# Diffusion in a Pore of Varying Cross Section

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**The ratio of the effective to the normal diffusivity of a material diffusing within porous solids is less than unity. In the simple theory the porosity and tortuosity, or labyrinth, factors are used to explain the magnitude of this ratio and to account respectively for the reduced cross-sectional area and the increased diffusion distance. However, abnormally large values of the tortuosity factor are obtained from experimentally measured effective diffusivities within pelleted or extruded porous solids. This work is concerned with the quantitative effect of periodic pore constrictions on the effective diffusivity. The pore model assumed for this study is a hyperbola of revolution giving a pore constriction at the vertex of the hyperbola. Solutions to the steady state diffusion equation in a pore of this shape were obtained at various values of $\beta$, the ratio of the maximum to the minimum cross-section in the pore. Comparison of the rate of diffusive transport in this pore and an equivalent cylindrical pore indicates that $\delta$, the ratio of the effective to the normal diffusivity, is about 0.33 at $\beta = 25$ for large pores. At the same value of $\beta$, $\delta$ would be smaller for diffusion in the Knudsen region.**

The effective diffusivity $D_e$ of a gas being transported within a porous solid by a diffusive mechanism is smaller than the normal diffusion coefficient $D_b$. Efforts to relate the ratio $D_e/D_b$ quantitatively to the variables characterizing the porous medium can be broadly classified into two types. The more fundamental method begins with the derivation of an expression for the value of $D_e/D_b$ in dilute suspension of particles of simple geometric shapes. Maxwell (*5*) considered uniform spheres and Rayleigh (*7*) infinite cylinders normal to the direction of flow, leading to the following equations, respectively:

$$\frac{D_e}{D_b} = \frac{2\epsilon}{3 - \epsilon} \tag{1}$$

$$\frac{D_e}{D_b} = \frac{\epsilon}{2 - \epsilon} \tag{2}$$

where $\epsilon$ = volume fraction voids. Using a continuum model, Bruggeman (*1*) extended the range of validity of the Maxwell expression to higher values of $\epsilon$, to obtain the equation

$$\frac{D_e}{D_b} = \epsilon^{\frac{3}{2}} \tag{3}$$

De La Rue and Tobias (*3*) found excellent agreement between the Bruggeman equation and their experimental values of the electrical conductivity of suspensions of spheres in the range of porosities from 1.0 to 0.5. Hoogschagen's (*4*) experimental values of $D_e/D_b$ for randomly packed beds of glass spheres in the porosity range from 0.35 to 0.4 lie between the values predicted by the Maxwell and Bruggeman equations, although slightly closer to the latter.

The other commonly used method is to relate $D_e/D_b$ to the porosity and a labyrinth, or tortuosity, factor $\tau$ by the following expression:

$$\frac{D_e}{D_b} = \frac{\epsilon}{\tau} \tag{4}$$

Equation (4) is essentially a defining equation for $\tau$. From a geometrical point of view, this form appears reasonable because $\epsilon$ allows for the reduced area for diffusive flow and $\tau$ accounts for the fact that the actual diffusion path between two points within a porous medium is generally greater than the distance between points. For loose powders and randomly packed glass spheres the labyrinth factors range from 1.42 to 1.58 (*4*), an indication that the actual diffusion path is $\sqrt{\tau}$, or from 1.19 to 1.26 times longer than the distance in the direction of net flow. The ratio of the channel length to the geometric depth in a system of closely packed uniform spheres is 1.304 (*2*).

Both these methods appear to be invalid when applied to tableted or extruded porous media, wherein labyrinth factors from 5 to as high as 300 are obtained with values of 10 to 12 being common (*4*). Interpreting such high values of the labyrinth factors simply as an increased diffusion length is hard to justify physically. In this investigation diffusion in a pore of varying cross section is compared with that in an "equivalent" cylindrical pore in order to determine whether periodic constrictions in the pore channel may reasonably account for unusually high labyrinth factors. In the model adopted, no account will be taken of the porosity or tortuosity factor, only of constrictions in the channel cross sectional area; moreover, the analysis will not directly apply when the Knudsen diffusivity must be used.

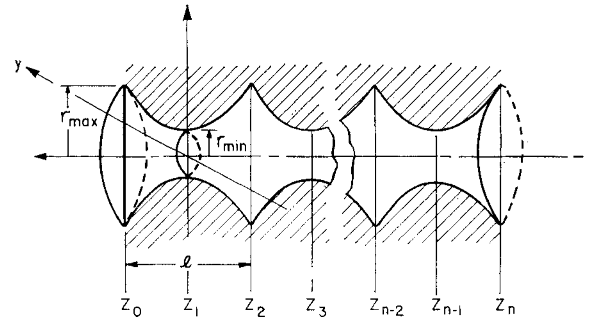

Fig. 1. Model of pore with periodic pore constrictions.

