Chapter 2

Diffusion

Transport of mass, heat and momentum takes place by two mechanisms, *convection* and *diffusion*. Convection is the process by which material or heat is transported due to the mean motion of the carrier fluid. Diffusion is the process by which material is transported by the random thermal motion of the molecules within the fluid, even in the absence of any mean flow. The random thermal motion takes place on the microscopic length scale in the fluid, which is the molecular size in a liquid, and the mean free path in a gas. Examples of convection and diffusion are as follows.

1. A mixed flow reactor with an impeller, in which a reaction catalysed by a solid catalyst takes place, as shown in figure 2.1. The pipes at the inlet and outlet of a reactor transport material by convection into and out of the reactor. Within the reactor, transport takes place by convection due to the motion of the impeller, and the flow patterns generated therein. However, if we closely examine the surface of a catalyst, the fluid flow takes place tangential to the catalyst surface, and there is no flow perpendicular to the surface of the catalyst. Therefore, the transport of the reactant from the fluid to the solid surface, and the transport of product from the solid surface to the fluid, can take place only by diffusion.

2. A shell-and-tube heat exchanger, in which a hot fluid flows through the tube and a cold fluid flows on the shell side. The heat is transported into the exchanger by convection by the fluid at the inlet of the tube side, and by convection by the fluid at the outlet of the shell side. However, the transport from the shell side to the tube side cannot take place by convection. This is because the fluid flow is tangential to the wall of the tube, and there is no convective transport perpendicular to the wall of the tube. The transport across the tube wall takes place due to diffusion in the fluids and due to conduction in the wall of the tube.

3. Fluid flowing through a pipe which is pumped using a pump at the inlet. The action of the pump results in a pressure gradient down the tube, with a

> higher pressure at the inlet and a lower pressure at the outlet. The net flux of momentum (momentum transported per unit area per unit time) into the tube is the product of the pressure difference and the average velocity of the fluid. (There is a contribution to the flux due to the force exerted by the fluid velocity at the interface, but this contribution is equal at the inlet and outlet, and so there is no net flux due to this). The transport of momentum at the inlet is due to convection, and is absent when there is no fluid flow. The total rate of input of momentum into the tube due to the pump is balanced by the viscous (frictional) force exerted by the walls of the tube on the fluid. This frictional transfer at the wall cannot take place by convection, since there is no fluid flow perpendicular to the walls of the tube. Therefore, this takes place by the diffusion of momentum.

It is evident that the convection is directional, and takes place only along the direction of flow. However, the random velocity fluctuations of the molecules which cause diffusion are isotropic, and have no preferred direction. Therefore, diffusion takes place in the direction in which there is a gradient in the concentration, temperature or mean velocity. Transport takes place by a combination of convection and diffusion in the bulk flow, but can take place only diffusion at bounding surfaces, since there is no mean flow perpendicular to the surface. The mechanisms of mass, momentum and thermal diffusion are discussed in further detail in the following sections.

2.1 Mass diffusion

2.1.1 Mass diffusion in gases

It is easiest to understand the concept for a gas mixture in two bulbs separated by a tube. One of the bulbs contains the pure solvent A, while the other contains a mixture of A and a small amount of the solute B. It will be assumed, for simplicity, that A and B have equal molecular mass and diameter, and the initial pressures and temperatures in the two bulbs are equal. When the stop cork between the two is opened, there is no net transfer of mass between the two bulbs, since the pressures and temperatures are equal. However, there will be a transfer of the solute B from one bulb to the other until the concentrations in the two bulbs are equal. Consider a surface across which there is a variation in the concentration, as shown in figure 2.4. There is a constant transport of molecules across this surface due to the thermal motion of the molecules. The **flux** of molecules at the surface is defined as the number of molecules passing across the surface per unit area per unit time. If the solute concentration and temperature are constant, the total flux of molecules passing downward across the surface is equal to the flux passing through in the upward direction. However, if there is a variation of concentration across the surface as shown in figure 2.4, then there is a net transport of solute molecules in the direction in which the concentration decreases, that is, in the downward direction. This is because the molecules that travel downward through the surface are transported from a distance of

