Diffusion of finite-sized Brownian particles in porous media

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The effective diffusion coefficient D_e for porous media composed of identical obstacles of radius R in which the diffusing particles have finite radius βR ($\beta \geqslant 0$) is determined by an efficient Brownian motion simulation technique. This is accomplished by first computing D_e for diffusion of "point" Brownian particles in a certain system of interpenetrable spherical obstacles and then employing an isomorphism between D_e for this interpenetrable sphere system and D_e for the system of interest, i.e., the one in which the Brownian particles have radius βR. [S. Torquato, J. Chem. Phys. **95**, 2838 (1991)]. The diffusion coefficient is computed for the cases $\beta = 1/9$ and $\beta = 1/4$ for a wide range of porosities and compared to previous calculations for point Brownian particles ($\beta = 0$). The effect of increasing the size of the Brownian particle is to hinder the diffusion, especially at low porosities. A simple scaling relation enables one to compute the effective diffusion coefficient D_e for finite β given the result of D_e for $\beta = 0$.

I. INTRODUCTION

Understanding the transport of macromolecules in disordered porous media (i.e., particles which are of the order of the size of the pores) is of importance in a variety of applications, including gel size-exclusion chromatography, separation of catalytic processes in zeolites, solvent swelling rubbers, and reverse osmosis membrane separation.[1–4] Transport of finite-sized particles in porous media is hindered (relative to the case of "point-sized" particles) due, in part, to the fact that the finite-sized particle is excluded from a fraction of the pore volume. Hindered diffusion of macromolecules has been recently studied by Sahimi and Jue[4] for a lattice model of porous media. Torquato[5] subsequently investigated the problem of diffusion-controlled trapping of finite-sized Brownian particles for a continuum model of traps (i.e., suspensions of spherical traps). There have been numerous studies dealing with the prediction of the effective diffusion coefficient D_e of continuum models of porous media in which the diffusing particles have zero radius,[6–9] i.e., point particles. In contrast, we are not aware of any investigation attempting to determine D_e of continuum models with finite-sized Brownian particles.

In this paper, we determine by Brownian motion simulation the effective diffusion coefficient D_e for porous media composed of a statistical distribution of identical spherical obstacles of radius R at number density ρ when the diffusing particles are spheres with radius βR, $\beta \geqslant 0$. In particular, we will employ the accurate first-passage-time technique developed by the authors to obtain the effective conductivity of composite media for "point" diffusing particles.[7,8]

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II. ISOMORPHISM BETWEEN TRANSPORT OF FINITE-SIZED AND POINT BROWNIAN PARTICLES

Torquato[5] utilized the fact that the trapping of a spherical tracer particle of radius βR in a medium of hard spherical traps of radius R is isomorphic to the trapping of a point particle of zero radius in a particular system of interpenetrable spherical traps to determine the trapping rate of the former system. We briefly describe this isomorphism which will be applied to the problem at hand. Consider the diffusion of a spherical tracer particle of radius b in the space exterior to a random distribution of hard spherical inclusions or obstacles of radius a at number density ρ. (The ensuing argument is not limited to hard obstacles, and hence applies to partially penetrable or overlapping obstacles.) As the result of exclusion-volume effects, the volume fraction available to the center of the tracer particle of radius b (for $b > 0$) is smaller than the porosity ϕ_1 (i.e., the volume fraction available to a point particle of zero radius). A key observation is that the diffusion of a tracer particle of radius b is isomorphic to the diffusion of a point particle in the space exterior to spheres of radius $a + b$ (centered at the same locations as the original obstacles of radius a) at number density ρ, possessing a hard core of radius a surrounded by perfectly penetrable concentric shell of thickness b. The latter system is precisely the penetrable-concentric shell (PCS) or "cherry-pit" model introduced by Torquato,[10] in which the dimensionless ratio

