Transport with multiple-rate exchange in disordered media

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We investigate transport of particles subject to exchange using the continuous-time random-walk framework. Transition is controlled by macroscale, and exchange by both macroscale and microscale disorder. A wide class of exchange mechanisms is represented using the multiple-rate exchange model. Particles are transported along random trajectories viewed as one-dimensional lattices. The solution of the transport problem is obtained in the form of the crossing-time density, $h(t;L)$, at an exit surface L; h is dependent on two functions, g and f. g characterizes exchange controlled by microscale disorder. The joint density f is central for the solution as it relates the microscale and macroscale disorder along random trajectories. For the case of transition and exchange disorder, we show that power-law exponent η (characterizing microscale disorder) and power-law exponents α_τ and α_μ (characterizing macroscale disorder), define two regions delimited by a line $\alpha_\tau=\alpha_\mu(\eta+1)$: One in which the asymptotic transport is dominated by transition, and one in which it is dominated by the exchange. For the case of transition disorder with uniform exchange, both transition and exchange can influence the late-time behavior of $h(t)$. Microscale exchange processes will unconditionally influence the late-time behavior of $h(t)$ only if $\eta<0$. If $\eta>0$, exchange will dominate at late time provided that transition is asymptotically Gaussian.

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I. INTRODUCTION

Transport in random media is of interest for understanding a variety of phenomena, in natural as well as engineered systems. Transport often involves particles that are dynamically inert, but in some way interact (or are subject to exchange) with the porous matrix. Studies of transport with exchange in homogeneous porous media have a long tradition in chromatography [1,2]. Moreover, a significant body of literature has focused on understanding the effect of microscale disorder on exchange, e.g., Refs. [3–5]. The ''multiple-rate'' concept provides a unifying model for different exchange mechanisms, applicable to a wide range of microscale disorder properties. This concept was first introduced for modeling dielectric relaxation [6], and subsequently extended to homogeneous porous media [7].

Few studies to date have considered transport with exchange in disordered media. A first comprehensive analysis was provided by Hughes and Sahimi [8,9] who considered transport with multiple transport paths assuming relatively simple (first-order) exchange; their analysis is based on master equations and the effective media approximation. Although Hughes and Sahimi stress the relevance of their results for geological media, it is well known that such systems often exhibit more complex exchange than the first order, e.g. [10,11]. Several recent studies [12–14] addressed transport with more complex exchange in disordered media, however, these results are still limited to a few specific exchange models.

The present work provides, for what we believe to be the first time, a continuous-time random-walk model for transport with exchange in disordered media. Using the multiple-rate concept, we can account for a wide range of exchange mechanisms, relevant for a variety of microstructural properties. General solutions are derived either in terms of the Laplace transform of the crossing-time density $h(t)$, or in terms of its moments. In the general case of microscale disorder with infinite exchange times, the solution cannot be obtained in an analytical form, and Monte Carlo simulations are required. Illustration examples address transport anomalies, in particular extended tailing of $h(t)$, which arises due to combined effects of transition and exchange. We summarize conditions under which anomalous transport arises asymptotically, controlled by macroscale disorder (transition), or by microscale disorder (exchange).

II. MODEL

A. Problem formulation and assumptions

Let a dynamically inert *pair* of particles be injected simultaneously into a disordered medium at time $t=0$ at $\mathbf{x}=\mathbf{a}$ in $\mathcal{R}^1$, $\mathcal{R}^2$, or $\mathcal{R}^3$, where $\mathbf{x}$ is a Cartesian position vector. The particle pair consists of one ''interacting'' particle (IP for shorthand) and one ''noninteracting'' particle (NIP for shorthand). For $t>0$, the particle pair advances toward, ultimately crossing, an exit surface L, following a trajectory $\mathbf{X}(\ell,\mathbf{a})$, where ℓ is the intrinsic length along $\mathbf{X}$. Let θ denote the IP crossing time, and τ the NIP crossing time at L. We denote the probability density function (PDF) for θ as $h(t)$ and for τ as $f(t)\equiv f_\tau(t)$; $h(t)dt$ is the probability that $t<\theta<t+dt$, and $f(t)dt$ the probability that $t<\tau<t+dt$ at L.

The two main assumptions for our analysis are as follows.

Transition is characterized by a nonzero mean drift; hence $\int f(\tau)d\tau=1$ for any $\mathbf{a}$ and any realization.

If $\mathbf{a}_1=\mathbf{a}_2$ for two NIPs, then $\mathbf{X}(\ell,\mathbf{a}_1)=\mathbf{X}(\ell,\mathbf{a}_2)$ in any realization; consequently, zero exchange implies $\theta=\tau$, and nonzero exchange $\theta>\tau$.

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Typical examples where the above assumptions apply would be flow-driven tracer transport by steady random flow in natural systems, such as geological media [15], or geomorphological networks [16]. Our second assumption implies that a random flow pattern is steady state, and that all fluctuations on the scale smaller than the support scale of a flow velocity (other than those related to exchange) are neglected. The above assumptions have been found appropriate for heterogeneous aquifers [17], fractured rock [12], river networks [16], but also for laboratory-scale chromatographic columns [1], in other words, over a variety of transport scales.

Let $P(\mathbf{x})$ denote the *exchange parameter vector*[1] that varies in space. Given the trajectory $\mathbf{X}$, and $P(\mathbf{x})$, we wish to quantify the IP crossing-time density h. If the medium is homogeneous in terms of exchange ($P=\text{const}$), and transition is Gaussian, the problem reduces to the one of chromatography with known solutions for h, e.g., [1]. Our emphasis here is on transition and exchange *disorder* (with possible non-Gaussian features) as would be applicable, for instance, to natural environments.

