Combined Surface and Pore Volume Diffusion in Porous Media

The recent theory for pore volume diffusion in porous media (Bhatia, 1985, 1986) is further extended to include surface diffusion with adsorption-desorption phenomena proceeding at finite rates. The short-range memory effects, previously discussed in terms of a correlation between successive pores traversed, are included here and are found to be important for surface diffusion as well. A tortuosity for surface diffusion is defined and found to be larger than 3, in the range of 5 to 7, because of internal correlation effects in the random network structure examined. Under conditions of gradients in pore surface area it is shown that the surface transport equation is

$$\frac{\partial(S_0C_{s0})}{\partial t} = \nabla_x \cdot S_0\, D_{se}\, \nabla_x\, C_{s0} + S_0[k_aC_0(M - C_{s0}) - (k_d + k_s)C_{s0}]$$

and the relation between the effective surface diffusivity D_{se} and the pore structure parameters is derived. The equation for pore volume diffusion requires further justification when adsorption-desorption occurs at finite rates, and is also derived here.

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Introduction

In modeling diffusion in porous solids it is now a widely accepted practice to use the continuum description incorporating an empirically determined effective diffusivity. Various analyses have been performed (Johnson and Stewart, 1965; Pismen, 1974; Whitaker, 1983) to estimate the effective diffusivity; however, the results have been generally unsatisfactory and there remains a discrepancy between the theoretical predictions and experimental values (Feng and Stewart, 1973; Horak and Schneider, 1971; McGreavy and Siddiqui, 1980). Consequently it has become customary to introduce a parameter called the tortuosity defined by

$$\gamma = \frac{\epsilon\bar{D}}{D_e} \tag{1}$$

and consign all uncertainties into this parameter by allowing it to deviate from its theoretical value of 3 (Johnson and Stewart, 1965; Feng and Stewart, 1973). The difference is normally qualitatively ascribed to nonidealities such as dead ends and deviation from cylindrical pore shape, although definitive support for this is lacking. Some calculations have been made (Petersen, 1958; Michaels, 1959) of the adverse influence of pore constrictions, but it has been observed (Bhatia, 1985) that the actual effect may be less because regions between constrictions are ascribed a smaller than true pore radius by mercury porosimetry. When Knudsen diffusion is important (and it generally is for catalyst particles or coal chars) the lowering of the effective diffusivity may be largely accounted for by using the smaller than actual pore radius. In support, it is to be noted that Patel and Butt (1975) have used converging-diverging pore shapes but still find fitted tortuosities of about 6 and higher.

An alternative theory has recently been proposed by Bhatia (1985, 1986) in which it is demonstrated that history effects are important during diffusion in porous solids, but which have been ignored in prior analyses. In these recent works a random walk formulation was adopted which allows for a short-range memory effect by considering the correlation among successive steps, with each step comprising the navigation of a complete pore segment. It was shown that this short-range memory effect is sufficient to explain the discrepancy between observed and predicted tortuosities. According to the new theory, tortuosity values for pore volume diffusion are expected to lie in the range of 6–9 for catalyst particles, consistent with experimental observations (Amberg and Echigoya, 1961; Wang and Smith, 1983), and to be 30 and upward for carbonaceous materials as observed by Turkdogan et al. (1970) and Yang et al. (1977). In addition it was shown that the tortuosity is a "process parameter," dependent upon temperature, pressure, and the diffusing species, and not a porous medium property alone. Similar results have been independently predicted by Reyes and Jensen (1985) using percolation theory, which also includes the effect of dead ends in its formulation. However since most porous solids of interest have about 30% porosity or higher, they are well above the percolation thresholds of 4 to 9% measured by Amberg and Echigoya (1961), so that the effect of dead ends should be small. Indeed, the similarity of the results of Bhatia (1986) and Reyes and Jensen (1985) also suggests that correlation effects dominate and that dead ends, not included in the former analysis, are of much less concern at these porosities. Under these conditions the analytical treatment of Bhatia (1986) appears attractive and provides a satisfactory description of pore volume diffusion. It is also to be noted that the results of Bhatia are consistent with those of Abbasi et al. (1983), who have performed Monte Carlo calculations of the effective diffusivity using a packed-spheres model, confirming the importance of correlations.

The analysis of Bhatia (1986) for pore volume diffusion and surface reaction assumed rapid adsorption with low surface coverage under conditions of negligible surface diffusion. When the dynamics of adsorption-desorption and surface diffusion are important the resulting overall conservation equations are somewhat different, although they may readily be written as done by Aris (1983). However, while an effective surface diffusivity may be used intuitively, it is not known *a priori* how it depends upon the pore structure, and what the value is of the tortuosity for surface diffusion. These quantities can best be obtained by an extension of the prior analysis to include as well the dynamics of these various surface phenomena.

Like pore volume diffusion, surface diffusion is also represented by Fick's law, and it is common to write

$$N_s = -b\, D_s \frac{dC_s}{dX} \tag{2}$$

where N_s is the flux in the x direction across a line of width b (Schneider and Smith, 1968; Gilliland et al., 1974), and the surface diffusivity D_s includes the effect of surface roughness. However, the surface diffusivity is also known to vary with the concentration C_s, approaching a constant limiting value for low C_s where Henry's law holds (Schneider and Smith, 1968). In this low concentration region Schneider and Smith (1968) and Komiyama and Smith (1974) also write

$$D_{se} = \frac{\epsilon}{\gamma_s} D_s \tag{3}$$

where D_{se} is the effective surface diffusivity for a porous solid and γ_s is the tortuosity for surface diffusion. In general, however, it is difficult to estimate γ_s from measurements of D_{se} because the intrinsic surface diffusivity D_s is not easily predicted, unlike the molecular or Knudsen diffusivities for pore volume diffusion. Thus, it would be useful to develop a theory to predict the surface tortuosity for interpreting the experimental effective surface diffusivity D_{se} and its variation with pore structure.

It is the purpose of this paper to extend the prior development (Bhatia, 1986) to include the dynamics of adsorption-desorption as well as surface diffusion. Although the methodology is similar the details are different since new phenomena are involved which do not enter into the prior work. As a result a fresh analysis such as that undertaken here is necessary. The analysis provides an explicit expression for the tortuosity for surface diffusion and shows that this parameter is a porous medium property, independent of process conditions, unlike the tortuosity for pore volume diffusion. The tortuosity for surface diffusion has hitherto received only little theoretical attention (Ho and Strieder, 1981) and this new development therefore forms an important extension of the prior theory.

Statistical Description of the Porous Medium

The porous medium model is the same as that considered previously (Bhatia, 1986) and its statistical characterization has been discussed in detail in that work. However, for ready reference we provide the basic features here.

As in the previous analysis, consider the porous medium as a network of randomly oriented cylindrical capillary segments of arbitrary size distribution. The mean capillary length $\tilde{\ell}$ is much smaller than the macroscopic length scale L, and the number of pores meeting at each intersection is equal to N. Define ψ as the dimensionless pore length and r^* as the dimensionless pore radius, and let $\tilde{\omega}$ be the set $[r^*, \psi]$. The orientation of a pore at an intersection is specified by a unit vector $\tilde{U}$ along its axis, given by

$$\tilde{U} = \sin\theta_1 \cos\theta_2\, \tilde{\imath} + \sin\theta_1 \sin\theta_2\, \tilde{\jmath} + \cos\theta_1\, \tilde{k} \tag{4}$$

where θ_1, θ_2 are measured in spherical coordinates. Denote by $\tilde{\theta}_i$ the set $[\theta_{i1}, \theta_{i2}]$ corresponding to the ith pore at an intersection, and let $\tilde{\tilde{\theta}}$ be the set $[\tilde{\theta}_1, \tilde{\theta}_2, \ldots, \tilde{\theta}_N]$ which contains the orientations of all the N pores meeting at an intersection. Similarly let $\tilde{\tilde{\omega}}$ be the set $[\tilde{\omega}_1, \tilde{\omega}_2, \ldots, \tilde{\omega}_N]$.

