Habilitation Thesis

Diffusion in random velocity fields with applications to hydrogeology

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1 Introduction

Stochastic modeling became a leading paradigm in studies of complex systems since several decades. Random media, random environments, or random fields are central topics for thousands of research papers in physics, technology, geophysics, and life sciences. For instance, a search for the topic "random media" in Web of Science returns almost four thousands results with about thousand citations per year in the last two decades (Figure 1, left panel). A similar dynamics shows the topic "groundwater contamination" (right panel of Figure 1), which is one of the investigation directions where the "randomness" paradigm was intensively used in the last decades.

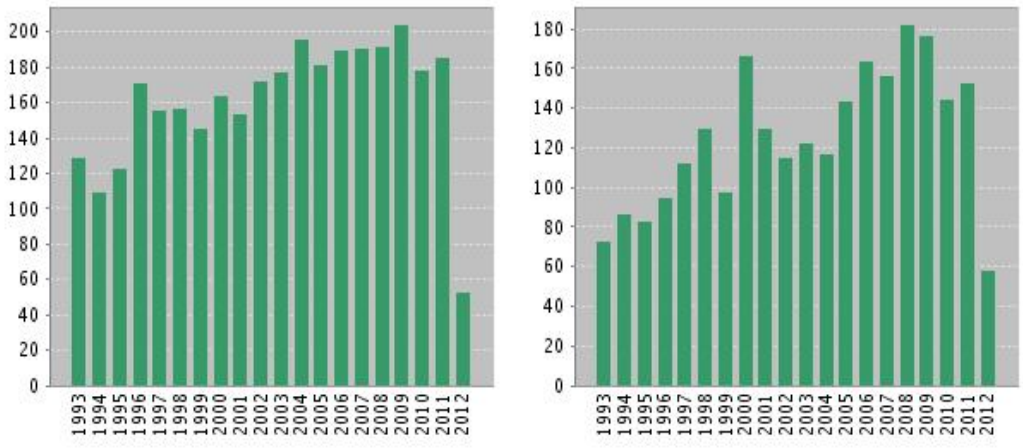


Figure 1: A Web of Science search for topic "random media" returns 3,847 results with an average number of citations per year of 1147.20 in the period 1993-2012 (left). For the same period, the topic "groundwater contamination" occurs 2,885 times, with 590.27 average citations per year (right).

The groundwater is contained in aquifer systems consisting of spatially heterogeneous hydrogeological formations. The scarcity of direct measurements of their hydraulic conductivity is compensated by spatial interpolations and empirical correlations, further modeled as space random fields [12]. The groundwater flow caused by piezometric pressure gradients is usually modelled by Darcy law for the filtration velocity in porous media and the randomness of the hydraulic conductivity induces the randomness of the flow velocity [18]. Contaminant solutes are transported by advection, diluted by diffusion and hydrodynamic dispersion, and undergo various chemical reactions. Under simplifying assumptions, also supported by experiments, the hydrodynamic dispersion is approximated as a Gaussian diffusion [53] and

summing up the molecular diffusion at the pore-scale one arrives at a "local-scale" diffusive model [8]. Hence, the primary mechanism responsible for the fate of contaminants in groundwater can be described as a diffusion in random velocity fields.

The process of diffusion in a random velocity field is the mathematical object underlying currently used stochastic models of transport in turbulence, plasma physics, and hydrogeology (Section 2). As shown in the following (Section 3), a specific feature of this process are the memory effects induced by position-velocity correlations, which can be straightforwardly quantified by correlations of the increments of the process. Their relationship with the ergodicity issue, for the usual setup of passive transport in hydrogeology (Section 4), has been investigated numerically through Monte Carlo simulations based on the "global random walk" algorithm (Section 5). The findings were consistent with theoretical results on statistical homogeneity properties and ergodicity, derived within the same passive transport setup (Section 6).

The global random walk consists of an arbitrarily large superposition of weak Euler schemes for the Itô equation and is therefore accurate, stable, and free of numerical diffusion (Section 7). Coupling this algorithm with finite element solutions to the flow equations resulted in a considerable speedup over the finite element solution to both flow and transport equations in non-reactive transport simulations (Section 8). The coupling procedure will also be a key tool in solving evolution equations for the probability density of the random concentrations in reactive transport. Such equations are derived form models of local mixing and upscaled processes of diffusion in random fields. The feasibility of the approach proposed to model probability densities is illustrated for the one-dimensional transport of the cross-section space average concentration in saturated aquifers (Section 9). Some conclusions and future prospects are presented in Section 10.

The approach based on diffusion in random fields and applications to transport in hydrogeological systems as well as in other random environments have been developed in the frame of the research projects EU Project EV5V-CT92-0214 (1994-1996), High Performance Computing Project JICG41 at Research Centre Jülich (since 2003), Romanian Academy grant 31/7006 (1996-1998), Project 01-8-CPD-042 / BIOTECH Programm of the Romanian Ministry for Education and Research (2001-2004), Deutsche Forschungsgemeinschaft grants SU 415/1-1, SU 415/1-2 (2005-2008), and Bundesministerium für Bildung und Forschung grant RUS 09/B12 (2009-2011).

The following sections contain a systematic presentation and discussion of the main results. A detailed presentation can be found in a couple of journal papers. The most relevant are the 15 papers included as Appendices, referred to as P1 to P15.

2 Physical problem

2.1 Random environments

Mathematical models of transport in random environments (e.g. continuous diffusion processes with random coefficients or random walks with random jump probabilities [9]) are often used for phenomena which are not reproducible experimentally under macroscopically identical conditions or in cases where the incomplete knowledge of the physical parameters precludes deterministic descriptions.

To the first class belongs the turbulence, characterized by an intrinsic randomness, which is modelled by random velocity fluctuations [61, 49, 32, 31]. In plasma physics the turbulent state of systems of charged particles is described by random electric potentials and magnetic fields [7, 6].

Transport in groundwater belongs to the second class. The way randomness enters modeling in hydrogeology is through stochastic parameterizations of incompletely known hydraulic conductivity fields which induce random Darcy velocity fields [28, 18].

2.2 Scale effect and memory effects

A common feature of transport processes in random environments is the apparent increase of diffusion coefficients with the scale of observation. In hydrogeology, the increase from Darcy scale, to laboratory, and to field scale of the diffusion coefficients inferred from measurements through different approaches (by fitting concentrations with solutions of advection-diffusion equations, from spatial moments of tracer concentrations, or by analysis of concentration series recorded at different travel distances from the source) has been called "scale effect" [27, 14, 16]. Similar scale dependence characterizes the so called "running diffusion coefficients" in plasma physics [5] and the "turbulent diffusivity" in turbulence [61, 50].

Another characteristic of transport in random media is the presence of various memory effects associated with the departure of the transport process from a genuine Gaussian diffusion. Memory effects manifested by non-Markovian evolution were explicitly associated with the stochastic nature of the environment in plasma physics [6]. In the frame of stochastic sub-surface hydrology, the departure from Fickian, linear-time behavior of the second moment of the solute plume may be interpreted as a memory effect [54]. The prototype memory-free process is the Wiener process with independent increments. Therefore, a direct quantification of memory effects is provided by correlations of increments of the transport process.

3 Diffusion with space-variable drift

3.1 Fokker-Planck equation

Scale effect and memory effects are already present in case of diffusion processes with deterministic coefficients if the drift coefficient varies in space.

The density of the transition probability $g(\mathbf{x}, t \mid \mathbf{x}_0, t_0)$ of a real diffusion process $\{X_i(t), t \geq 0, X_i \in \mathbb{R}, i = 1, 2, 3\}$ is the solution of the Cauchy problem for the Fokker-Planck equation,

$$\partial_t \; g + \partial_{x_i}(V_i g) = \partial_{x_i}\partial_{x_j}(D_{ij} g), \quad g(\mathbf{x}, t_0 \mid \mathbf{x}_0, t_0) = \delta(\mathbf{x} - \mathbf{x}_0). \tag{3.1}$$

The transition probability g governs the evolution of the concentration,

$$c(\mathbf{x}, t) = \int g(\mathbf{x}, t \mid \mathbf{x}_0, t_0) c(\mathbf{x}_0, t_0) d\mathbf{x}_0, \tag{3.2}$$

where $c(\mathbf{x}_0, t_0)$ is the initial concentration. If $c(\mathbf{x}_0$ is normalized to unity, so is c, and both can be interpreted as one-point probability densities.

A diffusion process satisfies uniformly in $\mathbf{x}$ and t, for all $\epsilon > 0$ [22, 36],

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|\mathbf{x}' - \mathbf{x}| \geqslant \epsilon} g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}' = 0, \tag{3.3}$$

$$V_i(\mathbf{x}, t) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|\mathbf{x}' - \mathbf{x}| < \epsilon} (x_i' - x_i) g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}', \tag{3.4}$$

$$D_{ij}(\mathbf{x}, t) = \frac{1}{2} \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|\mathbf{x}' - \mathbf{x}| < \epsilon} (x_i' - x_i)(x_j' - x_j) g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}'. \tag{3.5}$$

Condition (3.3) prevents instantaneous jumps and ensures the almost sure continuity of the sample paths $X(t)$, (3.4) defines the drift coefficients, and (3.5) the diffusion coefficients [36].

In (P1) we restricted the class of diffusion process by imposing conditions for finite first and second moments of g at finite times:

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|\mathbf{x}' - \mathbf{x}| \geqslant \epsilon} x_i' \; g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}' = 0, \tag{3.6}$$

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|\mathbf{x}' - \mathbf{x}| \geqslant \epsilon} x_i' x_j' \; g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}' = 0. \tag{3.7}$$

With (3.6-3.7), the integrals in (3.4-3.5) extend over the entire $\mathbb{R}^3$. In fact, the local averages, over spheres of radius ϵ, are used in (3.3-3.5) to avoid the hypothesis that the first two moments exist [22, p. 276]. However, the latter is always true in case of diffusion in random fields with finite-range correlations, as well as for samples of fractional Gaussian noise velocity fields.

The conditions (3.6) and (3.7) are fulfilled, for instance, by the one-dimensional Gaussian diffusion with affine mean and linear variance,

$$\mu(t) = \int xc(x,t)dx = x_0 + V(t-t_0),$$
$$s(t) = \int [x-\mu(t)]^2 c(x,t)dx = 2D(t-t_0),$$

constant drift and diffusion coefficients, $V = \frac{d}{dt}\mu(t)$, $D = \frac{1}{2}\frac{d}{dt}s(t)$, and transition probability density invariant to spatial translations,

$$g(x,t \mid x_0,t_0) = (4\pi Dt)^{-1/2} \exp\left(-(x-x_0-V(t-t_0))^2/4D(t-t_0)\right). \quad (3.8)$$

3.2 Dispersion and memory terms

For diffusion processes with variable coefficients, the relations between moments and coefficients are given by the following Proposition, proved in (P1, Appendix A).

Proposition 3.1 *The components of the first moment, μ_i, and of the covariance, s_{ij}, $i,j = 1,2,3$, of a general diffusion precess satisfying (3.3-3.5) and the conditions for finite moments (3.6-3.7) are given by:*

$$\mu_i(t,t_0) = \int x_i c(\mathbf{x},t)d\mathbf{x} = \mu_i(t_0) + \int_{t_0}^{t} \overline{V_i}(t')dt', \quad (3.9)$$

$$s_{ij}(t,t_0) = \int (x_i-\mu_i(t))(x_j-\mu_j(t))c(\mathbf{x},t)d\mathbf{x}$$
$$= s_{ij}(t_0) + 2\int_{t_0}^{t} dt' \int D_{ij}(\mathbf{x},t')c(\mathbf{x},t')d\mathbf{x} + s_{u,ij}(t,t_0) + m_{ij}(t,t_0), \quad (3.10)$$

$$s_{u,ij}(t,t_0) = \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \int c(\mathbf{x}_0,t_0)d\mathbf{x}_0 \int\int (u_i(\mathbf{x}',t'')u_j(\mathbf{x},t')$$
$$+ u_j(\mathbf{x}',t'')u_i(\mathbf{x},t'))g(\mathbf{x},t' \mid \mathbf{x}',t'')g(\mathbf{x}',t'' \mid \mathbf{x}_0,t_0)d\mathbf{x}d\mathbf{x}', \quad (3.11)$$

$$m_{ij}(t,t_0) = \int_{t_0}^{t} dt' \int c(\mathbf{x}_0,t_0)d\mathbf{x}_0 \int ((x_{0j}-\mu_j(t_0))u_i(\mathbf{x},t')$$
$$+ (x_{0i}-\mu_i(t_0))u_j(\mathbf{x},t'))g(\mathbf{x},t' \mid \mathbf{x}_0,t_0)d\mathbf{x} \quad (3.12)$$

where $\overline{V_i}(t) = \int V_i(\mathbf{x},t)c(\mathbf{x},t)d\mathbf{x}$ *and* $u_i(\mathbf{x},t) = V_i(\mathbf{x},t) - \overline{V}_i(t)$. □

According to Proposition 3.1, the covariance s_{ij} is decomposed in "dispersion terms" $s_{u,ij}$, positive definite, expressed through correlations of the drift coefficients, (3.11), and "memory terms", consisting of correlations between drift coefficients and initial positions (3.12), which are no longer positive definite (see Fig. 1 in P1).

To recast the result of Proposition 3.1 in terms of trajectories, we need the following Lemma.

Lemma 3.1 *Let be* $B = B_1 \times \cdots \times B_n$, $B_i \in \mathcal{B}$ *(the Borel* σ *-algebra on* $\mathbb{R}$*),* $1_{B_i}(y)$ *the characteristic functions of the sets* B_i, $i = 1, 2, 3$ *(*$1_{B_i}(y) = 1$ *if* $y \in B_i$ *and* $1_{B_i}(y) = 0$ *if* $y \notin B_i$*),* $\{X_t(\omega) = X(t, \omega), t \geq 0, \omega \in \Omega\}$ *a stochastic process defined on the canonical probability space* $(\Omega, \mathcal{A}, P)$*,* $\langle \cdot \rangle$ *the stochastic average with respect to* P*, and* $\delta(\cdot)$ *the singular Dirac function. Then,*

$$P_{t_1,...,t_n}(B) = \int_{B_1} dx_1 ... \int_{Bn} dx_n \, \langle \delta(x_1 - X_{t_1}(\omega)) ... \delta(x_n - X_{t_n}(\omega)) \rangle \qquad (3.13)$$

is a consistent n-dimensional distribution of the process $\{X_t(\omega)\}$.

