Universal scaling for diffusion-controlled reactions among traps

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The determination of the mean survival time τ (i.e., inverse reaction rate) associated with diffusion-controlled reactions among static traps is a problem of long-standing interest, dating back to the classical work of Smoluchkowski. For the broad class of model particulate- and digitized-based models considered here, we find a universal curve for the mean survival time τ for a wide range of porosities. The functional form of this universal scaling relation is motivated by rigorous bounds on τ and is expressible as a simple function of porosity, specific surface, and mean pore size. © *1997 American Institute of Physics.* [S0021-9606(97)50321-7]

I. INTRODUCTION

Diffusion and reaction in heterogeneous media arise in a host of phenomena in the physical and biological sciences.[1–7] Considerable attention has been devoted to instances in which the heterogeneous medium consists of two regions: a pore region in which the reactants diffuse and a trap region. Examples are found in such widely different processes as migration of atoms and defects in solids,[1] heterogeneous catalysis,[2] colloid or crystal growth,[2] cell metabolism,[3] fluorescence quenching,[5] and the decay of nuclear magnetism in fluid-saturated porous media.[6,7]

The fundamental task is to solve the diffusion equation subject to various initial conditions and boundary conditions at the pore-trap interface. It is the complexity of this interface which makes the solution of the diffusion equation nontrivial, even when the trap phase consists of simple geometrical elements such as spheres. An important class of reactions in which the mass transport step is the rate determining step is referred to as *diffusion-controlled reactions*. Smoluchkowski[8] considered an idealized diffusion-controlled problem in which a single spherical trap of radius a is surrounded by a uniform sea of infinitesimal diffusing particles. When one considers an infinitely dilute suspension of such traps at concentration ϕ_2, one can use Smoluchkowski's single-sphere solution of the concentration field to find that the steady-state mean survival time τ is given by

$$\tau = \frac{a^2}{3D\phi_1\phi_2}, \tag{1}$$

where D is the diffusion coefficient. The mean survival time τ, generally speaking, is the average time taken for a diffusing particle to survive before it gets trapped and is equal to the inverse of the trapping rate k.

At nondilute concentrations, there is competition between the traps for the diffusing species, and consequently this represents the most difficult regime in which to model the mean survival time. Considerable theoretical and computational effort has been expended to quantify τ or k for concentrated suspensions of spherical traps. This includes exact analytical expressions for periodic trap arrangements,[9] approximate formulas[10–14] and rigorous bounds[7,15–19] for random distributions of traps, and random-walk simulation methods.[13,20–23]

For heterogeneous media consisting of traps of irregular shape and size, it is even more difficult to predict τ using theoretical methods. It is important to note that the product τD for general media has dimensions of length squared, revealing that τ is intimately related to characteristic length scales of the pore space.

The purpose of this paper is to develop a universal curve for the mean survival time τ for a wide class of model microstructures that is valid from relatively low to high trap concentrations (or, equivalently, low to relatively high porosities). That is, we seek a means to scale data for τ in such a way that the scaled data for different model microstructures collapse onto a single curve.

Based on rigorous bounds for τ, we have found the following simple universal scaling relation:

$$\frac{\tau}{\tau_o} = \frac{8}{5}x + \frac{8}{7}x^2, \tag{2}$$

where

$$\tau_o = \frac{3\phi_2}{D\phi_1 s^2}, \tag{3}$$

$$x = \frac{\langle \delta \rangle^2}{\tau_o D}, \tag{4}$$

$\phi_1 = 1 - \phi_2$ is the porosity, s is the specific surface, and $\langle \delta \rangle$ is the mean pore size defined in Sec. II. We have tested this relation for eight very different particulate-based and digitized (lattice)-based model microstructures and found that the data indeed collapse onto a single curve, within small fluctuations. Thus, for any microstructure within this class, knowledge of the porosity ϕ_1, specific surface s and mean pore size $\langle \delta \rangle$ enables one to estimate τ using relation (2). More generally, given any of the three quantities from among the four quantities τ, ϕ_1, s, and $\langle \delta \rangle$, the remaining one can be estimated employing expression (2).

In Sec. II, we discuss briefly the basic equations and rigorous bounds. In Sec. III we describe the eight model microstructures. The survival times for five of these models

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have already been computed. However, τ has not been evaluated heretofore for the remaining three models. We do so here using efficient first-passage time simulation techniques. In Sec. IV the universal scaling relation is formulated and tested for the aforementioned eight model microstructures. This requires us to compute the mean pore size $\langle \delta \rangle$ for the first time for a majority of the models. Finally, in Sec. V we study the predictive capability of relation (2) and discuss its validity. We also comment on the case when the traps are not perfect absorbers.