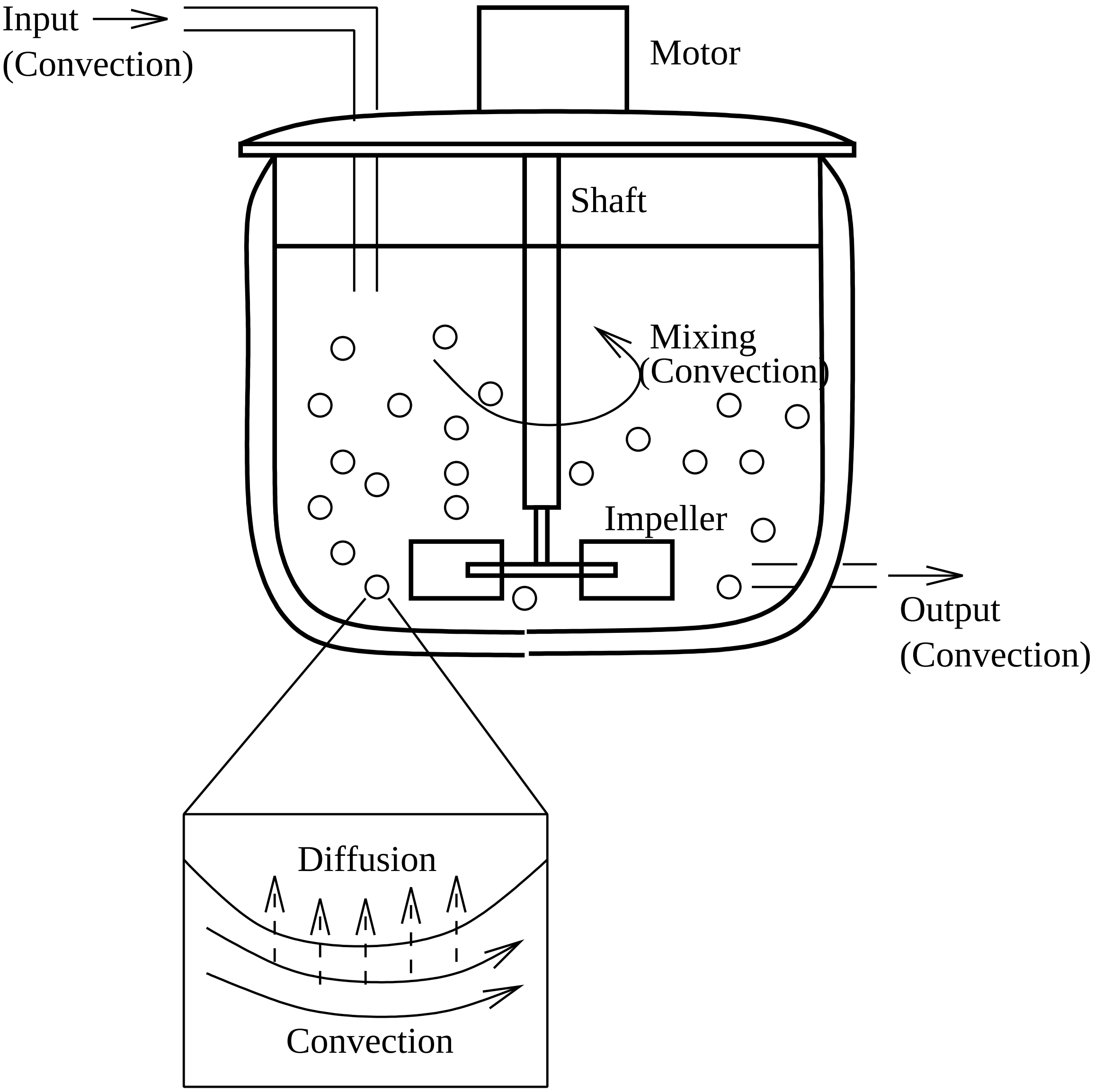

Figure 2.1: Convection and diffusion in a stirred reactor with catalyst pellets.

