Systems of Many Particles: The Maxwell–Boltzmann Distribution

This section derives the velocity distribution of particles of any kind that have translational kinetic energy because they are in thermal equilibrium. You (or your instructor) may wish to skip this section, since it has no direct biological application. It is included for completeness and to show an example of probability distributions in several variables, which are sometimes found in biological problems. The result obtained in this section is used in Sec. 3.10 to derive an important theorem about the equipartition of energy.

It was shown that the probability ratio for a particle to have energy \( U_r \) or \( U_s \) is given by Eq. 3.28:

\[
P(U_s)/P(U_r) = \left[ \Omega(U_s)/\Omega(U_r) \right] e^{-(U_r-U_s)/k_B T}.
\]

For the discussion of the Nernst equation and the atmosphere, the factor \( \Omega(U_s)/\Omega(U_r) \) was set equal to unity without any real justification. This section examines that factor in the classical limit—when the energy levels are so closely spaced that classical physics can be used.

To simplify the notation, suppose that the zero of the energy scale is picked so that \( U_r = 0 \). Then Eq. 3.28 becomes

\[
P(U_s) = \frac{P(0)}{\Omega(0)} \Omega(U_s) e^{-U_s/k_B T}.
\]
When the levels become very closely spaced, it is impossible to identify which level the particle is in. Instead, it is necessary to speak of a range of energy between \( U \) and \( U + \Delta U \). In this case, \( P(U)\Delta U \) is the probability that the particle has energy in the interval, and \( \Omega(U,\Delta U) \) is the number of microstates in the interval:

\[
P(U)\Delta U = \frac{P(0)}{\Omega(0)} \Omega(U,\Delta U) e^{-U/k_BT}.
\]

The factor \( \Omega(U,\Delta U) \) is the number of microstates in which the particle can be when its energy is between \( U \) and \( U + \Delta U \). We state the result and then try to make it plausible. The factor is

\[
\Omega(U,\Delta U) = \frac{\Delta p_x\Delta p_y\Delta p_z \Delta x\Delta y\Delta z}{h^3},
\]

where \( p_x = mv_x \) is the \( x \) component of the particles momentum, etc., and \( x, y, z \) are its location in space. The factor \( h \) is Planck’s constant \( h \) divided by \( 2\pi \):

\[
h = 1.0545727 \times 10^{-34} \text{ J s}.
\]

This result for \( \Omega \) includes only energy resulting from translation, that is, for a particle moving in three dimensions in a box or in solution. Additional microstates corresponding to rotation and other internal motions may be important in extended bodies such as molecules.

Here are some justifications for Eq. 103.2. In classical mechanics the state of a particle undergoing translational motion in three dimensions is specified at any instant by its position \((x,y,z)\) and velocity or momentum \((p_x,p_y,p_z)\). Its subsequent motion can be calculated if its initial position and momentum are known along with the force on the particle at later times. The initial position and momentum are the constants of integration needed when integrating Newton’s second law. The state of the particle at any instant, given by the six values \(x,y,z,p_x,p_y,p_z\), corresponds to a point in six-dimensional phase space.

Imagine a collection of gas molecules in a box. Even in the classical case, we might not care about the motion of each individual molecule. We might simply want to know the average number in some small volume of the box. This average is given by the total number of molecules times the probability of any molecule being in the small volume. If the volume is small enough, then the probability is proportional to the volume and can be written as \( P(x,y,z)\,dxdydz \). This is a joint probability distribution (Appendix M). It is the probability that a molecule is in the volume element \( dxdydz \), that is, simultaneously between \( x \) and \( x + dx \) and between \( y \) and \( y + dy \) and between \( z \) and \( z + dz \). In a small box, \( P(x,y,z) \) would be the reciprocal of the volume of the box. However, \( P \) can depend on position. For example, in a box tall enough so that exponential variations in the atmosphere are important, \( P(x,y,z) \) would depend on height.
This joint probability distribution is independent of the momentum of the molecules. One could extend the concept and ask for the probability that a molecule is in the volume element \( dxdydz \) while at the same time having momentum components between \( p_x \) and \( p_x + dp_x \), \( p_y \) and \( p_y + dp_y \), and \( p_z \) and \( p_z + dp_z \). This probability is proportional to both \( dxdydz \) and \( dp_xdp_ydp_z \), and therefore to the volume in phase space \( dxdydzdp_xdp_ydp_z \):

\[
P(x, y, z, p_x, p_y, p_z) \propto dxdydzdp_xdp_ydp_z.
\]

This is rather cumbersome to write out, so the abbreviation

\[
P(\mathbf{r}, \mathbf{p}) \propto d^3\mathbf{r} d^3\mathbf{p}
\]

is often used.