II. BASIC EQUATIONS AND VARIATIONAL BOUNDS

The random heterogeneous medium is a domain of space $\mathscr{V}(\omega) \in \mathbb{R}^3$ (where the realization ω is taken from some probability space) of volume V which is composed of two regions: the pore or trap-free region $\mathscr{V}_1(\omega)$ (in which diffusion occurs) of volume fraction (porosity) ϕ_1 and a trap 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 trap-free region is defined by

$$I(\mathbf{r},\omega)=\begin{cases}1, & \mathbf{r}\in\mathscr{V}_1(\omega)\\ 0, & \mathbf{r}\in\mathscr{V}_2(\omega)\end{cases}. \tag{5}$$

The characteristic function of pore-trap interface is defined by

$$M(\mathbf{r},\omega)=|\nabla I(\mathbf{r},\omega)|. \tag{6}$$

For statistically homogeneous media, the ensemble averages (indicated with angular brackets) of (5) and (6) yield

$$\phi_1=\langle I\rangle=\lim_{V_1,V\to\infty}\frac{V_1}{V}, \tag{7}$$

$$s=\langle M\rangle=\lim_{S,V\to\infty}\frac{S}{V}, \tag{8}$$

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

A. Trapping equations

Consider the steady-state diffusion of reactants among static traps with a prescribed rate of production of the reactants per unit pore volume, which is taken to be unity. The reactants diffuse in the trap-free region with diffusion coefficient D and without any bulk reaction. When the reactants come in contact with the pore-trap interface, they will be absorbed with a probability that depends on the value of the surface rate constant κ (which has dimensions of length/time.) Using homogenization theory, it has been shown that the mean survival time τ of a diffusing particle is given by

$$\tau=\frac{\langle u\rangle}{\phi_1 D}, \tag{9}$$

where the scaled concentration field of the reactants $u(\mathbf{r})$ satisfies the diffusion equation

$$\Delta u=-1, \quad \text{in } \mathscr{V}_1 \tag{10}$$

$$D\frac{\partial u}{\partial n}+\kappa u=0, \quad \text{on } \partial\mathscr{V}. \tag{11}$$

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

$$\langle u\rangle=\langle uI\rangle=\lim_{V\to\infty}\frac{1}{V}\int_{\mathscr{V}_1}u(\mathbf{r})\,d\mathbf{r}. \tag{12}$$

It is useful to introduce the dimensionless surface rate constant

$$\overline{\kappa}=\frac{\kappa\ell}{D} \tag{13}$$

and distinguish between two extreme regimes,

$$\begin{aligned}&\overline{\kappa}\gg 1 \quad \text{(Diffusion-Controlled)},\\ &\overline{\kappa}\ll 1 \quad \text{(Reaction-Controlled)},\end{aligned} \tag{14}$$

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 limit $\overline{\kappa}\to\infty$, the traps are perfect absorbers. In the reaction-controlled regime, the characteristic time associated with surface reaction is large compared with the diffusion time to the pore-trap interface. In the limit $\overline{\kappa}\to 0$, the traps are perfect reflectors. The results of this study are primarily concerned with the diffusion-controlled limit ($\overline{\kappa}\to\infty$).

B. Variational bounds

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 they: (i) enable one to test the merits of theories and computer experiments; (ii) as successfully more microstructural information is incorporated, the bounds become progressively narrower; and (iii) one of the bounds can typically provide a good estimate of the property for a wide range of conditions, even when the reciprocal bound diverges from it. Prager[15,24] pioneered the use of bounds to obtain estimates of effective properties of heterogeneous media in the early 1960's.

