

Diffusion

Diffusion is a net transport of molecules or energy or momentum or ... from a region of higher concentration to one of lower concentration by random (molecular) motion. We will look at diffusion in gases primarily.

Mean free path

Molecules in a gas move with a kinetic or thermal velocity related to their temperature. Thinking in terms of the billiard ball analogy, molecules move some distance before colliding with another molecule and then the two molecules ricochet off in other directions. The typical distance the molecules move between collisions is called the mean free path (λ). λ depends on the number density of the molecules and their collisional crosssection, A_c . In defining λ , one can think of it in terms of the volume per molecule, V_m , which is the inverse of the number density of molecules, N , in units of molecules per cubic m in mks units.

$$V_m = \frac{1}{N} \quad (1)$$

This is the same N we defined in the equation of state for an ideal gas in microscopic units early in the class

$$P = N k_B T \quad (2)$$

One can think of this volume per molecule as a cylinder whose area is the collisional crosssectional area and the length of the cylinder is the mean free path. Therefore this volume per molecule can also be defined as

$$V_m = A_c \lambda \quad (3)$$

So we can combine (1) and (3) to get an equation for the mean free path

$$\lambda = \frac{1}{A_c N} \quad (4)$$

Brownian motion or random walk

The next step in understanding diffusion is to understand the net effect of the random motion of the molecules that results from these collisions. The question we have to answer is *“What is the typical distance a molecule will move away from its initial position after some number of collisions with other molecules?”*

This is written as the standard deviation of its position after some number of collisions. After one collision it will have moved on average λ in some direction. After two collisions, it will have moved the sum of two vectors each of (mean) length, λ , but the direction of each of the two vectors is random. So the sum of the two vectors must be described in some probabilistic way.

We add two vectors and ask what is the length of the sum of the two vectors. Vector 1, \vec{x}_1 , is the vector describing the position change in the position of the molecule between the 0th collision and the 1st collision. It is given as

$$\vec{x}_1 = \Delta x_1 \hat{x} + \Delta y_1 \hat{y} + \Delta z_1 \hat{z} \quad (5)$$

To understand the net result of a random or “drunkard’s” walk which is the sum of a series of random steps, we begin by considering the square of the sum of the first two random steps written in Cartesian coordinates and then generalizing to an arbitrary number of steps...

$$X_{n=2} \equiv |\vec{x}_1 + \vec{x}_2| = \left[(\Delta x_1 + \Delta x_2)^2 + (\Delta y_1 + \Delta y_2)^2 + (\Delta z_1 + \Delta z_2)^2 \right]^{1/2}$$

$$X_{n=2}^2 = |\vec{x}_1 + \vec{x}_2|^2 = (\Delta x_1 + \Delta x_2)^2 + (\Delta y_1 + \Delta y_2)^2 + (\Delta z_1 + \Delta z_2)^2 \quad (6)$$

$$X_{n=2}^2 = (\Delta x_1^2 + 2\Delta x_1 \Delta x_2 + \Delta x_2^2) + (\Delta y_1^2 + 2\Delta y_1 \Delta y_2 + \Delta y_2^2) + (\Delta z_1^2 + 2\Delta z_1 \Delta z_2 + \Delta z_2^2)$$

$$X_{n=2}^2 = (\Delta x_1^2 + \Delta y_1^2 + \Delta z_1^2) + 2(\Delta x_1 \Delta x_2 + \Delta y_1 \Delta y_2 + \Delta z_1 \Delta z_2) + (\Delta x_2^2 + \Delta y_2^2 + \Delta z_2^2)$$

$$X_{n=2}^2 = |\hat{x}_1|^2 + |\hat{x}_2|^2 + 2(\Delta x_1 \Delta x_2 + \Delta y_1 \Delta y_2 + \Delta z_1 \Delta z_2) \quad (7)$$

Now we need to consider the expected value or mean value of $X_{n=2}^2 = \langle X_{n=2}^2 \rangle$.