$$\epsilon = \frac{a}{a+b} \tag{1}$$

is referred to as the "impenetrability" parameter since it is a measure of the relative size of the hard core: $\epsilon = 0$ and $\epsilon = 1$ corresponding to "fully penetrable" and "totally impenetrable" spheres, respectively. Therefore, the volume fraction available to the tracer particle $\phi_1(\rho,a+b) = 1-\phi_2(\rho,a+b)$ is equal to the volume fraction available to a point tracer in the PCS model, where $\phi_2(\rho,a+b)$ is the unavailable volume fraction. When $b=0$, the unavailable volume fraction $\phi_2(\rho,a) = \rho 4\pi a^3/3$ and ϕ_1 is just the standard porosity of the system. The quantity $\phi_2(\rho,a+b)$ is clearly greater than $\phi_2(\rho,a)$ but is less than $\rho 4\pi(a+b)^3/3$ because the concentric shells of thickness b may overlap. The volume fraction $\phi_2(\rho,a+b)$ in the PCS model is nontrivially related to ρ and radius $(a+b)$.

Recently, Torquato *et al.*[11] studied the so-called "nearest-neighbor" distribution functions, $E_v(r)$ and $H_v(r)$, for a random system of identical spherical obstacles. The "exclusion" probability function $E_v(r)$ is defined to be the probability of finding a spherical cavity of radius r, empty of the centers of the spherical obstacles and is related to "void" nearest-neighbor probability density $H_v(r)$ by the relation[12]

$$H_v(r) = -\frac{\partial E_v(r)}{\partial r}. \tag{2}$$

$H_v(r)dr$ is the probability that at an arbitrary point in the system the center of the nearest spherical obstacle lies at a distance between r and $r+dr$. Alternatively, $E_v(r)$ can be defined to be the fraction of volume available to a "test" particle of radius $b=r-a$ when inserted into a system of spherical obstacles of radius a at number density ρ and therefore equal to $\phi_1(\rho,a+b)$. Therefore, knowledge of E_v will enable us to compute the volume fraction of the PCS model.[5] Similarly, the nearest-neighbor probability density $H_v(r)$ can be alternatively defined to be specific surface (surface area per unit volume) available to a test particle of radius $b=r-a$, denoted by $s(\rho,a+b)$.

The exact integral representation of $E_v(r)$ and $H_v(r)$ was given by Torquato *et al.*[11] in d dimensions in terms of the n-body distribution functions which statistically characterize the microstructure of the system. It is generally impossible to determine the complete set of these distribution functions for $d \geqslant 2$, and therefore, the exact evaluation of $E_v(r)$ or $H_v(r)$ is not possible in two and higher dimensions. For distribution of hard spherical obstacles, Torquato *et al.* obtained two different sets of expressions for these quantities: one within the framework of Percus–Yevick approximation and the other within the framework of the Carnahan–Starling approximation. These approximations were compared to the scaled-particle approximations[13] and Monte Carlo simulations[14] and it was found that the Carnahan–Starling expressions gave excellent and the best agreement with the data. Specifically, the most accurate approximations found by Torquato *et al.*[11] are given by

$$E_v(x,\eta) = (1-\eta)\exp[-\eta(8ex^3+12fx^2+24gx+h)], \quad x \geqslant \tfrac{1}{2} \tag{3}$$

$$H_v(x,\eta) = \frac{12\eta}{a}(ex^2+fx+g)E_v(x,\eta), \quad x \geqslant \tfrac{1}{2} \tag{4}$$

where

$$x = \frac{r}{2a}, \tag{5}$$

$$\eta = \rho\frac{4\pi}{3}a^3, \tag{6}$$

$$e(\eta) = \frac{(1+\eta)}{(1-\eta)^3}, \tag{7}$$

$$f(\eta) = \frac{-\eta(3+\eta)}{2(1-\eta)^3}, \tag{8}$$

$$g(\eta) = \frac{\eta^2}{2(1-\eta)^3}, \tag{9}$$

$$h(\eta) = \frac{-9\eta^2+7\eta-2}{2(1-\eta)^3}. \tag{10}$$

Relations (3) and (4) in conjunction with the isomorphisms described earlier are utilized to determine the volume fraction and specific surface, respectively, available to a test particle of radius b in a system of hard spherical obstacles of radius a at number density ρ, i.e., one has in terms of the dimensionless variables[5,12]