B. Transition

We view $\mathbf{X}$ as a one-dimensional lattice with N equidistant sites. Based on our assumptions, transition along $\mathbf{X}$ is simply a sequence of steps, where the site and step indices coincide. The step duration $\Delta\tau_i$ at site i varies randomly. If a flow field is considered, then $\Delta\tau_i=\Delta\ell/V_i$, V_i being the magnitude of $\mathbf{V}_i$ at site i. The waiting-time density for transport on the lattice is site dependent, with $\psi_i(t)=\delta(t-\Delta\tau_i)$.[2]

Let $\gamma_i(t)$ denote the NIP crossing-time density at the ith site; it is computed as

$$\gamma_i(t)=\int_0^t \psi_i(t-t')\,\gamma_{i-1}(t')\,dt'. \tag{1}$$

At L, we have (suppressing index "N")

$$\gamma(t,\tau)=\delta(t-\tau), \quad \tau=\sum_{i=1}^{N}\Delta\tau_i. \tag{2}$$

Note that γ [Eq. (2)] corresponds to the "renormalized waiting-time density" for the canonical exponential waiting-time density of the continuous-time random walk, in the limit $N\to\infty$ [18].

[1] P summarizes, for instance, diffusion rates, equilibrium constants, intra-aggregate porosity, etc.

[2] For a classical random walk the simplest displacement density is $1/2(\delta_{i,i-1}+\delta_{i,i+1})$, whereas here we have $\delta_{i,i+1}$, i.e., the probability to move to site $i+1$ from site i is one, and the transition proceeds monotonically along the lattice. Hence any given site can be visited only once.

C. Exchange

The IP also follows trajectory $\mathbf{X}$, however, it is subject to exchange, and hence its movement is delayed relative to the NIP.

We consider sufficiently diluted systems such that exchange is linear. Consistent with the definition of linear exchange [1,13] we introduce a site-dependent waiting-time density for an IP as

$$\hat{\psi}_i=\exp\{-\Delta\tau_i s[1+\hat{g}_i(s)]\}, \tag{3}$$

where the hat denotes Laplace transform and s the Laplace transform variable. The function $g_i(t)$ characterizes in a general way *linear* exchange processes at site i. Thus Eq. (3) quantifies a "nonseparable" continuous-time random walk, e.g. [18]. In the absence of exchange, $g_i=0$, and the transport of NIP and IP coincides. In the homogeneous case, a single (site-independent) waiting-time density $\psi(t)$ characterizes exchange for the entire lattice.

The function g_i provides a mesoscale characterization of exchange processes, which take place on the microscale. Considerable effort has been made to better understand the relation between microscopic structure and mesoscale observations as quantified by g_i. O'Shaugnessy and Procaccia [3] and Havlin and Ben-Avraham [4], for instance, have shown how anomalous, subdiffusive behavior arises in porous media due to fractal microporous structures. Sheintuch and Brandon [19] and Giona and co-workers [5] have worked out many of the details of mass uptake into synthetic fractal microporous beads. Some environmental problems may also be determined by the release of material from natural materials that have fractal pore spaces. A growing body of work suggest that the pore space of many rocks is well characterized as a fractal over many orders of magnitude, e.g. [20–22]. Effective diffusivities in crystalline rock show a decrease with sample size that may be consistent with fractal pore structure [23].

In order to formulate the exchange as a multiple-rate process, we first normalize $g_i(t)$ as

$$g_i^*(t)=g_i(t)/\beta_i, \quad \beta_i=\int_0^\infty g_i(t)\,dt, \tag{4}$$

where β_i is referred to as the capacity coefficient of site i. The function g_i^* is referred to as the *exchange-time density*, i.e., a density function for the IP exchange time at site i; g_i^* is also referred to as the "memory function" [24].

A suitable form for g_i is a linear superposition of exponential densities [6,18],

$$g_i(t)=\int_0^\infty k\,\phi_i(k)\exp(-kt)\,dk \tag{5}$$

with

$$\beta_i=\int_0^\infty \phi_i(k)\,dk,$$

where $\phi_i(k)/\beta_i$ is a site-dependent density of the rate coefficient k. Note that $\beta_i=\int g_i(t)dt=\int \phi_i(k)dk$, i.e., β_i is the zeroth moment of both g_i and b_i. Assuming particular forms of $\phi_i(k)$, we recover most of the models currently used in engineering practice [24] (see Appendix B for a few examples).

D. Transition with exchange

From the recurrence relation we can write

$$\hat{\gamma}_N \equiv \hat{\gamma}=\prod_{i=1}^{N} \hat{\psi}_i , \tag{6}$$

where we assume, for simplicity, that at $\mathbf{x}=\mathbf{a}$ the waiting-time density is $\delta(t)$.

Substitution of Eq. (3) into Eq. (6) yields

$$\hat{\gamma}(s)=\exp\left\{ -s\left[\tau+\sum_{i=1}^{N} \hat{g}_i(s)\Delta\tau_i \right] \right\}. \tag{7}$$

We refer to γ as the *retention function*, as it quantifies the extent to which an IP is retarded relative to its NIP pair. For $g_i=0$, there is no exchange and γ [Eq. (7)] degenerates to Eq. (2); for $\hat{g}_i=\text{const}=\beta$, we get $\gamma(t,\tau)=\delta[t-\tau(1+\beta)]$, which is the statement of transition with simplest (equilibrium) exchange, e.g. [13].

The retention function $\gamma(t)$ is obtained by inverting Eq. (7) and may be written as

$$\gamma(t)=\delta(t-\tau)\circ\kappa(t)=\kappa(t-\tau), \tag{8}$$

where $\circ$ denotes the convolution operator, and

$$\kappa(t)=\mathcal{L}^{-1}[e^{-F(s)}], \quad F(s)=\left[s\sum_{i=1}^{N} \Delta\tau_i\hat{g}_i(s) \right], \tag{9}$$

with $\mathcal{L}^{-1}$ denoting inverse Laplace transform. Thus τ is the centering for the density $\kappa(t)$. The function $F(s)$ determines the form of κ. The asymptotic behavior of κ can be evaluated as $1-\hat{\kappa}\approx F(s)$ for $s\to 0$ (see Sec. IV for specific examples).

