First-passage-time calculation of the conductivity of continuum models of multiphase composites

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We formulate a Brownian-motion simulation technique to compute exactly the effective conductivity $\sigma_e$ of general continuum (off-lattice) models of $n$-phase heterogeneous media having phase conductivities $\sigma_1, \ldots, \sigma_n$, where $\sigma_i$ can be finite or infinite. The appropriate first-passage-time equations at the multiphase interface are derived to reduce significantly the computation time. The method is illustrated by calculating $\sigma_e$ for regular and random arrays of $d$-dimensional, nonoverlapping spheres ($d=2$ and 3) for a wide range of conductivity ratios (including perfectly insulating and superconducting particles) and volume fractions.

The problem of predicting the effective conductivity (and, by mathematical analogy, the dielectric constant, magnetic permeability, and diffusion coefficient) of multiphase composites has received considerable theoretical attention in recent years.\(^1\)–\(^6\) Comparatively speaking, there is a dearth of work on "exact" simulations of the property of interest, especially for continuum models (e.g., random distributions of particles in a matrix). Such "computer experiments" could provide unambiguous tests on theories which, except for specially prepared artificial media, are never exact.

Conventional simulations approaches for continuum models (e.g., finite differences and finite elements) are severely limited by high computational costs and thus questions concerning finite-size effects and accuracy are typically left unresolved.

In this Rapid Communication, we develop a Brownian motion simulation technique that efficiently yields the effective conductivity $\sigma_e$ of general continuum models of macroscopically isotropic, $d$-dimensional, $n$-phase composite media having conductivities $\sigma_1, \ldots, \sigma_n$ (where $0 \leq \sigma_i \leq \infty \ \forall i$) and volume fractions $\phi_1, \ldots, \phi_n$. This is done by keeping track of the mean-square displacement and mean time associated with Brownian trajectories in the limit of large times. Unlike recent random-walk algorithms which simulate the detailed zig-zag motion of the walker with small, finite step sizes,\(^7\) the present formulation facilitates the calculation by utilizing the appropriate first-passage-time equations in the homogeneous phases and multiphase interface. It has been demonstrated by Torquato and Kim\(^8\) that in the related diffusion-controlled trapping problem, the use of first-passage-time equations results in an execution time that is at least 1 order of magnitude faster than procedures which simulate the detailed zig-zag motion of the random walker. First-passage-time analysis also has the advantage that boundary conditions at the interface (the critical part of the calculation) are exact and do not have to be arrived at by physical reasoning or conjecture.

The essence of the first-passage-time methodology is to construct the largest concentric sphere of radius $R$ (around a randomly chosen point in phase $i$) which just touches the multiphase interface. The mean time $\tau$ taken for the Brownian particle (initially at the imaginary sphere center) to first strike a randomly chosen point on the sphere surface is simply given by

$$\tau(R) = \frac{R^2}{2d\sigma_i}.$$  \(^{(1)}\)

(In other words, when walking in the homogeneous regions there is no need to spend unnecessary computing time "wandering in the wilderness" by simulating the detailed motion of the random walker with finite step sizes.) The process is repeated, each time keeping track of $R^2$ and thus $\tau$, until the walker comes within a very small distance of the multiphase interface. At this juncture, one must compute the mean time associated with crossing the boundary, $\tau$, and the probability of crossing the boundary, both of which depend upon the phase conductivities and the local geometry. (These interface quantities are obtained by solving boundary-value problems described below.) At some future time, the Brownian particle will again walk entirely in one phase and the above procedure is repeated. The effective conductivity $\sigma_e$ scaled by the conductivity of the reference medium taken to be phase 1, can be shown\(^9\) to be given by

$$\frac{\sigma_e}{\sigma_1} = \frac{\left( \sum_i \tau_i(R_i) + \sum_i \tau_i(R_i) \right)}{\left( \sum_i \tau(R_i) + \sum_i \tau_i(R_i) \right)} \bigg|_{x^2 \rightarrow \infty}.$$  \(^{(2)}\)

\[\text{FIG. 1. Small neighborhood of the interface boundary between phases 1 and 2.}\]
Here $\tau_1(R)$ denotes the mean first hitting time for a walker in a homogeneous sphere of radius $R$ and conductivity $\sigma_1$, summations over $i$ is for Brownian paths in homogeneous regions, summations over $j$ is for paths crossing the interface, and angular brackets denote ensemble averages.

