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Anomalous walker diffusion through composite systems

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Abstract. Diffusion of a non-biased walker through a composite (multi-phase) system is shown to be anomalous for length scales less than the correlation length ξ (i.e., when the path length is measured with a ruler of length less than ξ) and Gaussian for length scales greater than ξ. The values of ξ and the fractal dimension d_w of the walker path in the anomalous regime reflect the phase properties and phase domain morphology of the composite. They are related to the diffusion coefficient D_w for walker diffusion in the Gaussian regime by $D_w \propto \xi^{2-d_w}$, and to the macroscopic transport coefficient σ through the relation $\sigma \propto D_w$. The correlation length ξ thus gives the size above which the composite is effectively homogeneous *with respect to the transport property of interest*. Walker behaviour is compared for disordered (random), particulate–matrix, and labyrinthine two-phase microstructures.

1. Introduction

The transport properties of a material reflect the composition and morphology of the microstructure†. An additional parameter is the correlation length ξ, which sets the length scale above which the transport property is independent of sample size or volume over which the property is measured. As ξ is itself a complex function of the material composition and morphology, it gives the size at which the material is effectively homogeneous *with respect to the property of interest*, and cannot be determined by visual inspection of the microstructure.

The value ξ may be determined experimentally by measuring the transport coefficient over progressively smaller volumes; for example, the electrical conductivity or resistivity of a material changes from its constant, macroscopic value when the applied a.c. frequency corresponds to the correlation length [2]. For a computer-generated or digitized microstructure, ξ may *only* be found by application of the 'walker diffusion method' [3] in which a random walker, subject to appropriate rules, diffuses through the composite material. This is demonstrated below for two-dimensional composites with disordered (random), particulate–matrix, and labyrinthine two-phase microstructures, respectively. The walker diffusion is shown to be 'anomalous' for length scales less than ξ (i.e., the fractal dimension d_w of the walker path is greater than two) and Gaussian ($d_w = 2$) for length scales greater than ξ, thus permitting easy identification of the correlation length as the transition between the two diffusion regimes.

As mentioned above, accurate measurement of transport properties requires that the linear dimension of the sample exceed ξ. A corollary to this is that the sample does not possess a characteristic length scale less than ξ (this statement will be qualified later); thus the

† For reviews on various aspects of this subject see [1].

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corresponding macroscopic transport property must be a power-law function of ξ, where the exponent is determined by the behaviour of the random walker in the anomalous regime. While this is in some sense a trivial statement, it suggests that expressions for related macroscopic properties can be similarly derived as power-law functions of ξ, with different exponents that appropriately describe the system at the length scales of the anomalous regime.

The work presented here relies on the walker diffusion method [3] of calculation of effective transport coefficients (these include the electrical conductivity σ, thermal conductivity κ, diffusion coefficient D, magnetic permeability μ, etc, although the symbol σ will be used exclusively for convenience). This method exploits the isomorphism between the transport equations and the diffusion equation for a collection of non-interacting walkers (hence the name). The phase domains in a composite microstructure correspond to distinct populations of walkers, where the walker density of a population is given by the value of the transport coefficient of the corresponding phase domain. The principle of detailed balance ensures that the population densities are maintained, and provides the following rule for walker diffusion over a digitized microstructure: a walker at site (or pixel) i attempts a move to a randomly chosen adjacent site j during the time interval $\tau = (4d)^{-1}$, where d is the Euclidean dimension of the space; this move is successful with probability $p_{ij} = \sigma_j/(\sigma_i + \sigma_j)$, where σ_i and σ_j are the transport coefficients for the phases comprising sites i and j, respectively. The path of a walker thus reflects the composition (population density) and morphology of the domains that are encountered, and may be described by a diffusion coefficient D_w that is related to the macroscopic transport coefficient σ by

$$\sigma = \langle \sigma(\boldsymbol{r}) \rangle D_w \tag{1}$$

where $\langle \sigma(\boldsymbol{r}) \rangle$ is the volume average of the constituent transport coefficients. The diffusion coefficient D_w is calculated from the equation

$$D_w = \langle R^2 \rangle / (2dt) \tag{2}$$

where the set $\{R\}$ of walker displacements, each occurring over the time interval t, comprises a Gaussian distribution that must necessarily be centred well beyond ξ.

