Simulation of diffusion and trapping in digitized heterogeneous media

David A. Coker\textsuperscript{a)} and Salvatore Torquato\textsuperscript{b)}

Princeton Materials Institute and Department of Civil Engineering and Operations Research, Princeton University, Princeton, New Jersey 08544

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We present an efficient and fast simulation technique to determine the mean survival time $\tau$ of a Brownian particle diffusing among a digitized lattice-based domain of traps. Following the first-passage time ideas of Torquato and Kim [Appl. Phys. Lett. 55, 1847 (1989)], the algorithm is based on the known solution for the mean first passage time of a Brownian particle in a cube. The mean survival time, the inverse of the trapping rate, is obtained for a variety of configurations involving digitized spheres. Since the survival time is highly sensitive to the surface area and associated resolution, the results provide a means of determining the relation between the survival time of a real material and its digitized representation. In general, lower resolution images give rise to a diminished mean survival time and, thus, a lower bound on the true mean survival time $\tau$. Digitization can affect other transport properties in which the interface plays a major role, e.g., the fluid permeability associated with flow in porous media. We demonstrate both analytically and computationally that the mean survival time for the digitized medium converges to the continuum value in the high-resolution limit. © 1995 American Institute of Physics.

I. INTRODUCTION

Determining the effective transport, electromagnetic, or mechanical properties of disordered heterogeneous media, such as composites, suspensions, porous materials, and biological media, is a long standing problem in science. In recent years much theoretical progress has been made towards predicting the effective properties of such media based on statistical knowledge of the underlying microstructure or morphology. Much of the rigorous theoretical progress\textsuperscript{1-10} has been made in constructing improved bounds that are dependent on statistical information describing the microstructure via various types of $n$-point statistical correlation functions. As predictive as these techniques may be, it is also desirable to directly obtain the desired quantity given the explicit configuration of the underlying microstructure. Such simulations provide benchmark results against which rigorous bounds and approximate theories can be tested. In some instances, direct simulations can be used to determine quantities that are either not obtainable or difficult to obtain experimentally, but at the same time are of fundamental importance.

With recent experimental advances in fields such as scanning and transmission electron microscopy,\textsuperscript{11} scanning tunneling electron microscopy,\textsuperscript{12} and synchrotron based tomography,\textsuperscript{13} it is possible to obtain high resolution two- and three-dimensional microstructural phase information of a given sample. In addition, these methods are noninvasive leaving the sample intact and unaltered, allowing complimentary studies either by any of the above techniques or through direct experimental measurement of the same sample. The microstructural information ($n$-point correlation functions) obtained from these techniques characterizes a sample\textsuperscript{14} and provides a means to predict and understand the effective properties of various media through the use of well-established property/microstructure theories.\textsuperscript{1-6,8-10}

As experimental or digitized data is of finite resolution, it is important to understand the relationship between a property extracted or measured from a digitized representation and the same property for the actual material. For the sake of simplicity, the question of noise and other such artifacts in the data are ignored here. In this study, it assumed that the data provides a true representation of the material at a specified resolution.

To understand the effect of resolution on the measured property of a digitized medium, an efficient algorithm based on first-passage time ideas of Torquato and Kim\textsuperscript{7} is presented that measures the mean survival time, $\tau$, for a digitized system of traps. The system is comprised of two phases: a trap region (material) and a trap-free (void) region. Reactive particles are introduced into the trap-free or void region where they may diffuse with a specified diffusion coefficient. Upon contact with the trap region, the diffusing particles can be absorbed. The mean survival time $\tau$ is the average time taken for a Brownian or diffusing particle to survive in a system of partially absorbing traps before it is trapped. The kinetics associated with diffusion and reaction are found in such widely different processes such 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.\textsuperscript{9,10,15-19} A closely associated quantity frequently mentioned in the literature is the trapping rate, $k$, which is merely the inverse of the mean survival time

$$k = \frac{1}{\tau}. \quad (1.1)$$

This study focuses on the steady-state case where the absorption rate of the diffusing particles equals their rate of production and the traps are assumed to be perfect absorbers.

