Diffusion in Packed Beds of Porous Particles

Stephen Whitaker
Laboratoire Energétique et Phénomènes
de Transfert
Université de Bordeaux I
33405 Talence Cedex, France

The determination of the effective diffusivity for small porous particles (the intraparticle diffusion coefficient) by direct experimental methods is generally not possible. Because of this, one is forced to measure the overall effective diffusivity for packed beds of porous particles and subsequently extract the particle effective diffusivity by means of a theoretical analysis of the two-region diffusion process. In a recent study by Park et al. (1987), experiments using arrested-flow chromatography were described and a method of obtaining the particle effective diffusivity was presented. Based on solutions of the overall diffusion equation

$$\epsilon \frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial z^2} \tag{1}$$

and experimental measurements, values of D_e were determined for a variety of packed beds of porous particles. In order to calculate values of the particle effective diffusivity, semiempirical equations were developed on the basis of the classic works of Maxwell (1873), Rayleigh (1892), Burger (1919), and Jeffrey (1973). All of these represent high void fraction theories for steady heat conduction in two-phase systems.

Rather than modify special theories in order to extract particle effective diffusivities from measured values of D_e, it would seem wise to make use of the general solution to the problem (Whitaker, 1983). The system under consideration is shown in Figure 1, where the β phase represents the homogeneous gas phase and the σ phase represents the porous particle phase. The diffusion equation for the gas phase contained within the porous particles must be volume-averaged and this is done in terms of the averaging volume $\mathcal{V}_\sigma$ indicated in Figure 1. An expanded view of the σ phase averaging volume is shown in Figure 2 where the κ phase represents the rigid solid and the γ phase is used to identify the gas within the porous particles. A detailed analysis of diffusion in porous catalysts (Whitaker, 1987) leads to a governing equation for the σ phase, and for dilute solutions or equimolar counterdiffusion the physics of the process under investigation can be described by

$$\frac{\partial c_\sigma}{\partial t} = \mathcal{D}_\sigma \nabla^2 c_\sigma \quad \text{in the } \sigma \text{ phase} \tag{2}$$

$$\text{B.C.1:} \quad c_\sigma = c_\beta \quad \text{at the } \sigma - \beta \text{ interface} \tag{3}$$

$$\text{B.C.2:} \quad \mathbf{n}_{\sigma\beta} \cdot \epsilon_\gamma \mathcal{D}_\sigma \nabla c_\sigma = \mathbf{n}_{\sigma\beta} \cdot \mathcal{D}_\beta \nabla c_\beta \quad \text{at the } \sigma - \beta \text{ interface} \tag{4}$$

$$\frac{\partial c_\beta}{\partial t} = \mathcal{D}_\beta \nabla^2 c_\beta \quad \text{in the } \beta \text{ phase} \tag{5}$$

Here c_σ represents the intrinsic phase average concentration (Gray, 1975) of the diffusing species in the σ phase, and c_β represents the point concentration of the diffusing species in the β phase. One must keep in mind that $\mathcal{D}_\sigma$ represents an effective diffusivity for the porous particles.

It is also important to keep in mind that $\mathcal{D}_\beta$ represents the molecular diffusivity of the diffusing species in the β phase, and that the patching together of volume-averaged transport equations and point transport equations is not necessarily an obvious process. The details are given in the original paper. The structure of the boundary value problem given by Eqs. 2–5 is almost identical to a transient heat conduction problem, and it would be identical if it were not for the presence of the particle void fraction, ϵ_γ, in the boundary condition given by Eq. 4. Clearly the steady state diffusion problem is analogous to the heat conduction problem, and this has important consequences for the solution of the closure problem (Crapiste et al., 1986).

