TRANSPORT AND DISPERSION IN RANDOM MEDIA

Sidney Redner*

corrections

Abstract. Transport and dispersion phenomena of dynamically-neutral tracer in flow through random media are discussed. For purely convective transport, a deterministic self-similar model is introduced for which the distribution of transit times for the tracer to traverse the network can be calculated. As a function of detailed geometric features of the system, the transit time distribution may be governed by a single time scale, or there may be an infinite sequence of dynamical transitions, in which progressively more time scales are needed to characterize the distribution. To treat the combined effects of convection and molecular diffusion on the transport of tracer, we study a "hydrodynamically-biased" continuum random walk on percolation clusters. A calculational method is outlined which gives the exact moments of the transit time distribution for a given network configuration. For $L \times L$ networks at the bond percolation threshold, the $k^{\rm th}$ moment of the transit time, $\langle t^k \rangle$, at zero flow rate are governed only by a single diffusional time scale, $\tau_D \sim L^{k(2+\theta)}$, where θ is the anomalous diffusion exponent. At high flow rates, $\langle t^k \rangle$ scales as $\tau_c \tau_D^{k-1}$, where $\tau_C \sim L^{d_f}$ is a convective time scale. This two-time-scale behavior is explained on the basis of a simple heuristic argument and from detailed analytical calculations. We also consider dispersion in macroscopically heterogeneous media. For simple geometries, we illustrate the subtleties involved in determining the rules for composing homogeneous, but dissimilar elements. We also discuss some intriguing aspects of dispersion in layered media in the presence of random velocity fields, where superdiffusive behavior arises.

1. Introduction. Hydrodynamic dispersion is a fundamental transport process in which dynamically-neutral tracer disperses in a flow field under the combined action of convection and molecular diffusion.[1-11] The subtle interplay between these two mechanisms gives rise to a transport phenomenon which is considerably more complicated, but richer phenomenologically, than either simple diffusion or biased diffusion. A crucial feature is that dispersion can be dominated by the small fraction of tracer that is caught in relatively rare, stagnant regions within the flow field. Our goal, in this paper, is to provide a simple discussion of some of the intriguing features of dispersion and transport phenomena in random media.

Given the inherent difficulties in accounting for both convection and molecular diffusion in dispersion phenomena, it is worthwhile to consider simpler situations which are tractable analytically.[9] We therefore first consider dispersion in a self-similar hierarchical model

* Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215. The Center for Polymer Studies is supported in part by grants from the ARO, NSF, and ONR.

in the absence of molecular diffusion. A general correspondence between the flow of fluid when each bond of the system is considered to be a one-dimensional tube, and the flow of electrical current when the bonds are considered to be identical resistors is described. This connection will be exploited repeatedly. For the hierarchical model, we introduce an adjustable "asymmetry" parameter which controls the width of the distribution of transit times for tracer to pass through the multiplicity of fluid paths through the network. We then formally solve for the distribution of transit times, and obtain explicit expressions for the moments of the transit time.

As the asymmetry of the hierarchical model is varied, the width of the transit time distribution also varies correspondingly, leading to two classes of behavior. On the other hand, for a sufficiently narrow distribution, $\langle T_N^k \rangle \sim c_k \langle T_N \rangle^k$, where $\langle T_N^k \rangle$ is the k^{th} moment of the transit time distribution on the N^{th}-order hierarchy, and c_k is a numerical coefficient. This implies that a localized pulse of tracer spreads out at the same rate at which the pulse convects downstream. For a sufficiently broad distribution, $\langle T_N^k \rangle / \langle T_N \rangle^k \to \infty$ as $N \to \infty$, leading to enhanced dispersion which is dominated by the small fraction of tracer that passes through the the slowest bond in the network.

We next consider dispersion in low-porosity media where both of convection *and* diffusion drive the transport of tracer.[11] This type of medium is modeled by a percolation model, in which a lattice of identical tubes are either occupied with probability p, or absent with probability $1 - p$. The analogy between electrical current and fluid flow is used to develop a random resistor network description of fluid transport and dispersion. In the presence of a steady-state background flow imposed by an external pressure drop, we calculate the detailed microscopic rules which govern the motion of the tracer at the level of single tubes and tube junctions. These rules are based on describing the combined convective and diffusive motion of the tracer in a tube in terms of a convection-diffusion equation (CDE), with the magnitude of the convection is proportional to the flow velocity in the bond. This gives rise to a "hydrodynamically-biased" continuum random walk as a model for tracer motion; this accounts for the finite macroscopic flow in a physically meaningful way. Together with the assumption of perfect mixing of fluid at tube junctions, we are able to construct a calculational approach which yields, in principle, the *exact* values for moments of transit times for tracer to traverse an arbitrary network.

For percolating networks at the percolation threshold on $L \times L$ square lattices, our numerical results suggest that at zero flow velocity, the transit time moments are all characterized by a single diffusive time scale, i.e., $\langle t^k \rangle \sim \langle t \rangle^k$. However, at high flow rates, *two* characteristic times, a convective and a diffusive time scale are needed to account for the behavior of the moments. This two-time-scale hypothesis is justified by a simple physical argument.

Finally, we consider a number of striking aspects of dispersion in macroscopically heterogeneous media. We seek to develop the composition rules for transport laws when homogeneous, but distinct subunits are superposed. For relatively simple geometries, this appears to be a non-trivial task. Moreover, when macroscopic geometrical inhomogeneity *and* inhomogeneity in velocity fields occur together, *super*diffusive behavior can occur in which the mean-square displacement grows faster than linearly in time. We discuss some of the basic features of this new type of transport phenomenon.