\textsuperscript{a)}E-mail: coker@cherrypit.princeton.edu
\textsuperscript{b)}E-mail: torquato@matter.princeton.edu
For traps of arbitrary configuration, determining the trapping rate theoretically is a very difficult problem as there is competition between the traps for the diffusing particles. Therefore, direct computer simulations offer a means to measure the mean survival time for a given configuration of traps. In addition, the mean survival time is chosen for study as it is a prototypical problem that is sensitive to the specific geometry of the traps. For a system of digitized traps, this geometric sensitivity also appears as a dependency of the measured mean survival time on the resolution of the digitized representation. Determining this dependence is one goal of the present work.

Torquato and co-workers used first-passage time techniques to measure the mean survival time, \( \tau \), of continuum models (e.g., random distributions of continuum spherical traps). This method to obtain \( \tau \), in principle, is exact and provides an order of magnitude savings in computer time compared to conventional random-walk techniques. The basic idea is that the zigzag random motion of the diffusing particle need not be simulated in detail. In the first-passage sphere algorithm (FPS), one first constructs the largest possible concentric sphere at the location of the diffusing particle which does not overlap any traps. A location on the surface of the sphere where the particle will land is then chosen at random. It is easily shown that the mean first-passage time, \( \tau \), (the average time that it takes the diffusing particle to first strike the surface of the imaginary sphere) is proportional to the square of the radius. This process is repeated until the particle is trapped and the survival time is obtained by averaging over many walks and many configurations. This then allows for an efficient and robust simulation technique as the diffusing particle may take large steps without the need to extrapolate to zero step size in order to obtain the correct results. This method is not limited to the determination of mean survival times and can be applied to a variety of processes governed by a steady-state diffusion equation. Thus, this method can be applied and extended to determine the effective dielectric constant, magnetic permeability, diffusion coefficients, and electrical conductivities. In particular, the first passage sphere algorithm was used to determine the conductivity of multiphase composites by Kim and Torquato.

Since digitized media are constructed of boxes or cubes, it is natural to generalize the FPS algorithm to account for the cubic nature of the system. Therefore, in this investigation, the FPS algorithm is modified to incorporate the use of first passage cubes (FPC). This algorithm retains the efficiency associated with the FPS algorithm, but replaces the concentric spheres with concentric cubes oriented parallel to the lattice of the digitized traps. Our algorithm is the three-dimensional analog of the two-dimensional algorithm of Siegel and Langer which involved the use of first-passage squares to measure the average time for a diffusing particle to traverse a system of rectangular throats and square cavities. We shall apply our algorithm to more complex three-dimensional geometries, such as media comprised of non-overlapping traps as well as bicontinuous overlapping traps.

The paper is organized as follows. In Sec. II, solutions to the diffusion equation are presented that determine the mean first passage time and hitting probability density function for a Brownian particle introduced at the center of a cube of size \( 2L \). In Sec. III, the FPC algorithm is presented with a discussion of necessary approximations and their effects. The effect of resolution is discussed in Sec. IV where our digitized sphere is defined and a simple model is presented demonstrating the effect of finite resolution on the mean survival time. Simulation results for transport interior to a sphere, transport exterior to a BCC lattice of spheres, and transport exterior to random overlapping spheres are given in Sec. V. A discussion of the results follows in Sec. VI.

II. BROWNIAN MOTION IN A CUBE

Consider a Brownian particle (random walker) in three dimensions starting at a position \( \mathbf{r} \). Surrounding, this particle is a bounding surface specified by \( \Omega(\mathbf{r},t) \). The walker diffuses through the medium and, on average, first reaches the surface \( \Omega \) at a time \( t \), the first passage time. The probability distribution \( P(\mathbf{r},t) \) for the first passage time is a function of both the initial position and \( \Omega \) and satisfies the diffusion equation:

\[
\nabla^2 P(x,y,z,t) = \frac{\partial}{\partial t} P(x,y,z,t). \tag{2.1}
\]

The FPS algorithm relies on the ability to solve (2.1) with respect to the following boundary conditions:

\[
\begin{align*}
P(x,y,z,t=0) &= 0 \quad |x,y,z|<L \\
P(x=\pm L,y,z,t=0) &= 1 \\
P(x,y=\pm L,z,t=0) &= 1 \\
P(x,y,z=\pm L,t=0) &= 1.
\end{align*}
\tag{2.2}
\]