Transition under the present conditions implies that a particle at site i at time t', will in the next step occupy site $i+1$ at time $t'+t$ with probability 1.[3] The time t is random due to, on one hand, randomness of the flow field, and on the other hand, the exchange processes.

In applications, the exit surface L is specified, and τ is a random variable. Moreover, the function $g_i(t)$ depends on the exchange parameter vector P_i. We, therefore, regard Eqs. (8),(9) as the *conditional* solution, for a given realization of $g_i(t;P_i)$ and τ. In the following section, we shall account for the randomness in τ and P_i.

[3]As a consequence, site occupancy and first-passage time densities are proportional.

III. UNCONDITIONAL SOLUTIONS

Given the retention function $\gamma(t)$ (8), we wish to compute the unconditional IP crossing-time density at the Nth site (i.e., at L), $h(t)$.[4]

A. Zero exchange

Since τ is a random variable for a given realization of a disordered medium, γ [Eq. (2)] is a conditional solution for the transport of a NIP. The unconditional solution is $\langle\gamma(t,\tau)\rangle=f_\tau(t)$, where $f(\tau)\equiv f_\tau$; hence in this case $h(t)\equiv f_\tau(t)$.

The density $f(\tau)$ is difficult to determine in a general way, for arbitrary boundary conditions and disorder. For geological formations, for instance, $f(\tau)$ has been computed analytically assuming Gaussian transport [17]. Non-Gaussian features of the conducting properties of geological media have been established in a few cases where comprehensive data sets were available [25]. $f(\tau)$ with non-Gaussian features has been identified for complex disorder as can be found in fractured rock [12,26]. Non-Gaussian features of transport have also been found in river networks, e.g. [16].

In view of the variety of statistical/structural features of disordered media, in particular for natural systems, we require a general and flexible form for $f_\tau\equiv f(\tau)$ that can capture in a generic way both the Gaussian and non-Gaussian features of NIP transport. We propose the following form defined in the Laplace domain as

$$\hat{f}_\tau(s)=\exp[ca^\alpha-ds-c(a+s)^\alpha], \tag{10}$$

where a, c, d, $\alpha>0$, and ca^α is included for normalization. We refer to Eq. (10) as a ''truncated one-sided stable'' density, or simply a ''truncated stable'' density; for $a=0$, Eq. (10) reduces to the standard one-sided stable density, e.g., Ref. [18]. Further discussion on the properties of Eq. (10) is given in Appendix A.

B. Factorized case

For many applications, it may be sufficient to factorize the nonhomogeneity of g, such that β is site dependent, while g^* is not, i.e.,

$$g_i(t)=\beta_i g^*(t). \tag{11}$$

The assumption (11) in effect reduces the ''nonseparable'' continuous-time random-walk model (3) to a ''separable'' one as originally proposed in Ref. [27].

Substituting Eq. (11) into Eq. (7), we get

$$\hat{\gamma}(s)=\exp\{-s[\tau+\mu\hat{g}^*(s)]\}, \tag{12}$$

where

$$\mu\equiv\sum_{i=1}^{N} \beta_i\Delta\tau_i . \tag{13}$$

[4]In the notation, e.g., of Hughes [18], we would write $h(L|\mathbf{a},t)$.

Thus, to compute the unconditional density $h(t)$, we require the joint density $f(\tau,\mu)$.

In view of Eq. (12), we have

$$\hat{h}(s)=\hat{f}_{\tau\mu}[s,s\hat{g}^*(s)], \tag{14}$$

where $\hat{f}_{\tau\mu}$ denotes the Laplace transform of the joint density $f(\tau,\mu)\equiv f_{\tau\mu}$, if such can be identified. Note that this solution is applicable irrespective of whether the cumulants of $g(t)$ are finite or infinite.

A simplified alternative to using the joint density $f_{\tau\mu}$, is to set bounds on $h(t)$, by treating two limiting cases: one where τ and μ are perfectly correlated (functionally dependent), and the other where τ and μ are uncorrelated.

In the perfectly correlated case, only if μ is linear in τ as $\mu=\beta\tau$, can we obtain an expression corresponding to Eq. (14). In view of Eq. (12), we then have

$$\hat{h}(s)=\hat{f}_{\tau}[\mathcal{F}(s)], \tag{15}$$

where $\mathcal{F}(s)\equiv s[1+\beta\hat{g}^*(s)]$. Expression (15) is a Laplace transform solution of the *subordination* problem in the terminology of Feller [28], where $\theta[\tau(L)]$, and $\tau(L)$ is the directing process. A relationship similar to Eq. (15) was first derived for homogeneous media in chromatography [1,2]. Hence Eq. (14) generalizes Eq. (15) from homogeneous to disordered media with ''separable'' random properties.

In the uncorrelated case, we get

$$\hat{h}(s)=\hat{f}_{\tau\mu}[s,s\hat{g}^*(s)]=\hat{f}_{\tau}(s)\hat{f}_{\mu}[s\hat{g}^*(s)]. \tag{16}$$

Expression (16) is a more general solution of the subordination problem, where $\theta(\tau,\mu)$, and τ and μ are the directing processes.

C. Finite exchange cumulants

If the cumulants of $g_i(t)$ are finite to order ''*M*,'' the unconditional arrival time density $h(t)$ can be obtained in terms of integrated cumulants of $g_i(t)$ along the lattice.

