JOURNAL OF CATALYSIS 93, 192–196 (1985)

Directional Autocorrelation and the Diffusional Tortuosity of Capillary Porous Media

The estimation of effective diffusivities and flux rates in porous materials such as catalyst particles and coal chars is a problem of fundamental importance in chemical reaction engineering, and much attention has been devoted to this issue. Several models are now available and most of them favor the visualization of the porous medium as a random network of capillaries requiring the use of a tortuosity factor to account for the effects of capillary orientation. Thus, Johnson and Stewart (*1*) solve for the flux in a single capillary of arbitrary radius and having the same length as the pellet, and integrate the result over the pore size distribution. A tortuosity factor is then introduced. Satterfield (*2*) instead proposes a pore diffusivity based on an average radius, and this is then divided by the tortuosity. Feng and Stewart (*3*), and more recently Wang and Smith (*4*), define a pore volume averaged diffusivity

$$\langle D\rangle = \frac{1}{\varepsilon}\int_0^\infty D(r)f(r)\,dr, \tag{1}$$

where $f(r)\,dr$ is the void fraction of pores in the radius interval $[r, r + dr]$. The effective diffusivity is then obtained from

$$D_e = \frac{\varepsilon\langle D\rangle}{\tau}, \tag{2}$$

where τ is the tortuosity factor. Another model (*5*) called the dusty gas model utilizes even more parameters and is less popular.

Among the theoretical calculations of the tortuosity factor the most widely accepted (*2, 6–8*) is that of Stewart and co-workers (*1, 3*) which predicts a value of $\tau = 3$, assuming pores with random orientations. Experimental evidence, however, appears to indicate values of τ larger than 3, usually by a significant factor. In addition, the values of τ estimated from diffusion measurements generally depend on which of the aforementioned models is used to fit the data, even for the same experiment (*4, 9*). Values of τ of about 4.4 have been reported by Horak and Schneider (*9*), and ranging from 3 to 11 by Satterfield and Cadle (*10*), using the Johnson and Stewart (*1*) approach. Most recently Wang and Smith (*4*) tested several methods and found consistent values only when a volume averaged diffusivity as defined by Eq. (1) was used. In their experiments τ varied only between 6 and 8 for two catalysts under varying conditions of temperature. Wang and Smith (*4*) also reported unreasonably low and varying values of τ when the diffusivity was instead based on an averaged radius ($2\varepsilon/S$). Similar results were also observed by Horak and Schneider (*9*). In other work Amberg and Echigoya (*11*) reported values of τ also in the range of 6 to 8 from experiments which were fortuitously in the bulk diffusion regime. Thus, their results for τ are not dependent on an estimation of a mean pore diffusivity. More recently McGreavy and Siddiqui (*12*) also find values of τ in the same range.

One of the key reasons used (*2, 13, 14*) to justify values of τ larger than the expected value of 3 is the possibility of pore constrictions which have been shown (*13, 14*) to have an adverse effect on the flux rate in individual pores. The extent of this effect depends largely on the relative size and volume of the constriction. In con-

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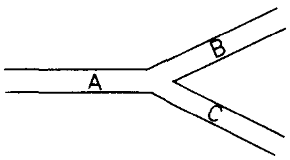

FIG. 1. Intersection of randomly oriented capillaries.

nected pore structures with a substantial pore volume in the Knudsen regime, as occurs in most catalyst particles, the extent of this effect may, however, be less than that predicted; for during mercury porosimetry regions between constrictions are penetrated only at a pressure corresponding to the smaller size of the constriction and therefore ascribed a smaller than actual radius. Thus, upon taking the pore volume average diffusivity, as in Eq. (1), the lowering of the effective diffusivity may be essentially accounted for. This suggests the possibility that other factors may also play a role in the underlying reasons for the high experimental tortuosity estimates, besides simple deviation from the ideal of cylindrical capillaries. This observation is also supported by the results of Patel and Butt (*15*) who introduced various converging–diverging capillary shapes into their pore structure models but still report fitted tortuosities of about 6 and larger.

