Trapping of finite-sized Brownian particles in porous media

S. Torquato[a)]
Courant Institute of Mathematical Sciences, New York University, New York, New York 10012

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It is shown that the trapping of finite-sized spherical Brownian particles of radius βR in a system of *interpenetrable* spherical traps of radius R is isomorphic to the trapping of "point" Brownian particles ($\beta = 0$) in a particular system of *interpenetrable* spherical traps of radius $(1+\beta)R$. This isomorphism in conjunction with previous trapping-rate data for $\beta = 0$ is employed to compute the trapping rate for the case $\beta = 1/4$ in a system of *hard* spherical traps as a function of trap volume fraction. The effect of increasing the size of the Brownian particles is to increase the trapping rate relative to the instance of point Brownian particles.

I. INTRODUCTION

The transport of particles in porous media which are of the order of the size of the pores is of importance in a variety of chemical and physical applications.[1-5] Some examples include separation or catalytic processes in zeolites, reverse osmosis membrane separation, and gel size-exclusion chromatography. Diffusion measurements in porous media, in particular, can serve as a tool in characterizing the pore structure over a range of molecular and macroscopic length scales.[6] Transport of finite-sized particles in porous media is hindered (relative to an unbounded system) due, in part, to the fact that the finite-sized particle is excluded from a fraction of the pore volume. Recently, Sahimi and Jue[4] related the effective diffusivity of macromolecules for a lattice model of porous media to the size of the molecules and the mean pore size.

The problem of diffusion-controlled reactions among perfectly absorbing, static traps is still attracting the attention of researchers, even though it has been around for 75 years.[7] A key macroscopic quantity here is the trapping rate k which is equal to the inverse of the average survival time of a Brownian particle. Virtually all previous studies consider "point" Brownian particles, i.e., particles with zero radius. Considerable attention has been paid to correcting the dilute-limit Smoluchowski result for k of continuum (off-lattice) models at arbitrary trap concentrations, i.e., when competition between traps cannot be neglected.[8-13] To our knowledge, determination of the trapping rate k when the diffusing particles have *nonzero* radii relative to the traps has not been considered for continuum models at arbitrary trap volume fractions. It is expected that because of exclusion-volume effects, the finite-sized Brownian particles will not survive as long as point particles and hence the former should possess a higher trapping rate.

The purpose of this note is to determine the trapping rate k among a random distribution of identical spherical traps of radius R at number density ρ when the diffusing particles are spheres with radius βR, $\beta \geqslant 0$. It is shown that once the solution for the trapping rate is known for the case of point Brownian particles ($\beta = 0$), one can then obtain the corresponding result for the finite-sized case (arbitrary β). This isomorphism combined with the trapping rate data of Lee *et al.*[13] for $\beta = 0$ in a system of interpenetrable traps is used to compute k for $\beta = 1/4$ in a system of *hard* spherical traps as a function of trap volume fraction.

II. TRAPPING OF FINITE-SIZED BROWNIAN PARTICLES

The trapping rate $k(\beta)$ associated with a random distribution of identical spherical traps of radius R at number density ρ in which there are diffusing spherical particles of radius βR can be determined from $k(0)$ for a particular system of interpenetrable spheres by exploiting a simple observation. To introduce this observation, consider the diffusion of a tracer particle of radius b in the space exterior to a system of *hard spherical inclusions* of radius a with number density ρ. (As will become apparent, the ensuing argument is not restricted to hard inclusions and hence applies to partially penetrable or overlapping inclusions.) Because of exclusion-volume effects, the fraction of volume available to the center of the tracer particle of radius b for $b > 0$ is less than the porosity (i.e., the fraction of volume available to a point tracer). The key observation is that the process with $b \geqslant 0$ is isomorphic to the diffusion of a point tracer in the space exterior to inclusions of radius $a + b$ (centered at the same positions the original inclusions of radius a) at number density ρ possessing a hard core of radius a, surrounded by a perfectly concentric shell of thickness b. The latter description is precisely the penetrable-concentric shell (PCS) model introduced previously by the author to study the effect of "connectedness" of the particle phase on the effective conductivity of such a suspension.[14] The dimensionless ratio

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

is referred to as the "impenetrability" parameter or index since it is a relative measure of the size of the hard core. The values $\epsilon = 0$ and $\epsilon = 1$ corresponding to "fully penetrable" and "totally impenetrable" spheres, respectively. The fraction of volume available to the center of the tracer particle $\phi_1(\rho, a+b)$ is equal to the volume fraction available to a point tracer in the PCS model. Therefore, the fraction of volume unavailable to a tracer particle $\phi_2(\rho, a+b)$ is simply given by