Since by definition

$$m_j=\lim_{s\to 0}\left[(-1)^j\frac{\partial^j\hat{h}}{\partial s^j}\right]=\lim_{s\to 0}\left[(-1)^j\frac{\partial^j(\hat{\gamma})}{\partial s^j}\right],$$

$$j=0,1,2,3,\ldots,M \tag{17}$$

the key to computing $h(t)$ is knowledge of the joint density $f(\tau,\mu_0,\mu_1,\mu_2,\ldots,\mu_M)$, where

$$\mu_j=\sum_i\ \beta_i w_{ji}\Delta\tau_i,\quad w_{ji}=\lim_{s\to 0}\left[(-1)^j\frac{\partial^j\hat{g}_i^*}{\partial s^j}\right]. \tag{18}$$

We refer to μ's as ''exchange trajectories,'' since they characterize exchange in an integrated sense along the entire lattice. It may be noted that finite cumulants of g_i to order ''*M*,'' imply finite cumulants of h to order ''$M+1$.''

The moments of $f(\tau,\mu_0,\mu_1,\mu_2,\ldots,\mu_M)$ are defined as

$$\langle\tau\rangle,\ \langle\mu_j\rangle,\ \langle\tau\mu_j\rangle,\ \langle\mu_j\mu_k\rangle,\ \langle\tau\mu_j\mu_k\rangle,\ \text{etc.}$$

If exchange is homogeneous (i.e., cumulants are site independent), then $f(\tau,\mu_0,\mu_1,\ldots,\mu_M)$ reduces to the NIP crossing-time density $f(\tau)$. We refer to $f(\tau,\mu_0,\mu_1,\ldots,\mu_M)$ (or any of its marginal densities) as ''exchange trajectory density.'' $f(\tau,\mu_0,\mu_1,\ldots,\mu_M)$ characterizes transport on the macroscale, reflecting the structural, or morphological, features of transition and the P field. In effect, f provides the link between the mesoscale and the observation (macro)scale.

In the general case, the joint density $f(\tau,\mu_0,\mu_1,\ldots,\mu_M)$ can be obtained using Monte Carlo simulations (see discussion below).

D. General case

In the general case, where cumulants of $g_i(t)$ are not necessarily finite, we can obtain $h(t)$ by ensemble averaging $\gamma(t)$, i.e., $h(t)=\langle\gamma(t)\rangle$, using Monte Carlo numerical simulations. To summarize the simulation steps, we assume here that transition is driven by a steady-state, random-flow field $\mathbf{V}(\mathbf{x})$, with a nonzero mean drift, i.e., $\langle\mathbf{V}(\mathbf{x})\rangle\neq 0$, where $\langle\ \rangle$ denotes ensemble averaging.

Let $\boldsymbol{\omega}(\omega_V,\omega_P)$ where ω_V is as element of the sample space for the flow field realization, $\mathbf{V}$, and ω_P an element of the sample space for the exchange parameter vector $P(\mathbf{x})$. We assume that the statistics of $\mathbf{V}$ and P fields are given (mean, covariances, cross covariances, etc.).

For each $\boldsymbol{\omega}$ (realization of $\mathbf{V}$ and P), NIPs are injected at a given location, and followed, whereby the trajectories $\mathbf{X}$ are computed. The trajectories $\mathbf{X}$ are discretized as one-dimensional lattices with equidistant time steps. At each site the exchange parameters P are sampled along a trajectory as $P[\mathbf{X}(\not{},\mathbf{a})]$ to obtain P_i and g_i, and $\hat{\gamma}$ is computed by quadratures from (7). Then $h(t)$ can be obtained either by computing $\hat{h}=\langle\hat{\gamma}(s)\rangle$ with numerical inversion, or by inverting $\hat{\gamma}$ for each $\boldsymbol{\omega}$ and then averaging, i.e., $h(t)=\langle\gamma(t)\rangle$.

Further details on Monte Carlo simulations in the context of geological media can be found in Ref. [13]. Note that the use of Eq. (7) simplifies numerical simulations significantly, since a three-dimensional transport-exchange problem is reduced to a three-dimensional flow problem and a one-dimensional exchange problem.

IV. ILLUSTRATION EXAMPLES

A. Moments of *h*: Transition with exchange disorder

Using the definition of g_i in terms of ϕ_i [Eq. (5)], the moment of order ''j'' μ_j [Eq. (18)] can be written as

$$\mu_j=\sum_i\ \Delta\tau_i(-1)^j\left.\frac{\partial^j\hat{g}_i}{\partial s^j}\right|_{s=0}=\sum_i\ \Delta\tau_i j!\int_0^\infty\frac{\phi_i(k)}{k^j}dk. \tag{19}$$

In our following discussion, we assume that $a\neq 0$ in Eq. (10), and the μ_0 and μ_1 are finite for all i; our focus is on the computation of the first two moments of h defined by

$$\langle\theta\rangle=\langle\tau\rangle+\langle\mu_0\rangle,$$

$$\sigma_\theta^2\equiv\langle\theta^2\rangle-\langle\theta\rangle^2=\sigma_\tau^2+2\sigma_{\tau\mu_0}+\sigma_{\mu_0}^2+2\langle\mu_1\rangle, \tag{20}$$

where

$$\langle \mu_0 \rangle = \left\langle \sum_i \beta_i \Delta \tau_i \right\rangle, \quad \langle \mu_1 \rangle = \left\langle \sum_i \frac{\beta_i \Delta \tau_i}{k_i} \right\rangle \tag{21}$$

and $\sigma_{\tau\mu_0} \equiv \langle \tau\mu_0 \rangle - \langle \tau \rangle \langle \mu_0 \rangle$, $\sigma^2_{\mu_0} \equiv \langle \mu_0^2 \rangle - \langle \mu_0 \rangle^2$, $\sigma^2_\tau \equiv \langle \tau^2 \rangle - \langle \tau \rangle^2$. Note that finite μ_1 implies finite average exchange time.

Consider the simple *binary exchange disorder* model [9] where exchange takes place at a random fraction of the lattice sites. For the binary model

$$g_i(t) = \omega g(t) \quad \text{or} \quad \phi_i(k) = \omega \phi(k), \tag{22}$$

where ω is a random variable taking values 1 and 0, with probability p for $\omega = 1$, and probability $1-p$ for $\omega = 0$; $g(t)$ and ϕ are site-independent.