Since the position of the interface between the porous particles and the surrounding gas phase is unknown, one seeks a volume-averaged diffusion equation for the packed bed of porous particles using the averaging volume shown in Figure 3. The analysis requires that the volume-averaged forms of Eqs. 2 and 4 be added to obtain the one-equation model given by

$$\frac{\partial \{c\}}{\partial t} = \mathsf{D}_{eff} \colon \nabla\nabla\{c\} \tag{6}$$

The author's permanent address is Department of Chemical Engineering, University of California, Davis, CA 95616.

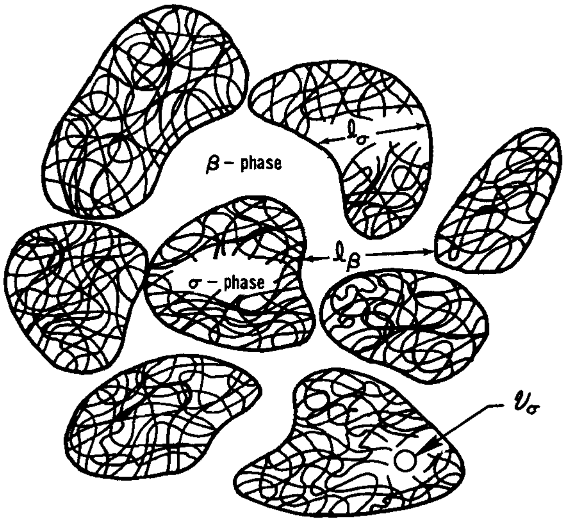

Figure 1. Packed bed of porous particles.

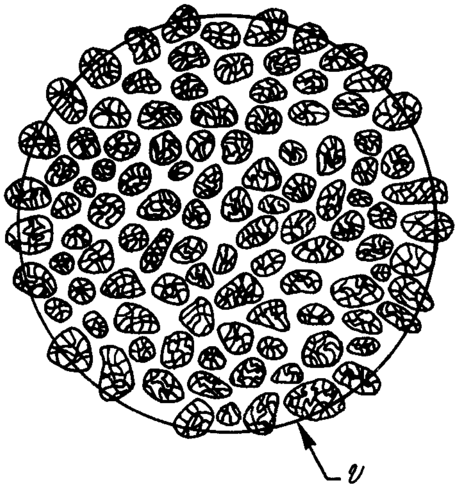

Figure 3. Averaging volume for two-region diffusive transport.

Here the overall intrinsic phase average concentration is defined as

$$\{c\} = \frac{\epsilon_\beta \langle c_\beta \rangle^\beta + \epsilon_\gamma \epsilon_\sigma \langle c_\sigma \rangle^\sigma}{\epsilon_\beta + \epsilon_\gamma \epsilon_\sigma} \tag{7}$$

in which ϵ_β represents the volume fraction of the β phase (the void fraction of the packed bed), ϵ_γ represents the volume fraction of the γ phase contained within the σ phase (the void fraction of the porous particles), and ϵ_σ represents the volume fraction occupied by the porous particles ($\epsilon_\sigma = 1 - \epsilon_\beta$). The overall porosity appearing in Eq. 1 can be expressed as

$$\epsilon = \epsilon_\beta + \epsilon_\gamma \epsilon_\sigma = \epsilon_\beta + \epsilon_\gamma (1 - \epsilon_\beta) \tag{8}$$

The β and σ phase intrinsic phase average concentrations are defined by

$$\langle c_\beta \rangle^\beta = \frac{1}{V_\beta} \int_{V_\beta} c_\beta \, dV, \quad \langle c_\sigma \rangle^\sigma = \frac{1}{V_\sigma} \int_{V_\sigma} c_\sigma \, dV \tag{9}$$

where V_β is the volume of the β phase contained in the averaging volume illustrated in Figure 3 and V_σ has an analogous meaning. The passage from the two-equation system for $\langle c_\beta \rangle^\beta$ and $\langle c_\sigma \rangle^\sigma$ to the one-equation model given by Eq. 6 is not automatic, and the details are given elsewhere (Whitaker, 1983).

