We introduce the idea of a three-dimensional probability-density function by showing how to find it from data referred to a Cartesian coordinates system. The probability density associated with a particular molecular velocity is just a number—a number that depends only on the velocity. Given a velocity, the probability density associated with that velocity must be independent of our choice of coordinate system. We can express the three-dimensional probability density using any coordinate system. We turn now to expressing velocities and probability density functions using spherical coordinates.

Just as we did for the Cartesian velocity components, we deduce the cumulative probability functions \(f_v(v)\), \(f_{\theta}(\theta)\), and \(f_{\varphi}(\varphi)\) for the spherical-coordinate components. Our deduction of \(f_v(v)\) from the experimental data uses \(v\)-values that are associated with all possible values of \(\theta\) and \(\varphi\). Corresponding statements apply to our deductions of \(f_{\theta}(\theta)\), and \(f_{\varphi}(\varphi)\). We also obtain their derivatives, the probability-density functions \(df_v(v)/dv\), \(df_{\theta}(\theta)/d\theta\), and \(df_{\varphi}(\varphi)/d\varphi\). From the properties of probability-density functions, we have

\[
\int_0^\infty \frac{df_v(v)}{dv} dv = \int_0^\pi \frac{df_{\theta}(\theta)}{d\theta} d\theta = \int_0^{2\pi} \frac{df_{\varphi}(\varphi)}{d\varphi} d\varphi = 1
\]

Let \(\omega\)' be the arbitrarily small increment of volume in velocity space in which the \(v\), \(\theta\), and \(\varphi\)-components of velocity lie between \(v\) and \(v + dv\), \(\theta\) and \(\theta + d\theta\), and \(\varphi\) and \(\varphi + d\varphi\). Then the probability that the velocity of a randomly selected molecule lies within \(\omega\)' is

\[
dP(\omega') = \int \left(\frac{df_v(v)}{dv}\right) \left(\frac{df_{\theta}(\theta)}{d\theta}\right) \left(\frac{df_{\varphi}(\varphi)}{d\varphi}\right) dv d\theta d\varphi
\]

Note that the product

\[
\left(\frac{df_v(v)}{dv}\right) \left(\frac{df_{\theta}(\theta)}{d\theta}\right) \left(\frac{df_{\varphi}(\varphi)}{d\varphi}\right)
\]

is not a three-dimensional probability density function. This is most immediately appreciated by recognizing that \(dv d\theta d\varphi\) is not an incremental “volume” in velocity space. That is, \(\text{int}^{\infty}_0 (dv d\theta d\varphi) = 1\)

We let \(\rho(v, \theta, \varphi)\) be the probability-density function for the velocity vector in spherical coordinates. When \(v\), \(\theta\), and \(\varphi\) specify the velocity, \(\rho(v, \theta, \varphi)\) is the probability per unit volume at that velocity. We want to use \(\rho(v, \theta, \varphi)\) to express the probability that an arbitrarily selected molecule has a velocity vector whose magnitude lies between \(v\) and \(v + dv\), while its \(\theta\)-component lies between \(\theta\) and \(\theta + d\theta\), and its \(\varphi\)-component lies between \(\varphi\) and \(\varphi + d\varphi\). This is just \(\rho(v, \theta, \varphi)\) times the velocity-space “volume” included by these ranges of \(v\), \(\theta\), and \(\varphi\).

When we change from Cartesian coordinates, \(\text{mathop{\limits{\rightharpoonup}}=}\) to spherical coordinates, \(\text{mathop{\limits{\rightharpoonup}}=}\), the transformation is
\[ v_x = v \sin \theta \cos \varphi, \quad v_y = v \sin \theta \sin \varphi, \quad v_z = v \cos \theta. \] (See Figure 1.) As sketched in Figure 2, an incremental increase in each of the coordinates of the point specified by the vector \( (v, \theta, \varphi) \) advances the vector to the point \( (v + dv, \theta + d\theta, \varphi + d\varphi) \). When \( dv \), \( d\theta \), and \( d\varphi \) are arbitrarily small, these two points specify the diagonally opposite corners of a rectangular parallelepiped, whose edges have the lengths \( dv \), \( v d\theta \), and \( v \sin \theta d\varphi \). The volume of this parallelepiped is \( v^2 \sin \theta dv d\theta d\varphi \). Hence, the differential volume element in Cartesian coordinates, \( dv_x dv_y dv_z \), becomes \( v^2 \sin \theta dv d\theta d\varphi \) in spherical coordinates.

