Knudsen Diffusion in Constricted Pores: Monte Carlo Simulations

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INTRODUCTION

The effective diffusivity describing the rate of gas transport in a porous solid such as a catalysis pellet or adsorbent is typically 1 to 3 orders of magnitude less than the normal diffusion coefficient. This reduced D_e is the result of numerous factors including porosity, pore cross-sectional shape, pore size distribution and direction orientation, degree of interconnectivity, and pore constrictions. The effective diffusivity is usually related to the bulk or Knudsen diffusivity and the porosity with the use of a tortuosity factor:

$$D_e = D_{AB,k}\,\varepsilon/\tau \tag{1}$$

The magnitude of τ cannot be predicted from first principles but is usually found to vary from 1 to 8 when measured experimentally. For bulk diffusion in beds of smooth, uniform spheres, Hoogschagen (1955) found τ to be between 1.4 and 1.6. For Knudsen diffusion in porous media comprised of uniform silica microspheres, Huizenga and Smith (1986) measured tortuosity values of 1.45 to 1.51 when the mean pore radius is defined as twice the ratio of pore volume to surface area. These values serve as a lower bound on τ with most materials of practical interest having higher values.

In many materials, high tortuosity factors are believed to be the result of severe pore constrictions. Several investigators have analyzed the effect of pore constrictions on D_{AB} in the bulk diffusion regime. Petersen (1958) modeled a constricted pore as a series of hyperbolas of revolution around the pore axis. The reduction of D_{AB} in a single pore due to constrictions was obtained via an analytical solution to obtain δ, the convergence factor, as a function of β, the ratio of maximum pore cross-sectional area to minimum cross-sectional area. The convergence factor, δ, is the ratio of the diffusivity in the constricted pore to that in an equivalent uniform cylindrical pore (i.e., $D_c/D_{AB,k}$). A β value of one corresponds to a uniform pore, and thus δ will equal one. As the value of β increases, the pore will become more constricted and δ will decrease. Petersen postulates that for Knudsen transport in a constricted pore, the value of δ would be lower than that for bulk diffusion at the same β value. Michaels (1959) analyzed bulk diffusion in a model pore comprised of capillaries of two diameters connected in series. Findings similar to those of Petersen were obtained at the expense of introducing a second parameter related to the relative lengths of the capillaries. Michaels noted that by failing to account for entrance and exit effects at each capillary intersection, his model would underpredict constriction effects. Currie (1960) modeled a constricted pore with a sinusoidal shape and obtained a δ-β relationship similar to that of Petersen.

Only one investigation appears to have addressed the problem of Knudsen diffusion in constricted pores. Haynes and Brown (1971) use the capillary-in-series model of Michaels to assess the effect of pressure on the constriction factor in both the bulk and Knudsen diffusion regimes. Potential problems associated with the use of the capillary-in-series model (i.e., entrance/exit effects) were not addressed. However, the question of how to define the characteristic pore radius to be used in calculating the Knudsen diffusion coefficient was discussed.

Monte Carlo simulation techniques have found favor for the analysis of Knudsen transport in geometries of nonuniform shape. In general, the motion of an individual molecule is tracked as it randomly migrates through the appropriate pore model. When repeated for a very large number of molecules, an effective diffusivity may be obtained. Early work using Monte Carlo simulations of low pressure gas transport were conducted by Milleron (1959, 1965) to assess the performance of vacuum system components. Abbasi et al. (1983) and Nakano and Evans (1983) have studied both Knudsen and bulk transport in a variety of model porous media. Smith and Huizenga (1984) have simulated Knudsen transport in a random assemblage of spheres pore model. Results generated in these studies reflect the average transport rate through a wide range of pore sizes and shapes which occur in a given porous solid. Therefore, the effect of pore constrictions on the diffusion rate could not be ascertained.

To address the question of Knudsen diffusion in constricted pores, Monte Carlo simulations are performed for molecules migrating through a physically realistic, constricted-pore model. The relationship between the convergence factor, δ, and the ratio of maximum to minimum pore cross-sectional area is determined for various definitions of the mean pore radius.

CALCULATION SCHEME

Due to the general applicability of the Monte Carlo simulation scheme which we use, our only criteria for selecting a pore model is the degree with which it approximates real-world constricted pores. Of course, no single model will actually represent all pores, but we feel that the model of Petersen, which uses a hyperbola of revolution, adequately describes a pore formed by the compaction of spheres. Also, this model elim-

