Diffusion in Disordered Systems with Multiple Families of Transport Paths

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We propose a new model for transport in disordered solids and rocks which contain N distinct families of transport paths ($N \geq 2$), and study the behavior of its effective transport properties. The model is relevant to transport in metals, polycrystals, porous catalysts, coalbed methane reservoirs, and geological systems with fractures and pores.

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Transport in random systems such as disordered solids and porous media is relevant to a wide variety of phenomena, and has been studied for a long time [1]. However, to date, most studies have been restricted to disordered systems in which the disorder is associated with a *single* family of transport paths, characterized by a single transport coefficient and a single transport equation.

In a great many cases, this simple description is totally inadequate. Most natural rocks consist of interconnected and intertwined networks of *fractures* and *pores* [2,3], which implies *two* distinct porosities, and in some cases, e.g., carbonate rocks, one needs *three* degrees of porosity to characterize rock [4]. Transport in the fracture network is very different from that in the pore network. Catalyst particles and coalbed methane reservoirs usually contain very large pores (*macropores*) and very small pores (*micropores*) [5]. Transport in the micropores is hindered in comparison with that in the macropores [6] because the size of the molecules is comparable with the size of the micropores. Moreover, while it is easy for molecules to enter the macropores from the micropores, the reverse is not true; i.e., the rates of exchange between macropores and micropores are unequal. In metals and polycrystals, transport often proceeds simultaneously through *two* distinct families of paths, the *bulk* and the *grain boundaries, dislocations, and internal cracks* [7]. Transport in such systems *cannot* be described by a single classical transport equation. 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. Despite its significance, virtually no studies have been made of transport in disordered media with multiple distinct families of transport paths. In this Letter, we present what we believe to be the first theory of transport in *disordered* systems to account for multiple transport paths [8].

The model.— We propose the following evolution equation for representing transport in N distinct families of transport paths:

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

Here $\mathbf{P}_i(t)$ is an N-dimensional column vector, the sth component of which 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 $\mathbf{W}_{ij}$ 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. We insist that $(1,1,\ldots,1)\mathbf{E}_i = 0$ to conserve probability. In particular, for $N=2$, $\mathbf{E}_i = \mathbf{K}(\mu_i, \nu_i)$, where

$$\mathbf{K}(\mu,\nu) = \begin{pmatrix} -\mu & \nu \\ \mu & -\nu \end{pmatrix} . \quad (2)$$

We assume that (a) all sites are topologically equivalent; (b) $\mathbf{W}_{ij} = 0$ unless sites i and j are nearest neighbors; (c) $\mathbf{W}_{ij} = \mathbf{W}_{ji}$; and (d) the matrices $\mathbf{W}_{ij}$ and $\mathbf{E}_i$ are independent, identically distributed random variables, but are mutually independent.

In the present Letter, we develop an exact but implicit solution of the problem for a d-dimensional system, obtain an exact and explicit solution for $d=1$, and propose an effective-medium approximation (EMA) for arbitrary d and outline some of its predictions. We point out that even the $d=1$ limit of our problem with $N \geq 2$ is nontrivial and far more complex than the $N=1$ case [9]. For example, whereas any percolationlike disorder divides a linear chain into finite segments and prohibits macroscopic transport, in the present problem one can have macroscopic transport even if m ($m < N$) paths have been disrupted by percolation disorder. The $N=2$ limit is particularly important since it has close connections with a well-known model [10] that has been used in the petroleum industry for modeling transport in reservoir rocks. Suppose that percolation disorder divides one transport path into finite segments. Then, the uninterrupted path represents the backbone of the system in which transport occurs, while the finite segments act as capacitors which are charged by exchange with the adjacent path. As such, the uninterrupted path represents the fractures of a reservoir that provide effective transport paths, while the finite segments behave like the porous matrix. The one-dimensional model of Coats and Smith (CS) [10], popular in the oil industry, has been used based on such an interpretation. But while the CS model was a one-

dimensional empirical and phenomenological model (no heterogeneity was allowed), our formulation not only provides, *for the first time*, a rigorous foundation for the CS and similar models, it also offers the novelty of higher-dimensional geometry, and the possibility of including the effect of heterogeneities in the model. In what follows the Laplace transform is indicated by a caret, and λ is the Laplace transform variable. A diagonal matrix with diagonal elements (in order) $\rho_1,\rho_2,\ldots,\rho_N$ is denoted by $\mathrm{diag}\{\rho_n\}$.

