Stochastic transport in heterogeneous media with multiple families of transport paths

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We examine in detail a model for transport in heterogeneous solids and porous media which contain N distinct families of transport paths (with $N \geq 2$), recently proposed by the authors [Phys. Rev. Lett. **70**, 2581 (1993)]. The model is relevant to transport in metals, polycrystals, porous catalysts, coalbed methane reservoirs, and geological systems with fractures and pores. We develop a number of exact results for the one-dimensional case and, more generally, study the behavior of its effective transport properties using an effective-medium approximation, which yields several exact results in one spatial dimension.

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I. INTRODUCTION

Transport in heterogeneous media is relevant to many phenomena in physics and engineering, and has been long studied [1]. A wide variety of concepts and techniques have been developed and applied, yielding considerable insight into, and information about, transport in disordered media. However, to date, most studies have been restricted to heterogeneous media in which the disorder is associated with a *single* family of transport paths, characterized by a single transport coefficient. For example, isotropic porous media are characterized by a single porosity, and permeability or electrical conductivity, and the transport process is described by a single transport equation.

In a great many cases, this simple description is totally inadequate [1,2], and transport *cannot* be described by a single classical transport equation. There are several systems of scientific and industrial importance in which transport takes place through two or more distinct families of transport paths. For example, most natural rock masses consist of interconnected and intertwined networks of *fractures* and *pores* [1–3], which implies *two* distinct porosities, one of which is contributed by the fractures (normally about 0.01–0.06), while the other one is contributed by the pores (usually about 0.1–0.15). In some cases, e.g., carbonate rocks, one needs *three* degrees of porosity for characterizing rock [4]. Although most of the porosity is contributed by the pores, the fractures provide the most effective transport paths. Moreover, transport along the pores and fractures are very different. For example, if the fracture network is sample spanning, it may be thought of as the backbone of the system in which transport occurs, while the porous matrix may act as a capacitor which is charged by exchange with adjacent fractures. We shall discuss this further in Sec. VII where we derive some exact results for a one-dimensional system. A second example is provided by porous catalyst particles which usually contain very large pores (*macropores*) and very small pores (*micropores*) [5]. The existence of two distinct types of pores gives rise to considerable complications in modeling transport in porous catalysts. For example, transport in the micropores is hindered (restricted) in comparison with that in the macropores [6] because the size of the transporting molecules is often comparable with the size of the micropores. Moreover, while it is easy for the molecules to enter the macropores from the micropores, the reverse is not true, implying that the rates of exchange between the two types of pores are not equal.

Metals and polycrystals provide another example to which our study is directly relevant. In these materials, transport often proceeds simultaneously through *two* distinct families of paths, the *bulk* and the *grain boundaries, dislocations and internal cracks* [7]. Finally, coalbed methane reservoirs provide another important example of a system with distinct families of transport paths. Such reservoirs are made of large fractures and very small pores. It is widely accepted that production of methane gas, originally adsorbed on the coalbed matrix, occurs by desorption from the matrix and its subsequent diffusion towards fractures. However, the pores are so small that they do not allow the influx of water from the fractures, and their sizes are also comparable to the size of the methane molecules. Thus molecular transport in the fractures of coalbed methane reservoirs is very different from that in the pores.

In general, if there are N distinct families of transport paths, the system should be modeled by N coupled transport equations, with the coupling needed to account for the *exchange* between the various transport paths. As we shall show below, aside from its practical importance, the rigorous investigation of the properties of such transport processes for dimensions $d \geq 2$ is a difficult problem of considerable mathematical interest. Recently, we presented [8] a theory of transport in disordered systems to account for multiple transport paths. In the degenerate case of zero disorder, our model is equivalent to a random-walk process with N internal states [9,10], while in the degenerate case of a single transport path it

reduces to the randomized master equation [11–13].

In this paper we describe the model in detail in Sec. II. We address the problem of matching the ensemble-averaged system (averaged over the spatial disorder) to a uniform system with time correlations or memory effects in Sec. III. If such a uniform system is determined, the macroscopically observable transport properties are easily extracted; this is discussed in Sec. IV. The required matching may be achieved approximately using an effective-medium approximation (EMA), which is discussed in Sec. V, leading to predictions of macroscopic transport properties whose determination is described in Sec. VI. Exact analysis in one dimension, presented in Sec. VII, confirms some of the predictions of the EMA. Section VIII contains some discussion and predictions based on scaling arguments.

II. MODEL

We consider the following evolution equation, which is the natural generalization of the familiar master equation on a d-dimensional lattice to accommodate the existence of N distinct transport paths:

$$\frac{\partial \mathbf{P}_i(t)}{\partial t}=\sum_j [\mathbf{W}_{ij}\mathbf{P}_j(t)-\mathbf{W}_{ji}\mathbf{P}_i(t)]+\mathbf{E}_i\mathbf{P}_i(t) . \quad (1)$$

Here $\mathbf{P}_i(t)$ is a column vector, the dimension of which corresponds to the number of distinct transport paths. The sth component of $\mathbf{P}_i(t)$ gives the probability that at time t, a randomly moving particle will be found in path s at lattice site i. The *transition matrix* $\mathbf{W}_{ij}$ governs the rate at which the bond joining sites i and j is crossed. The ss' component of this matrix gives the rate at which particles in path s' at site j move to path s at site i. The *exchange matrix* $\mathbf{E}_i$ gives the rate of transition between transport paths at site i.

To ensure that probabilities are conserved, we require that

$$\frac{\partial}{\partial t}(1,1,\ldots,1)\sum_i \mathbf{P}_i(t)=0 . \quad (2)$$

It is easy to verify directly from Eq. (1) that this is guaranteed if we insist that

$$(1,1,\ldots,1)\mathbf{E}_i=\mathbf{0} . \quad (3)$$

If the underlying lattice is translationally invariant, if the transition matrix $\mathbf{W}_{ij}$ is a function only of the relative position of sites i and j, and if the exchange matrix $\mathbf{E}_i$ is independent of position, Eq. (1) is easily solved by Fourier analysis. To illustrate the more general situation, consider a one-dimensional system with two paths for which transitions between sites are restricted to nearest-neighbor sites, so that for $j=i\pm1$,

$$\mathbf{W}_{ij}=\begin{bmatrix}\alpha_{ij} & 0\\ 0 & \beta_{ij}\end{bmatrix}, \quad \mathbf{E}_i=\begin{bmatrix}-\mu_i & \nu_i\\ \mu_i & -\nu_i\end{bmatrix} . \quad (4)$$

In this case, Eq. (1) is equivalent to two scalar equations which are spatially discretized versions of the usual equations of continuum double diffusion in one space dimension.

As our model of a disordered medium with N distinct families of transport paths, we make the following assumptions.

(a) All lattice sites are topologically equivalent. The set of nearest neighbors of site i will be denoted by $\{i\}$, so that $j\in\{i\}$ means that site j is a nearest neighbor of site i. The coordination number of the lattice (the number of nearest neighbors for each site) will be denoted by z.

(b) The transition matrix $\mathbf{W}_{ij}$ is nonzero only when the sites i and j are nearest neighbors.

(c) The transition matrices are symmetric: $\mathbf{W}_{ij}=\mathbf{W}_{ji}$.

(d) The transition matrices $\mathbf{W}_{ij}$ are independent, identically distributed random variables.

(e) The exchange matrices $\mathbf{E}_i$ are independent, identically distributed random variables.

(f) The $\mathbf{W}_{ij}$ and $\mathbf{E}_k$ matrices are mutually independent.

It is not assumed that for a given matrix $\mathbf{W}_{ij}$ or $\mathbf{E}_k$ the individual components are independent. Assumptions (d)–(f) may be relaxed, but are imposed here for simplicity.

