.

Path decomposition of discrete macrodispersion coefficient

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Forschungszentrum Jülich / Internal Report ICG-IV 00501
November 2001

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Abstract

Technical aspects of modeling the long time behavior of diffusion in random velocity fields are discussed from theoretical and numerical points of view. First, a general mathematical model of diffusion in random environments is presented. In this frame, the hypothesis which make possible a Lagrangian description are explicitly presented and the conditions for asymptotic diffusive behavior are analyzed. Next, the Global Random Walk algorithm for numerical modeling of diffusion is described. The issues of numerical modeling of diffusion in random velocity fields suggest a deeper analysis of computations of effective diffusion coefficients. In the following, the effective diffusion coefficient is expressed as a function of velocity correlations along the paths starting in grid points inside the contaminant plume and developed for several time iterations. This approach provides us with a new tool to analyze the asymptotic behavior and to characterize the numerical codes which generate discrete random fields.

Contents

1 Introduction

The stochastic approach of diffusion in random media is based on three assumptions: the heterogeneity of the natural porous media can be described by random space functions, for large times the transport process behaves asymptotically diffusive and, diffusion in a single realization of the medium produces the same concentration distribution as that given by average over the ensemble of realizations. Mathematically, this corresponds to the "self-averaging property" of the process [Avellaneda et al., 1991]. Then one expects that the stochastic model has predictive force for individual realizations of the porous medium [Attinger et al., 1999]. "A major motivation of stochastic analysis of transport in a heterogeneous porous medium has been to derive an effective equation for the concentration that may be used to make decision in real life contamination events" [Kapoor and Gelhar 1994a]. First, the existence of the asymptotic diffusive behavior and the self-averaging property must be checked. Further, the fluctuations of concentration in individual realizations should be studied, in order to find the superior bound which delimits the "unsafe zone" [Kapoor and Gelhar 1994b].

In this report we restrict our discussion to transport of passive scalars, i.e. without sorption or chemical reactions, and to saturated aquifers. The Darcy velocity field with high variability, due to the heterogeneity of the aquifer, is described by a random space function. The mathematical theory of diffusion processes provides a rigorous frame in which diffusion in random velocity fields can be defined as a stochastic process. Although general necessary conditions for diffusive behavior can be stated, sufficient condition can be established mainly for simple examples, as Langevin-kind equations or the stratified aquifer model of Matheron and de Marsily. In more complex cases, the connection between the Lagrangian statistical description and experimentally measured velocity correlations is obtained by the use of strong assumptions, which essentially produces the same effect as the Corsin conjecture of factorizing in average over the ensemble of realizations of the random field [Suciu, 2001]. The Eulerian approach based on advection-diffusion equations allows a more accurate mathematical presentation of the problem but hypotheses for asymptotic diffusive behavior are still mater of controversies [Kapoor and Gelhar 1994a, Dagan and Fiori, 1997]. In some analytical approaches, using special (Gaussian) forms for correlation function involved, the approach towards the asymptotic state can be described [Attinger et al., 1999]. In general, this is not easy and the travel time/distance at which the transport can be described by the effective diffusion equation as well as the validity of this equation for single aquifer can not be established on the basis of the mathematical model only. Overall, the mathematical stochastic models require strong continuity properties of random functions used as models for velocities and trajectories [Taylor, 1921] which is unlikely to hold in real processes.

Numerical models are used to verify and to go beyond the limits of mathematical theory of stochastic processes. When diffusion in random fields processes are numerically simulated, both the problem of asymptotic behavior and of "self-averaging" property are difficult to be solved and they imply high computing resources. In [Schwarze et al., 2001], to obtain the approach to asymptotic value of longitudinal effective diffusion coefficient, 3200 particle trajectories were simulated with "particle tracking" (PT) procedure, for times corresponding at 5000 correlation lengths. In other studies [Salandin and Fiorotto, 1998], the reliability of the computations is achieved using 20 000 trajectories (500 realizations of the field and 40 particles in each realization), up to 20 correlations lengths but the asymptotic regime is not reached. The computational effort needed to obtain statistically significant results "has serious implication" when the behavior in a single realization is studied [Bellin et al., 1992]. Because comparison with

field measurements rises questions about the validity of effective equation for single realization [Vanderborght and Vereecken, 2001] sometimes a more pragmatic approach is adopted in which no effective equation is used and direct simulations of transport and concentration variations are preferred [Tompson et al., 1998].

Global random walk algorithm (GRW) [Vamoş et al. 2001a, Vamoş et al. 2001b] is not concerned with limitations related to number of particles. Unlike the usual random walk algorithms, PT included, the trajectories of the particles must not be simulated individually and stored. With GRW, all particles lying at a given grid point are simultaneously scattered in space according the random walk (which simulates the local diffusion) and transported with velocity of the random field realization. This is done by the use of the Bernoulli repartitions or by determinist rules. In this way the maximum number of particle representable on a computing platform can be handled, without increasing computing time. Using large grids, GRW allows simulation of large times behavior and the checking of "self-averaging".

Section 2 presents a frame of mathematical theory of transport in random media and discusses the basic definitions, (random variables, processes and fields, concentration field and concentration variance, drift and diffusion coefficients) equations (Liouville, Fokker-Plank, master, Itô, Langevin) and properties (self-averaging, existence of effective diffusion coefficients, Corsin conjecture and relation between Lagrangian an Eulerian statistics). These basic notions are used to draw the main lines of the model of "diffusion by continuous movements" of Taylor [1921], on which the actual models of Lagrangian passive transport are based. In Section 3 the random walk and GRW algorithms are presented and their relation with continuous diffusion processes is discussed. A simulation of asymptotic behavior of diffusion in random velocity filed is presented in Section 4. The Section 5 presents the new numerical tool in analyzing asymptotic behavior, based on a "path decomposition" of the effective diffusion coefficient as function of velocity correlations. Section 6 contains some conclusion of this report and ideas for further works.

2 Elements of theory of transport in random media

2.1 Random variables, processes and fields

2.1.1 Random variables

Stochastic description of systems associates probabilities to states and to transitions between states. The heuristic definition of probability can be introduced as the limit for large number of trials of the relative frequency of occurrence of an event. Further, the probability can be axiomatically defined as an positive and additive function of sets of events so that the occurrence of any one event from the set of all possible events, i.e. the "sure event", has the probability one. A parameter describing the state of the system with the associate probability is modeled by a random variable. The random variable is the basic mathematical object used to build stochastic descriptions of real processes. Stochastic processes, random fields and dynamical systems are random variables, defined on particular spaces of events.

The mathematical model of random variables uses σ-algebras of sets and measures defined on σ -algebras. The σ-algebra $\mathcal{A}$ is a set of subsets of a generic set Ω which is closed with respect to intersection and countable reunion operations. The pair $(\Omega, \mathcal{A})$ is a *measurable space;* the set $A \subset \Omega$ is a *measurable set* with respect to $\mathcal{A}$ if $A \in \mathcal{A}$. A *measure* P on a σ-algebra $\mathcal{A}$ is defined as a positive and countable additive function of sets on $\mathcal{A}$, $P : \mathcal{A} \longmapsto \mathbb{R}_+$. The

triplet $(\Omega, \mathcal{A}, P)$ defines a *measure space*. When $P(\Omega) = 1$ then P is a normalized measure and $(\Omega, \mathcal{A}, P)$ becomes a *probability space*.

Let $(\Omega, \mathcal{A}, P)$ be a probability space and $(X, \mathcal{B})$ a measurable space with property $\{x\} \in \mathcal{B}$, $\forall x \in X$. A *random variable* is an $(\mathcal{A}, \mathcal{B})$-measurable application $\eta : \Omega \longmapsto X$, i.e. endowed with the property

$$\{\eta \in B\} \in \mathcal{A}, \forall B \in \mathcal{B}, \tag{2.1}$$

where $\{\eta \in B\} = \{\omega \in \Omega \mid \eta(\omega) \in B\}$.

In physics terminology, X is the *phase space,* the sets $B \in \mathcal{B}$ are realizations, Ω is the *space of elementary events*, the sets $A \in \mathcal{A}$ are *events* and $P(A)$ is the *probability of occurrence of the event* A [Gardiner, 1983, Wentzell, 1981].

The *distribution* of the random variable η is a measure $P_\eta : \mathcal{B} \longmapsto \mathbb{R}_+$, defined by

$$P_\eta(B) = P(\{\eta \in B\}),\ \forall B \in \mathcal{B}. \tag{2.2}$$

The distribution of the realization B is thus defined as the probability of occurrence of the event $\{\eta \in B\}$. In particular, $P_\eta(X) = P(\{\eta \in X\}) = P(\Omega) = 1$, which shows that the distribution organizes the phase space X as a probability space, $(X, \mathcal{B}, P_\eta)$.

The notion of distribution allows the connection of the mathematical model of random variable with experimental data and numerical models. For example, we consider the measurements of the positions of a particle at different distances along a straight line. The number of occurrences of a measured value, inside the interval Δx centered in x, N_{occ} divided by total number of measurements N, i.e. the relative frequency N_{occ}/N, approximates the repartition of a random variable describing the measurement.

Probabilistic descriptions of practical interest are given by *stochastic average* defined as a Lebesgue integral,

$$M(\eta) = \int_\Omega \eta(\omega) P(d\omega), \tag{2.3}$$

the *variance*, $M((\eta - M(\eta))^2)$, *n order moments*, $n > 2$, $M((\eta - M(\eta))^n)$ and *correlation functions* of two variables η and ς, $Cor(\eta, \varsigma) = M(\ \eta\varsigma - M(\eta)M(\varsigma))$.

When $B = X$ then $\{\eta \in X\} = \Omega$ and a change of variables theorem shows that the average over the space of elementary events, M_Ω, equals the average over the phase space, M_X,

$$M_\Omega(f) = \int_\Omega f(\eta(\omega)) P(d\omega) = \int_X f(x) P_\eta(dx) = M_X(f)\ , \tag{2.4}$$

where, $x = \eta(\omega)$ [Malliavin, 1993, p180]. Both averages are mathematical models of "average over the statistical ensemble".

2.1.2 Random functions, processes and fields

Let Λ be a set of parameters, $(\Omega, \mathcal{A}, P)$ a probability space and $(Y, \mathcal{B})$ a measurable space. A *random function* is defined as a random variable on Ω taking values in the "Cartesian product" space Y^Λ,

$$\boldsymbol{\eta} : \Omega \longmapsto Y^\Lambda,\ \boldsymbol{\eta}(\omega) = y^\omega,\ y^\omega \in Y^\Lambda,\ \forall\ \omega \in \Omega. \tag{2.5}$$

If $\mathcal{B}^\Lambda$ is a σ -algebra in Y^Λ, the $(\mathcal{A}, \mathcal{B}^\Lambda)$ -measurability of the random variable $\boldsymbol{\eta}$ is given by the condition $\{\boldsymbol{\eta} \in C\} \in \mathcal{A}$ for every set $C \in \mathcal{B}^\Lambda$. The *distribution of the random function* is defined by (2.2) as

$$P_{\boldsymbol{\eta}}(C) = P(\{\boldsymbol{\eta} \in C\}),\ \forall C \in \mathcal{B}^\Lambda, \tag{2.6}$$

and organizes the space Y^{Λ} as a probability space, $(Y^{\Lambda}, \mathcal{B}^{\Lambda}, P_{\boldsymbol{\eta}})$. The function $y^{\omega} : \Lambda \longmapsto Y$ is called a *sample* (or *realization*) of the random function and its values, $y^{\omega}(\lambda) = y_{\lambda}$, $\lambda \in \Lambda$, are points in the space Y, called the *state space*. The *phase space* for the random function $\boldsymbol{\eta}$ is the space of functions Y^{Λ} and the realization are sets of functions y^{ω} in Y^{Λ}. The definition of the random function as a random variable on a space of function is referred to as the definition *in the sense of Doob*, originally introduced in [Doob, 1953, Cap.2]. When $\Lambda \subseteq \mathbb{R}$ and λ has the meaning of physical time, the random function is called a *stochastic process*. The samples of a stochastic process are called *trajectories*. When $\Lambda \subset \mathbb{R}^d$, the random function is a *d-dimensional random field* (this is the mathematical object used as model for velocity field in turbulent diffusion and transport in heterogeneous porous media [Dobrushin and Pecherski, 1981, p.261, Wentzel, 1981, pp.25-26, Taylor, 1921]).

The value of y^{ω} for a fixed parameter λ defines a random variable, $\eta_{\lambda}(\omega) = y^{\omega}(\lambda)$, $\eta_{\lambda} : \Omega \longmapsto Y$. The phase space of η_{λ} coincides with the state space Y. The family of random variables $\{\eta_{\lambda} \mid \eta_{\lambda} : \Omega \longmapsto Y\}_{\lambda \in \Lambda}$ defines a random function in the *Wiener sense.* Another useful representation of the random function is as a *two variables function*, $\eta_{\lambda}(\omega) = \eta(\lambda, \omega)$, $\eta : \Lambda \times \Omega \to Y$. The sufficient condition of measurability is that for every fixed ω the function η be (left or right) continuous as function of λ [Wentzell, 1981, p.22]. General conditions of equivalence of these definitions are presented in [Iosifescu and Tăutu, 1972, p.164]. While the Wiener and two variables function definitions are useful in specific application, the Doob definition remains the main tool to build a coherent frame for a general theory of Markov and diffusion processes.

The distribution of the random function is completely defined by a *hierarchy of consistent finite dimensional distributions*. The *n-dimensional distributions* are the distributions of the random vectors $\{\eta_{\lambda_1}, ..., \eta_{\lambda_n}\}$, obtained from $\boldsymbol{\eta}$ for fixed values of the parameter λ,

$$P_{\lambda_1 ... \lambda_n}(B) = P(\{\eta_{\lambda_1} \in B_1, ..., \eta_{\lambda_n} \in B_n\}),\ B \in \mathcal{B}^n,\ \ B_i \in \mathcal{B}. \tag{2.7}$$

The distributions (2.7) are called *consistent* when they verify the conditions

$$P_{\lambda_{i_1}, ..., \lambda_{i_n}}(B_{i_1} \times ... \times B_{i_n}) = P_{\lambda_1 ... \lambda_n}(B_1 \times ... \times B_n), \tag{2.8}$$

for all permutations $\{i_1, ..., i_n\}$ of indices $\{1, ..., n\}$ and any $B_1, ..., B_n \in \mathcal{B}$, and

$$P_{\lambda_1 ... \lambda_n \lambda_{n+1}}(B_1 \times ... \times B_n \times Y) = P_{\lambda_1 ... \lambda_n}(B_1 \times ... \times B_n). \tag{2.9}$$

The existence of the process in the sense of Doob (2.5) and the definition of the distribution $P_{\boldsymbol{\eta}}$ are stated in the **Kolmogorov Theorem on finite-dimensional distributions:**

Theorem 1. *If $P_{\lambda_1 ... \lambda_n}$ are probability measures on $(\mathbb{R}^n, \mathcal{B}^n)$, associated to finite sets of parameters $\lambda_1, ..., \lambda_n$ from the set of parameters Λ, and if $P_{\lambda_1 ... \lambda_n}$ verify the consistency conditions* (2.8-9),

Then, there exists a random function $\boldsymbol{\eta}$ in the probability space $(\mathbb{R}^{\Lambda}, \mathcal{B}^{\Lambda}, P_{\boldsymbol{\eta}})$, uniquely defined in the sense of Doob, and the distribution is defined by

$$P_{\boldsymbol{\eta}}(C_n) = P_{\lambda_1 ... \lambda_n}(B), \text{for all } C_n \in \mathcal{B}^{\Lambda},\ C_n = \{(y_{\lambda_1} .... y_{\lambda_n}) \in B \mid B \in \mathcal{B}^n\}, \tag{2.10}$$

and, reciprocally, finite dimensional distributions distributions associated to a random function by (2.10) *are consistent.*

The simplest example of random function is the infinite sequence of independent random variables. Let $\Lambda = \mathbb{Z}$, where $\mathbb{Z}$ is the set integer numbers, and $(Y, \mathcal{B}, P_0)$ a state space. The

Cartesian product space endowed with the product probability measure $P = \bigotimes_{-\infty}^{\infty} P_0$, $(Y^{\mathbb{Z}}, \mathcal{B}^{\mathbb{Z}}, P)$ is the phase space for the random function

$$\boldsymbol{\eta} : Y^{\mathbb{Z}} \longmapsto Y^{\mathbb{Z}},\ \boldsymbol{\eta}(\mathbf{y}) = \mathbf{y}',\ y'_i = y_{i+1},\ \ -\infty < i < \infty,$$

defining a translation along the components of infinite vectors from $Y^{\mathbb{Z}} = \{(y_n)_{n\in\mathbb{Z}} \mid y_n \in Y\}$. It is straightforward that P verify (2.10) and the finite dimensional distributions are consistent.