For a cubic bounding surface of size \( 2L \) centered about the origin. Defining the quantity \( P_1(t) = P(x-\gamma-y-z=0,t) \) as the probability distribution associated with introducing the Brownian particle at the origin, the mean first passage time, \( \tau_c \), may be defined as:

\[
\tau_c = \int_0^\infty t \frac{\partial}{\partial t} P_1(t) dt. \tag{2.3}
\]

Here it should be noted that \( \tau_c \) is also the solution to the steady-state diffusion problem \( \nabla^2 \tau = -1 \) with appropriate boundary conditions. The random walk inside the cube is illustrated in Fig. 1.

The solution of (2.1) in three dimensions may be written as:

\[
P_1(t) = 1 - \frac{64}{\pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n}{\gamma(n)} \exp \left( -\frac{\gamma^2(n)\pi^2 t}{4L^2} \right). \tag{2.4}
\]
FIG. 1. Example of random walk in a cube.

\[ \tau_c = 2L^2 - \frac{16L^2}{\pi^3} \sum_{p=0}^{\infty} \frac{(-1)^p}{\gamma(p) \cosh(\gamma(p)(\pi/2))} \]

\[ - \frac{64L^2}{\pi^3} \sum_{m,p=0}^{\infty} \frac{(-1)^m(-1)^p}{\gamma(m) \gamma(p) \theta^2 \cosh(\theta(n/2))} \]

(2.5)

where

\[ \gamma(n) = 2n + 1 \quad \text{and} \quad \theta^2 = \gamma^2(m) + \gamma^2(p). \]

(2.6)

The series (2.5) for \( \tau_c \) can be summed numerically to give

\[ \tau_c \approx 0.22485L^2. \]

(2.7)

Thus, the average time for a Brownian particle introduced at the origin to reach a face of the cube is proportional to surface area of the cube. For comparison, the corresponding result for a Brownian particle introduced at the center of a sphere of radius \( R \) is given by

\[ \tau_s = \frac{R^2}{6}. \]

(2.8)

Generalizations of (2.4) and (2.5) may also be obtained for the case of a walker introduced at an arbitrary location inside the cube. The solution follows directly by writing

\[ q(x,y,t) = \hat{q}(x,t) \hat{q}(y,t) \]

(2.14)

Therefore, this expression for \( \hat{q} \) determines the hitting probability density \( q(x,y,t) \) at a given time \( t \). For the purposes of the FPC algorithm, the value of \( q(x,y,t=\tau_c) \) is of primary interest as this describes the distribution of hitting spots at the mean first passage time.

III. SIMULATION OF BROWNIAN MOTION

The result (2.7) relating the mean first passage time to the size of a cube, \( L \), allows for a direct and simple algorithm to measure the trapping rate of a digitized heterogeneous medium. As digitized data is comprised of voxels (cubic pixels), the FPC approach is more appropriate to voxel based data than previous algorithms based upon first passage spheres \(^{21}\) as the natural geometric building block of digitized structures is the unit cube. Therefore, the FPC approach is taken in order to develop a robust and efficient algorithm capable of dealing with digitized images.

The medium is assumed to be of two phases with one phase identified as void (trap-free region) and the other identified as material (trap region). For definiteness, the material voxels are assigned the value "1" and the void voxels are assigned the value "0." The Brownian particle diffuses through the void phase until it comes in contact with the material phase where it is absorbed or trapped. As explained
in the introduction, the average time to be absorbed is the mean survival time, \( \tau \), with the associated trapping rate, \( k = \tau^{-1} \).

To determine the mean survival time, a number of Brownian particles are introduced in the void region. Each is allowed to diffuse according to the following algorithm which takes advantage of the mean first passage results for a cube.

1. Given a particle in the void region at a particular location, construct the largest possible cube centered about the walker that does not encompass any of the material phase. The cube is oriented parallel to the lattice grid as rotations of the cube are not allowed. The cube is constructed using a growth algorithm whereby the cube grows in units of the lattice spacing until contacting the material phase. This allows for a local search of the surrounding volume which is much quicker than a global search algorithm.

