Random-walk simulation of the dielectric constant of a composite material

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(Received 19 March 1990)

We evaluate, by a random-walk method, the dielectric constant ϵ_e of a composite material consisting of impenetrable, spherical conducting inclusions embedded in an insulating matrix. The random-walk method permits an accurate evaluation of ϵ_e up to volume fractions corresponding to near to close packing of the inclusions. We compare the ϵ_e results for different types of random configurations with those for the simple-cubic and face-centered-cubic lattice configurations.

Many composite materials are composed of discrete inclusions embedded in a homogeneous matrix.[1] When the inclusions are sufficiently large to be characterized by their own material properties, such as a dielectric constant, the properties of the composite material will depend on the material properties of both phases, as well as the volume fraction and arrangement in space of the inclusion phase. In this paper we present a simulation method to evaluate the effective dielectric constant, ϵ_e, of composites based on a recently introduced random walk method.[2-4] The method has been successfully applied to composites consisting of inclusions which can overlap;[2-4] here we show that it can provide accurate results for discrete-inclusion composites.

There are many approaches to the prediction of the effective dielectric constant of a composite material. Among these are the following: (1) approximate methods based on mean-field approaches, such as those of Maxwell,[5] Maxwell-Garnett,[6] Clausius,[7] Mossotti,[8] and Bruggeman[9] (these methods are of uncertain quality at high inclusion volume fractions); (2) analytic approaches via diagrammatic expansions,[10,11] which are limited to dilute inclusions; (3) rigorous variational techniques[12] which lead to upper and lower bounds on ϵ_e (when the dielectric constants of the constituent phases are very different, the bounds are not close); and (4) an analytic-simulation method[13] based on a multipolar expansion of the fields around each inclusion arising from the presence of the other inclusions (if a sufficient number of multipoles are included, then this simulation method will converge even at high-volume fractions of the inclusions and provide accurate ϵ_e values).

In developing the analytic-simulation method,[13] we found that the most difficult case (in terms of the number of multipoles required to converge the results at a given volume fraction) corresponded to conducting inclusions in an insulating matrix, since here the electric field varies very rapidly in the gap between closely separated inclusions. The simulations were carried out for N spherical inclusions of radius R enclosed in a volume V, from which we define the volume fraction as $\phi=(4\pi R^3/3)(N/V)$. For ϕ above 0.45, the number of multipoles required for convergence was larger than could be practically included with our computational resources. Here, we extend the results for conducting inclusions to higher-volume fractions, by employing the random-walk method, and show that it can be used to obtain accurate results for these nonoverlapping inclusion composites.

We validate the random-walk method by simulating ϵ_e for a simple-cubic lattice and comparing the data with that of McPhedran and McKenzie[14] obtained by a multipole simulation. These authors were able to include a very large number of multipoles in their simulation because they found empirically that only the $l,m=0$ component among the $(2l+1)$ moments for order l in a spherical multipolar basis contribute to the effective dielectric constant. Thus, their results are very accurate even at volume fractions in the neighborhood of close packed. Based on these results, we then present the data for simulations of random distributions of inclusions at high-volume fractions.

The random-walk methodology has been carefully described by Tobochnik, Laing, and Wilson.[4] The method relies on the equivalence of Laplace's equation and the diffusion equation. In particular, the dielectric constant for the conductor-in-insulator matrix case can be related to the diffusion constant of a random walker which walks in the matrix phase of the composite with unit diffusion constant and in the inclusion phase with infinite diffusion constant. The diffusion constant D_e of the composite is obtained by monitoring the mean-square displacement of the walker versus time and using the relation

$$\langle r^2\rangle = 6D_e t \ . \tag{1}$$

For the conductors-in-insulators case, Einstein's connection between ϵ_e and D_e has been shown to be[15,3]

$$\epsilon_e = (1-\phi)D_e \ . \tag{2}$$

Thus, a simulation of D_e provides ϵ_e.

