Random-walk-based estimates of transport properties in small specimens of composite materials

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(Received 19 October 2001; revised manuscript received 26 December 2002; published 21 April 2003)

A method based on random walks is developed for estimating the dc conductance and similar transport properties in small specimens of composite materials. The method is valid over a much wider range of material structures than are asymptotic methods, and requires only that the internal structure of the material be known. The error in its estimates is limited primarily by CPU speed. It is found to work best for composites consisting of a bulk conducting phase and inclusions of lower conductivity.

DOI: 10.1103/PhysRevE.67.041104 PACS number(s): 05.60.Cd, 46.65.+g, 74.25.Fy

I. INTRODUCTION

Given a specimen of disordered material whose multiple phases have different physical properties, asymptotic methods can be used to estimate the conductivity of the material and hence the conductance of a specimen [1–3]. These methods serve as laws of large numbers for physical properties on random structures, and work by averaging away the effects of disorder and replacing a multiphase material by the one with uniform physical properties and the same external geometry. For them to work, they require that the internal structure of the material be relatively uniform, so that local property fluctuations can be averaged away.

In problems in materials science, specimens exist which do not meet these uniformity criteria. The specimen may consist of a small number of relatively large inclusions in a more conductive matrix, or may take the form of a thin sheet whose properties are uniform over the long dimensions but not over the short dimension. This nonuniformity will produce between-specimen variability and within-specimen variability that may have importance in applications, and which cannot be estimated by asymptotic means. Ideally, a method of estimating specimen conductance should be dependent upon very few assumptions concerning inclusion shape, uniformity, or complexity of structure, and should be straightforward to implement.

A second potential use of a small sample method arises when attempting to fit an asymptotic method to a specimen with a specific internal geometry. Some asymptotic methods are analytically derived without reference to specific specimen geometries, and considerable effort may be required to determine exactly what a material should look like to have those properties [4]. In practice, many asymptotic methods are often applied to data, and then a choice is made on the basis of goodness of fit [5–9]. Use of a small specimen estimate upon one large specimen or many small specimens of known structure could also be used to establish if that structure can lead to a particular class of asymptotic behavior.

A robust, random-walk-based estimator for the dc conductance of a composite specimen of known internal structure will be derived. This procedure can also be used to estimate any physical property analogous to conductance [10], such as electrical permittance, thermal conductance, and diffusion.

II. RANDOM-WALK-BASED METHODS FOR LARGE SAMPLES

The conductivity of large samples can be estimated through simulation routines based upon the Einstein correspondence between diffusivity and random walks [11]. In the ant-in-the-labyrinth algorithm [12,13], points are randomly chosen within a conductive phase of a composite. Each of these points is used as the starting point for a simple random walk with fixed step length and randomly chosen orientation at each step, which is used to simulate a diffusion. When the random walk hits an inclusion, its step length changes if the inclusion is conducting, and the walk stops at the surface if the inclusion is insulating. The walk is run for a fixed number of time steps, and the average Euclidean distance traveled is proportional to the conductivity of the composite.

For smaller specimens of composite, this algorithm can only be used under restrictive conditions. If the specimen has a symmetrical internal structure and a rectangular overall shape, then, by imposing periodic boundary conditions, the conductance can be found by the large sample method. If the specimen is not rectangular (e.g., it is cylindrical) or if the internal structure is irregular (e.g., it is a subset of a random sphere packing), then this method cannot be used.

