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Dispersion in porous media, continuous-time random walks, and percolation

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A promising approach to the modeling of anomalous (non-Gaussian) dispersion in flow through heterogeneous porous media is the continuous-time random walk (CTRW) method. In such a formula on the waiting time distribution $\psi(t)$ is usually assumed to be given by $\psi(t) \sim t^{-1-\alpha}$, with α fitted to the experimental data. The exponent α is also related to the power-law growth of the mean-square displacement of the solute with the time t $\langle R^2(t)\rangle \sim t^{\zeta}$. Invoking percolation and using a scaling analysis, we relate α to the geometrical exponents of percolation (ν, β, and β_B) as well as the exponents μ and e that characterize the power-law behavior of the effective conductivity and permeability of porous media near the percolation threshold. We then explain the cause of the nonuniversality of α in terms of the nonuniversality of μ and e in continuum systems, and in percolation models with long-range correlations, and propose bounds for it. The results are consistent with the experimental data, both at the laboratory and field scales.

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I. INTRODUCTION

When a solute is brought into contact with a miscible solvent, it slowly diffuses into the solvent, and after some time develops a diffused mixed zone. If the volumes of the two fluids do not change upon mixing, then the net transport of the solute across any arbitrary plane is represented by Fick's second law of diffusion

$$\frac{\partial C}{\partial t} = D_m \nabla^2 C, \tag{1}$$

where C is the solute concentration, t the time, and D_m the molecular diffusivity of the solute in the solvent. If the solvent is also flowing, then there will be additional *convective* mixing that is due to the nonuniform velocity field, which, in turn, is caused by the morphology of the medium. The resulting mixing process is called hydrodynamic dispersion, or dispersion for brevity.

Dispersion is important to a wide variety of processes. One important example of much current interest, due to the phenomenon of global warming, is the storage and sequestration of CO_2 in deep saline aquifers, in which dispersion plays an important role. Dispersion is also important to miscible displacements in enhanced oil recovery, to salt water intrusion in coastal aquifers where it helps the mixing of fresh and salt waters, and to the *in situ* characterization of aquifers by the classical method of injecting fluid tracers into the porous formations and measuring their travel times between two specific locations. Dispersion also plays a fundamental role in spreading industrial and nuclear wastes and polluting subsurface waters. In particular, burying nuclear waste deep in porous rock has been suggested as a way of sequestering its pollution, but the leakage of the waste into groundwater aquifers, which spread by dispersion, has been a major concern.

In laboratory-scale porous media dispersion is driven by a kinematic mechanism whereby pore throats are divided and rejoined at the pore bodies of the pore space. The tangling and divergence of streamlines is accentuated by the widely varying orientations of flow passages and coordination numbers of the pore space. Dispersion in such porous media is also driven by a dynamic mechanism because the speed with which a given pore throat is traversed depends on its hydraulic conductance and orientation, as well as the local pressure field. The net result is wide variations in the lengths of the streamlines and their downstream transverse separations that contribute to dispersion. The two mechanisms indicate that there is a geometrical aspect of dispersion with respect to the direction of the mean flow velocity: a longitudinal effect due to the difference between the velocity components in the direction of the mean flow and a transverse effect due to the differences between local velocity components orthogonal to the direction of the mean flow. On the other hand, over length scales that are much larger than the laboratory scale (those in which the spatial distribution of the permeability is broad) dispersion is dominated by the fluctuations in the flow velocities, with diffusion playing no significant role.

Dispersion is said to be *diffusive* or *Gaussian* if it is described by the convective-diffusion equation (CDE)

$$\frac{\partial C}{\partial t} + \langle \mathbf{v}\rangle \cdot \nabla C = D_L \frac{\partial^2 C}{\partial x^2} + D_T \nabla_T^2 C, \tag{2}$$

where $\langle \mathbf{v}\rangle$ is the macroscopic mean velocity, and ∇_T^2 the Laplacian in the transverse directions. Here D_L and D_T represent, respectively, the longitudinal (in the direction of macroscopic flow) and transverse (perpendicular to the direction of macroscopic flow) dispersion coefficients. As Eq. (2) indicates, D_L and D_T represent effective diffusivities that are, however, distinct from D_m, the molecular diffusivity, or D_e, the effective diffusivity in a pore space *in the absence of a flow field*. For the sake of simplicity we delete $\langle\cdot\rangle$ and denote the magnitude of the average fluid velocity by v. Due to its high significance dispersion has been studied by a wide variety of techniques and models [1]. They include mean-field approximations [2], several types of pore network models [3–7], volume- [8] and ensemble-averaging methods [9], the stochastic spectral method [10], particle-tracking techniques [11], the critical-path analysis [12], and the continuous-time random walk (CTRW) model [13–15].

