7.3: The Maxwell Distribution For Velocities

The most probable distribution of velocities of particles in a gas is given by Equation 7.2.9 with $\epsilon = \frac{p^2}{2m} = \frac{1}{2}mv^2$. Thus we expect the distribution function for velocities to be

$$f(v)d^3v = C\ \exp\left(-\frac{mv^2}{2kT}\right)d^3v \tag{7.3.1}$$

This is known as the **Maxwell distribution**. Maxwell arrived at this by an ingenious argument many years before the derivation we gave in the last section was worked out. He considered the probability of a particle having velocity components (v_1, v_2, v_3). If the probability of a particle having the x-component of velocity between v_1 and $v_1 + dv_1$ is $f(v_1)dv_1$, then the probability for (v_1, v_2, v_3) would be

$$\text{Probability of } (v_1, v_2, v_3) \ = \ f(v_1)f(v_2)f(v_3)dv_1dv_2dv_3 \tag{7.3.2}$$

Since the dynamics along the three dimensions are independent, the probability should be the product of the individual ones. Further, there is nothing to single out any particular Cartesian component, they are all equivalent, so the function f should be the same for each direction. This leads to 7.3.2. Finally, we have rotational invariance in a free gas with no external potentials, so the probability should be a function only of the speed $v = \sqrt{v_1^2 + v_2^2 + v_3^2}$. Thus we need a function $f(v)$ such that $f(v_1)f(v_2)f(v_3)$ depends only on v. The only solution is for $f(v)$ to be of the form

$$f(v_1) \ \propto \ \exp-(\alpha v_1^2) \tag{7.3.3}$$

for some constant α. The distribution of velocities is thus

$$fd^3v \ = \ C\exp(-\alpha v_1^2)d^3v \tag{7.3.4}$$

Since the total probability $\int fd^3v$ must be one, we can identify the constant C as $\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}$.

We now consider particles colliding with the wall of the container, say the face at $x = L_1$, as shown in Fig. 7.3.1. The momentum imparted to the wall in an elastic collision is $\Delta p_1 = 2mv_1$. At any given instant roughly half of the molecules will have a component v_1 towards the wall. All of them in a volume $A \times v_1$ (where A is the area of the face) will reach the wall in one second, so that the force on the wall due to collisions is

$$F \ = \ \frac{1}{2}\left(\frac{N}{V}\right)A \ \times \ v_1 \ \times \ (2mv_1) \ = \ \left(\frac{N}{V}\right)Amv_1^2 \tag{7.3.5}$$

Averaging over v_1^2 using Equation 7.3.4, we get the pressure

$$p \ = \ \frac{\langle F\rangle}{A} = \left(\frac{N}{V}\right)m\langle v_1^2\rangle \ = \ \left(\frac{N\ m}{2\alpha V}\right) \tag{7.3.6}$$

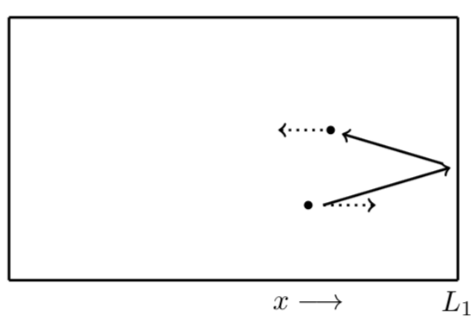

Figure 7.3.1: A typical collision with the wall of the container at $x = L_1$. The velocity component v_1 before and after collision is shown by the dotted line.

Comparing with the ideal gas law, we can identify α as $\frac{m}{2kT}$. Thus the distribution of velocities is

$$f(v)d^3v \;=\; \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT}\right) d^3v \tag{7.3.7}$$

$$f(v)d^3v \;=\; \left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}} \exp\left(-\frac{\epsilon}{kT}\right) d^3p$$

This is in agreement with Equation 7.2.9.