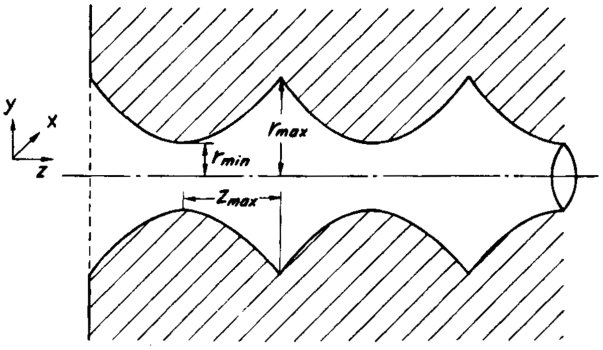

Figure 1. Constricted-pore model and coordinate system.

inates the sudden expansions and contractions of the capillary-in-series models. Following Petersen, the equation describing a unit cell of the constricted pore is:

$$x^2 + y^2 + z^2 = 0.5 \tag{2}$$

The half-length of a pore unit cell, $z_{\max}$ is related to β by:

$$z_{\max} = 0.707\sqrt{\beta^2 - 1} \tag{3}$$

The mean pore radius, defined as twice the pore volume to surface area, is:

$$\bar{r} = \frac{2\,z_{\max} + 4\,z_{\max}^3/3}{[2\,z_{\max}\sqrt{z_{\max}^2 + 0.5} + \ln(z_{\max} + \sqrt{z_{\max}^2 + 0.5}) - \ln(0.5)]} \tag{4}$$

Our model pore and associated coordinate system is illustrated in Figure 1.

Our Monte Carlo simulation of Knudsen diffusion through the pore model follows the technique proposed by Evans et al. (1980). The basis of the calculation is that a concentration (pressure) gradient is imposed across the pore in one direction. The pressure on one side of the pore is taken to be some arbitrary value such that the mean free path of the diffusing gas is much greater than $r_{\max}$ and a vacuum is maintained on the other side. A molecule entering the pore may either be transmitted through the pore or be reflected back to the high-pressure side. In either instance, a large number of molecule-pore wall collisions may occur before the molecule exits the pore. The effective diffusivity in the constricted pore, D_c, may be related to the fraction of molecules, f_t, which will penetrate a certain distance, L, into the pore via a flux balance:

$$D_c = \frac{f_t}{4}\sqrt{\frac{8RT}{\pi MW}}L \tag{5}$$

Thus, the reduction in D_c is directly proportional to the decrease in the fraction of molecules which reach a given distance into the pore. We should note that Eq. 5 is only strictly valid for discrete values of L corresponding to multiples of $2\,z_{\max}$. In other words, the flux of molecules in the pore may only be compared to the inlet flux at locations in the pore with cross-sectional area equal to the pore mouth.

The random migration of molecules in the pore is calculated on a step by step basis. To start, a set of x, y, z coordinates are randomly selected at a distance of $2\,z_{\max}$ outside of the pore mouth. Three direction cosines are randomly selected to define the initial trajectory in space. The molecule's movement is tracked along this trajectory until it intersects the exterior of the solid or the interior wall of the pore. If the molecule has missed the pore mouth, a new starting set of coordinates and new direction cosines are selected. If the molecule intersects the pore wall, the coordinates of the intersection point are calculated. Next, a new set of direction cosines is selected such that the azimuthal angle fits a cosine probability distribution and the angle of rotation fits a uniform distribution between 0 and 2π. The molecule is now tracked until another pore wall collision occurs or the molecule leaves the pore. The movement of each molecule is followed until the molecule exits through either end of the pore and the maximum depth of pore penetration is recorded. Following Evans and coworkers, the fraction of molecules, f_t, which penetrate a distance L into the pore may be plotted vs. $1/L$ to yield a straight line with slope proportional to the appropriate transport coefficient.

For each value of β, the movement of 10,000 molecules was tracked. Simulations conducted using larger and smaller numbers of trials indicate that 10,000 trials represent a satisfactory compromise between the statistical signficance of the results and computation time. Plots of f_t vs. $1/L$ were always linear using this number of trials. This is illustrated in Figure 2, a group of typical plots of f_t vs. $1/L$ for various β values. The number of unit cells connected together to form our model pore was varied between 3 and 20 with no significant effect (i.e., $< 2\%$) on the value of δ for a particular value of β. Figure 2 also demonstrates this independence of the number of pore unit cells. We should note that the values of $1/L$ for runs with different numbers of unit cells were corrected for comparison purposes. Therefore, all results will be reported based on simulations of a pore comprised of five unit cells.

