Maxwell–Boltzmann distribution

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Maxwell–Boltzmann

Probability density function

Cumulative distribution function

Parameters $a > 0$

Support $x \in [0; \infty)$

PDF $\sqrt{\frac{2}{\pi}} \frac{x^2 e^{-x^2/(2a^2)}}{a^3}$

CDF $\text{erf} \left( \frac{x}{\sqrt{2}a} \right) - \sqrt{\frac{2}{\pi}} \frac{x e^{-x^2/(2a^2)}}{a}$

where $\text{erf}$ is the Error function
Mean $\mu = 2a\sqrt{\frac{2}{n}}$

Mode $\sqrt{2a}$

Variance $\sigma^2 = \frac{a^2(3\pi - 8)}{\pi}$

Skewness $\gamma_1 = \frac{2\sqrt{2}(16 - 5\pi)}{(3\pi - 8)^{3/2}}$

Ex. kurtosis $\gamma_2 = 4\left(\frac{-96 + 40\pi - 3\pi^2}{(3\pi - 8)^2}\right)$

Entropy $\frac{1}{2} - \gamma - \ln(a\sqrt{2\pi})$

In physics, particularly statistical mechanics, the Maxwell–Boltzmann distribution describes particle speeds in gases, where the particles move freely between short collisions, but do not interact with each other, 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 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-Juttner distribution below.

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

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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):

\[
\frac{N_i}{N} = \frac{g_i \exp(-E_i/kT)}{\sum_j g_j \exp(-E_j/kT)}
\]

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**

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 \( g_i \) is constant for all \( i \). The relationship between kinetic energy and momentum for massive particles is

\[
E = \frac{p^2}{2m}
\]

where \( p^2 \) is the square of the momentum vector \( p = [p_x, p_y, p_z] \). We may therefore rewrite Equation 1 as:
\[
\frac{N_i}{N} = \frac{1}{Z} \exp \left[ -\frac{p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2}{2m k T} \right]
\]  

(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 \( N_i/N \) is **proportional** to the **probability density function** \( f_p \) for finding a molecule with these values of momentum components, so:

\[
f_p(p_x, p_y, p_z) = \frac{c}{Z} \exp \left[ -\frac{p_x^2 + p_y^2 + p_z^2}{2m k T} \right].
\]  

(4)

The **normalizing constant** \( c \), can be determined by recognizing that the probability of a molecule having *any* 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:

\[
c = \frac{Z}{(2\pi m k T)^{3/2}}.
\]  

(5)

Substituting Equation 5 into Equation 4 gives:

\[
f_p(p_x, p_y, p_z) = \left( \frac{1}{2\pi m k T} \right)^{3/2} \exp \left[ -\frac{p_x^2 + p_y^2 + p_z^2}{2m k T} \right].
\]  

(6)

The distribution is seen to be the product of three independent **normally distributed** variables \( p_x, p_y, \) and \( p_z \), with variance \( m k T \). Additionally, it can be seen that the magnitude of momentum will be distributed as a Maxwell–Boltzmann distribution, with \( a = \sqrt{m k T} \). 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:

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

(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:\[^{[4]}\]

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

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 $f_v$ is proportional to the momentum probability density function by

$$f_v d^3v = f_p \left( \frac{dp}{dv} \right)^3 d^3v$$

and using $p = mv$ we get

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

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 $v = [v_x, v_y, v_z]$ is

$$f_v(v_x, v_y, v_z) \ d v_x \ d v_y \ d v_z.$$  

Like the momentum, this distribution is seen to be the product of three independent normally distributed $\frac{kT}{m}$ variables $v_x, v_y,$ and $v_z$, but with variance $\frac{m}{kT}$. 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:

$$f_v(v_x, v_y, v_z) = f_{v_x}(v_x) f_{v_y}(v_y) f_{v_z}(v_z),$$

where the distribution for a single direction is

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

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 $\mu_v = 0$ and standard deviation $\sigma_v = \sqrt{\frac{3kT}{m}}$.

**Distribution for the speed**
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.

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

$$dV = dV_x dV_y dV_z = v^2 \sin \phi \, dv \, d\theta \, d\phi$$

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

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

for the speed. This equation is simply the Maxwell distribution with distribution parameter

$$\alpha = \sqrt{\frac{kT}{m}}.$$

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**

$$u = \frac{v}{v_p}, \quad v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

Relative speed is defined as $u$, where $v_p$ 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:

\[
v_p = \sqrt{\frac{2kT}{nm}} = \sqrt{\frac{2RT}{M}}
\]

Where \( R \) is the gas constant and \( M = N A m \) is the molar mass of the substance.