2. Transport and dispersion on the asymmetric hierarchical model. Consider the flow of fluid on the hierarchical model shown in Fig. 1. The system is a hierarchy of both singly-connected bonds and blobs; this appears to capture many of the essential geometrical features of the percolating backbone at the percolation threshold. An important aspect of this asymmetric hierarchy is that the curved bonds at a given level have a conductance decreased by a factor ϵ compared to the straight bonds at the same level.

We are interested in the properties of fluid flow and dispersion of tracer through this system when each bond is considered to be a one-dimensional tube. To this end, we now outline a general analogy between Poiseuille flow in the tube network and electrical current flow in a corresponding resistor network. For a resistor with conductance G, we choose the radius r and the length ℓ of the corresponding tube by $r^2 \sim G^{1/3}$ and $\ell \sim G^{-1/3}$. This gives a flow conductance, $g \sim r^4/\ell$, varying as G. In addition, when a unit pressure drop is imposed across the bond, the average fluid velocity $v \sim g/r^2$ varies as $G^{2/3}$, and the transit time $\tau \sim \ell/v$ therefore varies as G^{-1}. Thus the bond transit time is strictly proportional to the

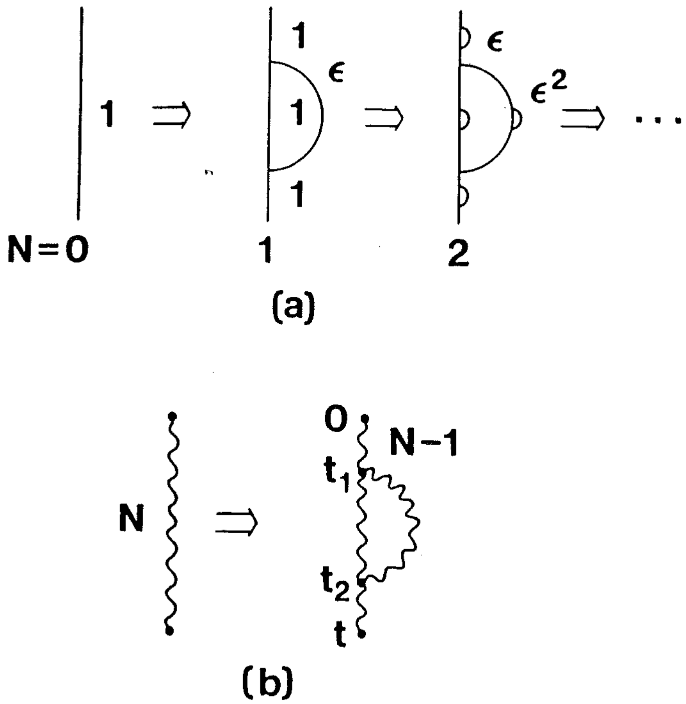

Figure 1. (a) The self-similar hierarchical model, in which a bond of conductance 1 at level N is replaced at level $N+1$ by four new bonds with conductances as indicated in the figure. Shown are the hierarchies at the $N = 0$, 1, and 2 levels. In (b) the corresponding decomposition of an N^{th}-order structure into four $(N-1)^{\text{th}}$-order structures. The labeling of the times used in the integral recurrence relation (2a) is indicated.

inverse of the flux in the bond. Since each bond has the same volume, the tracer spends an equal amount of time, on average, in each bond of the network. This parameterization also ensures that, in the convective limit, tracer enters a particular bond with a probability proportional to the flux in the bond.

The "asymmetry" parameter ϵ controls the width of the distribution of transit times for tracer particles to convect across the network. When $\epsilon = 1$ (symmetric limit), both paths of the first-order structure have the same transit time and there is no dispersion, while for $\epsilon \neq 1$, the variety of distinct paths available for the tracer causes a delta function input of tracer to evolve into a broadened distribution. Note that as $\epsilon \to 0$, one fluid path will have a diverging transit time while the other transit time remains finite. Consequently, the limit $\epsilon \to 0$ is a singular perturbation as flow in the slowest bond dominates in dispersion phenomena.

Let us now calculate the average time required for tracer to traverse the N^{th}-order structure, $\langle T_N \rangle$, when a unit potential difference (or pressure drop) is imposed across the two endpoints of the model. By decomposing the N^{th}-order structure into the four $(N-1)^{\text{th}}$ order structures as indicated in Fig. 1, the transit times on each of the lower-order structures will be rescaled by the factors $a \equiv (3+2\epsilon)/(1+\epsilon)$, $b \equiv 3+2\epsilon$, a, and $c \equiv (3+2\epsilon)/\epsilon$, respectively. Since the tracer takes the straight path with probability $p_{st} = 1/(1+\epsilon)$, and the curved path with probability $p_{cu} = \epsilon/(1+\epsilon)$, we find the simple recursion relation

$$\langle T_N \rangle = p_{st}(2a+b)\langle T_{N-1} \rangle + p_{cu}(2a+c)\langle T_{N-1} \rangle \equiv a_1 \langle T_{N-1} \rangle, \tag{1a}$$

with $a_1 = 4a$. Using $\langle T_0 \rangle = 1$, we thus obtain

$$\langle T_N \rangle = \langle T_1 \rangle^N = (a_1)^N. \tag{1b}$$

To compute the distribution of transit times, denote by $P_N(V;t)$ the probability density for traversing an N^{th}-order hierarchy in a time t when a potential drop V is applied across the system. This distribution satisfies the integral recurrence relation

$$P_N(V;t) = \int_0^{t_2} dt_1 \int_0^{t} dt_2 \Big[p_{st} P_{N-1}\big(\frac{V}{a};t_1\big) P_{N-1}\big(\frac{V}{b};t_2-t_1\big) P_{N-1}\big(\frac{V}{a};t-t_2\big) + p_{cu} P_{N-1}\big(\frac{V}{a};t_1\big) P_{N-1}\big(\frac{V}{c};t_2-t_1\big) P_{N-1}\big(\frac{V}{a};t-t_2\big)\Big]. \tag{2a}$$