$$\phi_1(\eta,\epsilon) = E_v\left(\frac{1}{2\epsilon},\eta\right), \tag{11}$$

$$s(\eta,\epsilon) = H_v\left(\frac{1}{2\epsilon},\eta\right). \tag{12}$$

It is important to note that this formalism can be extended to include cases in which the test particle of radius βR is inserted into a system of interpenetrable spheres of radius R having hard cores of radius λR surrounded by perfectly penetrable shells of thickness $(1-\lambda)R$. This is isomorphic[5] to the insertion of a test particle of radius $b=(1-\lambda+\beta)R$ into a system of hard spherical obstacles of radius $a=\lambda R$, and hence

$$\phi_1(\eta,\epsilon,\beta) = E_v\left(\frac{1+\beta}{2\lambda},\eta\lambda^3\right), \tag{13}$$

$$s(\eta,\epsilon,\beta) = H_v\left(\frac{1+\beta}{2\lambda},\eta\lambda^3\right). \tag{14}$$

In summary, application of the aforementioned isomorphism enables one to obtain the effective diffusion coefficient for Brownian particles of radius b in a system of hard spherical inclusions of radius a, $D_e[\phi_2(\rho,a);b]$, from the corresponding result for point particles in the PCS model from the relation

$$D_e[\phi_2(\rho,a);b] = D_e[\phi_2(\rho,a+b);0]. \tag{15}$$

More generally, if the Brownian particles of radius βR are diffusing in a system of interpenetrable spherical obstacles of radius R with impenetrable cores of radius λR, then,[5] using the notation of Eq. (13), one has

$$D_e[\phi_2(\eta,\lambda,0);\beta] = D_e[\phi_2(\eta,\epsilon,\beta);0]. \tag{16}$$

We perform calculations (in the subsequent section) for the specific cases in which the spherical obstacles are mutually impenetrable.

III. CALCULATION OF THE EFFECTIVE DIFFUSION COEFFICIENT BY FIRST-PASSAGE-TIME TECHNIQUE

The authors[7-9] developed a first-passage-time technique to efficiently compute the effective conductivity σ_e of continuum model of n-phase composite media having phase conductivities $\sigma_1,...,\sigma_n$. Whereas Refs. 7 and 8 dealt with composite media composed of hard particles, Ref. 9 treated media composed of fully penetrable or overlapping particles. In all of these works, the Brownian particle had zero radius. Mathematically, the problem of diffusion is the same as the problem of two-phase conduction in which phase 2 is a perfectly insulating phase, i.e., $D_e = \sigma_e$, $D = \sigma_1$ and $\sigma_2 = 0$. Here we shall apply the first-passage-time technique to compute D_e for porous media composed of hard spherical obstacles of radius R when the Brownian particles have radius βR. As discussed earlier, this is equivalent to diffusion of point particles in an equivalent PCS model according to Eq. (16). We shall briefly summarize the first-passage-time technique.[7-9] The reader is referred to Refs. 7–9 for specific details.

Consider a Brownian particle (diffusion tracer with zero radius) moving in a homogeneous region with diffusion coefficient D. The mean hitting time $\tau(Y)$, which is defined to be the mean time taken for a Brownian particle initially at the center of the sphere of radius Y to hit the surface for the first time, is $\tau(Y) = Y^2/6D$. This implies that once $\tau(Y)$ is known as a function of the mean square displacement Y^2, then the diffusion coefficient is computed by $D = Y^2/6\tau(Y)$. Likewise, the effective diffusion coefficient D_e associated with diffusion in a fluid-saturated porous medium can be expressed as

$$D_e = \frac{X^2}{6\tau(X)}\bigg|_{X^2\to\infty}. \tag{17}$$

Here $\tau(X)$ is the total mean time associated with the total mean square displacement X^2 of a Brownian particle moving in the space exterior to particle phase, phase 2. The limit $X^2\to\infty$ is taken since we consider an infinite porous medium. In the actual computer simulation, this is realized by taking X^2 sufficiently large. Therefore, in order to compute the effective diffusion coefficient D_e, it is sufficient to obtain X^2 as a function of $\tau(X)$. Note that X^2 is an average over many Brownian motion trajectories and system realizations.