For diatomic nitrogen (\( \text{N}_2 \), the primary component of air) at room temperature (300 K), this gives \( v_p = 422 \text{ m/s} \)

The mean speed is the mathematical average of the speed distribution

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

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

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

The typical speeds are related as follows:

\[
0.886 \langle v \rangle = v_p < \langle v \rangle < v_{rms} = 1.085 \langle v \rangle.
\]

**Distribution for relativistic speeds**
Maxwell–Juttner speed distribution (relativistic Maxwellian) for electron gas at different temperatures

As the gas becomes hotter and $kT$ approaches or exceeds $mc^2$, the probability distribution for

$$\gamma = 1/\sqrt{1 - u^2/c^2}$$

in this relativistic Maxwellian gas is given by the Maxwell–Juttner distribution[6]:

$$f(\gamma) = \frac{\gamma^2 \beta}{\theta K_2(1/\theta)} \exp \left( -\frac{\gamma}{\theta} \right)$$  \hspace{1cm} (11)

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–Juttner equation is covariant, but not manifestly so, and the temperature of the gas does not vary with the gross speed of the gas.[7]

See also

- Maxwell–Boltzmann statistics
- Boltzmann distribution
- Maxwell speed distribution
- Boltzmann factor
- Rayleigh distribution
- Ideal gas law
- James Clerk Maxwell
- Ludwig Eduard Boltzmann
- Kinetic theory

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Further reading


Maxwell–Boltzmann statistics

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Distribution of particle speed for $10^6$ oxygen particles at -100, 20 and 600 degrees Celsius. Speed distribution can be derived from Maxwell–Boltzmann distribution.

In statistical mechanics, Maxwell–Boltzmann statistics describes the statistical distribution of material particles over various energy states in thermal equilibrium, when the temperature is high enough and density is low enough to render quantum effects negligible.

The expected number of particles with energy $\varepsilon_i$ for Maxwell–Boltzmann statistics is $N_i$, where:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT}} = \frac{N}{Z} \cdot g_i e^{-\varepsilon_i/kT}$$

where:

- $N$ is the number of particles in state $i$
- $\varepsilon_i$ is the energy of the $i$-th state
- $g_i$ is the degeneracy of energy level $i$, the number of particle's states (excluding the "free particle" state) with energy $\varepsilon_i$
- $\mu$ is the chemical potential
- $k$ is Boltzmann's constant
- $T$ is absolute temperature
- $N$ is the total number of particles

$$N = \sum_i N_i$$

- $Z$ is the partition function

$$Z = \sum_i g_i e^{-\varepsilon_i/kT}$$

- $e^{(...)}$ is the exponential function

Equivalently, the distribution is sometimes expressed as
\[ N_i = \frac{1}{e^{(\varepsilon_i - \mu)/kT}} = \frac{N}{Z} e^{-\varepsilon_i/kT} \]

where the index \( i \) now specifies a particular state rather than the set of all states with energy \( \varepsilon_i \), and

\[ Z = \sum_i e^{-\varepsilon_i/kT} \]

Fermi–Dirac and Bose–Einstein statistics apply when quantum effects are important and the particles are "indistinguishable". Quantum effects appear if the concentration of particles \((N/V) \geq n_q\). Here \( n_q \) is the quantum concentration, for which the interparticle distance is equal to the thermal de Broglie wavelength, so that the wavefunctions of the particles are touching but not overlapping. Fermi–Dirac statistics apply to fermions (particles that obey the Pauli exclusion principle), and Bose–Einstein statistics apply to bosons. As the quantum concentration depends on temperature; most systems at high temperatures obey the classical (Maxwell–Boltzmann) limit unless they have a very high density, as for a white dwarf. Both Fermi–Dirac and Bose–Einstein become Maxwell–Boltzmann statistics at high temperature or at low concentration.

Maxwell–Boltzmann statistics are often described as the statistics of "distinguishable" classical particles. In other words the configuration of particle \( A \) in state 1 and particle \( B \) in state 2 is different from the case where particle \( B \) is in state 1 and particle \( A \) is in state 2. This assumption leads to the proper (Boltzmann) distribution of particles in the energy states, but yields non-physical results for the entropy, as embodied in the Gibbs paradox. This problem disappears when it is realized that all particles are in fact indistinguishable. Both of these distributions approach the Maxwell–Boltzmann distribution in the limit of high temperature and low density, without the need for any ad hoc assumptions. Maxwell–Boltzmann statistics are particularly useful for studying gases. Fermi–Dirac statistics are most often used for the study of electrons in solids. As such, they form the basis of semiconductor device theory and electronics.

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- 2 Another derivation (not as fundamental)
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### A derivation of the Maxwell–Boltzmann distribution

Suppose we have a container with a huge number of very small identical particles. Although the particles are identical, we still identify them by drawing numbers on them in the way lottery balls are being labelled with numbers and even colors.

All of those tiny particles are moving inside that container in all directions with great speed. Because the particles are speeding around, they do possess some energy. The Maxwell–Boltzmann distribution is a mathematical function that speaks about how many particles in the container have a certain energy.

It can be so that many particles have the same amount of energy \( \varepsilon_i \). The number of particles with the same energy \( \varepsilon_i \) is \( N_i \). The number of particles possessing another energy \( \varepsilon_j \) is \( N_j \). In physical speech this statement is lavishly inflated into something complicated which states that those many particles with the same energy \( \varepsilon_i \) all occupy a so called "energy level" \( \varepsilon_i \). The concept of energy level is used to graphically/mathematically describe and analyse the properties of particles and events experienced by them. Physicists take into consideration the ways particles arrange themselves and thus there is more than one way
of occupying an energy level and that's the reason why the particles were tagged like lottery ball, to know
the intentions of each one of them.

To begin with, let's ignore the degeneracy problem: assume that there is only one single way to put \( N_i \) particles into energy level, \( i \). What follows next is a bit of combinatorial thinking which has little to do in accurately describing the reservoir of particles.

