Diffusion of Large Molecules in Porous Media

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The results of computer simulations of transport of macromolecules in a disordered porous medium, represented by a network of capillary tubes with random radii, are reported. We develop a method for determining the macroscopic diffusivity D which, in principle, is exact. The effects of both convection and diffusion are taken into account. We find $D/D_\infty \sim \exp(-a/r_m)$, *independent* of the morphology of the medium or the microscopic transport laws, where a is the effective size of the molecules, D_∞ the diffusivity in an unbounded solvent, and r_m the mean effective size of the pores, consistent with experimental data.

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Many processes of current scientific and industrial interest involve the transport of macromolecules in restricted environments such as porous catalysts, Vycor glasses, and membranes.[1,2] A partial list of such processes includes separation or catalytic processes in zeolites or pillared clays, reverse osmosis membrane separation, solvent swelling rubbers, polyelectrolyte gels, enzyme immobilization in porous solids, and size exclusion chromotography. In addition, diffusion measurements in porous materials can serve as an analytical tool in the characterization of the geometry of pore structure over a range of molecular and macroscopic length scales.[3,4] Numerous experimental and theoretical studies have found the transport of macromolecules in solution in a porous medium to be less efficient than unhindered transport in an unbounded solution. This reduced efficiency, which was first pointed out by Renkin and co-workers,[5,6] is generally caused by the macromolecule's being excluded from a fraction of the pore volume, and by the hydrodynamic resistance hindering the transport of molecules through the porous medium.

Several theoretical models of transport in small pores have been developed. For example, hydrodynamic theories of mass transfer have been applied to the transport processes across synthetic and biological membranes,[7-9] diffusion in pores of silica alumina,[10] and in porous glasses.[11] Useful statistical and hydrodynamic theories of macromolecular transport in small pores have been developed by several authors.[12-14] Scaling concepts have also been used to study transport of large molecules in small pores.[15-17] However, these works have major shortcomings which limit their usefulness. Models that are based on statistical hydrodynamic principles[12-14] are applicable to only a single pore, and it is not clear how one can extend these to porous media that are essentially random networks of interconnected pores. For example, many catalyst particles such as zeolites, and many porous glasses that are prepared from phase-separated borosilicate glass by acid leaching of the boron,[4] have such a structure. Transport paths in such networks are highly tortuous, whereas tortuosity is totally absent in a single tube. On the other hand, models that are based on scaling arguments[15-17] can predict only the power-law behavior of the diffusion coefficient, and do not give exact numerical coefficients. Moreover, they are purely phenomenological in the sense that they do not provide any insight about the dependence of the transport coefficients on the morphology of the pore space, e.g., its pore-size distribution. In this Letter, we report the results of computer simulations of transport of large molecules in random networks of interconnected pores. Our results represent the first step towards a comprehensive theory of transport of large molecules in porous media with interconnected pores.

We model the porous medium by a square network in which each bond represents a cylindrical tube of constant length L. The effective radius r of each cylinder is distributed according to a probability density function $f(r)$, which represents the pore-size distribution of the medium; in this paper we use $f(r)=2\alpha^2 r\exp(-\alpha^2 r^2)$, where $r_m=\pi^{1/2}/2\alpha$ is the mean pore size. This distribution mimics many qualitative features of experimentally measured pore-size distributions.[18] It poses no major difficulty to carry out the same simulations with a three-dimensional network, and we shall report the results of such a study in a future paper. We consider the general case in which there is a macroscopic one-dimensional flow through the network. Thus, transport of the molecules is due to the combined effects of convection and molecular diffusion. The flux J of the molecules in each tube is given by $J=VC-D_t\,\partial C/\partial x$, where V is the apparent average flow velocity of the molecules in the tube, D_t is their apparent effective diffusivity, and C is their concentration. If we assume that one has Poiseuille (laminar) flow in each tube, then[13,14]

$$V=\bar{V}[1+2\lambda-4.92\lambda^2+O(\lambda^3)]\,, \tag{1}$$

where $\bar{V}=\Delta PR^2/8\mu L$ is the mean Poiseuille flow velocity in a tube of radius R along which a pressure drop of ΔP has been imposed, μ is the viscosity of the solvent, and $\lambda=a/R$. It has been assumed that the molecules can be represented as hard spheres of radius a or, if they are not spherical, they can be represented with an effective hydrodynamic radius a. The apparent effective diffusivity