The first random function build by the use of Kolmogorov theorem was the *Wiener process* [Wentzell, 1981, pp.83-84]. The 1-dimensional Wiener process is the random function $\mathbf{w} : \Omega \longmapsto \mathbb{R}^{[0,\infty)}$, $\mathbf{w}(\omega) = y^{\omega}$, with trajectories on real axis, $y^{\omega} : [0,\infty) \longmapsto \mathbb{R}$, defined by the following three properties:

(w1) $w_0(\omega) = 0$, $\forall \omega \in \Omega$, (the process starts from 0),

(w2) for fixed times, $0 \leq t_0 \leq t_1 \leq \cdots \leq t_n$, the corresponding random variables $w_{t_1} - w_{t_0}$, $w_{t_2} - w_{t_1}, \cdots, w_{t_n} - w_{t_{n-1}}$, are independent (independent increments), and

(w3) the random variables $w_t - w_s$, $0 \leq s \leq t$, have Gaussian distribution with zero mean and variance $(t-s)$,

$$P_{(w_t - w_s)}(B) = [2\pi(t-s)]^{-1/2} \int\limits_{B\subset\mathbb{R}} \exp\{-(y_t - y_s)^2/2(t-s)\} dy_s. \tag{2.11}$$

The distribution of the sequence of independent increments from the property (w2) is the product of distributions (2.11). By the means of a linear transformation of the vector of independent increments, one obtains the finite-dimensional distribution of the random vector $(w_{t_1}, \cdots, w_{t_n})$ as,

$$P_{w_{t_1}\cdots w_{t_n}}(B) = \prod_{i=1}^{n} [2\pi(t_i - t_{i-1})]^{-1/2} \int\limits_{B\subset\mathbb{R}^n} \exp\left[-\sum_{i=1}^{n} \frac{(y_i - y_{i-1})^2}{2(t_i - t_{i-1})}\right] dy_1 \cdots dy_n, \tag{2.12}$$

where $t_0 = 0$ and $y_0 = 0$ [Wentzell, 1981, p.13].

The Wiener process is a random variable defined on the probability space $(\mathcal{C}_0(\mathbb{R}^{[0,\infty)}), \mathcal{B}^{[0,\infty)}, P_{\mathbf{w}})$, where $\mathcal{C}_0(\mathbb{R}^{[0,\infty)})$ is the set of continuous real functions defined on $[0,\infty)$, starting at $t = 0$ from the point 0, and $P_{\mathbf{w}}$ is the distribution completely defined by finite-dimensional distributions (2.12) through (2.10) and Kolmogorov theorem. The averages over the phase space $M(f)(t)$ from (2.4) (and the higher order moments) are given by their values at fixed times t, by integration with respect to the measures (2.12).

2.1.3 Densities for finite dimensional probabilities

Let $(Y, \mathcal{B})$ be a state space, μ a measure on $\mathcal{B}$ and P_η the distribution of the random variable $\eta : \Omega \longmapsto X$. If the measure P_η is absolutely continuous with respect to μ, i.e. $P_\eta(B) = 0$ for every $B \in \mathcal{B}$, with $\mu(B) = 0$, then the Radon-Nikodym theorem defines the *probability density* p_η of the distribution P_η:

$$\int\limits_B p_\eta(y)\mu(dy) = P_\eta(B). \tag{2.13}$$

By (2.13), one associates to the set function P_η the point function p_η, which is Lebesgue integrable with respect to the measure μ and uniquely defined up to sets of null Lebesgue measure, i.e. it belongs to the set of integrable functions, $p_\eta \in L^1(Y, \mathcal{B}, \mu)$. Also, as a density

of a probability measure, p_η has the normalization property $\int_Y p_\eta(y)dy = 1$. In the case of real random variables, i.e. $Y \subseteq \mathbb{R}$, $\mu(dy) = dy$ is the Lebesgue measure on the Borel σ-algebra $\mathcal{B}$ (defined on the set of all open sets from Y) and, from (2.13), one obtains $P_\eta(dy) = p_\eta(y)dy$.

From Radon-Nikodym theorem one obtains also the densities of higher order finite dimensional distributions. Let $\boldsymbol{\eta} : \Omega \longmapsto Y^\Lambda$, be a random function defined on the probability space $(\Omega, \mathcal{A}, P)$, with trajectories $y^\omega : \Omega \longmapsto Y$, $y^\omega(\lambda) = \eta_\lambda(\omega)$, into the measurable space $(Y, \mathcal{B})$. When we consider the set $B = B_1 \times \cdots \times B_n$, $B_i \in \mathcal{B}$, and the characteristic function of the set B_i, $1_{B_i}(y)$ (defined by, $1_{B_i}(y) = 1$ when $y \in B_i$ and $1_{B_i}(y) = 0$ when $y \notin B_i$), the n-dimensional distribution (2.7) can be written as

$$P_{\lambda_1,...,\lambda_n}(B) = \int_\Omega 1_{B_1}(\eta_{\lambda_1}(\omega))...1_{Bn}(\eta_{\lambda n}(\omega))P(d\omega). \tag{2.14}$$

The value of the function 1_{B_i} in $\eta_{\lambda i}(\omega)$ can formally be written using the Dirac function [Kolmogorov and Fomine, 1975, p.200],

$$1_{Bi}(\eta_{\lambda i}(\omega)) = \int_{\mathbb{R}} \delta(y_i - \eta_{\lambda i}(\omega))1_{B_i}(y)dy_i = \int_{B_i} \delta(y_i - \eta_{\lambda i}(\omega))dy_i, \tag{2.15}$$

With (2.15), (2.14) becomes

$$P_{\lambda_1,...,\lambda_n}(B) = \int_{B_1} dy_1 ... \int_{Bn} dy_n M_\Omega[\delta(y_1 - \eta_{\lambda 1}(\omega))...\delta(y_n - \eta_{\lambda n}(\omega))], \tag{2.16}$$

where M_Ω is the averaging operator defined in (2.4). If B is a set of null measure in $\mathcal{B}^n$, then at least one of the integrals from (2.16) vanishes, thus $P_{\lambda_1,...,\lambda_n}(B)$ is an absolutely continuous measure with respect to the Lebesgue measure on $\mathcal{B}^n$. Then, in conditions of the Radon-Nikodym theorem, (2.16) defines the *n-dimensional density* (i.e. the density of the n-dimensional distribution $P_{\lambda_1,...,\lambda_n}$), as an integrable function from $L^1(Y^n)$, through

$$p(y_1, \lambda_1; ...; y_n, \lambda_n) = M_\Omega[\delta(y_1 - \eta_{\lambda 1}(\omega))...\delta(y_n - \eta_{\lambda n}(\omega))]. \tag{2.17}$$

The formula (2.17) is used in [van Kampen, 1981, Cap.3] to introduce the hierarchy of finite-dimensional distributions associated with a stochastic process and is also used in studies on turbulent diffusion [Lundgren and Pointin, 1975, Romanof, 1988]. For $n = 1$ and fixed λ, (2.17) gives the 1-dimensional density

$$p(y, \lambda) = M_\Omega[\delta(y - \eta_\lambda(\omega))] = \int_\Omega \delta(y - \eta_\lambda(\omega))P(d\omega). \tag{2.18}$$

The density (2.18) verify the normalization condition $\int_Y p(y, \lambda)dy = 1$. Indeed, because $\eta_\lambda(\omega) \in Y$, $\forall\ \omega \in \Omega$ we have $1_Y(\eta_\lambda(\omega)) \equiv 1$. Then,

$$\int_Y p(y, \lambda)dy = \int_\Omega P(d\omega) \int_{\mathbb{R}} 1_Y(y)\delta(y - \eta_\lambda(\omega))dy = \int_\Omega P(d\omega)1_Y(\eta_\lambda(\omega)) = \int_\Omega P(d\omega) = 1.$$

From (2.17) it follows that $p(y_1, \lambda_1; ...; y_n, \lambda_n)$ is an invariant function with respect to permutation of pairs (y_i, λ_i) and it verifies the relation

$$\int_Y p(y_1, \lambda_1; ...; y_n, \lambda_n)dy_n = p(y_1, \lambda_1; ...; y_{n-1}, \lambda_{n-1}). \tag{2.19}$$

Thus, the finite-dimensional densities defined by (2.17) have the consistency property for densities [van Kampen, 1981, Cap.3]. From this, it follows that the distributions

$$P_{\lambda_1,...,\lambda_n}(B) = \int\limits_{B_1} dy_1 ... \int\limits_{Bn} p(y_1, \lambda_1; ...; y_{n-1}, \lambda_{n-1}) dy_n \tag{2.20}$$

verify the consistency conditions (2.8-9), and the Kolmogorov theorem ensures the existence of the random function $\boldsymbol{\eta}$. The average, moments and correlation functions can be calculated as integrals weighted with the probability densities (2.17).

2.2 Markov processes

Let $\boldsymbol{\eta}$ be a stochastic process with real trajectories, $\boldsymbol{\eta} : \Omega \longmapsto Y^T$, $Y \subseteq \mathbb{R}$, $T \subseteq \mathbb{R}$.

The conditional probability density is obtained from (2.20) and the usual Bayesian definition from the theory of probability [Gardiner, 1983, Chap.3], as

$$p(y_1, t_1; ...; y_r, t_r \mid y_{r+1}, t_{r+1}; ...; y_n, t_n) = \begin{array}{c} p(y_1, t_1; ...; y_n, t_n)/ \\ p(y_{r+1}, t_{r+1}; ...; y_n, t_n). \end{array} \tag{2.21}$$

Markov processes are characterized by the dependence of conditional probabilities on only one of the previous states and not on the hole history of the process $\boldsymbol{\eta}$. For $t_1 > \cdots > t_{n,}$ the Markov property is expressed by

$$p(y_1, t_1; ...; y_r, t_r \mid y_{r+1}, t_{r+1}; ...; y_n, t_n) = p(y_1, t_1; ...; y_r, t_r \mid y_{r+1}, t_{r+1}). \tag{2.22}$$

From (2.21-22) one obtains

$$p(y_1, t_1; ...; y_n, t_n) = p(y_1, t_1 \mid y_2, t_2) ... p(y_{n-1}, t_{n-1} \mid y_n, t_n) p(y_n, t_n). \tag{2.23}$$

From the relation (2.23) and Kolmogorov theorem it follows that Markov processes are completely described by the 1-dimensional probability and conditional probability for two states, called *transition probability*. For $t_1 > t_2 > t_3$ and using (2.22), the consistency condition (2.19) written for Markov processes becomes the *Chapman-Kolmogorov equation,*

$$p(y_1, t_1 \mid y_3, t_3) = \int\limits_Y p(y_1, t_1 \mid y_2, t_2) p(y_2, t_2 \mid y_3, t_3) dy_2. \tag{2.24}$$

The property (2.23) of Markov processes establishes a connection between the 1-dimensional distribution at successive times. From the definition of finite-dimensional densities (2.7) and the consistency property (2.9), it follows that $P_{t_1}(B) = P(\eta_{t_1} \in B) = P(\eta_{t_1} \in B; \eta_{t_2} \in Y)$, for every $B \in \mathcal{B}$. With formula (2.20) and relation (2.23), written for two successive times, we obtain

$$\begin{aligned} P_{t_1}(B) &= \int\limits_B p(y_1, t_1) dy_1 = \int\limits_B dy_1 \int\limits_Y p(y_1, t_1; y_2, t_2) dy_2 \\ &= \int\limits_B dy_1 \int\limits_Y p(y_1, t_1 \mid y_2, t_2) p(y_2, t_2) dy_2. \end{aligned}$$

Thus, the 1-dimensional density at t_1 can be calculated from the corresponding density at t_2 and transition probability with the relation

$$p(y_1, t_1) = \int\limits_Y p(y_1, t_1 \mid y_2, t_2) p(y_2, t_2) dy_2. \tag{2.25}$$

2.3 Diffusion processes

2.3.1 Definition, drift and diffusion coefficients

Let $\boldsymbol{\eta} : \Omega \longmapsto Y^T$, $Y \subseteq \mathbb{R}^3$, $T \subseteq \mathbb{R}$, be a Markov process defined on the probability space $(\Omega, \mathcal{A}, P)$ valued into the trajectories space $\{y^\omega \in Y^T \mid y^\omega : T \longmapsto Y,\ y^\omega = \boldsymbol{\eta}(\omega),\ \omega \in \Omega\}$, where $(Y, \mathcal{B})$ is a measurable space, $Y \subseteq \mathbb{R}^3$ and $\mathcal{B}$ is the Borel σ-algebra. For this process one defines the densities of finite dimensional distributions, absolutely continuous with respect to Lebesgue measure, using (2.17) and the corresponding transition densities.

The Markov process defined in above, is a *diffusion process* in the sense of Kolmogorov [Gardiner, 1983, Sect.3.3, 3.4], if for any $\varepsilon > 0$ the transition probabilities satisfy, uniformly in x and t as $\Delta t \longrightarrow 0$, the conditions

$$i)\ \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|y-x| \geq \varepsilon} p(y, t + \Delta t \mid x, t) dy = 0,$$

$$ii)\ \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|y-x| < \varepsilon} (y_i - x_i) p(y, t + \Delta t \mid x, t) dy = A_i(x, y) + \mathcal{O}(\varepsilon),$$

$$iii)\ \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int\limits_{|y-x| < \varepsilon} (y_i - x_i)(y_j - x_j) p(y, t + \Delta t \mid x, t) dy = 2B_{ij}(x, t) + \mathcal{O}(\varepsilon).$$

The condition $i)$ ensures *the continuity with probability* 1 for the trajectories of the Markov process [Gardiner 1983, p.46, Wentzell, 1981, p.167]. This property means that for almost all values of ω (excepting sets of null measure, $E \in \mathcal{A}$, $P(E) = 0$) the trajectories y^ω are continues time functions. Continuous Markov processes are called "diffusion processes in a large sense" [Falkner, 1997].

If there exist partial derivatives of A_i, $B_{i,j}$ and transition probabilities p, then, in the limit $\varepsilon \longrightarrow 0$, from $i) - iii)$ the *Fokker-Planck*, equation

$$\partial_t p(x, t \mid x_0, t_0) = -\nabla[A p(x, t \mid x_0, t_0)] + \nabla^2[\tilde{B}(x, t)\, p(x, t \mid x_0, t_0)], \tag{2.26}$$

is derived, where A is the *drift vector* and $\tilde{B}$, the *diffusion tensor*. For positively defined A and $\tilde{B}$, the equation (3.1) can be solved if initial condition $p(x, t \mid x_0, t) = \delta(x - x_0)$ and suitable boundary conditions are assumed [Gardiner, 1983, Sect.3.42].

