Journal of Statistical Physics, Vol. 65, No. 5/6, 1991

Diffusion and Reaction among Traps: Some Theoretical and Simulation Results

S. Torquato[1,2]

Diffusion and reaction in heterogeneous media arise in a host of phenomena in the physical and biological sciences. The determination of the mean survival time τ (i.e., inverse trapping rate) and relaxation times T_n, $n = 1, 2, 3,...$ (i.e., inverse eigenvalues), associated with diffusion among partially absorbing, static traps with surface rate constant κ are problems of long-standing interest. The limits $\kappa = \infty$ and $\kappa = 0$ correspond to the diffusion-controlled case (i.e., perfect absorbers) and reaction-controlled case (i.e., perfect reflectors), respectively. This paper reviews progress we have made on several basic aspects of this problem: (i) the formulation of rigorous bonding techniques and computational methodologies that enable one to estimate the mean survival time τ and principal relaxation time T_1; (ii) the quantitative characterization of the microstructure of nontrivial continuum (i.e., off-lattice) models of heterogeneous media; and (iii) evaluation of τ and T_1 for the same models. We also describe a rigorous link between the mean survival time τ and a different effective parameter of the system, namely the fluid permeability tensor $\mathbf{k}$ associated with Stokes flow through the same porous medium.

KEY WORDS: Diffusion; traps.

1. INTRODUCTION

Physical problems involving simultaneous diffusion and reaction in heterogeneous media abound in physical and biological sciences.[1-3] Considerable attention has been devoted to instances in which the heterogeneous media consist of two regions: a pore region in which

[1] Courant Institute of Mathematical Sciences, New York University, New York, New York 10012.

[2] Current and permanent address: Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina 27695-7910.

0022-4715/91/1200-1173$06.50/0

diffusion occurs and a trap region (see refs. 1–14 and references therein). Examples are found in such widely different processes as heterogeneous catalysis, fluorescence quenching, 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.

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 at 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 pore–trap 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 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, i.e., the traps are perfect absorbers. In the opposite extreme of vanishing surface reaction ($\kappa = 0$), the traps are perfect reflectors. Without loss of generality we set the bulk rate constant equal to zero, since the solution of (1.1) with $\kappa_B \neq 0$ is simply related to the one with $\kappa_B = 0$ (see Section 2).

This paper is concerned with the study of relation (1.1) with condition (1.2) for two different situations:

(i) The *steady-state* solution with $\kappa_B = 0$.

(ii) The *time-dependent* solution with $\kappa_B = G = 0$.

The quantities of central interest are the *mean survival time* τ of a Brownian particle of problem (i) and the *relaxation times* T_n, $n = 1, 2, \ldots$ (or eigenvalues) of problem (ii). The times τ and T_1 are intimately linked to characteristic length scales of the pore region. Whereas the mean survival time τ is determined by the "average pore size," the *principal* relaxation time T_1 is governed by diffusion occurring in the largest cavities (pores) in the system. A key fundamental question is, what precisely is the relationship between the pore statistics and these time scales?

The purpose of this paper is to review progress we have made on several aspects of this problem:

1. The derivation of rigorous bounds on the mean survival time τ and principal relaxation time T_1 in terms of statistical correlation functions.
2. The quantitative characterization of the microstructure of nontrivial continuum (i.e., off-lattice) models of heterogeneous media.
3. The formulation of efficient Brownian-motion simulation techniques to obtain the mean survival time.
4. The connection of the steady-state trapping problem to the problem of Stokes flow through the same porous medium.
5. The calculation of τ and T_1 using the aforementioned methods for nontrivial model microstructures.

In Section 2, we describe the basic equations and discuss the relationship between the steady-state and time-dependent problems. Section 3 discusses rigorous bounds on τ and T_1 in the diffusion-controlled limit ($\kappa = \infty$). Section 4 treats bounds on τ and T_1 for arbitrary values of the surface rate constant κ. In Section 5 a recently derived expression is described which rigorously links the mean survival time τ to a different effective parameter of the system, namely, the fluid permeability tensor $\mathbf{k}$ associated with Stokes flow through the same porous medium. Section 6 reviews advances made in the quantitative characterization of the microstructure of heterogeneous media. In Section 7, we describe Brownian motion simulation techniques that yield the mean survival time accurately and with a very fast execution time. Finally, in Section 8 we discuss the evaluation of bounds on τ and T_1 for a variety of continuum models and compare these bounds, when possible, to simulation data.

2. BASIC EQUATIONS AND RELATIONSHIP BETWEEN SURVIVAL AND RELAXATION PROBLEMS

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

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

The characteristic function of the pore–trap 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 (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.

2.1. Steady-State Survival Problem

Consider the 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 $G(\mathbf{x}) = \gamma D \bar{C}(\mathbf{x})$ for statistically homogeneous media in the diffusion-controlled case (i.e., infinite surface reaction) has been expressed by Rubinstein and Torquato,[10] using the method of homogenization, in terms of a certain scaled concentration field [where $\bar{C}(\mathbf{x})$ is a mean concentration field]. The trapping constant is given by

$$\gamma = \langle u \rangle^{-1} \tag{2.5}$$

where u solves

$$\Delta u = -1 \qquad \text{in} \quad \mathcal{V}_1 \tag{2.6}$$

$$u = 0 \qquad \text{on} \quad \partial\mathcal{V} \tag{2.7}$$

Here Δ is the Laplacian operator and we extend u in the trap region $\mathcal{V}_2$ to be zero. As before, angular brackets denote an ensemble average. Ergodicity enables us to equate ensemble and volume averages so that

$$\langle u \rangle = \langle uI \rangle = \lim_{V \to \infty} \frac{1}{V} \int_{\mathcal{V}_1} u(\mathbf{r})\, d\mathbf{r} \tag{2.8}$$

The trapping constant is trivially related to the *average survival time* τ of a Brownian particle by the relation[15]

$$\tau = \frac{1}{\gamma \phi_1 D} \tag{2.9}$$

and therefore use of (2.5) yields

$$\tau = \frac{\langle u \rangle}{\phi_1 D} \tag{2.10}$$

Note that the inverse survival time τ^{-1} is simply the *trapping rate*. From ref. 12 it is seen that the expression (2.10) still holds for the finite-surface-reaction boundary condition at the pore–solid interface, i.e., u solves

$$\Delta u = -1, \qquad \text{in} \quad \mathcal{V}_1 \tag{2.11}$$

$$D\frac{\partial u}{\partial n} + \kappa u = 0, \qquad \text{on} \quad \partial\mathcal{V} \tag{2.12}$$

Here κ is the *surface rate constant* having dimensions of length/time. Of course in the case of (2.12) the mean survival time τ depends not only on D, but also on κ.

2.2. Relaxation Problem

The relaxation times associated with the decay of physical quantities such as concentration field and nuclear magnetization density are intimately related 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 obeys the following time-dependent diffusion equation in the *finite* but *large* pore region:

$$\frac{\partial c}{\partial t} = D\Delta c \qquad \text{in} \quad \mathcal{V}_1 \tag{2.13}$$

$$c(\mathbf{r}, 0) = c_0 \qquad \text{in} \quad \mathcal{V}_1 \tag{2.14}$$

$$D\frac{\partial c}{\partial n} + \kappa c = 0 \qquad \text{on} \quad \partial\mathcal{V} \tag{2.15}$$

where $\mathbf{n}$ is the unit outward normal from the pore region. Note that we could have included a bulk reaction term $\kappa_B c$ on the lhs of (2.13), 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 (2.13)–(2.15) can be given as an expansion in orthonormal eigenfunctions $\{\psi_n\}$ (see, e.g., ref. 16):

$$\frac{c(\mathbf{r}, t)}{c_0} = \sum_{n=1}^{\infty} a_n e^{-t/T_n} \psi_n(\mathbf{r}) \tag{2.16}$$

where

$$\Delta\psi_n = -\lambda_n\psi_n \qquad \text{in} \quad \mathcal{V}_1 \tag{2.17}$$

$$D\frac{\partial\psi_n}{\partial n} + \kappa_s\psi_n = 0 \qquad \text{on} \quad \partial\mathcal{V} \tag{2.18}$$

$$T_n = \frac{1}{D\lambda_n} \tag{2.19}$$

The T_n are the relaxation times. The initial condition and (2.16) yield

$$\sum_{n=1}^{\infty} a_n\psi_n(\mathbf{r}) = 1 \tag{2.20}$$

The eigenfunctions ψ_n are orthonormal such that

$$\frac{1}{\phi_1}\langle\psi_m\psi_n I\rangle = \delta_{mn} \tag{2.21}$$

so that

$$a_n = \frac{1}{\phi_1}\langle\psi_n I\rangle \tag{2.22}$$

Because the set of eigenfunctions is complete, we also have

$$\sum_{n=1}^{\infty} a_n^2 = 1 \tag{2.23}$$

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

$$\bar{\kappa} = \frac{\kappa l}{D} \tag{2.24}$$

and distinguish between two extreme regimes,

$$\begin{aligned} &\bar{\kappa} \gg 1 \qquad \text{(diffusion-controlled)} \\ &\bar{\kappa} \ll 1 \qquad \text{(reaction-controlled)} \end{aligned} \tag{2.25}$$

where l is a characteristic pore length scale. In the diffusion-controlled regime, the diffusing species takes a long time to diffuse to the pore–trap 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–trap interface.

