5.62 Physical Chemistry II
Spring 2008

Kinetic Theory of Gases – Transport Coefficients

We begin by considering the important case of <u>**diffusion**</u>. Diffusion is a very important transport property for chemists because it describes the mass transport necessary to bring molecules into sufficiently close proximity for chemical reactions to occur. Imagine a one component gas in a fixed volume at fixed T and p but with possible (slight) variation in the density $\rho(z,t)$ in the z-direction at time t.

$\rho(z + \lambda_z)$

$\rho(z)$

$\rho(z - \lambda_z)$
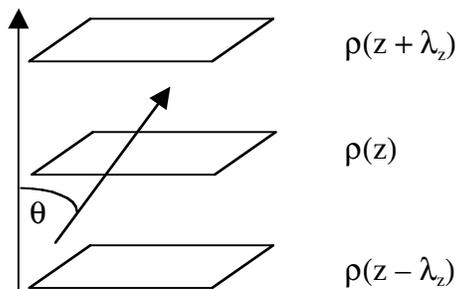
We *imagine* 3 planes at some position z separated by the mean free path and enquire about the simplest description of the <u>net</u> flux of particles j_z^m in the z-direction. The flux has units of mass per unit area per unit time.

At the <u>microscopic level</u>, over a distance on the order λ, a particle trajectory is likely to be interrupted by a single collision that deflects its path to a different height z, which is in a region of different density. We make the assumption that the microscopic flux, denoted $\tilde{j}_z^m(z,t)$, has the form of local effusion flux determined in Lecture #31:

$$\tilde{j}_z^m(z,t) = j_{angle}(\Omega,t) = \frac{\bar{v}}{4\pi}\cos\vartheta\,\rho(z,t)$$

With this form of the flux, we can determine the net flux of particles at the average z-position moving in the positive z-direction:

$$j_z^m(z,t) = -\underbrace{\tilde{j}_z^m(z+\lambda_z,t)}_{\boxed{\begin{array}{c}\text{down}\\\text{from}\\\text{above}\end{array}}} + \underbrace{\tilde{j}_z^m(z-\lambda_z,t)}_{\boxed{\begin{array}{c}\text{up}\\\text{from}\\\text{below}\end{array}}} = -\frac{\bar{v}}{4\pi}\cos\vartheta\left[\rho(z+\lambda_z,t) - \rho(z-\lambda_z,t)\right]$$

The mean free path λ_z may be considered small so we expand the density around the middle position:

$$\rho(z \pm \lambda_z, t) \approx \rho(z,t) \pm \lambda_z \left(\frac{\partial \rho}{\partial z} \right)_t$$

Accordingly, the net mass flux is:

$$j_z^m(z,\theta,t) = -\frac{\overline{v}}{4\pi} \cos \vartheta \, 2\lambda_z \left(\frac{\partial \rho}{\partial z} \right)_t.$$

The mean free path in the z direction can be taken as $\lambda_z = \lambda \cos \vartheta$. The average mass flux is given by the angular average:

$$j_z^m(z,t) = \left\langle \tilde{j}_z^m(z,\theta,t) \right\rangle = -\frac{\overline{v}}{4\pi} 2\lambda \left(\frac{\partial \rho}{\partial z} \right)_t \int_0^{2\pi} d\varphi \int_0^{\frac{\pi}{2}} d\vartheta \sin \vartheta \cos^2 \vartheta.$$

The angular integration gives the value $2\pi/3$ so we obtain the result:

$$j_z^m(z,t) = -\frac{\overline{v}\lambda}{3} \left(\frac{\partial \rho}{\partial z} \right)_t$$

Several approximations have been made. First, we have used a macroscopic quantity, the density, that is defined for many particles, on a microscopic scale to describe the frequency of collisions between a pair of particles. Second, we have assumed that the local velocity and density are uncorrected. This is valid in dilute gases. Third, we have been a bit sloppy about taking the z component of a straight-line trajectory. Fourth, we have no basis for choosing the z-interval to be exactly $2\lambda_z$; it could be slightly smaller or larger. So at best, our results only apply for dilute gases and they will yield a numerical coefficient uncertain by a factor of ~2.

Since the diffusion coefficient is defined as the constant of proportionality between the flux and the spatial density gradient that causes the relaxation we obtain:

$$D = \frac{\lambda \overline{v}}{3}.$$

For hard spheres we know $\lambda = \dfrac{1}{\sqrt{2}\pi d^2 \rho}$ and $\bar{v} = \left(\dfrac{8kT}{\pi m}\right)^{\frac{1}{2}}$ so we find

$$D \propto \frac{\sqrt{T}}{\rho}$$

There will be deviations from this hard sphere expression if the particle interaction is described by a more realistic potential. At low density, this deviation will occur at low temperatures when the relative velocity is lower and hence more strongly samples the repulsive or attractive regions of the potential. Even for hard spheres D will deviate from ρ^{-1} behavior at higher density because the m.f.p. will decrease more strongly than ρ^{-1} as the density increases.

