4.5: Combining the One-dimensional Probability Density Functions

In Section 4.4, we derive the probability density function for one Cartesian component of the velocity of a gas molecule. The probability density functions for the other two Cartesian components are the same function. For $\overrightarrow{v}=(v_x,v_y,v_z)$, we have $v^2=v_x^2+v_y^2+v_z^2$, and

$$\begin{aligned}\frac{df_x(v_x)}{dv_x}&=\left(\frac{\lambda}{2\pi}\right)^{1/2}\exp\left(\frac{-\lambda v_x^2}{2}\right)\\ \frac{df_y(v_y)}{dv_y}&=\left(\frac{\lambda}{2\pi}\right)^{1/2}\exp\left(\frac{-\lambda v_y^2}{2}\right)\\ \frac{df_z(v_z)}{dv_z}&=\left(\frac{\lambda}{2\pi}\right)^{1/2}\exp\left(\frac{-\lambda v_z^2}{2}\right)\end{aligned}$$

We now want to derive the three-dimensional probability density function from these relationships. Given these probability density functions for the Cartesian components of $\overrightarrow{v}$, we can find the probability density function in spherical coordinates

$$\begin{aligned}&\left(\frac{df_x(v_x)}{dv_x}\right)\left(\frac{df_y(v_y)}{dv_y}\right)\left(\frac{df_z(v_z)}{dv_z}\right)\\ &=\left(\frac{\lambda}{2\pi}\right)^{3/2}\exp\left(\frac{-\lambda v_x^2}{2}\right)exp\left(\frac{-\lambda v_y^2}{2}\right)exp\left(\frac{-\lambda v_z^2}{2}\right)\\ &=\left(\frac{\lambda}{2\pi}\right)^{3/2}\exp\left(\frac{-\lambda v^2}{2}\right)\\ &=\rho(v,\theta,\varphi)\end{aligned}$$

Since the differential volume element in spherical coordinates is $v^2\sin\theta\, dvd\theta d\varphi$, the probability that a molecule has a 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 $\varphi+d\varphi$ becomes

$$\begin{aligned}&\left(\frac{df_v(v)}{dv}\right)\left(\frac{df_\theta(\theta)}{d\theta}\right)\left(\frac{df_\varphi(\varphi)}{d\varphi}\right)dvd\theta d\varphi\\ &=\rho(v,\theta,\varphi)\,v^2\sin\theta dvd\theta d\varphi\\ &=\left(\frac{\lambda}{2\pi}\right)^{3/2}v^2\exp\left(\frac{-\lambda v^2}{2}\right)\sin\theta dvd\theta d\varphi\end{aligned}$$

(We found the same result in Section 4.3, of course.) We can find the probability-density function for the scalar velocity by eliminating the dependence on the angular components. To do this, we need only sum up, at a given value of v, the contributions from all possible values of θ and φ, recalling that $0\le\theta<\pi$ and $0\le\varphi<2\pi$. This sum is just

$$\begin{aligned}&\frac{df_v(v)}{dv}\int_{\theta=0}^{\pi}\left(\frac{df_\theta(\theta)}{d\theta}\right)d\theta\int_{\varphi=0}^{2\pi}\left(\frac{df_\varphi(\varphi)}{d\varphi}\right)d\varphi=\\ &=\left(\frac{\lambda}{2\pi}\right)^{3/2}v^2exp\left(\frac{-\lambda v^2}{2}\right)\int_{\theta=0}^{\pi}\sin\theta d\theta\int_{\varphi=0}^{2\pi}d\varphi\end{aligned}$$

Since $\int_{\theta=0}^{\pi}\left(\frac{df_\theta(\theta)}{d\theta}\right)d\theta=\int_{\varphi=0}^{2\pi}\left(\frac{df_\varphi(\varphi)}{d\varphi}\right)d\varphi=1$, $\int_0^\pi\sin\theta d\theta=2$, and $\int_0^{2\pi}d\varphi=2\pi$, we again obtain the Maxwell-Boltzmann probability-density function for the scalar velocity:

$$\frac{df_v(v)}{dv}=4\pi\left(\frac{\lambda}{2\pi}\right)^{3/2}v^2exp\left(\frac{-\lambda v^2}{2}\right)$$

Unlike the distribution function for the Cartesian components of velocity, the Maxwell-Boltzmann distribution for scalar velocities is not a normal distribution. Possible speeds lie in the interval $0\le v<\infty$. Because of the v^2 term, the Maxwell-Boltzmann equation is asymmetric; it has a pronounced tail at high velocities.