In the actual computer simulation, in the preponderance of cases where the Brownian particle is far enough from the boundary of the obstacles (or the pore–solid interface), we employ the time-saving first-passage-time technique which is now described. First, one constructs the largest imaginary concentric sphere of radius r around the diffusing particle which just touches the interface. The Brownian particle then jumps in one step to a random point on the surface of this imaginary concentric sphere and the process is repeated, each time keeping track of r_i^2 (or the mean hitting time) where r_i is the radius of the ith first-passage sphere, until the particle is within some prescribed very small distance $\delta_1 R$ of the interface boundary. Once the Brownian particle is very close to the interface, then it will take a large number of steps (and large computation time) to move again far enough from the interface since the first-passage sphere would be of very small radius. To avoid this difficulty at this juncture, the Brownian particle makes a big jump in one step to a random point on the available surface of the first-passage sphere of radius r ($\delta_1 < r/R < 1$) (see Fig. 1), spending the mean hitting time τ_s as discussed below. Thus the expression for the effective diffusion coefficient used in practice is given by

$$D_e = \frac{\langle \Sigma_i r_i^2 + \Sigma_j r_j^2\rangle}{6\langle \Sigma_i \tau(r_i) + \Sigma_j \tau_s(r_j)\rangle}\bigg|_{X^2\to\infty}, \tag{18}$$

since $X^2 = \langle \Sigma_i r_i^2 + \Sigma r_j^2\rangle$. Here $\tau(r)$ denotes the mean hitting time for a diffusion tracer with the diffusion coefficient D associated with a first-passage sphere of radius r. The summations over the subscripts i and j are for the first-passage sphere entirely exterior to the obstacles and the first-passage sphere encompassing the interface boundary (as illustrated in Fig. 1), respectively. Alternatively, since $\tau(r) = r^2/6D$, we have

$$\frac{D_e}{D} = \frac{\langle \Sigma_i \tau(r_i) + \Sigma_j \tau(r_j)\rangle}{\langle \Sigma_i \tau(r_i) + \Sigma_j \tau_s(r_j)\rangle}\bigg|_{X^2\to\infty}. \tag{19}$$

Note that, for an infinite medium, the initial position of the Brownian particle is arbitrary. Equation (19) is the basic equation to be used in our Brownian motion simulation to compute the effective diffusion coefficient D_e associated with random distributions of spherical obstacles.

The key quantity that should be determined in employing the aforementioned first-passage time technique is the mean hitting time $\tau_s(r)$ for a diffusion tracer associated with

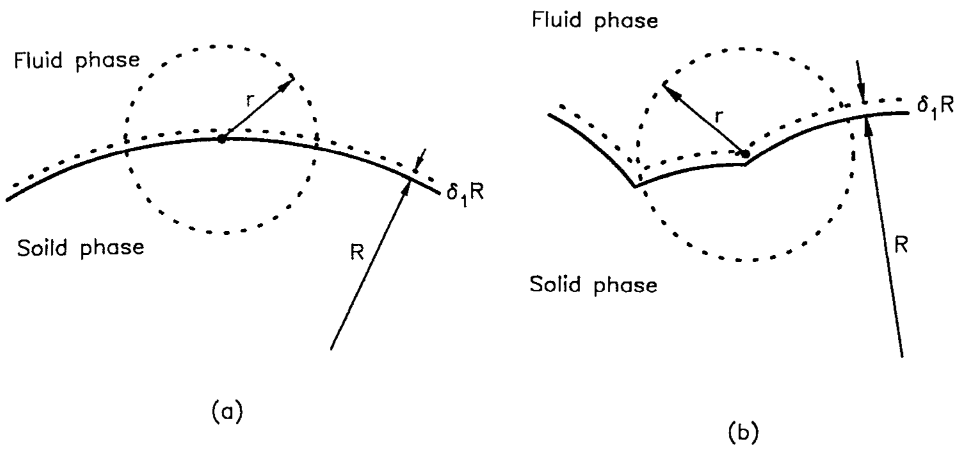

FIG. 1. Two-dimensional depiction of the first-flight sphere of radius r in a small neighborhood of (a) *smooth* and (b) *nonsmooth* fluid–solid interface.