An important question, the focus of this paper, is the modeling of *anomalous dispersion* (i.e., when dispersion cannot be described by the CDE [16]). When dispersion is anomalous, the mean-square displacement of the solute, $\langle R^2(t)\rangle$, varies with the time t as $\langle R^2(t)\rangle \sim t^\zeta$ with $\zeta \neq 1$. While numerical simulations may be used to study anomalous dispersion, the question of developing a fundamental formulation of the problem is still under study. The stochastic spectral method [10] and the ensemble-averaging technique [9] do provide analytical formulations, but are limited by certain constraints, such as the porous media having high porosity, or the spatial distribution of their permeability having certain properties. On the other hand, the CTRW formulation of dispersion [13–15] is a promising approach that has been shown to be capable of providing accurate predictions for the experimental data that cannot be modeled by the CDE. But, as described below, the current CTRW formulation is still phenomenological in the sense that its key quantity, the waiting-time distribution, must still be fitted to the experimental data.

In this paper we propose to combine the CTRW formulation with percolation theory to develop a model in which the key parameter of the former approach is expressed in terms of the percolation exponents that describe the power-law properties of flow and transport properties near the percolation threshold. We show that such an approach also explains the nonuniversality of the key parameter of the CTRW formulation, as well as providing bounds on its numerical value.

The rest of this paper is organized as follows. In the next section we provide a brief description of the CTRW formulation of dispersion. Section III describes how the CTRW formulation is combined with a percolation approach. In Sec. IV we test the prediction of the model against some experimental data measured in laboratory-scale porous media. Section V explains the origin of the observed nonuniversality of the CTRW's key parameter. We then extend in Sec. VI the discussion to dispersion in field-scale porous media. The paper is summarized in Sec. VII.

II. CONTINUOUS-TIME RANDOM WALK FORMULATION

The starting point of the CTRW model is a master equation (ME) [13,17]

$$\frac{\partial C(\mathbf{s},t)}{\partial t} = \sum_{\mathbf{s}'} W(\mathbf{s},\mathbf{s}')C(\mathbf{s}',t) - \sum_{\mathbf{s}'} W(\mathbf{s}',\mathbf{s})C(\mathbf{s},t), \tag{3}$$

where $C(\mathbf{s},t)$ is the solute concentration or, provided that it is suitably normalized, the probability that a solute particle is at $\mathbf{s}$ at time t, and $W(\mathbf{s},\mathbf{s}')$ is the transition rate, the probability of moving from $\mathbf{s}$ to $\mathbf{s}'$ that implicitly contains the effect of the flow velocity on the motion of the solute. $\mathbf{s}$ and $\mathbf{s}'$ are not necessarily the sites of a lattice. The crucial aspect of the formulation is specifying $W(\mathbf{s},\mathbf{s}')$, which entails detailed knowledge of the heterogeneities of porous media. Below a length scale ℓ_c the heterogeneities are unresolved and, thus, one must resort to a statistical description of the set $\{W(\mathbf{s},\mathbf{s}')\}$. To do so, one ensemble averages Eq. (3) that, as is well known [18], leads to a generalized master equation (GME), which is a *nonlocal* equation with memory (see also Ref. [19])

$$\frac{\partial C_m(\mathbf{s},t)}{\partial t} = \sum_{\mathbf{s}'}\int_0^t \varphi(\mathbf{s}-\mathbf{s}',t-t')C_m(\mathbf{s}',t')dt' - \sum_{\mathbf{s}'}\int_0^t \varphi(\mathbf{s}'-\mathbf{s},t-t')C_m(\mathbf{s},t')dt', \tag{4}$$

where $C_m(\mathbf{s},t)$ is the ensemble-averaged concentration. The function $\varphi(\mathbf{s},t)$ is given by Eqs. (8) and (15) below. Note that φ is stationary in space, depending only on $\mathbf{s}-\mathbf{s}'$.

A CTRW is described by

$$P(\mathbf{s},t) = \sum_{\mathbf{s}'}\int_0^t \psi(\mathbf{s}-\mathbf{s}',t-t')P(\mathbf{s}',t')dt', \tag{5}$$

where $P(\mathbf{s},t)$ is the probability per time that a random walker has arrived at $\mathbf{s}$ at time t, and $\psi(\mathbf{s},t)$ is the probability per unit time for a displacement $\mathbf{s}$ with a difference of arrival times of t, with $P(\mathbf{s},0) = P_0 = \delta_{\mathbf{s},0}\delta(t-0^+)$. It was shown [20] a long time ago that the GME is equivalent to a CTRW. The correspondence between Eqs. (4) and (5) is given by

$$C_m(\mathbf{s},t) = \int_0^t \Psi(t-t')P(\mathbf{s},t')dt'. \tag{6}$$

Here $\Psi(t)$ is given by

$$\Psi(t) = 1 - \int_0^t \psi(t')dt', \tag{7}$$

with $\psi(t) = \sum_{\mathbf{s}} \psi(\mathbf{s},t)$. $\varphi(\mathbf{s},t)$ is related to $\psi(\mathbf{s},t)$ in the Laplace transform space by

$$\tilde{\varphi}(\mathbf{s},\lambda) = \frac{\lambda\tilde{\psi}(\mathbf{s},\lambda)}{1-\tilde{\psi}(\lambda)}, \tag{8}$$

where λ is the Laplace transform variable conjugate to t. The formulation so far is valid for a lattice of N sites with periodic boundary conditions in which the sites' positions are given by, $\mathbf{s} = \sum_{j=1}^3 s_j a_j$ with $s_j = 1,2,\ldots,N$, and a_j being the lattice constants. If N is very large, the lattice constant can be arbitrarily small, approaching the continuum limit.