The explicit solution of Eq. (1) for a given realization of the disorder is unlikely to be available (except in one dimension) and indeed is not of particular interest. We require a statistical characterization of the large-scale effective transport properties of the system. In one dimension, some exact results can be derived (see Sec. VII), but apart from this case (and perhaps for the Bethe lattice and similar structures [14]), exact solution of this problem is unlikely. We develop in Sec. III an exact but implicit formalism for matching the random system to a uniform system with an effective transition matrix which is the same for all bonds and an effective exchange matrix which is the same for all sites. A discussion of the physical interpretation and history of the exact formalism and the EMA in the case of a single family of transport paths has been given previously [13]. Before embarking on an analysis of the problem, we summarize here some notational conventions.

(a) If $f(t)$ is a scalar-valued, vector-valued, or matrix-valued function of the time t, its Laplace transform is

$$\hat{f}(\lambda)=L\{f(t):\, t\to\lambda\}=\int_0^\infty f(t)e^{-\lambda t}dt . \quad (5)$$

(b) For brevity, the explicit dependence on the Laplace transform variable λ will often be suppressed.

(c) The zero and identity matrices are denoted by $\mathbf{0}$ and $\mathbf{I}$, respectively.

(d) The diagonal matrix with diagonal elements (in order) $\rho_1,\rho_2,\ldots,\rho_N$ is denoted by $\mathrm{diag}\{\rho_1,\rho_2,\ldots,\rho_N\}$ or, more briefly, by $\mathrm{diag}\{\rho_n\}$.

III. GENERAL FORMALISM

We attempt to match the random system to an "equivalent" uniform system. The matching procedure is performed in the Laplace transform domain. As $\mathbf{W}_{ij}=\mathbf{W}_{ji}$, the original equation (1) becomes

$$\lambda\hat{\mathbf{P}}_i-\mathbf{P}_i(0)=\sum_{j\in\{i\}}\mathbf{W}_{ij}[\hat{\mathbf{P}}_j-\hat{\mathbf{P}}_i]+\mathbf{E}_i\hat{\mathbf{P}}_i\ . \tag{6}$$

This equation is to be matched to the equation

$$\lambda\hat{\mathbf{P}}_i^0-\mathbf{P}_i(0)=\sum_{j\in\{i\}}\mathbf{W}^0[\hat{\mathbf{P}}_j^0-\hat{\mathbf{P}}_i^0]+\mathbf{E}^0\hat{\mathbf{P}}_i^0\ . \tag{7}$$

Here a superscript zero is used to distinguish the probability in the original system from that in the uniform system and to flag the two matrices which characterize the uniform system. However, we insist that both systems have the same initial condition, hence the presence of the same term $\mathbf{P}_i(0)$ on the left-hand side of Eqs. (6) and (7).

The effective transition matrix $\mathbf{W}^0=\mathbf{W}^0(\lambda)$ and the effective exchange matrix $\mathbf{E}^0=\mathbf{E}^0(\lambda)$ are functions of the Laplace transform variable λ. Hence, in the time domain, the random system is actually being matched to a *generalized master equation* with N families of transport paths:

$$\frac{\partial}{\partial t}\mathbf{P}_i^0(t)=\int_0^t\sum_{j\in\{i\}}\check{\mathbf{W}}(t-t')[\mathbf{P}_j^0(t')-\mathbf{P}_i^0(t')]dt'+\int_0^t\check{\mathbf{E}}(t-t')\mathbf{P}_i^0(t')dt'\ , \tag{8}$$

where

$$\check{\mathbf{W}}(t)=L^{-1}\{\mathbf{W}^0(\lambda);\lambda\rightarrow t\} \tag{9}$$

and

$$\check{\mathbf{E}}(t)=L^{-1}\{\mathbf{E}^0(\lambda);\lambda\rightarrow t\} \tag{10}$$

are *memory kernels*. We know from earlier analyses of the problem with a single family of transport paths [13] that when transport is confined to a fractal subset of the lattice (e.g., a percolation cluster at length scales smaller than the correlation length of percolation), the memory kernel can be slowly decaying, leading to subdiffusive motion, in which the mean-square displacement of a diffusing particle on a periodic lattice grows more slowly than linearly with time.

The initial condition can be removed by subtracting Eqs. (6) and (7), and after a little rearrangement we obtain

$$(z\mathbf{I}+\mathbf{A})[\hat{\mathbf{P}}_i(\lambda)-\hat{\mathbf{P}}_i^0(\lambda)]-\sum_{j\in\{i\}}[\hat{\mathbf{P}}_j(\lambda)-\hat{\mathbf{P}}_j^0(\lambda)]=-\sum_{j\in\{i\}}\boldsymbol{\Delta}_{ij}[\hat{\mathbf{P}}_i(\lambda)-\hat{\mathbf{P}}_j(\lambda)]+\boldsymbol{\Gamma}_i\hat{\mathbf{P}}_i(\lambda)\ , \tag{11}$$

where

$$\mathbf{A}=(\mathbf{W}^0)^{-1}(\lambda\mathbf{I}-\mathbf{E}^0)\ , \tag{12}$$

$$\boldsymbol{\Delta}_{ij}=(\mathbf{W}^0)^{-1}\mathbf{W}_{ij}-\mathbf{I}\ , \tag{13}$$

$$\boldsymbol{\Gamma}_i=(\mathbf{W}^0)^{-1}(\mathbf{E}_i-\mathbf{E}^0)\ . \tag{14}$$

The matrix Green's function $\mathbf{G}_{ij}(\mathbf{A})$ for the difference operator on the left-hand side of Eq. (11) satisfies

$$(z\mathbf{I}+\mathbf{A})\mathbf{G}_{ik}(\mathbf{A})-\sum_{j\in\{i\}}\mathbf{G}_{jk}(\mathbf{A})=-\delta_{ik}\mathbf{I}\ . \tag{15}$$

Equation (11) has the formal solution

$$\hat{\mathbf{P}}_i(\lambda)-\hat{\mathbf{P}}_i^0(\lambda)=\sum_j\sum_{k\in\{j\}}\mathbf{G}_{ij}(\mathbf{A})\boldsymbol{\Delta}_{jk}[\hat{\mathbf{P}}_j(\lambda)-\hat{\mathbf{P}}_k(\lambda)]-\sum_j\mathbf{G}_{ij}(\mathbf{A})\boldsymbol{\Gamma}_j\hat{\mathbf{P}}_j(\lambda)\ , \tag{16}$$

which is exact, but only determines $\hat{\mathbf{P}}_i(\lambda)$ implicitly. However, it expresses the fluctuations in the solution of the random system from the solution of the uniform one as a sum over the fluctuations in the transition matrices $\mathbf{W}_{ij}$ (via $\boldsymbol{\Delta}_{jk}$) and the exchange matrices $\mathbf{E}_i$ (via $\boldsymbol{\Gamma}_i$), and is a convenient starting point for the construction of EMA's.

IV. THE UNIFORM SYSTEM

We defer for the moment the discussion of the implementation of the EMA to assemble some properties of the uniform system described by Eq. (7). These properties are needed to translate the EMA predictions of $\mathbf{W}^0(\lambda)$ and $\mathbf{E}^0(\lambda)$ into observable quantities and will also prepare us for some subtleties which arise in the exact analysis in one space dimension (see Sec. VII). Our attention here focuses on periodic lattices. It is possible to adapt the analysis to treelike pseudolattices [14], but we shall not do this here.