Proof By Fubini's theorem, integration permutes with stochastic averaging [36, p. 59]. Then, if $Bn = \mathbb{R}$, the integral with respect to dx_n in (3.13) equals 1 (as value of the Dirac functional) and one obtains the marginal distribution $P_{t_1,...,t_{n-1}}$. Obviously, (3.13) is invariant to permutations in the order of integrals. Thus, (3.13) fulfils the formal consistency conditions for finite-dimensional probability distributions [22, 36].

The next step is to show that (3.13) is the n-dimensional distribution of $\{X_i(t)\}$. With

$$1_{Bi}(X_{t_i}(\omega)) = \int_{\mathbb{R}} \delta(x_i - X_{t_i}(\omega)) 1_{B_i}(x) dx_i = \int_{B_i} \delta(x_i - X_{t_i}(\omega)) dx_i,$$

one obtains

$$\begin{aligned} P_{t_1,...,t_n}(B) &= \int_{\Omega} 1_{B_1}(X_{t_1}(\omega)) ... 1_{Bn}(X_{t_n}(\omega)) P(d\omega) \\ &= P(\{X_{t_1} \in B_1, ..., X_{t_n} \in B_n\}), \end{aligned}$$

which shows that (3.13) is indeed a measure of cylindrical sets on $\mathcal{B}^n$, that is, the distribution of the n-dimensional random vector $\{X_{t_1} \cdots X_{t_n}\}$. □

The integrand from (3.13) was used by van Kampen [62] to define consistent finite-dimensional probability densities. Similar stochastic averages of δ functions are often used in the literature and referred to as "probability densities" (e.g., [49]). Averages with respect to such singular densities are well defined as Dirac functionals.

Modeling motions in random environments requires relations between spatial moments of probability densities and the statistics of the process

trajectories (e.g., [42, p. 287]). Lemma 3.1 allows a systematical derivation of such relations.

Proposition 3.2 *Consider* $\Omega = \mathbb{R}^3 \times \Omega_D$, *where* Ω_D *is the space of events of the diffusion process starting from a fixed initial position. Let* $\langle\cdot\rangle = \langle\langle\cdot\rangle_D\rangle_{X_0} = \langle\cdot\rangle_{DX_0}$ *be the expectation defined as average over* Ω_D *and over the initial positions* $\mathbf{X}(0) \in \mathbb{R}^3$.
Then, for a constant diffusion coefficient D *and stationary drift coefficients* $V_i(\mathbf{x})$, *the diagonal components of the covariance (3.10) have the equivalent representation:*

$$\begin{aligned} s_{ii}(t,t_0) &= s_{ii}(t_0) + 2D(t-t_0) \\ &\quad + 2\int_{t_0}^{t} dt' \int_{t_0}^{t'} \langle u_i(\mathbf{X}(t'))u_i(\mathbf{X}(t''))\rangle_{DX_0} dt'' \\ &\quad + 2\int_{t_0}^{t} \langle [X_i(t_0) - \langle X_i(t_0)\rangle_{DX_0}] u_i(\mathbf{X}(t'))\rangle_{DX_0} dt'. \end{aligned} \tag{3.14}$$

Proof The term $2D(t-t_0)$ is obtained from the second tern of (3.10) for D constant. By virtue of Lemma 3.1 the average with respect to the joint probability density $g(\mathbf{x},t' \mid \mathbf{x}',t'')g(\mathbf{x}',t'' \mid \mathbf{x}_0,t_0)c(\mathbf{x}_0,t_0) = p(\mathbf{x},t';\mathbf{x}',t'';\mathbf{x}_0,t_0)$ in (3.11), for $i=j$, equals the average with respect to $\langle\delta(x - X_{t'}(\omega))\delta(x' - X_{t''}(\omega))\delta(x_0 - X_{t_0(\omega)})\rangle_{DX_0}$, which gives the term in the second line of (3.14). The third line of (3.14) is obtained similarly by equating the average with respect to $g(\mathbf{x},t' \mid \mathbf{x}_0,t_0)c(\mathbf{x}_0,t_0) = p(\mathbf{x},t';\mathbf{x}_0,t_0)$ in (3.12) by the average with respect to $\langle\delta(x - X_{t'}(\omega))\delta(x_0 - X_{t_0(\omega)})\rangle_{DX_0}$. □

For given coefficients V_i and D of the Fokker-Planck equation (3.1) it is possible to construct a process satisfying the Itô equation (e.g. [36, p. 144])

$$X_i(t) = X_{0i} + \int_{t_0}^{t} V_i(\mathbf{X}(t'))dt' + W_i(t-t_0), \tag{3.15}$$

where W_i is any Wiener process with mean $E(W_i) = 0$ and variance $E(W_i^2) = 2D(t-t_0)$. Equation (3.15) describes the diffusion process in a weak sense, that is, only the coefficients are specified but not the Wiener process [36]. If sufficient conditions for the existence of weak solutions to (3.15) are fulfilled, the process has the same probability distribution as the diffusion process governed by the corresponding Fokker-Planck equation. Doob [22, Chap. VI, Sec. 3] also proved the equivalence of Itô and Fokker-Planck representations in a strong sense. That means, under more restrictive conditions, the path-wise unique solutions of the Itô equation are diffusion precesses satisfying (3.3-3.5) and, given a diffusion process with transition probability solving

the Fokker-planck equation, the associated Itô equation admits path-wise unique solutions [36, Theorems 4.6.1, and 4.7.1].

Remark 3.1 When the variance of the process (3.15) is computed for a fixed Wiener process (e.g., by Itô formula, as in P2, p.5) one obtains, in addition to the terms of (3.14), a term consisting of correlations between the Wiener process and the velocity fluctuations (equation (27) in P2). This term is canceled, for instance, when a weak solution to (3.15) is constructed by successive approximations with independent Wiener processes in each iteration (P2, p. 9). However, the representation (3.14) holds, via Lemma 3.1, for either strong or weak solutions to Itô equation if the diffusion process satisfies the supplementary conditions (3.6) and (3.7). The "global random walk" scheme presented in Section 7 below approximates such a process.

To emphasize the role of the initial conditions, it is useful to rewrite (3.14) as

$$s_{ii}(t,t_0) = s_{ii}(t_0) + \widetilde{s}_{ii}(t,t_0) + m_{ii}(t,t_0) \tag{3.16}$$

where the sum of second and third term of (3.14) is expressed in terms of displacements $\widetilde{X}_i(t) = X_i(t) - X_i(t_0)$,

$$\widetilde{s}_{ii}(t,t_0) = \langle (\widetilde{X}_i(t) - \langle \widetilde{X}_i(t) \rangle_{DX_0})^2 \rangle_{DX_0}$$

The term $\widetilde{s}_{ii}$ describes an enhanced dispersion (with respect to the local one $2D(t-t_0)$ in (3.14)), which explains the scale effect presented in Section 2.2. The last term in (3.16),

$$m_{ii}(t,t_0) = 2\langle (X_i(t_0) - \langle X_i(t_0) \rangle_{DX_0})(\widetilde{X}_i(t) - \langle \widetilde{X}_i(t) \rangle_{DX_0}) \rangle)\rangle_{DX_0}, \tag{3.17}$$

describes the memory effects mentioned in Section 2.2.

3.3 Memory effects and transition probabilities

Similarly to (3.16), for any three successive times, $t_1 < t_2 < t_3$, the variances of the increments of the process are related by

$$\widetilde{s}_{ii}(t_1,t_3) = \widetilde{s}_{ii}(t_1,t_2) + \widetilde{s}_{ii}(t_2,t_3) + m_{ii}(t_1,t_2,t_3), \tag{3.18}$$

where

$$\begin{aligned}
&\widetilde{s}_{ii}(t_3,t_1) = \mathrm{var}\{X_i(t_3) - X_i(t_1)\},\\
&\widetilde{s}_{ii}(t_1,t_2) = \mathrm{var}\{X_i(t_2) - X_i(t_1)\},\\
&\widetilde{s}_{ii}(t_2,t_2) = \mathrm{var}\{X_i(t_3) - X_i(t_2)\},\\
&m_{ii}(t_1,t_2,t_3) = 2\mathrm{cov}\{(X_i(t_2) - X_i(t_1)), (X_i(t_3) - X_i(t_2))\},
\end{aligned}$$

var$\{\cdot\}$ denotes the variance, and cov$\{\cdot\}$ the covariance. In fact, (3.18) is the general "binomial" rule saying that the variance of the sum of two random variables is the sum of variances plus two times their covariance (e.g., [48, p.213]) and as such is valid for any stochastic process $X(t)$. The relation (3.16) above is retrieved for the increments of the process (3.15) with the expectation $E\{\cdot\}$ defined as in Proposition 3.2 by $\langle\cdot\rangle_{DX_0}$.

The condition of vanishing memory terms, $m_{ii}(t_1, t_2, t_3) = 0$, leads to

$$E\{(X_i(t_2)-X_i(t_1))(X_i(t_3)-X_i(t_2))\} = E\{X_i(t_2)-X_i(t_1)\}E\{X_i(t_3)-X_i(t_2)\},$$

which expresses the uncorrelatedness of the increments of the process. As follows from (3.18), vanishing memory terms is equivalent with the additivity of the variance of the increments $\widetilde{\Sigma}_{ii}$ with respect to nonoverlapping time intervals (P3, p. 5). In the particular case of diffusion process with constant coefficients, the increments are uncorrelated, $m_{ii}(t_1, t_2, t_3) = 0$, and (3.18) expresses the linearity of the variance $\widetilde{s}_{ii}(t_m, t_n) = 2D(t_n - t_m)$, $t_n > t_m$. It is also easy to see that the uncorrelatedness of the increments is a consequence of the translation invariance of the transition probability density (3.8). Moreover, it has been shown that the only Itô-diffusion process with space-homogeneous transition probabilities are Gaussian diffusion processes with constant drift and diffusion coefficients [1].

In general, according to Theorem II.3.2 of Doob [22, p. 74], for any real process with $E\{|X(t)|^2\} < \infty$ and uncorrelated increments there exists a wide sense version of $X(t)$ (i.e. with the same first two moments) which is a Gaussian process with independent increments [22, p. 100]. By the definition of the statistical independence, this process has space-homogeneous transition probabilities. Since the converse is clearly true, i.e. processes with homogeneous transition probabilities have uncorrelated increments, we have the following corollary (P3, p. 5).

Corollary 3.1 *If the memory terms of a real process with finite first and second moments vanish for arbitrary successive time increments, then, the transport process is a wide-sense version of a Gaussian processes with spatially homogeneous transition probabilities.* □

Thus, memory-free processes have homogeneous transition probabilities. Inhomogeneous transition probabilities as memory effects, were identified in case of rare and extreme events (where the memory-free limit are independent identically distributed variables), for non-Markovian processes (generalized Langevin equation, diffusion equations with memory, or fractional diffusion), and of coarse, for processes of diffusion in random fields (P3, p. 5).

4 Diffusion in random fields model of passive transport in aquifers

Models of transport in highly heterogeneous media such as atmosphere, plasmas, industrial devices, or groundwater are based on stochastic partial differential equations of parabolic type [3, 4, 9, 42, 5, 15, 29, 2]. In case of transport in saturated aquifers, essential features of the transport, such as scale dependence, may be described by the simple advection-diffusion equation without sources and with constant diffusion coefficients (e.g., [18, 35, 21, 23]),

$$\partial_t c + \mathbf{V}\nabla c = D\nabla^2 c, \tag{4.1}$$

where $c(\mathbf{x}, t)$ is the concentration field, D is a local diffusion coefficient, and $\mathbf{V}(\mathbf{x})$ is a sample of a random velocity field. The latter is a solution of continuity and Darcy equations

$$\nabla\mathbf{V} = 0, \;\; \mathbf{V} = -K\nabla\psi, \tag{4.2}$$

where ψ is the piezometric head and K is the hydraulic conductivity, which is a sample of a space random function. This model reflects the specificity of transport in groundwater, where, unlike in case of turbulence, the flow is laminar and randomness is introduced by a stochastic parametrization of the flow equations (4.2).

Equation (4.1) has the form of the Fokker-Planck equation. (Note that in case of variable diffusion coefficients, the advection-diffusion equations also can be written as a Fokker-Planck equation by adding drift terms proportional with the gradients of the coefficients [36]). Thus, the concentration $c(\mathbf{x}, t)$, normalized to unity may be interpreted as a probability density function of the diffusion process described by the Itô (3.15).

For a given realization of the velocity field, corresponding to a realization of the hydraulic conductivity, (4.1) describes the diffusion with space variable drift analyzed in Section 3. To model diffusion in random velocity fields, the space of events from Proposition 3.2 is enlarged to the Cartesian product $\Omega = \mathbb{R}^3 \times \Omega_D \times \Omega_V$, where Ω_V is the space of realizations of the random velocity field. Correspondingly, the expectation will be formally written as $\langle\cdot\rangle = \langle\langle\langle\cdot\rangle_D\rangle_{X_0}\rangle_V = \langle\cdot\rangle_{DX_0V}$. With these, we define three centered processes of mean zero, $X_i^{eff}(t)$, $X_i^{ens}(t)$, $X_i^{cm}(t)$, $i = 1, 2, 3$, so that their variance describes the "effective" and the "ensemble" dispersion, $S_{ii}(t)$ and $\Sigma_{ii}(t)_{ii}$,

and the fluctuations of the center of mass, $R_{ii}(t)$ (P4, pp. 1-2):

$$\begin{aligned} X_i^{eff}(t) &= X_i(t) - \langle X_i(t)\rangle_{DX_0}, \quad S_{ii}(t) = \langle (X_i^{eff}(t))^2\rangle \\ X_i^{ens}(t) &= X_i(t) - \langle X_i(t)\rangle_{DX_0V}, \quad \Sigma_{ii}(t) = \langle (X_i^{ens}(t))^2\rangle \\ X_i^{cm}(t) &= \langle X_i(t)\rangle_{DX_0} - \langle X_i(t)\rangle_{DX_0V}, \quad R_{ii}(t) = \langle (X_i^{cm}(t))^2\rangle \end{aligned} \tag{4.3}$$

By Lemma 3.1, the variances of the three processes in (4.3) correspond to the expectation (average over velocity realizations) of the second spatial moment of the single-realization concentration $c(\mathbf{x},t)$, $S_{ii}(t)$, the second moment of the ensemble average concentration $\langle c(\mathbf{x},t)\rangle_V$, $\Sigma_{ii}(t)$, and the variance of the first spatial moment of $c(\mathbf{x},t)$, $R_{ii}(t)$. These quantities are related by

$$S_{ii} = \Sigma_{ii} - R_{ii}. \tag{4.4}$$

This identity was used by Le Doussal and Machta [39], in the context of measurements methods for diffusion coefficients, to define "quenched" and "annealed" coefficients, $S_{ii}/(2t)$ and $\Sigma_{ii}/(2t)$ respectively. Attinger et al. [2] considered the same quantities to define effective and ensemble dispersion coefficients, $\frac{1}{2}dS_{ii}/dt$ and $\frac{1}{2}d\Sigma_{ii}/dt$ respectively. Kitanidis [35] also obtained the identity (4.4) after computing $S_{ii}(t)$ and $\Sigma_{ii}(t)$ by averaging an advection-diffusion equation with random coefficients.