III. RANDOM-WALK-BASED METHODS FOR SMALL SAMPLES

For this and further sections, the transport property considered will be dc conduction. To develop theory and methods, the specimen whose conductance is to be estimated is a square region D in $\mathbb{R}^2$ with sides of unit length. This boundary is divided into four parts (Fig. 1): the side A_1 through which the current enters, the opposite side A_0 through which the current leaves, and two insulated sides S_1 and S_2 through which no current may pass. Any inclusions will be assumed to have boundaries that are Lipschitz-continuous functions, and so do not possess too many corners or very rough sections. If the inclusions have random size, it will be assumed that there is a fixed minimum size. The k inclusions present

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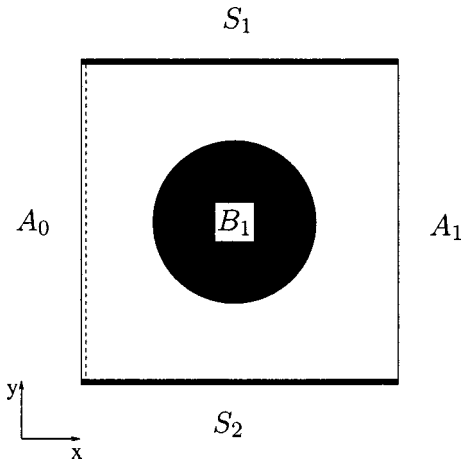

FIG. 1. The specimen considered here is a unit square in the plane. The current enters through A_1 and leaves at A_0, and the sides S_1 and S_2 are insulated. The inclusion B_1 may be insulating or conducting, but not superconducting. The dotted line is the location of the initial points for the diffusions and random walks discussed in Sec. III B 1.

are designated $B_1, \ldots, B_k$. The inclusion conductivity is $\sigma_1 \in [0,\infty)$ and the continuous phase conductivity is $\sigma_0 \in (0,\infty)$. No assumptions will be made about the arrangement of the inclusions within the specimen, except that their locations, shapes, and orientations are known.

A. The existence of a solution

The flow of dc current through the specimen is determined by a potential ϕ, which must satisfy

$$\nabla \cdot \sigma \nabla \phi = 0, \tag{1}$$

where $\sigma: \mathbb{R}^2 \to [0,\infty)$ is an L^∞ function and the boundary conditions are

$$\phi = 1 \quad \text{on} \quad A_1 \quad (x=1), \tag{2}$$

$$\phi = 0 \quad \text{on} \quad A_0 \quad (x=0), \tag{3}$$

$$\frac{\partial \phi}{\partial n} = 0 \quad \text{on} \quad S_1, S_2, \tag{4}$$

$$\sigma \frac{\partial \phi}{\partial n} \quad \text{is} \quad C^1 \quad \text{on the boundary of} \quad B_1, \ldots, B_k, \tag{5}$$

where n is a normal vector to S_1, S_2, or B_i. The $B_1, \ldots, B_k$ are considered to be parts of the boundary if the inclusions are insulating. Since Eq. (1) is an elliptical partial differential equation with an L^∞ coefficient and since the boundary conditions are Lipschitz, there exists a unique solution ϕ to the equation [14] which will be Hölder continuous if not twice differentiable at almost every point in the specimen [15]. Note that this existence result and several further results can be generalized to specimens in $\mathbb{R}^3$ having reasonable (i.e., smooth, nonfractal) boundaries but arbitrary shape and structure.

If there are no inclusions, the solution will be $\phi(x,y) = x$ at any point in D. In general, the solution ϕ cannot be expressed in terms of elementary functions or power series, but it is possible to directly estimate the value of ϕ at any point using random walks in the plane.

B. Estimation of conductance using a continuous random walk

By using discrete approximations to continuous random walks, the random geometry of a specimen can be unraveled, rather than averaged away. The method was developed as a generalization of the discrete lattice methods for resistor networks developed by Doyle and Snell [16]. While these methods are developed for a planar specimen, they generalize to any three-dimensional (or higher) specimen for which a potential ϕ can be shown to exist.

1. Estimating the conductance

The relative conductance of two unit square specimens satisfies

$$\frac{\varsigma_1}{\varsigma_2} = \frac{I_1}{I_2},$$

where ς_j is the conductance of specimen j and I_j is its current flux across the line $x=0$, as defined by

$$I_j = \int_0^1 \sigma(0,y) \frac{\partial \phi_j}{\partial x}(0,y)\, dy.$$

An estimator of ς_1/ς_2 can be constructed which avoids estimating the derivative directly.