First-passage-time equations which apply in a very small neighborhood of the interface between two phases, say phase 1 and phase 2 (see Fig. 1), are given by

$$\nabla^2 p_1 = 0 \text{ in } \Omega = \Omega_1 \cup \Omega_2,$$

$$p_1(x) = 1 \text{ on } \partial \Omega_1,$$

$$p_1(x) = 0 \text{ on } \partial \Omega_2,$$

$$p_1(x)_{|\Gamma} = p_1(x)_{|\Gamma} \text{ on } \Gamma,$$

$$\frac{\partial p_1}{\partial n_1} = \frac{\partial p_1}{\partial n_2} \text{ on } \Gamma,$$

$$p_2(x) = 1 - p_1(x),$$

$$(3)$$

$$\sigma_1 \nabla^2 \tau_s = -1 \text{ in } \Omega_1,$$

$$\tau_s(x) = 0 \text{ on } \partial \Omega_1,$$

$$\tau_s(x)_{|\Gamma} = \tau_s(x)_{|\Gamma} \text{ on } \Gamma,$$

$$\frac{\partial \tau_s}{\partial n_1} = \frac{\partial \tau_s}{\partial n_2} \text{ on } \Gamma.$$  

Here $p_1(x)$ [$p_2(x)$] is the probability that the walker initially at $x$ near $x_0$, the center of the imaginary sphere of radius $R$, hits $\partial \Omega_1$ [$\partial \Omega_2$] for the first time without hitting $\partial \Omega_2$ [$\partial \Omega_1$]. $\tau_s(x)$ is the mean hitting time for the walker initially at $x$ to hit $\partial \Omega_1$ [$\partial \Omega_2$] for the first time, $\Gamma$ denotes the interface surface, $n_i$ is the outward normal from region $\Omega_i$, $i = 1, 2, \ldots, d$ signifies the approach to $\Gamma$ from the region $\Omega_i$, and $a = \sigma_2/\sigma_1$. In the simulation, the interface quantities $p_1, p_2,$ and $\tau_s$ are computed when the walker comes within a prescribed small distance $\delta$ of the interface, where $a$ is the local radius of curvature and $\delta < 1$.

The solutions of Eqs. (3)-(5) for an interface with an infinite radius of curvature (straight line for $d = 2$ or plane for $d = 3$) is straightforward and for $d \geq 2$ is given by an infinite series involving $d$-dimensional spherical harmonics. We seek, however, a solution for curved interfaces since this will result in more accurate calculations and because the radius $R$ in practice does not have to be as small as it would have to be in the zero-curvature case, thus reducing the computation time. The general solution is intractable analytically but we have devised an approximate analytical solution (based upon the zero-curvature solution) which turns out to give excellent agreement with a numerical evaluation of Eqs. (3)-(5) using the boundary-element method. Figure 2 shows an example of this comparison for the mean hitting time $\tau_s$ for $d = 2$ in a case of large curvature. The general solutions are lengthy and hence are not given here.

In order to assess the accuracy of our algorithm, we have computed the effective conductivity $\sigma_e$ for the $d$-dimensional cubic lattice of spheres ($d = 2$ and 3) of radius $a$ and conductivity $\sigma_2$ in a reference medium (matrix) of conductivity $\sigma_1$, for both finite and infinite values of the conductivity ratio $a = \sigma_2/\sigma_1$ and a wide range of particle volume fraction $\phi_2$ values. For such idealized models, exact numerical results are available. We set $\delta = 0.0001$, employed 2000-6000 random walks, and let the dimensionless total mean-square displacement $X^2/a^2$ vary from 10 to 100, depending on the value of $\phi_2$ and $a$. Our simulation results were found to be in excellent agreement with the previous exact results for both finite and infinite values of $a$, with a maximum error of less than 1%. Each datum for $\sigma_e$ required, on average, only 8 CPU minutes on a CRAY Y-MP or 1 CPU hour on a VAX station 3100. For the special case of superconducting particles ($a = \infty$), we studied the behavior of $\sigma_e$ when the particles are very near their percolation-threshold or close-packing values (i.e., $\phi_2^c = \pi/4$ for $d = 2$ and $\phi_2^c = \pi/6$ for $d = 3$) and found that the simulation predicted the proper singular behavior in this critical region. Figure 3 compares some of our data with the exact results. Additional data (including insulating particles $a = 0$) are given elsewhere.