With Eq. (22), Eq. (19) reduces to

$$\mu_j = \tau\omega(-1)^j \frac{\partial^j \hat{g}}{\partial s^j}\bigg|_{s=0} = \tau\omega j! \int_0^\infty \frac{\phi(k)}{k^j} dk. \tag{23}$$

For the first two moments of h (20), we require $\mu_0 = \tau\omega\beta_0$ and $\mu_1 = \tau\omega/k_H$ where k_H is the harmonic mean exchange rate.

Assuming for simplicity that the transition and exchange disorder are uncorrelated (i.e., $\sigma_{\tau\mu_0} = 0$), we write expressions for the first two moments of h (20), applicable for the binary exchange model, as

$$\overline{\theta} = \langle \tau \rangle (1 + p\beta_0), \quad \sigma^2_\theta = \sigma^2_\tau (1 + p^2 {\beta_0}^2) + 2\langle \tau \rangle p \frac{\beta_0}{k_H}. \tag{24}$$

Hence the first moment of h is dependent only on p and β_0, and not affected by the choice of the exchange model; also, for $k_H \to 0$, we have $\sigma^2_\theta \to \infty$. If exchange is uniform, then $p = 1$; in the absence of exchange, $p = 0$, and $\sigma^2_\theta = \sigma^2_\tau$, consistent with the fact that NIP and IP transport coincides.

We compute the second moment σ^2_θ for three common exchange models summarized in Appendix B:

For the *first-order model* (B1), we get

$$\sigma^2_\theta = \sigma^2_\tau (1 + p^2 {\beta_0}^2) + 2\langle \tau \rangle p \frac{\beta_0}{k_0}, \tag{25}$$

where $\beta_0 k_0$ is the forward and k_0 the backward rate constants; thus $k_H = k_0$.

For *diffusion in spheres* (B2), we get

$$\sigma^2_\theta = \sigma^2_\tau (1 + p^2 {\beta_0}^2) + 2\langle \tau \rangle p \frac{\beta_0 r_p^2}{15 D_a}, \tag{26}$$

where r_p is the sphere radius and D_a is the apparent diffusion coefficient for the spheres, which accounts for possible sorption. In this case, $k_H = 15 D_a / r_p^2$.

For the *multiple-rate Gamma model* (B5),

$$\sigma^2_\theta = \sigma^2_\tau (1 + p^2 {\beta_0}^2) - 2\langle \tau \rangle p \frac{\beta_0 b}{\xi + 2}, \tag{27}$$

where ξ and b are parameters of the γ density. In this case $k_H = -(\xi+2)/b$ with $\xi < -2$. Note that for $\xi \geqslant -2$, σ^2_θ is not defined.

B. Density *h*: Non-Gaussian transition with uniform exchange

It is a common practice in applications to assume transition disorder with uniform exchange, where transition disorder is Gaussian, and exchange is assumed to have finite cumulants, e.g., [17]. We emphasize here non-Gaussian transition with uniform exchange, with cumulants that are not necessarily finite.

For illustration, we consider two cases using the truncated stable density in Eq. (10) with $d = 0$, $c = 1$, $\alpha = 1/2$, various a, and with $g(t)$ given by two different functions. To obtain $h(t)$ we invert the analytical solution numerically. The first example of $g(t)$ is applicable for diffusion into rock from parallel fractures. This density is provided in Ref. [24] and is given by Eq. (5) with ϕ_i defined in Eq. (39) where l is large but finite. Because of diffusion into a finite region, $g(t)$ behaves as $t^{-1/2}$ (i.e., $\eta = -1/2$) between $t = 0$ and approximately the diffusion time scale of l^2/D, which in this case is 3.3×10^{-6} [T]. Results are shown in Fig. 1(a). The function $h(t)$ shows three possible power-law regimes at late time (i.e., after the peak), with not all present for any particular set of parameters. Regime 1 causes $h(t)$ to scale as $t^{-\alpha-1}$. This regime exists, in general, over times where $g(t)$ is not power law but before the truncation of the stable density from Eq. (10), determined largely by the value of a. In Fig. 1(a) we see Regime 1 only at latest times (after l^2/D) for the case of $a = 0$. Given the value of $\alpha = 1/2$, $h(t) \sim t^{-1/2}$ in that region. Regime 2 causes $h(t)$ to scale as $t^{-\alpha(\eta+1)-1}$. This regime exists, in general, over times where both $g(t)$ and the stable density from Eq. (10) are power law. We see this behavior for $a = 0$ and times less than l^2/D, where $h(t) \sim t^{-5/4}$. Regime 3 causes $h(t)$ to scale as $t^{-\eta-2}$. This regime exists, in general, over times where $g(t)$ is power law, but where the stable density from Eq. (10) has been truncated. This behavior exists, in our example, at times prior to l^2/D and when $a > 0$.

The second example density, $g(t) \sim t^{-1.8}$ (i.e., $\eta = 0.8$), results from diffusion (from fractures) into rock matrix with a large range of physical properties. Such behavior has been observed, for example, in fractured dolomite [24,29]. In this second example, power-law behavior in $g(t)$ is confined between both a minimum and a maximum time (1 and 10^7 [T], respectively). The key difference, however, between the second example and the first is the value of η, which is less than 0 in the first example, and greater than zero in the second. Results are shown in Fig. 1(b). Similar to the first example, there is more than one power-law regime for $h(t)$. However, since $\eta > 0$, the late-time behavior is always dominated by α unless the density is truncated. Regime 1, where $h(t) \sim t^{-\alpha-1}$, exists at all late time, provided that $\alpha \ll 1$. Since $\eta > 0$, there is no Regime 2. Regime 3, where $h(t) \sim t^{-\eta-2}$, can only exist if a is not negligible. Given a large

