Chapter 10

Transport Processes

10.1 Mean Free Path

The mean free path for a particle, denoted by λ, is a the average distance traveled by a particle between collisions with other particles. The average number of collisions per unit length is thus $\frac{1}{\lambda}$ and the probability that a collision occurs in an interval dr is therefore $\frac{dr}{\lambda}$.

If $P_0(r)$ denotes the probability that no collision occurs in an interval of length r, then the probability that no collision occurs in an interval of length $r + dr$ is

$$P_0(r+dr) = P_0(r)\left(1 - \frac{dr}{\lambda}\right)$$

We can use this relationship to determine an expression for $P_0(r)$. For example, if dr is small,

$$P_0(r+dr) = P_0(r) + \left(\frac{d}{dr}P_0(r)\right)dr$$

Thus,

$$P_0(r) + \left(\frac{d}{dr}P_0(r)\right)dr = P_0(r)\left(1 - \frac{dr}{\lambda}\right)$$

$$\frac{d}{dr}P_0(r) = -\frac{1}{\lambda}P_0(r) \quad \rightarrow \quad P_0(r) = e^{-\frac{r}{\lambda}}$$

The probability that no collision occurs thus follows a Poisson distribution. Furthermore, we see that as the distance r increases, the probability that no collision occurs decreases. In other words, the greater the distance the particle moves, the lower the probability that it experiences no collisions. Similarly, if the value of λ decreases, the probability the particle experiences a collision increases. All of this makes sense.

The probability that a particle experiences its first collision in an interval between r and $r+dr$ is equal to the product of the probability that the particle experienced no collision traveling a distance r and then experienced a collision when traveling the additional distance dr. Thus, the probability that a particle experiences its first collision in an interval between r and $r+dr$ is $P_0(r)\frac{dr}{\lambda}$.

We can use this expression to calculate the average distance travelled between collisions.

$$\langle r\rangle = \int_0^\infty r\left(P_0(r)\frac{dr}{\lambda}\right) \quad \rightarrow \quad \langle r\rangle = \frac{1}{\lambda}\int_0^\infty r e^{-\frac{r}{\lambda}}dr$$

$$\langle r\rangle = \frac{1}{\lambda}\left(\lambda^2\right) \quad \rightarrow \quad \langle r\rangle = \lambda$$

As expected, the mean distance travelled between collisions is equal to the mean free path.

Let's now consider a gas containing two types of particles, A and B. Particles A have mass m_A, radius r_A, and density ρ_A. Similarly, particles B have mass m_B, radius r_B, and density ρ_B. Let's further assume that the speed of each particle in the gas is described by the Maxwell-Boltzmann speed distribution derived previously.

$$P(v)dv = \left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{\beta m v^2}{2}} 4\pi v^2 dv$$

In this expression, the variable m denotes the mass of a particle of the gas and v is the speed of particle of the gas. We can use this expression to express the average relative speed of two particles of our gas as

$$\overline{v}_r = \int P_A\left(v_A\right) P_B\left(v_B\right)\left|v_A - v_B\right| dv_A dv_B$$

$$\overline{v}_r = \left(\frac{\beta m_A}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\beta m_B}{2\pi}\right)^{\frac{3}{2}}\int e^{-\frac{\beta\left(m_A v_A^2 + m_B v_B^2\right)}{2}}\left(4\pi v_A v_B\right)^2\left|v_A - v_B\right| dv_A dv_B$$

It's easier to write this integral in terms of the center of mass velocity, denoted as v_{CM} and the relative velocity, denoted as v_r.

$$v_{CM} = \frac{m_A v_A + m_B v_B}{m_A + m_B} \qquad v_r = v_A - v_B$$

$$\overline{v}_r = \left(\frac{\beta M}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\beta \mu}{2\pi}\right)^{\frac{3}{2}}\int_0^\infty\int_0^\infty v_r e^{-\frac{\beta}{2}\left(MV_{CM}^2 + \mu v_r^2\right)} dv_r dV_{CM}$$

