# Maxwell–Boltzmann distribution

In physics, particularly statistical mechanics, the **Maxwell–Boltzmann distribution** describes particle speeds in gases, where the particles move freely without interacting with one another, except for very brief elastic collisions in which they may exchange momentum and kinetic energy, but do not change their respective states of intramolecular excitation, as a function of the temperature of the system, the mass of the particle, and speed of the particle. Particle in this context refers to the gaseous atoms or molecules – no difference is made between the two in its development and result.[1]

It is a probability distribution (derived assuming isotropy) for the speed of a particle constituting the gas - the magnitude of its velocity vector, meaning that for a given temperature, the particle will have a speed selected randomly from the distribution, but is more likely to be within one range of some speeds than others.[2]

The Maxwell–Boltzmann distribution applies to ideal gases close to thermodynamic equilibrium with negligible quantum effects and at non-relativistic speeds. It forms the basis of the kinetic theory of gases, which provides a simplified explanation of many fundamental gaseous properties, including pressure and diffusion.[3] However - there is a generalization to relativistic speeds, see **Maxwell-Jüttner distribution** below.

The distribution is named after James Clerk Maxwell and Ludwig Boltzmann.

## Physical applications

Usually the Maxwell–Boltzmann distribution refers to molecular speeds, but also applies to the distribution of the momenta and energy of the molecules.

For 3-dimensional vector quantities, the components are treated independent and normally distributed with mean equal to 0 and standard deviation of $a$. If $X_i$ are distributed as $X \sim N(0, a^2)$, then

$$Z = \sqrt{X_1^2 + X_2^2 + X_3^2}$$

is distributed as a Maxwell–Boltzmann distribution with parameter $a$. Apart from the scale parameter $a$, the distribution is identical to the chi distribution with 3 degrees of freedom.

## Distributions (various forms)

The original derivation by Maxwell assumed all three directions would behave in the same fashion, but a later derivation by Boltzmann dropped this assumption using kinetic theory. The Maxwell–Boltzmann distribution (for energies) can now most readily be derived from the Boltzmann distribution for energies (see also the Maxwell–Boltzmann statistics of statistical mechanics):[1][4]

$$\frac{N_i}{N} = \frac{g_i \exp\left(-E_i/kT\right)}{\sum_j g_j \exp\left(-E_j/kT\right)} \qquad \textbf{(1)}$$

where:

- $i$ is the microstate (indicating one configuration particle quantum states - see partition function).
- $E_i$ is the energy level of microstate $i$.
- $T$ is the equilibrium temperature of the system.
- $g_i$ is the degeneracy factor, or number of degenerate microstates which have the same energy level
- $k$ is the Boltzmann constant.
- $N_i$ is the number of molecules at equilibrium temperature $T$, in a state $i$ which has energy $E_i$ and degeneracy $g_i$.
- $N$ is the total number of molecules in the system.

Note that sometimes the above equation is written without the degeneracy factor $g_i$. In this case the index $i$ will specify an individual state, rather than a set of $g_i$ states having the same energy $E_i$. Because velocity and speed are related to energy, Equation (**1**) can be used to derive relationships between temperature and the speeds of molecules in a gas. The denominator in this equation is known as the canonical partition function.

## Distribution for the momentum vector

The following is a derivation wildly different from the derivation described by James Clerk Maxwell and later described with fewer assumptions by Ludwig Boltzmann. Instead it is close to Boltzmann's later approach of 1877.

For the case of an "ideal gas" consisting of non-interacting atoms in the ground state, all energy is in the form of kinetic energy, and $g_\mathrm{i}$ is constant for all $i$. The relationship between kinetic energy and momentum for massive particles is

$$E = \frac{p^2}{2m} \qquad \textbf{(2)}$$

where $p^2$ is the square of the momentum vector $\mathbf{p} = [p_x, p_y, p_z]$. We may therefore rewrite Equation (**1**) as:

$$\frac{N_i}{N} = \frac{1}{Z}\exp\left[-\frac{p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2}{2mkT}\right] \qquad \textbf{(3)}$$

where $Z$ is the partition function, corresponding to the denominator in Equation (**1**). Here $m$ is the molecular mass of the gas, $T$ is the thermodynamic temperature and $k$ is the Boltzmann constant. This distribution of $N_\mathbf{i}/N$ is proportional to the probability density function $f_\mathbf{p}$ for finding a molecule with these values of momentum components, so:

$$f_\mathbf{p}(p_x, p_y, p_z) = \frac{c}{Z}\exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right] \qquad \textbf{(4)}$$