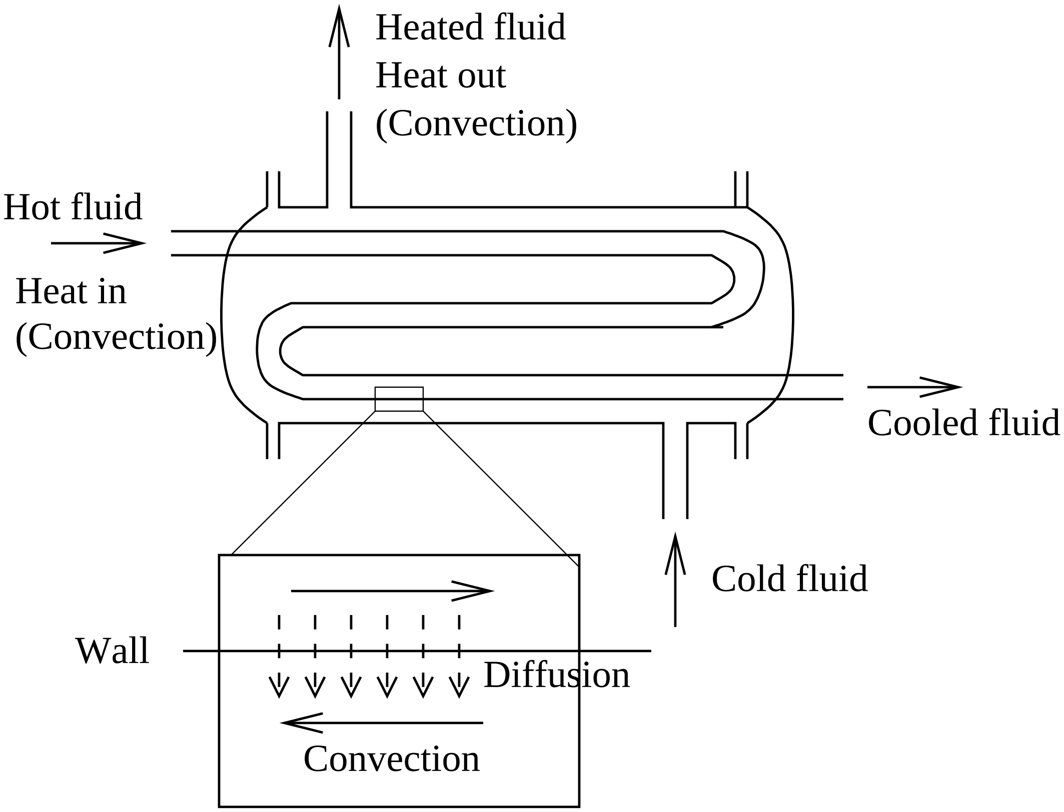

Figure 2.2: Convection and diffusion in a heat exchanger.

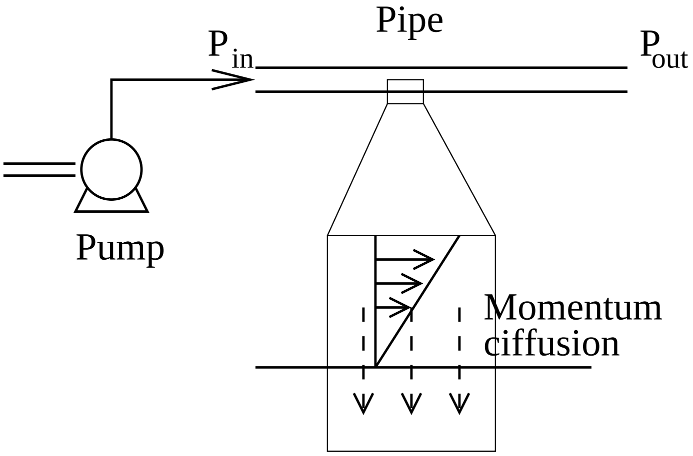

Figure 2.3: Momentum diffusion at the wall of a pipe.

about one mean free path above the surface, where the concentration is higher, whereas the molecules which travel upward are transported from a distance of about one mean free path below the surface, where the concentration is lower. The net flux of molecules, which is the net number of molecules transported downward through the surface per unit area per unit time, can be estimated as follows.

In figure 2.4 molecules are transported across the surface from above to below because a fraction of the molecules above the surface have a velocity in the downward direction. The mass flux across the surface (mass transported per unit area per unit time) is proportional to the concentration (number of molecules per unit volume times the molecular mass), since a larger concentration will result in a larger number of molecules traveling across the surface. The mass flux is also proportional to the root-mean-square of the fluctuating velocity of the molecules, since a higher fluctuating velocity will result in more molecules traveling across the surface. On this basis, we would expect the expression for the mass flux to be given by,

$$Z = A_z c v_{rms} \tag{2.1}$$

where v_{rms} is the root-mean-square speed and c is the concentration. More exact calculations reveal that the factor A_z is $\frac{1}{4}$, but we shall not be concerned with these numerical factors at this stage.

The important point to note is that the molecules reaching the surface in figure 2.4 have arrived had their last collision, on average, a distance $(2\lambda/3)$ above the plane, where the mean free path, λ, is

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n} \tag{2.2}$$

The total flux of molecules is

$$j_{z-} = \frac{1}{4} v_{rms} \left(c_0 + \frac{2}{3} \lambda \left. \frac{dc}{dz} \right|_{z=0} \right) \tag{2.3}$$

where c_0 is the concentration at the surface $z = 0$, and $(c_s - a_2 \lambda (dc/dz)|_{z=0})$ is the average concentration of the molecules traveling downward through the surface. The constant a_2 is a constant of $O(1)$, since the molecules that travel downward are transported from a location which is of the order of one mean free path λ above the surface. This constant can be evaluated exactly using kinetic theory of gases, but this is not necessary since we are only interested in obtaining the order of magnitude of the diffusion coefficient. In equation 2.3, a Taylor series expansion has been used for the average concentration of the molecules that are transported through the surface, and this expansion has been truncated at the second term. This is a good approximation if the mean free path, λ, is small compared to the length over which the concentration varies.

