PHYSICAL REVIEW E VOLUME 59, NUMBER 3 MARCH 1999

# Walker diffusion method for calculation of transport properties of composite materials

Clinton DeW. Van Siclen*
*Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho 83415*

(Received 5 August 1998)

The morphology of a multiphase microstructure greatly influences the macroscopic transport properties of the composite material. These properties are shown to be related to the diffusion coefficient of a random (nonbiased) walker. The proper diffusion rules are found by considering an isomorphic image of the microstructure in which distinct populations of walkers correspond to the phase domains, with the walker density of a population proportional to the transport coefficient of the corresponding domain. To demonstrate the method, it is applied to disordered two-phase percolating composites. [S1063-651X(99)14603-8]

PACS number(s): 05.60.−k, 44.30.+v, 91.60.Pn, 66.30.−h

A primary goal of materials physics is the discovery of relationships between the microstructure of a material and its macroscopic properties. Transport properties in particular are greatly influenced by the microstructure geometry, here considered to be the phase distribution and phase domain morphology. Classic examples of this dependence are the metal-insulator system, which cannot conduct unless the conducting phase percolates, and porous media, where the pore size and pore-space connectedness and tortuosity determine the electrical resistivity and fluid permeability of oil-bearing rock, and the efficacy of materials designed for catalysis or chemical separation.

Transport phenomena arise from the occurrence of two vector fields, say $\mathbf{E}(\mathbf{r})$ and $\mathbf{J}(\mathbf{r})$, that satisfy the set of equations

$$\nabla\times\mathbf{E}=0,\quad \nabla\cdot\mathbf{J}=0,\quad \mathbf{J}=\sigma(\mathbf{r})\mathbf{E},\quad \mathbf{E}=-\nabla\phi. \tag{1}$$

The quantity $\phi$ is a scalar potential, and $\sigma(\mathbf{r})$ is the local transport coefficient connecting the two local fields (and is a second-rank tensor in general). When $\mathbf{E}$ and $\mathbf{J}$ are the electric field and the current density, respectively, $\sigma$ is the electrical conductivity of the material. Other pairs of vector fields are connected by the dielectric constant $\epsilon$, the magnetic permeability $\mu$, the thermal conductivity $\kappa$, and the particle diffusion coefficient $D$.

The local transport coefficients collectively produce the measured transport coefficient which describes the transport property for the material as a whole. The macroscopic transport coefficients are not generally simple functions of the volume fractions of the phases present in the composite, but reflect the geometry of the microstructure as well.

Two general approaches to the calculation of macroscopic transport coefficients are found in the literature. In the first, effective values or bounds are obtained from a statistical description of the microstructure [1]; in the second, ‘‘exact’’ values are calculated for a model system isomorphic with the microstructure. The latter approach is usually accomplished by simply solving the set of equations (1) for a given applied field $\mathbf{E}$ at the system boundary (or potential difference across the system). The continuum medium is replaced by a network of discrete circuit elements corresponding to the $\sigma(\mathbf{r})$, and the potential $\phi_i$ at each node $i$ is found by solving a system of coupled algebraic equations, each of which is a discretized version of the equation,

$$\nabla\cdot[\sigma(\mathbf{r})\nabla\phi(\mathbf{r})]=0. \tag{2}$$

With the $\phi_i$ in hand, the field $J_i$ at each node is easily calculated from the discretized version of the equation,

$$\mathbf{J}(\mathbf{r})=-\sigma(\mathbf{r})\nabla\phi(\mathbf{r}). \tag{3}$$

The macroscopic transport coefficient $\sigma$ is then obtained from the relation $\langle\mathbf{J}\rangle=\sigma\mathbf{E}$.

