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COMMUNICATIONS

Effective diffusivity in periodic porous materials

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Diffusion of a solute in a periodic porous solid is analyzed. An expression for the effective diffusion coefficient is derived for a solute diffusing in a porous medium formed by a simple cubic lattice of spherical cavities connected by narrow tubes. This expression shows how the effective diffusion coefficient depends on microgeometry of the porous material. Generalizations to nonspherical cavities, other lattices, and nonequal diffusion coefficients in the cavities and in the tubes are discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1615758]

Motivated by recent successes in the design of periodic porous materials,[1] we study solute diffusion in a solvent-filled periodic array of identical cavities connected by narrow tubes and derive an expression for the effective diffusivity. The wide range of architectures in a new class of man-made porous materials promises a large number of applications in chemistry and biology. One of the potential applications is in controlled drug release: By regulating the microstructure of a porous material one can tune the molecular diffusivity of a drug and, hence, the rate of its efflux from the encapsulating matrix.[2,3]

Recently, we have derived the effective diffusivity for the case of periodic arrays of touching spherical cavities.[4] Our analysis was based on the recent results for the escape of Brownian particles through the entropic barrier.[5] Here, we combine the general approach presented in Ref. 4 with the analysis of the particle translocation through a narrow tube connecting two reservoirs.[6] This enables the derivation of the expression for the effective diffusivity, D_{eff}, in a porous medium formed by spherical cavities arranged in a lattice and connected by tubes. The derived structure/property relationship shows how D_{eff} depends on the microgeometry of the medium. Straightforward generalizations of our analysis to other lattices, nonspherical cavities, and nonequal diffusion coefficients in the cavities and in the tubes are discussed at the end of the paper.

Consider a particle diffusing in a porous medium formed by a simple cubic lattice of spherical cavities of radius R connected by tubes of length L and radius a, which is much smaller than R. The particle diffusion constant in the unconstrained solvent is D_0. The effective diffusivity characterizes diffusion of a particle on times when its mean square displacement is much larger than the square of the lattice period, $(2R+L)^2$. To derive an expression for D_{eff} one has to find the mean square displacement by solving the diffusion equation in real geometry. To perform this calculation one has to solve the diffusion equation in the cavity and in the tube and match the two solutions at the tube entrance. This is an extremely complicated task, which cannot be carried out. One can find a discussion of different approximate approaches to the problem in Ref. 7.

While the problem cannot be solved analytically in the general case, an expression for D_{eff} can be derived when $a \ll R$. In this case, diffusion can be replaced by a lattice random walk between the neighboring sites, which coincide with the centers of the spheres. Indeed, when $a \ll R$, the time required for a particle to find an entrance to a tube is much larger than the characteristic relaxation time of the distribution in the cavity to equilibrium. This means that every small volume inside the cavity is visited many times by the particle before it enters the tube. As a consequence, its average position in the cavity coincides with the center of the sphere.

Replacing diffusion by the random walk we can find the effective diffusivity by means of the relation

$$D_{eff}=\frac{(2R+L)^2}{6T}, \tag{1}$$

where T is the average time between successive steps of the random walk. We derive an expression for T as a function of the problem parameters, R, a, L, and D_0 in two steps. First, we derive an expression for T using auxiliary quantities that characterize the particle life in the cavity and in the tube.

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Expressing these auxiliary quantities in terms of the original parameters of the problem we find an expression for the effective diffusivity.

The idea of replacing the diffusion in a periodic porous medium by random walk has been previously exploited by Callaghan *et al.* in their pore hopping theory, which was developed for the interpretation of the pulsed gradient spin-echo nuclear magnetic resonance results.[8] For these authors, the hopping rate was an adjustable parameter. In our analysis, the hopping rate is derived as a function of the solute diffusivity and the geometric parameters of the medium.

To escape from the cavity, the particle has to first find an entrance to one of the tubes that connect the cavity with its six nearest neighbors. To derive the average searching time, we use the result for the survival probability of a particle diffusing in a cavity of volume V with a small circular absorbing disk of radius a on its wall.[5] It was shown that the survival probability decays as a single exponential, $S(t)=\exp(-kt)$, where the rate constant is given by $k=4aD_0/V$. Consequently, the average time finding one disk is $k^{-1}=V/(4aD_0)$. When there are six entrances (absorbing disks) the average searching time is $1/(6k)$.