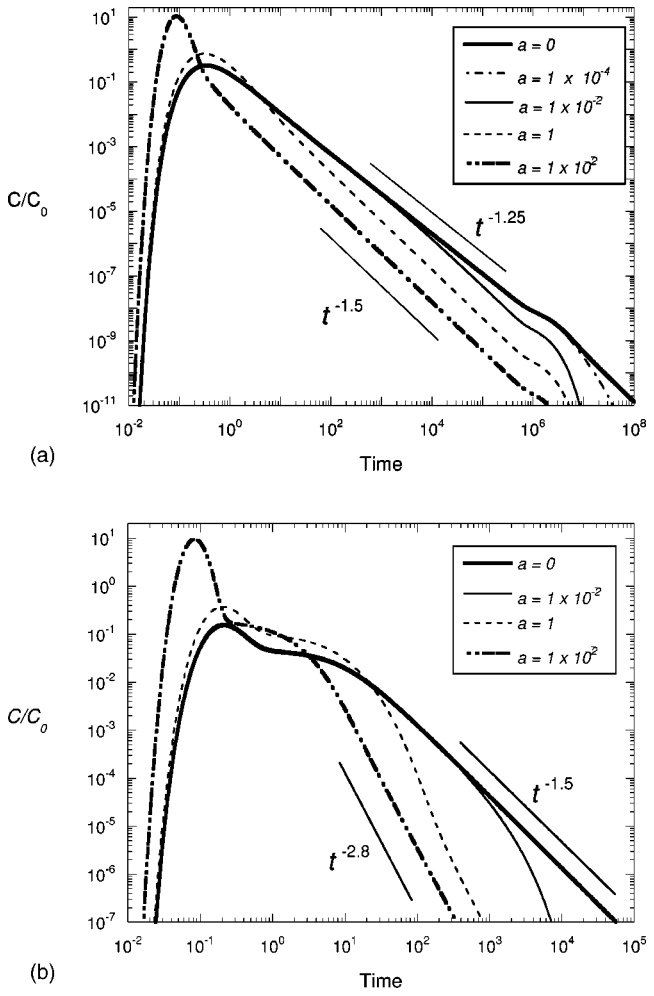

FIG. 1. Interaction between macroscale transition and microscale exchange. The transition is characterized by the truncated stable density (10) with $d=0$, $c=1$, $\alpha=\frac{1}{2}$ and a range of a [1/T] values. The exchange is characterized by two forms of g: (a) $g(t)$ as defined in Eq. (B4); (b) power-law $g(t)\sim t^{-1.8}$ ($\eta=0.8$).

enough a, the late-time behavior of $h(t)$ between $t_{\min}$ and $t_{\max}$ is determined by η.

C. Density *h*: Non-Gaussian transition with exchange disorder

We limit our discussion here to the factorized case (16). Closed-form solutions for $h(t)$ [Eq. (16)] can be obtained only in a few special cases, when γ is available in closed form and $f(\tau)$ and $f(\mu)$ assume trivial forms, such as δ functions. In the case where γ is available in closed form, with $f(\tau)$ and $f(\mu)$ given, h can be solved in a relatively simple manner, by numerical quadratures, possibly combined with numerical inversion of $\hat{f}$. In the general case, h can be either studied through its cumulants (if these are finite), or evaluated using numerical inversion and Monte Carlo simulations. In the following, we illustrate the asymptotic behavior of $h(t)$, using the limiting properties of its Laplace transform $\hat{h}$ for $s\to 0$.

Consider the case where a characteristic exchange time cannot be defined, i.e., the first moment of $g(t)$ is infinite; this corresponds to the case (B7), with $\eta<1$. We consider here the range $-1<\eta<1$ applicable for most practical problems. Let the trajectory densities assume the forms (10) and (A4) with $\alpha_m=0$ $(m=\tau,\mu)$, i.e., one-sided stable densities, where for simplicity, we neglect centering ($d_m=0$). Then we have $s\hat{g}\sim s^{\eta+1}$, and Eq. (16) yields for $s\to 0$,

$$1-\hat{h}(s)\approx c_\tau s^{\alpha_\tau}+c_\mu s^{\alpha_\mu(1+\eta)}. \tag{28}$$

Asymptotic behavior of $h(t)$ will thus be determined by the relative magnitude of the exponents α_τ and $\alpha_\mu(\eta+1)$.

Consider first the special case $\alpha_\tau=\alpha_\mu\equiv\alpha$. Then for $\eta>0$, the asymptotic transport (for fixed, finite L) is dominated by the trajectory density exponent α. For $\eta<0$, asymptotic transport is dominated by a combination of the exponents α and η, i.e.,

$$h(t)\sim t^{-\alpha(\eta+1)-1},\quad t\to\infty. \tag{29}$$

Since $\alpha<1$, then for $\eta<0$ we have $\alpha(\eta+1)<1$ and all the moments of $h(t)$ other than the zeroth moment, are infinite.

In the case $\alpha_\tau<\alpha_\mu$, and for $0<\eta<1$, the transport is always asymptotically dominated by transition. If $\alpha_\tau>\alpha_\mu$ and $-1<\eta<0$, the transport is always asymptotically dominated by exchange. The dependence of asymptotic transport on the exponents α_τ, α_μ, and η, can be clearly summarized on a (α_μ,α_τ) plot as given by the simple linear relationship $\alpha_\tau=\alpha_\mu(\eta+1)$. For any given $-1<\eta<1$, a line from the origin given by $\alpha_\tau=\alpha_\mu(\eta+1)$ defines a dominance ''delimiter,'' or ''jump'': below the line, any combination of α_τ and α_μ implies an asymptotic dominance of exchange, whereas above the line any combination of α_τ and α_μ implies an asymptotic dominance of transition.