The symmetric overall effective diffusivity tensor in Eq. 6 is given by

$$\mathbf{D}_{eff} = \left(\frac{\epsilon_\beta \mathcal{D}_\beta + \epsilon_\gamma \epsilon_\sigma \mathcal{D}_\sigma}{\epsilon_\beta + \epsilon_\gamma \epsilon_\sigma} \right) \mathbf{I} + \frac{\mathcal{D}_\beta + \epsilon_\gamma \mathcal{D}_\sigma}{\mathcal{V} (\epsilon_\beta + \epsilon_\gamma \epsilon_\sigma)} \int_{A_{\beta\sigma}} \frac{1}{2} (\boldsymbol{n}_{\beta\sigma} \boldsymbol{f} + \boldsymbol{f} \boldsymbol{n}_{\beta\sigma}) \, dA \tag{10}$$

where $\mathcal{V}$ is the averaging volume shown in Figure 3 and $A_{\beta\sigma}$ is the interfacial area contained within that volume. Once can follow the work of Ryan et al. (1981) or Nozad et al. (1985) to demonstrate that the $\underset{\sim}{f}$ field need only be solved for a unit cell using the following boundary-value problem

$$\nabla^2 \boldsymbol{f} = 0 \quad \text{in the } \beta \text{ phase} \tag{11}$$

$$\text{B.C.1:} \quad \boldsymbol{f} = \boldsymbol{g} \quad \text{at the } \sigma - \beta \text{ interface} \tag{12}$$

$$\text{B.C.2:} \quad \boldsymbol{n}_{\sigma\beta} \cdot \nabla \boldsymbol{f} = \kappa \boldsymbol{n}_{\sigma\beta} \cdot \nabla \boldsymbol{g} + (\kappa - 1) \boldsymbol{n}_{\sigma\beta} \quad \text{at the } \sigma - \beta \text{ interface} \tag{13}$$

$$\nabla^2 \boldsymbol{g} = 0$$

$$\text{Periodicity:} \ \boldsymbol{f}(\boldsymbol{r} + \ell_i) = \boldsymbol{f}(\boldsymbol{r}), \quad \boldsymbol{g}(\boldsymbol{r} + \ell_i) = \boldsymbol{g}(\boldsymbol{r}), \quad i = 1, 2, 3 \tag{14}$$

$$\text{Averages:} \quad \langle \boldsymbol{f} \rangle^\beta = 0, \quad \langle \boldsymbol{g} \rangle^\sigma = 0 \tag{15}$$

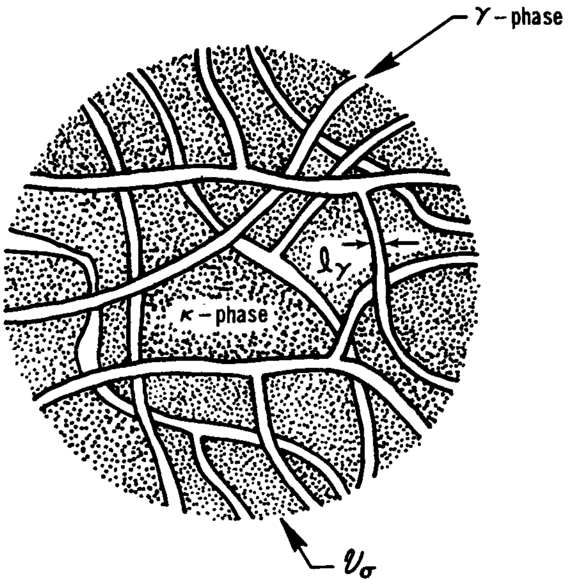

Figure 2. Averaging volume for porous particle phase.

The closure analysis has been restricted to the quasi-steady state on the basis of constraints given in the original papers. Because of this, the closure problem for the transient two-region diffusion problem is identical to the closure problem for transient heat conduction in a two-phase system. The parameter κ in Eq. 15 is defined by

$$\kappa = \epsilon_\gamma \mathscr{D}_\sigma / \mathscr{D}_\beta \tag{16}$$

while in the heat transfer problem κ is given by the ratio of thermal conductivities, k_σ / k_β.