A. Matrix Green's function for periodic lattices

For d-dimensional periodic lattices, the site index i is replaced by a vector $\mathbf{r}$ with integer components. The lattice Green's function can be constructed by discrete Fourier analysis and we find in particular that the lattice Green's function at the origin is $\mathbf{G}_{00}(\mathbf{A})=-\mathbf{g}(\mathbf{A})$, where

$$\mathbf{g}(\mathbf{A})=\frac{1}{(2\pi)^d}\int_{-\pi}^{\pi}\cdots\int_{-\pi}^{\pi}\{z[1-\Lambda(\mathbf{k})]\mathbf{I}+\mathbf{A}\}^{-1}d^d\mathbf{k} \tag{17}$$

and

$$\Lambda(\mathbf{k})=z^{-1}\sum_{\mathbf{r}\in\{0\}}\exp(i\mathbf{k}\cdot\mathbf{r})\ . \tag{18}$$

We introduce a matrix $\mathbf{Q}$ to diagonalize $\mathbf{A}$, so that

$$\mathbf{Q}^{-1}\mathbf{A}\mathbf{Q}=\mathrm{diag}\{a_n\}\ . \tag{19}$$

One example of $\mathbf{Q}$ is given below in Sec. VI B. Then [15]

$$\mathbf{g}(\mathbf{A})=\mathbf{Q}\,\mathrm{diag}\{g(a_n)\}\mathbf{Q}^{-1}\ , \tag{20}$$

where

$$g(a)=\frac{1}{(2\pi)^d}\int_{-\pi}^{\pi}\cdots\int_{-\pi}^{\pi}\frac{d^d\mathbf{k}}{z[1-\Lambda(\mathbf{k})]+a} \tag{21}$$

is the value at the origin of the (scalar) lattice Green's function discussed in the Appendix. In particular, in one dimension we have

$$g(a)=[a(4+a)]^{-1/2}\ . \tag{22}$$

B. Mean-square displacement

The Laplace transform $\langle \hat{\mathbf{R}}^2(\lambda) \rangle$ of the column vector mean-square displacement

$$\langle \mathbf{R}^2(t) \rangle = \sum_{\mathbf{r}} |\mathbf{r}|^2 \mathbf{P}_{\mathbf{r}}(t) \tag{23}$$

is $-\nabla_{\mathbf{k}}^2 \tilde{\mathbf{P}}(\mathbf{k},\lambda)|_{\mathbf{k}=0}$, where

$$\tilde{\mathbf{P}}(\mathbf{k},\lambda) = \sum_{\mathbf{r}} \exp(i\mathbf{k}\cdot\mathbf{r}) \mathbf{P}_{\mathbf{r}}(\lambda) \ . \tag{24}$$

For the initial condition

$$\mathbf{P}_{\mathbf{r}}(0) = \delta_{\mathbf{r}0}\mathbf{u} \ , \tag{25}$$

taking the discrete Fourier transform of Eq. (7) we deduce that

$$\tilde{\mathbf{P}}(\mathbf{k},\lambda) = \mathbf{F}(\mathbf{k},\lambda)^{-1}\mathbf{u} \ , \tag{26}$$

where

$$\mathbf{F}(\mathbf{k},\lambda) = \lambda \mathbf{I} + z[1-\Lambda(k)]\mathbf{W}^0(\lambda) - \mathbf{E}^0(\lambda) \tag{27}$$

and $\Lambda(\mathbf{k})$ is defined by Eq. (18). We differentiate the equation

$$\mathbf{F}(\mathbf{k},\lambda)\mathbf{F}(\mathbf{k},\lambda)^{-1} = \mathbf{I} \tag{28}$$

with respect to the components of $\mathbf{k}$, let $\mathbf{k} \to \mathbf{0}$, and note that $-\nabla_{\mathbf{k}}^2 \Lambda(\mathbf{k})|_{\mathbf{k}=0} = 1$ if all bonds have unit length (as is assumed here), to deduce that

$$\langle \hat{\mathbf{R}}^2(\lambda) \rangle = z[\lambda \mathbf{I} - \mathbf{E}^0(\lambda)]^{-1} \mathbf{W}^0(\lambda) [\lambda \mathbf{I} - \mathbf{E}^0(\lambda)]^{-1} \mathbf{u} \ . \tag{29}$$

The dominant large-t behavior of $\langle \mathbf{R}^2(t) \rangle$ can be deduced via Tauberian theorems [16] from the dominant small-λ behavior of $\langle \hat{\mathbf{R}}^2(\lambda) \rangle$, although the latter has to be calculated carefully since $\mathbf{E}^0(0)$ is a singular matrix.

C. Propagator from the origin

In analyzing site occupancy probabilities it is convenient to introduce the *propagator matrix* $\mathbf{M}_{\mathbf{r}}(t)$, defined by

$$\mathbf{P}_{\mathbf{r}}(t) = \mathbf{M}_{\mathbf{r}}(t)\mathbf{u} \ , \tag{30}$$

so that

$$\hat{\mathbf{M}}_{\mathbf{r}}(\lambda) = \frac{1}{(2\pi)^d} \int_{-\pi}^{\pi} \cdots \int_{-\pi}^{\pi} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{F}(\mathbf{k},\lambda)^{-1} d^d\mathbf{k} \ . \tag{31}$$

After a little algebra, one may show that the Laplace transform of the propagator from the origin is given by

$$\hat{\mathbf{M}}_0(\lambda) = g(\mathbf{A})\mathbf{A}(\lambda\mathbf{I} - \mathbf{E}^0)^{-1} = g(\mathbf{A})(\mathbf{W}^0)^{-1} \ , \tag{32}$$

where as before $\mathbf{A} = (\mathbf{W}^0)^{-1}(\lambda\mathbf{I} - \mathbf{E}^0)$, so that $\mathbf{A}$ is a function of λ.

V. EFFECTIVE-MEDIUM APPROXIMATION

In essence, an EMA is constructed by selecting uniform system characteristics ($\mathbf{W}^0$ and $\mathbf{E}^0$) so that the effects of the fluctuations vanish on the average. This prescription can in practice only be approximately satisfied. The extent to which it is satisfied is controlled by the numbers of bonds and sites from which the fluctuation condition is constructed. We confine our attention to two cases, conveniently described as *transition disorder* and *exchange disorder*. The general case in which both transition and exchange disorder are present is much more difficult and is not treated here.

A. Transition disorder

This type of disorder corresponds to, e.g., randomness in the shapes and sizes of the microscopic elements of the transport paths. For example, in rock masses the pores are usually characterized by a pore size distribution, and the fractures by a distribution of their hydraulic conductances or apertures. For laminar flow, the flow rate q in a pore is proportional to the fourth power of its effective radius, whereas for a fracture q is proportional to the nth power of its aperture, where n can vary anywhere from 3 to 6 [1]. That is why flow in the fracture network is very different from that in the porous matrix. Thus we assume that the exchange matrices are the same for each site (so $\mathbf{\Gamma}_i \equiv \mathbf{0}$) and we write $\mathbf{E}_i \equiv \mathbf{E}^0$. We construct the *single-bond* EMA by allowing only one bond to have a transition matrix which differs from $\mathbf{W}^0$. If this bond joins sites 0 and 1, Eq. (16) reduces to

$$\hat{\mathbf{P}}_i(\lambda) - \hat{\mathbf{P}}_i^0(\lambda) = \mathbf{G}_{i0}(\mathbf{A})\mathbf{\Delta}_{01}[\hat{\mathbf{P}}_0(\lambda) - \hat{\mathbf{P}}_1(\lambda)] + \mathbf{G}_{i1}(\mathbf{A})\mathbf{\Delta}_{10}[\hat{\mathbf{P}}_1(\lambda) - \hat{\mathbf{P}}_0(\lambda)] \ . \tag{33}$$

If we note that $\mathbf{G}_{01}(\mathbf{A}) = \mathbf{G}_{10}(\mathbf{A})$ and let

$$\mathbf{G}_{00}(\mathbf{A}) = \mathbf{G}_{11}(\mathbf{A}) = -\mathbf{g}(\mathbf{A}) \tag{34}$$

we may deduce from Eq. (33) an explicit expression for the variation in $\hat{\mathbf{P}}_i(\lambda)$ across the 0-1 bond:

$$\hat{\mathbf{P}}_0 - \hat{\mathbf{P}}_1 = \left\{ \mathbf{I} + \frac{2}{z}[\mathbf{I} - \mathbf{A}\mathbf{g}(\mathbf{A})]\mathbf{\Delta}_{01} \right\}^{-1} (\hat{\mathbf{P}}_0^0 - \hat{\mathbf{P}}_1^0) \ . \tag{35}$$