To carry out the simulation of D_e for nonoverlapping spherical inclusions, we first generate configurations of spheres by a Metropolis Monte Carlo algorithm.[16] This method yields liquid-state disorder for $\phi < 0.45$ and disordered-solid-like configurations at higher-volume fractions. At very high-volume fractions, near hexagonal close packing, the Metropolis method is too time consuming to make it practical to obtain well-randomized configurations, and so we use the following alternative procedure. A face-centered-cubic (fcc) lattice is randomized by taking the Wigner-Seitz cell about each inclusion and randomly displacing each particle within the largest spherical region that can be inscribed in its Wigner-Seitz cell. We typically used 864 inclusions in a given configuration, performed ten independent random walks on each configuration, with the walkers started at a randomly chosen point close to the center of the simulation cell, and then repeated this procedure for 100 configurations. Each configuration (the primary cell) is periodically replicated and a walker which steps out of the primary cell is allowed to continue its walk in the image cells. The slopes of the mean squared displacement versus time plots are quite linear after an initial induction time and before the mean-square displacement becomes so large that typical walkers are leaving the primary cell. The slopes can be estimated to an accuracy of about 5%.

The random walk was carried out by a mean-first-passage-time (MFPT) method.[4,17] In this method, for a walker exterior to any inclusion, a sphere centered on the walker is expanded until it touches the closest inclusion. Then, the walker steps to a randomly chosen point on the surface of this sphere with the time assigned to the step chosen from the MFPT distribution characterizing the distribution of times to transit this distance via diffusion.[4] A new sphere is drawn around the new starting point for the walker and the above procedure is repeated until the walker is captured by an inclusion. When a walker is inside an inclusion, it is placed on a randomly chosen point on the inclusion's surface. No time is counted for this event, since the inclusions' conductivity (diffusivity) is taken as infinitely large. The MFPT method is a useful alternative to the conventional lattice walk method used to simulate the walker's diffusive motion. It eliminates the necessity of carrying out walks with very small lattice spacings, which would be required at high-volume fractions. Also, elimination of the effect of the lattice spacing on the results, by varying the lattice constant of the walk, does not have to be carried out.

In order to implement the MFPT approach for nonoverlapping inclusions, a criterion must be established for when the walker is considered to be inside an inclusion. Figure 1 defines the inclusion radius R, an outer radius R_c, and a length a_c. Consider the walker with the closest inclusion, and define "a" as the minimum distance from this inclusion's surface to the walker's location. If a is greater than a_c, then the MFPT walk is carried out. Otherwise, the walker is placed on the surface of the outer sphere with radius R_c at a random location. If a is between zero and a_c, then the walker is placed randomly on R_c. A time equal to the diffusion time for a length

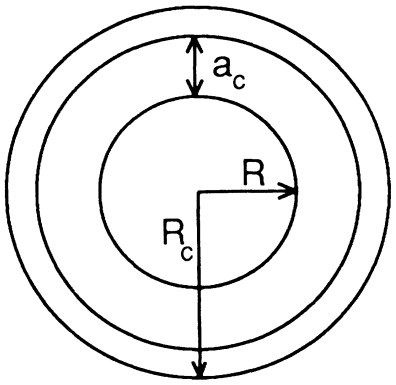

FIG. 1. An inclusion of radius R, with two concentric spheres of radii, $R + a_c$ and R_c, used to decide when a walker is captured by the inclusion, as discussed in the text.

$R_c - R$ is counted toward the total diffusion time for this step. We found that this procedure yields accurate results as long as (1) $R_c - R$ is chosen to be small with respect to the gap between neighboring inclusions and (2) R_c is slightly bigger than $a_c + R$.

The method was checked against the multipole data obtained by McPhedran and McKenzie[14] for a simple-cubic (sc) lattice of conducting inclusions. The comparison is shown in Table I. For the highest-volume fraction used ($\phi = 0.523$), where we note that simple cubic close packing is $\phi = \pi/6 \sim 0.523\,60$, the choices $a_c = 0.00008$ and $R_c - R = 0.000\,081$ give results accurate to about 5%. The accuracy is better for lower-volume fractions without the use of such small a_c and $R_c - R$ values.