Thermal conductivity   The situation with respect to energy transport is very similar to that for mass transport. The local energy density is given by: $\rho e(z,t) = c_v \rho T(z,t)$ where e(z,t) is the local energy per unit mass of the gas, ρ is the gas density, c_V is the heat capacity per unit mass of the gas, and T is temperature. Therefore the microscopic energy flux is

$$\tilde{j}_z^e(z,\theta,t) = \frac{\bar{v}}{4\pi}\cos\theta\, T(z,t) e(z,t) = \frac{\bar{v}\rho c_v}{4\pi}\cos\vartheta\, T(z,t).$$

The superscript "e" specifies energy flux density.

In exact analogy to the procedure followed for mass transport we approximate:

$$j_z^e(z,t) = -\tilde{j}_z^e(z+\lambda_z,t) + \tilde{j}_z^e(z-\lambda_z,t) = -\frac{\bar{v}\rho c_v}{4\pi}\cos\vartheta\left[T(z+\lambda_z,t) - T(z-\lambda_z,t)\right]$$

so that for small m.f.p.:

$$\tilde{j}_z^e(z,\theta,t) = -\frac{\bar{v}\rho c_v}{4\pi}\cos^2\vartheta\, 2\lambda\left(\frac{\partial T}{\partial z}\right)_t.$$

The average over angles gives the same numerical factor as before ($2\pi/3$), thus

$$j_z^e(z,t) = -\frac{\bar{v}\rho c_v \lambda}{3}\left(\frac{\partial T}{\partial z}\right)_t.$$

Accordingly, the thermal conductivity is found to be:

$$\kappa = \frac{\overline{v}\rho c_v \lambda}{3}$$

Again the numerical factor cannot be trusted. The important prediction is

$$\kappa = D\rho c_v .$$

Viscosity. The final example is the transport of momentum. In this case, the physical quantity of interest is the x-component of momentum because the shear force is applied in the x direction. We have for the microscopic momentum (p) flux:

$$\tilde{j}_z^p(z,t) = \frac{\overline{v}\rho}{4\pi} \cos\vartheta\, v_x(z,t)$$

where ρ is the mass density and $v_x(z,t)$ is the local velocity in the gas in the direction of the shear force. Balancing this microscopic flux gives:

$$j_z^p(z,\theta,t) = -\tilde{j}_z^p(z+\lambda_z,t) + \tilde{j}_z^p(z-\lambda_z,t) = -\frac{\overline{v}\rho}{4\pi} \cos\vartheta\left[v_x(z+\lambda_z,t) - v_x(z-\lambda_z,t) \right]$$

and for small m.f.p. after averaging over angles exactly as before,

$$j_z^p(z,t) = -\frac{\overline{v}\rho\lambda}{3}\left(\frac{\partial v_x(z,t)}{\partial z} \right)_t .$$

The shear viscosity coefficient is the constant of proportionality between the momentum flux $j_z^p(z,t)$ and the gradient in v_z in the direction (x) of the shear force, $\frac{\partial v_x}{\partial z}(z,t)$. Thus, the shear viscosity is given by:

$$\eta = \frac{\overline{v}\rho\lambda}{3} = \frac{\overline{v}}{3\sqrt{2}\pi d^2}$$

where d is the diameter of a hard sphere molecule.

An important prediction of kinetic theory is that the shear viscosity of a dilute gas does not depend on density.

We have relationships between the transport coefficients:

$$\eta = \rho D, \qquad \kappa = c_v \eta, \qquad \frac{\kappa}{\rho c_v} = D.$$

<u>Macroscopic conservation equation</u>.   We have obtained results for three transport equations; for mass, momentum, and energy. These equations are:

$$j_z^m = -D\left(\frac{\partial \rho}{\partial z}\right), \quad j_z^e = -\kappa\left(\frac{\partial T}{\partial z}\right), \quad j_z^p = F_x = -\eta\left(\frac{\partial v_x}{\partial z}\right).$$

We can use these expressions for the flux to obtain conservation equations for the associated quantities of mass, energy, and momentum.