2.3. Relationship Between Survival and Relaxation Problems

Torquato and Avellaneda[16] have shown that mean survival time τ is bounded from above and below in terms of the principal relaxation T_1. Indeed τ is linked to all of the relaxation time (i.e., eigenvalues). These statements are given in the form of two propositions.

Proposition 1. For statistically homogeneous media of arbitrary topology at porosity ϕ_1, the following relation holds:

$$\tau = \sum_{n=1}^{\infty} a_n^2 T_n \tag{2.26}$$

where the a_n are the averages of the eigenfunctions ψ_n given by (2.22).

The reader is referred to ref. 16 for details of the rather straightforward proof of this proposition. The key idea is to take the Laplace transform in time of (2.16) and observe that

$$u(\mathbf{r}) = \frac{D\hat{c}(\mathbf{r}, 0)}{c_0} \tag{2.27}$$

where

$$\hat{c}(\mathbf{r}, s) = \int_0^{\infty} c(\mathbf{r}, t)\, e^{-st}\, dt \tag{2.28}$$

and $u(\mathbf{r})$ is the field satisfying (2.11) and (2.12). Averaging (2.27) and use of (2.16) yields the proposition.

It useful to introduce a Laplace-variable-dependent mean survival time

$$\tau(s) = \frac{\langle \hat{c}(\mathbf{r}, s) \rangle}{c_0 \phi_1} \tag{2.29}$$

implying the existence of "frequency-dependent" mean survival time. Note that $\tau(0)$ is just the standard *steady-state* or *static* mean survival time defined by (2.10)–(2.12).

Proposition 2. For any statistically homogeneous medium at 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:

$$a_1^2 T_1 \leqslant \tau \leqslant T_1 \tag{2.30}$$

where a_1 is given by (2.22).

The reader is referred to ref. 16 for the proof.

3. VARIATIONAL BOUNDS ON THE SURVIVAL AND RELAXATION TIMES FOR INFINITE SURFACE REACTION

For general random media, the complexity of the microstructure prevents one from obtaining the effective properties of the system exactly. Therefore, any rigorous statement about the properties must be in the form of an inequality, i.e., rigorous bounds on the effective properties. Bounds are useful since: (i) they enable one to test the merits of theories and computer experiments; (ii) they become progressively narrower as successfully more microstructural information is incorporated; and (iii) one of them can typically provide a good estimate of the property for a wide range of conditions, even when the reciprocal bound diverges from it.

Prager[5,17] pioneered the use of bounds to obtain estimates of effective properties in the early 1960s.

3.1. Bounds on Survival Time

Rubinstein and Torquato[10] derived variational principles for the mean survival time τ in the diffusion-controlled case ($\kappa = \infty$). They formulated the variational principles both in terms of ensemble averages and volume averages. Here we state only the ensemble-averaged relations. The ensemble-averaged upper bound is given by

$$\tau \leqslant \frac{\langle \nabla v \cdot \nabla v I \rangle}{D\phi_1}, \qquad \forall v \in A \tag{3.1}$$

$$A = \{\text{smooth, stationary } v;\ \Delta v = -1 \text{ in } \mathcal{V}_1\} \tag{3.2}$$

The ensemble-averaged lower bound is given by

$$\tau \geqslant \frac{\langle uI \rangle^2}{D\phi_1 \langle \nabla v \cdot \nabla v I \rangle}, \qquad \forall v \in B \tag{3.3}$$

$$B = \{\text{smooth, stationary } v;\ v = 0 \text{ on } \partial\mathcal{V} \text{ and } \langle vI \rangle = \langle uI \rangle\} \tag{3.4}$$

In order to obtain specific bounds, one must derive trial fields which meet the admissibility conditions of (3.2) and (3.3). Note that if both conditions (3.2) and (3.3) are met simultaneously, one would be solving the exact problem, which, as already noted, is generally not possible. These variational principles were applied by formulating four different classes of bounds: interfacial-surface, multiple-scattering, security-spheres, and void bounds.[10,11] These bounds are given in terms of various types of statistical correlation functions and are briefly described below.

Interfacial-Surface Upper Bounds:

$$\tau \leqslant \tau^{(2U)}[\phi_1, \sigma, S_2, F_{sv}, F_{ss}] \tag{3.5}$$

Multiple-Scattering Upper Bounds:

$$\tau \leqslant \tau^{(3U)}[\phi_1, \sigma, G_2, G_3] \tag{3.6}$$

Void Upper Bounds:

$$\tau \leqslant \tau^{(2U)}[\phi_1, S_2] \tag{3.7}$$

Security-Spheres Lower Bounds:

$$\tau \geqslant \tau^{(2L)}[\phi_1, H_P] \tag{3.8}$$

The right-hand sides of (3.5)–(3.8) represent functionals of certain correlation functions. The n-point probability function $S_n(\mathbf{x}^n)$ gives the probability of finding n points with positions $\mathbf{x}^n \equiv \{\mathbf{x}_1,..., \mathbf{x}_n\}$ in $\mathscr{V}_1$, the trap-free region. The surface–void correlation function $F_{sv}(\mathbf{x}_1, \mathbf{x}_2)$ gives the correlation associated with having a point at $\mathbf{x}_1$ on the interface $\partial\mathscr{V}$ and another point at $\mathbf{x}_2$ in the trap-free region $\mathscr{V}_1$. The surface–surface correlation function $F_{ss}(\mathbf{x}_1, \mathbf{x}_2)$ gives the correlation associated with having a point at $\mathbf{x}_1$ and another point at $\mathbf{x}_2$ both on the interface. (The interfacial-surface bound was first derived by Doi[18] using an approach different than the one used by Rubinstein and Torquato.) The point/q-particle function $G_n(\mathbf{x}_1; \mathbf{r}^q)$ gives the correlation associated with having a point at $\mathbf{x}_1$ in $\mathscr{V}_1$ and a configuration of q inclusions with coordinates $\mathbf{r}^q$, $n = 1 + q$. The quantity $H_P(r)$ is the so-called *particle* nearest-neighbor distribution function[19] and for sphere distributions is defined such that $H_P(r)\,dr$ is the probability of finding a nearest neighbor in a shell dr at a distance r from a sphere located at the origin.

3.2. Lower Bound on Principal Relaxation Time

For the diffusion-controlled case, the principal relaxation time $T_1 = 1/D\lambda_1$ is known to be bounded from below[20] by the following expression:

$$T_1 \geqslant \frac{\langle \psi^2 I \rangle}{D\langle \nabla\psi \cdot \nabla\psi I \rangle} \tag{3.9}$$

where

$$\psi = 0 \qquad \text{on} \quad \partial\mathscr{V} \tag{3.10}$$

Here ψ is a trial eigenfunction.

Prager[5] employed a trial eigenfunction satisfying (3.10) which gave the specific lower bound

$$T_1 \geqslant \frac{\langle \delta^2 \rangle}{D} \tag{3.11}$$

where the general nth moment is defined by

$$\langle \delta^n \rangle = \int_0^\infty \delta^n P(\delta)\, d\delta \tag{3.12}$$

and $P(\delta)$ is the *pore size distribution function.* The quantity $P(\delta)\, d\delta$ is the probability that a randomly chosen point in the pore region $\mathcal{V}_1$ lies at a distance between δ and $\delta + d\delta$ from the nearest point on the interface $\partial\mathcal{V}$. The function $P(\delta)$ normalizes to unity and at extreme values, one has

$$P(0) = \frac{\sigma}{\phi_1} \qquad \text{and} \qquad P(\infty) = 0 \tag{3.13}$$

4. BOUNDS ON THE SURVIVAL AND RELAXATION TIMES FOR FINITE SURFACE REACTION

For diffusion-controlled processes ($\bar{\kappa} = \infty$), Prager[5] obtained simple lower bounds on the mean survival time τ and the principal relaxation time T_1. Here we generalize these results for situations in which the surface reaction rate κ is finite by employing the appropriate variational principles.

4.1. Lower Bound on Survival Time

Rubinstein and Torquato[10] derived a variational lower bound on the mean survival time τ in the diffusion-controlled limit. This lower bound has been generalized by Torquato and Avellaneda[16] to treat finite surface reaction. The following variational lower bound on the mean survival time τ exists:

$$\tau \geqslant \frac{\langle uI \rangle^2}{D\phi_1[\langle \nabla v \cdot \nabla v I \rangle + (\kappa/D)\langle v^2 M \rangle]} \tag{4.1}$$

This bound is proved in ref. 16. Here the average of the trial concentration field v is equal to the actual concentration field u that solves (2.11) and (2.12), i.e.,

$$\langle vI \rangle = \langle uI \rangle \tag{4.2}$$

Consider a trial field of the form

$$v = \frac{\langle u \rangle J(\delta)}{\phi_1 \int_0^\infty J(\delta)\, P(\delta)\, d\delta} \tag{4.3}$$

Insertion of (4.3) into (4.1) yields

$$\tau \geqslant \frac{[\int_0^\infty J(\delta)\, P(\delta)\, d\delta]^2}{D\phi[\int_0^\infty (dJ/d\delta)^2\, P(\delta)\, d\delta + (\kappa\sigma/D\phi_1)\, J^2(0)]} \tag{4.4}$$

Let the deterministic function J be given by

$$J(\delta) = c^*\delta + d^* \tag{4.5}$$

where c^* and d^* are constants to be optimized and n is an arbitrary integer. Substitution of (4.5) into (4.4) yields the *optimized lower* bound on τ:

$$\tau \geqslant \frac{\langle \delta \rangle^2}{D} + \frac{\phi_1}{\kappa\sigma} \tag{4.6}$$

For $\bar{\kappa} \to \infty$, (4.6) reduces to the diffusion-controlled-limit bound obtained by Prager.[5] Not surprisingly, finite surface reaction yields a survival time which is larger than the one for the diffusion-controlled limit.