If necessary joint measurability conditions which allow permutations of averages are fulfilled (e.g. [64]) the second moment of the mean concentration can be expressed as (see P5 and, for the case $D = 0$, P6)

$$\Sigma_{ii} = S_{ii}(0) + \langle X_{ii}\rangle_{X_0} + M_{ii} + Q_{ii}, \tag{4.5}$$

where where $S_{ii}(0) = \langle (X_{0i} - \langle X_{0i}\rangle_{X_0})^2\rangle_{X_0}$, $X_{ii} = \langle (\widetilde{X}_i - \langle \widetilde{X}_i\rangle_{DV})^2\rangle_{DV}$ is the "one-particle dispersion" (defined by averaging with respect to D and V for a fixed initial position), $M_{ii} = \langle m_{ii}\rangle_V$ is the ensemble mean of the memory term (3.17), and $Q_{ii} = \langle (\langle \widetilde{X}_i\rangle_{DV} - \langle \widetilde{X}_i\rangle_{DX_0V})^2\rangle_{X_0}$ is the spatial variance of the one-particle center of mass $\langle \widetilde{X}_i\rangle_{DV}$, computed by averages over X_0.

As follows from (3.15), the trajectory $\mathbf{X}(t')$ depends on the Lagrangian velocity field $V_i(\mathbf{X}(t))$, which consists of observations at random locations on the trajectory of the random Eulerian velocity (which is defined in a fixed reference frame) [64]. If the Lagrangian field is statistically homogeneous the one-particle center of mass $\langle \widetilde{X}_i\rangle_{DV}$ and dispersion X_{ii} are independent of X_0. Then M_{ii} and Q_{ii} vanish and from (4.4) and (4.5) one obtains

$$S_{ii} = S_{ii}(0) + X_{ii} - R_{ii}. \tag{4.6}$$

The validity of the Lagrangian homogeneity hypothesis and of the the relation (4.6), first derived by Dagan [19], is crucial for the interpretation of the field measurements and for the inference of the up-scaled diffusion coefficients.

5 Monte Carlo results

An ideal tracer experiment, consisting of passive transport of substance under different deterministic initial conditions, was simulated numerically with the method presented in Section 7 below. A two-dimensional advection-diffusion problem was solved by simultaneously tracking large collections of computational particles (ten billions in most cases, e.g., P5-P9) by an approach equivalent to a superposition of weak Euler schemes for the Itô equation (implementation details are given in Appendix A of P7).

For a given statistically homogeneous log-normal random hydraulic conductivity K with exponential correlation and finite correlation length λ, the velocity field was approximated to the first order in the variance of $\ln K$. The approximation (equations (21-22) in P4), obtained by a formal asymptotic expansion of the flow equations (4.2) [29, 18], was computed numerically by the Kraichnan's approach [38] as sum between a constant mean $(U, 0)$ and a superposition of random periodic fluctuations (e.g. equation (8) in P8). In this way one obtains fast estimations of samples of random velocity fields which allowed us to compute ensembles of thousands of transport simulations at moderate computational costs. For finite number of random periodic modes the fluctuations of the estimated dispersion quantities may have an artificial logarithmic increase (P10, Appendix A). As an empirical recipe, the number of modes was chosen to be of the order of the total computation time (P10). The convergence of the Monte Carlo estimates was ensured by using several hundreds of simulations (P11, Fig. 4).

5.1 Ergodic properties of the center of mass process

Figure 2 shows the long-time decay of the variance R_{ii} of the center of mass process $X_i^{cm}(t)$. This implies, according to (4.4), that at large times the expectation of the second moment of the concentration may be approximated by the second moment of the mean concentration, $S_{ii} \approx \Sigma_{ii}$. Figure 2 also shows the decrease of R_{ii} with increasing supports of the initial concentration. One expects therefore that, for sufficiently large contaminant sources, the approximation $S_{ii} \approx \Sigma_{ii}$ also holds at finite times. Following the terminology introduced by Dagan [19], large plumes, for which the expected second moment can be approximated by the second moment of the ensemble mean concentration, are usually called "ergodic" plumes in the hydrogeological literature. One hypothesizes also that the mean second moment S_{ii} as well as the unaveraged moment s_{ii} of an ergodic plume can be approximated, according to (4.6), by the one-particle dispersion X_{ii} (P6 and P9).

Another ergodic property was formulated by Sposito et al. [55]. The

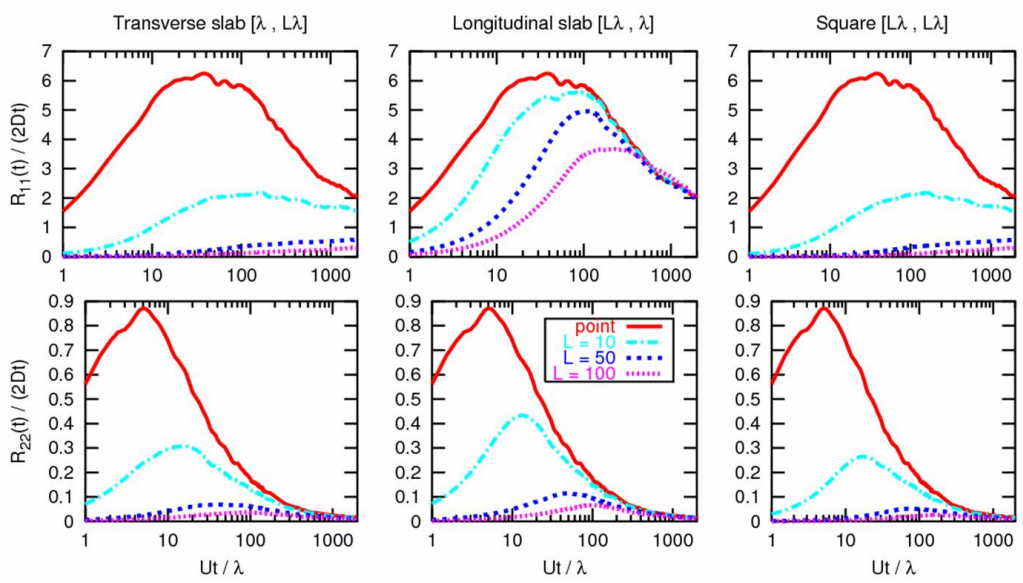


Figure 2: The variance of the center of mass $R_{ii}/(2Dt)$, $i = 1, 2$, decreases uniformly with increasing source dimension and goes to zero for large times.

transport in groundwater is called "asymptotically ergodic" if the solution of (4.1) for a given realization of the velocity field approaches that of the "macrodispersion" model, an up-scaled advection-diffusion equation supposed to exist when the random fields have finite correlation scales. Various meanings of ergodicity in hydrogeological literature are particular cases of the general formulation proposed in (P7): an observable of the transport process is *ergodic with respect to a stochastic model* if the root mean square distance from the model prediction is smaller than a given threshold. The squared distance can be decomposed as sum between the squared deviation of the ensemble mean of the observable from the reference stochastic model and the variance of the observable about its mean (definition (5) in P7). The usual statistical inference for ergodic estimators of the mean [63] is retrieved in this formulation when the observable is an average over the parameter range (time or space) and the stochastic model is the ensemble mean of the random function (see also P6, paragraph 8). The self-averaging property from statistical physics [9] corresponds to the particular case when the observable is the (unaveraged) process itself and the stochastic model is the ensemble mean of the process. Self-averaging is thus ensured by a vanishing variance in the long time limit.

The behavior $R_{ii} \to 0$ for $t \to 0$ corresponds to the self-averaging of the process $X_i^{cm}(t)$. The self-averaging of the center of mass corresponds

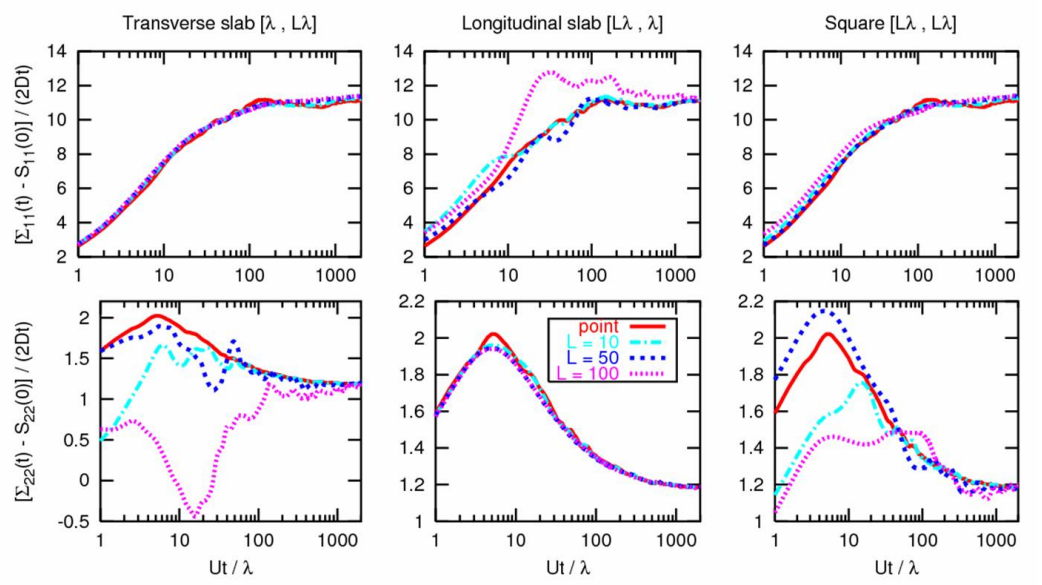


Figure 3: For sources with large dimensions on the i-direction the ensemble dispersion Σ_{ii} depends on the initial conditions.

to a self-averaging property of the mean Lagrangian velocity $\langle u_i(\mathbf{X}(t'))\rangle_{DX_0}$ (P1, Figure 2). The variance of $(X_i^{cm})^2(t)$ also was found to decrease in time and with increasing source size (P5, fig. 1). This implies the self-averaging of the dispersion coefficient of the center of mass $(X_i^{cm})^2/(2t)$ (see P2, equation (23)). Since, according to Slutsky's theorem [63] a vanishing variance is a sufficient condition for ergodicity, the self-averaging implies the usual ergodicity, that is, the convergence of the time and space averages of the observables $X_i^{cm}(t))$, $\langle u_i(\mathbf{X}(t'))\rangle_{DX_0}$, and $(X_i^{cm})^2/(2t)$.

5.2 Dependence on initial conditions

The variance of the process $X_i^{ens}(t)$, i.e. the second moment of the mean concentration Σ_{ii}, computed for different shapes and sizes of the source is shown in Figure 3. Significant dependence on initial conditions of the ensemble dispersion corrected for the initial second moment, $\Sigma_{ii} - S_{ii}(0)$, manifests in case of asymmetric sources with large extension on the i-axis while the initial conditions have negligible influence for sources with direction of largest extension perpendicular to the i-axis. This behavior was attributed to the mean memory terms, which may be significantly large in the first case and negligible in the second (according to (4.5), where the influence of the Q_{ii} term was found to be negligible, see P1, P5, P6).

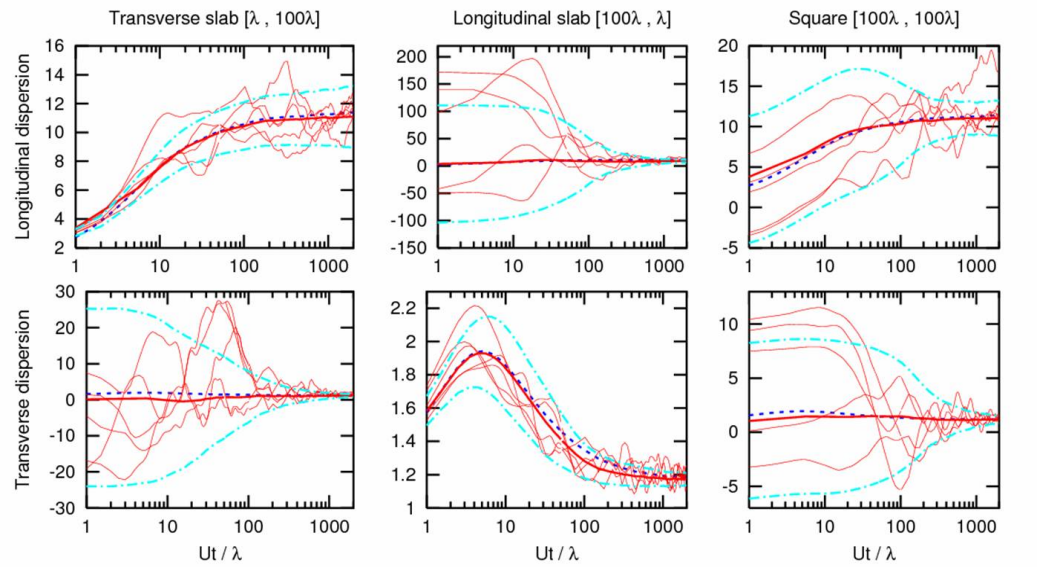


Figure 4: Single-realization dispersion $(s_{ii}-S_{ii}(0))/(2Dt)$ (thin lines), one-particle dispersion $X_{ii}/(2Dt)$ (dot lines), ensemble averages $(S_{ii}-S_{ii}(0))/(2Dt)$ (thick lines), and $(S_{ii}-S_{ii}(0)\pm SD(s_{ii}))/(2Dt)$ (line-points).