If we have an ensemble of identical systems we can at any instant describe the ensemble as a collection of points in phase space. The density of points per unit volume of phase space is proportional to the probability function \( P(\mathbf{r}, \mathbf{p}) \). Liouville's theorem of advanced classical mechanics (Reif, 1965, Appendix 13) shows that for an ensemble of systems conserving energy, the density of points in phase space does not change with time. This means that if the density of points in phase space is uniform it remains that way. This is consistent with the postulates of Sec. 3.4, with the equilibrium state corresponding to an ensemble with a uniform density of points in phase space.

Quantum mechanics does not allow precise determination of both the position and the momentum of a particle. The Heisenberg uncertainty principle gives the limitation in precision of the simultaneous measurement of both quantities:

\[
(\Delta x)(\Delta p_x) \geq \hbar.
\]

Similar relations hold for the \( y \) direction and \( z \) direction. This says that there is a fundamental limitation on how small one can make the products \( dxdp_x \), \( dydp_y \), and \( dzdp_z \). Because \( \hbar \) is so small, we can conceive of intervals \( dxdp_x \) that are quite small on a classical scale but that contain many multiples of \( \hbar \). If each element of phase space of size \( \hbar \) (in one dimension) is associated with a quantum-mechanical energy level, then the factor \( dxdp_x/\hbar \) is the number of levels in interval \( dx \). In three dimensions, the number of levels is

\[
\frac{dxdydz dp_x dp_y dp_z}{\hbar^3},
\]

that is, the volume in phase space divided by \( \hbar^3 \).

For a single particle moving in three dimensions and in thermal equilibrium, therefore, Eq. 103.1 becomes

\[
P(U)dU = C \left( e^{-U/k_B T} \right) dxdydz dp_x dp_y dp_z.
\]
[In writing this equation, the factor $P(0)/h^2\Omega(0)$ has been called the constant $C$.] This is the probability that the particle is between $x$ and $x+dx$, between $y$ and $y+dy$, and between $z$ and $z+dz$, and has momentum components between $p_x$ and $p_x+dp_x$, $p_y$ and $p_y+dp_y$, and $p_z$ and $p_z+dp_z$. This is called a joint probability distribution; see Appendix M. The total energy $U$ in the exponent is related to position and momentum by

$$ U = E_k + E_p, $$

$$ U = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + E_p(x, y, z). \quad (103.5) $$

This is a rather complex equation, and it will take several pages to show what it means. There are two different ways to proceed: we can either calculate the probability that the particle has energy between $U$ and $U+dU$, or we can ask for the probability that the position and momentum are in the range just described. The latter is easier and will be done first. It is only necessary to write the left-hand side as

$$ P(\mathbf{r}, \mathbf{p}) \, d^3r \, d^3p $$

and substitute Eq. 103.5 in the exponent.

We will work through a specific example: an oxygen molecule at 300 K. Since 1 mol of O$_2$ has a mass of $32 \times 10^3$ kg, the mass of a single molecule is the mass of 1 mol divided by Avogadro’s number:

$$ m = \frac{32 \times 10^3}{6 \times 10^{23}} = 5.31 \times 10^{-26} \text{ kg}. $$

The factor $2mk_BT$, which occurs in the expressions below, is

$$ 2mk_BT = (2)(5.31 \times 10^{-26})(1.38 \times 10^{-23})(300) $$

$$ = 4.40 \times 10^{-26} \text{ kg}^2 \text{ m}^2 \text{ s}^{-2}. $$

If the potential energy does not depend on position, then the exponent is

$$ \frac{U}{k_BT} = \frac{p_x^2 + p_y^2 + p_z^2}{2mk_BT}. $$

The factor $P(\mathbf{r}, \mathbf{p})$ is given by

$$ Ce^{-U/k_BT} = C \exp \left[ -\frac{p_x^2 + p_y^2 + p_z^2}{2mk_BT} \right]. $$