4.2. Lower Bound on Principal Relaxation Time

The first eigenvalue $\lambda_1 = (T_1 D)^{-1}$ [cf. (2.19)] is bounded from above by the relation

$$(T_1 D)^{-1} \leqslant \frac{(1/V)\int_{\mathcal{V}_1} \nabla\psi^* \cdot \nabla\psi^*\, d\mathbf{r} + (\kappa/DV)\int_{\partial\mathcal{V}} (\psi^*)^2\, dS}{(1/V)\int_{\mathcal{V}_1} (\psi^*)^2\, d\mathbf{r}} \tag{4.7}$$

where ψ^* is a trial eigenfunction and dS indicates a surface integration over the pore–solid interface. This variational bound is derived in ref. 16. Now consider a trial eigenfunction of the form

$$\psi^*(\mathbf{r}) = G(\delta) \tag{4.8}$$

where $\delta(\mathbf{r})$, as in Section 2, 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 (4.8) into (4.7) yields, in the infinite-volume limit,

$$(T_1 D)^{-1} \leqslant \frac{\int_0^\infty (dG/d\delta)^2 P(\delta)\, d\delta + (\kappa\sigma/D\phi_1) G^2(0)}{\int_0^\infty G^2(\delta) P(\delta)\, d\delta} \tag{4.9}$$

To begin with, we choose

$$G(\delta) = a^*\delta + b^* \tag{4.10}$$

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 (4.10) and optimizing b^* gives a lower bound on $T_1 = 1/D\lambda_1$,

$$T_1 \geqslant \frac{\langle\delta^2\rangle + 2\langle\delta\rangle b_* + b_*^2}{D(1 + (\kappa\sigma/D\phi_1) b_*^2)} \tag{4.11}$$

where

$$b_* = \frac{[1 - (\kappa\sigma/D\phi_1)\langle\delta^2\rangle] + \{[1 - (\kappa\sigma/D\phi_1)\langle\delta^2\rangle]^2 + (4\kappa\sigma/D\phi_1)\langle\delta\rangle^2\}^{1/2}}{2(\kappa\sigma/D\phi_1)\langle\delta\rangle} \tag{4.12}$$

Here σ is the specific surface and σ/ϕ_1 is the *interfacial surface area per unit pore volume.* Note that the bound (4.11) depends upon the first and second moments of $P(\delta)$. For fast diffusion, bound (4.11) has the asymptotic form

$$T_1 \geqslant \frac{\phi_1}{\kappa\sigma} + \frac{2(2\langle\delta\rangle^2 - \langle\delta^2\rangle)}{D}, \qquad (\bar{\kappa} \ll 1 \tag{4.13}$$

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

$$T_1 \geqslant \frac{\langle\delta^2\rangle}{D} + \frac{3\phi_1\langle\delta\rangle^2}{4\kappa\sigma\langle\delta^2\rangle}, \qquad \bar{\kappa} \gg 1 \tag{4.14}$$

Note that in the limit $\bar{\kappa} \to \infty$, relation (4.14) recovers the diffusion-controlled limit result of Prager.[5] Again, finite κ leads to larger relaxation times relative to the diffusion-controlled limit.

5. RELATIONSHIP OF THE TIMES T_1 AND τ TO THE FLUID PERMEABILITY

If a porous medium saturated with a viscous fluid of viscosity μ is subjected to an applied pressure gradient ∇p_0, then the induced average

velocity $\mathbf{Q}$ is proportional to ∇p_0, i.e., $\mathbf{Q} = -\mathbf{k} \cdot \nabla p_0/\mu$, where $\mathbf{k}$ is the fluid permeability tensor. This is referred to as Darcy's law.[21] Torquato[15] proved that the mean survival time τ for statistically anisotropic porous media of arbitrary topology is rigorously related to the fluid permeability $\mathbf{k}$ arising in Darcy's law for Stokes flow through the same porous medium by the relation

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

Relation (5.1) states that the permeability tensor $\mathbf{k}$ minus the isotropic tensor $D\phi_1\tau\mathbf{U}$ is negative-semidefinite, where $\mathbf{U}$ is the unit dyadic. In the isotropic case, (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. Relation (5.1) is remarkable in that it relates overall momentum transport on the one hand to overall diffusion transport on the other.

How sharp is the inequality of (5.1)? The equality of (5.1) is achieved[15] for one of the eigenvalues for transport in parallel channels of arbitrary cross-sectional shape:

$$k_{33} = D\phi_1 \tau = \frac{\phi_1^3}{c\sigma^2} \tag{5.3}$$

where c is a shape-dependent constant (e.g., $c = 2$ for circles, $c = 5/3$ for equilateral triangles, and $c = 1.78$ for squares), σ is the specific surface, and the channels are aligned in the x_3 direction. Note that since there is no flow in the other principal directions for this anisotropic geometry, i.e., $k_{11} = k_{22} = 0$, the bound of (5.1) is clearly satisfied.

For any microstructure with a completely disconnected pore space, k is zero, while τ is nonzero. Less trivially, for any cubic array of narrow tubes, $k = D\phi_1\tau/3$. For the case of transport exterior to a dilute bed of spheres, $k = 2D\phi_1\tau/3$, and thus the bound of (5.1) is relatively sharp. For porous media with low prosity and significant tortuosity, 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 *et al.*[22] very recently to reexamine the problem of 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. (2.29)], we also have

$$\mathbf{k} \leqslant D\phi_1 T_1 \mathbf{U} \tag{5.4}$$

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

It is useful to recall our earlier definition (2.29) of the *Laplace-variable-dependent* mean survival time

$$\tau(s) = \frac{\langle \hat{c}(\mathbf{r}, s) \rangle}{c_0 \phi_1} \tag{5.5}$$

Torquato and Avellaneda[16] also define the analogous *Laplace-variable-dependent* fluid permeability tensor

$$\mathsf{k}(s) = \frac{\nu \langle \hat{\mathbf{v}}(\mathbf{r}, s) \rangle}{v_0} \tag{5.6}$$

where $\hat{\mathbf{v}}$ is the Laplace transform of the solution of the time-dependent tensor Stokes equations, ν is the kinematic viscosity, and v_0 is some reference speed. It is proved that

$$\mathbf{k}(s) \leqslant D\phi_1 \tau(s)\, \mathbf{U} \tag{5.7}$$

Note that in the static case ($s = 0$), we recover Torquato's original result (5.1). The importance of (5.7) lies in the fact that $\mathbf{k}(s)$ can be related to the so-called dynamic permeability[23,24] $\tilde{\mathbf{k}}(\omega)$, 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. It turns out that the dynamic permeability and the Laplace-variable-dependent permeability (5.6) are related by[16] $\tilde{\mathbf{k}}(\omega) = \mathbf{k}(s = -i\omega)$, where $i = \sqrt{-1}$.

6. MICROSTRUCTURE CHARACTERIZATION

Sections 3 and 4 described some of the different types of statistical correlation functions (S_n, G_n, F_{sv}, F_{ss}, H_p, P) that have arisen in rigorous bounds on the mean survival time τ and principal relaxation time T_1. These correlation functions are also fundamental to the study of other effective properties of heterogeneous media.[17,18,25–27] Until recently, application of such bounds (although in existence for almost 30 years in some cases) was virtually nonexistent because of the difficulty involved in ascertaining the correlation functions. Are these different types of correlation functions related to one another? Can one write down a single expression that contains complete statistical information? As has been demonstrated, the answers to the last two queries are in the affirmative.

6.1. Unified Theoretical Approach

For simplicity, consider first a statistical distribution of N identical d-dimensional spheres of radius R (phase 2) in volume V distributed throughout a "matrix" (phase 1). (More complicated models are described below.) In the context of the trapping problem, the matrix phase is the trap-free region. Such a model is not as restrictive as one might initially surmise, especially since the particles may be allowed to overlap in varying degrees, thereby allowing interparticle clustering and thus the generation of interesting microstructures with long winding chains or large clusters. Therefore, the *matrix* need not be continuous. The d-dimensional spheres are spatially distributed according to the *specific* N-particle probability density $P_N(\mathbf{r}^N)$ which normalizes to unity. The ensemble average of any many-body function $F(\mathbf{r}^N)$ is then given by

$$\langle F(\mathbf{r}^N)\rangle = \int F(\mathbf{r}^N)\, P_N(\mathbf{r}^N)\, d\mathbf{r}^N$$

The reduced n-particle *generic* probability density is defined by

$$\rho_n(\mathbf{r}^n) = \frac{N!}{(N-n)!} \int P_N(\mathbf{r}^N)\, d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N \tag{6.1}$$

Thus, $\rho_n(\mathbf{r}^n)$ characterizes the probability of finding any n spheres with positions $\mathbf{r}^n$. If the medium is statistically homogeneous, the $\rho_n(\mathbf{r}^n)$ will depend upon the relative displacements $\mathbf{r}_{12},\ldots,\mathbf{r}_{1n}$, where $\mathbf{r}_{1i}=\mathbf{r}_i-\mathbf{r}_1$. In such instances, it is implied that the "thermodynamic limit" has been taken, i.e., $N\to\infty$, $V\to\infty$, such that the number density $\rho = N/V = \rho_1(\mathbf{r}_1)$ is some finite constant.