From Figure 3 we can conclude that the second moment of the mean concentration depends on the size, geometry, and orientation of the source and it does approximate the one-particle dispersion only in special cases. Unless the cases of narrow sources with small extension on i -th direction and small memory terms (3.17), $\Sigma_{ii} \neq S_{ii}(0) + X_{ii}$. This indicates that *the Lagrangian stationarity, which would imply (4.6), fails even though the velocity field considered in simulations is statistically homogeneous.*

5.3 Non-ergodic effective dispersion at finite times

The variance (3.16) of the effective process $X_i^{eff}(t)$ computed for fixed realizations of the velocity field shows large sample to sample fluctuations in cases where Σ_{ii} is also strongly influenced by the initial conditions (Figure 4). The one-particle dispersion X_{ii} shown in Figure 4 was approximated by $\Sigma_{ii}-S_{ii}(0)$ in ergodic situations consisting of large slab sources perpendicular to the i-axis. The deviation $S_{ii}-X_{ii}$ from the one-particle dispersion of the mean of s_{ii} is one to two orders of magnitude smaller than its standard deviation $SD(s_{ii})$. These are the two quantities which determine the deviation from ergodic behavior in the general formulation from Section 5.1.

Ergodicity may be expected, within acceptable small root mean square

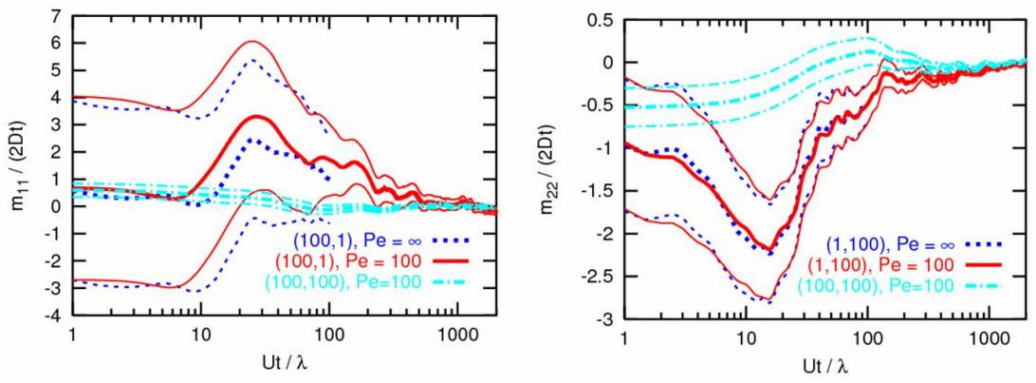


Figure 5: Longitudinal (left) and transverse (right) memory terms in non-ergodic cases, for finite and infinite Peclet numbers. Solid lines correspond to M_{ii} and thin lines correspond to $(M_{ii} \pm SD(m_{ii})/R^{1/2})/(2Dt)$, where $R = 1024$ is the number of Monte Carlo simulations used in statistical estimates.

distances, for longitudinal dispersion in case of large transverse slab sources and for transverse dispersion in case of longitudinal slab sources. However, the Monte Carlo results contradict a common belief on ergodicity issue: *large transverse plumes do not necessarily imply the ergodicity of both longitudinal and transverse dispersion*. On the contrary, increasing the plume dimensions might result in dramatic non-ergodic behavior, mainly for the transverse dispersion. This is an issue of concern for the assessment of the up-scaled diffusion coefficients in studies of reactive transport in groundwater (P10).

5.4 Loss of memory and asymptotic ergodicity

In ergodic cases from Figure 4 (slab sources perpendicular to i-axis) the approximation $s_{ii} \approx X_{ii}$ may be considered. Since memory terms also can be neglected (see (3.17)), it follows that in ergodic situations $s_{ii} - S_{ii}(0) \approx X_{ii}$ is an approximate form of (3.16). Thus, in non-ergodic cases (3.16) can be approximated by $s_{ii} - S_{ii}(0) \approx X_{ii} + m_{ii}$, which allows estimations of means and standard deviations of the memory terms m_{ii} (for more details on this approximation see P1, p. 8). Since the deviation of the mean, $S_{ii} - S_{ii}(0) - X_{ii}$, is negligible as compared with the standard deviation $SD(s_{ii})$ (see Section 5.3), $SD(m_{ii}) \approx SD(s_{ii})$ quantifies the non-ergodicity of s_{ii} with respect to X_{ii}.

The results presented in Figure 5 show that memory effects at finite times are stronger for asymmetric sources, and almost identical with those for pure advection (Pe= 100). *The mean-square convergence of m_{ii} to zero indicates the asymptotic ergodicity of the actual dispersion s_{ii}.*

6 Theoretical results

6.1 Statistical homogeneity properties

The failure of Lagrangian homogeneity (Section 5.2) means that the mean $\langle \widetilde{X}_i \rangle_{DV}$ and the variance X_{ii} of the increment $\widetilde{X}_i(t) = X_i(t) - X_i(t_0)$ depend on the deterministic initial position $X_i(t_0)$. Since the transition density $g(\mathbf{x}, t|\mathbf{x}_0, t_0)$ is the probability density of $\widetilde{X}_i$, the statistical homogeneity of $\widetilde{X}_i$ is equivalent to the invariance to space translations of the ensemble averaged transition density $\langle g \rangle_V$.

The usual set-up for statistical homogeneity is as follows. Let V be a homogeneous random function defined on the canonical probability space $(\Omega, \mathcal{A}, P)$, usually denoted by $V(\omega, \mathbf{x}) = \omega(\mathbf{x})$. Measure-preserving shifts on Ω are defined through $(\tau_{\mathbf{x}_0}\omega)(\mathbf{x}) = \omega(\mathbf{x} + \mathbf{x}_0)$, $P \circ \tau_{\mathbf{x}_0}^{-1} = P$. A composed function $F(V)$ is also homogeneous if it depends on ω and $\mathbf{x}_0$ only through measure preserving shifts $F = F(\tau_{\mathbf{x}_0}\omega)$ [64].

Let us consider the transition density solving (4.1) in a translated reference system, $\widetilde{\mathbf{x}} = \mathbf{x} - \mathbf{x}_0$,

$$\partial_t g(\widetilde{\mathbf{x}}, t|\mathbf{0}, t_0) + \nabla(\mathbf{V}(\widetilde{\mathbf{x}} + \mathbf{x}_0) g(\widetilde{\mathbf{x}}, t|\mathbf{0}, t_0)) = D\nabla^2 g(\widetilde{\mathbf{x}}, t|\mathbf{0}, t_0). \tag{6.1}$$

As follows from (6.1), g depends on velocity statistics only through $\tau_{\mathbf{x}_0}\omega = \mathbf{V}(\widetilde{\mathbf{x}} + \mathbf{x}_0)$, hence, it is statistically homogeneous if the Eulerian velocity field $\mathbf{V}(\mathbf{x}, \omega)$ is homogeneous. If, in addition, the solutions of (4.1) are unique in a classical sense, then $g(\mathbf{x}, t|\mathbf{x}_0, t_0, \omega) = g(\mathbf{x} - \mathbf{x}_0, t|\mathbf{0}, t_0, \tau_{\mathbf{x}_0}\omega)$ and the measure-preserving property of $\tau_{\mathbf{x}_0}$ implies the translation invariance of the mean transition density, that is, $\langle g \rangle_V (\mathbf{x}, t|\mathbf{x}_0, t_0) = \langle g \rangle_V (\mathbf{x} - \mathbf{x}_0, t|\mathbf{0}, t_0)$.

According to (3.15), to Fokker-Plank equation (6.1) one associates an Itô equation solving for displacements $\widetilde{X}_i(t) = X_i(t) - x_{0i}$ from the deterministic initial position $X_i(t_0) = x_{0i}$,

$$\widetilde{X}_i(t) = \int_0^t V_i(\widetilde{\mathbf{X}}(t') + \mathbf{x}_0) dt' + W_i(t). \tag{6.2}$$

If the solutions to (6.2) are pathwise unique, then the displacement field $\widetilde{\mathbf{X}}(t; \mathbf{x}_0, \omega) = \widetilde{\mathbf{X}}(t; \mathbf{0}, \tau_{\mathbf{x}_0}\omega)$ is homogeneous [64, Remark 6.7 and Prposition 6.1]. Homogeneity of $\widetilde{\mathbf{X}}(t)$ implies homogeneity of the Lagrangian velocity field, $V_i^L(\mathbf{x}_0, t) = V_i(\mathbf{X}(t)) = V_i(\widetilde{\mathbf{X}}(t) + \mathbf{x}_0)$, which depends on statistics of $\widetilde{\mathbf{X}}$ through measure-preserving shifts. Conversely, assuming the homogeneity of $V_i(\mathbf{x}_0, t)$, (6.2) implies the homogeneity of $\widetilde{\mathbf{X}}$ (see also P3, p. 2).

We have thus the following Proposition which summarizes these homogeneity properties of the process of diffusion in random velocity fields.

Proposition 6.1 *If (1) the Eulerian velocity field* $\mathbf{V}(\mathbf{x},\omega)$ *is statistically homogeneous and (2) the Fokker-Plank equation (4.1) admits unique classical solutions for (3) deterministic initial conditions, then*
(a) The mean transition density $\langle g\rangle_{_V}$ *is invariant to spatial translations,* $\langle g\rangle_{_V}(\mathbf{x},t|\mathbf{x}_0,t_0)=\langle g\rangle_{_V}(\mathbf{x}-\mathbf{x}_0,t|\mathbf{0},t_0)$.

If, in addition, (4) the associated Itô equation (3.15) admits pathwise unique solutions, then
(b) the following statements are equivalent:
(b1) The displacement field $\widetilde{\mathbf{X}}=X_i(t)-x_{0i}$ *is statistically homogeneous.*
(b2) The Lagrangian velocity field $V_i^L(\mathbf{x}_0,t)$ *is statistically homogeneous.*
(b3) The ensemble mean transition density $\langle g\rangle_{_V}$ *is translation-invariant.* □

The statements (b1) and (b2) in Proposition 6.1 can be proved independently, without requiring the existence of a density g for the transition probability. The first proof of homogeneity property (b2) and of the equality between Lagrangian and Eulerian means was given by Lumley [41] for purely advective transport, under the implicit assumption of analytical velocity realizations. Port and Stone [51] extended this result by considering diffusion in random advection fields and provided a rigorous proof for the equality of the Lagrangian and Eulerian one-point probability distributions under milder conditions, i.e continuity of the first-order spatial derivatives of the velocity samples. Zirbel [64] extended previous homogeneity results to statistical stationarity in case of space-time velocity fields and generalized the results of Port and Stone by replacing the Wiener process by a family of martingales which allow including the diffusion in the random environment.

The results obtained so far do not go beyond the equality of the one-dimensional probability distributions of the Lagrangian and Eulerian velocity fields. Since the higher distributions do not coincide, the probability laws of the Lagrangian and Eulerian fields are in general different [64]. The invariance to spatial translations of the mean density $\langle g\rangle_{_V}$ (Proposition 6.1, (a)) is also a one-point statistical property, which implies the homogeneity of $\langle\widetilde{X}_i\rangle_{_{DV}}$ and X_{ii}, cancels the mean of the memory terms (3.17), and ensures the validity of the expression (4.6) for the second moment.

These homogeneity properties hold true under the uniqueness conditions (2) and (4) in Proposition 6.1. The irregularity of the velocity samples for the exponentially correlated $\ln K$ field used in Monte Carlo simulations (see P3, pp. 2-3 and Figure 1), which do not ensure the uniqueness of the solutions, may explain the non-vanishing mean memory terms indicated by Figures 3 and 5.

Also essential is the assumption of deterministic initial conditions (assumption (3) in Proposition 6.1). In case of random initial conditions, the

velocity with the spatial argument translated by $\mathbf{x}_0(\omega)$ in equations (6.1) and (6.2) is not a measure-preserving shift and we are no longer in the frame of the usual homogeneity setup. Since the mean memory terms are time integrals of the Lagrangian velocity covariance (equation (15) in P3), they are non-vanishing as long as the velocity is correlated. This implies that translation-invariance of the mean transition probabilities associated to successive increments of the process may be expected only in case of uncorrelated velocity fields or asymptotically in the long time limit, for velocity fields with finite correlation scales. Then, by Corollary 3.1, the transport process is a wide-sense version of a Gaussian diffusion.

6.2 First-order approximations

Theoretical investigations in subsurface hydrology are often based on first-order approximations of the variances of the effective, ensemble, and center of mass processes defined in (4.3) [29, 17, 2, 21, 23]. Such approximations are essentially asymptotic expansions truncated at the first order in the variance of the velocity field. Approximations obtained by Eulerian approaches, based on Fourier representations of solutions to partial differential equations similar to (4.1) [29, 2, 13, 23], are in good agrement with those derived from trajectory equations of type (3.15) [10, 23] (see also P8 and P10). This is just as we would expect from the Itô - Fokker-Planck equivalence (e.g., Proposition 3.2). Itô representation is to be preferred here since it renders the computations easier and leads to simpler physical interpretations (P3).

In the following, the first-order approximation approach is illustrated for the ensemble process X_i^{ens}. Approximations for the effective, X_i^{eff}, and center of mass, X_i^{cm}, processes can be obtained similarly (P2, Section 4). The Itô process starting from $\mathbf{x}_0 = \mathbf{0}$, in non-dimensional form, reads

$$X_i(t) = \delta_{i,1} t + \epsilon \int_0^t u_i(\mathbf{X}(t'))dt' + Pe^{-1/2} W_i(t), \tag{6.3}$$

where $Pe = U\lambda/D_0$ is the Péclet number with respect to the correlation length in the mean flow direction $\lambda = \lambda_{11}$, $U = \langle V_1 \rangle_V$, $u_i = V_i - \delta_{i,1}U$, $\langle u_i \rangle_V = 0$, $\langle u_i^2 \rangle_V = \sigma^2$, and $\epsilon = \sigma/U$ are velocity fluctuations. Within the order of magnitude hypothesis $Pe^{-1/2} = \mathcal{O}(\epsilon^\alpha)$, $\alpha > 0$, the ensemble process $X_i^{ens}(t) = X_i(t) - \langle X_i(t) \rangle_{DV}$ is described, according to (6.3), by

$$X_i^{ens}(t) = \epsilon \int_0^t u_i(\mathbf{X}(t'))dt' + \epsilon^\alpha W_i(t).$$

Taking the half time derivative of the variance of X_i^{ens} (see (4.3)), which defines ensemble dispersion coefficients $D_{ii}^{ens}(t) = \frac{1}{2} d\Sigma_{ii}(t)/dt$ [2], one obtains

a Taylor-Green-Kubo formula (P3):

$$D_{ii}^{ens}(t) = \epsilon^{2\alpha} + \epsilon^2 \int_0^t \langle u_i(\mathbf{X}(t)) u_i(\mathbf{X}(t')) \rangle_{DV} dt'. \tag{6.4}$$

The convergence of the integral in (6.4) for $t \to \infty$ ensures finite correlation times τ_{ii} of the Lagrangian velocity. Finite τ_{ii} is a criterion for diffusive limit, formulated for instance by Fannjiang and Komorowski [26]. If this criterion is fulfilled, then the long time limit of (6.4) defines asymptotic dispersion coefficients of the process X_i^{ens}.