The variable $M = m_A + m_B$ is the total mass of the particles and the variable $\mu = \frac{m_A m_B}{m_A + m_B}$ is the reduced mass of the particles. Performing the integration then yields

$$\overline{v}_r = \left(\frac{\beta M}{2\pi}\right)^{\frac{1}{2}} \left(\frac{\beta\mu}{2\pi}\right)^{\frac{3}{2}} \left(\frac{1}{2}\right)^{\frac{1}{2}} \int_0^{\infty} v_r e^{\frac{-\beta\mu v_r^2}{2}} dv_r$$

$$\overline{v}_r = \left(\frac{\beta M}{2\pi}\right)^{\frac{1}{2}} \left(\frac{\beta\mu}{2\pi}\right)^{\frac{3}{2}} \left(\frac{1}{2}\right)^{\frac{1}{2}} \left(\frac{1}{\mu\beta}\right)$$

$$\overline{v}_r = \left(\frac{8}{\pi\mu\beta}\right)^{\frac{1}{2}}$$

If the particles are identical and each have mass m,

$$\mu = \frac{m}{2} \quad \rightarrow \quad \overline{v}_r = \left(\frac{8}{\pi\frac{m}{2}\beta}\right)^{\frac{1}{2}} \quad \rightarrow \quad \overline{v}_r = \left(\frac{16}{\pi m\beta}\right)^{\frac{1}{2}}$$

$$\overline{v}_r = \sqrt{2}\left(\frac{8}{\pi m\beta}\right)^{\frac{1}{2}}$$

The average speed of a particle in an ideal gas can be determined from the Maxwell-Boltzmann speed distribution.

$$\overline{v} = \int vP(v)dv$$

$$\overline{v} = \int v\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{\beta m v^2}{2}} 4\pi v^2 dv \quad \rightarrow \quad \overline{v} = 4\pi\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} \int_0^{\infty} e^{-\frac{\beta m v^2}{2}} v^3 dv$$

$$\overline{v} = 4\pi\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} \frac{2}{\beta^2 m^2} \quad \rightarrow \quad \overline{v} = \left(\frac{8}{\pi m\beta}\right)^{\frac{1}{2}}$$

Thus, for identical particles

$$\overline{v}_r = \sqrt{2}\overline{v}$$

We can now determine the frequency of collisions between particles in the gas. Let's assume that all B particles are at rest and an A particle is moving through the gas at speed $\overline{v}_r$. As it moves, the A particle will sweep out a *collision cylinder* of radius $r_{AB} = \frac{r_A + r_B}{2}$ and volume $\pi r_{AB}^2 \overline{v}_r t$ in a time interval t. The number of B particles that collide with this A particle in the time interval t is thus $f_{AB}t$, where f_{AB} is the collision frequency.

$$f_{AB} = \rho_B \pi r_{AB}^2 \overline{v}_r$$

Similarly, for collisions between particles of type A is

$$f_{AA} = \rho_A \pi r_{AA}^2 \overline{v}_r$$

Thus, for a gas of identical particles, the mean free path is

$$\lambda = \frac{\overline{v}}{f_{AA}} \quad \rightarrow \quad \lambda = \frac{\overline{v}_r}{\sqrt{2} f_{AA}} \quad \rightarrow \quad \lambda = \frac{1}{\sqrt{2}\rho_A \pi r_{AA}^2}$$

We can also write this equation in terms of the pressure and temperature of the gas using Equation 5.2.

$$\rho_A = \frac{N_A}{V} \quad \rightarrow \quad \lambda = \frac{k_B T}{\sqrt{2}\pi r_{AA}^2 P}$$

The total number of collisions per unit volume per second between particles of type A and type B is the product of this collision frequency and the density of the type A particles.

$$n_{AB} = f_{AB}\rho_A \quad \rightarrow \quad n_{AB} = \rho_A \rho_B \pi r_{AB}^2 \overline{v}_r$$

$$n_{AB} = \rho_A \rho_B \pi r_{AB}^2 \left(\frac{8}{\pi \mu \beta}\right)^{\frac{1}{2}}$$

Similarly, the total number of collisions between type A particles is

$$n_{AA} = f_{AA}\rho_A \quad \rightarrow \quad n_{AA} = \frac{1}{2}\left(\rho_A \pi r_{AA}^2 \overline{v}_r\right)\rho_A$$

The additional factor of $\frac{1}{2}$ prevents over-counting. Simplifying this expression then gives us

$$n_{AB} = \frac{1}{2}\rho_A^2 \pi r_{AA}^2 \left(\frac{16}{\pi m_A \beta}\right)^{\frac{1}{2}}$$

10.1.1 Diffusion

A bottle containing a volatile chemical is opened very briefly in the center of a large room, releasing many molecules of the chemical into the air. The mean free path of these molecules (*i.e.*, the average distance travelled between collisions with other molecules) is 10^{-5}m, and they collide on average 10^7 times per second. After each collision, the molecules are equally likely to move in any direction.

