

Diffusion theory for transport in porous media: Transition-probability densities of diffusion processes corresponding to advection-dispersion equations

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Abstract. Local-scale spatial averaging of pore-scale advection-diffusion equations in porous media leads to advection-dispersion equations (ADEs). While often used to describe subsurface transport, ADEs may pose special problems in the context of diffusion theory. Standard diffusion theory applies only when characteristic coefficients, velocity, porosity, and dispersion tensor, are smooth functions of space. Subsurface porous-media properties, however, naturally exhibit spatial variability. Transitions between material types are often abrupt rather than smooth, such as sand in contact with clay. In such composite porous media, characteristic coefficients in spatially averaged transport equations may be discontinuous. Although commonly called on to model transport in these cases, standard diffusion theory does not apply. Herein we develop diffusion theory for ADEs of transport in porous media. Derivation of ADEs from probabilistic assumptions yields (1) necessary conditions for convergence of diffusion processes to ADEs, even when coefficients are discontinuous, and (2) general probabilistic definitions of physical quantities, velocity, and dispersion tensor. As examples of how the new theory can be applied to theoretical and numerical problems of transport in porous media, we evaluate several random walk methods that have appeared in the water resources literature.

1. Introduction

The need to forecast long-term transport phenomena such as groundwater remediation at complex field sites is placing more stringent demands on models of transport in porous media. Detailed site characterizations based on geostatistical simulations that are conditional to subsurface core and geophysical data are producing ever more realistic models of heterogeneity, perhaps including most of the intricacies that strongly govern scale-dependent dispersion [e.g., Carle *et al.*, 1998; Copty and Rubin, 1995; McKenna and Poeter, 1995; Sheibe and Freyburg, 1995]. These models commonly include large contrasts in hydraulic conductivity (K) characterized by both gradational and abrupt contacts between geologic materials (e.g., clean sand resting on a clay bed) and with $\ln K$ variances as high as 24. Furthermore, the volume fraction of low- K media composed of silts and clays, where diffusion tends to dominate over advection, is often substantial, at 20–80%. Accurate modeling of advection and dispersion in such composite media is challenging because (1) the heterogeneity must be highly resolved in three dimensions, often entailing 10^5 – 10^6 nodes or more, and (2) even small errors in the numerical solution can result in significant, erroneous distribution of con-

taminant mass among the high- K and low- K materials [LaBolle *et al.*, 1996a, b].

The random walk particle method (RWPM) is attractive for simulating transport in highly resolved heterogeneous media because of its computational efficiency and lack of numerical dispersion [Prickett *et al.*, 1981; Uffink, 1985; Ahlstrom *et al.*, 1977; Kinzelbach, 1988; Tompson *et al.*, 1987; LaBolle *et al.*, 1996a]. Standard diffusion theory underlying the RWPM, however, relies on the assumption that material properties vary smoothly in space. This paper is motivated by the desire to eventually develop and apply an RWPM to simulate local-scale transport in composite media. To accomplish this in a mathematically rigorous way, one must first develop diffusion theory for local-scale, spatially averaged subsurface diffusion processes in composite media.

Herein we develop new diffusion theory for problems of subsurface transport in composite media described by advection-dispersion equations (ADEs) and demonstrate relevance of the theory to analyses published previously in the water resources literature. In the spirit of Kolmogorov [1931], we derive ADEs from principles of probability to yield (1) necessary conditions for convergence of diffusion processes in composite porous media to ADEs with discontinuous coefficients and (2) probabilistic definitions of velocity and dispersion tensor that are consistent with the mass balance principles referred to in the physics literature as detailed balance. We finish with an evaluation of several RWPMs that have appeared in the water resources literature.

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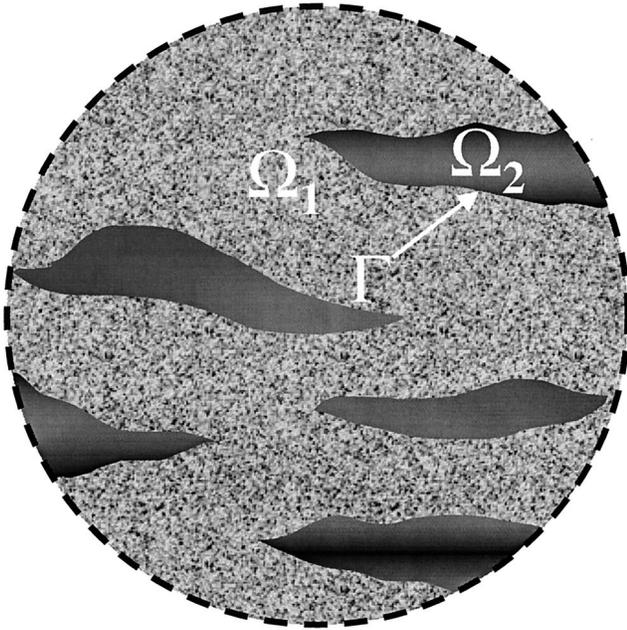


Figure 1. Porous media system composed of subdomains Ω_1 and Ω_2 with contrasting material properties that give rise to discontinuous characteristic transport coefficients at the interface Γ .

2. Background and Problem Description

Rigorous treatment of transport in porous media must begin with diffusion theory applied at the pore scale. In flowing pore water, diffusion theory predicts transport according to advection-diffusion equations. Fundamentals of this theory were first introduced by *Einstein* [1905] in his classic paper on molecular diffusion in liquids. Therein, Einstein mathematically defined a diffusion process through probabilistic assumptions regarding the apparent stochastic motion of Brownian particles and showed that the densities of such processes obey diffusion equations for the time evolution of concentration. While this work laid the foundations of diffusion theory, the mathematics of diffusion processes have since been improved and formalized in probability theory, the theory of stochastic differential equations, and the theory of stochastic processes. Diffusion theory has seen diverse hydrogeological applications and has played a key role in developing theories of water flow [*Scheidtger*, 1974; *Bhattacharya et al.*, 1976], theories for effective-medium properties and macroscopic transport in heterogeneous media [*Matheron and de Marsily*, 1980; *Dagan*, 1984; *Van Den Broeck*, 1990; *Brenner*, 1991; *Bhattacharya and Gupta*, 1990] and RWPM's for numerical simulation [*Prickett et al.*, 1981; *Uffink*, 1985; *Ahlstrom et al.*, 1977; *Kinzelbach*, 1988; *Tompson et al.*, 1987; *LaBolle et al.*, 1996a].