In terms of the Laplace transform, $\tilde{P}_N(V;z) = \int P_N(V;t)e^{-zt}dt$, we obtain the functional recursion relation

$$\tilde{P}_N(z) = \left[\tilde{P}_{N-1}(az)\right]^2 \left(p_{st}\tilde{P}_{N-1}(bz) + p_{cu}\tilde{P}_{N-1}(cz)\right), \tag{2b}$$

where the argument V has been dropped since it can be rescaled to an identical value for all the P_N's.

On the other hand, the Laplace transform is the moment generating function

$$\tilde{P}_N(z) = \langle e^{-zt}\rangle = 1 - z\langle T_N\rangle + \frac{z^2}{2}\langle T_N^2\rangle - \ldots \tag{3}$$

so that by expanding (2b) in a power series, one obtains recursion relation in which the k^{th} moment on the N^{th}-order structure, $\langle T_N^k\rangle$, can be decomposed in terms of all moments up to order k on the $(N-1)^{\text{th}}$-order structure. For example, for the case $k=2$, we obtain

$$\langle T_N^2\rangle = a_2\langle T_{N-1}^2\rangle + b_2\langle T_{N-1}\rangle^2, \tag{4a}$$

with

$$a_2 = \left(\frac{1+4\epsilon+\epsilon^2}{\epsilon}\right)\left(\frac{3+2\epsilon}{1+\epsilon}\right)^2; \qquad b_2 = 10\left(\frac{3+2\epsilon}{1+\epsilon}\right)^2. \tag{4b}$$

If we iterate Eq. (4a), we ultimately arrive at

$$\langle T_N^2\rangle = (1-c_2)a_2^N + c_2(a_1^2)^N, \tag{5}$$

with $c_2 = b_2/(a_1^2 - a_2) = 10\epsilon/(12\epsilon - \epsilon^2 - 1)$.

When $a_1^2 > a_2$, which occurs when $\epsilon > 0.08392\ldots \equiv \epsilon_2$, the second term in (5) dominates and we have, as $N \to \infty$

$$\langle T_N^2\rangle \sim c_2(a_1^2)^N = c_2\langle T_N\rangle^2. \tag{6}$$

(Note that this gives $\langle T_N^2\rangle = \langle T_N\rangle^2$ when $\epsilon = 1$.) Thus for $\epsilon > \epsilon_2$, both $\langle T_N\rangle$ and $\sqrt{\langle T_N^2\rangle}$ are governed by a single characteristic time as $N \to \infty$. However for $\epsilon \le \epsilon_2$, the first term in (5) dominates, so that as $N \to \infty$

$$\langle T_N^2\rangle \sim (1-c_2)a_2^N. \tag{7}$$

This limiting behavior for the second (and higher) moments for large N as $\epsilon \to 0$ stems from the small fraction of tracer which enters the slowest bond of the network. That is, taking the square of the time required to traverse the slowest bond in the network, and multiplying by the probability of entering this bond, gives a contribution to the second moment that equals $(9/\epsilon)^N$ for $\epsilon \to 0$, and this coincides with (7) in the $\epsilon \to 0$ limit. Thus the second moment is indeed dominated by the tracer which passes through the slowest bond in the network. Moreover, as $\epsilon \to 0$, $\langle T_N \rangle \sim 12^N$, so that the ratio $\langle T_N^2 \rangle / \langle T_N \rangle^2$ diverges as $(16\epsilon)^{-N}$. Consequently there is more than one time scale that characterizes the transit time distribution.

Similar, but more tedious, considerations apply for the higher moments. The general picture that emerges is that there exists a series of dynamical transitions as a function of ϵ in which the scaling behavior of the moments change. That is, there is an increasing sequence $\{\epsilon_k\}$, with $\epsilon_2 = 0.08392\ldots$, $\epsilon_3 = 0.14727\ldots$, $\epsilon_4 = 0.188003\ldots$, with $\lim_{k\to\infty} \epsilon_k = 1/3$, such that for $\epsilon_k \le \epsilon < \epsilon_{k+1}$ moments of order $j < k$, are governed by a single time scale, namely

$$\langle T_N^j \rangle \sim c_j (a_1^j)^N = c_j \langle T_N \rangle^j, \tag{8a}$$