The particle that has entered the tube will either return to the initial cavity or traverse the tube and escape to the neighboring cavity. The probabilities for these two events are denoted P_r and P_{tr}, respectively. Since the particle eventually escapes from the tube, $P_{tr}+P_r=1$. The average times spent in the tube by translocating and returning particles are $\overline{t_{tr}}$ and $\overline{t_r}$. Using these probabilities and average times for each events, we can write time T as an infinite series

$$T=\sum_{n=1}^{\infty}\left[\frac{n}{6k}+(n-1)\overline{t_r}+\overline{t_{tr}}\right]P_r^{n-1}P_{tr}, \tag{2}$$

where the nth term is the contribution due to the particle translocation on the nth attempt. The series can be summed up, leading to the mean time for escaping to one of the six nearest neighboring cavities

$$T=\frac{1+6k\overline{t}}{6kP_{tr}}, \tag{3}$$

where $\overline{t}$ is the average lifetime in the tube given by

$$\overline{t}=\overline{t_{tr}}P_{tr}+\overline{t_r}P_r. \tag{4}$$

Combining Eqs. (3) and (1) we arrive at

$$D_{eff}=\frac{(2R+L)^2kP_{tr}}{1+6k\overline{t}}. \tag{5}$$

To finish the derivation, we need to express k, P_{tr}, and $\overline{t}$ in terms of R, a, L, and D_0. Expressions for the translocation probability and the average lifetime have been previously derived[6]

$$P_{tr}=\frac{1}{2+\dfrac{4L}{\pi a}}, \tag{6}$$

$$\overline{t}=\frac{\pi aL}{8D_0}. \tag{7}$$

Substituting these expressions into Eq. (5) we obtain

$$D_{eff}=\frac{6a^2(2R+L)^2D_0}{(4R^3+9a^2L)(\pi a+2L)}. \tag{8}$$

This is one of the main results of this note. It shows how the effective diffusivity depends on the geometrical parameters of the porous media. The expressions for k, P_{tr}, and $\overline{t}$ used to obtain D_{eff} in Eq. (8) from the expression in Eq. (5) have been tested against Brownian dynamics simulations in Refs. 5 and 6. The tests have demonstrated excellent agreement between the theoretical predictions and the numerical results. For this reason the expressions in Eq. (8) may be considered as an exact result when $a\ll R$.

For $L=0$, the effective diffusion constant in Eq. (8) reduces to our recent result for a cubic lattice of contacting spheres, $D_{eff}=6aD_0/(\pi R)$.[4] In the opposite limiting case, as $L\to\infty$, the effective diffusion constant approaches

$$D_{eff}=\tfrac{1}{3}D_0. \tag{9}$$

This corresponds to diffusion in a cubic lattice formed by the intersecting tubes.

The dependence of D_{eff} on L is nonmonotonous. D_{eff} first decreases with L, then reaches a minimum, and then increases approaching its limiting value $D_0/3$ as $L\to\infty$. In this limiting case D_{eff} does not depend on the tube radius. When $a\to 0$, D_{eff} reaches its minimal value of $D_{eff}=6a^2D_0/R^2$ at $L=2R$. This value is $\pi a/R$ times smaller than the value of D_{eff} at $L=0$, i.e., for contacting spheres connected by apertures of radius a.

The effective diffusion constant of a solute in a porous medium is always smaller than that in the unconstrained solvent. It is frequently written in the form

$$D_{eff}=\frac{D_0}{\tau}, \tag{10}$$

where τ is the tortuosity, which is a fudge factor that accounts for the effect of the constrictions.[3,9] Our result for the effective diffusivity leads to the explicit expression for the tortuosity as a function of the geometrical parameters of the porous media

$$\tau=\frac{(4+9\tilde{a}^2\tilde{L})(\pi\tilde{a}+2\tilde{L})}{6\tilde{a}^2(2+\tilde{L})^2}, \tag{11}$$

where $\tilde{a}$ and $\tilde{L}$ are dimensionless diameter and length of the tubes:

$$\tilde{a}=\frac{a}{R},\quad \tilde{L}=\frac{L}{R}. \tag{12}$$

An interesting feature of the L-dependence of the tortuosity is the asymmetry of its fast initial increase and subsequent slow decrease when it goes to the $\tilde{L}\to\infty$ asymptotic value, $\tau=3$ (Fig. 1).