Torquato[28] has introduced the general n-point distribution function $H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q)$ which is defined to be the correlation associated with finding m points with positions $\mathbf{x}^m$ on certain surfaces within the medium, $p-m$ with positions $\mathbf{x}^{p-m}$ in certain spaces exterior to the spheres, and q sphere centers with positions $\mathbf{r}^q$, $n=p+q$, in a statistically *inhomogeneous* medium of N identical d-dimensional spheres. Torquato found a series representation of H_n for such media which enables one to compute it; namely, he found that

$$H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q) = (-1)^m \frac{\partial}{\partial a_1} \cdots \frac{\partial}{\partial a_m} G_n(\mathbf{x}^p; \mathbf{r}^q) \tag{6.2}$$

where

$$G_n(\mathbf{x}^p; \mathbf{r}^q) = \sum_{s=0}^{\infty} (-1)^s\, G_n^{(s)}(\mathbf{x}^p; \mathbf{r}^q) \tag{6.3}$$

$$G_n^{(s)}(\mathbf{x}^p;\mathbf{r}^q)=\frac{1}{s!}\prod_{l=1}^{q}\prod_{k=1}^{p}e(y_{kl};a_k)\int\rho_{q+s}(\mathbf{r}^{q+s})\prod_{j=q+1}^{q+s}m^{(p)}(\mathbf{x}^p;\mathbf{r}_j)\,d\mathbf{r}_j \tag{6.4}$$

$$m^p(\mathbf{x}^p;\mathbf{r}_j)=1-\prod_{i=1}^{P}[1-m(y_{ij};a_i)] \tag{6.5}$$

$$m(y_{ij};a)=\begin{cases}1, & y_{ij}<a\\ 0, & \text{otherwise}\end{cases} \tag{6.6}$$

$$e(y_{ij};a)=1-m(y_{ij};a) \tag{6.7}$$

$$y_{ij}=|\mathbf{x}_i-\mathbf{r}_j| \tag{6.8}$$

The key idea in arriving at (6.2) is the consideration of adding p "test" particles of radii $b_1,\ldots,b_p$ in the system of N spherical inclusions of radius R, with $p\ll N$. Since the ith test particle is capable of excluding the centers of the actual inclusions from spheres of radius a_i (where for $b_i>0$, $a_i=R+b_i$ and for $b_i=0$, $a_i=R-c_i$, $0\leqslant c_i\leqslant R$), then it is natural to associate with each test particle a subdivision of space into two regions: D_i, the space available to the ith test particle (i.e., the space outside N spheres of radius a_i centered at $\mathbf{r}^N$) and the complement space D_i^*. Let $\mathscr{S}_i$ denote the surface between D_i and D_i^*. Thus, more specifically, $H_n(\mathbf{x}^m;\mathbf{x}^{p-m};\mathbf{r}^q)$ gives the correlation associated with finding the center of a test particle of radius b_1 at $\mathbf{x}_1$ on $\mathscr{S}_1,\ldots$, and the center of a test particle of radius b_m at $\mathbf{x}_m$ on $\mathscr{S}_m$, and the center of a test particle of radius b_{m+1} at $\mathbf{x}_{m+1}$ in $D_{m+1},\ldots$, and the center of a test particle of radius b_p at $\mathbf{x}_p$ in D_p, and of finding any q inclusions with configuration $\mathbf{r}^q$, where $\mathbf{x}^{p-m}\equiv\{\mathbf{x}_{m+1},\ldots,\mathbf{x}_p\}$ and $n=p+q$. Note that it is only in the limit $b_i\to 0$ or $a_i\to R$ that D_i is the space exterior to the actual inclusions, i.e., the matrix phase.

According to relations (6.2)–(6.4), one needs to know the n-particle probability densities ρ_n in order to compute the general n-point distribution function H_n for distributions of interpenetrable spheres. The ρ_n have been extensively investigated in the context of the statistical mechanics of liquids and solids.[29] Here of course the microscopic scale refers to the arrangement and motion of molecules. Thus, the powerful machinery and results of statistical mechanics can be brought to bear on the problem of characterizing the microstructure of random heterogeneous media.

From the general quantity $H_n(\mathbf{x}^m;\mathbf{x}^{p-m};\mathbf{r}^q)$ one can obtain all of the aforementioned correlation functions and their generalizations, i.e.,

$$S_n(\mathbf{x}^n)\equiv S_n^{(1)}(\mathbf{x}^n)=\lim_{a_i\to R,\forall i}H_n(\varnothing;\mathbf{x}^n;\varnothing) \tag{6.9}$$

$$G_n(\mathbf{x}_1;\mathbf{r}^q)=\lim_{a_1\to R}H_n(\varnothing;\mathbf{x}_1;\mathbf{r}^q) \tag{6.10}$$

$$F_{sv}(\mathbf{x}_1, \mathbf{x}_2) = \lim_{a_i \to R, \forall i} H_2(\mathbf{x}_1; \mathbf{x}_2; \varnothing) \tag{6.11}$$

$$F_{ss}(\mathbf{x}_1, \mathbf{x}_2) = \lim_{a_i \to R, \forall i} H_2(\mathbf{x}_1, \mathbf{x}_2; \varnothing; \varnothing) \tag{6.12}$$

and

$$H_P(r) = \lim_{a_1 \to 0} \frac{\partial}{\partial a_1} \lim_{|\mathbf{x}_1 - \mathbf{r}_1| \to 0} H_2(\varnothing; \mathbf{x}_1; \mathbf{r}_1) \tag{6.13}$$

Here $\varnothing$ denotes the empty set. For particulate media the S_n are termed the n-point *matrix* probability functions. Note that the series for S_n obtained in this way is identical to the one derived by Torquato and Stell.[30] Representations of the remaining quantities (point/n-particle quantities, surface correlation functions, and the nearest-neighbor distribution functions) were obtained for the first time from (6.2). Moreover, one can obtain the pore-size distribution function $P(\delta)$ from the "void" nearest-neighbor distribution function[19] $H_V(r)$ for a single test particle of radius $b_1 = r - R$ at $\mathbf{x}_1$:

$$H_V(r) = H_1(\mathbf{x}_1; \phi; \phi) \tag{6.14}$$

$H_V(r)\,dr$ may be interpreted to be the probability that, at an arbitrary point in the system, the center of the nearest inclusion of radius R lies at a distance between r and $r + dr$. This is identical to the function defined in the scaled-particle theory of Reiss *et al.*[31] The functions $P(\delta)$ and $H_V(r)$ for identical spheres of radius R are related in a simple manner:

$$P(\delta) = \frac{H_V(\delta + R)}{\phi_1} \tag{6.15}$$

Note that Torquato[28] has also given the general asymptotic properties of the general H_n for cases in which a subset of the n points are far from one another and has given successive upper and lower bounds on the H_n. The reader is referred to this reference for further details on these topics.

The concept of a distribution of particles is very general if it is not restricted to impenetrable particles. The intersection of particles need not have any physical meaning, but is simply a device for generating complex shapes from simple elements. An example of an interpenetrable-sphere model is the so-called penetrable-concentric-shell or "cherry-pit" model.[32] Here each D-dimensional sphere of diameter $2R$ is composed of an impenetrable core of diameter $2\lambda R$, encompassed by a perfectly penetrable shell of thickness $(1 - \lambda)R$ (cf. Fig. 1). The extreme limits $\lambda = 0$ and 1 correspond, respectively, to cases of fully penetrable and totally

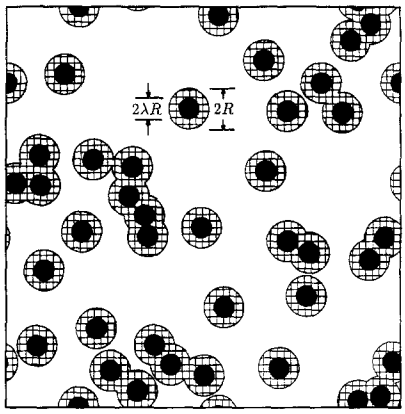

Fig. 1. A distribution of identical disks of radius R in the penetrable-concentric-shell model or cherry-pit model.[32] Each disk is composed of an inner impenetrable core ("pit") of diameter $2\lambda R$ (indicated by the black circular region) encompassed by a perfectly penetrable concentric shell of thickness $(1-\lambda)R$, $0 \leqslant \lambda \leqslant 1$.

impenetrable spheres. In some instances these limits shall be simply referred to as overlapping and impenetrable (hard) spheres, respectively. This is a versatile model in that it enables one to vary the degree of "connectedness" of the particle phase by varying the impenetrability index λ.

For fully penetrable spheres ($\lambda = 0$) at number density ρ (i.e., number of particles per unit volume), there is a complete absence of spatial correlation between the particles and thus one has the exact simple relation valid for all n:

$$\rho_n(\mathbf{r}^n) = \rho^n, \qquad \forall n \tag{6.16}$$

For $d = 2$ and $d = 3$, the particle phase percolates at $\phi_2^c \simeq 0.68$ and $\phi_2^c \simeq 0.3$, respectively (see, e.g., ref. 33). For $d = 3$, the medium is actually bicontinuous for the range $0.3 \leqslant \phi_2 \leqslant 0.97$, where $\phi_2 = 0.97$ or $\phi_1 = 0.03$ corresponds to the percolation threshold of the matrix,[34] i.e., for $\phi_1 < 0.03$ the matrix is disconnected.

