Diffusivity in periodic arrays of spherical cavities

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(Received 1 November 2002; accepted 27 January 2003)

[DOI: 10.1063/1.1561615]

This note deals with diffusion of a solute in a porous medium formed by a periodic array of identical, solvent-filled, touching spherical cavities. We derive an expression for the effective diffusivity, D_{eff}, as a function of the medium microgeometry and the solute diffusivity in the bulk solvent. The expression shows the effective transport property can be directly linked to the microgeometry of the porous material.

Recent advances in materials science lead to a new class of porous solids with periodic architectures.[1] Synthesis with templating by organic compounds can yield materials with unimodal pore size distribution.[1–3] Templating with colloidal crystals leads to solids with periodic arrays of identical voids.[4,5] Lithography can produce arrays of cavities connected by narrow channels.[6–8] In addition to periodic porous solids, fluid-based networks of vesicles and channels have been reported.[9,10] The new materials with controlled microgeometry can be used to design unique environments for a number of biological and chemical processes.[1,2,6,11]

Well-defined architecture of these materials enables theoretical descriptions of their transport properties. In particular, the classical problem of the effective diffusivity in porous medium can be solved at very low cost to produce accurate expressions linking the effective diffusion constant to the geometric parameters of the medium. Here, we derive an expression for the effective diffusivity in a periodic medium formed by an array of spherical cavities of radius R connected by small round apertures of radius a, $a \ll R$. We show how D_{eff} depends on the radii a and R, as well as on the type of the lattice formed by the cavities.

The effective diffusivity characterizes diffusion of solute molecules on times when their mean square displacement is much larger than R^2.[12–14] To derive an expression for D_{eff} one has to find the mean square displacement by solving diffusion equation with very complex boundary conditions. This problem has no analytical solution. However, this difficulty can be dealt with when $a \ll R$. In this case, diffusion can be replaced by a lattice random walk between neighboring sites, which coincide with the centers of the cavities. To justify this statement, we note that when $a \ll R$, a particle has to find a small window in order to escape from the cavity. In other words, the particle must overcome a high entropy barrier.[15] The escape takes time of the order of $R^3/(aD_0)$, where D_0 is the solute diffusion constant in the bulk solvent.[16] This time is large compared to the time R^2/D_0 that characterizes the relaxation of the distribution in the cavity to the equilibrium. As a consequence, the particle visits every small volume inside the cavity many times before it escapes, and its average position in the cavity coincides with the cavity center.

Thus, on times much larger than R^2/D_0 motion of the particle can be viewed as a random walk between centers of neighboring spheres. After sufficiently many steps this random walk becomes equivalent to diffusion with the effective diffusion constant given by

$$D_{\mathrm{eff}} = \frac{\alpha l^2}{T}, \tag{1}$$

where l is the distance between centers of two contacting spheres

$$l = 2\sqrt{R^2 - a^2} \approx 2R, \tag{2}$$

T is the average time between successive steps of the random walk which is the average particle lifetime in the cavity, and α is a geometrical factor that depends on the lattice type, for a simple cubic lattice $\alpha = 1/6$.

The average lifetime T is required to finish the derivation. To find this time we use a recent result for the survival probability of a particle diffusing in a cavity of volume V with a circular absorbing disk on its wall. When the disk radius a is small compared to the cavity size the survival probability is exponential, $S(t) = \exp(-kt)$, with the rate constant given by $k = 4aD_0/V$.[16] The average particle lifetime in this cavity is $1/k$. The average lifetime of the particle in the cavity with n absorbing disks is $1/(nk)$. When the particle comes to a window connecting two neighboring cavities it has equal probabilities to end up on both sides of the window. Therefore, the average lifetime in the cavity connected with n neighboring cavities is

$$T = \frac{2}{nk} = \frac{2\pi R^3}{3naD_0}. \tag{3}$$

Substituting this average lifetime into Eq. (1) and using Eq. (2) we arrive at

$$D_{\text{eff}}=\frac{6a\alpha nD_0}{\pi R}. \tag{4}$$

For a simple cubic (SC) lattice $n=6$, $\alpha n=1$, and the effective diffusivity takes the form

$$D_{\text{eff,SC}}=\frac{6aD_0}{\pi R}. \tag{5}$$

Using this we can write D_{eff} in Eq. (4) as

$$D_{\text{eff}}=\alpha nD_{\text{eff,SC}}. \tag{6}$$

The expressions above are main results of this note. They show how D_{eff} depends on R and a as well as the type of the lattice.

Our approach is similar to the pore hopping theory developed by Callaghan *et al.* for the interpretation of their pulsed gradient spin–echo nuclear magnetic resonance results in porous media.[17] The difference between the two theories lies in the fact that we evaluate the hopping rate which is an uncertain parameter for Callaghan *et al.*[17]

The expressions for D_{eff} derived above allow one to find the tortuosity factor, τ, which is a fudge factor that accounts for combined effect of constrictions.[12,14] It appears in the traditional presentation of the effective diffusion constant in a porous media in the form

$$D_{\text{eff}}=\frac{D_0}{\tau}. \tag{7}$$

For the model under study

$$\tau=\frac{\pi R}{6a\alpha n}. \tag{8}$$

When cavities form a simple cubic lattice, the tortuosity becomes

$$\tau_{\text{SC}}=\frac{\pi R}{6a}. \tag{9}$$

Since $R\gg a$, the tortuosity factor is much larger than unity.

In conclusion, we have developed a theory for the effective diffusivity in arrays of spherical cavities. Our results can be straightforwardly generalized to voids of other shapes, such as cubes connected by small apertures and to the periodic arrays of voids connected by narrow tubes. This theory will be presented in a forthcoming paper.

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