In the case densities f_τ and f_μ have finite moments, i.e., $a_m\neq 0$ $(m=\tau,\mu)$, asymptotic transport is dominated by the exchange-time density exponent η, i.e.,

$$h(t)\sim t^{-\eta-2},\quad t\to\infty. \tag{30}$$

For a rate distribution ϕ other than the power law, and γ distribution, it can be shown that asymptotically, the slope of $g(t)$ is zero (albeit the convergence to zero may be slow). As a simple example, consider g given in Eq. (B1). For sufficiently large time (or small s), $\hat{g}_i\approx\beta_i$, and

$$h(t)=\int_0^1 f_\tau(\tau)f_\mu(t-\tau)d\tau, \tag{31}$$

where $\mu=\Sigma_i\beta_i\Delta\tau_i$; this case has been analyzed, e.g., in Ref. [13]. If $\beta_i=\beta$, i.e., site dependence is neglected, we have

$$h(t)=\frac{1}{R}f_\tau(t/R), \tag{32}$$

where $R\equiv 1+\beta$ is commonly referred to as the retardation factor. The classical subsurface transport model (convective diffusive, or advective dispersive with constant diffusion coefficient, for a pulse in a semi-infinite domain, with constant

linear equilibrium sorption, e.g., Ref. [30]) is then recovered from Eq. (32) where f_τ is given in Eq. (10) with $a\neq 0$, $d=0$, $\alpha=1/2$.

V. CONCLUSIONS

In the factorized (''separable'') case, θ is dependent on τ and μ, i.e., $\theta(\tau,\mu)$, and the solution is obtained as $\hat{h}=\hat{f}_{\tau\mu}(s,s\hat{g})$; this generalizes the classical result of chromatography obtained for the homogeneous case as $\hat{h}=\hat{f}_\tau(s+s\hat{g})$ [1]. μ accounts for macroscale disorder in a relatively simple manner, by integrating the variable exchange parameter β (''total capacity'') along the entire lattice. In this case, $\theta(\tau,\mu)$ is subordinated to θ with two operational times, τ and μ [28]. In the ''nonseparable'' case where all exchange parameters exhibit disorder, while cumulants of g are finite, $\theta(\tau,\mu_0,\mu_1,\mu_2,\ldots)$ is subordinated to θ, with an infinite series of operational variables τ, $\mu_0,\mu_1,\mu_2,\ldots$ [28]. In other words, θ depends on $\mu_m(L)$ $(m=0,1,2,...)$, in which case the solution for h is derived in the form of cumulants. In the most general case where cumulants of g_i are not defined, the solution can be obtained only using Monte Carlo simulations, based on one-dimensional lattices (trajectories).

Asymptotic solutions of h [Eq. (16)] were obtained by introducing a ''truncated stable'' density f [Eq. (10)] for exchange trajectories τ and μ (in this case simplified as uncorrelated). Two significant features of the truncated stable density (10) [or Eq. (A4)] in the present context are: (i) it can be directly used in [Eq. (16)] for setting bounds on the density h; (ii) by suitable choice of parameters, it reduces to familiar densities with finite or infinite moments, providing a smooth transition between the two. Of particular interest is the one-sided stable (Levy) density (for $a=0$ and $0<\alpha<1$), and inverse-Gaussian density $(a\neq 0,d=0,\alpha=1/2)$ characteristic for a classical convection-diffusion process.

An interesting asymptotic case is when both microscale exchange is characterized by power-law asymptotic behavior with exponent η, and macroscale transition is characterized by a power-law with exponents α_τ and α_μ. The line $\alpha_\tau=\alpha_\mu(\eta+1)$ defines two regions in the exponent plane (α_τ,α_μ), one in which the asymptotic transport is dominated by transition, and one in which it is dominated by exchange. For the case of transition disorder with uniform exchange, both transition (summarized in the exponent α) and exchange (summarized in the exponent η) can influence the late-time behavior of $h(t)$. Since exchange is subordinated to transition, it will unconditionally influence the late-time behavior of $h(t)$ only if $\eta<0$. If $\eta>0$, exchange will dominate at late time provided that transition becomes Gaussian in the limit. However, if transition is never Gaussian and $\eta>0$, then transition effects will determine the asymptotic behavior of $h(t)$. In the case transition is never Gaussian and $\eta<0$, then both the transition and exchange will determine late-time behavior of the density $h(t)$.

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APPENDIX A: ONE-SIDED TRUNCATED STABLE DENSITY

Suitable choice of the parameters reduces f [Eq. (10)] to familiar forms, either with finite, or infinite moments. The Dirac δ function is obtained from [Eq. (10)] as a degenerate case with $\alpha=1$. Setting $d=0$ and $\alpha=1/2$, we obtain the solution of the convection-diffusion (or advection-dispersion) equation for pulse injection in a semi-infinite domain in the form

$$f_\tau(\tau)=\frac{ce^{c\sqrt{a}}}{2\sqrt{\pi t^3}}\exp\left(-a\tau-\frac{c^2}{4\tau}\right), \tag{A1}$$

where

$$a=\frac{U^2}{4D},\quad c=\frac{L}{\sqrt{D}} \tag{A2}$$

with L being the distance, U the mean drift, and D the dispersion coefficient [31].

Setting $a=0$, reduces f_τ [Eq. (10)] to the one-sided stable (Levy) density, where d is the centering parameter, c is the width parameter, and α the exponent [18]. If we denote the Levy density as $f_L(\tau)\equiv f(\tau;a=0)$, and set $d=0$, we can write

$$f_\tau(\tau)=f_L(\tau)e^{-a\tau+ca^\alpha}.$$

Since $f_L(\tau)\sim\tau^{-\alpha-1}$ for $\tau\to\infty$, we have

$$f_\tau(\tau)\sim\tau^{-\alpha-1}e^{-a\tau}. \tag{A3}$$

Thus the parameter a determines the ''cutoff.'' Up to $a\tau\approx 0.1$, f coincides with the Levy density, after which its tail starts deviating from a power law, gradually reducing to zero at $a\tau\approx 100$.