Exact formulation for $d=1$.—In one dimension, the site index i is an integer and the only nonzero transition matrices are $\mathbf{W}_{i,i+1}=\mathbf{W}_{i+1,i}$. Taking a Laplace transform of Eq. (1) yields

$$\lambda\hat{\mathbf{P}}_i-\mathbf{P}_i(0)=\mathbf{W}_{i,i+1}[\hat{\mathbf{P}}_{i+1}-\hat{\mathbf{P}}_i]+\mathbf{W}_{i,i-1}[\hat{\mathbf{P}}_{i-1}-\hat{\mathbf{P}}_i]+\mathbf{E}_i\hat{\mathbf{P}}_i. \quad (3)$$

As the initial condition we use $\mathbf{P}_i(0)=\delta_{i,0}\mathbf{u}$, and introduce the propagator matrix $\mathbf{M}_i(t)$ defined by $\mathbf{P}_i(t)=\mathbf{M}_i\times(t)\mathbf{u}$, so that

$$\lambda\hat{\mathbf{M}}_i-\delta_{i,0}\mathbf{I}=\mathbf{W}_{i,i+1}[\hat{\mathbf{M}}_{i+1}-\hat{\mathbf{M}}_i]+\mathbf{W}_{i,i-1}[\hat{\mathbf{M}}_{i-1}-\hat{\mathbf{M}}_i]+\mathbf{E}_i\hat{\mathbf{M}}_i. \quad (4)$$

Consider first sites to the right of the origin ($i>0$). Let $\mathbf{N}_i(\lambda)=\mathbf{W}_{i,i+1}[\hat{\mathbf{M}}_i(\lambda)-\hat{\mathbf{M}}_{i+1}(\lambda)]\hat{\mathbf{M}}_i(\lambda)^{-1}$. Equation (4) yields the recurrence relation

$$\mathbf{N}_{i-1}=(\mathbf{N}_i+\lambda\mathbf{I}-\mathbf{E}_i)(\mathbf{N}_i+\lambda\mathbf{I}+\mathbf{W}_{i,i-1}-\mathbf{E}_i)^{-1}\mathbf{W}_{i,i-1}. \quad (5)$$

Since the random matrices on the right are determined from the iteration in terms of the transition rate and exchange matrices to the right of site $i-1$, we can show 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 $i<0$. We can show from Eq. (4) in the case $i=0$ that $\hat{\mathbf{M}}_0(\lambda)=(\lambda\mathbf{I}+\mathbf{N}_+ +\mathbf{N}_- -\mathbf{E})^{-1}$, where $\mathbf{N}_-$ and $\mathbf{N}_+$ are independent, each having the distribution of $\mathbf{N}$, and arising respectively from the environment on the left and the right of the origin. If $\langle\cdot\rangle$ denotes an average over all realizations of the random medium, as our probe of the behavior of the system we examine $\langle\hat{\mathbf{M}}_0(\lambda)\rangle$ in the limit $\lambda\to0$ ($t\to\infty$). 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, after some algebra we obtain

$$\langle(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E})(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W}-\mathbf{E})^{-1}(\mathbf{N}+\lambda\mathbf{I}-\mathbf{E})\rangle=\lambda\mathbf{I}-\langle\mathbf{E}\rangle. \quad (6)$$

Thus, unlike the empirical models [10], we find an *exact* solution for a *disordered* medium with N distinct families of transport paths. We pursue the implications of these results in two cases.

Pure transition disorder.—This type of disorder corresponds to, e.g., randomness in the shapes and sizes of the transport paths. For example, in rock masses the pores are characterized by a size distribution and the fractures by a distribution of hydraulic conductivities, both of which result in random $\mathbf{W}_{ij}$. Consider first the case in which $\mathbf{E}_i=0$, but allow the transition matrices to have nonzero off-diagonal terms, so that changes of path are forbidden without changes of site, but may occur otherwise. From Eq. (6), $\langle(\mathbf{N}+\lambda\mathbf{I})(\mathbf{N}+\lambda\mathbf{I}+\mathbf{W})^{-1}(\mathbf{N}+\lambda\mathbf{I})\rangle=\lambda\mathbf{I}$, with the averages over $\mathbf{N}$ and $\mathbf{W}$ able to be taken independently. $\mathbf{N}$ vanishes with probability 1 as $\lambda\to0$ and so we find that to leading order in λ, $\langle\mathbf{N}\mathbf{w}\mathbf{N}\rangle\sim\lambda\mathbf{I}$, where $\mathbf{w}=\langle\mathbf{W}^{-1}\rangle$ and the average 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 $\langle\mathbf{n}\mathbf{w}\mathbf{n}\rangle=\mathbf{I}$. Thus