## MODEL

The shapes of pores formed within porous media pelleted or extruded from particulate material are complex especially if the particles are deformed in the process. However, it seems reasonable that the network of channels formed by the interconnected interstitial spaces between particles will vary in cross section. The extent of variation will depend in part upon the amount of compaction and the shape of particles comprising the aggregate. It is proposed herein to study diffusion in an idealized model (Figure 1) of a pore which retains the property of variable cross section along its length. The pore walls are hyperbolas of revolution about the $Z$ axis. A pore of any length is made from repeating units represented by $Z_0$, $Z_2$, $Z_2Z_4$ . . . $Z_{n-2}Z_n$. It is clear that if the concentration in the $xy$ planes at $Z_0$ and $Z_n$ are held at $C_0$ and $C_n$, respectively, where $C_0 > C_n$, then a net transport of material will take place from $Z_0$ to $Z_n$. Moreover, if the fluid in the pore is held at constant temperature and total pressure and if $D_b$ is assumed to be independent of concentration, symmetry demands that the concentration will drop in equal increments in the $xy$ planes at $Z_1$, $Z_2$ . . . $Z_{n-1}$ at steady state. Therefore, the problem is simplified to solving Laplace's equation for the region between $Z_0$ and $Z_1$.

A pore of this shape can be most conveniently described in oblate spheroidal coordinates (*6*). The origin for the coordinate system will be taken at $Z_1$ along the $Z$ axis as shown in Figure 1 and in greater detail in Figure 2. Since angular symmetry has been assumed, two coordinates will be needed which will describe a mutually orthogonal set of hyperbolas and ellipses with focuses at $x = \pm 1.0$. The coordinates $\xi$ and $\eta$ are defined as

$$\frac{x^2}{(1+\xi^2)} + \frac{Z^2}{\xi^2} = 1 \qquad (5)$$

for the ellipses and

$$\frac{x^2}{(1-\eta^2)} - \frac{Z^2}{\eta^2} = 1 \qquad (6)$$

for the hyperbolas.

The walls of the pore are defined by the hyperbolas asymptotic to lines $x = \pm Z$, and correspond to setting $\eta = 0.707$ in Equation (6). This choice seemed most appropriate to describe a constriction formed from roughly spherical particles.

The concentration profile in the pore is given by the solution to the Laplace equation

$$\nabla^2 \psi = 0 \qquad (7)$$

where $\psi$ is a dimensionless concentration in terms of the concentrations at the boundaries $Z_0$ and $Z_1$ as defined below.

$$\psi \equiv \frac{C(Z) - C(Z_1)}{C(Z_0) - C(Z_1)}$$

$$= \frac{C(Z) - C(0)}{C(Z_0) - C(0)} \qquad (8)$$

when the origin is taken through $Z_1$. The boundary conditions are

$$\psi(Z_0) = 1 \quad \left(\frac{d\psi}{d\eta}\right)_{\eta=0.707} = 0$$

$$\psi(0) = 0 \quad \left(\frac{d\psi}{d\eta}\right)_{\eta=1} = 0 \qquad (9)$$

As the first boundary condition $\psi(Z_0) = 1$ introduces mathematical difficulties, it is proposed to solve the Laplace equation twice for each ratio of $r_{max}$ to $r_{min}$: one solution subject to the boundary condition $\psi(\xi_0) = 1$ where $\xi_0$ characterizes the ellipse going through the point $\eta = 0.707$, $Z_0$; and the other solution subject to the boundary condition $\psi(\xi_0') = 1$ where $\xi_0'$ characterizes the ellipse going through $\eta = 1$, $Z_0$. These solutions are readily obtained and the desired solution lies between them.

In oblate spheroidal coordinates

$$\nabla^2\psi = \frac{1}{(\xi^2+\eta^2)}\left\{\frac{\partial}{\partial\xi}\left[(1+\xi^2)\frac{\partial\psi}{\partial\xi}\right]\right.$$

$$\left. + \frac{\partial}{\partial\eta}\left[(1-\eta^2)\frac{\partial\psi}{\partial\eta}\right]\right\} = 0 \qquad (10)$$

