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 single-particle distribution function $F(\mathbf{v})$ is given by Maxwell distribution:

$$F(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)$$

To find the probability of N particles within interval (v_1, v_2), we then integrate that probability function

$$\int_{v_1}^{v_2} N \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)\, d^3\mathbf{v}$$

where $d^3\mathbf{v} = dv_x\, dv_y\, dv_z$. This can be simplified into

$$4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{v_1}^{v_2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)\, dv$$

Maxwell Distribution 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

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

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

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

should apply. This functional equation is solved by

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

Substituting this solution back, we obtain

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

All that left is normalization

$$\int\limits_{\mathbb{R}^3} B\exp\left[-A\left(v_x^2 + v_y^2 + v_y^2\right)\right]\, d^3\mathbf{v} = 1$$

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

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

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

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

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

$$dN = \frac{1}{V} N\ dV = \frac{N v_{x+}}{V}\ dt\ dA$$

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

$$p = m v_{x+} \implies dp = 2 m v_{v+}$$

Hence the total change of momentum of particles dN

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

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

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

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

$$\langle G(\mathbf{v})\rangle = \int\limits_0^{2\pi}\int\limits_0^{\pi}\int\limits_0^{\infty} G(v)F(v)v^2 \sin\theta\ dv\ d\theta\ d\phi = 4\pi \int\limits_0^{\infty} v^2 G(v) F(v)\ dv$$

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

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

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

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

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

$$\langle v^2 \rangle = 3\frac{k_b T}{m} = \frac{3}{2A} \implies A = \frac{m}{2k_B T}$$

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

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

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

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

$$\int\limits_{\mathbb{R}^3} G(\mathbf{V})\, d^3\mathbf{V} = \iint\limits_{\mathbb{R}^3} N_1 N_2 F_1(\mathbf{v}) F_2(\mathbf{v}+\mathbf{V})\, d^3\mathbf{v}\, d^3\mathbf{V}$$

To avoid ambiguity, we shall write it more explicitly as

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

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

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

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

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

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

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

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

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

Using the equation above

$$\exp\left[-\frac{m_2}{2k_BT_2}\Omega^2\right] \exp\left[\Omega^2 \frac{m_2^2}{k_B^2T_2^2}\frac{1}{4}\frac{2k_BT_1T_2}{m_1T_2+m_2T_1}\right]\left[\pi\frac{2k_BT_1T_2}{m_1T_2+m_2T_1}\right]^{1/2}$$

Combining the exponent, we get

$$\exp\left[\Omega^2\left(\frac{m_2^2k_BT_1T_2}{2k_BT_2^2(m_1T_2+m_2T_1)} - \frac{m_2}{2k_BT_2}\right)\right]\left[\pi\frac{2k_BT_1T_2}{m_1T_2+m_2T_1}\right]^{1/2}$$

Next simply evaluate the terms inside parenthesis

$$\exp\left[\Omega^2\left(\frac{m_2\left\{m_2k_BT_1T_2 - m_1k_BT_2 - m_2k_BT_1T_2\right\}}{2k_BT_2^2(m_1T_2+m_2T_1)}\right)\right][\ldots]^{1/2}$$

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

$$\exp\left[-\frac{m_2m_1k_BT_2T_2}{2k_BT_2^2(m_1T_2+m_2T_1)}\Omega^2\right]\left[\pi\frac{2k_BT_1T_2}{m_1T_2+m_2T_1}\right]^{1/2}$$

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,

$$\int\limits_{\mathbb{R}^3} G(\mathbf{V})\, d^3\mathbf{V} = N_1N_2\left(\frac{m_1m_2}{4\pi^2k_B^2T_1T_2}\right)^{3/2}$$
$$\int\limits_{\mathbb{R}^3}\left[\exp\left[-\frac{m_2m_1k_BT_2T_2}{2k_BT_2^2(m_1T_2+m_2T_1)}V_i^2\right]\left[\frac{2\pi k_BT_1T_2}{m_1T_2+m_2T_1}\right]^{1/2}\right]^3 d^3\mathbf{V}$$

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

$$\int\limits_{\mathbb{R}^3} G(\mathbf{V})\, d^3\mathbf{V} = \int\limits_{\mathbb{R}^3} N_1N_2\left(\frac{1}{2\pi k_B}\frac{m_1m_2}{m_1T_2+m_2T_1}\right)^{3/2}$$
$$\exp\left[-\frac{m_2m_1}{2(m_1T_2+m_2T_1)}V^2\right]\, d^3\mathbf{V}$$

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

$$G(\mathbf{V}) = N_1N_2\left(\frac{1}{2\pi k_B}\frac{m_1m_2}{m_1T_2+m_2T_1}\right)^{3/2}\exp\left[-\frac{m_2m_1}{2(m_1T_2+m_2T_1)}V^2\right]$$

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. □