A probability density $p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ is now defined such that, given an intersection at the dimensionless position $\tilde{\eta}$, $p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\, d\tilde{\tilde{\omega}}\, d\tilde{\tilde{\theta}}$ is the probability that the parameters in the set $\tilde{\tilde{\omega}}$ characterizing the pores meeting at that point lie in $(\tilde{\tilde{\omega}}, \tilde{\tilde{\omega}} + d\tilde{\tilde{\omega}})$ and the corresponding orientations lie in $(\tilde{\tilde{\theta}}, \tilde{\tilde{\theta}} + d\tilde{\tilde{\theta}})$, where

$$d\tilde{\tilde{\omega}} = \prod_{j=1}^{N} dr_j^*\, d\psi_j$$

$$d\tilde{\tilde{\theta}} = \prod_{j=1}^{N} d\theta_{j1}\, d\theta_{j2}$$

An average of an arbitrary function $J(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$, given in intersection at $\tilde{\eta}$, is now given by

$$\langle J \rangle = \int\!\!\int J(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\, p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\, d\tilde{\tilde{\omega}}\, d\tilde{\tilde{\theta}} \tag{5}$$

Further, define the conditional probability density $p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}_{,i}, \tilde{\tilde{\theta}}_{,i}/\tilde{\omega}_i, \tilde{\theta}_i)$ for the remaining $N - 1$ pores, given $\tilde{\omega}_i$, $\tilde{\theta}_i$ for the ith pore at an intersection at $\tilde{\eta}$, as

$$p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}_{,i}, \tilde{\tilde{\theta}}_{,i}/\tilde{\omega}_i, \tilde{\theta}_i) = \frac{p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})}{\int\int p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\, d\tilde{\tilde{\omega}}_{,i}\, d\tilde{\tilde{\theta}}_{,i}} \qquad (6)$$

where $\tilde{\tilde{\omega}}_{,i} = [\tilde{\omega}_1, \tilde{\omega}_2, \ldots, \tilde{\omega}_{i-1}, \tilde{\omega}_{i+1}, \ldots, \tilde{\omega}_N]$. A similar definition holds for $\tilde{\tilde{\theta}}_{,i}$. The corresponding conditional average of $J(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ is given as

$$\langle J \rangle_{,i} = \int\int J(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}_{,i}, \tilde{\tilde{\theta}}_{,i}/\tilde{\omega}_i, \tilde{\theta}_i)d\tilde{\tilde{\omega}}_{,i}\, d\tilde{\tilde{\theta}}_{,i} \qquad (7)$$

Defining $\beta(=r^{*2}\psi)$ as a dimensionless pore volume gives the density of pore intersections

$$p_i(\alpha, \tilde{\eta}) = \frac{2\epsilon}{N\langle \beta \rangle \pi r_a^2 \bar{\ell}} \qquad (8)$$

Denoting $g(\alpha, \tilde{\eta}, \tilde{\omega}_1, \tilde{\theta}_1)d\tilde{\omega}_1\, d\tilde{\theta}_1$ as the local number density of pores with parameters in $(\tilde{\omega}_1, \tilde{\omega}_1 + d\tilde{\omega}_1)$, and orientations in $(\tilde{\theta}_1, \tilde{\theta}_1 + d\tilde{\theta}_1)$, gives

$$g(\alpha, \tilde{\eta}, \tilde{\omega}_1, \tilde{\theta}_1) = \frac{N p_i(\alpha, \tilde{\eta})}{2} \int\int p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})d\tilde{\tilde{\omega}}_{,1}\, d\tilde{\tilde{\theta}}_{,1} \qquad (9)$$

To zero order, considering the pore orientation to be random and uncorrelated with the size parameters,

$$g_0(\tilde{\eta}, \tilde{\omega}, \tilde{\theta}) = h(\tilde{\eta}, \tilde{\omega})\frac{\sin\theta_1}{4\pi}, \quad \begin{matrix} 0 \le \theta_1 \le \pi \\ 0 \le \theta_2 \le 2\pi \end{matrix} \qquad (10)$$

and

$$g_1(\tilde{\eta}, \tilde{\omega}, \tilde{\theta}) = \frac{\psi}{2}\tilde{U} \cdot \nabla g_0 \qquad (11)$$

as proved in the prior work (Bhatia, 1986). In Eqs. 10 and 11, $h(\tilde{\eta}, \tilde{\omega})$ is the probability density, per unit volume, that a pore with one end at $\tilde{\eta}$ has size parameters defined by $\tilde{\omega}$, and g_0, g_1 are the first two coefficients of the asymptotic expansion

$$g(\alpha, \tilde{\eta}, \tilde{\omega}, \tilde{\theta}) = g_0(\tilde{\eta}, \tilde{\omega}, \tilde{\theta}) + \alpha g_1(\tilde{\eta}, \tilde{\omega}, \tilde{\theta}) + 0(\alpha^2) \qquad (12)$$

in which α being small has been treated as a perturbation parameter.

With the above statistical characterization it is now possible to undertake an analysis of the transport both on the surface and in the gas phase of the pores.

Analysis of Surface Transport

In this section we examine the dynamics of surface transport in the Henry's law region in which the surface diffusivity is independent of adsorbed concentration. For higher concentrations in which D_s depends on the adsorbed concentration, the analysis is similar, requiring further algebraic detail as discussed in a later section. As in the prior work we proceed by first developing the general equations for the transport, next examine the transition and reaction intensities, and then perform an asymptotic analysis to obtain the final continuum description.

General equations for surface transport

The derivation of the equations for surface transport as before proceeds through the familar techniques of stochastic processes (Van Kampen, 1983); however, our treatment is more general than the prior developments in stochastic processes because each intersection of the pore network is characterized by its own state variables (the sizes and orientations of the pores meeting at the intersection). In addition the states of neighboring intersections are correlated, for they share a common pore.

In the prior treatment (Bhatia, 1986) diffusion through the pore volume was considered as a random walk from one intersection to another, with each step comprising the successful navigation of a complete pore segment. For surface transport one may use the same analogy with the steps now being executed by diffusion along the pore surface. In a manner similar to the prior work we now make the following definitions: $Q_{sj}(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ is the probability that after j steps and at time lying in $(t, t + dt)$, a particle diffusing along the pore surfaces arrives at an intersection located at $\tilde{\eta}$ having pores with parameters given by $\tilde{\tilde{\omega}}$ and orientation by $\tilde{\tilde{\theta}}$. Also, $p_t(t, \tilde{\omega}_i/\tilde{\tilde{\omega}})dt$ is the probability that a particle arriving at $t = 0$ at an intersection with parameters $\tilde{\tilde{\omega}}$ leaves during $(t, t + dt)$ from the end of the ith pore characterized by the parameter set $\tilde{\omega}_i$. As will be shown subsequently, $p_t(t, \tilde{\omega}_i/\tilde{\tilde{\omega}})$ is homogeneous in time in the low surface concentration Henry's law region. In addition, we define $p_d(t/\tilde{\tilde{\omega}})dt$ as the probability (also homogeneous) that upon arriving at the intersection at $t = 0$, the particle disappears at time in $(t, t + dt)$. Disappearance may occur either by reaction or by desorption into the fluid phase.

With the above definitions the subsequent derivations are precisely the same as in Eqs. 17 to 31 of the prior work (Bhatia, 1986) but with $p_d(t/\tilde{\tilde{\omega}})$ replacing $p_r(s/\tilde{\tilde{\omega}})$ and the rate of arrival after zero steps $Q_{s0}(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ now given by

$$Q_{s0}(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) = P_s(\tilde{\eta}, 0)\delta(t) + k_a C_0(\tilde{\eta}, t) \cdot \left[\frac{MS_0}{p_i(0, \tilde{\eta})} - P_{s0}(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\right] + 0(\alpha) \qquad (13)$$

Here, the righthand side of Eq. 13 reflects the fact that particles may arrive at an intersection after zero steps either by initial placement or by adsorption. In this equation we have used a Langmuir-Hinshelwood isotherm with an adsorption rate constant k_a and a maximum surface concentration M. $C_0(\tilde{\eta}, t)$ is the local gas-phase concentration to zero order in α (an equation for C_0 will be derived later), and S_0 is the surface area per unit volume to zero order. The surface area per unit volume is defined by

$$S = N\pi r_a \bar{\ell} p_i(\alpha, \tilde{\eta})\langle r^*\psi \rangle \qquad (14)$$

In Eq. 13 $P_{s0}(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ represents the probability density, to zero order, of finding a particle at an intersection located at $\tilde{\eta}$, at time t, given that the state of the intersection is defined by $\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}$.

