Diffusion on two-dimensional percolation clusters: Influence of cluster anisotropy

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(Received 6 February 1991)

This paper investigates the influence of geometric anisotropy of two-dimensional percolation clusters on diffusion. Monte Carlo simulation indicates that the ensemble of all random walks starting from any given origin is typically anisotropic as determined by the local geometry of the cluster. Single-particle (or tracer) diffusion is described by the position-correlation matrix (PCM). A mean-field equation is developed for the PCM of the random walker in terms of the moment of inertia tensor of the cluster as a function of the chemical distance from the origin. In contrast, the ensemble of all random walks starting from all possible origins, weighted by the stationary probabilities, leads to essentially isotropic diffusion due to self-averaging over many regions within the cluster. The diffusion of an ensemble of particles in the latter case may be characterized by the velocity-correlation matrix (VCM). It is proved that the VCM is symmetric when a detailed balance condition holds and stationary initial conditions are used. An evolution equation for the VCM is constructed using a generalized Langevin equation with a power-law friction kernel. The kernel is a phenomenological characterization of the diffusion process in a fractal medium.

I. INTRODUCTION

It is well known that many naturally occurring as well as manufactured disordered media are not homogeneous at small length scales, but rather are self-similar fractals.1 The structure of these self-similar objects will look the same at different levels of magnification. Consequently, the physical properties of these systems will obey scaling laws such as the mass \( M \) depending on the scale of observation \( L \) as

\[
\bar{M}(L) \sim AL^{d_f},
\]

where the bar denotes a configurational average. The exponent \( d_f \) is called the fractal dimension1 and is less than the dimension \( d \) of the embedding space. Examples of self-similar fractals include surfaces of some molecular aggregates, natural and synthetic macromolecules, dust particles, porous media, catalyst pellets, alloys, etc. The role of diffusion in such media is extremely important either explicitly or implicitly in practical applications. For example, diffusion can implicitly control the effectiveness of an embedded catalyst, and the conductivity of a disordered alloy is related to the carrier's self-diffusion. Monte Carlo simulation of random walks on disordered structures shows that diffusion is anomalously slow2 in the fractal regime. In other words, the mean-square displacement of the random walker \( \langle R(t)^2 \rangle \) is not proportional to the time \( t \), but rather to \( t \) raised to a fractional exponent. Thus

\[
\langle R(t)^2 \rangle \sim At^{2/d_w},
\]

where \( d_w > 2 \) is the anomalous diffusion exponent. In the anomalous regime, long-range correlations in the step displacements must exist and furthermore, the central limit theorem breaks down, resulting in the probability distribution for the distance from the origin to deviate from a Gaussian.3,4 These and many other interesting features of diffusion on fractals have been reviewed by Havlin and Ben Avraham.5

While much progress has been made toward deriving the evolution equations for diffusion on fractals, the analysis has hitherto been based on the assumption that the diffusion process is isotropic.6 This assumption is reasonable since on average one expects a homogeneously disordered system to be rotationally invariant in its properties. However, the isotropy is regained only after a complete configurational average over the disorder is performed. Therefore we expect that anisotropic properties may be important in a given system without a configurational average. Another motivation for our study is the possi-
bility that the local anisotropy may play a role in many physical processes, although a large system may appear isotropic macroscopically because of self-averaging.

Studies by Family, Vicsek, and Meakin have shown that two-dimensional critical percolation clusters are typically anisotropic. They define the anisotropy $A_N$ of a cluster of $N$ sites as $A_N = \lambda_{\text{min}}/\lambda_{\text{max}}$, where $\lambda_{\text{min}}$ and $\lambda_{\text{max}}$ are, respectively, the minimum and maximum eigenvalue of the radius of gyration tensor. Since their estimates of the average asymptotic anisotropy $\bar{A}$ for growing and equilibrium clusters are approximately 0.48 and 0.40, respectively, the clusters are geometrically highly anisotropic. The main purpose of this paper is to investigate the influence of such anisotropy on the diffusion process. More specifically, we investigate if the diffusion is anisotropic and if so, its dependence on the structure of the cluster.

We first describe the diffusion process by means of the position-correlation matrix (PCM), which is ideally suited to describe tracer diffusion in a medium. We derive a mean-field evolution equation for single-particle diffusion on a given cluster in terms of the moment of inertia tensor as a function of the chemical distance from the starting site. The equation is evaluated using data from Monte Carlo experiments of random walks on twodimensional percolation clusters. Asymptotic properties of the solution are investigated. The diffusion is also described using a velocity-correlation matrix (VCM), which is suited to describe a stationary ensemble of diffusers in developments based on linear response theory. The cornerstone of this theory is the fluctuation dissipation theorem, which relates the frequency-dependent diffusivity to the equilibrium VCM. We have previously studied the velocity-autocorrelation function (VACF) for random walks on percolation clusters. This has proven to be extremely useful in identifying the long-time properties of the friction kernel of a generalized Langevin equation (GLE). The GLE is useful in describing the dynamics of a Brownian particle on a fractal. The advantage of the GLE is that the friction kernel serves as an effective constitutive property of the fractal medium. A power-law friction kernel can be used to approximate anomalous diffusion on two-dimensional critical percolation clusters. The GLE can be employed to simulate diffusion on fractals and possibly to derive the partial differential equations governing anomalous diffusion.

The outline of this paper is as follows. In Sec. II, the anisotropy of percolation clusters is studied using the moment of inertia tensor. The anisotropy as a function of size is found to be dependent upon the ensemble used. More specifically, the anisotropy of an ensemble of equilibrium percolation clusters differs from that of growing clusters. Furthermore, the anisotropy of an ensemble of growing clusters itself is dependent on the growth model employed. New quantities are introduced to measure the anisotropy in order to relate the geometric properties of a cluster to the diffusion process. In Sec. III, we derive the mean-field evolution equation for the PCM and show that a configurational average reproduces the correct scaling behavior for anomalous diffusion. We also compare the calculated mean-field approximation to the results obtained from the exact enumeration method. In Sec. IV, we use the results of Sec. II to construct an approximate GLE to describe the dynamics on fractals using a simple power-law friction kernel. An equation of motion for the VCM follows directly from the GLE and is solved analytically. The solution shows good agreement with the VACF of blind-ant random walks obtained via computer simulations of diffusion on two-dimensional percolation clusters. Section V summarizes the developments of this paper.

II. ANISOTROPIC PROPERTIES OF PERCOLATION CLUSTERS

A. Static anisotropy

Since the initial work of Family, Vicsek, and Meakin, there have been a number of studies on the anisotropy of percolation clusters. In two dimensions, a natural measure of the anisotropy is the ratio of the smallest to the largest eigenvalue of the radius of gyration tensor. However, other kinds of amplitude ratios have been introduced by Aronovitz and co-workers that allow for the generalization to higher dimensions and easier analytical study. One difference is that they define an amplitude as a ratio of averages instead of an average of a ratio. For example, anisotropic amplitudes can be defined in terms of the ratio of averaged polynomials involving the eigenvalues, the simplest being given by the average of the difference divided by the average of the sum of the eigenvalues. In order to relate the anisotropy of the diffusion process to that of the percolation cluster itself, we have studied the cluster anisotropy in multiple ways.