2. Add \( 0.225L_i^2 \) to the total time, where \( L_i \) is the size of the cube constructed at timestep \( i \). For the simulation (2.7) has been computed to nine decimal places to maintain sufficient accuracy. It is important to mention here that the simulation generates a large number of cubes allowing the use of the mean first passage time for each cube rather than choosing the time from the distribution \( P_1(t) \) and then averaging over these times.

3. A new position for the particle is chosen on the face of the cube using the hitting probability density function, \( q(x,y,\tau_c) \). However, to speed up the calculation an approximation to the hitting probability density is used. Defining the function, \( \tilde{q}(x,y) \) as the infinite time limit of \( q(x,y,t) \), it is possible to obtain a simple analytic expression describing the density of hitting spots.

\[
\tilde{q}(x,y) = \lim_{t \to \infty} q(x,y,t) = \frac{\pi^2}{16} \cos \left( \frac{\pi x}{2L} \right) \cos \left( \frac{\pi y}{2L} \right)
\]

which is a generalization of the formula in two dimensions investigated by Siegel and Langer.\(^2\) Thus \( \tilde{q}(x,y) \) provides a convenient analytic approximation to the true probability density function \( q(x,y,\tau_c) \).

In Fig. 2, the true hitting probability density function is compared with the infinite time approximation. Here it is seen that \( \tilde{q}(x,y) \) slightly underestimates the density of hitting spots near the center of the face and consequently overestimates the density near the edge of the face. This is easy to understand physically as any particle that has remained in the cube for a long time has a greater chance of diffusing towards the corners. Therefore, the walker on average moves further away from the center of the cube during a given timestep thus slightly decreasing the mean survival time, \( \tau \), causing an associated increase in the mean trapping rate, \( k \).

In two dimensions, the approximation is much better as noted by Siegel and Langer.\(^2\)

4. Continue this process at each new location if the particle did not land on the face of a material voxel. Once the walker lands on the face of a material voxel, it is trapped and the iterative process stops with total time recorded. The mean survival time is then obtained by averaging over many such walks. This procedure is illustrated using two dimensional squares in Fig. 3.
or resolution. Therefore, the walker need only be within 
$\delta X 10^{-6}$ of a material voxel to become trapped. This adds 
negligibly to the total time which scales as the square of the 
distance. Several different thicknesses were chosen and the 
results were seen to be relatively insensitive to thicknesses 
below $\delta X 10^{-4}$. The use of a boundary layer is supported as 
well in previous work by both Zheng and Chiew$^{24}$ and 
Torquato and Kim.$^{7}$

IV. RESOLUTION

As this algorithm was developed for the future analysis 
of real digitized media with a finite resolution, it is important 
to address the question: how does finite resolution effect 
the measured properties and how does this finite resolution value 
relate to the continuum value? To provide a partial answer to 
this question, a simple model was developed through which 
a semi-quantitative estimate of the resolution induced error 
can be obtained. A complete description of the construction 
of the digitized spheres is presented since the resolution 
model is based upon this definition.

A useful assumption in analyzing trapping problems is 
that the trapping rate scales with the surface area. Therefore, 
the more surface area, the more likely a Brownian particle 
becomes trapped decreasing the mean survival time. In the 
case of smooth spheres, the trapping rate of an isolated 
sphere is directly proportional to its surface area, 
Smoluchowski.$^{25}$ If this surface is coarsened with feature 
sizes comparable to the radius of the sphere, the trapping rate 
would greatly increase. However, as the features become 
finer and finer, the trapping rate becomes insensitive to the 
surface features and mimics the behavior of the correspond-
ing smooth object. An intuitive example is the extreme case 
of a fractal-like surface where the scale of the surface fea-
tures goes to zero yet the surface area is infinite; however, 
the trapping rate remains finite and in this case is equivalent 
to the corresponding smooth sphere. Another way of under-
standing this is that in the case of a Brownian particle start-
ing far away from a trap, the small features do not strongly 
effect the trapping rate as this is dictated by the amount of 
free volume accessible to the walker. Therefore, the trapping 
rate depends not only on the surface area but also on the 
scale of any surface features. To quantify this observation, 
we have developed a simple model based on a digitized 
sphere. To make the model more powerful for analyzing the 
simulations, the sphere conforms to the volume preserving 
algorithm used to generate the various digitized media.