For totally impenetrable spheres ($\lambda = 1$) at number density ρ, the impenetrability condition alone does not uniquely determine the ensemble. To fix the ensemble, one must specify further information about the process of manufacture. For example, stating that the hard-sphere system is also in thermal equilibrium (which, roughly speaking, may be regarded as the most random distribution of spheres subject to the impenetrability constraint) completely specifies the distribution. Vastly more is known about the equilibrium ρ_n than about the infinitely many sets of nonequilibrium

$\rho_{n'}$.[29] In light of this knowledge and because the former is a reasonable model of heterogeneous media, many of the results for the H_n have been obtained for equilibrium ensembles.

For various models of identical d-dimensional interpenetrable spheres the lower-order n-point matrix probability functions[35-37] S_n, surface correlation functions[38] F_{sv} and F_{ss}, particle nearest-neighbor distribution function[19] H_P, and the void nearest-neighbor distribution function[19] H_V have been evaluated. As an illustrative example, consider the determination of H_V or, equivalently, the pore size distribution $P(\delta)$. Torquato *et al.*[19] derived various approximate expressions for the void nearest-neighbor function H_V for *totally impenetrable spheres*. The most accurate of these approximations is given by

$$H_V(x) = \frac{12\eta}{R}(ex^2 + fx + g)\, E_V(x), \qquad x > \frac{1}{2} \tag{6.17}$$

where

$$E_V(x) = (1-\eta)\exp[-\eta(8ex^3 + 12fx^2 + 24gx + h)], \qquad x > \frac{1}{2} \tag{6.18}$$

$$e = \frac{(1+\eta)}{(1-\eta)^3} \tag{6.19}$$

$$f = -\frac{\eta(3+\eta)}{2(1-\eta)^3} \tag{6.20}$$

$$g = \frac{\eta^2}{2(1-\eta)^3} \tag{6.21}$$

$$h = \frac{-9\eta^2 + 7\eta - 2}{2(1-\eta)^3} \tag{6.22}$$

$$x = \frac{r}{2R} \tag{6.23}$$

Here

$$\eta = \rho \frac{4\pi}{3} R^3 \tag{6.24}$$

is a reduced density that for impenetrable spheres is identical to the sphere volume fraction ϕ_2. However, for interpenetrable spheres, $\eta \neq \phi_2$. Relation (6.17) was found to be in excellent agreement with computer simulations[39] for a wide range of volume fractions ϕ_2. Here $E_V(x)$ is the "void" *exclusion*

probability, i.e., the probability of finding a cavity of dimensionless radius $x = r/2R$ empty of inclusion centers. Notice that when $x = 1/2$, (6.17) and (6.18) give the exact results

$$H_V(1/2) = \sigma = 3\phi^2/R \tag{6.25}$$

$$E_V(1/2) = \phi_1 = 1 - \phi_2 = 1 - \eta \tag{6.26}$$

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. (6.17) and (6.18)] by simply replacing R (on the rhs of the relations) with λR. For example, carrying out this substitution and taking the limit $\lambda \to 0$ gives the appropriate simple *exact* results for fully penetrable or overlapping spheres:

$$H_V(x) = \frac{12\eta x^2}{R} \exp(-8\eta x^3), \qquad x \geqslant 0 \tag{6.27}$$

$$E_V(x) = \exp(-8\eta x^3), \qquad x \geqslant 0 \tag{6.28}$$

From the relations above, we have for $x = 1/2$ that

$$H_V(1/2) = \sigma = (3/R)\,\eta\phi_1 \tag{6.29}$$

$$E_V(1/2) = \phi_1 = 1 - \phi_2 = \exp(-\eta) \tag{6.30}$$

In Fig. 2 we plot the dimensionless pore size distribution $P(\delta)$ in the cherry-pit model for $\lambda = 0$, 0.8, and 1, and an inclusion volume fraction

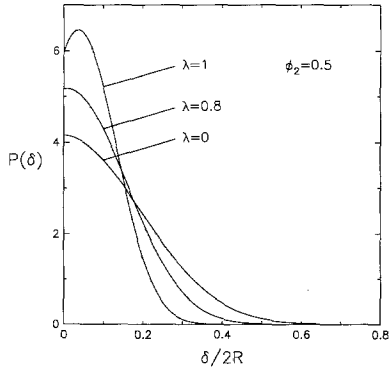

Fig. 2. The pore size distribution $P(\delta)$ versus the dimensionless distance $\delta/2R$ for distributions of spheres of radius R in the penetrable-concentric-shell or cherry-pit model[32] for three different values of the impenetrability parameter λ: $\lambda = 0$, 0.8, and 1. The pore region is the space exterior to the spheres. Here the porosity ϕ_1 is equal to the trap volume function $\phi_2 = 0.5$.

$\phi_2 = 0.5$, using relations (6.15) and (6.17) for spheres of unit diameter ($2R = 1$).

Thus far we have described results for continuum models consisting of distributions of *iden*tical spheres. Are there corresponding results for more complex continuum models? Recently, the formalism of Torquato[28] for the general n-point distribution function H_n has been extended by Lu and Torquato[40] to treat sphere systems with a polydispersivity in sphere diameter. Polydispersivity constitutes an important microstructural feature of a wide class of heterogeneous media. The results of Lu and Torquato contain as special cases the lower-order S_n for polydispersed systems obtained by Stell and Rikvold.[37] Torquato and Sen[41] and Lado and Torquato[42] have recently computed the two-point matrix probability function S_2 for the *anisotropic* microgeometries consisting of oriented cylinders and spheroids of aspect ratio b/a, respectively. The latter result is particularly interesting in that one can obtain $S_2(\mathbf{x})$ for a spheroidal system with aspect ratio b/a from $S_2(x)$ for an equivalent sphere system at the same volume fraction. Indeed, this isomorphism applies to S_n for any n, namely,[43]

$$S_n\left(\mathbf{x}_{12},\ldots,\mathbf{x}_{1n};\frac{b}{a}\right) = S_n\left(\sigma_0\frac{x_{12}}{\sigma(\theta_{12})},\ldots,\sigma_0\frac{x_{1n}}{\sigma(\theta_{1n})};1\right) \tag{6.31}$$

where $\sigma_0 = 2a$,

$$\sigma(\theta) = \frac{2a}{[1-(1-a^2/b^2)\cos^2\theta]^{1/2}} \tag{6.32}$$

is an angle-dependent "sphere diameter," and $x_{ij} = |\mathbf{x}_j - \mathbf{x}_i|$. This isomorphism was first exploited by Lebowitz and Perram[44] in the context of statistical thermodynamics of aligned hard spheroids. Note that scaling relations such as (6.31) apply as well to the point/q-particle distribution function $G_n(\mathbf{x};\mathbf{r}^q)$ for oriented spheroidal systems.

7. BROWNIAN-MOTION SIMULATION TECHNIQUES

Relative to the amount of theoretical work being conducted on predicting effective properties, there is a paucity of work on "exact" simulations of the effective property of interest, especially for "continuum" models. Such "computer experiments" could provide unambiguous tests on theories for well-defined continuum model microstructures. Computer simulations could also yield information on quantities of theoretical importance that are not readily measurable in the laboratory.

Unfortunately, most computer-simulation studies carried out in the past have attempted to solve the local governing differential equations for the fields (e.g., electric, temperature, concentration, etc.), subject to the appropriate boundary conditions at the multiphase interface of the computer-generated heterogeneous system, using some numerical technique such as finite differences or finite elements. This is repeated for all possible configurations and then the fields are configurationally averaged, since the effective properties depend upon ensemble averages of the fields. This is a very *inefficient* way of getting the average behavior, since there is a significant amount of information lost in going from the local to the average fields. Accordingly, such calculations become computationally exorbitant, even when performed on a supercomputer.

Brownian-motion simulation techniques[8,9,45–49] provide a means of directly determining effective transport properties of disordered heterogeneous media for processes governed by a steady-state diffusion equation. Hence, the algorithm can be applied to determine the effective electrical and thermal conductivity, dielectric constant, magnetic permeability, diffusion coefficient associated with flow past fixed obstacles, and the mean survival time associated with diffusion and reaction among traps. In the case of the trapping problem, the simulation method is demonstrated to have an execution time that is at least an order of magnitude faster than previous simulation methodologies.

Consider the diffusion-controlled trapping problem first. The diffusing particles undergo Brownian motion in the trap-free region $\mathcal{V}_1$ until they come in contact with a trap. The mean survival time τ is related to the total mean square displacement before trapping $\overline{r^2}$ by the relation

$$\tau = \frac{\overline{r^2}}{2dD} \tag{7.1}$$

where d is the space dimension. Lee *et al.*[45] computed $\overline{r^2}$ for distributions of spherical traps of radius R by performing "continuum" random walks of fixed step size a. They obtained simulation data for several step sizes and extrapolated to the limit $a/R \to 0$. The so-called Grid method[50] was employed to significantly reduce the computer time required to check for trapping. Using the same technique, Miller and Torquato[46] computed k_D for spherical traps with a polydispersivity in size and compared these results to theoretical predictions of k_D. Let us call this simulation procedure "method I". (It should be noted that Richards[8,9] had earlier carried our lattice random walks for the same models.) This procedure is already considerably faster than finite-difference or finite-elements schemes.

