

Maxwell Distribution

Maxwell assumes that the random velocity of particles can be described by some probability distribution. He then derived the formula for average number of particles whose velocity lies between $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$. The 3D distribution function $f(\mathbf{v})$ is given by Maxwell distribution:

$$f(\mathbf{v}) d^3\mathbf{v} = N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mv^2}{2kT} \right) d^3\mathbf{v}$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$ and $d^3\mathbf{v} = dv_x dv_y dv_z$. The single component distribution is given by

$$f(v_x) dv_x = N \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left(-\frac{mv_x^2}{2kT} \right) dv_x$$

This can be transformed into speed distribution function as

$$f(v) dv = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp \left(-\frac{mv^2}{2kT} \right) dv$$

Maxwell's Derivation

Maxwell first noted that the distribution function $F(\mathbf{v})$ with respect to x -axis does not affect $F(\mathbf{v})$ with respect to y -axis and z -axis, since they are at right angle, orthogonal, and independent. Hence, He wrote that a particle velocity lies at $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$ as

$$F(\mathbf{v}) d^3\mathbf{v} = f(v_x)f(v_y)f(v_z) dx dy dz$$

Then also argued that the probability only depend on the magnitude of \mathbf{v} , thus

$$f(v_x)f(v_y)f(v_z) = g(v_x^2 + v_y^2 + v_z^2)$$

should apply. This functional equation is solved by

$$f(\alpha) = B e^{-A\alpha^2} d\alpha$$

Substituting this solution back, we obtain

$$F(\mathbf{v}) = B \exp [-A (v_x^2 + v_y^2 + v_z^2)]$$

All that left is normalization

$$\int_{\mathbb{R}^3} B \exp [-A (v_x^2 + v_y^2 + v_z^2)] d^3\mathbf{v} = 1$$

The integral may be evaluated as three product of the same integral

$$\int_{\mathbb{R}^3} \exp [-A (v_x^2 + v_y^2 + v_z^2)] d^3\mathbf{v} = \left(\int_{-\infty}^{\infty} e^{-A\alpha^2} d\alpha \right)^3$$

with α as dummy variable. This is Gaussian integral if $A = 1$, since it is not however, we substitute $\omega = A\alpha^2$ and $d\omega = \sqrt{A}d\alpha$

$$\int_{\mathbb{R}^3} \exp [-A (v_x^2 + v_y^2 + v_z^2)] d^3\mathbf{v} = \left(\frac{1}{\sqrt{A}} \int_{-\infty}^{\infty} e^{-A\omega^2} d\omega \right)^3 = \left(\frac{\pi}{2} \right)^{3/2}$$

It follows that the normalization constant is $B = (A/\pi)^{3/2}$. Putting it all together

$$F(\mathbf{v}) = \left(\frac{A}{\pi} \right)^{3/2} e^{-Av^2}$$

with $v^2 = v_x^2 + v_y^2 + v_z^2$. All that left then is to find the value of A , which is determined by some physical quantity—for no mathematics technique can determine the value of A .

To do so, let us do some physics. Consider an area orthogonal to x -axis dA of a container V with N particles of gases. The number of particles moving at positive x -axis is

$$dN = \frac{N}{V} dV = \frac{N}{V} v_{x+} dA dt$$

where dV is the volume occupied by dN particle

$$dV = v_{x+} dt dA$$

Each particle hits the wall with momentum p and reflected—perfectly—back, thus changing its momentum

$$p = mv_{x+} \implies dp = 2mv_{x+}$$

Hence the total change of momentum of particles dN

$$dp_x = dp dN = \frac{2mv_{x+}^2 N}{V} dt dA$$

Since force is the change of momentum, we can say

$$F_x = \frac{dp_x}{dt}$$

Finally we can determine the one of macroscopic observable, which is pressure

$$P = \frac{F_x}{dA} = \frac{2mN}{V} \langle v_{x+}^2 \rangle$$

The expression for pressure P is not yet complete. We need to evaluate the term $\langle v_{x+}^2 \rangle$. To do so, consider an observable $G(\mathbf{v})$, which is a function of v alone. The observed value $\langle G(\mathbf{v}) \rangle$ is

$$\langle G(\mathbf{v}) \rangle = \int_{\mathbb{R}^3} G(\mathbf{v}) F(\mathbf{v}) d^3\mathbf{v}$$