The integrals from $ii)$-$iii)$ have the meaning of local averages, $M_{|y-x|<\varepsilon}[f(y) \mid x, t](t + \Delta t; x, t)$, of some functions $f(y)$ defined on Y. These averages are calculated inside a sphere of radius ε, at time moment $t + \Delta t$ and conditioned by the value x at t for the trajectories of the process. Using the mean theorem and the condition $i)$, one estimates the average over the state space at $t + \Delta t$ as it follows:

$$\begin{aligned} M[f(y) \mid x, t](t + \Delta t; x, t) &= \int\limits_{|y-x|<\varepsilon} f(y) p(y, t + \Delta t \mid x, t) dy \\ &+ M_{|y-x| \geq \varepsilon}[f(y) \mid x, t](t + \Delta t; x, t) \int\limits_{|y-x| \geq \varepsilon} p(y, t + \Delta t \mid x, t) dy \\ &= M_{|y-x|<\varepsilon}[f(y) \mid x, t](t + \Delta t; x, t) + o(\Delta t). \end{aligned} \tag{2.27}$$

We found that for continuous processes the local average is of the same magnitude order for $\Delta t \to 0$ as the average over the entire state space (the Euler order relations, o, $\mathcal{O}, \mathcal{O}_s$ and $\sim$, are used in the sense of definitions from [Georgescu, 1995, Sect.1.2]). In $ii)$-$iii)$ there is no relation between ε and Δt. Usually one assumes $\varepsilon = o(\Delta t)$ [Wentzell, 1981, Cap.11]. In

this case, when the initial time is t and the initial condition for equation (2.26) is given by $p(y,t \mid x,t) = \delta(y-x)$, from (2.27), and conditions *ii*) and *iii*), we have

$$A_i(x,t) = \frac{d}{ds} M[(y_i - x_i) \mid x,t](t+s;x,t) \mid_{s=0}, \tag{2.28}$$

respectively,

$$B_{ij}(x,t) = \frac{1}{2}\frac{d}{ds} M[(y_i - x_i)(y_j - x_j) \mid x,t](t+s;x,t) \mid_{s=0} . \tag{2.29}$$

This proves that for continuous processes (i.e. verifying the condition *i*) the existence of the coefficients (2.28-29), into the hypothesis of order relation $\varepsilon = o(\Delta t)$, is equivalent with the diffusion conditions *ii*)-*iii*). The coefficients (2.28-29) are "forward" derivatives with respect to time of mean value and variance of $(y_i - x_i)$, conditioned by initial state (x,t) (the variance is obtained when the product $M[(y_i - x_i) \mid x,t]M[(y_j - x_j) \mid x,t]$, which is of the order $o(s)$ for $s \to 0$, is subtracted from the mean in (2.29)). Only in these conditions, the diffusion coefficients can be defined as time derivatives of displacement variances as in [Taylor, 1921, Dagan, 1989].

The typical diffusion process is the 1-dimensional *Gauss process* ($Y \subseteq \mathbb{R}$), defined by its average x_0 and variance $\sigma^2 = 2D(t - t_0)$, $D > 0$, and the Gauss density

$$p(x,t \mid x_0,t_0) = [4\pi D(t-t_0)]^{-\frac{1}{2}} \exp[-(x-x_0)^2/4D(t-t_0)]. \tag{2.30}$$

The Gauss process has two important properties. Its mean value and variance are linear functions of duration of the process, $(t-t_0)$, and their derivatives are constant. The consequence is a remarkable reproducibility property: processes starting from any initial time have, after an identical time interval, an identical variance. In was shown that their image in state space is a fractal set [Lasota Mackey, 1985, p.206]. Also, using (2.30) and the corresponding (set function) measure, $P_{x,t}(B) = \int_B p(y,t+\Delta t \mid x,t)dy$, it is easy to check that for every finite constant K,

$$P_{x,t}(\{\frac{1}{\Delta t}(\mid y - x \mid) > K\}) \underset{\Delta t \to 0}{\longrightarrow} 1,$$

i.e. the limit defining the time derivative is "almost sure infinite" al all times t. This argument proves that the trajectories of Gaussian diffusion process are nowhere differentiable with probability 1.

Using (2.28-29), one obtains the coefficients for the Fokker-Planck equation which corresponds the process with transition density (2.30). The result is the *diffusion equation*

$$\partial_t p = D\partial_x^2 p. \tag{2.31}$$

More generally, if the average is $x_0 + u(t - t_0)$, the *advection-diffusion equation*

$$\partial_t p + u\partial_x p = D\partial_x^2 p \tag{2.32}$$

is obtained.

The solutions of parabolic equations, as (2.31-32), are uniquely determined by initial and boundary conditions [Gardiner, 1983, Chap.5, Lasota and Mackey, 1994, Chap.11, Crank, 1975, Carslaw and Jaeger, 1959]. For instance, the transition probability (2.30) is a solution for the

equation (2.31) with initial condition $p(y,t_0 \mid x,t_0) = \delta(y-x)$ and conditions to infinity $\lim_{|x|\to\infty} p(y,t_0 \mid x,t_0) = 0$, $\lim_{|x|\to\infty} \partial_x p(y,t_0 \mid x,t_0) = 0$. The 1-dimensional probability density

$$p(x,t) = \int_{\mathbb{R}} p(x,t \mid x_0,t_0)p(x_0,t_0)dx_0$$

also verifies the equation (2.31), with initial condition $p(x,t_0) = p(x_0,t_0)$. This proves that the transition probability density, $p(x,t \mid x_0,t_0)$, is the Green function for the equation (2.31).

The continuity condition *i)* can be generalized as

$$i') \lim_{\Delta t\to 0} \frac{1}{\Delta t} \int_{|y-x|\geq\varepsilon} p(y,t+\Delta t \mid x,t)dy = W(y \mid x,t),$$

where W is the *jump probability* from the state x into the state y at time t [Gardiner, 1983, van Kampen, 1981]. Instead of (2.26) on obtains in the same conditions, *the integro-differential form of Chapman-Kolmogorov equation*,

$$\begin{array}{ll} \partial_t p(x,t \mid x_0,t_0) = & \\ -\nabla[\mathbf{A}p(x,t \mid x_0,t_0)] & a) \text{ Liouville} \\ +\nabla^2[\tilde{\mathbf{B}}\,(x,t)\,p(x,t \mid x_0,t_0)] & b) \text{ diffusion} \\ +\int_Y dy[W(x \mid y,t)p(y,t \mid x_0,t_0) - W(y \mid x,t)p(x,t \mid x_0,t_0)]. & c) \text{ master} \end{array} \tag{2.33}$$

When $W \geq 0$, almost everywhere (a.e.), then the integro-differential equation has solutions in the same initial and boundary conditions as the Fokker-Planck equation [Gardiner, 1983, Sect.3.7]. The equation (2.33) shows that generally the trajectory of a Markov process can be represented as the sum of a three functions: a continuous and derivable function, the determinist component, with a probability density function solution of the Liouville equation (2.33a), when $\tilde{B} \equiv \tilde{0}$ and $W \equiv 0$, a continuous and nowhere derivable function, with a probability density function solution of the diffusion equation (2.33b), when $A \equiv 0$ and $W \equiv 0$, and a jump function (discontinuous at all times), with a probability density function solution of the *master equation* (2.33c), when $A \equiv 0$ and $\tilde{B} \equiv \tilde{0}$. Under some conditions, the master equation approximates the diffusion equation [Gardiner, 1983, Cap.7] and, reciprocally, there are situations when the master equation can be approximated by a diffusion equation [van Kampen, 1981, Cap.10].

The asymptotic behavior of solutions is governed by the following theorem.

Theorem 2. [Gardiner, 1983, Sect.3.7]**:** *If the 1-dimensional stationary density is $p_s(x) \neq 0$ a.e., the state space Y is simply connected and the diffusion tensor $\tilde{B}$ and jump probability W are a.e. positively defined, then the solutions of integro-differential Chapmann-Kolmogorov equation* (2.33) *tend to the stationary solution p_s: $\|p(x,t) - p_s(x)\|_{L^1(Y)} \longrightarrow 0$, as $t \to \infty$.* □

2.3.2 Lagrangean framework

Gaussian white noise. The solution of the advection-diffusion equation (2.32) is of the form (2.30) where the mean value x_0 must be replaced by $x_0 + u(t-t_0)$. Because the coefficients (2.28-29) do not significantly change in small time intervals, all diffusion processes behave locally as a process described by advection-diffusion equation with constant coefficients (2.32) [Gardiner, 1983, Sect.3.5.2]. The transition dx between the states of this process, for infinitesimal time intervals dt, can be interpreted using the definitions (2.28-29) as a superposition between a translation udt and a fluctuation the mean of which is $\sqrt{\sigma^2} = \sqrt{2Ddt}$, i.e.,

$$dx\,(t) = udt + \sqrt{2D}\sqrt{dt}. \tag{2.34}$$

The second term in right hand of (2.34) is significant as compared with the first term only when $\sqrt{dt} = \mathcal{O}(dt)$. This order relation comes in conflict with the usual rules of differential calculus. That is why new rules, called "Itô calculus" are introduced. Heuristically, one looks for a stochastic process $\boldsymbol{\zeta}$, $\boldsymbol{\zeta} : \Omega \longmapsto Z^I$, $Z \subseteq \mathbb{R}$, $I \subseteq \mathbb{R}$, so that, at fixed time moments t, $\zeta_t(\omega) = \zeta(t, \omega)$ is a random variable describing the "fluctuation velocity" in (2.34),

$$\zeta(t, \omega)dt = \sqrt{dt}. \tag{2.35}$$

Using (2.35), the integral form of (2.34) becomes

$$x\left(t\right) = x_{_0} + \int\limits_{t_{_0}}^{t} udt + \sqrt{2D} \int\limits_{t_{_0}}^{t} \zeta(t, \omega)dt. \tag{2.36}$$

The solution of (2.36) corresponds to the process with transition probabilities verifying (2.32) only when it has the same mean value and variance, i.e.,

$$M[\zeta(t, \omega)] = 0 \tag{2.37}$$

and,

$$2D \int\limits_{t_{_0}}^{t} dt' \int\limits_{t_{_0}}^{t} dt'' M[\zeta(t', \omega)\zeta(t'', \omega)] = 2D(t - t_{_0}).$$

The last relation holds only when the correlation function of random variables $\zeta(t', \omega)$ and $\zeta(t'', \omega)$ has the singular form of Dirac function,

$$M[\zeta(t', \omega)\zeta(t'', \omega)] = \delta\left(t' - t''\right). \tag{2.38}$$

The process $\boldsymbol{\zeta}$ with zero mean and Dirac correlated, as required by (2.37-38), is called *Gaussian white noise* [van Kampen, 1981, Cap.8]. One remarks that, with the following change of variables

$$dw\left(t, \omega\right) = \zeta(t, \omega)dt, \tag{2.39}$$

and with $x_{_0} = 0$ and $u = 0$, from (3.12-13) on obtains the property w3) of the Wiener process defined in Section 2.1.2. Sometimes, the relation (2.39) is also used to define the white noise as "derivative" of the Wiener process [Lasota and Mackey, 1985, p.293], but this has only an intuitive meaning because, as we have seen in previous section the Wiener process, as all Gaussian processes, is not derivable.

Itô stochastic equation. The Itô calculus uses the properties of the Wiener process. From (2.39) and (2.35) one obtains $(dw(t, \omega))^2 = dt$, thus the new rule is that dt and $(dw)^2$ are of the same order of magnitude.

As defined by (2.12), *the Wiener process* is a Gaussian process with the transition probabilities given by (2.30), diffusion coefficient $D = 0.5$, and starting from $x_{_0} = 0$ at $t_{_0} = 0$. The representation as a two variables function, $w(t, \omega)$, $w : [0, \infty] \times \Omega \longmapsto Y$, and (2.39) allows the generalization of (2.34) as a *Itô stochastic differential equation*

$$dx(t) = a(x(t), t)dt + \tilde{b}(x(t), t)dw(t), \tag{2.40}$$

where for sake of simplicity we dropped the dependence on ω. If for every fixed ω there exists a unique solution of (2.40), $x(t) = X(w(t,\omega), x_0, t_0) = X(t, \omega, x_0, t_0)$, which satisfies the initial condition $x_0 = x(t_0)$, then the time function $x(t)$ is the trajectory of a stochastic process $\boldsymbol{\chi} : \Omega \times Y \longmapsto Y^{[0,\infty]}$, defined in the Cartesian product space $\Omega \times Y$.

Considering the density of initial states given by $p(x_0, t_0)$ and using the definition (2.18) we obtain the 1-dimensional density at t,

$$\begin{aligned} p(x,t) &= M_{\Omega\times Y}[\delta(x - X(t,\omega,x_0,t_0))] \\ &= \int_Y M_\Omega[\delta(x - X(t,\omega,x_0,t_0))]p(x_0,t_0)dx_0. \end{aligned}$$

Comparing (2.41) and (2.25), we find that the transition probability density of the process $\boldsymbol{\chi}$ is given by

$$p(x,t \mid x_0,t_0) = M_\Omega[\delta(x - X(t,\omega,x_0,t_0))]. \tag{2.41}$$

The average of a function $f(x)$, conditioned by the initial state (x_0, t_0), is an integral weighted with the previous transition density,

$$M[f(x) \mid x_0,t_0](t;x_0,t_0) = \int_Y f(x)p(x,t \mid x_0,t_0)dx = \int_\Omega P(d\omega) \int_Y f(x)\delta(x - X(t,\omega,x_0,t_0))dx = M_\Omega[f(X(t,\omega,x_0,t_0))],$$

thus,

$$M[f(x(t)) \mid x_0,t_0](t;x_0,t_0) = M_\Omega[f(X(t,\omega,x_0,t_0))]. \tag{2.42}$$

When the coefficients a and $\tilde{b}$ are determinist functions or endowed with special statistical properties (the so called "nonanticipative functions"), using (2.42), the coefficients of (2.28-29) of the Fokker-Planck equation can be related to the coefficients of the Itô equation (2.40) by

$$A(x,t) = a(x,t), \text{ and } \tilde{B}(x,t) = \tfrac{1}{2}\tilde{b}\tilde{b}^{\mathrm{T}}(x,t). \tag{2.43}$$

In this case, the probability density of the process $\boldsymbol{\chi}$ obeys a Fokker-Planck equation with coefficients (2.43) [Gardiner, 1983, chap.4].

The descriptions realized by the Fokker-Planck equation and probability densities as space-time functions are called *Eulerian statistics* and the description which uses the trajectories of fictitious particles given by Itô equation and averages over realizations as (2.42), are *Lagrangian statistics* [Avellaneda et al., 1991]. In Lagrangian statistics the definition *iii*) of the diffusion coefficients becomes

$$B_{ij}(x,t) = \frac{1}{2}\frac{d}{ds}(\tilde{\sigma}^2)_{ij}(t+s;x,t) \mid_{s=0}, \tag{2.44}$$

where $(\tilde{\sigma}^2)_{ij}(t+s;x,t)$ are the variance coefficients computed at $t+s$, over the trajectories starting from (x,t) (conditional averages computed with (2.42)) [Suciu, 2001].

2.3.3 Langevin equation

A useful example of Itô equation is the *Langevin equation*,

$$dx(t) = -kx(t)dt + \sqrt{2D}dw(t), \tag{2.45}$$

where $x \in \mathbb{R}$, $k > 0$ and $D > 0$. The solutions of (2.45) are trajectories of the Ornstein-Uhlenbeck process. Solving (2.45), in initial condition $x(t_0) = x_0$ [Gardiner, 1983, Sect.4.4.4], one obtains the mean value

$$M_\Omega[x(t)] = x_0 \exp(-k(t - t_0)), \tag{2.46}$$

and variance

$$\sigma^2(x(t)) = \frac{D}{k}[1 - \exp(-2k(t - t_0))]. \tag{2.47}$$

The coefficients of the corresponding Fokker-Planck equation are, from (2.43), $A = -kx$ and $B = D$. The equivalence between Langevin and Fokker-Planck equation can be rigorously proved [van Kampen, 1981, p.241]. Comparing with the Gaussian process with variance $\sigma^2 = 2D(t - t_0)$ linearly increasing in time and without stationary state, from (2.46-47) we can see that the Ornstein-Uhlenbeck process has a stationary state with zero mean and constant variance D/k. This process fulfils the conditions from Theorem 2 ($D > 0$), and all solutions tend to the stationary solution when $(t - t_0) \longrightarrow \infty$.

2.3.4 Asymptotic diffusive behavior

Both diffusion processes described by equations (2.31-32) and Ornstein-Uhlenbeck process have the remarkable *self-averaging property* [Avellaneda et al., 1991],

$$\lim_{t\to\infty} \frac{\sigma^2(t)}{t} = 2D^*, \tag{2.48}$$

where D^* is an *effective diffusion coefficient*.

The self-averaging property is common for diffusion processes. For diffusion processes described by equations (2.31-32) the effective coefficient (2.48) coincides with the diffusion coefficient D. For the Ornstein-Uhlenbeck process with variance given by (2.47), (2.48) gives $D^* = 0$, which shows that the diffusion ceases when the asymptotic stationary state is reached.

The definition (2.48) can be used to check the existence of *asymptotic diffusive behavior* for more complex processes described by Itô stochastic differential equation of form (2.40) even when the correspondence with a Fokker-Planck equation can not be established and the properties $i) - iii)$, defining diffusion processes, do not hold.

2.3.5 Green-Kubo formula

The following example is a process with nontrivial asymptotic diffusive behavior, used as model for equilibrium thermodynamics, entropy law and Gibs relation for "canonical ensemble" [Mackey, 1989, Suciu2000, Suciu2001].

