2 \tag{9}$$

In three dimensions, the velocity vector $\vec{v}$ has three components, which we will label v_x, v_y, v_z. Consider a system of just one particle. What is the probability that it has a particular velocity $\vec{v} = (v_x, v_y, v_z)$? As in the example above, we know that the probability $P(\vec{v})$ will look like:

$$P(\vec{v}) = c(T) \times \exp\left(-\frac{m|\vec{v}|^2}{2k_B T}\right) = c(T) \times \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) \tag{10}$$

To make the probabilities add up to 1, we need to set $c(T)$ appropriately. This time, our probabilities form a continuous function of the parameters v_x, v_y, v_z instead of the discrete case of the two-state system in Example 1.1. So we demand:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(v_x, v_y, v_z) dv_x dv_y dv_z = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} c(T) \times \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) dv_x dv_y dv_z \tag{11}$$

We now change variables to spherical coordinates (u, θ, ϕ)[1], and use u to denote the magnitude of $\vec{v}$:

$$u^2 = v_x^2 + v_y^2 + v_z^2 \tag{12}$$

$$v_x = u \sin\theta \cos\phi \tag{13}$$

$$v_y = u \sin\theta \sin\phi \tag{14}$$

$$v_z = u \cos\theta \tag{15}$$

$$dv_x dv_y dv_z = u^2 \sin\theta \, du \, d\theta \, d\phi \tag{16}$$

Substituting all of these relations into the integral 11,

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[1]For more on how to do conversions like this (from rectangular coordinates (x, y, z) to spherical coordinates (u, θ, ϕ) or other coordinate systems), please see the Wikipedia page.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} c(T) \times \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) dv_x dv_y dv_z \tag{17}$$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} c(T) \times \exp\left(-\frac{mu^2}{2k_B T}\right) u^2 \sin\theta \, du \, d\theta \, d\phi \tag{18}$$

$$= 4\pi c(T) \int_0^{\infty} u^2 \exp\left(-\frac{mu^2}{2k_B T}\right) du \tag{19}$$

The time has come to learn how to do this integral. Luckily, here's a neat trick. Let $\alpha = m/(2k_B T)$. Then this integral can be written as

$$4\pi c(T) \int_0^{\infty} u^2 \exp(-\alpha u^2) du \tag{20}$$

$$= 4\pi c(T) \int_0^{\infty} \left(-\frac{d}{d\alpha} \exp(-\alpha u^2)\right) du \tag{21}$$

$$= -4\pi c(T) \frac{d}{d\alpha} \left(\int_0^{\infty} \exp(-\alpha u^2) du\right) \tag{22}$$

One last time, let $w = \sqrt{\alpha} u$ so that the integral inside the parentheses can be written as

$$\int_0^{\infty} \exp(-\alpha u^2) du = \frac{1}{\sqrt{\alpha}} \int_0^{\infty} \exp(-w^2) dw \tag{23}$$

In discussion, you learned a trick to evaluate the integral of a Gaussian! So if we applied that trick here, we get that

$$\int_0^{\infty} \exp(-w^2) dw = \frac{\sqrt{\pi}}{2} \tag{24}$$

and

$$4\pi c(T) \int_0^{\infty} u^2 \exp\left(-\frac{mu^2}{2k_B T}\right) du \tag{25}$$

$$= -4\pi c(T) \frac{d}{d\alpha} \left(\frac{\sqrt{\pi}}{2} \alpha^{-1/2}\right) = c(T) \times \pi^{3/2} \alpha^{-3/2} = c(T) \times \left(\frac{2\pi k_B T}{m}\right)^{3/2} \tag{26}$$

At long last,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} c(T) \times \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right) dv_x dv_y dv_z = c(T) \times \left(\frac{2\pi k_B T}{m}\right)^{3/2} = 1 \tag{27}$$

and therefore

$$c(T) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \tag{28}$$

Now we can assemble all of the pieces to get the Maxwell-Boltzmann distribution. Look back at Eq. 17. We substitute $c(T)$ now:

$$\int_0^{\infty} 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2k_B T}\right) du \tag{29}$$

The integrand is the quantity known as the Maxwell-Boltzmann distribution, and it describes the probability of finding a particle with magnitude of velocity (otherwise known as speed) u. Observe that this distribution is skewed, and the lower the temperature is, the more the distribution is skewed towards slower speeds:

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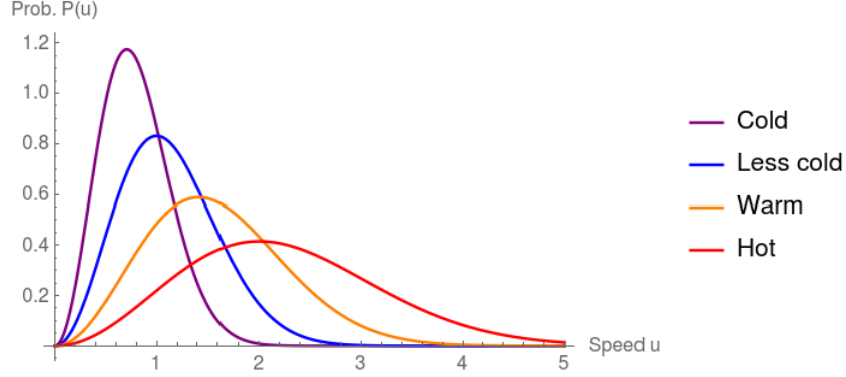
3 Average Energy, RMS Velocity, etc.

For a system of a gas of N molecules moving essentially independently, we are interested in the average energy of the system denoted $\langle E_{\text{total}} \rangle$. E_{total} is the total energy of the system, the sum of the kinetic energies of the individual molecules:

$$E_{\text{total}} = \sum_{i=1}^{N} \frac{1}{2} m |\vec{v}_i|^2 \tag{30}$$

So we want to take the expectation value of this energy with respect to the probability distributions found above:

$$\langle E_{\text{total}} \rangle = \left\langle \sum_{i=1}^{N} \frac{1}{2} m |\vec{v}_i|^2 \right\rangle = \sum_{i=1}^{N} \frac{1}{2} m \langle |\vec{v}_i|^2 \rangle = \frac{1}{2} m N \langle u^2 \rangle \tag{31}$$

To calculate $\langle u^2 \rangle$ with respect to the Maxwell-Boltzmann distribution specified by the integrand in Eq. 29, we just need to do the integral:

$$\langle u^2 \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty u^4 \exp\left(-\frac{mu^2}{2k_B T} \right) du \tag{32}$$

And we can use the same trick used back in Eq. 20, writing $\alpha = m/(2k_B T)$,

$$\langle u^2 \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{d^2}{d\alpha^2} \int_0^\infty \exp(-\alpha u^2) du = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{\sqrt{\pi}}{2} \frac{d^2}{d\alpha^2} (\alpha^{-1/2}) \tag{33}$$

where I have used the result in Eq. 24. Taking the derivatives,

$$\langle u^2 \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{\sqrt{\pi}}{2} \frac{3}{4} \alpha^{-5/2} = \frac{3}{2} \left(\frac{m}{2k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^{5/2} = 3 \frac{k_B T}{m} \tag{34}$$

Substituting this result back into Eq. 31,

$$\langle E_{\text{total}} \rangle = \frac{1}{2} m N \left(3 \frac{k_B T}{m} \right) = \frac{3}{2} N k_B T \tag{35}$$

The RMS speed refers to $\sqrt{\langle u^2 \rangle}$, which is given by Eq. 34:

$$u_{\text{RMS}} = \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \tag{36}$$

We might also be interested in the average *speed* $\langle u \rangle$, which we can compute as

$$\langle u \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty u^3 \exp\left(-\frac{mu^2}{2k_B T} \right) du = \sqrt{\frac{8k_B T}{\pi m}} \tag{37}$$

4 Equipartition Theorem

Definition 1. A degree of freedom is termed "quadratic" if it is parameterized by a variable x and its contribution to the total energy is proportional to x^2.

This definition is not too restrictive because if the energy is some function $U(x)$ is sufficiently smooth, then we can always perform a series expansion of it around some value x_0 where $U(x)$ has a local minimum:

$$U(x) = c_0 + c_1(x - x_0) + \frac{1}{2}c_2(x - x_0)^2 + \ldots \tag{38}$$

and if $(x - x_0) < 1$, we can approximate the behavior of this function around x_0 pretty well, since higher-order terms will get smaller. For example, if we are interested in the potential energy of a spring, we know that there is some natural length to the spring, L_0 for which the potential energy stored in the spring is minimized. From there, we are interested in what the potential looks like around that minimum. So:

$$U(L) \approx c_0 + c_1(L - L_0) + \frac{1}{2}c_2(L - L_0)^2 \tag{39}$$

But remember that

$$c_n = f^{(n)}(L)\Big|_{L=L_0} \tag{40}$$

so since we are expanding around a minimum at L_0, $c_1 = f^{(1)}(L_0) = 0$. So now we are down to

$$U(L) \approx c_0 + \frac{1}{2}c_2(L - L_0)^2 \tag{41}$$

Another feature of physics is that additive offsets in energies are not meaningful. To clarify what this means, only differences in energy can be measured. Another way to view this is that forces are related to the gradient of the potential energy:

$$\vec{F} = -\frac{\partial}{\partial x}U(x,y,z)\hat{\mathbf{i}} - \frac{\partial}{\partial y}U(x,y,z)\hat{\mathbf{j}} - \frac{\partial}{\partial z}U(x,y,z)\hat{\mathbf{k}} \tag{42}$$