The Kubo relation (6.4) has been derived in (P3, equation (7)) in case of homogeneous Lagrangian velocity fields. In absence of Lagrangian homogeneity, (6.4) is still valid if $u_i(\mathbf{X}(t))$ is replaced by $v_i(\mathbf{X}(t)) = u_i(\mathbf{X}(t)) - \langle u_i(\mathbf{X}(t)) \rangle_V$. In the derivation of (6.4), cross-correlations between the Wiener process W_i and the velocity fluctuations v_i cancel, according to Remark 3.1, because the diffusion process fulfils the supplementary conditions (3.6) and (3.7). If we are only interested in a first order of approximation, there is no distinction between the two situations, since the approximated Lagrangian velocity is sttistically homogeneous (P2, Section 4).

A consistent formal asymptotical expansion of the dispersion coefficients (6.4) can be obtained as follows. Consider the asymptotic series of the trajectory (6.3), $\mathbf{X}(t) = \mathbf{X}^{(0)}(t) + \epsilon \Delta \mathbf{X}(t) + \cdots$, where $\mathbf{X}^{(0)}(t) = (t, 0, 0)$ is the trajectory of the mean flow, and the formal Taylor expansion of u_i,

$$u_i(\mathbf{X}) = u_i(\mathbf{X}^{(0)}) + \epsilon u_i'(\mathbf{X}^{(0)}) \Delta \mathbf{X} + \cdots, \tag{6.5}$$

where u_i' denotes the Fréchet derivative. Then, assuming $\alpha \geq 1$, from (6.4) and (6.5) one obtains,

$$D_{ii}^{ens} \sim \epsilon^{2\alpha} + \epsilon^2 \tau_{ii}^{(0)} + \epsilon^4 F(u_i(\mathbf{X}^{(0)}), u_i'(\mathbf{X}^{(0)})) + \cdots, \tag{6.6}$$

where $\tau_{ii}^{(0)}$ are the Lagrangian correlation times and F is a functional of the Lagrangian velocity u_i and of its Fréchet derivative u_i'. The truncation to the first-order in ϵ^2, written in dimensional variables, gives (P3, p. 4),

$$D_{ii}^{ens} \sim D_0 + \sigma^2 \lambda_{ii} / U. \tag{6.7}$$

Remark 6.1 Consistent first-order expansions may be obtained from the first iteration of the Itô equation about the reference solution $\mathbf{X}^{(0)}(t)$ (P2, P8). Formally, this consists of replacing $u_i(\mathbf{X}(t))$ by $u_i(t)$ in (6.4).

Rigorous proofs of existence for up-scaled processes with constant coefficients similar to (6.7) (limit theorems) can be found in a series of papers by Kesten, Papanicolaou, Fannjiang, Komorowski [34, 26, 37], among others.

The first iteration of the Itô equation about the process of diffusion taking place in the mean flow field, $\mathbf{Z}^{(0)}(t) = \mathbf{X}^{(0)}(t) + \epsilon^{\alpha}\mathbf{W}(t)$ leads to

$$D_{ii}^{ens}(t) = D_0 + \int_0^t dt' \int\int \langle u_i(\mathbf{x})u_i(\mathbf{x}')\rangle_{DV} g(\mathbf{x},t;\mathbf{x}',t')d\mathbf{x}d\mathbf{x}'. \tag{6.8}$$

where $p(\mathbf{x},t;\mathbf{x}',t')$ is the Gaussian joint probability density of the diffusion process $\mathbf{Z}^{(0)}(t)$ (P3, equation (11); also P2, equation (34)). This approximation is an inconsistent asymptotic expansion, because it mixes the orders of magnitude, by including the contribution ϵ^{α} in the zero-th order $\mathbf{Z}^{(0)}$. However, (6.8) leads to the same asymptotic behavior (6.7) (P8, Figure 2). In addition, the inconsistent approximation, unlike the consistent one, accounts for enhanced diffusion (i.e. scale effect) in single realizations of the velocity field (P. 8, p.2). Non the less, such approximations allow the computation of the dispersion coefficients in power-law correlated velocity fields as linear combinations of scale-dependent coefficients for diffusion in velocity fields with short-range correlations (P4, equation (42)).

6.3 Anomalous diffusion and ergodicity

The ergodicity of the center of mass process $X_i^{cm}(t)$ (shown, for instance in Figure 2) has been associated, at an heuristic level, with that of the space-random fields with finite correlation range and with the normal diffusive behavior of the process at large times [19]. In the more general case of space-time random fields, arguments have been put forward that temporally ergodic flows satisfy the diffusion limit criterion of convergent integral in (6.4) and that the violation of this criterion may lead to anomalous diffusion [26]. For time-independent fields and small velocity fluctuations, some relations between the ergodicity of the random fields, that of the effective dispersion coefficients, and the type of diffusive behavior are readily available in the frame of the consistent first-order approximation.

Consider first velocity fields with short range correlations. In such cases the integral range is finite and the space-random velocity is necessarily ergodic [12]. Typical examples are exponential and Gaussian short range correlations, for which, according to Remark 6.1, the first-order approximation of the Lagrangian correlation behaves like $\mathrm{cov}_u(t) \sim e^{-t}$ and $\mathrm{cov}_u(t) \sim e^{-t^2}$, respectively. The corresponding correlation times τ_{ii} are finite and define constant dispersion coefficients, given by (6.6) truncated at the order ϵ^2.

An ergodic estimator in the first-order of approximation of the dispersion coefficient for the "reduced" process $Y_i = X_i^{ens} - W_i$ can be obtained by replacing in (6.4) the Lagrangian covariance $\mathrm{cov}_{\mathbf{u}}(t-t') = \langle u_i(t)u_i(t')\rangle_V$ by

a time average of the product $u_i(t)u_i(t')$,

$$D^*_{Y,ii}(t) = \int_0^t dt' \frac{1}{T-t} \int_0^{T-t} u_i(t+s)u_i(t'+s)ds = \int_0^t \mathrm{cov}^T_{\mathbf{u}}(t,t')dt'. \quad (6.9)$$

Since to the first-order the velocity fields are Gaussian of mean zero (e.g., [29]), the forth moments are completely determined by the correlation function (e.g., [63, equation (3.29)]). The limit, in the mean square sense, $\langle[\mathrm{cov}^T_{\mathbf{u}}(t,t') - \mathrm{cov}_{\mathbf{u}}(t-t')]^2\rangle_V \to 0$ as $T \to \infty$ exists if and only if the condition of Slutsky's theorem for ergodic variance is fulfilled [63, p. 234], i.e.

$$\frac{1}{T}\int_0^T (\mathrm{cov}_{\mathbf{u}}(s))^2 ds \underset{T\to\infty}{\longrightarrow} 0. \quad (6.10)$$

The validity of (6.10) implies the mean square convergence of the estimator $D^*_{Y,ii}$ towards the ensemble coefficient $D^{ens}_{Y,ii}$.

Consider now *fractional Gaussian noise* velocities with power-law correlations $\mathrm{cov}_{\mathbf{u}}(t) \sim t^{-\beta}$, $0 < \beta < 2$. The process Y_i has the variance $\Sigma_{ii} \sim t^{2-\beta}$. If $\beta \neq 1$, Y_i is a *fractional Brownian motion* with *Hurst exponent* $H = 1 - \beta/2$, $0 < H < 1$, $H \neq 1/2$ (*superdiffusion* if $0 < \beta < 1$ and *subdiffusion* if $1 < \beta < 2$). If $\beta = 1$ (the case of "$1/x$" noise), then $\Sigma_{ii} \sim t \ln t - t$. In all these cases of anomalous diffusion, the increments of the process are correlated and the memory terms $M_{ii} \sim t^{2-\beta}$ persist indefinitely (P3, p.6). Deng and Barkai [20] proved the ergodicity of the variance in the particular case of fractional Brownian motion. Since the condition (6.10) holds for all $\beta > 0$, ergodicity is also a corollary of Slutsky's theorem.

Summarizing, we have the following result.

Corollary 6.1 *Ensemble dispersion coefficients for diffusion processes in either short-range correlated or fractional Gaussian noise random fields are ergodic within the precision of the consistent first-order approximation.* □

Remark 6.2 Consider the single-trajectory quantity

$$\Sigma^*_{ii}(t) = 2\int_0^t (t-\tau)d\tau \left(\frac{1}{t-\tau}\int_0^{t-\tau} u_i(s)u_i(s+\tau)ds\right).$$

The expression in the brackets is an ergodic estimator of the velocity covariance $\mathrm{cov}_{\mathbf{u}}(t)$, and, if it is accurate enough, then

$$\Sigma^*_{ii}(t) = 2\int_0^t d\tau \int_0^{t-\tau} u_i(s)u_i(s+\tau)ds \approx 2\int_0^t (t-\tau)\mathrm{cov}_{\mathbf{u}}(\tau)d\tau. \quad (6.11)$$

The right hand side of the approximate equality in (6.11) is the Taylor's formula valid for a stationary ensemble variance Σ_{ii} [46, equation (9.30')]. Thus, Σ^*_{ii} is a *self-averaging* estimator of Σ_{ii} which can be used to estimate dispersion coefficients on a single trajectory of the process through $\Sigma^*_{ii}/(2t)$ (see also P11, equations (2) and (3)).

7 Global random walk

7.1 Global random walk algorithm

The global random walk algorithm (GRW) used in the Monte Carlo simulations presented in Section 5 solves diffusion problems by moving large collections of computational particles on regular lattices. Instead of moving particles sequentially, GRW redistributes all particles from a lattice site, through advective displacements and diffusion jumps, in a single numerical procedure. GRW can thus be thought as a superposition of weak solutions to Itô equation projected on the lattice: instead of computing individual trajectories, it approximates the evolution of the probability distribution of the Itô diffusion by that of the number of particles at lattice sites (P12).

In a one-dimensional GRW algorithm, the number of particles n at lattice sites i and successive time steps k and $k+1$ is given by the rules

$$n(j,k) = \delta n(j+v_j, j, k) + \delta n(j+v_j-d, j, k) + \delta n(j+v_j+d, j, k), \quad (7.1)$$

$$n(i,k+1) = \delta n(i,i,k) + \sum_{j\neq i} \delta n(i,j,k), \quad (7.2)$$

where $v_j = [V_j \delta t/\delta x]$ are discrete displacements due to advection by the local velocity field, computed as the integer part $[\cdot]$ of the non-dimensionalized velocity, δt and δx are the time and space steps, $j+v_j$ are new positions after advective displacements, and d are natural numbers describing discrete diffusive jumps $d\delta x$. The number of particles undergoing diffusion jumps, $\delta n(j+v_j \pm d, j, k)$, and the number of particles waiting at $j+v_j$ over the k-time step, $\delta n(j+v_j, j, k)$, are binomial random variables. The space and time steps, δx and δt, are related to the diffusion coefficient D through

$$D = r\frac{(d\delta x)^2}{2\delta t}, \quad (7.3)$$

where r is a rational number, $0 \leq r \leq 1$.

The relation (7.3) is the Kolmogorov's definition of the diffusion coefficient (3.5) projected on the lattice, where the parameter r plays the role of the transition probability. Indeed, according to (7.1), the trajectory of each particle is governed by

$$\hat{X}_{k+1} = \hat{X}_k + v\delta x + \xi, \quad (7.4)$$

where the discrete process ξ is an *unbiased random walk* with amplitude $|\xi| = d\delta x$ and transition probabilities

$$\mathrm{P}\{\xi = \pm\sqrt{2D\delta t}\} = \frac{r}{2}, \ \mathrm{P}\{\xi = 0\} = 1 - r. \quad (7.5)$$

Proposition 7.1 *The discrete process $\hat{X}$ approximates a continuous diffusion process $X(t)$ with finite first two moments satisfying (3.3-3.7).*

Proof The definition of a diffusion process can be reformulated in terms of transition probabilities and conditional expectations, without requiring that the transition probability has a density (e.g., [36, p. 68 and p. 142]).

Condition (3.3), reformulated as $\lim_{\delta t\to 0}\frac{1}{\delta t}\text{Prob}\{|\hat{X}_{k+1}-\hat{X}_k|>\epsilon\}=0$, is fulfilled if for every $\epsilon>0$ there exists a small δt such that $\text{Prob}\{|\hat{X}_{k+1}-\hat{X}_k|>\epsilon\}=0$. According to (7.4), $|\hat{X}_{k+1}-\hat{X}_k|=|v\delta x+\xi|$ takes on a maximum value of $(|v|+d)\delta x$. Using (7.5), one finds that if $\delta t\le\delta t^*=\frac{rd^2\epsilon^2}{2D(|v|+d)^2}$, then $(|v|+d)\delta x\le\epsilon$ with probability 1. Thus, the condition (3.3) is fulfilled because $\text{Prob}\{|\hat{X}_{k+1}-\hat{X}_k|>\epsilon\}=1-\text{Prob}\{|\hat{X}_{k+1}-\hat{X}_k|\le\epsilon\}=0$. Since transitions outside the interval $(-\epsilon,\epsilon)$ have probability zero if $\delta t\le\delta t^*$, the conditions (3.6-3.7) for the first two moments of $\hat{X}_{k+1}-\hat{X}_k$ are fulfilled as well.

Condition (3.4), reformulated as an expectation for fixed $\hat{X}_k$ and $\delta t\le\delta t^*$, yields

$$\lim_{\delta t\to 0}\frac{1}{\delta t}E\{\hat{X}_{k+1}-\hat{X}_k\}=\lim_{\delta t\to 0}\frac{1}{\delta t}E\{V\delta t+\Delta v\delta x+\xi\}=V+\lim_{\delta t\to 0}\frac{1}{\delta t}\Delta v\delta x, \tag{7.6}$$

where the truncation error of the advective displacement is defined by $\Delta v=v-V\frac{\delta t}{\delta x}$, $-1\le\Delta v\le 1$, and (7.4) implies $E\{\xi\}=0$.