A. Definition of digitized sphere

In the sphere generating algorithm, a given voxel is either 
material or void dependent on the criteria

$$x^2+y^2+z^2<(1+\epsilon)R^2$$

(4.1)

where $\epsilon$ (a small parameter), is chosen to preserve volume. 
Adding this parameter to preserve volume is a very natural 
choice, as many experimental techniques that digitize a me-
dium rely on matching the phase volumes to other experi-
mental measurements. In addition, previous results for typi-
cal continuum simulations involving spheres are given as 
functions of the volume fraction or reduced density, $\eta$, which

is the number of traps per unit volume multiplied by the 
volume of a single trap. Therefore, by matching reduced den-
sity or volume fraction of a single sphere, our simulations 
closely reproduce the situation in previous simulations in-
volving continuum media. This volume preserving definition 
is also consistent with that used by Garboczi et al.$^{26}$ and 
Martys and Garboczi$^{27}$ in their studies of systems of non-
overlapping disks in two dimensions. It should be noted that 
the surface area, approximately 1.5 times greater than that of 
the continuum counterpart, is not affected by the value of $\epsilon$ 
for the diameters used in this study (greater than 10) as small 
adjustments in $\epsilon$ are equivalent to adding or subtracting a 
single cube on the surface which does not effect the surface 
area. Therefore, $\epsilon$ provides a convenient parameter to probe 
the effect of resolution on the trapping rate simulations of 
digitized media removing the question about the effect of 
volume differences. The resolution of the sphere is essen-
tially determined by the radius, $R$, as the voxel size $\delta$ 
is assumed fixed. Therefore, increasing $R$ corresponds to gen-

FIG. 4. Two-dimensional projection of digitized sphere with diameter=15.

erating a more finely resolved sphere. In Fig. 4, a sample two 
dimensional projection of a typical sphere generated by the 
above criteria is shown.

B. Resolution model

To understand the effect of resolution on the mean sur-

vival time, the following simple model is presented. Given a 
digitized sphere with corresponding continuum radius, $R$, 
construct the following three spheres with their centers coincid-

ing with that of the digitized sphere: (1) a sphere of radius 
$R_1$ that encompasses all digitized sphere voxels and that may 
include some void space as well, (2) a sphere of radius $R_2$ 
that is as large as possible without encompassing any void 
space, and (3) a sphere of radius $R'$ that is the corresponding 
continuum sphere. These definitions are illustrated in Fig. 5. 
From these definitions, it is clear that $R_2$$R$ $R_1$. In the 
situation where Brownian particles are introduced at the cen-
ter of the digitized sphere, the mean first passage time for 
the continuum sphere, $\tau$, is given by (2.8). Therefore, using the 
above definitions for $R_1$, the following is found to be true for 
Brownian particles introduced at the center

where \( r_1 \) is the mean first passage time of a continuum sphere with radius \( R_i \) using (2.8). As the resolution becomes finer and finer, \( r_1 \) and \( r_2 \) converge uniformly to \( r_s \) as both \( R_1 \) and \( R_2 \) converge to \( R \). From the definitions of \( R_1 \) and \( R_2 \) the mean first passage time for the digitized sphere, \( r^* \), should be bounded through the expression

\[
T_0 < T^* < T_1
\]

which implies that \( r^* \) converges to \( r_s \) as the resolution becomes finer. Therefore, \( r_1 - r_2 \) bounds the difference between the continuum first passage time and that of the digitized sphere.