[a] Permanent address: Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC 27695-7910.

$$\phi_2(\rho,a+b)=1-\phi_1(\rho,a+b). \tag{2}$$

When $b=0$, the volume fraction of the hard cores is simply given by

$$\phi_2(\rho,a)=\rho\frac{4\pi}{3}a^3 \tag{3}$$

and $\phi_1(\rho,a)$ is then just the standard porosity of the system. Now $\phi_2(\rho,a+b)$ is 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, i.e.,

$$\rho\frac{4\pi}{3}a^3<\phi_2(\rho,a+b)\leqslant\rho\frac{4\pi}{3}(a+b)^3. \tag{4}$$

Therefore, employing the aforementioned isomorphism, one can obtain the trapping rate for Brownian particles of radius b in a system of hard spherical traps of radius a, $k[\phi_2(\rho,a);b]$, from the corresponding result for point particles in the PCS model from the relation

$$k[\phi_2(\rho,a);b]=k[\phi_2(\rho,a+b);0]. \tag{5}$$

As shall be shown, this relation is not restricted to the case of hard inclusions as used in the above argument. The trapping rate in the PCS model has been computed by Lee *et al.*[13] using Monte Carlo simulations, but these authors did not make use of the isomorphism described here to compute the k for finite-sized Brownian particles. In what follows, the data of Lee *et al.* are employed in this way. However, in order to do so, one must first obtain the appropriate expression for the *volume fraction* ϕ_2 in the isomorphic PCS model.

In order to accomplish this task, we will apply the recent results of Torquato *et al.*[15] for the so-called "nearest-neighbor" distribution functions[16] $E_v(r)$ and $H_v(r)$ for a random system of identical spherical inclusions of radius a at number density ρ and employ the aforementioned isomorphism. The "exclusion" probability function

$$E_v(r)=-\frac{\partial H_v(r)}{\partial r} \tag{6}$$

is equal to the probability that a spherical cavity (centered at some arbitrary point) is empty of inclusion centers. $H_v(r)dr$ is the probability that at an arbitrary point in the system the center of the nearest inclusion lies at a distance r and $r+dr$. Now $E_v(r)$ can be reinterpreted as the fraction of volume available to a "test" particle of radius $b=r-a$ when inserted into a system of spherical inclusions of radius a at number density ρ, and thus is equal to $\phi_1(\rho,a+b)$.

Similarly, the nearest-neighbor probability density $H_v(r)$ can be interpreted as the surface (per unit volume) available to a test particle of radius $b=r-a$, denoted by $s(\rho,a+b)$. The quantity $s(\rho,a)$ is then simply the specific surface (surface area per unit volume) of the inclusion-pore interface.

Torquato *et al.*[15] obtained, among other results, exact integral representations of $E_v(r)$ and $H_v(r)$ in terms of the n-body distribution functions which statistically characterize the structure of the system. However, since the higher-order distribution functions are generally never known, an exact evaluation of $E_v(r)$ and $H_v(r)$ is not possible in two and higher dimensions. Accordingly, Torquato *et al.* derived two different sets of accurate expressions for the quantities within the framework of the Percus–Yevick and Carnahan–Starling approximations, respectively, for systems of hard spherical inclusions. These results were compared to scaled-particle approximations[17] and computer-simulation experiments.[18] It was found[15] that the Carnahan–Starling expressions generally gave excellent and the best agreement with data (Percus–Yevick relations giving the next best agreement):

$$E_v(x,\eta)=(1-\eta)\exp[-\eta(8ex^3+12fx^2+24gx+h)],\quad x\geqslant\frac{1}{2}, \tag{7}$$

$$H_v(x,\eta)=\frac{12\eta}{a}E_v(x,\eta),\quad x\geqslant\frac{1}{2}, \tag{8}$$

where

$$x=\frac{r}{2a}, \tag{9}$$

$$\eta=\rho\frac{4\pi}{3}a^3, \tag{10}$$

$$e(\eta)=\frac{(1+\eta)}{(1-\eta)^3}, \tag{11}$$

$$f(\eta)=\frac{-\eta(3+\eta)}{2(1-\eta)^3}, \tag{12}$$

$$g(\eta)=\frac{\eta^2}{2(1-\eta)^3}, \tag{13}$$

$$h(\eta)=\frac{-9\eta^2+7\eta-2}{2(1-\eta)^3}. \tag{14}$$

Relations (7) and (8) in conjunction with the isomorphism described above are now employed to obtain the volume fraction and specific surface available to a test particle of radius b in a system of hard spherical inclusions of radius a at number density ρ. Thus, in terms of dimensionless independent variables, we have