Rubinstein and Torquato[18] derived variational principles for the mean survival time τ in the diffusion-controlled case ($\overline{\kappa}=\infty$). These variational principles were applied by formulating four different classes of bounds: *interfacial-surface, multiple-scattering, security-spheres, and void bounds.*[18] Each of these bounds is given in terms of various types of statistical correlation functions. For example, the interfacial-surface upper bound on τ is given in terms of two-point

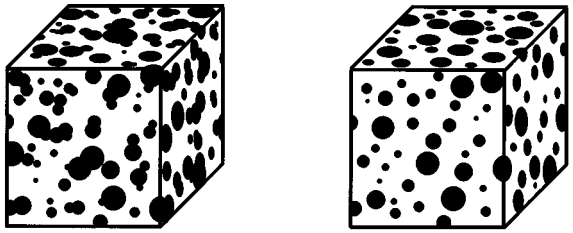

FIG. 1. Two random-sphere models. (a) Model 1: identical overlapping spheres; (b) Model 2: identical nonoverlapping spheres in equilibrium.

correlation functions that involve information about the interface and pore region. For media composed of spherical traps, the *upper bounds* tend to be very sharp for low to moderate values of the trap concentration.

The variational principle leading to *lower bounds* on τ has been generalized by Torquato and Avellaneda[19] to treat finite surface reaction. Using this variational principle, they found the following lower bound on the mean survival time:

$$\tau \geqslant \frac{\langle \delta \rangle^2}{D} + \frac{\phi_1}{\kappa s}. \tag{15}$$

For $\overline{\kappa} \to \infty$, (15) reduces to the diffusion-controlled-limit bound

$$\tau \geqslant \frac{\langle \delta \rangle^2}{D} \tag{16}$$

obtained originally by Prager.[15] Here the general nth moment of δ is defined by

$$\langle \delta^n \rangle = \int_0^\infty \delta^n P(\delta) d\delta \tag{17}$$

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 $\mathscr{V}_1$ lies at a distance between δ and $\delta + d\delta$ from the nearest point on the interface $\partial\mathscr{V}$. $P(\delta)$ normalizes to unity and at extreme values, one has

$$P(0) = \frac{s}{\phi_1} \quad \text{and} \quad P(\infty) = 0. \tag{18}$$

It was shown that this lower bound is relatively sharp at high trap concentrations (i.e., low porosities) in the case of spherical traps. The universal scaling that we formulate in Sec. IV is based on this lower bound.

III. MODEL HETEROGENEOUS MEDIA AND COMPUTATIONS OF τ

A. Model microstructures

We will consider the following eight model microstructures (shown in Figs. 1–3) in which the black phase is the trap region and the white phase is the diffusion region:

(1) random distributions of identical overlapping spheres;
(2) random distributions of identical nonoverlapping spheres;

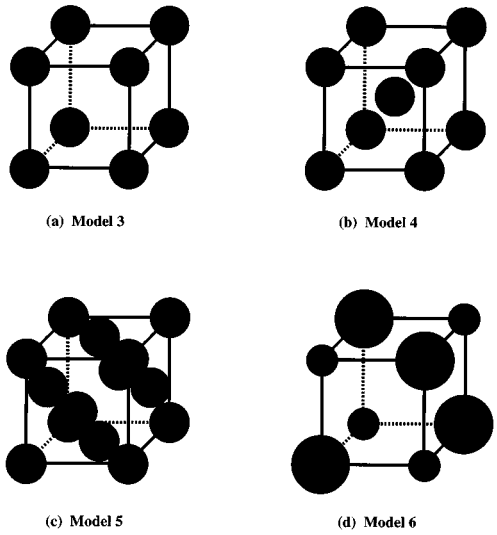

FIG. 2. Four periodic-sphere models. (a) Model 3: simple cubic lattice of identical spheres; (b) Model 4: body-centered cubic lattice of identical spheres; (c) Model 5: face-centered cubic lattice of identical spheres; (d) Model 6: simple cubic lattice of bi-dispersed spheres.

(3) simple cubic lattice of identical nonoverlapping spheres;
(4) body-centered cubic lattice of identical nonoverlapping spheres;
(5) face-centered cubic lattice of identical nonoverlapping spheres;
(6) simple cubic lattice of nonoverlapping spheres of two different sizes;
(7) three-dimensional random checkerboard; and
(8) Gaussian construction.