For a given cluster, a random walker will start at a given origin and proceed to explore its surroundings. Therefore we generated site-percolation clusters using the growth method of Leath starting from a seed site which defines the origin. The cluster is grown in a series of shells by checking each perimeter site if it is occupied with probability $p$ (otherwise vacant). After all the perimeter sites have been checked, then all possible nearest-neighbor bonds are formed between the occupied sites. The process continues because the collection of all unchecked nearest-neighbor sites to the latest set of occupied sites will form a new set of perimeter sites. It follows that all sites within the cluster belong to a shell of a certain generation defined by the chemical distance from the origin. The chemical distance $l$ of a certain site with respect to the origin is defined as the length of the shortest path connecting through the bonds of the cluster between that site and the origin. The clusters can be grown to a predetermined number of sites or alternatively to a chemical distance $l_0$ such that all sites contained within the cluster have a chemical distance $l \leq l_0$. 
The Leath method\textsuperscript{15} is better suited for the study of the diffusion process than the method by Alexandrowicz,\textsuperscript{16} which was used in prior studies\textsuperscript{7} on the anisotropy of percolation clusters. In the latter method, the clusters are grown by selecting a perimeter site (growth site) at random for the determination if the site is occupied or vacant. When the site is found to be occupied, it is connected to the cluster and then its unchecked nearest neighbors immediately become members of the set of growth sites. The clusters grown in this way are not built up by shell by shell and represent another type of growth process.\textsuperscript{17} It is not unreasonable to expect that the properties of clusters as a function of their size may depend on the growth method, and therefore a distinction between equilibrium clusters and growing clusters becomes necessary.

An equilibrium cluster is a finite cluster that has stopped growing after all perimeter sites have been checked. Unless otherwise stated, all quoted results that are discussed below are for site percolation clusters on the square lattice at the critical threshold \((p = p_c \approx 0.593)\). Denoting by \(\bar{A}\) the average of the ratio of the smallest to largest eigenvalue of the radius of gyration tensor (or equivalently of the moment of inertia tensor) about the center of mass, we find \(\bar{A}(N)\) as a function of the cluster size \(N\) to be the same for both the Leath and Alexandrowicz growth methods. From a sample of 36 520 randomly generated equilibrium clusters, the asymptotic value for \(\bar{A}\) was found to be 0.395 \pm 0.015, which is in agreement with Family, Vicsek, and Meakin.\textsuperscript{7} This is because both the Alexandrowicz and Leath methods produce the same ensemble of equilibrium clusters as they differ only in the order that the perimeter sites are checked.

However, the growing clusters (i.e., all clusters other than the equilibrium ones) differ from the equilibrium clusters in that not all of their available perimeter sites have been checked. Thus the order in which the perimeter sites are checked can influence the properties of the growing clusters. Of course, many growing clusters may be close to finishing the growth process, and the most differences from the equilibrium clusters, if they exist at all, should be associated with indefinitely growing clusters. In order to approximate these, we may choose to consider the ensemble of subclusters of size \(N \leq N_{min}\) within larger clusters grown to at least a size \(N_{min}\), which is much larger than \(N_{cut}\). In the remainder of this section, we mean these relatively small subclusters by growing clusters.

As pointed out by Family, Vicsek, and Meakin\textsuperscript{7} the asymptotic amplitude of \(\bar{A}\) for the growing clusters has a different value than that for the equilibrium clusters. They found for the growing clusters using the Alexandrowicz method (GAM clusters) the asymptotic value for \(\bar{A}\) to be approximately 0.485, which is 22% higher than for the equilibrium clusters. Choosing \(N_{min} = 10000\) and \(N_{cut} = 5000\), we find, from 38 000 growing clusters using the Leath method (GLM clusters) and from 30 000 GAM clusters, approximately the same asymptotic value of 0.457 \pm 0.010. This value is 14% higher than the equilibrium clusters. Furthermore, the GAM and GLM clusters approach the asymptotic value of \(\bar{A}\) differently as a function of the number of sites.

The asymptotic form for the maximum and minimum principal moments of inertia are assumed to be given by

\[
I_{max}(N) = h_{max} N^{1+2/\delta_f} (1 + g_{max} N^{-\theta} + \cdots) \tag{2.1}
\]

and

\[
I_{min}(N) = h_{min} N^{1+2/\delta_f} (1 + g_{min} N^{-\theta} + \cdots), \tag{2.2}
\]

where the leading term follows from the definition of the moment of inertia \((\int r^2 dN)\) and the fractal scaling law \((N \sim r^{\delta_f})\), and \(\theta\) is the smallest correction exponent to the leading behavior. Letting \(\bar{A}(N)\) denote the ratio of \(I_{min}(N)\) over \(I_{max}(N)\), it follows that

\[
\bar{A}(N) = \bar{A}[1 + (g_{min} - g_{max}) N^{-\theta} + \cdots], \quad \bar{A} = \frac{h_{min}}{h_{max}}. \tag{2.3}
\]

By choosing a value of \(\theta\) and plotting \(\bar{A}(N)\) against \(N^{-\theta}\), we eventually obtain a straight line from trial and error and find initial estimates for the correction exponents and the asymptotic value of \(\bar{A}\). We then rewrite the above equations in the form

\[
y(N) = \frac{h_{min}}{h_{max}} \frac{I_{max}(N)}{I_{min}(N)} - 1 = (g_{min} - g_{max}) N^{-\theta} \tag{2.4}
\]

and plot \(y(N)\) versus \(N\) on a log-log scale for various asymptotic values of \(\bar{A}\) (close to the initial estimate) to arrive at our final estimates.

The asymptotic values for \(\bar{A}\) are found to be 0.4105 \pm 0.005 and 0.4085 \pm 0.005 for the GAM and GLM clusters, respectively. In Fig. 1 the comparison of the correction exponents between the GAM and GLM clusters is displayed. The correction exponents are determined to be 0.49 \pm 0.05 and 0.65 \pm 0.1 for the GAM and GLM clusters, respectively. The uncertainties on \(\bar{A}\) are obtained from observing when the plots in Fig. 1 produce poor fits, and the uncertainties in the correction exponent are obtained from these extreme limits on \(\bar{A}\). In the case of the GLM clusters the large uncertainty is a result of the insensitivity in finding the best linear least-squares fit. Furthermore, the second method of using Eq. (2.4) for estimating the correction exponent was not possible for the equilibrium clusters because of the large fluctuations in the data. In fact, from our data it was not possible to exclude an exponent value as high as 0.7 or as low as 0.4, although Family, Vicsek, and Meakin\textsuperscript{7} reported that the equilibrium clusters have a correction exponent of approximately 0.47, which is the same as the GAM clusters.

While the above results have been obtained about the
center of mass, we have also studied the anisotropic properties of percolation clusters about the seed site used in generating them. Effectively, we have studied the anisotropy in six different ensembles: equilibrium clusters, GAM and GLM clusters taking the origin of coordinates at the center of mass (as discussed above) and at the seed site. We have observed that the asymptotic value for $A$ and/or the approach as a function in the number of sites is in general dependent upon the choice of ensemble. Although we have observed differing differences between these ensembles, these results are not pertinent to the remainder of this paper.

We have further studied the static anisotropic properties of a cluster in terms of its moment of inertia tensor as a function of the chemical distance. The ensemble of clusters of chemical distance $l$ was constructed from the collection of subclusters within larger clusters of minimum size $l_0$. The origin is taken at the seed site which will be the starting point of the random walks. The local geometry of the cluster is described by the moment of inertia tensor given by

$$\overrightarrow{I}(l) = \begin{bmatrix}
I_x(l) & -P_{xy}(l) \\
-P_{xy}(l) & I_y(l)
\end{bmatrix},$$

where $I_x = \sum^{N(l)}_{i=1} y_i^2$ is the moment of inertia about the $x$ axis, $P_{xy} = \sum^{N(l)}_{i=1} x_i y_i$ is the product of inertia, etc. The principal moments of inertia ($I_{\text{min}}$ and $I_{\text{max}}$) and the principal axes can be found by diagonalizing the moment of inertia tensor. The principal moments of inertia are expressed in terms of the two rotationally invariant quantities $I_{\text{av}}$ and $\Delta I$ as

$$I_{\text{max}} = I_{\text{av}} + \Delta I, \quad I_{\text{min}} = I_{\text{av}} - \Delta I,$$

where

$$I_{\text{av}} = \frac{I_x + I_y}{2}, \quad (\Delta I)^2 = \left(\frac{I_x - I_y}{2}\right)^2 + P_{xy}^2.$$

Note that $\Delta I$ is equal to $(I_{\text{max}} - I_{\text{min}})/2$, which is equal to zero for an isotropic configuration.

