Diffusion and reaction in heterogeneous media: Pore size distribution, relaxation times, and mean survival time

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Diffusion and reaction in heterogeneous media plays an important role in a variety of processes arising in the physical and biological sciences. The determination of the relaxation times T_n $(n = 1,2,...)$ and the mean survival time τ is considered for diffusion and reaction among *partially* absorbing traps with dimensionless surface rate constant $\bar{\kappa}$. The limits $\bar{\kappa} = \infty$ and $\bar{\kappa} = 0$ correspond to the diffusion-controlled case (i.e., perfect absorbers) and reaction-controlled case (i.e., perfect reflectors), respectively. Rigorous lower bounds on the principal (or largest) relaxation time T_1 and mean survival time τ for arbitrary $\bar{\kappa}$ are derived in terms of the *pore size distribution* $P(\delta)$. Here $P(\delta)d\delta$ is the probability that a randomly chosen point in the pore region lies at a distance δ and $\delta + d\delta$ from the *nearest* point on the pore–trap interface. The aforementioned moments and hence the bounds on T_1 and τ are evaluated for distributions of interpenetrable spherical traps. The length scales $\langle\delta\rangle$ and $\langle\delta^2\rangle^{1/2}$, under certain conditions, can yield useful information about the times T_1 and τ, underscoring the importance of experimentally measuring or theoretically determining the pore size distribution $P(\delta)$. Moreover, rigorous relations between the relaxation times T_n and the mean survival time are proved. One states that τ is a certain weighted sum over the T_n, while another bounds τ from above and below in terms of the principal relaxation time T_1. Consequences of these relationships are examined for diffusion interior and exterior to distributions of spheres. Finally, we note the connection between the times T_1 and τ and the fluid permeability for flow through porous media, in light of a previously proved theorem, and nuclear magnetic resonance (NMR) relaxation in fluid-saturated porous media.

I. INTRODUCTION

Transport problems involving simultaneous diffusion and reaction in heterogeneous media abound in physical and biological sciences (see, e.g., the review article of Weiss[1] and references therein). Examples are found in such widely different processes as heterogeneous catalysis, cell metabolism, diffusion of molecules in DNA, migration of atoms and defects in solids, colloid or crystal growth, and the decay of nuclear magnetism in fluid-saturated porous media.

We consider the problem of diffusion and reaction among *partially absorbing* "traps" in which the concentration field of the reactants $c(\mathbf{r},t)$ at position $\mathbf{r}$ exterior to the traps and time t is generally governed by the equation

$$\frac{\partial c}{\partial t} = D\Delta c - \kappa_B c + G, \tag{1.1}$$

with the boundary condition at the fluid–trap (or pore–solid) interface given by

$$D\frac{\partial c}{\partial n} + \kappa c = 0 \tag{1.2}$$

and initial conditions. Here D is the diffusion coefficient of the reactant, κ_B is a bulk rate constant, κ is a surface rate constant, G is a generation rate per unit volume trap-free volume, and $\mathbf{n}$ is the unit outward normal from the pore space. Note that for infinite surface reaction ($\kappa = \infty$), the process is diffusion controlled and the Dirichlet boundary condition applies, i.e., the traps are perfect absorbers. In the opposite extreme of vanishing surface reaction ($\kappa = 0$), the Neumann boundary condition holds, i.e., the traps are perfect reflectors. Without loss of generality, we set the bulk rate constant equal to zero since the solution of Eq. (1.1) with $\kappa_B \neq 0$ is simply related to the one with $\kappa_B = 0$ (see Sec. II).

In this paper, we shall study Eq. (1.1) with condition (1.2) for two different cases:

(i) the *time-dependent* solution with $\kappa_B = G = 0$;

(ii) and the *steady-state* solution with $\kappa_B = 0$.

The quantities of central interest are the *relaxation times* T_n, $n = 1,2,...$ (or eigenvalues) of problem (i) and the *mean survival time* τ of a Brownian particle of problem (ii). The times T_1 and τ are linked intimately to characteristic length scales of the pore region. Whereas the *principal* relaxation time T_1 is governed by diffusion occurring in the largest cavities (pores) in the system, the mean survival time τ is determined by the "average pore size." The key fundamental question is "what precisely is the relationship between the pore statistics and these time scales?" It should be mentioned that there is recent interest in both T_1 and τ in connection with the nuclear magnetic resonance (NMR) response of fluid-saturated porous media,[2,3] where $c(\mathbf{r},t)$ in this problem represents the nuclear magnetization.

The principal findings of this article can be summarized as follows:

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(1) The derivation of rigorous lower bounds on both T_1 and τ in terms of lower-order moments $\langle\delta\rangle$ and $\langle\delta^2\rangle$ of the "pore size distribution" $P(\delta)$ for surface rate constants κ in the range $0<\kappa\leqslant\infty$. Here $P(\delta)d\delta$ is the probability that a randomly chosen point in the pore region lies at a distance δ and $\delta+d\delta$ from the *nearest* point on the pore–solid interface.

(2) The calculation of the moments of $\langle\delta\rangle$ and $\langle\delta^2\rangle$ for distributions of interpenetrable spherical traps and hence the evaluation of the aforementioned bounds on T_1 and τ for such microgeometries. Under certain conditions, the length scales $\langle\delta\rangle$ and $\langle\delta^2\rangle^{1/2}$ can yield useful information about the times T_1 and τ, thus underscoring the importance of experimentally measuring or theoretically determining the pore size distribution $P(\delta)$.

(3) Establishment of the rigorous relations between the relaxation times T_n and mean survival time τ. One relation states that τ is simply a weighted sum over T_n, while another relation bounds τ from above and below in terms of the principal relaxation time T_1.

(4) Application of the results of Eq. (3) for diffusion interior and exterior to distributions of spheres.

(5) In light of a recent theorem,[4] we note the connection between the times T_1 and τ and the fluid permeability for flow through the same porous medium and NMR relaxation in fluid-saturated porous media.

II. PORE SIZE DISTRIBUTION, LENGTH SCALES, AND TIME SCALES

A. Definition of fundamental quantities

The random porous medium is a domain of space $\mathscr{V}(\omega)\in\mathbf{R}^3$ (where the realization ω is taken from some probability space Ω) of volume V which is composed of two regions: the void (pore) region $\mathscr{V}_1(\omega)$ through which fluid is transported of volume fraction (porosity) ϕ_1 and a solid-phase region $\mathscr{V}_2(\omega)$ of volume fraction ϕ_2. Let V_i be the volume of region $\mathscr{V}_i$, $V=V_1+V_2$ be the total system volume, $\partial\mathscr{V}(\omega)$ be the surface between $\mathscr{V}_1$ and $\mathscr{V}_2$, and S be the total surface area of the interface $\partial\mathscr{V}$. The characteristic function of the pore region is defined by

$$I(\mathbf{r},\omega)=\begin{cases}1, & \mathbf{r}\in\mathscr{V}_1(\omega)\\ 0, & \mathbf{r}\in\mathscr{V}_2(\omega)\end{cases}. \tag{2.1}$$

The characteristic function of the pore–solid interface is defined by

$$M(\mathbf{r},\omega)=|\nabla I(\mathbf{r},\omega)|. \tag{2.2}$$

For statistically homogeneous media, the ensemble averages (indicated with angular brackets) of Eqs. (2.1) and (2.2) yield

$$\phi_1=\langle I\rangle=\lim_{V_1,V\to\infty}\frac{V_1}{V}, \tag{2.3}$$

$$\sigma=\langle M\rangle=\lim_{S,V\to\infty}\frac{S}{V}, \tag{2.4}$$

which are the porosity and specific surface (interface area per unit system volume V), respectively.

The pore size distribution[5] $P(\delta)$ is defined in such a way that $P(\delta)d\delta$ is the probability that a randomly chosen point in the pore region $\mathscr{V}_1(\omega)$ lies at a distance between δ and $\delta+d\delta$ from the *nearest* point on the pore–solid interface $\partial\mathscr{V}$. $P(\delta)$ normalizes to unity, i.e.,

$$\int_0^\infty P(\delta)d\delta=1. \tag{2.5}$$

At the extreme values of pore size, we have

$$P(0)=\frac{\sigma}{\phi_1}\quad\text{and}\quad P(\infty)=0, \tag{2.6}$$

where σ/ϕ_1 is the interfacial area per unit pore volume V_1. It is useful to define the cumulative distribution function as

$$F(\delta)=\int_\delta^\infty P(r)dr. \tag{2.7}$$

$F(\delta)$ is the fraction of pore space which has a pore diameter larger than δ. Clearly,

$$F(0)=1\quad\text{and}\quad F(\infty)=0. \tag{2.8}$$

The moments of $P(\delta)$ defined as

$$\langle\delta^n\rangle=\int_0^\infty \delta^n P(\delta)d\delta \tag{2.9}$$

are of central interest in this study. Integrating Eq. (2.9) by parts and using Eq. (2.7) gives the alternative representation of the moments in terms of the cumulative pore size distribution

$$\langle\delta^n\rangle=n\int_0^\infty \delta^{n-1}F(\delta)d\delta. \tag{2.10}$$

One of the transport problems examined in the ensuing section is that of diffusion among traps in which we are interested in computing the mean survival time and relaxation time. Letting D be the diffusion coefficient of the fluid, we define for such processes two time scales as follows:

$$t_S=\frac{\langle\delta\rangle^2}{D}, \tag{2.11}$$

$$t_R=\frac{\langle\delta^2\rangle}{D}. \tag{2.12}$$

It is shown in Sec. III that t_S is a measure of the mean survival time of a Brownian particle among traps with arbitrary surface reaction. Similarly, t_R is a measure of the relaxation time associated with the smallest eigenvalue (i.e., the dominant relaxation time) for unsteady diffusion among *perfectly absorbing* traps (i.e., traps with infinite surface reaction). For traps with arbitrary surface reaction, the dominant relaxation time depends on both t_T and t_R.