Consider a physical system consisting of a single particle, of mass m and moving under the action of a Newtonian force perturbed with a white noise,

$$\frac{dx}{dt} = v, \ \frac{dv}{dt} = -\gamma v + \sqrt{2D}\zeta, \tag{2.49}$$

where x is the position and v the velocity of the particle, $(x, v) \in \mathbb{R}^2$, $\gamma > 0$, $D > 0$ and $dw(t) = \zeta(t)\, dt$. (It is to be noted that, in this example, the physical dimension of D is L^2/T^3, where L stands for length and T for time units, i.e. D is a diffusion coefficient for velocity). The second equation (2.49) is the Langevin equation and its solutions are the trajectories of

an Ornstein-Uhlenbeck process describing the particle velocity. The density of the transition probability tends to a Gaussian stationary density, according to Theorem 2, [Gardiner, 1983, Sect.3.8.4],

$$p(v, t - t_0 \mid v_0) \underset{t-t_0\to\infty}{\longrightarrow} p_s(v) = \left[\frac{2\pi D}{\gamma}\right]^{-\frac{1}{2}} \exp\left[-\frac{v^2}{\frac{2D}{\gamma}}\right]. \tag{2.50}$$

For each velocity realization, the first equation (2.49) provides a trajectory of the particle $x(t) = \int_{t_0}^{t} v(t')dt'$. The average over the velocity ensemble gives the displacements variance

$$\sigma^2(x(t)) = \int_{t_0}^{t}\int_{t_0}^{t} M\{[(v - M(v))(t')][(v - M(v))(t'')]\}dt'dt''. \tag{2.51}$$

The limit (2.48) can be written, using the L'Hopital rule from differential calculus, as the limit of the derivative of the variance σ^2,

$$D^* = \lim_{t\to\infty} \frac{\sigma^2(t)}{2t} = \lim_{t\to\infty} \frac{1}{2}\frac{d}{dt}\sigma^2(t). \tag{2.52}$$

From (2.51-52) on obtains

$$D^* = \lim_{t\to\infty} \int_{t_0}^{t} M\{[(v - M(v))(t')][(v - M(v))(t)]\}dt', \tag{2.53}$$

and using (2.50) one finds the value $D^* = D/\gamma^2$ for the effective diffusion coefficient (the physical dimensions of D^* are now L^2/T) [Suciu 2001]. Thus the process describing the position of a particle moving with a velocity described by the Ornstein-Uhlenbeck process has the self-averaging property and behaves asymptotically diffusive.

The stationary density from (2.50) describing the equilibrium state has zero mean value, $[M(v)]^e = 0$ and the variance $[M(v^2)]^e = \int_{\mathbb{R}} v^2 p_s(v)dv = D/\gamma$. From (2.46), the mean value at $t''$of the velocity process staring at t' from v' is $\int_{\mathbb{R}} v'' p(v'', t'' - t' \mid v')dv'' = v' \exp[-\gamma(t'' - t')]$. The velocity correlation in the equilibrium state can be computed as

$$\begin{aligned}\{M[v(t')v(t'')]\}^e &= \int_{\mathbb{R}}\int_{\mathbb{R}} v'v''p(v'', t'' - t' \mid v')p_s(v')dv'dv'' \\ &= \int_{\mathbb{R}} v'p_s(v')dv' \int_{\mathbb{R}} v''p(v'', t'' - t' \mid v')dv'' \\ &= \exp[-\gamma(t'' - t')] \int_{\mathbb{R}} (v')^2 p_s(v')dv'.\end{aligned}$$

Thus we have the equilibrium correlation given by

$$\{M[v(t')v(t'')]\}^e = \frac{D}{\gamma}\exp[-\gamma(t'' - t')]. \tag{2.54}$$

Replacing the correlation from (2.53) with (2.54) we find that the effective diffusion coefficient can be derived from the equilibrium correlation with relation

$$D^* = \lim_{t\to\infty} \int_{t_0}^{t} \{M[v(t')v(t)]\}^e dt' = \frac{D}{\gamma^2}. \tag{2.55}$$

This is a *Green-Kubo formula* [Evans and Morris, 1990, chap.4] for transport coefficients.

The difference with respect to the Ornstein-Uhlenbeck positions process, described by the Langevin equation (2.45), is that the process described by (2.49), where the velocity is an Ornstein-Uhlenbeck process, has a nontrivial stationary state. In the stationary state the process behaves asymptotically diffusive with an effective diffusion coefficient given by (2.55). This example shows that the integral of velocity correlation (2.53) must be finite for large times, as a *necessary condition* for diffusive behavior. Also, the exponential decay of correlation (2.54), was a *sufficient condition* for the existence of the finite diffusion coefficient D^*.

The velocity correlation can be characterized by the *correlation time* τ_c,

$$\tau_c = \lim_{t\to\infty} \int_{t_0}^{t} \frac{\{M[v(t')v(t)]\}^e}{[M(v^2)]^e} dt'.$$

A finite correlation time is a necessary condition for an asymptotic diffusive behavior. In the case described by (2.29), the correlation time is $\tau_c = 1/\gamma$ and we have the relation $D^* = [M(v^2)]^e \tau_c$.

2.4 Diffusion by continuous movements

Taylor [1921] derived a process with asymptotic diffusive behavior, induced by a space random velocity field, as model for turbulent diffusion in atmosphere. This is a pioneering work in the theory of stochastic processes (it was only in '30 years that the mathematical bases of modern theory of diffusion processes where published by Kolmogorov). The paper of Taylor also was the staring point for a vast literature on turbulent diffusion, transport in porous media and plasma physics [Suciu, 2001].

We choose "Diffusion by continuous movements" as title for this Section, the same as the title of original paper of Taylor, with the intention to underline the strong continuity properties required by the mathematical theory. Because in many works on asymptotic diffusion the presentation of mathematical theory is incomplete and can be found only in a cumbersome way, following cross references over hundreds of papers published in the last three decades, we present here a minimal mathematical frame based on definitions and notions from previous sections of this report.

2.4.1 Movement in random fields.

The problem can be formulated as it follows. Let $\boldsymbol{\vartheta} : \Omega \longmapsto Y_V^{\Lambda}$, $Y_V \subseteq \mathbb{R}^3$, $\Lambda \subseteq \mathbb{R}^3$, be a random field, with a range of parameters in physical space. We make the following hypotheses about the properties of the random field:

H1) For every fixed $\omega \in \Omega$ the sample $V^{(\omega)}$, $V^{(\omega)} : \Lambda \longmapsto Y_V$, is a nonsingular vector field.

H2) For all the samples $\omega \in \Omega$ the functions $V^{(\omega)}(x)$, $V^{(\omega)} : \Lambda \longmapsto Y_V$, and their derivatives are continuous with respect to the space variable x.

The nonsigularity of the samples of the velocity files (*H1*) means that the field can not vanish. The continuity hypothesis *H2)* ensures the existence of a function of x and ω defined by the samples of the field, $V(x,\omega) = V^{(\omega)}(x)$, measurable with respect to (x,ω) which can be an

equivalent representation of the field $\boldsymbol{\vartheta}$. The measurability gives the property of commutation between the space integration and stochastic average

$$\int_{\Lambda} M_{\Omega}[V(x,\omega)]dx = M_{\Omega}[\int_{\Lambda} V(x,\omega)dx],$$

which is often used in applications [Suciu, 2001, Wentzell, 1981] (we will use it in the next Section, to derive the connection between Lagrangian and Eulerian correlations). Because the function $V(x,\omega)$ is defined by the sample $V^{(\omega)}$, using it in (2.17) one obtains a hierarchy of consistent distributions which define the distribution of a random field, in condition of the Kolmogorov theorem, as we have seen in Section 2.1.3. In these conditions the two variable function representation $V(x,\omega)$ is equivalent with the random field $\boldsymbol{\vartheta}$ [Iosifescu and Tăutu, 1973, p. 164, Suciu, 2001, p. 19].

Under the hypotheses *H1)* and *H2),* all the realizations ω of the random field $\boldsymbol{\vartheta}$ generate differentiable dynamical systems $\{S_t^{(\omega)}\}_{t\in\mathbb{R}}$, with trajectories in $Y_x \subseteq \mathbb{R}^3$, $x^{(\omega)}(t;x_0,t_0) = S_{t-t_0}^{(\omega)}(x_0) = X(t,\omega,x_0,t_0)$ [Arnold, 1978]. For physical reasons, the space Y_x, on which the trajectories are defined, and the space Λ, on which the velocity realizations are defined, coincide but we will use different notation to prevent confusions. The trajectories $x^{(\omega)}$ are solutions of the differentiable system

$$\frac{dx^{(\omega)}}{dt} = V^{(\omega)}(x^{(\omega)}). \tag{2.56}$$

The relation (2.56) may represent the description of a "fluid particle", as in continuum mechanics, or even of a real particle. The infinite set of dynamical systems corresponding to the realizations of the random field forms a statistical ensemble. The 1-dimensional density has the meaning of a concentration field, $p \equiv c$. When the physical system contains N particles, then $\int_{Y_x} c(x,t)dx = N$, and the normalization condition for 1-dimensional densities, $\int_{Y_x} p(x,t)dx = 1$, implies that concentration and probability density are related by

$$c(x,t) = N\ p(x,t). \tag{2.57}$$

The stochastic model of the previous statistical ensemble is the process $\boldsymbol{\chi} : \Omega \times Y_x \longmapsto Y_x^{\mathbb{R}}$, where, for fixed $\omega \in \Omega$ and $x_0 \in Y_x$, $\boldsymbol{\chi}(\omega,x_0) = X(t,\omega,x_0,t_0)$ is a trajectory of the dynamical system $\{S_t^{(\omega)}\}_{t\in\mathbb{R}}$. We consider that the space of elementary events (for random field) is organized as a probability space $(\Omega,\mathcal{A},P)$, endowed with a measure P, and the state of initial positions Y_x, is a probability space $(Y_x,\mathcal{B},P_x)$, with σ-algebra Borel $\mathcal{B}$, and probability measure P_x, defined by

$$P_x(B) = \int_B c(x_0,t_0)dx_0, \text{ for all sets } B \in \mathcal{B},$$

where the density $c(x_0,t_0)$ is given by the initial concentration. Then, we define the measure of the probability space $\Omega \times Y_x$ (of elementary events) of the process $\boldsymbol{\chi}$ as a normalized product measure, PP_x, and the stochastic average (2.3) becomes

$$M_{\Omega\times Y_x}(f) = \int_{\Omega} P(d\omega) \int_{Y_x} f(\omega,x_0)c(x_0,t_0)dx_0 = M_{\Omega}[\int_{Y_x} f(\omega,x_0)c(x_0,t_0)dx_0].$$

In the sequel, the shortcut "the process $\boldsymbol{\chi}$" refers to this model. The properties of $\boldsymbol{\chi}$ allows us to use the definitions and results concerning random variables (Section 2.1), Markov processes (Section 2.2) and diffusion processes (Section 2.3).

The dynamical system is a determinist process in $Y_x \subseteq \mathbb{R}^3$, with a "degenerate" transition probability [Suciu, 2001],

$$p^{(\omega)}(x, t \mid x_0, t_0; \omega) = \delta(x - X(t, \omega, x_0, t_0)), \tag{2.58}$$

which is a solution of the Liouville equation

$$\partial_t p^{(\omega)} + \nabla_x (V^{(\omega)} p^{(\omega)}) = 0, \tag{2.59}$$

with initial condition $p^{(\omega)}(x, 0 \mid x_0, 0; \omega) = \delta(x - x_0)$ [Gardiner, 1983, Sect. 4.3.4].

When the probability density of initial positions is given by the concentration $c(x_0, t_0)$, then the concentration at t (equal to 1-dimensional density, according (2.57)), in a single realization ω of the velocity field, is given by (2.25) in the form

$$c^{(\omega)}(x, t) = \int\limits_{Y_x} p^{(\omega)}(x, t \mid x_0, t_0; \omega) c(x_0, t_0) dx_0, \tag{2.60}$$

and is also a solution of (2.59). We recognize in relation (2.60) the definition of "concentration in a single realization of the Darcian velocity field" used the Lagrangian framework (see for instance [Dagan and Fiori, 1997], and eq. 1 in [Vanderborght, 2001]). Because (2.60) is a solution of the Liouville equation (2.59), there is no diffusion, i.e. the initial concentration $c(x_0, t_0)$ "is not diluted", as pointed out in [Vanderborght, 2001]. In a single realization of the velocity field the initial concentration is only advected with the velocity $V^{(\omega)}$, without any deformation of the concentration profile. Even when the effect of a diffusion superposed on the advection process is present in trajectories X, the relation (2.60) alone is not complete. It is necessary to perform an average over the realizations of the diffusion process to obtain the real concentration field, as we shall show in the next section. In this way, (2.60) becomes identical with the equation (5) in [Vanderborght, 2001]. We also can see that, as long as no diffusion is considered, equation (1) and (5) from [Vanderborght, 2001] are both identical with (2.60).

The concentration field corresponding to a fluid particle moving according to the process $\boldsymbol{\chi}$ is, from (2.57) and (2.18), the 1-dimensional density obtained as an average over the probability space $\Omega \times Y_x$,

$$\begin{aligned} c(x, t) &= M_{\Omega \times Y_x}[\delta(x - X(t, \omega, x_0, t_0))] \\ &= \int\limits_{Y_x} M_\Omega[\delta(x - X(t, \omega, x_0, t_0))] c(x_0, t_0) dx_0 \\ &= \int\limits_{Y_x} p(x, t \mid x_0, t_0) c(x_0, t_0) dx_0. \end{aligned} \tag{2.61}$$

where $p(x, t \mid x_0, t_0)$ is a transition probability as that defined by a relation of form (2.41), with the difference that now Ω is the probability space on which the random field $\boldsymbol{\vartheta}$ is defined, while in (2.41) it was the probability space of the Wiener process. Comparing with (2.60), we remark that the second line in (2.61) is the average over Ω of the concentration in a single realization $c^{(\omega)}(x, t)$, i.e. $c(x, t) = M_\Omega[c^{(\omega)}(x, t)]$. Thus, the equation (2.61) is the same with the equation (10) in [Vanderborght, 2001], when no local diffusion is considered.

The concentration correlation and variance can also be obtained as average over Ω. Using (2.60) and (2.58) we obtain

$$M_\Omega[c^{(\omega)}(x_1,t_1)c^{(\omega)}(x_2,t_2)] - M_\Omega[c^{(\omega)}(x_1,t_1)]M_\Omega[c^{(\omega)}(x_2,t_2)] =$$
$$\int\limits_{Y_x}\int\limits_{Y_x} M_\Omega[\delta(x_1 - X(t_1,\omega,x_{01},t_{01}))\delta(x_2 - X(t_2,\omega,x_{02},t_{02}))]c(x_{01},t_{01})c(x_{02},t_{02})dx_{01}dx_{02}$$
$$-c(x_1,t_1)c(x_2,t_2).$$

The first term in this relation can also be written as

$$M_{\Omega\times Y_x}[\delta(x_1 - X(t_1,\omega,x_{01},t_{01}))\delta(x_2 - X(t_2,\omega,x_{02},t_{02}))] = p(x_1,t_1;x_2,t_2) =$$
$$\int\limits_{Y_x}\int\limits_{Y_x} p(x_1,t_1;x_2,t_2|x_{01},t_{01};x_{02},t_{02})p(x_{01},t_{01};x_{02},t_{02})dx_{01}dx_{02},$$

where we used the definition (2.17) of 2-dimensional density and the definition (2.21) of conditional probability. When $t_{01} = t_{02} = t_0$, where t_0 is the initial moment, then the 2-dimensional density of the determinist initial concentration factorizes, $p(x_{01},t_0;x_{02},t_0) = c(x_{01},t_0)c(x_{02},t_0)$, and we finally obtain the concentration correlation function

$$M_\Omega[c^{(\omega)}(x_1,t_1)c^{(\omega)}(x_2,t_2)] - M_\Omega[c^{(\omega)}(x_1,t_1)]M_\Omega[c^{(\omega)}(x_2,t_2)] = \tag{2.62}$$
$$\int\limits_{Y_x}\int\limits_{Y_x} p(x_1,t_1;x_2,t_2|x_{01},t_0;x_{02},t_0)c(x_{01},t_0)c(x_{02},t_0)dx_{01}dx_{02} - c(x_1,t_1)c(x_2,t_2),$$

which corresponds to equation (23) from [Vanderborght, 2001]. For $t_1 = t_2$, (2.62) gives the variance of the concentration field.