Assume that there are no inclusions on the line $x=\epsilon$ (see Fig. 1), or in the region between A_0 and $x=\epsilon$, where ϵ is close to 0. A one-term Taylor series expansion of the potential ϕ of specimen i is

$$\phi_i(\epsilon,y) = \phi_i(0,y) + \left(\frac{\partial \phi_i}{\partial x}(0,y) \right) \epsilon + \left(\frac{\partial^2 \phi_i}{\partial x^2}(\xi(y),y) \right) \frac{\epsilon^2}{2}$$

for some values $\xi(y) \in \{(\delta,y): 0 \leqslant \delta \leqslant \epsilon\}$, and so

$$\int_0^1 \frac{\partial \phi_i}{\partial x}(0,y)\, dy = \frac{1}{\epsilon} \varphi_i - \frac{\epsilon}{2} R_i, \tag{6}$$

where

$$\varphi_i = \int_0^1 \phi_i(\epsilon,y)\, dy$$

and

$$R_i = \int_0^1 \frac{\partial^2 \phi_i}{\partial x^2}(\xi_i(y),y)\, dy.$$

If the conductance of the specimen is being compared to an inclusion-free specimen whose potential is $\phi_0(x,y) = x$, then $\int_0^1 (\partial \phi_0/\partial x)(0,y)\, dy = 1$ and the relative conductance can be

estimated using the leading term of Eq. (6). If the conductances of two specimens with potentials ϕ_i, $i=1,2$ are being compared, then

$$\frac{\varsigma_1}{\varsigma_2}=\frac{\varphi_1}{\varphi_2}+\frac{\epsilon^2}{2}\left(\frac{\varphi_1 R_2-\varphi_2 R_1}{\varphi_2(\varphi_2-(\epsilon/2)R_2)}\right) \tag{7}$$

and so φ_1/φ_2 is an estimator of the relative conductance of the two specimens.

2. Estimating the potential

Random walks can be used to approximate the solutions of elliptical boundary value problems if the local conductivity $\sigma(x,y)$ is a bounded measurable function [17,18].

Under the boundary conditions specified in Eqs. (2)–(5), if (x,y) is any point in a conducting region on the interior of the specimen, then

$$\phi(x,y)=\int_{A_1}\phi(1,\xi)P_1(d\xi)+\int_{A_0}\phi(0,\xi)P_0(d\xi), \tag{8}$$

where $P_i(d\xi)$ is the probability that a Brownian motion that begins at (x,y) reaches a small neighborhood around a point ξ on the boundary A_i before reaching any other point on A_0 or A_1. By fixing ϕ at 0 and 1 on A_0 and A_1, respectively, Eq. (8) reduces to

$$\phi(x,y)=\text{Prob}[\text{Brownian motion beginning at}\,(x,y)\ \text{crosses}\,A_1\ \text{before crossing}\,A_0], \tag{9}$$

which is known as the *escape probability to* A_1 *from* (x,y). This allows ϕ to be estimated at individual points in D [19,20] to arbitrary accuracy. Also, Eq. (9) shows that the integral φ used in Eqs. (6) and (7) is the mean escape probability to A_1 for points randomly chosen from a uniform distribution on the line $x=\epsilon$.

3. Approximating the Brownian motion

Realizations of a Brownian motion cannot be directly simulated, but must themselves be simulated via other stochastic processes. A combination of two different simulations is used, in order to balance the speed of execution against the need for accuracy in the crucial regions around the boundaries and interfaces in the specimen.