To derive Eq. (35), we note from symmetry that Eq. (15) reduces for $i = k = 0$ to

$$(z + \mathbf{A})\mathbf{G}_{00}(\mathbf{A}) - z\mathbf{G}_{01}(\mathbf{A}) = -\mathbf{I} \ . \tag{36}$$

The *single-bond* EMA is constructed by requiring that

$$\langle \hat{\mathbf{P}}_0(\lambda) - \hat{\mathbf{P}}_1(\lambda) \rangle = \hat{\mathbf{P}}_0^0(\lambda) - \hat{\mathbf{P}}_1^0(\lambda) \ , \tag{37}$$

where the angular brackets denote the average over the disorder in the transition matrices, and we arrive at the self-consistency condition [17]

$$\langle \{\mathbf{I} + (2/z)[\mathbf{I} - \mathbf{A}\mathbf{g}(\mathbf{A})]\mathbf{\Delta}\}^{-1} \rangle = \mathbf{I} \ , \tag{38}$$

where $\mathbf{g}(\mathbf{A})$ is given by Eq. (34) and we have for brevity dropped the bond index 01 from Δ_{01}.

A more general formalism for constructing higher-order EMA's may be constructed by generalizing previous analyses for problems with a single family of transport paths [13,18]. A marriage of EMA and renormalization ideas is also possible [19], which improves considerably the performance of EMA.

Consider for a moment only weak disorder, so that the random variable Δ is regarded as "small." Expanding

the inverse matrix in Eq. (38) as a power series we find that for self-consistency it suffices that $\langle[\mathbf{I}-\mathbf{Ag}(\mathbf{A})]\boldsymbol{\Delta}\rangle\approx\mathbf{0}$. Assuming that $\mathbf{I}-\mathbf{Ag}(\mathbf{A})$ is nonsingular, we recover the requirement that $\langle\boldsymbol{\Delta}\rangle\approx\mathbf{0}$, which reduces to $\mathbf{W}^0\approx\langle\mathbf{W}\rangle$. We shall see from an exact result in Sec. VII that this approximation, though valid in the limit of weak disorder, is poor in general.

B. Exchange disorder

This type of disorder corresponds to an asymmetry in the exchange rates. For example, the rate of molecular transport from the micropores to the macropores of a porous catalyst is not the same as that from the macropores to the micropores, because molecular sizes are often comparable to those of the micropores. Since the effective sizes of the pores are often distributed quantities, the rate of exchange between the macropores and micropores varies in space. The same is true about the fractures and pores of coalbed methane reservoirs. In this case we assume that the transition matrices are the same for each site (so $\Delta_{ij}\equiv 0$) and we write $\mathbf{W}_{ij}\equiv\mathbf{W}^0$. We make the *single-site* EMA by allowing only one site (site 0, say) to have an exchange matrix which differs from $\mathbf{E}^0$ which reduces Eq. (16) to

$$\hat{\mathbf{P}}_i(\lambda)-\hat{\mathbf{P}}_i^0(\lambda)=-\mathbf{G}_{i0}(\mathbf{A})\boldsymbol{\Gamma}_0\hat{\mathbf{P}}_0(\lambda)\ . \tag{39}$$

For $i=0$ we deduce that

$$\hat{\mathbf{P}}_0(\lambda)=\{\mathbf{I}-\mathbf{g}(\mathbf{A})\boldsymbol{\Gamma}_0\}^{-1}\hat{\mathbf{P}}_0(\lambda)\ . \tag{40}$$

This gives the self-consistency condition

$$\langle\{\mathbf{I}-\mathbf{g}(\mathbf{A})\boldsymbol{\Gamma}\}^{-1}\rangle=\mathbf{I}\ , \tag{41}$$

where the averaging is over the disorder in the exchange matrices and we have for brevity dropped the site index 0 from $\boldsymbol{\Gamma}_0$. A weak disorder (small $\boldsymbol{\Gamma}$) calculation can also be made, imitating the analysis for transition disorder, and we recover as the crudest approximation $\mathbf{E}^0(\lambda)\approx\langle\mathbf{E}\rangle$.

VI. EFFECTIVE-MEDIUM PREDICTIONS

Having assembled the general effective-medium formalism, we now examine some representative predictions of the approximation.

A. Systems without exchange matrices

Consider the case in which there is no exchange matrix (i.e., $\mathbf{E}_i=\mathbf{0}$), but allow the transition matrices $\mathbf{W}_{ij}$ to have off-diagonal terms. Then $\mathbf{A}=\lambda(\mathbf{W}^0)^{-1}\to\mathbf{0}$ as $\lambda\to 0$ and indeed $\mathbf{Ag}(\mathbf{A})\to\mathbf{0}$. [As discussed in the Appendix, $\mathbf{g}(\mathbf{A})$ has a finite limit as $\mathbf{A}\to\mathbf{0}$ if $d\geq 3$ and a modest divergence in lower dimensions.] Thus Eq. (38) reduces to a simple equation for the $\lambda\to 0$ limiting form of the effective transition rate matrix:

$$\langle\{(1-2/z)\mathbf{I}+(2/z)\mathbf{W}^0(0)^{-1}\mathbf{W}\}^{-1}\rangle=\mathbf{I}\ , \tag{42}$$

with the average taken over the distribution of the random variable $\mathbf{W}$. In space dimension $d\geq 2$, we have N^2 simultaneous nonlinear equations to solve for the N^2 elements of the matrix $\mathbf{W}^0(0)$. However, if $d=1$ (so that $z=2$), the equations greatly simplify and we find the prediction that

$$\mathbf{W}^0(0)=\langle\mathbf{W}^{-1}\rangle^{-1}\ . \tag{43}$$

This should be compared with the prediction of naive perturbation analysis (Sec. V A) that $\mathbf{W}^0(\lambda)=\langle\mathbf{W}\rangle$ for all λ.

From Eq. (32), the propagator from the origin is given by

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle=\mathbf{g}[\lambda(\mathbf{W}^0)^{-1}](\mathbf{W}^0)^{-1}\ . \tag{44}$$

If we introduce a matrix $\mathbf{V}$ to diagonalize $(\mathbf{W}^0)^{-1}$, so that

$$(\mathbf{W}^0)^{-1}=\mathbf{V}\,\mathrm{diag}\{\omega_n^2\}\mathbf{V}^{-1}\ , \tag{45}$$

we see that

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle=\mathbf{V}\,\mathrm{diag}\{\omega_n^2 g(\lambda\omega_n^2)\}\mathbf{V}^{-1}\ . \tag{46}$$

In one dimension, we have $\mathbf{W}^0(0)$ predicted explicitly by Eq. (43), while $g(a)\sim 1/(2a^{1/2})$ as $a\to 0$, so that we predict that

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle=\frac{1}{2\lambda^{1/2}}\mathbf{V}\,\mathrm{diag}\{\omega_n\}\mathbf{V}^{-1}\ . \tag{47}$$

We shall see in Sec. VII that this result is exact.

