RAPID COMMUNICATIONS

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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 σ_e of general continuum (off-lattice) models of n-phase heterogeneous media having phase conductivities $\sigma_1, \ldots, \sigma_n$, where σ_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 σ_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 σ_e of general continuum models of macroscopically isotropic, d-dimensional, n-phase composite media having conductivities $\sigma_1, \ldots, \sigma_n$ (where $0 \le \sigma_i \le \infty \ \forall i$) 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 τ 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

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

(In other words, when walking in the homogeneous regions there is no need to spend unnecessary computing time[8] "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 τ, 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, τ_s, 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 σ_e scaled by the conductivity of the reference medium taken to be phase 1, can be shown[9] to be given by

$$\frac{\sigma_e}{\sigma_1} = \left. \frac{\left\langle \sum_i \tau_1(R_i) + \sum_j \tau_1(R_j) \right\rangle}{\left\langle \sum_i \tau(R_i) + \sum_j \tau_s(R_j) \right\rangle} \right|_{X^2 \to \infty} . \tag{2}$$

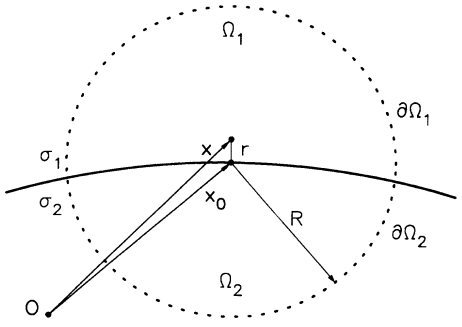

FIG. 1. Small neighborhood of the interface boundary between phases 1 and 2.

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Here $\tau_1(R)$ denotes the mean first hitting time for a walker in a homogeneous sphere of radius R and conductivity σ_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[9]

$$\begin{aligned}
&\nabla^2 p_1 = 0 \text{ in } \Omega\ (=\Omega_1 \cup \Omega_2)\,,\\
&p_1(\mathbf{x}) = 1 \text{ on } \partial\Omega_1\,,\\
&p_1(\mathbf{x}) = 0 \text{ on } \partial\Omega_2\,,\\
&p_1(\mathbf{x})|_1 = p_1(\mathbf{x})|_2 \text{ on } \Gamma\,,\\
&\left.\frac{\partial p_1}{\partial n_1}\right|_1 = \alpha \left.\frac{\partial p_1}{\partial n_1}\right|_2 \text{ on } \Gamma\,,
\end{aligned} \tag{3}$$

$$p_2(\mathbf{x}) = 1 - p_1(\mathbf{x})\,, \tag{4}$$

$$\begin{aligned}
&\sigma_i \nabla^2 \tau_s = -1 \text{ in } \Omega_i\,,\\
&\tau_s(\mathbf{x}) = 0 \text{ on } \partial\Omega\,,\\
&\tau_s(\mathbf{x})|_1 = \tau_s(\mathbf{x})|_2 \text{ on } \Gamma\,,\\
&\left.\frac{\partial \tau_s}{\partial n_1}\right|_1 = \alpha \left.\frac{\partial \tau_s}{\partial n_1}\right|_2 \text{ on } \Gamma\,.
\end{aligned} \tag{5}$$

Here $p_1(\mathbf{x})$ $[p_2(\mathbf{x})]$ is the probability that the walker initially at $\mathbf{x}$ near $\mathbf{x}_0$, the center of the imaginary sphere of radius R, hits $\partial\Omega_1$ $[\partial\Omega_2]$ for the first time without hitting $\partial\Omega_2$ $[\partial\Omega_1]$, $\tau_s(\mathbf{x})$ is the mean hitting time for the walker initially at $\mathbf{x}$ to hit $\partial\Omega$ $(=\partial\Omega_1+\partial\Omega_2)$ for the first time, Γ denotes the interface surface, n_i is the unit outward normal from region Ω_i, $\cdots|_i$ signifies the approach to Γ from the region Ω_i, and $\alpha=\sigma_2/\sigma_1$. In the simulation, the interface quantities p_1, p_2, and τ_s are computed when the walker comes within a prescribed small distance $a\delta$ of the interface, where a is the local radius of curvature and $\delta \ll 1$.