Since $e^a+b = e^a e^b$, this can also be written as

$$ \left( e^{-\frac{p_x^2}{2mk_BT}} \right) \left( e^{-\frac{p_y^2}{2mk_BT}} \right) \left( e^{-\frac{p_z^2}{2mk_BT}} \right) $$
1.0
0.8
0.6
0.4
0.2
0.0
exp\left(-\frac{p_x^2}{2mk_BT}\right)
for O_2 at 300 K.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig103.1.png}
\caption{Plot of $e^{-\frac{p_x^2}{2mk_BT}}$ for an oxygen molecule at 300 K.}
\end{figure}

Therefore, the probability can be written

$$P(r,p) \, r \, dp = C(e^{-\frac{p_x^2}{2mk_BT}}dp_x)(e^{-\frac{p_y^2}{2mk_BT}}dp_y)$$
$$\times (e^{-\frac{p_z^2}{2mk_BT}}dp_z)drdydz. \quad (103.6)$$

Consider the dependence of this expression on $p_x$. The probability that $p_x$ is in the interval $(p_x, dp_x)$ is proportional to $e^{-\frac{p_x^2}{2mk_BT}}dp_x$. The exponential term is plotted in Fig. 103.1. It is the same term that appears in the Gaussian probability distribution (Appendix I). It is a maximum when the exponent is zero and is symmetric about the origin because the exponent contains $p_x^2$. The area under the curve is finite and is equal to $\sqrt{2\pi mk_BT}$ (see Appendix I). The fact that the curve is nearly zero for momenta greater than $5 \times 10^{-23}$ kg m s$^{-1}$ reflects the fact that very few oxygen molecules at room temperatures have momenta exceeding that.

If we want to know the probability that the molecule has a velocity between +200 and +210 m s$^{-1}$ (the + sign meaning that it is travelling to the right), we can find it from Eq. 103.6. First, these velocities are multiplied by the mass of an oxygen molecule to get the range of $p_x$, which is from $+1.063 \times 10^{-23}$ to $+1.116 \times 10^{-23}$ kg m s$^{-1}$. These two values are represented by the vertical lines in Fig. 103.1. Suppose the molecules are confined to a box with dimensions $L_x$, $L_y$, and $L_z$. The probability that the molecule has a value of $p_x$ between $p_x$ and $p_x + dp_x$ while it can be anywhere within the box and have any value of $p_y$ or $p_z$, is obtained by
integrating over all the other variables:

\[ P(p_x) \, dp_x = \int_{p_y=-\infty}^{p_y=\infty} \int_{p_z=-\infty}^{p_z=\infty} \int_{x=0}^{L_x} \int_{y=0}^{L_y} \int_{z=0}^{L_z} P(\mathbf{r}, \mathbf{p}) \, dp_y \, dp_z \, dx \, dy \, dz \, dp_x. \]

It becomes a bit cumbersome to keep track of which integral sign has limits for which variable, so it is customary to rearrange the terms:

\[ P(p_x) \, dp_x = \left[ \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_{0}^{L_x} dx \int_{0}^{L_y} dy \int_{0}^{L_z} dz \, P(\mathbf{r}, \mathbf{p}) \right] \, dp_x. \]

If Eq. 103.6 is used for \( P(\mathbf{r}, \mathbf{p}) \), this becomes

\[ P(p_x) \, dp_x = C \int_{-\infty}^{\infty} dp_y \, e^{-\frac{p_y^2}{2mk_B T}} \int_{-\infty}^{\infty} dp_z \, e^{-\frac{p_z^2}{2mk_B T}} \times \int_{0}^{L_x} dx \int_{0}^{L_y} dy \int_{0}^{L_z} dz \, e^{-\frac{p_x^2}{2mk_B T}} \, dp_x. \]