The flux of molecules in the upward direction is

$$j_{z+} = \frac{1}{4} v_{rms} \left(c_0 - \frac{2}{3} \lambda \left. \frac{dc}{dz} \right|_{z=0} \right) \tag{2.4}$$

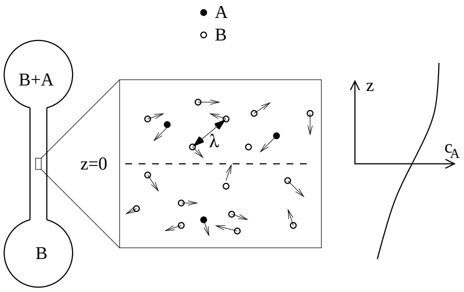

Figure 2.4: Mass diffusion due to concentration gradient in a gas.

since the molecules are transported from a distance of the order of one mean free path below the surface $z = 0$. The total flux of molecules is given by

$$\begin{aligned} j_z &= j_{z+} - j_{z-} \\ &= \frac{1}{3} - \frac{\lambda}{d^2} v_{mean} \left.\frac{dc}{dz}\right|_{z=0} \\ &= -D \left.\frac{dc}{dz}\right|_{z=0} \end{aligned} \tag{2.5}$$

where D, the diffusion coefficient, has dimensions of $\mathcal{L}^2\mathcal{T}^{-1}$. The root mean square velocity of the molecules in a gas can be estimated as

$$v_{rms} = \sqrt{\frac{3kT}{m}} \tag{2.6}$$

where T is the absolute temperature, k is the Boltzmann constant and m is the mass of the molecule. The 'mean' velocity is defined slightly differently, as the average of the magnitude of the velocity of all the particles. This turns out to be,

$$v_{mean} = \sqrt{\frac{8kT}{\pi m}} \tag{2.7}$$

A more exact expression for the diffusion coefficient is obtained using the kinetic theory of gases, which provides the value of a, but the functional dependence of the flux on the temperature, molecular diameter and the concentration gradient is captured by the simple explanation leading to equation 2.5. For a mixture of two components, with masses m_1 and m_2 and diameters d_1 and d_2, exact expressions for the diffusion coefficient can be obtained using methods from the kinetic theory of gases. For spherical molecules, the coefficient of diffusion is

$$D_{12} = \frac{3}{8nd_{12}^2} \left(\frac{kT(m_1 + m_2)}{2\pi m_1 m_2} \right)^{1/2} \tag{2.8}$$

where $d_{12} = (d_1 + d_2)/2$. The coefficient of 'self diffusion', which is the diffusion or a molecule in a gas composed of molecules of the same type, can be obtained by setting $d_1 = d_2 = d$ and $m_1 = m_2 = m$ in equation 2.8,

$$D_{11} = \frac{3}{8nd^2}\left(\frac{kT}{\pi m}\right)^{1/2} \tag{2.9}$$

The diffusion coefficient can be estimated if we know, approximately, the root mean square velocity of the molecules, and the mean free path. Let us consider the specific example of hydrogen gas at room temperature. The mass of one mole (6.023×10^{23} molecules) is 2 gm (2×10^{-3} kg), and therefore the mass of one molecule is 3.32×10^{-27} kg. The Boltzmann constant $k = 1.38\times10^{-23}$ J/K. At a temperature of 398 K, $\sqrt{kT/m} \sim 1.286\times10^{3}$ m/s. Oxygen has a molecular mass of 32 gm per mole, which is 16 times that of hydrogen. Therefore, we would expect the root mean square velocity in oxygen to be four times less than hydrogen, which is 321 m/s. The speed of sound in nitrogen is slightly higher, because it has a molecular mass (28 gm per mole) slightly less than oxygen. Our calculations show that the molecular velocity is close to the speed of sound (about 1290 m/s in hydrogen, and about 330 m/s in air), as expected.

The mean free path of a molecule is the distance travelled between successive collisions. This can be estimated as follows. Consider a molecule in a gas traveling between two successive collisions as shown in figure **??**. As it travels, the molecule sweeps out a cylindrical volume of radius equal to its diameter along the path, and volume $\pi d^2 L$, where d is the molecular diameter and L is the length of the path traveled by the molecule. The molecule will collide with a second molecule if the center of the second molecule is located within the cylinder. The total number of second molecules within this volume is $(\pi d^2 L)\times n$, where n is the number density of the gas molecules (number per unit volume). The length L after which a molecule encounters another molecule will vary from collision to collision, but on average, a collision will take place when the number is second molecules in the volume swept by the first molecule is approximately 1. This gives us $(n\pi d^2\lambda) \sim 1$, where λ is the mean free path (average distance between collisions). A more detailed calculation, carried out on the basis of the kinetic theory of gases, yields $\lambda = (\sqrt{2}\pi n d^2)^{-1}$.