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle\sim2^{-1}\lambda^{-1/2}\langle\mathbf{n}^{-1}\rangle. \quad (7)$$

For $N=1$ the scalar analog of $\mathbf{n}$ is a constant [9] rather than a genuine random variable, and this should also occur here. The determination of $\mathbf{n}$ thus becomes an algebraic problem [11]. If any component of $\langle\mathbf{W}^{-1}\rangle$ is infinite the analysis must be modified, a scenario not considered here.

Pure exchange disorder.—This type of disorder corresponds to an asymmetry in the exchange rates as in, e.g., porous catalysts. To simplify the discussion, we restrict our attention to $N=2$, with the assumptions that (i) $\mathbf{W}=\mathrm{diag}\{u,v\}$ and (ii) $(\mu,\nu)=\omega(\mu^*,\nu^*)$, with the random variable ω taking the values 1 and 0 with probabilities p and $1-p$, respectively, corresponding to exchange taking place at a random fraction p of the lattice sites.

Preliminary analysis of the uniform case suggests that in the limit $\lambda\to0$, $\mathbf{N}\sim-\chi\mathbf{K}(\mu^*,\nu^*)$. This is consistent provided the random variable χ has the same distribution as $(\omega+\chi)/[1+(\mu^*/u+\nu^*/v)(\omega+\chi)]$, with ω and χ independent. Thus, we find that $p\langle\chi^{-1}(\chi+1)^{-1}\rangle=\langle\mu^*/u+\nu^*/v\rangle$ and so in the limit of small p, we have the exact asymptotic result that

$$\langle\chi^{-1}\rangle\sim p^{-1}\langle\mu^*/u+\nu^*/v\rangle. \quad (8)$$

Exact solution and effective-medium approximation.—We attempt to match the random system to an "equivalent" uniform system. Equation (3) is to be matched to that of a uniform system, denoted by a superscript zero, which, however, has the same initial condition as the random system

$$\lambda\hat{\mathbf{P}}_i^0-\mathbf{P}_i(0)=\sum_j\mathbf{W}^0[\hat{\mathbf{P}}_j^0-\hat{\mathbf{P}}_i^0]+\mathbf{E}^0\hat{\mathbf{P}}_i^0. \quad (9)$$

The effective matrices $\mathbf{W}^0=\mathbf{W}^0(\lambda)$ and $\mathbf{E}^0=\mathbf{E}^0(\lambda)$ are functions of the Laplace transform variable λ [12]. Hence, in the time domain, the random system is being matched to

$$\frac{\partial}{\partial t}\mathbf{P}_i^0(t)=\int_0^t\sum_j\check{\mathbf{W}}(t-t')[\mathbf{P}_j^0(t')-\mathbf{P}_i^0(t')]dt'+\int_0^t\check{\mathbf{E}}(t-t')\mathbf{P}_i^0(t')dt', \quad (10)$$

where $\check{\mathbf{W}}(t)=L^{-1}\{\mathbf{W}^0(\lambda)\}$ and $\check{\mathbf{E}}(t)=L^{-1}\{\mathbf{E}^0(\lambda)\}$. If

transport is confined to a fractal subset of the system (e.g., a percolation cluster at length scales smaller than the correlation length), $\check{\mathbf{W}}(t)$ and $\check{\mathbf{E}}(t)$ can be slowly decaying [12,13]. For example, fracture networks of rocks often have a fractal structure [1], while the pore networks do not. However, if the time scales for transport in distinct paths are very different (for example, transport in the fractures is much faster than that in the pores), then the macroscopic behavior of the system can be very complex (see below).