while moments of order $j \ge k$, scale anomalously, *i.e.*,

$$\langle T_N^j \rangle \sim z_j a_j^N. \tag{8b}$$

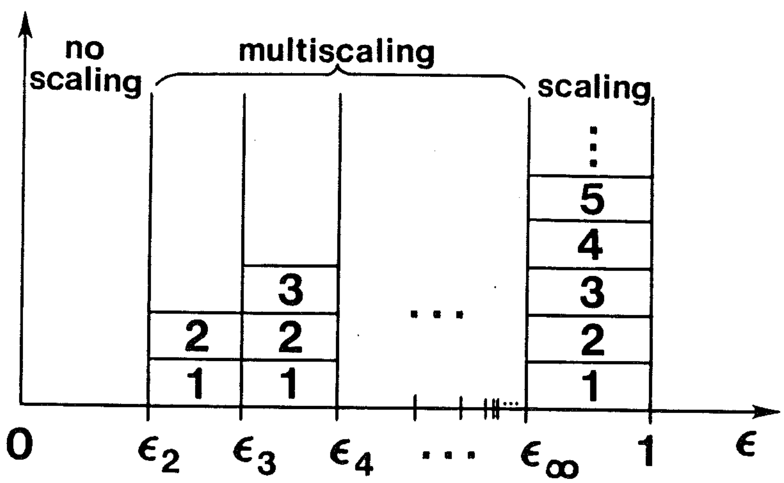

Figure 2. "Phase diagram" for the behavior of the transit time moments of the hierarchical model as a function of the asymmetry parameter ϵ. The labelled blocks indicate the orders of the transit time moments which obey one-parameter scaling.

In general, for $\epsilon > 1/3$, the relation $\langle T_N^k \rangle \sim c_k \langle T_N \rangle^k$ holds for all k. That is, a single time scale, $\langle T_N \rangle$, characterizes *all* the moments of the transit time distribution. We term this behavior in the weakly asymmetric limit as the "scaling" regime. On the other hand for $\epsilon < \epsilon_2$, each moment scales independently. This behavior arises solely from the small fraction of tracer which enters the slowest bond in the network. In the limit $\epsilon \to 0$, this fraction gives the following contribution to the k^{th}-moment

$$\left(\epsilon \cdot \left(\frac{3}{\epsilon}\right)^k\right)^N, \tag{9}$$

which coincides with the limit $\epsilon \to 0$ behavior of a_k^N. We term this new type behavior as "multiscaling".

In the scaling regime, the functional recursion relation for the Laplace transform of the transit time distribution can be simplified by using $\langle T_N^k \rangle \sim c_k \langle T_N \rangle^k$ in (3) to yield, for large N

$$\tilde{P}_N(z) = \langle e^{-zt} \rangle = 1 - z\langle T_N \rangle + c_2 \frac{z^2}{2} \langle T_N \rangle^2 - \ldots \equiv \tilde{g}(z\langle T_N \rangle). \tag{10}$$

That is, $\tilde{P}_N(z)$ is a function only of the scaling combination $z\langle T_N\rangle = z(4a)^N$. Using (10) in (2b), we find the following functional relation for the scaling function $\tilde{g}(z)$

$$\tilde{g}(z) = \left[\tilde{g}\left(\frac{z}{4}\right)\right]^2 \left(p_{\rm st}\tilde{g}(\frac{bz}{4a}) + p_{\rm cu}\tilde{g}(\frac{cz}{4a})\right), \tag{11}$$

with asymptotic solution as $z \to \infty$

$$\tilde{g}(z) \sim A\exp(-(z/z_0)^\alpha), \tag{12}$$

where $A = \sqrt{1+\epsilon}$, z_0 is arbitrary, and α is determined by the root of $4^\alpha = 2 + (1+\epsilon)^\alpha$. When $\epsilon = 1$, this gives $\alpha = 1$, which corresponds to a delta function for the transit time distribution. On the other hand, for $\epsilon < 1$, α is also less than 1, and this quasi-exponential decay in z implies a broadened distribution of transit times.

3. Dispersion in the presence of percolation disorder. For a poorly connected medium, percolation offers a simple and accurate description of many transport properties.[12] We will again exploit the analogy between fluid flow in a random network of tubes and electrical current flow in the corresponding random resistor network to develop a formalism to compute the distribution of transit times for tracer to pass through a percolating network. Our approach is based on first solving for the steady-state fluid flow in the network when a fixed pressure drop is imposed across the opposite edges of the system, and then solving for the motion of tracer through the network under the action of the imposed flow. The detailed rules for tracer motion are based on a picture in which the tracer obeys the convection-diffusion equation (CDE) in each tube with the magnitude of the convection is proportional to the local pressure drop in the bond, and on the assumption that there is perfect mixing of tracer at the junctions between multiple bonds.

Thus we are considering a *hydrodynamically-biased, continuum* random walk with an inhomogeneous bias proportional to the current flow in the bond on the backbone of the network, and with isotropic diffusive motion on the dead ends where there is no flow. We are considering the continuum description in order to account for the longitudinal dispersion within each time, *i.e.*, we have implicitly taken the ratio of the bond length to the mean-free path to be infinite. This feature should provide a more accurate description of motion in a real random network, as compared to a discrete random walk model. An additional noteworthy point is the contrast between the hydrodynamically-biased and *globally*-biased random walk models.[13,14] In the latter model, it is typically assumed that there is a uniform bias everywhere, *including* the dead ends. This leads to dead end residence times which grows exponentially with the length of the dead end ℓ, rather than growing as ℓ^2 if there were unbiased diffusion. Consequently, trapping in the dead ends plays an anomalously large role in determining the motion of a random walker. This might be appropriate for an extremely dilute system where hydrodynamics is not relevant, but not for typical fluid flow.

In order to solve the problem of tracer motion through a percolating network, we first require the solution to the CDE for a single one-dimensional tube.[11] The CDE is

$$\frac{\partial c(x,t)}{\partial t} + u\frac{\partial c(x,t)}{\partial x} - D_{\rm mol}\frac{\partial^2 c(x,t)}{\partial x^2} = 0, \tag{13}$$

where $c(x,t)$ is the tracer concentration at position x and time t, u is the flow velocity, and $D_{\rm mol}$ is the molecular diffusion coefficient. We require the solution to the CDE with boundary conditions appropriate for injection of tracer at one end of the tube, and removal of the tracer at the other end. This corresponds to a unit flux at the inlet end, $j(x = 0,t) = \delta(t)$, and zero concentration at the outlet end, $c(x,t=0) = 0$. Notice that the flux $j(x,t) = uc(x,t) - D_{\rm mol}\frac{\partial c(x,t)}{\partial x}$ has a contributions arising from both convection and dispersion.