2.1. Governing Equations

The process of local-scale, spatial averaging of pore-scale advection-diffusion equations commonly gives rise to ADEs of the form [*Scheidtger*, 1974; *Bear*, 1972; *Koch and Brady*, 1985; *Plumb and Whitaker*, 1990; *Quintard and Whitaker*, 1993]

$$\frac{\partial}{\partial t} [\Theta(\mathbf{x})c(\mathbf{x}, t)] + \frac{\partial}{\partial x_i} [\Theta(\mathbf{x})v_i(\mathbf{x}, t)c(\mathbf{x}, t)]$$

$$- \frac{\partial}{\partial x_i} \left[\Theta(\mathbf{x})D_{ij}(\mathbf{x}, t) \frac{\partial c(\mathbf{x}, t)}{\partial x_j} \right] = 0 \quad (1)$$

where $c(\mathbf{x}, t)$ is aqueous concentration [$M L^{-3}$], $\Theta(\mathbf{x})$ is effective porosity, $\mathbf{v}(\mathbf{x}, t)$ is average groundwater-velocity vector [$L T^{-1}$], and $\mathbf{D}(\mathbf{x}, t)$ is a hydrodynamic dispersion tensor [$L^2 T^{-1}$]. When there is free flow of mass across material interfaces in composite media (Figure 1), continuity requires

$$\frac{\partial}{\partial t} (\Theta c_1) = - \frac{\partial}{\partial x_i} (\Theta v_{1i} c_1) + \frac{\partial}{\partial x_i} \left(\Theta D_{1ij} \frac{\partial c_1}{\partial x_j} \right) \quad \text{in } \Omega_1 \quad (2a)$$

$$\frac{\partial}{\partial t} (\Theta c_2) = - \frac{\partial}{\partial x_i} (\Theta v_{2i} c_2) + \frac{\partial}{\partial x_i} \left(\Theta D_{2ij} \frac{\partial c_2}{\partial x_j} \right) \quad \text{in } \Omega_2 \quad (2b)$$

$$c_1 = c_2 \quad \text{on } \Gamma \quad (2c)$$

$$\begin{aligned} \Theta_1 n_{1i} \left(v_{1i} c_1 - \Theta D_{1ij} \frac{\partial c_1}{\partial x_j} \right) \Big|_1 \\ = \Theta_2 n_{2i} \left(v_{2i} c_2 - \Theta D_{2ij} \frac{\partial c_2}{\partial x_j} \right) \Big|_2 \end{aligned} \quad (2d)$$

where subscripts 1 and 2 represent smoothly varying quantities or fields in Ω_1 and Ω_2 , respectively; \mathbf{n}_i is a unit outward normal in Ω_i to the interface denoted by Γ ; and $|_i$ means the approach to Γ in Ω_i . Similar equations arise in the description of thin films optics, the electrical and thermal properties of composite materials, and numerous other applications. Such problems have received considerable attention in the literature, particularly diffusive transport between flowing and stagnant water in rock [*Neretnieks*, 1980; *Bibby*, 1981; *Grisak and Pickens*, 1981; *Neretnieks et al.*, 1982; *Mutch et al.*, 1993], soil particles [*van Genuchten and Wierenga*, 1976; *Koch and Brady*, 1985; *Quintard and Whitaker*, 1993], and low-permeability granular materials [*Gillham et al.*, 1984; *Sudicky et al.*, 1985; *Wilson et al.*, 1993; *Berglund and Cvetkovic*, 1995].

2.2. Diffusion Processes and Kolmogorov's Equations

As with advection and diffusion at the pore scale, one can also develop diffusion processes that correspond to local-scale, spatially averaged transport equations in the form of (1). Diffusion processes are Markov processes with continuous sample paths. In the context of subsurface transport, it is conceptually appealing to consider a realization of a diffusion process $\mathbf{X}(t)$ as a continuous function of time describing the "average" trajectory of a solute molecule (or particle) in three-dimensional Euclidean space. Standard diffusion theory relates the dynamics of a diffusion process to *Kolmogorov's* [1931] equations, diffusion equations which describe its probabilistic evolution in time.

The Markov property can be expressed in terms of conditional probabilities as [*Azwiniski*, 1970]

$$p(\mathbf{x}_n, t_n | \mathbf{x}_{n-1}, t_{n-1}, \dots, \mathbf{x}_0, t_0) = p(\mathbf{x}_n, t_n | \mathbf{x}_{n-1}, t_{n-1}) \quad (3a)$$

$$\int_{\mathbf{x}_n \in \Omega} p(\xi, t_n | \mathbf{x}_{n-1}, t_{n-1}) d\xi = P[\mathbf{X}(t_n) \in \Omega | \mathbf{X}(t_{n-1}) = \mathbf{x}_{n-1}] \quad (3b)$$

where \mathbf{x}_n , \mathbf{x}_{n-1} , and \mathbf{x}_0 are values of \mathbf{X} at discrete times $t_n \geq t_{n-1} \geq t_0$, and the conditional (or transition) probability density function, $p(\mathbf{x}_n, t_n | \mathbf{x}_{n-1}, t_{n-1})$ is positive with integral

one. The Markov process \mathbf{X} is a diffusion process if its transition-probability density satisfies [Arnold, 1974]

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int (z_i - x_i) p(\mathbf{z}, t + \Delta t | \mathbf{x}, t) d\mathbf{z} = A_i(\mathbf{x}, t) \quad (4a)$$

$$\lim_{\Delta t \rightarrow 0} \frac{1}{2\Delta t} \int (z_i - x_i)(z_j - x_j) p(\mathbf{z}, t + \Delta t | \mathbf{x}, t) d\mathbf{z} = D_{ij}(\mathbf{x}, t) \quad (4b)$$

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|z-x| \geq \varepsilon} p(\mathbf{z}, t + \Delta t | \mathbf{x}, t) d\mathbf{z} = 0 \quad \forall \varepsilon > 0 \quad (4c)$$

where \mathbf{z} and \mathbf{x} are values of \mathbf{X} , \mathbf{A} [$L T^{-1}$] is a drift vector, and \mathbf{D} [$L^2 T^{-1}$] is a diffusion or dispersion tensor. Condition (4c) ensures that the process \mathbf{X} has continuous sample paths.