The results of the random-walk method for the disordered configurations, generated by the Metropolis method, are shown in Fig. 2. Also on Fig. 2 are data gen-

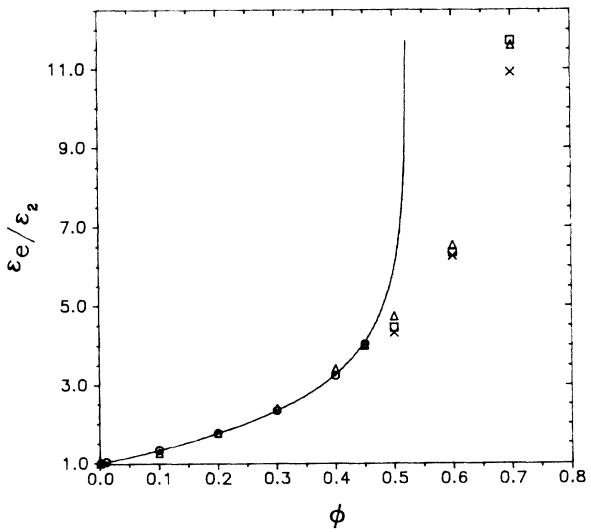

FIG. 2. ϵ_e/ϵ_2 vs inclusion volume fraction ϕ. The solid line is generated by the multipole method of Ref. 14 for the sc lattice. The Δ's (x's) are generated by the random-walk method for the Metropolis (randomized lattice) configurations. The open squares are generated by the random-walk method for the fcc lattice. The open circles are generated for the Metropolis configurations by the multipole-simulation method of Ref. 13.

TABLE I. A comparison between the multipole-method results of McPhedran and McKenzie and the random-walk-method results of the present work for the simple-cubic lattice.

ϕ	0.05	0.1	0.2	0.3	0.4	0.5	0.52	0.522	0.523
ϵ_e[a]	1.1	1.4	1.8	2.3	3.2	5.8	9.1	10.4	11.8
ϵ_e[b]	1.158	1.334	1.756	2.333	3.261	5.887	8.863	10.140	11.700

[a]Evaluated by random-walk method.
[b]Multipole-method data of Ref. 14.

erated by our recent multipolar simulations.[13] The multipolar simulations converge only up to $\phi=0.45$, and over this range of volume fractions the two methods are in good agreement. For higher-volume fractions, it is of interest to observe that the Metropolis configuration results are quite close to the face-centered-cubic lattice results of McPhedran and McKenzie. Note, however, that at volume fractions close to fcc closest packing, $\phi=0.74$, the Metropolis method does not give independent random configurations for the numbers of Monte Carlo steps we found practical to use. Thus, we also generated configurations by a method which provides better randomization; namely, the randomization of each inclusion within its Wigner-Seitz cell, as discussed above. To the accuracy of the random-walk method, these results are equivalent to those obtained for the fcc and Metropolis randomization configurations. At these very high-volume fractions, there is no way of providing extensive configuration randomization. The data at $\phi=0.5$ are of interest in that they suggest that the result for Metropolis configurations is higher than the fcc lattice result. This behavior is not expected, since random close packing occurs at $\phi\sim0.63$;[18] thus, $\epsilon_e(\phi)$ should be increasing faster with ϕ than $\epsilon_e(\phi)$ for the fcc lattice. Though, note that this conclusion is based on data which is at the limit of the accuracy of the random-walk method.

The developments presented here show that the random-walk method can be used at very high-volume fractions, even for the difficult insulator-in-conductor case. A further advantage of the method is that nonspherical geometries can also be simulated. When the two phases have arbitrary dielectric constants, the random-walk method can be carried out by random walks both inside and outside the inclusions,[4] though this will require substantially more computer time than that required for the conductor-in-insulator case. On the other hand, composites consisting of inclusions which are themselves composite are readily treated by the multipole-simulation method,[13] while these composites would be tedious to treat by the random-walk method. Finally, we note that there is as yet no random-walk method to discuss frequency-dependent dielectric properties, as is important for the prediction of optical properties of composites. These problems are readily addressed by the multipole methodology.[19]

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