For an initially empty system of length L, the CDE is conveniently solved by introducing the Laplace transform, $\tilde{c}(x,s) = \int_0^\infty c(x,t)e^{-st}dt$ to yield a solution of the form

$$\tilde{c}(x,s) = Ae^{\alpha x} + Be^{\beta x}, \tag{14}$$

where $\alpha, \beta = (u \pm \sqrt{u^2 + 4D_{\rm mol}s})/2D_{\rm mol}$, and from the boundary conditions, we determine the constants to be $A = [D_{\rm mol}(\beta - \alpha e^{(\alpha-\beta)L})]^{-1}$ and $B = [D_{\rm mol}(\alpha - \beta e^{-(\alpha-\beta)L})]^{-1}$. For a unit flux input and an absorbing boundary at the outlet, we have the fundamental correspondence that the first passage probability density, $P(t)$, coincides with the outlet flux. Thus the Laplace transform of $P(t)$ is

$$\tilde{P}(s) = \tilde{j}(x = L, s) = \frac{m_s e^m}{m \sinh m_s + m_s \cosh m_s}, \tag{15}$$

where $m = uL/2D_{\rm mol}$ is the Peclet number, and where $m_s = \sqrt{m^2 + sL^2/D_{\rm mol}}$.

Since $\tilde{P}(s)$ is the generating function of the transit time moments, they can be extracted from the series expansion of $\tilde{P}(s)$ in powers of s. We thereby obtain

$$\langle t \rangle = \frac{L^2}{D_{\rm mol}}\left(\frac{1}{2m} - \frac{1}{4m^2}[1 - e^{-2m}]\right), \tag{16a}$$

$$\langle t^2 \rangle = \left(\frac{L^2}{D_{\rm mol}}\right)^2\left(\frac{1}{4m^2} - \frac{1}{8m^4}[2 - (6m+1)e^{-2m} - e^{-4m}]\right), \tag{16b}$$

and so on. The limiting forms of the moments are instructive: For the first moment, we find

$$\langle t \rangle \to \frac{L^2}{2D_{\rm mol}} \qquad m \to 0, \tag{17a}$$

$$\to \frac{L}{U} - \frac{D_{\rm mol}}{U^2} \qquad m \to \infty, \tag{17b}$$

while for the second moment,

$$\langle t^2 \rangle \to \frac{5}{12}\left(\frac{L^2}{D_{\rm mol}}\right)^2 \qquad m \to 0, \tag{18a}$$

$$\to \frac{L^2}{U^2} - \frac{2D^2}{U^4} + \mathcal{O}(e^{-m}) \qquad m \to \infty, \tag{18b}$$

and the limiting behavior for an arbitrary moment has the form

$$\langle t^k \rangle \to x_k \left(\frac{L^2}{D_{\rm mol}}\right)^k \qquad m \to 0, \tag{19a}$$

$$\to \frac{L^k}{U^k} + \ldots \qquad m \to \infty, \tag{19b}$$

where the x_k are constants. Thus at small Peclet numbers, the transit time moments are all governed by the diffusion time, $L^2/D_{\rm mol}$, while at high Peclet numbers the moments are governed by the convection time, L/U.

We now extend this calculational approach to treat a network of nodes i connected by one-dimensional tubes ij of length l_{ij} and cross-sectional area S_{ij}. For simplicity we henceforth take the l_{ij} to have a common value l; however, the general case can be treated straightforwardly. The nodes at one end of the network are all connected to an inlet node I, and those at the other end to an outlet node O. We first compute the background flow field by applying a fixed pressure drop between the inlet and outlet nodes. Due to the complete mixing of the tracer at the nodes of the network, each tube "sees" the rest of the system only through the tracer concentration at its two ends. Thus, as we shall describe, the tracer motion in the network can be accounted for in terms of a (non-symmetric) matrix equation for the node concentrations.

As in the single tube problem, we require the first passage probability density, $P(t)$, for the tracer to arrive at the outlet node, given that there is a unit delta function injection of flux at the inlet node. This first passage problem may be solved in terms of the set of tracer concentrations, $\{c_i(t)\}$, at the nodes of the network. To solve for the $\{c_i(t)\}$, first consider tube ij in which the tracer concentration within the tube, $c_{ij}(x,t)$, satisfies the one-dimensional CDE, where the convection term u now varies in space according to the magnitude of the background flow, *i.e.*, $u = u_{ij}$. We now solve this system of equations for an initially empty system, subject to the boundary conditions appropriate for continuity of the tracer concentrations at all junctions. That is, $\tilde{c}_{ij}(x,s) = \tilde{c}_i$ at $x = 0$, and $\tilde{c}_{ij} = \tilde{c}_j$ at $x = l$. In close analogy with the case of a single tube, the solution is of the form $\tilde{c}_{ij}(x,s) = A_{ij}e^{\alpha_{ij}x} + B_{ij}e^{\beta_{ij}x}$, with $\alpha_{ij}, \beta_{ij} = (u_{ij} \pm \sqrt{u_{ij}^2 + 4D_{\rm mol}s})/2D_{\rm mol}$, and

$$A_{ij} = \frac{\tilde{c}_j - \tilde{c}_i e^{\beta_{ij}l}}{e^{\alpha_{ij}l} - e^{\beta_{ij}l}} \qquad B_{ij} = \frac{\tilde{c}_i e^{\alpha_{ij}l} - \tilde{c}_j}{e^{\alpha_{ij}l} - e^{\beta_{ij}l}}. \tag{20}$$

