J Stat Phys (2010) 140: 544–564
DOI 10.1007/s10955-010-9992-x

Incorporation of Effects of Diffusion into Advection-Mediated Dispersion in Porous Media

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Received: 23 June 2009 / Accepted: 12 May 2010 / Published online: 28 May 2010

Abstract The distribution of solute arrival times, $W(t;x)$, at position x in disordered porous media does not generally follow Gaussian statistics. A previous publication determined $W(t;x)$ in the absence of diffusion from a synthesis of critical path, percolation scaling, and cluster statistics of percolation. In that publication, $W(t;x)$ as obtained from theory, was compared with simulations in the particular case of advective solute transport through a two-dimensional model porous medium at the percolation threshold for various lengths x. The simulations also did not include the effects of diffusion. Our prediction was apparently verified. In the current work we present numerical results related to moments of $W(x;t)$, the spatial solute distribution at arbitrary time, and extend the theory to consider effects of molecular diffusion in an asymptotic sense for large Peclet numbers, $\mathrm{P_e}$. However, results for the scaling of the dispersion coefficient in the range $1 < \mathrm{P_e} < 100$ agree with those of other authors, while results for the dispersivity as a function of spatial scale also appear to explain experiment.

Keywords Percolation theory · Porous media · Solute dispersion · Long-tailed distribution

1 Introduction

Classical continuum theory [1] of porous media predicts that a pulse of solutes introduced uniformly into a column with mean flow velocity $\boldsymbol{v}$ will subsequently obey Gaussian spreading about a mean flow distance, $\boldsymbol{v}t$. Such spreading is not normally seen [2–12], with solute arrival enhanced at short *and* long times [11, 12]. The long-time tail in the arrival-time distribution can at least be approximated by a power-law, a justification for pursuing analyses

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based on non-classical fractional order partial differential equations [13–21]. The question of the appropriate analytical form for the arrival time distribution is not resolved yet, with both power-law [22, 23] and multi-fractal [24] forms suggested in the literature. Our goal is different: to try to generate a result from first principles for the arrival time distribution which can be used for realistic prediction of experimental results, rather than to resolve a theoretical distinction per se. The work here builds on that of [25], which considered dispersion only by advection (flow), to include effects of diffusion. In [25] concepts from critical path analysis [26, 27] were fused with the cluster statistics of percolation theory [28] and descriptions of the topology of large clusters [29, 30] near the percolation threshold. Contrary to expectations, comparison with experiment here appears to indicate that our treatment is useful even for systems with small disorder.

Our work is consistent with the historical interpretation that dispersion arises from two inputs: 1) spatially variable flow velocities, 2) effects of molecular diffusion. Effects of variable velocity can be understood in different ways. Quoting from [31] (who draw on works of Sahimi and co-authors [32–35]) "Moreover, the critical path analysis [26] indicates that transport in a well-connected system in which the hydraulic conductivity distribution is broad, is actually dominated by a small subset of the system in which the magnitude of the conductivities is larger than a certain threshold. Heterogeneous porous media can therefore be mapped onto equivalent percolation networks."

Quoting from [36], "Dispersion can be dominated by the small fraction of tracer that is caught in relatively rare, stagnant regions within the flow field," both "in the convective limit [37]," and in cases where diffusion is important [38, 39]. While treatments of [37–39] appeared to be falsified by careful comparison of predictions with experiment [40], some of the same authors [41] had already by 1988 considered the possibility that the relevant velocity variability related to percolation disorder.

Although we agree broadly with the quote from [31] we do not rely on a simple mapping. Our treatment [25], representing the cluster statistics of percolation theory in terms of local conductances (allowing flow optimization analogous to critical path analysis), then incorporates tortuosity as well, revealing that the critical path in an infinite system has zero velocity. In this framework we find contributions to solute fluxes *at the same arrival time* from paths below and above the percolation threshold, characterized by as many as three different values of a controlling conductance. For small enough system sizes, none of these values need be particularly close to the percolation threshold so that, in contrast to the quoted approaches, we need not distinguish between sources of slow velocities.

A classical partial differential equation, called frequently the advection-dispersion equation, treats advection and diffusion effects distinctly [1],

$$\frac{\partial C}{\partial t} = \nabla \cdot D_h \nabla C - \boldsymbol{v} \cdot \nabla C \tag{1}$$

Here $C = C(x, t)$ is the concentration as function of space and time. Diffusion processes show up in the first term, the second accounts for advection of a concentration gradient. D_h is called the hydrodynamic dispersion. In homogeneous media, $C(x, t)$ from (1) is a Gaussian centered at $\boldsymbol{v}t$ with variance $D_h t$. In case $\boldsymbol{v} = 0$, $D_h \propto D_m$ [36], with D_m the molecular diffusion constant. Equation (1) was derived on a homogeneous continuum, conditions not satisfied in porous media, leading to problems in its application.

In heterogeneous media, D_h can vary from point to point and $\boldsymbol{v}$ is a random field, generated by solving

$$\nabla \cdot \boldsymbol{v} \propto -\nabla \cdot K \nabla P = 0 \tag{2}$$

In (2) K is the hydraulic conductivity and P is the pressure. A large amount of research capital has been spent solving numerically the system of (1) and (2) [42–46], but without advancing the understanding of the problems of (1), since typically the needed behaviors of D_h must be built into the equations themselves. Other authors have pursued a "stochastic" differential equations approach, to solving (1) and (2) (which is really a form of perturbation theory either for K (or $\log(K)$) [47, 48] or for the associated Liouville equation [49–51]. The latter method is typically based on the cumulant expansion of van Kampen [52].

Although the first term represents diffusion effects, for (1) to generate rough correspondence with experiment, the coefficient, D_h, must be larger than the static diffusion constant. Effects of diffusion appear enhanced by flow so that D_h typically acquires a velocity dependence [32–35]. Even in stochastic theories, solutions to (1) require asymptotically [53] a Gaussian form for $C(x,t)$, which is not typically observed [2–12, 16, 23] (or is found at too large a spatial scale [53]). Finally, D_h must include a dependence on the spatial scale of the measurement [4–8, 10].

A quantity designed, in the Lagrangian representation, to quantify discrepancy between experiment and the Gaussian solution, is the longitudinal dispersion coefficient [54, 55],

$$D_l(t) = \frac{1}{2}\frac{d}{dt}\sigma^2(t) \propto \frac{\sigma^2(t)}{t} \tag{3}$$

where the proportionality follows if $\sigma^2(t)$, *the variance of the spatial solute distribution*, is a power of the time, t. For Gaussian dispersion, the linear relationship $\sigma^2(t) \propto t$ makes $D_l(t)$ time independent. Since field experiments are pinned to an Eulerian representation, dispersion is also reported as the ratio of $\sigma^2(t)$ to the mean *travel length*, x. The two representations are not always equivalent, since the mean solute velocity, $v_s \equiv x/t$ is not, in general, scale-independent (e.g., [29, 32–35]). The typical dependence of $D_l(t)$ is,

$$D_l(t) \propto t^{\alpha} \tag{4}$$

with $0 < \alpha < 1$. Reference [11] cites early works on the Continuous Time Random Walk [56, 57] which show that (4) results from a power-law tail of the arrival time distribution. Because we find the entire distribution, and because it is not precisely a power-law, we do not seek the kind of simple analytical relationship between it and the dispersion coefficient quoted in [11].