Adapting Maxwell's Argument to a Relativistic Gas

Maxwell's argument leading to Equation 7.3.7 is so simple and elegant that it is tempting to see if there are other situations to which such a symmetry-based reasoning might be applied. The most obvious case would be a gas of free particles for which relativistic effects are taken into account. In this case, $\epsilon = \sqrt{p_2 + m_2}$ and it is clear that $e^{-\beta\epsilon}$ cannot be obtained from a product of the form $f(p_1)f(p_2)f(p_3)$. So, at first glance, Maxwell's reasoning seems to fail. But this is not quite so, as the following line of reasoning will show.

As a first step, notice that the distribution in Equation 7.3.7 is for a gas which has no overall drift motion. This is seen by noting that

$$\langle v_i \rangle \;=\; \int d^3p \frac{p_i}{m} \left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}} \exp\left(-\frac{\epsilon}{kT}\right) \;=\; 0 \tag{7.3.8}$$

We can include an overall velocity $\vec{u}$ by changing the distribution to

$$f(p) = \left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}} \exp\left(-\frac{(\vec{p} - m\vec{u})^2}{2mkT}\right) \tag{7.3.9}$$

It is easily verified that $\langle v_i \rangle = u_i$. It is important to include the overall motion in the reasoning since the symmetry is the full set of Lorentz transformations in the relativistic case and they include velocity-transformations.

Secondly, we note that in the relativistic case where we have the 4-momentum p_μ, $\mu = 0,\ 1,\ 2,\ 3$ and what is needed to sum over all states is not the integration over all p_μ, rather we must integrate with the invariant measure

$$d\mu = d^4p\delta(p^2 - m^2)\Theta(p_0) \tag{7.3.10}$$

where Θ is the step function,

$$\Theta(x) = \begin{cases} 1 & \text{for x>0} \\ 0 & \text{for x<0} \end{cases} \tag{7.3.11}$$

Further the δ-function can be expanded as

$$\delta(p^2 - m^2) = \delta(p_0^2 - \vec{p}^2 - m^2) = \frac{1}{2p_0}\left[\delta(p_0 - \sqrt{\vec{p}^2 + m^2}) + \delta(p_0 + \sqrt{\vec{p}^2 + m^2})\right] \tag{7.3.12}$$

The integration over p_0 is trivial because of these equations and we find that

$$\int d\mu f(p_\mu) \;=\; \int \frac{d^3p}{2\sqrt{\vec{p}^2 + m^2}} f(\sqrt{\vec{p}^2 + m^2},\ \vec{p}) \tag{7.3.13}$$

Now we seek a function which can be written in the form $f(p_0)f(p_1)f(p_2)f(p_3)$ involving the four components of p_μ and integrate it with the measured Equation 7.3.10. The function f must also involve the drift velocity in general. In the relativistic case, this is the 4-velocity U^μ, whose components are

$$U_0 = \frac{1}{\sqrt{1 - \vec{u}^2}}, \qquad U_i = \frac{u_i}{\sqrt{1 - \vec{u}^2}} \tag{7.3.14}$$

The solution is again an exponential

$$f(p) = C\exp(-\beta\, p_\mu U^\mu) \;=\; C\exp\left(-\beta(p_0 U_0 - \vec{p}\cdot\vec{U})\right) \tag{7.3.15}$$

With the measure from Equation 7.3.10, we find

$$\int d\mu\; f(p)\; B(p) = C\; \int \frac{d^3p}{2\epsilon_p} \exp\Big(-\beta(\epsilon_p U_0 - \vec{p}\cdot\vec{U})\Big)\; B(\epsilon_p, \vec{p}) \tag{7.3.16}$$

for any observable $B(p)$ and where $\epsilon_p = \sqrt{p_2 + m_2}$. At this stage, if we wish to, we can consider a gas with no overall motion, setting $\vec{u} = 0$, to get

$$\langle B\rangle \;=\; C\; \int \frac{d^3p}{2\epsilon_p} \exp(-\beta\epsilon_p)\; B(\epsilon_p, \vec{p}) \tag{7.3.17}$$

This brings us back to a form similar to Equation 7.2.9, even for the relativistic case.