Since both G and F are a function of v alone, the integral can be easily evaluated in spherical coordinate

$$\langle G(\mathbf{v}) \rangle = \int_0^{2\pi} \int_0^\pi \int_0^\infty G(v) F(v) v^2 \sin \theta dv d\theta d\phi = 4\pi \int_0^\infty v^2 G(v) F(v) dv$$

Next we will determine the expectation value of $\langle v \rangle$ and $\langle v^2 \rangle$. For $\langle v \rangle$, we have

$$\langle v \rangle = \frac{4A^{3/2}}{\sqrt{\pi}} \int_0^{\infty} v^3 e^{-Av^2} dv = \frac{2A^{3/2}}{\sqrt{\pi}A^4} \Gamma(2) = \frac{2}{\sqrt{A\pi}}$$

As for $\langle v^2 \rangle$, we find

$$\langle v^2 \rangle = \frac{4A^{3/2}}{\sqrt{\pi}} \int_0^{\infty} v^4 e^{-Av^2} dv = \frac{2A^{3/2}}{\sqrt{\pi}A^5} \Gamma\left(\frac{5}{2}\right) = \frac{3}{2A}$$

Eliminating A

$$\left. \begin{aligned} \frac{1}{A} &= \frac{\pi}{4} \langle v \rangle^2 \\ \frac{1}{A} &= \frac{2}{3} \langle v^2 \rangle \end{aligned} \right\} \langle v^2 \rangle = \frac{3\pi}{8} \langle v \rangle^2$$

As we stated before, our choice of axis is the one such that they are orthogonal, and independent. Thus,

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{\langle v_x^2 + v_y^2 + v_z^2 \rangle}{3}$$

Since $\langle v_{x+}^2 \rangle = \langle v_x^2 \rangle / 2$

$$\langle v_{x+}^2 \rangle = \frac{\langle v^2 \rangle}{6}$$

Substituting this into our expression for P

$$P = \frac{mN}{3V} \langle v^2 \rangle = \frac{2N}{3V} u$$

where u is the average kinetic energy per particles

$$u = \frac{1}{2} m \langle v^2 \rangle$$

The equation above implies that for two gases with the same pressure, the equation

$$\frac{m_1 N_1}{3V_1} \langle v_1^2 \rangle = \frac{m_2 N_2}{3V_2} \langle v_2^2 \rangle$$

should apply. Since we are considering an ideal gas, we can therefore invoke Avogadro's hypothesis and obtain

$$m_1 \langle v_1^2 \rangle = m_2 \langle v_2^2 \rangle$$

In other words, ideal gas with the same mass, number of particles, pressure, and volume, have the same amount of kinetic energy and obey both our equation of pressure P and kinetic energy u . Now, using the equation of ideal gas, we have the relation

$$\frac{NkT}{V} = \frac{mN}{3V} \langle v^2 \rangle = \frac{2N}{3V} u$$

Solving for u and $\langle v^2 \rangle$

$$u = \frac{3}{2} kT \quad \text{and} \quad \langle v^2 \rangle = 3 \frac{kT}{m}$$

Result for u also prove the same conclusion obtained from thermodynamics. Finally, we can solve for A by using both results we obtained from $\langle v^2 \rangle$

$$\langle v^2 \rangle = 3 \frac{kT}{m} = \frac{3}{2A} \implies A = \frac{m}{2kT}$$

To put a nice little bow over everything, we write the complete form of Maxwell distribution

$$f(\mathbf{v}) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mv^2}{2kT} \right) \quad \blacksquare$$

where, as before, $v^2 = v_x^2 + v_y^2 + v_z^2$

Boltzmann's Derivation

We will now derive the Maxwell distribution using Boltzmann's method. Let $n_{\mathbf{k}}$ be the number of particle whose velocity lies within $(\epsilon\mathbf{v}, \epsilon\mathbf{v} + \epsilon)$, so

$$n_{\mathbf{k}} = \epsilon f(\mathbf{k}\mathbf{v})$$

and as $\epsilon \rightarrow 0$

$$n = f(\mathbf{v}) \lim_{\epsilon \rightarrow 0} \epsilon = f(\mathbf{v}) d^3v$$

As before, we want to find the equilibrium distribution function, $f(\mathbf{v})$ in this case, by maximizing the said distribution function, constrained by N and Nu function. The N constraint simply evaluate into

$$N = \int_{\mathbb{R}^3} f(\mathbf{v}) d^3v$$

Recall that Nu stands for total energy. In the present case, we involve velocity into our consideration, hence the energy in question is the kinetic energy, which is evaluated by

$$Nu = \frac{m}{2} \langle v^2 \rangle = \frac{m}{2} \int_{\mathbb{R}^3} v^2 f(\mathbf{v}) d^3v$$