Models 1–5 represent five different mircrostructures consisting of identical spherical traps of radius a. In the overlapping-sphere model (model 1), the sphere centers are spatially uncorrelated and thus the spheres may overlap to form clusters. In the nonoverlapping-sphere model 2, the spheres are assumed to be in thermal equilibrium subject to the impenetrability constraint. Models 3–5 take the identical spherical traps to be located on the sites of simple, body-centered, and face-centered cubic lattices, respectively. In model 6 two different-sized spherical traps of radii a_1 and a_2 are arranged on the sites of a simple cubic lattice as shown in Fig. 2. Figure 3 depicts the two digitized-based

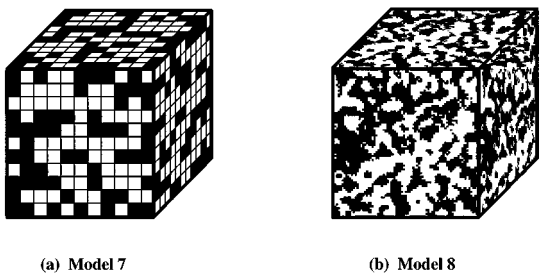

FIG. 3. Two random digitized-based models. (a) Model 7: random checkerboard; (b) Model 8: Gaussian construction.

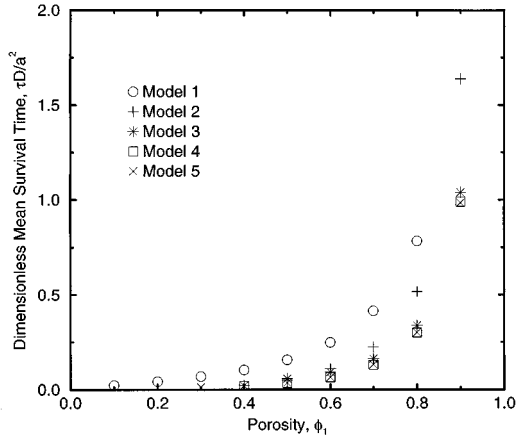

FIG. 4. The dimensionless mean survival time $\tau D/a^2$ versus porosity ϕ_1 for the identical-sphere models 1–5. Here a is the sphere radius.

models. In the random checkerboard construction (model 7), a unit cube is tessellated into smaller cubes of length b and is randomly assigned to be a void element (white) according to the prescribed porosity ϕ_1. The Gaussian construction (model 8) of Crossley, Schwartz and Banavar[26] is generated by smoothing random white-noise images using Gaussian kernels. This results in a microstructure characterized by a wide range of length scales.

B. Computations of the mean survival time τ

The mean survival time τ has been previously computed for the random-sphere models 1 and 2 by Lee *et al.*[20] using random-walk simulation techniques. The survival time for the periodic models was calculated by Felderhof[9] using multipole-expansion techniques.

Figure 4 shows the mean survival time versus porosity for models 1–5. It is seen that there is significant scattering of the data at large values of ϕ_1. The reason for this is that systems at the same porosity can have appreciably different pore size distributions.

The mean survival time for models 6–8 is computed in the present study for the first time for different values of the porosity ϕ_1. This is accomplished using efficient first-passage time simulation methods developed for continuum models (e.g., spherical or ellipsoidal traps)[21,23,25] and for digitized models.[27] The basic idea behind such techniques is that instead of simulating the detailed zigzag motion of a diffusing particle, one surrounds the Brownian particle with the largest possible concentric sphere of radius R, for the continuum models, or cube of length L, for the digitized models, which does not overlap any trap. The diffusing particle then jumps to a point on the surface of this first-passage region according to a specific probability law. The average time taken for the Brownian particle to first strike the imaginary surface is simply proportional to R^2, in the case of a first-passage sphere, or L^2, in the case of a first-passage cube. One repeats this process until the Brownian particle gets trapped and the mean survival time is just the sum of all of the mean hitting times (averaged over many walkers and configurations). In the case of model 6, we applied the first-passage sphere procedure, and in the digitized-based (i.e., nonparticulate) model microstructures (models 7 and 8) we used first-passage cubes.[27]

Table I summarizes our results for model 6 and Table II gives our results for models 7 and 8. In Fig. 5, we plot the dimensionless mean survival time $\tau D/b^2$ versus porosity ϕ_1 for the digitized-based models 7 and 8. Here we see that there is significant scatter of the data *for a wide range of porosities*.

TABLE I. The dimensionless mean survival time $\tau D/a_1^2$ as a function of porosity ϕ_1 for a bi-dispersion of spherical traps of radii a_1 and a_2 arranged in simple cubic lattice (model 6). The porosity ϕ_1 is varied by fixing a_1 and varying a_2.

ϕ_1	a_2/a_1	$\tau D/a_1^2$
0.3	2.3085	0.0505
0.4	2.1829	0.0759
0.5	2.0409	0.1122
0.6	1.8759	0.1695
0.7	1.6752	0.2697
0.8	1.4096	0.4782
0.9	0.9656	1.005

TABLE II. The dimensionless mean survival time $\tau D/b^2$ as a function of porosity ϕ_1 for the two digitized-based models 7 and 8, where b is the length of a voxel.