Equations (3) and (9) are combined to yield

$$(z\mathbf{I}+\mathbf{A})(\hat{\mathbf{P}}_i-\hat{\mathbf{P}}_i^0)-\sum_j[\hat{\mathbf{P}}_j-\hat{\mathbf{P}}_j^0]=-\sum_j\Delta_{ij}[\hat{\mathbf{P}}_i-\hat{\mathbf{P}}_j]+\Gamma_i\hat{\mathbf{P}}_i\,, \quad (11)$$

where $\mathbf{A}=(\mathbf{W}^0)^{-1}(\lambda\mathbf{I}-\mathbf{E}^0)$, $\Delta_{ij}=(\mathbf{W}^0)^{-1}\mathbf{W}_{ij}-\mathbf{I}$, and $\Gamma_i=(\mathbf{W}^0)^{-1}[\mathbf{E}_i-\mathbf{E}^0]$, with $\mathbf{I}$ the identity matrix and z the coordination number. We introduce a matrix Green function $\mathbf{G}_{ij}(\mathbf{A})$ by

$$(z\mathbf{I}+\mathbf{A})\mathbf{G}_{ik}(\mathbf{A})-\sum_j\mathbf{G}_{jk}(\mathbf{A})=-\delta_{ik}\mathbf{I}\,. \quad (12)$$

We use a matrix $\mathbf{Q}$ to diagonalize $\mathbf{A}$, so that $\mathbf{Q}^{-1}\mathbf{A}\mathbf{Q}=\mathrm{diag}\{a_n\}$. Then, $\mathbf{G}_{00}(\mathbf{A})=-\mathbf{g}(\mathbf{A})$, where

$$\mathbf{g}(\mathbf{A})=\frac{1}{2\pi}\int_{-\pi}^{\pi}\{z[1-\Lambda(\mathbf{k})]\mathbf{I}+\mathbf{A}\}^{-1}dk \quad (13)$$

$$=\mathbf{Q}\,\mathrm{diag}\{g(a_n)\}\mathbf{Q}^{-1}\,, \quad (14)$$

with $\Lambda(\mathbf{k})=z^{-1}\sum_{\mathbf{r}}\exp(i\mathbf{k}\cdot\mathbf{r})$. Equation (11) has the formal solution

$$\hat{\mathbf{P}}_i-\hat{\mathbf{P}}_i^0=\sum_j\sum_k\mathbf{G}_{ij}(\mathbf{A})\Delta_{jk}[\hat{\mathbf{P}}_j-\hat{\mathbf{P}}_k]-\sum_j\mathbf{G}_{ij}(\mathbf{A})\Gamma_j\hat{\mathbf{P}}_j\,, \quad (15)$$

which is exact but only implicit.

We defer for the moment the discussion of the construction of the EMA to assemble some properties of the uniform system described by Eq. (9) which will be needed later. The Laplace transform $\langle\hat{\mathbf{R}}^2(\lambda)\rangle$ of the column vector mean-square displacement $\langle\mathbf{R}^2(t)\rangle=\sum_l l^2\mathbf{P}_l(t)$ for the initial condition $\mathbf{P}_l(0)=\delta_{l0}\mathbf{u}$ is given by

$$\langle\hat{\mathbf{R}}^2(\lambda)\rangle=z[\lambda\mathbf{I}-\mathbf{E}^0(\lambda)]^{-1}\mathbf{W}^0(\lambda)[\lambda\mathbf{I}-\mathbf{E}^0(\lambda)]^{-1}\mathbf{u}\,. \quad (16)$$

The large-t behavior of $\langle\mathbf{R}^2(t)\rangle$ can be deduced from the small-λ behavior of $\langle\hat{\mathbf{R}}^2(\lambda)\rangle$, although, unlike the $N=1$ case, the latter has to be calculated carefully since $\mathbf{E}^0(0)$ is singular. One may show that $\hat{\mathbf{M}}_0(\lambda)=\mathbf{g}(\mathbf{A})\mathbf{A}(\lambda\mathbf{I}-\mathbf{E}^0)^{-1}=\mathbf{g}(\mathbf{A})(\mathbf{W}^0)^{-1}$. As before, we confine our attention to two cases.

Pure transition disorder.—Here we assume that the exchange matrices are the same for each site (so $\Gamma_i\equiv\mathbf{0}$) 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 different from $\mathbf{W}^0$ [14]. If this bond joins sites 0 and 1, Eq. (15) leads to $\hat{\mathbf{P}}_0-\hat{\mathbf{P}}_1=\{\mathbf{I}+[\mathbf{I}-\mathbf{A}\mathbf{g}(\mathbf{A})]\Delta_{01}\}^{-1}\times[\hat{\mathbf{P}}_0^0-\hat{\mathbf{P}}_1^0]$. The *single-bond* EMA is constructed by requiring that $\langle\hat{\mathbf{P}}_0(\lambda)-\hat{\mathbf{P}}_1(\lambda)\rangle=\hat{\mathbf{P}}_0^0(\lambda)-\hat{\mathbf{P}}_1^0(\lambda)$. Therefore, we obtain

$$\langle\{\mathbf{I}+(2/z)(\mathbf{I}-\mathbf{A}\mathbf{g}(\mathbf{A})]\Delta\}^{-1}\rangle=\mathbf{I}\,, \quad (17)$$

where $\Delta=\Delta_{01}$ [15].