The number of different ways of performing an ordered selection of one single object from \( N \) objects is obviously \( N \). The number of different ways of selecting two objects from \( N \) objects, in a particular order, is thus \( N(N-1) \) and that of selecting \( n \) objects in a particular order is seen to be \( N!/(N-n)! \). The number of ways of selecting 2 objects from \( N \) objects without regard to order is \( N(N-1)/2! \). It can be seen that the number of ways of selecting \( n \) objects from \( N \) objects without regard to order is the binomial coefficient: \( N!/(n!(N-n)!)) \). If we now have a set of boxes labelled \( a, b, c, d, e, ..., k \), then the number of ways of selecting \( N_a \) objects from a total of \( N \) objects and placing them in box \( a \), then selecting \( N_b \) objects from the remaining \( N-N_a \) objects and placing them in box \( b \), then selecting \( N_c \) objects from the remaining \( N-N_a-N_b \) objects and placing them in box \( c \), and continuing until no object is left outside is

\[
W = \frac{N!}{N_a!(N-N_a)!} \times \frac{(N-N_a)!}{N_b!(N-N_a-N_b)!} \times \frac{(N-N_a-N_b)!}{N_c!(N-N_a-N_b-N_c)!} \times \cdots \times \frac{N!}{N_k!(N-N_a-N_b-N_c-...-N_{k-1}-N_k)!}
\]

and because not even a single object is to be left outside the boxes, implies that the sum made of the terms \( N_a, N_b, N_c, N_d, N_e, ..., N_k \) must equal \( N \), thus the term \( (N-N_a-N_b-N_c-...-N_{i-1}-N_i)! \) in the relation above evaluates to \( 0! \). \((0!)=1\) which makes possible to write down that relation as

\[
W = \frac{N!}{\prod_{i=a,b,c,...}^{k} \frac{1}{N_i!}}
\]

Now going back to the degeneracy problem which characterize the reservoir of particles. If the \( i \)-th box has a "degeneracy" of \( g_i \), that is, it has \( g_i \) "sub-boxes", such that any way of filling the \( i \)-th box where the number in the sub-boxes is changed is a distinct way of filling the box, then the number of ways of filling the \( i \)-th box must be increased by the number of ways of distributing the \( N_i \) objects in the \( g_i \) "sub-boxes".
Summary recap of the case of $N_i$ particles above, ignoring degeneracy.

The number of ways of placing $N_i$ distinguishable objects in $g_i$ "sub-boxes" is $g_i^{N_i}$. Thus the number of ways that a total of $N$ particles can be classified into energy levels according to their energies, while each level $g_i$ having $g_i$ distinct states such that the $i$-th level accommodates $N_i$ particles is:

$$W = \frac{N!}{N_a!(N - N_a)!} \times \frac{(N - N_a)!}{N_b!(N - N_a - N_b)!} \times \frac{(N - N_a - N_b)!}{N_c!(N - N_a - N_b - N_c)!} \times \ldots$$

$$\times \frac{(N - \ldots - N_i)!}{N_k!(N - \ldots - N_i - N_k)!} =$$

$$= \frac{N!}{N_a!N_b!N_c!\ldots N_k!(N - \ldots - N_i - N_k)!}$$

$$W = N! \prod_{i=a,b,c,...}^k \frac{1}{N_i!}$$

The number of ways of placing $N_i$ distinguishable objects in $g_i$ "sub-boxes" is $g_i^{N_i}$. Thus the number of ways $W$ that a total of $N$ particles can be classified into energy levels according to their energies, while each level $g_i$ having $g_i$ distinct states such that the $i$-th level accommodates $N_i$ particles is:

$$W = N! \prod_{i=a,b,c,...}^k \frac{g_i^{N_i}}{N_i!}$$

This is the form for $W$ first derived by Boltzmann. Boltzmann's fundamental equation $S = k \ln W$ relates the thermodynamic entropy $S$ to the number of microstates $W$, where $k$ is the Boltzmann constant. It was pointed out by Gibbs however, that the above expression for $W$ does not yield an extensive entropy, and is therefore faulty. This problem is known as the Gibbs paradox. The problem is that the particles considered by the above equation are not indistinguishable. In other words, for two particles $(A$ and $B$) in two energy sublevels the population represented by $[A,B]$ is considered distinct from the population $[B,A]$ while for indistinguishable particles, they are not. If we carry out the argument for indistinguishable particles, we are led to the Bose-Einstein expression for $W$:

$$W = \prod_{i} \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$$

Both the Maxwell-Boltzmann distribution and the Bose-Einstein distribution are only valid for temperatures well above absolute zero, implying that $g_i \gg 1$. The Maxwell-Boltzmann distribution also requires low density, implying that $g_i \gg N_i$. Under these conditions, we may use Stirling's approximation for the factorial:

$$N! \approx N^N e^{-N}.$$
Using the fact that \((1 + N_i/g_i)^{g_i} \approx e^{N_i} \) for \(g_i \gg N_i\) we can again use Stirlings approximation to write:

\[
W \approx \prod_i \frac{(N_i + g_i)^{N_i + g_i}}{N_i^{N_i} g_i^{g_i}} \approx \prod_i \frac{g_i^{N_i}(1 + N_i/g_i)^{g_i}}{N_i^{N_i}}
\]

This is essentially a division by \(N!\) of Boltzmann's original expression for \(W\), and this correction is referred to as **correct Boltzmann counting**.