In the neighborhood of boundaries and interfaces, the Brownian motion is simulated by a simple random walk. The step length in the ith phase is chosen to be proportional to the conductivity σ_i of that phase. The direction of each step is chosen independently from a uniform distribution on the unit disk. If a step intersects an insulating boundary, then the step terminates at the boundary and takes the next step that will send it free from the insulating surface. If the step crosses a boundary from a phase of conductivity σ_i to a phase of conductivity $\sigma_j>0$ at a fraction ρ of its length, then the step length changes from δ_i to

$$\left(\rho+(1-\rho)\frac{\sigma_j}{\sigma_i}\right)\delta_i, \tag{10}$$

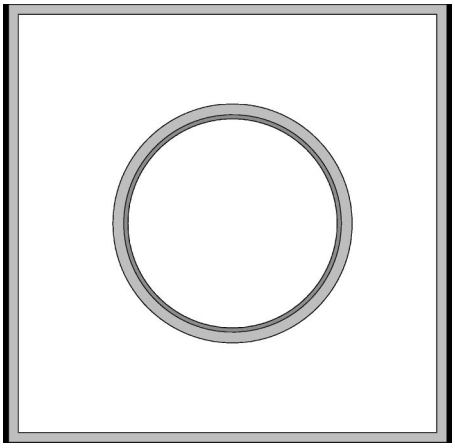

FIG. 2. On the white regions, the random walk proceeds via a walk on spheres. On the lightly shaded regions, the walk proceeds by steps of fixed length δ_0, and the regions have thickness $5\delta_0$. Within the inner shaded ring, the walk proceeds by steps of length $(\sigma_1/\sigma_0)\delta_0$, where σ_1 is the inclusion conductivity and σ_0 is the continuous phase conductivity. Steps crossing the boundary between the two shaded regions have their length altered via Eq. (10).

as in Hong *et al.* [13]. The subset of phase i in D where the simple random walk is used is defined to be all points within $5\delta_i$ of a boundary or interface. For a single spherical inclusion, these neighborhoods are shown in Fig. 2.

In the remainder of D, the diffusion is simulated by using the random walk on spheres [21], as implemented in the plane. In the ith phase, a sphere having diameter $2.5\delta_i$ less than the distance to the nearest boundary or interface is constructed at the end of the previous step, and the next step in the simulation is a point randomly chosen from a uniform distribution on the surface of this disk.

Each walk begins from a point (ϵ,U) on the line $x=\epsilon$, where U is chosen from a uniform distribution on the interval $[0,1]$. If each choice of starting point and subsequent step direction are mutually independent, then φ is estimated by

$$\hat{\varphi}=\frac{1}{N}\sum_{i=1}^{N}\Phi_i, \tag{11}$$

where each $\Phi_i\sim$binomial $[1,\phi(\epsilon,U_i)]$. This is an unbiased estimator when the conductance relative to the empty square specimen is estimated, since

$$E[\hat{\varphi}]=E[E[\Phi_1|U_1]]=E[\phi(\epsilon,U_1)]=\varphi.$$

IV. COMPARISON WITH EFFECTIVE MEDIUM THEORIES

Effective medium theories [22,23] and similar large sample theories replace a disordered specimen of two phases by a specimen of single phase of intermediate conductivity with the same dimensions. The method developed here can be seen as replacing the original specimen with a new specimen of only the matrix phase, having the same conductance as the composite specimen but having a different shape.

If a rectangular specimen consists of a single phase, its overall conductance is inversely proportional to d, the distance between A_0 and A_1. Since the conductance ς is approximately proportional to the escape probability φ, d is approximately proportional to φ^{-1}. This can be shown directly for diffusion on a line by results from diffusion theory [24], but these results only hold when no inclusions are present. Since the results developed here hold when inclusions are present, the determination of φ for a specimen is analogous to finding d for a pure matrix specimen having the same conductance as the original composite specimen.