In general, the moment of inertia about an axis making an angle of $\phi$ with respect to the $x$ axis is given by

$$I(l, \phi) = I_x(l) \cos^2 \phi + I_y(l) \sin^2 \phi - 2P_{xy}(l) \cos \phi \sin \phi.$$  

(2.8)

In particular, the major principal axis makes an angle of $\psi$ defined by $I(l, \psi(l)) = I_{\text{max}}(l)$ on the interval $0 \leq \psi < \pi$. Since the form of Eq. (2.8) is the same for any choice of the $x$ and $y$ axes, we could equally well have chosen the $x$ axis to be the major principal axis. In this case,

$$I(l, \phi') = I_{\text{max}}(l) \cos^2 \phi' + I_{\text{min}}(l) \sin^2 \phi',$$

where $\phi'$ is relative to the major principal axis. In two dimensions, the angle $\phi'$ is simply equal to $\phi - \psi$, so that Eq. (2.9) can be written as

$$I(l, \phi | \psi) = I_{\text{av}}(l | \psi) + \Delta I(l | \psi) \cos 2(\phi - \psi),$$

(2.10)

where $I_{\text{av}}$ and $\Delta I$ are now functions of the conditional argument $\psi$.

For disordered systems on an underlying lattice, there may be anisotropic effects induced by the lattice as well as by the disorder. The anisotropy of a cluster will generally be a function of the orientation of its principal axes on the lattice. Thus let us consider the (unprimed) coordinate system to be fixed with respect to the crystalline axes of the lattice and the new (primed) coordinate system to be such that the $x'$ axis makes an arbitrarily chosen angle $\phi$ from the $x$ axis. The quantities associated with a specific configuration that do not depend on $\phi$, such as $I_{\text{av}}$ and $\Delta I$, are called rotationally invariant. They will, however, in general depend on $\psi$.

In a disordered system, all possible orientations must be averaged over if a configurational average is desired. For example, the disorder average of $I_{\text{av}}$ may be expressed as

$$\overline{I_{\text{av}}(l)} = \int_0^{2\pi} I_{\text{av}}(l | \psi) f(\psi) d\psi,$$

(2.11)

where $f(\psi)$ is the probability density for the angle $\psi$. The function $f(\psi)$ may in general depend on the lat-
tice structure. Thus certain properties of clusters [e.g., \(I_{av}(l | \psi)\)] may depend on their orientation relative to the crystalline axes, and the average property of an ensemble of clusters [e.g., \(I_{av}(l)\)] may also depend on the fraction of clusters (relative frequency) that have a particular orientation.

In this work, however, we have found that \(f(\psi)\) is uniform for both the square and triangular lattices, implying that no preferred angle exists between the principal and crystal axes. We introduce three orientation-dependent measures of the anisotropy of a cluster given by

\[
a(l | \psi) = \frac{I_{av}(l | \psi)}{I_{av}(l)}, \quad b(l | \psi) = \frac{\Delta I(l | \psi)}{I_{av}(l)}
\]

as well as

\[
A(l | \psi) = \frac{I_{min}(l | \psi)}{I_{max}(l | \psi)} = \frac{a(l | \psi) - b(l | \psi)}{a(l | \psi) + b(l | \psi)}.
\]

Thus, by knowing how the anisotropic properties of clusters are affected by the relative orientation \(\psi\) between the crystal and principal axes, together with the frequency of occurrence \(f(\psi)\), the contribution to the anisotropy from the lattice can be separated from that due to disorder.

We show in Fig. 2 the simulation results of the configurational average over 20,000 clusters for the three quantities \(a, b,\) and \(A\) as functions of \(l\) and \(\psi\). Since the square lattice has fourfold and inversion symmetries, the entire \(\psi\) dependence can be deduced for the functions \(a(l, \psi), b(l, \psi),\) and \(A(l, \psi)\) from their dependence over a range of \(45^\circ\) starting from \(0^\circ, 45^\circ, 90^\circ,\) or \(135^\circ\). Therefore we plot in Fig. 2 the results for \(l = 5, 44, 122,\) and 200 over those restricted angular ranges, respectively. It appears that for \(l = 5\) there is a strong oscillatory dependence on \(\psi\) in three functions; however, for \(l = 44\) there is only a slight hint of oscillation, and there is virtually no dependence on the cluster orientation for larger clusters. These results imply that the orientation dependence in the functions \(a, b,\) and \(A\) can be neglected for large \((l > 100)\) percolation clusters.

Since \(f(\psi)\) is also uniform, we conclude that the square lattice does not induce any anisotropy in the ensemble of percolation clusters (except for small clusters with \(l < 100)\). This result corroborates the conclusion previously found in a different way by Quandt and Young. The asymptotic values for \(b\) and \(A\) are estimated to be \(0.371 \pm 0.006\) and \(0.442 \pm 0.006,\) respectively. We have also found no orientational dependence on \(a, b,\) and \(A\) for the triangular lattice (from 20,000 clusters at \(p = p_c = 0.5),\) where the asymptotic values for \(b\) and \(A\) are estimated to be \(0.369 \pm 0.01\) and \(0.436 \pm 0.01,\) respectively. These results suggest that the underlying lattice does not play an important role in the anisotropic properties of percolation clusters.

B. Dynamic anisotropy

After a cluster has been randomly generated, we study the anisotropy of random walks on the cluster starting at the seed site. Whereas the geometric or static anisotropy essentially depends on the distribution of the sites in space, the dynamic anisotropy (as probed by random walks) depends, in addition, on the topological aspect of connectivity of sites. In this paper we investigate so-called blind-ant \(^5\) random walks; however, we expect that these results will apply to a wider class of models. At each time step the blind ant has equal probability in attempting to hop to a nearest neighbor. If an attempt to hop is made onto a site that is not a part of the cluster, then the walker does not move. Using the exact enumeration method, \(^6, 11\) all Brownian paths are summed over by successive multiplications of a transition probability matrix. The anisotropy of the Brownian motion is obtained from the position-correlation matrix.

The position-correlation matrix is defined by

\[
\mathcal{P}(t) = \langle \mathbf{R}(t)\mathbf{R}^T(t) \rangle = \begin{bmatrix}
\langle X(t)X(t) \rangle & \langle X(t)Y(t) \rangle \\
\langle Y(t)X(t) \rangle & \langle Y(t)Y(t) \rangle
\end{bmatrix},
\]

where \(\mathbf{R}\) is the displacement vector of a walker, \(T\) denotes the transpose operation, and the angular brackets denote an ensemble average over all walks from the same starting point. The anisotropic characteristics of the PCM is
analyzed in a similar way to the moment of inertia tensor. The mean-square displacement projected onto an axis making an angle of \( \phi \) with respect to the \( x \) axis is given by

\[
(q(t, \phi)^2) = \langle [\mathbf{R}(t) \cdot \hat{e}_r(\phi)]^2 \rangle,
\]

(2.15)

where \( \hat{e}_r(\phi) \) is the radial unit vector in the \( x-y \) plane. The PCM can be diagonalized at any given time to obtain the eigenvalues \( (q(t)^2)_{\text{min}} \) and \( (q(t)^2)_{\text{max}} \). Although we have studied \( \psi(t) \), defined as the angle between the \( x \) axis and the axis of greatest displacement, we have not found any simple relation to the geometric features of the cluster in terms of its chemical distance.

The eigenvalues of the PCM are expressed in terms of two rotationally invariant quantities. The first is just the usual mean-square displacement given by

\[
(R(t)^2) = (q(t)^2)_{\text{max}} + (q(t)^2)_{\text{min}},
\]

(2.16)

and the second is a measure of the anisotropy given by

\[
(\Delta Q(t)) = (q(t)^2)_{\text{max}} - (q(t)^2)_{\text{min}}.
\]

(2.17)

The dynamical quantities \( (R^2) \) and \( (\Delta Q) \) are analogous to the static quantities \( I_{\varphi} \) and \( \Delta I \), respectively.