The average displacement in one-dimension for a molecule for a single step (*i.e.*, between each collision) is zero ($\overline{s} = 0$) since any molecule is equally probable to move in any direction after a collision. We can also show this to be true through integration. The average value of function f over all solid angles is

$$\overline{f} = \frac{1}{4\pi}\int f\sin\theta\, d\theta\, d\phi$$

For displacements of the molecules along the z-axis, the z-component of a step of length α would be

$$\overline{f}_z = \frac{1}{4\pi}\int (\alpha\cos\theta)\sin\theta\, d\theta\, d\phi$$

$$\overline{f}_z = \frac{\alpha}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} (\cos\theta)\,(\sin\theta)\, d\theta \quad \rightarrow \quad \overline{f}_z = \frac{\alpha}{2}\int_0^{\pi} (\cos\theta)\,(\sin\theta)\, d\theta$$

$$\overline{f}_z = 0$$

For displacements along the x-axis and y-axis we have

$$\overline{f}_x = \frac{1}{4\pi}\int (\alpha\sin\theta\cos\phi)\sin\theta\, d\theta\, d\phi$$

$$\overline{f}_x = \frac{\alpha}{2\pi}\int_0^{2\pi} \cos\phi\, d\phi \int_0^{\pi} \sin^2 d\theta\, d\theta \quad \rightarrow \quad \overline{f}_x = 0$$

$$\overline{f}_y = \frac{1}{4\pi}\int (\alpha\sin\theta\sin\phi)\sin\theta\, d\theta\, d\phi$$

$$\overline{f}_y = \frac{\alpha}{2\pi}\int_0^{2\pi} \sin\phi\, d\phi \int_0^{\pi} \sin^2 d\theta\, d\theta \quad \rightarrow \quad \overline{f}_y = 0$$

The average displacement is indeed zero in all directions. The square of the dispersion for a single step is

$$\overline{(\Delta s)^2} = \overline{s^2} - \overline{s}^2 \quad \rightarrow \quad \overline{(\Delta s)^2} = \overline{s^2}$$

$$\overline{s_z^2} = \frac{1}{4\pi}\int (\alpha\cos\theta)^2\sin\theta\, d\theta\, d\phi \quad \rightarrow \quad \overline{s_z^2} = \frac{\alpha^2}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} \left(\cos^2\theta\right)(\sin\theta)\, d\theta$$

$$\overline{s_z^2} = \frac{\alpha^2}{4\pi}\,(2\pi)\left(\frac{2}{3}\right) \quad \rightarrow \quad \overline{s_z^2} = \frac{\alpha^2}{3}$$

A similar calculation shows that

$$\overline{s_x^2} = \overline{s_y^2} = \frac{\alpha^2}{3}$$

$$\overline{s^2} = \overline{s_x^2} + \overline{s_y^2} + \overline{s_z^2} \quad \rightarrow \quad \overline{s^2} = \alpha^2$$

Thus, for the molecules of the volatile chemical in this example

$$\overline{s^2} = \left(10^{-5}\text{m}\right)^2 \quad \rightarrow \quad \overline{s^2} = 10^{-10}\text{m}^2$$

The displacement after N steps (or collisions) can be determine from the displacement for a single step. For movement along the z-axis we have

$$\overline{z} = N\overline{s_z} \quad \rightarrow \quad \overline{z} = N\left(0\right) \quad \rightarrow \quad \overline{z} = 0$$

The dispersion after N steps is

$$\overline{\left(\Delta z\right)^2} = N\overline{\left(\Delta s\right)_z^2} \quad \rightarrow \quad \overline{\left(\Delta z\right)^2} = \frac{N\alpha^2}{3}$$

Since the molecules of gas in this example collide 10^7 times a second, the dispersion after one second is

$$\overline{\left(\Delta z\right)^2} = \left(10^7\right)\frac{\left(10^{-5}\text{m}\right)^2}{3} \quad \rightarrow \quad \overline{\left(\Delta z\right)^2} = 3.3 \times 10^{-4}\text{m}^2$$

The standard deviation of the distribution of volatile molecules varies as the square-root of the number of collisions. For motion along the z-axis,

$$\sigma_z = \sqrt{\overline{\left(\Delta z\right)^2}} \quad \rightarrow \quad \sigma_z = \sqrt{N\overline{\left(\Delta s\right)_z^2}}$$

We can use this expression to calculate the number of collisions or equivalently the time required for a certain level of diffusion to occur. For example, suppose we are on the z-axis a distance of 6m away from the bottle. The number of collisions required for 32% of the molecules to be farther from the bottle than you would correspond to the number of collisions resulting in a standard deviation of 6m.

$$\left(6\text{m}\right)^2 = N\left(3.3 \times 10^{-4}\text{m}^2\right) \quad \rightarrow \quad N = 1.08 \times 10^{12}$$

The time required for this number of collisions is

$$t = \frac{1.08 \times 10^{12}}{10^7} \quad \rightarrow \quad t = 1.08 \times 10^5\text{s}$$

That's about 30 hours.