A rather different method for calculating exact values of transport coefficients is inspired by the Einstein relation $\sigma \propto D$ between the conductivity $\sigma$ of a material and the diffusion coefficient $D$ of the mobile electric charges. Schwartz and Banavar [2] obtained the conductivity of a conducting pore-insulating grain system by measuring the displacement over time of a walker diffusing randomly through the pore space while obeying ‘‘blind ant’’ boundary conditions at the pore-grain interface. The ratio of the diffusion coefficients for the walker in the pore space and the walker in a purely conducting system, multiplied by the volume fraction of pore space, then equals the ratio of the conductivities for the pore-grain and pure conductor systems. Bunde *et al.* [3] and Hong *et al.* [4] calculated the composite conductivity of random, two-phase conducting systems by having the walker diffuse randomly within each phase with diffusion coefficient proportional to the conductivity of that phase. They made the *ansatz* that an attempted move across a domain boundary from phase $i$ to phase $j$ is accomplished with probability $D_j/(D_i+D_j)=\sigma_j/(\sigma_i+\sigma_j)$. The walker diffusion coefficient $D$, which is proportional to the composite conductivity, is then found from the walker displacement over a time that equals the sum of time spent by the walker in each phase. This model for multi-phase systems was also used by Tobochnik, Laing, and Wilson [5] and Kim and Torquato [6], who adapted the first-passage-time method to minimize the computer time required to track a walker diffusing within a large phase domain.

The present work also obtains the macroscopic transport coefficients via a diffusing walker, but does not use the Einstein relation and so avoids the *ansatz* mentioned above.

---

*Electronic address: cvs@inel.gov

While the method is developed here for discrete systems (or digitized microstructures), it is applicable to continuum systems as well.

Consider a collection of noninteracting random walkers. When a driving force $-\nabla\phi(\mathbf{r})$ is imposed, a diffusion current density $\mathbf{J}(\mathbf{r})$ is created, where

$$\mathbf{J}(\mathbf{r})=-D(\mathbf{r})\rho(\mathbf{r})\nabla\phi(\mathbf{r}) \tag{4}$$

and $D(\mathbf{r})$ and $\rho(\mathbf{r})$ are the local walker diffusion coefficient and local walker density, respectively. As this diffusion equation resembles the transport equation (3), the product $D(\mathbf{r})\ \rho(\mathbf{r})$ is identified with the local transport coefficient $\sigma(\mathbf{r})$. More specifically, $D(\mathbf{r})\rho^0(\mathbf{r})\equiv\sigma(\mathbf{r})$, where $\rho^0(\mathbf{r})$ is the (local) equilibrium walker density in the absence of a driving force.

Thus a connection is made between a composite comprised of phase domains, each characterized by a transport coefficient value, and an isomorphic configuration of walker ''domains'' or populations, each characterized by values for equilibrium walker density and walker diffusion coefficient. In analogy with the local relation above, the macroscopic transport coefficient $\sigma$ equals the product of the average walker population $\langle\rho^0(\mathbf{r})\rangle$ of the isomorph and the diffusion coefficient $D$ of a walker moving through the isomorph.

To maintain the equilibrium populations, the diffusing walker must obey the principle of detailed balance. This requires that the walker at site $i$ attempt a move in a randomly chosen direction, and that the move to adjacent site $j$ be successful with probability $p_{ij}=\rho_j^0/(\rho_i^0+\rho_j^0)$. For the walker diffusing within a domain, $p_{ij}=1/2$, so that the time $\tau_i$ associated with a move attempt is given by the relation

$$D_i=\frac{1}{2d}\frac{\lambda^2}{2\tau_i}, \tag{5}$$

where $D_i$ is the diffusion coefficient for the walker within the domain, $d$ is the dimension of the space, and $\lambda$ is the site width (or pixel size).

In order that the walker *trajectory* fully reflect the microstructure geometry, the local diffusion coefficient $D(\mathbf{r})$ is everywhere set equal to 1 [7]. Thus the walker at a site $i$ attempts a move to a randomly chosen adjacent site $j$ during the time interval $\tau=(4d)^{-1}$ ($\lambda=1$ for convenience); that move is successful with probability $p_{ij}=\sigma_j/(\sigma_i+\sigma_j)$. The walker diffusion coefficient $D$ is then calculated from the total displacement of the walker over the time corresponding to the number of attempted moves. The macroscopic transport coefficient $\sigma=\langle\sigma(\mathbf{r})\rangle D$, showing that the geometric aspects of the microstructure are completely accounted for in the parameter $D$. [But $D$ is also a functional of the local values $\sigma(\mathbf{r})$ and so must be recalculated when those change even when the geometry does not. The exception to this is a simple scaling of all $\sigma(\mathbf{r})$ with no change in the geometry, which does not affect $D$.]