Using the new equation for Q_0 one may follow the derivations in Eqs. 17 to 31 of Bhatia (1986) to obtain the results, in terms of Laplace transforms,

$$
\begin{aligned}
sP_s(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) - P_s(\tilde{\eta}, 0)
&= -\left[\frac{p_d(s/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})} + \frac{\sum_{i=1}^{N} p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})}\right] P_s(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\
&\quad + \sum_{i=1}^{N} \left\langle \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P_s(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\rangle_{,i} \\
&\quad + \sum_{i=1}^{N} \sum_{m=1}^{2} \frac{\alpha^m}{m!} \psi_i^n (\tilde{U}_i \cdot \nabla)^m \left\langle \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P_s(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\rangle_{,i} \\
&\quad + k_a \mathcal{L}\left[C_0\left(\frac{S_0 M}{p_{i0}} - P_{s0}\right)\right] + 0(\alpha) \qquad (15)
\end{aligned}
$$

$$
\begin{aligned}
s(SC_s)(\tilde{\eta}, s) - (SC_s)(\tilde{\eta}, 0)
&= -\left\{\frac{p_d(s/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})} P_s(\eta, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\right\} \\
&\quad - \alpha \sum_{i=1}^{N} \nabla \cdot \left\{\frac{\tilde{U}_i' \psi_i p_t(s, \omega_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P_s(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\} \\
&\quad + \frac{\alpha^2}{2} \sum_{i=1}^{N} \nabla\nabla : \left\{\tilde{U}_i'\tilde{U}_i'\psi_i^2 \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P_s(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\} \\
&\quad + k_a \mathcal{L}[SC_0(M - C_{s0})] + 0(\alpha) \qquad (16)
\end{aligned}
$$

replacing Eqs. 31 and 30, respectively, of the prior work. In Eq. 15 P_s replaces P of the earlier paper, and is defined by

$$P_s(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) = \sum_{j=0}^{\infty} \int_0^t Q_{sj}(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) p_n(t - \tau/\tilde{\tilde{\omega}})\, d\tau \qquad (17)$$

in which $p_n(t/\tilde{\tilde{\omega}})$ is the probability (homogeneous) of finding a particle in the neighborhood of the intersection, given that it arrived there at $t = 0$. Thus $P_s(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ is the probability of finding a particle in the neighborhood of an intersection at $\tilde{\eta}$, given that the intersection is characterized by the pore parameter set $\tilde{\tilde{\omega}}$ and orientations $\tilde{\tilde{\theta}}$. Further, in Eq. 16 C_s is the local surface concentration, defined by

$$C_s(\tilde{\eta}, t) = \frac{\{P_s(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\}}{S} \qquad (18)$$

where the braces represent a volumetric expectancy given by

$$\{P_s(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\} = p_i(\alpha, \tilde{\eta}) \langle P_s(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\rangle \qquad (19)$$

The operator $\mathcal{L}$ in Eqs. 15 and 16 represents the Laplace transform.

In order to obtain an equation for the surface concentration $C_s(\tilde{\eta}, t)$ it is necessary to eliminate the probability P_s from the volumetric averages in Eq. 16. As in the previous work this can be accomplished through an asymptotic analysis of Eq. 15. Before this, however, it is necessary to develop the forms of the intensity functions $[p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}})/p_n(s/\tilde{\tilde{\omega}})]$ and $[p_d(s/\tilde{\tilde{\omega}})/p_n(s/\tilde{\tilde{\omega}})]$ in these equations.

Intensity functions for surface transport

To obtain the intensity functions required to further develop Eqs. 14 and 15 it is necessary to solve simultaneously the diffusion equations for the various pore segments meeting at an intersection, with mutually common boundary conditions at the intersection. The rationale for this has been provided in the earlier paper as well as by Pismen (1974), in both of which pore volume diffusion was analyzed. For surface transport we examine the case in which a molecule is initially placed on the surface at the intersection and diffuses into the connecting pores, while simultaneously desorbing. Assuming a first-order surface reaction, the diffusion equations for the N pores meeting at the intersection are given by

$$\frac{\partial n_i}{\partial t} = D_s \frac{\partial^2 n_i}{\partial z_i^2} - (k_d + k_s) n_i \quad i = 1, 2, \ldots, N \qquad (20)$$

and are to be solved with the initial condition

$$n_i(z_i, 0) = \frac{\delta(z_i)}{q_i N} \qquad (21)$$

and boundary conditions

$$\text{at } z_i = 0: \quad n_1 = n_2 = \cdots = n_N; \quad \sum_{i=1}^{N} q_i D_s \left[\frac{\partial n_i}{\partial z_i}\right]_{z_i=0} = 0 \qquad (22)$$

$$\text{at } z_i = \ell_i: \quad n_i = 0 \qquad (23)$$

where D_s is the surface diffusivity, assumed to be concentration-independent since we are dealing with the Henry's law region (Schneider and Smith, 1968), and q_i is the perimeter of the ith pore ($2\pi r_i$). The transition rate through any pore is then given by

$$p_t(t, \tilde{\omega}_i/\tilde{\tilde{\omega}}) = -q_i D_s \left[\frac{\partial n_i}{\partial z_i}\right]_{z_i=\ell_i} \qquad (24)$$

and the probability of finding the molecule in the neighborhood of the intersection at time t is given by

$$p_n(t/\tilde{\tilde{\omega}}) = \sum_{i=1}^{N} q_i \int_0^{\ell_i} n_i\, dz_i \qquad (25)$$

Clearly, since the time of placement of the particle does not enter into Eqs. 20 to 23, p_t and p_n are homogeneous in time. The rate of disappearance $p_d(t/\tilde{\tilde{\omega}})$ is then related to p_t and p_n through

$$p_n(t/\tilde{\tilde{\omega}}) + \sum_{i=1}^{N} \int_0^t p_t(\tau, \tilde{\omega}_i/\tilde{\tilde{\omega}})\, d\tau + \int_0^t p_d(\tau/\tilde{\tilde{\omega}})\, d\tau = 1 \qquad (26)$$

Equations 20 to 26 may be solved after taking Laplace transforms to yield expressions for $[p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}})/p_n(s/\tilde{\tilde{\omega}})]$ and $[p_d(s/\tilde{\tilde{\omega}})/p_n(s/\tilde{\tilde{\omega}})]$ as required in Eqs. 15 and 16. These expressions are identical to Eqs. 38 and 39 of Bhatia (1986) but with q_i replacing A_i, D_s replacing D_i, p_d replacing p_r, and $(k_d + k_s)$ replacing k_i. As shown in the earlier work, in order to obtain the usual effective diffusion relationship we are only interested in the intensity functions in the limit $\ell_i\sqrt{(s + k_d + k_s)/D_s} \rightarrow 0$, i.e., when all individual pore level Thiele moduli are negligible. This therefore becomes a restriction on the validity of the effective diffusion equation for porous solids. Upon taking the above limit the results are similar to Eqs. 43 and 44 of the earlier paper, and we obtain

$$\frac{p_t}{p_n} = \frac{2D_s^*D_eq_i^*}{L^2\alpha^2\psi_i\sum_{i=1}^{N} q_i^*\psi_i} + 0(\alpha^0) \tag{27}$$

$$\frac{p_d}{p_n} = \frac{\phi_2^2D_e}{L^2} + 0(\alpha^2) \tag{28}$$

where $\phi_2 = [L^2(k_d + k_s)/D_e]^{1/2}$, $q_i^* = r_i^*$, and $D_s^* = D_s/D_e$. Equation 27 may be rewritten as

$$\frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})} = \frac{2D_e\Gamma_i}{L^2\alpha^2\psi_i\sum_{i=1}^{N}\lambda_i} \tag{29}$$

where $\Gamma_i = D_s^*q_i^*$ and $\lambda_i = q_i^*\psi_i$, replacing δ_i and β_i, respectively, in Eq. 45 of the prior paper. With the definition of the intensity functions in Eqs. 28 and 29 it is now possible to proceed with the asymptotic analysis of Eqs. 15 and 16 and obtain an equation for the surface transport in terms of the surface concentration C_s.