An important quantity, which has been used in the numerical simulations of dispersion [3,4,11], is the first passage-time distribution (FPTD) $Q(\mathbf{s},t)$, the probability density of a solute particle arriving at $\mathbf{s}$ at time t for the first time. Introducing the FPTD into the CTRW formulation is necessary because, while the solution of Eqs. (5) through (8) may be derived for a system with periodic boundary conditions, such conditions do not necessarily exist in actual experiments. One has

$$P(\mathbf{s},t) = P_0 + \int_0^t Q(\mathbf{s},t')P(0,t-t')dt'. \tag{9}$$

The solution of Eq. (9) in the Laplace transform yields

$$\tilde{Q}(\mathbf{s},\lambda) = \frac{\tilde{P}(\mathbf{s},\lambda)-\delta_{\mathbf{s},0}}{\tilde{P}(0,\lambda)}. \tag{10}$$

The breakthrough curve $j(t,L)$ measured at time t and, say $s_1 = L$ (L is the length of the porous medium), which is measured routinely in experiments, is given by

$$j(t,L) = \sum_{s_2}\sum_{s_3} Q(s_1 = L,s_2,s_3). \tag{11}$$

The inverse Laplace transform of the solutions presented so far must be computed numerically [21].

One must now identify $\psi(\mathbf{s},t)$ and its relation with the transition rates. One first writes down an ME as a random walk equation to obtain a transition length and time distribution

$$\psi_{\mathbf{s},\mathbf{s}'}(t) = W(\mathbf{s}',\mathbf{s}) \exp\left[-t \sum_{\mathbf{s}''} W(\mathbf{s}'',\mathbf{s})\right]. \qquad (12)$$

Then, summing over all $\mathbf{s}'$, one obtains

$$\psi_{\mathbf{s}}(t) = \sum_{\mathbf{s}'} W(\mathbf{s}',\mathbf{s}) \exp\left[-t \sum_{\mathbf{s}'} W(\mathbf{s}',t)\right] \equiv -\frac{dQ_s}{dt}, \qquad (13)$$

with

$$\psi(t) = -\frac{d}{dt}[[Q_s]], \qquad (14)$$

where $[[\cdot]]$ denotes an ensemble average. For an ordered porous medium, $W(\mathbf{s}',\mathbf{s}) = W(\mathbf{s}'-\mathbf{s})$ and $W_s = \sum_{\mathbf{s}'} W(\mathbf{s}',\mathbf{s}) =$ constant. Then $\psi(t) = W_s \exp(-W_s t)$, $\tilde{\psi}(\lambda) = W_s/(W_s+\lambda)$, and

$$\tilde{\varphi}(\mathbf{s},\lambda) = W(\mathbf{s}). \qquad (15)$$

One can also determine an effective transition rate by an effective-medium approximation [19]. More generally though, the porous medium may have a fixed $W(\mathbf{s}'-\mathbf{s})$, but with a random spatial distribution of the sites $\mathbf{s}$. Thus, if the site density is N_s, one has [22]

$$[[Q_s]] = \exp\left\{-N_s \int \{1-\exp[-W(\mathbf{s})t]\} d^3s\right\}. \qquad (16)$$

A transition rate is then specified and Eq. (15) is evaluated [23] to derive an expression for $\psi(t)$.

The CTRW may be extended to the continuum limit. If the first two moments of $\psi(\mathbf{s},t)$ exist, one has [24] in the Laplace transform space

$$\lambda\tilde{C}_m(\mathbf{s},\lambda) - C_m(\mathbf{s},0) = -\mathbf{v}_*(\lambda)\cdot\nabla\tilde{C}_m(\mathbf{s},\lambda) + \mathbf{D}_*(\lambda) : \nabla\nabla\tilde{C}_m(\mathbf{s},\lambda), \qquad (17)$$