RESULTS AND DISCUSSION

The decrease in the Knudsen diffusivity as a function of β, (maximum cross-sectional area/minimum cross-sectional area) has been calculated for a β range of 1 to 25. The convergence factor, δ, which we define to be the ratio of D_c to D_k in a straight uniform cylinder of some characteristic radius, is plotted in Figure 3 vs. β. As Haynes and Brown (1971) indicate, there are two different ways to define the characteristic pore radius. We can define this pore radius as that which we would obtain using mercury porosimetry or adsorption isotherm analysis. This would correspond to the radius of the smallest con-

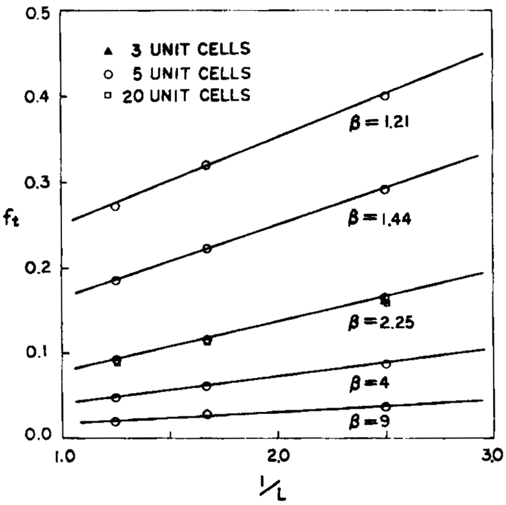

Figure 2. Fraction transmitted vs. reciprocal penetration depth for varying values of β and number of pore unit cells.

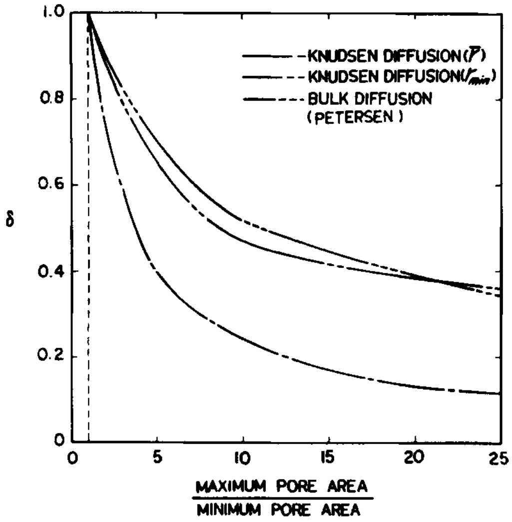

Figure 3. Variation of convergence factor as a function of pore cross-sectional area ratio, diffusion regime, and characteristic pore radius definition.

striction (i.e., r_{min}). The second choice would be to define the radius as twice the ratio of pore volume to pore surface area as both Satterfield (1970) and Huizenga and Smith (1984) have suggested. Only for Knudsen diffusion is this question of the proper characteristic pore radius a concern, since D_{AB} for tubes is independent of r.

Figure 3 contains plots of the convergence factor vs. β for both of the characteristic pore radius definitions, $\bar{r}$ and r_{min}. In addition, the δ-β relationship for ordinary diffusion, as calculated by Petersen, is presented. It is interesting to note that the curves for bulk diffusion and Knudsen diffusion based on r_{min} are very similar. Haynes and Brown report that the convergence factor should be identical for bulk and Knudsen diffusion when the characteristic pore size is r_{min}. The probable reason for this small discrepancy between the findings of Haynes and Brown and these results is to be found in the problems associated with using a Knudsen diffusivity derived for a long capillary in conjunction with a series of short capallaries of different diameters connected in series (i.e., ignoring entrance and exit effects).

When the mean pore radius is defined as $\bar{r}$, the effect of β on the convergence factor is much more pronounced than for r_{min}. This would imply that as the diffusion regime changes from Knudsen to ordinary (i.e., as the pressure is increased), the value of the convergence factor, δ, will decrease. Haynes and Brown cite this fact to suggest that one should use the mean pore radius calculated from porosimetry/isotherm analysis to minimize the effect of pressure on the tortuosity factor. Although a consistency of δ and τ over the range of diffusion regimes is certainly desirable, the available information seems to indicate that this is improbable, regardless of the definition of r. If one uses the minimum pore radius to calculate D_k, the value of δ for both Knudsen and bulk diffusion will be similar. However, for a pore geometry as simple as a random packing of uniform solid spheres, the tortuosity factor, τ, can vary by a factor of two between the two regimes (Huizenga and Smith, 1984). In contrast, if twice the ratio of pore volume to surface area is used, the convergence factor will be a stronger function of β for Knudsen transport than for bulk diffusion.

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NOTATION

D_{AB} = bulk diffusion coefficient
D_c = diffusion coefficient in a constricted pore
D_e = effective diffusivity
D_k = Knudsen diffusion coefficient
f_t = fraction of molecules transmitted a distance L into a pore
L = total pore length
MW = gas molecular weight
r = pore radius
r_{min} = minimum pore radius
r_{max} = maximum pore radius
$\bar{r}$ = mean pore radius
R = gas constant
T = temperature
x,y,z = spatial coordinates

GREEK LETTERS

β = maximum pore cross-sectional area/minimum cross-sectional area
δ = convergence factor, $D_c/D_{AB,k}$
ε = porosity
τ = tortuosity factor

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