$$\langle X_{n=2}^2 \rangle = \langle |\hat{x}_1|^2 + |\hat{x}_2|^2 + 2(\Delta x_1 \Delta x_2 + \Delta y_1 \Delta y_2 + \Delta z_1 \Delta z_2) \rangle$$

$$\langle X_{n=2}^2 \rangle = \langle |\hat{x}_1|^2 \rangle + \langle |\hat{x}_2|^2 \rangle + 2(\langle \Delta x_1 \Delta x_2 \rangle + \langle \Delta y_1 \Delta y_2 \rangle + \langle \Delta z_1 \Delta z_2 \rangle) \quad (8)$$

The expected value of the length the molecule moves between collisions is the mean free path, λ .
So

$$\langle X_{n=2}^2 \rangle = \lambda^2 + \lambda^2 + 2(\langle \Delta x_1 \Delta x_2 \rangle + \langle \Delta y_1 \Delta y_2 \rangle + \langle \Delta z_1 \Delta z_2 \rangle)$$

$$\langle X_{n=2}^2 \rangle = 2\lambda^2 + 2(\langle \Delta x_1 \Delta x_2 \rangle + \langle \Delta y_1 \Delta y_2 \rangle + \langle \Delta z_1 \Delta z_2 \rangle) \quad (9)$$

Now the question is what to do with the expected value of the cross terms. If the collisions are really random as we think and assume they are, then there is no preferred direction and therefore no correlation between Δx_1 and Δx_2 or Δy_1 and Δy_2 which means

$$\langle \Delta x_1 \Delta x_2 \rangle = 0, \quad \langle \Delta y_1 \Delta y_2 \rangle = 0, \quad \langle \Delta z_1 \Delta z_2 \rangle = 0 \quad (10)$$

Therefore

$$\langle X_{n=2}^2 \rangle = 2\lambda^2 \quad (11)$$

Generalizing this relation to X^2 after n collisions gives

$$\langle X_n^2 \rangle = n\lambda^2 \quad (12)$$

The square root of this equation gives us the root of the mean square distance or *rms* distance a molecule will move away from its initial location after n collisions.

$$\langle X_n^2 \rangle^{1/2} = \sqrt{n} \lambda \quad (13)$$

Time and velocity

Now we must introduce time into the diffusion process. In order to calculate diffusive fluxes and rates of diffusion, we need to know how long it will a molecule take to move a distance X away from its initial location. From (13) we see that the number of collisions required for the molecule to move a distance X is given by

$$n = \left(\frac{X}{\lambda}\right)^2 \quad (14)$$

The typical time for a molecule to move one mean free path, which is the time between collisions, is

$$\tau_\lambda = \frac{\lambda}{v_t} \quad (15)$$

where v_t is the thermal velocity of the molecule. Therefore the typical time for the molecule to move a distance, X , is

$$\tau_\lambda = n\tau_\lambda = n \frac{\lambda}{v_t} = \left(\frac{X}{\lambda}\right)^2 \frac{\lambda}{v_t} = \frac{X^2}{v_t \lambda} \quad (16)$$

The average velocity of the molecule in moving a distance X is

$$v_x = \frac{X}{n\tau} = \frac{Xv_t\lambda}{X^2} = v_t \frac{\lambda}{X} \quad (17)$$

So the farther the molecule moves from its initial position, the slower it moves on average. This makes diffusion a very slow process over large distances (but it is quite fast over very short distances).

Diffusive Flux

Suppose we have a horizontal gradient in the density of some quantity, B , which is ρ_B . What is the flux of high ρ_B into the low ρ_B area and visa versa via diffusion? Consider two points separated by a distance, Δx . The difference in ρ_B between the two points is $\Delta\rho_B = d\rho_B/dx \Delta x$. The general definition of a flux is the density times the velocity, $\rho_B \vec{v}$ (check units). (17) provides the diffusive velocity. The **net** flux is the diffusive flux in the $+x$ direction minus the diffusive flux in the $-x$ direction

$$F_{Bnet} = \rho_B(x - \Delta x/2) v(x - \Delta x/2) - \rho_B(x + \Delta x/2) v(x + \Delta x/2) \quad (18)$$

$$F_{Bnet} = \left(\rho_B - \frac{d\rho_B}{dx} \frac{\Delta x}{2}\right) \frac{v_t \lambda}{\Delta x} - \left(\rho_B + \frac{d\rho_B}{dx} \frac{\Delta x}{2}\right) \frac{v_t \lambda}{\Delta x}$$