D_t is written as $D_t = D_m + D_c$, where[13,14]

$$D_m = D_\infty[1 + \tfrac{9}{8}\lambda\ln\lambda + 0.461\lambda + \tfrac{9}{4}\lambda^2\ln\lambda + O(\lambda^3)] \tag{2}$$

is the apparent effective molecular diffusivity of the molecules in the tube, and

$$D_c = \frac{R^2\bar{V}^2}{48D_\infty}[1 - 1.862\lambda + 9.68\lambda^2 + O(\lambda^3)] \tag{3}$$

is the contribution of convection to D_t. Here $D_\infty = kT/6\pi\mu a$ is the effective diffusivity of the particles in an *unbounded* solvent, where T is the temperature of the system and k is Boltzman's constant. Equations (1)-(3) are asymptotically exact, and the terms in the brackets represent the corrections to the usual expressions for V and D_t due to the finite size of the molecules. The concentration C obeys a one-dimensional convective-diffusion equation,

$$\frac{\partial C}{\partial t} + V\frac{\partial C}{\partial x} = D_t\frac{\partial^2 C}{\partial x^2}. \tag{4}$$

If we introduce the Laplace transform

$$\hat{C}(x,s) = \int_0^\infty C(x,t)e^{-st}dt, \tag{5}$$

then Eq. (4), subject to the boundary conditions $C(x=0,t) = C_1(t)$ and $C(x=L,t) = C_2(t)$, can be easily solved. The solution is given by

$$\hat{C}(x,s) = Ae^{\alpha x} + Be^{\beta x}, \tag{6}$$

where

$$\alpha,\beta = [V \pm (V^2 + 4D_t s)^{1/2}]/2D_t,$$

$$A = [\hat{C}_2 - \hat{C}_1\exp(\beta L)]/[\exp(\alpha L) - \exp(\beta L)],$$

and

$$B = [\hat{C}_1\exp(\alpha L) - \hat{C}_2]/[\exp(\alpha L) - \exp(\beta L)].$$

Assuming that the molecules do not accumulate at the nodes of the network, one must have

$$\sum_{j\in\{i\}} S_{ij}\hat{J}_{ij} = 0, \tag{7}$$

where $\{i\}$ denotes the set of nearest-neighbor sites of the node i, $\hat{J}_{ij}$ the (Laplace transformed) flux leaving node i along tube ij, $\hat{J}_{ij} = V_{ij}\hat{C}_i - D_t\,\partial\hat{C}_i/\partial x$, and S_{ij} is the cross-section area of tube ij. Equation (7) is valid for every interior node of the network. For the inlet nodes we impose the condition $\sum S_{ij}\hat{J}_{ij} = 1$, corresponding to a δ-function input of flux. Equations (6) and (7) yield a set of linear equations for the (Laplace transformed) nodal concentrations $\hat{C}_i$, which can be solved for any value of s. From the solution of this set, one can calculate all quantities of interest such as the macroscopic effective diffusivity D. We have assumed that there is complete mixing of the molecules at the nodes of the network, so that to each node we assign a unique concentration C_i. Aside from this assumption, which is at least a good approximation (a matter which is currently under study), our treatment of the problem in the random network is exact.

Thus, the procedure to calculate the macroscopic effective diffusivity D of the molecules is as follows. We first determine the flow field through the network by applying a fixed pressure drop between the inlet and outlet nodes. If there is Poiseuille flow in each tube, then the fluid flow problem is isomorphic to current flow in a random resistor network. Thus, we have a set of linear equations for the nodal pressures which we solve by Gaussian elimination. After determining the background flow field, we calculate the apparent mean flow velocities, Eq. (1), and the apparent effective diffusivities D_t for all tubes for a given molecular size a and a pore-size distribution $f(r)$. We then use Eqs. (6) and (7), with the boundary conditions mentioned above, to solve for the (Laplace transformed) nodal concentrations $\hat{C}_i$. Unlike the set of linear equations for nodal pressures, the matrix of coefficients for the nodal concentrations is *not* symmetric. We fix s and solve this set by Gaussian eliminations. We then use a numerical inversion to convert the solution to the time domain. From the distribution of nodal concentrations we determine the macroscopic effective diffusivity. We used $L_x \times L_y$ networks where $L_x = 40$, $L_y = 30$, and x is the direction of macroscopic flow. We used periodic boundary conditions in the y direction, and the results represent the average over up to twelve different network realizations. More extensive simulations are, of course, necessary, but we believe that the qualitative features of our results will not change with more extensive simulations.