Averaged transport equation

Substituting of Eqs. 28 and 29 in Eqs. 15 and 16 results in

$$\begin{aligned}\alpha^2\frac{\partial P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})}{\partial\tau} &= -\alpha^2\phi_2^2P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\\ &- \frac{2}{\lambda_\tau}\left[\sum_{i=1}^{N}\frac{\Gamma_i}{\psi_i}\right]P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) + 2\sum_{i=1}^{N}\left\langle\frac{\Gamma_i}{\psi_i\lambda_\tau'}P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\rangle_{,i}\\ &+ 2\sum_{i=1}^{N}\sum_{m=1}^{2}\frac{\alpha^m\Gamma_i\psi_i^{m-1}}{m!}(\tilde{U}_i\cdot\nabla)^m\left\langle\frac{P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')}{\lambda_\tau'}\right\rangle_{,i}\\ &+ \left(\frac{L^2k_a}{D_e}\right)\alpha^2C_0(\tilde{\eta}, \tau)\left(\frac{MS_0}{p_{i0}} - P_{s0}\right) + 0(\alpha^3)\end{aligned} \tag{30}$$

$$\begin{aligned}\alpha^2\frac{\partial(SC_s)}{\partial\tau} &= -\alpha^2\phi_2^2\{P_s\} - 2\alpha N\nabla\cdot\left\{\frac{\tilde{U}_1\Gamma_1}{\lambda_\tau}P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\right\}\\ &+ Na^2\nabla\nabla:\left\{\frac{\Gamma_1\psi_1}{\lambda_\tau}\tilde{U}_1\tilde{U}_1P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\right\} + \alpha^2\left(\frac{k_aL^2}{D_e}\right)\\ &\cdot S_0C_0(\tilde{\eta}, \tau)(M - C_{s0}) + 0(\alpha^3)\end{aligned} \tag{31}$$

in which $\lambda_\tau = \Sigma_{i=1}^{N}\lambda_i$. Equations 30 and 31 are quite similar to Eqs. 47 and 48 of the prior work, but contain also the additional adsorption term on the righthand side. To obtain an equation in the surface concentration C_s it is necessary to perform an asymptotic analysis of Eqs. 30 and 31 by expanding C_s and P_s in terms of powers of the small parameter α as in Eq. 12, and equating terms of the same order. This yields a series of subproblems the solution of which gives the averaged transport equation, to zero order in α,

$$\begin{aligned}\frac{\partial(S_0C_{s0})}{\partial t} &= \nabla_x\cdot\frac{S_0}{\gamma_1}(D_s - D_{sc})\nabla_xC_{s0}\\ &+ S_0[k_aC_0(M - C_{s0}) - (k_d + k_s)C_{s0}]\end{aligned} \tag{32}$$

in which we have returned to dimensional time and space, and where

$$\gamma_1 = 3 \tag{33}$$

$$\frac{D_{sc}}{D_s} = \frac{2}{\langle r\ell\rangle}\left\langle\frac{r_1^2}{\left[1 + (r_1/\ell_1)\left\langle\left[\sum_{j=1}^{N} r_j/\ell_j\right]^{-1}\right\rangle_{,1}^{0}\right]\left[\sum_{j=1}^{N} r_j/\ell_j\right]}\right\rangle^{0} \tag{34}$$

Details of the derivation of Eqs. 32 to 34 are given in appendix A.

Equation 32 is a generalization of the usual equation for surface transport as used for example by Aris (1983). However, our result, in addition to rigorously justifying the use of the intuitive form as the continuum limit, provides a relation for the effective surface diffusivity in terms of its actual value D_s. This relation is given by

$$D_{se} = \frac{D_s}{\gamma_1}\left(1 - \frac{D_{sc}}{D_s}\right) \tag{35}$$

in which (D_{sc}/D_s) is as given by Eq. 34 and expresses the effect of internal correlations (a short-range memory effect) on the effective surface diffusivity. In terms of this effective surface diffusivity the surface transport equation is

$$\begin{aligned}\frac{\partial(S_0C_{s0})}{\partial t} &= \nabla_x\cdot S_0D_{se}\nabla_xC_{s0}\\ &+ S_0[k_aC_o(M - C_{s0}) - (k_d + k_s)C_{s0}]\end{aligned} \tag{36}$$

Under conditions of uniform surface area per unit volume (i.e., no gradients in the pore structure parameters) S_0 may be factored out of the above equation to yield the form used for the steady state by Aris (1983).

Analysis of Pore Volume Transport

In the surface transport equation (cf. Eq. 32 or 36) the adsorption term contains the local concentration of the diffusing species in the pores. An equation must also be developed for this quantity $C_0(\tilde{\eta}, t)$. Under conditions of negligible surface diffusion, low surface coverage, and rapid adsorption, the required equation for pore volume diffusion was derived in the prior work, resulting in a new expression for the effective diffusivity. When these assumptions are relaxed the expression for the effective pore volume diffusivity obtained in the prior paper still holds; however, the intensities involved are no longer homogeneous as previously assumed, and some justification of the final form is necessary. Further, the adsorption-desorption effects cannot be incorporated quite easily into the intensity as previously done, but must be split up into the probability of arrival after zero steps, and the rate of disappearance, as for surface transport. Because of these differences the equation for pore volume diffusion in the presence of adsorption-desorption at finite rates is derived here in outline form, keeping in mind that the approach and details of the method are similar to the prior work.

General equations for pore volume diffusion

For pore volume diffusion with adsorption-desorption at finite rates it will be shown in a subsequent section that the transition probability p_t and the probability p_n are homogeneous in time, to zero order; however the probability of disappearance, p_d, is no longer homogeneous but is also a function of the time of arrival, in the form

$$p_d(\tilde{\eta}, \tau, y/\tilde{\tilde{\omega}}) = A(\eta, \tau)F(y/\tilde{\tilde{\omega}}) \tag{37}$$

in which τ is the arrival time and y is the time elapsed. Thus, $p_d(\tilde{\eta}, \tau, y/\tilde{\tilde{\omega}})\, dy$ is the probability that a molecule arriving at time τ at an intersection located at $\tilde{\eta}$ with parameters $\tilde{\tilde{\omega}}$ disappears by adsorption after an elapsed time y lying in $(y, y + dy)$. For generality Eq. 26 is modified to

$$p_n(\tilde{\eta}, t, \tau/\tilde{\tilde{\omega}}) = 1 - \sum_{i=1}^{N} \int_0^{t-\tau} p_t(y, \tilde{\omega}_i/\tilde{\tilde{\omega}})\, dy + \int_0^{t-\tau} p_d(\tilde{\eta}, \tau, y/\tilde{\tilde{\omega}})\, dy \tag{38}$$

in which p_n is written also as a function of τ, although to the leading order in α it shall be homogeneous since $\Sigma_{i=1}^{N} p_t \gg p_d$.

Following the prior analysis it is now possible to derive the general transport equations, in the Laplace domain, in terms of the probability $P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ and the local concentration $C(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$. Skipping the mathematical details, which are given in appendix B, we present these equations as:

$$\begin{aligned} sP(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) - P(\tilde{\eta}, 0) = &- \left[\sum_{i=1}^{N} \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})}\right] P(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\ &- \frac{F(s/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})} \mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})A(\tilde{\eta}, t)] + k_d P_s(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\ &+ \sum_{i=1}^{N} \left\langle \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}') \right\rangle_{,i} + \sum_{i=1}^{N} \sum_{m=1}^{\infty} \frac{\alpha^m \psi_i^m}{m!} \\ &\cdot (\tilde{U}_i \cdot \nabla)^m \left\langle \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}') \right\rangle_{,i} + 0\left(\frac{\alpha^2 \dot{A} P F}{p_n}\right) \end{aligned} \tag{39}$$

and

$$\begin{aligned} s(\epsilon C)(\tilde{\eta}, s) - (\epsilon C)(\tilde{\eta}, 0) = &- \left\{\frac{F(s/\tilde{\omega})}{p_n(s/\tilde{\tilde{\omega}})} \mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})A(\tilde{\eta}, t)]\right\} \\ &+ k_d\{P_s\} - \alpha \sum_{i=1}^{N} \nabla \cdot \left\{\tilde{U}_i' \psi_i \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\} \\ &+ \frac{\alpha^2}{2} \sum_{i=1}^{N} \nabla\nabla : \left\{\tilde{U}_i' \tilde{U}_i' \psi_i^2 \frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P(\tilde{\eta}, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\} \\ &+ 0\left(\frac{\alpha^2 \dot{A} P F}{p_n}\right) \end{aligned} \tag{40}$$

It is now necessary to express the probability P in terms of the local concentration C in Eq. 40 in order to obtain an equation for the concentration field. Before this, however, we shall develop the expressions for the intensity functions.