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[9] (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 τ_s for $d=2$ in a case of large curvature. The general solutions[9] are lengthy and hence are not given here.

In order to assess the accuracy of our algorithm, we have computed the effective conductivity σ_e for the d-dimensional cubic lattice of spheres ($d=2$ and 3) of radius a and conductivity σ_2 in a reference medium (matrix) of conductivity σ_1, for both finite and infinite values of the conductivity ratio $\alpha=\sigma_2/\sigma_1$ and a wide range of particle volume fraction ϕ_2 values. For such idealized models, exact numerical results are available.[1] 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 ϕ_2 and α. Our simulation results were found to be in excellent agreement with the previous exact results for both finite and infinite values of α, with a maximum error of less than 1%. Each datum for σ_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 ($\alpha=\infty$), we studied the behavior of σ_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[1] in this critical region. Figure 3 compares some of our data with the exact results. Additional data (including insulating particles $\alpha=0$) are given elsewhere.[9]

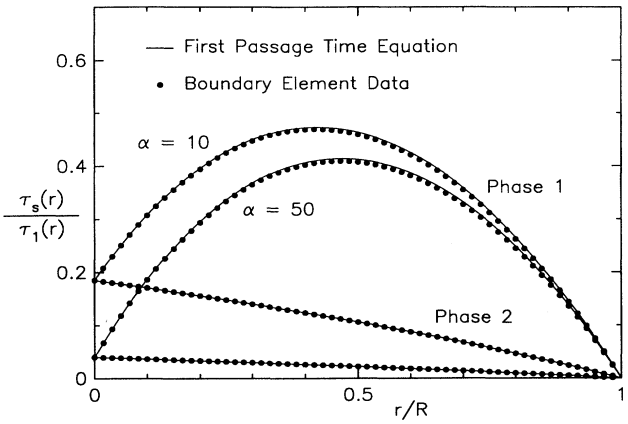

FIG. 2. First-passage-time equation (solid lines) and the boundary-element data (circles) for τ_s/τ_1 vs the scaled distance r/R from the interface for selected $\alpha=\sigma_2/\sigma_1$ in the $d=2$ case. Ratio of radius of curvature to first flight radius is 10.

We also apply our algorithm to obtain σ_e for random distributions of nonoverlapping (i.e., spatially correlated) d-dimensional spheres ($d=2$ and 3) of conductivity σ_2 in a matrix of conductivity σ_1, useful models for which there are still very few exact results, especially at large α and ϕ_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.[10] 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[11] and is about 86% of the random close-packing value[12] ϕ_2^c. For $d=3$, we examined the range $0 \leq \phi_2 \leq 0.6$. Above the fluid-solid phase transition[13] $\phi_2 \approx 0.49$, 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[14] to obtain

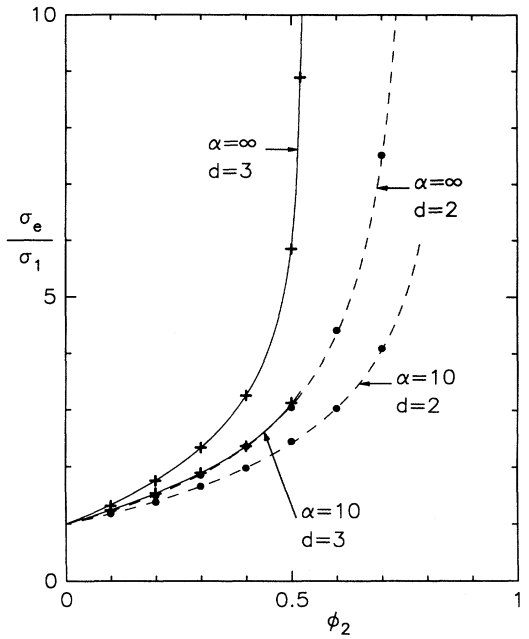

FIG. 3. σ_e/σ_1 for a square array of disks ($d=2$) and a simple-cubic array of spheres ($d=3$) as a function of the disk area fraction ϕ_2 at selected $\alpha=\sigma_2/\sigma_1$. Dashed and solid lines are the exact results (Ref. 1) and circles and crosses are our data. For $d=2$, the datum for $\alpha=\infty$ near the percolation threshold is not shown.