A more efficient Brownian-motion simulation technique recently

formulated by Torquato and Kim[48] makes use of first-passage-time equations. The basic idea is that the zigzag random motion of the diffusing particle need not be simulated in detail. First (referring to Fig. 3), one constructs the largest possible concentric sphere of radius r_i about the walker which does not overlap any trap particles, and then a point on the sphere surface of radius r_i is chosen randomly. The radius r_i is related to the mean hitting time T_i, the average time taken by the Brownian particle to first strike the surface of the sphere of radius r_i, by

$$r_i^2 = 6DT_i \tag{7.2}$$

This process is repeated until the random walker is trapped and the survival time is obtained by summing over all the r_i^2, i.e., the mean survival time for a single walk and a configuration of traps is given by

$$\tau = \sum_{i=1} T_i = \frac{\sum r_i^2}{2dD} \tag{7.3}$$

The mean survival time is then obtained by averaging over many walks and configurations. In practice, trapping can never be achieved in the

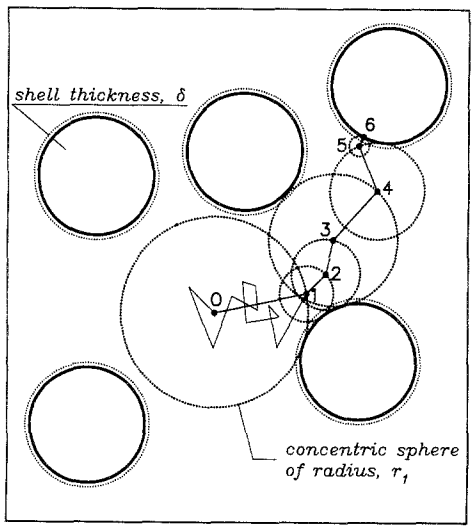

Fig. 3. Two-dimensional schematic representation of the first-passage-time technique employed by Torquato and Kim.[48] The zigzag motion of the random walker need not be simulated step by step. Instead one constructs the largest concentric sphere of radius r_i which does not overlap any trap; the next position of the walker is taken to be on the concentric sphere surface (and is chosen randomly). This process is repeated, each time keeping track of r_i^2, until the walker gets trapped (i.e., comes within a small distance δ of a trap).

course of the simulation. We assume the walker is trapped if it lies within a small distance δ from the trap surface. Let us call this first-passage-time approach "method II."

Table I compares the computing time required to obtain the scaled inverse mean hitting time τ_s/τ for a system of equisized, fully-penetrable spheres at the reduced densities $\eta = 0.3$ and $\eta = 0.5$ ($\eta = \rho 4\pi R^3/3$), using the two aforementioned different algorithms: methods I and II. Here τ_s is the dilute-limit Smoluchowski[4] result, i.e.,

$$\tau_s = R^2/3\phi_2 \tag{7.4}$$

For a reduced density $\eta = 0.3$, method II is about 16 times faster than method I. For $\eta = 0.5$, it is about 10 times faster than method I. Thus, the first-passage-time method is extremely fast and accurate.

The first-passage-time method of Torquato and Kim[48] has been recently applied by Miller *et al.*[49] to determine the trapping rate associated with diffusion-controlled reactions among *oriented spheroidal traps* of arbitrary aspect ratio b/a. They studied prolate ($b/a > 1$) and oblate ($b/a < 1$) cases for both *overlapping* (i.e., spatially uncorrelated) and *hard* (i.e., spatially correlated) traps.

We have also employed such first-passage-time analyses to compute effective conductivities of *general n-phase* heterogeneous media. In this case, one can show that

$$\frac{\sigma_e}{\sigma_1} = \frac{\overline{r^2(t)}|_{\text{inhomogeneous}}}{\overline{r^2(t)}|_{\text{homogeneous}}} \tag{7.5}$$

Here the denominator of the right-hand side represents the mean square displacement in a reference homogeneous medium of conductivity σ_1 and

Table I. Comparison of Computing Time Required by Two Different Brownian-Motions Algorithms to Obtain the Scaled Inverse Mean Survival Time τ_s/τ (i.e., Scaled Trapping Rate) for a System of Identical Fully Penetrable Traps at Reduced Densities $\eta = 0.3$ and 0.5[a]

	$\eta = 0.3$		$\eta = 0.5$	
Algorithm	CPU Time (hours)	τ_s/τ	CPU Time (hours)	τ_s/τ
Method I[45]	12.08	2.476	6.85	3.301
Method II[48]	0.77	2.469	0.72	3.330

[a] Simulations were performed on a VAX station 3200 using 490 traps, 50 configurations, and 1000 random walkers per configuration. Here $\delta/R = 0.0001$.

the numerator represents the corresponding quantity for the heterogeneous medium. Simulations of σ_e involve two new features: (1) different walking speeds in each phase, and (2) a nonzero probability of reflection at the interface between the different materials. Thus, the first-passage-time equations for the mean hitting times and the reflection probabilities in the neighborhood of the two-phase interface must be derived. This has recently been done by Kim and Torquato and was applied for random distributions of inclusions.[51]

8. CALCULATIONS OF SURVIVAL AND RELAXATION TIMES FOR CONTINUUM MODELS

Here we shall discuss calculations of bounds on the mean survival time τ and the principal relaxation time T_1 for the simple cases of diffusion interior to spheres and more complex models of diffusion exterior to *spherical* and *nonspherical* particles. Bounds on τ for particulate traps are compared to "exact" Brownian-motion simulation data.

2.1. Diffusion Interior to Spheres

Consider diffusion occurring interior to nonoverlapping (i.e., disconnected) spherical cavities of radius R with finite surface rate constant κ. For such a simple microgeometry, we know many results exactly.[16] For example, we have

$$\tau = \frac{R^2}{15D} + \frac{R}{3\kappa} \tag{8.1}$$

$$\psi_n(r) = \frac{B_n}{r} \sin(r\sqrt{\lambda_n}) \tag{8.2}$$

where

$$B_n^2 = \frac{2R^2(R^2\lambda_n + K)}{3(R^2\lambda_n + K^2 - K)} \tag{8.3}$$

$$K = 1 - \frac{\kappa}{D} = R\sqrt{\lambda_n}\cot(R\sqrt{\lambda_n}) \tag{8.4}$$

and the associated eigenfunction coefficients are

$$a_n = \frac{3B_n}{R^3\lambda_n} \sin(r\sqrt{\lambda_n}) \tag{8.5}$$

The following asymptotic expressions hold for the principal relaxation time $T_1 = 1/D\lambda_n$:

$$T_1 \sim \frac{R}{3\kappa} + \frac{R^2}{15D} + \frac{17R^3\kappa}{525D^2} \qquad \left(\frac{\kappa R}{D} \ll 1\right) \tag{8.6}$$

$$T_1 \sim \frac{R^2}{\pi^2 D} + \frac{2R}{\pi^2 \kappa} \tag{8.7}$$

Moreover, the pore size distribution $P(\delta)$ is given by

$$P(\delta) = \begin{cases} \dfrac{3(R-\delta)^2}{R^3}, & \delta < R \\ 0, & \delta > R \end{cases} \tag{8.8}$$

This expression combined with (3.12) yields the moments as[16]

$$\langle \delta^n \rangle = \frac{6R^n}{(n+1)(n+2)(n+3)} \tag{8.9}$$

The lower bound (4.6) on the mean survival time is easily calculated as

$$\tau \geqslant \frac{R^2}{16D} + \frac{R}{3\kappa} \tag{8.10}$$

Comparison of this result to the exact result (8.1) reveals that the bound is remarkably sharp. The reason for this is that the mean square displacement of a Brownian particle (because it is confined to be in a trap-free region characterized by a single size) is well described by the square of the first moment $P(\delta)$. Similarly, the lower bounds (4.13) and (4.14) on the principal relaxation time T_1 yield exactly

$$T_1 \geqslant \frac{R}{3\kappa} + \frac{R^2}{20D} \qquad \left(\frac{\kappa R}{D} \ll 1\right) \tag{8.11}$$

$$T_1 \geqslant \frac{R^2}{10D} + \frac{5R}{32\kappa} \qquad \left(\frac{\kappa R}{D} \gg 1\right) \tag{8.12}$$

Again, comparison to the exact results (8.6) and (8.7) shows that the bounds (8.11) and (8.12) are quite sharp.

It is instructive to examine Proposition 2 [relation (2.30)] for the case of diffusion interior to spheres of radius R. For the perfectly nonabsorbing limit[16] ($\kappa R/D \to 0$),

$$T_1 = a_1^2 T_1 = \tau \sim \frac{R}{3\kappa} \tag{8.13}$$

and hence the bounds in (2.30) are exact since the lowest mode dominates completely. For the perfectly absorbing limit ($\kappa R/D \to \infty$), we have from the exact results

$$a_1^2 T_1 \sim \frac{6a^2}{\pi^4 D}, \qquad T_1 \sim \frac{a^2}{\pi^2 D}, \qquad \tau \sim \frac{a^2}{15D} \tag{8.14}$$

or from (2.30)

$$\frac{6a^2}{\pi^4 D} \leqslant \frac{a^2}{15D} \leqslant \frac{a^2}{\pi^2 D} \tag{8.15}$$

The bounds of (8.15) are relatively sharp.