Intensity functions for pore volume diffusion

The rate of disappearance of a molecule from the pore volume is no longer homogeneous, as is evident from the conservation equation

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial z_i^2} - \frac{2k_a}{r_i} c_i(M - C_s), \quad i = 1, 2, \ldots, N \tag{41}$$

which models the diffusion and adsorption in the N pores meeting at an intersection under conditions of negligible bulk flow. In Eq. 41, D_i is the diffusion coefficient in the ith pore of radius r_i, and the adsorption term provides the inhomogeneity since the local surface concentration C_s is also a function of time. The above equation is to be solved with the initial condition

$$t = \tau: \quad c_i = \frac{\delta(z_i)}{NA_i} \tag{42}$$

and boundary conditions

$$\text{at } z_i = 0: \quad c_i = c_2 = c_N; \sum_{i=1}^{N} A_i D_i \left[\frac{\partial c_i}{\partial z_i}\right]_{z_i=0} = 0 \tag{43}$$

$$\text{at } z_i = \ell_i: \quad c_i = 0, \quad i = 1, 2, \ldots, N \tag{44}$$

Equation 42 specifies that the molecule is placed at the intersection at time $t = \tau$. Its subsequent temporal behavior is modeled by Eq. 41. The solution of this equation is no longer as easy as in the previous cases because C_s is also a function of t. However, some simplification may be made. Substitution of

$$y = t - \tau \tag{45}$$

converts Eq. 41 to

$$\frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial z_i^2} - \frac{2k_a}{r_i} c_i[M - C_s(\tilde{\eta}, \tau + y)] \tag{46}$$

and Eq. 42 to

$$y = 0: \quad c_i = \frac{\delta(z_i)}{NA_i} \tag{47}$$

where y is the time elapsed. Recognizing, as before, that the arrival time τ is much larger than the time elapsed, y, (by a factor of the order of magnitude of $1/\alpha^2$) Eq. 46 may be replaced by

$$\frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial z_i^2} - k_i c_i \tag{48}$$

where $k_i = 2k_a[M - C_s(\tilde{\eta}, \tau)]/r_i$, and is a function of τ but not of y. The transition rate is related to c_i through

$$p_t(t, \tilde{\omega}_i/\tilde{\tilde{\omega}}) = -A_i D_i \left[\frac{\partial c_i}{\partial z_i}\right]_{z_i=\ell_i} \tag{49}$$

and the probability p_n is obtained from

$$p_n(t/\tilde{\tilde{\omega}}) = \sum_{i=1}^{N} A_i \int_0^{\ell_i} c_i(z_i, t)\, dz_i \tag{50}$$

while the probability p_d is related to p_n and p_t through Eq. 38. It is now straightforward to take Laplace transforms with respect to y in Eq. 48, and obtain the functions p_t, p_n, and p_d in the Laplace domain. However, as before we are interested only in the limit that all pore level Thiele moduli are negligible, for it was shown earlier (Bhatia, 1986) that only in this limit is the usual effective diffusion equation applicable. Thus, we seek the solutions in the limit $\ell_i\sqrt{s + k_i/D_i} \to 0$, and

$$p_n(s/\tilde{\tilde{\omega}}) = \frac{1}{2}\frac{\sum_{i=1}^{N} A_i\ell_i}{\sum_{i=1}^{N} A_i D_i/\ell_i} \tag{51}$$

$$p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}) = \frac{A_i D_i/\ell_i}{\sum_{i=1}^{N} A_i D_i/\ell_i} \tag{52}$$

$$p_d(\tilde{\eta}, \tau, s/\tilde{\tilde{\omega}}) = \frac{\sum_{i=1}^{N} A_i k_i \ell_i}{2\sum_{i=1}^{N} A_i D_i/\ell_i} \tag{53}$$

In Eqs. 51 to 53 only p_d is a function of the arrival time τ since k_i contains $C_s(\tilde{\eta}, \tau)$, while D_i is independent of τ. Thus, p_n and p_t are homogeneous while p_d is not. The probability p_d may also be rewritten in the form of Eq. 37 with

$$A(\tilde{\eta}, \tau) = 1 - \frac{C_s(\tilde{\eta}, \tau)}{M} \tag{54}$$

and

$$F(s/\tilde{\tilde{\omega}}) = \frac{1}{2}\frac{\sum_{i=1}^{N} 2k_a M A_i \ell_i/r_i}{\sum_{i=1}^{N} A_i D_i/\ell_i} \tag{55}$$

Equations 51, 52, and 55 combine to yield

$$\frac{p_t(s/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})} = \frac{2D_e\delta_i}{L^2\alpha^2\psi_i \sum_{i=1}^{N}\beta_i} \tag{56}$$

$$\frac{F(s/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})} = \frac{D_e\phi_1^2}{L^2\epsilon_a}\rho(\tilde{\tilde{\omega}}) \tag{57}$$

where $\phi_1 = [2L^2 k_a M\epsilon_a/r_a D_e]^{1/2}$, and the rest of the notation is as in the previous paper (Bhatia, 1986). Equations 56 and 57 provide the required intensity functions for pore volume diffusion.

Asymptotic analysis

Substitution of Eqs. 54, 56, and 57 into Eqs. 39 and 40 results in

$$\begin{aligned}
\alpha^2 \frac{\partial P(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})}{\partial \tau} = {} & -\alpha^2 \frac{\phi_1^2}{\epsilon_a}\rho(\tilde{\tilde{\omega}}) \\
& \cdot \left[1 - \frac{C_s(\tilde{\eta}, \tau)}{M}\right] P(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\
& + \alpha^2\left(\frac{L^2 k_d}{D_e}\right) P_s(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\
& - \frac{2}{\beta_\tau}\left[\sum_{i=1}^{N}\delta_i/\psi_i\right] P(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\
& + 2\sum_{i=1}^{N}\left\langle \frac{(\delta_i/\psi_i)}{\beta'_\tau} P(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\rangle_{,i} \\
& + 2\sum_{i=1}^{N}\sum_{m=1}^{2}\frac{\alpha^m\delta_i\psi_i^{m-1}}{m!}(\tilde{U}_{i'}\nabla)^m \\
& \cdot \left\langle \frac{P(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')}{\beta'_\tau}\right\rangle_{,i} + 0(\alpha^3)
\end{aligned} \tag{58}$$

and

$$\begin{aligned}
\alpha^2\frac{\partial(\epsilon C)}{\partial\tau} = {} & -\alpha^2\frac{\phi_1}{\epsilon_a}\left(1 - \frac{C_s}{M}\right)\{\rho P\} \\
& + \alpha^2\left(\frac{L^2 k_d}{D_e}\right)\{P_s\} \\
& - 2\alpha N\nabla \cdot \left\{\frac{\delta_1}{\beta_\tau}\tilde{U}_1 P\right\} + N\alpha^2\nabla\nabla : \\
& \cdot \left\{\frac{\delta_1\epsilon_1}{\beta_\tau}\tilde{U}_1\tilde{U}_1 P\right\} + 0(\alpha^3)
\end{aligned} \tag{59}$$

These equations are quite similar to Eqs. (47) and (48) of the prior work, except for the presence of the factor $[1 - (C_s/M)]$ in the first term on the righthand side and the desorption term in the new equations. The asymptotic analysis is therefore identical, yielding the same expressions for y_1 in terms of the state-independent y_0, with the new terms not affecting these results. Upon substituting the expressions for y_0 and y_1 in terms of P_0 into Eq. 59 and balancing terms to order α^2, one obtains after some algebra the final form, in dimensional time and space,

$$\begin{aligned}
\frac{\partial(\epsilon_0 C_0)}{\partial t} = {} & \nabla_x \cdot \frac{\epsilon_0}{\gamma_1}(\bar{D} - D_c)\nabla_x C_0 \\
& - S_0[k_a C_0(M - C_s) - k_d C_s]
\end{aligned} \tag{60}$$

where

$$\bar{D} = \frac{\langle A1D(r)\rangle^0}{\langle A1\rangle^0} \tag{61}$$

$$D_c = \frac{2}{\langle A1 \rangle^0} \cdot \left\langle \frac{A_1^2 D_1^2}{\left[1 + (A_1 D_1/\ell_1)\left\langle \left[\sum_{i=1}^{N} A_i D_i/\ell_i\right]^{-1} \right\rangle_{,1}^{0}\right]\left[\sum_{i=1}^{N} A_i D_i/\ell_i\right]} \right\rangle^0 \tag{62}$$

Equations 61 and 62 give the same expressions for $\overline{D}$ and D_c, respectively, as in Bhatia (1986). Thus, the effective pore volume diffusivity is the same as that predicted previously. However, this new analysis was required because the intensity functions are no longer homogeneous when adsorption-desorption phenomena proceed at finite rates. The previous analysis for rapid adsorption-desorption considered only homogeneous intensity functions and is no longer directly applicable to the new situation considered here.