Although (1) appears a poor choice as a fundamental transport equation at arbitrary scales, its validity at the pore scale is not questioned [7]. At the pore scale, the relative importance of advection and diffusion on solute transport are thus gauged [41] "by [use of] the Peclet number, $\mathrm{P_e} = vl/D_m$ [58, 59]. Here v is the average fluid velocity, l is a characteristic internal length of the medium, and D_m is the molecular diffusion constant. One may think of $\mathrm{P_e}$ as the ratio of the molecular diffusion time l^2/D_m to the convection time l/v over a distance l." In disordered media v varies greatly in space. At the pore scale, l corresponds to a pore dimension, but at scales larger than centimeters, a generalization is not straightforward [60]. At the pore scale we calculate $\mathrm{P_e}$ using pore length scales, diffusion constants, and velocities. At larger scales we do not yet choose an analogy to $\mathrm{P_e}$. In real media, of course, $\mathrm{P_e}$ must be related to observable quantities.

Calculation of the distribution of arrival times, $W(t;x)$, of solute transported in steady flow [25] has a close relationship to that of finding the distribution of hydraulic conductivity values in finite-sized systems [61, 62]. In particular, both are based on the relevance of the cluster statistics of percolation theory to a distribution of water and associated solute fluxes.

Such an application leads directly to a formulation of solute transport in terms of both critical path analysis and percolation scaling [25].

The primary new work here is to incorporate effects of diffusion into those calculations [25], but a second addition is to generate numerical results for the spatial solute distribution at an arbitrary time, allowing calculation of $D_l(t)$ and derived quantities. The subsequent comparison with experiment allows, at least at larger length scales, evaluation of the relevance of diffusion to experiment, and the relevance of our theoretical results to systems with varying degrees of heterogeneity.

2 Model of the Porous Medium

Calculations below will exploit concepts of critical path analysis from percolation theory with a specific model of the porous medium and corresponding distribution of local conductances. We chose a truncated random fractal model [63]. Although such random fractal models are popular [63–66], the associated power-law distribution of local conductances is not critical to the results we obtain; in fact, in at least one case we investigate, *the same time-dependence for the dispersion is obtained with a log-normal distribution of conductance values* [31]. Two advantages of the power-law distribution are that it facilitates calculations and allows representation of a wide-range of heterogeneities through variation of a single parameter, the fractal dimensionality, D. A third advantage is that, with appropriate substitutions, it can be applied [67] equally to geologic length scales (meters to kilometers). When our results (in the absence of diffusion) are compared with experiment, we will make use of that option.

In the truncated random fractal model [63], pore sizes are distributed according to a power law described by the fractal dimensionality of the pore space, D. Regular structures such as Sierpinski gaskets and carpets are not envisioned. Truncation means that a minimum pore-size, r_0, cuts off the power law distribution. Assumption of self-similarity makes any pore shape distribution independent of pore size and, on the average, a pore length proportional to its radius. The discrete model [63] was adapted [68] to generate a continuous distribution of pore sizes. The volume fraction of the medium, $F(r)\,dr$ occupied by pores between radius r and $r + dr$ is given by,

$$F(r) \propto r^{2-D} \quad r_0 < r < r_m \tag{5}$$

where r_0 and r_m are the minimum and maximum pore radii, respectively. The porosity of the medium is found by integrating $F(r)$ between limits r_0 and r_m with result,

$$\phi = \frac{3-D}{r_m^{3-D}} \int_{r_0}^{r_m} dr\, r^{2-D} = \left(\frac{r_0}{r_m}\right)^{3-D} \tag{6}$$

Equation (6) is identical to the result of [63].

Application of critical path analysis to such a network to find the hydraulic conductivity at saturation, K, develops a critical radius, r_c, as the smallest pore on that infinite cluster which has the largest possible value of the smallest pore. In terms of the critical volume fraction for percolation, $V_c = p_c$, r_c is defined as follows,

$$V_c = \int_{r_c}^{r_m} F(r)\,dr \tag{7}$$

Thus, all the pores with radius $r_c \le r \le r_m$ just barely percolate. An analogous integral with lower limit r relates that r to arbitrary volume fraction, V. For Poiseuille flow, g is proportional to r^4 and inversely proportional to the pore length, itself proportional to r. Thus $g \propto r^3$ and $p - p_c \propto (g^{1-D/3} - g_c^{1-D/3})/g_c^{1-D/3}$, a result relevant for transforming cluster statistics of percolation [28] to a form involving a minimum, or controlling, conductance.

3 Fusing Critical Path Concepts with Percolation Scaling and Cluster Statistics of Percolation Theory to Generate $W(t)$

3.1 Finding a Distribution of Limiting Conductance Values

The cluster statistics of percolation theory give [28] the number of clusters, n_s, per unit volume with s total interconnected sites (or bonds) for any value of the site probability, p. In particular, n_s is approximated as [28],

$$n_s \approx s^{-\tau} \exp\left\{-\left[(p - p_c)s^{\sigma}\right]^2\right\} \tag{8}$$

with σ and τ standard exponents from percolation theory [28]. What is needed is a form of the cluster statistics in which p (p_c) is replaced by g (g_c) and cluster volume by cluster length N. Here N is a number (equal to the number of controlling resistances along one dimension of the cluster); the linear extent of the cluster is then Nl, where l is a typical separation of controlling resistances. One finds [25, 62], using the above result for $p - p_c$,

$$n_N = \frac{1}{N^{d+1}} \exp\left\{-\left[\left(\frac{Nl}{L}\right)^{\frac{1}{\nu}} \left|1 - \left(\frac{g}{g_c}\right)^{\frac{3-D}{3}}\right|\right]^2\right\} \tag{9}$$

The exponent for the correlation length $\nu = 0.88$ in 3-D and $4/3$ in 2-D [32], will be important for later calculations. The probability, $W(g; x)$, that a given system of Euclidean length, $Nl = x$, is spanned by a cluster with controlling conductance g is then proportional to the integral of $N^d n_N$ over clusters of all sizes larger than or equal to the volume in question. The result can be expressed in terms of the exponential integral [25],

$$\mathrm{Ei}[z] = \int_z^{\infty} \frac{\exp[-y]}{y}\, dy$$

as

$$W(g; x) \propto \frac{1}{\beta} \mathrm{Ei}\left[\alpha \left(\frac{x}{L}\right)^{\beta}\right] \tag{10}$$

where the parameters α and β are given by,

$$\alpha = \left|1 - \left(\frac{g}{g_c}\right)^{\frac{3-D}{3}}\right|^2 \quad \text{and} \quad \beta = \frac{2}{\nu} \tag{11}$$

Here L^3 is a representative elementary volume (REV), which corresponds to the smallest volume for which statistical arguments, such as percolation theory, are accurate, and $l \approx L$ was assumed [25]. We then set $L = 1$, meaning that $x = 1$ corresponds to the REV scale.