B. Calculations of the pore size distribution and moments for transport exterior to random beds of identical spheres

For porous media of general morphology, the theoretical determination of the pore size distribution is quite complex. Indeed, the calculation of $P(\delta)$ for the simple model of flow around a random bed of mutually impenetrable identical spheres is nontrivial.[6] Here we shall apply the recent theoretical results of Torquato, Lu, and Rubinstein[6,7] for the so-called "nearest-neighbor" distribution functions to obtain $P(\delta)$ for random distributions of identical interpenetrable spheres of radius a which comprise phase 2 or the solid phase. Using this information, we then compute the first and second moments $\langle\delta\rangle$ and $\langle\delta^2\rangle$ for such systems as a function of the solid volume fraction ϕ_2.

The quantities $P(\delta)$ and $F(\delta)$ are actually trivially related to the "void" nearest-neighbor distribution function $H_v(r)$ and void exclusion probability $E_v(r)$, respectively, studied by Torquato *et al.* for systems of spherical inclusions. H_v and E_v are related by

$$H_v(r) = -\frac{\partial E_v(r)}{\partial r}. \tag{2.13}$$

$E_v(r)$ is the probability of finding a spherical region of radius r (centered at some arbitrary point) empty of centers of the inclusions of radius a. This is equivalent to the probability of inserting a "test" particle of radius $b = r - a$ (at some arbitrary position) in the system of spheres of radius a. $H_v(r)dr$ is the probability that the center of the *nearest* inclusion of radius a is at a distance between r and $r + dr$ from the center of the test particle of radius $b = r - a$. Note that

$$H_v(a) = \sigma, \quad E_v(a) = \phi_1, \quad H_v(\infty) = E_v(\infty) = 0. \tag{2.14}$$

Recognizing that b corresponds to δ in the present paper and employing the aforementioned definitions for the statistical quantities, we have

$$P(\delta) = \frac{H_v(\delta + a)}{\phi_1}, \tag{2.15}$$

$$F(\delta) = \frac{E_v(\delta + a)}{\phi_1}. \tag{2.16}$$

The moments defined by Eq. (2.9) for this model are also given by

$$\langle\delta^n\rangle = \frac{1}{\phi_1}\int_a^\infty (r-a)^n H_v(r)dr, \tag{2.17}$$

or

$$\langle\delta^n\rangle = \frac{n}{\phi_1}\int_a^\infty (r-a)^{n-1} E_v(r)dr. \tag{2.18}$$

Torquato *et al.* derived exact integral representations of $H_v(r)$ and $E_v(r)$ for identical spheres that interact with an arbitrary potential in terms of n-body distribution functions. However, because the higher-order n-body distribution functions are not known for arbitrary potential, an exact evaluation of H_v and E_v is generally not possible. For the case of mutually totally impenetrable spheres at number density ρ, these authors obtained the following approximations for H_v and E_v that were in excellent agreement with computer simulations:[8]

$$E_v(x) = (1-\eta)\exp[-\eta(8ex^3 + 12fx^2 + 24gx + h)], \quad x > \tfrac{1}{2} \tag{2.19}$$

$$H_v(x) = \frac{12\eta}{a}(ex^2 + fx + g)E_v(x), \quad x > \tfrac{1}{2} \tag{2.20}$$

where

$$e = \frac{(1+\eta)}{(1-\eta)^3}, \tag{2.21}$$

$$f = -\frac{\eta(3+\eta)}{2(1-\eta)^3}, \tag{2.22}$$

$$g = \frac{\eta^2}{2(1-\eta)^3}, \tag{2.23}$$

$$h = \frac{-9\eta^2 + 7\eta - 2}{2(1-\eta)^3}, \tag{2.24}$$

$$x = \frac{r}{2a}. \tag{2.25}$$

Here

$$\eta = \rho\frac{4\pi}{3}a^3 \tag{2.26}$$

is a reduced density that for impenetrable spheres is identical to the sphere volume fraction ϕ_2. For interpenetrable spheres, $\eta \neq \phi_2$.

The concept of a random bed of spheres becomes very general if the spheres are allowed to *overlap* or *interpenetrate* one another to some degree. A useful interpenetrable-sphere model is the so-called *penetrable-concentric-shell* (PCS) or *cherry-pit* model[9] in which each sphere of radius a is composed of a *hard* core of diameter λa, encompassed by a perfectly penetrable concentric shell of thickness $(1-\lambda a)$, $0 \leqslant \lambda \leqslant 1$. The extreme limits of the *impenetrability parameter* λ, $\lambda = 0$ and $\lambda = 1$, correspond to the cases of *fully penetrable* (i.e., spatially uncorrelated or Poisson distributed centers) and *totally impenetrable* spheres, respectively. The cherry-pit model enables one to vary the "connectedness" of the particle phase by varying λ; e.g., for $\lambda = 0$ and $\lambda = 1$, the particle phase percolation thresholds, respectively, correspond to $\phi_2^c \simeq 0.3$ (Ref. 10) and $\phi_2^c \simeq 0.64$ (Ref. 11). As observed by Torquato *et al.*, the quantities $H_v(x)$ and $E_v(x)$ for arbitrary λ can be obtained from the corresponding quantities for $\lambda = 1$ [i.e., Eqs. (2.19) and (2.20)] by simply replacing a (on the right-hand side of the relations) with λa. For example, carrying out this substitution and taking the limit $\lambda \to 0$, give the appropriate simple results for fully penetrable spheres

$$E_v(x) = \exp(-8\eta x^3), \quad x \geqslant 0, \tag{2.27}$$

$$H_v(x) = \frac{12\eta x^2}{a}\exp(-8\eta x^3), \quad x \geqslant 0. \tag{2.28}$$

Note from Eq. (2.14) and the relations above, we have the well-known results

$$E_v(1/2) = \phi_1 = 1 - \phi_2 = \exp(-\eta), \tag{2.29}$$

$$H_v(1/2) = \sigma = \frac{3}{a}\eta\phi_1. \tag{2.30}$$

In Fig. 1, we plot the dimensionless pore size distribution $P(\delta)$ in the PCS model for $\lambda = 0$, 0.8, and 1, and an inclusion volume fraction $\phi_2 = 0.5$ using relations (2.15) and (2.20) for spheres of unit diameter (i.e., $2a = 1$). Figure 2 shows corresponding plots for the cumlative pore size distribution $F(\delta)$.

Relations (2.17)–(2.20) enable us to compute the moments $\langle\delta^n\rangle$ for spheres in the cherry-pit model at various

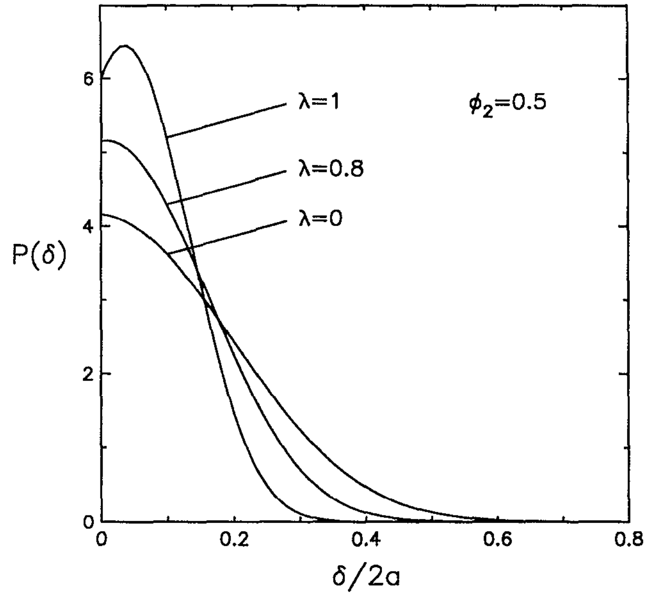

FIG. 1. The pore size distribution $P(\delta)$ vs the dimensionless distance $\delta/2a$ for distributions of spheres of radius a in the penetrable-concentric-shell or cherry-pit model (Ref. 9) for three different values of the impenetrability parameter λ ($\lambda = 0, 0.8$, and 1). The pore region is the space exterior to the spheres. Here the porosity ϕ_1 is equal to the trap volume function $\phi_2 = 0.5$.