So even if I modify $U(x,y,z)$ by a constant to $U(x,y,z) + \text{const}$, the *derivatives* with respect to x, y, z will not change. Therefore the forces will not change either. This means that we can always take the constant term in the series expansion of $U(x)$ to be $c_0 = 0$, leaving us with

$$U(x) \approx \frac{1}{2}c_2(x - x_0)^2 \tag{43}$$

which is purely quadratic.

Since this analysis is completely general and this formulation is ubiquitous in physics and chemistry, we often begin an analysis by assuming that the potential has a simple quadratic form. The potential energy is generally not exactly quadratic, as there are higher-order terms, but including them tends to make problems difficult to solve analytically. Continuing forward, we look at what happens to $\langle E_{\text{total}} \rangle$. Suppose that a gas molecule has D quadratic degrees of freedom. Indexing each of those degrees of freedom by j,

$$\langle E_{\text{total}} \rangle = N \sum_{j=1}^{D} \frac{1}{2}c_j \langle x_j^2 \rangle \tag{44}$$

For example, if we are talking about a gas of H2, which we may model as two spheres connected by a spring, then at high temperatures, $D = 6$ because the molecule has 3 translational velocity components (so x_1, x_2, x_3 are the three components of velocity v_x, v_y, v_z and c_0, c_1, c_2 are the mass m), 2 angular velocity components (so x_4, x_5 are the two components of angular velocity ω_x, ω_y and c_4, c_5 are the moment of inertia I), and 1

vibrational degree of freedom (so x_6 is the bond length ΔL and c_6 is the spring constant k). To calculate $\langle x_j^2 \rangle$, we think back to what the distribution for a single velocity component would have looked like.

$$f(v_x) = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_B T} \right) \tag{45}$$

We were once interested in $\langle u^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$. The average value of one of these components was:

$$\int_{-\infty}^{\infty} v_x^2 f(v_x) dv_x = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} v_x^2 \exp\left(-\frac{mv_x^2}{2k_B T} \right) = \frac{k_B T}{m} \tag{46}$$

After multiplying this by $Nm/2$, we conclude that it contributes $k_B T/2$ to $\langle E_{\text{total}} \rangle$. What about a rotational velocity? The energy term for that looks like

$$E = \frac{1}{2} I \omega_x^2 \tag{47}$$

By making the substitution $m \to I$ and $v_x \to \omega_x$:

$$f(\omega_x) = \left(\frac{I}{2\pi k_B T} \right)^{1/2} \exp\left(-\frac{I\omega_x^2}{2k_B T} \right) \tag{48}$$

$$\int_{-\infty}^{\infty} \omega_x^2 f(\omega_x) d\omega_x = \left(\frac{I}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} \omega_x^2 \exp\left(-\frac{I\omega_x^2}{2k_B T} \right) = \frac{k_B T}{I} \tag{49}$$

After multiplying this by $NI/2$, we conclude that it contributes $k_B T/2$ to $\langle E_{\text{total}} \rangle$. In general, following the general form for $\langle E_{\text{total}} \rangle$ in Eq. 44, we see that its distribution will be:

$$f(x_j) = \left(\frac{c_j}{2\pi k_B T} \right)^{1/2} \exp\left(-\frac{c_j x_j^2}{2k_B T} \right) \tag{50}$$

and

$$\int_{-\infty}^{\infty} x_j^2 f(x_j) dx_j = \left(\frac{c_j}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{\infty} x_j^2 \exp\left(-\frac{c_j x_j^2}{2k_B T} \right) = \frac{k_B T}{c_j} \tag{51}$$

Substituting into Eq. 44,

$$\langle E_{\text{total}} \rangle = N \sum_{j=1}^{D} \frac{1}{2} c_j \frac{k_B T}{c_j} = \frac{1}{2} N D k_B T \tag{52}$$

This yields the equipartition theorem.

Theorem 1. Let x_j be a quadratic degree of freedom. Then the average total energy contribution due to that degree of freedom is given by $\frac{1}{2} k_B T$.

This is termed "equipartition" because each degree of freedom contributes the same amount, $N k_B T/2$.