$$\phi_1(\eta,\epsilon)=E_v\left(\frac{1}{2\epsilon},\eta\right), \tag{15}$$

$$s(\eta,\epsilon)=H_v\left(\frac{1}{2\epsilon},\eta\right), \tag{16}$$

where we have used the fact that $x=\epsilon/2$, ϵ being the impenetrability parameter given by Eq. (1).

More generally, consider the insertion of a test particle of radius βR into a system of *interpenetrable* spheres of radius R having hard cores of radius λR surrounded by perfectly penetrable concentric shells of thickness $(1-\lambda)R$. This is isomorphic to the insertion of a test particle of radius $b=(1-\lambda+\beta)R$ into a system of hard spherical inclusions of radius $a=\lambda R$. Therefore, for the general interpenetrable-inclusion case, one has

$$\phi_1(\eta,\epsilon,\beta)=E_v\left(\frac{1+\beta}{2\lambda},\eta\lambda^3\right), \tag{17}$$

$$s(\eta,\epsilon,\beta)=H_v\left(\frac{1+\beta}{2\lambda},\eta\lambda^3\right), \tag{18}$$

where

$$\epsilon=\frac{\lambda}{1+\beta}, \tag{19}$$

$$\eta=\rho\frac{4\pi R^3}{3}. \quad (20)$$

The quantities E_v and H_v are given by relations (7) and (8), respectively. Note for totally impenetrable or hard inclusions ($\lambda=1$), $\epsilon=1/(1+\beta)$, and Eqs. (17) and (18) become identical to Eqs. (15) and (16), respectively. Expressions (17) and (18) are new within the framework of the Carnahan–Starling approximations (7) and (8), respectively. Rikvold and Stell,[19] however, were the first to approximate $\phi_1(\eta,\lambda,\beta)$ and $s(\eta,\lambda,\beta)$ using the scaled-particle approximations of Reiss *et al.*[17] Observe that $\eta\lambda^3$ [where η is now given by Eq. (20)] represents the volume fraction occupied by the hard cores. The largest attainable value of $\eta\lambda^3$ is given by the close-packing value for the microstructure under consideration. The largest close-packing value for $\eta\lambda^3$ is $\sqrt{2}\pi/6\simeq 0.740$, corresponding to face-centered-cubic close packing of the hard cores. A value of $\eta\lambda^3$ equal to 0.64 corresponds approximately to the random-close-packing value.[15]

For point test particles ($\beta=0;\epsilon=\lambda$), relations (17) and (18) yield, respectively, the porosity and specific surface as

$$\phi_1(\eta,\lambda,0)=E_v\left(\frac{1}{2\lambda},\eta\lambda^3\right), \quad (21)$$

$$s(\eta,\lambda,0)=H_v\left(\frac{1}{2\lambda},\eta\lambda^3\right). \quad (22)$$

In the extreme limits of fully penetrable ($\lambda=0$) and totally impenetrable ($\lambda=1$) spheres, Eqs. (21) and (22) give exact results, i.e.,

$$\phi_1=\exp(-\eta),\quad s=\frac{3}{R}\eta\phi_1,\quad \text{for } \lambda=0, \quad (23)$$

$$\phi_1=1-\eta,\quad s=\frac{3}{R}\eta,\quad \text{for } \lambda=1. \quad (24)$$

If the test particles of radius βR and the interpenetrable inclusions of radius R are regarded to be the Brownian particles and traps, respectively, then Eq. (5) for the trapping rate can be recast as

$$k\,[\phi_2(\eta,\lambda,0);\beta]=k\,[\phi_2(\eta,\epsilon,\beta);0]. \quad (25)$$

To summarize, if the trapping rate associated with the diffusion of point particles in a system of interpenetrable, identical traps with radius $(1+\beta)R$, impenetrability index $\epsilon=\lambda/(1+\beta)$, and trap volume fraction $\phi_2(\eta,\epsilon,\beta)$ [the right-hand side of Eq. (25)] is known, then the trapping rate associated with the diffusion of finite-sized particles of radius βR in a system of interpenetrable, identical traps with radius R, impenetrability index λ, and trap volume fraction $\phi_2(\eta,\lambda,0)$ [the left-hand side of Eq. (25)] is also known.