the first-passage sphere of radius r encompassing the interface boundary (see Fig. 1). The authors[7] recently showed that it is given by the solution of a Poisson boundary-value problem. They also gave an accurate analytical solution for $\tau_s(r)$ that depends on the pore–solid geometry contained within the first-passage sphere of radius r and the molecular diffusion coefficient D. In the following, we state their essential results in the language of this paper. In the case that the interface encompassed by the first-passage sphere is *smoothly* curved [as in Fig. 1(a)], the mean hitting time $\tau_s(r)$ for a diffusion tracer at $\mathbf{x}$ associated with the first-passage sphere of radius r centered at $\mathbf{x}_0$ at the interface is given by

$$\tau_s(r) = \frac{r^2}{6D}\frac{4\pi r^3/3}{V}\left[1 + \frac{1}{2}h^2 - \frac{3}{2}\sum_{m=0}^{\infty} C_{2m+1} h^{2m+1}\right], \tag{20}$$

where

$$C_{2m+1} = \frac{(-1)^{m+1}(2m)!}{2^{2m+1}(m!)^2}\frac{(4m+3)}{(2m-1)(m+2)(m+1)}. \tag{21}$$

Here $h = |\mathbf{x} - \mathbf{x}_0|/r$ and V is the volume of the region inside the first-passage sphere that lies entirely in the fluid phase. Note that the first-passage sphere is centered at $\mathbf{x}_0$ at the interface boundary instead of the location of the diffusion tracer $\mathbf{x}$ since the former lends itself to a more tractable solution. If the interface boundary encompassed by the first-passage sphere is *nonsmooth* as in the surface of the union of two or more overlapping obstacles [as illustrated in Fig. 1(b)], it is more practical from a computational point of view to use a modified version of Eq. (20), which is as follows:[9]

$$\tau_s(r) = \frac{r^2}{6D}\frac{4\pi r^3/3}{V}. \tag{22}$$

In the application of Eq. (22), the first-passage sphere is centered at the location of the diffusion tracer $\mathbf{x}$, unlike in Eq. (20).

IV. SIMULATION DETAILS

Here we apply the first-passage time technique to compute the effective diffusion coefficient D_e of a porous media composed of equilibrium distributions of hard spherical obstacles of radius R in which the diffusing particles are taken to have radius equal to $R/4$ and $R/9$. This is done by computing D_e associated with point diffusing particles in porous media composed of spheres in the PCS model with $\lambda = 0.8$ or $\lambda = 0.9$ and utilizing the results of Sec. II. For these special cases, relation (16) yields

$$D[\phi_2(\eta,1,0);1/4] = D[\phi_2(\eta,0.8,0.25);0], \tag{23}$$

and

$$D[\phi_2(\eta,1,0);1/9] = D[\phi_2(\eta,0.8,1/9);0]. \tag{24}$$

In order to compute the effective diffusion coefficient D_e from computer simulations, we must first generate realizations of the particle distributions and then employ the first-passage-time technique, i.e., determine the effective diffusion coefficient for each realization (using many diffusion tracer particles) and subsequently average over a sufficiently large number of realizations to obtain D_e.

In particular, we shall generate equilibrium distributions of spheres in the PCS model for fixed λ and number density ρ by employing a conventional Metropolis algorithm.[15] N spherical obstacles having hard-core radius λR are initially placed at the lattice sites of body-centered cubical array in a unit cell of size L^3. The unit cell is surrounded by the periodic images of itself. Each obstacle is then moved by a small distance to a new position which is accepted or rejected according to whether the inner hard cores overlap or not. This process is repeated until equilibrium is reached. In our simulation, $N = 125$ and each obstacle is moved 450 times before sampling for the first equilibrium realization. Subsequent equilibrium realizations were sampled at intervals of 50 moves per obstacle, ensuring that equilibrium is achieved.[8]