Since $f(\mathbf{v})$ is a function of v alone, we can make the change of variable $d^3v = v^2 \sin \theta dv; d\theta d\phi$. Thus, our constraint equations read

$$4\pi \int_0^\infty v^2 f(\mathbf{v}) dv = N, \quad 4\pi \int_0^\infty v^4 f(\mathbf{v}) dv = Nu$$

We then consider the number of configuration \mathcal{P} , which is given by

$$\mathcal{P} = N! \left(\prod_{\mathbf{k}=-\infty}^{\infty} n_{\mathbf{k}}! \right)^{-1}$$

Taking the logarithm and applying Stirling's approximation,

$$\ln \mathcal{P} = N \ln N - N - \sum_{\mathbf{k}=-\infty}^{\infty} (n_{\mathbf{k}} \ln n_{\mathbf{k}} - n_{\mathbf{k}})$$

Taking the limit $\epsilon \rightarrow 0$

$$\begin{aligned}\ln \mathcal{P} &= N \ln N - N - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] d^3v - \lim_{\epsilon \rightarrow 0} \int_{\mathbb{R}^3} f(\mathbf{v}) \ln(\epsilon) d^3v \\ &\quad + \int_{\mathbb{R}^3} f(\mathbf{v}) d^3v \\ \ln \mathcal{P} &= N \ln N - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] d^3v - N \lim_{\epsilon \rightarrow 0} \ln(\epsilon)\end{aligned}$$

To maximize the logarithm of \mathcal{P} , we defined permutability measure by

$$\Omega = - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] d^3v$$

and maximize it with the N and Nu constraint. We use the first form of those constraints, since they look simpler, and use the second form to evaluate the resulting maximized function, since we can't evaluate it using the first form. Anyway, the auxiliary function reads as

$$F(f) = \int_{\mathbb{R}^3} \left[f \ln(f) + \lambda_1 f + \lambda_2 \frac{m}{2} v^2 f \right] d^3v$$

As for its derivative,

$$\frac{dF}{df} = \int_{\mathbb{R}^3} \left[\ln(f) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 \right] d^3v = 0$$

which implies

$$\ln(f) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 = 0$$

Thus

$$f(\mathbf{v}) = \exp \left(-1 - \lambda_1 - \lambda_2 \frac{m}{2} v^2 \right) = C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right)$$

We now use this to evaluate both constraints and determine the value for each constant. For the N constraint

$$\begin{aligned}N &= 4\pi \int_0^\infty v^2 C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) dv = \frac{4\pi C}{2} \left(\frac{2}{m\lambda_2} \right)^{3/2} \frac{\sqrt{\pi}}{2} \\ &= C \left(\frac{2\pi}{m\lambda_2} \right)^{3/2}\end{aligned}$$

Then the Nu constraint

$$\begin{aligned}Nu &= 4\pi \int_0^\infty v^4 C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) dv = \frac{4\pi C m}{4} \left(\frac{2}{m\lambda_2} \right)^{5/2} \frac{3\sqrt{\pi}}{4} \\ &= \frac{3}{4} C m \left(\frac{2\pi^{3/5}}{m\lambda_2} \right)^{5/2}\end{aligned}$$

Solving both for N and equating them

$$\begin{aligned}C \left(\frac{2\pi}{m\lambda_2} \right)^{3/2} &= \frac{3}{4u} C m \left(\frac{2\pi^{3/5}}{m\lambda_2} \right)^{5/2} \\ \frac{4u}{3} &= \frac{2m}{m\lambda_2} \\ \lambda_2 &= \frac{3}{2u}\end{aligned}$$

On using this to the previously evaluated N constraint

$$N = C \left(\frac{2\pi}{m} \frac{2u}{3} \right)^{3/2} \implies C = N \left(\frac{3m}{4\pi u} \right)^{3/2}$$

Hence

$$f(\mathbf{v}) = C \exp \left(-\frac{\lambda_2 m}{2} v^2 \right) = N \left(\frac{3m}{4\pi u} \right)^{3/2} \exp \left(-\frac{3m}{4u} v^2 \right) \quad \blacksquare$$

Maxwell Distribution for Relative Velocities

Maxwell distribution also works on composite system. This is due to it also works on relative velocities. We shall prove this.