From this, the Laplace transform of the flux leaving node i along tube ij is

$$\tilde{j}_{ij} = S_{ij}\left(u_{ij}\tilde{c}_{ij} - D_{\rm mol}\frac{\partial \tilde{c}_{ij}}{\partial x}\right)_{x=l}. \tag{21}$$

We may now express this flux in terms of the concentrations $\tilde{c}_i$ and $\tilde{c}_j$ at the two ends of the tube. Thus writing $\tilde{J}_{ij} = G^+_{ij}\tilde{c}_i - G^-_{ij}\tilde{c}_j$, we have

$$G^+_{ij}(s) = D_{\rm mol}S_{ij}(m + m_s \coth m_s)/l, \tag{22a}$$

$$G^-_{ij}(s) = D_{\rm mol}S_{ij}\left(m_s e^{-m}/\sinh m_s\right)/l. \tag{22b}$$

For simplicity we have dropped in subscript ij on m and m_s. For nodes of negligible volume with no accumulation of tracer possible, then the $\tilde{c}_i$ satisfy the current conservation conditions (for the interior nodes of the network),

$$\sum_j \tilde{j}_{ij} = \sum_j (G^+_{ij}\tilde{c}_i - G^-_{ij}\tilde{c}_j) = 0, \tag{23a}$$

while at the inlet node,

$$\sum_j \tilde{J}_{Ij} = \sum_j (G^+_{Ij}\tilde{c}_I - G^-_{Ij}\tilde{c}_j) = 1, \tag{23b}$$

corresponding to a delta function input of flux. Due to the absorbing boundary condition at the outlet node, the Laplace transform of the first passage probability density, $P(t)$, again coincides with the flux exiting via the outlet node

$$\tilde{P}(s) = -\sum_j \tilde{J}_{Oj} = \sum_j G^-_{Oj}\tilde{c}_j. \tag{24}$$

For any value of s, Eqs. (23) and (24) are the analogues of the Kirchhoff equations, $\sum_j g_{ij}(v_i - v_j) = 0$, for the potentials v_i in an electrical network. The primary difference between the two cases is that in the tracer problem, the effective tube conductances are direction dependent, leading to non-symmetric network equations.

Eqs. (23) may be solved in a number of ways. In [15], they were solved by a "probability propagation" algorithm which was motivated by a physical picture in which individual packets of first passage probability are propagated along all possible paths through the system. By this technique, the network first-passage probability $\tilde{P}(s)$ can be obtained exactly, in principle, up to geometric convergence inherent in summing over progressively longer and longer paths. For a well-connected network with little backflow or stagnation effects, probability propagation leads to an efficient method as the computation time is proportional to the system volume. Consequently, this method is intrinsically superior to a computational approach which propagates individual particles through the network. In fact, a finite simulation based on such an approach must lead to incorrect results, as the low-probability paths, which can dominate the higher transit-time moments, will not be sampled. For a poorly-connected medium, however, backflow and stagnation cause the propagation of first passage probability to become relatively inefficient. In this case, it is more efficient to solve the network equations (23) directly.[10,11]

Our simulation results are based on solving square lattice networks of identical tubes at the percolation threshold, with the linear dimension L ranging from 2 to 70. For each configuration, we first find the background flow field by solving for the node potentials of the corresponding random resistor network with a unit external potential drop applied. Then we solve for the tracer motion according to the calculational scheme outlined above. The primary results of the simulation are the following. In the limit of zero flow rate (no convection) the tracer motion reduces to a continuum version of anomalous diffusion[16] on percolation clusters. Owing to the self-similar geometry, one expects that the diffusion equation does not apply, but rather, that the transport is described by anomalous diffusion in which

$$\langle t^k \rangle \sim (\tau_D)^k \sim L^{k(2+\theta)}. \tag{25}$$

Our data are consistent with the previously-estimated value $2+\theta \approx 2.86$ in two dimensions.[14]

The behavior in the high Peclet number regime is considerably more interesting. First, the reduced moment $\langle t^k \rangle^{1/k}$ now *depends* on k, indicating that there is no unique time scale which characterizes the transit time distribution. However, it is possible to give a very simple argument which appears to account for this unusual scaling of the moments. Consider the Y-shaped network of three tubes, each of volume v (Fig. 3), where the incoming fluid flux q branches into two tubes of respective fluxes ϵq and $(1-\epsilon)q$. It is pedagogically useful to think of the "slower" branch as approaching a dead end as the limit $\epsilon \to 0$ is taken. The tracer flux through each branch may be viewed as the sum of diffusive and convective processes which occur independently and simultaneously. The total transition rate into the slower branch is then the sum of its diffusive rate, equal to the inverse diffusion time $D_{\rm mol}/l^2$, and its convective rate, equal to the inverse convection time $u/l = \epsilon q/v$, where u is the velocity in the upper branch. For the "faster" branch, the transition rate is dominated by the convective rate, q/v. As $\epsilon \to 0$, the transition rate into the slower branch is controlled by diffusion and therefore tends to $D_{\rm mol}/l^2$. Correspondingly, the relative entrance probabilities tend to $p_u = D_{\rm mol}v/l^2q + \mathcal{O}(q^{-2})$ and $p_l = 1 - p_u$. Thus the moments of the transit time distribution are, to leading order in q^{-1},

