6.2: Probability Density Functions for Velocity Components in Spherical Coordinates

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 $f_v\left(v\right)$, $f_\theta\left(\theta\right)$, and $f_\varphi\left(\varphi\right)$ for the spherical-coordinate components. Our deduction of $f_v\left(v\right)$ from the experimental data uses v-values that are associated with all possible values of θ and φ. Corresponding statements apply to our deductions of $f_\theta\left(\theta\right)$, and $f_\varphi\left(\varphi\right)$. We also obtain their derivatives, the probability-density functions $df_v\left(v\right)/dv$, $df_\theta\left(\theta\right)/d\theta$, and $df_\varphi\left(\varphi\right)/d\varphi$. From the properties of probability-density functions, we have

$$\int^{\infty}_0{\left(\frac{df_v\left(v\right)}{dv}\right)dv}=\int^{\pi}_0{\left(\frac{df_\theta\left(\theta\right)}{d\theta}\right)d\theta}=\int^{2\pi}_0{\left(\frac{df_\varphi\left(\varphi\right)}{d\varphi}\right)d\varphi}=1$$

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

$$dP\left(υ/\right)=\left(\frac{df_v\left(v\right)}{dv}\right)\left(\frac{df_\theta\left(\theta\right)}{d\theta}\right)\left(\frac{df_\varphi\left(\varphi\right)}{d\varphi}\right)dvd\theta d\varphi$$

Note that the product

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

is not a three-dimensional probability density function. This is most immediately appreciated by recognizing that $dvd\theta d\varphi$ is not an incremental "volume" in velocity space. That is, υ/ $\neq dvd\theta d\varphi$

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

When we change from Cartesian coordinates, $\overrightarrow{v}=\left(v_x,v_y,v_z\right)$, to spherical coordinates, $\overrightarrow{v}=\left(v,\theta,\varphi\right)$, the transformation is $v_x=v\mathrm{sin}\theta\,\mathrm{cos}\varphi$, $v_y=v\mathrm{sin}\theta\,\mathrm{sin}\varphi$, $v_z=v\mathrm{cos}\theta$. (See Figure 1.) As sketched in Figure 2, an incremental increase in each of the coordinates of the point specified by the vector $\left(v,\ \theta,\varphi\right)$ advances the vector to the point $\left(v+dv,\theta+d\theta,\varphi+d\varphi\right)$. 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, $vd\theta$, and $v\mathrm{sin}\theta\,d\varphi$. The volume of this parallelepiped is $v^2\mathrm{sin}\theta\,dvd\theta d\varphi$. Hence, the differential volume elementdifferential volume element in Cartesian coordinates, $dv_xdv_ydv_z$, becomes $v^2\mathrm{sin}\theta\,dvd\theta d\varphi$ in spherical coordinates.

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

$$dv_xdv_ydv_z=\left|J\left(\frac{v_x,v_y,v_z}{v,\theta,\varphi}\right)\right|dvd\theta d\varphi$$

where the Jacobian is a determinate of partial derivatives

$$\begin{aligned}J\left(\frac{v_x,v_y,v_z}{v,\theta,\varphi}\right)&=\left|\begin{array}{ccc}\partial v_x/\partial v & \partial v_x/\partial \theta & \partial v_x/\partial \varphi\\ \partial v_y/\partial v & \partial v_y/\partial \theta & \partial v_y/\partial \varphi\\ \partial v_z/\partial v & \partial v_z/\partial \theta & \partial v_z/\partial \varphi\end{array}\right|\\&=v^2\mathrm{sin}\theta\end{aligned}$$

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

$$dP\left(\upsilon\prime\right) = \rho\left(v,\theta,\varphi\right) v^2 \sin\theta \, dv d\theta d\varphi$$

