4.3: Maxwell's Derivation of the Gas-velocity Probability-density Function

To this point, we have been developing our ability to characterize the gas-velocity distribution functions. We now want to use Maxwell's argument to find them. We have already introduced the first step, which is the recognition that three-dimensional probability-density functions can be expressed as products of independent one-dimensional functions, and that $\rho_\theta\left(\theta\right)$, and $\rho_\varphi\left(\varphi\right)$ are the constants $1/2$ and $1/2\pi$. Now, because the probability density associated with any given velocity is just a number that is independent of the coordinate system, we can equate the three-dimensional probability-density functions for Cartesian and spherical coordinates: $\rho\left(v_x,v_y,v_z\right)=\rho\left(v,\ \theta,\varphi\right)$ so that

$$\rho_x\left(v_x\right)\rho_y\left(v_y\right)\rho_z\left(v_z\right)=\frac{\rho_v\left(v\right)}{4\pi}$$

We take the partial derivative of this last equation with respect to v_x. The probability densities $\rho_y\left(v_y\right)$ and $\rho_z\left(v_z\right)$ are independent of v_x. However, v is a function of v_x, because $v^2=v^2_x+v^2_y+v^2_z$. We find

$$\frac{d\rho_x\left(v_x\right)}{dv_x}\rho_y\left(v_y\right)\rho_z\left(v_z\right)=\frac{1}{4\pi}{\left(\frac{\partial \rho_v\left(v\right)}{\partial v_x}\right)}_{v_yv_v}=\frac{1}{4\pi}\left(\frac{d\rho_v\left(v\right)}{dv}\right){\left(\frac{\partial v}{\partial v_x}\right)}_{v_yv_z}$$

Since $v^2=v^2_x+v^2_y+v^2_z$, $2v{(\partial v/\partial v_x)}_{v_yv_z}=2v_x$ and

$${\left(\frac{\partial v}{\partial v_x}\right)}_{v_yv_z}=\frac{v_x}{v}$$

Making this substitution and dividing by the original equation gives

$$\frac{d\rho_x\left(v_x\right)}{dv_x}\frac{\rho_y\left(v_y\right)\rho_z\left(v_z\right)}{\rho_x\left(v_x\right)\rho_y\left(v_y\right)\rho_z\left(v_z\right)}=\frac{v_x}{v}\frac{1}{\rho_v\left(v\right)}\frac{d\rho_v\left(v\right)}{dv}$$

Cancellation and rearrangement of the result leads to an equation in which the independent variables v_x and v are separated. This means that each term must be equal to a constant, which we take to be $-\lambda$. We find

$$\left(\frac{1}{v_x\rho_x\left(v_x\right)}\right)\frac{d\rho_x\left(v_x\right)}{dv_x}=\left(\frac{1}{v\rho_v\left(v\right)}\right)\frac{d\rho_v\left(v\right)}{dv}=-\lambda$$

so that

$$\frac{d\rho_x\left(v_x\right)}{\rho_x\left(v_x\right)}=-\lambda v_xdv_x$$

and

$$\frac{d\rho_v\left(v\right)}{\rho_v\left(v\right)}=-\lambda vdv$$

From the first of these equations, we obtain the probability density function for the distributions of one-dimensional velocities. (See Section 4.4.) The three-dimensional probability density function can be deduced from the one-dimensional function. (See Section 4.5.)

From the second equation, we obtain the three-dimensional probability-density function directly. Integrating from $v=0$, where $\rho_v\left(0\right)$ has a fixed value, to an arbitrary scalar velocity, v, where the scalar-velocity function is $\rho_v\left(v\right)$, we have

$$\int^{\rho_v\left(v\right)}_{\rho_v\left(0\right)}{\frac{d\rho_v\left(v\right)}{\rho_v\left(v\right)}}=-\lambda\int^v_0{vdv}$$

or

$$\rho_v\left(v\right)=\rho_v\left(0\right)exp\left(\frac{-\lambda v^2}{2}\right)$$

The probability-density function for the scalar velocity becomes

$$\frac{df_v\left(v\right)}{dv}=v^2\rho_v\left(v\right)=\rho_v\left(0\right)v^2exp\left(\frac{-\lambda v^2}{2}\right)$$

This is the result we want, except that it contains the unknown parameters $\rho_v\left(0\right)$ and λ. The value of $\rho_v\left(0\right)$ must be such as to make the integral over all velocities equal to unity. We require

$$\begin{aligned}1&=\int^{\infty}_0{\left(\frac{df_v\left(v\right)}{dv}\right)}dv\\&=\rho_v\left(0\right)\int^{\infty}_0{v^2\mathrm{exp}\left(\frac{-\lambda v^2}{2}\right)}dv\\&=\frac{\rho_v\left(0\right)}{4\pi}{\left(\frac{2\pi}{\lambda}\right)}^{3/2}\end{aligned}$$

so that

$$\rho_v\left(0\right)=4\pi{\left(\frac{\lambda}{2\pi}\right)}^{3/2}$$

where we use the definite integral $\int^{\infty}_0{x^2\mathrm{exp}\left(-ax^2\right)}dx=\left(1/4\right)\sqrt{\pi/a^3}$. (See Appendix D.) The scalar-velocity function in the three-dimensional probability-density function becomes

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

The probability-density function for the scalar velocity becomes

$$\begin{aligned}\frac{df_v\left(v\right)}{dv}&=v^2\rho_v\left(v\right)\\&=4\pi{\left(\frac{\lambda}{2\pi}\right)}^{3/2}v^2\mathrm{exp}\left(\frac{-\lambda v^2}{2}\right)\end{aligned}$$

The three-dimensional probability density in spherical coordinates becomes

$$\begin{aligned}\rho\left(v,\ \theta,\varphi\right)&=\rho_v\left(v\right)\rho_{\theta}\left(\theta\right)\rho_{\varphi}\left(\varphi\right)\\&={\left(\frac{\lambda}{2\pi}\right)}^{3/2}\mathrm{exp}\left(\frac{-\lambda v^2}{2}\right)\end{aligned}$$

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 $\varphi+d\varphi$ becomes

$$\begin{aligned}dP\left(\upsilon\prime\right)&=\left(\frac{df_v\left(v\right)}{dv}\right)\left(\frac{df_{\theta}\left(\theta\right)}{d\theta}\right)\left(\frac{df_{\varphi}\left(\varphi\right)}{d\varphi}\right)dvd\theta d\varphi\\&=\rho\left(v,\theta,\varphi\right)v^2\mathrm{sin}\theta dvd\theta d\varphi\\&=\left(\frac{1}{4\pi}\right)\rho_v\left(v\right)v^2\mathrm{sin}\theta dvd\theta d\varphi\\&={\left(\frac{\lambda}{2\pi}\right)}^{3/2}v^2exp\left(\frac{-\lambda v^2}{2}\right)\mathrm{sin}\theta dvd\theta d\varphi\end{aligned}$$

In Section 4.6, we again derive Boyle's law and use the ideal gas equation to show that $\lambda=m/kT$.