where : indicates a tensor product. $\mathbf{v}_*(\lambda)$ and $\mathbf{D}_*(\lambda)$ are, respectively, the effective flow velocity vector and the dispersion tensor. In many cases, one writes $\psi(\mathbf{s},t) = p(\mathbf{s})\psi(t)$, where $p(\mathbf{s})$ and $\psi(t)$ are the probability distributions for the length of the solute's jump and the waiting time before the jump is made, respectively. The decoupling is justified if the flow velocity correlates very weakly [13,17] with $|\mathbf{s}|$, which is the case in many situations. Writing [24,25], $\mathbf{v}_*(\lambda) = \tilde{M}(\lambda)\mathbf{v}_\psi$ and $\mathbf{D}_*(\lambda) = \tilde{M}(\lambda)\mathbf{D}_\psi$ with $\tilde{M} \equiv t_c\lambda\tilde{\psi}(\lambda)/[1-\tilde{\psi}(\lambda)]$, one obtains

$$\mathbf{v}_\psi = \frac{1}{t_c}\int \mathbf{s}\, p(\mathbf{s}) d^d s, \qquad (18)$$

$$\mathbf{D}_\psi = \frac{1}{2t_c}\int \mathbf{s}\mathbf{s}\, p(\mathbf{s}) d^d s, \qquad (19)$$

with t_c being a characteristic time. The mass flux $\mathbf{J}$ is then given by

$$\tilde{\mathbf{J}}(\mathbf{s},\lambda) \equiv \tilde{M}(\lambda)[\mathbf{v}_\psi\tilde{C}_m(\mathbf{s},\lambda) - \mathbf{D}_\psi\cdot\nabla\tilde{C}_m(\mathbf{s},\lambda)]. \qquad (20)$$

In a very large number of applications of the CTRW [13,15,17, 19–26], including to dispersion [13,17], the following power law has been used

$$\psi(t) \sim t^{-1-\alpha}. \qquad (21)$$

Equation (21) completes the CTRW formulation of dispersion: one fits the CTRW expression for the flux J or the breakthrough curve j to the data and estimates α, the critical parameter of the formulation. α is *nonuniversal*, implying that it depends on the porous media's morphology. We now propose combining percolation theory [27] with the CTRW formulation to develop a method for estimating the exponent α, relating it to the morphology of the pore space, and putting bounds on its value.

III. ESTIMATING α BASED ON PERCOLATION THEORY

Even on the scale of a laboratory sample, porous media are highly heterogeneous [28], hence giving rise to broad distributions of the pore conductances. Thus, one can invoke the critical-path analysis (CPA), first proposed by Ambegaokar, Halperin, and Langer [29], who argued that transport in a disordered medium with a *broad* distribution of conductances (one in which the conductances vary by at least a few orders of magnitude) is dominated by those with magnitudes larger than some characteristic conductance σ_c, defined as the smallest conductance such that the set of conductances $\{\sigma|\sigma > \sigma_c\}$ forms a conducting sample-spanning cluster (SSC), called the critical path. In other words, transport is dominated by the highly conducting regions, and it is their connectivity that is important to macroscopic transport. Since the low-conducting regions make little or no contribution to the overall transport, their connectivity is not important and, thus, they can be removed. Therefore, transport in a disordered medium with a broad conductance distribution reduces to a percolation problem with threshold conductance σ_c, even if the medium may seem to be in a state far from its percolation threshold.

According to the CTRW formulation of dispersion, if the distribution $\psi(t)$ is given by Eq. (21) then the mean-square displacement $\langle R^2(t)\rangle$ of a solute particle is given by

$$\langle R^2(t)\rangle \sim \begin{cases} t^{2\alpha} & \alpha < 1, \\ t^{3-\alpha} & 1 < \alpha < 2, \end{cases} \qquad (22)$$

where $\alpha < 1$ corresponds to porous media that are highly heterogeneous. On the other hand, for dispersion on the SSC at the percolation threshold p_c one has [30]

$$\langle R^2(t)\rangle \sim t^{\zeta}, \qquad (23)$$

where, as shown shortly, ζ is related to the standard percolation exponents. A comparison of Eqs. (22) and (23) indicates that if the percolation model and the CPA are applicable, then estimating the exponent α of Eq. (21) is tantamount to determining the exponent ζ that characterizes the power-law dependence of $\langle R^2(t)\rangle$ on the time t in the SSC at the percolation threshold p_c. Anomalous dispersion corresponds to $\zeta \neq 1$.

Relating the CTRW to percolation systems deserves some discussion since the CTRW is obtained by ensemble averaging of the master equation, and one might question the applicability of such averaging to a poorly connected system, such as one near or at the percolation threshold. However, three points are worth mentioning here. (i) One can rigorously map *diffusion* in the percolation system onto a CTRW [19], in which case the power law (22) arises naturally. (ii) The CPA maps a disordered medium that is seemingly far from its percolation threshold to which the CTRW formulation is applicable, onto one at the percolation threshold, if the medium is heterogeneous. This is the crucial aspect of what we are proposing in the present paper. (iii) Data for dispersion in porous media with extremely low connectivity have been shown to be described well by the CTRW formulation [1].