10.2 Transport of Molecular Quantities

Viscosity involves the transport of momentum, diffusion involves the transport of mass, and thermal conductivity involves the transport of energy.

10.2.1 Viscosity

Let's now consider a system consisting of two parallel plates a distance a away from each other along the z-axis. The lower plate is kept at rest while the upper plate is moving at speed V in the x-axis direction. A gas is contained within the volume between the two plates.

The average distance traveled by a particle of the gas since its last collision is λ. Therefore, the position of this last collision is

$$z' = z - \frac{v_z \lambda}{v}$$

In this equation, v_z is the z-axis component of the velocity and v is the magnitude of the velocity. We can relate the momentum of a particle of the gas at position z to the momentum of a particle of the gas at position z' through the following approximation:

$$p\left(z'\right) = p\left(z - \frac{v_z \lambda}{v}\right) \quad \rightarrow \quad p\left(z'\right) = p\left(z\right) - \frac{v_z \lambda}{v}\frac{dp}{dz} + \ldots$$

The net flow of momentum, denoted as $\psi(z)$, is given by integrating the product of $p\left(z'\right)$ and the number of molecules crossing the surface from the height z' over all possible velocities.

$$\psi(z) = \int p\left(z'\right) v_z \rho \left[\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{m\beta}{2}\left[(v_x - v(z))^2 + v_y^2 + v_z^2\right]}\right] dv_x dv_y dv_z$$

Substitution of the expression for $p\left(z'\right)$ then gives us

$$\psi(z) = \int \left[p\left(z\right) - \frac{v_z \lambda}{v}\frac{dp}{dz}\right] v_z \rho \left[\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{m\beta}{2}\left[(v_x - v(z))^2 + v_y^2 + v_z^2\right]}\right] dv_x dv_y dv_z$$

The integral with $p\left(z\right)$ is zero since $p\left(z\right)$ does not depend on v_x, v_y, or v_z. This leaves us with

$$\psi(z) = \left(-\rho\lambda \frac{dp}{dz}\right)\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \int \frac{v_z^2}{v} e^{-\frac{m\beta}{2}\left[(v_x - v(z))^2 + v_y^2 + v_z^2\right]} dv_x dv_y dv_z$$

If $v(z)$ is small compared to v_x, which will likely be the case, we can ignore its contribution to the integral. Let's also assume that the system is isotropic so that

$$v_x^2 = v_y^2 = v_z^2 \quad \rightarrow \quad v^2 = 3v_x^2$$

$$\psi(z) = \left(-\rho\lambda \frac{dp}{dz}\right)\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \int \frac{1}{3} v e^{-\frac{m\beta v^2}{2}} 4\pi v^2 dv$$

$$\psi(z) = \left(-\rho\lambda\frac{dp}{dz}\right)\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}}\frac{4}{3}\pi\left(\frac{2}{m^2\beta^2}\right)$$

$$\psi(z) = -\frac{1}{3}\left(\rho\lambda\frac{dp}{dz}\right)\left(\frac{8}{m\pi\beta}\right)^{\frac{1}{2}}$$

We recognize the final term in this expression as the average velocity, $\overline{v}$.

$$\overline{v} = \left(\frac{8}{m\pi\beta}\right)^{\frac{1}{2}} \quad \rightarrow \quad \psi(z) = -\frac{1}{3}\lambda\rho\overline{v}\frac{dp}{dz}$$

We can now generalize this expression and convert $\psi(z)$ to $\vec{\psi}(z)$ by swapping the derivative with a gradient

$$\vec{\psi}(z) = -\frac{1}{3}\rho m\lambda\overline{v}\nabla v$$

This is Newton's Law of viscosity, which is usually written as

$$\vec{\psi}(z) = -\eta\nabla v$$

In this equation, the variable η is the coefficient of viscosity and is independent of pressure and density. From inspection we see that

$$\eta = \frac{1}{3}\rho m\lambda\overline{v} \quad \rightarrow \quad \eta = \frac{1}{3}\rho m\left[\frac{1}{\sqrt{2}\rho\pi r^2}\right]\left[\left(\frac{8k_BT}{m\pi}\right)^{\frac{1}{2}}\right]$$

$$\eta = \frac{1}{3}\left(\frac{4}{\pi^3}\right)^{\frac{1}{2}}\frac{(mk_BT)^{\frac{1}{2}}}{r^2}$$

As we might have anticipated, viscosity increases with temperature.