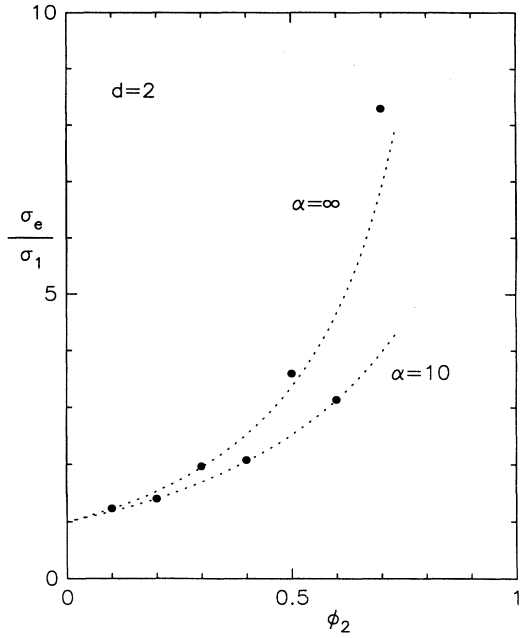

FIG. 4. σ_e/σ_1 for an equilibrium distribution of hard disks ($d=2$) as a function of the disk area fraction ϕ_2 at selected $\alpha=\sigma_2/\sigma_1$. Dotted lines are four-point lower bounds (Refs. 2 and 5) and circles are our data.

hard-sphere realizations. Note that $\phi_2=0.6$ corresponds to approximately 95% of the random close-packing value[12] ϕ_2^c for $d=3$. Generation of configurations at ϕ_2^c (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 $\delta=0.0001$, and let the scaled total mean-square displacement X^2/a^2 vary from 10 to 100, depending upon ϕ_2 and α. 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 σ_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 σ_e with $\alpha=10$ and ∞ 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 ζ_2.[15] The upper bounds are not shown since it is now well established[5,9,14,16] that microstructure-sensitive lower bounds will provide a good estimate of σ_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 σ_e with $\alpha=10$ and ∞. Included in the figure is an analytical approximation due to Torquato[16] and the evaluation of Milton's three-point lower bound by Miller and Torqua-

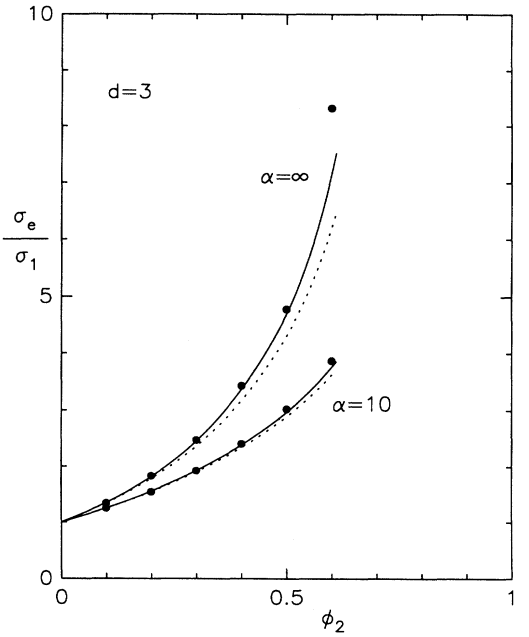

FIG. 5. σ_e/σ_1 for an equilibrium distribution of hard spheres ($d=3$) as a function of the sphere volume fraction ϕ_2 at selected $\alpha=\sigma_2/\sigma_1$. Solid and dotted lines are Torquato's approximation (Ref. 16) and three-point lower bounds (Refs. 2 and 14), respectively, and circles are our data.

to.[14] Both analytical expressions involve the microstructural parameter ζ_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 ϕ_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 σ_e for distributions of d-dimensional overlapping (i.e., spatially uncorrelated) spheres[17] (also known as the "Swiss-cheese model"[18]). Since our algorithm can accurately yield behavior near the percolation threshold, we are also computing transport percolation exponents[18] for these models.

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