$$\langle t^k \rangle = p_f t_f^k + p_s t_s^k \simeq \frac{D_{\rm mol} v}{l^2 q}\left(\frac{v}{q} + \frac{l^2}{D_{\rm mol}} + \frac{v}{q}\right)^k + 1 \cdot \left(\frac{v}{q} + \frac{v}{q}\right)^k, \tag{26}$$

where the subscript f and s refer to the faster and slower branches, respectively. We rewrite this result in the simpler (and suggestive) form

$$\langle t^k \rangle \sim \tau_C \tau_D^{k-1}, \tag{27}$$

where $\tau_C = \langle t \rangle = 3v/q$, is the "convection" time, which, in turn, is equal to the total volume of the system divided by the flux, and $\tau_D = l^2/D_{\rm mol}$ is the "diffusion" time in the slower branch. Thus the contribution of the slowest bond dominates in all but the first moment, and for this particular case, the slowest bond contribution is of the same order as that of the rest of the network, leading to a transit time which is exactly proportional to the volume of the system.[11,17,18]

To make a correspondence with the transit time moments on percolating clusters, we identify τ_C and τ_D with percolation quantities. From the theorem that the average transit

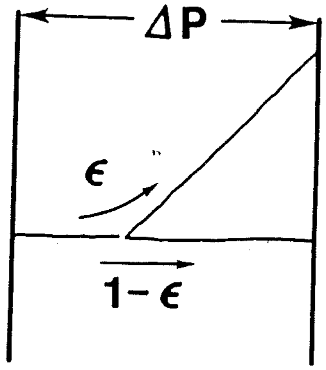

Figure 3. A simple network containing a primarily diffusive path and a primarily convective path. Each tube is of volume v.

time at high flow rates is proportional to the volume of the system, we have $\tau_C \sim L^{d_f}/I$, *i.e.*, the average number of bonds in a percolating cluster of an $L \times L$ system divided by the total current flow I. From our numerical results at zero flow rate, there appears to be a unique diffusive time scale $\tau_D \sim L^{2+\theta}$, which governs all the transit time moments in the diffusive limit. Combining these two results, we anticipate that

$$\langle t^k \rangle \sim \frac{1}{I} L^{d_f+(k-1)(2+\theta)}. \tag{28}$$

This form provides an excellent account of our numerical data.

4. Dispersion in Macroscopically Heterogeneous Media. Thus far we have considered situations systems for which the disorder was on the scale of a single bond. We now discuss some novel transport phenomena that can arise when fluid is flowing through a medium in which the disorder is correlated on a *macroscopic* scale. Consider, for example, a stratified medium in which fluid is diffusing perpendicular to the layers (Fig. 4). Let us compute the first passage time for tracer to traverse a finite number of layers. For N layers of lengths L_i, with respective diffusion coefficients D_i and D_2, we need to solve the diffusion equation with the boundary conditions of unit injection of flux at the left end of block 1, zero concentration at the far end of block N, and continuity of the concentrations and fluxes at all the interfaces. Using standard techniques, the Laplace transform of the first passage probability across a 2-layer composite is,

$$\tilde{P}(s) = [\cosh x_1 \cosh x_2 + \frac{D_1}{D_2} \sinh x_1 \sinh x_2]^{-1}, \tag{29}$$

where $x_i = \sqrt{sL_i^2/D_i}$, and s is the Laplace transform variable. (Notice that for $D_1 = D_2$, Eq. (29) reduces to the first passage probability for a homogeneous block of length $L_1 + L_2$.) The corresponding average first passage time is

$$\langle t \rangle = \frac{L_1^2}{2D_1} + \frac{L_2^2}{2D_2} + \frac{L_1 L_2}{D_2}, \tag{30}$$

which, interestingly, is *not* symmetric in the indices 1 and 2. Therefore $\langle t \rangle$ *cannot* be recast in terms of effective geometric and transport parameters, *e.g.*, as $\langle t \rangle = L_{\text{eff}}^2/D_{\text{eff}}$, which one might have expected if the composite could be described by an effective diffusion equation.

A similar calculation for the N-layer system yields, for the average first passage time through the composite

$$\langle t \rangle = \sum_{i=1}^{N} \frac{L_i^2}{D_i} + \frac{1}{2} \sum_{i<j}^{N} \frac{L_i L_j}{D_j}. \tag{31}$$

This form has a number of striking implications. Even for simple special cases, such as a periodic array of alternating blocks, it is not possible to recast this expression into a form that suggestive of an effective diffusion equation description for the composite. Roughly speaking, the essential problem is that lengths appear as quadratic products, while diffusion constants tend to combine inversely, leading to an anomalous composition rule for $\langle t \rangle$. More generally, it should prove interesting to learn how to write the composition rules and macroscopic description for both series and parallel superposition of homogeneous, but different, subsystems.

For the case of transport parallel to the layers, extremely intriguing behavior can arise, as Matheron and de Marsily[19] were apparently the first to recognize. Consider, as they did, many independent and homogeneous layers of differing thickness, in which the fluid velocity in each layer is a random variable which is drawn from a symmetric distribution with a zero mean (Fig. 4). The tracer therefore obeys the convection-diffusion equation, in which the (layer-dependent) convection term is given by the velocity in the layer. In the longitudinal direction, the spread of dynamically-neutral tracer was found to increase as $t^{3/4}$. This remarkable result arises because in a finite time, a random walker explores only a finite number of layers, N, within which the mean velocity is of order $N^{1/2}$ and fluctuating in sign.[19,20] This non-stationary average velocity leads to an anomalous time dependence of the longitudinal displacement.