We carried out two types of computer experiments. In the first one, we fixed the molecular size a and varied the pore sizes. We start with a given molecular size, use $f(r)$ mentioned above (with $\alpha = 1$), and calculate D. We then hold a fixed and multiply all pore radii by a constant factor, thus changing $\lambda = a/r_m$, calculate D, and so on. The results are shown in Fig. 1 where we used the experimentally typical values $a = 400$ nm and $D_\infty \sim 5\times10^{-9}$ cm^2/sec. In the second experiment, we hold $f(r)$ fixed (i.e., pore radii are held fixed) and vary a. The results are shown in Fig. 2. In these two figures the effect of convection has been taken into account. Moreover, in Fig. 2, the effective diffusivities with and without convection are compared and, as expected, convection enhances transport, so that D is larger when convection is present. The first simulations correspond to our using the same macromolecules with different porous media, while the second simulations correspond to our measuring the diffusivities of various molecules in the same porous medium. Both are typical of the past laboratory measurements. As can be seen, as λ increases, D decreases sharply and appears to vanish as $\lambda \to 1$.

Figure 3 represents the dependence of $\ln(D/D_\infty)$ on λ in the limit of a vanishing flow field when a is held fixed

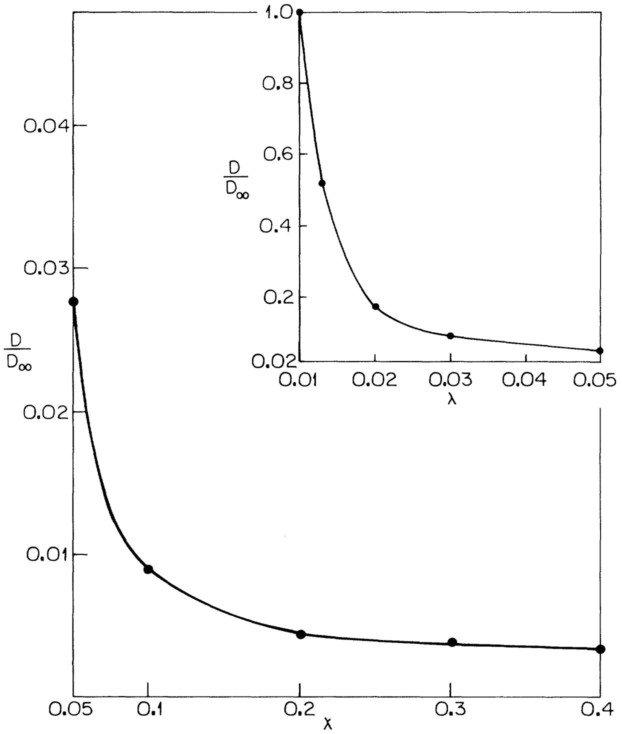

FIG. 1. The dependence of D/D_∞ on the ratio $\lambda = a/r_m$, if the size of the molecule is held fixed and the pore sizes are varied. Here D_∞ is the bulk diffusivity for a molecule in an unbounded solvent.

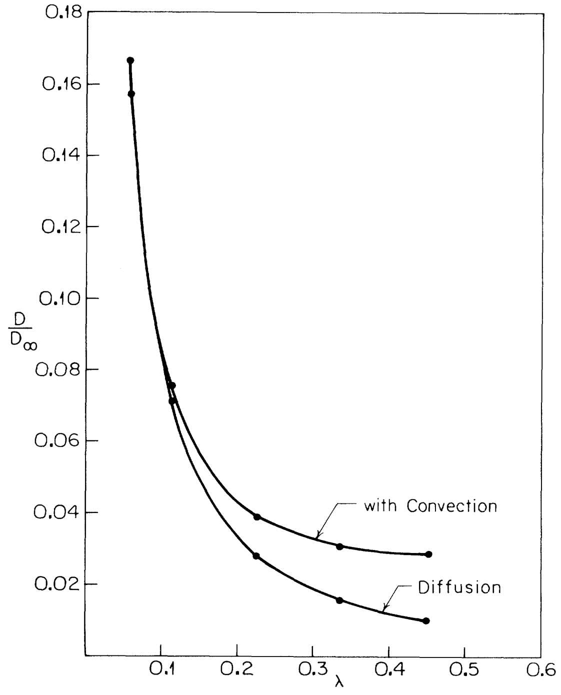

FIG. 2. The dependence of D/D_∞ on λ, if the porous medium is fixed and the molecular size is varied.