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 $\rho_v\left(v\right)$, $\rho_\theta\left(\theta\right)$, and $\rho_\varphi\left(\varphi\right)$ such that $\rho\left(v,\ \theta,\varphi\right) = \rho_v\left(v\right) \rho_\theta\left(\theta\right) \rho_\varphi\left(\varphi\right)$. The probability that the v-, θ-, and φ-components of velocity lie between v and $v + dv$, θ and $\theta + d\theta$, and φ and $\varphi + d\varphi$ becomes

$$\begin{aligned} dP\left(\upsilon\prime\right) &= \left(\frac{df_v\left(v\right)}{dv}\right) \left(\frac{df_\theta\left(\theta\right)}{d\theta}\right) \left(\frac{df_\varphi\left(\varphi\right)}{d\varphi}\right) dv d\theta d\varphi \\ &= \rho\left(v,\theta,\varphi\right) v^2 \sin\theta dv d\theta d\varphi \\ &= \rho_v\left(v\right) \rho_\theta\left(\theta\right) \rho_\varphi\left(\varphi\right) v^2 \sin\theta dv d\theta d\varphi \end{aligned}$$

Since v, θ, and φ are independent, it follows that

$$\begin{aligned} \frac{df_v\left(v\right)}{dv} &= v^2 \rho_v\left(v\right) \\ \frac{df_\theta\left(\theta\right)}{d\theta} &= \rho_\theta\left(\theta\right) \sin\theta \\ \frac{df_\varphi\left(\varphi\right)}{d\varphi} &= \rho_\varphi\left(\varphi\right) \end{aligned}$$

Moreover, the assumption that velocity is independent of direction means that $\rho_\theta\left(\theta\right)$ must actually be independent of θ; that is, $\rho_\theta\left(\theta\right)$ must be a constant. We let this constant be α_θ; so $\rho_\theta\left(\theta\right) = \alpha_\theta$. By the same argument, we set $\rho_\varphi\left(\varphi\right) = \alpha_\varphi$. Each of these probability-density functions must be normalized. This means that

$$1 = \int^{\infty}_0 v^2 \rho_v\left(v\right) dv$$

$$1 = \int^{\pi}_0 \alpha_\theta \sin\theta \, d\theta = 2\alpha_\theta$$

$$1 = \int^{2\pi}_0 \alpha_\varphi d\varphi = 2\pi\alpha_\varphi$$

from which we see that $\rho_\theta\left(\theta\right) = \alpha_\theta = 1/2$ and $\rho_\varphi\left(\varphi\right) = \alpha_\varphi = 1/2\pi$. It is important to recognize that, while $\rho_x\left(v_x\right)$, $\rho_y\left(v_y\right)$, and $\rho_z\left(v_z\right)$ are probability density functions, $\rho_\theta\left(\theta\right)$ and $\rho_v\left(v\right)$ are not. (However, $\rho_\varphi\left(\varphi\right)$ is a probability density function.) We can see this by noting that, if $\rho_\theta\left(\theta\right)$ were a probability density, its integral over all possible values of θ $\left(0 < \theta < \pi\right)$ would be one. Instead, we find

$$\int^{\pi}_0 \rho_\theta\left(\theta\right) d\theta = \int^{\pi}_0 d\theta/2 = \pi/2$$

Similarly, when we find $\rho_v\left(v\right)$, we can show explicitly that

$$\int^{\infty}_0 \rho_v\left(v\right) dv \neq 1$$

Our notation now allows us to express the probability that an arbitrarily selected molecule has a velocity vector whose magnitude lies between v and $v + dv$, while its θ-component lies between θ and $\theta + d\theta$, and its φ-component lies between φ and $\varphi + d\varphi$ using three equivalent representations of the probability density function:

$$dP\left(\upsilon\prime\right) = \rho\left(v,\theta,\varphi\right) v^2 \sin\theta dv d\theta d\varphi \ - \rho_v\left(v\right) \rho_\theta\left(\theta\right) \rho_\varphi\left(\varphi\right) v^2 \sin\theta dv d\theta d\varphi \ = \left(\frac{1}{4\pi}\right) \rho_v\left(v\right) v^2 \sin\theta \, dv d\theta d\varphi$$

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

$$\rho\left(v,\ \theta,\varphi\right)=\rho_v\left(v\right)\rho_\theta\left(\theta\right)\rho_\varphi\left(\varphi\right)=\frac{\rho_v\left(v\right)}{4\pi}$$

This shows explicitly that $\rho\left(v,\ \theta,\varphi\right)$ is independent of θ and φ; if the speed is independent of direction, the probability density function that describes velocity must be independent of the coordinates, θ and φ, that specify its direction.