Defining $\psi(\xi, \eta) = E(\xi)M(\eta)$ causes the equation to separate into

$$(1-\eta^2)\frac{d^2M}{d\eta^2} - 2\eta\frac{dM}{d\eta}$$

$$- \lambda^2 M = 0 \qquad (11)$$

and

$$(1+\xi^2)\frac{d^2E}{d\xi^2} + 2\xi\frac{dE}{d\xi}$$

$$+ \lambda^2 E = 0 \qquad (12)$$

To satisfy the boundary condition, $(dM/d\eta)_{\eta=1} = 0$, clearly $\lambda^2$ in Equation (11) must be set equal to zero in order to avoid a trivial solution. If the separation constant $\lambda^2 = 0$, then in order to satisfy all boundary conditions, $M = 1$ and

$$\psi(\xi) = \frac{\tan^{-1}\xi}{\tan^{-1}\xi_0} \qquad (13)$$

The diffusive flow is always normal to the $\xi$ = constant lines and the net transport $N$ through the pore is

$$N = [C(\xi_1) - C(0)] \iint_s \frac{D_b}{h_\xi}\left(\frac{d\psi}{d\xi}\right) ds \qquad (14)$$

$$= [C(\xi_1) - C(0)] \int_0^{2\pi} d\phi$$

$$\cdot \int_{\eta_1=0.707}^{1} D_b\left(\frac{d\psi}{d\xi}\right)\frac{h_\phi h_\eta}{h_\xi}\, d\eta \qquad (15)$$

where

$$h_\phi = \sqrt{(\xi^2+1)(1-\eta^2)}$$

$$h_\eta = \sqrt{\frac{(\xi^2+\eta^2)}{(1-\eta^2)}} \qquad (16)$$

$$h_\xi = \sqrt{\frac{\xi^2+\eta^2}{\xi^2+1}}$$

Substituting, simplifying, and integrating gives

$$N = \frac{2\pi[C(\xi_1) - C(0)](1-\eta_1)D_b}{\tan^{-1}\xi_0} \qquad (17)$$

The rate of transport in a channel of varying cross section is given in Equation (17). A question of interest may now be raised. If the hyperbolic-shaped pore is replaced by an equivalent system of cylindrical pores, what values of the diffusivity $D_e$ should be used in order to compute the correct rate of diffusive transport?

If there are $m$ cylindrical pores of radius $r_{avg}$ and of length $Z_0$, the rate of diffusive transport is

$$N = \frac{D_e \pi r_{avg}{}^2 m[C(Z_0) - C(0)]}{Z_0} \qquad (18)$$

the radius $r_{avg}$ is generally obtained from the volume and surface area of the true pore system by the equation

$$r_{avg} = \frac{2V}{S} \qquad (19)$$

Equation (19) is correct if the pores are smooth, cylindrical, and separate. The number of pores $m$ must be chosen so that the total pore volume of the equivalent pore system is equal to the true pore volume; therefore

$$m = \frac{V}{\pi r_{avg}^2 Z_0} \qquad (20)$$

Substituting Equations (19) and (20) into (18) and simplifying gives

$$N = \frac{[C(Z_0) - C(0)]D_e V}{Z_0^2} \qquad (21)$$

where $V$ = volume of the hyperbolic pore model

$$= \pi(1 - \eta_1^2)\left[Z_0 + \frac{Z_0^3}{3(\eta_1^2)}\right] \qquad (22)$$

and $\eta_1 = 0.707$. The desired ratio $D_e/D_b$ is obtained by setting $N$ of Equation (21) equal to its correct value, obtained from Equation (17), which upon rearrangement is

$$\frac{D_e}{D_b} = \frac{1.172 Z_0^2}{\left(Z_0 + \frac{Z_0^3}{1.5}\right)\tan^{-1}\xi_0} \qquad (23)$$

The parameter $\xi_0$ takes the two values ($\xi_0$ and $\xi_0'$) described previously under boundary conditions. The $D_e/D_b$ ratio is plotted in Figure 3 as a function of the $A_{max}/A_{min}$ ratio, which will be referred to hereafter as $\beta$ where $A_{max}$ refers to the maximum cross-sectional area at the entrance to the pore and $A_{min}$ refers to the minimum cross-sectional area at the pore constriction. The lower curve corresponds to the boundary condition $\psi(\xi_0) = 1$, whereas the upper curve corresponds to $\psi(\xi_0') = 1$. The dashed curve is an interpolated curve going through the point $D_e/D_b = 1$ at $\beta = 1$ and represents a reasonably accurate solution to the original problem. It should be pointed out that the $D_e/D_b$ ratio is not particularly sensitive to pore shape; for example a pore unit having about twice the length-to-diameter ratio of the pore shown in Figure 2 is bounded by the hyperbola corresponding to $\eta = 0.9$ and $\beta = 25$ and has a value of $D_e/D_b$ equal to 0.39 instead of 0.33 at $\eta = 0.707$ and the same value of $\beta$.