8.2. Diffusion Exterior to Particles

Figure 4 shows the simulation data of Lee *et al.*[45] for dimensionless trapping rate or, equivalently, dimensionless inverse survival time τ_s/τ in the penetrable-concentric-shell or cherry-pit model in the diffusion-controlled limit ($\bar{\kappa} = \infty$) for various values of the impenetrability parameter λ. For fixed volume fraction ϕ_2, the trapping rate increases with increasing λ because the surface area available for reaction increases. In Fig. 5 we compare, for the fully-penetrable case ($\lambda = 0$), Richards'[8] survival probability theory, the interfacial-surface lower bound computed by Torquato,[52] and

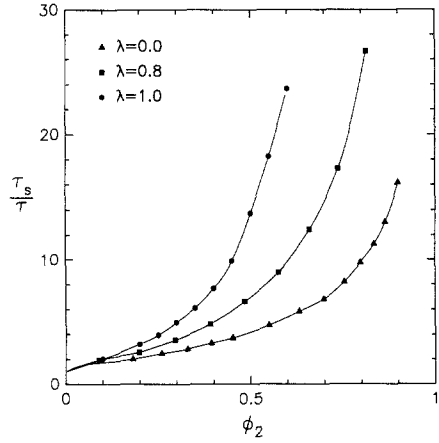

Fig. 4. Dimensionless trapping rate or inverse survival time τ_s/τ in the cherry-pit model,[32] versus trap volume fraction ϕ_2 for values of the impenetrability parameter $\lambda = 0, 0.8$, and 1 as simulated by Lee *et al.*[45] Dashed lines are spline fits of the simulation data (solid symbols). Here $\tau_s = R^2/3\phi_2$ and R is the sphere radius.

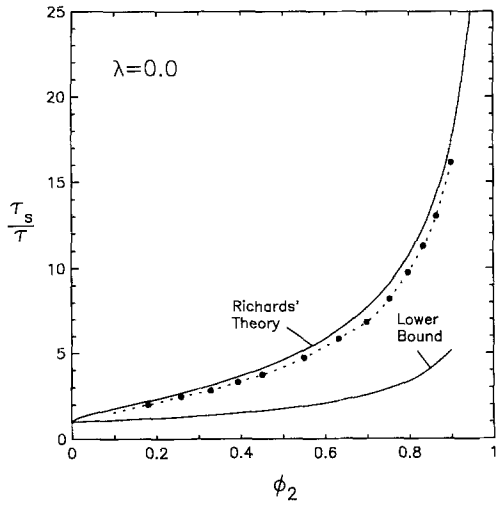

Fig. 5. Dimensionless trapping rate or inverse survival time τ_s/τ for fully penetrable traps ($\lambda = 0$) versus trap volume fraction ϕ_2. The dotted line is a spline fit of the simulation data of Lee *et al.*[45] (solid circles). Included in the plot is Richards' theory[8] and the interfacial-surface lower bound computed by Torquato.[52] Here $\tau_s = R^2/3\phi_2$.

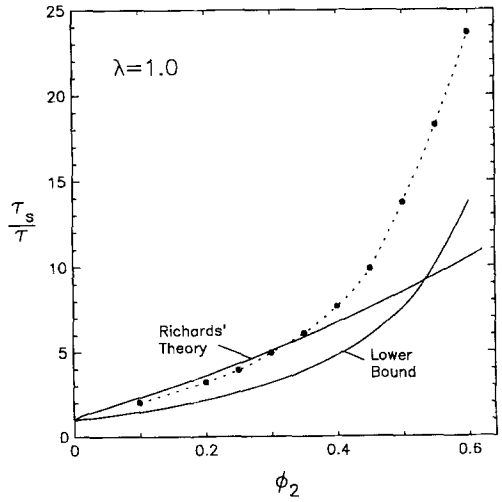

Fig. 6. Dimensionless trapping rate or inverse survival time τ_s/τ for totally impenetrable traps ($\lambda = 1$) versus trap volume fraction ϕ_2. The dotted line is a spline fit of the simulation data of Lee *et al.*[45] (solid circles). Included in the plot is Richards' theory[9] and the interfacial-surface lower bound computed by Torquato.[52] Here $\tau_s = R^2/3\phi_2$.

the simulation data.[45] Richards' theory is in excellent agreement with data for all ϕ_2. (We note that Szabo,[13] using a different method, obtained an expression for the trapping rate which is identical to Richards' expression.) Figure 6 gives the corresponding comparison for the case of totally impenetrable traps ($\lambda = 1$). Here the survival probability theory of Richards[9] actually dips below the data and indeed violates the lower bound computed by Torquato[52] for $\phi_2 > 0.52$. (Various definitions of the trapping rate exist in the literature; see Richards and Torquato[53] for a discussion of the relationships between these different definitions. In particular, the definition used in refs. 8 and 9 is different from the one of ref. 52.)

Figure 7 depicts the simulation data of Miller *et al.*[49] for dimensionless trapping rate or inverse survival time $a^2/\tau D$ versus $\log(b/a)$ for both *impenetrable* and *overlapping* oriented spheroids of aspect ratio b/a at $\phi_2 = 0.3$. Included in the figure are the corresponding calculations of the two-point void lower bound (3.7) on τ^{-1} as obtained Torquato and Lado[43]:

$$\frac{a^2}{\tau D} \geqslant \frac{\phi_1 \phi_2^2}{4\langle x \rangle_o} f\left(\frac{b}{a}\right) \tag{8.16}$$

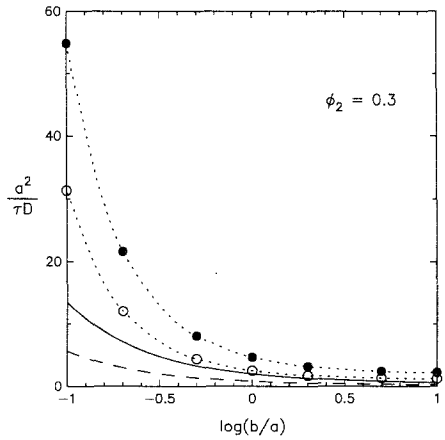

Fig. 7. Dimensionless trapping rate or inverse survival time $a^2/\tau D$ versus the log of the aspect ratio b/a for hard, oriented spheroids and overlapping, oriented spheroids at a spheroid volume fraction $\phi_2 = 0.3$. Filled and unfilled circles are the hard and overlapping simulation data, respectively, of Miller *et al.*[49]; dotted lines are spline fits of the data. Solid and dashed lines, respectively, are the lower bounds for hard and overlapping spheroidal traps obtained by Torquato and Lado.[43]

where $\langle x \rangle_o$ is the first moment of the two-point probability function for the equivalent spherical system of radius a and volume fraction defined by

$$\langle x \rangle_o = \int_0^\infty x[S_2(x) - \phi_1^2]\, dx \tag{8.17}$$

Note surprisingly, the trapping rate, for fixed ϕ_2, decreases with increasing aspect ratio; prolate and oblate results are always below and above the sphere results ($b/a = 1$), respectively. This is related to the fact that surface area available for reaction decreases as b/a increases for fixed ϕ_2. Whereas τ^{-1} gradually changes as the aspect ratio b/a is varied for prolate spheroidal traps, τ^{-1} dramatically increases as the spheroids become disklike ($b/a \ll 1$). For the case of *impenetrable oblate* traps, the data for the range $0.1 \leqslant b/a \leqslant 1$ obey the following power law:

$$a^2/\tau D \sim (b/a)^{-\alpha} \tag{8.18}$$

where the exponent α (approximately unity) weakly depends on ϕ_2 ($\alpha = 0.99$ at $\phi_2 = 0.1$, $\alpha = 1.07$ at $\phi_2 = 0.3$, and $\alpha = 1.11$ at $\phi_2 = 0.5$).

In Fig. 8 we compare the lower bound (4.6) on the dimensionless survival time $\tau D/R^2$ (where R is sphere radius) in the diffusion-controlled case ($\bar{\kappa} = \kappa R/D = \infty$) to the simulation data of Lee *et al.*[45] for the cherry-pit model[32] in the extreme limits of the impenetrability parameter λ. Com-

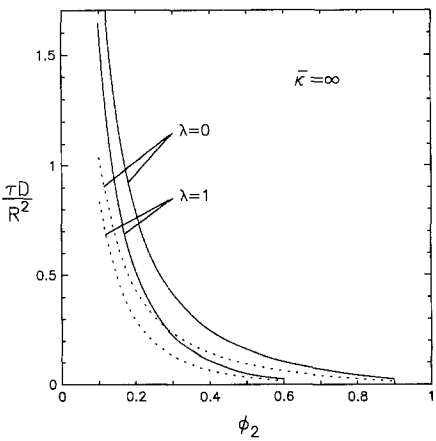

Fig. 8. Comparison of the lower bound (4.6) on the dimensionless survival time $\tau D/R^2$ in the diffusion-controlled limit ($\bar{\kappa} = \infty$) versus trap volume fraction ϕ_2 (dotted lines) to the simulation data (solid lines) of Lee *et al.*[45] for spherical traps of radius R in the cherry-pit model[32] in the extreme limits of the values of the impenetrability parameter λ, i.e., $\lambda = 0$ and $\lambda = 1$. Here $\bar{\kappa} = \kappa R/D$.

parison 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 a Brownian particle as ϕ_2 is made larger or as the porosity $\phi_1 = 1 - \phi_2$ is made smaller.

In Fig. 9 we plot the lower bound (4.11) on the dimensionless relaxation time $T_1 D/a^2$ versus 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 fixed volume fraction.

