6.11: The Probability Density Function for the Relative Velocity

From our development of the Maxwell-Boltzmann probability density functions, we can express the probability that the velocity components of particle 1 lie in the intervals v_{1x} to $v_{1x}+dv_{1x}$; v_{1y} to $v_{1y}+dv_{1y}$; v_{1z} to $v_{1z}+dv_{1z}$; while those of particle 2 simultaneously lie in the intervals v_{2x} to $v_{2x}+dv_{2x}$; v_{2y} to $v_{2y}+dv_{2y}$; v_{2z} to $v_{2z}+dv_{2z}$ as

$$\left(\frac{df\left(v_{1x}\right)}{dv_{1x}}\right)\left(\frac{df\left(v_{1y}\right)}{dv_{1y}}\right)\left(\frac{df\left(v_{1z}\right)}{dv_{1z}}\right)\left(\frac{df\left(v_{2x}\right)}{dv_{2x}}\right)\left(\frac{df\left(v_{2y}\right)}{dv_{2y}}\right)\left(\frac{df\left(v_{2z}\right)}{dv_{2z}}\right)$$
$$\times dv_{1x}dv_{1y}dv_{1z}dv_{2x}dv_{2y}dv_{2z}$$
$$=\left(\frac{df\left(v_1\right)}{dv_1}\right)\left(\frac{df\left(v_2\right)}{dv_2}\right)dv_1dv_2$$

We want to express this probability using the relative velocity coordinates. Since the velocity of the center of mass and the relative velocity are independent, we might expect that the Jacobian of this transformation is just the product of the two individual Jacobians. This turns out to be the case. The Jacobian of the transformation

$$\left(\dot{x}_1,\dot{y}_1,\dot{z}_1,\dot{x}_2,\dot{y}_2,\dot{z}_2\right)\rightarrow\left(\dot{x}_0,,\dot{y}_0,\dot{z}_0,\dot{x}_{12},\dot{y}_{12},\dot{z}_{12}\right)$$

is a six-by-six determinate. It is messy, but straightforward, to show that it is equal to the product of two three-by-three determinants and that the absolute value of this product is one. Therefore, we have

$$\begin{aligned} dv_{1x}dv_{1y}dv_{1z}dv_{2x}dv_{2y}dv_{2z} &= d\dot{x}_1d\dot{y}_1d\dot{z}_1d\dot{x}_2d\dot{y}_2d\dot{z}_2 \\ &= d\dot{x}_0d\dot{y}_0d\dot{z}_0d\dot{x}_{12}d\dot{y}_{12}d\dot{z}_{12}\end{aligned}$$

We transform the probability density by substituting into the one-dimensional probability density functions. That is,

$$\begin{aligned}\left(\frac{df\left(v_1\right)}{dv_1}\right)\left(\frac{df\left(v_2\right)}{dv_2}\right) &= \left(\frac{m_1}{2\pi kT}\right)^{3/2}\exp\left(\frac{-m_1\left(v^2_{1x}+v^2_{1y}+v^2_{1z}\right)}{2kT}\right)\times\left(\frac{m_2}{2\pi kT}\right)^{3/2}\exp\left(\frac{-m_2\left(v^2_{2x}+v^2_{2y}+v^2_{2z}\right)}{2kT}\right) \\ &= \left(\frac{m_1m_2}{4\pi^2k^2T^2}\right)^{3/2}\times\exp\left(\frac{-m_1\left(v^2_{1x}+v^2_{1y}+v^2_{1z}\right)-m_2\left(v^2_{2x}+v^2_{2y}+v^2_{2z}\right)}{2kT}\right) \\ &= \left(\frac{m_1m_2}{4\pi^2k^2T^2}\right)^{3/2}\times\exp\left(\frac{-\frac{m_1m_2}{\mu}\left(\dot{x}^2_0+\dot{y}^2_0+z^2_0\right)-\mu\left(\dot{x}^2_{12}+\dot{y}^2_{12}+\dot{z}^2_{12}\right)}{2kT}\right)\end{aligned}$$

where the last expression specifies the probability density as a function of the relative velocity coordinates.

Next, we make a further transformation of variables. We convert the velocity of the center of mass, $\left(\dot{x}_0,\dot{y}_0,\dot{z}_0\right)$, and the relative velocity, $\left(\dot{x}_{12},\dot{y}_{12},\dot{z}_{12}\right)$, from Cartesian coordinates to spherical coordinates, referred to the $Oxyz$ axis system. (The motion of the center of mass is most readily visualized in the original frame $Oxyz$. The relative motion, $\overrightarrow{v}_{12}$, is most readily visualized in the Particle-One Centered Frame, $O_1x''y''z''$. In $O_1x''y''z''$, the motion of particle 2 is specified by $\dot{x}''_2=\dot{x}_{12}$, $\dot{y}''_2=\dot{y}_{12}$, and $\dot{z}''_2=\dot{z}_{12}$. The motion of the center of mass is specified by $\dot{x}''_0=\mu\dot{x}_{12}/m_1$, $\dot{y}''_0=\mu\dot{y}_{12}/m_1$, and $\dot{z}''_0=\mu\dot{z}_{12}/m_1$. Since it is the relative motion that is actually of interest, it might seem that we should refer the spherical coordinates to the $O_1x''y''z''$ frame. This is an unnecessary distinction because all three coordinate frames are parallel to one another, and $\overrightarrow{r}_0$ and $\overrightarrow{r}_{12}$ are the same vectors in all three frames.) Letting