	$\tau D/b^2$	
ϕ_1	Random checkerboard	Digitized Gaussian construction
0.1	0.0246	0.2249
0.2	0.0306	. . .
0.3	0.0385	0.4841
0.4	0.0497	. . .
0.5	0.0665	0.9163
0.6	0.0941	. . .
0.7	0.1456	1.952
0.8	0.2619	. . .
0.9	0.6696	6.763

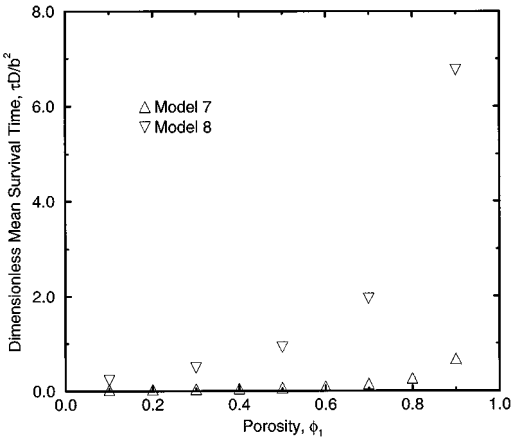

FIG. 5. The dimensionless mean survival time $\tau D/b^2$ versus porosity ϕ_1 for the two random digitized-based models 7 and 8. Here b is the voxel length.

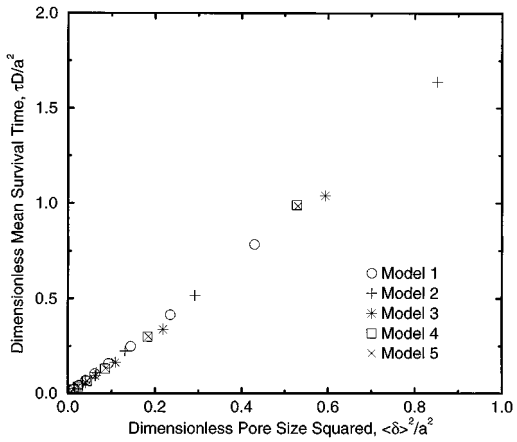

FIG. 6. The dimensionless mean survival time $\tau D/a^2$ versus the mean pore size squared $\langle \delta \rangle^2/a^2$ for the identical-sphere models 1–5. Here a is the sphere radius.

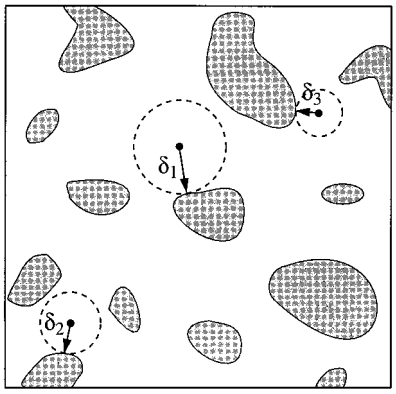

FIG. 7. Schematic illustrating the evaluation of the dimensionless mean pore size $\langle \delta \rangle$ by throwing many random points in the void phase and recording the radii of the ''first-passage'' spheres. The average radius of the first-passage spheres is the mean pore size.

IV. UNIVERSAL SCALING FOR THE MEAN SURVIVAL TIME

In this section, we formulate a universal curve for the mean survival time τ. We begin by considering model microstructures involving identical spherical traps (models 1–5). We then develop the universal scaling relation for general media.

A. Media consisting of identical spherical traps

From Fig. 4 one can see that systems of identical spheres (models 1–5) can have appreciably different values of τ at the same value of the porosity ϕ_1. The lower bound (16) suggests that *it is more appropriate to compare different sphere systems at the same average pore size* $\langle \delta \rangle$. Thus, the more appropriate independent variable is $\langle \delta \rangle$, as opposed to ϕ_1. Indeed, apart from small fluctuations, all of the data for models 1–5 collapse onto one curve when $D\tau/a^2$ is plotted versus $\langle \delta \rangle^2/a^2$, as shown in Fig. 6. The average pore sizes for the random-sphere models 1 and 2 were given in Ref. 19. For general media, $\langle \delta \rangle$ is easily obtained from Monte Carlo simulations.[28] Specifically, the mean pore size $\langle \delta \rangle$ for each of the models 3–8 is evaluated by throwing randomly in the void phase 5×10^4 to 10^6 points. For each of these points, the radius of the largest concentric sphere that does not overlap any trap is recorded. The average value of the radii of these ''first-passage'' spheres is the mean pore size (see Fig. 7).