The nonmonotonic behavior of D_{eff} and the tortuosity is due to the competition of two factors which enter into the expression in Eq. (5). The factor $(2R+L)^2$ increases with L while the factor $P_{tr}/(1+k\overline{t})$ decreases as L increases. From Eq. (8) one can see that for $L\ll R^3/a^2$ $D_{eff}\approx k(2R+L)^2P_{tr}=(\pi ak/2)(2R+L)^2/(\pi a+2L)$. This expression shows that

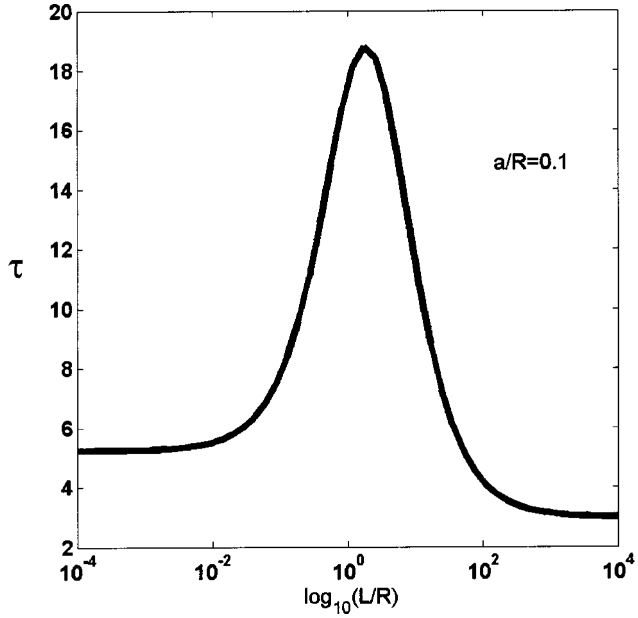

FIG. 1. Tortuosity as a function of the tube length.

D_{eff} monotonically decreases with L when $L<2R$, reaches a minimum at $L=2R$, and then increases when $L>2R$. The increase of D_{eff} slows down at $L \gg R^3/a^2$. As $L\to\infty$ D_{eff} approaches its limiting value given in Eq. (9).

Our results can be extended to the cavities of different shapes as well as to the lattices of other types. For example, for cubic cavities of size b arranged in a simple cubic lattice and connected by cylindrical tubes of length L and radius a, which is small compared to b, $a \ll b$, D_{eff} is given by

$$D_{eff}=\frac{4\pi a^2(b+L)^2 D_0}{(2b^3+\pi a^2 L)(\pi a+2L)}. \tag{13}$$

Generalization of the expression in Eq. (5) to the case of simple cubic lattices of spherical cavities in d dimensions $(d=1,2,3)$ is

$$D_{eff}=\frac{6a^2(2R+L)^2 D_0}{(4R^3+3da^2 L)(\pi a+2L)}. \tag{14}$$

In the discussion above it has been assumed that the particle diffusion coefficients in the cavities and in the tubes are equal. The derivation can be generalized to the case of nonequal diffusion coefficients, $D_c \neq D_t$, where D_c and D_t are the diffusion coefficients in the cavities and in the tubes, respectively. In this case k and $\bar{t}$ are given by the same expressions as earlier, in which D_0 should be replaced by D_c, and $P_{tr}=[2+4LD_c/(\pi a D_t)]^{-1}$. Substituting these relations into Eq. (5) one finds

$$D_{eff}=\frac{6a^2(2R+L)^2 D_c D_t}{(4R^3+9a^2 L)(\pi a D_t+2LD_c)}. \tag{15}$$

This expression is a generalization of D_{eff} in Eq. (8) to the case of nonequal diffusion coefficients. The expression in Eq. (15) can be used when the size of the diffusing solute is comparable with the tube diameter and $D_t \ll D_c$.

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