The closure problem has been solved for the two-dimensional, spatially periodic system shown in Figure 4 and this system produces isotropic values of the effective diffusivity tensor represented by Eq. 10. Under these circumstances the dimensionless form of Eq. 10 can be expressed as

$$\frac{\epsilon D_{eff}}{\mathscr{D}_\beta} = (\epsilon_\beta + \epsilon_\sigma \kappa) + \mathbf{I}:\left[\frac{1-\kappa}{\mathscr{V}} \int_{A_{\beta\sigma}} \frac{1}{2}(\boldsymbol{n}_{\beta\sigma}\boldsymbol{f} + \boldsymbol{f}\boldsymbol{n}_{\beta\sigma})\, dA\right] \tag{17}$$

where Eq. 8 has been used to express the total porosity as ϵ. To be absolutely clear about the correspondence between the diffusion process and the heat conduction process, we note that the effective thermal conductivity for two-phase isotropic systems is given by (Nozad et al., 1985)

$$\frac{K_{eff}}{\kappa_\beta} = (\epsilon_\beta + \epsilon_\sigma \kappa) + \mathbf{I}:\left[\frac{1-\kappa}{\mathscr{V}} \int_{A_{\beta\sigma}} \frac{1}{2}(\boldsymbol{n}_{\beta\sigma}\boldsymbol{f} + \boldsymbol{f}\boldsymbol{n}_{\beta\sigma})\, dA\right] \tag{18}$$

The dimensionless effective diffusivity represented by Eq. 17 is plotted as a function of κ for several values of ϵ_β in Figure 5. The crucial characteristic of the results shown in Figure 5 is that the dependence of $(\epsilon_\beta + \epsilon_\gamma \epsilon_\sigma) D_{eff} / \mathscr{D}_\beta$ on the parameter κ is essentially linear. This makes the theory especially easy to use.

One might be concerned with the simplistic model illustrated in Figure 4 as opposed to the more realistic system shown in Figure 1. However, there is ample theoretical evidence (Ryan et al., 1981; Nozad et al., 1985; Strieder and Aris, 1973; among others) and experimental evidence (Hoogschagen, 1955; Currie, 1960; Kim et al., 1987) that the dimensionless effective transport coefficients given by Eqs. 17 and 18 are dominated by ϵ_β and κ and are influenced only slightly by particle geometry. One must be careful to confine this observation to systems that give rise to isotropic diffusion or conduction since it is not valid for anisotropic systems (Kim et al., 1987). In addition, this observation is not valid for large values of κ; however, for the diffusion problem under consideration κ is bounded between zero and one.

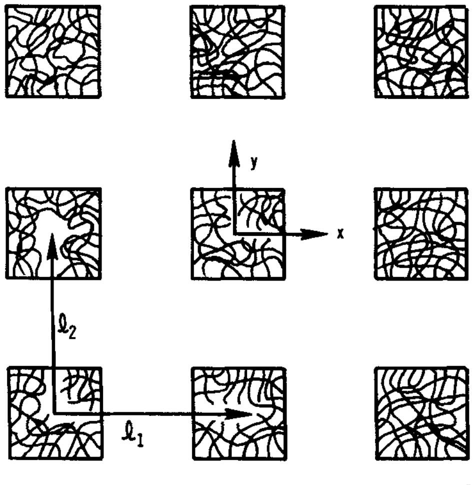

Figure 4. Two-dimensional model of a packed bed of porous particles.