For a percolating conductor-insulator system, the principle of detailed balance is equivalent to the blind ant boundary condition. That this is the correct boundary condition (rather than the ''myopic ant'') is evident by considering the conductivities of thin (one-dimensional) and thick (three-dimensional) straight conducting wires encased in insulation. The diffusion coefficient $D$ of a walker in the thick wire is unchanged when the walker trajectory is projected onto a one-dimensional space, and equals the diffusion coefficient for the walker in the thin wire when the conductivities of the two wires are equal. Thus the excursions of the walker in the thick wire transverse to the wire axis correspond to attempts by the blind walker in the thin wire to enter the insulator.

The conductivity $\sigma$ of a conductor-insulator system is given by $\sigma/\sigma_C=\phi_C D=\phi_C' D'$, where $\sigma_C$ is the conductivity of the conducting phase, $\phi_C$ and $\phi_C'$ are the volume fractions of the conducting phase and the percolating conductor clusters (comprised of contiguous conducting sites), respectively, and $D'$ is the diffusion coefficient for walker diffusion on a percolating cluster. This same relation holds for a system containing an infinite superconducting cluster. Systems comprised of separated, superconducting domains embedded in an ordinary conductor, however, are problematic, as those domains absorb the walkers.

Perhaps surprisingly, this walker diffusion method based on walker populations gives results identical to those obtained by the method mentioned above that relies on an *ansatz* for moving a walker across a phase boundary. This follows from the fact that, for a given system and starting point, walkers in the two cases make identical trajectories over $N$ attempted moves. For a total walker displacement of $R$ in a two-phase system, the latter method gives

$$\sigma=D=\frac{1}{2d}\frac{R^2}{[n\tau_A+(N-n)\tau_B]}, \tag{6}$$

where $n$ is the number of attempted moves from a site with conductivity $\sigma_A$, and $\tau_A=(4d\sigma_A)^{-1}$ and $\tau_B=(4d\sigma_B)^{-1}$ are the time increments associated with an attempted move from sites with conductivity $\sigma_A$ and $\sigma_B$, respectively; while the former method gives

$$\sigma=\langle\sigma(\mathbf{r})\rangle D=\langle\sigma(\mathbf{r})\rangle\frac{1}{2d}\frac{R^2}{N\tau} \tag{7}$$

with $\tau=(4d)^{-1}$. The quantities $n$ and $N-n$ in Eq. (6) are proportional to the walker populations of the two phases such that $n/N=\phi_A\rho_A^0\langle\rho^0(\mathbf{r})\rangle^{-1}$ and $(N-n)/N=\phi_B\rho_B^0\langle\rho^0(\mathbf{r})\rangle^{-1}$, where $\phi_A$ and $\phi_B$ are the volume fractions of phases $A$ and $B$, respectively. Use of these ratios and the relations $\rho_A^0=\sigma_A$, $\rho_B^0=\sigma_B$, and $\langle\rho^0(\mathbf{r})\rangle=\langle\sigma(\mathbf{r})\rangle$ then converts Eq. (6) into Eq. (7).

Both terms in the denominator of Eq. (6) contribute even when one phase is an insulator; failure to recognize this will result in a value for $\sigma$ too large by a factor $\phi_C^{-1}$, where $\phi_C$ is the volume fraction of the conducting phase.

The diffusion procedure described above is computationally inefficient since not all attempted moves by the walker are successful. This is overcome by statistically weighing the behavior of the walker such that every attempt is successful but the move is accomplished over a variable time interval.