The number of gas molecules per unit volume, from the ideal gas law, is $n \sim (p/kT)$, where p is the pressure. For a gas at STP, $p = 1.013\times10^5$N/m^2, $T = 300K$ and $k = 1.3087\times10^{-23}$J/K, and the number of molecules per unit volume is 2.5×10^{25}m^{-3}. The diameter of a hydrogen molecule is 1.372×10^{-10}m, and therefore the mean free path of a hydrogen molecule at STP is approximately 5×10^{-7}m, or 0.5 microns. The diameter of larger molecules is also of the same order, though somewhat larger; for example, the diameter of a nitrogen molecule is 3.8×10^{-10}m, and that of oxygen is 3.7×10^{-10}m. Therefore, the mean free paths are correspondingly lower, about $6\times10^{-8}m$.

The diffusion coefficient can be estimated as the product of the mean free path and the v_{rms}, is estimated as a constant times 6×10^{-4}m^2/s for hydrogen, and about 2×10^{-5}m^2/s for nitrogen and oxygen. These are, approximately in agreement with values reported in literature; for small molecules H_2 and He, Cussler reports the diffusion coefficient to be 1.132×10^{-4}m^2/s, while for large molecules such as nitrogen and oxygen the diffusion coefficient is about 10 times less, at $1.81 \times 10^{-5}\mathrm{m}^2/\mathrm{s}$. These vary from the diffusion coefficient predicted by equation 2.8 are in agreement with those reported in experiments to within about 2 %. The value $10^{-5} m^2/s$ can be considered a typical diffusion coefficient for commonly encountered gases.

It is useful to examine the assumptions that were used to derive the expression for the diffusion coefficient in 2.5.

1. The first assumption was that the mean free path is small compared to the length scale for diffusion, which is the distance between the two bulbs in this case, so that the expression for the concentration above the surface in 2.4 can be truncated at the first term. The truncation of the Taylor series expansion for the concentration in equation 2.4, which is valid if the length scale of the flow is large compared to the mean free path, is applicable for all applications at STP except those in microfluidics where the channel and tube sizes are of the order of microns.

2.1.2 Mass diffusion in liquids

The estimate of the diffusion coefficient for liquids calculated in a similar manner is not accurate. Since the mean molecular velocity in liquids and gases are about equal at the same temperature, whereas the mean free path is of the order of one molecular diameter, it would be expected that the diffusion coefficients in liquids is only about ten times less than that in gases. However, the diffusion coefficients of small molecules in liquids are about four orders of magnitude lower than that in gases. For example, the diffusion coefficient of nitrogen in water is $1.88 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$, while that of hydrogen in water is $4.5 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$. The diffusion coefficient of larger molecules, such as polymers, in water is smaller still. The diffusion coefficient of heamoglobin in water is $6.9 \times 10^{-11}\mathrm{m}^2/\mathrm{s}$.

Equation 2.5 cannot be used for an accurate prediction of the diffusion coefficients in liquids because ‘cooperative motion’ is necessary for the diffusion of molecules within a liquid. The molecules in a liquid are closely packed, and so the translation of one molecules requires the cooperative motion of many other molecules. This is in contrast to a gas, where the molecules translate freely between successive collisions. An estimate for the diffusion coefficient can be obtained using the Stokes-Einstein equation for the diffusivity,

$$D = \frac{kT}{3\pi\mu d} \tag{2.10}$$

where d is the diameter of the molecule that is diffusing, and μ is the viscosity of the suspending fluid. This formula is strictly applicable only for colloidal particles in a fluid when the particle diameter is large compared to the diameter of the fluid, but is also used as a model equation for predicting the diffusivity of small molecules in a liquid. For nitrogen in water of viscosity $10^{-3}\mathrm{kg/m/s}$, this gives $D = 1.15 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$, whereas for hydrogen in water the diffusivity is $D = 3 \times 10^{-9}\mathrm{m}^2/\mathrm{s}$. Though the order of magnitude of this prediction is in

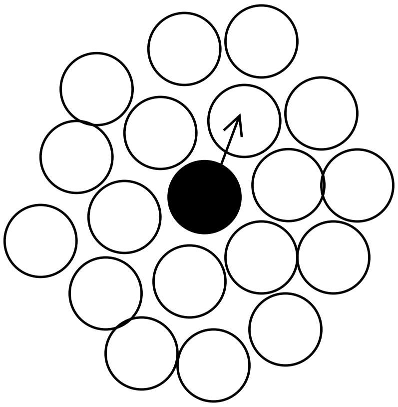

Figure 2.5: The requirement for cooperative motion for the diffusion of mass in a liquid.

agreement with the experimentally measured diffusion coefficinet, the numerical values are not exact. This is because the formula is strictly applicable only for large colloidal particles in a fluid, and not for small molecules.