10.2.2 Thermal conductivity

Now assume that the plates are both fixed (not moving) but there is a difference in temperature between them. Now rather than there being a gradient of momentum between the plates, there is a gradient in temperature, and thus the average energy per molecule, denoted as $\bar{\epsilon}$ will vary with position.

$$\frac{d\bar{\epsilon}}{dz} = \frac{d\bar{\epsilon}}{dT}\frac{dT}{dz} \quad \rightarrow \quad \frac{d\bar{\epsilon}}{dz} = \frac{C_V}{N}\nabla T$$

Thus,

$$\psi(z) = -\frac{1}{3}\rho\lambda\overline{v}\frac{C_V}{N}\nabla T$$

This is Fourier's heat law, which is usually written as

$$\psi(z) = -k\nabla T$$

The variable k in this equation is the thermal conductivity. From inspection we see that

$$k = \frac{1}{3}\rho\lambda\overline{v}\frac{C_V}{N} \quad \to \quad k = \frac{\eta C_V}{mN} \quad \to \quad \kappa = \frac{\eta C_V}{M}$$

10.2.3 Diffusion

Consider a system consisting of two gasses, A and B, confined in a cylinder aligned along the z-axis. The density of each gas is a function of position along the z-axis and the sum of these densities is constant.

$$\rho_A(z) + \rho_B(z) = \rho = \text{constant}$$

Each gas also has its own distribution of velocities, $f_A(\vec{v})$ and $f_B(\vec{v})$. A particle of gas A arrives, on average, at a position z from $z' = z - \frac{v_z\lambda_A}{v}$, where λ_A is the mean free path of a particle of gas A. The density of molecules of gas A at position z' is

$$\rho_A(\vec{v}, z') = \rho_A(z') f_A(\vec{v})$$

$$\rho_A(\vec{v}, z') = \rho_A(z) f_A(\vec{v}) - \frac{v_z\lambda_A}{v}\frac{d\rho_A}{dz} f_A(\vec{v}) + \ldots$$

The number of molecules passing through a unit plane perpendicular to the z-axis in the +z direction per second is thus

$$v_z\rho_A(\vec{v}, z') = \rho_A v_z(z) f_A(\vec{v}) - \frac{v_z^2\lambda_A}{v}\frac{d\rho_A}{dz} f_A(\vec{v}) + \ldots$$

The net flow is obtained through integration

$$\psi_A(z) = \int \left[\rho_A v_z(z) f_A(\vec{v}) - \frac{v_z^2\lambda_A}{v}\frac{d\rho_A}{dz} f_A(\vec{v}) + \ldots\right] dv_x dv_y dv_z$$

If we assume the gas is isotropic

$$\psi_A(z) = \int \left[\rho_A v_z(z) f_A(\vec{v}) - \frac{\frac{1}{3}v^2\lambda_A}{v}\frac{d\rho_A}{dz} f_A(\vec{v}) + \ldots\right] 4\pi v^2 dv$$

Since

$$f_A = \left(\frac{m_A\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{m_A\beta}{2}v^2}$$

$$\psi_A(z) = -\left(\frac{4\pi\lambda_A}{3}\right)\frac{d\rho_A}{dz}\left(\frac{m_A\beta}{2\pi}\right)^{\frac{3}{2}} \int_0^\infty v^3 e^{-\frac{m_A\beta}{2}v^2} dv$$

$$\psi_A(z) = -\left(\frac{4\pi\lambda_A}{3}\right)\frac{d\rho_A}{dz}\left(\frac{m_A\beta}{2\pi}\right)^{\frac{3}{2}}\frac{2}{m_A^2\beta^2}$$

$$\psi_A(z) = -\frac{1}{3}\lambda_A\overline{v}_A\frac{d\rho_A}{dz} \quad \rightarrow \quad \vec{\psi}_A(z) = -\frac{1}{3}\lambda_A\overline{v}_A\nabla\rho_A$$

This is Fourier's heat law, which is usually written as

$$\vec{\psi}_A(z) = -D\nabla\rho$$

The variable D in this equation is the diffusion coefficient. From inspection we see that

$$D_A = \frac{1}{3}\lambda_A\overline{v}_A$$

$$D_A = \frac{1}{3}\left[\frac{1}{\sqrt{2}\rho_A\pi r_{AA}^2}\right]\left[\left(\frac{8k_BT}{m_A\pi}\right)^{\frac{1}{2}}\right]$$