sphere volume fractions ϕ_2. Tables I–III give the first two moments as functions of ϕ_2 for $\lambda = 0, 0.8$, and 1, respectively. The last column in each of the tables gives the respective ratio $\langle\delta^2\rangle/\langle\delta\rangle^2 = t_R/t_S$ which is simply related to the dimensionless variance

$$\frac{\langle\delta^2\rangle - \langle\delta\rangle^2}{\langle\delta\rangle^2} = \frac{\langle\delta^2\rangle}{\langle\delta\rangle^2} - 1.$$

As exclusion-volume effects increase (i.e., as the degree of impenetrability λ increases), the moments $\langle\delta\rangle$ and $\langle\delta^2\rangle$ and

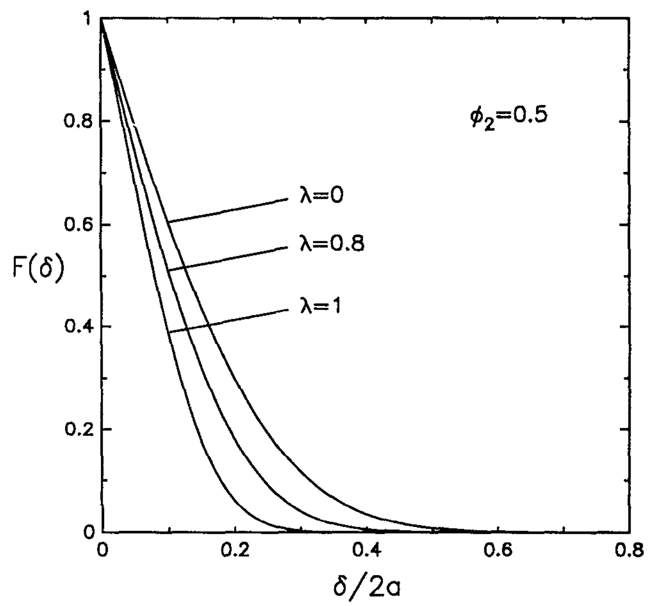

FIG. 2. The same as in Fig. 1, except for the cumulative distribution function $F(\delta)$.

TABLE I. Lower-order moments for diffusion exterior to idential spherical traps in the penetrable concentric shell or "cherry-pit" model (Ref. 9). Here the impenetrability parameter $\lambda = 0$ (i.e., fully penetrable spheres).

ϕ_2	$\frac{\langle\delta\rangle}{a}$	$\frac{\langle\delta^2\rangle}{a^2}$	$\frac{\langle\delta^2\rangle}{\langle\delta\rangle^2}$
0.1	1.018	1.395	1.346
0.2	0.6558	0.6098	1.418
0.3	0.4857	0.3472	1.472
0.4	0.3803	0.2196	1.518
0.5	0.3058	0.1458	1.559
0.6	0.2484	0.0987	1.600
0.7	0.2011	0.0663	1.639
0.8	0.1594	0.0427	1.681
0.9	0.1183	0.0242	1.729

the variance decrease at fixed volume fraction ϕ_2 as expected.

C. Pore size distribution and moments for transport interior to disconnected spherical pores

For the simple microgeometry consisting of nonoverlapping (i.e., disconnected) spherical pores of radius a, the pore size distribution is given by

$$P(\delta) = \begin{cases} \dfrac{3(a-\delta)^2}{a^3}, & \delta < a \\ 0, & \delta > a \end{cases}. \tag{2.31}$$

This expression combined with Eq. (2.9) yields the moments as

$$\langle\delta^n\rangle = \frac{6a^n}{(n+1)(n+2)(n+3)}. \tag{2.32}$$

III. BASIC EQUATIONS AND BOUNDS FOR THE RELAXATION AND SURVIVAL TIMES

A. Basic equations

1. Relaxation problem

The relaxation times associated with the decay of physical quantities such as concentration field and nuclear magnetization are related intimately to the characteristic length scales of the pore region. Let $c(\mathbf{r},t)$ generally denote the physical quantity of interest at local position $\mathbf{r}$ and time t. It

TABLE II. The same as in Table I except for $\lambda = 0.8$.

ϕ_2	$\frac{\langle\delta\rangle}{a}$	$\frac{\langle\delta^2\rangle}{a^2}$	$\frac{\langle\delta^2\rangle}{\langle\delta\rangle^2}$
0.1	0.9661	1.255	1.343
0.2	0.5957	0.501 6	1.414
0.3	0.4200	0.258 5	1.465
0.4	0.3136	0.148 2	1.507
0.5	0.2390	0.088 3	1.546
0.6	0.1830	0.052 3	1.559
0.7	0.1383	0.031 0	1.621
0.8	0.1011	0.017 0	1.663
0.9	0.0670	0.007 72	1.720

TABLE III. The same as in Table I except for $\lambda = 1$ (i.e., totally impenetrable spheres).

ϕ_2	$\frac{\langle\delta\rangle}{a}$	$\frac{\langle\delta^2\rangle}{a^2}$	$\frac{\langle\delta^2\rangle}{\langle\delta\rangle^2}$
0.1	0.9228	1.139	1.338
0.2	0.5407	0.4084	1.397
0.3	0.3624	0.1887	1.436
0.4	0.2543	0.0948	1.466
0.5	0.1803	0.0484	1.489
0.6	0.1259	0.0239	1.508

obeys the following time-dependent diffusion equation in the *finite*, but *large* pore region:

$$\frac{\partial c}{\partial t} = D\Delta c \quad \text{in} \quad \mathscr{V}_1, \tag{3.1}$$

$$c(\mathbf{r},0) = c_0 \quad \text{in} \quad \mathscr{V}_1, \tag{3.2}$$

$$D\frac{\partial c}{\partial n} + \kappa c = 0 \quad \text{on} \quad \partial\mathscr{V}, \tag{3.3}$$

where κ is the *surface rate* constant (having dimensions of length/time), Δ is the Laplacian operator, and $\mathbf{n}$ is the unit outward normal from the pore region. Note that we could have included a bulk reaction term $\kappa_B c$ on the left-hand side of Eq. (3.1), but since the solution $c(\mathbf{r},t)$ of such a situation multiplied by $\exp(\kappa_B t)$ gives the corresponding solution with $\kappa_B = 0$, we do not include bulk reaction.

The solution of Eqs. (3.1)–(3.3) can be given as an expansion in orthonormal eigenfunctions $\{\psi_n\}$:

$$\frac{c(\mathbf{r},t)}{c_0} = \sum_{n=1}^{\infty} a_n e^{-t/T_n}\psi_n(\mathbf{r}), \tag{3.4}$$

where

$$\Delta\psi_n = -\lambda_n\psi_n \quad \text{in} \quad \mathscr{V}_1, \tag{3.5}$$

$$D\frac{\partial\psi_n}{\partial n} + \kappa_s\psi_n = 0 \quad \text{on} \quad \partial\mathscr{V}, \tag{3.6}$$

$$T_n = \frac{1}{D\lambda_n}. \tag{3.7}$$

T_n are the relaxation times. The initial condition and Eq. (3.4) yield

$$\sum_{n=1}^{\infty} a_n\psi_n(\mathbf{r}) = 1. \tag{3.8}$$

The eigenfunctions ψ_n are orthonormal such that

$$\frac{1}{V_1}\int_{\mathscr{V}_1}\psi_m(\mathbf{r})\psi_n(\mathbf{r})d\mathbf{r} = \delta_{mn}, \tag{3.9}$$

so that

$$a_n = \frac{1}{V_1}\int_{\mathscr{V}_1}\psi_n(\mathbf{r})d\mathbf{r}, \tag{3.10}$$

where $V_1 = \phi_1 V$ is the total pore volume. Because the set of eigenfunctions is complete, we also have

$$\sum_{n=1}^{\infty} a_n^2 = 1. \tag{3.11}$$

Ultimately, we will pass to the limit $V_1 \to \infty$, $V \to \infty$.

At long times, the smallest eigenvalue λ_1 dominates and therefore the principal relaxation time T_1 shall be of central interest. The precise dependence of T_1 on the pore geometry is generally very complex. It is useful to introduce the dimensionless surface rate constant

$$\bar{\kappa} = \frac{\kappa l}{D} \tag{3.12}$$

and distinguish between two extreme regimes

$$\bar{\kappa} \gg 1 \quad \text{(diffusion controlled)},$$
$$\bar{\kappa} \ll 1 \quad \text{(reaction controlled)}, \tag{3.13}$$

where l is a characteristic pore length scale which may be taken to $\langle\delta\rangle$ or $\langle\delta^2\rangle^{1/2}$. In the diffusion-controlled regime, the diffusing species takes a long time to diffuse to the pore–solid interface relative to the characteristic time associated with the surface reaction, i.e., the process is governed by diffusion. In the reaction-controlled regime, the characteristic time associated with surface reaction is large compared with the diffusion time to the pore–solid interface.