Evolution of the probability density $p(\mathbf{x}, t)$ of a diffusion processes satisfying (4a)–(4c) is given by a diffusion equation referred to as Kolmogorov's forward (or the Fokker-Planck) equation (for a derivation, see pp. 126–129 of Jazwinski [1970])

$$\frac{\partial p(\mathbf{x}, t)}{\partial t} + \frac{\partial}{\partial x_i} [A_i(\mathbf{x}, t) p(\mathbf{x}, t)] - \frac{\partial^2}{\partial x_i \partial x_j} [D_{ij}(\mathbf{x}, t) p(\mathbf{x}, t)] = 0 \quad (5)$$

with initial condition $p(\mathbf{x}, t_0)$, $t \geq t_0$. In applications of diffusion theory to subsurface transport, (1) has normally been treated as a special case of Kolmogorov's forward equation (5) with $p(\mathbf{x}, t) = \Theta(\mathbf{x})c(\mathbf{x}, t)$ [Tompson et al., 1987; Bhattacharya and Gupta, 1990]. Using this relationship in (5), one finds that equivalence between (5) and (1) is obtained by specifying the drift as [Tompson et al., 1987]

$$A_i(\mathbf{x}, t) = v_i(\mathbf{x}, t) + \Theta^{-1}(\mathbf{x}) \frac{\partial}{\partial x_j} [\Theta(\mathbf{x}) D_{ij}(\mathbf{x}, t)] \quad (6)$$

As the need for gradient terms in (6) suggests, standard theory [Einstein, 1956; Kolmogorov, 1950; Feller, 1968, 1971; Itô and McKean, 1961] applies only to ADEs when coefficients porosity Θ and dispersion tensor \mathbf{D} are smooth functions of space. This theory cannot generally address diffusion processes in composite porous media in which abrupt transitions between materials with contrasting hydraulic and transport properties lead to discontinuous characteristic coefficients. In some cases, limitations of standard theory have been discounted or have gone unnoticed. This has led to published results and the proliferation of numerical models with unintended, unphysical meaning [see LaBolle et al., 1996a]. Clearly, development of a rigorous theory that applies to local-scale, spatially averaged equations of transport in composite porous media is important to forecasting long-term transport phenomena. In the following section we develop (1) more general results for subsurface transport described by ADEs and (2) conditions necessary to ensure conservation of mass and convergence of diffusion processes to these equations in the presence of material interfaces (discontinuous coefficients).

3. Diffusion Processes and Advection-Dispersion Equations

Here we derive ADEs from principles of probability. Similar derivations for concentration described by Kolmogorov's forward equation are given by Einstein [1905] (for constant coef-

ficients), Kolmogorov [1931] (for spatially varying coefficients), and in various texts on stochastic processes (e.g., pp. 48–50 of Gardiner [1990] and pp. 126–129 of Jazwinski [1970]). However, these results do not generally apply to subsurface transport described by ADEs. To generalize theory for transport in composite porous media, we use the mathematical abstraction of a “weak” form of ADEs. This new form of the governing equations can be found by forming the integral of (1) against a smooth test function $f(\mathbf{x}, t)$:

$$\int_0^t \int f \left[\frac{\partial(\Theta c)}{\partial s} - \frac{\partial}{\partial x_i} \left(\Theta D_{ij} \frac{\partial c}{\partial x_j} \right) + \frac{\partial}{\partial x_i} (\Theta v_i c) \right] d\mathbf{x} ds = 0 \quad (7)$$

and integrating by parts to yield

$$\int f c d\mu(\mathbf{x}) \Big|_0^t - \int_0^t \int \frac{\partial f}{\partial s} c d\mu(\mathbf{x}) ds + \int_0^t \int \frac{\partial f}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} - v_i c \right) d\mu(\mathbf{x}) ds = 0 \quad (8)$$

where the quantity $d\mu(\mathbf{x})$ is referred to as a measure and $d\mu(\mathbf{x}) = \Theta d\mathbf{x}$. This measure arises naturally in the formulation of a probabilistic description of transport in a phase that occupies a fraction Θ of the entire domain. Distributions c satisfying (8) for smooth and bounded f are said to converge weakly to (1). Derivation of (8) will relate the physical quantities \mathbf{v} , \mathbf{D} , and Θ to concepts from probability, that is, transition-probability densities of diffusion processes that correspond to this new governing equation.

3.1. Transition-Probability Densities of Diffusion Processes Corresponding to ADEs

For derivation of (8) we begin with the time derivative of the probability density $p_\varepsilon(\mathbf{x}, t) d\mu(\mathbf{x})$ integrated in space and time against the test function $f(\mathbf{x}, t)$:

$$\begin{aligned} \varepsilon^2 \int_0^t \int \frac{\partial p_\varepsilon(\mathbf{x}, s)}{\partial s} f(\mathbf{x}, s) d\mu(\mathbf{x}) ds + o(\varepsilon^2) \\ = \int_0^t \int [p_\varepsilon(\mathbf{x}, s + \varepsilon^2) - p_\varepsilon(\mathbf{x}, s)] f(\mathbf{x}, s) d\mu(\mathbf{x}) ds \end{aligned} \quad (9)$$

where $\varepsilon^2 = \Delta t$. Integrating the left-hand side by parts yields

$$\begin{aligned} \varepsilon^2 \int_0^t \int \frac{\partial p_\varepsilon(\mathbf{x}, s)}{\partial s} f(\mathbf{x}, s) d\mu(\mathbf{x}) ds + o(\varepsilon^2) \\ = \varepsilon^2 \int f(\mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) d\mu(\mathbf{x}) \Big|_0^t \\ - \varepsilon^2 \int_0^t \int \frac{\partial f(\mathbf{x}, s)}{\partial s} p_\varepsilon(\mathbf{x}, s) d\mu(\mathbf{x}) ds \end{aligned} \quad (10)$$

