Derivation of the Maxwell-Boltzmann distribution

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May 5, 2022

Introduction

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

Derivation

Particle motion is random and so the velocity components are independent of one another. Following Maxwell, 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:

$$p_{v_x}(v_x)p_{v_y}(v_y)p_{v_z}(v_z)dv_x dv_y dv_z \tag{1}$$

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:

$$p_{v_x}(v_x)p_{v_y}(v_y)p_{v_z}(v_z) = p(v) \tag{2}$$

With speed v given by:

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{3}$$

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 (2) is:

$$Ce^{-Kv_x^2}Ce^{-Kv_y^2}Ce^{-Kv_z^2} = C^3e^{-Kv^2} \tag{4}$$

With:

$$p_{v_i}(v_i) = Ce^{-Kv_i^2} \tag{5}$$

And:

$$p(v) = C^3e^{-Kv^2} \tag{6}$$

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

$$\begin{aligned} x &\leftarrow v_x \\ y &\leftarrow v_y \\ z &\leftarrow v_z \\ r &\leftarrow v \end{aligned} \tag{7}$$

Equation (2) then becomes:

$$p_x(x)p_y(y)p_z(z) = p(r) \tag{8}$$

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

$$\begin{aligned} 1 =& \int_{-\infty}^{\infty} p_x(x)p_y(y)p_z(z)dxdydz \\ =& C^3 \int_{-\infty}^{\infty} e^{-K(x^2+y^2+z^2)} dxdydz \end{aligned} \tag{9}$$

The integral in (9) is more readily computed in spherical coordinates:

$$\begin{aligned} 1 =& C^3 \int_0^{2\pi} d\theta \int_0^{\pi} \sin(\phi)d\phi \int_0^{\infty} e^{-Kr^2} r^2 dr \\ =& 4\pi C^3 \int_0^{\infty} r^2 e^{-Kr^2} dr = \int_0^{\infty} \rho_r dr \\ =& C^3 \left(\frac{\pi}{K}\right)^{3/2} \end{aligned} \tag{10}$$

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

$$C = \sqrt{\frac{K}{\pi}} \tag{11}$$

Which means that the probability density ρ_r is:

$$\rho_r = 4\pi r^2 \left(\frac{K}{\pi}\right)^{3/2} e^{-Kr^2} \tag{12}$$

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

$$\langle r^2 \rangle = \int_0^{\infty} r^2 \rho_r dr = \frac{3}{2K} \tag{13}$$

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

$$kT = \frac{1}{3} m \langle r^2 \rangle \tag{14}$$

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

$$K = \frac{m}{2kT} \tag{15}$$

The probability density ρ_r then becomes:

$$\rho_r = \left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mr^2}{2kT}} 4\pi r^2 \tag{16}$$

Converting back to the original variables ($v \leftarrow r$) equation (16) becomes:

$$\rho_v = \left(\frac{m}{2kT\pi}\right)^{3/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2 \tag{17}$$

Which is the Maxwell-Boltzmann distribution.