On average, an attempted move by the walker at site $i$ is successful with probability

$$\pi_i=\frac{1}{2d}\sum_{k=1}^{2d}p_{ik}, \tag{8}$$

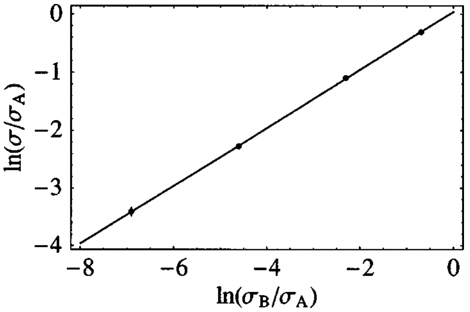

FIG. 1. Calculated values of the conductivity ratio $\sigma/\sigma_A$ of two-dimensional, two-phase random composites, where phase $A$ has volume fraction $\phi_A = p_c$ and conductivity $\sigma_A$, and phase $B$ has volume fraction $\sigma_B = (1-p_c)$ and conductivity $\sigma_B$. The four data points are taken for $\sigma_B/\sigma_A = 0.5$, 0.1, 0.01, and 0.001.

where the summation is over all adjacent sites. Then the time interval $T_i$ associated with a successful move is, on average, $\tau/\pi_i$. That successful move is made to site $j$ (rather than another adjacent site) with probability $P_{ij} = p_{ij}/(2d\pi_i)$. Thus the actual behavior of the walker is well approximated by a sequence of moves in which the direction of each move from a site $i$ is determined randomly by the set of probabilities $\{P_{ij}\}$, where

$$P_{ij} = \left(\frac{\sigma_j}{\sigma_i + \sigma_j}\right)\left[\sum_{k=1}^{2d}\left(\frac{\sigma_k}{\sigma_i + \sigma_k}\right)\right]^{-1}, \tag{9}$$

and the time interval over which the move occurs is

$$T_i = \left[2\sum_{k=1}^{2d}\left(\frac{\sigma_k}{\sigma_i + \sigma_k}\right)\right]^{-1}. \tag{10}$$

This variable residence time algorithm was used to obtain the analytical result $\sigma = \langle \sigma(\mathbf{r})^{-1}\rangle^{-1}$ for various one-dimensional composites. It was also used to calculate the conductivity of two-dimensional, two-phase random composites at the percolation threshold $p_c$ of the higher-conductivity phase, where Straley [8] has predicted that $\sigma/\sigma_A \propto (\sigma_B/\sigma_A)^{1/2}$. These numerical results are presented in Fig. 1 along with a ‘‘best fit’’ straight line having slope 0.5005 ± 0.0025 to compare with Straley’s critical exponent of $\frac{1}{2}$.

Each data point in Fig. 1 is obtained from the average value of $\sigma/\sigma_A$ calculated for fifteen different 200×200-site (periodically continued) random configurations having $\phi_A = p_c = 0.592\,75$. The length of the error bar superposed on each point is two standard deviations (only one error bar is not obscured by the plotted points, however). The walker diffusion coefficient $D$ for a single configuration was calculated by fitting $5\times10^4$ walker displacements $r$ to a Gaussian distribution [so $r$ is plotted against $2\pi r p(r,t)$, where $p$ is the Gaussian distribution function], where each displacement was determined after a time interval $t = 10^5$ (this corresponds to the time required for the walker to make 10×200×200 moves in a single-phase system). In every case the fit was extremely good. It is believed that this fitting procedure yields a more accurate value for $D$ than is given by the expression $D = \langle r^2\rangle/(2dt)$, particularly when the number of measurements is limited.

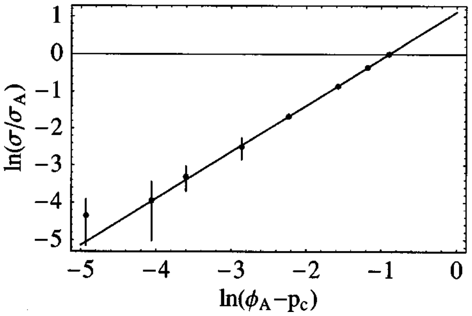

FIG. 2. Calculated values of the conductivity ratio $\sigma/\sigma_A$ of two-dimensional, random conductor-insulator systems, where the conducting phase has conductivity $\sigma_A$ and volume fraction $\phi_A$. The eight data points are taken for $\phi_A = 1.0$, 0.9, 0.8, 0.7, 0.65, 0.62, 0.61, and 0.60.