2. Anomalous walker diffusion

For displacements $R < \xi$, the walker diffusion is anomalous rather than Gaussian due to the heterogeneity of the microstructure at length scales less than ξ (note that the specimen or periodic length L replaces ξ here and in the work that follows when $L < \xi$). There is, however, an additional characteristic length $\xi_0 < \xi$ below which the microstructure is again effectively homogeneous; this may correspond, for example, to the average phase domain size. A walker displacement of ξ requiring a travel time $t_\xi = \xi^2/(2dD_w)$ is then comprised of $(\xi/\xi_0)^{d_w}$ segments of length ξ_0, each requiring a travel time of $t_0 = \xi_0^2/(2dD_0)$, where D_0 is the walker diffusion coefficient calculated from displacements $R < \xi_0$. Setting

$$t_\xi = (\xi/\xi_0)^{d_w} t_0 \tag{3}$$

gives the relation

$$D_w = D_0(\xi/\xi_0)^{2-d_w} \tag{4}$$

between the walker diffusion coefficient D_w and the correlation length ξ. This equation has been derived previously in the context of percolation theory [4] and for conducting pore–insulating matrix systems [5], where d_w is then the fractal dimension of the walker path on a percolating cluster near the percolation threshold, and through a system of connected pores comprising a fractal structure, respectively. (The assumption is made that the trajectory of a

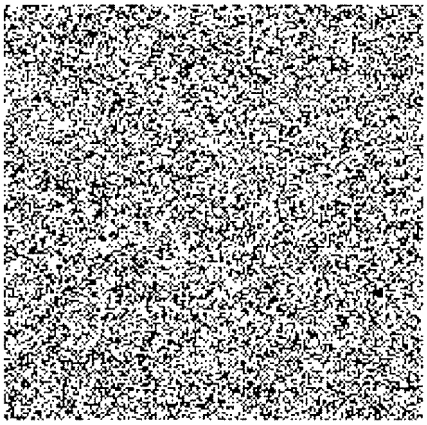

Figure 1. Disordered (random) two-phase composite (size 200×200). The white phase A has volume fraction equal to the percolation threshold p_c. For an infinite system, the correlation length ξ goes to infinity as the conductivity of the black phase B goes to zero.

walker confined to a fractal structure will itself be fractal. This is certainly so in the former case (a disordered conductor–insulator system near the percolation threshold) [6], and has been demonstrated indirectly [7, 8] for self-similar models made up of the Sierpiński gasket and its generalizations to all Euclidean dimensions.) Equations (1) and (4) together show that all transport properties of a heterogeneous material have a power-law dependence on the correlation length, reflecting the absence of a natural length scale between ξ_0 and ξ. Like ξ, the exponent d_w is a complex function of the material composition and morphology. Because D_w is a functional of the ratios σ_i/σ_j of the constituent phase property values, the dependence of ξ and d_w on the phase properties is expected to likewise take the form of ratios.

The dimension d_w of a walker path that is fractal over length scales $\xi_0 < R < \xi$ may be determined from the generalization of equation (3),

$$t_R = (\langle R^2 \rangle / \xi_0^2)^{d_w/2} t_0. \tag{5}$$

Composites, however, do not in general give rise to walker trajectories that can be characterized by a single fractal dimension, whereupon d_w in equation (5) must be replaced by the length-scale dependent dimension $d_w(R)$. In any case, $d_w = 2$ for $R > \xi$, which allows an unambiguous graphical determination of the correlation length.