To determine ζ we carry out a scaling analysis that represents an extension of our previous work [30]. Let us first recall the power laws that govern the various quantities near p_c. The correlation length ξ_p of percolation follows $\xi_p \sim (p-p_c)^{-\nu}$. The accessible fraction $X^A(p)$, the fraction of the bonds or pores that are on the SSC, follows $X^A(p) \sim (p-p_c)^{\beta}$, while the backbone fraction $X^B(p)$ (the fraction of bonds on the backbone, the flow-carrying part of the SSC) is given by $X^B(p) \sim (p-p_c)^{\beta_B}$. The exponent ν, β, and β_B are universal with $\nu = 4/3$ and 0.89, $\beta = 5/36$ and 0.41, and $\beta_B \simeq 0.48$ and 1.05 for two-dimensional (2D) and three-dimensional (3D) systems, respectively. The electrical conductivity σ and permeability K of the SSC follow the power laws $\sigma \sim (p-p_c)^{\mu}$ and $K \sim (p-p_c)^{e}$. For lattice percolating in which the hydraulic or electrical conductance is either 0 or a finite value for all the bonds $e = \mu \simeq 1.3$ and 2.0 in 2D and 3D. But in certain continuum percolation systems in which the conductance distribution is broad (varying over orders of magnitude), μ and e take on nonuniversal values [19,31,32]. The breakdown of the universality of μ and e is, in fact, a key to our development in this paper.

We first note that every porous medium contains a certain fraction of dead-end pores. Solute transport into and out of such pores is by diffusion only. Thus, we consider two distinct cases. (i) Diffusion of the solute into the dead-end pores contributes significantly to dispersion, and cannot be neglected. This is usually the case for column experiments carried out with laboratory-scale porous media, a fact that has been known since the 1960s [33]. (ii) Diffusion into the dead-end pores is not significant. This is the case when either the flow velocity in the laboratory experiment is high enough to overcome any effect by diffusion into and out of the dead-end pores, or when dispersion is dominated by the velocity fluctuations induced by large-scale spatial variations of the permeability and porosity, as it happens in field-scale porous media, such as groundwater aquifers.

An important characteristic of dispersion is the *dispersivity* α_L, defined by $\alpha_L = D_L/v$. Two average flow velocities may be defined. One, v_c, is defined in terms of the travel times of the solute in the SSC. Then $v_c \sim K/X^A$, and near p_c

$$v_c \sim (p-p_c)^{e-\beta} \sim \xi_p^{-\theta_c}, \tag{24}$$

where $\theta_c = (e-\beta)/\nu$. On the other hand, if an average particle velocity v_B is defined in terms of the solute travel time along the backbone, then, $v_B \sim K/X^B$. Thus, near p_c

$$v_B \sim (p-p_c)^{e-\beta_B} \sim \xi_p^{-\theta_B}, \tag{25}$$

where $\theta_B = (e-\beta_B)/\nu$. For length scales $L \ll \xi_p$, we should replace ξ_p in Eqs. (24) and (25) by L. We also define a Péclet number Pe by

$$\mathrm{Pe} = \frac{v\xi_p}{D_e}, \tag{26}$$

where D_e is the effective diffusivity of the solute in the porous medium $D_e \sim (p-p_c)^{\mu-\beta} \sim \xi_p^{-\theta}$, with $\theta = (\mu-\beta)/\nu$ being the anomalous diffusion exponent [34], and v is either v_c or v_B. For $L \ll \xi_p$, we replace ξ_p in Eq. (26) by L. To relate the CTRW parameter α to the percolation exponents we focus on $\langle \Delta x^2 \rangle$, the mean-square displacements in the longitudinal direction.

(i) Suppose that diffusion into the dead-end pores contributes significantly to dispersion, as in the column experiments. de Gennes [35] showed (see also Ref. [27] for a simpler derivation of his result) that the longitudinal dispersion coefficient D_L (in the direction of macroscopic flow) is given by $D_L \sim (v_c\xi_p)^2/D_e$. This is similar to the classical theory of dispersion in pores with stagnant regions [36], which play a role similar to the dead-end pores in porous media. The work by Aris [36] showed the same type of dependence of D_L on v_c and D_e exists in such pores, except that in a porous medium the relevant length scale is the percolation correlation length ξ_p, not the pore size as in Aris' work [36]. Thus, using Eq. (24) and $D_e \sim \xi_p^{-\theta}$, we obtain, $D_L \sim \xi_p^{2-2\theta_c+\theta}$. For $L \ll \xi_p$ the only relevant length scale is L and, therefore, we must replace ξ_p with L. Hence

$$D_L \sim L^{2-2\theta_c+\theta}. \tag{27}$$

Since L is now the only relevant length scale in the percolating system, all the length scales must be proportional to L. Thus, Eq. (27) is rewritten as $D_L \sim \langle \Delta x^2 \rangle^{(2-2\theta_c+\theta)/2}$. As D_L represents an effective diffusivity, one must have $D_L \sim d\langle \Delta x^2 \rangle/dt$. Thus, one obtains, $d\langle \Delta x^2 \rangle/dt \sim \langle \Delta x^2 \rangle^{(2-2\theta_c+\theta)/2}$, which, after integration, yields $\langle \Delta x^2 \rangle \sim t^{2/(2\theta_c-\theta)}$, implying that

$$\zeta = \frac{2}{2\theta_c-\theta} = \frac{2\nu}{2e-\mu-\beta}. \tag{28}$$

Therefore, if we use the numerical values of e and μ for lattice percolation, we obtain

$$\zeta \simeq \begin{cases} 2.3 & \text{2D porous media,} \\ 1.1 & \text{3D porous media.} \end{cases} \tag{29}$$

