

6.3: 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 $\rho_\theta(\theta)$, and $\rho_\varphi(\varphi)$ 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: $\rho(v_x, v_y, v_z) = \rho(v, \theta, \varphi)$ so that

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

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

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

Since $v^2 = v_x^2 + v_y^2 + v_z^2$, $2v(\partial v / \partial v_x)_{v_y v_z} = 2v_x$ and

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

Making this substitution and dividing by the original equation gives

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

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

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

so that

$$\frac{d\rho_x(v_x)}{\rho_x(v_x)} = -\lambda v_x dv_x$$

and

$$\frac{d\rho_v(v)}{\rho_v(v)} = -\lambda v dv$$

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 $\rho_v(0)$ has a fixed value, to an arbitrary scalar velocity, v , where the scalar-velocity function is $\rho_v(v)$, we have

$$\int_{\rho_v(0)}^{\rho_v(v)} \frac{d\rho_v(v)}{\rho_v(v)} = -\lambda \int_0^v v dv$$

or

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

The probability-density function for the scalar velocity becomes

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

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

$$\begin{aligned} 1 &= \int_0^\infty \left(\frac{df_v(v)}{dv}\right) dv \\ &= \rho_v(0) \int_0^\infty v^2 \exp\left(\frac{-\lambda v^2}{2}\right) dv \\ &= \frac{\rho_v(0)}{4\pi} \left(\frac{2\pi}{\lambda}\right)^{3/2} \end{aligned}$$

so that

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

where we use the definite integral $\int_0^\infty x^2 \exp(-ax^2) dx = (1/4) \sqrt{\pi/a^3}$. (See Appendix D.) The scalar-velocity function in the three-dimensional probability-density function becomes

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

The probability-density function for the scalar velocity becomes

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

The three-dimensional probability density in spherical coordinates becomes

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

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

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

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

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