Problem 1C.2

The wall collision frequency. It is desired to find the frequency Z with which the molecules in an ideal gas strike a unit area of a wall from one side only. The gas is at rest and at equilibrium with a temperature T and the number density of the molecules is n. All molecules have a mass m. All molecules in the region $x < 0$ with $u_x > 0$ will hit an area S in the yz-plane in a short time Δt if they are in the volume $Su_x\Delta t$. The number of wall collisions per unit area per unit time will be

$$\begin{aligned} Z &= \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{+\infty}(Su_x\Delta t)f(u_x,u_y,u_z)du_x du_y du_z}{S\Delta t} \\ &= n\left(\frac{m}{2\pi\kappa T}\right)^{3/2}\left(\int_0^{+\infty}u_x\exp(-mu_x^2/2\kappa T)\,du_x\right) \\ &\quad \left(\int_{-\infty}^{+\infty}\exp(-mu_y^2/2\kappa T)\,du_y\right)\left(\int_{-\infty}^{+\infty}\exp(-mu_z^2/2\kappa T)\,du_z\right) \\ &= n\sqrt{\frac{\kappa T}{2\pi m}} = \frac{1}{4}n\bar{u} \end{aligned} \tag{1C.2-1}$$

Verify the above development.

Solution

Suppose we have an xyz-coordinate system immersed in an ideal gas. In order for molecules to strike the yz-plane within a certain time interval Δt, the molecules have to be within a distance of $u_x\Delta t$ to do so, u_x being the x-component of their velocity. If we consider a small area on the yz-plane S, then all the molecules within the volume $Su_x\Delta t$ will collide with this area. The Maxwell–Boltzmann distribution function,

$$f(u_x,u_y,u_z) = n\left(\frac{m}{2\pi\kappa T}\right)^{3/2}\exp\left(-\frac{mu^2}{2\kappa T}\right), \tag{1}$$

allows us to find the number of molecules in an ideal gas at rest between certain velocities. $f(u_x,u_y,u_z)\,du_x\,du_y\,du_z$ represents the number of molecules per unit volume that has velocity between $\langle u_x,u_y,u_z\rangle$ and $\langle u_x+du_x,u_y+du_y,u_z+du_z\rangle$. So then this quantity times the volume $(Su_x\Delta t)f(u_x,u_y,u_z)\,du_x\,du_y\,du_z$ represents the number of molecules in the volume $Su_x\Delta t$ that has velocity between $\langle u_x,u_y,u_z\rangle$ and $\langle u_x+du_x,u_y+du_y,u_z+du_z\rangle$. Integrating over all possible velocities, we obtain the total number of molecules within the volume that will collide with the surface.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\infty}(Su_x\Delta t)f(u_x,u_y,u_z)\,du_x\,du_y\,du_z$$

The molecules are assumed to travel from left to right only, so the integral in du_x only goes from 0 to ∞. Dividing this by the area S, we get the number of collisions per unit area.

$$\frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\infty}(Su_x\Delta t)f(u_x,u_y,u_z)\,du_x\,du_y\,du_z}{S}$$

Dividing this by the time interval Δt, we get the number of collisions per unit area per unit time Z.

$$Z = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\infty}(Su_x\Delta t)f(u_x,u_y,u_z)\,du_x\,du_y\,du_z}{S\Delta t}$$

Bring out the constant from the integral and cancel it with the one in the denominator.

$$Z = \frac{\cancel{S\Delta t}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} u_x f(u_x, u_y, u_z)\, du_x\, du_y\, du_z}{\cancel{S\Delta t}}$$

Substitute the formula for $f(u_x, u_y, u_z)$ in equation (1).

$$Z = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} u_x n \left(\frac{m}{2\pi\kappa T}\right)^{3/2} \exp\left(-\frac{mu^2}{2\kappa T}\right) du_x\, du_y\, du_z.$$

Bring the constant in front of the integral.

$$Z = n\left(\frac{m}{2\pi\kappa T}\right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} u_x \exp\left(-\frac{mu^2}{2\kappa T}\right) du_x\, du_y\, du_z.$$

Let $a = m/2\kappa T$ to make the integral easier to write and substitute $u^2 = u_x^2 + u_y^2 + u_z^2$.

$$Z = n\left(\frac{a}{\pi}\right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} u_x e^{-a(u_x^2+u_y^2+u_z^2)}\, du_x\, du_y\, du_z.$$

Split up the triple integral into three single integrals.

$$Z = n\left(\frac{a}{\pi}\right)^{3/2} \left(\int_{0}^{\infty} u_x e^{-au_x^2}\, du_x\right)\left(\int_{-\infty}^{\infty} e^{-au_y^2}\, du_y\right)\left(\int_{-\infty}^{\infty} e^{-au_z^2}\, du_z\right)$$

The integrals in du_y and du_z are known. Use the substitution,

$$v = au_x^2$$

$$dv = 2au_x\, du_x \quad \rightarrow \quad \frac{dv}{2a} = u_x\, du_x,$$

to solve the first one.

$$Z = n\left(\frac{a}{\pi}\right)^{3/2} \left(\int_{0}^{\infty} e^{-v}\frac{dv}{2a}\right)\left(\sqrt{\frac{\pi}{a}}\right)\left(\sqrt{\frac{\pi}{a}}\right)$$

Evaluate it.

$$Z = n\left(\frac{a}{\pi}\right)^{3/2} \left(\frac{1}{2a}\right)\left(\sqrt{\frac{\pi}{a}}\right)\left(\sqrt{\frac{\pi}{a}}\right)$$

Simplify the result.

$$Z = \frac{n}{2}\frac{1}{\sqrt{\pi a}}$$

Substitute the expression for a.

$$Z = \frac{n}{2}\sqrt{\frac{2\kappa T}{\pi m}} = \frac{n}{4}\sqrt{\frac{8\kappa T}{\pi m}}$$

Therefore,

$$Z = \frac{1}{4}n\bar{u},$$

where $\bar{u}$ is the mean molecular speed.