Substituting this result into (9) gives

$$\begin{aligned} & \varepsilon^2 \int f(\mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) \, d\mu(\mathbf{x}) \Big|_0^t \\ & - \varepsilon^2 \int_0^t \int \frac{\partial f(\mathbf{x}, s)}{\partial s} p_\varepsilon(\mathbf{x}, s) \, d\mu(\mathbf{x}) \, ds \\ & - \int_0^t \int [p_\varepsilon(\mathbf{x}, s + \varepsilon^2) - p_\varepsilon(\mathbf{x}, s)] f(\mathbf{x}, s) \, d\mu(\mathbf{x}) \, ds \\ & + o(\varepsilon^2) = 0 \end{aligned} \tag{11}$$

Substituting the relationship

$$p_\varepsilon(\mathbf{x}, s + \varepsilon^2) = \int p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s) p_\varepsilon(\mathbf{z}, s) \, d\mu(\mathbf{z}) \tag{12}$$

into the last term in (11) yields

$$\begin{aligned} & \int [p_\varepsilon(\mathbf{x}, s + \varepsilon^2) - p_\varepsilon(\mathbf{x}, s)] f(\mathbf{x}, s) \, d\mu(\mathbf{x}) \\ & = \int \left[\int p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s) p_\varepsilon(\mathbf{z}, s) \, d\mu(\mathbf{z}) - p_\varepsilon(\mathbf{x}, s) \right] f(\mathbf{x}, s) \, d\mu(\mathbf{x}) \\ & = \int \int p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s) p_\varepsilon(\mathbf{z}, s) f(\mathbf{x}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & - \int p_\varepsilon(\mathbf{x}, s) f(\mathbf{x}, s) \, d\mu(\mathbf{x}) \\ & = \int \int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) f(\mathbf{z}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & - \int p_\varepsilon(\mathbf{x}, s) f(\mathbf{x}, s) \, d\mu(\mathbf{x}) \end{aligned} \tag{13}$$

Inserting the relationship

$$\int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) \, d\mu(\mathbf{z}) = 1 \tag{14}$$

into the last integral in the right-hand side of (13) gives

$$\begin{aligned} & \int [p_\varepsilon(\mathbf{x}, s + \varepsilon^2) - p_\varepsilon(\mathbf{x}, s)] f(\mathbf{x}, s) \, d\mu(\mathbf{x}) \\ & = \int \int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) f(\mathbf{z}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & - \int \left[\int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) \, d\mu(\mathbf{z}) \right] p_\varepsilon(\mathbf{x}, s) f(\mathbf{x}, s) \, d\mu(\mathbf{x}) \\ & = \int \int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) f(\mathbf{z}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & - \int \int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) f(\mathbf{x}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & = \int \int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) [f(\mathbf{z}, s) - f(\mathbf{x}, s)] \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \end{aligned} \tag{15}$$

Substituting (15) into (12) yields

$$\begin{aligned} & \varepsilon^2 \int f(\mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) \, d\mu(\mathbf{x}) \Big|_0^t \\ & - \varepsilon^2 \int_0^t \int \frac{\partial f(\mathbf{x}, s)}{\partial s} p_\varepsilon(\mathbf{x}, s) \, d\mu(\mathbf{x}) \, ds \\ & - \int_0^t \int \int [f(\mathbf{z}, s) - f(\mathbf{x}, s)] p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) \\ & \cdot d\mu(\mathbf{z}) p_\varepsilon(\mathbf{x}, s) \, d\mu(\mathbf{x}) \, ds + o(\varepsilon^2) = 0 \end{aligned} \tag{16}$$

For the last integral in (16) we have

$$\begin{aligned} & \int \int [f(\mathbf{z}, s) - f(\mathbf{x}, s)] p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & = \int \int [f(\mathbf{x}, s) - f(\mathbf{z}, s)] p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s) p_\varepsilon(\mathbf{z}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & = - \int [f(\mathbf{z}, s) - f(\mathbf{x}, s)] p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s) p_\varepsilon(\mathbf{z}, s) \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & = \frac{1}{2} \int \int [f(\mathbf{z}, s) - f(\mathbf{x}, s)] [p_\varepsilon(\mathbf{x}, s) p(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) \\ & - p_\varepsilon(\mathbf{z}, s) p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s)] \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & = \frac{1}{2} \int \int [p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) - p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s)] p_\varepsilon(\mathbf{z}, s) \\ & \cdot [f(\mathbf{z}, s) - f(\mathbf{x}, s)] \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & - \frac{1}{2} \int \int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) [f(\mathbf{z}, s) - f(\mathbf{x}, s)] \\ & \cdot [p_\varepsilon(\mathbf{z}, s) - p_\varepsilon(\mathbf{x}, s)] \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & = \frac{1}{2} \int \int [p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) - p_\varepsilon(\mathbf{x}, s + \varepsilon^2 | \mathbf{z}, s)] p_\varepsilon(\mathbf{x}, s) \\ & \cdot [f(\mathbf{z}, s) - f(\mathbf{x}, s)] \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \\ & - \frac{1}{2} \int \int p_\varepsilon(\mathbf{z}, s + \varepsilon^2 | \mathbf{x}, s) [f(\mathbf{z}, s) - f(\mathbf{x}, s)] \\ & \cdot [p_\varepsilon(\mathbf{z}, s) - p_\varepsilon(\mathbf{x}, s)] \, d\mu(\mathbf{z}) \, d\mu(\mathbf{x}) \end{aligned} \tag{17}$$

Formally expanding $f(\mathbf{z}, t)$ and $p(\mathbf{z}, t)$ in Taylor series yields

$$f(\mathbf{z}, t) = f(\mathbf{x}, t) + (z_i - x_i) \frac{\partial f(\mathbf{x}, t)}{\partial x_i} + \dots \tag{18a}$$

$$p_\varepsilon(\mathbf{z}, t) = p_\varepsilon(\mathbf{x}, t) + (z_i - x_i) \frac{\partial p_\varepsilon(\mathbf{x}, t)}{\partial x_i} + \dots \tag{18b}$$