In the weak disorder limit ("small" Δ), expansion of the inverse matrix in Eq. (17) as a power series shows that for self-consistency it suffices that $\langle[\mathbf{I}-\mathbf{A}\mathbf{g}(\mathbf{A})]\Delta\rangle\approx\mathbf{0}$, so that $\mathbf{W}^0\approx\langle\mathbf{W}\rangle$. We shall see that this approximation, though valid in the limit of weak disorder, is poor in general.

Exchange disorder.—We now assume that the transition matrices are the same for each site ($\Delta_{ij}\equiv\mathbf{0}$) and we write $\mathbf{W}_{ij}\equiv\mathbf{W}^0$. In the *single-site* EMA only one site (site 0, say) has an exchange matrix which differs from $\mathbf{E}^0$, and thus $\hat{\mathbf{P}}_i(\lambda)-\hat{\mathbf{P}}_i^0(\lambda)=-\mathbf{G}_{i0}(\mathbf{A})\Gamma_0\hat{\mathbf{P}}_0(\lambda)$. For $i=0$ we deduce that $\hat{\mathbf{P}}_0(\lambda)=\{\mathbf{I}-\mathbf{g}(\mathbf{A})\Gamma_0\}^{-1}\hat{\mathbf{P}}_0(\lambda)$, yielding

$$\langle\{\mathbf{I}-\mathbf{g}(\mathbf{A})\Gamma\}^{-1}\rangle=\mathbf{I}\,, \quad (18)$$

where $\Gamma=\Gamma_0$. We now examine some representative predictions of EMAs in $d=1$, and compare them with the exact results. The EMA predictions for $d>1$ will be given elsewhere [14].

No exchange matrices.—If $\mathbf{E}_i=\mathbf{0}$, but $\mathbf{W}_{ij}$ can have off-diagonal terms, then $\mathbf{A}=\lambda(\mathbf{W}^0)^{-1}\to\mathbf{0}$ as $\lambda\to 0$ and indeed $\mathbf{A}\mathbf{g}(\mathbf{A})\to 0$. Thus, Eq. (17), in the limit $\lambda\to 0$, reduces to $\langle\{\mathbf{W}^0(0)^{-1}\mathbf{W}\}^{-1}\rangle=\mathbf{I}$ and we find that $\mathbf{W}^0(0)=\langle\mathbf{W}^{-1}\rangle^{-1}$, which should be compared with the naive perturbation prediction that $\mathbf{W}^0(\lambda)=\langle\mathbf{W}\rangle$ for *all* λ.

Since $\langle\hat{\mathbf{M}}_0(\lambda)\rangle=\mathbf{g}(\lambda(\mathbf{W}^0)^{-1})(\mathbf{W}^0)^{-1}$, we introduce a matrix $\mathbf{V}$ to diagonalize $(\mathbf{W}^0)^{-1}$, so that $(\mathbf{W}^0)^{-1}=\mathbf{V}\times\mathrm{diag}\{\omega_n^2\}\mathbf{V}^{-1}$, and

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle=\mathbf{V}\,\mathrm{diag}\{\omega_n^2 g(\lambda\omega_n^2)\}\mathbf{V}^{-1}\,. \quad (19)$$

Since $g(a)\sim 1/2a^{1/2}$ as $a\to 0$, we predict that

$$\langle\hat{\mathbf{M}}_0(\lambda)\rangle=\frac{1}{2\lambda^{1/2}}\mathbf{V}\,\mathrm{diag}\{\omega_n\}\mathbf{V}^{-1}\,. \quad (20)$$

We shall see below that this result is *exact*.

Diagonal exchange matrices for $N=2$.—Here we take $\mathbf{W}=\mathrm{diag}\{u,v\}$, $\mathbf{W}^0=\mathrm{diag}\{u^0,v^0\}$, $\mathbf{E}^0=\mathbf{K}(\mu^0,\nu^0)$, and we write $\kappa=\mu/u+\nu/v$ and $\kappa^0=\mu^0/u^0+\nu^0/v^0$. As $\lambda\to 0$, the eigenvalues a_1 and a_2 of $\mathbf{A}$ have the limits $a_1\to 0$ and $a_2\to\kappa^0$. 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 $\lambda\to 0$ we obtain simple expressions for $\mathbf{A}\mathbf{g}(\mathbf{A})=\mathbf{g}(\mathbf{A})\mathbf{A}$.