Using (4.1), it is possible to determine \( R_1 \) and \( R_2 \) in terms of \( \varepsilon \). The following expressions involve the lattice spacing \( \delta \); however, in our simulations \( \delta \) is always set to unity. Thus, the following is found to be true

\[
R_1 = \sqrt{R^2 + y_m^2}
\]

\[
R_2 = \sqrt{(R - \delta)^2 + y_m^2 + \varepsilon(\delta)}
\]

\[
y_m = \left[ \sqrt{\left( K - \frac{\delta}{2} \right)} + \frac{\delta}{2} \right]
\]

where \( [z] \) denotes the greatest integer less than \( z \) and \( y_m \) is a quantity dependent on \( \varepsilon \) that measures the size of the largest square on the sphere normal to a coordinate axis. The expression for \( R_2 \) is an estimate that has a relative error of at most \( \delta/(\sqrt{3}K) \) due to inexact knowledge of \( y_m \). Therefore, an estimate of the variability of the mean first passage time for the digitized sphere is given by

\[
\tau_1 - \tau_2 < \frac{R_1^2 - R_2^2}{R^2} - \frac{R^2 + y_m^2 - (R - \delta)^2 - y_m^2}{R^2}
\]

\[
= 2\left( \frac{\delta}{R} - \frac{\delta^2}{2R^2} \right)
\]

which is independent of \( y_m \) due to the approximation in determining \( R_2 \). However, as we are primarily interested in the variability as a function of \( R \) this is a reasonable approximation. The results from this model are shown in Fig. 6. This model exhibits power law behavior and clearly shows that a digitized sphere must have a radius of at least 40 lattice units in order for the trapping rate of the lattice sphere to be in reasonable agreement with the trapping rate associated with the continuum sphere. Due to the fact that surface features serve to enhance the trapping rate and in effect decrease the mean survival time, it is expected that \( (\tau_1 - \tau_2)/\tau_s \) is an estimate of what we shall refer to as the diminished mean survival time.

Combining the predictions from this model for a particle diffusing interior to a digitized sphere and the general notion mentioned previously that the trapping rate should increase with increasing surface area, we assert that the simulated mean survival time for a digitized system of traps provides a lower bound for the continuum system. Consequently, the simulated trapping rate for the digitized system would provide an upper bound on the continuum trapping rate. That this is indeed the case will be shown later for a variety of systems involving digitized spherical traps.

V. SIMULATION RESULTS

Since this study is concerned with the development of a simulation technique capable of determining the trapping rate from digitized images of real materials, it is important to establish the accuracy and limitations of the FPC algorithm.
by investigating several digitized systems having a corresponding continuum system with well studied properties. In this investigation several systems involving spheres are investigated: (A) transport interior to a sphere, (B) transport exterior to a BCC lattice of spheres, and (C) transport exterior to a random overlapping spheres. This serves two purposes: (1) sphere systems are some of the most thoroughly studied with both analytic and computational results and (2) systems involving spheres allow easy comparison with the results from the resolution model. The spheres used in the simulations are digitized as discussed earlier and shown in Fig. 4. In general, these spheres exhibit larger surface area than their continuum counterparts, typically by a factor of 1.5. The parameter $\varepsilon$ in (4.1) is chosen such that the volume of the digitized sphere is less than but within 0.3% of the continuum sphere. This additional criterion on the volume is applied to remove the enhanced trapping effect due to a larger sphere volume. With this in mind, the above FPC algorithm is applied to a variety of systems involving both randomly overlapping and periodically distributed configurations of spheres at various reduced densities and trap volume fractions. As mentioned above, the mean first passage time for a particle in a digitized medium should be less than the corresponding continuum value; therefore, the simulation results are given with respect to the continuum value through the dimensionless mean first passage time defined as

$$\frac{\Delta \tau}{\tau} = \frac{\text{continuum time} - \text{simulation time}}{\text{continuum time}},$$

(5.1)

which is always a positive quantity.

A. Transport Interior to a Sphere

First we study transport interior to digitized spheres. The spheres are constructed at various radii. Two scenarios are examined and in each $5 \times 10^5$ walkers are introduced.

In the first scenario, Brownian particles are introduced at the center of the sphere and allowed to diffuse until coming in contact with the sphere wall. This corresponds exactly to the resolution model system. The mean first passage time for the continuum sphere is given by (2.8). The simulation results are presented in Fig. 7 where the quantity $\Delta \tau/\tau$ is defined from (5.1) with the continuum value given by (2.8).