An independent test of whether (10) predicts experimental hydraulic conductivity distributions was made in [69] where $W(g;x)$ was approximated by,

$$W(g;x) \propto \ln\left[\left(\frac{L}{l+x}\right)^{\frac{1}{\nu}} \frac{1}{|(1-[\frac{g}{g_c}]^{1-D/3})|}\right] \tag{12}$$

Thus the asymptotic behavior of $\mathrm{Ei}(x)$ involves a logarithmic divergence in $W(g;x)$ at $g = g_c$. Since a logarithmic divergence is integrable, $W(g;x)$ is normalizable over the controlling conductance, g.

The solute concentration of the water introduced is assumed uniform. Thus, although the probability that a given isotropic system is spanned by a cluster of minimum conductance g is given by (10) and (11), the mass of solute advected through such clusters characterized by minimum conductance g must be proportional to the expected water flux, itself proportional to $gW(g;x)$. This assertion is consistent with the following quote from [70] for massive particles: "It is often assumed that the particle flux for a given channel is proportional to the fluid flux there, which is highly plausible in the limit of small particle radius [32, 71, 72]. Furthermore, recent studies [73, 74] on the microscopic motion of particles in model porous media show that this approximation is valid even when the radius of the particle is close to that of the channel."

3.2 Relationship of $W(g;x)$ to $W(t;x)$

In order to use $W(g;x)$ to give information on arrival times, we must relate the controlling conductance, g, of a path to the time, t, solute takes to travel along that path, $t(g)$. Absent diffusion, the solution for $t(g)$ is deterministic and [25],

$$gW(g;x)\,dg = W(t;x)\,dt \quad \text{or} \quad W(t;x) = \frac{gW(g;x)}{dt/dg} \tag{13}$$

3.3 Calculation of Cluster Transit Time, t_g

In the following, we decouple the effects of the conductance distribution and connectivity [25] by treating the conductances in series. Then the total *time* of travel is the sum of the travel times through the individual pores along a quasi-one-dimensional path. This means that it is necessary to find the transit times of individual pores.

The time that a solute requires to traverse one pore is proportional to $1/u$, where u is the typical velocity in that pore. Then uA, where A is the cross-sectional area of that particular pore, must (aside from numerical factors) be proportional to Q, where Q is the volume flux of water through the pore. Thus the time required for water-transported solutes to traverse a pore is, $t \propto r/u \propto rA/Q$, where rA is proportional to r^3, or the volume of the pore. Q for all pores along a quasi-one-dimensional critical percolation path is identical and equal to Q_c, which is proportional to g_c. Similarly Q for all pores along a quasi-one-dimensional path near critical percolation is proportional to g, where g is the controlling (smallest) conductance on such a path. The probability that a given pore has radius r is proportional to [68] r^{-D-1} (though the fractional volume in such pores is proportional to $r^3 r^{-D-1} = r^{2-D}$). Q is a volume per unit time, but the time factor is explicitly removed (and called t_0) below so that Q is effectively only a volume. Under those stipulations, Q is r^3 and t_0 is a fundamental advection time scale over a relevant pore. The value of t_0 is not required as

only functional dependences are relevant below. Using these inputs it is possible to write the following expression of proportionality [25],

$$t(r) \propto t_0 \int_r^{r_m} dr' \frac{r'^3}{Q} \frac{r'^{-D-1}}{r^{-D}} = t_0 \left[\int_r^{r_c} dr' \frac{r'^3}{Q} \frac{r'^{-D-1}}{r^{-D}} + \int_{r_c}^{r_m} dr' \frac{r'^3}{Q} \frac{r'^{-D-1}}{r^{-D}} \right] \tag{14}$$

Division of the integral into two terms is useful for expressing the time in terms of the critical time for percolation. Equation (14) must now be modified to account for effects of topology on the transit time. The scaling of the time was noted to follow [25],

$$t \propto |V - V_c|^{-(\nu D_b - \nu)} \left(\frac{x}{L} \right)^{D_b} \tag{15}$$

While one might assume that a solute transit time would involve $d_{\min}$, an exponent that describes the shortest path length [75] across the cluster, [29] showed that the scaling of the time depends on the fractal dimensionality of the backbone, D_b. In the present context V and V_c may be considered to correspond to the volumetric moisture content, θ, and its critical value for percolation, θ_t, and the final results obtained can refer either to saturated or unsaturated media. The combined effects of streamline fluxes and tortuosity is given by the product of (14) and (15). Evaluating the integrals in (14) and combining with (15) yields, (note an additional factor g_c/g in [25] that is in error),

$$t = \left(\frac{x}{L} \right)^{D_b} \frac{t_0}{3 - D} \frac{1}{(1 - \theta_t)^{A-\nu}} \left[\left(1 + \frac{\theta_t}{1 - \theta_t} \right) \left(\frac{g_c}{g} \right)^{1-D/3} - 1 \right] \left[\frac{1}{|(\frac{g}{g_c})^{1-D/3} - 1|} \right]^{(D_b - 1)\nu}$$

$$\equiv \left(\frac{x}{L} \right)^{D_b} t_g \tag{16}$$

where t_g, a cluster transit time, is defined by (16).

While $W(g; x)$ contains a logarithmic divergence, $t(g)$ in (16) contains a power-law divergence at $g = g_c$.

3.4 Results for $W(t; x)$ Excluding Effects of Diffusion

Analytical solution of (13) for $W(t; x)$ using (16) for $t(g)$ is impossible since inversion of $t(g)$ to find $g(t)$ is not possible. Numerical calculations were complicated by the fact that at some times, only one value of g contributes to $W(t; x)$, while at other times two, or even three values of g do so. For each contribution one must apply an analogue to (13). Results for $W(t; x)$ (from [25]) are shown in Figs. 1a, b, for various combinations of fractal dimensionality and critical volume fraction for percolation, $V_c = \theta_t$. The result for $W(t; x)$ is rather insensitive to each parameter.

Results for $W(t; x)$ differ significantly according to the relevant critical exponents for the percolation problem that is relevant. Sahimi [32] has argued (and we agree) that wetting and drying of porous media should be classed as invasion percolation problems. While Sahimi and Yortsos [76] also argued that the distinction between random and invasion percolation is not critical to many phenomena, insofar as the fractal dimensionality of the backbone, D_b, is relevant (see (16) and the discussion before it referring to [29]) this distinction is relevant to dispersion. In media that are saturated except for entrapped air, for example, D_b from invasion percolation should be used.

Values for the fractal dimensionality of the backbone, D_b, and the minimal path, $D_{\min}$, in various percolation models are taken from [30]. Using these values of D_b it is possible to predict $W(t; x)$ for both invasion and random percolation applications.

