Self Diffusion Coefficient of Ideal Gas

We present a short derivation of the self diffusion coefficient of an ideal gas using some methods of kinetic theory. The derivation is a special case of that provided in Chapter 13 of [1]. We begin with the principle of diffusion writ mathematically. The principle of diffusion states that particles diffuse from a region of high concentration/number density to a region of low concentration/number density. Given a three dimensional number distribution of particles the principle can be written as

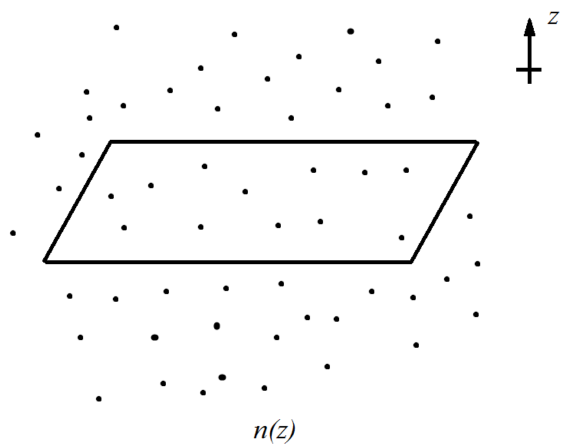
$$\mathbf{J} = -D\,\nabla n(\mathbf{x}) \tag{1}$$

where $\mathbf{J}$ is the flux, the number of particles flowing through a unit area per unit time, $n(\mathbf{x})$ is the number density, and D is the diffusion coefficient. Our goal is to compute this diffusion coefficient for an ideal gas.

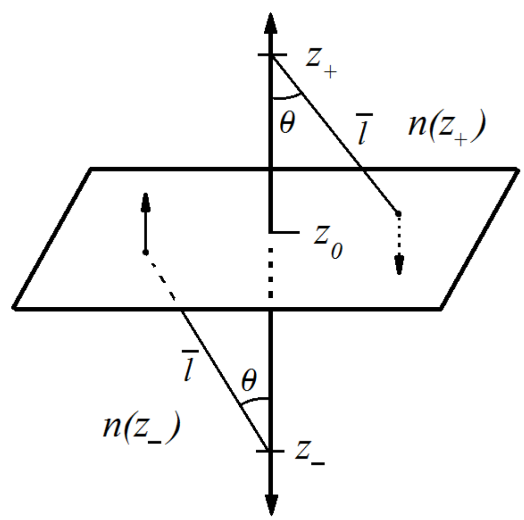
Our starting point is depicted in Fig. 1. In (a) we show a number of particles distributed across a surface of finite area laid perpendicular to the z axis. In our picture of diffusion we assume that the particles move both upwards and downwards, and we want to calculate the net flux of particles diffusing through the surface.

The flux of particles, the number of particles moving through a unit area per unit time, can be written in terms of the density as

$$\frac{dN}{dA\,dt} = n(\mathbf{x})\,\mathbf{v} \tag{2}$$



(a)



(b)

Figure 1: (a) Diffusion across surface: Particles defined by a volume number density $n(z)$ diffusing across a rectangular surface. (b) Detailed diffusion across surface: Particles diffusing through surface from both sides. $n(z_-)$ are the particles diffusing downwards and $n(z_+)$ are the particles diffusing upwards. The relevant surface is at $z = z_0$. $\bar{l}$ is the mean free path of a particle.

For our case, only motion in the z direction is relevant, so we can replace the vectors with their z component values. Also, we want to compute the flux at the surface, so we take $z = z_0$. However, there are two different fluxes we need to consider. There is a flux coming downwards through the surface from above and a flux going upwards through the surface from below. For conceptualy simplicity it will be useful to calculate these quantities separately and then add them together. The computations are similar so we need only calculate one and then extrapolate to the other case.

For the flux coming from below we assume that before the particle reaches the surface at $z = z_0$, it has traveled a mean-free-path of $\bar{l}$[1]. We also define the density for our flux as the density of the particle's point of origin. From the figure, then taking z_- as the point of origin of the particle we have

$$z_0 = z_- + \bar{l}\cos\theta \tag{3}$$

which incorporates the fact that the particle can come from any azimuthal direction in crossing the origin. The flux of particles moving upwards through the surface at $z = z_0$ is then

$$\frac{dN}{dA\,dt}\Big|_{(-)} = n(z_-)\,v_z \simeq n(z_0)\,v_z - \bar{l}\cos\theta\left(\frac{\partial n}{\partial z}\right)_{z_0} v_z \tag{4}$$

where in the last equality we expanded $n(z_-)$ in a series around z_0. For this expansion we assumed that the spatial length over which the number density varies is much larger than the length of the mean path since the number density is a macroscopic quanity and the mean free path is microscopic. But because the number density, the flux and the principle of diffusion are macroscopic concepts, we need to conduct an averaging over our microscopic degrees of freedom, namely v_z, in order to compute the net flux through the surface. As per statistical mechanics we assume the velocities of the particles are thermally distributed. So computing the average of our upward flux we find