We observe from a configurational average over 100 clusters that the ratio of averages given by \( \langle \Delta Q(t) \rangle \rangle \langle R(t)^2 \rangle \rangle \) calculated up to \( t = 1000 \) remains approximately equal to 0.36 for \( t > 100 \). We notice that this number is close to the asymptotic value of the analogous geometric quantity \( b \). Furthermore, the ratio of the averages given by \( \langle q_{\text{min}}(t)^2 \rangle / \langle q_{\text{max}}(t)^2 \rangle \rangle \) remains approximately equal to 0.46 for \( t > 100 \), which is also close to the asymptotic value of the analogous geometric quantity \( A \). We expect that the agreement will become even better if the number of clusters in the sample is increased. The implication of these results is that a random walk starting from the origin has a typical amount of prolateness (anisotropy) at long times. Thus the geometrical anisotropy of the clusters directly influences the degree of prolateness in the random walks.

However, the directions of the principal axes of diffusion vary in a complicated, seemingly nonsensible fashion. We further find that if we use all possible starting points weighted by the stationary distribution, the anisotropy is self-averaged out. Therefore, in experiments where the diffusors start from a localized area in the cluster (so-called tracer experiments), the anisotropic nature of the diffusion should manifest itself, while in cases where diffusors start from many points on a cluster, the measured averages do not reflect the anisotropy.

III. MEAN-FIELD APPROXIMATION FOR THE PCM

As shown in Sec. II, the mean-square displacement of a Brownian particle in an anisotropic medium is not adequate to fully describe a diffusion process. In an anisotropic environment, we intuitively expect a particle to diffuse faster along directions with the least number of restrictions (corresponding to areas with a high connectivity between sites). Clearly the local bond or site density of the percolation clusters will be a major factor in the diffusive profile. We consider blind-ant\textsuperscript{5,11} random walks starting from the seed site of a given cluster, and derive a mean-field equation for the PCM on clusters embedded in two dimensions.

Since we are primarily concerned with behavior at large times and chemical distances, we will regard \( l \) and \( t \) as continuous variables. Furthermore, we choose the units of distance and time such that \( l_{\text{max}} = vt \), where the average step speed \( v \) is unity. Thus as time progresses, the walker continuously experiences more structure of the cluster up to a chemical distance equal to \( t \).

Let \( p(x, y, l; t) \) denote the joint probability density that the walker at time \( t \) has the coordinates \( (x, y) \) and chemical distance \( l \). In essence, we have coarse grained the structure of the clusters into separate bins defined by the chemical-distance shells. Thus integration over \( l \) recovers the usual position probability density \( p(x, y, t) \).

The contribution from the chemical-distance shell \( l \) for the mean-square displacement projected onto the \( x \) direction is given by

\[
\langle X(t; l)^2 \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy p(x, y, l; t).
\]

(3.1)

Taking all the chemical-distance shells collectively, we have

\[
\langle X(t)^2 \rangle = \int_0^l \langle X(t; l)^2 \rangle dl,
\]

(3.2)

where we have accounted for the fact that the walker can be located at a chemical distance between \( 0 \) and \( l \) at time \( t \). We now make a mean-field approximation to the function \( p(x, y, l; t) \) given by

\[
p(x, y, l; t) \approx \bar{p}(l, t) n(x, y; l),
\]

(3.3)

where \( n(x, y; l) \) is the density of sites at location \( (x, y) \) and chemical distance \( l \), i.e., \( n(x, y; l) = 0 \) if \( (x, y) \) is not in the shell \( l \) and \( n(x, y; l) = 1 \) otherwise. The entire time dependence has been put in \( \bar{p}(l, t) \), which gives the mean probability density per site that the walker is located at chemical distance \( l \) at time \( t \). In other words, if \( p(l, t) \) is the probability density for the random walker to be located in chemical-distance shell \( l \) at time \( t \), then

\[
\bar{p}(l, t) = p(l, t) G(l),
\]

(3.4)

where \( G(l) \) is the total number of sites at chemical distance \( l \) given by

\[
G(l) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} n(x, y; l) dx dy.
\]

(3.5)

Physically, we have ignored the fluctuation in probability among sites of a cluster that are at the same chemical distance from the origin. This approximation should be valid if the fluctuations in \( p(x, y, l; t) \) are small com-
pared to the mean value $\bar{p}(l,t)$. In Fig. 3 we plot the normalized distribution of the ratio of the actual probability density $p(x,y,t;I)$ at a site to the probability density per site $\bar{p}(l,t)$ within a given chemical-distance shell. This distribution was obtained from 600 random clusters generated using the Alexandrowicz method. The unnormalized histogram tallied the occurrence of all ratios (within a chemical-distance shell) for all 600 clusters generated. We find that the distributions obtained are the same for different chemical distances and times as long as $y = l(t)/(t^{1/d_x})$ is constant. The exponent $d_x$ is defined through the relation $(l(t)/t^2) \sim t^{2/d_x}$ and we find that the distribution broadens as the scaling variable $y$ increases. This sort of behavior suggests multifractal characteristics in the diffusion process. We see that the approximation is fair for $y \approx 3$ and less and poor for $y > 3$. However, the region where the approximation becomes poor is fortunately in the tail of the distribution $p(l,t)$ to find the particle. We have thus far coarse grained the dynamics in terms of the chemical-distance shells.

Incorporating Eqs. (3.3) and (3.1) we find that

$$\langle X(t)^2 \rangle \approx \bar{p}(l,t) \int_{-\infty}^{\infty} dx \, x^2 \int_{-\infty}^{\infty} dy \, n(x,y;l).$$  

(3.6)

The moment of inertia about the $y$ axis for a cluster of chemical distance up to $l$ is given by

$$I_y(l) = \int_0^l dl' \int_{-\infty}^{\infty} dx \, x^2 \int_{-\infty}^{\infty} dy \, n(x,y;l'),$$

(3.7)

where the origin of coordinates is located at the starting position of the walker. Thus Eq. (3.2) reduces to

$$\langle X(t)^2 \rangle \approx \int_0^l dl \, \bar{p}(l,t) \, I'_y(l),$$

(3.8)

where the prime denotes the derivative of a function with respect to its argument. Similarly, the entire PCM is expressed by

$$\tilde{P}(t) \approx \int_0^l dl \, \tilde{p}(l,t) \, \tilde{T}'(l)$$

$$= \int_0^l dl \, \tilde{p}(l,t) \begin{bmatrix} I_{y}(l) & P_{y}(l) \\ P_{y}(l) & I_{y}(l) \end{bmatrix},$$

(3.9)

where $\tilde{T}'(l) dl$ is just the moment of inertia tensor of the $l$th chemical-distance shell rotated by $90^\circ$.

Now we proceed to make another mean-field approximation to Eq. (3.9) by replacing $\tilde{p}(l,t)$ by its configurational average denoted by $\bar{p}(l,t)$. The physical motivation for this additional approximation is that we expect the PCM to be predominately controlled by the moment of inertia tensor and that all clusters will share a similar mean probability density per site $\bar{p}(l,t)$.

A subtle point to this approximation is that the simple substitution of the configurational average $\bar{p}(l,t)$ in place of $\tilde{p}(l,t)$ would not allow for proper normalization. This is because the normalization of $\tilde{p}$ is dependent on cluster configuration:

$$\int_0^l G(l) \bar{p}(l,t) \, dl = \int_0^l p(l,t) \, dl = 1.$$  

(3.10)

Thus, in order to preserve this form of normalization, we must replace $\tilde{p}(l,t)$ by $\bar{p}(l,t)/C(t)$, where $C(t)$ is a normalization coefficient defined by

$$C(t) = \int_0^l G(l) \bar{p}(l,t) \, dl,$$

(3.11)

which depends on the structure of the cluster through $G(l)$. Therefore this second mean-field approximation retains some of the cluster to cluster fluctuations within the normalization coefficient.