B. Two-path systems with diagonal exchange matrices

We report some results for a periodic lattice of arbitrary dimension d, with two families of transport paths and diagonal exchange matrices, so that we have

$$\mathbf{W}=\begin{bmatrix}u & 0\\ 0 & v\end{bmatrix},\quad \mathbf{W}^0=\begin{bmatrix}u^0 & 0\\ 0 & v^0\end{bmatrix}\ , \tag{48}$$

$$\mathbf{E}=\begin{bmatrix}-\mu & \nu\\ \mu & -\nu\end{bmatrix},\quad \mathbf{E}^0=\begin{bmatrix}-\mu^0 & \nu^0\\ \mu^0 & -\nu^0\end{bmatrix}\ , \tag{49}$$

$$\mathbf{A}=\begin{bmatrix}u^{-1}(\lambda+\mu) & -u^{-1}\nu\\ -v^{-1}\mu & v^{-1}(\lambda+\nu)\end{bmatrix}\ . \tag{50}$$

For brevity, we write

$$\kappa=\frac{\mu}{u}+\frac{\nu}{v},\quad \kappa^0=\frac{\mu^0}{u^0}+\frac{\nu^0}{v^0}\ . \tag{51}$$

The eigenvalues of $\mathbf{A}$ are the solutions a_1 and a_2 of the equation

$$\left\{\frac{\lambda+\mu^0}{u^0}-a\right\}\left\{\frac{\lambda+\nu^0}{v^0}-a\right\}-\left\{\frac{\mu^0}{u^0}\right\}\left\{\frac{\nu^0}{v^0}\right\}=0 \tag{52}$$

and so as $\lambda\to 0$ we have

$$a_1\to 0,\quad a_2\to\kappa^0\ . \tag{53}$$

Corresponding eigenvectors for $\lambda=0$ are $\binom{\nu^0}{\mu^0}$ and $\binom{-v^0}{u^0}$, and so the diagonalizing matrices are

$$\mathbf{Q}=\begin{bmatrix}\nu^0 & -v^0\\ \mu^0 & u^0\end{bmatrix},\quad \mathbf{Q}^{-1}=\frac{1}{\kappa^0\mu^0\nu^0}\begin{bmatrix}u^0 & v^0\\ -\mu^0 & \nu^0\end{bmatrix}\ . \tag{54}$$

Although $\mathbf{g}(\mathbf{A})=\mathbf{Q}\,\mathrm{diag}\{g(a_n)\}\mathbf{Q}^{-1}$, it is not convenient to calculate $\mathbf{g}(\mathbf{A})$ this way, since $g(a_1)$ diverges as $\lambda\to 0$ for $d=1$ and 2. However, we note for later reference that as $\mathbf{A}\mathbf{g}(\mathbf{A})=\mathbf{g}(\mathbf{A})\mathbf{A}=\mathbf{Q}\,\mathrm{diag}\{a_n g(a_n)\}\mathbf{Q}^{-1}$, and $ag(a)\to 0$ as $\lambda\to 0$, in the limit $\lambda\to 0$ we obtain

$$\mathbf{A}\mathbf{g}(\mathbf{A})=\mathbf{g}(\mathbf{A})\mathbf{A}=\frac{g(\kappa^0)}{u^0v^0}\begin{bmatrix}\mu^0v^0 & -\nu^0v^0\\ -\mu^0u^0 & \nu^0u^0\end{bmatrix}. \tag{55}$$

Similarly in the limit $\lambda\to 0$,

$$\mathbf{g}(\mathbf{A})^{-1}=\frac{1}{g(\kappa^0)\kappa^0u^0v^0}\begin{bmatrix}\mu^0v^0 & -\nu^0v^0\\ -\mu^0u^0 & \nu^0u^0\end{bmatrix}. \tag{56}$$

C. Two-path systems with exchange disorder only

Consider first *exchange disorder only,* so that $\mathbf{W}=\mathbf{W}^0$ and we may therefore take $u^0=u$ and $v^0=v$ as known constants. The analysis is simplified by noting that since

$$\mathbf{\Gamma}=(\mathbf{W}^0)^{-1}(\mathbf{E}-\mathbf{E}^0)=\mathbf{A}(\lambda\mathbf{I}-\mathbf{E}^0)^{-1}(\mathbf{E}-\mathbf{E}^0)\ , \tag{57}$$

Eq. (41) is equivalent to the assertion that

$$\langle\{\mathbf{I}-\mathrm{diag}\{a_n g(a_n)\}\mathbf{Q}^{-1}(\lambda\mathbf{I}-\mathbf{E}^0)^{-1}(\mathbf{E}-\mathbf{E}^0)\mathbf{Q}\}^{-1}\rangle=\mathbf{I}\ . \tag{58}$$

Although $(\lambda\mathbf{I}-\mathbf{E}^0)^{-1}$ diverges as $\lambda\to 0$,

$$(\lambda\mathbf{I}-\mathbf{E}^0)^{-1}(\mathbf{E}-\mathbf{E}^0)=\frac{1}{\mu^0+\nu^0+\lambda}\begin{bmatrix}-\mu+\mu^0 & \nu-\nu^0\\ \mu-\mu^0 & -\nu+\nu^0\end{bmatrix} \tag{59}$$

has a finite small-λ limit. After some algebra, the matrix self-consistency condition (58) reduces to four scalar equations:

$$\left\langle\frac{1}{D^0}\left[1-\frac{\mu^0-\mu}{u^0}\right]\right\rangle=\left\langle\frac{1}{D^0}\left[1-\frac{\nu^0-\nu}{v^0}\right]\right\rangle=1 \tag{60}$$

and

$$\left\langle\frac{\mu^0-\mu}{D^0u^0}\right\rangle=\left\langle\frac{\nu^0-\nu}{D^0v^0}\right\rangle=0\ , \tag{61}$$

with $D^0=1+g(\kappa^0)(\kappa-\kappa^0)$. Although it may appear that the problem is overdetermined, since

$$\langle\{1+g(\kappa^0)(\kappa-\kappa^0)\}/D^0\rangle=1\ , \tag{62}$$

it is easy to prove that if the pair of conditions (61) hold, then $\langle 1/D^0\rangle=1$ and the conditions (60) are also satisfied. It follows that

$$\mu^0=\left\langle\frac{\mu}{1+g(\kappa^0)(\kappa-\kappa^0)}\right\rangle \tag{63}$$

and

$$\nu^0=\left\langle\frac{\nu}{1+g(\kappa^0)(\kappa-\kappa^0)}\right\rangle\ , \tag{64}$$

where κ^0 is determined from the equation

$$\left\langle\frac{1}{1+g(\kappa^0)(\kappa-\kappa^0)}\right\rangle=1\ . \tag{65}$$

Although we have not exhibited it explicitly here, we emphasize that the last three equations apply only in the limit $\lambda\to 0$. The general case of positive λ is somewhat more complicated.

To illustrate the predictions of the EMA, consider the case of *binary disorder,* where (μ,ν) takes the values (μ^*,ν^*) and (0,0) with probabilities p and $1-p$, respectively, and for brevity write $\kappa^*=\mu^*/u^0+\nu^*/v^0$. Equation (65) becomes

$$(1-p)=(1-\kappa^0/\kappa^*)[1-g(\kappa^0)\kappa^0]\ . \tag{66}$$

In one dimension, this leads to a quadratic equation for κ^0, but in higher dimensions the scalar lattice Green's function g is not an elementary function and the equation has to be solved numerically. To illustrate the dependence of the problem on the lattice dimension, we consider the "dilute limit", $p\to 0$, in which μ^0 and ν^0 (and so κ^0) should vanish. The asymptotic form of κ^0 as $p\to 0$ depends on the lattice dimension d. As discussed in the Appendix, for $d\geq 3$, $g(0)=z^{-1}(1-R)^{-1}<\infty$, with R the return probability for Pólya's random walk on the lattice, and so we predict that

$$\kappa^0\sim[1+g(0)\kappa^*]^{-1}\kappa^*p\ , \tag{67}$$

from which it follows that within the EMA, $\mu^0(0)\sim p\mu^*/[1+\kappa^*g(0)]$ and $\nu^0(0)\sim p\nu^*/[1+\kappa^*g(0)]$. It is interesting to note that even in the limit of arbitrarily small p, the naive perturbation prediction that $\kappa^0=\langle\kappa\rangle$ (i.e., $\kappa^0=p\kappa^*$) is not recovered.