Consider two system with N_1 and N_2 Particles. We then want to find the probability of pairs of particles whose relative velocity is \mathbf{V} . We define such probability density function as

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} = \iint_{\mathbb{R}^3} N_1 N_2 F_1(\mathbf{v}) F_2(\mathbf{v} + \mathbf{V}) d^3\mathbf{v} d^3\mathbf{V}$$

To avoid ambiguity, we shall write it more explicitly as

$$G(\mathbf{V}) = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k^2 T_1 T_2} \right)^{3/2} \exp \left[-\frac{m_1}{2kT_1} (v_x^2 + v_y^2 + v_z^2) \right] \\ \exp \left[-\frac{m_2}{2kT_2} (\{v_x + V_x\}^2 + \{v_y + V_y\}^2 + \{v_z + V_z\}^2) \right]$$

Then, as is the case from before, the integral can be evaluated as product of three identical integrals

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3\mathbf{V} = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k^2 T_1 T_2} \right)^{3/2} \\ \int_{\mathbb{R}^3} \left[\int_{-\infty}^{\infty} \exp \left(-\frac{m_1}{2kT_1} \omega^2 - \frac{m_2}{2kT_2} \{\omega + \Omega\}^2 \right) d\omega \right]^3 d^3\mathbf{V}$$

...Sary integrals. Let's first try to evaluate the term inside square parenthesis

$$\int_{-\infty}^{\infty} \exp \left[-\left(\frac{m_1}{2kT_1} + \frac{m_2}{2kT_2} \right) \omega^2 - 2\frac{m_2}{2kT_2} \Omega \omega - \frac{m_2}{2kT_2} \Omega^2 \right] d\omega$$

Since the last term is a constant, we can take it outside the integral

$$\exp \left[-\frac{m_2}{2kT_2} \Omega^2 \right] \int_{-\infty}^{\infty} \exp \left[-\left(\frac{m_1 T_2 + m_2 T_1}{2kT_1 T_2} \right) \omega^2 - \frac{m_2 \Omega}{kT_2} \omega \right] d\omega$$

The integral itself can be evaluated using the general form of Gaussian integral

$$\int_{-\infty}^{\infty} \exp (-\alpha x^2 + \beta x + \gamma) dx = \sqrt{\frac{\pi}{\alpha}} \exp \left(\frac{\beta^2}{4\alpha} + \gamma \right)$$

Using the equation above

$$\exp \left[-\frac{m_2}{2kT_2} \Omega^2 \right] \exp \left[\Omega^2 \frac{m_2^2}{k^2 T_2^2} \frac{1}{4} \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right] \left[\pi \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2}$$

Combining the exponent, we get

$$\exp \left[\Omega^2 \left(\frac{m_2^2 k T_1 T_2}{2kT_2^2(m_1 T_2 + m_2 T_1)} - \frac{m_2}{2kT_2} \right) \right] \left[\pi \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2}$$

Next simply evaluate the terms inside parenthesis

$$\exp \left[\Omega^2 \left(\frac{m_2 \{m_2 k T_1 T_2 - m_1 k T_2 - m_2 k T_1 T_2\}}{2kT_2^2(m_1 T_2 + m_2 T_1)} \right) \right] [\dots]^{1/2}$$

where I have taken some liberties to not write the last term constant due to \hbox{ overfull } problem. Anyway, we obtain

$$\exp \left[-\frac{m_2 m_1 k T_2 T_2}{2kT_2^2(m_1 T_2 + m_2 T_1)} \Omega^2 \right] \left[\pi \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2}$$

Before substituting back into our original integral, note that Ω is the dummy variable we used for the term \mathbf{V} ; or rather V_i , where i is i -th component of Cartesian coordinate. Hence,

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3 \mathbf{V} = N_1 N_2 \left(\frac{m_1 m_2}{4\pi^2 k^2 T_1 T_2} \right)^{3/2} \int_{\mathbb{R}^3} \left[\exp \left[-\frac{m_2 m_1 k T_2 T_2}{2kT_2^2(m_1 T_2 + m_2 T_1)} V_i^2 \right] \left[\pi \frac{2kT_1 T_2}{m_1 T_2 + m_2 T_1} \right]^{1/2} \right]^3 d^3 \mathbf{V}$$

Recall that $V^2 = V_x^2 + V_y^2 + V_z^2$, then we can simplify our equation

$$\int_{\mathbb{R}^3} G(\mathbf{V}) d^3 \mathbf{V} = \int_{\mathbb{R}^3} N_1 N_2 \left(\frac{1}{2\pi k} \frac{m_1 m_2}{m_1 T_2 + m_2 T_1} \right)^{3/2} \exp \left[-\frac{m_2 m_1}{2(m_1 T_2 + m_2 T_1)} V^2 \right] d^3 \mathbf{V}$$