The heterogeneity of the microstructure is indicated as well by the irregular shape of the growing cluster comprised of all sites visited by a diffusing walker. At time t the cluster contains $S(t)$ sites and has a radius of roughly $\langle R(t)^2 \rangle^{1/2}$. The cluster size $S(t)$ is assumed to scale with radius as $\langle R(t)^2 \rangle^{D_s/2}$, where D_s is the dynamic mass fractal dimension of the cluster. The time dependence of $S(t)$ is made explicit by using equation (5) to obtain

$$S(t) \propto t^{D_s/d_w} = t^{d_s/2} \tag{6}$$

where the spectral (or fracton) dimension $d_s = 2D_s/d_w$ [8, 9]. The values D_s and d_s are expected to change at the crossover time t_ξ given by equation (3), as the cluster radius is then approximately ξ.

3. Application to disordered composites

An analytic expression for ξ may be found for the special case of a two-dimensional, two-phase disordered (random) composite at the percolation threshold $p_c = 0.592\,75$ of the higher conductivity phase. This composite has electrical conductivity $\sigma = (\sigma_A \sigma_B)^{1/2}$, where σ_A and

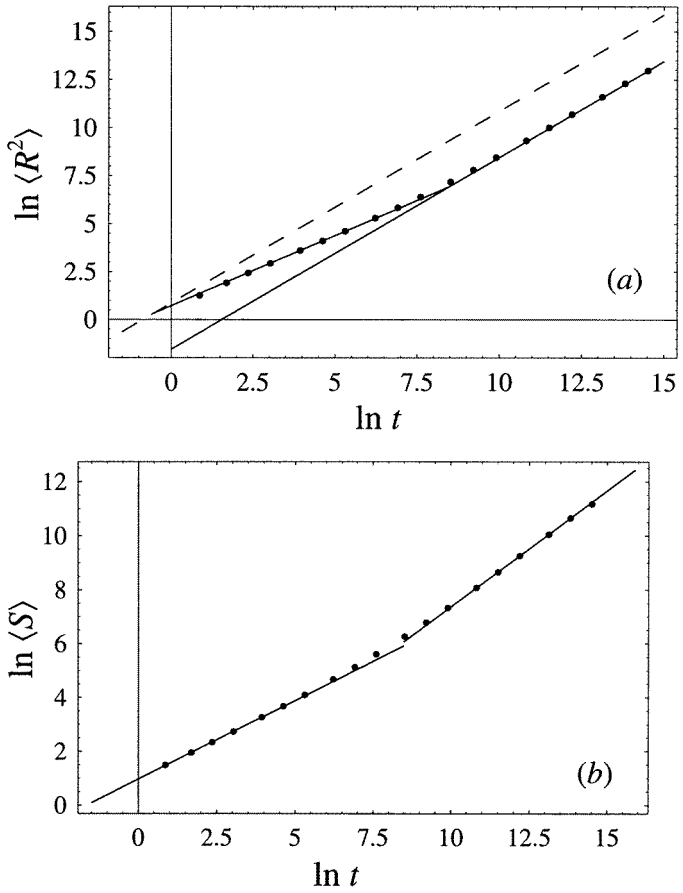

Figure 2. Average values for (*a*) walker displacement-squared $R(t)^2$ and (*b*) number $S(t)$ of visited sites for walks over the indicated time intervals t through disordered, two-phase composites (as shown in figure 1) with phase conductivity ratio $\sigma_B/\sigma_A = 10^{-3}$. The bend in the sequence of data points occurs at the crossover time t_ξ separating the anomalous (walker path dimension $d_w > 2$) and Gaussian ($d_w = 2$) regimes, and so locates the correlation length ξ in (*a*) and the critical cluster size in (*b*) where the dynamic mass fractal dimension D_s of the cluster of visited sites changes. The solid lines are fits to the data points in each regime; the dashed line in (*a*) indicates the walker behaviour under the random medium approximation.