Since we have no simulation results for T_1, it is natural to ask, how sharp are the bounds obtained for T_1 in the cherry-pit model? Consider this question first for the case of fully penetrable spheres; 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 is proportional to $(a/L)^2$ for $L \gg 1$ or, equivalently, the principal relaxation time T_1 is proportional to $(L/a)^2$ for $L \gg 1$. The reason for this divergent behavior is that T_1 is determined by the large fluctuations of the ensemble of configurations, corresponding to the existence of very large pores, and such behavior is 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.[54] The associated average survival probability behaves

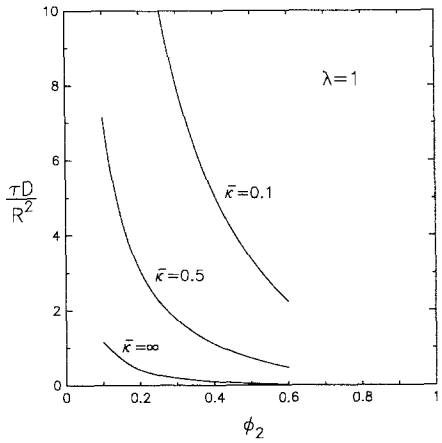

Fig. 9. Lower bound (4.11) on the dimensionless relaxation time $T_1 D/R^2$ versus the trap volume fraction ϕ_2 in the cherry-pit model[32] for impenetrability $\lambda = 0, 0.8$, and 1 with $\bar{\kappa} = \kappa R/D = \infty$.

like the stretched exponential $\exp[-\text{constant } t^{d/(d+2)}]$ in d dimensions as $t \to \infty$.[54,55] 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. For practical purposes, $P(\delta)$ for the Poisson system has finite support,[16] i.e., it is supported in the interval $[0, \delta_0]$. For example, from Fig. 2 for $\phi_1 = \phi_2 = 0.5$, $\delta_0/2R \simeq 0.7$ for $\lambda = 0$ ("Poisson" distribution) and use of the relation[16] that $T_1 \leqslant c\delta_0^2/D$ (where c is a bounded constant) suggests that the lower bound $\langle \delta^2 \rangle / D$ on T_1 in Fig. 9 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.

To summarize, the lower bound (4.11) 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 (4.11) on the mean survival time

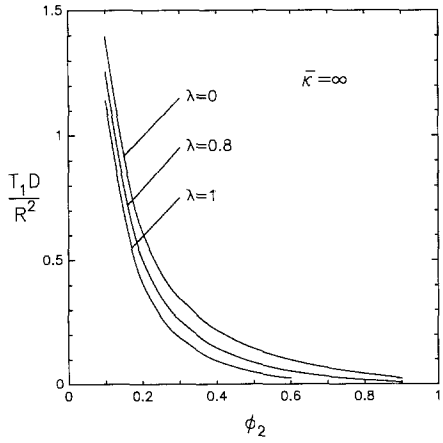

Fig. 10. Lower bound (4.6) on the dimensionless survival time $\tau D/R^2$ versus ϕ_2 for totally impenetrable traps ($\lambda = 1$) for several values of the dimensionless surface rate constant $\bar{\kappa} = \kappa R/D$: $\bar{\kappa} = \infty$, 0.5, and 0.1.

τ is a more robust estimator of τ since it is related to the entire spectrum of eigenvalues (see Eq. (2.26) below).

The lower bound (4.6) on the dimensionless survival time $\tau D/R^2$ versus ϕ_2 for totally impenetrable traps ($\lambda = 1$) for several values of the dimensionless surface rate constant $\bar{\kappa}(\infty, 0.5, 0.1)$ is depicted in Fig. 10. Observe that the lower bound on τ increases with decreasing surface reaction. This is consistent with the fact that 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 to that for τ and hence is not shown graphically.

ACKNOWLEDGMENTS

It has been a privilege to have worked with my colleagues J. Rubinstein, M. Avellaneda, S. B. Lee, C. A. Miller, I. C. Kim, F. Lado, and P. M. Richards on the various trapping problems described here. The author gratefully acknowledges the support of the Office of Basic Energy Sciences, U. S. Department of Energy under grant DE-FG05-86ER 13842. He also acknowledges the partial support of the U. S. Air Force grant AFOSR-90-0090 during his sabbatical leave at the Courant Institute of Mathematical Sciences.

REFERENCES

1. D. F. Calef and J. M. Deutch, *Annu. Rev. Chem. Phys.* **34**:493 (1983).
2. H. C. Berg, *Random Walks in Biology* (Princeton University Press, Princeton, New Jersey, 1983).
3. G. H. Weiss, *J. Stat. Phys.* **42**:3 (1986).
4. M. von Smoluchkowski, *Phys. Z.* **17**:557 (1916).
5. S. Prager, *Chem. Eng. Sci.* **18**:227 (1963).
6. B. U. Felderhof and J. M. Deutch, *J. Chem. Phys.* **64**:4551 (1976).
7. R. I. Cukier and K. F. Freed, *J. Chem. Phys.* **78**:2573 (1983).
8. P. M. Richards, *J. Chem. Phys.* **85**:3520 (1986).
9. P. M. Richards, *Phys. Rev. B* **35**:248 (1987).
10. J. Rubinstein and S. Torquato, *J. Chem. Phys.* **88**:6372 (1988).
11. A. Szabo, R. Zwanzig, and N. Agmon, *Phys. Rev. Lett.* **61**:2496 (1988).
12. S. Torquato and J. Rubinstein, *J. Chem. Phys.* **90**:1644 (1989).
13. A. Szabo, *J. Phys. Chem.* **93**:6929 (1989).
14. J. R. Banavar and L. M. Schwartz, *Phys. Rev. Lett.* **58**:1411 (1987).
15. S. Torquato, *Phys. Rev. Lett.* **64**:2644 (1990).
16. S. Torquato and M. Avellaneda, *J. Chem. Phys.* **95**:6477 (1991).
17. S. Prager, *Physica* **29**:129 (1963).
18. M. Doi, *J. Phys. Soc. Japan* **40**:56 (1976).
19. S. Torquato, B. Lu, and J. Rubinstein, *Phys. Rev. A* **41**:2059 (1990).

20. R. Courant and D. Hilbert, *Methods of Mathematical Physics*, Vol. I (Wiley-Interscience, New York, 1953).
21. A. E. Scheidegger, *The Physics of Flow through Porous Media* (University of Toronto Press, Toronto, 1974).
22. D. J. Wilkinson, D. L. Johnson, and L. M. Schwartz, *Phys. Rev. B*, in press.
23. D. L. Johnson, J. Koplik, and R. Dashen, *J. Fluid Mech.* **176**:379 (1987).
24. P. Sheng and M. Y. Zhou, *Phys. Rev. Lett.* **61**:159 (1988).
25. G. W. Milton, *Phys. Rev. Lett.* **46**:542 (1981).
26. S. Torquato, *J. Chem. Phys.* **84**:6345 (1986).
27. J. Rubinstein and S. Torquato, *J. Fluid Mech.* **206**:25 (1989).
28. S. Torquato, *J. Stat. Phys.* **45**:843 (1986).
29. J. P. Hansen and I. R. McDonald, *Simple Theory of Liquids* (Academic Press, New York, 1986).
30. S. Torquato and G. Stell, *J. Chem. Phys.* **77**:2071 (1982).
31. H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**:369 (1959).
32. S. Torquato, *J. Chem. Phys.* **81**:5079 (1984).
33. S. W. Haan and R. Zwanzig, *J. Phys. A* **10**:1547 (1977), and references therein.
34. W. T. Elam, A. R. Kerstein, and J. J. Rehr, *Phys. Rev. Lett.* **52**:1516 (1984).
35. S. Torquato and G. Stell, *J. Chem. Phys.* **82**:980 (1985).
36. S. Torquato and F. Lado, *J. Phys. A: Math. Gen.* **18**:141 (1985).
37. G. Stell and P. A. Rikvold, *Chem. Eng. Commun.* **51**:233 (1987).
38. S. Torquato, *J. Chem. Phys.* **85**:4622 (1986).
39. S. Torquato and S. B. Lee, *Physica A* **164**:347 (1990).
40. B. Lu and S. Torquato, *Phys. Rev. A* **43**:2078 (1991).
41. S. Torquato and A. K. Sen, *J. Appl. Phys.* **67**:1145 (1990).
42. F. Lado and S. Torquato, *J. Chem. Phys.* **93**:5912 (1990).
43. S. Torquato and F. Lado, *J. Chem. Phys.* **94**:4453 (1991).
44. J. L. Lebowitz and J. W. Perram, *Mol. Phys.* **50**:1207 (1983).
45. S. B. Lee, I. C. Kim, C. A. Miller, and S. Torquato, *Phys. Rev. B* **39**:11833 (1989).
46. C. A. Miller and S. Torquato, *Phys. Rev. B* **39**:710 (1989).
47. L. H. Zheng and Y. C. Chiew, *J. Chem. Phys.* **90**:322 (1989).
48. S. Torquato and I. C. Kim, *Appl. Phys. Lett.* **55**:1847 (1989).
49. C. A. Miller, I. C. Kim, and S. Torquato, *J. Chem. Phys.* **94** (1991).
50. S. B. Lee and S. Torquato, *J. Chem. Phys.* **89**:3258 (1988).
51. I. C. Kim and S. Torquato, *Phys. Rev. A* **43**:3198 (1991).
52. S. Torquato, *J. Chem. Phys.* **85**:7178 (1986).
53. P. M. Richards and S. Torquato, *J. Chem. Phys.* **87**:4612 (1987).
54. I. M. Lifshitz, S. A. Gredeskal, and L. A. Pastur, *Introduction to the Theory of Disordered Systems* (Wiley, New York, 1988).
55. M. D. Donsker and S. R. S. Varadhan, *Commun. Pure Appl. Math.* **28**:525 (1975).