Note that the Taylor series expansion in (18b) is usually unjustified when p is not smooth. However, in this case one does expect p to have one generalized derivative; that is, p should have one derivative that is continuous with discontinuities at

subdomain boundaries. For such functions, one expects (18b) to be correct. Substituting (18a) and (18b) into (17) and retaining terms to order $(z_i - x_i)(z_j - x_j)$ gives

$$\begin{aligned}
 & \frac{1}{2} \iint [p_\varepsilon(\mathbf{z}, s + \varepsilon^2|\mathbf{x}, s) - p_\varepsilon(\mathbf{x}, s + \varepsilon^2|\mathbf{z}, s)] \\
 & \quad \cdot p_\varepsilon(\mathbf{x}, s)(z_i - x_i) \frac{\partial f(\mathbf{x}, s)}{\partial x_i} d\mu(\mathbf{z}) d\mu(\mathbf{x}) \\
 & \quad - \frac{1}{2} \iint p_\varepsilon(\mathbf{z}, s + \varepsilon^2|\mathbf{x}, s)(z_i - x_i) \\
 & \quad \cdot \frac{\partial f(\mathbf{x}, s)}{\partial x_i} (z_j - x_j) \frac{\partial p_\varepsilon(\mathbf{x}, s)}{\partial x_j} d\mu(\mathbf{z}) d\mu(\mathbf{x}) \\
 & = \frac{1}{2} \iint [p_\varepsilon(\mathbf{z}, s + \varepsilon^2|\mathbf{x}, s) - p_\varepsilon(\mathbf{x}, s + \varepsilon^2|\mathbf{z}, s)] \\
 & \quad \cdot p_\varepsilon(\mathbf{x}, s)(z_i - x_i) \frac{\partial f(\mathbf{x}, s)}{\partial x_i} d\mu(\mathbf{z}) d\mu(\mathbf{x}) \\
 & \quad - \frac{1}{2} \iint p_\varepsilon(\mathbf{z}, s + \varepsilon^2|\mathbf{x}, s)(z_i - x_i) \frac{\partial f(\mathbf{x}, s)}{\partial x_i} (z_j - x_j) \\
 & \quad \cdot \frac{\partial p_\varepsilon(\mathbf{x}, s)}{\partial x_j} d\mu(\mathbf{z}) d\mu(\mathbf{x}) \tag{19}
 \end{aligned}$$

Substituting (19) into (16) yields

$$\begin{aligned}
 & \varepsilon^2 \int f(\mathbf{x}, s) p_\varepsilon(\mathbf{x}, s) d\mu(\mathbf{x}) \Big|_0^t \\
 & - \varepsilon^2 \int_0^t \int \frac{\partial f(\mathbf{x}, s)}{\partial s} p_\varepsilon(\mathbf{x}, s) d\mu(\mathbf{x}) ds \\
 & + \frac{1}{2} \int_0^t \iint (z_i - x_i)(z_j - x_j) p_\varepsilon(\mathbf{z}, s + \varepsilon^2|\mathbf{x}, s) \\
 & \quad \cdot \frac{\partial f(\mathbf{x}, s)}{\partial x_i} \frac{\partial p_\varepsilon(\mathbf{x}, s)}{\partial x_j} d\mu(\mathbf{z}) d\mu(\mathbf{x}) ds \\
 & - \frac{1}{2} \int_0^t \iint (z_i - x_i)[p_\varepsilon(\mathbf{z}, s + \varepsilon^2|\mathbf{x}, s) - p_\varepsilon(\mathbf{x}, s + \varepsilon^2|\mathbf{z}, s)] \\
 & \quad \cdot p_\varepsilon(\mathbf{x}, s) \frac{\partial f(\mathbf{x}, s)}{\partial x_i} d\mu(\mathbf{z}) d\mu(\mathbf{x}) ds + o(\varepsilon^2) = 0 \tag{20}
 \end{aligned}$$

Finally, in the limit, (20) converges to (8) provided $p_\varepsilon(\mathbf{x}, t)$ converges to $c(\mathbf{x}, t)$ and \mathbf{v} and \mathbf{D} are chosen as

$$\begin{aligned}
 & \lim_{\varepsilon \rightarrow 0} \frac{1}{2\varepsilon^2} \int (z_i - x_i)[p_\varepsilon(\mathbf{z}, t + \varepsilon^2|\mathbf{x}, t) - p_\varepsilon(\mathbf{x}, t + \varepsilon^2|\mathbf{z}, t)] d\mu(\mathbf{z}) \\
 & = v_i(\mathbf{x}, t) \tag{21a}
 \end{aligned}$$

$$\begin{aligned}
 & \lim_{\varepsilon \rightarrow 0} \frac{1}{2\varepsilon^2} \int (z_i - x_i)(z_j - x_j) p_\varepsilon(\mathbf{z}, t + \varepsilon^2|\mathbf{x}, t) d\mu(\mathbf{z}) \\
 & = D_{ij}(\mathbf{x}, t) \tag{21b}
 \end{aligned}$$

Equations (21a) and (21b) are the main theoretical results of this paper. They give general probabilistic definitions of physical quantities, velocity and dispersion tensor, in terms of the transition-probability density function of a diffusion process that simulates ADEs. These conditions must be satisfied by the transition-probability density of a diffusion process corresponding to ADEs. As derivation of (8) was not restricted to smooth \mathbf{v} , \mathbf{D} , or Θ , the new theory does not preclude representing (2) by a diffusion process satisfying (21a) and (21b). For ADEs, these definitions of the physical quantities, velocity and dispersion tensor, are more general than, and can replace, the usual definitions for drift and dispersion given in (4a) and (4b). Next we consider a probabilistic analogy to mass balance that is referred to in the physics literature as ‘‘detailed balance.’’ We will show that the principle of detailed balance arises naturally from the definition of velocity given in (21a).