The diffusion coefficients in liquids and gases increase with temperature. In gases, the diffusion coefficient increases proportional to $T^{1/2}$, due to an increase in the root mean square velocity. Equation 2.10 indicates that the diffusion coefficient increases proportional to T if the viscosity is a constant, due to an increase in the energy of the fluctuations. However, the viscosity of liquids decreases with temperature, and so the diffusion coefficient increases faster than T with an increase in the temperature.

2.1.3 Diffusion in multicomponent systems

So far, we have restricted attention to the diffusion of a solute in a solvent, and assumed that the solute concentration is small compared to that of the solvent. In this case, the motion of the solute does not cause a movement in the center of mass, and so there is no convective motion. However, when the solute and solvent concentrations are comparable, as well as in multicomponent systems, the motion of the solute could result in the motion of the center of mass. In this case, the constituents in the mixture have mean motion, which is the motion of the center of mass, as well as diffusive motion, which is motion relative to the center of mass.

2.2 Momentum diffusion

The stress τ_{xz} is defined as the force per unit area exerted in the x direction at the surface with unit normal in the z direction due to a variation in the x component of the velocity with the z coordinate. The stress can also be

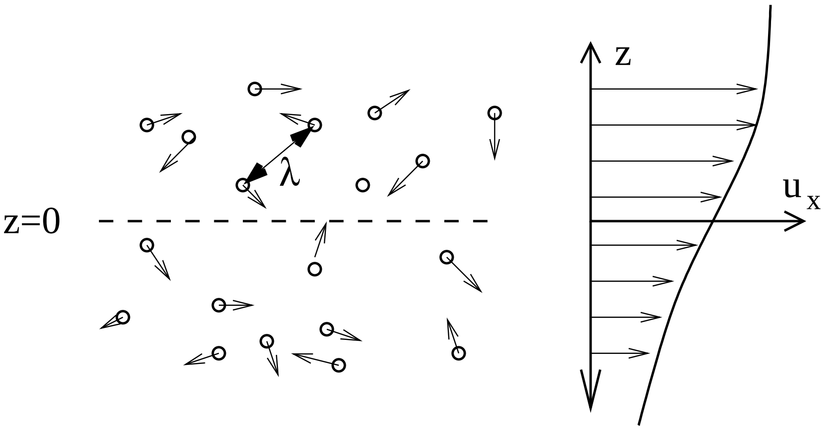

Figure 2.6: Flux of x momentum in the z direction due.

considered as a momentum flux (transfer of momentum per unit area per unit time), since both have units of $\mathcal{M}\mathcal{L}^{-1}\mathcal{T}^{-2}$, though the stress as defined here is actually the negative of the flux of momentum for reasons explained a little later.

The flux of momentum at a surface can be estimated using arguments similar to that for mass diffusion. When there is a gradient in the tangential fluid velocity near a surface, the transport of momentum takes place because the molecules traveling downward through the surface travel from a distance of the order of one mean free path above the surface, where the mean velocity is higher, and the flux of streamwise momentum downward through the surface is the product of (the number of molecules traveling through the surface per unit area per unit time) and the (average momentum of the molecules).

$$j^m_{z-} = (a^m_1 n v_{rms}) \left(m \left(v_x|_{z=0} + a^m_2 \lambda \left. \frac{dv_x}{dz} \right|_{z=0} \right) \right) \tag{2.11}$$

where a^m_1 and a^m_2 are O(1) numbers. In a similar, the flux of streamwise momentum upward through the surface is

$$j^m_{z+} = (a^m_1 n v_{rms}) \left(m \left(v_x|_{z=0} - a^m_3 \lambda \left. \frac{dv_x}{dz} \right|_{z=0} \right) \right) \tag{2.12}$$

The total flux of momentum through the surface is the sum of these two contributions,

$$j^m = -2a^m n v_{rms}) m \lambda \left. \frac{dv_x}{dz} \right|_{z=0} \tag{2.13}$$

The shear stress τ_{xz} is defined as the force per area, in the x direction, acting at a surface whose unit normal is in the $+z$ direction. The flux j^m, as defined, is the flux of streamwise (x) momentum upward through the surface, whose outward unit normal is in the downward ($-z$) direction. Therefore, the stress is the negative of the rate of transfer of momentum,

$$\begin{aligned}\tau_{xz} &= 2a^m n m v_{rms} \lambda \frac{dv_x}{dz} \\ &= \mu \frac{dv_x}{dz} \qquad (2.14)\end{aligned}$$

where μ is the 'coefficient of viscosity' is $2a^m n m v_{rms}$. The 'momentum diffusivity' can be obtained by recasting the right side of the above expression in terms of the gradient in the momentum density, (nmv_x).

$$\begin{aligned}\tau_{xz} &= 2a^m v_{rms} \lambda \frac{d(nmv_x)}{dz} \\ &= \nu \frac{d(nmv_x)}{dz} \qquad (2.15)\end{aligned}$$

where $\nu = (\mu/\rho)$ is the 'kinematic viscosity' or the 'momentum diffusivity'.