Thus our final mean-field expression for the PCM is given as

$$\tilde{P}(t) \approx \frac{\int \tilde{T}'(l) \bar{p}(l,t) \, dl}{\int G(l) \bar{p}(l,t) \, dl}.$$  

(3.12)

At this point, a nice physical picture of the diffusion process emerges. If $\bar{p}(l,t)$ were independent of $l$, then the PCM would just equal the radius of gyration tensor. Therefore $\bar{p}(l,t)$ is a time-dependent weighting function that determines the relative importance of the sites within chemical distance shell $l$. 

![Diagram](image-url)
The usefulness of Eq. (3.12) for the PCM becomes clear when we consider the scaling properties of \( \bar{p}(l, t) \).

The function \( \bar{p}(l, t) \) is expected to have the same scaling behavior as \( p(l, t)/G(l) \), where the bar denotes the configurational average as usual. Havlin et al.\(^5\) showed from exact enumeration of random walks that \( \bar{p}(l, t) \) has a scaling form given by

\[
\bar{p}(l, t) = y^d \exp(-b y^\beta), \quad \beta = 1.9 \pm 0.1 \quad (3.13)
\]

when using the similarity variable \( y = l/t^{1/d_w} \) as before. In the above \( d_t \) is the exponent that describes the scaling of the number of sites with the chemical distance. Noting that \( G(l) \sim l^{d_t - 1} \), we make the scaling anzatz that

\[
\bar{p}(l, t) = \Phi(y) t^{-d_s/2}, \quad (3.14)
\]

where \( d_s = 2d_t/d_w \) is equal to the spectral dimension.

We performed the exact summation of random walks starting from the seed on square-lattice site percolation clusters generated using the Leath\(^\text{15}\) method at \( p = p_c \approx 0.593 \). We have studied 400 clusters of chemical distance 200 and 400 clusters of chemical distance 400, using four different time frames at times 500, 1000, 2500, and 5000. With the values of \( d_s \approx 1.39 \) and \( d_w \approx 2.54 \) as determined by Havlin et al.,\(^5\) we indeed observed scaling. The smoothed plot for the scaling function \( \Phi(y) \) is shown in Fig. 4. In addition to \( \bar{p}(l, t) \), we have observed scaling in the following fluctuations given by

\[
\sigma[p(x, y, l, t) - \bar{p}(l, t)] = \Delta \phi(y) t^{-d_s/2}, \quad (3.15)
\]

\[
\sigma[p(l, t)^2 - \bar{p}(l, t)^2]^{1/2} = \Delta \Phi(y) t^{-d_s/2}, \quad (3.16)
\]

where \( \sigma \) in Eq. (3.15) refers to the root mean square of an ensemble of sites \( (x, y) \) contained in shell \( l \) of one cluster. The scaling functions \( \Delta \phi(y) \) and \( \Delta \Phi(y) \) are also presented in Fig. 4. We find that the fluctuations defined above are of the same order as the mean probability density per site and furthermore, from Fig. 3 we can expect these deviations from the mean to be a few orders of magnitude for large \( y \). However, the essential physics can still be captured in Eq. (3.12) since \( \bar{p}(l, t) \) varies over many decades.

\[ |\ln[\Phi(y)]| \] is plotted against \( y \) on a log-log plot in Fig. 5. The scaling function \( \Phi(y) \) is found to be approximately a stretched exponential for large values of \( y \) with the power \( \beta = 1.65 \pm 0.05 \). We note here that this value of \( \beta \) is consistent with the theoretical prediction of Havlin et al.\(^5\) that \( \beta = d_w/(d_w - 1) \), although they were considering the scaling of \( p(l, t) \) [not \( \bar{p}(l, t) \)]. Although the data in Figs. 4 and 5 pertain to clusters grown using the Leath method, we have obtained the same results from clusters grown using the Alexandrowicz method. With a total of 1400 clusters using the Alexandrowicz (600) and Leath (800) methods of growing, we found that the best data

---

**FIG. 4.** Scaling functions \( \Phi(y) \), \( \Delta \phi(y) \), and \( \Delta \Phi(y) \) as discussed in the text are plotted against the similarity variable \( y = l/t^{1/d_w} \), with \( l \) having a range from 0 to 400. The symbols specify different times: \( \bigcirc \), \( t=500 \); \( \bigcirc \), \( t=1000 \); \( \bigtriangleup \), \( t=2500 \); \( \bullet \), \( t=5000 \); and the solid lines are obtained from smoothing the collapsed data. In this plot \( d_s = 1.30 \) and \( d_w = 2.50 \).

---

**FIG. 5.** \( |\ln \Phi(y)| \) is plotted against the similarity variable \( y \) on a logarithmic scale. The symbols specify different times: \( \bigcirc \), \( t=500 \); \( \bigcirc \), \( t=1000 \); \( \bigtriangleup \), \( t=2500 \); \( \bullet \), \( t=5000 \); and the solid line is obtained from smoothing the collapsed data. We see that the scaling function \( \Phi(y) \) is asymptotically a stretch exponential with the power \( \beta = 1.65 \pm 0.05 \) when choosing \( d_s = 1.30 \) and \( d_w = 2.50 \).
collapse was obtained when $d_s = 1.30 \pm 0.02$ and $d_{sw} = 2.47 \pm 0.05$ yielding the power $\beta = 1.65 \pm 0.05$ as above. The uncertainties in these numbers were determined from the extreme limits on successful data collapse.

As a consistency check, we consider the configurational average of the PCM as given in Eq. (3.12). First, we consider the mean-square displacement which is given by the trace of the PCM. In this case, we have

$$
\langle R(t)^2 \rangle \approx \frac{2 \int_0^t l' \Phi(l, t) dl}{\int_0^t G(l) \Phi(l, t) dl}.
$$

(3.17)

Performing a configurational average over an ensemble of clusters of a given chemical distance, the scaling behavior of the time dependence can be obtained from Eq. (3.17) by simply replacing $I'_w(l)$ and $G(l)$ by their configurational averages. As shown in Appendix A, $I'_w(l) \propto c \delta^l$ where $d_t$ satisfies the scaling law

$$
d_t = (2 + d_f) d_t / d_f.
$$

(3.18)

Using $d_f = 1.896...$ and the known estimate of $d_t$ ($1.87 \pm 0.04$), the scaling law predicts $d_t$ to be $3.43 \pm 0.08$ (which agrees with the exponent value of $3.36 \pm 0.01$ as determined by our simulation). Using the above scaling forms, and changing the integration variable from $l$ to $y$, the configurational average of the mean-square displacement at long times is given as

$$
\frac{\int_0^{y^{1/4w}} y^{d_t-1} \Phi(y) dy}{\int_0^{y^{1/4w}} y^{d_f-1} \Phi(y) dy}.
$$

(3.19)

Since the integrands decay exponentially at long times, the upper limit of integration may be approximated by infinity. Noting further that $d_t / d_w$ is equal to $d_f / d_w$, we finally obtain

$$
\langle R^2(t) \rangle \sim t^{2/d_w}.
$$

(3.20)

Thus the correct power-law dependence of the mean-square displacement on time is recovered from the trace of the PCM matrix. Using the same arguments as above except replacing $I'_w(l)$ in Eq. (3.17) with $\Delta I'(l)$, it follows that the leading time dependence for $\langle \Delta Q(t) \rangle$ is the same as the mean-square displacement. Thus, in the case of tracer diffusion, anisotropic effects increase with time as the walkers explore more and more of the cluster.

Equation (3.9) should be an excellent approximation for the PCM in the long-time limit for finite clusters. In the blind-ant model, we note that at long times $\tilde{p}(l, t)$ approaches the asymptotic value of $1/N$ ($N$ being the size of the cluster) independent of $l$ and thereby reduces the PCM of Eq. (3.9) to the radius of gyration tensor.