If $a\neq 0$, the moments of f_τ [Eq. (2)] are finite, the first two being

$$\langle\tau\rangle=c\alpha a^{\alpha-1},$$

$$\sigma_\tau^2\equiv\langle\tau^2\rangle-\langle\tau\rangle^2=c(1-\alpha)\alpha a^{\alpha-2}.$$

Since a can be chosen arbitrarily small, a and α determine the ''degree'' of ''non-Gaussianity'' of the density f, and thus can be useful for interpreting observations in a wide range of media with a variety of structures.

In view of the dependence of μ [Eq. (13)] on $\Delta\tau_i$, we propose a general density f_μ in the Laplace domain, in analogy to f_τ [Eq. (10)], as

$$\hat{f}_\mu(s)=\exp[ca^\alpha-ds-c(a+s)^\alpha], \tag{A4}$$

where a, c, d, $0<\alpha\leqslant 1$ are parameters for μ, in general different from those for τ. A special case of interest is if $\mu=\beta\tau$ ($\beta=$const), with $\alpha=1/2$ and $a\neq 0$ in which case [Eq.

(A4)] can be inverted analytically and is the solution of the convection-diffusion equation, with retardation, for a pulse in a semi-infinite domain [30].

Finally, we note that f_τ (10) is comparable to the Laplace transform of the Gamma density (f_G) with nonzero centering:

$$\hat{f}_G = b^{-\xi}(b+s)^{\xi}e^{-ds},$$

where b,d,ξ are parameters. b is here the "cutoff" parameter corresponding to our a in Eq. (10).

APPENDIX B: A FEW TYPICAL EXCHANGE MODELS

1. First-order model

This model has been widely used in the analysis of chromatographic columns [1], in the oil industry [32], and for subsurface transport [33,34]. The rate density ϕ and the memory function g are defined as

$$\phi(k) = \beta_0 \delta(k-k_0), \quad g(t) = \beta_0 k_0 e^{-k_0 t}, \tag{B1}$$

where β_0 and k_0 are constants. The master equation formulation for multiple transport paths with random exchanges of Hughes and Sahimi [8,9], is also based on this model.

As shown, e.g., in Ref. [2], g [Eq. (B1)] is applicable for a variety of diffusion-sorption linear models where the kinetic transfer is characterized by a *single* rate (equal to k_0) or equivalently a single time scale (equal to $1/k_0$).

2. Diffusion in spheres

This is a classical model in reactor engineering [2]. Similar to the first-order model, the diffusion model is characterized by a single exchange rate. The rate density ϕ and the memory function g are defined by [24]

$$\phi(k) = \sum_{m=1}^{\infty} \frac{6\beta_0}{m^2\pi^2}\,\delta\left(k - m^2\pi^2\frac{D_a}{r_p^2}\right),$$

$$g(t) = \sum_{m=1}^{\infty} 6\beta_0 \frac{D_a}{r_p^2}\exp\left(-m^2\pi^2\frac{D_a}{r_p^2}t\right), \tag{B2}$$

where r_p is the sphere radius and D_a is the apparent diffusion coefficient for the spheres, which accounts for possible sorption.

3. Diffusion into infinite blocks

Another widely used model is for retention in fractured rock with the rate density ϕ_i of the form [24]

$$\phi_i(k) = \lim_{t\to\infty} \sum_{j=1}^{\infty} \frac{8A_i l}{(2j-1)^2\pi^2}\,\delta_j\left[k - \frac{(2j-1)^2\pi^2}{4}\frac{D_a}{l^2}\right], \tag{B3}$$

which yields

$$g_i(t) = A_i\sqrt{\frac{D_a}{\pi t}}, \quad \hat{g}_i(s) \sim \frac{1}{\sqrt{s}}, \tag{B4}$$

where A_i is a site-dependent retention parameter group; D_a is an apparent diffusion coefficient in the (immobile) rock matrix, which accounts for sorption; and δ_j is a Dirac δ function. The corresponding continuum form of the nonhomogeneous retention function γ is given elsewhere, e.g. [12,14]. For this model, γ quantifies parallel-plate advection-diffusion into an infinite medium (rock) [35], and is equivalent to a one-sided stable density with exponent $\frac{1}{2}$ [28].

4. Gamma model

This model accounts for a distribution of exchange rates, which has provided a good description of desorption in environmental engineering, e.g. [36,37]. The rate density ϕ and the memory function g are defined as [24]

$$\phi(k) = \frac{\beta_0}{\gamma(-\xi-1)}\frac{e^{-bk}}{b^{\xi+1}k^{\xi+2}},$$

$$g(t) = \frac{-\beta_0(\xi+1)}{b}(t/b+1)^{\xi}, \tag{B5}$$

where ξ and b are parameters of the gamma density.

5. Power-law model

A particularly useful form of the rate density ϕ is given by the power law [6,24]

$$\phi(k) \sim k^{\eta-1}, \tag{B6}$$

which yields

$$g(t) \sim t^{-\eta-1}, \quad \hat{g}(s) \sim s^{\eta}. \tag{B7}$$

Giona and co-workers [5] showed that mass uptake by diffusion into a finitely ramified fractal with a constant-concentration external boundary evolves as $\sim t^{d_s/2}$ and $\sim s^{-d_s-1}$, where d_s is the spectral dimension. Since $\hat{g}(s) = \hat{M}_r(s)/\hat{M}(s)$, e.g. [2], where $\hat{M}_r(s)$ is the mass retained in the immobile water and $\hat{M}(s)$ is the mass retained in the mobile water, $\eta = -d_s/2$ and

$$g(t) \sim t^{d_s/2-1}, \hat{g}(s) \sim s^{d_s/2}.$$

For diffusion into a slab of homogeneous rock $d_s = 1$, and we recover the model (B6) with $\eta = -1/2$.

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