If the inclusions in a specimen are insulating, then the matrix phase is formed into a network of conductor. If the inclusions are spherical, then the basic structure of this network can be described by a Voronoi tessellation [25]. If conductances are assigned to the branches of that network, then this can produce a discrete analog of the network itself [26]. Random walks can be used to estimate a distance across a network of this form, designated as the resistance distance [27]. The averaged escape probability φ represents a continuous generalization of this discrete metric.

V. SOURCES AND CONTROL OF ERROR

There are three main sources of error in the procedure. The control of these errors is limited by CPU speed.

A. Errors from estimating the potential

The error in the estimation of φ is best expressed as the standard deviation of the estimator $\hat{\varphi}$. The variance of $\hat{\varphi}$ is given by

$$\begin{aligned} N\,\mathrm{var}[\hat{\varphi}] &= E[\mathrm{var}[\Phi_1|U_1]] + \mathrm{var}[E[\Phi_1|U_1]] \\ &= (E[\phi(\epsilon,U_1)] - E[\phi(\epsilon,U_1)^2]) \\ &\quad + (E[\phi(\epsilon,U_1)^2] - E[\phi(\epsilon,U_1)]^2) \\ &= \varphi(1-\varphi), \end{aligned}$$

and so the standard deviation of $\hat{\varphi}$ is

$$\sigma[\hat{\varphi}] = \sqrt{\frac{\varphi(1-\varphi)}{N}}.$$

By choosing N large, this error can be made as small as needed.

B. Errors from estimating the derivative

The absolute value of the error term in Eq. (7) is bounded above by

$$\left(\frac{\max(\varphi_1,\varphi_2)}{\min(\varphi_2,\epsilon I_2)}\right)\max(R_1,R_2)\epsilon^2.$$

The first term in this product attains a near constant value as ϵ decreases, as long as R_i is small. The middle term in the product is small when ϵ is small, since then the equipotential lines between A_0 and $x=\epsilon$ are nearly straight. When this is the case, $\partial^2\phi_i/\partial y^2(x,y)$ is near zero in this region. If the line $x=\epsilon$ passes very close to the boundaries of inclusions with internal conductivity greatly different from matrix conductivity, then this error is increased.

C. Errors from approximating the diffusion

Simulation of the diffusion by the random walk on spheres is exact. Errors arise only in boundary and transition regions, where the random walk changes its step length or stops. These errors cannot be quantified using existing methods, especially in a simulation of a diffusion through a system of this complexity. They can be minimized by choosing the step size to be as small as feasible; Schwartz and Banavar [28] suggest a step size of 0.01 times the diameter of the smallest inclusion, but this was found to produce small positive bias in the relative conductance estimates in simulation experiments. This bias was eliminated by choosing step sizes of 0.0001–0.0005 times the diameter of the smallest inclusion.

VI. SIMULATION EXPERIMENTS AND COMPARISON WITH THEORY

Two sets of simulation experiments were carried out, one based on a regular arrangement of disks and the other based on disordered arrangements.

In each case, 10^6 random walks are simulated on a Sun Ultra 10 CPU. The program is written in C, incorporating the ran2 random number generator from Ref. [29]. The time required is proportional to p and to the number of spheres used for any fixed ratio of σ_1/σ_2. Each walk is allowed to take atmost 50×10^6 steps. Each data point requires between 5 and 90 h to estimate, but this will be reducible through further refinements to the diffusion approximation (e.g., parallelization or improved implementation of the random walk on spheres). While these times may not compare favorably with finite element methods in some circumstances, coding this algorithm may be much easier in circumstances where no finite element code exists, and it can just as easily be applied to specimens in three dimensions. Also, when inclusions are insulating, abrupt conductivity transitions are dealt within a simple way by the random walk, and dense mesh structures at the boundaries are not required.