Condition (3.5) is verified exactly:

$$\frac{1}{2}\lim_{\delta t\to 0}\frac{1}{\delta t}E\{(\hat{X}_{k+1}-\hat{X}_k)^2\}=\frac{1}{2}\lim_{\delta t\to 0}\frac{1}{\delta t}E\{V^2\delta^2 t+2V\xi\delta t+\xi^2\}=D, \tag{7.7}$$

where one uses (7.5), which implies $E\{\xi\}=0$ and $E\{\xi^2\}=2Dt$. □

According to Proposition 7.1, the GRW algorithm (7.1-7.3) fulfills the requirements for an exact decomposition of the variance of the second moments of the concentration as sum of dispersion and memory terms (see Remark 3.1). As shown by (7.3) and (7.7), the algorithm is *free of numerical diffusion* by construction. The main source of errors is the truncation of the advective displacement from the last term in (7.6). A priori error estimates are not available for the GRW algorithm but one expects that refining the space and time steps reduces the truncation errors (e.g., P12, figure 1). A posteriori error estimates can be obtained by comparisons with a biased-GRW (P13).

In case of a constant velocity, there are no truncation errors at all if one chooses $V\delta t=v\delta x$, which cancels Δv in (7.6). The first three moments of the random walk ξ with jump probabilities given by (7.5) satisfy

$$|E(\xi)|+\left|E(\xi^3)\right|+\left|E(\xi^2)-\delta t\right|=0\le C\delta t^2,$$

for any positive constant C, condition required for a consistent first-order truncation of the Itô-Taylor expansion [36, Section 5.12]. We have thus the following corollary to the Proposition 7.1.

Corollary 7.1 *If V is a real constant, then the discrete process (7.4) is a weak Euler scheme with convergence order $\mathcal{O}(\delta t)$ for the Itô equation $dX(t)=Vdt+dW(t)$, $E(dW)=0$ and $E((dW)^2)=2D\delta t$.* □

By virtue of Corollary 7.1, in case of constant V the GRW algorithm is a superposition of weak Euler schemes which approximates the one-point probability density of the Itô process by particle density at lattice sites.

The mean of the binomial random variables $\delta n(j+v_j \pm d, j, k)$ with parameters $n(j,k)$ and $r/2$ (see (7.5)), i.e. the mean number of unbiased right/left jumps from the lattice site j at time t, equals $\frac{1}{2}rn(j,k)$ [48, p. 156]. Taking the mean over an ensemble of GRW runs (denoted in the following by an overline) and using (7.1) one obtains

$$\overline{\delta n(j+v_j \pm d, j, k)} = \frac{1}{2} r\ \overline{n(j,k)}, \quad \overline{\delta n(j, j+v_j, k)} = (1-r)\ \overline{n(j,k)}. \tag{7.8}$$

In case of constant D and $V = 0$, according to (7.1-7.2), the evolution of the mean number of particles is described by an explicit finite difference scheme for the diffusion equation $\partial_t c = D\partial_x^2 c$,

$$\overline{n(i,k+1)} = \frac{r}{2}\overline{n(i+d,k)} + (1-r)\overline{n(i,k)} + \frac{r}{2}\overline{n(i-d,k)}. \tag{7.9}$$

The continuous solution can be approximated by $c(x_i, t_k) = \overline{n(i,k)}/\delta x$ (P12). In weak formulations, $c(x_i, t_k)$ is usually approximated by a sum of Dirac measures [40, 25]. Since the initial value problem is well-posed (as consequence of conservation of the number of particles) and the scheme (7.9) is stable ($r \leq 1$ fulfils the von Neumann's criterion), it is also convergent, according to Lax-Richtmyer Equivalence Theorem [56]. The convergence order is $\mathcal{O}(\delta t)$ in time and $\mathcal{O}(\delta x^2)$ in space.

7.2 Implementation and numerical convergence

The exact GRW algorithm is implemented by extracting the random variables $\delta n(j + v_j \pm d, j, k)$ from the cumulative binomial distribution function (see P12, pp. 532-533). Several other implementations were also proposed in (P12), for instance, the "deterministic GRW", where one gives up the particle indivisibility and n are arbitrary positive real numbers evolving according to (7.9), approximations of the binomial distributions by *erf*-functions for large n, or the reduced fluctuations GRW algorithm. The latter proved its efficiency in large scale simulations of transport in groundwater (P5, P7).

In the reduced fluctuations GRW, the number of left jumps is given by

$$\delta n(j + v_j - d, j, k) = \begin{cases} n/2 & \text{if } n \text{ is even} \\ [n/2] + \theta & \text{if } n \text{ is odd,} \end{cases} \tag{7.10}$$

where $n = n(j,k) - \delta n(j + v_j, j, k)$, $[n/2]$ is the integer part of $n/2$, and θ is a random variable taking the values 0 and 1 with probability 1/2. The number of right jumps is given by the difference $n - \delta n(j + v_j - d, j, k)$.

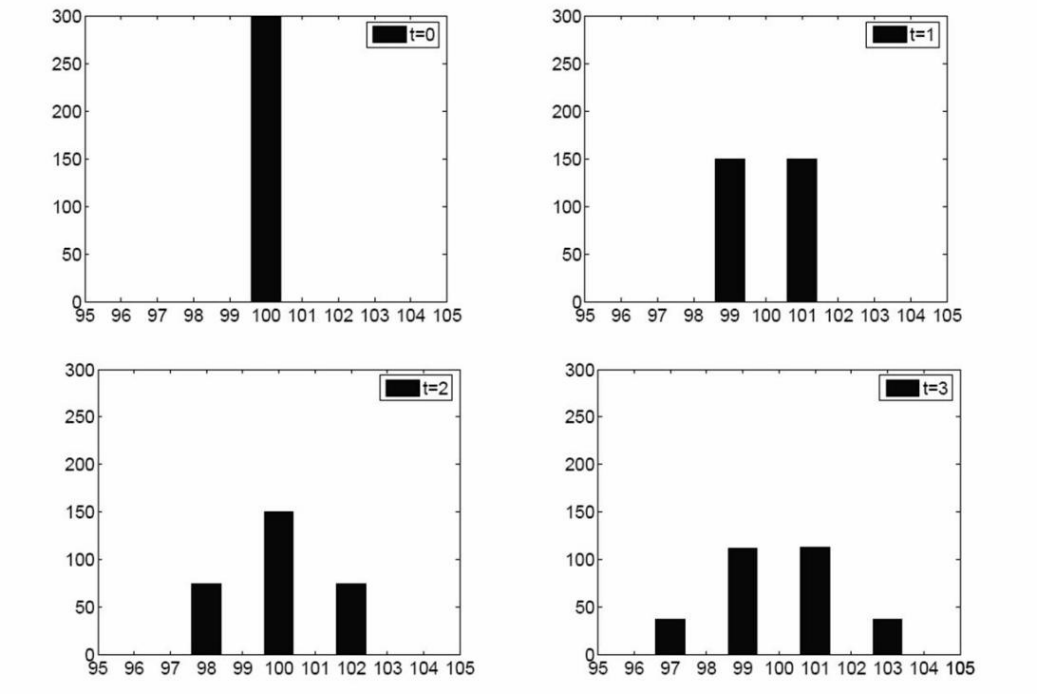


Figure 6: Distribution of $N = 300$ particles staring from $x = 100$ after the first three GRW time steps for $D = 1$ and fixed parameters $r = 1$ and $d = 1$.

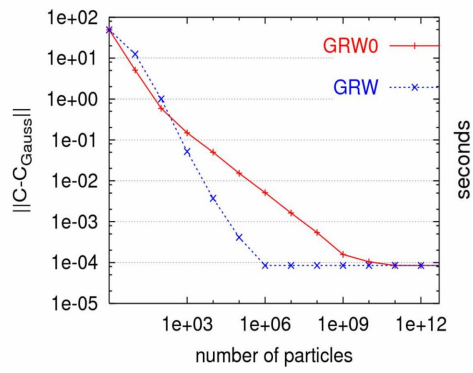


Figure 7: Convergence with the number of particles of the exact GRW algorithm (GRW0) and of the reduced fluctuations algorithm (GRW), for a one-dimensional Gaussian diffusion problem.

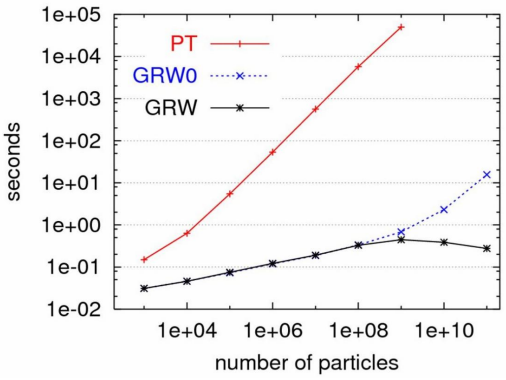


Figure 8: Comparison of CPU times for simulations carried out with GRW, GRW0, and PT of a three-dimensional Gaussian diffusion problem over ten dimensionless time steps.

In practice, (7.10) is implemented by summing up reminders of division by 2 and multiplication by r of $n(j.k)$, which avoids the need to use random number generators (P14, p. 3).

The GRW solution to the initial value problem for a Gaussian diffusion is illustrated in Figure 6. By increasing the number of particles the unaveraged GRW solution approaches the solution of the finite difference scheme (7.9). It was found that the GRW algorithm is *self-averaging*, in the sense that if the total number of particles N is large enough, no ensemble averaging over GRW runs is necessary to obtain smooth solutions (P12, Figure 5). Thus, the GRW solution converges like $\mathcal{O}(\delta x^2)$ $+\mathcal{O}(1/\sqrt{N})$. The decay with N of the error norm is a bit faster in case of reduced fluctuations GRW (Figure 7). The number of particles required for self-averaging increases with the simulation time and the dimension of the spatial domain. In case of large scale simulations in groundwater is vas found to be $N \sim 10^{10}$ [57].

Compared with sequential particle tracking procedures (PT), consisting of ensembles of (generally) strong solutions to Itô equation, GRW has the advantage of providing smooth solutions by using huge numbers of particles, at low computational costs. This is shown by a comparison of CPU time used to solve the same problem given in Figure 8. While for PT the CPU time increases linearly with N and requires increasing numbers of processors (up to 256 for $N = 10^9$ on a Cray T3E parallel computer), the computing time increases significantly only for more than $N > 10^8$ in case of exact GRW algorithm (GRW0) and is practically constant in case of reduced fluctuations GRW.

Two-and three-dimensional GRW algorithms can be constructed by repeating the one-dimensional procedure for each spatial direction, in case of constant diffusion coefficients, or by using independent random walks, in case of variable diffusion coefficients (Figure 9). In the latter case, one uses space-time variable r_x and r_y, $r_x + r_y \leq 1$, and for given d_x, d_y, δx and δy, the time step is chosen to satisfy

$$\delta t \leq \left(\frac{2D_x^{\max}}{(d_x \delta x)^2} + \frac{2D_y^{\max}}{(d_y \delta y)^2} \right)^{-1}.$$

where $D_x^{\max} = \max\{D_x(x,y,t)\}$ and $D_y^{\max} = \max\{D_y(x,y,t)\}$. This implementation yields accurate solutions even if the diffusion coefficients are highly variable and random (for instance, in simulations of diffusion in human skin, modeled as a three-layer two-dimensional model with Gaussian distributed diffusion coefficients [59]).

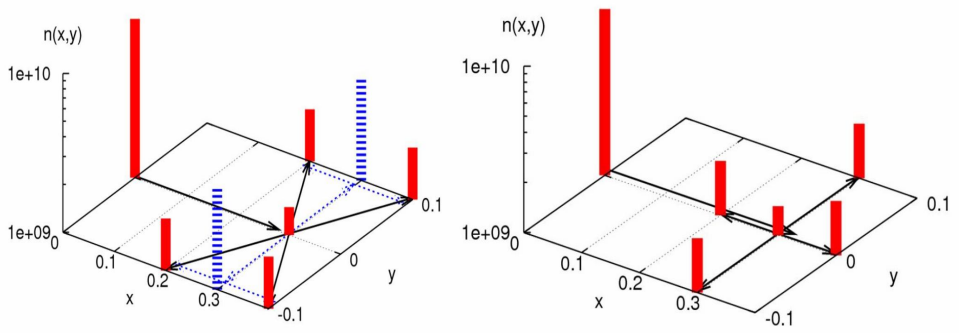


Figure 9: Two-dimensional GRW for constant diffusion coefficient, built as a superposition of two one-dimensional GRW procedures (left) and GRW for variable diffusion coefficients, based on two independent random walks on x- and y-directions (right).

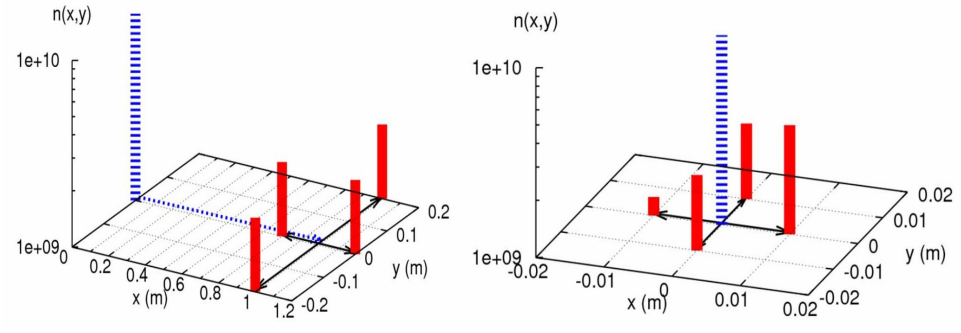


Figure 10: GRW state at $t = \delta t = 0.5$ (left) and BGRW state at $t = \delta t = 0.0025$ (right), for the same problem of transport in groundwater (P13).

7.3 Biased-GRW algorithm

If the velocity and the diffusion coefficients vary in space, overshooting errors may occur when the particles jump over more than one lattice site (see Figure 10). Overshooting can be avoided if advection is simulated by a bias in the random walk probability and only jumps to the nearest sites are allowed. This results in a biased global random walk (BGRW) algorithm (P13). Since BGRW moves all the particles lying at a lattice site in a single numerical procedure, N can be as large as necessary to ensure the self-averaging, which is the main difference with respect to the biased-random walks on lattices which move particles sequentially [33, 24]).