σ_B are the conductivities of the majority and minority phases, respectively [10]. Substitution of this relation and equation (4) into equation (1) gives

$$\xi = \xi_0 \left[\frac{(\sigma_A \sigma_B)^{1/2}}{D_0[\sigma_A p_c + \sigma_B(1 - p_c)]} \right]^{1/(2-d_w)} . \tag{7}$$

Figure 1 shows a computer-generated representation of such a binary composite, where the black sites (pixels) are of the minority phase B. Figure 2 presents values for (*a*) $\langle R(t)^2 \rangle$ and (*b*) $\langle S(t) \rangle$ calculated by the walker diffusion method (and using the variable residence time algorithm [3]) for 500 × 500-site periodic composites with the ratio $\sigma_B/\sigma_A = 10^{-3}$. The average values $\langle R(t)^2 \rangle$ and $\langle S(t) \rangle$ are determined from 12 different, randomly generated composites; those 12 values each of $R(t)^2$ and $S(t)$ are themselves average values found from 10^5 walks, each of duration t, over a single composite. In every case the error bar of two

Table 1. The walker path dimension d_w, spectral dimension d_s, dynamic mass fractal dimension D_s, correlation length ξ, walker diffusion coefficient D_w, and conductivity σ of two-dimensional, two-phase disordered composites with volume fraction of the majority phase A at the percolation threshold and phase conductivity ratio σ_B/σ_A.

	Anomalous regime ($d_w > 2$)				Gaussian regime ($d_w = 2$)		
σ_B/σ_A	d_w	d_s	D_s	ξ	$d_s = D_s$	D_w	σ/σ_A
1	—	—	—	—	1.80	1.0000	1.0000
0.01	2.42	1.23	1.49	15	1.77	0.1676	0.1000
0.001	2.73	1.17	1.59	32	1.72	0.0533	0.0316
0.0001	2.85	1.16	1.65	93	1.59	0.0169	0.0100

standard deviations is obscured by the plotted point.

The correlation length ξ and crossover time t_ξ distinguishing the anomalous and Gaussian regimes are easily identified by the bend in the array of data points. The linear least-squares fit to the $\langle R(t)^2 \rangle$ points lying within the anomalous regime gives $d_w = 2.73$ (slope $= 2/d_w$); substitution of this and values for ξ_0 ($\ln \xi_0^2$ is taken to be the y-intercept of the fit) and D_0 (taken to be $\xi_0^2/4$) into equation (7) gives $\xi = 32$, in excellent agreement with a visual estimate of ξ. The linear least-squares fit to the $\langle R(t)^2 \rangle$ points lying within the Gaussian regime gives $d_w = 2$ (slope $= 1$) as expected, and y-intercept equal to $\ln(4D_w)$. The parallel dashed line has y-intercept equal to $\ln(4D_{\mathrm{RMA}})$, where D_{RMA} is the random medium approximation (RMA) [3] value for the walker diffusion coefficient. The RMA does not account for correlations between subsequent moves and so is exact only in the limit $t \to 0$. Clearly, the anomalous walker behaviour shown in figure 2(*a*) is inevitable for disordered composites (including conductor–insulator systems), simply because D_w will always differ from D_{RMA}.

Figure 2(*b*) shows the power-law growth of $S(t)$ with spectral dimension d_s (slope $= d_s/2$) that changes gradually near the crossover time t_ξ. For very large t, the number $S(t)$ of visited sites is limited by the size of the system, which is indicated in figure 2(*b*) by the extent of the best-fit line in the Gaussian regime (note that the last data point is affected by this limit).

The calculated values of ξ, the dimensions d_w, d_s, and D_s in the anomalous and Gaussian regimes, D_w, and σ are presented in table 1 together with values for disordered composites with $\sigma_B/\sigma_A = 1$, 10^{-2}, and 10^{-4}. Of primary interest is the *progression* of values as σ_B/σ_A decreases rather than the numbers themselves, since the latter (excepting those for D_w and σ) derive from slopes determined by linear least-squares fits to collections of data points that judiciously (i.e., subjectively) exclude those at very short times and at times around t_ξ.

Similar calculations were made for systems with $L < \xi$. As expected, the dimensions d_w, d_s, and D_s describing the walker behaviour in the anomalous regime did not change, while D_w and σ increased (the best-fit line to the Gaussian data in figure 2(*a*) moved upwards in accordance with equation (4)).