We wish to find the \(N_i\) for which the function \(W\) is maximized, while considering the constraint that there is a fixed number of particles \((N = \sum N_i)\) and a fixed energy \((E = \sum N_i \varepsilon_i)\) in the container. The maxima of \(W\) and \(\ln(W)\) are achieved by the same values of \(N_i\), and, since it is easier to accomplish mathematically, we will maximize the latter function instead. We constrain our solution using **Lagrange multipliers** forming the function:

\[
f(N_1, N_2, \ldots, N_n) = \ln(W) + \alpha(N - \sum N_i) + \beta(E - \sum N_i \varepsilon_i)
\]

\[
\ln W = \ln \left[ \prod_{i=1}^n \frac{g_i^{N_i}}{N_i!} \right] \approx \sum_{i=1}^n (N_i \ln g_i - N_i \ln N_i + N_i)
\]

Finally

\[
f(N_1, N_2, \ldots, N_n) = \alpha N + \beta E + \sum_{i=1}^n (N_i \ln g_i - N_i \ln N_i + N_i - (\alpha + \beta \varepsilon_i) N_i)
\]

In order to maximize the expression above we apply **Fermat's theorem (stationary points)**, according to which local extrema, if exist, must be at critical points (partial derivatives vanish):

\[
\frac{\partial f}{\partial N_i} = \ln g_i - \ln N_i - (\alpha + \beta \varepsilon_i) = 0
\]

By solving the equations above \((i = 1 \ldots n)\) we arrive to an expression for \(N_i\):

\[
N_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i}}
\]

Substituting this expression for \(N_i\) into the equation for \(\ln W\) and assuming that \(N \gg 1\) yields:

\[
\ln W = \alpha N + \beta E
\]

or, differentiating and rearranging:

\[
dE = \frac{1}{\beta} d\ln W - \frac{\alpha}{\beta} dN
\]
Boltzmann realized that this is just an expression of the second law of thermodynamics. Identifying $dE$ as the internal energy, the second law of thermodynamics states that for variation only in entropy ($S$) and particle number ($N$):

$$dE = T \, dS + \mu \, dN$$

where $T$ is the temperature and $\mu$ is the chemical potential. Boltzmann's famous equation $S = k \ln W$ is the realization that the entropy is proportional to $\ln W$ with the constant of proportionality being Boltzmann's constant. It follows immediately that $\beta = 1/kT$ and $\alpha = -\mu/kT$ so that the populations may now be written:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT}}$$

Note that the above formula is sometimes written:

$$N_i = \frac{g_i}{e^{\varepsilon_i/kT}/Z}$$

where $Z = \exp(\mu/kT)$ is the absolute activity.

Alternatively, we may use the fact that

$$\sum_i N_i = N$$

to obtain the population numbers as

$$N_i = N \frac{g_i e^{-\varepsilon_i/kT}}{Z}$$

where $Z$ is the partition function defined by:

$$Z = \sum_i g_i e^{-\varepsilon_i/kT}$$

**Another derivation (not as fundamental)**

In the above discussion, the Boltzmann distribution function was obtained via directly analysing the multiplicities of a system. Alternatively, one can make use of the canonical ensemble. In a canonical ensemble, a system is in thermal contact with a reservoir. While energy is free to flow between the system and the reservoir, the reservoir is thought to have infinitely large heat capacity as to maintain constant temperature, $T$, for the combined system.

In the present context, our system is assumed to have the energy levels $\varepsilon_i$ with degeneracies $g_i$. As before, we would like to calculate the probability that our system has energy $\varepsilon_i$.

If our system is in state $S_1$, then there would be a corresponding number of microstates available to the reservoir. Call this number $\Omega_R(S_1)$. By assumption, the combined system (of the system we are interested in and the reservoir) is isolated, so all microstates are equally probable. Therefore, for instance, if $\Omega_R(S_1) = 2 \Omega_R(S_2)$, we can conclude that our system is twice as likely to be in state $S_1$ than $S_2$. In general, if $P(S_i)$ is the probability that our system is in state $S_i$.
\[
\frac{P(s_1)}{P(s_2)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)}.
\]

Since the entropy of the reservoir \( S_R = k \ln \Omega_R \), the above becomes

\[
\frac{P(s_1)}{P(s_2)} = \frac{e^{S_R(s_1)/k}}{e^{S_R(s_2)/k}} = e^{(S_R(s_1) - S_R(s_2))/k}.
\]

Next we recall the thermodynamic identity (from the first law of thermodynamics):

\[
dS_R = \frac{1}{T} (dU_R + P \, dV_R - \mu \, dN_R)
\]

In a canonical ensemble, there is no exchange of particles, so the \( dN_R \) term is zero. Similarly, \( dV_R = 0 \). This gives

\[
S_R(s_1) - S_R(s_2) = \frac{1}{T} (U_R(s_1) - U_R(s_2)) = -\frac{1}{T} (E(s_1) - E(s_2)).
\]

where \( U_R(s_i) \) and \( E(s_i) \) denote the energies of the reservoir and the system at \( s_i \), respectively. For the second equality we have used the conservation of energy. Substituting into the first equation relating \( P(s_1), P(s_2) \):

\[
\frac{P(s_1)}{P(s_2)} = \frac{e^{-E(s_1)/kT}}{e^{-E(s_2)/kT}}.
\]

which implies, for any state \( s \) of the system

\[
P(s) = \frac{1}{Z} e^{-E(s)/kT},
\]

where \( Z \) is an appropriately chosen "constant" to make total probability 1. (\( Z \) is constant provided that the temperature \( T \) is invariant.) It is obvious that