The normalizing constant $c$, can be determined by recognizing that the probability of a molecule having *some* momentum must be 1. Therefore the integral of equation (**4**) over all $p_x$, $p_y$, and $p_z$ must be 1.

It can be shown that:

$$c = \frac{Z}{(2\pi mkT)^{3/2}} \qquad \textbf{(5)}$$

Substituting Equation (**5**) into Equation (**4**) gives:

$$f_\mathbf{p}(p_x, p_y, p_z) = \left(\frac{1}{2\pi mkT}\right)^{3/2}\exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right] \qquad \textbf{(6)}$$

The distribution is seen to be the product of three independent normally distributed variables $p_x$, $p_y$, and $p_z$, with variance $mkT$. Additionally, it can be seen that the magnitude of momentum will be distributed as a Maxwell–Boltzmann distribution, with $a = \sqrt{mkT}$. The Maxwell–Boltzmann distribution for the momentum (or equally for the velocities) can be obtained more fundamentally using the H-theorem at equilibrium within the kinetic theory framework.

## Distribution for the energy

Using $p^2 = 2mE$, and the distribution function for the magnitude of the momentum (see below), we get the energy distribution:

$$f_E\,dE = f_p\left(\frac{dp}{dE}\right)\,dE = 2\sqrt{\frac{E}{\pi}}\left(\frac{1}{kT}\right)^{3/2}\exp\left[\frac{-E}{kT}\right]\,dE. \quad (7)$$

Since the energy is proportional to the sum of the squares of the three normally distributed momentum components, this distribution is a gamma distribution and a chi-squared distribution with three degrees of freedom.

By the equipartition theorem, this energy is evenly distributed among all three degrees of freedom, so that the energy per degree of freedom is distributed as a chi-squared distribution with one degree of freedom:[5]

$$f_\epsilon(\epsilon)\,d\epsilon = \sqrt{\frac{1}{\epsilon\pi kT}}\;\exp\left[\frac{-\epsilon}{kT}\right]\,d\epsilon$$

where $\epsilon$ is the energy per degree of freedom. At equilibrium, this distribution will hold true for any number of degrees of freedom. For example, if the particles are rigid mass dipoles, they will have three translational degrees of freedom and two additional rotational degrees of freedom. The energy in each degree of freedom will be described according to the above chi-squared distribution with one degree of freedom, and the total energy will be distributed according to a chi-squared distribution with five degrees of freedom. This has implications in the theory of the specific heat of a gas.

The Maxwell–Boltzmann distribution can also be obtained by considering the gas to be a type of quantum gas.

## Distribution for the velocity vector

Recognizing that the velocity probability density $f_\mathbf{v}$ is proportional to the momentum probability density function by

$$f_\mathbf{v} d^3v = f_\mathbf{p}\left(\frac{dp}{dv}\right)^3 d^3v$$

and using **p** = m**v** we get

$$f_\mathbf{v}(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left[-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}\right],$$

which is the Maxwell–Boltzmann velocity distribution. The probability of finding a particle with velocity in the infinitesimal element $[dv_x, dv_y, dv_z]$ about velocity $\mathbf{v} = [v_x, v_y, v_z]$ is

$$f_\mathbf{v}\left(v_x, v_y, v_z\right)\,dv_x\,dv_y\,dv_z.$$

Like the momentum, this distribution is seen to be the product of three independent normally distributed variables $v_x$, $v_y$, and $v_z$, but with variance $\frac{kT}{m}$. It can also be seen that the Maxwell–Boltzmann velocity distribution for the vector velocity $[v_x, v_y, v_z]$ is the product of the distributions for each of the three directions:

$$f_v\left(v_x, v_y, v_z\right) = f_v(v_x)f_v(v_y)f_v(v_z)$$

where the distribution for a single direction is

$$f_v(v_i) = \sqrt{\frac{m}{2\pi kT}}\exp\left[\frac{-mv_i^2}{2kT}\right].$$

Each component of the velocity vector has a normal distribution with mean $\mu_{v_x} = \mu_{v_y} = \mu_{v_z} = 0$ and standard deviation $\sigma_{v_x} = \sigma_{v_y} = \sigma_{v_z} = \sqrt{\frac{kT}{m}}$, so the vector has a 3-dimensional normal distribution, also called a "multinormal" distribution, with mean $\mu_\mathbf{v} = \mathbf{0}$ and standard deviation $\sigma_\mathbf{v} = \sqrt{\frac{3kT}{m}}$.

## Distribution for the speed

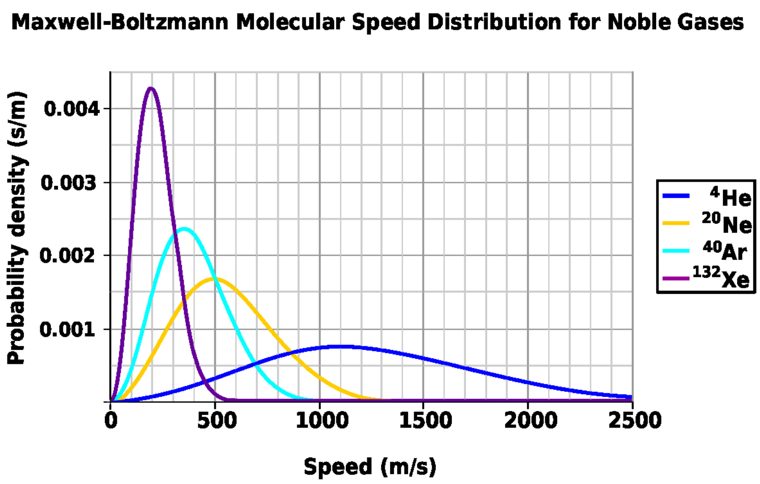
Usually, we are more interested in the speeds of molecules rather than their component velocities. The Maxwell–Boltzmann distribution for the speed follows immediately from the distribution of the velocity vector, above. Note that the speed is

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

and the increment of volume is

$$dv_x\, dv_y\, dv_z = v^2 \sin\phi\, dv\, d\theta\, d\phi$$

where $\theta$ and $\phi$ are the "course" (azimuth of the velocity vector) and "path angle" (elevation angle of the velocity vector). Integration of the normal probability density function of the velocity, above, over the course (from 0 to $2\pi$) and path angle (from 0 to $\pi$), with substitution of the speed for the sum of the squares of the vector components, yields the probability density function




The speed probability density functions of the speeds of a few noble gases at a temperature of 298.15 K (25 °C). The *y*-axis is in s/m so that the area under any section of the curve (which represents the probability of the speed being in that range) is dimensionless.

$$f(v) = \sqrt{\frac{2}{\pi}\left(\frac{m}{kT}\right)^3}\, v^2 \exp\left(\frac{-mv^2}{2kT}\right)$$

for the speed. This equation is simply the Maxwell distribution with distribution parameter $a = \sqrt{\frac{kT}{m}}$.

We are often more interested in quantities such as the average speed of the particles rather than the actual distribution. The mean speed, most probable speed (mode), and root-mean-square can be obtained from properties of the Maxwell distribution.

## Distribution for relative speed

Relative speed is defined as $u = \frac{v}{v_p}$, where $v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$ is the most probable speed. The distribution of relative speeds allows comparison of dissimilar gasses, independent of temperature and molecular weight.

## Typical speeds

Although the above equation gives the distribution for the speed or, in other words, the fraction of time the molecule has a particular speed, we are often more interested in quantities such as the average speed rather than the whole distribution.