We next assess the approximations made in Eq. (3.12) through studying the evolution of the PCM first by numerically calculating the right-hand side of this equation for a set of randomly generated clusters and then comparing these results with the actual ones obtained from the exact enumeration method. In the anomalous diffusion regime ($a \ll t^{1/d_w} \ll \xi$), we may incorporate the scaling form for $\tilde{p}(l, t)$ explicitly. This reduces Eq. (3.12) to

$$
\tilde{T}(t) \approx \int_0^t T'(l) \Phi(l/t^{1/d_w}) dl.
$$

(3.21)

The evaluation of the right-hand side of Eq. (3.21) consisted of generating a cluster, calculating the number of sites and the moment of inertia tensor for each chemical-distance shell, and then numerically summing the integrals using the smoothed numerical fit for the scaling function $\Phi$. To facilitate this, the scaling function is stored in a table consisting of $y$ and $\Phi(y)$. The scaling variable is calculated for each chemical distance at each time of interest. The method of linear extrapolation was used to find $\Phi(y)$ for values of $y$ not contained in the table. Furthermore, we only expect reasonable comparison for $t^{1/d_w} \gg a$ where the scaling form for $\tilde{p}(l, t)$ is valid.

A plot of $\langle R(t)^2 \rangle$ against $t$ as well as $\langle \Delta Q(t) \rangle$ against $t$ on a logarithmic scale is given in Fig. 6 for both the mean-field approximation and the actual data. In this case the bar denotes an average over 23 clusters. Also in Fig. 7 the typical accuracy of the approximation for

**FIG. 6.** We compare the mean-field-theory (MFT) results to the exact results of a configurational average over 23 clusters for the dynamical quantities $\langle R(t)^2 \rangle$ and $\langle \Delta Q(t) \rangle$ vs time on a logarithmic scale. The mean-field result for $\langle R(t)^2 \rangle$ is denoted by $\circ$ and $\langle \Delta Q(t) \rangle$ is denoted by $\times$. The solid lines going through the symbols are the exact results.
IV. GENERALIZED LANGEVIN EQUATION

The mean-field equation for the PCM described in Sec. III is adequate for describing the typical random motion of one particle confined to a percolation cluster. In this section, we describe the typical random motion in a given medium of a collection of noninteracting particles, using a generalized Langevin equation of irreversible thermodynamics. From the GLE, an evolution equation for the velocity-correlation matrix can be expressed in the language of fractional calculus. The equation is solved for the velocity-autocorrelation function and is compared with the blind-ant VACF obtained from simulations on two-dimensional critical percolation clusters.

The VCM $\overline{X}(t)$ is defined by

$$\overline{X}(t) = \langle V(t)V^T(0) \rangle_{eq},$$

where $V(t)$ is the velocity of the particle at time $t$, and the subscript $eq$ denotes the expectation with respect to the equilibrium state. The frequency-dependent diffusion tensor $\overline{D}(\omega)$ is determined from the VCM via the first fluctuation dissipation theorem to be

$$\overline{D}(\omega) = \int_0^\infty e^{-i\omega t} \overline{X}(t) dt.$$  \hfill (4.2)

This fluctuation dissipation relation reduces the problem of calculating the frequency-dependent diffusivity for a fractal medium to that of determining the VCM. Furthermore, according to the Einstein relation the ac conductivity is proportional to the frequency-dependent diffusivity of the charge carriers.

The VCM can be numerically calculated using the exact enumeration method. The time $t$ is taken to be discrete and the velocity of a particle at time $t$ is defined as

$$V(t) = R(t + 1) - R(t).$$

(4.3)

Basically, with each cluster of $N$ sites there is an associated transition probability matrix $W$ whose elements $w_{ij}$ represent the probability of the random walker to be at site $i$ at time $t$ given that it is at site $j$ at time $t$. If the initial starting probabilities on the cluster are given by an $N$-dimensional state vector $p$, then the occupation probability vector $p(t)$ at time $t$ is determined by

$$p(t) = W^tp,$$

(4.4)

which is a simple Markoff chain. Since Eq. (4.2) is valid only when the VCM describes fluctuations from the equilibrium state, the initial state vector is chosen to be the stationary state $p_\infty$, which satisfies $Wp_\infty = p_\infty$.

We now elucidate the properties of the VCM tensor. First it is symmetric, i.e.,

$$\langle V_x(t)V_y(0) \rangle = \langle V_y(t)V_x(0) \rangle.$$  \hfill (4.5)

This symmetry follows from the detailed balance property of the transition probability matrix $W$ for blind-ant random walks. The proof of this symmetry property is presented in Appendix B. The symmetry property of the VCM implies that the frequency-dependent diffusivity and conductivity tensors are symmetric.

Furthermore, it has been established that when $\langle R(t)^2 \rangle \sim t^{1-\gamma}$, where $0 < \gamma < 1$, the VACF satisfies

$$\int_0^\infty \langle V(t)\cdot V(0) \rangle dt = \int_0^\infty \text{Tr} \overline{X}(t) dt = 0,$$  \hfill (4.6)

and (for the blind-ant model) has the asymptotic property

$$\text{Tr} \overline{X}(t) \sim -at^{-1+\gamma} \quad (t \to \infty, \ a > 0).$$

(4.7)

The negative long-time tail in the VACF implies that a particle will tend to reverse its direction of motion relative to its initial step. Thus a particle on an infinite percolating cluster retains an infinitely long memory of its initial velocity. Although the random motion of a particle can be represented by a stochastic Markoff process as discussed above, the disadvantage of this approach is that the entire cluster configuration needs to be expressed
via the transition matrix. However, by reducing the size of the state space from the entire configurational details down to the particle's velocity, we may describe the antipersistent motion which makes the diffusion anomalous using a non-Markovian random process.

To describe the random motion with memory in the particle's velocity, the classical Langevin equation is not appropriate and a generalized Langevin equation becomes necessary. The GLE is given by

$$\frac{d\mathbf{V}}{dt} = - \int_0^t \alpha(t-\tau) \cdot \mathbf{V}(\tau) \, d\tau + \frac{\mathbf{F}(t)}{m},$$

(4.8)

where $m$ is the mass of the particle, $\mathbf{F}(t)$ is the random force on the particle, and $\alpha(t)$ is the effective friction kernel tensor induced by the disorder. In the Langevin formalism, the friction kernel accounts for all systematic random forces that are correlated with the particle's velocity and the remaining random force $\mathbf{F}(t)$ is assumed to be uncorrelated to the initial velocity such that

$$(\mathbf{V}(0)\mathbf{F}(t)) = \bar{0}.$$  

(4.9)

The random force $\mathbf{F}(t)$ must further satisfy the second fluctuation dissipation theorem expressed as

$$(\mathbf{F}(0)\mathbf{F}(t)) = m^2 \alpha(t) \cdot \bar{\mathbf{v}}(0)$$

(4.10)
in order to enforce the ensemble to be stationary.

We have observed numerically that when stationary initial conditions are used the diagonal components of the VCM are nearly equal and that the off-diagonal components are typically two orders of magnitude smaller. Although the Brownian motion is typically anisotropic about any given point within the percolation network, the result of using a stationary initial distribution is to average over all the locally preferred directions, thereby regaining essentially isotropic diffusion. Since the ensemble-averaged diffusion on two-dimensional percolation clusters is approximately isotropic, we can consider the friction kernel to be a scalar and the motion along any direction is then described by a scalar GLE

$$\frac{dV}{dt} = - \int_0^t \alpha(t-\tau) V(\tau) d\tau + \frac{F(t)}{m}. $$

(4.11)

We have previously shown for the random process of Eq. (4.10) that if the VACF has the asymptotic property of Eq. (4.7), as in the case of the blind-ant model, then the friction kernel decays asymptotically as $\alpha(t) \sim bt^{-(1+\gamma)}$, where $b$ is a positive constant. We now make the assumption that we can model the diffusion process on the infinite percolation cluster with a friction kernel given strictly by

$$\alpha(t) = \frac{\alpha_0}{\Gamma(\gamma)} t^{-1+\gamma},$$

(4.12)

valid at all times where $\Gamma(x)$ is the gamma function. The power-law friction kernel of Eq. (4.12) has the nice property that enables the GLE to be written in terms of a fractional derivative. The fractional derivative of order $\mu$ of a function $f(t)$ is defined by Oldham and Spanier as

$$D^\mu f(t) \equiv \frac{1}{\Gamma(-\mu)} \int_0^t (t-\tau)^{-\mu-1} f(\tau) \, d\tau.$$  

(4.13)

Using the above definition, we can find the solution to any GLE that falls in the class given by

$$\frac{dv}{dt} = -\alpha_0 D^{-\gamma} v(t) + \frac{F(t)}{m}.$$

(4.14)

Although Eq. (4.14) is an approximation to the true GLE needed to derive the VACF, it has the advantage that it can be solved analytically.