It is interesting that the $y$ intercept of the straight line in Fig. 1 is 0.0427 ± 0.0107 rather than zero. Calculations with $\sigma_B = \sigma_A$ gave $\sigma/\sigma_A = 0.9999 \pm 0.0015$, suggesting that the computational procedure is not systematically overestimating the conductivity ratio. Perhaps the discrepancy is due to the tendency of the walker to prefer the higher-conductivity regions that are inevitable in imperfectly random configurations. Van Siclen [9] has shown that such composition fluctuations are present over a large range of length scales for computer-generated, nominally random configurations.

The variable residence time algorithm was also used to calculate the conductivity of two-dimensional, random conductor-insulator systems, where the volume fraction $\phi_A$ of the conducting phase was varied from unity to near the percolation threshold. These results are presented in Fig. 2 along with a ‘‘best fit’’ straight line having slope $\mu = 1.2534 \pm 0.0053$ and $y$ intercept 1.1214 ± 0.0083. This fit (to the four rightmost points) is consistent with the relation

$$\frac{\sigma}{\sigma_A} = \left(\frac{\phi_A - p_c}{1 - p_c}\right)^{\mu} \tag{11}$$

with the critical exponent $\mu$ in good agreement with the value 1.28 ± 0.05 found experimentally by Watson and Leath [10].

Each data point in Fig. 2 is obtained from the average value of $\sigma/\sigma_A$ calculated for thirty different 200×200-site (periodically continued) random configurations having a fixed value of $\phi_A$ above the percolation threshold. For each configuration, the walker is initially placed at a randomly selected conducting site (not necessarily on a percolating cluster) since all conducting sites have equal walker densities $\rho^0$. Thus the length of the error bar (two standard deviations) superposed on each point reflects the size distribution of conducting clusters (to one of which the walker is confined) for random systems with conductor volume fraction $\phi_A$. In particular, the error bars are large for $\phi_A$ near $p_c$ since there is a broad size distribution of conducting clusters on which the walker may be randomly placed and consequently a broad range of possible values for the walker diffusion coefficient $D$; in fact, the average values for $\sigma/\sigma_A$ incorporate values $\sigma \propto D = 0$ obtained when the walker is placed on an isolated conducting site. However, the calculated values for $D$ near

$p_c$ are questionable in any case since walker diffusion is anomalous on such fractal-like clusters [11].

Alternatively the points in Fig. 2 could be obtained by confining the walker to a percolating cluster. Then $\sigma/\sigma_A = \phi'_A D'$, where $\phi'_A$ is the volume fraction of percolating clusters and $D'$ is the diffusion coefficient of the walker on a percolating cluster. This relation reflects the fact that the average diffusion coefficient for those walkers at conducting sites not belonging to a percolating cluster goes to zero as the measurement time interval $t$ goes to infinity. But $D'$ simultaneously increases and so must be calculated for large $t$.

A ''random medium'' approximation (RMA) for transport coefficients of disordered composites may be derived from the variable residence time algorithm. The probability $P_m$ that the walker is found at a site of phase $m$ is proportional to the equilibrium walker population corresponding to that phase, so that

$$P_m = \rho_m^0 \phi_m \left[ \sum_{n=1}^{N} \rho_n^0 \phi_n \right]^{-1} = \sigma_m \phi_m \langle \sigma(\mathbf{r}) \rangle^{-1}, \qquad (12)$$

where $N$ is the number of different phases present in the composite. (In this and the following expressions, the subscripts refer to the phase to which the site belongs rather than to the unique identification of the site.) From Eq. (10), the time interval over which the walker at a site of phase $m$ moves to an adjacent site is, on average,

$$T_m = \left[ 4d \sum_{n=1}^{N} \phi_n \left( \frac{\sigma_n}{\sigma_m + \sigma_n} \right) \right]^{-1} = \left[ 4d \left\langle \frac{\sigma_n}{\sigma_m + \sigma_n} \right\rangle_n \right]^{-1}. \qquad (13)$$

Thus the time interval over which an arbitrary move occurs in a random system is

$$T = \sum_{m=1}^{N} P_m T_m \qquad (14)$$

and the transport coefficient $\sigma = \langle \sigma(\mathbf{r}) \rangle D = \langle \sigma(\mathbf{r}) \rangle (2dT)^{-1}$.