$$\begin{aligned}
\left\langle \frac{dN}{dA\,dt}\Big|_{(-)} \right\rangle &= \int d^3\mathbf{v}\, n(z_-) v_z\, p(\mathbf{v}) \\
&= \left(\frac{\beta m}{2\pi}\right)^{3/2} \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_0^{\infty} dv_z\, n(z_-) v_z\, e^{-m\beta\mathbf{v}^2/2} \\
&\simeq \left(\frac{\beta m}{2\pi}\right)^{3/2} \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_0^{\infty} dv_z \left[n(z_0)\,v_z - \bar{l}\cos\theta\left(\frac{\partial n}{\partial z}\right)_{z_0} v_z\right] e^{-m\beta\mathbf{v}^2/2} \\
&= \text{(I)} + \text{(II)}
\end{aligned} \tag{5}$$

where the v_z integral runs over only positive values because we are only considering upward moving particles and we defined the two terms as (I) and (II) respectively. (I) can be easily computed to yield

$$\text{(I)} = \frac{1}{4} n(z_0)\bar{v}, \tag{6}$$

where

$$\bar{v} = 2\sqrt{\frac{2}{\pi\beta m}} \tag{7}$$

is the average speed of particles in an ideal gas. To compute (II) we must use the fact that θ is defined in the velocity, and not position, coordinate system. Namely, $v_z = |\mathbf{v}|\cos\theta$. With this definition we can write (II) as

$$\text{(II)} = -\bar{l}\left(\frac{\partial n}{\partial z}\right)_{z_0} \left(\frac{\beta m}{2\pi}\right)^{3/2} \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_0^{\infty} dv_z\, \frac{v_z^2}{|\mathbf{v}|}\, e^{-m\beta\mathbf{v}^2/2} \tag{8}$$

By the isotropic symmetry of the Bolztmann distribution we expect the integral to be 1/3 of its value with $\mathbf{v}^2/|\mathbf{v}| = |\mathbf{v}|$ in the integrand. Because the v_z integral runs over half of its domain, we must also include a

[1] See [1] Ch.13 for justification.

factor of $1/2$. So we find

$$\text{(II)} = -\frac{1}{6}\bar{l}\,\overline{v}\left(\frac{\partial n}{\partial z}\right)_{z_0} \tag{9}$$

and the total flux in the upwards direction is

$$\left\langle \frac{dN}{dA\,dt}\Big|_{(-)} \right\rangle = \frac{1}{4}n(z_0)\overline{v} - \frac{1}{6}\bar{l}\,\overline{v}\left(\frac{\partial n}{\partial z}\right)_{z_0}. \tag{10}$$

Performing a similar calculation we find the flux in the downwards direction is

$$\left\langle \frac{dN}{dA\,dt}\Big|_{(+)} \right\rangle = -\frac{1}{4}n(z_0)\overline{v} - \frac{1}{6}\bar{l}\,\overline{v}\left(\frac{\partial n}{\partial z}\right)_{z_0}. \tag{11}$$

The total flux in the z direction is the sum[2] of these two quantities. We then have

$$\begin{aligned} J_z(z_0) &\equiv \left\langle \frac{dN}{dA\,dt}\Big|_{(+)} \right\rangle + \left\langle \frac{dN}{dA\,dt}\Big|_{(-)} \right\rangle \\ &= -\frac{1}{3}\bar{l}\,\overline{v}\left(\frac{\partial n}{\partial z}\right)_{z_0}. \end{aligned} \tag{12}$$

And by Eq.(1), we find that the self-diffusion coefficient of an ideal gas is

$$D = \frac{1}{3}\bar{l}\,\overline{v}. \tag{13}$$

Writing this quantity explicilty in terms of the thermal equlibrium temperature, pressure, and the mass of an individual particle we find

$$D = \frac{1}{3}\frac{k_B T}{\sqrt{2}\pi r^2 p} 2\sqrt{\frac{2k_B T}{\pi m}} = \frac{2}{3r^2 p}\sqrt{\frac{1}{m}\left(\frac{k_B T}{\pi}\right)^3} \tag{14}$$

Note: This derivation of the diffusion coefficient was corrected around mid century. The new accepted derivation is [2].

References

[1] J. H. Jeans, *The dynamical theory of gases*. University Press, 1921.

[2] S. Chapman and T. G. Cowling, *The mathematical theory of non-uniform gases: an account of the kinetic theory of viscosity, thermal conduction and diffusion in gases*. Cambridge university press, 1970.

[2] It is the sum and not the difference because both quantities are defined with z in the positive direction.