The essence of the first-passage-time algorithm has been described in Sec. III. Here we need be more specific about the conditions under which a Brownian particle is considered to be in the small neighborhood of the interface boundary and hence when the first-passage quantity τ_s needs to be computed by Eq. (20) or (22). An imaginary thin concentric shell of thickness $\delta_1 R$ is drawn around each cluster consisting of PCS spheres of radius R. If a Brownian particle enters this thin shell, we employ the first-passage-time equation (20) or (22). We then construct an imaginary first-passage sphere of radius r which is taken to be the distance to the next nearest neighboring obstacle or some prescribed smaller distance $\delta_2 R$ with $\delta_1 < r/R \leqslant \delta_2 < 1$. In employing Eq. (20) or (22), the determination of the volume portion V of the first-passage sphere exterior to the obstacle is essential. However, for the case of nonsmooth interface boundary as shown in Fig. 1(b), the exact analytical determination of V is generally impossible. The authors[9] recently employed the so-called *template method* to determine this quantity numerically. One uniformly and randomly throws M_t measuring points inside the first-passage sphere and counts the occasions M that the measuring points happen to be thrown exterior to the obstacle. V is then simply determined to be $V = 4\pi r^3/3 \cdot M/M_t$. Of course, for the case of smooth interface boundary as shown in Fig. 1(a), V is exactly computed analytically without any difficulty.

After a sufficiently large total mean square displacement, Eq. (18) is then employed to yield the effective diffusion coefficient for each Brownian trajectory and each realization. Many different Brownian trajectories are considered per realization. The effective diffusion coefficient D_e is finally determined by averaging the diffusion coefficients over all realizations. Finally, note that so-called Grid method[16] was used to reduce the computation time needed to check if the tracer is near an obstacle.

In our simulations, we have taken $\delta_1 = 0.0001$ and $\delta_2 = 0.01$. We considered 100 to 200 equilibrium realizations and 100 random walks per realization, and have let the dimensionless total mean square displacement X^2/R^2 vary from 2 to 10, depending on the value of ρ. Our calculations were carried out on a VAX station 3100 and on a CRAY Y-MP.

TABLE I. Comparison of the scaled effective diffusion coefficient D_e/D for point Brownian particles for different values of the impenetrability parameter λ in the PCS or cherry-pit model. The cases $\lambda = 0.8$ and $\lambda = 0.9$ were computed in the present work. The limits $\lambda = 0$ and $\lambda = 1$ correspond to fully penetrable and totally impenetrable spheres, respectively, and were computed earlier by us (Refs. 8 and 9).

Particle volume fraction, ϕ_2	Scaled effective diffusion coefficient, D_e/D			
	$\lambda = 0$	$\lambda = 0.8$	$\lambda = 0.9$	$\lambda = 1$
0.1	0.855	0.856	0.856	···
0.2	0.714	0.718	···	0.724
0.3	0.593	0.596	0.598	···
0.4	0.461	0.463	···	0.491
0.5	0.346	0.359	0.368	···
0.6	0.248	0.257	···	0.287
0.7	0.160	0.167	0.178	···
0.8	0.076	0.092	···	···
0.9	0.022	0.027	···	···

V. RESULTS AND DISCUSSION

Our simulation data are compared to the best available rigorous three-point upper bound due to Beran,[17] which, for the effective diffusion coefficient D_e in the diffusion problem considered, is given by

$$\frac{D_e}{D} \leqslant \phi_2 - \frac{\phi_1 \phi_2}{(3 - \phi_1 - 2\zeta_2)}. \tag{25}$$

Here ζ_2 is a three-point parameter involving the multidimensional integral over a three-point correlation function that we discuss below. Note that the corresponding lower bound vanishes for diffusion past obstacles.