$$F_{Bnet} = \left(-\frac{d\rho_B}{dx} \frac{\Delta x}{2}\right) \frac{v_t \lambda}{\Delta x} - \left(\frac{d\rho_B}{dx} \frac{\Delta x}{2}\right) \frac{v_t \lambda}{\Delta x} = -2 \frac{d\rho_B}{dx} \frac{\Delta x}{2} \frac{v_t \lambda}{\Delta x}$$

$$F_{Bnet} = -v_t \lambda \frac{d\rho_B}{dx} \quad (19)$$

Diffusivity and Equations of Diffusion

What is the definition of diffusivity? The diffusion equations were derived by Adolf Fick in 1855. Fick's First Law is that the diffusive flux, F , of some substance, B , is given by

$$\vec{F}_B = -D \frac{d\rho_B}{dx} \hat{x} \quad (20)$$

or more generally

$$\vec{F}_B = -D \vec{\nabla} \rho_B \quad (21)$$

where D is the diffusivity in units of m^2/s . F has units of B-units/ m^2/s . This equation form is known as “down-gradient” diffusion because the flux is in the opposite direction of the gradient. Comparing (19) and (20), it is clear that

$$D = v_t \lambda \quad (22)$$

For completeness, Fick's Second Law is known as the diffusivity equation which describes the time rate of change of the density of some quantity, B , due to diffusion

$$\frac{\partial \rho_B}{\partial t} = \nabla \cdot [D \nabla \rho_B(\vec{r}, t)] \quad (23)$$

If the diffusivity, D , does not vary with position then

$$\frac{\partial \rho_B}{\partial t} = D \nabla^2 \rho_B(\vec{r}, t) \quad (24)$$

Note that (23) and (24) are simply versions of the flux divergence equation

$$\frac{\partial \rho_B}{\partial t} = -\nabla \cdot \vec{F}_B + \dot{B} \quad (25)$$

where \dot{B} represents a source term because plugging (20) into (25) with no source term yields

$$\frac{\partial \rho_B}{\partial t} = -\nabla \cdot (-D \nabla \rho_B) = \nabla \cdot (D \nabla \rho_B)$$

which is the same as (23).

Putting it all together

The diffusivity, D , can be thought of as a distance times a velocity. Given the derivations we just did about the random motions of molecules in a gas, we can write

$$D = X v_x = \frac{X v_t \lambda}{X} = v_t \lambda = \frac{v_t}{A_c N} \quad (26)$$

The thermal velocity has at least 2 definitions. The rms velocity is

$$v_{t-rms} = \sqrt{\frac{3k_B T}{m}} \quad (27)$$

The average magnitude of the velocity is

$$v_{t-mag} = \sqrt{\frac{8k_B T}{m\pi}} \quad (28)$$

From the ideal gas law,

$$N = \frac{P}{k_B T} \quad (29)$$

Combining these

$$D = \frac{v_t}{A_c N} = \sqrt{a \frac{k_B T}{m}} \frac{k_B T}{A_c P} = \sqrt{\frac{a}{m}} \frac{(k_B T)^{3/2}}{A_c P} \quad (30)$$

where a is the constant for the relevant thermal velocity, either 3 or $8/\pi$. $a^{1/2}$ is either 1.73 or 1.60. The biggest uncertainty in using this equation is probably the collisional cross-section.

The Diffusivity of Air

The diffusivity of air at 300 K and 1000 mb, is $2.216 \times 10^{-5} \text{ m}^2/\text{s}$.

We can calculate the diffusivity of air from (30). The cross-sectional area of a N_2 molecule is $\sim 2.08 \times 10^{-10} \times 1.6 \times 10^{-10} \sim 4 \times 10^{-20} \text{ m}^2$. The collisional cross-section of two N_2 molecules colliding should be about 10^{-19} m^2 . Using this value yields a diffusivity of air of $2 \times 10^{-4} \text{ m}^2/\text{s}$. This is a factor of 10 too high indicating that the cross-sectional area at 300 K is actually about 10^{-18} m^2 and the simple cross-sectional area I used is too low by about a factor of 10.