Proceeding to solve for the VACF resulting from Eq. (4.14), we obtain an expression for the VACF given by

$$\frac{d\chi(t)}{dt} = -\alpha_0 D^{-\gamma} \chi(t),$$

(4.15)

where use of Eq. (4.9) has been made. On taking the Laplace transform of Eq. (4.15) and using the initial condition $\chi(0) = 1$, we find

$$\hat{\chi}(s) = \frac{s^\gamma}{s^{1+\gamma} + \alpha_0^2},$$

(4.16)

where the caret denotes the Laplace transform. We first note from Eq. (4.16) that

$$\hat{\chi}(0) = \int_0^\infty \chi(t) dt = 0,$$

(4.17)

which satisfies the condition of Eq. (4.6) for anomalous diffusion on the infinite percolating cluster at the critical threshold. Furthermore, Eq. (4.16) can be inverted analytically (Appendix C) to obtain the VACF for all time as

$$\chi(t) = -\frac{\alpha_0}{\pi} \sin \pi \gamma \int_0^\infty \frac{r^\gamma e^{-tr}}{r^{2(1+\gamma)} + \alpha_0^2 + 2 \alpha_0 \cos \pi(1+\gamma)r^{1+\gamma}} \, dr + \frac{2}{1+\gamma} \exp(at \cos \phi) \cos(at \sin \phi).$$

(4.18)

The long-time behavior of the VACF is obtained from an asymptotic analysis of Eq. (4.18) as shown in Appendix C and is given by

$$\lim_{t \to \infty} \chi(t) \sim -\frac{\gamma \Gamma(\gamma) \sin \pi \gamma}{\alpha_0 \pi} t^{-(1+\gamma)},$$

(4.19)

which agrees with Eq. (4.7) ensuring anomalous diffusion.

The integral in Eq. (4.18) has been numerically performed and the resulting VACF is compared in Fig. 8 with the actual blind-ant VACF obtained from the exact enumeration method. The choice of the exponent
FIG. 8. We compare the VACF as calculated using Eq. (4.18) to the simulation results. The solid line is the prediction of Eq. (4.18) and the squares represent data obtained for blind-ant random walks by exact enumeration. We see that there is excellent agreement for the choice of $\alpha = 3.00$ and $\gamma = 0.27$. The initial period before the power-law behavior is attained is not shown in this log-log plot as the VACF does not have a definite sign.

$\gamma = 0.27$ and the constant $\alpha_0 = 3.00$ was used to match the data from computer simulation. Although no attempt was made to optimize the fit, the predictions of the GLE are in excellent agreement with the simulation data for times greater than 10. Thus the simple power-law friction kernel appears to be an excellent approximation to model the anomalous diffusion and the GLE of Eq. (4.14) provides an adequate equation of motion for the VACF.

We now briefly consider the problem of relating the friction kernel tensor to the cluster structure in situations where the anisotropic effects are not insignificant. Whereas this problem is difficult to solve in general, the connection is readily made for cases where the average of tracer diffusion over an ensemble of clusters yields the same VACF as stationary diffusion on a single cluster. Under such conditions we have

$$\chi(t) = \frac{1}{2} \frac{d^2}{dt^2} \bar{P}(t)$$

and the friction tensor can be related to the cluster geometry.

Finally, we remark that, while the GLE provides a useful characterization of the fractal medium and an adequate equation of motion for the VACF, it can also be used to simulate fractal diffusion when proper identification of the random force can be made.

V. SUMMARY

This paper is a continuation of our efforts$^9,10$ to establish evolutionary laws for diffusion in fractal media. In our previous efforts, we have investigated the properties of the VACF for anomalous diffusion, which conveys information about the nature of the random motion and can further be used in conjunction with the principles of linear-response theory to derive expressions for the frequency-dependent diffusivity. The three main developments of this paper are (i) the study of the anisotropy of percolation clusters and tracer diffusion on those clusters (Sec. II), (ii) the formulation of a mean-field equation for the PCM for tracer diffusion (Sec. III), and (iii) the formulation of an equation of motion using fractional calculus for the VACF (which governs the anomalous diffusion) (Sec. IV).

From the study of random walks starting from one origin we find that the geometric anisotropic properties of the clusters directly influence the anisotropy of the diffusion process around the local region. The typical walk is anisotropic about any given origin, although any principal direction of the diffusion is equally probable. Thus, when many starting points are averaged over (using a stationary initial condition), the diffusion appears essentially isotropic because self-averaging over many regions removes the global anisotropy. For this reason, to determine the frequency-dependent diffusivity via the VCM, a scalar representation for the diffusion process is adequate, although the physical picture is that a collection of many different skewed random motions are actually occurring.

We describe tracer diffusion on a cluster in terms of the PCM which yield the second moments of the probability density of position $p(x,y;t)$. We derive a mean-field approximation in terms of the moment of inertia as a function of the chemical distance from the origin. The anisotropy in the PCM reflects the changing anisotropy of successive shells within the cluster as the diffusing particle explores a greater chemical distance. The simplest model for diffusion on a given cluster features the exact specification of its moment of inertia and number of sites as a function of chemical distance. Then the PCM is just the radius of gyration tensor of the cluster where the sites within a chemical distance $l$ are weighted by the average probability per site $\bar{P}(l,t)$ that a random walker is located at a site in the $l$th shell at time $t$. The quantity $\bar{P}(l,t)$ is a configurationally averaged probability and does not depend on the details of a particular cluster. In addition to giving us a nice physical picture of the diffusion process, the mean-field approximation of Eq. (3.12) for the PCM captures the essential physics quite accurately and therefore has potential to serve as a basis in further theoretical developments such as the derivation of an evolution equation for $P(x,y;t)$.

We have considered a certain class of generalized Langevin equations for anomalous diffusion in fractal media featuring a random force and a friction kernel that decays as a simple power law at all times. From the GLE of Eq. (4.14) we obtain an equation of motion for the VACF which is neatly cast in the notation of fractional calculus. The resulting equation Eq. (4.15) is solved analytically and its solution is compared to the
VACF obtained from simulations of blind-ant random walks on two-dimensional percolation clusters. Except for very short times (less than ten steps), the agreement is excellent. Restricting the random walks to the blind-ant model, the specification of the amplitude and exponent of the friction kernel serves to characterize the fractal medium as far as diffusion is concerned. We also note that the GLE can be effectively used to simulate diffusion in fractal media once the statistical properties of the random force are determined. This aspect is currently under investigation. The GLE has the potential to serve as a starting point for deriving the partial differential equations of diffusion (the analogs of the Fokker-Planck and Smoluchowski equations), which are convenient for treating boundary-value problems. An additional usefulness of the GLE approach is that it serves as a general formalism for the study of fluctuations in macroscopic variables.

ACKNOWLEDGMENTS

We thank F. Family for correspondence and for informing us of work done previously on the anisotropy of critical percolation clusters. D. R. and R. M. are grateful to the School of Chemical Engineering at Purdue University for a grant that made this research possible. H. N. and D. J. are grateful to the Office of Naval Research for a grant that made this research possible.