2. Survival problem

A different but related diffusion problem is the one associated with steady-state diffusion of reactants among static traps with a prescribed rate of production of the reactants per unit pore volume $G(\mathbf{x})$. The trapping constant γ arising in the relation $G(\mathbf{x}) = \gamma D\overline{C}(\mathbf{x})$ for statistically homogeneous media has been expressed by Rubinstein and Torquato[12] (using the method of homogenization) in terms of a certain scaled concentration field [where $\overline{C}(\mathbf{x})$ is a mean concentration field]. The trapping constant is given by

$$\gamma = \langle u\rangle^{-1}, \tag{3.14}$$

where u solves

$$\Delta u = -1 \quad \text{in} \quad \mathscr{V}_1, \tag{3.15}$$

$$u = 0 \quad \text{on} \quad \partial\mathscr{V}. \tag{3.16}$$

As before, angular brackets denote an ensemble average. Ergodicity enables us to equate ensemble and volume averages so that

$$\langle u\rangle = \lim_{V\to\infty}\frac{1}{V}\int_{\mathscr{V}_1} u(\mathbf{r})d\mathbf{r}. \tag{3.17}$$

The trapping constant is trivially related to the *average survival time* τ of a Brownian particle by the relation[4]

$$\tau = \frac{1}{\gamma\phi_1 D} \tag{3.18}$$

and therefore use of Eq. (3.16) yields

$$\tau = \frac{\langle u\rangle}{\phi_1 D}. \tag{3.19}$$

Upon examination of derivation of Eq. (3.16) [or, equivalently, Eq. (3.19)] in Ref. 12, it is seen that expression (3.19) still holds for the more general boundary condition (3.3) at the pore–solid interface, i.e., u in Eq. (3.19) also solves

$$\Delta u = -1, \quad \text{in} \quad \mathscr{V}_1, \tag{3.20}$$

$$D\frac{\partial u}{\partial n}+\kappa u=0, \quad \text{on } \partial\mathscr{V}. \tag{3.21}$$

Of course in the case of Eq. (3.20), the mean survival time τ depends not only on D, but on κ.

In the case of the diffusion-controlled limit ($\bar{\kappa}=\infty$), variational principles have recently been derived to bound τ from below and above.[12] Moreover, accurate computer simulations of τ in this limit for distributions of identical interpenetrable spheres,[13] interpenetrable spheres with a polydispensivity in size,[14] and interpenetrable oriented spheroids[15] have been obtained using efficient random-walk techniques.

B. Bounds on the relaxation and survival times in terms of moments of the pore size distribution $P(\delta)$

For diffusion-controlled processes ($\bar{\kappa}=\infty$), Prager[16] obtained in the early 1960s simple lower bounds on the mean survival time τ and the relaxation time T_1 in terms of the characteristic time scales t_S and t_R, respectively, defined in Sec. II. Here we generalize these results for situations in which the surface reaction rate κ is finite by employing the appropriate variational principles.

1. Lower bound on principal relaxation time

The first eigenvalue $\lambda_1=(T_1D)^{-1}$ [cf. (3.5)] is bounded from above by the relation

$$(T_1D)^{-1} \leqslant \frac{(1/V)\int_{\mathscr{V}_1}\nabla\psi^*\cdot\nabla\psi^*\,d\mathbf{r}+(\kappa/DV)\int_{\partial\mathscr{V}}(\psi^*)^2dS}{(1/V)\int_{\mathscr{V}_1}(\psi^*)^2d\mathbf{r}}, \tag{3.22}$$

where ψ^* is a trial eigenfunction and dS indicates a surface integration over the pore–solid interface. This variational bound is derived in Appendix B. Now consider a trial eigenfunction of the form

$$\psi^*(\mathbf{r})=G(\delta), \tag{3.23}$$

where $\delta(\mathbf{r})$, as in Sec. II, is the minimum distance to the pore–solid interface and $G(\delta)$ is some nonstochastic function of δ. We emphasize, however, that δ is a random function of $\mathbf{r}$ since it varies from point to point in a stochastic fashion. Substitution of Eq. (3.23) into Eq. (3.22) yields, in the infinite-volume limit,

$$(T_1D)^{-1} \leqslant \frac{\int_0^\infty(dG/d\delta)^2P(\delta)d\delta+(\kappa\sigma/D\phi_1)G^2(0)}{\int_0^\infty G^2(\delta)P(\delta)d\delta}. \tag{3.24}$$

To begin with, we choose

$$G(\delta)=a^*\delta+b^*, \tag{3.25}$$

where a^* and b^* are constants to be optimized. Observe that δ vanishes at the interface and therefore the constant b^* is the only contribution at the interface. Without loss of generality, a^* is set equal to unity. Substitution of Eq. (3.25) and optimizing b^* gives a lower bound on $T_1=1/D\lambda_1$:

$$T_1 \geqslant \frac{\langle\delta^2\rangle+2\langle\delta\rangle b_*+b_*^2}{D\,[1+(\kappa\sigma/D\phi_1)b_*^2]}, \tag{3.26}$$

where

$$b_*=\frac{[1-(\kappa\sigma/D\phi_1)\langle\delta^2\rangle]+\sqrt{[1-(\kappa\sigma/D\phi_1)\langle\delta^2\rangle]^2+(4\kappa\sigma/D\phi_1)\langle\delta\rangle^2}}{2(\kappa\sigma/D\phi_1)\langle\delta\rangle}. \tag{3.27}$$

Here σ is the specific surface and σ/ϕ_1 is the *interfacial surface area per unit pore volume.* Note that the bound (3.26) depends on the first and second moments of $P(\delta)$. For fast diffusion, bound (3.26) has the asymptotic form

$$T_1 \geqslant \frac{\phi_1}{\kappa\sigma}+\frac{2(2\langle\delta\rangle^2-\langle\delta^2\rangle)}{D} \quad (\bar{\kappa}\ll 1). \tag{3.28}$$

In the slow diffusion regime, Eq. (3.26) yields the asymptotic expression

$$T_1 \geqslant \frac{\langle\delta^2\rangle}{D}+\frac{3\phi_1\langle\delta\rangle^2}{4\kappa\sigma\langle\delta^2\rangle} \quad (\bar{\kappa}\gg 1). \tag{3.29}$$

Note that in the limit $\bar{\kappa}\to\infty$, relation (3.29) recovers the diffusion-controlled limit result of Prager[16] which is just the characteristic time t_R given by Eq. (2.12). Not surprisingly, finite surface reaction leads to larger relaxation times relative to the diffusion-controlled limit.

For transport interior to nonoverlapping spherical pores of radius a, the moments are known exactly from Eq. (2.32) and therefore Eqs. (3.28) and (3.29) yield, respectively,

$$T_1 \geqslant \frac{a}{3\kappa}+\frac{a^2}{20D} \quad (\bar{\kappa}\ll 1), \tag{3.30}$$

$$T_1 \geqslant \frac{a^2}{10D}+\frac{5a}{32\kappa} \quad (\bar{\kappa}\gg 1). \tag{3.31}$$

Comparison of the relation above to the exact asymptotic expansions given in Appendix A reveals that the bounds (3.30) and (3.31) are extremely sharp. Indeed, in the infinitely weak surface reaction case, the first term of Eq. (3.30) is exact. This is expected since the mean-square displacement of a Brownian particle (because it is confined to be in a pore region characterized by a single size) is well described by the lower-order moments of $P(\delta)$. The bounds of course will not be as sharp for connected pore regions, especially when there is a wide pore size distribution. Specific calculations for transport *exterior* to distributions of spheres are given below.

We could have chosen a more complex form for $G(\delta)$. For example, let us choose

$$G(\delta)=a^*\delta^n+b^*. \tag{3.32}$$

Then Eq. (3.24) yields in the diffusion-controlled limit (with $b^*=0$)

$$T_1 \geq \frac{n^2\langle\delta^{2n-2}\rangle}{D\langle\delta^{2n}\rangle} \quad (\bar{\kappa}=\infty). \tag{3.33}$$

For the class of microgeometries examined in this study, Eq. (3.33) is optimum for $n=1$ for integer n. We include it here since there may be microstructures for which $n=1$ is not optimal. Moreover, we could have left $G(\delta)$ arbitrary and obtained the optimum $G(\delta)$ from the resulting Euler–Lagrange equation as was done by Prager for the case $\bar{\kappa}=\infty$. This procedure is avoided here because the choice (3.25) leads to simple expressions for T_1 and Prager found, by using it, very little improvement over the simple trial field δ in the diffusion-controlled limit.

