Derivation of the Maxwell-Boltzmann distribution

Derek W. Harrison

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Introduction

The Maxwell-Boltzmann distribution of particle speeds is derived using the kinetic theory of gases.

Derivation

Following Maxwell, the probability of some particle having an x-component velocity between v_x and $v_x + dv_x$ is:

$$p_{v_x}(v_x)dv_x \tag{1}$$

Motion of the particles is random and so the velocity components are independent of one another. The probability some particle has velocities between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and between v_z and $v_z + dv_z$ is then:

$$p_{v_x}(v_x)p_{v_y}(v_y)p_{v_z}(v_z)dv_x dv_y dv_z \tag{2}$$

Since the motion of the particles is random velocity distributions are symmetric about the origin and therefore it follows that the probability some particle has velocities between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and between v_z and $v_z + dv_z$ should depend only on speed v:

$$p_{v_x}(v_x)p_{v_y}(v_y)p_{v_z}(v_z) = p(v) \tag{3}$$

With the speed v given by:

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{4}$$

It is reasonable to assume that the velocity components are normally distributed. Based on the reasoning and the requirement that solutions are finite one can deduce that the solution of (3) is:

$$Ce^{-Kv_x^2}Ce^{-Kv_y^2}Ce^{-Kv_z^2} = C^3 e^{-Kv^2} \tag{5}$$

With:

$$p_{v_i}(v_i) = Ce^{-Kv_i^2} \tag{6}$$

And:

$$p(v) = C^3 e^{-Kv^2} \tag{7}$$

To facilitate the following steps of the derivation a change of variables is made:

$$\begin{aligned} x &\leftarrow v_x \\ y &\leftarrow v_y \\ z &\leftarrow v_z \\ r &\leftarrow v \end{aligned} \tag{8}$$

Equation (3) then becomes:

$$p_x(x)p_y(y)p_z(z) = p(r) \tag{9}$$

To determine the constant C the integral of (2) over the whole velocity space is equated with 1 and the resulting equation is solved for C:

$$\begin{aligned} 1 =& \int_{-\infty}^{\infty} p_x(x)p_y(y)p_z(z)dxdydz \\ =& C^3 \int_{-\infty}^{\infty} e^{-K(x^2+y^2+z^2)}dxdydz \end{aligned} \tag{10}$$

The integral in (10) is more readily computed in spherical coordinates:

$$\begin{aligned} 1 =& C^3 \int_0^{2\pi} d\theta \int_0^{\pi} \sin(\phi)d\phi \int_0^{\infty} e^{-Kr^2}r^2dr \\ =& 4\pi C^3 \int_0^{\infty} r^2e^{-Kr^2}dr = \int_0^{\infty} \rho_r dr \\ =& C^3 \left(\frac{\pi}{K}\right)^{3/2} \end{aligned} \tag{11}$$

Where ϕ is the polar angle, θ the azimutal angle and ρ_r the probability density. The constant C is therefore:

$$C = \sqrt{\frac{K}{\pi}} \tag{12}$$

Which means that the probability density ρ_r is:

$$\rho_r = 4\pi r^2 \left(\frac{K}{\pi}\right)^{3/2} e^{-Kr^2} \tag{13}$$

The average squared speed of the system of particles $\langle r^2\rangle$ is then:

$$\langle r^2\rangle = \int_0^{\infty} r^2\rho_r dr = \frac{3}{2K} \tag{14}$$

From kinetic theory and experimental observations the temperature and average particle speed of the system are related by:

$$kT = \frac{1}{3}m\langle r^2\rangle \tag{15}$$

With m the mass of a particle and k the Boltzmann constant. Which means that the constant K is equal to:

$$K = \frac{m}{2kT} \tag{16}$$

The probability density ρ_r then becomes:

$$\rho_r = \left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mr^2}{2kT}} 4\pi r^2 \tag{17}$$

Converting back to the original variables ($v \leftarrow r$) equation (17) becomes:

$$\rho_v = \left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2 \tag{18}$$

Which is the Maxwell-Boltzmann distribution.