In the second scenario, Brownian particles are introduced at random locations within a digitized sphere and allowed to diffuse until coming in contact with the sphere wall. The mean first passage time for the continuum system has the exact value $\tau_{\text{is}}$ of

$$\tau_{\text{is}} = \frac{R^2}{15}.$$  

(5.2)

The results are shown in Fig. 8 where the definition (5.1) is used with (5.2) playing the role of the continuum value. The results from the model are shown in Fig. 8 only for comparison. The results presented here support the trend predicted by the resolution model in Sec. IV even when the walker is not introduced at the origin.
overlapping spheres is given in Felderhof. The results comparing the mean survival time from the simulation with the continuum theory using the dimensionless diminished mean survival time (5.1) are shown in Fig. 9 with the continuum values obtained from Felderhof. Again the trend towards a smaller effect at finer resolutions is clearly seen where the resolution is defined with respect to the sphere radius.

C. Transport exterior to random overlapping spheres

A system comprised of overlapping spherical traps is strongly suggestive of real materials. This system is bicontinuous for trap volume fractions in the range $0.3 < \phi_2 < 0.97$ or, in terms of the reduced density, $0.36 < \eta < 3.51$. (For this model, the reduced density $\eta$ is related to $\phi_2$ by the relation $1 - \phi_2 = \exp(-\eta).$) As the microstructure is quite complex, exact expressions for the mean survival time do not exist. However, previous studies by Lee et al.,28 as well as Zheng and Chiew,24 including a study involving first passage spheres (Torquato and Kim7) provide a consistent estimate of the mean survival time at various reduced densities for systems involving overlapping continuum spheres. Therefore, this system is ideal to study in order to determine the effect of digitization of real materials on the mean survival time. Figure 10 contains an example of a two-dimensional slice through a three-dimensional distribution of equisized overlapping digitized spheres at the reduced density $\eta=0.3$. One feature worth noting in the digitized image is the lack of cusps that would be visible in a system of continuum spheres.

Again using (5.1), the diminished mean survival time for two reduced densities ($\eta=0.3,1.4$) is given in Fig. 11. In this case, the continuum survival times are from Lee et al.28 and Torquato and Kim7 rather than theoretical results. Typically, 2000–3000 walkers are used per configuration with a total of 100–200 configurations. The mean survival time is obtained with an error less than 1% due to the large number of configurations and walkers. The results clearly show a resolution dependence that is consistent with that seen in the simpler systems studied above. The striking feature of the mean survival times for the overlapping sphere system is the strong dependence on the reduced density.

VI. DISCUSSION

The results presented in Sec. V indicate that a finite resolution representation serves to decrease the mean survival
time $\tau$ for a Brownian particle in a system of digitized traps. This is not only true for systems of isolated spheres, but also for the system of randomly overlapping spheres which has a microstructure reminiscent of real materials. The convergence to the continuum limit is slow when viewed as a function of resolution which we define as the sphere diameter. Therefore, high resolution digital representations are required to obtain measured mean survival times approximately equal to the continuum value.

For a Brownian particle diffusing interior to a digitized sphere, the model system provides an upper bound on the diminished survival time. The mean survival time $\tau$ is more strongly influenced by the digitization in the case where Brownian particles are introduced at random locations within the digitized sphere in comparison to the scenario where particles are introduced only at the origin. This is easily understood since a particle starting at any random location within the sphere effectively sees a smaller sphere radius in the neighborhood it is walking and consequently an effectively poorer resolution.

In the case of particles diffusing exterior to a system of digitized spheres for both the BCC lattice and random overlapping configurations, the diminished mean survival time is clearly a function of resolution as seen in Figs. 9 and 11. Again, the resolution is defined in terms of the sphere radius. The better the resolution at a given volume fraction, the weaker the effect. The dependence on the resolution in the BCC lattice is much more pronounced due to the fact that the spheres do not overlap. In the case of overlapping spheres, the effect is somewhat weaker due to the fact that the geometry of the system is much more complicated as discussed in the next paragraph.