2. Lower bound on survival time

Rubinstein and Torquato[12] derived a variational lower bound on the mean survival time τ in the diffusion-controlled limit. We now generalize these lower bounds to treat finite surface reaction. The following variational upper bound on the inverse mean survival time τ^{-1} exists

$$(\tau D\phi_1)^{-1}\langle u\rangle^2 \leq \frac{1}{V}\int_{\mathscr{V}_1}\nabla v\cdot\nabla v\, d\mathbf{r} + \frac{\kappa}{VD}\int_{\partial\mathscr{V}} v^2 dS. \tag{3.34}$$

This bound is proved in Appendix B. Here the average of trial concentration field v is equal to the actual concentration field u that solves Eqs. (3.20) and (3.21), i.e.,

$$\langle v\rangle = \langle u\rangle. \tag{3.35}$$

Consider a trial field of the form

$$v = \frac{\langle u\rangle J(\delta)}{\phi_1\int_0^\infty J(\delta)P(\delta)d\delta}. \tag{3.36}$$

Insertion of Eq. (3.36) into Eq. (3.34) and passing to the infinite-volume limit yields

$$(\tau D)^{-1} \leq \frac{\int_0^\infty (dJ/d\delta)^2 P(\delta)d\delta + (\kappa\sigma/D\phi_1)J^2(0)}{[\int_0^\infty J(\delta)P(\delta)d\delta]^2}. \tag{3.37}$$

Let the deterministic function J be given by

$$J(\delta) = c^*\delta + d^*, \tag{3.38}$$

where c^* and d^* are constants to be optimized. Substitution of Eq. (3.38) into Eq. (3.37) yields the *optimized lower bound* on τ:

$$\tau \geq \frac{\langle\delta\rangle^2}{D} + \frac{\phi_1}{\kappa\sigma}. \tag{3.39}$$

It is noteworthy that Eq. (3.39) is considerably simpler than bound (3.26) for the relaxation time (3.26). For $\bar{\kappa}\to\infty$, Eq. (3.39) reduces to the diffusion-controlled-limit bound obtained by Prager[16] which is just the characteristic time t_S given by Eq. (2.11). Again, finite κ yields a survival time which is larger than the one for the diffusion-controlled limit.

For transport inside spherical pores of radius a, Eqs. (2.32) and (3.39) give

$$\tau \geq \frac{a^2}{16D} + \frac{a}{3\kappa}. \tag{3.40}$$

Comparison of this result to the exact result of Appendix A shows that the bound is remarkably sharp for reasons already mentioned.

Before presenting calculations of the bounds on τ and T_1 for diffusion exterior to spheres, it is useful to make an interesting and general remark. The variational bound on T_1 [relation (3.24)] is strikingly similar to the variational bound on τ [relation (3.37)], the major difference being the denominator. Now if we let $G(\delta) = J(\delta)$, these bounds suggest that τ may be generally bounded from above by T_1. [This is most easily seen by comparing Eqs. (3.29) and (3.39) in the diffusion-controlled limit.] This physically interesting result is proved in the next subsection.

3. Calculations of bounds on τ and T_1 for transport exterior to spheres

The advantages of bounds such as Eqs. (3.26) and (3.39) are their simplicity and the fact that they can be applied to arbitrary isotropic microgeometries. For the special case of diffusion exterior to spherical traps in the PCS or cherry-pit model for $\lambda = 0$, 0.8, and 1, Tables I–III [and relations (3.26) and (3.39)] provide lower bounds on τ and T_1 for this model. In Fig. 3, we compare the lower bound (3.39) on the dimensionless survival time $\tau D/a^2$ (where a is a sphere radius) in the diffusion-controlled case ($\bar{\kappa} = \kappa a/D = \infty$) to the simulation data of Lee *et al.*[13] for the cherry-pit model[9] in the extreme limits of the impenetrability parameter λ. Comparison to simulation results for τ shows that the lower bounds on τ become relatively sharper as the trap volume fraction ϕ_2 increases. The reason for this is that the square of the moment $\langle\delta\rangle$ provides an increasingly better estimate of the actual mean-square displacement of

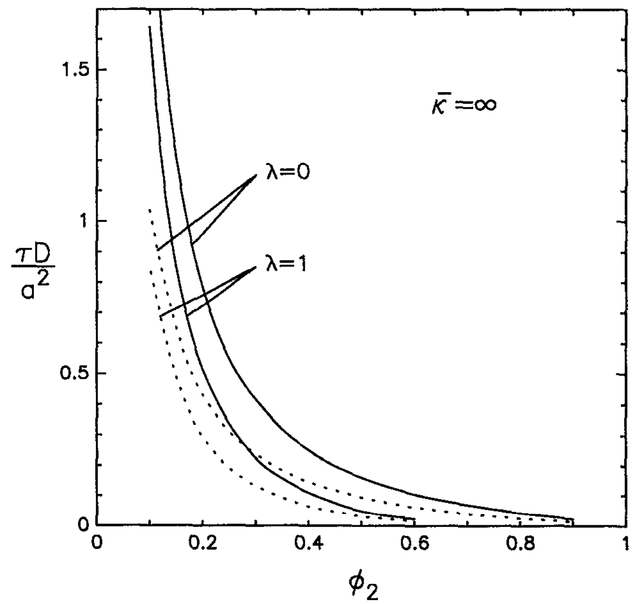

FIG. 3. Comparison of the lower bound (3.39) on the dimensionless survival time $\tau D/a^2$ in the diffusion-controlled limit ($\bar{\kappa}=\infty$) vs trap volume fraction ϕ_2 (dotted lines) to the simulation data (solid lines) of Lee *et al.* (Ref. 13) for spherical traps of radius a in the cherry-pit model (Ref. 9) in the extreme limits of the impenetrability parameter λ, i.e., $\lambda = 0$ and $\lambda = 1$. Here $\bar{\kappa} = \kappa a/D$.

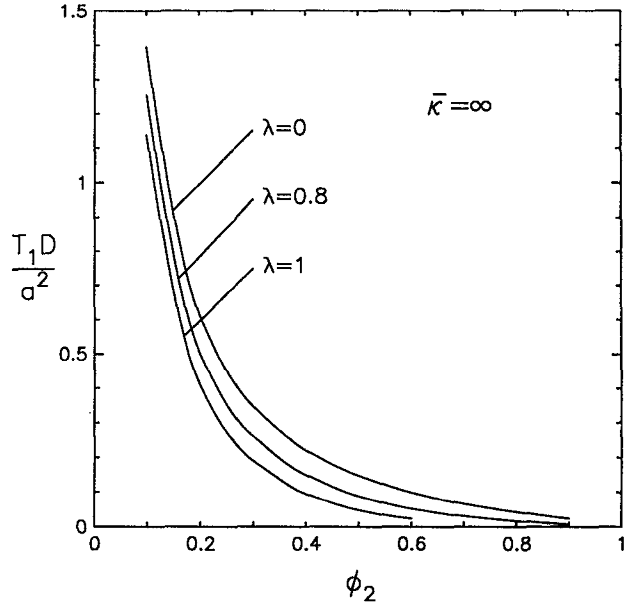

FIG. 4. Lower bound (3.26) on the dimensionless relaxation time $T_1 D/a^2$ vs the trap volume fraction ϕ_2 in the cherry-pit model (Ref. 9) for impenetrability parameter $\lambda = 0$, 0.8, and 1 with $\bar{\kappa} = \kappa a/D = \infty$.

a Brownian particle as ϕ_2 is made larger or as the porosity $\phi_1 = 1 - \phi_2$ is made smaller. For example, for $\lambda = 1$ (totally impenetrable traps), the actual result is about two times as large as the bound (3.33) for $\phi_2 = 0.1$ and 1.48 times as large as the bound for $\phi_2 = 0.6$. Real porous media are characterized by small porosities ϕ_1 or large solid phase volume fractions ϕ_2, the regime in which the bounds are relatively sharp.

In Fig. 4, we plot the lower bound (3.26) on the dimensionless relaxation time $T_1 D/a^2$ vs the trap volume fraction ϕ_2 in the cherry-pit model for $\lambda = 0$, 0.8, and 1 with $\bar{\kappa} = \kappa a/D = \infty$. As in the survival problem, the relaxation time T_1 increases with decreasing impenetrability for the fixed volume fraction.

An important question is the following: in light of the fact that we have no simulation results for T_1, how sharp are the bounds we obtain for T_1 in the cherry-pit model? To begin with, let us consider this query for the fully penetrable-sphere case, i.e., Poisson distributed sphere centers with reduced density η. The principal eigenvalue λ_1 of the Laplacian operator for such a system of spheres of radius a in a cubical box of length L satisfies

$$\lambda_1 \propto \left(\frac{a}{L}\right)^2 \quad \text{for} \quad L \gg 1,$$

or equivalently,

$$T_1 \propto \left(\frac{L}{a}\right)^2 \quad \text{for} \quad L \gg 1.$$

The reason for such behavior is that T_1 is determined by the large fluctuations of the ensemble of configurations, corresponding to the existence of very large pores. This divergence of T_1 is in fact accompanied by the appearance of a continuous spectrum in the infinite-volume limit. The corresponding density of states near $\lambda_1 = 0$ is known as the "Lifshitz spectrum" in the theory of disordered systems.[17] The associated average survival probability behaves like $\exp[-\text{constant}\, t^{3/5}]$ in three dimensions as $t \to \infty$.[17,18] Although such large pore fluctuations are exceedingly rare, they exist with nonzero probability for this Poisson system and this is reflected in the fact that the pore size distribution $P(\delta)$ has *infinite* support. However, such fluctuations do not exist in most real porous and heterogeneous media since the range of pore sizes is bounded, i.e., $P(\delta)$ typically possesses finite support. Indeed, in a Monte Carlo simulation of T_1 for a Poisson system of spheres, large fluctuations are eliminated since one considers a constant number of particles in a cubical box (with periodic boundary conditions), each realization consistent with a value of the volume fraction ϕ_2. Supposing that $P(\delta)$ is supported in the interval $(0,\delta_0)$, i.e., every point in the pore space lies at most a distance δ_0 away from the interface, it can be shown by a probabilistic renewal argument[19] that the average survival probability decays exponentially with time. One concludes from this, using dimensional considerations, that

$$T_1 \leqslant \frac{c\delta_0^2}{D}, \tag{3.41}$$

where c is a constant dependent on the porosity and microgeometry. Unfortunately, the exact value of this constant is difficult to determine. For practical purposes, $P(\delta)$ for the Poisson system has finite support. For example, from Fig. 1 for $\phi_1 = \phi_2 = 0.5$, $\delta/2a \simeq 0.7$ for $\lambda = 0$ ("Poisson" distribution) and application of Eq. (3.41) with bounded c and $\delta_0 = 1.4a$ suggests that the lower bound $\langle \delta^2 \rangle / D$ on T_1 in Fig. 4 provides a coarse estimate of T_1. Similar arguments apply to the cherry-pit model in general even though pore size fluctuations will be smaller for a nonzero impenetrability parameter.