The two-dimensional BGRW is defined by the rule

$$\begin{aligned} n(i,j,k) &= \delta n(i,j \mid i,j,k) \\ &+ \delta n(i+1,j \mid i,j,k) + \delta n(i-1,j \mid i,j,k) \\ &+ \delta n(i,j+1 \mid i,j,k) + \delta n(i,j-1 \mid i,j,k), \end{aligned} \tag{7.11}$$

where $n(i,j,k)$ is the number of particles at the site $(x,y) = (i\delta x, j\delta y)$ at the time $t = k\delta t$. To the components of the drift (velocity) and diffusion coefficients of the transport problem, $V_x(x,y,t)$, $V_y(x,y,t)$, $D_x(x,y,t)$ and $D_y(x,y,t)$, one associates dimensionless parameters

$$v_x = V_x\frac{\delta t}{\delta x},\ v_y = V_y\frac{\delta t}{\delta y},\ r_x = D_x\frac{2\delta t}{\delta x^2},\ r_y = 2D_y\frac{2\delta t}{\delta y^2}. \tag{7.12}$$

Instead of (7.8), the average over BGRW runs of the terms in (7.11) are now related by

$$\begin{aligned} \overline{\delta n(i,j \mid i,j,k)} &= (1 - r_x - r_y)\ \overline{n(i,j,k)}, \\ \overline{\delta n(i \pm 1,j \mid i,j,k)} &= \frac{1}{2}(r_x \pm v_x)\overline{n(i,j,k)}, \\ \overline{\delta n(i,j \pm 1 \mid i,j,k)} &= \frac{1}{2}(r_y \pm v_y)\overline{n(i,j,k)}. \end{aligned} \tag{7.13}$$

The last four terms in (7.13) are averages of binomial random variables, like in the unbiased GRW algorithm, and the reduced fluctuations BGRW is implemented similarly to (7.10).

Defining the particle density $\rho(x,y,t) = \overline{n}(i,j,k)$, summing up the contributions coming from the first neighbors to a lattice site, and using (7.11-7.13)

one obtains

$$\frac{\rho(x,y,t+\delta t)-\rho(x,y,t)}{\delta t}+$$
$$\frac{V_x\rho(x+\delta x,y,t)-V_x\rho(x-\delta x,y,t)}{2\delta x}+\frac{V_y\rho(x,y+\delta y,t)-V_y\rho(x,y-\delta y,t)}{2\delta y}=$$
$$\frac{D_x\rho(x+\delta x,y,t)-2D_x\rho(x,y,t)+D_x\rho(x-\delta x,y,t)}{\delta x^2}+$$
$$\frac{D_y\rho(x,y+\delta y,t)-2D_y\rho(x,y,t)+D_y\rho(x,y-\delta y,t)}{\delta y^2}. \tag{7.14}$$

The relation (7.14) is the forward-time centered-space finite difference scheme for the Fokker-Plank equation

$$\partial_t\rho+\partial_x(V_x\rho)+\partial_y(V_y\rho)=\partial_x^2(D_x\rho)+\partial_y^2(D_y\rho). \tag{7.15}$$

As follows from (7.13), the BGRW algorithm is subject to the following restrictions

$$r_x+r_y\leq 1,\ \ |v_x|\leq r_x,\ \ |v_y|\leq r_y. \tag{7.16}$$

By the last two inequalities in (7.16), the Courant numbers $V_x\delta t/\delta x$ and $V_y\delta t/\delta y$ are sub-unity, which ensures that the BGRW algorithm is free of overshooting errors. If, in addition, one imposes the conditions $r_x\leq 0.5$ and $r_y\leq 0.5$, the von Neumann's criterion for stability is also satisfied, Thus, the convergence of the scheme (7.14) is implied by the Lax-Richtmyer Equivalence Theorem [56]. Summarizing, we have the following proposition.

Proposition 7.2 *Under the conditions stated above, the solution of the BGRW algorithm (7.11-7.13) for an initial value problem converges with the order $\mathcal{O}(\delta x^2)$ to the solution of the Fokker-Planck equation (7.15).* □

As shown by (7.14), the BGRW algorithm is equivalent with a finite difference scheme even if the velocity field is a space-time function, unlike in case of unbiased GRW, for which the equivalence holds only for constant velocity. Instead, since advection is accounted for by biased jump probabilities, BGRW is no longer equivalent to an Euler scheme for the Itô equation.

The advection-diffusion equation which corresponds to Fick's law,

$$\partial_t\rho+\partial_x(V_x^*\rho)+\partial_y(V_y^*\rho)=\partial_xD_x\partial_x\rho+\partial_yD_y\partial_y\rho,$$

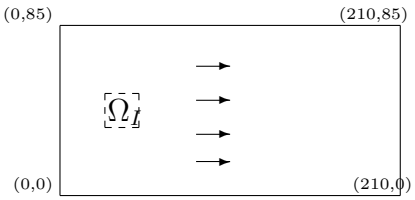
becomes equivalent to (7.15) if the drift coefficients are replaced by $V_x-\partial_xD_x$ and $V_y-\partial_yD_y$ [36] and the corresponding BGRW algorithm can be derived similarly.

The BGRW algorithm is highly accurate but more expensive than the unbiased GRW, because of the restriction of sub-unity Courant numbers in (7.16). Therefore, BGRW was mainly used to validate the faster but less accurate unbiased GRW algorithm (see [58], P8, and P13).

8 Coupled MFEM-GRW simulations

8.1 A typical problem of transport in aquifers

Consider a two-dimensional flow and transport problem associated to (4.1) and (4.2) and its solutions obtained by the mixed finite element method (MFEM) proposed in [52, 11]. The computational domain is $\Omega = [0, 210] \times [0, 85]$ and $T = 200$ is the final time. The constant diffusion coefficient is set to $D = 0.01$ (lengths are measured in m, times in days, and concentrations are normalized by the maximum initial concentration, as in typical field-scale transport problems for saturated aquifers (P7)). The initial and boundary conditions for both pressure and concentration are given in Fig. 5.



$\Omega_I = [40, 45] \times [40, 45]$

Initial conditions

$$c_I(x, y) = \begin{cases} 0.04 & if (x, y) \in \Omega_I \\ 0 & otherwise \end{cases}.$$

Boundary conditions

$$\psi(x, y, t) = \begin{cases} 3.5 & at\ x = 0 \\ 0 & at\ x = 210 \end{cases},$$

elsewhere $\mathbf{V} \cdot \mathbf{n} = 0,\ \nabla c \cdot \mathbf{n} = 0.$

Figure 11: Computational domain, boundary conditions, and initial conditions for the flow and transport problem [52].

Log-normal K fields with variance σ are generated as a superposition of N_p random periodic modes

$$\ln(K(\mathbf{x})) = \sigma \sqrt{\frac{2}{N_p}} \sum_{l=1}^{N_p} a(\mathbf{q}_l) \sin(\mathbf{q}_l \cdot \mathbf{x} + \alpha_l),$$

where the wave vectors $\mathbf{q}_l$ are mutually independent Gaussian random variables, with probability distribution proportional with the spectral density of the $\ln K$ field, and the phases θ_l are random variables uniformly distributed in the interval $[0, 2\pi]$. (P14). The generated random field $u(\mathbf{x})$ has the mean zero, the variance σ^2, and an isotropic correlation described by the function $C(r) = \sigma^2 e^{-r/\lambda}$, where r is the lag distance and λ is the correlation length.

For accurate simulations of the $\ln K$ field N_p has to be of the order of the total simulation time (P7, P9). However, for the validation of the approach presented in the following, a smoother $\ln K$ field with $N_p = 1$ will be considered. The resulting hydraulic conductivity K and the velocity field given by the MFEM solution to (4.2) are presented in Figure 12.

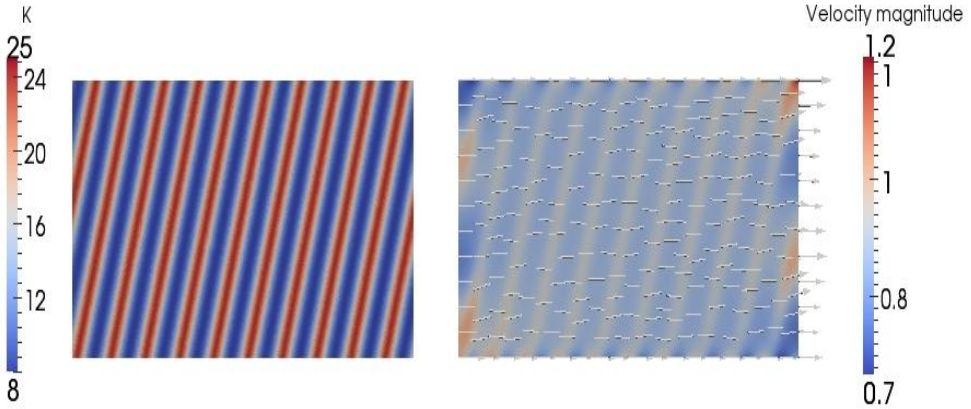


Figure 12: $K(\mathbf{x})$ (left) and corresponding $\mathbf{V}(\mathbf{x})$ (right) for a single sine-mode.

8.2 MFEM-GRW coupling

The large scale GRW simulations presented in (P7) were carried out with the a first-order approximated velocity field (GRW-Kraichnan approach) which is accurate only if the variance σ^2 of the $\ln K$ field is small enough. It is therefore desirable to have a coupled approach consisting of GRW simulations, free of numerical diffusion, with exact and accurate velocity fields produced by MFEM methods. The MFEM-GRW coupling method proposed in (P14) consists of the following steps:

- compute MFEM solutions to the flow and Darcy equations,
- import the velocity field from the MFEM basis into GRW:
  - find the MFEM element containing the lattice site $\mathbf{x}$,
  - compute
$$\mathbf{V}(\mathbf{x}) = \sum_{k=1}^{3} f_k \frac{\mathbf{x} - \mathbf{x}_k}{2a},$$
    where f_i are basis coefficients, $\mathbf{x}_k$ are position vectors of the corners, and a is the area of the triangular MFEM element,
- use $\mathbf{V}(\mathbf{x})$ as input in GRW transport simulations.

The coupled MFEM-GRW achieves a speed-up of computation of a factor of ten compared to the full MFEM solution to both flow and transport problems (P14, p. 9).

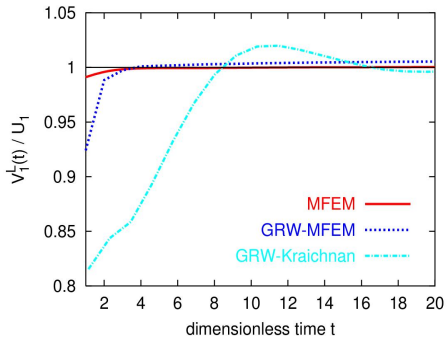


Figure 13: Mean Lagrangian velocity components $V_1^L = d\mu_x/dt$ normalized with the MFEM mean Eulerian velocity $U_1 = 0.871$ m/day, computed by full MFEM, coupled GRW-MFEM, and GRW-Kraichnan approximation.

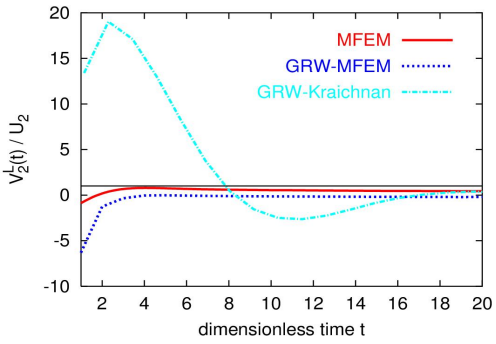


Figure 14: The same as in Figure 13, for mean Lagrangian velocity components $V_2^L = d\mu_y/dt$ normalized with the MFEM mean Eulerian velocity $U_2 = 0.014$ m/day.

8.3 Validation of the MFEM-GRW approach

For validation purposes, full MFEM solutions to both flow and transport, for a small grid-Peclet number $\mathrm{Pe}_{\mathrm{grid}} = 0.0871$, are compared with coupled MFEM-GRW solutions. The resolution of the velocity field in the GRW simulation is controlled by a new parameter $p = U\delta t/\delta x$ [57] and by the *mean Courant number* $U\delta t/d\delta x = p/d$, where $U = U_1$ is the longitudinal component of the Eulerian mean velocity and d is the amplitude of the diffusion jumps. A sub-unity value $p/d = 2/3$ ensured small overshooting errors.

The first and second centered spatial moments

$$\mu_\alpha(t) = \int\int \alpha c(x,y,t)dxdy,\ \ \mu_{\alpha\alpha}(t) = \int\int (\alpha - \mu_\alpha)^2 c(x,y,t)dxdy,$$

where α stands for x or y, were computed by integrating over the spatial support of the concentration $c(x,y,t)$.

Figures 13 and 14 show comparisons of the mean Lagrangian velocity components $V_\alpha^L = d\mu_\alpha/dt$ computed by the two approaches as well as by the GRW-Kraichnan approach. MFEM and MFEM-GRW results are close to each other, while the GRW-Kraichnan results are acceptable only after sufficiently large times.

The effective diffusion coefficients $D_{\alpha\alpha}^{eff} = \mu_{\alpha\alpha}/(2t)$ are compared in figures 15 and 16. The GRW-Kraichnan solutions show again large deviations

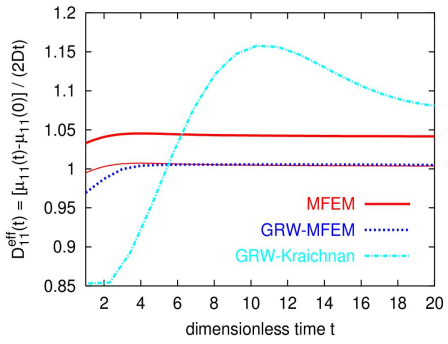


Figure 15: Longitudinal effective diffusion coefficients computed by full MFEM, coupled GRW-MFEM, and GRW-Kraichnan approximation.

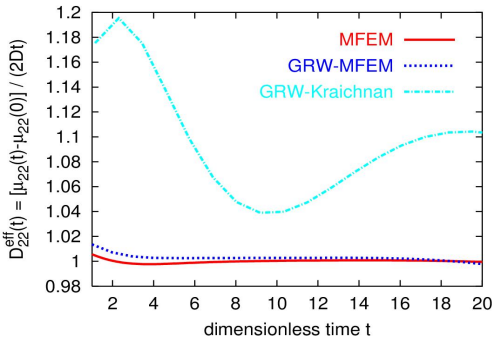


Figure 16: The same as in Figure 15, for transverse effective diffusion coefficients.

from the other two approaches. Nevertheless, even though they are inaccurate for single-realization simulations, large ensembles of GRW-Kraichnan solutions were found to be accurate enough for the purpose of Monte Carlo simulations [58]. MFEM results for the longitudinal effective diffusion coefficient show a small systematic deviation from those obtained by MFEM-GRW. This was found to be caused by the residual numerical diffusion in the MFEM scheme. The latter was evaluated by solving a transport problem for constant velocity and subtracting the nominal (input) diffusion coefficient from the diffusion coefficient computed by the MFEM method. After correcting for the residual numerical diffusion, the MFEM and MFEM-GRW results become quite close after a few dimensionless times (thin lines in Figure 16). This concludes the validation test of the coupled MFEM-GRW approach.