For $d\leq 2$, where Pólya walkers are certain to return to the starting site, $g(a)\to\infty$ as $a\to 0$ and the leading-order small-p form of κ^0 is predicted by the EMA to become independent of κ^*. For $d=2, g(a)\sim(4\pi)^{-1}c\ln(1/a)$, with c a lattice-dependent constant (see the Appendix), and we predict that

$$\kappa^0\sim[4\pi p]/[c\ln(1/p)]\ , \tag{68}$$

while for $d=1, g(a)\sim(4a)^{-1/2}$ and we predict that

$$\kappa^0\sim 4p^2\ . \tag{69}$$

Here again the perturbation prediction that $\kappa^0=\langle\kappa\rangle$ is not recovered. The more general case in which (μ,ν) takes the values (μ_1,ν_1) and (μ_2,ν_2) with probabilities p and $1-p$, respectively, where $\nu_1\ll\mu_1$ and $\nu_2\ll\nu_2$, is of practical interest since it may correspond to, e.g., transport in a porous catalyst with micropores and macropores, or coalbed methane reservoirs with tight pores and large fractures. As discussed above, transport in the micropores is hindered and slow and, moreover, while it is easy for the molecules to enter the macropores from the micropores, the reverse is not true and, therefore, the rates of exchange between the two types of pores are not in general equal. The EMA developed here should be particularly accurate for such problems, since the system is not critical and does not have a fractal structure.

D. Two-path systems with transition disorder only

The case of *transition disorder only* with two families of transport paths appears more subtle. If we attempt to

write $\mu^0=\mu=$const, we find that the self-consistency condition (38) reduces in the $\lambda=0$ limit to *three* independent scalar equations for the *two* unknown functions $u^0(0)$ and $v^0(0)$, which in general admit no solution. This suggests that for transition disorder, the uniform system which represents themacroscopic transport properties of the disordered system must either possess off-diagonal terms in the matrix $\mathbf{W}^0(\lambda)$ or have an exchange matrix $\mathbf{E}^0(\lambda)$ which differs from the exchange matrix for each realization of the system. In other words, matching a disordered system with several distinct families of transport paths to a uniform system induces not only memory, but also *additional couplings* absent from the original system. This explains why simply coupled diffusion equations are found to be poor models for transport in fractured porous rock [1–4].

VII. EXACT RESULTS IN ONE DIMENSION

Even the $d=1$ limit of our problem with $N\geq 2$ is nontrivial and far more complex than the $N=1$ case [11]. For example, whereas percolationlike disorder divides a linear chain into finite segments and prohibits macroscopic transport, in our problem one can have global transport even if m ($m<N$) paths have been disrupted by percolation disorder. The $N=2$ limit of our problem is particularly important and interesting since it can be related to some well-known models that have been used in the petroleum industry for treating transport and hydrodynamic dispersion in heterogeneous rocks. For example, Coats and Smith [20] developed a one-dimensional semiempirical model of dispersion (for a review see Sahimi [1]) in a porous medium containing flowing and stagnant regions. In their model, it is assumed that a fraction ϕ_f of the pore volume is available for flow, while $1-\phi_f$ is the stagnant fraction. The concentration of the solute in flowing and stagnant regions C_f and C_s are governed by

$$\frac{\partial C_f}{\partial t}+v\frac{\partial C_f}{\partial x}=D_L\frac{\partial^2 C_f}{\partial x^2}+k_c(C_s-C_f)\ , \tag{70}$$

$$\frac{\partial C_s}{\partial t}=k_c(C_f-C_s)\ , \tag{71}$$

where v is the average flow velocity, D_L the dispersion (effective diffusion) coefficient, and k_c the mass transfer coefficient between the flowing and stagnant regions. A comparison of Eqs. (70) and (71) with (1) indicates that the two models are closely related, if C_f and C_s are interpreted as the solute concentration in the fractures and pores, respectively, and if we assume that transport in the pores is negligible. In fact, using this interpretation, Eqs. (70) and (71) have been used for modeling transport in reservoir rocks with fractures and pores (for a review see Sahimi [1]). Of course, in our model we have ignored the effect of a flow field, but this can be easily incorporated into our model. However, while the Coats-Smith model is one dimensional and purely phenomenological (no disorder is allowed in the model), and does not provide any insight into how the morphologies of the fracture and pore networks control the overall transport process, our model offers higher-dimensional systems and inclusion of heterogeneities, and can be used for investigating the effect of such factors.

For a one-dimensional lattice, the site index i is an integer and the only nonzero transition matrices are $\mathbf{W}_{i,i+1}=\mathbf{W}_{i+1,i}$. We remind the reader that for brevity, we suppress the argument λ of Laplace transformed functions where no confusion will arise. As $\mathbf{W}_{ij}=\mathbf{W}_{ji}$, Eq. (1) becomes, for $d=1$,

$$\lambda\hat{\mathbf{P}}_i-\mathbf{P}_i(0)=\mathbf{W}_{i,i+1}(\hat{\mathbf{P}}_{i+1}-\hat{\mathbf{P}}_i)+\mathbf{W}_{i,i-1}(\hat{\mathbf{P}}_{i-1}-\hat{\mathbf{P}}_i)+\mathbf{E}_i\hat{\mathbf{P}}_i\ . \tag{72}$$

To accommodate an arbitrary partitioning between paths at the starting site, we write $\mathbf{P}_i(0)=\delta_{i,0}\mathbf{u}$ and, by analogy with Sec. IV C, we introduce the propagator matrix $\mathbf{M}_i(t)$ defined by $\mathbf{P}_i(t)=\mathbf{M}_i(t)\mathbf{u}$. Equation (72) becomes an equation for Laplace transform $\hat{\mathbf{M}}_i(\lambda)$ of the propagator matrix:

$$\lambda\hat{\mathbf{M}}_i-\delta_{i,0}\mathbf{I}=\mathbf{W}_{i,i+1}(\hat{\mathbf{M}}_{i+1}-\hat{\mathbf{M}}_i)+\mathbf{W}_{i,i-1}(\hat{\mathbf{M}}_{i-1}-\hat{\mathbf{M}}_i)+\mathbf{E}_i\hat{\mathbf{M}}_i\ . \tag{73}$$

Consider first the case of sites to the right of the origin ($i>0$). We introduce random matrices

$$\mathbf{N}_i(\lambda)=\mathbf{W}_{i,i+1}[\hat{\mathbf{M}}_i(\lambda)-\hat{\mathbf{M}}_{i+1}(\lambda)]\hat{\mathbf{M}}_i(\lambda)^{-1}\ , \tag{74}$$

which reduce Eq. (73) to the recurrence relation

$$\mathbf{N}_{i-1}=(\mathbf{N}_i+\lambda\mathbf{I}-\mathbf{E}_i)(\mathbf{N}_i+\lambda\mathbf{I}+\mathbf{W}_{i,i-1}-\mathbf{E}_i)^{-1}\mathbf{W}_{i,i-1}\ . \tag{75}$$

Iterating this relation gives a matrix generalization of a random continued fraction. Since the random matrices on the right-hand side of Eq. (75) are determined from the iteration in terms of the transition rate and exchange matrices to the right of site $i-1$, we are able to deduce that, where $\mathbf{N}$, $\mathbf{W}$, and $\mathbf{E}$ denote generic independent random variables corresponding to $\mathbf{N}_i$, $\mathbf{W}_{i,i\pm1}$, and $\mathbf{E}_i$ for arbitrary lattice sites, $\mathbf{N}$ has the same distribution as

$$(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E})(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W}-\mathbf{E})^{-1}\mathbf{W}\ .$$

A similar analysis may be made for $i<0$, and we easily show from Eq. (73) in the case $i=0$ that

$$\hat{\mathbf{M}}_0(\lambda)=(\lambda\mathbf{I}+\mathbf{N}_+ +\mathbf{N}_- -\mathbf{E})^{-1}\ , \tag{76}$$

where $\mathbf{N}_-$ and $\mathbf{N}_+$ are independent, each having the distribution of N, and arising, respectively, from the environment on the left and right of the origin.

