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:

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

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 $v_z + dv_z$:

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

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:

$$p_{v_x}(v_x)p_{v_y}(v_y)p_{v_z}(v_z) = p(v)$$
(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 independent of one another and normally distributed. From these assumptions one can deduce that a possible solution of (3) is:

$$Ce^{-Kv_x^2}Ce^{-Kv_y^2}Ce^{-Kv_z^2} = C^3e^{-Kv^2}$$
(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:

$$x \leftarrow v_x$$

$$y \leftarrow v_y$$

$$z \leftarrow v_z$$

$$r \leftarrow v$$
(8)

Equation (3) then becomes:

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

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:

$$1 = \int_{-\infty}^{\infty} p_x(x) p_y(y) p_z(z) dx dy dz$$

$$= C^3 \int_{-\infty}^{\infty} e^{-K(x^2 + y^2 + z^2)} dx dy dz$$
(10)

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

$$1 = C^{3} \int_{0}^{2\pi} d\theta \int_{0}^{\pi/2} \sin(\phi) d\phi \int_{0}^{\infty} e^{-Kr^{2}} r^{2} dr$$

$$= 4\pi C^{3} \int_{0}^{\infty} r^{2} e^{-Kr^{2}} dr = \int_{0}^{\infty} \rho_{r} dr$$

$$= C^{3} \left(\frac{\pi}{K}\right)^{3/2}$$
(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. 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 (e.g.: $v \leftarrow r$) equation (17) becomes:

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

Which is the Maxwell-Boltzmann velocity distribution.