In summary, the lower bound (3.26) on T_1 will yield a reasonable estimate of the relaxation time provided that the pore size range is finite. On the other hand, for systems possessing very wide fluctuations in pore size, the bound will not be sharp and one could argue that the consideration of a single relaxation time, based on the smallest eigenvalue, is no longer appropriate. However, the bound (3.39) on the mean survival time τ is a more robust estimator of τ since it is related to the entire spectrum of eigenvalues [see Eq. (4.1) below].

Figure 5 shows the lower bound (3.39) on the dimensionless survival time $\tau D/a^2$ vs ϕ_2 for totally impenetrable traps ($\lambda = 1$) for several values of the dimensionless surface rate constant $\bar{\kappa}$ (∞, 0.5, 0.1). Notice that the lower bound on τ increases with decreasing surface reaction. Clearly, the diffusing particles survive longer when the surface reaction is finite relative to the case $\bar{\kappa} = \infty$ (i.e., diffusion-controlled limit) since particles are not always absorbed when they strike the surface. The behavior of the bound on T_1 for finite $\bar{\kappa}$ is qualitatively similar and hence is not shown graphically.

It is noteworthy that if the case of fully penetrable traps ($\lambda = 0$) is considered to be a reference system, then the fol-

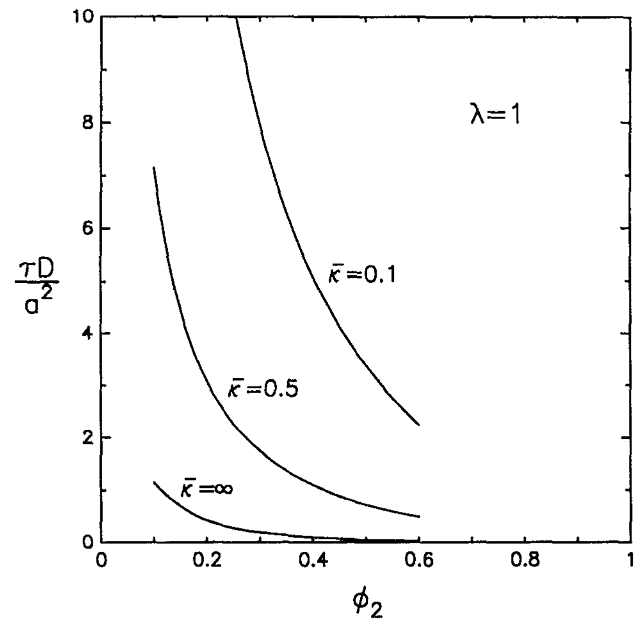

FIG. 5. Lower bound (3.39) on the dimensionless survival time $\tau D/a^2$ vs ϕ_2 for totally impenetrable traps ($\lambda = 1$) for several values of the dimensionless surface rate constant $\bar{\kappa} = \kappa a/D$ ($\bar{\kappa} = \infty$, 0.5, and 0.1).

lowing approximate scaling for the mean survival time $\tau(\lambda)$ for a system with impenetrability parameter λ holds quite accurately

$$\frac{\tau(0)}{\tau(\lambda)} \simeq \frac{\langle\delta\rangle^2_{\lambda=0}}{\langle\delta\rangle^2_{\lambda}}. \tag{3.42}$$

Thus Eq. (3.42) enables one to compute $\tau(\lambda)$ given $\tau(0)$ and the first moments of $P(\delta)$ for $\lambda = 0$ and arbitrary λ. In Fig. 6, we plot the right-hand side of Eq. (3.42) along with

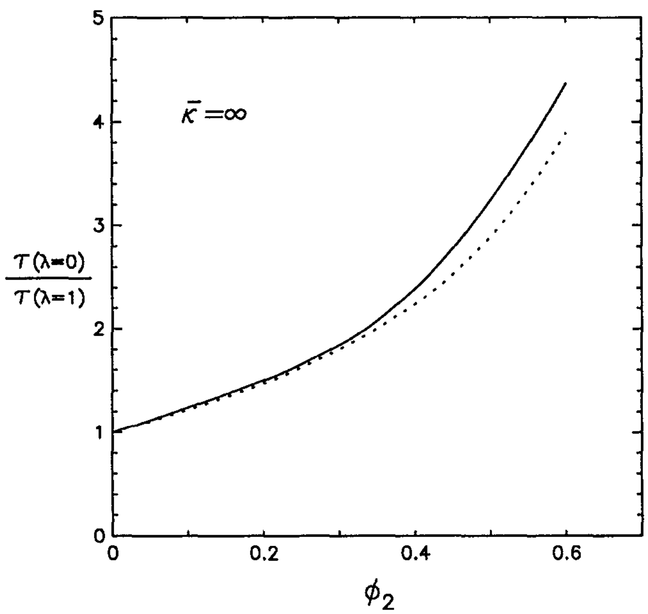

FIG. 6. Comparison of simulation data (solid lines) for the scaled survival time $\tau(\lambda = 0)/\tau(\lambda = 1)$ vs trap volume fraction ϕ_2 to the ratio $\langle\delta\rangle^2_{\lambda=0}/\langle\delta\rangle^2_{\lambda=1}$ (dotted lines) for the diffusion-controlled limit ($\bar{\kappa} = \infty$). $\lambda = 0$ and 1 and correspond to fully penetrable and totally impenetrable spheres, respectively, in the cherry-pit model (Ref. 9).

actual simulation results of the ratio of mean survival times for the case of $\lambda = 1$. The remarkable agreement obtained using this scaling relation indicates that lower-order moments of $P(\delta)$ contain useful information about diffusional properties of the system.

IV. RIGOROUS LINK BETWEEN THE RELAXATION TIMES AND MEAN SURVIVAL TIME

The previous section suggests that the mean survival time τ may be bounded from above by the relaxation time T_1 in general. Here we shall show that this is rigorously true and that there is a lower bound on τ in terms T_1. Indeed τ is linked to all of the relaxation times (i.e., eigenvalues). These statements are given and proven in the form of two propositions.

A. Proposition 1

For statistically homogeneous porous media of arbtirary topology at porosity ϕ_1, the following relation holds:

$$\tau = \sum_{n=1}^{\infty} a_n^2 T_n, \tag{4.1}$$

where a_n are the pore volume averages of ψ_n given by Eq. (3.10).

1. Proof

Consider initially a *large*, but *finite* pore region $\mathscr{V}_1$. Taking the Laplace transform of Eqs. (3.1)–(3.3) yields

$$s\hat{c}(\mathbf{r},s) = D\Delta\hat{c}(\mathbf{r},s) + c_0, \quad \text{in } \mathscr{V}_1 \tag{4.2}$$

$$D\frac{\partial\hat{c}}{\partial n} + \kappa\hat{c} = 0, \quad \text{on } \partial\mathscr{V}, \tag{4.3}$$

where

$$\hat{c}(\mathbf{r},s) = \int_0^\infty c(\mathbf{r},t)e^{-st}dt. \tag{4.4}$$

Setting $s = 0$ in Eqs. (4.2) and (4.3) gives

$$\Delta\hat{c}(\mathbf{r},0) = -\frac{c_0}{D}, \quad \text{in } \mathscr{V}_1, \tag{4.5}$$

$$D\frac{\partial\hat{c}}{\partial n} + \kappa\hat{c} = 0, \quad \text{on } \partial\mathscr{V}. \tag{4.6}$$

Letting

$$u(\mathbf{r}) = \frac{D\hat{c}(r,0)}{c_0} \tag{4.7}$$

in the relations immediately above yields the equations

$$\Delta u = -1, \quad \text{in } \mathscr{V}_1, \tag{4.8}$$

$$D\frac{\partial u}{\partial n} + \kappa u = 0, \quad \text{on } \partial\mathscr{V}, \tag{4.9}$$

which are identical to Eqs. (3.20) and (3.21) for the survival problem. Therefore, the solution of Eqs. (4.8) and (4.9) can be expressed in terms of the eigenfunctions $\{\psi_n\}$ which solve Eqs. (3.5) and (3.6) by taking Laplace transform of Eq. (3.4):

$$\frac{\hat{c}(\mathbf{r},s)}{c_0} = \sum_{n=1}^{\infty} a_n\psi_n(\mathbf{r})\frac{1}{(1/T_n) + s}. \tag{4.10}$$