The expression for μ in 2.14 contains an unknown coefficient, a^m, which can be determined using a more detailed calculation based upon the kinetic theory of gases. The viscosity for a dilute gas consisting of spherical molecules is

$$\begin{aligned}\mu &= \frac{5}{16d^2}\left(\frac{mkT}{\pi}\right)^{1/2} \\ \nu &= \frac{5}{16nd^2}\left(\frac{kT}{\pi m}\right)^{1/2} \qquad (2.16)\end{aligned}$$

It is evident from equations 2.8 and 2.16 that the self diffusivity D_{11} and the kinematic viscosity ν are proportional to each other, and the Schmidt number $Sc = (D_{11}/\nu) = (6/5)$ for monoatomic gases of spherical molecules. In real gases, the Schmidt number varies between 1.32 and 1.4 for most polyatomic gases, but has a lower value between 1.25 and 1.3 for monoatomic gases. This discrepancy is because the actual pair potential between the gas molecules is not the hard sphere potential, but resembles the Lennard-Jones 6-12 potential which has an attractive component. Values between 1.32 and 1.36 are obtained for gases which interact by the Lennard-Jones potential. However, in all cases, the momentum and mass diffusivity in gases are of the same order of magnitude. The momentum diffusivity also increases with temperature, because the root mean square velocity increases as $\sqrt{T}$, whereas the mean free path is independent of temperature and depends only on the density. The momentum diffusivity decreases as the density is increased, because the mean free path decreases.

The momentum diffusivity for liquids turns out to be much higher than the mass diffusivity of liquids, because the transport of momentum does not require the physical motion of individual molecules, and is therefore not restricted by the collective rearrengement required for the translation of a molecule. Consequently, the momentum diffusivity in liquids is only about one order of magnitude smaller than the mass diffusivity; for example, the kinematic viscosity of water is $1 \times 10^{-6}\mathrm{m}^2\ \mathrm{s}^{-1}$ at 20^oC and atmospheric pressure, whereas that for air is $1.5 \times 10^{-5}\mathrm{m}^2\ \mathrm{s}^{-1}$ under the same conditions. Therefore, the Schmidt number for liquids of small molecules is about 10^3. The momentum diffusivity in liquids also decreases with an increase in temperature, in contrast to gases where it increases with an increase in pressure. This is due to the difference in the structure of gases and liquids. Since the molecules in a liquid are densely packed, neighbouring molecules are located at the position corresponding to the potential energy minimum of the central molecule. In this case, the relative motion of the molecules is an activated process which has an energy barrier, and transport across this barrier is easier as the temperature is increased. This results in a lower stress requirement for a given strain rate, and consequently a lower kinematic viscosity.

Whereas the above simple calculation of the transport coefficients assumes the molecules are spherical, a more detailed calculation incorporates the potential energy of interaction of the molecules. The simplest form of the potential that can be used for spherical molecules is the Lennard-Jones potential, which has two parameters, the characteristic diameter σ and the energy scale ϵ. The potential has the form,

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.17}$$

where r is the distance between the molecules, and ϵ is the lowest energy. The transport coefficients are then given by,

$$\mu = \frac{2}{3\pi^{3/2}}\sqrt{\frac{mkT}{\Omega_\mu \sigma^2}} \tag{2.18}$$

where the correction factor Ω is a slowly varying function of (kT/ϵ).

2.3 Thermal diffusion

Thermal diffusion is the process of transfer of energy due to the random motion of molecules when there is a variation in the temperature in the system. In a gas, thermal diffusion takes place due to the physical motion of molecules across a surface in the gas when there is a temperature variation across the surface. In this case, the energy density e is defined as the average energy per unit volume, in a manner analogous to the concentration, which is the mass of solute per unit volume. Consider a surface at $z = 0$ across which there is a variation in the temperature, and therefore a variation in e. The flux of energy, which is the rate of transfer of energy per unit area downward throug the surface, analogous to equation 2.6, is given by

$$j^e_{z-} = a^e_1 v_{rms}\left(e_0 + a^e_2 \lambda \frac{de}{dz}\right) \tag{2.19}$$

where a_1^e and a_2^e are $O(1)$ numbers. The average rate of transport of energy per unit area upward through the surface, analogous to equation 2.3, is

$$j_{z+}^e = a_1^e v_{rms} \left(e_0 - a_2^e \lambda \frac{de}{dz} \right) \tag{2.20}$$