The **most probable speed**, $v_p$, is the speed most likely to be possessed by any molecule (of the same mass *m*) in the system and corresponds to the maximum value or mode of *f*(*v*). To find it, we calculate *df*/*dv*, set it to zero and solve for *v*:

$$\frac{df(v)}{dv} = 0$$

which yields:

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

Where $R$ is the gas constant and $M = N_A\, m$ is the molar mass of the substance.

For diatomic nitrogen ($N_2$, the primary component of air) at room temperature (300 K), this gives $v_p = 422$m/s

The mean speed is the mathematical average of the speed distribution

$$\langle v \rangle = \int_0^\infty v\, f(v)\, dv = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \frac{2}{\sqrt{\pi}} v_p$$

The root mean square speed, $v_{\mathrm{rms}}$ is the square root of the average squared speed:

$$v_{\mathrm{rms}} = \left( \int_0^\infty v^2\, f(v)\, dv \right)^{1/2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3}{2}} v_p$$

The typical speeds are related as follows:

$$0.886 \langle v \rangle = v_p < \langle v \rangle < v_{\mathrm{rms}} = 1.085 \langle v \rangle.$$

## Distribution for relativistic speeds

As the gas becomes hotter and $kT$ approaches or exceeds $mc^2$, the probability distribution for $\gamma = 1/\sqrt{1 - v^2/c^2}$ in this relativistic Maxwellian gas is given by the Maxwell–Jüttner distribution[6]:

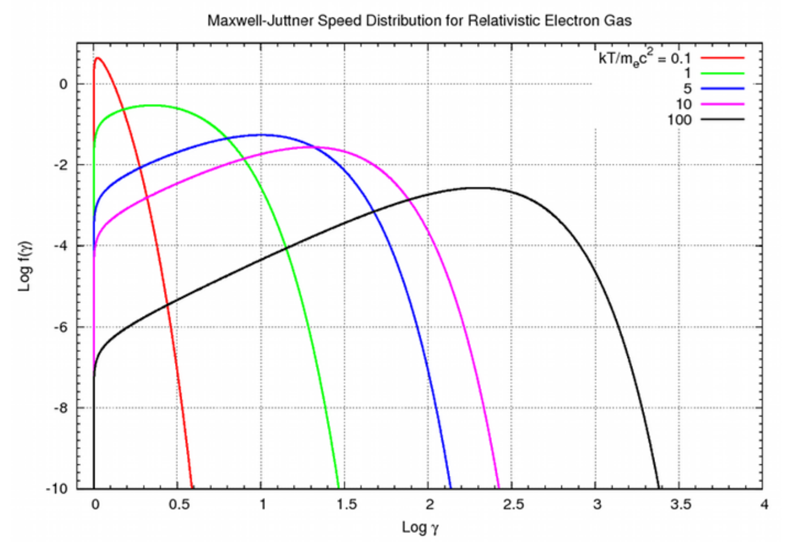
$$f(\gamma) = \frac{\gamma^2 \beta}{\theta K_2(1/\theta)} \exp\left( -\frac{\gamma}{\theta} \right)$$

where $\beta = \frac{v}{c} = \sqrt{1 - 1/\gamma^2}$, $\theta = \frac{kT}{mc^2}$, and $K_2$ is the modified Bessel function of the second kind.

Alternatively, this can be written in terms of the momentum as

$$f(p) = \frac{1}{4\pi m^3 c^3 \theta K_2(1/\theta)} \exp\left( -\frac{\gamma(p)}{\theta} \right)$$

where $\gamma(p) = \sqrt{1 + \left( \frac{p}{mc} \right)^2}$. The Maxwell–Jüttner equation is covariant, but not manifestly so, and the temperature of the gas does not vary with the gross speed of the gas.[7]



Maxwell–Jüttner speed distribution (relativistic Maxwellian) for electron gas at different temperatures

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## Further reading


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## External links

- "The Maxwell Speed Distribution" (http://demonstrations.wolfram.com/TheMaxwellSpeedDistribution/) from The Wolfram Demonstrations Project at Mathworld

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