Discussion

Effective surface diffusivity

For pore volume diffusion the correlation term D_c (Eqs. 60 and 62), and its effect on the tortuosity, has been discussed at length in the prior work. We therefore confine our attention here to the effective surface diffusivity defined in Eqs. 33 to 35 and which is a new result obtained in this work. However, we do note from the previous results that the tortuosity for pore volume diffusion is a process parameter that depends upon temperature, pressure, and the diffusing species, and is not a porous medium property alone. For surface diffusion we write the effective surface diffusivity as

$$D_{se} = \frac{D_s}{\gamma_s} \tag{63}$$

and, upon using Eqs. 33 and 35, obtain

$$\gamma_s = \frac{3}{1 - D_{sc}/D_s} \tag{64}$$

where (D_{sc}/D_s) is given by Eq. 34. Since Eq. 34 shows that the factor (D_{sc}/D_s) depends only on the pore structure, it is clear from Eq. 64 that the tortuosity for surface diffusion γ_s is a porous medium property alone and is independent of process conditions, unlike the tortuosity for pore volume diffusion. It may be observed here that Eq. 63 for the effective diffusivity is slightly different from Eq. 3 used by Schneider and Smith (1968) and Komiyama and Smith (1974), who preferred to write the surface concentration in terms of amount adsorbed per unit pore volume and therefore required the additional factor of local porosity, ϵ. Because the concentration measured per unit surface area is a more natural variable for the adsorbed species and because of the possibility of pore structure, and hence surface area, gradients, Eqs. 33 to 36 would seem to be a more appropriate representation of the surface diffusion problem.

To determine the effect of pore structure on the tortuosity γ_s, and hence the effective surface diffusivity, calculations were performed for a pore structure in which pore sizes at an intersection were uncorrelated. As in the prior calculations for pore volume diffusion (Bhatia, 1986) a log-normal pore volume distribution was chosen and the pore length was assumed uniform; for on compressing particles of uniform size, the pore lengths should be roughly the same as the diameter of the grains. Thus, the variation in pore lengths should be small and the averaging operations in Eq. 34 will be affected only by the pore radius distribution. For a log-normal pore volume distribution, the pore radius probability density is given by

$$p(r) = \frac{a}{r^3} \exp\left[-(\ln r/\mu)^2/\sigma^2\right], \qquad 0 < r < \infty \tag{65}$$

where $a = \mu^2 e^{-2\sigma^2}/(2\pi\sigma^2)^{1/2}$. Use of this distribution for the pore radius gives the required probability density for the calculation of the averages in Eq. 34 as

$$\left[\int\int p_0(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\, d\tilde{\tilde{\theta}} \prod_{i=1}^{N} d\psi_i\right] \prod_{i=1}^{N} dr_i^* = \prod_{i=1}^{N} p(r_i)\, dr_i \tag{66}$$

since ℓ_i is considered to be uniform. It is apparent from Eqs. 34, 64, and 66 that γ_s is a function of the standard deviation σ and is independent of the mean pore radius μ. Figure 1 shows the variation in tortuosity γ_s with σ for various values of the parameter N when the required integrals are evaluated in Eq. 34. It is seen that γ_s increases with increase in σ but much more slowly than the tortuosity for pore volume diffusion. Thus for $N = 4$, γ_s increases from 5 to 7 as σ increases from 0 to 1. For pore volume diffusion the corresponding increase in tortuosity was from 5 to 37 (Bhatia, 1986). This lower sensitivity to σ of γ_s is because the pore flux is now proportional to r instead of r^2 for pore volume diffusion. In addition, the surface diffusivity D_s is independent of r, while the pore diffusivity D depends on r through the Knudsen diffusivity. This dependency of D on r further increases the effect of σ on the tortuosity for pore volume diffusion.

In general, as observed in the prior work, $N = 4$ appears to be a reasonable value and the surface tortuosity is expected to lie in the range of 5 to 7, depending upon σ. It may be observed that for $\sigma = 0$, Eqs. 33, 34, and 64 yield

$$\gamma_s = \frac{3(N+1)}{(N-1)} \tag{67}$$

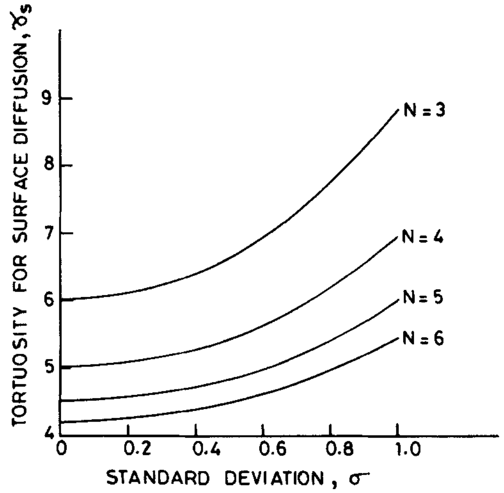

Figure 1. Effect of standard deviation on tortuosity for surface diffusion, at various values of *N*.

which is the same as that obtained for pore volume diffusion (Bhatia, 1985, 1986). Thus, the two tortuosities are the same only for a uniform-size network.

It should be emphasized that the tortuosity factors calculated here and previously are for a random network as pictured in the prior paper. At the other extreme, one may instead consider a more "symmetric" cross-linked network, also pictured in the prior paper. For this case, it may be seen that the effects of opposing pore segments cancel and the term containing P_{s1} in Eq. A2 does not contribute. The resulting surface tortuosity then turns out to be exactly 3, independent of the pore size distribution, as does the tortuosity for pore volume diffusion. The values of the tortuosities obtained for our random network and the value of 3 for the cross-linked structure may therefore be viewed as upper and lower bounds for actual pore structures. It does seem from the previous comparisons with experimental data for pore volume diffusion that the random network gives tortuosities close to the measured values and is the more realistic structure. However, for surface diffusion the same comparisons cannot be made because γ_s cannot be experimentally estimated since D_s cannot be accurately predicted, unlike the pore diffusivity $D(r)$. Experimental confirmation of the new theory for surface diffusion can therefore best be made by studying the effect of pore size distribution on D_{se}. Such studies have not yet been reported.

Concentration-dependent surface diffusivities

The theory for surface diffusion in pore networks proposed here assumes low surface coverages for which the intrinsic surface diffusivity approaches a constant limiting value. At larger surface concentrations D_s becomes a function of C_s and some extension of the theory is necessary. However, the modification is easily done by recognizing that p_t, p_d, and p_n are no longer homogeneous since D_s is a function of C_s and C_s depends upon time. However, by recognizing, as in Eq. B8, that the process time is much larger than the time elapsed between individual steps, the same simplifications may be used as in the development here for pore volume diffusion to show that Eqs. 32 to 36 hold for this case as well, but with D_s being a function of the adsorbed concentration C_s. The demonstration is just a matter of added algebra and has therefore been avoided in this, already quite algebraically involved, presentation.

Longer range correlations

While the treatment of this and the previous paper considers the (short-range) correlations between successive pores traversed, the significance of longer range correlations has been left unexamined. Such longer range correlations may arise if more than one step in the path of a diffusing molecule is repeated. To demonstrate how such longer range effects rapidly vanish it is necessary to consider only the probability of repeating two successive steps, which is $1/N^2$ when all pores are considered to be of the same size. On the other hand the probability of repeating a single step is $1/N$. For $N = 4$ the probability of repeating two successive steps is therefore 0.06 while the probability of repeating a single step is 0.25. Thus, we see that with increase in the number of steps to be repeated the probability of doing so decreases rapidly. Thus, longer range correlations vanish rapidly and the short-range effect considered here is the dominant one.