An analytic expression for ξ may also be found for the special case of a disordered (random) conductor–insulator system ($\sigma_B/\sigma_A = 0$). Here all quantities are derived from walker diffusion restricted to an infinite conducting cluster (note that equation (4) is not otherwise correct). Equation (1) may be written $\sigma = \sigma_A \phi'_A D_w$, where ϕ'_A is the volume fraction of sites belonging to the infinite cluster. Combining this with equation (4) and the relation [3, 11]

$$\frac{\sigma}{\sigma_A} = \left(\frac{\phi_A - p_c}{1 - p_c} \right)^{\mu} \tag{8}$$

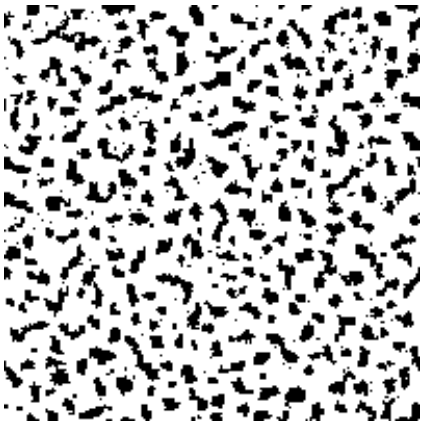

Figure 3. Two-phase composite with a particulate–matrix microstructure (size 200 × 200). The black phase B has volume fraction 0.25.

where $\phi_A > p_c$ is the volume fraction of conductor phase, produces

$$\xi = \xi_0 \left[\frac{1}{D_0 \phi'_A} \left(\frac{\phi_A - p_c}{1 - p_c} \right)^{\mu} \right]^{1/(2-d_w)} . \tag{9}$$

Near the percolation threshold, $\phi'_A \sim (\phi_A - p_c)^{\beta}$, so $\xi \sim (\phi_A - p_c)^{-\nu}$ with $\nu = (\mu - \beta)/(d_w - 2)$ as expected [6]. Equation (9) was verified by calculations similar to those described above. Due to the strong correlation between subsequent walker moves, approximate analytic values for ξ_0 and D_0 may be used in equation (9). For two-dimensional systems, these are $\xi_0 = 1$ and $D_0 = (4t_0)^{-1}$, where the time $t_0 = (1-\phi_A)^3 + 3\phi_A(1-\phi_A)^2/2 + \phi_A^2(1-\phi_A) + \phi_A^3/4$ is obtained by considering the first move of a walker placed randomly on an infinite cluster.

4. Application to particulate–matrix and labyrinthine composites

More generally, composites are comprised of phase domains arranged in a distinct microstructure. A typical morphology is shown in figure 3, where second-phase particles are embedded in a host matrix. Figure 4 presents values for (*a*) $\langle (R(t)^2 \rangle$ and (*b*) $\langle S(t) \rangle$ for this two-dimensional (200 × 200-site periodic) composite with $\sigma_B/\sigma_A = 10^3$. Each data point is the average of 12 values, where each of those 12 values is in turn the average $R(t)^2$ or $S(t)$ produced by 10^5 walks, each of duration t. In every case the error bar of two standard deviations is obscured by the plotted point. As found for the disordered composites above, the anomalous and Gaussian regimes are readily distinguished; the correlation length ξ and crossover time t_ξ are identified in figure 4(*a*) by the intersection of the sequence of data points with the solid line fit to those points lying in the Gaussian regime. The dashed line in figure 4(*a*) with a slope of 1 and y-intercept equal to ln 4 would be produced by a walker diffusing through a single-phase system ($D_w = 1$), and so gives the limiting behaviour at $t \to 0$ for the particulate–matrix system. An anomalous diffusion regime terminating at the correlation length ξ is therefore inevitable. The odd hump in the data in figure 4(*b*) may be due to 'capture' of the walker by the higher conductivity particles (phase B), as the corresponding value of $\langle S(t) \rangle$ is roughly the size of a typical particle. The two ends of the best-fit line derived from the data points in the Gaussian time regime indicate the crossover time t_ξ and the size of the system, respectively.