(ii) Suppose that the dead-end pores do not contribute significantly to dispersion. Thus, dispersion takes place only in flow through the backbone of the SSC, in which case [1] $D_L/D_e \sim \mathrm{Pe}$, implying that $D_L \sim \xi_p v_B \sim \xi_p^{1-\theta_B}$. Thus, for $L \ll \xi_p$

$$D_L \sim L^{1-\theta_B}. \tag{30}$$

Using the same type of analysis as in case (i), we obtain $\langle \Delta x^2 \rangle \sim t^{2/(1+\theta_B)}$. Thus

$$\zeta = \frac{2}{1+\theta_B} = \frac{2\nu}{\nu+e-\beta_B}, \tag{31}$$

implying that

$$\zeta \simeq \begin{cases} 1.26 & \text{2D porous media,} \\ 0.97 & \text{3D porous media} \end{cases} \tag{32}$$

if the numerical values of θ_B for lattice percolation are used. The power laws that relate the dispersivity α_L to the time can then be derived. Consider, for example, case (i) and Eq. (24). For length scales $L \ll \xi_p$ one has $v_c \sim L^{-\theta_c} \sim \langle x \rangle^{-\theta_c}$. On the other hand, $v_c = d\langle x \rangle/dt$. Thus, equating the two equations and integrating, one obtains $\langle x(t) \rangle$ and, hence, $v_c(t) \sim t^{-\theta_c/(1+\theta_c)}$. Since $\alpha_L = D_L/v_c$ and $D_L \sim t^{(2-2\theta_c+\theta)/(2\theta_c-\theta)}$, one obtains the power law that relates α_L to the time t. The final results for both cases (i) and (ii) are then given by

$$\alpha_L \sim \begin{cases} t^{(2+\theta)/[(2\theta_c-\theta)(1+\theta_c)]} & \text{case (i)}, \\ t^{1/(1+\theta_B)} & \text{case (ii)}. \end{cases} \tag{33}$$

IV. COMPARISON WITH LABORATORY EXPERIMENTAL DATA

Anomalous dispersion was first reported by Aronofsky and Heller [16], who reported on systematic deviations of their data from the description by the CDE. Scheidegger [37] also reported on some careful experiments on dispersion in porous columns, noting that the breakthrough solute concentration profile, when fitted to the CDE, deviated significantly and systematically from his data. Silliman and Simpson [38] reported convincing data for dispersion in laboratory experiments that indicated the scale dependence of the dispersivity, the hallmark of non-Fickian dispersion (see also below).

Cortis and Berkowitz [39] reanalyzed Scheidegger's data using the CTRW formulation. Scheidegger measured the breakthrough curves in Berea sandstone cores, 30 inches long with a diameter of 2 inches, and porosity of 0.204. The volume flux was 1.73 cm^3/min. The cores were first saturated fully with the solute tracers and subsequently flushed with clear liquid. Figure 1 presents the fit of the data by both the CDE and CTRW formulations [39], which we have replotted slightly differently. The most accurate fit with the CDE was obtained [39] with $D_L \simeq (1.58 \pm 0.84) \times 10^{-3}$cm^2/min. Equation (21) was used and the most accurate fit was obtained with $v_\psi \simeq (7.25 \pm 0.01) \times 10^{-1}$cm/min, $D_\psi \simeq (7.97 \pm 0.16) \times 10^{-2}$ cm^2/min, and

$$\alpha \simeq 1.59. \tag{34}$$

The error in the estimated α was negligible to two decimal places.

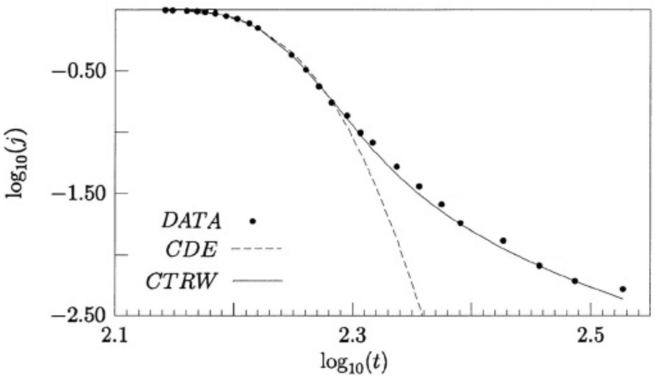

FIG. 1. Comparison of the fits of Scheidegger's data by the CTRW model and the CDE.