In the case of overlapping spheres there is also a dependence on the volume fraction of material at a given radius (or resolution) as seen in Fig. 11. Basically, the mean survival time is more strongly affected by a higher material fraction. This is due to the fact that at higher material fractions, the pore space accessible to the diffusing particles decreases. Any particle introduced into the system finds itself in a pore cavity that becomes characteristically smaller as the material volume fraction increases and thus redefines what is meant by resolution. Thus, the correct quantity of interest is not the radii of the spheres in the system, but rather the characteristic length scale of the pore cavities. One such measure of the volume accessible to a walker at each location in the void phase is the first moment of the pore-size distribution function $P(\delta)$ of Torquato and Avellaneda.\textsuperscript{10} The quantity $P(\delta)d\delta$ describes the probability that a randomly chosen point in the pore phase lies at a distance between $\delta$ and $\delta+d\delta$ from the nearest point on the pore-solid interface. The first moment $\langle\delta\rangle$ gives a measure of the mean cavity size seen by the diffusing particle in a medium with diffusion coefficient $D$ at any time during the random walk and provides a convenient lower bounds on the mean survival time,\textsuperscript{10}

$$\tau \geq \langle\delta\rangle^2/D.$$ The data presented in Ref. 10 shows that the first moment is nearly twice as large for $\eta=0.3$ than for $\eta=1.4$ which are the reduced densities shown in Fig. 11. Therefore, the particles at the higher reduced density are diffusing in an effectively poorer resolution system, thus explaining the difference in the diminished mean first passage time.

Therefore, we assert that the measured survival time of a digitized sample provides a lower bound on the true survival time and is equivalent to the true mean survival time in the case where the continuum medium exactly coincides with its digitized representation. The effect on the mean survival time is not necessarily dependent on the resolution defined through the typical grain size, but is highly dependent on the resolution defined through the average pore size. This distinction is very important and can be easily overlooked. One reason for this is that grain size is a natural parameter that typically defines a given material. However, for diffusivity and permeability simulations, the pore space hosts the dynamics and thus dictates the principal length scales.

Another interesting consequence of this investigation is the effect of digitization on the n-point correlation functions. The n-point correlation functions describe the probability of finding n points in the same phase (say, void). In general, the n-point correlation functions should only be weakly affected by the digitization, as they represent information that is averaged over many grains or traps and thus smear out much of the dependence on edge characteristics. The two-point correlation function, $S_2(r)$, for an isotropic medium is only a function of distance. The properties

$$\lim_{r \to 0} S_2(r) = \phi_1^2, \quad \lim_{r \to \infty} S_2(r) = \phi_1$$

remain invariant under digitization as the digitizing procedure is assumed to preserve phase volume as discussed in the introduction. However, the slope of the two-point correlation function at zero distance, $S_2'(0)$, is directly proportional to the specific surface area (surface area per unit volume) and will be strongly affected by the digitization. In our estimation, independent of resolution, this value can be as much as 50% larger than the continuum value depending on the nature of the sample.

Finally, we note that digitization can affect other transport properties in which the interface plays a major role. One such example is the fluid permeability associated with viscous flow in porous media. Here it is appropriate to mention a remarkable rigorous result from the development of cross-property bounds. Torquato\textsuperscript{19} has shown that the fluid permeability, $K$, of an isotropic porous medium is bounded from above by the mean survival time $\tau$ according to the relation

$$K \leq D \phi_1 \tau,$$

(6.1)

where $D$ is the diffusion constant and $\phi_1$ is the volume fraction of the void phase. Interestingly, the equality sign of (6.1) is achieved for transport interior to parallel channels of arbitrary cross section.\textsuperscript{19} I.e., for such geometries the trapping and flow problems are identical. For general geometries, these two transport problems are related but not identical. Although the governing differential equations are generally different for both problems, they share a common feature, namely, the fields (concentration or velocity) vanish at the pore-solid interface. Therefore, in both problems, the interface plays a major role in determining the effective proper-
ties. This fact is well known in the case of the fluid permeability.\textsuperscript{1,2} Relation (6.1) implies that the permeability determined from the digitized representation may be decreased in a manner similar to the mean survival time. This may explain some of the discrepancy between the simulated permeability and the measured value reported in Schwartz et al.,\textsuperscript{20} where the simulated permeability for a digitized medium was about 30\% less than the measured value.

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