

Derivation of the Maxwell-Boltzmann velocity distribution

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Introduction

The Maxwell-Boltzmann velocity distribution of particles is derived using the kinetic theory of gases.

Derivation

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

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

Continuing the reasoning one can compute the probability of some particle having velocities between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and between v_z and $v_z + dv_z$:

$$p_{v_x}(v_x)p_{v_y}(v_y)p_{v_z}(v_z)dv_xdv_ydv_z \quad (2)$$

From the symmetry of the problem one can reason 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 :

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

With the speed v given by:

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \quad (4)$$

It is reasonable to assume that the velocity components are independent of one another and normally distributed. From these assumptions one can deduce that a possible solution of (3) is:

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

With:

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

And:

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

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

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

Equation (3) then becomes:

$$p_x(x)p_y(y)p_z(z) = p(r) \quad (9)$$

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 :

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

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

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

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

$$C = \sqrt{\frac{K}{\pi}} \quad (12)$$

Which means that the probability density ρ_r is:

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

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

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

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

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

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

$$K = \frac{m}{2kT} \quad (16)$$

The probability density ρ_r then becomes:

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

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

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

Which is the Maxwell-Boltzmann velocity distribution.