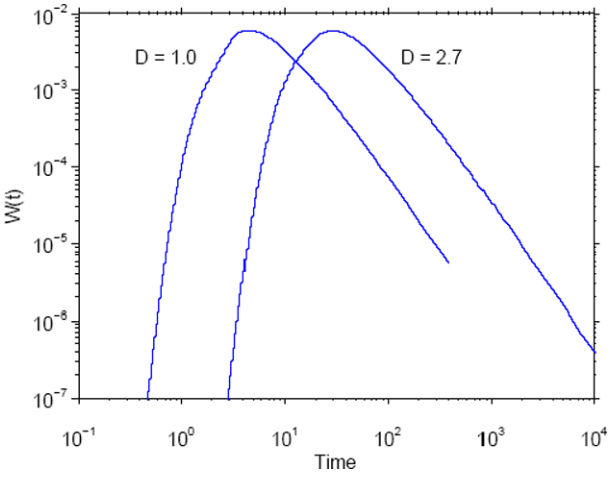

Fig. 1a Derived values of $W(t)$ for two different values of the fractal dimensionality of the pore space, D. $D = 1$ signifies a nearly ordered medium, while $D = 2.7$ generates a rather disordered medium, thus showing the relative insensitivity of the form of $W(t)$ to the heterogeneity of the pore space

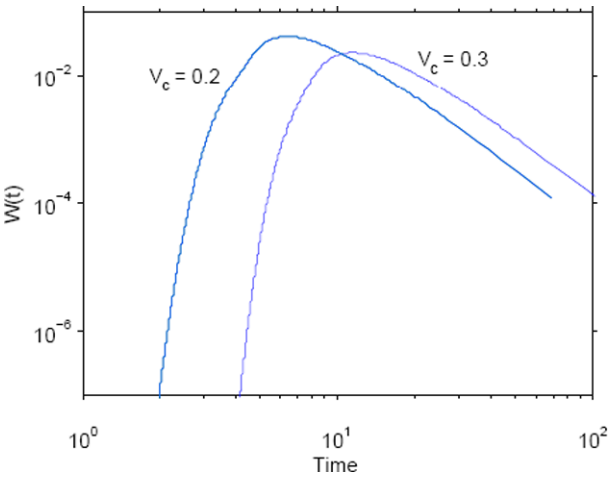

Fig. 1b (Color online) A similar demonstration of the relative insensitivity of the form of $W(t)$ to the critical volume fraction for percolation

3.5 Spatial Distribution at an Instant in Time

Calculation of the spatial distribution, $W(x;t)$, of solutes at a given time is closely related to calculation of the distribution of arrival times at a given point in space. However, we cannot simply integrate over all g holding x constant, since each g value is associated with its own particular velocity.

Consider again the statistics, $W(g,x)$, of clusters of size at least x dominated by minimum conductances, g. $W(g,x)$ represents once again the probability that an arbitrary particle will initiate its motion on such a cluster and can also travel at least x on that cluster. If the solute is on a cluster described by $W(g,x)$, its distance of travel, x, and mean velocity, $\langle v\rangle$ will be related by, $x = \langle v\rangle t$, where t is the time since the solute was initially introduced, and $\langle v\rangle$ is dependent on scale, x, as well as g. For consistency we require this distance x to be identical to x in $W(g,x)$. The pore size dependence of the mean velocity is independent of the distance of travel, and can be roughly estimated using the framework already introduced above as being inversely proportional to $t(g)$ (in particular as $t_0/t(g)$). Now, $x \propto t^{1/D_b}$, so

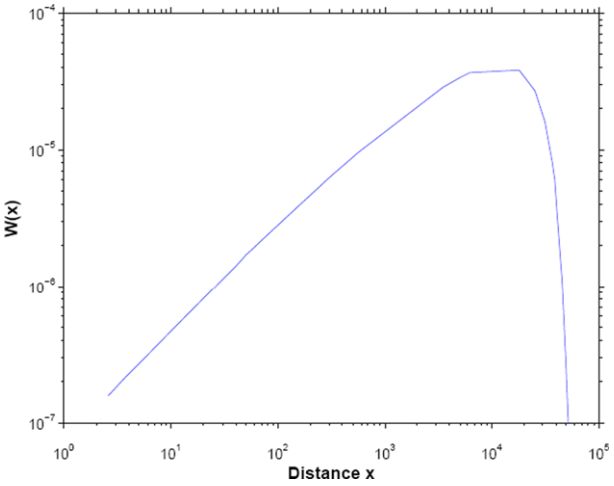

Fig. 2 (Color online) A typical form of the spatial solute distribution, $W(x)$

that $\langle v \rangle = x/t \propto t^{(1/D_b - 1)} \propto x^{1-D_b}$. Using these inputs we found [25] that,

$$\langle v \rangle \propto \left(\frac{t_0}{t_g}\right)\left(\frac{L}{x}\right)^{D_b - 1} v_0 \tag{17}$$

where v_0 is a pore scale velocity. Then one can write for the distance traveled,

$$x = L\left(\frac{t}{t_g}\right)^{\frac{1}{D_b}} \tag{18}$$

where $L \approx v_0 t_0$. The probability that the particle has actually gone this distance x (at time t) is then given by the probability distribution $W(g, x)$ given in (10) and (11), but with the value of $x(t)$ inserted from (18). Then the logarithmic approximation of $W(g, x)$ (12) would look like,

$$W(g; x) \propto \ln\left[\left(\frac{L}{l + L[\frac{t}{t_g}]^{\frac{1}{D_b}}}\right)\frac{1}{|(1 - (\frac{g}{g_c})^{1-D/3})|}\right] \tag{19}$$

In exponential integral form the argument is also expressed as such a product and again both factors must be expressed consistently in terms of the same g value. Then one can make a direct translation between $W(g; x(t, g))$ and $W(x; t)$ in the same way as in (13),

$$W(x; t) = \frac{g W(g, x(t, g))}{dx/dg} \tag{20}$$

where dx/dg is obtained from (18) in terms of dt_g/dg from (16), and where the final step involves solving for g in terms of x and t using (18). Thus the results will include the value of the time as a parameter, just as (13) included the value of the spatial coordinate as a parameter. The appearance of $W(x; t)$ for one combination of parameters is given in Fig. 2. Using (20) the moments of the spatial solute distribution, in particular the variance, $\sigma^2(x)$, may be calculated with time t a parameter.

The variance of the solute distribution is determined from,

$$\sigma^2(x) = \langle x^2 \rangle - \langle x \rangle^2 \tag{21}$$

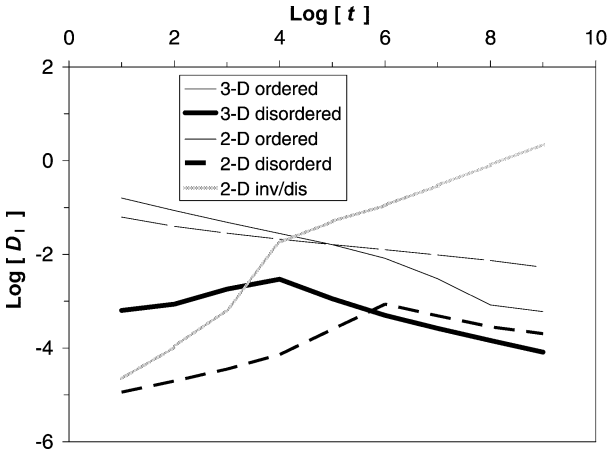

Fig. 3 Dependence of dispersion coefficient, $D_l(t)$, on time for 2-D invasion percolation (large disorder) and for random percolation systems in two and three dimensions (each with differing values of D_b), each with both large and small disorder ($D = 2.95$ or $D = 1$)

where the averages are performed over $W(x;t)$ from (20). Specifically, the dispersion coefficient (from (3)) $D_l(t) = \sigma^2(x)/t$, whereas the dipersivity, $\alpha_l(x) = D_l(t)/v(t) = \sigma^2(x)/\langle x \rangle$. $D_l(t)$ so generated is not quite a power law, so it would have been better to use the derivative form from (3).

