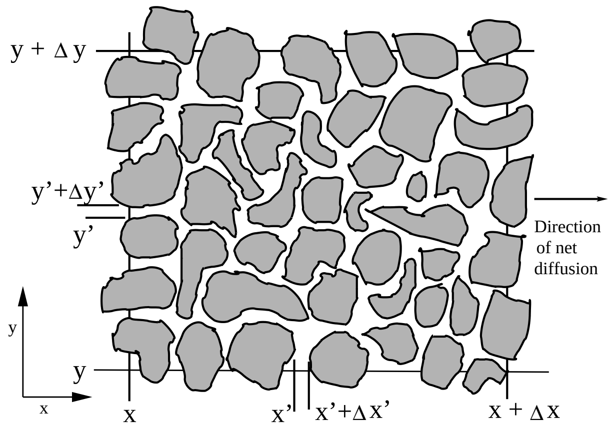

Figure 1: Cross sectional view of porous media.

This material is essentially reproduced from the book by Petersen, which is out of print [E.E. Petersen, *Chemical Reaction Analysis,* Prentice Hall, Englewood Cliffs, New Jersey, 1965]. Our objective is to introduce the basis behind an effective diffusion coefficient and this is best demonstrated with a nonreacting system that involves equimolal counter diffusion. To simplify the equations, we will drop the subscript of j on the concentration terms and assume we are writing these for component A in the mixture of A and B. We will select cartesian coordinates as illustrated in Figure 1. The volume element for this example is $\Delta x \Delta y \Delta z$, which is small compared to the size of the system and large compared to the channels within the porous region. By assuming the solid regions are general cylinders, the diffusive flow at every value of z is identical and concentrations are independent of z. The size of our model system is small compared to the total system so we will assume an average concentration along the coordinates x and $x + \Delta x$; these are prescribed as constants and independent of y. Further we will assume no flux of our diffusing species across the planes at y and $y + \Delta y$. These boundary conditions force the diffusive flux to flow only in the $x-$direction. These statements lead to

$$\bigtriangledown^2 c = 0 \text{ for equimolar counter diffusion}$$

$$c \neq f(z)$$

$$c = c_o \text{ at } x \qquad c = c_1 \text{ at } x + \Delta x$$

$$\frac{\partial c}{\partial y} = 0 \text{ at } y \text{ and } y + \Delta y$$

Our components (A and B) are really diffusing through the channels and we have to solve the Laplace equation ($\bigtriangledown^2 c = 0$) through these channels. This requires we define new coordinates x', y', and z'; they have the property that their differentials $\Delta x'$, $\Delta y'$ and $\Delta z'$ are small compared to Δx, Δy and Δz. The solution for this new coordinate system is $c(x', y')$ and the rate of diffusion (of component A) in the $x-$direction through the volume element $\Delta x \Delta y \Delta z$ is

$$I_A = -D_A \Delta z \int_0^{\Delta y} \left[\frac{\partial c(x', y')}{\partial x'} \right]_{y'} dy' \tag{1}$$

where D_A is the binary diffusion coefficient of A in the AB mixture and the integration may be carried out at any value of x'.

Many times problems can be simplified and the results made more general by using dimensionless variables and coordinates. The concentration and the position are made dimensionless using

$$\psi \equiv \frac{c(x', y') - c(x)}{c(x + \Delta x) - c(x)} \qquad \eta \equiv \frac{x'}{\Delta x} \qquad \xi \equiv \frac{y'}{\Delta y}$$

After substituting into Eqn. 1

$$I_A = -D_A \Delta z \Delta y \frac{c(x + \Delta x) - c(x)}{\Delta x} \int_0^1 \left[\frac{\partial \psi(\eta, \xi)}{\partial \eta} \right]_{\xi} d\xi \tag{2}$$

The integral in Eqn. 2 is only a function of the pore geometry. This happens in the new coordinates because the Laplacian and the boundary conditions are now independent of the substance diffusing and the concentrations. The best part is the integral is a constant, which we will call f_1, that only depends on the geometry of the channels within the volume $\Delta x \Delta y \Delta z$. This leads us to rewrite Eqn. 2 as

$$I_A = -D_A \Delta z \Delta y \frac{dc(x)}{dx} f_1(\text{geometry}) \tag{3}$$

Note Eqn. 3 is the cartesian coordinate version of Eqn. 7.8 in the text that was developed for spherical coordinates and is reproduced here

$$I_j = -d_j 4\pi r^2 \frac{dc_j}{dr} \xi \qquad \text{Text Eqn 7.8}$$

Now if we recast this problem using the same volume $\Delta x \Delta y \Delta z$, only now we assume it is filled with hypothetical material that we treat as an "equivalent" homogeneous medium with an effective diffusivity D_e. This new equivalent homogenous medium (see

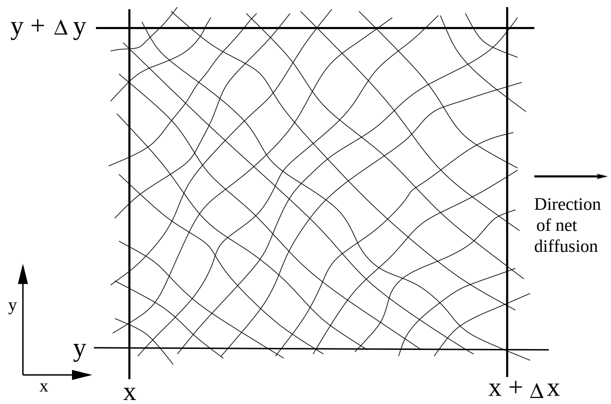

Figure 2: Cross sectional view of the equivalent homogeneous media.

Figure 2) has the same boundary conditions that were imposed on the porous medium in Figure 1. Therefore the solution to the Laplace equation leads to

$$I_A = -D_e \Delta z \Delta y \frac{dc(x)}{dx} \tag{4}$$

Comparing Eqns. 3 and 4 leads to

$$D_e = D_A f_1(\text{geometry}) \tag{5}$$

and we see that the ratio of the effective and molecular diffusivity is equal to a geometric factor that is characteristic of the porous medium. If one has a precise description of the pore geometry, the integral in Eqn. 2 can be evaluated. It has more generally been defined in terms of two parameters, the tortuosity factor, τ, and the porous solid porosity, ϵ, as described in the text.

$$f_1(\text{geometry}) = \frac{\epsilon}{\tau}$$