The labyrinthine two-phase morphology shown in figure 5 is also typical of real microstructures. Figure 6 presents values for (*a*) $\langle R(t)^2 \rangle$ and (*b*) $\langle S(t) \rangle$ for this two-dimensional (200 × 200-site periodic) composite with $\sigma_B/\sigma_A = 10^{-3}$, obtained in the same manner as for the particulate–matrix system. Again, the correlation length ξ and crossover time t_ξ separating

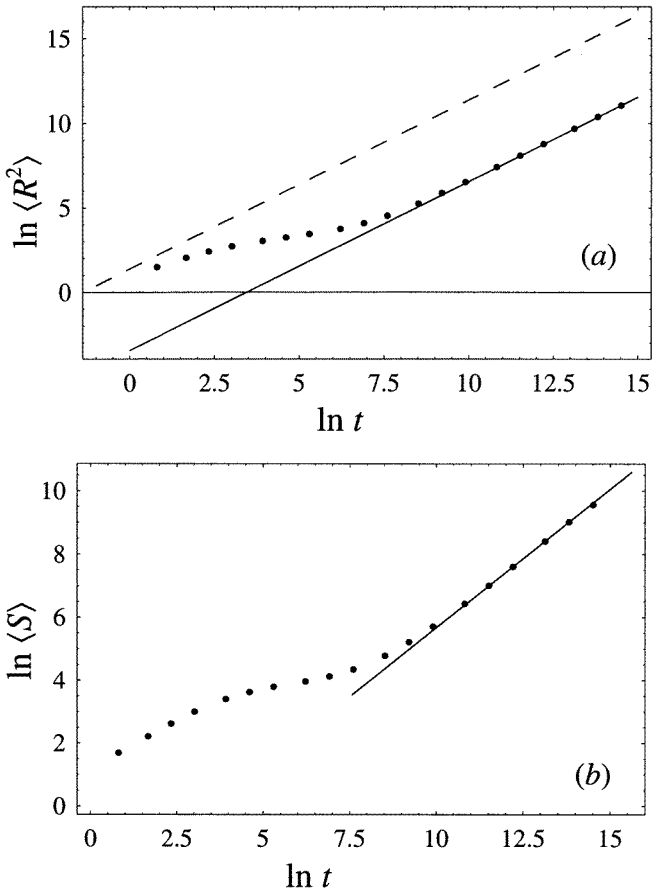

Figure 4. Average values for (*a*) walker displacement-squared $R(t)^2$ and (*b*) number $S(t)$ of visited sites for walks over the indicated time intervals t through the composite shown in figure 3 (particulate–matrix microstructure) with phase conductivity ratio $\sigma_B/\sigma_A = 10^3$. The solid lines are fits to the data points in the Gaussian regime; the dashed line in (*a*) indicates the walker behaviour in a single-phase material.

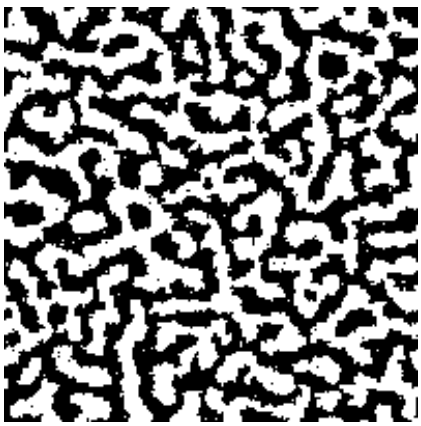

Figure 5. Two-phase composite with a labyrinthine microstructure (size 200×200). Each phase has volume fraction 0.5.