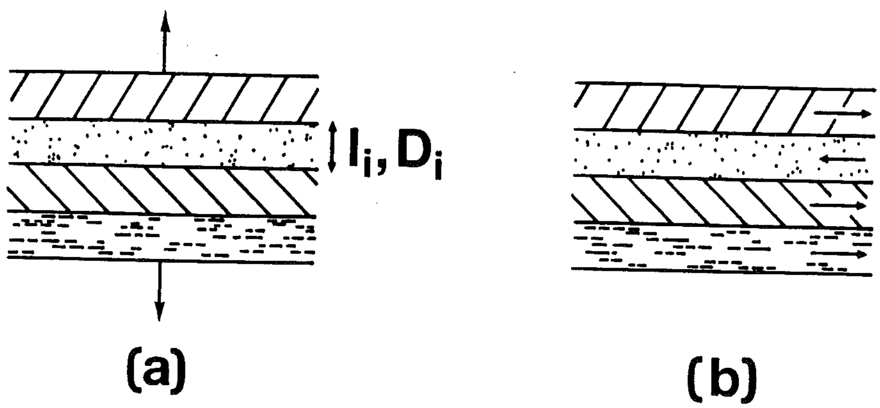

Figure 4. Schematic illustration of a stratified medium. In (a), transport perpendicular to the layers is depicted. In (b) there is a constant fluid velocity within each layer which is a random variable that is symmetrically distributed about a zero mean.

More quantitatively, assume that the mixing of fluid between different layers is driven by molecular diffusion, which is the same in all layers. Then in a time t the random walk visits $D_\perp t$ layers. The average velocity within these layers is simply

$$\langle v \rangle_t = \frac{1}{\sqrt{D_\perp t}} \sum_{i=1}^{\sqrt{D_\perp t}} v_i \sim (D_\perp t)^{-1/4}, \tag{32}$$

where the subscript denotes a restricted average over only t layers. The rms longitudinal displacement at time t, is then

$$\sqrt{\langle x(t)^2 \rangle} \sim \langle v \rangle_t t \sim D_\perp^{-1/4} t^{3/4}. \tag{33}$$

This simple, but striking result raises many interesting and open questions. First, we would like to find the probability distribution for the longitudinal displacement. Our simulations suggest that this distribution can be fit to a quasi-exponential form

$$P(x,t) \propto \frac{1}{t^\nu} \exp[-(x/t^\nu)^\delta] \tag{34}$$

with $\nu = 3/4$, and with the exponent $\delta \lesssim 1.75$. This exponent value for δ is unexpected, since in most examples δ and ν satisfy the relation $\delta = (1-\nu)^{-1}$. On the other hand, a Lifshitz-type argument based on considering the walks which contribute to the extreme large-distance tail of the distribution suggests that $\delta = 4/3$. If this is indeed the case, then the form of the probability distribution is likely to be masked by very slow crossover effects, and this seems to be observed in our simulations.

Some interesting generalizations of the random walk in a stratified medium include considering d'-dimensional strata in a d-dimensional system. There exist only a very few results about the dynamics of random walks in such media. It should also prove fruitful to consider an *isotropic* version of the stratified random walk. For example consider a random walk on a random "Manhattan" grid, in which the directionality along any Avenue or Street is fixed along its entire length, but random in orientation. For this system, a simple generalization of the arguments leading to Eq. (33) suggest that the exponent ν is $2/3$, and that $\delta = 3$. These types of superdiffusive behavior in systems with correlated, but disordered velocity fields should prove to be a rich area for future investigations.

5. Summary and discussion. We have treated a variety of dispersion phenomena within the framework of simple network and random walk models. For random tube networks models of disordered media, we have argued that dispersion can be dominated by the infinitesimal fraction of fluid which is stuck in the "slowest" flow regions of the system. In such a case, the distribution of times for tracer to pass through a network exhibits a tail at long times which dominates in the behavior of the higher moments of the transit time. For the specific example of dispersion on the asymmetric hierarchical model, the moments of the transit time exhibit two very different classes of behavior. In the scaling regime, all moments of the transit time distribution are governed by a single time scale. In the multiscaling regime, dispersion is dominated by the small fraction of tracer that enters the slowest bond in the network. This leads to each moment of the transit time scaling independently of all other moments.

We have also investigated dispersion on percolation clusters, where the transport of tracer involves a competition between pure diffusion in the dead ends and hydrodynamically-biased diffusion on the backbone. The tracer moves through each tube under the action of the background steady-state flow according to the rules of the convection-diffusion equation in each tube with complete mixing of tracer at the tube junctions. This general approach represents what we believe to be the correct generalization of the classical random walk on a percolation cluster to the case of finite flow rates and also to the continuum limit. We have thus developed and implemented numerically a computational recipe which yields a formally exact solution for the the transit time distribution of the tracer on a given configuration, for arbitrary values of the fluid flow velocity. Furthermore, we have postulated a scaling form for the transit time moments which is in excellent agreement with our numerical data on percolation clusters.

Finally, we have discussed the phenomenon of transport in macroscopically heterogeneous media. Even at the most elementary level of consideration, these systems exhibit a variety of novel diffusive and superdiffusive transport laws. There are still a wide variety of intriguing and puzzling questions for which satisfactory, first-principles explanations are still lacking. We believe that some of the theoretical approaches outlined in this paper will be useful in providing some clues towards understanding transport in these types of media.

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