3.2. Detailed Balance

The principle of detailed balance is a probabilistic analogy to mass balance for steady state solutions to (1), with time-independent transport coefficients and $\mathbf{v} = \mathbf{0}$, in which the mass (or probability) flux vanishes (for a discussion of detailed balance as it relates to Kolmogorov’s equations, see pp. 148–155 of *Gardiner* [1990]). For the mass flux to vanish, transitions of mass from one location to another must balance, on the average, with reverse transitions at any instant in time. A statement of detailed balance in terms of conditional probabilities may be written as

$$p(\mathbf{z}, t + \Delta t|\mathbf{x}, t) p_s(\mathbf{x}) = p(\mathbf{x}, t + \Delta t|\mathbf{z}, t) p_s(\mathbf{z}) \tag{22}$$

where $p_s(\mathbf{x}) = c(\mathbf{x})$ is a steady state solution to an ADE with time-independent transport coefficients and $\mathbf{v} = \mathbf{0}$. A process satisfying (22) will maintain detailed balance regardless of whether or not coefficients are smooth.

The form of (22) closely resembles that of (21a). In particular, consider diffusion in a closed system with domain Ω . Here the steady state solution (invariant distribution) is a uniform concentration distribution (probability density) such that $p_s(\mathbf{x}) = p_s(\mathbf{z})$, for any \mathbf{x} and \mathbf{z} in Ω (this is not necessarily true for Kolmogorov’s equations with zero drift). This result in combination with (22) leads to the following detailed balance condition:

$$p(\mathbf{z}, t + \Delta t|\mathbf{x}, t) = p(\mathbf{x}, t + \Delta t|\mathbf{z}, t) \tag{23}$$

Subtracting $p(\mathbf{x}, t + \Delta t|\mathbf{z}, t)$ from both sides of (23), multiplying by $(2\Delta t)^{-1}(\mathbf{z} - \mathbf{x})\Theta$, integrating over all \mathbf{z} , and taking the limit as $\Delta t \rightarrow 0$ yields

$$\lim_{\Delta t \rightarrow 0} \frac{1}{2\Delta t} \int (z_i - x_i)[p(\mathbf{z}, t + \Delta t|\mathbf{x}, t) - p(\mathbf{x}, t + \Delta t|\mathbf{z}, t)] d\mu(\mathbf{z}) = 0 \tag{24}$$

which is (21a) for the case of $\mathbf{v} = \mathbf{0}$. For this case, (21a) is a statement that detailed balance holds microscopically, in the limit of small Δt (as opposed to the definition of drift in (4a), which displays no obvious connection with the physics and is less general for ADEs). Equation (21a) also shows how lack of detailed balance relates to the advective flux. It is no surprise that the probabilistic definition of velocity embraces the principle of mass balance.

Equation (24) is a necessary condition to simulate the dynamic dispersion process described by (2) with $\mathbf{v} = \mathbf{0}$. A diffu-

sion process can satisfy (24) by satisfying (23), that is, by maintaining a symmetric transition-probability density. However, symmetry is not a necessary condition; standard RWPMs based on numerical integration of stochastic differential equations (e.g., as discussed by *Tompson et al.* [1987] and *Kinzelbach* [1988]) will satisfy (24) when coefficients are smooth but do not necessarily maintain a symmetric transition-probability density. The concept of detailed balance is used in the following examples, in which we evaluate several RWPMs presented in the water resources literature.

4. Examples: Random Walk Simulation Methods

Here we apply the results above to evaluate RWPMs for ADEs with discontinuous coefficients [*Uffink*, 1985; *Ackerer*, 1985; *Cordes et al.*, 1991; *Semra et al.*, 1993] about which the literature reports conflicting claims of success. The approximations considered here address the simple problem of random walk simulation of one-dimensional dispersive transport in an infinite domain with instantaneous point source at x_0 , constant Θ , constant coefficients within subdomains Ω_1 ($x < 0$) and Ω_2 ($x > 0$), and discontinuous dispersion coefficient at $x = 0$ ($D_1 > D_2$). In this case the coupled boundary-value problem in (2) reduces to

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x} \left(D_1 \frac{\partial c_1}{\partial x} \right) \quad \text{in } \Omega_1 \quad (25a)$$

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x} \left(D_2 \frac{\partial c_2}{\partial x} \right) \quad \text{in } \Omega_2 \quad (25b)$$

$$c_1 = c_2 \quad \text{on } x = 0 \quad (25c)$$

$$\lim_{x \rightarrow 0^-} D_1 \frac{\partial c_1}{\partial x} = \lim_{x \rightarrow 0^+} D_2 \frac{\partial c_2}{\partial x} \quad (25d)$$

$$c_1(-\infty, t) = c_2(+\infty, t) = 0 \quad (25e)$$

$$c_1(x, 0) = \delta(x - x_0) \quad x_0 \in \Omega_1 \quad (25f)$$

$$c_2(x, 0) = \delta(x - x_0) \quad x_0 \in \Omega_2 \quad (25g)$$

In applications of the RWPMs to be presented, Markov-chains will be constructed within subdomains by discrete-time Euler approximations to stochastic differential equations as

$$\Delta X(t) = B(x) \Delta W(t) \quad (26)$$

where $B^2 = 2D$ and $W [T^{1/2}]$ is a Wiener process (Brownian motion). Furthermore, the Wiener process will be “discretized” and simulated by a uniformly distributed random variable U with mean zero and variance Δt . Individual approximation methods discussed below differ by their construction of Markov chains at the boundary between subdomains.

4.1. Methods

The method of *Uffink* [1985] constructs transition-probability densities by superposition of uniform densities according to an analytical solution to (25) [see *LaBolle et al.*, 1996a]. Particles that may cross the interface in the following time step use this modified transition-probability density.

The method of *Ackerer* [1985] splits the time step of a random walker into two smaller time steps for all particles that would cross the interface over a span Δt . The first step occurs over a time interval Δt_1 that moves the particle to the inter-

face. The second step occurs over a time interval $\Delta t_2 = \Delta t - \Delta t_1$, starts from the interface, and is performed such that there is a 50% probability of entering either Ω_1 or Ω_2 with uniform transition-probability density on the intervals $[-(6D_1\Delta t_2)^{1/2}, 0]$ and $[0, (6D_2\Delta t_2)^{1/2}]$, respectively.