A. Asymptotic methods for ordered inclusions

If the inclusions in a very large specimen of heterogeneous material form an ordered array, improvements on Rayleigh's [30] estimate for the conductivity of the composite material were given by Perrins *et al.* [31] in the case of a square array of disks in the plane,

$$\frac{\sigma_c}{\sigma_0} = 1 - \frac{2p}{T + p - \dfrac{0.305827p^4T}{T^2 - 1.402958p^8} - \dfrac{0.013362p^8}{T}}, \quad (12)$$

where

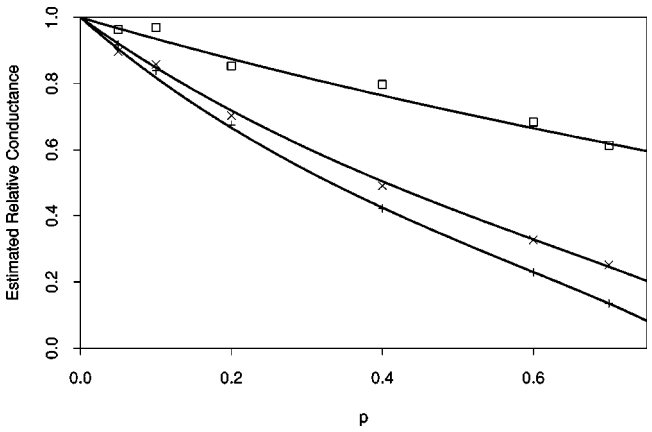

FIG. 3. Comparison of asymptotic estimates [lines, as found from Eq. (12)] with simulation estimates for specimens with a single inclusion whose conductivity satisfies $\sigma_1/\sigma_0=0.0$ (+), $\sigma_1/\sigma_0=0.1$ (×). and $\sigma_1/\sigma_0=0.5$ (□). Note that error decreases as p and σ_1/σ_0 decrease. All estimates are made relative to a specimen of pure conductor.

$$T=\frac{\sigma_0-\sigma_1}{\sigma_0+\sigma_1}.$$

If the specimen is small and the inclusions form an ordered square pattern centered inside the specimen, then Eq. (12) also yields the conductance of the specimen, relative to the conductance of a specimen of pure matrix of the same size and shape. In almost no other circumstance can an analytically derived relationship be found for small specimen conductance.

B. Ordered inclusions

The conductance of a specimen whose inclusions are arranged in a centered square array within the specimen (e.g., Fig. 5, left) is estimated relative to the conductance of a pure conductor specimen. Results are compared with Eq. (12) for $\sigma_1<\sigma_0$ in Fig. 3 and for $\sigma_1>\sigma_0$ in Fig. 4.

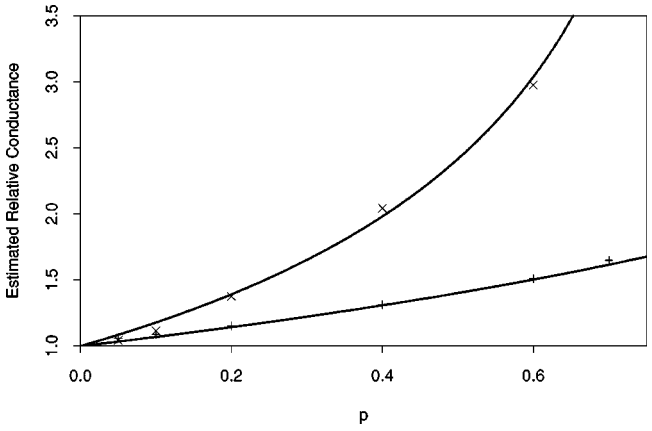

FIG. 4. Comparison of asymptotic estimates [lines, as found from Eq. (12)] with simulation estimates for specimens with a single inclusion whose conductivity satisfies $\sigma_1/\sigma_0=2$ (+) and $\sigma_1/\sigma_0=10$ (×). Note that error decreases as p and σ_1/σ_0 decrease. All estimates are made relative to a specimen of pure conductor.