The coupled MFEM-GRW approach may be especially useful in Monte Carol simulations of passive transport for large variances of the log-hydraulic conductivity. Another useful application is the assessment of the numerical diffusion in MFEM methods by comparisons of solutions for passive transport problems. MFEM schemes with acceptable small numerical diffusion can be further used to solve reactive transport problems (an application to aerosol filters modeled as random media is presented in Section 4 of (P14)). The MFEM-GRW approach will be also a valuable tool in solving evolution equations for the probability density of the random concentration, as that sketched in Section 9.1 below.

9 GRW solutions to PDF evolution equations

9.1 Modeled PDF evolution equations

The evolution of the probability density function (PDF) of the random concentration in groundwater systems can be modeled, similarly to approaches developed in turbulence and combustion theory [49, 15, 32, 31, 44], by Itô equations for trajectories of "fluid particles", X_i, $i = 1, 2, 3$,

$$dX_i(t) = \mathcal{V}_i(t)dt + d\tilde{W}_i(t),\ E\{\tilde{W}_i^2(t)\} = 0,\ E\{\tilde{W}_i^2(t)\} = 2\int_0^t \mathcal{D}_{ii}(t')dt', \tag{9.1}$$

where $\mathcal{V}_i$ and $\mathcal{D}_{ij}$ are up-scaled velocity fields and dispersion coefficients, and by Itô equations describing time-random concentrations $C(\mathbf{X}, t)$ carried by fluid particles,

$$\begin{aligned} dC(t) &= A(t)dt + B(t)dW(t) + S_1(C(t), \overline{C}(t)), \\ d\overline{C}(t) &= S_2(C(t), \overline{C}(t)), \end{aligned} \tag{9.2}$$

where C and $\overline{C}$ are mobile and immobile species concentration related by reaction terms S_1 and S_2 and $W(t)$ is the standard Wiener process [60].

A general form of the drift term in (9.2) is

$$A(t) = -a(t)(C(t) - \langle C\rangle) + \Delta^{diff}\langle C\rangle,$$

where $\Delta^{diff}\langle C\rangle$ describes the attenuation of the mean concentration through diffusion [45]. The diffusion coefficient in (9.2) has the generic form [49]

$$B(t) \propto \sqrt{\langle (C(t) - \langle C\rangle)^2\rangle}.$$

By Itô - Fokker-Planck equivalence one associates to the position (X_i) and concentration $(C, \overline{C})$ Itô equations a Fokker-Planck equation describing the *joint concentration-position* PDF $p(c, \mathbf{x}, t)$,

$$\partial_t p + \mathcal{V}\nabla p + \nabla_c(Ap) = \mathcal{D}\nabla^2 p + \nabla_c^2(Bp) - \nabla_{c,\overline{c}}((S_1 + S_2)p). \tag{9.3}$$

The reaction terms S_1 and S_2 are in a closed form, the same as in the concentration balance equation. The drift and diffusion coefficients in physical space ($\mathcal{V}$, $\mathcal{D}$) and in the concentration space (A, B) are unclosed and require modeling. $\mathcal{V}$ and $\mathcal{D}$ can in principle be obtained from homogenization MFEM approximations for non-periodic media and random coefficients (e.g., [47]). MFEM solutions imported into GRW and mixing models for A and B can be used to solve the equation (9.3) for the evolution of the joint PDF in physical and concentration spaces by a coupled MFEM-GRW approach similar to that described in the previous section.

9.2 GRW solutions to modeled PDF equations

The feasibility of the GRW-PDF approach has been illustrated in [60] for the passive transport problem considered in (P7). The Monte Carlo results were processed statistically to infer various correlations and PDFs (P15). The strong correlation between the longitudinal dispersion coefficient and the cross-section space-average concentration and the smallness of the other input-output correlations (P15, Figure 6) supply numerical support for a one dimensional model (9.1), with constant constant $\mathcal{V}$ and time-variable $\mathcal{D}$.

The coefficient $\mathcal{D} = \mathcal{D}_{11}$ has been estimated according to Remark 6.2, using a single trajectory of diffusion in a realization of the Kraichnan velocity field, with the discrete version of (6.11),

$$\mathcal{D} = X_t^2/(2S\tau), \;\; X_t^2 = \sum_{s=1}^{S} \delta X_s^2 + 2 \sum_{r=1}^{S-1} \sum_{s=1}^{S-r} \delta X_s \delta X_{s+r}, \;\; \delta X_s = X_{s\tau} - X_{(s-1)\tau}.$$

The drift term in (9.1) was set to the constant mean $\mathcal{V} = 1$ m/day.

The drift term $A(t)$ in (9.2) was specified by $a(t) = \mathcal{D}(t)/\lambda$, $\lambda = 1$ m. The attenuation of the mean concentration by the local diffusion of coefficient $D = 0.01$ m^2/day, $\Delta^{diff}\langle C \rangle$, was evaluated from one-dimensional GRW solutions. In absence of a model for the diffusion in the concentration space, a coefficient $B = 10^{-6}$ day$^{-\frac{1}{2}}$ was chosen, which corresponds to (7.3), with the time and concentration steps used in simulation, $r = 1$, and $d = 1$.

The initial condition for the Fokker-Planck equation (9.3) was the concentration PDF after the first time step in the Monte Carlo simulations (P15), multiplied by $N = 10^{24}$ particles for the purpose of the GRW simulation.

Figure 17 shows contour plots for $n = 1$ and $n = 10^6$ particles in the (x, c) plane at successive times and Figure 18 shows the evolution of the simulated concentration PDF.

Integrating over c the solution $p(c, x, t)$ of the Fokker-Planck equation (9.3) gives the marginal $p(x, t)$, which is the mean concentration corresponding to (9.1). The comparison with Monte Carlo results from Figure 19 shows that the GRW solution fulfils this consistency condition.

The comparison in Figure 20 between the input dispersion coefficient, those computed during the GRW simulation, and the Monte Carlo reference value indicates that the "ergodic" estimation based on (6.11) is an acceptable approximation for the transport problem considered here.

As shown by Figure 21, the cumulative probability distribution is still different from that obtained by Monte Carlo simulations. This is a somewhat expected result, because the GRW simulation is incompletely parameterized. Nevertheless, these results provide a numerical support for the feasibility of the GRW-PDF approach.

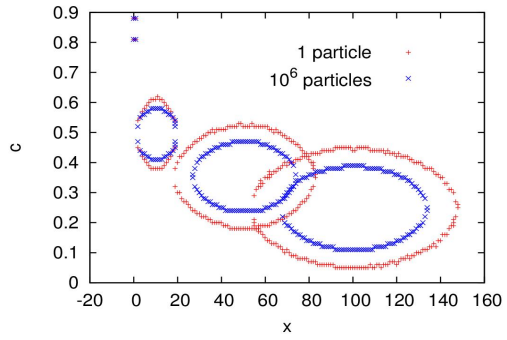


Figure 17: Contours in (x, c) plane at $t = 0$, 10, 50, and 100 days.

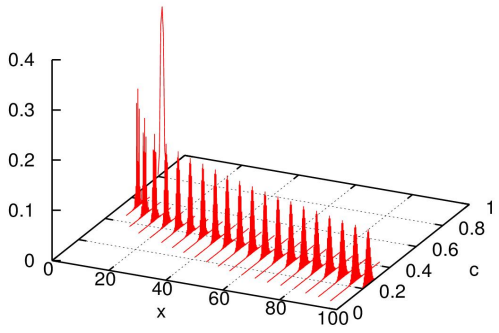


Figure 18: Transport of $p(c)$ along $x = \mathcal{V}t$ over 100 days.

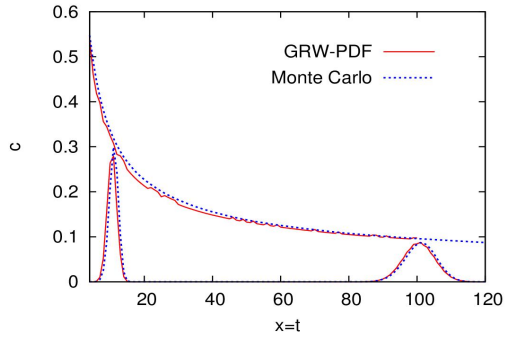


Figure 19: $\langle C \rangle(x)$, at $t = 10$ days, $t = 100$ days (peaks), and $\langle C \rangle(x = \mathcal{V}t)$ (monotone curves) compared with Monte Carlo results.

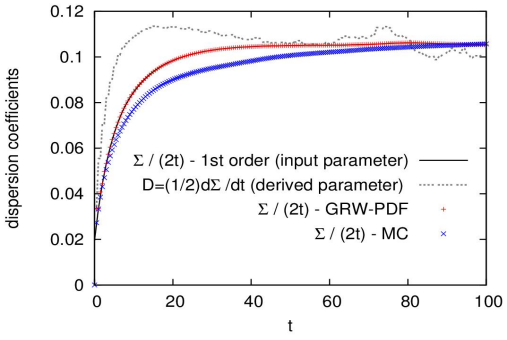


Figure 20: Input and computed dispersion coefficients compared with Monte Carlo results.

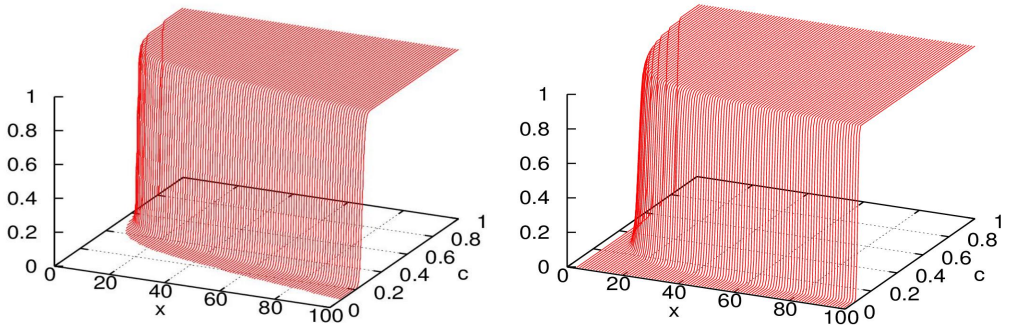


Figure 21: Cumulative distribution function at the center of mass $x = \mathcal{V}t$ transported in time by the GRW-PDF algorithm (left) compared with the Monte Carlo estimate (right).

10 Conclusions

The model of diffusion in random velocity fields can be parameterized by experimentally inferred local dispersion coefficients and by space dependent drift coefficients. The latter are solutions of boundary value problems for the flow equations, with hydraulic conductivity parameters provided as samples of a random space function, inferred by geostatistical interpretation of field-scale measurements.

Diffusion in random velocity fields is a stochastic process with memory. The relevant memory effects are quantified by correlations of the increments of the process, determined by correlations of the velocity field. The memory may be transitory, for short-range velocity correlations, or indefinitely persistent, in case of power-law correlations.

Memory effects cause a "non-ergodic" behavior of the actual dispersion and concentration with respect to theoretical models given by stochastic averages, such as the one-particle dispersion and the macrodispersion model. Therefore, in practical applications aiming at monitoring groundwater contamination, theoretical averages are not enough and the one-dimensional PDF of the random concentration is often required.

Efficient solutions to PDF evolution equations can be obtained by GRW or by coupled MFEM-GRW approaches. The challenge is to identify suitable mixing models for the dynamics of the concentration at fixed locations. Mixing models used in turbulence and combustion theory may be a starting point, however, they cannot be simply transferred and applied to transport problems in sub-surface hydrology.

An option for a better modeling of the local mixing could be to evaluate directly the mean diffusion flux from which mixing models of type (9.2) are usually derived [15, 45]. This evaluation can be done dynamically through independent GRW simulations of local diffusion processes in physical space, at every lattice site and time step of the GRW-PDF code. The efficiency of the GRW algorithm makes possible such imbedded simulations, at reasonable computational costs.

The next step should be to get closer to measurements. Time series of concentrations may be interpreted as polydispersive processes consisting of superpositions of Gaussian processes associated to local thermodynamic equilibrium states at different scales [30]. A mechanism which is able to generate time series with the same polydisperse parameters may serve as a mixing model. Such an approach is justified by the hierarchical structure of scales and by the low flow velocity in groundwater systems.

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APPENDIX

List of papers included in the Appendix

P 1 Suciu N., C. Vamos, F. A. Radu, H. Vereecken, and P. Knabner (2009), Persistent memory of diffusing particles,*Phys. Rev. E, 80*, 061134, doi:10.1103/PhysRevE.80.061134.

P 2 Suciu, N., C. Vamos, H. Vereecken, K. Sabelfeld, and P. Knabner (2008), Ito equation model for disperion of solutes in heterogeneous media, *Rev. Anal. Num. Th. Approx. (Romanian Academy), 37*, 221-238.

P 3 Suciu N. (2010), Spatially inhomogeneous transition probabilities as memory effects for diffusion in statistically homogeneous random velocity fields, *Phys. Rev. E, 81*, 056301, doi:10.1103/PhysRevE.81.056301.

P 4 Suciu, N., S. Attinger, F.A. Radu, C. Vamos, J. Vanderborght, H. Vereecken, P. Knabner (2011), Solute transport in aquifers with evolving scale heterogeneity, *Preprint No. 346*, Mathematics Department - Friedrich-Alexander University Erlangen-Nuremberg (http://fauams5.am.uni-erlangen.de/papers/pr346.pdf).

P 5 Suciu N., C. Vamos, H. Vereecken, K. Sabelfeld, and P. Knabner (2008), Memory effects induced by dependence on initial conditions and ergodicity of transport in heterogeneous media, *Water Resour. Res. 44*, W08501, doi:10.1029/2007WR006740.

P 6 Suciu N., and C. Vamoş (2007), Comment on "Nonstationary flow and nonergodic transport in random porous me-

dia" by G. Darvini and P. Salandin, *Water Resour. Res., 43*, W12601, doi:10.1029/2007WR005946.

P 7 Suciu, N., C. Vamos, J. Vanderborght, H. Hardelauf, and H. Vereecken (2006), Numerical investigations on ergodicity of solute transport in heterogeneous aquifers, *Water Resour. Res., 42*, W04409, doi:10.1029/2005WR004546.

P 8 Suciu N., C. Vamoş, and J. Eberhard (2006), Evaluation of the first-order approximations for transport in heterogeneous media, *Water Resour. Res. 42*, W11504, doi: 10.1029/2005WR004714.

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