Appendix A: Derivation of the Averaged Surface Transport Equation

The simplification of Eqs. 30 and 31 is facilitated by recognizing that α, being small, may profitably be used as a perturbation parameter. Expanding P_s and C_s in terms of powers of α, as in Eq. 12, and substituting into Eq. 31 yields the subproblems

$$\nabla \cdot \left\{ \frac{\tilde{U}_1 \Gamma_1}{\lambda_\tau} p_{s0} \right\}^0 = 0 \tag{A1}$$

$$\begin{aligned} \frac{\partial (S_0 C_{s0})}{\partial \tau} = & - \phi_2^2 \{P_{so}\}^0 \\ & - 2N \nabla \cdot \left\{ \frac{\tilde{U}_1 \Gamma_1}{\lambda_\tau} P_{s1} \right\}^0 - 2N \nabla \cdot \left\{ \frac{\tilde{U}_1 \Gamma_1}{\lambda_\tau} P_{s0} \right\}^1 \\ & + N \nabla \nabla : \left\{ \frac{\Gamma_1 \psi_1}{\lambda_\tau} \tilde{U}_1 \tilde{U}_1 P_{so} \right\}^0 \\ & + \left(\frac{k_a L^2}{D_e} \right) S_0 C_0 (M - C_{s0}) \end{aligned} \tag{A2}$$

upon equating like powers of α. In Eqs. A1 and A2 the volumetric averages have been expanded as

$$\{J\} = \{J_0\}^0 + \alpha[\{J_0\}^1 + \{J_1\}^0] + 0(\alpha^2) \tag{A3}$$

where

$$\{J_m\}^0 = p_{i0}(\tilde{\eta}) \int\int J_m(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) p_0(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\, d\tilde{\tilde{\omega}}\, d\tilde{\tilde{\theta}} \qquad m = 0, 1, 2, \ldots \tag{A4}$$

$$\begin{aligned} \{J_0\}^1 = \int\int J_0(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) [& p_{i1}(\tilde{\eta}) p_0(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\ & + p_{i0}(\tilde{\eta}) p_1(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})]\, d\tilde{\tilde{\omega}}\, d\tilde{\tilde{\theta}} \end{aligned} \tag{A5}$$

It is Eq. A2 that we seek, but before it becomes usable P_{s0} must be removed from the averages and expressed in terms of C_{s0}. To this end a similar expansion in Eq. 30 yields

$$\frac{1}{\lambda_\tau} \left[\sum_{i=1}^{N} \frac{\Gamma_i}{\psi_i} \right] P_{s0}(\tilde{\eta}, \tau / \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) = \sum_{i=1}^{N} \left\langle \frac{\Gamma_i}{\psi_i \lambda'_\tau} P_{s0}(\tilde{\eta}, \tau / \tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}') \right\rangle_{,i}^{0} \tag{A6}$$

$$\begin{aligned} \sum_{i=1}^{N} \Gamma_i (\tilde{U}_i \cdot \nabla) \left\langle \frac{P_{s0}(\tilde{\eta}, \tau / \tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')}{\lambda'_\tau} \right\rangle_{,i}^{0} & \\ = \frac{1}{\lambda_\tau} \left[\sum_{i=1}^{N} \frac{\Gamma_i}{\psi_i} \right] & P_{s1}(\tilde{\eta}, \tau / \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}}) \\ - \sum_{i=1}^{N} & \left\langle \frac{\Gamma_i}{\psi_i \lambda'_\tau} P_{s1}(\tilde{\eta}, \tau / \tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}') \right\rangle_{,i}^{0} \\ - \sum_{i=1}^{N} & \left\langle \frac{\Gamma_i}{\psi_i \lambda'_\tau} P_{s0}(\tilde{\eta}, \tau / \tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}') \right\rangle_{,i}^{1} \end{aligned} \tag{A7}$$

which must be manipulated to express P_{s0} and P_{s1} in terms of C_{s0}. In the above equations we have expressed the expansion of the averages as

$$\langle J \rangle = \langle J_0 \rangle^0 + \alpha[\langle J_0 \rangle^1 + \langle J_1 \rangle^0] + 0(\alpha^2) \tag{A8}$$

where

$$\langle J_m\rangle^n = \int\int J_m(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})p_n(\tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})\, d\tilde{\tilde{\omega}}\, d\tilde{\tilde{\tilde{\theta}}} \qquad m, n = 0, 1, 2, \ldots \qquad \text{(A9)}$$

Equations A6 and A7 are quite similar to Eqs. 56 and 57 of the prior work (Bhatia, 1986) and the same solutions hold. Thus, one finds tht the quantity y_0 defined by

$$y_0 = \frac{P_{S0}(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})}{\lambda_\tau} \qquad \text{(A10)}$$

is state independent (i.e., independent of $\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}$) and is a function only of $\tilde{\eta}$ and τ. The solution of Eq. A7 gives

$$y_1 = f_0(\tilde{\eta}, \tau) + \sum_{i=1}^{N} \frac{\Gamma_i(\tilde{U}_i \cdot \nabla y_0)}{\left[1 + (\Gamma_i/\psi_i)\left\langle\left[\sum_{j=1}^{N} \Gamma_j/\psi_j\right]^{-1}\right\rangle_{,i}^{0}\right]\left[\sum_{j=1}^{N} \Gamma_j/\psi_j\right]} \qquad \text{(A11)}$$

where

$$y_1(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) = \frac{P_{S1}(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})}{\lambda_\tau} \qquad \text{(A12)}$$

and $f_0(\tilde{\eta}, \tau)$ is a state-independent part. $y_0(\tilde{\eta}, \tau)$ may be related to C_{s0} through Eqs. 14, 18, and 19 to yield

$$y_0 = \pi r_a \bar{\ell} C_{s0} \qquad \text{(A13)}$$

Thus, Eqs. A10 to A13 relate P_{s0} and P_{s1} to C_{s0}. These may now be substituted along with Eqs. 4, 5, 9, 10, and 19 into Eq. A1 to show that it is always satisfied. Substitution of these equations along with Eq. 11 into Eq. A2, and manipulations similar to those in the prior article yield the final result in Eqs. 32 to 34.

Appendix B: Derivation of the General Pore Volume Transport Equations

As a starting point of the analysis we write, as in the previous work,

$$Q_j(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) = \sum_{i=1}^{N} \int_0^t \cdot \langle Q_{j-1}(\tilde{\eta} + \alpha\psi_i\tilde{U}_i, \tau/\tilde{\tilde{\omega}}', \tilde{\tilde{\tilde{\theta}}}')p_i(t - \tau, \tilde{\omega}_i/\tilde{\tilde{\omega}}')\rangle_{,i}\, d\tau \qquad \text{(B1)}$$

$$P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) = \sum_{j=0}^{\infty} \int_0^t Q_j(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})p_n(t, \tau/\tilde{\tilde{\omega}})\, d\tau \qquad \text{(B2)}$$

where Q_j and P have the same definitions as before. In Eq. B2 we now substitute the expression for p_n in Eq. 38, and take Laplace transforms to obtain

$$sP(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) = \sum_{j=0}^{\infty} Q_j(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) - \sum_{j=0}^{\infty}\sum_{i=1}^{N} Q_j(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})p_i(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}) - \sum_{j=0}^{\infty} F(s/\tilde{\tilde{\omega}})\mathcal{L}[A(\tilde{\eta}, t)Q_j(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})] \qquad \text{(B3)}$$

Recognizing that $p_n(t, \tau/\tilde{\tilde{\omega}})$ is essentially homogeneous, i.e., it is a function of $(t - \tau)$, Eq. B2 yields

$$\sum_{j=0}^{\infty} Q_j(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) = \frac{P(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})}{\cdot\, p_n(s/\tilde{\tilde{\omega}})} \qquad \text{(B4)}$$

and further

$$\mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})A(\tilde{\eta}, t)] = \sum_{j=0}^{\infty} \int_0^\infty e^{-st}A(\tilde{\eta}, t) \cdot \left[\int_0^t Q_j(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})p_n(t - \tau/\tilde{\tilde{\omega}})\, d\tau\right] dt \qquad \text{(B5)}$$

Interchanging the integrals in the righthand side of Eq. B5:

$$\mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})\mathrm{A}(\tilde{\eta}, t)] = \sum_{j=0}^{\infty} \int_0^\infty \cdot \left[\int_\tau^\infty e^{-st}A(\tilde{\eta}, t)p_n(t - \tau/\tilde{\tilde{\omega}})\, dt\right] Q_j(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})\, d\tau \qquad \text{(B6)}$$