We calculated $D_l(t)$ and $\alpha_l(t)$ numerically for two and three dimensional systems using values [30] for D_b appropriate for random percolation and invasion percolation (with and without trapping) and for the cases of large ($D = 2.95$) and small disorder ($D = 1$). However we represent in figures only models with distinct combinations of critical exponents; excluding those invasion percolation examples with the same D_b as in random percolation. Note that $D_l(t)$ can be either an increasing or decreasing function of, t (Fig. 3). Thus, when $D_l(t)$ can be represented as a power law in time, the relevant power may be negative or positive. These values are summarized in Table 1. Note that for 2-D random percolation systems with large disorder we find a power of 0.37 for small times (about 5 decades). In [31] the dispersion coefficient was given as a function of system size for 2-D random percolation simulations on a lattice using a log-normal distribution of local conductances. D_l was found there to behave as x^{ε} with $0.56 < \varepsilon < 0.68$. Using the 2-D value of $D_b = 1.6432$ [30], this would correspond to powers of time between $0.56/D_b = 0.34$ and $0.68/D_b = 0.41$, and our results are in nearly precise agreement.

The dispersivity is usually reported as a power, δ, of the system size, x. We give graphically determined values of this power in Table 1. More importantly, we plot the dispersivity vs. system size x in Fig. 4 for all distinct sets of values of ν, D_b, and D. We also reproduce a rule of thumb from a review of experiments [8].

To generate a power, δ, we let Excel optimize the linear fit on a log-log representation. But blind application of such a procedure to some cases can lead to an overestimation of δ. The range of values given in each case represents relative extremes in disorder of the pore space, i.e., $1 < D < 2.95$. For a typical porosity (of soils) of 0.4, this range of fractal dimensionalities corresponds to a maximum to minimum pore-size ratio that ranges from about 1.3 to 27,000. But for applications at larger length scales [67], where more and less highly conductive regions can correspond to different sediment types, smaller volume fractions of the more highly conducting sediments lead to smaller contrasts in conductance (more nearly 4 orders of magnitude). In any case, we refer to these two extremes as small and large disorder, respectively.

Table 1 Output parameters describing dispersion for various percolation models with input parameters from [30]

Model	$D_{\min}$	D_b	$D_l(t)$	$D_l(t)/\langle v\rangle$
3D				
Site NTIP	1.37	1.87	$-0.30 < \alpha < -0.16$	$1.13 < \delta < 1.16$
Site TIP	1.37	1.86	$-0.30 < \alpha < -0.16$	$1.14 < \delta < 1.15$
Bond TIP	1.46	1.46	$0.053 < \alpha < 0.081$	$1.14 < \delta < 1.15$
RP	1.37	1.87	$-0.30 < \alpha < -0.16$	$1.13 < \delta < 1.16$
2D				
NTIP	1.1293	1.6422	$-0.13 < \alpha < 0.37$*	$1.07 < \delta < 1.51$
Site TIP	1.214	1.217	$0.4 < \alpha < 0.41$	$1.04 < \delta < 1.33$
Bond TIP	1.217	1.217	$0.4 < \alpha < 0.41$	$1.04 < \delta < 1.33$
RP	1.1307	1.6432	$-0.13 < \alpha < 0.37$*	$1.07 < \delta < 1.51$

RP = random percolation, IP = invasion percolation, T = trapping, and NT = non-trapping

*The wide spreads in these values incorporates the slope breaks shown in Figs. 3 and 4.

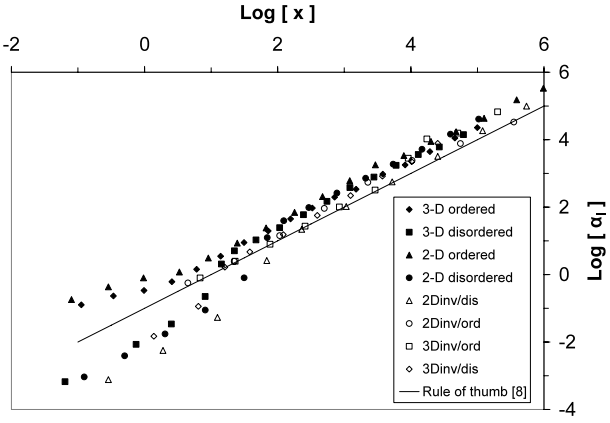

Fig. 4 Scaling of the dispersivity, $\alpha_l(x)$ with x for 2-D and 3-D random and invasion percolation models (each with differing values of D_b), each with either small or large disorder ($D = 1$ or $D = 2.95$). An approximate relationship for predicting $\alpha_l(x)$ [8] is also included. Note that quasi-universal behavior of $\alpha_l(x)$ sets on at an x that corresponds to the change in slope in the time dependence of $D_l(t)$

Experimental values of the power α have been noted typically to be small ($\ll 1$) and positive, while experimental values of δ have been summarized as lying between 0.76 and 1.53 [6, 7, 10]. Thus our values of these parameters are in accord with experimental values. For a more convincing demonstration consider the comparison in Fig. 5 of several of our results with nearly 1000 experiments [7, 16, 77, 78]. This agreement (roughly 8 orders of magnitude of dispersivity over 6 orders of magnitude of length) was produced without use of adjustable parameters, although $L = 1$ was taken to be 1 meter. The relevance of the same length scale to nearly 1000 experiments all over the world was very surprising to us and will be discussed in a future publication.

Whether negative values of the power α should be trusted depends on whether the central limit theorem applies; this is in principle an interesting question but we cannot answer it here. At small enough times and spatial extents the central limit theorem need not apply, whereas the power-law scaling relationship (8) between t and x makes $\sigma^2(x)/x$ a positive power of x even when $\sigma^2(x)/t$ is not a positive power of t. Note that some numerical simulations appear consistent with Gaussian behavior in time but inconsistent with Gaussian behavior in space [79]. Figures 2–5 are shown here for the first time.