Biggar and Nielsen [40] reported breakthrough curves for both saturated and unsaturated porous media. In their experiments the columns were filled with Aiken clay loam 0.23–0.5 mm aggregates in saturated conditions. Two breakthrough curves for the saturated porous medium were measured with injection speeds of 3.4 cm/h and 0.058 cm/h. The most accurate fit of the data for the latter case by the CDE was obtained with $D_L \simeq (9.70 \pm 0.17) \times 10^{-4}$cm^2/min. The regression of the data by Cortis and Berkowitz [39] using the CTRW model yielded $v_\psi \simeq 3.33 \times 10^{-3}$cm/min, $D_\psi \simeq 2.02 \times 10^{-4}$cm^2/min, and

$$\alpha \simeq 1.29, \tag{35}$$

with insignificant errors to two decimal places for the three quantities. The corresponding exponent for the data at higher injection speed was $\alpha \simeq 1.67$ [39].

Thus, for both sets of data we have $1 < \alpha < 2$, implying that it is the second equation in Eq. (22) that is relevant to our discussions and, therefore, $\alpha = 3 - \zeta$. As pointed out earlier, in the column experiments of the type carried out by Scheidegger [37] and Biggar and Nielsen [40] diffusion into the dead-end pores is important and cannot be ignored since the fluid velocity is not too high. Thus, it is case (i) that is relevant to their experiments. Indeed, estimates (29) yield $0.7 < \alpha < 1.9$, consistent with Eqs. (34) and (35). But one must also explain the differences between the percolation estimates and Eqs. (34) and (35). The power laws of percolation theory are valid for infinitely large systems, whereas the experimental systems are finite. Thus finite-size effects might play a role in the difference between the percolation predictions and what one obtains by fitting the experimental data. We believe, however, that there is a deeper reason for the deviations, which we now address.

V. NONUNIVERSALITY OF THE CTRW EXPONENT

Estimates (34) and (35) indicate clearly that α is not universal. On the other hand, it is also known [19,31,32] that many continuum models of disordered media give rise to nonuniversal values of μ and e, and porous media certainly represent continuum systems. Since the main difference between the porous media used in the experiments of Scheidegger and Biggar and Nielsen is their morphologies, the nonuniversality of α may be due to the morphology of the two porous media. Thus, one must use the nonuniversal estimates of μ and e in Eqs. (28) and (31).

In particular, consider a percolation system in which the local conductances g follow a distribution given by

$$h(g) \sim g^{-\gamma}, \tag{36}$$

where $0 < \gamma < 1$. Distribution (36) is not a pathological one and is actually quite common [1,31,32]. Several authors [19,31,41] have shown that, given distribution (36), μ and e are nonuniversal. Let us denote the nonuniversal exponents by μ_n and e_n. Feng *et al.* [31] showed that

$$\max(\mu_l + y, \mu) \leqslant \mu_n \leqslant \mu + y, \tag{37}$$

$$\max(\mu_l + y, \mu) \leqslant e_n \leqslant \mu + y, \tag{38}$$

where $y = \gamma/(1-\gamma)$, μ and e are the universal values of the two exponents, and $\mu_l = 1 + (d-2)\nu$, with d being the system's dimensionality. Kogut and Straley [41] argued that the upper bound for μ may be an exact result.

Thus, consider Scheidegger's experiments. Using estimate (35) we obtain, $\zeta \simeq 1.41$ which, when substituted in Eq. (28), yields $\mu_n \simeq e_n \simeq 1.42\nu + \beta$ if we use the suggestion by Kogut and Straley [41]. Thus, if Scheidegger's porous medium was 2D, one obtains $\mu_n \simeq e_n \simeq 1.82$, much larger than the universal (lattice) value of 1.3, but corresponding to a conductance distribution with $\gamma \simeq 2/5$. On the other hand, if the porous medium was 3D, then $\mu_n \simeq e_n \simeq 1.69$, which could not be produced by any $\gamma > 0$, and in fact violates the theoretical requirement that the conductivity and permeability exponents in d dimensions must be larger than those in $(d-1)$ dimensions. Thus, Scheidegger's porous sample was essentially 2D, as are most laboratory-scale porous media. Indeed, it had an aspect ratio (the ratio of column's length and diameter) of 15. A similar analysis for Biggar and Nielsen's data indicates that their porous medium had a 2D geometry with $\gamma \simeq 1/4$, but assuming a 3D geometry would again violate what is known about μ and e. Such considerations imply that the theory that we are proposing is self-consistent, in the sense that it produces results that are consistent with what is known about μ and e, and automatically rules out other possibilities that violate rigorous theories concerning these exponents.