In summary, we see that we get universal behavior (to a very good approximation) when τ is plotted against the independent variable $\langle \delta \rangle^2$ in appropriate dimensionless form.

B. General media

For identical spherical traps of radius a, the mean survival time τ was scaled by the time scale a^2/D and the square of the average pore size, $\langle \delta \rangle^2$, was scaled by a^2. For media with an arbitrary topology, one must choose the appropriate characteristic time and length scales. A simple but useful choice for the time scale is τ_o, defined by the expression

$$\tau_o = \frac{3\phi_2}{D\phi_1 s^2}, \tag{19}$$

with $(\tau_o D)^{1/2}$ being the corresponding length scale. The motivation behind choice (19) is the fact that for a dilute system of spherical traps with a polydispersivity in size, the quantity

$$\tau_o = \frac{\langle a^3 \rangle^2}{3D\phi_1\phi_2\langle a^2 \rangle^2} \tag{20}$$

is a rigorous *upper bound* on the mean survival time.[18,22] Here $\langle a^n \rangle$ is the nth moment of the sphere size distribution function. Now since the specific surface of such a polydispersed- sphere system is given by[22]

$$s = 3\phi_2 \frac{\langle a^2 \rangle}{\langle a^3 \rangle}, \tag{21}$$

then by substituting (21) into (20) we obtain (19). Thus, for this particular multi-scale system, a natural length scale is s^{-1}. For arbitrary topologies, it is not unreasonable to employ the same choice (19) to scale τ.

By scaling the data for models 1–8 using (19), we again find that all of the data collapse onto a single curve, apart from small fluctuations. Figure 8 depicts this universal scaling which is well represented by the simple expression

$$\frac{\tau}{\tau_o} = \frac{8}{5}x + \frac{8}{7}x^2, \tag{22}$$

where

$$x = \frac{\langle \delta \rangle^2}{\tau_o D} \tag{23}$$

is the dimensionless mean pore size squared. The solid curve in the figure is relation (22).

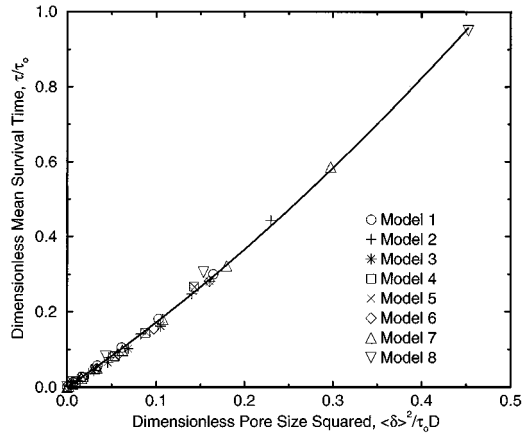

FIG. 8. The dimensionless mean survival time τ/τ_o versus dimensionless mean pore size squared $\langle\delta\rangle^2/\tau_o D$ for all models 1–8. Solid curve is universal scaling relation (22). Here $\tau_o=3\phi_2/D\phi_1 s^2$.

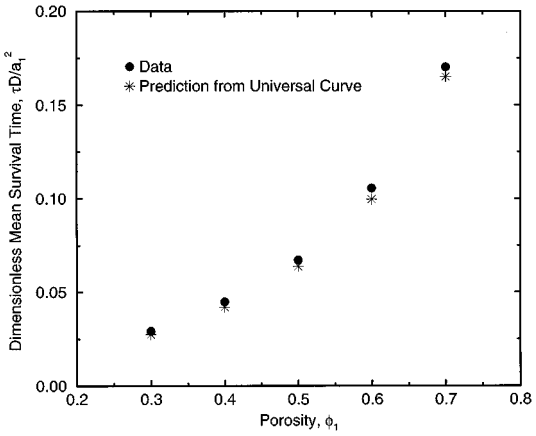

FIG. 9. Prediction of the dimensionless mean survival time $\tau D/a_1^2$ versus the porosity ϕ_1 for the random overlapping bi-dispersed spheres from relation (22) when $\langle\delta\rangle$, ϕ_1, and s are given.