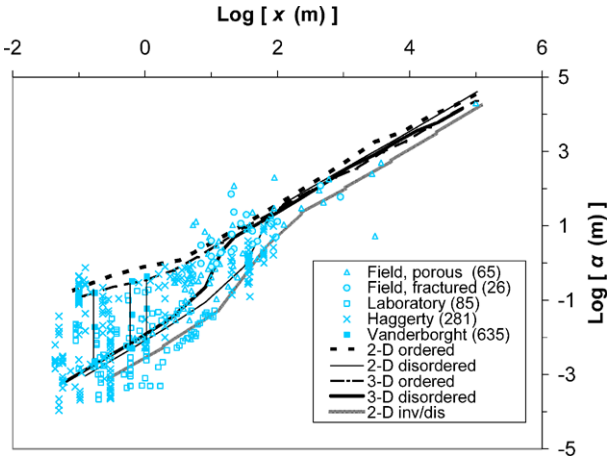

Fig. 5 (Color online) Comparison of dispersivity predictions with experiment for 2-D and 3-D random percolation models, each with either small or large disorder. Since only the 2-D invasion percolation system with large disorder lies outside these limits (see Fig. 4), it is the only invasion percolation model shown. Original data compilations are from Neuman [7], Haggarty [77], Pachepsky et al., [16], and Vanderborght and Vereecken [78]. The number of experiments is given in parentheses for each entry in the *legend*. The data set of [78] is so large that we only represent their values of the mean and standard deviations of a log-normal distribution of $\alpha_l(x)$ values, and connect them with *vertical lines*

4 Treatment of Diffusion Effects

We treat the effects of diffusion only at the pore scale. Equation (1) is, at the pore scale, consistent with treatments based on the Peclet number, $\mathrm{P_e}$. We wish to represent the probability, f, that a particle diffuses off a given path characterized by a given flux at some particular pore with radius r (and length l proportional to r). Equation (1) derives from the idea that probability fluxes are proportional to concentration gradients; thus probabilities per unit time for individual particles are constant. This implies that the probability that a particle can exit a given pore by diffusion is the ratio of the advection time, t_A to the molecular diffusion time, t_D. $t_D = D_m/r^2$, while $t_A = r/v$ [25]. Then the probability, f_i, that a given particle leaves pore i by diffusion is (also found in [80]),

$$f_i \propto \frac{t_A}{t_D} = \frac{1}{\mathrm{P_e}} = \frac{D_m r}{Q} \tag{22}$$

A compatible result that the time for escape from a dead-end is proportional to $\mathrm{P_e}$ was found in [81], as transition rates and survival times are inverses of each other. The final equality arises from the identity $Q = Av \propto r^2 v$ for the fluid flux Q. The assumed proportionality of pore length and radius makes $A/l \propto r$. On a path with conserved Q, the largest radius on the path dominates on account of its smallest value of $\mathrm{P_e}$. The probability, P, that the particle remains on the flow path at a given pore is then $1 - f$. In order to stay on the given flow path it must stay on at every opportunity, a product of $1 - f$ over all the pores along the flow path. Provided that f is small enough (high Peclet numbers) we can use the relationship $\exp(-dx) \approx 1 - dx$ to transform the product

$$\prod_i (1 - f_i) \tag{23}$$

to

$$\exp\left[-\sum_i f_i\right] = \exp\left[-\sum_i \frac{1}{\mathrm{P_e}}\right] \tag{24}$$

We can simplify the sum inside the exponential by representing it as the product of a typical value of $\mathrm{P_e}^{-1}$ and a number corresponding to the frequency of opportunities to "jump" to another flow path. This number is essentially the number of correlation lengths, L, traversed, and can be found by taking the product of the number of pores visited on a path $(x/r_m)^{df}|1-(g/g_c)^{1-D/3}|^{-df}$ and the fraction of pores that provide close contact with other paths r_m/L. Here, in accord with the observations of [40] we neglect any cases for which the particle diffuses into a pore with no flow (although this underestimates the dispersion somewhat). Now the probability that a particle *does not leave* (through diffusion) a path at any point up to the Euclidean distance x is

$$\exp\left[-\frac{r_m}{L}\left(\frac{x}{r_m}\right)^{d_{\min}}\left|\frac{1}{(\frac{g}{g_c})^{1-D/3}-1}\right|^{d_{\min}}\left(\frac{1}{\mathrm{P_{e_c}}}\right)\right] \tag{25}$$

The exponent $d_{\min}$ is the fractal dimensionality of the optimal path [75]. We have assumed that the spatial tortuosity factor is relevant to counting the number of opportunities for diffusion-induced transitions off the path. It is possible that for consistency the choice here should also be the mass fractal dimensionality, D_b as chosen for the total time of transit (since that argument takes into account branching of the paths [29]), but we do not yet have simulations with which we can test our results and make a choice. In addition to the obvious tendency for factor (25) to reduce the contribution of highly tortuous paths (with g near g_c) to large travel times, it also reduces the tendency of very slow paths (with small controlling g and thus small $\mathrm{P_e}$) to contribute to large travel times. Equation (13) must now be multiplied by result (25) to generate,

$$W(t)\,dt = \frac{g\,W(g)}{dt/dg}\exp\left[-\frac{r_m}{L}\left(\frac{x}{r_m}\right)^{d_f}\left|\frac{1}{(\frac{g}{g_c})^{1-D/3}-1}\right|^{d_f}\left(\frac{1}{\mathrm{P_{e_c}}}\right)\right] \tag{26}$$

For $\mathrm{P_e}=\infty$, factor (25) equals 1 and results (13) for pure advection are recovered exactly. For large $\mathrm{P_e}$ (>300, for example, as quoted in [34, 35]) the product of $r_m/\mathrm{P_e}L_0$ may be as small as $1/3000$, and the exponential factor will have little influence until the system is thousands of pores on a side, so it is likely that our treatment of jumps to other flow paths is adequate. Thus it might seem that the claimed lower bound of $\mathrm{P_e}\approx 300$ for which diffusion may be neglected [34, 35] should be approximately verified here as well. This question turns out to be more complex, if our analysis is correct. Our use of $r_m/\mathrm{P_e}L_0$ may ultimately be equivalent to other investigators' use of $\mathrm{P_e}^{-1}$ (in view of the equivalent interpretation in terms of diffusion out of a pore), and to first approximation we treat the two quantities equivalently. Assuming that this choice was appropriate, the $\mathrm{P_e}$ scaling of $D_l(t)$ that we generate has the right power (ca. 1.2) in the right range of $\mathrm{P_e}$ values $1<\mathrm{P_e}<100$ [40, 82–85]. However, assumption of this equivalence also means that the effects of diffusion on $W(t;x)$ are seen at very large values of $\mathrm{P_e}$ (see Fig. 6). Figure 7 shows effects of varying $\mathrm{P_e}$ on $D_l(t)$ with Fig. 8 giving the dependence of the maximum $D_l(t)$ on $\mathrm{P_e}$.