The three-point parameter ζ_2 for spheres in the PCS model was computed in the extreme limits $\lambda = 0$[18] and $\lambda = 1$,[19] but heretofore has not been computed for intermediate values $0 < \lambda < 1$. Torquato[6] has observed that the low-volume-fraction expansions of ζ_2 provides very good estimates over the wide range of ϕ_2 even with only the linear term (i.e., $\zeta_2 = \text{constant}\cdot\phi_2$) for a wide class of statistically isotropic suspensions of spheres. We will exploit this observation and compute ζ_2 through first order in ϕ_2 as a function of λ for large λ. Using the method of Torquato,[10] we find that ζ_2 through first order in ϕ_2 for large λ is given by

$$\zeta_2 = C\phi_2, \tag{26}$$

where

$$C = \frac{3}{8} - 10(1-\lambda^3) - 9(1-\lambda^4) + \frac{3}{2}(1-\lambda^6) + \frac{3\lambda}{8(1+2\lambda)^2} - \frac{3}{16}\ln(1+2\lambda). \tag{27}$$

When $\lambda = 1$, Eq. (26) recovers the exact relation[20] $\zeta_2 = [5/12 - 3\ln(3/16)]\phi_2 \simeq 0.210\,68\phi_2$.

Table I shows the simulation data for the scaled effective diffusion coefficient D_e/D for point particles in porous media composed of spheres in the PCS model for $\lambda = 0.8$ and

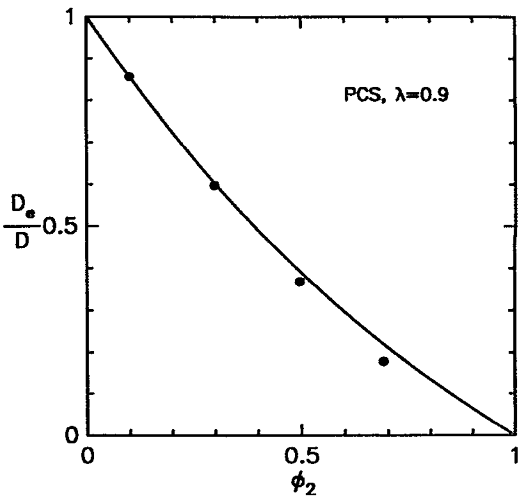

FIG. 3. Comparison of the simulation data for the scaled effective diffusion coefficient D_e/D for a point particle (with $\beta = 0$) in porous media composed of spheres in the PCS or cherry-pit model with an impenetrability parameter $\lambda = 0.9$ to the corresponding three-point upper bound (25).

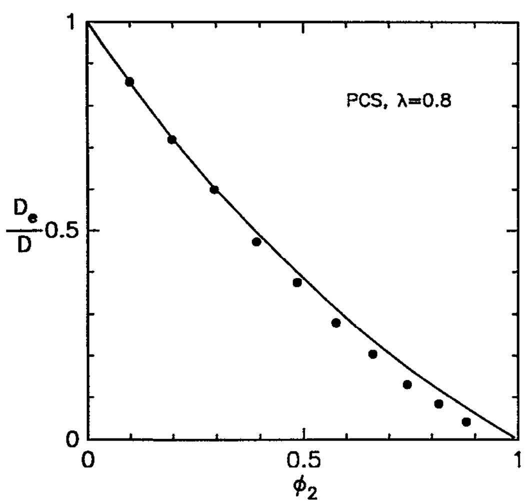

FIG. 2. Comparison of the simulation data for the scaled effective diffusion coefficient D_e/D for a point particle (with $\beta = 0$) in porous media composed of spheres in the PCS or cherry-pit model with an impenetrability parameter $\lambda = 0.8$ to the corresponding three-point upper bound (25).

TABLE II. The scaled effective diffusion coefficient D_e/D for Brownian particles of radius $R/4$ in porous media composed of hard spherical obstacles of radius R.

Particle volume fraction, ϕ_2	Scaled effective diffusion coefficient, D_e/D
0.051	0.856
0.102	0.720
0.154	0.600
0.205	0.472
0.256	0.375
0.307	0.280
0.358	0.203
0.410	0.130
0.461	0.083
0.512	0.041

TABLE III. The scaled effective diffusion coefficient D_e/D for Brownian particles of radius $R/9$ in porous media composed of hard spherical obstacles of radius R.