Using these, the total energy flux is

$$\begin{aligned} j_z^e &= -2a^e v_{rms} \lambda \frac{de}{dz} \\ &= -D^e \frac{de}{dz} \end{aligned} \tag{2.21}$$

where D^e is the 'thermal diffusivity', which has dimensions of L^2T^{-1}. The thermal conductivity is obtained by expressing the energy in terms of the temperature, $e = mnC_vT$, where C_v is the specific heat at constant volume, defined as the energy per unit mass, to obtain

$$j_z^e = -K \frac{dT}{dz} \tag{2.22}$$

where

$$K = 2a^e v_{rms} \lambda mnC_v \tag{2.23}$$

The thermal conductivity has units of $MLT^{-3}\theta^{-1}$, where θ is the dimension of temperature. A more exact calculation can be carried out using kinetic theory in order to remove the uncertainity in the value of a^e, and the result for a monoatomic gas of spherical molecules is

$$K = \frac{5}{2} C_v \mu \tag{2.24}$$

$$K = \frac{75}{64d^2} \left(\frac{k^3T}{\pi m} \right)^{3/2} \tag{2.25}$$

In deriving the above thermal conductivity, the value $C_v = (3k/2m)$ has been used. The diffusivity and thermal conductivity are related by

$$D^e = \frac{K}{nmC_v} = \frac{K}{\rho C_v} \tag{2.26}$$

where ρ is the mass density.

Equation 2.25 for the thermal conductivity is in agreement with experimental results for monoatomic gases to within 1 % at STP. Equation 2.25 is not applicable for diatomic and polyatomic gases, especially for gases of polar molecules, since there is an exchange between the translational and internal energy modes. The ratio of the momentum and thermal diffusivity, $C_p\mu/K$, is known as the Prandtl number. This ratio is predicted to be (2/3) for monoatomic gases of spherical molecules, and experimentally observed values vary between 0.66 for unimolecular gases such as neon and argon, to a maximum of about 0.95 for water at boiling point at atmospheric pressure. For polyatomic molecules, there is a transfer of energy between the translational and internal modes, and a correlation of the type $Pr = C_p/(C_p + 1.25R)$ is found to provide good predictions.

It is clear that the thermal diffusivity for gases is of the same magnitude as the mass and momentum diffusivity, because the mechanism of energy transport (fluctuating motion of the gas molecules) is the same as that for mass and momentum transport. However, in liquids, the mechanism of energy transport could be very different from that of mass and momentum transport. Whereas the transport of mass requires the physical transport of molecules across a surface, the transport of energy does not. One mechanism is the vibrational motion of molecules transferring energy to neighbouring molecules. A second mechnism, in liquid metals, is the transport of energy through the electron cloud around the metal atoms. Transport of energy due to the latter mechanism is a very rapid process, resulting in a high thermal diffusivity. Due to this, the Prandtl number of liquid metals is very low. For example, the Prandtl number of liquid mercury is 0.015 indicating that the thermal diffusivity is about 60 times higher than the momentum diffusivity. In contrast, large organic molecules have Prandtl number between 10^2 and 10^4. The Prandtl number for water is about 7.

Problems:

1. Compute the mean free path and the mean molecular velocity of hydrogen molecules (molecular diameter $2.915\AA$) and chlorine molecules (molecular diameter $4.115\AA$) at 300 K temperature and 10^5 Pa pressure. What is the ratio of the mean free path and the molecular diameter? Compute the viscosity from kinetic theory.

2. In the kinetic theory of gases, there are two dimensionless numbers that relate the macroscopic flow properties to the molecular properties. The Mach number is defined as (U/c), where U is the flow velocity and c is the speed of sound. The Knudsen number is defined as (λ/L), where λ is the mean free path and L is the macroscopic length scale. If the speed of sound in a gas is approximately equal to the molecular velocity, how is the ratio of convection and diffusion in a gas (the Peclet number for concentration and diffusion or the Reynolds number for momentum diffusion) related to the Mach number and the Knudsen number?

3. Calculate the diffusion coefficients of hydrogen (molecular diameter $2.915\AA$), methane (molecular diameter $3.822\AA$) and water vapour and chlorine (molecular diameter $4.115\AA$) in air at 300K and 10^5 Pa. Use the approximate molecular diameter $3.617\AA$ for air.

4. Estimate the mass flux in a gas with uniform density and a gradient in temperature.

   What is the mass flux when there is both a gradient in density and temperature? What is the relation between the density and temperature gradients when the mass flux is zero?

5. The haemoglobin molecule has a diffusivity of 0.069×10^{-9} m^2/s in water. Using the Stokes-Einstein relation, estimate the diameter of this molecule. Assume water has a viscosity of 10^{-3} kg/m/s.

6. Use the Stokes-Einstein relation to determine the diffusion coefficient of hydrogen (molecular diamter $2.915\AA$), oxygen (molecular diameter $3.433\AA$) and benzene (molecular diameter $5.270\AA$ in water at 300K. Compare with the measured values of 4.5×10^{-9}, 2.1×10^{-9} and 1.02×10^{-9} m^2/s respectively. For which molecule would you expect the best and worst agreement with measured values?