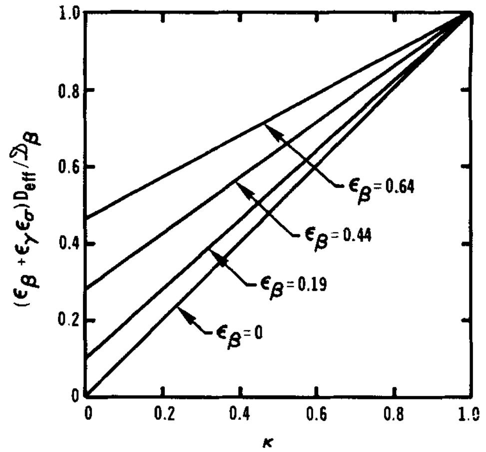

Figure 5. Theoretical values of effective diffusivity for one-equation model.

In order to determine the effective diffusivity for the porous particles illustrated in Figure 1, one performs an experiment of the type described by Park et al. (1987), and one measures the total porosity and the packed bed void fraction. This produces values of $\epsilon D_{eff} / \mathscr{D}_\beta$ and ϵ_β, and the value of κ is then extracted from Figure 5. In order to construct a more accurate version of Figure 5 one only needs to locate a point on the ordinate and then use a linear relation between $\epsilon D_{eff} / \mathscr{D}_\beta$ and κ. The points on the ordinate can be located experimentally by measuring the effective diffusivity for a packed bed of nonporous particles having the same void fraction, ϵ_β, as the packed bed of porous particles. Alternatively one can use the theoretical values listed in Table 1. As an example, we consider the data given in the first entry of Table 4 in Park et al. (1987): $\epsilon_\beta = 0.40$, $\epsilon_\gamma = 0.65$, $\mathscr{D}_\beta = 0.77 \times 10^{-4}\ \mathrm{m^2/s}$, $\epsilon D_{eff} = 0.413 \times 10^{-4}\ \mathrm{m^2/s}$.

From Table 1 we have

$$\left(\frac{\epsilon D_{eff}}{\mathscr{D}_\beta}\right)_{\kappa=0} = 0.250 \tag{19}$$

and this leads to the linear relation illustrated in Figure 5 given

Table 1. Overall Effective Diffusivities for $\kappa = 0$

ϵ_β	$\epsilon D_{eff} / \mathscr{D}_\beta$
0.05	0.047
0.15	0.098
0.25	0.154
0.35	0.216
0.40	0.250
0.50	0.329
0.60	0.420
0.70	0.471

Table 2. **Internal Tortuosity Factors for Porous Particles**

Column No.	Packing Material	κ	Parallel Diffusion	Modified Maxwell	Modified Burger	Modified Rayleigh	Modified Jeffrey	General Solution
VII	Varian FB	0.381	1.16	1.56	1.42	1.62	1.56	1.37
VIII-1	Varian FB	0.349	1.28	1.72	1.56	1.78	1.73	1.50
VIII-2	Varian FB	0.345	1.27	1.71	1.55	1.77	1.71	1.48
IX-1	Common FB	0.0635	3.55	5.29	4.53	5.55	5.74	3.59
IX-2	Common FB	0.0635	3.59	5.35	4.58	5.61	5.81	3.57
X	Common FB	0.0807	2.66	3.97	3.40	4.15	4.22	2.83
XI	Common FB	0.0662	3.42	5.07	4.35	5.32	5.49	3.44
XII	CSS-1000LDS	0.340	1.30	1.72	1.57	1.79	1.72	1.54
XIII	CSS-1000LDS	0.373	1.19	1.58	1.44	1.63	1.58	1.41
XIV	CSS-1000LDS	0.340	1.30	1.72	1.57	1.79	1.73	1.54
XV	CSS-1000LDS	0.369	1.20	1.59	1.45	1.65	1.60	1.42

by

$$\left(\frac{\epsilon D_{eff}}{\mathcal{D}_\beta}\right) = (0.250)(1 - \kappa) + \kappa \tag{20}$$

The measured value of $\epsilon D_{eff}/\mathcal{D}_\beta$ is 0.536 and from Eq. 20 we have

$$\kappa = \frac{\epsilon_\gamma \mathcal{D}_\sigma}{\mathcal{D}_\beta} = 0.381 \tag{21}$$