If the ratio of $D_e/D_b$ in Equation (23) is defined as equal to $\delta$, the convergence factor, that is, a factor which accounts for reduction in $D_e$ due to constrictions in the pore along its length. If the $\delta$ factor is taken into account, Equation (4) can be redefined as

$$\frac{D_e}{D_b} = \frac{\epsilon\delta}{\tau} \qquad (24)$$

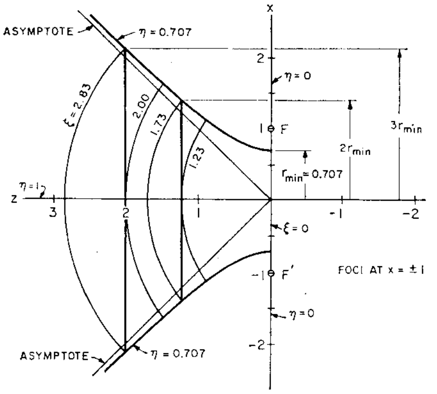

**Fig. 2. Detail of pore repeating unit for cases of $R_{max}/R_{min}$ equal to 2 and 3.**

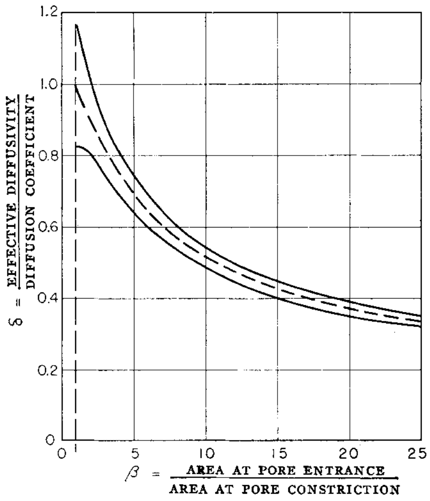

**Fig. 3. Effective diffusivity as a function of convergence ratio, shown by the dashed curve. The upper curve is for ($\xi_0'$) = 1 and the lower for ($\xi_0$) = 1.**

For porosities greater than about 0.4, corresponding to the region from dilute dispersions to loosely packed beds, the Bruggeman form is applicable where $\tau \propto \epsilon^{-1/2}$ and $\delta = 1$.

When solids are compacted owing to pelleting or extruding, it is postulated that constrictions are produced within the solid and $\delta$ becomes less than unity. The ratio of $D_e/D_b$, therefore, is less than predicted by the Bruggeman equation. Postulating pore constrictions and the $\delta$ factor forms a more satisfactory explanation for the greatly reduced values of $D_e$ than attempting to interpret them on the basis of a tortuosity factor alone. Estimation of the magnitude of $\delta$ factors by the model assumed in this paper are not valid if under the conditions of the diffusion process the mean free path of the gas molecules is of the same order of magnitude as the diameter of pores. In this region the Knudsen form of the diffusion coefficient must be used where $D_k$ is a function of the pore radius. It is clear, however, that in the Knudsen region the magnitude of $\delta$ would be smaller for a given value of the $\beta$ than the values plotted in Figure 3.

Although the concept of pore constrictions in compacted materials provides the basis for a reasonably attractive explanation of abnormally high tortuosity factors, unfortunately there appears to be at present no satisfactory experimental technique to characterize independently the structure of pores within compacted materials in sufficient detail to test the method presented here.

## NOTATION

$A_{max}$ = maximum cross-sectional area of pore
$A_{min}$ = minimum cross-sectional area of pore
$C$ = concentration
$D_b$ = normal diffusion coefficient
$D_e$ = "effective" diffusion coefficient
$h_\eta$, $h_\xi$, $h_\phi$ = scaling factors in oblate spheroidal coordinate system defined by Equation (16)
$N$ = rate of diffusive transport through the pore
$r_{avg}$ = radius of equivalent cylindrical pore
$r_{max}$ = maximum radius of pore
$r_{min}$ = minimum radius of pore
$S$ = pore wall surface
$V$ = volume of pore
$X$ = Cartesian coordinate
$Y$ = Cartesian coordinate
$Z$ = Cartesian coordinate
$Z_0$ = pore length

### Greek Letters

$\beta$ = $A_{max}/A_{min}$
$\delta$ = convergence factor
$\epsilon$ = porosity
$\eta$ = oblate spheroidal coordinate
$\lambda$ = separation constant
$\xi$ = oblate spheroidal coordinate
$\tau$ = tortuosity or labyrinth factor
$\psi$ = dimensionless concentration
$\nabla^2$ = Laplacean operator

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