The hypotheses *H1*) and *H2*), allow us to describe the movement in random fields by the trajectories of the dynamical system (2.56) and to use the Lagrangian statistics to look for the existence of the diffusive behavior. Because the particle moves along the trajectories of a differentiable dynamical system $\{S_t^{(\omega)}\}_{t\in\mathbb{R}}$, for each realization ω of the random field, the process $\boldsymbol{\chi}$ is continuous, i.e. it verifies the property *i*) of diffusion processes (see section 2.3.1). The coefficients (2.28-29) of the Fokker-Planck equation (equivalent with diffusion properties *ii*) and *iii*)) can be computed using the conditional averages of the form (2.42).

For fixed ω, the values of the function $V(x,\omega)$ in points x lying on the trajectory of the process $\boldsymbol{\chi}$, which starts in the initial point x_0, define the function $V(t,\omega,x_0,t_0) = V(X(t,\omega,x_0,t_0),\omega)$, and the solution of (2.56) is

$$(X(t,\omega,x_0,t_0) - x_0) = \int\limits_{t_0}^{t} dsV(s,\omega,x_0,t_0). \tag{2.63}$$

The drift coefficient (2.28), conditioned by a state (x_0,t_0), is obtained using (2.63) and conditional average (2.42), as

$$A(x_0,t_0) = \frac{d}{dt}M_\Omega[(X(t,\omega,x_0,t_0) - x_0)] \mid_{t=t_0}$$
$$= \frac{d}{dt}\{\int\limits_{t_0}^{t} dsM_\Omega[V(s,\omega,x_0,t_0)]\} \mid_{t=t_0}.$$

Thus, the local mean velocity, $\overline{V}(x_0,t_0) = M_\Omega[V(t_0,\omega,x_0,t_0)]$, defines the drift coefficient of the Fokker-Planck equation,

$$A(x_0,t_0) = \overline{V}(x_0,t_0). \tag{2.64}$$

The diffusion coefficients can also be computed using (2.63) and the Lagrangian definition (2.44). The tensor of displacements' variance, conditioned by the state (x_0,t_0), is

$$\begin{aligned}\tilde{\sigma}^2(t;x_0,t_0) = \int_{t_0}^{t} ds \int_{t_0}^{t} ds' \{ & M_\Omega[V(s,\omega,x_0,t_0)V(s',\omega,x_0,t_0)] \\ & - M_\Omega[V(s,\omega,x_0,t_0)]M_\Omega[V(s',\omega,x_0,t_0)]\},\end{aligned} \tag{2.65}$$

and from (2.44) we obtain the diffusion tensor

$$\tilde{B}(x_0,t_0) = \frac{1}{2}\frac{d}{dt}\tilde{\sigma}^2(t;x_0,t_0)\mid_{t=t_0} = \tilde{0}. \tag{2.66}$$

The coefficients (2.64) and (2.66) have the same form in all points (x,t), and the Fokker-Planck equation take the form (2.33a) of the Liouville equation,

$$\partial_t c(x,t) + \nabla_x(\overline{V}(x,t)c(x,t)) = 0. \tag{2.67}$$

The equation (2.67) is just the average over velocity realizations of the Liouville equation (2.59) associated with dynamical systems in each realization of the field. Since the coefficients $\tilde{B}$ defined by local time derivative (2.44) vanish, there is no local diffusive behavior for the considered particle moving in random velocity field.

2.4.2 The existence of asymptotic diffusive behavior

When the asymptotic diffusive behavior property (2.48) holds, one expects that, at large scale, the process $\boldsymbol{\chi}$, described locally by the Liouville equation (2.67), may be approximated by a diffusion equation. Also, one expects that behavior in single realization is similar with the average over realizations of the random field. Only in these conditions, the stochastic model predicts the evolution of the concentration field for transport in heterogeneous media. We will see that even when the asymptotic diffusive behavior can be proved, the existence of an effective diffusion equation and the asymptotic diffusive behavior in all realizations of the field still remains open problems.

In order to check the asymptotic diffusive behavior, one uses the Lagrangian correlation of the velocity field, defined by the integrand in the expression of variance (2.65). Because we have proved in the previous section that there is no local diffusive behavior, we define now the tensor function of *Lagrangian correlation* as a complete average over the entire probability space $\Omega \times Y_x$, of the process $\boldsymbol{\chi}$,

$$\begin{aligned}\tilde{R}_L(s,s') = & M_{\Omega\times Y_x}[V(s,\omega,x_0,t_0)V(s',\omega,x_0,t_0)] - \\ & M_{\Omega\times Y_x}[V(s,\omega,x_0,t_0)]M_{\Omega\times Y_x}[V(s',\omega,x_0,t_0)].\end{aligned} \tag{2.68}$$

With (2.68) the variance (2.65), averaged over Y_x, becomes

$$\tilde{\sigma}^2(t) = \int_{t_0}^{t} ds \int_{t_0}^{t} \tilde{R}_L(s,s')ds'. \tag{2.69}$$

In particular, when the Lagrangian correlation is a *homogeneous* time function, $\tilde{R}_L(s,s') = \tilde{R}_L(\tau)$, where $\tau = s - s'$, and $\tilde{R}_L$ is an *even function* of τ, $\tilde{R}_L(-\tau) = \tilde{R}_L(\tau)$, (2.69) can be written as

$$\tilde{\sigma}^2(t) = 2\int_0^t (t-\tau)\tilde{R}_L(\tau)d\tau.$$

This is the well known "Taylor formula" [Monin and Yaglom, 1965, eq. (9.30′)].

The asymptotic diffusive behavior (2.48) requires the order relation $\sigma^2 = \mathcal{O}(t)$ for $t \longrightarrow \infty$. From (2.69) we find the necessary condition

$$\lim_{t\to\infty}\int_{t_0}^t \tilde{R}_L(s,s')ds' < \infty,$$

the same as the condition for the process presented in Section 2.3.5. Similarly with (2.52), the condition (2.48) defines the effective diffusion coefficient by

$$\tilde{D}^* = \lim_{t\to\infty}\frac{\tilde{\sigma}^2(t)}{2t} = \lim_{t\to\infty}\frac{1}{2}\frac{d}{dt}\tilde{\sigma}^2(t) = \lim_{t\to\infty}\int_{t_0}^t \tilde{R}_L(t,s')ds', \tag{2.70}$$

i.e. the effective coefficient is given by a Green-Kubo type relation.

In these conditions *one asserts* that it is possible to approximate asymptotically the advection equation (2.59) with the advection diffusion equation

$$\partial_t\ c(x,t) + V^*\nabla c(x,t) = \tilde{D}^*\nabla^2 c(x,t). \tag{2.71}$$

where $V^* = M_{Y_x}[\overline{V}(x_0,t_0)] = M_{\Omega\times Y_x}[V(t_0,\omega,x_0,t_0)]$ is the mean velocity. This is the general framework of all theories of "Lagrangian passive transport in turbulent fields" and Green-Kubo type approaches from statistical mechanics [Taylor, 1921, Monin and Yaglom, 1965, chap.9]. One remarks that while the existence of derivatives (2.28-29) determines the Fokker-Planck equation, the existence of the limit (2.70) does not ensure the existence of the diffusion equation as an asymptotic approximation of exact Liouville equation (2.67). Also, due to the absence of local diffusion, in this model the asymptotic diffusive behavior in single realization makes no sense. Indeed, using (2.63) and (2.65), without average over realizations, $\sigma^2 = \mathcal{O}(t^2)$ for $t \longrightarrow \infty$.

In experiments, the velocity field is measured in fixed space points, which corresponds to an Eulerian description. To pass to an Eulerian description we write Lagrangian correlation (2.68) as

$$\tilde{R}_L(s,s') = \int_{Y_x}\int_{Y_x} dxdx' M_{\Omega\times Y_x}[\delta(x - X(s,\omega,x_0,t_0))\delta(x' - X(s',\omega,x_0,t_0))V(x,\omega)V(x',\omega)] \tag{2.72}$$

$$-\int_{Y_x} dx M_{\Omega\times Y_x}[\delta(x - X(s,\omega,x_0,t_0))V(x,\omega)]\int_{Y_x} dx' M_{\Omega\times Y_x}[\delta(x' - X(s',\omega,x_0,t_0))V(x',\omega)].$$

In (2.72) we considered the extensions to $\mathbb{R}^3$ of function $V(x,\omega)$, $V(x,\omega):\Lambda\longmapsto Y_V$ defined by $V(x,\omega)=0$ for $x\notin Y_x$ (we remember that Λ and Y_x coincide), we used the commutation between the space integral and stochastic average given by *H2)*, and the Dirac function to write

$$V(s,\omega,x_0,t_0)=\int\limits_{\mathbb{R}^3}\delta(x-X(s,\omega,x_0,t_0))V(x,\omega)dx=\int\limits_{Y_x}\delta(x-X(s,\omega,x_0,t_0))V(x,\omega)dx.$$

The *Corsin Conjecture* (in the form used by Saffman [1969] in problems of turbulent diffusion) says that the averages over $\Omega\times Y_x$ factorizes as it follows:

$$\begin{array}{l}M_{\Omega\times Y_x}[\delta(x-X(s,\omega,x_0,t_0))\delta(x'-X(s',\omega,x_0,t_0))V(x,\omega)V(x',\omega)]=\\ M_{\Omega\times Y_x}[\delta(x-X(s,\omega,x_0,t_0))\delta(x'-X(s',\omega,x_0,t_0))]M_{\Omega\times Y_x}[V(x,\omega)V(x',\omega)],\end{array}\tag{2.73}$$

and

$$\begin{array}{l}M_{\Omega\times Y_x}[\delta(x-X(s,\omega,x_0,t_0))V(x,\omega)]=M_{\Omega\times Y_x}[\delta(x-X(s,\omega,x_0,t_0))]M_{\Omega\times Y_x}[V(x,\omega)],\\ M_{\Omega\times Y_x}[\delta(x'-X(s',\omega,x_0,t_0))V(x',\omega)]=M_{\Omega\times Y_x}[\delta(x'-X(s',\omega,x_0,t_0))]M_{\Omega\times Y_x}[V(x',\omega)].\end{array}\tag{2.74}$$

According to (2.17), the first factor in (2.73) defines the 2-dimensional density of the process $\boldsymbol{\chi}$

$$p(x,s;x',s')=M_{\Omega\times Y_x}[\delta(x-X(s,\omega,x_0,t_0))\delta(x'-X(s',\omega,x_0,t_0))],\tag{2.75}$$

and the first factors in (2.74) define the 1-dimensional density

$$p(x,s)=M_{\Omega\times Y_x}[\delta(x-X(s,\omega,x_0,t_0))].\tag{2.76}$$

The second factor in (2.73) can be written as

$$\begin{aligned}M_{\Omega\times Y_x}[V(x,\omega)V(x',\omega)]&=M_\Omega[V(x,\omega)V(x',\omega)]\int\limits_{Y_x}c(x_0,t_0)dx_0=M_\Omega[V(x,\omega)V(x',\omega)]\\&=\int\limits_{Y_V}\int\limits_{Y_V}vv'M_\Omega[\delta(v-V(x,\omega))\delta(v'-V(x',\omega))]dvdv',\end{aligned}$$

where we used the commutation property *H2)* and the Dirac function, as in (2.72). Introducing the 2-dimensional density of the field $\boldsymbol{\vartheta}$, defined by (2.17),

$$p_v(v,x;v',x')=M_\Omega[\delta(v-V(x,\omega))\delta(v'-V(x',\omega))],$$

we have

$$M_{\Omega\times Y_x}[V(x,\omega)V(x',\omega)]=\int\limits_{Y_V}\int\limits_{Y_V}vv'p_v(v,x;v',x')dvdv'.\tag{2.77}$$

Similarly, for the second factors in (2.74) we obtain:

$$\begin{array}{l}M_{\Omega\times Y_x}[V(x,\omega)]=\int\limits_{Y_V}vp_v(v,x)dv=\overline{V}(x),\\ M_{\Omega\times Y_x}[V(x',\omega)]=\int\limits_{Y_V}v'p_v(v',x')dv'=\overline{V}(x').\end{array}\tag{2.78}$$

Using (2.73-78) in (2.72), we finally obtain

$$\tilde{R}_L(s,s') = \int\limits_{Y_x}\int\limits_{Y_x} dxdx' p(x,s;x',s')\tilde{R}_E(x,x'), \tag{2.79}$$

where $\tilde{R}_E$ is the *Eulerian correlation* tensor

$$\tilde{R}_E(x,x') = \int\limits_{Y_V}\int\limits_{Y_V} [vv' - \overline{V}(x)\overline{V}(x')]p_v(v,x;v',x')dvdv'. \tag{2.80}$$

To establish the connection between the Lagrangian and Eulerian descriptions by means of relations of the form (2.79) is one of the main aims in modeling turbulent diffusion and transport processes in heterogeneous porous media [Isichenko, 1992, Reuss and Misguish, 1996].

2.4.3 Diffusion in random fields and macrodispersion

Sometimes at *local scales* the transport processes in natural porous media are well described by advection-diffusion equations but at larger, *global scales,* the diffusion coefficients experimentally derived, during the calibration of the model, present an apparent increase as compared to the local ones. This is the so-called "scale effect" [Saffman, 1969, Fried, 1975]. This effect can be explained by the heterogeneity of the aquifer properties. The main question is: may the transport be globally described by an effective diffusion equation? This could be the case when the variability of the Darcy velocity produces a hydrodynamic dispersion of the solute which, at a suitable large scale, behaves similarly to a diffusion process. This phenomenon is sometimes called "macrodispersion" and the corresponding effective diffusion coefficient "macrodispersion coefficient" [Dagan, 1989]. The macrodispersion problem requires a two scale description: the Darcy scale where the process of local diffusion is important and a macrodispersion scale, where the solute transport is dominated by the variability of the advection velocity. A stochastic two-scale model can be obtained considering a diffusion process in random velocity field.

Let the velocity field be described by the random function $\boldsymbol{\vartheta} : \Omega_V \longmapsto Y_V^{\Lambda}$, $Y_V \subseteq \mathbb{R}^3$, $\Lambda \subseteq \mathbb{R}^3$, and consider the Wiener process $\mathbf{w} : \Omega_w \longmapsto Y_w^{[0,\infty]}$, $Y_w \subseteq \mathbb{R}^3$. For every fixed $\omega_{_V} \in \Omega_V$ one considers the Itô equation

$$dx^{(\omega_{_V})}(t) = V(x^{(\omega_{_V})}(t), \omega_{_V})dt + (2D)^{\frac{1}{2}}dw(t). \tag{2.81}$$

If there is a unique solution of (2.81), for every trajectory of $\mathbf{w}$ and sample of $\boldsymbol{\vartheta}$, $x^{(\omega_{_V},\omega_w)}(t) = X(t,\omega_w,\omega_{_V},x_{_0},t_{_0})$, with the initial condition $x_{_0} = x^{(\omega_{_V}\omega_w)}(t_{_0})$, then using $X(t,\omega_w,\omega_{_V},x_{_0},t_{_0})$ one defines a stochastic process $\boldsymbol{\chi}$, in the direct product probability space, $\boldsymbol{\chi} : \Omega_V \times \Omega_w \times Y_x \longmapsto Y_x^{[0,\infty]}$, $Y_x \subseteq \mathbb{R}^3$. To do that, the nonsingularity (*H1*) and continuity (*H2*) properties of $\boldsymbol{\vartheta}$, from Section 2.4.1, should be supposed.

The concentration is given by the 1-dimensional density of the process $\boldsymbol{\chi}$,

$$c(x,t) = M_{\Omega_V\times\Omega_w\times Y_x}[\delta(x - X(t,\omega_w,\omega_{_V},x_{_0},t_{_0}))]. \tag{2.82}$$

The definition (2.82) generalizes (2.61-62) from Section 2.4.1. So, (2.61) becomes identical with (10) and (2.62) generalizes (23) from [Vanderborght, 2001].