Each of these integrals can be evaluated. They are

\[ \int_{-\infty}^{\infty} dp_y \, e^{-\frac{p_y^2}{2mk_B T}} = (2\pi mk_B T)^{1/2}, \]

\[ \int_{-\infty}^{\infty} dp_z \, e^{-\frac{p_z^2}{2mk_B T}} = (2\pi mk_B T)^{1/2}, \]

\[ \int_{0}^{L_x} dx = L_x, \]

\[ \int_{0}^{L_y} dy = L_y, \]

\[ \int_{0}^{L_z} dz = L_z. \]

When these values are substituted, the expression becomes

\[ P(p_x) \, dp_x = C (2\pi mk_B T)(L_x L_y L_z) e^{-\frac{p_x^2}{2mk_B T}} \, dp_x. \]

The next step is to determine the constant \( C \). The easiest way is to use the fact that the particle must have some value of \( p_x \), so that \( \int_{-\infty}^{\infty} P(p_x) \, dp_x = 1 \). Therefore,

\[ C (2\pi mk_B T)(L_x L_y L_z) \int_{-\infty}^{\infty} dp_x \, e^{-\frac{p_x^2}{2mk_B T}} = 1. \]

This integral is just like the other momentum integrals above and has the value \((2\pi mk_B T)^{1/2}\):

\[ C (2\pi mk_B T)^{3/2}(L_x L_y L_z) = 1. \]
1.0
0.8
0.6
0.4
0.2
0.0

\[ \exp(-px^2/2mkBT) \text{ for O}_2 \text{ at 300 K} \]

\[ 1.16 \]
\[ 1.14 \]
\[ 1.12 \]
\[ 1.10 \]
\[ 1.08 \]
\[ 1.06 \]
\[ 1.04 \]
\[ 1.02 \]
\[ 1.00 \]

\[ px \text{ in units of } 10^{-23} \text{ kg m s}^{-1} \]

**FIGURE 103.2.** Expanded scale for a portion of the plot in Fig. 103.1, showing the exponential between 200 and 210 m s\(^{-1}\) (\(p_x = 1.063 \times 10^{-23}\) and \(1.116 \times 10^{-23}\) kg m s\(^{-1}\)).

It is customary to call \(L_xL_yL_z\) the volume of the box, \(V\). Then

\[ C = \frac{1}{V(2\pi mk_BT)^{3/2}}. \]  \hspace{1cm} (103.7)

When this is put in the expression for \(P(p_x)\), the result is

\[ P(p_x)dp_x = \frac{1}{(2\pi mk_BT)^{1/2}}e^{-p_x^2/2mk_BT}dp_x. \]  \hspace{1cm} (103.8)

The probability that \(p_x\) has a value between \(p_1\) and \(p_2\) is then

\[ P(p_1, p_2) = (2\pi mk_BT)^{-1/2} \int_{p_1}^{p_2} dp_x e^{-p_x^2/2mk_BT}. \]

For the case we are considering, this integral is most easily evaluated by assuming that the integrand is nearly constant because the two values of \(p\) are so close together. The integrand is plotted over this range in Fig. 103.2; the integral is equal to the shaded area. If that area is assumed to be a rectangle of height 0.774 (the value of the integrand at \(p = 1.063 \times 10^{-23}\) kg m s\(^{-1}\)), the area is \(4.10 \times 10^{-25}\); if it is approximated by a trapezoid, the width of the base must be multiplied by the average height, and the area is \(4.04 \times 10^{-25}\). The probability that the velocity or momentum is between these limits is therefore

\[ P = (4.04 \times 10^{-25})(1.38 \times 10^{-15})^{-1/2} = 0.011. \] The
probability that a particle has an \( x \) component of velocity between 200 and 210 m s\(^{-1}\) to the right is about 1%.

If we had asked for the probability that the particle had this velocity and at the same time was in the left half of the box (say, between \( x = 0 \) and \( x = L_x/2 \)), the answer would have been

\[
\int_{p_x}^p dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_0^{L_z/2} dx \int_0^{L_y} dy \int_0^{L_z} dz P(r, p).
\]

This works out to be

\[
\frac{(2\pi mk_BT)(L_x/2)(L_y)(L_z)}{(2\pi mk_BT)\sqrt{2}(L_xL_yL_z)} \int_{p_x}^p e^{-p_x^2/2m_kT} dp_x.
\]

The only difference between this and the previous case is the factor of \( 1/2 \) introduced because only half the volume is considered. The final result is 0.005.