Consider first *pure exchange disorder*, so that $\mathbf{W}=\mathbf{W}^0$ and we may take $u^0=u$ and $v^0=v$ as known constants. Since

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

Eq. (18) is equivalent to asserting that

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

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

$$(\lambda \mathbf{I}-\mathbf{E}^0)^{-1}(\mathbf{E}-\mathbf{E}^0)=[\mu^0+\nu^0+\lambda]^{-1}\mathbf{K}(\mu-\mu^0,\nu-\nu^0)$$

has a finite small-λ limit. Then, it can be shown that as $\lambda \to 0$

$$\langle [1+g(\kappa^0)(\kappa-\kappa^0)]^{-1}\rangle = 1 , \tag{21}$$

with

$$\mu^0=\langle \mu[1+g(\kappa^0)(\kappa-\kappa^0)]^{-1}\rangle , \tag{22}$$

$$\nu^0=\langle \nu[1+g(\kappa^0)(\kappa-\kappa^0)]^{-1}\rangle . \tag{23}$$

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 $\kappa^*=\mu^*/\mu^0+\nu^*/\nu^0$. Equation (21) becomes $(1-p)=(1-\kappa^0/\kappa^*)[1-g(\kappa^0)\kappa^0]$, yielding a quadratic equation for κ^0. In the "dilute limit" $p \to 0$, μ^0 and ν^0 (and so κ^0) should vanish. Since for $d=1$, $g(a)\sim(4a)^{-1/2}$, we predict that $\kappa^0 \sim 4p^2$. Thus, even in the limit of arbitrarily small p, the naive perturbation prediction that $\kappa^0=\langle\kappa\rangle=p\kappa^*$ is not recovered. Moreover, EMA yields an exact result here. To see this, note that we have from Eqs. (22) and (23) that $\mu^0/\mu^*=\nu^0/\nu^*=p/[1+g(\kappa^0)(\kappa^*-\kappa^0)]$, and the EMA predicts that $\lim_{\lambda \to 0}\mathbf{N}=-\chi^0\mathbf{K}(\mu^*,\nu^*)$, where $\mathbf{K}$ is defined by Eq. (2) and

$$\chi^0=\frac{p[1-\kappa^0 g(\kappa^0)]}{2\kappa^0 g(\kappa^0)[1+g(\kappa^0)(\kappa^*-\kappa^0)]} , \tag{24}$$

and thus as $a \to 0$ we predict that $\kappa^0 \sim 4p^2$. Consequently, as $p \to 0$, we have $\chi^0 \sim 2p/\kappa^*$, with $\kappa^*=\mu^*/\mu^0+\nu^*/\nu^0$. Thus, we find that the EMA prediction χ^0 and the random variable χ of the exact analysis satisfy

$$\lim_{p \to 0}\chi^0\langle 1/\chi\rangle = 2 . \tag{25}$$

The EMA thus yields the exact scaling in the limit $p \to 0$.

The case of *transition disorder only* with $N=2$ (or *any* $N \geq 2$) is more subtle. Writing $\mu^0=\mu=$const, we find that Eq. (17) 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 the global 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, *for the first time,* why simply coupled diffusion equations are found to be poor models for transport in fractured rocks [1].

In summary, we proposed a model for transport in heterogeneous media with multiple families of transport paths. We derived an exact (but implicit) solution of the model for arbitrary dimensionality and number of transport paths which demonstrates, for the first time, why simply coupled transport equations that have been used so far cannot describe transport in such media. We derived an exact and explicit solution for $d=1$, thus providing, for the first time, a rigorous foundation for a popular empirical model [10] that has been used in the past for describing transport in rock masses. We outlined the construction of a class of EMAs that should be useful for describing transport in disordered media that are not too close to their percolation threshold. Finally, our model allows one to investigate the effect of multiple time scales for distinct transport paths. For example, transport along the fractures of rocks is much faster than that in the pores, and therefore even if the fracture network is fractal, unlike the $N=1$ case, the macroscopic behavior of transport in the rock may not be subdiffusive.

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