A. The uniform $d=1$ case

Before examining the case in which transition matrices $\mathbf{W}$ or exchange matrices $\mathbf{E}$ are random, let us consider briefly the case in which both of these matrices are uniform, taking the values $\mathbf{W}^0$ and $\mathbf{E}^0$. This provides some insight into the algebraic structure of the problem. From the preceding considerations, the (uniform) $\mathbf{N}$ matrix satisfies the equation

$$\mathbf{N}=(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E}^0)(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W}^0-\mathbf{E}^0)^{-1}\mathbf{W}^0 \tag{77}$$

$$=\mathbf{W}-\mathbf{W}(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W}^0-\mathbf{E}^0)^{-1}\mathbf{W}^0 . \tag{78}$$

It is perhaps not immediately apparent to the reader how one may solve such a nonlinear matrix equation and indeed, even in the case of two paths, in any direct attack the algebra becomes complex. Fortunately, from Eq. (32) in Sec. IV we have an explicit solution for the propagator at the origin. Comparing this with Eq. (76), we find that

$$\mathbf{N}=\tfrac{1}{2}\{\mathbf{E}^0-\lambda\mathbf{I}+\mathbf{W}^0\mathbf{g}(\mathbf{A})^{-1}\} , \tag{79}$$

where $\mathbf{A}=(\mathbf{W}^0)^{-1}(\lambda\mathbf{I}-\mathbf{E}^0)$. To verify that this explicit formula is consistent with Eq. (77), we need only substitute the solution (79) into Eq. (77), eliminate $(\mathbf{W}^0)^{-1}(\lambda\mathbf{I}-\mathbf{E}^0)$ in favor of $\mathbf{A}$, diagonalize the system using the $\mathbf{Q}$ matrix, and recall the explicit formula (22) for $g(a)$ in one dimension. We now see in particular that for the uniform system with two paths, borrowing the notation of Eqs. (48) and (49),

$$\lim_{\lambda\to 0}\mathbf{N}=\frac{1-\kappa^0 g(\kappa^0)}{2\kappa^0 g(\kappa^0)}\begin{bmatrix}\mu^0 & -\nu^0\\ -\mu^0 & \nu^0\end{bmatrix} , \tag{80}$$

with $\kappa^0=\mu^0/u^0+\nu^0/v^0$. The $\lambda\to 0$ limit of the $\mathbf{N}$ matrix thus has the same symmetry properties as the exchange matrix $\mathbf{E}^0$.

B. The disordered $d=1$ case

Where angular brackets denote the average over all realizations of the random environment, as our probe of the behavior of the system we examine in the Laplace transform domain the ensemble-averaged matrix propagator at the origin,

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle=\langle(\lambda\mathbf{I}+\mathbf{N}_+ +\mathbf{N}_- -\mathbf{E})^{-1}\rangle . \tag{81}$$

We seek the dominant behavior in the limit $\lambda\to 0$ (corresponding to $t\to\infty$). In the absence of disorder, as in normal diffusion, $\mathbf{M}_0(t)$ decays as $t^{-1/2}$, corresponding to $\hat{\mathbf{M}}_0(\lambda)$ diverging as $\lambda^{-1/2}$. For sufficiently modest disorder in the environment, $\langle\hat{\mathbf{M}}_0(\lambda)\rangle$ should diverge in the same manner. This suggests that $\langle(\lambda\mathbf{I}+\mathbf{N}_+ +\mathbf{N}_- -\mathbf{E})^{-1}\rangle$ should become a singular matrix as $\lambda\to 0$, with its determinant vanishing as $\lambda^{1/2}$.

Since $\mathbf{N}$ and $(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E})(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W}-\mathbf{E})^{-1}\mathbf{W}$ have the same distribution, averaging over environments gives the following two equivalent conditions:

$$\langle\mathbf{N}\rangle=\langle(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E})(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W}-\mathbf{E})^{-1}\mathbf{W}\rangle , \tag{82}$$

$$\langle(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E})(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W}-\mathbf{E})^{-1}(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E})\rangle =\lambda\mathbf{I}-\langle\mathbf{E}\rangle . \tag{83}$$

We now pursue the implications of the preceding exact results in some special cases.

C. Systems without exchange matrices in $d=1$

As in Sec. VI, we consider the special case in which the exchange matrices are zero, but we allow the transition matrices to have nonzero off-diagonal terms, so that changes of path are forbidden without changes of site, but may occur with changes of site. From Eq. (83),

$$\langle(\mathbf{N}+\lambda\mathbf{I})(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W})^{-1}(\mathbf{N}+\lambda\mathbf{I})\rangle=\lambda\mathbf{I} , \tag{84}$$

with the averages over $\mathbf{N}$ and $\mathbf{W}$ able to be taken independently. This is consistent with the hypothesis that $\mathbf{N}$ vanishes with probability 1 as $\lambda\to 0$ and so we find that to leading order in λ,

$$\langle\mathbf{NwN}\rangle\sim\lambda\mathbf{I} , \tag{85}$$

where we have written $\mathbf{w}=\langle\mathbf{W}^{-1}\rangle$ and the average in Eq. (85) is now taken only over the distribution of $\mathbf{N}$. It is now seen that $\mathbf{N}$ is $O(\lambda^{1/2})$ and we write $\mathbf{N}\sim\lambda^{1/2}\mathbf{n}$, where $\langle\mathbf{nwn}\rangle=\mathbf{I}$. Equation (81) thus gives

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle\sim 2^{-1}\lambda^{-1/2}\langle\mathbf{n}^{-1}\rangle . \tag{86}$$

In the single-path problem [11] the scalar analog of $\mathbf{n}$ is a constant rather than a genuine random variable (a manifestation of a limiting law of probability) and this should also occur here. The determination of $\mathbf{n}$ thus becomes a simple algebraic problem. In the special case in which $\mathbf{w}$ is diagonalizable, so that we may write $\mathbf{w}=\mathbf{V}\,\mathrm{diag}\{\omega_k^2\}\mathbf{V}^{-1}$, it is easy to verify that $\mathbf{n}=\mathbf{V}\,\mathrm{diag}\{1/\omega_k\}\mathbf{V}^{-1}$ is a solution of $\mathbf{nwn}=\mathbf{I}$ and it follows that

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle\sim\frac{1}{2\lambda^{1/2}}\langle\mathbf{n}^{-1}\rangle=\frac{1}{2\lambda^{1/2}}\mathbf{V}\,\mathrm{diag}\{\omega_n\}\mathbf{V}^{-1} . \tag{87}$$

Comparing this with Eq. (47), we see that the EMA of Sec. V returns an exact result in this case. If any component of $\langle\mathbf{W}^{-1}\rangle$ is infinite the analysis must be modified and "nonuniversal" behavior characterized by different critical exponents ensues, a scenario not considered here.

D. A two-path system in $d=1$

We turn now to the mathematically more difficult case in which exchange matrices are present. To simplify the discussion, we restrict our attention to the two-path problem ($N=2$), with two additional assumptions.

(a) $(\mu,\nu)=\omega(\mu^*,\nu^*)$, where ω is a non-negative random variable and μ^* and ν^* are constants. If the random variable ω takes the value 1 with probability p and the value 0 with probability $1-p$, we have *binary exchange disorder,* with exchange taking place at a random fraction p of the lattice sites.

(b) $\mathbf{W}=\mathrm{diag}\{u,v\}$, where for the moment we allow u and v to be random variables.