This is probably the most useful representation for the experimentally determined effective diffusivity for the porous particles; however, in order to compare our results with those published by Park et al. (1987) we use the internal tortuosity factor defined by

$$\tau_{int} = \frac{\epsilon_\gamma \bar{D}}{\epsilon_\gamma \mathcal{D}_\sigma} = \frac{\epsilon_\gamma \bar{D}}{\kappa \mathcal{D}_\beta} \tag{24}$$

Here $\bar{D}$ is a diffusivity based on a pore-size distribution function given by Eq. 16 of Park et al. and tabulated in their Table 5. The computed values of τ_{int} based on the general solution (Whitaker, 1983) are listed here in Table 2 along with the computed values of κ. The values computed using the general theory are in the same neighborhood as the results predicted by the various semiempirical formulas; however, one must keep in mind that the results for the general solution are based on a rigorous theory with only ϵ_β, ϵ_γ, and D_{eff} used as input parameters. No adjustments were made on the basis of external tortuosities determined in packed beds of nonporous particles.

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Notation

$A_{\beta\sigma}$ = $\beta - \sigma$ interfacial area contained within averaging volume $\mathcal{V}$, m^2
c = undefined concentration of the diffusing species, modes/m^3
c_β = point concentration of the diffusing species in the β phase, mol/m^3
c_σ = intrinsic phase average concentration of the diffusing species within the porous particles, mol/m^3
$\langle c_\beta\rangle^\beta$ = intrinsic phase average concentration of the diffusing species in the β phase, mol/m^3
$\langle c_\sigma\rangle^\sigma$ = intrinsic phase average concentration of the diffusing species in the σ phase, mol/m^3
$\{c\}$ = overall intrinsic phase average concentration in the packed bed, mol/m^3
D_e = overall effective diffusivity, m^2/s
$\mathcal{D}_\sigma$ = point effective diffusivity for the σ phase, m^2/s
D_{eff} = overall effective diffusivity tensor, m^2/s
D_{eff} = overall effective diffusivity for isotropic systems, m^2/s
f = vector field that maps $\nabla\langle c_\beta\rangle^\beta$ onto $c_\beta - \langle c_\beta\rangle^\beta$, m
g = vector field that maps $\nabla\langle c_\sigma\rangle^\sigma$ onto $c_\sigma - \langle c_\sigma\rangle^\sigma$, m
k_β = thermal conductivity of β phase, kcal/m · ks
k_σ = thermal conductivity of σ phase, kcal/m · ks
K_{eff} = effective thermal conductivity for isotropic systems, kcal/m · ks
ℓ_i = lattice vectors ($i = 1, 2, 3$) describing a spatially periodic porous medium, m
$\mathbf{n}_{\alpha\beta}$ = unit outwardly directed unit normal vector pointing from σ phase toward β phase
$\mathbf{n}_{\beta\sigma}$ = unit normal vector, $\underset{\sim}{n}_{\beta\sigma} = -\underset{\sim}{n}_{\sigma\beta}$
$\mathbf{r}$ = position vector, m
t = time, s
$\mathcal{V}_o$ = averaging volume for σ phase, m^3
$\mathcal{V}$ = averaging volume for packed bed, m^3
V_β = volume of β phase contained within $\mathcal{V}$, m^3
V_σ = volume of σ phase contained within $\mathcal{V}$, m^3

Greek letters

$\epsilon = \epsilon_\beta + \epsilon_\gamma\epsilon_\sigma$, total porosity
ϵ_β = volume fraction of β phase (porosity of packed bed)
ϵ_γ = volume fraction of γ phase (porosity of porous particles)
ϵ_σ = volume fraction of σ phase, $\epsilon_\sigma = 1 - \epsilon_\beta$
$\kappa = \epsilon_\gamma\mathcal{D}_\sigma/\mathcal{D}_\beta$ for diffusion process, k_σ/k_β for heat conduction process

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