\[
Z = \sum_s e^{-E(s)/kT},
\]

where the index \( s \) runs through all microstates of the system. \( Z \) is sometimes called the Boltzmann sum over states (or "Zustandssumme" in the original German). If we index the summation via the energy eigenvalues instead of all possible states, degeneracy must be taken into account. The probability of our system having energy \( \varepsilon \) is simply the sum of the probabilities of all corresponding microstates:

\[
P(\varepsilon) = \frac{1}{Z} g_i e^{-\varepsilon_i/kT}
\]

where, with obvious modification,

\[
Z = \sum_j g_j e^{-\varepsilon_j/kT},
\]

this is the same result as before.
Comments

- Notice that in this formulation, the initial assumption "... suppose the system has total N particles..." is dispensed with. Indeed, the number of particles possessed by the system plays no role in arriving at the distribution. Rather, how many particles would occupy states with energy $\varepsilon_i$ follows as an easy consequence.

- What has been presented above is essentially a derivation of the canonical partition function. As one can tell by comparing the definitions, the Boltzmann sum over states is really no different from the canonical partition function.

- Exactly the same approach can be used to derive Fermi–Dirac and Bose–Einstein statistics. However, there one would replace the canonical ensemble with the grand canonical ensemble, since there is exchange of particles between the system and the reservoir. Also, the system one considers in those cases is a single particle state, not a particle. (In the above discussion, we could have assumed our system to be a single atom.)

Limits of applicability

The Bose–Einstein and Fermi–Dirac distributions may be written:

$$N_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT} + 1}.$$  

Assuming the minimum value of $\varepsilon_i$ is small, it can be seen that the condition under which the Maxwell–Boltzmann distribution is valid is when

$$e^{-\mu/kT} \gg 1.$$  

For an ideal gas, we can calculate the chemical potential using the development in the Sackur–Tetrode article to show that:

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{S,V} = -kT \ln \left( \frac{V}{N\Lambda^3} \right)$$

where $E$ is the total internal energy, $S$ is the entropy, $V$ is the volume, and $\Lambda$ is the thermal de Broglie wavelength. The condition for the applicability of the Maxwell–Boltzmann distribution for an ideal gas is again shown to be

$$\frac{V}{N\Lambda^3} \gg 1.$$  

See also

- Bose–Einstein statistics
- Fermi–Dirac statistics

References

Bibliography
Let's look at our good friend the Gaussian integral. If you're in a statistical mechanics course, you are going to become a master of these things by the time you're done.

Okay, so

\[ I(\alpha) = \int_{-\infty}^{\infty} dx \, e^{-\alpha x^2} \]

Let's square it. Then we get that

\[ I(\alpha)^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \, e^{-\alpha(x^2 + y^2)} \]

After making a change of coordinates to polar and integrating over the entire plane, we get that the integral is given by

\[ I(\alpha) = \frac{\pi}{\sqrt{\alpha}} \]

Okay, but what about terms like \(x^2\)? Well...

\[ \int x^2 e^{-\alpha x^2} = -\frac{d}{d\alpha} I(\alpha) \]

Which then means that

\[ \int x^2 e^{-\alpha x^2} = -\frac{d}{d\alpha} I(\alpha) \]

This works for all even powers. This is a rather handy trick to know, and is pretty standard.

**Terms and Formulae**

**Terms**

- **Boltzmann constant** - A constant, \( k \), involved in the equation for average velocity. \( k = 1.38 \times 10^{-23} \) J/K

- **Diffusion** - Diffusion is the spread of one substance through another.

- **Effusion** - Effusion is the rate at which a gas passes through a small hole into a vacuum.

- **Kinetic energy** - \( E_k = \frac{1}{2}mv^2 \)

- **Kinetic molecular theory** - A theory that models the interaction between individual gas molecules. See the summary for more details.

- **Maxwell-Boltzmann speed distribution** - The distribution attained when molecule speed is set against the number of molecules sharing that speed.

- **Mean free path** - The mean distance a molecule travels before it impacts another molecule; given the huge number of collisions in a gas, the mean free path is vastly smaller than any typical room or container. The equation for mean free path:

\[
\lambda = \frac{V}{\sqrt{2\pi d^2 N}}
\]
\( m_p \) - The most probable velocity at which the most molecules in a gas travel. The formula for most probable velocity is:

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

**Root mean square velocity** - An equation to measure the typical velocity of molecules in a gas.

\[
v_{rms} = \sqrt{\frac{2}{3}} \sqrt{\frac{RT}{M}} = \sqrt{\frac{2}{3}} \sqrt{\frac{kT}{m}}
\]

**Formulae**

Average velocity \( \bar{v} \)

\[
\bar{v} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}
\]

Kinetic energy

\[
E_k = \frac{1}{2} mv^2
\]

Mean free path

\[
\lambda = \sqrt{\frac{2m d^2 N}{}}
\]

Formule for most probable velocity

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

Formula for root mean square velocity

\[
v_{rms} = \sqrt{\frac{2}{3}} \sqrt{\frac{RT}{M}} = \sqrt{\frac{2}{3}} \sqrt{\frac{kT}{m}}
\]
Maxwell–Boltzmann distribution

Maxwell–Boltzmann

Probability density function

Cumulative distribution function

Parameters $\alpha > 0$

Support $x \in [0; \infty)$
In physics, particularly statistical mechanics, the Maxwell–Boltzmann distribution describes particle speeds in gases, where the particles move freely between short collisions, but do not interact with each other, 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 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-Juttner distribution below.