$$v^2_0=\dot{x}^2_0+\dot{y}^2_0+z^2_0$$
$$v^2_{12}=\dot{x}^2_{12}+\dot{y}^2_{12}+z^2_{12}$$

the Cartesian velocity components are expressed in spherical coordinates by

$$\dot{x}_0=v_0\sin\theta_0\,\cos\varphi_0$$
$$\dot{y}_0=v_0\sin\theta_0\,\sin\varphi_0$$

$$\dot{z}_0 = v_0 \cos\theta_0$$

$$\dot{x}_{12} = v_{12} \sin\theta_{12} \cos\varphi_{12}$$

$$\dot{y}_{12} = v_{12} \sin\theta_{12} \sin\varphi_{12}$$

$$\dot{z}_{12} = v_{12} \cos\theta_{12}$$

The angles θ_0, θ_{12}, φ_0, and φ_{12} are defined in the usual manner relative to the $Oxyz$ axis system. The Jacobian of this transformation is a six-by-six determinate; which can again be converted to the product of two three-by-three determinates. We find

$$d\dot{x}_0 d\dot{y}_0 d\dot{z}_0 d\dot{x}_{12} d\dot{y}_{12} d\dot{z}_{12} =$$

$$= v_0^2 \sin\theta_0 \, dv_0 d\theta_0 d\varphi_0 v_{12}^2 \sin\theta_{12} \, dv_{12} d\theta_{12} d\varphi_{12}$$

The probability that the components of the velocity of the center of mass lie in the intervals v_0 to $v_0 + dv_0$; θ_0 to $\theta_0 + d\theta_0$; φ_0 to $\varphi_0 + d\varphi_0$; while the components of the relative velocity lie in the intervals v_{12} to $v_{12} + dv_{12}$; θ_{12} to $\theta_{12} + d\theta_{12}$; φ_{12} to $\varphi_{12} + d\varphi_{12}$; becomes

$$\left(\frac{m_1 m_2}{4\pi^2 k^2 T^2}\right)^{3/2} exp\left(\frac{-m_1 m_2 v_0^2}{2\mu kT}\right) exp\left(\frac{-\mu v_{12}^2}{2kT}\right) \times$$

$$v_0^2 \sin\theta_0 \, dv_0 d\theta_0 d\varphi_0 v_{12}^2 \sin\theta_{12} \, dv_{12} d\theta_{12} d\varphi_{12}$$

We are interested in the probability increment for the relative velocityrelative velocity:probability density function irrespective of the velocity of the center of mass. To sum the contributions for all possible motions of the center of mass, we integrate this expression over the possible ranges of v_0, θ_0, and φ_0. We have

$$\left(\frac{df(v_{12})}{dv_{12}}\right)\left(\frac{df(\theta_{12})}{d\theta_{12}}\right)\left(\frac{df(\varphi_{12})}{d\varphi_{12}}\right) dv_{12} d\theta_{12} d\varphi_{12} =$$

$$= \left(\frac{m_1 m_2}{4\pi^2 k^2 T^2}\right)^{3/2} \int_0^\infty v_0^2 exp\left(\frac{-m_1 m_2 v_0^2}{2\mu kT}\right) dv_0 \times \int_0^\pi \sin\theta_0 \, d\theta_0 \int_0^{2\pi} d\varphi_0$$

$$\times \left[v_{12}^2 exp\left(\frac{-\mu v_{12}^2}{2kT}\right) \sin\theta_{12} \, dv_{12} d\theta_{12} d\varphi_{12} \right]$$

$$= \left(\frac{\mu}{2\pi kT}\right)^{3/2} v_{12}^2 exp\left(\frac{-\mu v_{12}^2}{2kT}\right) \sin\theta_{12} \, dv_{12} d\theta_{12} d\varphi_{12}$$

This is the same as the probability increment for a single-particle velocity—albeit with μ replacing m; v_{12} replacing v; θ_{12} replacing θ; and φ_{12} replacing φ. As in the single-particle case, we can obtain the probability increment for the scalar component of the relative velocity by integrating over all possible values of θ_{12} and φ_{12}. We find

$$\frac{df(v_{12})}{dv_{12}} = 4\pi \left(\frac{\mu}{2\pi kT}\right)^{3/2} v_{12}^2 exp\left(\frac{-\mu v_{12}^2}{2kT}\right) dv_{12}$$

In §8, we find the most probable velocity, the mean velocity, and the root-mean-square velocity for a gas whose particles have mass m. By identical arguments, we obtain the most probable relative velocity, the mean relative velocity, and the root-mean-square relative velocity. To do so, we can simply substitute μ for m in the earlier results. In particular, the mean relative velocity is

$$\bar{v}_{12} = \langle v_{12} \rangle = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \approx 1.596 \left(\frac{kT}{\pi\mu}\right)^{1/21}$$

If particles 1 and 2 have the same mass, m, the reduced mass becomes $\mu = m/2$. In this case, we have

$$\langle v_{12} \rangle = \left(\frac{2(8kT)}{\pi m}\right)^{1/2} = \sqrt{2} \langle v \rangle$$

We can arrive at this same conclusion by considering the relative motion of two particles that represents the average case. As illustrated in Figure 9, this occurs when the two particles have the same speed, $\langle v\rangle$, but are moving at 90-degree angles to one another. In this situation, the length of the resultant vector—the relative speed— is just

$$\left|\overline{v}_{12}\right|=\left\langle v_{12}\right\rangle=\sqrt{2}\left\langle v\right\rangle.$$