To simplify the computations we suppose $M_{\Omega_V}[V(x,\omega_{_V})]=0$. Using the integral form of (2.81) and Itô calculus (the "correlation formula" in [Gardiner, 1983, eq. (4.242)]), one obtains the variance of the process $\boldsymbol{\chi}$, as average over the probability space $\Omega_V\times\Omega_w\times Y_x$,

$$\begin{aligned}\tilde{\sigma}^2(t)= \;& 2D(t-t_{_0})+\\ & \int\limits_{t_{_0}}^{t} ds \int\limits_{t_{_0}}^{t} ds' M_{\Omega_V\times\Omega_w\times Y_x}[V(s,\omega_w,\omega_{_V},x_{_0},t_{_0})V(s',\omega_w,\omega_{_V},x_{_0},t_{_0})].\end{aligned} \tag{2.83}$$

At finite times the second term from (2.83) behaves as $(t-t_{_0})^2$, which is an explanation of the "scale effect". Indeed, the effective diffusion coefficients are $\tilde{D}^*=\tilde{\sigma}^2(t)/(2t)\sim t$ and increase with travel time.

The Lagrangian correlation under the integral in (2.83) is an average over the product probability space $\Omega_V\times\Omega_w\times Y_x$. Using the Dirac function, we have

$$\begin{aligned}&\tilde{R}_L(s,s')=\\ &M_{\Omega_V\times\Omega_w\times Y_x}[\int\limits_{Y_x}\int\limits_{Y_x} dxdx' V(x,\omega_{_V})V(x',\omega_{_V})\delta(x-X(s,\omega_w,\omega_V,x_{_0},t_{_0}))\\ &\delta(x'-X(s',\omega_w,\omega_{_V},x_{_0},t_{_0})]=\int\limits_{Y_x}\int\limits_{Y_x} dxdx' M_{\Omega_V}\{V(x,\omega_{_V})V(x',\omega_{_V})\\ &M_{\Omega_w\times Y_x}[\delta(x-X(s,\omega_w,\omega_V,x_{_0},t_{_0}))\delta(x'-X(s',\omega_w,\omega_{_V},x_{_0},t_{_0})]\}.\end{aligned} \tag{2.84}$$

When one uses the Corsin conjecture in average over $\omega_{_V}$, the second factor from (2.84) defines the 2-dimensional probability of the process $\boldsymbol{\chi}$:

$$\begin{aligned}&p(x,s;x',s')=\\ &M_{\Omega_V\times\Omega_w\times Y_x}[\delta(x-X(s,\omega_w,\omega_{_V},x_{_0},t_{_0}))\delta(x'-X(s',\omega_w,\omega_{_V},x_{_0},t_{_0}))].\end{aligned} \tag{2.85}$$

The first factor from (2.84) gives the Eulerian correlation (2.80). From (2.80), (2.85) and (2.84) one obtains the relation

$$\tilde{R}_L(s,s')=\int\limits_{Y_x}\int\limits_{Y_x} dxdx' p(x,s;x',s')\tilde{R}_E(x,x'), \tag{2.86}$$

which gives the Lagrangian correlation as a space average of the Eulerian correlation, over the solute plume and weighted with the 2-dimensional density of the process $\boldsymbol{\chi}$.

If the Lagrangian correlation $\tilde{R}_L$ decreases to zero fast enough as $t\to\infty$, then the process $\boldsymbol{\chi}$ behaves asymptotically diffusive and from (2.48) it follows

$$\tilde{D}^*=D\tilde{1}+\lim_{t\to\infty}\int\limits_{t_{_0}}^{t} ds'\tilde{R}_L(t,s'). \tag{2.87}$$

When the coefficients (2.87) exist, one asserts that for large times the concentration (2.82) is described by the diffusion equation

$$\partial_t c(x,t)=\tilde{D}^*\nabla^2 c(x,t).$$

The Lagrangian correlation from (2.84), is an average over Ω_w of the correlation in the absence a of local diffusion. Thus, the effective diffusion coefficients for diffusion in random fields are not the sum between the local coefficient D and the effective coefficient computed in

the case without local diffusion (2.70). Because of the Gaussian form of distributions of the Wiener process, implicitly considered in (2.85), local diffusion make the decay of $\tilde{R}_L$ faster and enhances diffusive behavior [Suciu, 2001].

In a single realization of the velocity field, dropping the average over $\omega_{_V}$ in (2.84), we have

$$\tilde{R}_L^{(\omega_{_V})}(s,s') = \int\limits_{Y_x}\int\limits_{Y_x} dxdx' p^{(\omega_{_V})}(x,s;x',s')V(x,\omega_{_V})V(x',\omega_{_V}),$$

where

$$p^{(\omega_{_V})}(x,s;x',s') = M_{\Omega_w\times Y_x}[\delta(x-X(s,\omega_w,\omega_{_V},x_0,t_0))\delta(x'-X(s',\omega_w,\omega_{_V},x_0,t_0))]$$

is the 2-dimensional density of the diffusion process in the realization $\omega_{_V}$ of the random field. Thus, the Lagrangian correlation in a single realization $\tilde{R}_L^{(\omega_{_V})}$ is given by a space average over the solute plume (i.e. weighted with the probability density $p^{(\omega_{_V})}$ describing the diffusion process in a single realization). It is straightforward that the correlation (2.84) is the average over realizations of the correlations in individual realizations,

$$\tilde{R}_L(s,s') = M_{\Omega_{_V}}[\tilde{R}_L^{(\omega_{_V})}(s,s')].$$

The effective diffusion coefficient in a single realization is

$$\tilde{D}^{*(\omega_{_V})} = D\tilde{1} + \lim_{t\to\infty}\int\limits_{t_0}^{t} ds'\tilde{R}_L^{(\omega_{_V})}(t,s').$$

and comparing with (2.87) we find the relation

$$\tilde{D}^* = M_{\Omega_{_V}}[\tilde{D}^{*(\omega_{_V})}]. \tag{2.88}$$

Due to (2.88), the existence of self-averaging in all realizations implies the self-averaging of the process $\boldsymbol{\chi}$ describing diffusion in random fields. Also, when the process $\boldsymbol{\chi}$ has the self-averaging property, then all the coefficients $\tilde{D}^{*(\omega_{_V})}$ from the average over Ω_V in (2.88) have finite values (otherwise the average cannot be finite). This means that all the realizations $\omega_{_V}$ have the self-averaging property. If the Lagrangian correlation in each realization equals the Lagrangian correlation of the process $\boldsymbol{\chi}$, $\tilde{R}_L^{(\omega_{_V})} = \tilde{R}_L$, for all $\omega_{_V} \in \Omega_V$, then the effective diffusion coefficients have the same value $\tilde{D}^*$ in all realizations. A weaker (necessary) condition for equality of effective diffusion coefficients in all realizations is

$$\lim_{t\to\infty}\int\limits_{t_0}^{t} ds'(\tilde{R}_L^{(\omega_{_V})}(t,s') - \tilde{R}_L(t,s')) = 0, \text{ for all } \omega_{_V} \in \Omega_V.$$

The conclusion of this discussion is that the existence of the finite diffusion coefficient (2.87) of the process $\boldsymbol{\chi}$ do not ensure the validity of the effective diffusion equation in a single realization of the random field. The use of an effective diffusion equation to describe the solute transport is justified when the Lagrangian correlation $\tilde{R}_L^{(\omega_{_V})}$ can be estimated from measurements, as space average over the plume, and it behaves in time so that the effective diffusion

coefficient $\tilde{D}^{*(\omega_V)}$ exists. But in this case the construction of the process $\boldsymbol{\chi}$ is no more necessary. This could avoid some conceptual inconveniences. Indeed, in Section 2.4.1, this process was derived under the assumptions of nonsingularity of the velocity field (*H1*) and the continuity of each realization as a space function (*H2*). In most of stochastic approaches [Schwarze et. all, 2001, Schwarze 1999] Lagrangian stationarity is also assumed. This supposes, implicitly, the nonsingularity and continuity of the velocity field, because only in these conditions the existence of a stochastic process $\boldsymbol{\chi}$ can be inferred and Lagrangian correlation can be defined. In some cases, these hypotheses could be unrealistic and scarcity of experimental data makes it difficult to validate the stochastic model.

2.4.4 The model of Matheron and de Marsily

An example where a Lagrangian description and the connection with the Eulerian statistics can be rigorously derived is the stratified aquifer model of Matheron and de Marsily [1980]. The model describes the movement in the plan $\mathbb{R}^2$ of a particle, due to a 2-dimensional diffusion process, with longitudinal diffusion coefficient D_L and transversal diffusion coefficient D_T, on which one superposes a horizontal random field function only on transverse coordinate, $V(z,\omega_V)$:

$$\begin{aligned} dx^{(\omega_V)}(t) &= V(z(t),\omega_V)dt + D_L dw(t), \\ dz(t) &= D_T dw(t). \end{aligned} \tag{2.89}$$

In this case, the tensor of Lagrangian correlations (2.84) reduces to the component corresponding to horizontal velocities,

$$\begin{aligned} &R_L(s,s') = \\ &\int\limits_{\mathbb{R}}\int\limits_{\mathbb{R}} dzdz' M_{\Omega_V\times\Omega_w\times\mathbb{R}^2}[\delta(z-Z(s,\omega_w,z_0,t_0))\delta(z'-Z(s',\omega_w,z_0,t_0))V(z,\omega_V)V(z',\omega_V)] = \\ &\int\limits_{\mathbb{R}}\int\limits_{\mathbb{R}} dzdz' M_{\Omega_w\times\mathbb{R}^2}[\delta(z-Z(s,\omega_w,z_0,t_0))\delta(z'-Z(s',\omega_w,z_0,t_0))]M_{\Omega_V}[V(z,\omega_V)V(z',\omega_V)]. \end{aligned} \tag{2.90}$$

Because the transverse diffusion in (2.89) is not influenced by the horizontal random field, the vertical component of the trajectory $Z(s,\omega_w,z_0,t_0)$ in (2.90) does not depend on ω_V. In this case, the average over Ω_V factorizes and the connection between Lagrangian and Eulerian correlations (2.86) holds without the hypothesis of Corsin's factorization. The variance of the longitudinal displacements becomes

$$\begin{aligned} \sigma_x^2(t) = \; & 2D_L(t-t_0)+ \\ & \int\limits_{t_0}^{t} ds \int\limits_{t_0}^{t} ds' \int\limits_{\mathbb{R}}\int\limits_{\mathbb{R}} dzdz' p(z,s;z',s';D_T)R_E(z,z'), \end{aligned} \tag{2.91}$$

where

$$p(z,s;z',s';D_T) = M_{\Omega_w\times\mathbb{R}^2}[\delta(z-Z(s,\omega_w,z_0,t_0))\delta(z'-Z(s',\omega_w,z_0,t_0))]$$

is the Gaussian 2-dimensional density of the transverse diffusion process with coefficient D_T. When the same notations are used, (2.91) becomes identical with eq. (6) from [Matheron and de Marsily, 1980, Appendix 1].

The main feature of the model is that for Gaussian correlated fields, $R_E \sim e^{-(z-z')^2}$, the variance behaves as $\sigma_x^2 \sim t^{3/2}$. From (2.48) it follows that the behavior is superdiffusive at all times. This property is often used to check the validity of the numerical models of diffusion in random fields [Avellaneda et al., 1993, Honkonen, 1996]. In [Matheron and de Marsily, 1980] it

is proved that when the velocity V also has a vertical component, then the behavior becomes diffusive.

2.4.5 The Eulerian statistics of travel time

Here we present another case where, stating with a Lagrangian description, the final results can be exactly expressed by means of Eulerian averages. The Lagrangian description of stationary regime of solute transport in soils, when pore scale dispersion is neglected, can be obtained with an equation of form (2.63),

$$Z(t,\omega) = \int_0^t V(Z(s,\omega))ds, \tag{2.92}$$

where $Z(t,\omega)$ is the trajectory starting at $t_0 = 0$ from $z_0 = 0$. The velocity V is defined by a realization of the random field, as in Section 2.4.1, for points z belonging on the trajectory $Z(t,\omega)$, by $V(Z(t,\omega)) = V(z,\omega)$. In (2.92) we have supposed, as often it is in literature [Vanderborght et al., 1998], that the trajectories of solute particles are vertical.

One of the quantities which describe the process is the travel time $\tau(z)$ of a solute particle to reach a certain depth z, and its statistics (average and variance). From (2.92) we have

$$z = Z(\tau,\omega) = \int_0^\tau V(Z(s,\omega))ds,$$

which can be written as a function F, implicitly defining τ as function of z,

$$F(z,\tau(z)) = z - \int_0^\tau V(Z(s,\omega))ds \equiv 0. \tag{2.93}$$

The total derivative of F with respect of z is

$$\frac{dF}{dz} = \frac{\partial F}{\partial z} + \frac{\partial F}{\partial \tau}\frac{\partial \tau}{\partial z} = 0,$$

and, using the Leibnitz-Newton formula to write the derivative with respect to τ of the integral in (2.93) as $\partial F/\partial\tau = -V(Z(\tau,\omega)) = -V(z,\omega)$, we formally obtain the derivative of $\tau(z)$ with respect to z:

$$\frac{\partial \tau}{\partial z} = -\frac{\partial F}{\partial z}/\frac{\partial F}{\partial \tau} = 1/V(z,\omega). \tag{2.94}$$

From the hypothesis *H1)* it follows that in one-dimensional case V can not vanish, then $V > 0$. Then, F becomes a monotonous function of τ and, together with the hypothesis *H2)*, ensures the existence of the function $\tau(z)$, on the entire range of z, by the implicit function theorem from differential calculus. Integrating (2.94), we obtain

$$\tau(z) = \int_0^z \frac{\partial \tau}{\partial z}dz = \int_0^z \frac{1}{V(z,\omega)}dz. \tag{2.95}$$

Unlike the usual Lagrangian representations (see for instance [Vanderborght et al., 1998], equation (23)), (2.95) is an Eulerian representation for travel time, because the velocity is function of fixed depth z.

The mean travel time is obtained as average of (2.95) over realizations of the velocity field. Using the property of commutation of stochastic average and space integral (in conditions of (hypothesis *H2)*), the definition (2.18) of 1-dimensional density $p(v,z)$ and the Dirac function representation, we have

$$M_\Omega[\tau(z)] = \int_0^z dz \int_{-\infty}^{\infty} \frac{1}{v} M_\Omega[\delta(v - V(z,\omega)]dv = \int_0^z dz \int_{-\infty}^{\infty} \frac{1}{v} p(v,z)dv.$$

If one defines the harmonic average $v_H = 1/\ (\overline{1/v})$, where $\overline{1/v} = \int_{-\infty}^{\infty} 1/v\ p(v,z)dv$ is the Eulerian average of $1/v$, we finally obtain the average travel time

$$M_\Omega[\tau(z)] = \frac{z}{v_H}. \tag{2.96}$$

The variance of travel time can be also computed as an Eulerian average, with respect to the 2-dimensional density (2.17),

$$\begin{aligned}
\sigma^2[\tau(z)] &= M_\Omega[(\tau(z) - M_\Omega[\tau(z)])^2] = M_\Omega[(\tau(z))^2] - (M_\Omega[\tau(z)])^2 \\
&= \int_0^z \int_0^z dzdz' \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{v}\frac{1}{v'} M_\Omega[\delta(v - V(z,\omega)\delta(v' - V(z',\omega)]dvdv' - (\frac{z}{v_H})^2 \\
&= \int_0^z \int_0^z dzdz' \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\frac{1}{v}\frac{1}{v'} - (\frac{1}{v_H})^2) p(v,z;v',z')dvdv'.
\end{aligned}$$

The stochastic average in this expression defines the covariance of inverse velocities

$$cov_{\frac{1}{v};\frac{1}{v'}}(z,z') = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\frac{1}{v}\frac{1}{v'} - (\frac{1}{v_H})^2) p(v,z;v',z')dvdv.$$

With the hypothesis that the random field is stationary, we have $p(v,z;v',z') = p(v,z - z';v')$ and $cov_{\frac{1}{v};\frac{1}{v'}}(z,z') = cov_{\frac{1}{v};\frac{1}{v'}}(z - z')$. Using the normalized covariance notation $\rho(\Delta z) = cov_{1/v;1/v'}(z - z')\ /\ \sigma^2[1/v]$, where $\sigma^2[1/v] = cov_{1/v;1/v'}(0)$ is the corresponding constant variance, we can write the variance of the travel time as

$$\sigma^2[\tau(z)] = 2\sigma^2[1/v] \int_0^z (z - \Delta z)\rho(\Delta z)dz. \tag{2.97}$$

The average (2.86) and the variance (2.97) are identical with the relations (13-14) in [Shapiro and Cvetkovic, 1988]. In our approach, the results for the one-dimensional case are rigorously derived using the implicit function theorem, and the hypotheses *H1)* and *H2)* which ensure the existence of both the Lagrangian description (2.92) and the Eulerian representation (2.95) of the travel time.

