Problem 1C.3

Pressure of an ideal gas.[4] It is desired to get the pressure exerted by an ideal gas on a wall by accounting for the rate of momentum transfer from the molecules to the wall, assuming specular reflections.

(a) When a molecule traveling with a velocity $\mathbf{u}$ collides with a wall, its incoming velocity components are u_x, u_y, u_z, and after a specular reflection at the wall, its components are $-u_x$, u_y, u_z. Thus the net momentum transmitted to the wall by a molecule is $2mu_x$. The molecules that have an x-component of the velocity equal to u_x, and that will collide with the wall during a small time interval Δt, must be within the volume $Su_x\Delta t$. How many molecules with velocity components in the range from u_x, u_y, u_z to $u_x + \Delta u_x$, $u_y + \Delta u_y$, $u_z + \Delta u_z$ will hit an area S of the wall with a velocity u_x within a time interval Δt? It will be $f(u_x, u_y, u_z)du_x du_y du_z$ times $Su_x\Delta t$. Then the pressure exerted on the wall by the gas will be

$$p = \frac{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{0}^{+\infty}(Su_x\Delta t)(2mu_x)f(u_x, u_y, u_z)du_x du_y du_z}{S\Delta t} \tag{1C.3-1}$$

Explain carefully how this expression is constructed. Verify that this relation is dimensionally correct.

(b) Insert Eq. 1C.1-1 for the Maxwell–Boltzmann equilibrium distribution into Eq. 1C.3-1 and perform the integration. Verify that this procedure leads to $p = n\kappa T$, the ideal gas law.

Solution

Part (a)

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,

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

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 $\langle u_x + du_x, u_y + du_y, u_z + du_z\rangle$. The pressure on the surface is the force divided by area.

$$p = \frac{F_x}{S}$$

From Newton's second law we know that $F_x = ma_x = dP_x/dt$, where P_x is the component of momentum in the x-direction.

$$p = \frac{1}{S}\frac{dP_x}{dt}$$

[4] R. J. Silbey and R. A. Alberty, *Physical Chemistry*, Wiley, New York, 3rd edition (2001), pp. 639-640.

Since we are considering a finite time interval of Δt, we have

$$p = \frac{1}{S}\frac{\Delta P_x}{\Delta t}.$$

The total change in momentum is obtained by multiplying the total number of molecules by the change in momentum of each molecule.

$$p = \frac{1}{S\Delta t}\left(\text{total \# of molecules} \times \text{change in momentum of each molecule}\right).$$

We obtain the total number of molecules in the volume by integrating $(Su_x\Delta t)f(u_x, u_y, u_z)\, du_x\, du_y\, du_z$ over all possible velocities. As explained in the problem statement, the change in momentum of one molecule is $2mu_x$. Thus,

$$p = \frac{1}{S\Delta t}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} \underbrace{(2mu_x)}_{\text{change in momentum of each molecule}} \underbrace{(Su_x\Delta t)f(u_x, u_y, u_z)\, du_x\, du_y\, du_z}_{\text{total \# of molecules}}.$$

The molecules are assumed to travel from left to right only, so the integral in du_x only goes from 0 to ∞. Therefore,

$$p = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty}(Su_x\Delta t)(2mu_x)f(u_x, u_y, u_z)\, du_x\, du_y\, du_z}{S\Delta t}.$$

We will check the dimensions now. $(Su_x\Delta t)f(u_x, u_y, u_z)\, du_x\, du_y\, du_z$ represents a number of molecules, so it is dimensionless. Thus, the units of p should be equivalent to those of $2mu_x/S\Delta t$, what remains in the expression.

$$[p] \stackrel{?}{=} \left[\frac{2mu_x}{S\Delta t}\right]$$

We have

$$\begin{aligned} \frac{\text{N}}{\text{m}^2} &\stackrel{?}{=} \text{kg}\cdot\frac{\text{m}}{\text{s}}\cdot\frac{1}{\text{m}^2\cdot s} \\ \frac{\text{kg}}{\text{m}^2}\cdot\frac{\text{m}}{\text{s}^2} &\stackrel{?}{=} \frac{\text{kg}}{\text{m}\cdot\text{s}^2} \\ \frac{\text{kg}}{\text{m}\cdot\text{s}^2} &= \frac{\text{kg}}{\text{m}\cdot\text{s}^2} \end{aligned}$$

Therefore, the relation is dimensionally correct.

Part (b)

Bring the constants out in front of the integral and cancel $S\Delta t$.

$$p = 2m\frac{\cancel{S\Delta t}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} u_x^2 f(u_x, u_y, u_z)\, du_x\, du_y\, du_z}{\cancel{S\Delta t}}$$

Substitute Eq. 1C.1-1 in for $f(u_x, u_y, u_z)$.

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

Bring the constants in front.

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

Let $a = m/2\kappa T$ so that the integral is easier to write.

$$p = 2mn\left(\frac{a}{\pi}\right)^{3/2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} u_x^2 e^{-au^2}\, du_x\, du_y\, du_z$$

Substitute $u^2 = u_x^2 + u_y^2 + u_z^2$.

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

Split up the triple integral into three single integrals.

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

The last two integrals are known. Integrate the first one by parts as follows.

$$\begin{aligned} v &= u_x & dw &= u_x e^{-au_x^2}\, du \\ dv &= du_x & w &= -\frac{e^{-au_x^2}}{2a} \end{aligned}$$

The formula being used is $\int v\, dw = vw - \int w\, dv$, so we have

$$p = 2mn\left(\frac{a}{\pi}\right)^{3/2}\left[-\frac{u_x e^{-au_x^2}}{2a}\bigg|_0^{\infty} - \int_0^{\infty}\left(-\frac{e^{-au_x^2}}{2a}\right) du_x\right]\left(\sqrt{\frac{\pi}{a}}\right)\left(\sqrt{\frac{\pi}{a}}\right).$$

The first term in square brackets is zero. Bring the constant in front of the remaining integral.

$$p = 2mn\left(\frac{a}{\pi}\right)^{3/2}\left(\frac{1}{2a}\int_0^{\infty} e^{-au_x^2}\, du_x\right)\left(\sqrt{\frac{\pi}{a}}\right)\left(\sqrt{\frac{\pi}{a}}\right)$$

This last integral is known.

$$p = 2mn\left(\frac{a}{\pi}\right)^{3/2}\left(\frac{1}{2a}\cdot\frac{1}{2}\sqrt{\frac{\pi}{a}}\right)\left(\sqrt{\frac{\pi}{a}}\right)\left(\sqrt{\frac{\pi}{a}}\right)$$

Simplify the result.

$$p = \frac{mn}{2a}$$

Substitute the expression for a and cancel terms.

$$p = \frac{\cancel{m}n \cdot \cancel{2}\kappa T}{\cancel{2}\cancel{m}}$$

Therefore,

$$p = n\kappa T.$$