Since we are integrating over the same limit, we can conclude that

$$G(\mathbf{V}) = N_1 N_2 \left(\frac{1}{2\pi k} \frac{m_1 m_2}{m_1 T_2 + m_2 T_1} \right)^{3/2} \exp \left[-\frac{m_2 m_1}{2(m_1 T_2 + m_2 T_1)} V^2 \right]$$

The equation above shows that the probability distribution function for composite system has the same form as Maxwell distribution, hence Maxwell distribution function also works on composite system. \square

Physical Quantity

Few physical quantities that can be derived from the MB distribution function are as follows. First we have the average velocity

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

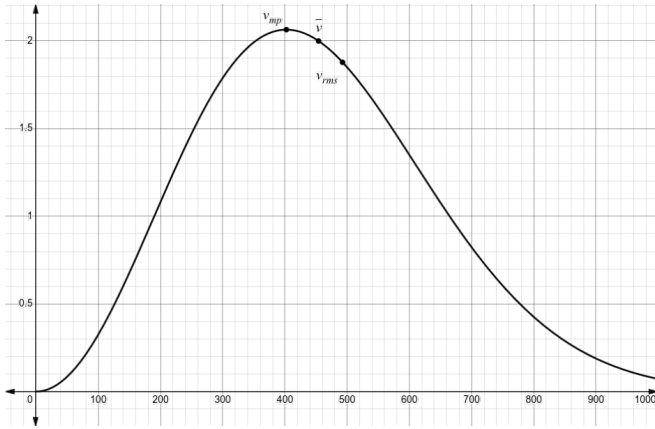


Figure: MB distribution function. In general, $v_{\text{mp}} < \langle v \rangle < v_{\text{rms}}$

then the most probable velocity

$$v_{\text{mp}} = \sqrt{\frac{2kT}{m}}$$

and the root-mean-square

$$v_{\text{rms}} = \sqrt{\frac{3kT}{2}}$$

We also have flux, that is a number of particles per unit area per unit time

$$\Gamma = \frac{1}{4} \rho \langle v \rangle$$

Derivation. The derivation of $\langle v \rangle$ and v_{rms} are quite trivial. For the expectation value of velocity

$$\begin{aligned} \langle v \rangle &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv \\ &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m} \right)^{4/2} \Gamma(2) = \sqrt{\frac{8kT}{\pi m}} \end{aligned}$$

And for root-mean-square-velocity

$$\begin{aligned} v_{\text{rms}} &= \left[4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2kT}\right) dv \right]^{1/2} \\ &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m} \right)^{5/2} \Gamma\left(\frac{5}{2}\right) = \sqrt{\frac{3kT}{2}} \end{aligned}$$

To find the most probable velocity, we maximize the distribution function. Hence, setting the derivative with respect to velocity to zero

$$4N \left(\frac{m}{2\pi kT} \right)^{3/2} \left[2v \exp\left(-\frac{mv^2}{2kT}\right) - v^2 \frac{mv}{kT} \exp\left(-\frac{mv^2}{2kT}\right) \right] = 0$$

Solving for velocity, we have

$$2v \exp\left(-\frac{mv^2}{2kT}\right) = \frac{mv^3}{kT} \exp\left(-\frac{mv^2}{2kT}\right)$$

$$v = \sqrt{\frac{2kT}{m}}$$

To derive flux, we need to recall

$$dN \frac{N}{V} v_{x+} dA dt$$

Using the definition of particle density $\rho = N/V$ and flux $\Gamma = N/At$, we conclude

$$\Gamma = \rho v_{x+}$$

We find the x component of the velocity by

$$\langle v_x \rangle = \int v_x f(v_x) dv_x$$

We find

$$\langle v_x \rangle = \left(\frac{m}{2\pi kT}\right)^{1/2} \int v_x \exp\left(-\frac{mv^2}{2kT}\right) dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \frac{1}{2} \left(\frac{2\pi kT}{m}\right)^{1/2} \Gamma(2) = \sqrt{\frac{2kT}{m}}$$

We could simply substitute this result into our flux equation, or alternatively we write

$$\langle v \rangle = \sqrt{\frac{8kT}{m}} = \sqrt{2} \langle v_x \rangle$$

and substituting into the flux equation for much cleaner result

$$\Gamma = \frac{1}{4} \rho \langle v \rangle$$