Another thing we can find with the Maxwell-Boltzmann distribution is the probability that the particle has an energy between \( U \) and \( U + dU \). To find this, it is necessary to return to Eq. 103.4 and write it in terms of \( U \) instead of the momentum. The exponential part, \( e^{-U/k_BT} \), is correct as it stands. We will restrict ourselves to the case that there is no potential energy so that \( U = E_k = p^2/2m = p_x^2 + p_y^2 + p_z^2 \). It is necessary to relate the fact that the energy may be between \( U \) and \( U + dU \), to the volume element \( dp \).

Instead of working with rectangular coordinates, it is more convenient to use the spherical coordinates shown in Fig. 103.3. The three independent variables are \( p \), the magnitude of the momentum; \( \theta \), the angle that \( p \) makes with the \( p_z \) axis; and \( \phi \), the angle that the projection of \( p \) in the \((p_x, p_y)\) plane makes with the \( p_x \) axis. The components can be written in terms of these new variables by considering the projections in Fig. 103.3:

\[
\begin{align*}
p_x &= p \sin \theta \cos \phi, \\
p_y &= p \sin \theta \sin \phi, \\
p_z &= p \cos \theta.
\end{align*}
\]

(103.9)

With these variables, the total energy is \( p^2/2m \) and does not depend on the angles.

In rectangular coordinates, the volume element \( dp \) was determined by lines along which only one of the three variables changed at a time. In spherical coordinates, the volume element is determined the same way. First, \( p \) is varied by an amount \( dp \) while \( \theta \) and \( \phi \) are fixed. Then \( \theta \) is changed by \( d\theta \) while \( p \) and \( \phi \) are fixed; the edge of the cube traced out has length \( p d\theta \). Finally, \( \phi \) is changed, giving an edge \( p \sin \theta d\phi \). The volume of the element is the product of these three edges, as long as the displacements are so small that the element is like a rectangular solid:

\[
d^3p = p^2 \sin \theta \; d\theta \; d\phi \; dp.
\]
The dimensions are cubic momentum. This replaces $dp_x dp_y dp_z$ in Eq. 103.6:

$$P(r, p) \frac{d^3 r}{d^3 p} = Ce^{-U/k_BT} dx dy dz \ p^2 \sin \theta \ d\theta \ d\phi \ dp.$$  \hspace{1cm} (103.10)

The angular integrations can be carried out because $U$ does not depend on $\theta$ and $\phi$. The limits of the $\phi$ integration are 0 to $2\pi$ and give the shaded strip shown in Fig. 103.4. The $\theta$ integration is carried from 0 to $\pi$ (north pole to south pole) to cover the entire surface of the sphere. The angular integrals are

$$\int_{0}^{2\pi} \ d\phi = 2\pi$$

and

$$\int_{0}^{\pi} \sin \theta \ d\theta = \left[-\cos \theta \right]_{0}^{\pi} = 2$$  \hspace{1cm} (103.11)

The angular integrals together are therefore $4\pi$. Equation 103.10 now has become

$$P(r, p) \frac{d^3 r}{d^3 p} = 4\pi C e^{-U/k_BT} \ dx dy dz \ p^2 \ dp.$$  \hspace{1cm} (103.12)

Note that the differential is now a fourth-order differential instead of a sixth-order differential, because two of the integrations have already been made.