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

### Contents

- **Physical applications**
- **Distributions (various forms)**
  - Distribution for the momentum vector
  - Distribution for the energy
  - Distribution for the velocity vector
  - Distribution for the speed
  - Distribution for relative speed
  - Typical speeds
  - Distribution for relativistic speeds
- **See also**
- **References**
- **Further reading**
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):

\[
\frac{N_i}{N} = \frac{g_i \exp \left( -\frac{E_i}{kT} \right)}{\sum_j g_j \exp \left( -\frac{E_j}{kT} \right)}
\]

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

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 \( g_i \) is constant for all \( i \). The relationship between kinetic energy and momentum for massive particles is
where $p^2$ is the square of the momentum vector $p = [p_x, p_y, p_z]$. We may therefore rewrite Equation 1 as:

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

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 $N_i/N$ is proportional to the probability density function $f_p$ for finding a molecule with these values of momentum components, so:

$$f_p(p_x, p_y, p_z) = \frac{c}{Z} \exp \left[ -\frac{p_{x}^2 + p_{y}^2 + p_{z}^2}{2mkT} \right]. \quad (4)$$

The normalizing constant $c$, can be determined by recognizing that the probability of a molecule having any 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:

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

Substituting Equation 5 into Equation 4 gives:

$$f_p(p_x, p_y, p_z) = \frac{1}{(2\pi mkT)^{3/2}} \exp \left[ -\frac{p_{x}^2 + p_{y}^2 + p_{z}^2}{2mkT} \right]. \quad (6)$$

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

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 \( f_v \) is proportional to the momentum probability density function by

\[ f_v d^3v = f_p \left( \frac{dp}{dv} \right)^3 d^3v \]

and using \( p = mv \) we get

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

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 \( v = [v_x, v_y, v_z] \) is

\[ f_v(v_x, v_y, v_z) \, dv_x \, dv_y \, dv_z. \]

Like the momentum, this distribution is seen to be the product of three independent normally distributed \( k/T \) variables \( v_x, v_y, \) and \( v_z \), but with variance \( m \). 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:

\[ f_v(v_x, v_y, v_z) = f_{v_x}(v_x) f_{v_y}(v_y) f_{v_z}(v_z) \]

where the distribution for a single direction is

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

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 \( \mu_v = 0 \) and standard deviation \( \sigma_v = \sqrt{\frac{3kT}{m}} \).

**Distribution for the speed**

\[
\begin{align*}
\text{Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases} \\
\text{Speed (m/s)} & \quad \text{Probability density (s/m)} \\
0 & \quad 0.001 \\
500 & \quad 0.002 \\
1000 & \quad 0.003 \\
1500 & \quad 0.004 \\
2000 & \quad 0.005 \\
2500 & \quad 0.006 \\
\end{align*}
\]

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.

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

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

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 \( v_p = 422 \text{ m/s} \).

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**, \( v_{\text{rms}} \) is the square root of the average squared speed:

\[
v_{\text{rms}} = \left( \int_{0}^{\infty} v^2 f(v) \, dv \right)^{1/2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3}{2}} v_p
\]

The typical speeds are related as follows:

\[
0.886\langle v \rangle = v_p < \langle v \rangle < v_{\text{rms}} = 1.085\langle v \rangle.
\]

**Distribution for relativistic speeds**
Maxwell–Juttner speed distribution (relativistic Maxwellian) for electron gas at different temperatures

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

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

(11)

where $\beta = \frac{v}{c} = \sqrt{1 - 1/\gamma^2} \theta = \frac{kT}{me^2}$ and $K_2\delta$ 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 $\gamma(p) = \sqrt{1 + \left(\frac{p}{me}\right)^2}$. The Maxwell–Juttner equation is covariant, but not manifestly so, and the temperature of the gas does not vary with the gross speed of the gas.\[11\]

### 4.9 The ideal gas

**Take-home message:** We can now derive the equation of state and other properties of the ideal gas.

We are now reaching the most important test of statistical physics: the ideal gas. For the moment we assume it is monatomic; the extra work for a diatomic gas is minimal.

**Remember** the one-particle translational partition function, at any attainable temperature, is

$$Z_1 = V \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2} \equiv V n_Q.$$
From this we can obtain the average energy per particle, \(\frac{3}{2}k_B T\), and since the particles are non-interacting, the energy of \(N\) particles in a box is just \(\frac{3}{2}Nk_B T\). This could be obtained from the expression we previously used for the \(N\)-particle partition function, 

\[Z_N = Z_1^N\,.
\]

But if we follow this through and calculate the Helmholtz free energy and the entropy, we find that the results do not make sense: specifically, if one has double the number of particles, in double the volume, the entropy and the Helmholtz free energy, like the energy, should double. These are extensive variables. But if we go ahead and calculate based on \(Z_N = Z_1^N\), we do not get extensive results, but terms like \(V \ln N\).

However we shouldn't have expected \(Z_N = Z_1^N\) to work, because the derivation was based on the idea that every one of the \(N\) particles was distinguishable. But at a completely fundamental level, every molecule is exactly the same as every other molecule of the same substance.