We also apply our algorithm to obtain $\sigma_e$ for random distributions of nonoverlapping (i.e., spatially correlated) $d$-dimensional spheres ($d = 2$ and 3) of conductivity $\sigma_2$ in a matrix of conductivity $\sigma_1$, useful models for which there are still very few exact results, especially at large $a$ and $\phi_2$. We generated equilibrium configurations of $N$ $d$-dimensional hard spheres of radius $a$ in a cubical cell with periodic boundary conditions using a standard Metropolis algorithm. For $d = 2$, we studied the volume fraction range $0 \leq \phi_2 < 0.7$; $\phi_2 = 0.7$ corresponds to a value very close to the fluid-solid phase transition and is about 86% of the random close-packing value. For $d = 3$, we examined the range $0 \leq \phi_2 \leq 0.6$. Above the fluid-solid phase transition, $\phi_2 \approx 0.49$, the system for $d = 3$ is in the metastable glassy state and generation of realizations becomes quite subtle. For $\phi_2 = 0.5$ and 0.6, we employed the careful procedure of Miller and Torquato to obtain
hard-sphere realizations. Note that $\phi_2 = 0.6$ corresponds to approximately 95% of the random close-packing value $12.3 \phi_2$ for $d = 3$. Generation of configurations at $\phi_2$ (for $d = 2$ and 3) is quite complex and hence was not carried out in the present work.

We employed 100–1000 random walks per realization, and averaged over 100–600 realizations, set $\epsilon = 0.0001$, and let the scaled total mean-square displacement $X^2/\alpha^2$ vary from 10 to 100, depending upon $\phi_2$ and $\alpha$. We studied the effect of system size and found that with $N = 100$ and 125, finite-size effects were negligible for $d = 2$ and 3, respectively. For $d = 2$ and 3, each datum for $\sigma_e$, accurate to within 2%, required on average about 1 and 5 CPU hours on a CRAY Y-MP. It is important to emphasize, however, that a reduction of the number of realizations by an order of magnitude reduces the computing time proportionally but with little loss in accuracy (i.e., approximately 5% accuracy level). Compared to previous techniques, our algorithm yields the effective conductivity accurately with a very fast execution time.

Figure 4 compares our hard-disk simulation data for $\sigma_e$ with $\alpha = 10$ and $\infty$ to evaluations of Milton’s four-point lower bound by Torquato and Lado.5 The bound incorporates nontrivial information about the microstructure through a parameter $\xi_2$.15 The upper bounds are not shown since it is now well established5,9,14,16 that microstructure-sensitive lower bounds will provide a good estimate of $\sigma_e$ when $\alpha \gg 1$, provided that the medium does not possess large conducting clusters. This indeed is borne out in Fig. 4. Additional data for $\alpha = 0$ and 50 are given in Ref. 9.

In Fig. 5, we depict our hard-sphere simulation data for $\sigma_e$ with $\alpha = 10$ and $\infty$. Included in the figure is an analytical approximation due to Torquato16 and the evaluation of Milton’s three-point lower bound by Miller and Torqua-
Both analytical expressions involve the microstructural parameter $\zeta_2$. Torquato’s expression is seen generally to provide an excellent estimate of the effective conductivity for a wide range of conditions. Note that the well-known Clausius-Mossotti formula underestimates the data, especially for $\alpha \gg 1$ and large $\phi_2$. For example, for $d = 3$, $\alpha = \infty$ and $\phi_2 = 0.6$; this formula is about 51% below the datum. Data for $\alpha = 0$ are also given in Ref. 9.

We are in the process of computing $\sigma_e$ for distributions of $d$-dimensional overlapping (i.e., spatially uncorrelated) spheres (also known as the “Swiss-cheese model”).

Since our algorithm can accurately yield behavior near the percolation threshold, we are also computing transport percolation exponents for these models.

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6. See also references contained within Refs. 1–5.
15. In Ref. 14, it was shown that exact low-density expansions of the parameter $\zeta_2$ for hard-sphere systems are accurate over virtually the entire volume fraction range. Thus, for $d = 2$, we employ $\zeta_2 = \phi/3 - 0.05707\phi^2$, first obtained in Ref. 5.