3 Numerical modeling by Global Random Walk

3.1 Random walk and diffusion equation

It is well known that diffusion processes can be numerically simulated with random walk (RW) algorithm. For simple diffusion processes the RW algorithm is identical with the finite difference (FD) scheme [Ames, 1977] but, as we shall discuss in the following, this equivalence is not valid for more complex diffusion processes.

To show that the RW algorithm gives a numerical solution of the diffusion equation, let us consider an infinite grid with nodes at $x_i = i\delta x$, $i \in \mathbb{Z}$, where $\delta x > 0$ is the space step. At time $t_k = k\delta t$, $k \in \mathbb{N}$, where $\delta t > 0$ is the time step, a particle jumps to the left or right neighboring node with equal probabilities. In this way, the RW motion can be described as a stochastic process with discrete state space. If we denote by $P(x_i, t_k)$ the probability distribution at t_k and by $P(x_i, t_k|x_j, t_l)$ the transition probability, then the consistency property of finite dimensional probabilities for discrete Markov processes gives a relation analogue with (2.25),

$$P(x_i, t_k) = \sum_j P(x_i, t_k|x_j, t_l)P(x_j, t_l), \tag{3.1}$$

where $t_k > t_l$. According to the RW law, the transition probabilities for successive time steps are given by

$$P(x_i, t_{k+1}|x_j, t_k) = \begin{cases} \frac{1}{2} \text{ for } i = j \pm 1 \\ 0 \text{ for } i \neq j \pm 1 \end{cases} . \tag{3.2}$$

For three time steps $k_1 > k_2 > k_3$, the Chapmann-Kolmogorov equation for discrete state space processes (analogue to (2.24)) is

$$P(x_{i_1}, t_{k_1}|x_{i_3}, t_{k_3}) = \sum_{i_2} P(x_{i_1}, t_{k_1}|x_{i_2}, t_{k_2})P(x_{i_2}, t_{k_2}|x_{i_3}, t_{k_3}),$$

and, with transition probabilities (3.2), it gives the master equation for the transition probability of the process starting in the state $(0, 0)$,

$$P(x_i, t_{k+1}|0, 0) = \frac{1}{2}\left[P(x_{i-1}, t_k|0, 0) + P(x_{i+1}, t_k|0, 0)\right], \tag{3.3}$$

which is a discrete form of master equation (2.33c). One proves (see for instance [Gardiner, 1983]) that when $\delta x \longrightarrow 0$ and $\delta t \longrightarrow 0$, and if the limit

$$\lim_{\delta x, \delta t \longrightarrow 0} \frac{\delta x^2}{2\delta t} = D \tag{3.4}$$

is finite, then the limit of the solution of (3.3) is the Gaussian transition probability with the density

$$p(x, t|0, 0) = (4\pi Dt)^{-1/2} \exp\left\{\frac{-x^2}{4Dt}\right\}. \tag{3.5}$$

The Gaussian process is a continuous Markov process and the probability density that a particle has the position x at time t, given by (2.25),

$$p(x, t) = \int_{\mathbb{R}} p(x, t|x', 0)p(x', 0)dx',$$

is the solution of the diffusion equation (2.31),

$$\partial_t p = D\partial_x^2 p,$$

with the initial condition $p_0(x) = p(x, 0)$ [Gardiner, 1983].

The connection between the RW process, described by the master equation (3.3), and the diffusion equation (2.31) is used to build up the RW algorithm. One considers N fictitious particles moving on the previously described infinite grid, their movement being governed by the RW law. At the initial time the distribution of the N particles approximates the values of the initial probability density $p_0(x)$. For each particle and each time step a random number taking the values -1 and $+1$ with a probability equal to $1/2$ is generated. If the random number is -1, then the particle moves to the left and if it is $+1$ the particle moves to the right. In this way the distribution of the N particles at the time t_k approximately describes the solution $p(x, t_k)$ of the diffusion equation (2.31). This approximation can be improved by increasing N and reducing δx and δt.

3.2 The GRW algorithm

The GRW algorithm [Vamoş et al., 20011a, 2001b] is identical with the RW algorithm in its mathematical principles, only the numerical implementation of the particles displacement is different. Hence, first we describe the RW algorithm for advection-equation (2.32). Using the relation between the concentration field c and the probability distribution p given by (2.57), in (2.32), we consider the advection-diffusion equation

$$\partial_t c + V(x)\partial_x c = D\partial_x^2 c, \tag{3.6}$$

where the advection velocity $V(x)$ is a space function and the diffusion coefficient D is a constant. According to (3.4), we relate the space step δx and the time step δt, for a given constant diffusion coefficient D, by

$$D = \frac{\delta x^2}{2\delta t}. \tag{3.7}$$

The particles in x_i jump either in $(x_i - \delta x)$ or in $(x_i + \delta x)$. Similarly, the realization of the random velocity field is described on the grid by a set of integers v_i, defined by

$$V(x_i) = \frac{\delta x}{\delta t} v_i, \tag{3.8}$$

so that the movement of particles in x_i due to advection field is given by $(x_i + v_i \delta x)$. The total displacement of particles is obtained, similarly to PT algorithm [Tompson and Gelhar, 1990], as sum of advective and diffusive displacements. After a time step δt, the particles starting from the node i reach either the node $(i + v_i - 1)$ or $(i + v_i + 1)$. The shortcoming of this approach is that $V(x_i)$ has only discrete values and if $V(x)$ has large variations, then $\delta x/\delta t$ must be small imposing a small space step. Therefore, in this case very large grids are needed. Also, the velocity $V(x_i)$ must be replaced by its average over a time step. For smooth variations, it was shown that

$$V_i = (V(x_i) + V(x_i + \delta t V(x_i)))/2 \tag{3.9}$$

approximates the average up to second order in δt [Roth and Hammel, 1996].

At a given time $t_k = k\delta t$, the N particles are distributed on the grid so that $n(i, k)$ is the number of particles at the node $x_i = i\delta x$. Moving each particle according to the RW law, the

distribution of the particles at the next time step $n(i,k+1)$ is obtained. Repeating S times the simulation under the same initial condition, we obtain for each node i and time k a sequence of values $n_s(i,k)$, $1 \leqslant s \leqslant S$. When S is large enough, we can approximate the solution $c(x,t)$ of the advection-diffusion equation (3.6) using the average over the S realizations of $n_s(i,k)$, denoted $\overline{n(i,k)}$. Assuming that the particles in the node x_i are assigned to an interval consisting of l space steps, the numerical solution of (3.6) is given by

$$c(x_i,t_k) = \frac{1}{l\,\delta x}\overline{n(i,k)}. \tag{3.10}$$

This is a simple case of a Monte Carlo method [Ames, 1977].

The GRW algorithm moves the particles in large groups, not individually. We denote by $\delta n(i,j,k)$ the number of particles which at time t_k are moved from x_j to x_i. Then the distribution of the particles at the next time is obtained from the relation

$$n(i,k+1) = \sum_j \delta n(i,j,k). \tag{3.11}$$

The particles laying at j at time k are scattered according to the relation,

$$n(j,k) = \delta n(j,j+v_j,k) + \delta n(j+v_j-d,j,k) + \delta n(j+v_j+d,j,k), \tag{3.12}$$

where the positive integer d describes the jumps of particles due to diffusion, $\delta n(j+v_j \pm d,j,k)$ are the numbers of particles undergoing advective displacements v_j and diffusive jumps d and $\delta n(j,j+v_j,k)$ is the number of particles which do not undergo diffusive jumps and remain at the grid point $j+v_j$ after an advective displacement. The GRW algorithm is defined if a procedure to calculate the values of the quantities in the right hand part of (3.12) is given.

We want that at a given time step only a fraction r of the number of particles jump in neighboring nodes, the rest of them remaining at the same node. To avoid the division of particles, r must be a positive rational number $r \leqslant 1$, such that $(1-r)N$ be an integer and equal to the total number of particles which do not undergo diffusive jumps at a time step. For increasing index j, we determine the number of particles remaining at the node x_{j+v_j} by means of the formula

$$\delta n(j,j+v_j,k) = \left[(1-r)\sum_{j' \leqslant j} n(j',k)\right] - \left[(1-r)\sum_{j'<j} n(j',k)\right], \tag{3.13}$$

where $[\cdot]$ is the integer part of the expression in the brackets. Taking the average over a great number of Monte Carlo realizations we obtain

$$\overline{\delta n(j,j+v_j,k)} = (1-r)\overline{n(j,k)} \tag{3.14}$$

Since $\delta n(j,j+v_j,k)$ is known, (3.12) relates the random variables $\delta n(j+v_j-d,j,k)$ and $\delta n(j+v_j+d,j,k)$ and only one of them has independent values.

As a consistency requirement, for a given diffusion process, the GRW algorithm must give the same mean square displacement as the RW algorithm. If δx_{RW} is the space step for the RW algorithm, then, because all the particles jump at the first neighbors, for a time step δt the mean square displacement of the particles in the node j is $\overline{n(j,k)}\delta x_{RW}^2$. For an equal time step, in GRW algorithm only the fraction r of the particles in the node j jump at the nodes

$j \pm d$ and, from (3.12) and (3.14), the mean square displacement is $r\ \overline{n(j,k)}(d\delta x)^2$. Imposing the condition $\overline{n(j,k)}\delta x_{RW}^2 = r\ \overline{n(j,k)}(d\delta x)^2$ and using (3.7) for δx_{RW}, the parameter r is given by

$$r = \frac{2D\delta t}{(d\delta x)^2}. \tag{3.15}$$

For given δx and δt and properly combining the values of both d and r, using (3.15) one can numerically describe all the possible values of the diffusion coefficient.

The GRW algorithm performs the evaluation of the random variables $\delta n(j + v_j \pm d, j, k)$ directly, not as a sum of the individual jumps of the $n \equiv n(j,k) - \delta n(j,j,k)$ particles. Since each of the n particles can reach the node $j + v_j - d$ with a probability equal to $1/2$, it follows that the probability for $\delta n(j + v_j - d, j, k)$ to take the value m, $0 \leqslant m \leqslant n$, is given by the Bernoulli distribution $b_n(m) = 2^{-n}C_n^m$. To assign to $\delta n(j+v_j-d, j, k)$ a random value satisfying the Bernoulli distribution, at each time step, a random number η with a uniform distribution in the interval $[0, 1]$ is generated. If we denote by $F_n(m) = \sum_{l=0}^{m} b_n(l)$, $0 < F_n(m) \leqslant 1$, the Bernoulli repartition, then $\delta n(j + v_j - d, j, k)$ takes the value m satisfying the condition $F_n(m-1) \leqslant \eta < F_n(m)$, where we use the convention $F_n(-1) = 0$.

To analyze the relation between the GRW and the FD algorithms, we consider the centered differences and time explicit scheme for diffusion equation obtained from (3.6) when $V(x) \equiv 0$. Considering the approximation in the order $\mathcal{O}(\delta x^2)$ of $\partial_x^2 c$ in (3.6), using finite difference between $d\delta x$ space steps and the parameter r defined by (3.15), the explicit FD scheme can be written as

$$c(i, k+1) = \frac{r}{2}c(i+d, k) + (1-r)c(i,k) + \frac{r}{2}c(i-d, k). \tag{3.16}$$

The solution of (3.16) is stable if the von Neumann stability criterion, $r \leqslant 1$, is fulfilled. Since from (3.15) we also have $\delta t = \mathcal{O}(\delta x^2)$, the FD scheme (3.16) is a consistent approximation of the exact partial differential equation within the approximation order $\mathcal{O}(\delta x^2)$. The stability and consistency imply the convergence of the order $\mathcal{O}(\delta x^2)$ for the initial value problem attached to (3.6) with $V(x) \equiv 0$ [Godunov and Ryabenkii, 1987]. For $v_i \equiv 0$, the GRW algorithm relation (3.11) becomes

$$n(i, k+1) = \delta n(i, i, k) + \delta n(i, i+d, k) + \delta n(i, i-d, k).$$

Taking into account (3.10) and (3.14), the average of this relation is identical with (3.16) if

$$\overline{\delta n(j \pm d, j, k)} = \frac{1}{2} r\ \overline{n(j,k)}. \tag{3.17}$$

But this is the RW law statement that the average number of particles jumping in a direction is equal to half the total number of particles. This proves that the FD solution is identical with the ensemble average of the GRW solutions. The parameter (3.15) defining the particles fraction jumping to the neighboring nodes in (3.17) is the same as the stability parameter of the FD scheme (2.9).

One can define a modified GRW algorithm which is identical with the FD algorithm for $V(x) \equiv 0$, if the particles can be divided and $n(j,k)$ is a real number, not an integer. Instead of (3.13) we introduce

$$\delta n(j, j, k) = (1-r)n(j,k) \tag{3.18}$$

and in analogy with (3.17) we consider

$$\delta n(j + v_j \pm d, j, k) = \frac{1}{2} r\ n(j,k). \tag{3.19}$$

Then (3.12) is identical satisfied and all the quantities in (3.11) are defined. In this case, $\delta n(j+v_j-d,j,k)$ is not anymore a random variable but its value is uniquely determined by (3.19) and coincides with the mean value of the corresponding random variable in GRW. Therefore we call this modified algorithm as a "deterministic" GRW (GRWD).

Another form of the GRW algorithm can be obtained by both preforming a deterministic scattering and preserving the particles indivisibility. We use (3.13) and instead of (3.19) we introduce

$$\delta n(j+v_j-d,j,k)=\begin{cases} n/2 & \text{if } n \text{ is even} \\ [n/2]+\theta & \text{if } n \text{ is odd} \end{cases}, \tag{3.20}$$

where $n=n(j,k)-\delta n(j,j,k)$, $[n/2]$ is the integer part of $n/2$ and θ is a random variable taking the values 0 and 1 with probability 1/2. The quantity $\delta n(j+v_j+d,j,k)$ is determined by (3.12). In comparison with GRW, this algorithm reduces the particles number fluctuations at only one particle and we call it GRWR. Since the fluctuations do not vanish, only the average of the GRWR solution is identical with the FD solution. The algorithms without fluctuations (GRWD) and with reduced fluctuations (GRWR) can be used to obtain numerical solutions for the advection-diffusion equation (3.6), as well as the stochastic algorithm GRW. The GRW algorithm is expected to be more accurate when the fluctuations significantly influence the simulated process [Horsthemke, 1984].

The GRW algorithm and its modified forms GRWD and GRWR use the relation (3.11) where $\delta n(i,j,k)$ is nonvanishing for every j satisfying $j+v_j\pm d=i$. Therefore, if $V(x)$ varies in space, the evolution of the concentration in a node is obtained, unlike in (3.16), by contributions from more than the first neighboring nodes. The terms in (3.11) are not apriori known, because they depend on the value of V in x_j. In this case, the GRW algorithm is no more equivalent with a FD scheme.

The implementation of the GRW algorithm as a computer code, encounters some problems related to the computation of the Bernoulli distribution $b_n(m)=2^{-n}C_n^m$ and of the corresponding repartition $F_n(m)=\sum_{i=0}^m b_n(i)$. When the number of particles is of order 10^6, the computation of $b_n(m)$ or $F_n(m)$ takes too much time to be performed at each computation step. Therefore the values of $F_n(m)$ are computed only once and stored in files for values $n=2^k$ with $1\leqslant k\leqslant 20$. Due to the symmetry of $F_n(m)$ with respect to $m=n/2$, only the values $F_n(m)\leq 0.5$ are stored. If $n<2^{21}$, a binary representation $n=\sum_{l=0}^{20}a(l)2^l$ is used. The 2^l particles of a group with $a(l)\neq 0$ are scattered in $\delta n_l(j+v_j-d,j,k)$ and $\delta n_l(j+v_j+d,j,k)$, as previously described, using a random number η uniformly generated in the interval $[0,1]$. The final result is obtained from

$$\delta n(j+v_j-d,j,k)=\textstyle\sum_{l=0}^{20}a(l)\delta n_l(j+v_j-d,j,k).$$

If $n\geqslant 2^{21}$, then there are several groups consisting of 2^{20} particles and for each group the procedure from above can be used. This method, referred to as GRW0 (first used in [Vamoş et al., 2001]), becomes time expensive for very large n. In this article a different method is used. The reduced variable $\xi=(m-n/2)/\sqrt{n/4}$ and the repartitions $F_n(\xi)$ are introduced. For $n\to\infty$, the repartition $F_n(\xi)$ tends to the normal Gaussian repartition, according to De Moivre-Laplace theorem [Papoulis, 1991]. A good approximation is obtained when for every $n\geqslant 2^{21}$ one uses the repartition corresponding to $n=2^{20}$ as function of the reduced variable ξ. For instance, the relative error of the values δn obtained using $F_{2^{20}}$ instead of $F_{2^{30}}$ is of the order 10^{-9}. In this way, GRW can handle a number of particles equal to the maximum number of particles that can be represented in the internal memory of the computer.