It is the purpose of this note to bring attention to the presence of a hitherto unrecognized autocorrelation effect during diffusion in capillary structures, and which can account for values of τ much larger than otherwise expected, under conditions of bulk as well as Knudsen diffusion. This autocorrelation effect is most readily evidenced if we admit that molecular transport in a capillary network must comprise of a sequence of individual steps each of which corresponds to the successful navigation of a *complete* pore segment. Since the second-order differential equation of diffusion (essentially a continuum approximation) is used to model the overall process, the individual pore lengths are considered negligible in comparison to the pellet size; and in the context of the random walk basis of the diffusion equation, successive pore segments become the individual steps of the "random walk." If successive steps are truly random, then indeed

$$\tau^{-1} = \langle \cos^2 \vartheta \rangle = \frac{1}{3}, \quad (3)$$

where ϑ is the angle between the pore axis and a reference laboratory axis. A closer examination, however, reveals that successive steps are not necessarily random, for shortly after traversing a complete pore segment and arriving at an intersection the diffusing molecule can, as a result of collisions, reverse direction. In such a case the next *full* pore segment effected may be *precisely* the last one, and this *no longer* has a random direction. Thus, there is a correlation among successive steps and some account must be made of this effect in the above calculation of the tortuosity factor.

As an illustration consider the events occurring at a pore junction such as that in Fig. 1, which depicts the intersection of three capillaries all of which are assumed to be oriented randomly, and in directions uncorrelated with each other. A molecule upon arriving at this junction after having diffused through, say, capillary A may initially have a velocity vector that has a higher likelihood of carrying it into pores B or C. However, since the distance traveled between collisions (either with the pore walls or with other molecules) is small compared to the length of the individual pore segments, as is usually the case (for this is the fundamental assumption behind the use of a diffusion equation in individual capillaries when calculating micropore or macropore effectiveness factors (*7, 16, 17*)), the molecule is likely to suffer many collisions and make several excursions back to the junction, and possibly into pore A, before ultimately, in its meanderings, exiting from the end of either pores A, B, or C onto the next intersection, and so on. The point of ultimate exit is therefore largely uncorrelated with the velocity vector on initially arriving at the junction of A, B, and C; and in the simplest case, if all three pores have the same radius and length, the probability is $\frac{1}{3}$ that the molecule exits from the end of capillary A, back to the intersection it had previously visited. Thus, upon successfully completing a given step, the probability is only $\frac{2}{3}$ that the next step is random. These probabilities will of course change if the number of pores meeting at an intersection is different from three as considered in this illustration.

A somewhat analogous situation, first described by Bardeen and Herring (*18*), exists in the migration of atoms in crystals, wherein a tracer atom upon making a jump in a lattice creates a vacancy at the site just left. It may therefore make its next jump back to the previous site instead of making a jump according to an isotropic set of probabilities. Various methods have been employed to calculate the correlation factor by which the diffusion coefficient is modified for the different lattice types, and many of these are reviewed in Manning (*19*) and Le Claire (*20, 21*). In general the problem is reduced to one of calculating the factor

$$F = \frac{1 + \langle\cos\vartheta_1\rangle}{1 - \langle\cos\vartheta_1\rangle}, \tag{4}$$

where ϑ_1 is the angle between successive jump directions, and $\langle\cos\vartheta_1\rangle$ the expected value of its cosine. The resulting value of $\langle\cos^2\vartheta\rangle$ is then modified to $F/3$ in calculating the diffusion coefficient. The same corrections carry over identically to our capillary network diffusion problem, and the tortuosity should therefore be modified to

$$\tau = \frac{3}{F}, \tag{5}$$

where F is given as in Eq. (4), with ϑ_1 being treated as the angle between successive pores traversed. If successive steps are truly randomly oriented then

$$\langle\cos\vartheta_1\rangle = \frac{1}{2}\int_0^\pi \cos\vartheta_1 \sin\vartheta_1\, d\vartheta_1$$
$$= 0.$$

Thus, $F = 1$ and $\tau = 3$. This, as shown above, is, however, not the true situation.