Preliminary analysis of the uniform case above suggests for the $\lambda\to 0$ limit the ansatz

$$\mathbf{N}\sim\chi\begin{bmatrix}\mu^* & -\nu^*\\ -\mu^* & \nu^*\end{bmatrix} . \tag{88}$$

This is consistent provided that the random variable χ has the same distribution as

$$\frac{\omega+\chi}{1+(\mu^*/u+\nu^*/v)(\omega+\chi)} ,$$

with ω and χ independent. Taking reciprocals, this re-

quires that

$$\left\langle \frac{1}{\chi} \right\rangle = \left\langle \frac{1}{\chi+\omega} \right\rangle + \left\langle \frac{\mu^*}{u} + \frac{\nu^*}{v} \right\rangle \tag{89}$$

and so we have the exact result that

$$\left\langle \frac{\omega}{\chi(\chi+\omega)} \right\rangle = \left\langle \frac{\mu^*}{u} + \frac{\nu^*}{v} \right\rangle . \tag{90}$$

For the binary disorder case ($\omega=1$ or 0 with probability p and $1-p$, respectively), we obtain

$$p\left\langle \frac{1}{\chi(\chi+1)} \right\rangle = \left\langle \frac{\mu^*}{u} + \frac{\nu^*}{v} \right\rangle . \tag{91}$$

In the limit of small p, we have

$$\left\langle \frac{1}{\chi} \right\rangle \sim \frac{1}{p}\left\langle \frac{\mu^*}{u} + \frac{\nu^*}{v} \right\rangle . \tag{92}$$

If u and v are constants, the natural scaling of χ is exactly that predicted by the EMA. To see this, consider the behavior of $\mathbf{N}$ for a uniform system given by Eq. (80). For binary exchange disorder, we have from Eqs. (63) and (64) that

$$\frac{\mu^0}{\mu^*} = \frac{\nu^0}{\nu^*} = \frac{p}{1+g(\kappa^0)(\kappa^*-\kappa^0)} \tag{93}$$

and the EMA predicts that

$$\lim_{\lambda\to 0} \mathbf{N} = \chi^0 \begin{bmatrix} \mu^* & -\nu^* \\ -\mu^* & \nu^* \end{bmatrix} , \tag{94}$$

where

$$\chi^0 = \frac{p[1-\kappa^0 g(\kappa^0)]}{2\kappa^0 g(\kappa^0)[1+g(\kappa^0)(\kappa^*-\kappa^0)]} . \tag{95}$$

For one dimension, $g(a)\sim 1/(2\sqrt{a})$ as $a\to 0$ and we predicted that $\kappa^0 \sim 4p^2$. Consequently, as $p\to 0$, we have

$$\chi^0 \sim 2p/\kappa^* , \tag{96}$$

with $\kappa^* = \mu^*/u^0 + v^*/v^0$. Thus we find that the effective-medium prediction χ^0 and the random variable χ of the exact analysis satisfy

$$\lim_{p\to 0} \chi^0 \langle 1/\chi \rangle = 2 . \tag{97}$$

VIII. SCALING ANALYSIS

We conclude by discussing possible qualitative behaviors for the scalar mean-square displacement

$$\sigma^2(t) = (1,1)\langle \mathbf{R}^2(t) \rangle \tag{98}$$

for a two-path model with

$$\mathbf{W}^0 = \begin{bmatrix} w_{11}^0 & w_{12}^0 \\ w_{21}^0 & w_{22}^0 \end{bmatrix}, \quad \mathbf{E}^0 = \begin{bmatrix} -\mu^0 & \nu^0 \\ \mu^0 & -\nu^0 \end{bmatrix} . \tag{99}$$

For brevity, the λ dependence of the components of these matrices has been suppressed. If the components u_1 and u_2 in the initial vector $\mathbf{u}$ add to unity, we have

$$\sigma^2(\lambda) = \frac{z\{[w_{11}^0+w_{21}^0][\nu^0+\lambda u_1]+[w_{12}^0+w_{22}^0][\mu^0+\lambda u_2]\}}{\lambda^2[\lambda+\mu^0+\nu^0]} . \tag{100}$$

For modest disorder, we expect that $\mathbf{W}^0(\lambda)$ and $\mathbf{E}^0(\lambda)$ will have nonzero limits as $\lambda\to 0$. In systems in which paths or path transitions may be blocked at some sites, experience in the single case [13] suggests that at the appropriate percolation threshold, $\mathbf{W}^0(\lambda)\propto\lambda^\alpha$ $(0\le\alpha<1)$, while if the entries in the effective exchange matrix $\check{\mathbf{E}}(t)$ do not change sign, we may have $\mathbf{E}^0(\lambda)\propto\lambda^{-\beta}(0\le\beta<1)$, corresponding to $\check{\mathbf{E}}(t)\propto t^{\beta-1}$. In any event, so long as $\mu^0/(\mu^0+\nu^0)$ and $\nu^0/(\mu^0+\nu^0)$ converge to finite limits (a and b, say) as $\lambda\to 0$, we find that to leading order,

$$\sigma^2(\lambda) \sim \frac{z}{\lambda^2}\{[w_{11}^0+w_{21}^0]b+[w_{12}^0+w_{22}^0]a\} . \tag{101}$$

Since $w_{ij}^0\propto\lambda^\alpha$, this corresponds to $\sigma^2(t)\sim t^{1-\alpha}$. Past experience has shown in a variety of contexts that EMA's perform well in noncritical or nonfractal systems. For pure exchange disorder, the medium cannot have effectively fractal structure and Eqs. (100) and (101) should be good approximations, independent of the dimension of the system.

However, a more interesting case arises if transport in one family is much faster than in the other(s). For example, transport in the fracture network of a reservoir is much faster than that in the pores, or diffusion in the macropores of a catalyst is much faster than that in the micropores. In reservoir rocks it is often true [1,3,21] that the fracture network has a fractal structure. Moreover, at the largest length scales (of order of a kilometer or more) the fracture network is found [21] to have the structure of the sample-spanning percolation cluster at the percolation threshold, while the pore network is well connected. In this case, not all entries of $\mathbf{W}^0(\lambda)$ behave as λ^α and one may expect a variety of interesting results to emerge. In particular, the system can behave quite differently on various time scales which would depend on how the transport process is partitioned between the two networks and whether these networks are macroscopically connected. We hope to be able to report the results of a numerical simulation of this problem in the near future.

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APPENDIX

The scalar lattice Green's functions $g(a)$ needed for the present calculations may be found in various disguises throughout the literature. For treatment compatible with our notation, and in particular with our definition (21), we refer the reader to an earlier paper [13], in which we discuss Green's functions for standard lattices and give some asymptotic forms as $a \to 0$. In particular in one dimension, we have

$$g(a) = a^{-1/2}(4+a)^{-1/2} \sim 1/(2a^{1/2}) , \tag{A1}$$

while in two dimensions, $g(a)$ can be expressed in terms of complete elliptic integrals and

$$g(a) \sim \frac{c}{4\pi} \ln(1/a) , \tag{A2}$$

with c taking the values 1, $1/\sqrt{3}$, and $\sqrt{3}$ for the square, triangular, and hexagonal lattices, respectively. In three or higher dimensions $g(a)$ has a finite limit as $a \to 0$. In three dimensions $g(0)$ is exactly known in terms of elliptic integrals or equivalently in terms of products of Γ functions of rational arguments and takes the values

0.448 22 (diamond) ,

0.252 73 (simple cubic) ,

0.174 15 (body-centered cubic) ,

0.112 06 (face-centered cubic) .

In general for dimensions three or higher,

$$g(0) = z^{-1}(1-R)^{-1} , \tag{A3}$$

where R is the return probability for Pólya's random walk on the lattice. For many lattices with $d \geq 3$, $g(0)$ is numerically close to (but not identical to) the bond percolation threshold of the lattice [22].

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$$= (\mathbf{Q}^{-1})^{-1}\{\,\mathrm{diag}\{\theta + a_n\}\}^{-1}\mathbf{Q}^{-1} .$$

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