Making the substitution $t = \tau + y$ in Eq. B6:

$$\mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})A(\tilde{\eta}, t)] = \sum_{j=0}^{\infty} \int_0^\infty e^{-s\tau}Q_j(\tilde{\eta}, \tau/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) \cdot \left[\int_0^\infty e^{-sy}A(\tilde{\eta}, \tau + y)p_n(y/\tilde{\tilde{\omega}})\, dt\right] d\tau \qquad \text{(B7)}$$

In the inner integral in Eq. B7 it may be recognized that the arrival time τ is much larger than the time elapsed y and

$$A(\tau + y) = A(\tau) + 0(\alpha^2\dot{A}) \qquad \text{(B8)}$$

since the arrival time τ has the scale (L^2/D_e) while the time elapsed has the scale $(\bar{\ell}^2/\bar{D})$. Thus, Eq. B7 simplifies to

$$\mathcal{L}[Q_j(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})A(\tilde{\eta}, t)] = \frac{\mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})A(\tilde{\eta}, t)]}{p_n(s/\tilde{\tilde{\omega}})} + 0(\alpha^2\dot{A}P) \qquad \text{(B9)}$$

A molecule may arrive at an intersection after zero steps either as a result of initial placement or by desorption from the local pore surface. Thus,

$$Q_0(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) = P(\tilde{\eta}, 0)\delta(t) + k_dP_s(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) \qquad \text{(B10)}$$

Equations B1, B3, B4, B 9, and B10 combine to yield

$$sP(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) - P(\tilde{\eta},0) = -\left[\sum_{i=1}^{N} \frac{P_i(s, \tilde{\omega}_i/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})}\right]P(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) - \frac{F(s/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})}\mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}})A(\tilde{\eta}, t)] + k_dP_s(\tilde{\eta},s/\tilde{\tilde{\omega}}, \tilde{\tilde{\tilde{\theta}}}) + \sum_{i=1}^{N} \cdot \left\langle\frac{p_i(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')} P(\tilde{\eta} + \alpha\psi_i\tilde{U}_i, s/\tilde{\tilde{\omega}}',\tilde{\tilde{\tilde{\theta}}}')\right\rangle_{,i} + 0\left(\frac{\alpha^2\dot{A}PF}{p_n}\right) \qquad \text{(B11)}$$

Defining the local concentration

$$C(\tilde{\eta}, t) = \{P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\}/\epsilon \tag{B12}$$

where the volumetric average in the braces is given as in Eq. 19, and multiplying Eq. B11 by $p_i(\alpha, \tilde{\eta})$ and integrating yields, as in the prior work,

$$\begin{aligned} s(\epsilon C)(\tilde{\eta}, s) - (\epsilon C)(\tilde{\eta}, 0) = {} & -\left\{\frac{F(s/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})}\mathcal{L}[P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})A(\tilde{\eta}, t)]\right\} \\ & + k_d\{P_s\} - \sum_{i=1}^{N}\left\{\frac{P_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}})}{p_n(s/\tilde{\tilde{\omega}})}P(\tilde{\eta}, s/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})\right\} \\ & + \sum_{i=1}^{N}\left\{\frac{p_t(s, \tilde{\omega}_i/\tilde{\tilde{\omega}}')}{p_n(s/\tilde{\tilde{\omega}}')}P(\tilde{\eta} + \alpha\psi_i U_i, s/\tilde{\tilde{\omega}}', \tilde{\tilde{\theta}}')\right\} \\ & + 0\left(\frac{\alpha^2 \dot{A} P F}{p_n}\right) \end{aligned} \tag{B13}$$

We may now, as before, exploit the smallness of α and expand Eqs. B11 and B13 to obtain Eqs. 39 and 40.

Notation

a = normalization factor
A = pore cross-sectional area
A^* = dimensionless cross-sectional area, r^2/r_a^2
$A(\tilde{\eta}, \tau)$ = defined in Eqs. 37 and 54
$\dot{A}$ = $dA/d\tau$
b = perimeter across which diffusion occurs
c_i = concentration in ith pore
C = pore concentration
C_s = surface concentration
$D(r)$ = diffusion coefficient in pore of radius r
$\bar{D}$ = volume-averaged pore diffusivity
D_e = effective diffusivity
D^* = dimensionless pore diffusivity D/D_e
D_s = surface diffusivity
D_s^* = D_s/D_e
D_{se} = effective surface diffusivity
f_0 = state-independent part of y_1
$F(s/\tilde{\tilde{\omega}})$ = defined in Eqs. 37 and 55
$g(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ = pore density function, Eq. 9
$h(\tilde{\eta}, \tilde{\tilde{\omega}})$ = defined in Eq. 10
k_a = adsorption rate constant
k_d = desorption rate constant
k_i = $2k_a(M - C_s)/r_i$
k_s = surface reaction rate constant
ℓ = pore length
$\bar{\ell}$ = mean pore length
$\mathcal{L}$ = Laplace transform
L = macroscopic length scale
M = maximum surface concentration
n_i = surface concentration in ith pore
N = number of pores meeting at an intersection
$p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ = probability density for size parameters and orientations for pores meeting at an intersection
$p(\alpha, \tilde{\eta}, \tilde{\tilde{\omega}}_{,i}, \tilde{\tilde{\theta}}_{,i}/\tilde{\omega}_i, \tilde{\theta}_i)$ = conditional probability density, Eq. 6
$p(r)$ = probability density for pore radius
$p_i(\alpha, \tilde{\eta})$ = local density of pore intersections at $\tilde{\eta}$
$p_d(\tilde{\eta}, \tau, y/\tilde{\tilde{\omega}})$ = rate of disappearance after an elapsed time y, having arrived at time τ
$p_t(t, \tilde{\omega}_i/\tilde{\tilde{\omega}})$ = rate of transition by ith pore after time t
$p_n(t/\tilde{\tilde{\omega}})$ = probability of finding molecule at an intersection after time t
$P(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ = probability density of finding particle at an intersection at $\tilde{\eta}$, at time t
$P_s(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ = probability density of finding particle on the surface near an intersection at $\tilde{\eta}$, at time t
q = pore perimeter, $2\pi r$
q^* = r/r_a
$Q_j(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ = arrival rate at an intersection at $\tilde{\eta}$, with pore parameters $\tilde{\tilde{\omega}}$ and pore orientations $\tilde{\tilde{\theta}}$, after j steps
$Q_{sj}(\tilde{\eta}, t/\tilde{\tilde{\omega}}, \tilde{\tilde{\theta}})$ = arrival rate at the surface near an intersection with pore parameters $\tilde{\tilde{\omega}}$, and pore orientations $\tilde{\tilde{\theta}}$, after j steps
r = pore radius
r^* = r/r_a
r_a = pore radius used for scaling
s = Laplace transform variable
S = surface area per unit volume
t = time
$\tilde{U}$ = pore orientation vector
$\tilde{X}$ = position vector
y = time elapsed
y_0 = defined in Eq. A10
y_1 = defined in Eq. A12
z = axial coordinate along pore

Greek letters

$\alpha = \bar{\ell}/L$
$\beta = r^{*2}$
$\beta_\tau = \Sigma_{i=1}^N \beta_i$
$\delta_i = A_i^* D_i^*$
ϵ = local porosity
ϵ_a = porosity used for scaling
γ = tortuosity for pore volume diffusion
γ_s = tortuosity for surface diffusion
$\gamma_1 = 3$
$\Gamma_i = D_s^* q^*$
$\lambda = q_i \psi_i$
$\lambda_\tau = \Sigma_{i=1}^N \lambda_i$
μ = mean pore radius
$\tilde{\eta}$ = dimensionless location vector, $\tilde{X}/L$
$\tilde{\omega}$ = pore parameter set
$\tilde{\tilde{\omega}}$ = parameters for all the pores at an intersection
$\phi_1 = [2L^2 k_a M \epsilon_a / r_a D_e]^{1/2}$
$\phi_2 = [L^2(k_d + k_s)/D_e]^{1/2}$
$\rho(\tilde{\tilde{\omega}}) = [\Sigma_{i=1}^N r_i^* \psi_i]/\Sigma_{i=1}^N A_i^* \psi_i$
σ = standard deviation
$\psi = \ell/\bar{\ell}$
$\tilde{\theta}$ = pore orientation
$\tilde{\tilde{\theta}}$ = orientations for all the pores at an intersection
τ = arrival time, dimensionless time $(D_e t/L^2)$

Subscripts

0,1 = order of term
i = ith pore at an intersection
$,i$ = all pores but the ith

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