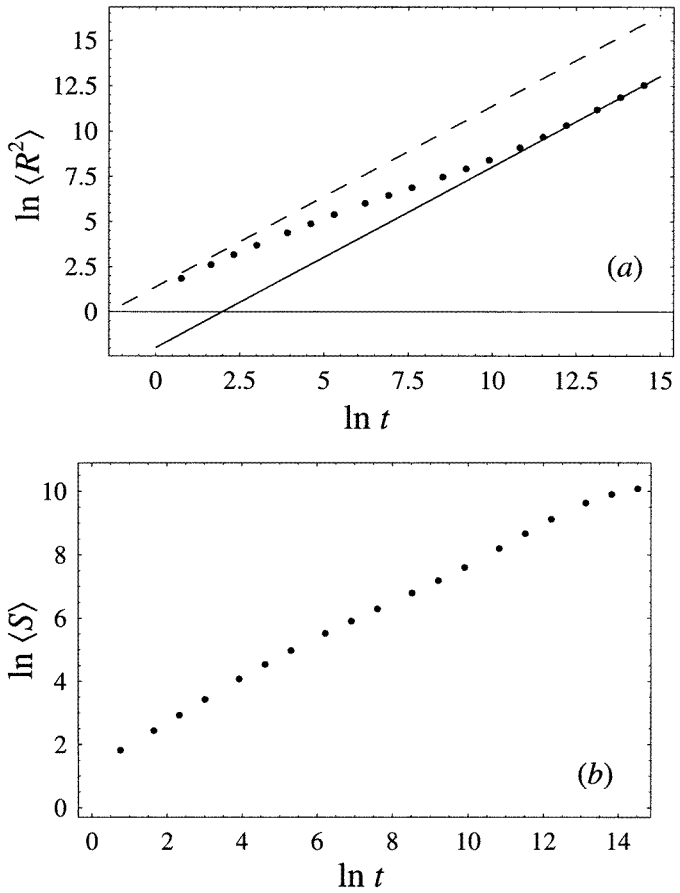

Figure 6. Average values for (*a*) walker displacement-squared $R(t)^2$ and (*b*) number $S(t)$ of visited sites for walks over the indicated time intervals t through the composite shown in figure 5 (labyrinthine microstructure) with phase conductivity ratio $\sigma_B/\sigma_A = 10^{-3}$. The solid line in (*a*) is a fit to the data points in the Gaussian regime, while the dashed line indicates the walker behaviour in a single-phase material.

the anomalous and Gaussian regimes are easily identified.

Values for the correlation length ξ, the walker diffusion coefficient D_w, and the conductivity σ for these particulate–matrix and labyrinthine systems are given in table 2. The larger values in the latter case are due to the percolating domain structure of the higher conductivity phase.

These examples demonstrate that a distinct correlation length (associated with a particular transport property) exists even for non-fractal composite microstructures. This is because the *heterogeneity* of the microstructure (as expressed by the morphology, phase domain distribution, etc, as well as by the ratios σ_i/σ_j) is *length-scale dependent* at all length scales up to ξ.

5. Discussion

While the concept of 'correlation length' underpins percolation theory, which essentially considers the properties of disordered, conductor–insulator systems, it is much less

Table 2. The correlation length ξ, walker diffusion coefficient D_w, and conductivity σ of the particulate–matrix and labyrinthine microstructures shown in figures 3 and 5, respectively.

Morphology	ξ	D_w	σ
Particulate–matrix	8	0.0080	$0.0020\sigma_B$
Labyrinthine	91	0.0347	$0.0174\sigma_A$

appreciated in experimental and applied research, where measurements are generally made on heterogeneous composite materials. Microscopic systems, such as multiphase alloy microstructures and porous rock, are typically characterized optically due to the availability of sophisticated imaging techniques and image analysis software. In this context, the work reported here makes the point that homogeneity is not 'in the eye of the beholder'; rather it is in reference to the particular property under study. At the other size extreme, megascopic systems such as oil reservoirs and aquifers cannot be studied in their entirety, so subsystems (or subvolumes), often of size less than ξ, are characterized instead. The measured physical property (e.g., fluid permeability) will then be subsystem size-dependent, and phenomenological equations of motion (e.g., Darcy's law) that require a homogeneous system may not be obeyed.

Equations (1) and (4) together show that the transport properties of a heterogeneous system are power law functions of ξ. That ξ (and d_w) depends on the constituent phase properties as well as on the phase domain morphology and distribution seems to fundamentally limit the usefulness of purely morphological (i.e., visual) descriptors such as fractal dimension and n-point correlation functions in the calculation of transport properties of composites.

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