APPENDIX A: SCALING PROPERTIES OF THE MOMENT OF INERTIA

Using simple scaling arguments we show that the configurational average of the moment of inertia \( I_{av} = (I_x + I_y)/2 \) satisfies a power law in terms of the maximum chemical distance given by

\[
I_{av}(l) \sim l^{d_1}.
\]

(A1)

The scaling behavior for \( I_{av} \) follows from

\[
I_{av}(l) = \frac{1}{2} \int_0^l r(l')^2 G(l') \, dl'
\]

(A2)

for a given cluster, where \( r(l) \) is the mean Euclidean distance from the origin to the sites in shell \( l \) of the cluster. Taking the configurational average and noting the scaling behavior \( G(l) \sim l^{d_1 - 1} \) and \( r(l) \sim l^{d_1/d_1} \), the leading behavior for \( I_{av}(l) \) is given by

\[
I_{av}(l) \sim l^{(2 + d_1) d_1/d_1}.
\]

(A3)

From Eqs. (A1) and (A3), we obtain the scaling law

\[
d_1 = (2 + d_1) d_1/d_1.
\]

(A4)

APPENDIX B: Symmetry of the Velocity-Correlation Matrix

The symmetry of the VCM, implying that \( \langle V_x(t) V_y(0) \rangle_{eq} \) is identically equal to \( \langle V_y(t) V_x(0) \rangle_{eq} \), arises because the transition probability matrix \( W \) satisfies detailed balance with respect to the stationary state \( p_{\infty} \equiv (p_1, \ldots, p_N) \). The detailed balance condition is expressed as

\[
W_{ij} p_i = W_{ji} p_j \quad \forall i, j,
\]

(B1)

where \( W_{ij} \) is the transition probability from site \( j \) to site \( i \) and \( p_j \) is the value of the stationary distribution at site \( j \). No summation is implied by the repeating indices.

We first show by mathematical induction that if \( W \) satisfies detailed balance as defined above, then \( W^n \) will also satisfy detailed balance. Assuming that the \( W^{n-1} \) matrix as well as the \( W \) matrix both obey detailed balance, it follows that

\[
(W^n)_{ij} p_j = \sum_k W_{ik}(W^{n-1})_{kj} p_j
\]

\[
= \sum_k W_{ik}(W^{n-1})_{kj} p_k
\]

\[
= \sum_k (W^{n-1})_{ik} W_{ki} p_i = (W^n)_{ji} p_i.
\]

(B2)

This proves that the \( W^n \) matrix must satisfy detailed balance for all \( n \geq 1 \).

We proceed by noting that

\[
\langle V_x(n) V_y(0) \rangle_{eq} = \langle [X(n + 1) - X(n)] [Y(1) - Y(0)] \rangle_{eq},
\]

(B3)

which implies that the VCM is symmetric if \( \langle X(n) Y(0) \rangle_{eq} \) is identically equal to \( \langle Y(n) X(0) \rangle_{eq} \) and if the use of the stationarity is made. Observing that

\[
\langle X(n) Y(0) \rangle_{eq} = \sum_{i,j} x_i y_j (W^n)_{ij} p_j
\]

\[
= \sum_{i,j} y_j x_i (W^n)_{ji} p_i = \langle Y(n) X(0) \rangle_{eq},
\]

(B4)

where \( (x_i, y_i) \) denote the position coordinates of site \( i \) of the cluster, we have established the symmetry of the VCM.

APPENDIX C: Solution for the VACF Using a Power-Law Friction Kernel

We have from Eq. (4.16) the Laplace transform for the VACF given as

\[
\tilde{\chi}(z) = \frac{z^\gamma}{z^{1+\gamma} + \alpha_0},
\]

(C1)

and choosing the principal branch such that \(-\pi < \arg z < \pi\), the only singularities are at

\[
z_\pm = a e^{\pm i\phi} \quad \text{with} \quad a = \alpha_0^{1/(1+\gamma)}, \quad \phi = \frac{\pi}{1 + \gamma}.
\]

(C2)
Since $0 < \gamma < 1$, we have $\pi/2 < |\phi| < \pi$, so that the singularities are in the left half of the complex plane. Except for these isolated singularities, $\tilde{\chi}(z)$ is analytic in the left half plane, and noting that the origin is a branch point, we can obtain $\chi(t)$ from the complex inversion formula

$$
\chi(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \tilde{\chi}(z)e^{zt}dz = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{zt} \frac{z^{\gamma}}{z^{1+\gamma} + \alpha_0}dz,
$$

where $c > 0$. The contour for evaluating the integral is shown in Fig. 9. Applying the residue theorem to this contour, we have

$$
\int_{c-iR}^{c+iR} + \int_{C_R} + \int_{C_R^*} + \int_{C_1} + \int_{C_2} + \int_{C_3}

= 2\pi i \sum_{k=1}^{3} \text{res}_k[\tilde{\chi}(z)e^{zt}].
$$

The contributions from $C_R$ and $C_R^*$ vanish on letting $R$ go to infinity while the contribution from $C_3$ vanishes on letting $\epsilon$ shrink to zero so that

$$
\chi(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \tilde{\chi}(z)e^{zt}

= \frac{-1}{2\pi i} \left( \int_{C_1} + \int_{C_2} \right) + \sum_{k=1}^{2} \text{res}_k[\tilde{\chi}(z)e^{zt}].
$$

Computing the residues at the simple poles we obtain

$$
\chi(t) = \frac{-\alpha_0}{\pi} \sin \pi \gamma \int_0^{\infty} \frac{r^{\gamma} e^{-tr}}{r^{2(1+\gamma)} + \alpha_0^2 + 2\alpha_0 \cos \pi(1+\gamma)r^{1+\gamma}} dr + \frac{2}{1+\gamma} \exp(at \cos \phi) \cos(at \sin \phi),
$$

which is the complete expression for $\chi(t)$. We now find the leading long-time behavior of $\chi(t)$ by first observing that the second term decays exponentially and is negligible compared to the integral term which arises from the branch point at the origin. Furthermore, the principal contribution of the integral at long times comes from the region close to the origin so that we have, on making a Taylor series expansion,

$$
\lim_{t\to\infty} \chi(t) \sim \frac{-\sin \pi \gamma}{\pi \alpha_0} \int_0^{\infty} e^{-tr} r^{\gamma} \left( 1 - \frac{2r^{1+\gamma} \cos(1+\gamma)}{\alpha_0} \right) dr,
$$

or to leading order

$$
\lim_{t\to\infty} \chi(t) \sim \frac{-\sin \pi \gamma}{\pi \alpha_0} \int_0^{\infty} r^{\gamma} e^{-tr} dr.
$$

Using the definition of the $\gamma$ function and using the property $\Gamma(1+z) = z\Gamma(z)$, we finally obtain

$$
\lim_{t\to\infty} \chi(t) \sim \frac{-\gamma \Gamma(\gamma)}{\alpha_0 \pi} t^{-(1+\gamma)}.
$$
DIFFUSION ON TWO-DIMENSIONAL PERCOLATION

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6. Almost all the analysis has been on identifying the mean-square displacement from the origin or on estimating probability densities of the random walker's position as a function of the distance from the origin and time. See, for example, B. O'Shaughnessy and I. Procaccia, Phys. Rev. A 32, 3073 (1985); and S. Havlin, D. Movshovitz, B. Trus, and G. H. Weiss, J. Phys. A 18, L719 (1985).
18. We have observed, for example, that, for a given set of clusters, the anisotropy amplitude $\tilde{A}$ with respect to the seed site is about 25% lower (more anisotropic) than that with respect to the center of mass. This is not surprising if one imagines a circular configuration, but an ellipsoidal configuration allows for the possibility that the ratio $A$ may increase or decrease depending on where the origin is translated. We are continuing the study of the anisotropy of percolation clusters in the $(p,N,t)$ ensemble.