V. APPLICATIONS AND DISCUSSION

In this section we apply the universal scaling relation and discuss its validity. Our results are applied to two different microstructures: bi-dispersed overlapping spherical traps and simple cubic lattices of identical spherical traps. In the first case we use the universal relation (22) to predict the mean survival time τ and in the second case we employ it to predict the mean pore size $\langle\delta\rangle$. We also remark on the case when the traps are not perfect absorbers.

Miller and Torquato[22] evaluated the mean survival time for a bi-dispersion of overlapping spherical traps of radii a_1 and a_2 at number densities ρ_1 and ρ_2, respectively. Note that these data were not utilized to obtain the universal scaling (22). Thus, we can test the predictive accuracy of our universal scaling for this particular model since we have the exact expressions for the porosity ϕ_1 and specific surface s (see Ref. 22) as well as the mean pore size $\langle\delta\rangle$:[19]

$$\phi_1=\exp\left[-\sum_{i=1}^{2}\frac{4\pi a_i^3\rho_i}{3}\right], \tag{24}$$

$$s=\left[\sum_{i=1}^{2}4\pi a_i^2\rho_i\right]\phi_1, \tag{25}$$

$$\langle\delta\rangle=\frac{1}{\phi_1}\int_0^\infty \exp\left[-\sum_{i=1}^{2}\frac{4\pi(r+a_i)^3\rho_i}{3}\right]dr. \tag{26}$$

Miller and Torquato obtained simulation data for the special instance in which $a_2/a_1=0.5$ and $\rho_2/\rho_1=8.0$. In this instance, the universal relation (22) predicts mean survival times which are in excellent agreement with the simulation data as shown in Fig. 9.

As a second application of the universal scaling relation (22), we will predict the mean pore size as function of porosity for simple cubic lattices of spherical traps of radius a utilizing Felderhof's exact results for the mean survival time τ for this model.[9] The specific surface for this model is given by $s=3(1-\phi_1)/a$. Figure 10 shows that the prediction of relation (22) for the mean pore size $\langle\delta\rangle$ of simple cubic lattices is in very good agreement with our direct Monte Carlo simulations of the same quantity.

The universal relation (22) should be applicable to a wide class of microstructures provided that the dimensionless variable x is within the range of the considered data set, i.e., $\langle\delta\rangle^2/\tau_0 D<0.5$. It must be emphasized that the range $0\leqslant x<0.5$ is representative of many realistic media for a wide range of porosities. We have studied various multiscale, hierarchical models for which $x>0.5$ but these are exceptional examples. Such work will be reported in a future paper.

Finally, it is useful to comment on the case in which the reaction is not diffusion-controlled, i.e., when the surface rate constant κ [cf. (11)] is finite. It is clear that in the reaction-controlled regime ($\overline{\kappa}\gg 1$), survival time data plotted against porosity as the independent variable (in appropriate dimensionless form) will show significant scatter for different model microstructures. The rigorous bound (15) reveals that $\phi_1/\kappa s$ is the proper independent variable in the limit $\overline{\kappa}\gg 1$. For arbitrary values of the dimensionless rate constant

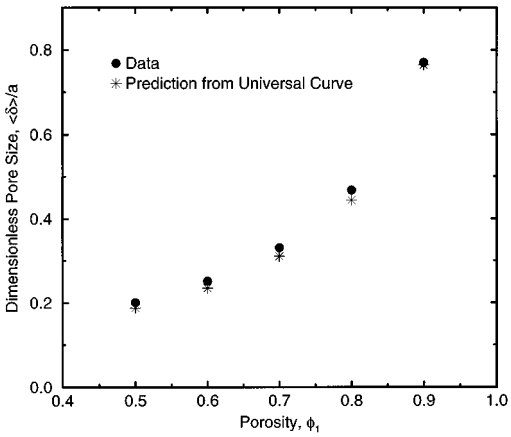

FIG. 10. Prediction of the dimensionless mean pore size $\langle\delta\rangle/a$ versus the porosity ϕ_1 for the simple cubic lattice from scaling relation (22) when τ, ϕ_1, and s are given.

$\overline{\kappa}$, one may consider using the entire right-hand side of the bound (15), i.e., $\langle \delta^2 \rangle / D + \phi_1 / \kappa s$, as the independent variable, which is known to provide excellent estimates of τ for systems with relatively disconnected pores.[19]

ACKNOWLEDGMENT

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