The exact form of \(Z_N\) in this case has no compact form. But there is an approximation which becomes exact in the limit of low number densities \(n \equiv N/V\): specifically \(n \ll n_Q\), where \(n_Q \equiv (mk_B T/2\pi \hbar^2)^{3/2}\) is the "quantum concentration" and is a measure of the number of energy levels available. The significance of this limit is that it is very unlikely that any two atoms are in the same energy level. This is called the classical limit.

\[Z_N = \frac{(Z_1)^N}{N!}\]

More details of how this works here.

Now, using Stirling’s approximation \(\ln(N!) \approx N \ln N - N\), we find

\[\langle F \rangle = -k_B T \ln Z_N = -Nk_B T (\ln Z_1 - \ln N + 1)\]

\[= -Nk_B T \left[ \ln \left( \frac{V}{N} \right) + \ln \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} + 1 \right]\]

\[= Nk_B T \left[ \ln \left( \frac{n}{n_Q} \right) - 1 \right].\]

Also

\[P = -\left( \frac{\partial F}{\partial V} \right)_{T,N}\]

\[= \frac{Nk_B T}{V}\]
and

$$S = -\left( \frac{\partial F}{\partial T} \right)_{V,N} = -Nk_B \left[ \ln \left( \frac{n}{n_Q} \right) - 1 \right] + Nk_B T \frac{dnQ}{dT} = Nk_B \left[ \ln \left( \frac{nQ}{n} \right) + \frac{5}{2} \right]$$  

The Sackur-Tetrode Equation

Since \( n_Q \) is composed only of constants and \( T \), it is intensive; the number density \( n \equiv V/N \) is the ratio of extensive quantities and so is also intensive. Hence \( F \) and \( S \) are clearly simply proportional to \( N \), and so extensive as required, and \( P \) is intensive. Since \( n_Q \gg n \) if the result is to be valid, \( S \) is also positive, as it should be!

The expression for \( P \) is clearly experimentally verifiable: it is the ideal gas law. That's good, but we expected to get that. More interestingly the Sackur-Tetrode equation for \( S \) can also be checked. First, if we unpick the dependence on \( V \) and \( T \), we get

$$S = Nk_B (\ln V + \frac{3}{2} \ln T + \text{const.})$$

which is in accord with the form derived from classical thermodynamics (see here). But more importantly it predicts the absolute entropy of a gas at a certain temperature, and this can be checked experimentally too. If we start with the solid at some very low temperature \( T_0 \), at which the entropy can be assumed to be very small, and we know the experimental specific heat capacity as a function of temperature and the latent heats of melting and vaporisation, we can numerically calculate the integral

$$\int_{T_0}^{T} \frac{dQ}{T} = S(T) - S(T_0) \approx S(T)$$

Good agreement is found. An example with numerical details can be found on pages 5&6 here, from Edward J. Groth of Princeton University.

Finally, we include vibrations and rotations as well as translations: since the one-particle energies are independent and add, \( \varepsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} \), the partition functions multiply: \( Z_1 = Z_{1tr} Z_{1rot} Z_{1vib} \) (the argument is like that for the \( N \)-particle partition function for distinguishable particles here) and so

$$Z_N = \frac{(Z_{1tr}^N)^N (Z_{1rot}^N)^N (Z_{1vib}^N)^N}{N!} = Z_{Ntr} (Z_{1rot}^N)^N (Z_{1vib}^N)^N$$

$$F = F_{tr} + F_{rot} + F_{vib}$$
and the energy and entropy also add.

References

- **Mandl** 7.1,7.4-6
- **Bowley and Sánchez** 6.5
- **Kittel and Kroemer** 3

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**The N-particle partition function for distinguishable particles**

Let's start with two spins. There are four states of the whole system, \( \uparrow \uparrow \) with energy \(-2\mu B\), \( \uparrow \downarrow \) and \( \downarrow \uparrow \), both with energy zero, and \( \downarrow \downarrow \) with energy \(2\mu B\). Thus the two-particle partition function is

\[
Z_2 = e^{2\mu B} + e^0 + e^{2\mu B} = e^{2\mu B} + 2 + e^{-2\mu B} \\
= (e^{\mu B} + e^{-\mu B})^2 = (Z_1)^2
\]

In general, for \( N \) particles, the energies range through \(-N\mu B, -(N-2)\mu B, \ldots, -(N-2n_i)\mu B, \ldots, N\mu B\) with there being \(N!/n_i!(N-n_i)!\) separate states with \(n_i\) down-spins. So

\[
Z_N = e^{-N\mu B} + \ldots + \frac{N!}{n_i!(N-n_i)!}e^{-(N-2n_i)\mu B} + \ldots + e^{N\mu B} \\
= (e^{-\mu B} + e^{\mu B})^N = (Z_1)^N
\]

There is a caveat, which can be ignored on first reading. The argument says that there are a number of different states with the same number of down spins. Since the spins are arranged on a lattice, this is correct; every spin can be distinguished from every other spin by its position. When we go on to consider a gas, however, this is no longer so, and the relation between \( Z_1 \) and \( Z_N \) changes. The treatment for indistinguishable particles is [here](#).