and r_m is varied. Also shown are the results with[5,6]

$$D_t/D_\infty = (1-\lambda)^2(1-2.104\lambda+2.09\lambda^3-0.95\lambda^5)\,, \qquad (8)$$

which has been found[12] to be relatively accurate for diffusion in straight tubes. For small values of λ, the two curves do not differ by more than a few percent, but for larger values of λ the difference becomes larger. Thus, the interconnected structure of the pore space can cause a large difference between the predictions of the two expressions for D_t/D_∞, whereas for straight pores, the predictions of the two expressions do not differ by more than a few percent. We may expect the results with Eq. (8) to be more accurate than those with Eq. (2) if $\lambda > 0.2$, since Eq. (2) is an asymptotic result which is very accurate only for $\lambda < 0.2$, whereas Eq. (8), which is a semiempirical relation, represents a good approximation to D_t/D_∞ even for relatively large values of λ. The shape of the curves in Fig. 3 suggests that $D/D_\infty \sim \exp(-\gamma\lambda^\delta)$, where γ and δ are constant, and from Fig. 3 we obtain $\delta = 1$. This value of δ must be compared with[15-17] $\delta = \frac{5}{3}$, which has been predicted for linear polymers in porous media. Thus, the value of δ depends on the structure (shape) of the macromolecules. As shown in Fig. 3, the value of δ is independent of the precise dependence of D_t on λ [i.e., we obtain the same δ with both Eqs. (2) and (8)]. We have also established that if the effective radii of the pores are distributed according to a Gaussian distribution, or are distributed uniformly in the interval $(0,b]$ (where b is a constant), the value of δ will remain unchanged. Thus, this exponential dependence of D on λ is probably independent of the morphology of the medium and the microscopic transport laws for D_t, and may represent a universal law. The value of $\delta = 1$ agrees completely with the experimental observations.[8,19] How-

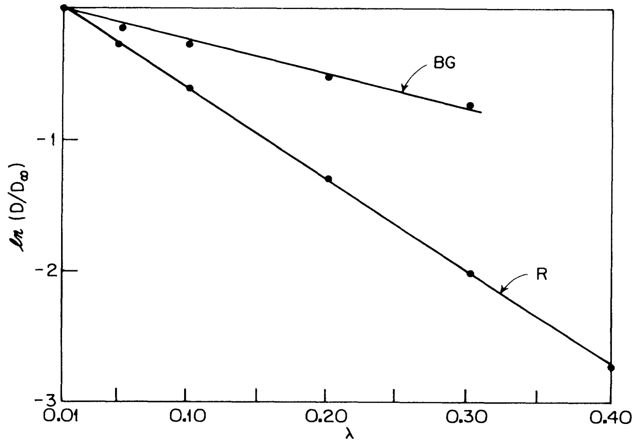

FIG. 3. The dependence of $\ln(D/D_\infty)$ on λ, in the absence of flow if the molecular size is fixed. Here BG refers to Eq. (2) (Ref. 13) and R refers to Eq. (8) (Ref. 6).

ever, unlike Fig. 2, we cannot make a direct comparison between the pure diffusion case (Fig. 3) and combined diffusion and convection case (Fig. 1), because in this case the molecular size is fixed and the pore-size distribution of the porous medium is varied, which, in turn, changes the flow field and, thus, the effective diffusivity in a nonlinear way.

Our model provides a method of estimating D transport of large molecules in more complex porous media. For example, during many catalytic processes, the pores of the catalyst are plugged as a result of an undesired reaction and the formation of deposits. Thus, at some point the catalyst loses its macroscopic connectivity, reaches its percolation threshold[20] and is completely deactivated. Estimation of the effective diffusivity of large molecules in a partially deactivated catalyst (i.e., a percolating system) is an important and yet unsolved problem. It is straightforward to include percolation effects in our model and apply it to catalyst deactivation processes. Moreover, it is currently controversial[21,22] whether the effective transport properties of macromolecules under nonreactive and reactive conditions are the same. Our model and method provide a rational framework to resolve such a controversy. Finally, it has been suggested[3] that for many dynamical processes of excited molecules in restricted environments, e.g., porous silicas, the mean pore size r_m is a significant length scale. The (possibly) universal exponential dependence of D/D_∞ on λ provides a relatively straightforward way of estimating r_m by performing diffusion and/or convection experiments, which may be easier and more accurate than other experimental methods such as[23] small-angle x-ray scattering, surface-area measurements, and electron micrographs. We are currently investigating these issues. The results will be reported elsewhere.[24]

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