When f becomes much less than 1 already over a single pore (for $\mathrm{P_e}\approx 1$) our treatment yields a probability of being transported to all neighboring pores as roughly equal, consistent with Gaussian spreading, and not with diffusion on a fractal. The fractal structure of the critical paths is important only during flow, not during diffusion. Although this point may

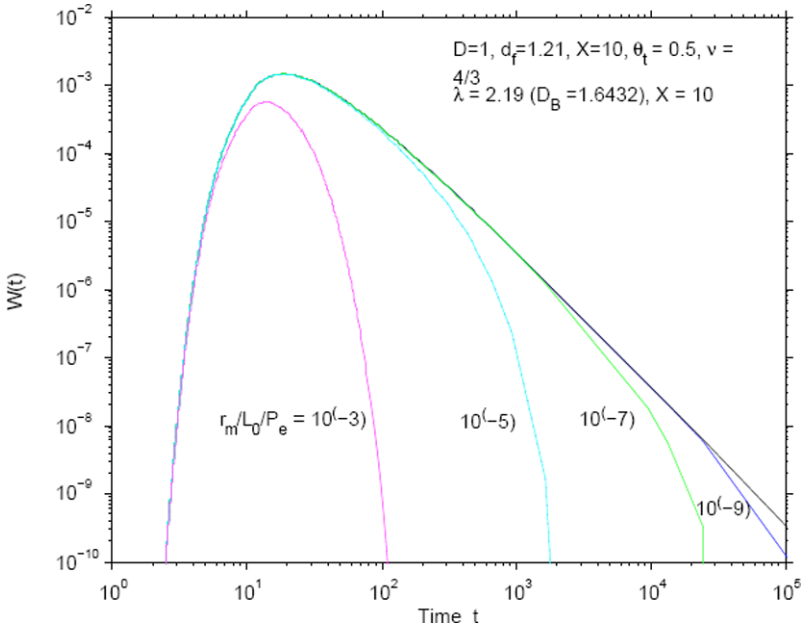

Fig. 6 (Color online) $W(t;x)$ for two-dimensional random percolation systems with increasing values of the Peclet number, P_e. For small values of P_e, roughly 10^{-3}, the long-time tail of $W(t;x)$ has nearly disappeared, and the superlinear scaling of the dispersion coefficient with P_e sets on

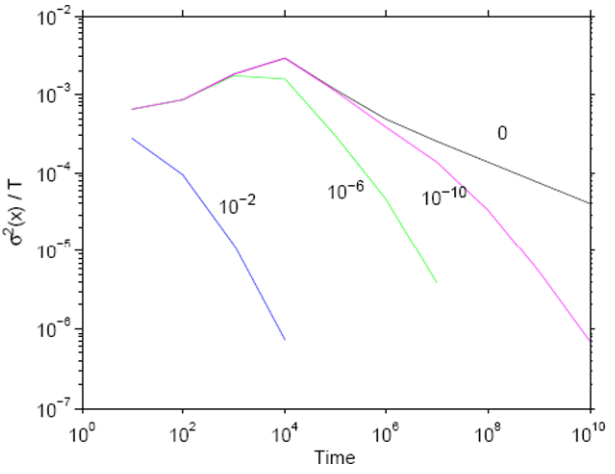

Fig. 7 (Color online) Dispersion coefficient for three-dimensional random percolation systems as function of time for various (inverse) Peclet numbers, which are given for each curve. Note that the infinite Peclet number solution has a maximum in this case. As a consequence, increase in the Peclet number past a given value (about 10^8) cannot yield an increase in the dispersion coefficient, which is already bounded

be argued theoretically in the context of electrical conductivity [86], perhaps the more convincing argument is based on experiment, which shows little or no evidence of the relevance of such fractal structures. Most electrical conductivity and diffusion measurements exhibit characteristics of universal scaling of percolation with no pore-size contribution at all [87].

When factor (25) is analyzed at large enough length scales, x, the exponential becomes rapidly very small. This means that, for any value of P_e, large enough length scales interrupt the coherence of the fractal solute paths and destroy the long tail in the solute arrival time

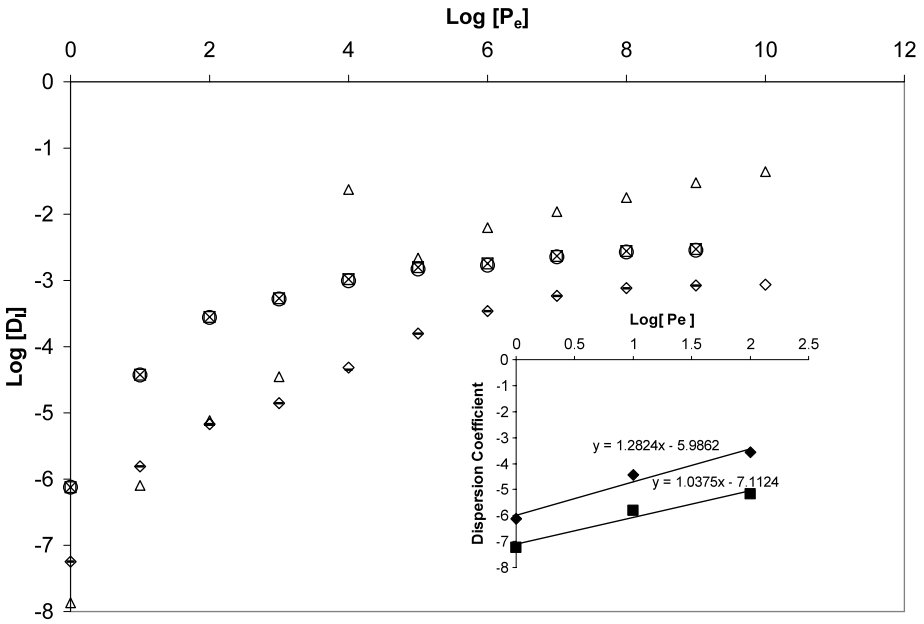

Fig. 8 Scaling of D_l with P_e for highly disordered media (largest pore sizes thousands of times larger than the smallest). Note that the value of D_l for infinite P_e is reached only after 8 orders of magnitude increase of P_e (for five systems), while D_l continues to rise in the sixth. Also the typical increase in D_l here is about three and a half orders of magnitude, at least two orders of magnitude more than for nearly ordered media (with largest pore size less than 50% larger than the smallest). *Open triangles* 2-D invasion, $d_{\min} = 1.22$, *open circles* 3-D invasion, $d_{\min} = 1.37$, *open diamonds* 2-D invasion, $d_{\min} = 1.13$, *dashes* 2-D random, $d_{\min} = 1.13$, *crosses* 3-D random, $d_{\min} = 1.46$, *open squares* 3-D random, $d_{\min} = 1.37$. The *inset* shows the Excel value of the slope for two cases

distribution. The arguments of [57] and [88] (quoted in [12]) then imply that, if the second moment of the arrival time distribution exists, the central limit theorem applies and Gaussian spreading is recovered. This discussion is reminiscent of [89] ("Effect of scale on solute dispersion in saturated porous media"), although their theoretical context was a discussion of Taylor-Aris dispersion in a single capillary [89, 90]. If such concepts apply at greater scales as well, our results for the dispersivity (Fig. 5) are not valid. Because of the agreement with experiment we conclude that the appropriate value of P_e^{-1} at larger length scales is extremely small and diffusion is seldom relevant.