Setting $s=0$ and utilizing Eq. (4.7) yields

$$u(\mathbf{r})=\sum_{n=1}^{\infty}\frac{a_n\psi_n(\mathbf{r})}{\lambda_n}. \tag{4.11}$$

Averaging Eq. (4.11) over the pore space gives

$$\frac{1}{V_1}\int_{\mathscr{V}_1}u(\mathbf{r})d\mathbf{r}=\sum_{n=1}^{\infty}\frac{a_n}{\lambda_n}\frac{1}{V_1}\int_{\mathscr{V}_1}\psi_n(\mathbf{r})d\mathbf{r}$$

$$=\sum_{n=1}^{\infty}\frac{a_n^2}{\lambda_n}. \tag{4.12}$$

The second line follows from condition (3.10). Passing to the limit $V_1\to\infty$, $V\to\infty$, using Eqs. (3.17) and (3.19) and the fact that $V_1=\phi_1 V$, enables us to rewrite Eq. (4.12) in terms of the mean survival time as

$$\tau=\sum_{n=1}^{\infty}\frac{a_n^2}{D\lambda_n}=\sum_{n=1}^{\infty}a_n^2T_n, \tag{4.13}$$

which proves the proposition.

2. Remark

The quantity $s\hat{c}(\mathbf{r},s)$ on the left-hand side of Eq. (4.2) can be physically interpreted as a bulk reaction term, with s playing the role of a bulk rate constant. In Sec. IV, it will be useful to introduce a Laplace-variable-dependent mean survival time

$$\tau(s)=\frac{\langle\hat{c}(\mathbf{r},s)\rangle}{c_0\phi_1}, \tag{4.14}$$

implying the existence of a frequency-dependent mean survival time. Note $\tau(0)$ is just the standard *steady-state* or *static* mean survival time defined above.

B. Proposition 2

For any statistically homogeneous porous medium with porosity ϕ_1, the mean survival time τ is bounded from above and below in terms of the principal relaxation time T_1 as follows:

$$a_1^2T_1\leqslant\tau\leqslant T_1, \tag{4.15}$$

where a_1 is given by Eq. (3.10), the pore volume average of the first eigenfunction ψ_1.

1. Proof

Since the eigenvalues are positive and $\lambda_1\leqslant\lambda_i$ ($T_1\geqslant T_i$) for $i\neq 1$, then

$$\sum_{n=1}^{\infty}a_n^2T_n\leqslant\sum_{n=1}^{\infty}a_n^2T_1 \tag{4.16}$$

and proposition 1 yields the upper bound

$$\tau\leqslant T_1. \tag{4.17}$$

Moreover, proposition 1 in conjunction with the inequality

$$\sum_{n=1}^{\infty}a_n^2T_n\geqslant a_1^2T_1 \tag{4.18}$$

yields

$$\tau\geqslant a_1^2T_1. \tag{4.19}$$

It is instructive to examine proposition 2 for the case of diffusion interior to spheres of radius a. For the perfectly nonabsorbing limit ($\kappa a/D\to 0$) (see Appendix A),

$$T_1=a_1^2T_1=\tau\sim\frac{a}{3\kappa} \tag{4.20}$$

and hence the bounds in Eq. (4.15) are exact since the lowest mode dominates completely. For the perfectly absorbing limit ($\kappa a/D\to\infty$), we have from Appendix A that

$$a_1^2T_1\sim\frac{6a^2}{\pi^4D},\quad T_1\sim\frac{a^2}{\pi^2D},\quad \tau\sim\frac{a^2}{15D}, \tag{4.21}$$

or from Eq. (4.15)

$$\frac{6a^2}{\pi^4D}\leqslant\frac{a^2}{15D}\leqslant\frac{a^2}{\pi^2D}. \tag{4.22}$$

The bounds of Eq. (4.22) are reasonably sharp.

Note that for a general porous medium, bound (4.17) can be used to estimate the principal relaxation time T_1 given that τ has been measured exactly provided, as discussed earlier in Sec. III, that the medium is characterized by a finite range of pore sizes.

V. RELATIONSHIP BETWEEN THE TIMES T_1 AND τ TO THE FLUID PERMEABILITY

Torquato[4] proved that the mean survival time τ for statistically anisotropic porous media of arbitrary topology is rigorously related to the fluid permeability tensor k arising in Darcy's law for slow viscous flow through the same porous medium by the relation

$$\mathsf{k}\leqslant D\phi_1\tau\mathsf{U}. \tag{5.1}$$

Relation (5.1) states that the permeability tensor k minus the isotropic tensor $D\phi_1\tau\mathsf{U}$ is negative semidefinite, where U is the unit dyadic. In the isotropic case, Eq. (5.1) simplifies as

$$k\leqslant D\phi_1\tau. \tag{5.2}$$

Thus knowing the mean survival time exactly, one can bound the fluid permeability and vice versa. The equality of Eq. (5.1) is achieved for one of the eigenvalues for transport in parallel channels of arbitrary cross-sectional shape. For porous media with low porosity and significant tortousity, bound (5.2) is not sharp essentially because τ, unlike k, is relatively insensitive to the presence of "narrow throats." Relation (5.2) motivated Wilkinson, Johnson, and Schwartz[3] very recently to reexamine the problem of nuclear magnetic resonance (NMR) relaxation in fluid-saturated porous media by focusing attention on τ instead of the relaxation times T_n.

In light of the upper bound of proposition 2 [Eq. (4.15)], we also have

$$\mathsf{k}\leqslant D\phi_1\tau\mathsf{U}\leqslant D\phi_1T_1\mathsf{U}. \tag{5.2}$$

Hence, although Eq. (5.2) provides an upper bound on k in terms of T_1, it is weaker than Eq. (5.1).

It is useful to recall our earlier definition (4.14) of the *frequency-dependent* mean survival time

$$\tau(s)=\frac{\langle\hat{c}(\mathbf{r},s)\rangle}{c_0\phi_1} \tag{5.3}$$

Elsewhere[20] we define the analogous frequency-dependent fluid permeability tensor

$$\mathsf{k}(s) = \frac{\nu[\hat{\mathsf{v}}(\mathbf{r},s)]}{v_0}, \tag{5.4}$$

where $\hat{\mathsf{v}}$ is the Laplace transform in time of the unsteady solution of the tensor Stokes equations, ν is the kinematic viscosity, and v_0 is some reference speed. There we will prove that

$$\mathsf{k}(s) \leq D\phi_1 \tau(s)\mathsf{U}. \tag{5.5}$$

Note that in the static case ($s=0$), we recover Torquato's original result (5.1). The importance of Eq. (5.5) lies in the fact that $\mathsf{k}(s)$ can be related to the so-called dynamic permeability[21,22] $\tilde{\mathsf{k}}(\omega)$ which is the constant of proportionality in the dynamic form of Darcy's law when the porous medium is subjected to an oscillatory pressure gradient with frequency ω. The precise relationship between $\mathsf{k}(s)$ and $\tilde{\mathsf{k}}(\omega)$ and the consequences of such a relation will be described in Ref. 20.

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APPENDIX A: RELAXATION AND SURVIVAL TIMES FOR TRANSPORT INTERIOR TO DISCONNECTED SPHERICAL PORES

It is useful to obtain the relaxation time T_1 and mean survival time τ for the simple case of transport interior to spherical pores of radius a since such results provide some physical insight into the behavior of these times for more complex geometries.

For the relaxation problem, it is easily shown that the eigenfunction [cf. Eq. (3.5)] is given by

$$\psi_n(r) = \frac{B_n}{r}\sin(\sqrt{\lambda_n}\, r), \tag{A1}$$

where

$$B_n^2 = \frac{2a^2(a^2\lambda_n + K)}{3(a^2\lambda_n + K^2 - K)}, \tag{A2}$$

$$K = 1 - \frac{\kappa}{D} = a\sqrt{\lambda_n}\cot(a\sqrt{\lambda_n}), \tag{A3}$$

and the associated coefficients are

$$a_n = \frac{3B_n}{a^3\lambda_n}\sin(\sqrt{\lambda_n}\, r). \tag{A4}$$

The following are asymptotic expressions for $T_1 = 1/D\lambda_1$:

$$T_1 \sim \frac{a}{3\kappa} + \frac{a^2}{15D} + \frac{17a^3\kappa}{525D^2} \quad \left(\frac{\kappa a}{D} \ll 1\right), \tag{A5}$$

$$T_1 \sim \frac{a^2}{\pi^2 D} + \frac{2a}{\pi^2\kappa} \quad \left(\frac{\kappa a}{D} \gg 1\right). \tag{A6}$$

For the survival problem, it is easily shown that the solution of Eqs. (3.14) and (3.20) is given by

$$u = \frac{a^2 - r^2}{6} + \frac{aD}{3\kappa}. \tag{A7}$$

Substitution into Eq. (3.19) exactly yields

$$\tau = \frac{a^2}{15D} + \frac{a}{3\kappa}. \tag{A8}$$

APPENDIX B: DERIVATION OF VARIATIONAL PRINCIPLES FOR T_1 AND τ

We give here a brief, self-contained derivation of the variational principles (3.22) and (3.34) for the relaxation and mean survival times. We shall assume in this derivation that V represents a finite reference cube in the porous medium and that periodic boundary conditions are satisfied by the trial fields on the cube boundaries. This assumption entails no loss in generality since boundary contributions become negligible in the limit $V \to \infty$.