The next step is to write $p^2 \ dp$ in terms of $U = p^2 / 2m$. Since

$$dU = \frac{2p dp}{2m} = \frac{p dp}{m},$$
$p^2 dp$ can be written as $p m dU$. Finally, the fact that $p = (2mU)^{1/2}$ is used to write

$$p^2 dp = m^{3/2} 2^{1/2} U^{1/2} dU.$$  

The probability as a function of $U$ is therefore

$$P(r, U) d^3r dU = C(4\pi 2^{1/2} m^{3/2}) e^{-U/k_B T} U^{1/2} dU dx dy dz. \quad (103.13)$$

This is the Maxwell-Boltzmann distribution as a function of energy for particles whose energy is $U = p^2/2m$. Figure 103.5 is a plot of $U^{1/2} e^{-U}$, which gives the general shape of this distribution. The probability of the particle having no energy is zero, while the probability that $p_x$ was zero is a maximum. The difference occurs because $d^3 p$ is proportional to $p^2 dp$, which vanishes for zero total momentum.

Finally, as an example of using these integrals, we will verify that the probability is still correctly normalized. Imagine that the particle is confined to a box with sides $L_x, L_y, L_z$ and total volume $V$. The spatial integrals again give $V$. The constant was determined for this condition in Eq. 103.7. Therefore

$$P(U) dU = \int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz P(r, U) dU$$

$$= \frac{1}{(2\pi m k_B T)^{3/2}} (4\pi 2^{1/2} m^{3/2}) e^{-U/k_B T} U^{1/2} dU.$$  

The possible values of $U$ range from 0 to infinity. Therefore we must evaluate

$$\int_0^\infty e^{-U/k_B T} U^{1/2} dU.$$
FIGURE 103.5. Plot of \( y = U^{1/2} e^{-U} \) to show the general shape of the Maxwell-Boltzmann energy distribution.

Standard tables of integrals show that

\[
\int_0^\infty x^n e^{-ax} \, dx = \frac{\Gamma(n+1)}{a^{n+1}}. \tag{103.14}
\]

The quantity \( \Gamma(n+1) \) is a tabulated function called the gamma function. In this case, \( n = \frac{1}{2} \), so that

\[
\int_0^\infty U^{1/2} e^{-U/k_BT} \, dU = \Gamma \left( \frac{3}{2} \right) (k_BT)^{3/2}.
\]

The \( \Gamma \) function is evaluated using the integral tables again

\[
\Gamma \left( m + \frac{1}{2} \right) = \frac{1 \times 3 \times 5 \cdots \times (2m-1)}{2^m} \pi^{1/2}.
\]

Setting \( m = 1 \) in this expression gives \( \Gamma \left( \frac{3}{2} \right) = \frac{1}{2} \sqrt{\pi} \). When this result is put in the expression for \( P(U) \), we have

\[
\int_0^\infty P(U) \, dU = \frac{1}{(2\pi m k_BT)^{3/2}} \left( 4\pi 2^{1/2} m^{3/2} \right) \left( \frac{1}{2} \pi^{1/2} \right) (k_BT)^{3/2} = 1.
\]

The algebra has been done correctly and the probability is still normalized.
103.1 Problems

Problem 1 Make plots of the classical trajectories in phase space (that is, $p_x$ vs $x$) for a particle of mass $m$ (a) in free fall, (b) bouncing with momentum $\pm p_x$ parallel to the $x$ axis between walls at $x = 0$ and $x = L$; (c) and undergoing harmonic oscillation along the $x$ axis: $x = x_0 \sin(\omega t)$.

Problem 2 Suppose that a water molecule in solution has a velocity in the $x$ direction between 200 and 201 m s$^{-1}$, while it is located within a region of 1 nm along the $x$ axis. In how many cells of phase space of size $h$ might it be located?

Problem 3 Use the technique described in Sec. 3.10 to show that the probability that a molecule is in one half of the box and has a positive value of $v_x$ is 0.25.

Problem 4 Use the fact that
\[ \int_0^{\infty} e^{-\lambda x^2} \, dx = \frac{1}{2} \left( \frac{\pi}{\lambda} \right)^{1/2} \]

to show that
\[ \int_{-\infty}^{\infty} e^{-p^2/(2mk_B T)} \, dp = (2\pi mk_B T)^{1/2}. \]

Problem 5 The Maxwell–Boltzmann probability distribution $P(U) \, dU$ can be expressed in the form $Ce^{-U/k_B T} \pi \pi p^2 dp$. Find an expression for the Maxwell–Boltzmann probability distribution for molecular speed, $P(v) \, dv$, where the speed is $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$.

103.2 References