For the range $1 < P_e < 300$ (or so) an ideal solution would be to develop a set of generalized network-like equations (actually discretized Chapman-Kolmogorov equations—see again references [89, 90]) that allow particles to transfer both to and from (fractal) flow paths. The basis of such equations is simply the conservation of probabilities when summing the probability fluxes onto and off of all paths in the network. To solve such equations for $W(t)$ one must sum over all the network paths whose arrival times sum to a given value. The actual sum over path times in a power-law distribution (due to the power-law tortuosity), however, should be dominated by the longest individual step, meaning that our simpler approach of identifying an extreme value may be a useful proxy. *This is indeed the basis of our fundamental hypothesis for incorporating diffusion into the present framework.*

Consider again Fig. 6 for $W(t; x)$ in the presence of diffusion. The power-law tail is cut off beyond a value of t which depends on P_e. Calculations imply that $D_l(t)$ according to (26)

Table 2 Tabulated values of calculated exponent describing scaling of $D_l(t)$ with P_e

Model	$D_{\min}$	D_b	P_e scaling exponent
3D			
Site NTIP	1.37	1.87	1.286
Site TIP	1.37	1.86	1.286
Bond TIP	1.46	1.46	1.285
RP	1.37	1.87	1.282
2D			
NTIP	1.1293	1.6422	1.038
Site TIP	1.214	1.217	1.377
Bond TIP	1.217	1.217	1.377
RP	1.1307	1.6432	1.038
Average	1.22 ± 0.14		

diminishes extremely rapidly at time values associated with the cut-off in $W(t; x)$ (Fig. 7). Such rapid diminution is likely inappropriate (difficulties with the central limit theorem), and we assumed that $D_l(t)$ should thus in most cases reach some maximum and then be independent of time for larger t values. Assumption of a constant value of $D_l(t)$ for larger times is consistent with the central limit theorem (analogously to [89] and [90]). Thus when we estimate the scaling of $D_l(t)$ with P_e, we choose the largest value of $D_l(t)$ for each given P_e value. For $1 < P_e < 100$, the maximum $D_l(t)$ always occurred at the initial time step, allowing straightforward representation of Peclet number scaling (Fig. 8) in this region. The inset shows Excel determined fits to straight lines for two systems.

5 Comparison with Experimental Summary of Peclet Number Scaling

The typical scaling of $D_l(t)$ with P_e in the range $1 < P_e < 100$, as reported in the following references [40, 82–85] is that $D_l(t)$ is proportional to $P_e^{1.2}$. Further the general conclusion of [83, 84], that "the influence of both heterogeneity and high Peclet numbers results in asymptotic behavior only being seen after movement through many throats," is certainly consistent with the general treatment here. Some of the above references are experimental, others are from simulations. However, while the power given is relatively consistent, there is some uncertainty as to the boundaries of the range of P_e for which the superlinear power should be valid with some authors giving a much narrower range ([85], for example). Our results show some curvature in the range $1 < P_e < 100$, but if we allow Excel to fit $D_l(t)$ to a power of P_e in this range, we get the results shown in the table below. Our average power is in very close agreement with the above published values, and for virtually the same range of Peclet numbers.

6 Discussion

Our calculations appear simultaneously to be consistent with many general results for dispersion in porous media. We also suggest that our calculations should apply to all strongly disordered systems, regardless of scale or type of disorder. Our results may even be relevant

to systems with minimal disorder. These arguments are supported by the agreement between our results and experiment for the dispersivity in Fig. 5 as well as the agreement between our results and simulations [31] for the dispersion coefficient in 2-D random percolation, since the simulations were done on a lattice with a different form of the conductance distribution. Figure 5 also suggests that diffusion is seldom significant at larger length scales, since theoretical results depicted were obtained for pure advection.

Our formulation is distinct from any that attribute long-tailed dispersion to geometric (fractal) or related structures extant in porous media [91–93]. It is also distinct from those [94], which develop a distribution of arrival times from considering the distribution of shortest paths connecting two sites on a percolation cluster (in view of the binary distribution of permeabilities considered there), although general features of the arrival time distribution are shared. Our perspective may be contrasted with that of reference [95], where the authors find that similar scaling of dispersion can result from long-range correlations in permeability fields in a percolation model. Finally, perhaps surprisingly, the distribution of clogging times (in two dimensions) [96] and particle penetration [97] in filtration processes resemble closely our results for arrival time distributions [25] in two dimensions as well as the spatial dependence of the dispersivity (here). While the basis for the calculations appears quite different, the slope of the tail of the calculated arrival time distribution (approximately -1.5) and simulated clogging time distribution (also -1.5) appear to be essentially identical. Considering that very nearly the same slope (-1.58) in the arrival time distribution tail is also observed for solute particles in two-dimensional flow simulations on a percolation structure [98] as well as for solute arrival time distributions (-1.5) in experiments of fracture flows [99] (where it has apparently been erroneously attributed to diffusion into and back out of the matrix [99]), we speculate that our arrival time distribution may have relevance to filtration processes and many field experiments (with dispersivity values in Fig. 5) as well.

The assumption of a local power-law in conductances was not relevant to the dispersion coefficient as the results of a 2-D simulation with a log-normal distribution of local conductances also gave a power-law behavior with the same exponent.

Some annoying fluctuations in our results exist. We presume these to be complications from the coarseness of our discretization procedures (decadal discretization in the case of Peclet numbers) when applied to selection of a maximum value of $D_l(t)$.

7 Conclusions

Previous calculations [25] of an arrival time distribution for solutes advected through disordered media were based on the synthesis of critical path analysis [26, 27], cluster statistics of percolation theory [28], and percolation scaling concepts [29, 30]. These calculations could be applied to any disordered media as well as possibly quite ordered media, as long as the effects of finite Peclet number transport could be ignored. The calculations appeared to allow a quantitative prediction of a distribution of solute arrival times, $W(t)$ [25]. In that case we were also somewhat surprised to see that a theoretical construction built on the assumption of wide ranges of pore sizes could generate the appropriate prediction for a medium constructed of single pore sizes, but at the percolation threshold [98].

Here we set out to 1) generate numerical results also for the spatial distribution of solutes at an arbitrary time, $W(x;t)$, and 2) incorporate effects of diffusion into dispersion by advection, albeit only in an asymptotic way. It appears that our treatment of dispersion by advection yields appropriate scaling of $D_l(t)$ with time and $\alpha_l(x)$ with spatial scale, while our asymptotic treatment of diffusion, at least in cases of strongly disordered media, yields

the correct scaling of $D_l(t)$ with Peclet number for P_e values up to 100 or so. For values of P_e between 100 and 1000 or so, we appear to underestimate the dependence of $D_l(t)$ on P_e, as [82–84] report a separate regime of approximately linear dependence of $D_l(t)$ on P_e, whereas our approximate power diminishes more rapidly. However, this regime is approximately reproduced in 2-D invasion percolation, for which we had no complications from a non-monotonic dependence of $D_l(t)$ on t.

Future work should address more quantitatively the intermediate and low Peclet number regimes, where we expect that a discretized Chapman-Kolmogorov equation of a similar form to that of the Continuous Time Random Walk equation may be appropriate. Such a development would put our treatment on a stronger theoretical footing and could provide bases for choosing a fractional calculus, Fokker-Planck equations, etc. Further research into the apparent reduction of $D_l(t)$ at large values of t (for most systems) is also necessary to establish whether the central limit theorem is violated.

Acknowledgements This research was supported by NSF grants EAR-0911482 and EAR-0810186.

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