III. CALCULATION OF THE TRAPPING RATE OF FINITE-SIZED BROWNIAN PARTICLES

It is desired to calculate the trapping rate for the diffusion of particles of radius $R/4$ in a system of totally impenetrable traps ($\lambda=1$) of radius R as function of the trap volume fraction ϕ_2. This is accomplished by utilizing the results of the previous section and the trapping-rate simulation data of Lee *et al.*[13] for the diffusion of point particles in a system of traps in the PCS model with $\lambda=0.8$. For this special case, relation (25) becomes

$$k\,[\phi_2(\eta,1,0);0.25]=k\,[\phi_2(\eta,0.8,0.25);0]. \quad (26)$$

This result combined with Eq. (21) and the data of Ref. 13 yield the trapping rate for $\beta=1/4$ in a system of hard traps as a function of the volume function of the hard traps $\phi_2(\eta,1,0)$ and is summarized in Fig. 1. Included in the figure is the corresponding result for point Brownian particles ($\beta=0$). Here

$$k_s=\frac{3\phi_2}{(1+\beta)^2R^2} \quad (27)$$

is the dilute-limit Smoluchowski result for interpenetrable spherical traps of radius $(1+\beta)R$ and ϕ_2 is the associated trap volume fraction. Not surprisingly, since finite-sized Brownian particles do not survive as long as point Brownian particles, on the average, the trapping rate for $\beta=1/4$ is larger than for $\beta=0$ at fixed ϕ_2.

Lee *et al.* actually computed $k(\beta=0)$ for three different values of the impenetrability index; $\lambda=0$, 0.8, and 1. Denoting this trapping rate simply by $k(\lambda,0)$, we note in passing that given the trapping rate for hard traps $k(1,0)$, one can obtain the corresponding result for traps with impenetrability index λ at the *same trap volume fraction* by the approximate simple scaling relation

$$\frac{k(1,0)}{k(\lambda,0)}\simeq\left[\frac{s(1)}{s(\lambda)}\right]^{\alpha}. \quad (28)$$

Here $s(1)$ and $s(\lambda)$ are the specific surfaces of PCS systems for $\lambda=1$ and arbitrary λ, respectively, at the same trap volume ϕ_2 and $\alpha(\lambda)$ is an exponent which depends only on λ (i.e., it is independent of ϕ_2); $\alpha\simeq 19/4$ for $\lambda=0.8$ and $\alpha\simeq 13/4$ for $\lambda=0$. The simple scaling relation (28) was not given in the paper by Lee *et al.*

As a final remark, we note that the isomorphism described here is also being applied to study the effective diffu-

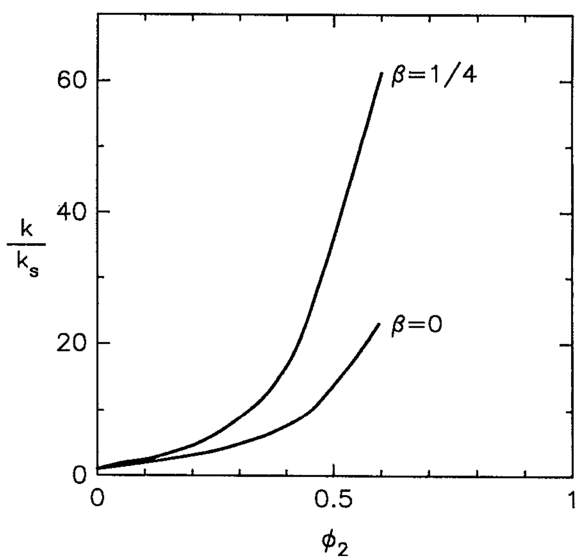

FIG. 1. The scaled trapping rate k/k_s as a function of the trap volume fraction ϕ_2 for point ($\beta=0$) and finite-sized ($\beta=1/4$) Brownian particles in a system of hard traps of radius R. Here β is the ratio of the radius of the Brownian particle to the radius of a trap.

sion coefficient of finite-sized Brownian particles in a bed of interpenetrable spheres.[20] Here hindered diffusion due to exclusion-volume effects results in a lower effective diffusion coefficient relative to the case of point Brownian particles.

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