Based on this analysis we also identify bounds for α. It has been shown [31,32,41] that nonuniversal values of μ and e for continuum percolation are *always* larger than the universal values for lattice percolation. Thus, according to Eqs. (28) and (29) *for laboratory-scale porous media* and based on dimensional considerations, one must have

$$0.7 \leqslant \alpha \leqslant 1.9. \tag{39}$$

Interestingly, $\alpha \simeq 0.7$ was reported by Bijeljic, Mostaghim, and Blunt [5] for carbonate rock as an example of highly heterogeneous porous media, and $\alpha \simeq 1.8$ very close to the proposed upper bound, for sandpacks as an example of relatively weakly heterogeneous porous media.

VI. DISPERSION AT FIELD SCALE

Despite considerable difficulty associated with measurements of D_L and α_L in field-scale porous media (FSPM), a considerable amount of data have been collected [42] that indicate unequivocally that both α_L and D_L depend on the length scale of measurements and time. Over 130 dispersivities were collected from the literature by Arya *et al.* [43], collected on length scales from less than 10 cm to more than 100 km. At least 75% of the data followed the scaling

$$\alpha_L \sim L^{\delta}, \tag{40}$$

with $\delta \simeq 0.88$, where L is the length scale of the measurements or distance from the source. Reanalysis of their data and those of others by Neuman [44] indicated that $L \gg 100$ m one has $\delta \simeq 0.92$.

The case relevant to FSPM is (ii) because in flow through such porous media diffusion into and out of the dead-end pores plays no significant role, as the distribution of the solute concentration is dominated by the fluctuations in the flow velocity field, which in turn is controlled by heterogeneities of FSPM. Equations (25) and (30) predict that

$$\alpha_L \sim L, \tag{41}$$

implying that $\delta = 1$, at most 13% larger than Arya *et al.*'s estimate, and only 9% larger than Neuman's [44]. Given the uncertainty in measuring α_L, the agreement between the percolation prediction and the data is good. Moreover, if we write

$$\alpha_L \sim t^{\chi}, \tag{42}$$

then, according to Eq. (33), $\chi = (1+\theta_B)^{-1}$. We then recognize that FSPM are essentially 2D porous media, as they are up to tens of kilometers long, but at most a few hundred meters thick. Therefore, it is the 2D value of θ_B that is relevant to Eq. (42) and thus $\chi \simeq 0.63$ if we use the numerical value of θ_B for lattice percolation. Indeed, in the numerical simulation of dispersion in FSPM [45] $\chi \simeq 0.5$–0.6 has been used, completely consistent with the percolation prediction.

For the FSPM the exponent ζ and, hence, the CTRW exponent $\alpha = 3 - \zeta$ (or $\alpha = \zeta/2$, depending on the conditions) should be expected to be nonuniversal. The reason is that numerous studies [1] have indicated that the spatial distribution of the permeability and porosity of FSPM are dominated by long-range nondecaying correlations that are well described by such self-affine fractal distributions as the fractional Brownian motion (FBM) and fractional Gaussian noise (FGN). Simulation of flow and transport in percolation systems in which the local permeabilities are distributed according to an FBM [32] indicated that the percolation exponents ν, β, and β_B, as well as the permeability exponents e are nonuniversal. Thus, if the CTRW formulation is to be used to model dispersion in FSPM [46], its critical parameter α should be expected to be nonuniversal, vary from field to field, and related to the Hurst exponent or other exponents that characterize long-range correlations in FSPM.

VII. SUMMARY

The key parameter in a CTRW formulation of anomalous dispersion in porous media is α, defined by the power law that describes the waiting time distribution of the CTRW, Eq. (21). We argued that percolation theory can provide expressions, in terms of its key exponents, for α for dispersion in both laboratory- and field-scale porous media. We also argued that the observed nonuniversality of α is due to the nonuniversality of the percolation exponents that occur in continuum models, as well as in percolation with long-range correlations.

One might argue that the percolation approach merely expresses the nonuniversal CTRW parameter α in terms of the exponents that are nonuniversal for continuum models. As such, one might argue that the percolation approach has no more predictive power than simply fitting α to the data. But, whereas in the CTRW formulation the parameter α is purely phenomenological, in the percolation approach it is expressed in terms of fundamental exponents that have rigorous theoretical foundation. Moreover, for laboratory-scale porous media the nonuniversality of α is explained in terms of the dependence of the percolation exponents e and μ on the parameter of the conductance distribution, which not only represents an important aspect of a pore space morphology, but is also measured routinely. Similarly, for dispersion in FSPM the nonuniversality of α is linked to the dependence of μ and e on the parameters that characterize long-range correlations in the pore space, such as the Hurst exponent H that is paramount to the FBM and FGN, and is also routinely estimated using well log data [1,47]. As such, we believe that the proposed link between percolation and the CTRW formulation of dispersion, and the explanation of the nonuniversality of α in terms of the nonuniversality of the percolation exponents is appealing, and puts the CTRW formulation of anomalous dispersion on a more rigorous foundation.

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