Like effective-medium approximations, this expression is less accurate as the conductivities of the phases diverge and as the percolation threshold of a high-conductivity phase is approached. This is because the derivation does not take into account the correlation between subsequent moves by the diffusing walker; indeed, if the walker environment were ''rerandomized'' after every move, the RMA would be exact.

For a two-phase disordered composite, the RMA gives

$$\sigma = \langle \sigma(\mathbf{r}) \rangle^2 \left[ \frac{\sigma_A \phi_A}{\phi_A + \left( \frac{2\sigma_B}{\sigma_A + \sigma_B} \right) \phi_B} + \frac{\sigma_B \phi_B}{\left( \frac{2\sigma_A}{\sigma_A + \sigma_B} \right) \phi_A + \phi_B} \right]^{-1}. \qquad (15)$$

When $\sigma_B = 0$ as in a conductor-insulator system, Eq. (15) reduces to $\sigma/\sigma_A = \phi_A^2$, which resembles Archie's Law [12] with a cementation index of 2.

By relating phase domains to walker populations, the walker diffusion method provides a way to calculate the transport properties of composite materials. The computational efficiency of the method is enhanced by the variable residence time algorithm. Some results from percolation theory have been reproduced to verify the method and algorithm. The walker diffusion method may be applied to continuum, anisotropic, and higher-dimensional systems as well as to discrete systems such as digitized microstructures. It is the only viable method for determining transport properties of complex systems such as fractals, and is the best ''exact'' method to use to evaluate the results from statistical methods of calculating transport coefficients.

This work was supported in part by the U.S. Department of Energy, Office of Environmental Management, under U.S. DOE Idaho Operations Office Contract No. DE-AC07-94ID13223.

---

[1] A variety of methods are presented by E. H. Kerner, Proc. Phys. Soc. London, Sect. B **69**, 802 (1956); L. M. Schwartz, Physica A **207**, 131 (1994); J. M. V. A. Koelman and A. de Kuijper, *ibid.* **247**, 10 (1997); R. Hilfer, Phys. Rev. B **44**, 60 (1991); Physica A **194**, 406 (1993); S. Torquato, J. Stat. Phys. **45**, 843 (1986); Appl. Mech. Rev. **44**, 37 (1991); **47**, S29 (1994).

[2] L. M. Schwartz and J. R. Banavar, Physica A **157**, 230 (1989); Phys. Rev. B **39**, 11 965 (1989).

[3] A. Bunde, A. Coniglio, D. C. Hong, and H. E. Stanley, J. Phys. A **18**, L137 (1985).

[4] D. C. Hong, H. E. Stanley, A. Coniglio, and A. Bunde, Phys. Rev. B **33**, 4564 (1986).

[5] J. Tobochnik, D. Laing, and G. Wilson, Phys. Rev. A **41**, 3052 (1990).

[6] I. C. Kim and S. Torquato, J. Appl. Phys. **68**, 3892 (1990); **69**, 2280 (1991).

[7] Any other choice is not viable. For example, setting $\rho^0(\mathbf{r}) = 1$ everywhere and $D(\mathbf{r}) = \sigma(\mathbf{r})$ gives $\sigma = D = \langle \sigma(\mathbf{r})^{-1} \rangle^{-1}$.

[8] J. P. Straley, Phys. Rev. B **15**, 5733 (1977).

[9] C. DeW. Van Siclen, Phys. Rev. E **56**, 5211 (1997).

[10] See Ref. [8] in B. P. Watson and P. L. Leath, Phys. Rev. B **9**, 4893 (1974).

[11] C.-W. Nan, Prog. Mater. Sci. **37**, 1 (1993).

[12] R. Hilfer, Adv. Chem. Phys. **XCII**, 299 (1996).