Each of these flux equations is of the form $j_z = -L\left(\dfrac{\partial Y}{\partial z}\right)$. Let us imagine the build up of the quantity Y in a volume element due to the passage of flux. The build up of Y in the volume element in a time dt equals the <u>net passage</u> of flux through the one face of the volume element in time dt.
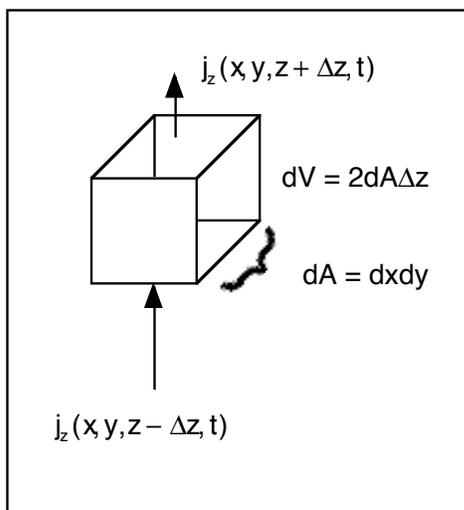
$$dV\left[Y(x,y,z,t+dt) - Y(x,y,z,t)\right] =$$
$$dAdt\left[j_z(x,y,z-\Delta z,t) - j_z(x,y,z+\Delta z,t)\right]$$

Expanding for small dt and Δz gives:
$$dV\left(\frac{\partial Y}{\partial t}\right) = -dA2\Delta z\left(\frac{\partial j_z}{\partial z}\right). \quad \text{Since}$$

dV=dA2Δz we obtain the conservation equation in the form

$$\left(\frac{\partial Y}{\partial t}\right) = -\left(\frac{\partial j_z}{\partial z}\right)$$

Thus the transport equations give rise to macroscopic relaxation equations that relate changes in conserved quantities in space and time.

Conservation law	Conserved quantity - Y	Flux equation $j_z = -L\left(\dfrac{\partial Y}{\partial z}\right)$	Transport equation $\left(\dfrac{\partial Y}{\partial t}\right) = L\left(\dfrac{\partial^2 Y}{\partial z^2}\right)$
Mass diffusion	$\rho(z,t)$	$j_z^m = -D\left(\dfrac{\partial \rho}{\partial z}\right)$	$\left(\dfrac{\partial \rho}{\partial t}\right) = D\left(\dfrac{\partial^2 \rho}{\partial z^2}\right)$
Momentum	$\rho v_x(z,t)$	$j_z^p = -\eta\left(\dfrac{\partial v_x}{\partial z}\right)$	$\left(\dfrac{\partial v_x}{\partial t}\right) = \eta\left(\dfrac{\partial^2 v_x}{\partial z^2}\right)$
Energy	$\rho c_v T(z,t)$	$j_z^e = -\kappa\left(\dfrac{\partial T}{\partial z}\right)$	$\left(\dfrac{\partial T}{\partial t}\right) = \dfrac{\kappa}{\rho c_v}\left(\dfrac{\partial^2 T}{\partial z^2}\right)$

These transport equations that have the form of:

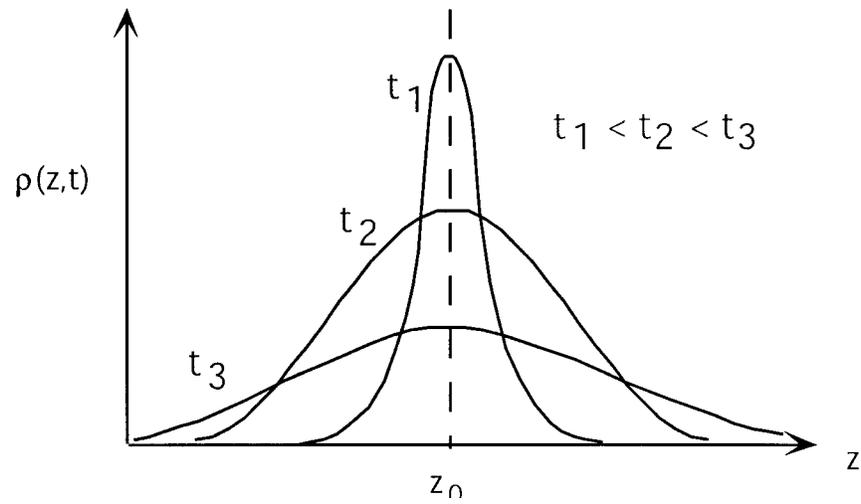$$\left(\frac{\partial Y}{\partial t}\right) = L\left(\frac{\partial^2 Y}{\partial z^2}\right)$$

are called "diffusion equations". For example Fick's law for mass diffusion has the form:

$$\left(\frac{\partial \rho}{\partial t}\right)_z = D\left(\frac{\partial^2 \rho}{\partial z^2}\right)_t.$$

This equation has a fundamental solution:

$$\rho(z,t) = \frac{\rho_0}{(4\pi Dt)^{\frac{1}{2}}}\exp\left[-\frac{(z-z_0)^2}{4Dt}\right]$$

for the initial conditions $\rho(z,t=0) = \rho_0\delta(z-z_0)$.

Evidently $\int_{-\infty}^{+\infty} dz \rho(z,t) = \rho_0$ because mass is conserved in the diffusion process.