Cordes et al. [1991] conclude that the methods of *Uffink* [1985] and *Ackerer* [1985] both fail and present another alternative. They reason that for a constant concentration in the vicinity of the interface, the same number of particles must cross the interface from either side in a given amount of time. They propose, on the basis of the difference in mean square displacements in Ω_1 and Ω_2 , fully reflecting a fraction of particles $(\sqrt{D_1} - \sqrt{D_2})/\sqrt{D_1}$ crossing from the region of high to low dispersion. For each particle that crosses the interface from the region of high dispersion to that of low dispersion, this operation can be performed by drawing a random number from a uniform distribution over the interval from 0 to 1; when this number is less than $(\sqrt{D_1} - \sqrt{D_2})/\sqrt{D_1}$, the particle is reflected about the interface with no loss of momentum.

More recently, *Semra et al.* [1993] conclude that the methods of *Uffink* [1985], *Ackerer* [1985], and *Cordes et al.* [1991] all fail to conserve mass; they present a third alternative. As with *Ackerer*'s method, they split the time step. Once at the interface, however, the transition-probability density is specified by a uniform distribution on the interval $[-(6D_1\Delta t_2)^{1/2}, (6D_2\Delta t_2)^{1/2}]$.

4.2. Comparison With Theory

To test the four RWPMs discussed above, we (1) examine their ability to maintain the invariant distribution (i.e., uniform number density) in a closed system with discontinuous dispersion coefficient, (2) compare simulation results with an analytical solution to (25a)–(25g), and (3) qualitatively evaluate the transition-probability densities for symmetry. The theory presented above suggests that those approximations that maintain a symmetric transition-probability density should be successful and correctly pass tests 1 and 2.

4.2.1. Invariant distribution. Consider a closed one-dimensional constant-concentration system with reflecting boundaries on both ends and a material interface located in the center such that the two equal-volume portions of the domain, Ω_1 and Ω_2 , are delineated by a discontinuity in dispersion coefficients [see *Semra et al.*, 1993; *LaBolle et al.*, 1996a]. When transport is purely dispersive, a correct approximation will maintain steady state uniform particle number density, that is, $N_1/N_2 \approx 1$, where N_1 and N_2 are the numbers of particles at locations $x < 0$ and $x > 0$, respectively. Figure 2 shows results from tests of the four methods for a one-dimensional system with reflecting boundaries at $x = -49$ and $x = 49$, $\Delta t = 0.005$, 588 particles, $D_1 = 5.0$ ($x < 0$,) and D_2 ($x > 0$) prescribed such that the ratio D_1/D_2 ranges from 2.5 to 20.0. The methods of *Ackerer* [1985] and *Cordes et al.* [1991] do not maintain uniform number density. The methods of *Uffink* [1985] and *Semra et al.* [1993] correctly maintain uniform number density.

4.2.2. Correspondence with an analytical solution. Figure 3 compares results for 100,000 realizations from a point source initial condition $x_0 = -5.5$ with an analytical solution to (25a)–(25g) at time $t = 6.0$ [see *LaBolle et al.*, 1996a] for parameter values $D_1 = 5.0$, $D_2 = 0.25$, and $\Delta t = 0.005$. Concentrations are approximated at discrete spatial locations by the normalized number of particles contained in a unit length along the x axis. Results from the methods of *Ackerer*

[1985] and *Cordes et al.* [1991] do not match the analytical solution. The methods of *Uffink* [1985] and *Semra et al.* [1993] correctly simulate the problem.

4.2.3. Symmetric transition-probability density. For an infinite system with an interface located at $x = 0$, $D_1 = 5.0$, $D_2 = 1.0$, and $\Delta t = 0.005$, the graphs in Figure 4 each plot 40,000 particle locations after a single time step versus initial location uniformly distributed over the interval $[-1/2, 1/2]$. Particle number density illustrates the transition-probability density in the region near the interface at $x = 0$. The methods of *Uffink* [1985] and *Semra et al.* [1993] show symmetric transition-probability densities; those of *Ackerer* [1985] and *Cordes et al.* [1991] do not.

4.3. Discussion

The RWPMs for ADEs given by *Uffink* [1985] and *Semra et al.* [1993] are successful and correspond with theory by maintaining symmetric transition-probability density. However, since one can conceive of a process that satisfies (24), in the limit, without symmetric transition-probability density, these results fail to explain how the methods of *Ackerer* [1985] and *Cordes et al.* [1991] violate theory. Although a detailed analysis of these methods is beyond the scope of this paper, consider that the method of *Ackerer* specifies a constant probability of reflection, independent of the contrast in dispersion coefficients between subdomains. Taking the limit as $D_2 \rightarrow 0$, the interface should approach a fully reflecting boundary, yet the method of *Ackerer* incorrectly does nothing to impede diffusion of particles across the interface from Ω_1 to Ω_2 .

The method of *Cordes et al.* [1991] falls short for more subtle reasons. Brownian motion is a rapidly fluctuating process. A particle undergoing Brownian motion at an interface will, in theory, attempt to cross that interface an infinite number of times in any finite time interval. Therefore, provided the probability of reflection is less than one and the time step approaches zero, that is, the simulated process approaches a theoretical Brownian motion, application of the method developed by *Cordes et al.* will have no effect. This suggests that a successful one-sided “reflection technique,” such as that proposed by *Cordes et al.*, would specify a probability of reflection that depends not only on the contrast in dispersion coefficients but also on time-step size.