Mathematically, this conversion is obtained using the absolute value of the \textbf{Jacobian}, \( \left| \frac{\partial (v_x, v_y, v_z)}{\partial (v, \theta, \varphi)} \right| \), of the transformation. That is,

\[
\left| \frac{dv_x dv_y dv_z}{dv d\theta d\varphi} \right| = \left| \frac{\partial (v_x, v_y, v_z)}{\partial (v, \theta, \varphi)} \right| = v^2 \sin \theta.
\]

Since the differential unit of volume in spherical coordinates is \( v^2 \sin \theta dv d\theta d\varphi \), the \textbf{probability that the velocity components lie within the indicated ranges} is

\[
\frac{df_v(v) df_\theta(\theta) df_\varphi(\varphi)}{dv d\theta d\varphi} = \rho(v, \theta, \varphi) v^2 \sin \theta dv d\theta d\varphi.
\]

We can develop the next step in Maxwell’s argument by taking his assumption to mean that the three-dimensional probability density function is expressible as a product of three one-dimensional functions. That is, we take Maxwell’s assumption to assert the existence of independent functions \( \rho_v(v) \), \( \rho_\theta(\theta) \), and \( \rho_\varphi(\varphi) \) such that \( \rho(v, \theta, \varphi) = \rho_v(v) \rho_\theta(\theta) \rho_\varphi(\varphi) \). The probability that the \( v \)-, \( \theta \)-, and \( \varphi \)-components of velocity lie between \( v \) and \( v + dv \), \( \theta \) and \( \theta + d\theta \), and \( \varphi \) and \( \varphi + d\varphi \) becomes

\[
\rho(v, \theta, \varphi) v^2 \sin \theta dv d\theta d\varphi.
\]

Since \( v \), \( \theta \), and \( \varphi \) are independent, it follows that

\[
\frac{df_v(v)}{dv} = v^2 \rho_v(v)
\]

\[
\frac{df_\theta(\theta)}{d\theta} = \rho_\theta(\theta) \sin \theta
\]

\[
\frac{df_\varphi(\varphi)}{d\varphi} = \rho_\varphi(\varphi)
\]
Moreover, the assumption that velocity is independent of direction means that \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) must actually be independent of \(\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}\); that is, \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) must be a constant. We let this constant be \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\); so \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) must be \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\). By the same argument, we set \(\langle \rho_v \rangle_{\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}}\) and \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\). Each of these probability-density functions must be normalized. This means that

\[
\int^\infty_0 v^2 \rho_v(v) dv = 1
\]

\[
\int^\pi_0 \alpha_\theta \sin \theta d\theta = 2\alpha_\theta
\]

\[
\int^{2\pi}_0 \alpha_\phi d\phi = 2\pi \alpha_\phi
\]

from which we see that \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}} = \alpha_\theta = \frac{1}{2}\) and \(\langle \rho_v \rangle_{\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}} = \alpha_\phi = \frac{1}{2}\pi\). It is important to recognize that, while \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) and \(\langle \rho_v \rangle_{\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}}\) are probability density functions, \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) and \(\langle \rho_v \rangle_{\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}}\) are not. (However, \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) and \(\langle \rho_v \rangle_{\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}}\) are probability density functions.) We can see this by noting that, if \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) were a probability density, its integral over all possible values of \(\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}\) would be one. Instead, we find

\[
\int^\pi_0 \rho_\theta(\theta) d\theta = \int^\pi_0 d\theta /2 = \pi /2
\]

Similarly, when we find \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\), we can show explicitly that

\[
\int^\infty_0 \rho_v(v) dv = 1
\]

Our notation now allows us to express the probability that an arbitrarily selected molecule has a velocity vector whose magnitude lies between \(\langle v \rangle \) and \(\langle v + dv \rangle\), while its \(\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}\)-component lies between \(\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}} + d\theta\), and its \(\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}\)-component lies between \(\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}} + d\phi\) using three equivalent representations of the probability density function:

\[
\frac{dP}{d\theta} = \rho_v(v, \theta, \phi) v^n \sin \theta dv d\theta d\phi
\]

The three-dimensional probability-density function in spherical coordinates is

\[
\rho(v, \theta, \phi) = \rho_v(v) \rho_\theta(\theta) \rho_\phi(\phi)
\]

This shows explicitly that \(\langle \rho_v \rangle_{\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}}\) is independent of \(\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}\) and \(\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}\); if the speed is independent of direction, the probability density function that describes velocity must be independent of the coordinates, \(\langle \theta \rangle_{\langle \theta \rangle_{\langle \theta \rangle}}\) and \(\langle \phi \rangle_{\langle \phi \rangle_{\langle \phi \rangle}}\), that specify its direction.