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**The N particle partition function for indistinguishable particles.**

Before reading this section, you should read over the [derivation](#) of which held for the paramagnet, where all \( N \) particles were distinguishable (by their position in the lattice).
Consider first the simplest case, of two particles and two energy levels. If the particles are distinguishable, as in the upper picture below, there are four states, two of which have energy $\varepsilon$, and the two-particle partition function is

$$Z_2 = e^0 + 2e^{-\varepsilon \beta} + e^{-2\varepsilon \beta} = (Z_1)^2$$

If the particles are indistinguishable, however, there are only three states, as in the lower picture, and the partition function is

$$Z_2 = e^0 + e^{-\varepsilon \beta} + e^{-2\varepsilon \beta} \neq (Z_1)^2$$

If we use $(Z_1)^2$, we over-count the state in which the particles are in different energy levels. In general there is no simple expression for the $N$-particle partition function for indistinguishable particles. However we note that $(Z_1)^N$ over-counts the states in which all $N$ particles are in different energy levels by exactly $N!$. So if we are in a position where there are many more accessible energy levels (that is, levels with energy less than a few $k_B T$) than there are particles, the probability of any two particles being in the same energy level is small, and almost all states will have all the particles in different levels. Hence a good approximation is

$$Z_N = \frac{(Z_1)^N}{N!}.$$

In the ideal gas, we can calculate the number of levels below, say, $2k_B T$, from $\int_0^{k_{\text{max}}} D(k) dk$ with $\hbar^2 k_{\text{max}}^2/2m = 2k_B T$, giving $2.1 n_Q V$. So we see that $n_Q$ is a measure of the number of states available, and we can use the approximation provided $n_Q V \gg N$ (or $n_Q \gg n$). This is the classical limit.
It is worth noting that, assuming a truly ideal gas which never condenses or solidifies, the Sackur-Tetrode equation is not valid for indefinitely low temperatures. It must be wrong, because as $T \to 0$, $n_Q \to 0$ and $S \to -\infty$.

But we know that $S \to 0$ as $T \to 0$, because all the particles occupy the lowest energy level. But of course that is exactly the regime in which $Z_N = (Z_1)^N/N!$ is no longer valid.

For a gas with the density of air at STP, $n \approx 3 \times 10^{25} \text{ m}^{-3}$. We have $n_Q \approx n$ for $T \approx 10^{-2} \text{ K}$, so real gases are essentially always classical.

Note too that $n_Q \approx 1/\lambda^3$, where $\lambda$ is the wavelength of a particle with energy $\frac{3}{2} k_B T$. This implies that the classical limit holds if the particle separation is large compared with their wavelength--a reasonable-sounding statement! (See the first tutorial sheet of last semester, PC210 qu. 1(b-d)).

An example of a non-classical gas is the conduction electrons in a metal; they are free to move within the metal and can be treated as a dense gas ($n \approx 10^{26} \text{ m}^{-3}$), but at room temperature $n_Q \approx 10^{27} \text{ m}^{-3}$. So the quantum nature of the electron (specifically the fact that it is a fermion) becomes all important.

### 4.10 The Maxwell-Boltzmann Distribution

**Take-home message:** The density of states can be used to derive the Maxwell-Boltzmann distribution of molecular speeds in a gas.

The speed $v$ of a particle is related to the wavenumber $k$ by $mv = \hbar k$. We already know the probability of a particle having $k$ in the range $k \to k + dk$, and so we can immediately write down the corresponding probability of the speed being in the range $v \to dv$:

$$P(k \to k + dk) = \frac{D(k) e^{-\varepsilon(k)/\beta}}{Z_1} dk$$

where $\varepsilon(k) = \hbar^2 k^2 / 2m$.

$$P(v \to v + dv) = \frac{V}{2\pi^2} \frac{e^{-\varepsilon(v)/\beta}}{Z_1} \left( \frac{m}{\hbar} \right)^3 v^2 dv$$

$\Rightarrow P(v) = \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$

This is called the Maxwell-Boltzmann distribution, and it is plotted below.
We can find the most probable speed (from \(dP(v)/dv = 0\)), as well as the mean speed and the rms speed:

\[
\begin{align*}
v_p &= \sqrt{\frac{2 k_B T}{m}} \approx 1.41 \sqrt{\frac{k_B T}{m}} \\
\langle v \rangle &= \sqrt{\frac{8 k_B T}{\pi m}} \approx 1.60 \sqrt{\frac{k_B T}{m}} \\
v_{\text{rms}} &= \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}} \approx 1.73 \sqrt{\frac{k_B T}{m}}
\end{align*}
\]

These are marked on the graph above.

Note that \(\hbar\) has disappeared from \(P(v)\), which can be derived from the Boltzmann distribution in a purely classical theory provided the normalisation is obtained from requiring the integral of \(P(v)\) to be one.

References

- Mandl 7.7
- Bowley and Sánchez 7.4
- Kittel and Kroemer 14

Gaussian Integrals – even powers \(e^{-\alpha x^n}\) where \(n\) is even:
\[ I(\alpha) = \int_{-\infty}^{\infty} dx e^{-\alpha x^2} \]

Let's square it. Then we get that
\[ I(\alpha)^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{-\alpha (x^2 + y^2)} \]

After making a change of coordinates to polar and integrating over the entire plane, we get that the integral is given by
\[ I(\alpha) = \sqrt{\pi/\alpha} \]

Okay, but what about terms like \( x^n \)? Well...
\[ \int x^2 e^{-\alpha x^2} = \int -\frac{d}{d\alpha} e^{-\alpha x^2} \]

Which then means that
\[ \int x^2 e^{-\alpha x^2} = -\frac{\partial}{\partial \alpha} I(\alpha) \]

This works for all even powers. This is a rather handy trick to know, and is pretty standard.