It is readily evident that, in general, for capillary networks the value of F will depend on the lengths and diameters, as well as total number, of the pores meeting at a junction. We consider here only the simplest case with all pores of the same length and diameter. Consider first intersections such as that in Fig. 1, but involving N pores, with no correlation among their orientations. The probability is then $1/N$ that the molecule executes a step identical to the previous one, and this event has $\vartheta_1 = 180°$, i.e., $\cos\vartheta_1 = -1$. If the molecule instead leaves by any of the other pores, $\langle\cos\vartheta_1\rangle = 0$ since they are randomly oriented. Thus, taking the overall average, $\langle\cos\vartheta_1\rangle = -1/N$ and

$$\tau = \frac{3(N+1)}{N-1}. \tag{6}$$

Thus, only the $N \rightarrow \infty$, i.e., we have a "thoroughly" interconnected structure, is $\tau = 3$. This, however, is clearly unrealistic and, although N may vary among the junctions in the pore structure, $N = 4$, on the average, is probably the most reasonable choice. This gives $\tau = 5$, a result in much better agreement with the experimental observations discussed previously. For $N = 2$, $\tau = 9$, while for $N = 6$, $\tau = 4.2$. Most experimental results appear to fall between these values. For $N \rightarrow 1$, $\tau \rightarrow \infty$ and molecules everywhere are trapped, as expected, for it may be recognized that this situation corresponds to isolated pores.

One may also consider intersections such as that shown in Fig. 2, in which a continuous pore is intersected by a randomly oriented pore. It is evident that for molecules arriving at the junction from either branch of the continuous pore $\langle\cos\vartheta_1\rangle = 0$, while for molecules arriving via the intersecting

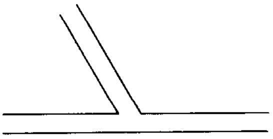

FIG. 2. Intersection of a continuous pore with a randomly oriented capillary.

pore $\langle \cos \vartheta_l \rangle = -\frac{1}{3}$. For pores of uniform length and diameter the probability is 0.5 that a molecule traveling in a pore encounters an intersection in which the capillary ends, and consequently, taking the overall average, $\langle \cos \vartheta_l \rangle = -\frac{1}{6}$, giving $\tau = 4.2$ upon application of Eqs. (4) and (5). Alternatively, if all intersections are of the crosslinked type as in Fig. 3, then it is readily calculated that $\tau = 3$. This situation is, however, a less likely event than those depicted in Figs. 1 and 2, particularly in view of the experimental findings discussed above.

Although we have calculated the above tortuosity factors for uniform size pore systems the full estimation of the effective diffusivity must also involve the correlation among the size parameters, as well as the possible variation in number, of the pores meeting at an intersection; a level of elaboration not readily possible by the use of Eq. (4) alone. The full accounting of these factors will also essentially subsume the effect of pore constrictions since the latter can be effectively viewed as smaller pores intersecting with larger ones. A detailed statistical framework for performing such calculations based on measurable pore volume distribution data is currently being developed in this laboratory and will be reported in a future publication. In this communication we have indicated this very interesting effect and provided a simple method for estimating its approximate magnitude. Finally, we note that this autocorrelation effect is not restricted to capillary networks alone, but is of general consequence for all interconnected structures that may be postulated to model the porous medium. Regardless of the nature of the structure a diffusing molecule is confined by the internal surfaces and, as a result, its path is never truly random, but probabilistically correlated with its past trajectory, because of the possibility of reversing direction.

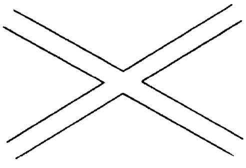

FIG. 3. Intersection in a crosslinked network.

APPENDIX: NOMENCLATURE

$D(r)$	diffusivity in pores of radius r
$\langle D \rangle$	volume averaged pore diffusivity
D_e	effective diffusivity in pellet
ε	porosity
$f(r)$	pore volume distribution
F	correlation factor defined in Eq. (4)
N	number of pores meeting at intersection
r	pore radius
S	surface area per unit volume
τ	tortuosity
ϑ	angle between pore axis and reference axis
ϑ_l	angle between successive steps.

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Received October 20, 1983

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