1. Variational principle for T_1

Consider first the problem of minimizing the functional

$$\mathscr{F}_1(\psi^*) = \frac{(1/V)\int_{\mathscr{V}_1} \nabla\psi^*\cdot\nabla\psi^*\, d\mathbf{r} + (\kappa/DV)\int_{\partial\mathscr{V}} (\psi^*)^2 dS}{(1/V)\int_{\mathscr{V}_1} (\psi^*)^2 d\mathbf{r}} \tag{B1}$$

over all scalar functions ψ^* defined in $\mathscr{V}_1$. Since the numerator in Eq. (B1) is convex, this problem is equivalent to the minimization of the modified functional

$$\mathscr{F}_2(\psi^*) = \frac{1}{V}\int_{\mathscr{V}_1} \nabla\psi^*\cdot\nabla\psi^*\, d\mathbf{r} + \frac{\kappa}{DV}\int_{\partial\mathscr{V}} (\psi^*)^2 dS - \lambda\int_{\mathscr{V}_1} (\psi^*)^2 d\mathbf{r}, \tag{B2}$$

where λ is a Lagrange multiplier. The first variation of $\mathscr{F}_2(\psi^*)$ is given by

$$\delta\mathscr{F}_2(\psi^*) = \frac{2}{V}\int_{\mathscr{V}_1} \nabla\psi^*\cdot\nabla(\delta\psi^*) d\mathbf{r} + \frac{2\kappa}{DV}\int_{\partial\mathscr{V}} \psi^*(\delta\psi^*) dS - 2\lambda\int_{\mathscr{V}_1} \psi^*(\delta\psi^*) d\mathbf{r} \tag{B3}$$

for an arbitrary variation $\delta\psi^*$. The minimizer of Eq. (B2) [and hence of Eq. (B1)] satisfies $\delta\mathscr{F}_2(\psi^*) = 0$ for all variations $\delta\psi^*$. Considering variations $\delta\psi^*$ that vanish on the pore surface, i.e., $\delta\psi^*(\mathbf{r}) = 0$ on $\partial\mathscr{V}$, notice that the middle term in Eq. (B3) vanishes. Performing integration by parts in the optimality relation $\delta\mathscr{F}_2(\psi^*) = 0$, we obtain the equation

$$-\Delta\psi^* = \lambda\psi^*, \tag{B4}$$

so that ψ^* is an eigenfunction with eigenvalue λ. Moreover, if one considers arbitrary variations $\delta\psi^*$ in Eq. (B3) and takes into account the equation satisfied by ψ^*, one finds, using integration by parts, that

$$\int_{\partial\mathscr{V}} \frac{\partial\psi^*}{\partial n}(\delta\psi^*)dS + \frac{\kappa}{D}\int_{\partial\mathscr{V}} \psi^*(\delta\psi^*)dS = 0, \quad (B5)$$

which implies that ψ^* satisfies the boundary condition

$$D\frac{\partial\psi^*}{\partial n} + \kappa\psi^* = 0 \quad \text{on } \partial\mathscr{V}. \quad (B6)$$

Therefore, ψ^* satisfies Eqs. (3.5) and (3.6) with eigenvalue λ. From Eqs. (B3), (B4), and (B6), we can characterize the Lagrange multiplier λ as the ratio

$$\lambda = \frac{(1/V)\int_{\mathscr{V}_1}\nabla\psi^*\cdot\nabla\psi^*\, d\mathbf{r} + (\kappa/DV)\int_{\partial\mathscr{V}}(\psi^*)^2 dS}{(1/V)\int_{\mathscr{V}_1}(\psi^*)^2 d\mathbf{r}}. \quad (B7)$$

On the other hand, the principal eigenvalue λ_1 and eigenfunction ψ_1 of problems (3.5) and (3.6) satisfy

$$\lambda_1 = \frac{(1/V)\int_{\mathscr{V}_1}\nabla\psi_1\cdot\nabla\psi_1\, d\mathbf{r} + (\kappa/DV)\int_{\partial\mathscr{V}}\psi_1^2 dS}{(1/V)\int_{\mathscr{V}_1}(\psi_1^2)^2 d\mathbf{r}} \quad (B8)$$

From the optimality of ψ^* for Eq. (B1), it follows that $\lambda \leqslant \lambda_1$. On the other hand λ is an eigenvalue and hence $\lambda_1 \leqslant \lambda$. We conclude therefore that

$$\min_{\psi^*} \mathscr{F}_1(\psi^*) = \lambda = \lambda_1 = \mathscr{F}_1(\psi_1) \quad (B9)$$

as desired. Consequently, the integral (B1) is minimized for $\psi^* = \psi_1$ and its minimum value is the principal eigenvalue λ_1.

2. Variational principle for τ

Next, we consider the functional

$$\mathscr{F}_3(v) = \frac{1}{V}\int_{\mathscr{V}_1}\nabla v\cdot\nabla v\, d\mathbf{r} + \frac{\kappa}{VD}\int_{\partial\mathscr{V}} v^2 dS \quad (B10)$$

and the problem of minimizing $\mathscr{F}_3(v)$ subject to the constraint

$$\frac{1}{V}\int_{\mathscr{V}_1} v\, d\mathbf{r} = c = \langle u\rangle, \quad (B11)$$

where u is the solution of Eqs. (3.20) and (3.21). Since $\mathscr{F}_3(v)$ is convex, the minimizer of this problem must also minimize the functional

$$\mathscr{F}_4(v) = \mathscr{F}_3(v) - \lambda\frac{1}{V}\int_{\mathscr{V}_1} v\, d\mathbf{r} \quad (B12)$$

over all functions v defined in $\mathscr{V}_1$, where λ is an appropriate Lagrange multiplier. In the previous problem, the trial fields are not required to satisfy Eq. (B11). The minimizer $\bar{v}$ of $\mathscr{F}_4(v)$ is such that

$$0 = \delta\mathscr{F}_4(v) = \frac{2}{V}\int_{\mathscr{V}_1}\nabla v\cdot\nabla(\delta v)d\mathbf{r} + \frac{2\kappa}{DV}\int_{\partial\mathscr{V}} v\cdot(\delta v)dS - \frac{\lambda}{V}\int_{\mathscr{V}}\delta v\, d\mathbf{r}. \quad (B13)$$

We conclude from this, using the arguments of the previous paragraph, that the minimizer satisfies the equations

$$\begin{cases} -\Delta v = \tfrac{1}{2}\lambda \ \text{ in } \mathscr{V} \\ D\dfrac{\partial v}{\partial n} + \kappa v = 0 \ \text{ on } \partial\mathscr{V} \end{cases}. \quad (B14)$$

We deduce from this equation that

$$\frac{2v}{\lambda} = u, \quad (B15)$$

where u is the solution of Eqs. (3.20) and (3.21). Averaging Eq. (B15) over the volume, we obtain $\langle 2v/\lambda\rangle = \langle u\rangle = \langle v\rangle$, since v satisfies the volume constraint (B11). Therefore $\lambda = 2$. Substitution of $\lambda = 2$ and $\delta v = v$ in Eq. (B13) yields

$$\langle u\rangle = \frac{1}{V}\int_{\mathscr{V}_1}\nabla v\cdot\nabla v\, d\mathbf{r} + \frac{\kappa}{DV}\int_{\partial\mathscr{V}} v^2 dS = \min_{v^*}\mathscr{F}_3(v^*), \quad (B16)$$

where the minimum is taken over functions where v^* satisfies $\langle v^*\rangle = \langle u\rangle$. Alternatively, from Eq. (3.19), $\langle u\rangle = \tau\phi_1 D$, so that from Eq. (B16)

$$\min_{v^*}\mathscr{F}_3(v^*) = \frac{\langle u\rangle^2}{\tau\phi_1 D}. \quad (B17)$$

This is the desired variational principle for the mean survival time τ.

Remark

This last variational principle for τ is valid for an *arbitrary* volume constraint with the trial field v, i.e., for an arbitrary constant c, we have

$$\frac{c^2}{\tau\phi_1 D} = \min_v\left(\frac{1}{V}\int_{\mathscr{V}_1}\nabla v\cdot\nabla v\, d\mathbf{r} + \frac{\kappa}{VD}\int_{\partial\mathscr{V}} v^2 dS\right) \quad (B18)$$

with v subject to

$$\frac{1}{V}\int_{\mathscr{V}_1} v\, d\mathbf{r} = c. \quad (B19)$$

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