Particle volume fraction, ϕ_2	Scaled effective diffusion coefficient, D_e/D
0.100	0.856
0.299	0.598
0.497	0.368
0.689	0.178

0.9. Table I also includes the previously obtained simulation data for totally impenetrable spheres[8] (i.e., PCS spheres with $\lambda = 1$) and the fully penetrable spheres[9] (i.e., PCS spheres with $\lambda = 0$) which were originally calculated in the context of the conductivity problem. For small sphere volume fractions, D_e/D varies little with the interpenetrability parameter λ, as would be expected, since overlap of the obstacles is negligible for $\phi_2 \ll 1$. For fixed but large ϕ_2, D_e/D increases slightly with increasing λ because there is less clustering of the obstacles as λ is made large.

Figures 2 and 3 depict the data for D_e/D in the PCS model for $\lambda = 0.8$ and 0.9, respectively, along with the corresponding upper bound (25) which was computed using Eq. (26). It can be seen that all the simulation data lie below the upper bound. Furthermore, the upper bound itself is shown to yield a good estimate to D_e/D over the whole range of volume fractions. This is consistent with the arguments of Torquato,[21] who observed that the upper bound should yield a good estimate of D_e/D provided that the pore phase is connected, as is the case for the volume fractions considered above for the PCS model.

Using the isomorphism described in Sec. II in conjunction with Eqs. (23) and (24), we can map our PCS results of D_e/D for point-diffusing particles into equivalent results for diffusion of finite-sized Brownian particles in porous media composed of hard (totally impenetrable) spherical obstacles. Tables II and III give our simulation data for finite-sized Brownian particles of radius $R/4$ and $R/9$, respectively. Figure 4 compares the scaled effective diffusion coefficient D_e/D for three different sized Brownian particles ($\beta = 0$, 1/9 and 1/4) in porous media composed of hard spheres of radius R. It is seen that diffusion is considerably hindered due to exclusion-volume effects. For example, at $\phi_2 = 0.5$, the scaled diffusion coefficient decreases by about a factor of 10 when β goes from zero to 1/4. Thus hindered diffusion becomes more pronounced at low porosities (i.e., high volume fraction of the obstacles), as would be expected.

We can obtain a simple scaling relation that enables one to calculate the effective diffusion coefficient $D_e[\phi_2(R);\beta]$ for finite β given the result of $D_e[\phi_2(R);0]$ for $\beta = 0$ in the case of hard spherical obstacles of radius R. First, we observe that D_e for finite β at the volume fraction $\phi_2/(1+\beta)^3$ is approximately equal to D_e for $\beta = 0$ at the volume fraction ϕ_2 in the equivalent PCS system. Second, note from Table I that D_e for point Brownian particles in the PCS system is relatively insensitive to the impenetrability parameter. Thus, we find that for the hard-sphere porous medium, the relation

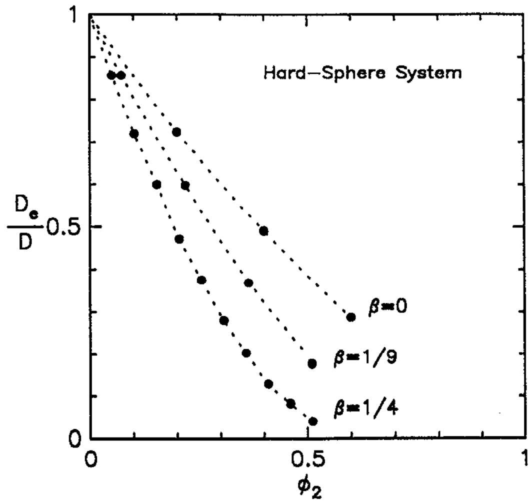

FIG. 4. The scaled effective diffusion coefficient D_e/D for porous media composed of totally impenetrable (hard) spheres of radius R for three different sized Brownian particles: $\beta = 0$, $\beta = 1/9$, and $\beta = 1/4$. Here βR is the radius of the Brownian particles. The cases $\beta = 1/9$ and $\beta = 1/4$ were computed in the present work. The instance $\beta = 0$ was evaluated in Ref. 8.

$$D_e[\phi_2/(1+\beta)^3;\beta] = D_e[\phi_2;0] \tag{28}$$

enables one to accurately estimate the effective diffusion coefficient $D_e[\beta]$ given the result $D_e[0]$. The results summarized in Fig. 4 validate relation (28).

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