Success with the method of *Uffink* [1985] confirms the ob-

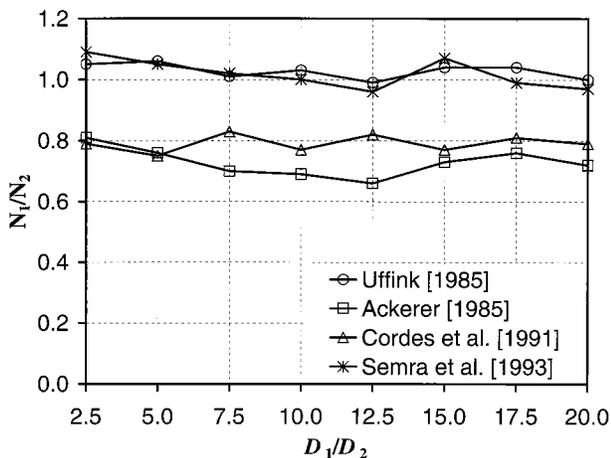


Figure 2. Ratios N_1/N_2 simulated by alternative Markov-chain approximations for various values of D_1/D_2 .

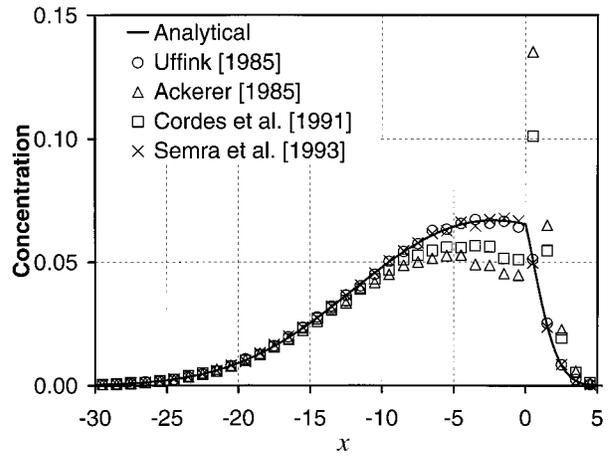


Figure 3. Comparison of concentrations from simulations by the alternative Markov-chain approximations with the analytical solution to equations (25a)–(25g) at $t = 6.0$ for $x_0 = -5.5$, $D_1 = 5.0$, and $D_2 = 0.25$. Methods of *Semra et al.* [1993] and *Uffink* [1985] produce results virtually identical to the analytical solution.

vious: transition-probability densities of Markov-chain approximations to ADEs may be constructed from an analytical solution to the governing initial boundary-value problem. However, in contrast to the simple one-dimensional problem considered above, analytical solutions are normally not at hand for more complex multidimensional problems. Success with the method of *Semra et al.* [1993] demonstrates that conditions (21a) and (21b) may be satisfied by other, more simple, techniques; knowledge of an analytical solution is not generally needed to construct successful approximation methods.

The RWPMs presented above apply to one-dimensional dif-

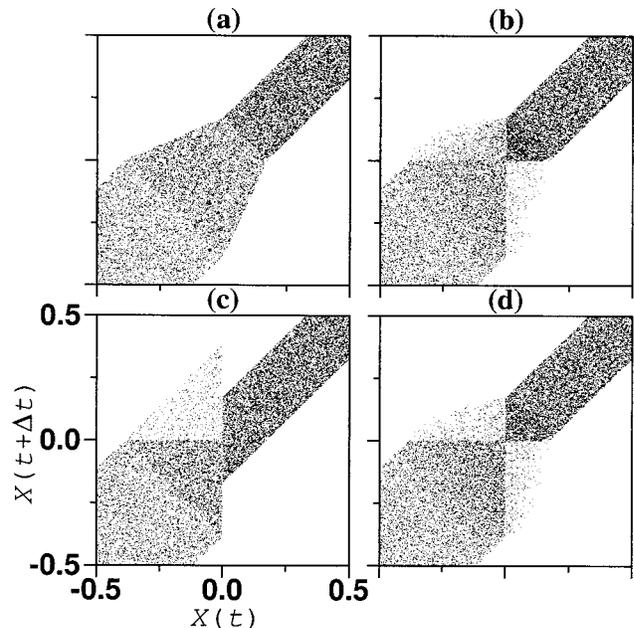


Figure 4. Transition-probability density illustrated by evolving Markov chains for 40,000 particles initially uniformly distributed over the interval from $[-1/2, 1/2]$ over a single time step using the approximations of (a) *Uffink* [1985], (b) *Ackerer* [1985], (c) *Cordes et al.* [1991], and (d) *Semra et al.* [1993].

fusion problems with constant coefficients in subdomains and discontinuous coefficients at material interfaces. Alternative methods must be developed for more general multidimensional problems that may include advection, smoothly varying coefficients in subdomains and discontinuous coefficients at material interfaces. Nevertheless, the transition-probability density of a successful Markov-chain approximation must satisfy conditions (21a) and (21b).

5. Summary and Conclusions

Diffusion theory has played an important role in developing theory for subsurface transport. Standard diffusion theory applies to subsurface transport described by ADEs when the coefficients velocity, porosity, and dispersion tensor are smooth functions of space. Subsurface porous-material properties, however, commonly exhibit abrupt transitions between material types, such as where sand is in contact with clay. Abrupt transitions between materials with contrasting hydraulic and transport properties may lead to discontinuous coefficients in macroscopic equations of transport. Although commonly called on to model transport in such cases, standard diffusion theory does not apply.

In this paper we have developed new diffusion theory for transport in porous media. Development of the theory relied on a weak form of ADEs, a mathematical abstraction that facilitates development of diffusion processes that apply when coefficients velocity, porosity, and dispersion tensor are discontinuous. Derivation of this equation from principles of probability related these coefficients to the transition-probability density of a diffusion process that simulates ADEs. A diffusion process that simulates subsurface transport described by ADEs must satisfy these relationships.

The new theory adds to our knowledge of diffusion processes corresponding to local-scale, spatially averaged equations of transport in porous media and is important to forecasting long-term transport phenomena. Conditions that arise from diffusion theory for ADEs are consistent with probabilistic mass balance principles, referred to in the physics literature as detailed balance. Theory and examples demonstrated that a diffusion process with symmetric transition-probability density satisfies the necessary conditions to simulate ADEs with discontinuous coefficients. Evaluation of several random walk methods for transport in one-dimensional composite porous media showed which methods are successful and correspond with theory. In a subsequent paper we will show how one can generalize stochastic differential equations to the case of discontinuous coefficients to yield simple Markov-chain approximations for subsurface transport that satisfy the necessary conditions presented here.

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