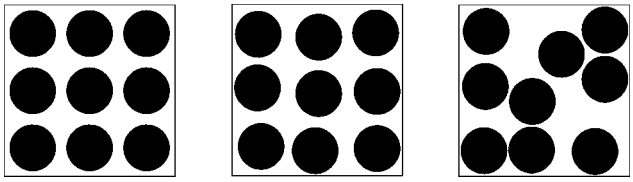

FIG. 5. From left to right: an ordered array of nine inclusions, a perturbed ordered array, and an arbitrarily arranged array. All inclusions are assumed to be insulating and of the same size. The volume fraction of inclusion in all three specimens is $p=0.5$.

In all cases where the inclusions are less conductive, the simulations and Eq. (12) are in very strong agreement. Variation around the asymptotic estimate increases with inclusion conductivity, and also as the size of the inclusions is reduced.

C. Disordered inclusions

The major purpose of using this algorithm on small samples is to determine the degree to which deviations from the ordered arrangement of inclusions affect the conductance. For a specimen with nine insulating disk inclusions, conductance estimates are found for an ordered specimen (Fig. 5, left), a specimen that is arbitrarily disordered (Fig. 5, right), and a specimen prepared by randomly perturbing the ordered arrangement (Fig. 5, center). The perturbed arrangement was prepared by dividing the specimen into nine subsquares and placing the inclusions randomly in each subsquare such that the inclusions used for the $p=0.5$ case were contained completely within each square. In all cases, p was adjusted by changing the radius of the inclusions.

When p is small, the inclusions are isolated in a large volume of matrix and the estimates for all three specimens are very similar. As p increases, the matrix becomes a structured conducting network, and the different arrangements of inclusions produce differences in the conductance that are

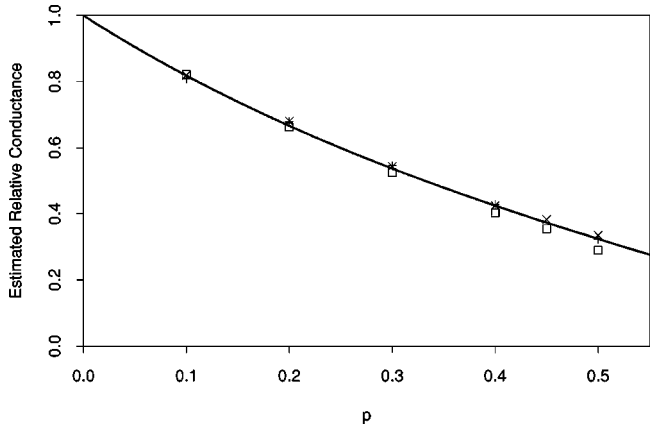

FIG. 6. Plot of the effects of inclusion arrangement on specimen conductance. All inclusions were centered at the same locations as those seen in Fig. 5, and sphere radii were reduced to give other values of p. The solid line is Eq. (12), while the points represent simulation estimates for the ordered (+), randomly perturbed (×), and arbitrarily arranged (□) specimens.

most noticeable in the arbitrarily ordered specimen (see Fig. 6). The greater number of choke points in the conductor network produces increasingly lower conductances as p approaches 0.5.

VII. CONCLUSIONS

(i) Escape probabilities can be used to estimate the conductance of small composite specimens, given their internal structure.

(ii) The procedure does not depend upon strong assumptions regarding internal specimen geometry, and can be easily implemented when the random walk on spheres is used.

(iii) The accuracy of the method can be understood and controlled, and is primarily limited by computing speed.

(iv) All results extend to specimens in $\mathbb{R}^3$.

ACKNOWLEDGMENTS

Comments from Bruce Ankenman, Takeru Igusa, Alan Karr, Ricardo Nochetto, and Mark Freidlin were important in the development of the method. This research was funded in part by NSF Grants Nos. DMS-9313013 and DMS-9208758 to the National Institute of Statistical Sciences.

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