For 2 and 3-dimensional problems, the GRW algorithms are implemented by performing the 1-dimensional global scattering procedures described in this section on x_1, x_2 and x_3 space axes, according to the values of velocity components and diffusion coefficients. A numerical proof of convergence, discussions about boundary conditions and performances of the algorithm are presented in [Vamoş et al., 2001b].

4 Numerical simulation of diffusion in random fields

If the advection velocity has large spatial variations then $V(x)$ can be modeled as a random velocity field. This approach is often used in studies of transport processes in heterogeneous porous media. Many authors agree that numerical simulations of diffusion in random fields are better achieved by RW algorithms than by usual FD or finite element algorithms [Moltyamer et al., Tompson and Gelhar, 1990, Tompson and Knapp, 1989, Tompson et al., 1998, Roth Hammel, 1996]. In this Section, we shall show that GRW allows the simulation of the 2-dimensional diffusion in single realizations of random velocity fields using moderate computing resources.

The transport in a random velocity field is a complex process consisting in diffusive movements of particles and their transport along the stream lines of the velocity field. A mathematical description of this process is given by the advection-diffusion equation (3.6) where D is a local diffusion coefficient and $V(x)$ a random field. Such models are used to describe the transport of pollutants in natural porous media. In the following, we consider the numerical simulation of the transport of a contaminant substance in a saturated aquifer, for a punctual injection case. The heterogeneity of the advection velocities is described by realizations of a random field. In this conditions, traditional methods (finite difference/element) are restricted at simplified aquifer models [Tompson and Knapp, 1989]. Better results in simulation of field experiments were obtained by means of the stochastic models based on PT method [Tompson and Gelhar,1990, Tompson et al., 1998]. For instance, when the simulations of the groundwater transport at field scale are performed with PT, the numerical diffusion and dispersion problems occurring in finite element/difference methods are completely eliminated [Moltyamer et al., 1993].

In PT algorithm, the diffusion process is described by the movement of an ensemble of fictitious particles in continuous space. For each particle the change of the position x in the time interval $(t_{k+1} - t_k)$, due to the realization $V(x)$ of the random velocity field and the local diffusion with coefficient D is described by the discrete form of the Itô equation (2.81),

$$x(t_{k+1}) - x(t_k) = V(x(t_k), t_k)\delta t + G\sqrt{2D\delta t}, \tag{4.1}$$

where G is a Gaussian random variable with mean zero and unit variance. For large number of particles one expects that their number density give an approximation of the concentration field $c(x, t_k)$ satisfying an advection-diffusion equation [Tompson and Gelhar, 1990]. This assertion is based on the relation between the Itô equation and the Fokker-Planck equation for the probability density of particle position [Gardiner, 1983]. According to (2.57) the probability density is proportional to the concentration, so that (3.6) is in fact the Fokker-Planck equation. The accuracy of the solution strongly depends on the number of tracked particles. Further, to obtain simulations of the stochastic model of diffusion in random velocity fields, presented in Section 2.4.3, one performs repeated computations and averages over large ensemble of realizations. As it is mentioned in literature [Sun, 1996], "a trade off should be made to

reduce the computation time without affecting the accuracy". Although improvements of the algorithm have been made, the high computational costs of PT simulations is still an open problem [Ghoniem and Sherman, 1985]. That is why sometimes a "semianalytical" evaluation of diffusive movement is used [Salandin and Fiorotto, 1998]. In [Zhang et al., 1993] for instance, on the basis of some numerical tests, the last term in (4.1) was taken as $4\sqrt{D\delta t}$.

The computational effort in the PT method is due to the fact that every particle is separately displaced and all the trajectories must be stored. That is why the GRW method, where groups of particles are simultaneously displaced, saves time and memory. GRW produces simulations of the diffusion in random fields without prohibitive computational costs [Vamoş et al., 2001b].

4.1 Simulation of asymptotic state in single realization

For the simulation of 2-dimensional diffusion in random fields we consider the same procedure to generate the field as in [Schwarze et al., 2001] (Kraichnan generator of hydraulic conductivity field and first order approximation). The velocity field is spatial stationary and divergence free and has the form $\mathbf{V}(x_1, x_2) = \mathbf{U} + \mathbf{u}(x_1, x_2)$, where $\mathbf{U} = (U, 0)$ is the mean velocity and $\mathbf{u}(x_1, x_2)$ the fluctuation. The "filtration velocity" is given by Darcy law

$$\mathbf{V} = -\frac{K}{\phi}\nabla H,$$

where K is the hydraulic conductivity, ϕ the porosity and ∇H is the hydraulic gradient. The correlation coefficients

$$R_{ll}(a) = \langle u_l(x_1, x_2)u_l(x_1 + a, x_2)\rangle \,/\, \langle u_l(x_1, x_2)u_l(x_1, x_2)\rangle\,,$$

where $l = 1, 2$ and $\langle\cdot\rangle$ denotes the average over the realizations of the random field, decay with a, corresponding to an exponential correlated logarithm of the hydraulic conductivity, with variance $\sigma^2_{\ln K} = 1$ and correlation length $\lambda = 1$ m. We also consider $U = 1$ m/day, and local diffusion coefficient $D = 0.01$ m^2/day (as in simulations represented in Fig. 11 and 14 from [Schwarze et al., 2001]).

The simulations consist in determining at each time step the positions of N particles on a grid using the relations (3.11) and (3.12), defining the GRW algorithm, and the computation of the corresponding spatial moments. Because the movement due to velocity fluctuations is much larger than diffusive motion, only the spreading of the plume over regions with different velocities is important and not the fluctuations of the number of particles. That is why the simulations were performed with the reduced fluctuations algorithm GRWR with $r = 1$. The use of GRWR algorithm requires reduced computing resources than GRW and GRWD algorithms. Unlike in GRW algorithm, only one random number will be generated (at every time step and when at a given node there is an odd number of particles). Because the indivisibility of particles is preserved, the plume has a smaller extension than in the case of GRWD algorithm and, consequently, smaller grids are necessary.

The computation domain is a rectangular grid with 10^7 nodes, $0 \leqslant i \leqslant 10000$ and $0 \leqslant j \leqslant 1000$, the space step is $\delta x = \delta y = 0.1$ m and the time step $\delta t = 0.5$ day. In two different realizations of the velocity field, $N = 10^{10}$ particles were released at the point $(i_0, j_0) = (50, 500)$. We checked that for greater values of N the simulation results remain unchanged. A period of 800 days was simulated, so that in this interval the particles travel a mean distance of 800 correlation lengths. The computations were performed with a PC (Pentium III, 600 MHz, 64 Mb RAM) and lasted about 3 hours for each simulation.

The asymptotic diffusive behavior is described by finite coefficients (2.48),

$$\lim_{t\to\infty}\frac{\sigma_{ll}^2(t)}{t}=2D_{ll}^{eff}. \tag{4.2}$$

In (4.2) we use the notation D_{ll}^{eff} for the components of the tensor of effective diffusion coefficients $\tilde{D}^{*(\omega_V)}$ from (2.88). Usually, one reserves the name "effective diffusion coefficients" for asymptotic coefficients in single realization, to avoid confusion with the asymptotic coefficients defined as averages over realizations ($\tilde{D}^*$ in (2.88)). The last quantities are called "ensemble diffusion coefficients" [Attinger et al., 1999, Vanderborght and Vereecken, 2001].

In Fig. 1 and 2, the evolution of $D_{11}^{eff}(t)$ and $D_{22}^{eff}(t)$, for the 2-dimensional GRWR simulations, are represented for the two realizations of the random field. The coefficients D_{11}^* and D_{22}^* are closed to the constant values predicted by theory presented in [Schwarze et al., 2001].

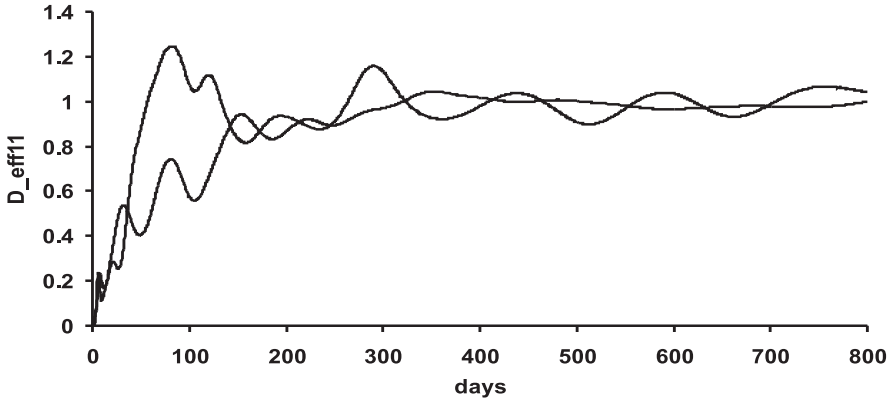


FIG. 1 Longitudinal effective diffusion coefficient in two different realizations.

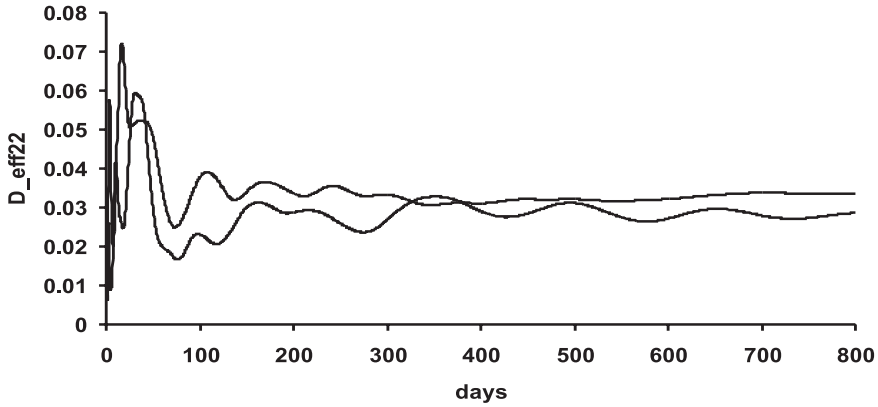


FIG. 2 Transversal effective diffusion coefficient in two different realizations.

The coefficients from Fig. 1 and 2 approach the asymptotic value, after cca. 200 days (correlation lengths), but heir value oscillates around the theoretical value. This behavior persists over travel times of hundreds of days. At small travel times, the oscillations can be explained by the fact that the space average weighted with the number of particles, which defines $\sigma_{ll}^2(t)$, varies with the extent of the plume and do not provides a good estimation of the statistical average. At large travel times, the oscillations can be caused either by numerical errors or by bad statistical properties of the realizations of the random field.

4.2 The analysis of overshoot errors

In simulations from Fig. 1 and 2, we used the discrete values of velocity given by (3.8), i.e. without corrections. Because in a time step δt the particles moving with velocity $V(x_i)$ can jump over several grid points, where the velocity has different values, the "overshoot errors" occur [Sun, 1996]. To analyze the influence of overshooting in our computations we used the approximation (3.9) for the average velocity in a time step. The discrete values of velocity, v_i, were replaced, according to (3.8) and (3.9), by

$$\bar{v}_i = (v_i + v_{i+v_i\delta x})/2. \tag{4.3}$$

The effective coefficient given by Green-Kubo formula (2.55) is related with the velocity variance $M[v^2]^e$ and correlation time τ_c by formula $D^* = M[v^2]^e\tau_c$. For diffusion in random fields it is not easy to obtain the correlation time for the Lagrangian correlation $\tilde{R}_L$. The exact formula (2.84) requires a complete knowledge of functions describing the velocity realizations and the particles' trajectories. Even when Corsin conjecture is used to obtain (2.86), the knowledge of the analytic Eulerian correlation function R_E and of the 2-dimensional density of the positions' process are necessary. However, some approximative relations can be derived in particular cases. For example, the asymptotic value of the effective coefficient (2.87), for exponential correlated logarithm of hydraulic conductivity, was estimated in [Gelhar and Axness, 1983] as

$$D_{11}^{eff} \cong D + U\lambda\sigma^2_{\ln K}. \tag{4.4}$$

The computations of the longitudinal coefficient D_{11}^{eff} with velocity discretization (3.8), i.e. without corrections, and with correction (4.3), for 800 days and a coarse discretization ($\delta x = \delta y = 1$ and $\delta t = 5$), are compared in Fig. 3. We remark that the method (3.8) overestimates the coefficient, which, according to (4.4) should be $D_{11}^{eff} \cong 1.1$, with cca. 20% and the corrections (4.3) give asymptotic values closed to the theoretical estimation. The overshooting is important mainly in longitudinal direction, as shown by the curve (×), where only the longitudinal advective velocities were corrected.

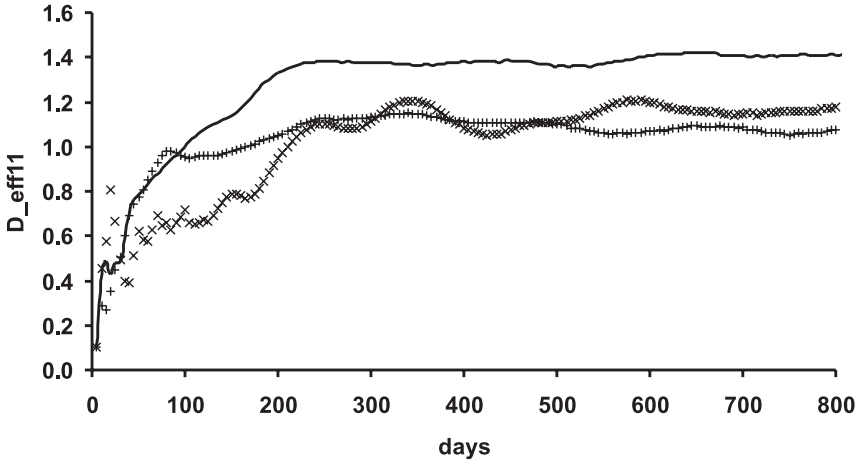


FIG. 3 Comparison between effective diffusion coefficients computed without corrections (full line), corrections with mean velocity over a time step (+) and correction for longitudinal direction only (×), for $D = 0.1$, $\delta x = 1$ and $\delta t = 5$.

In Fig. 4, we compared the methods (3.8) and (4.3) for smaller discretization steps ($\delta x = \delta y = 0.4$ and $\delta t = 2$) and for 1000 days. One remarks that there are no significant differences between the methods. The result may be explained by the randomness of velocity field which, for small discretization steps, could compensate the effect of overshooting.

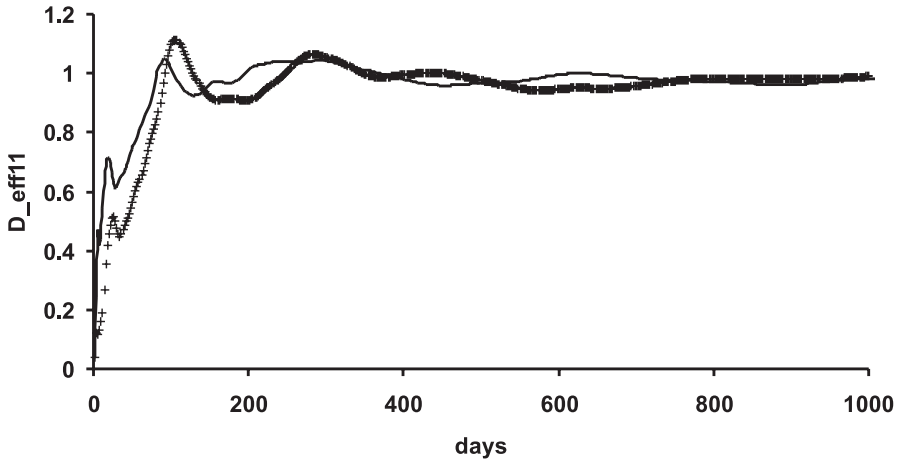


FIG. 4 Effective diffusion coefficient computed without corrections (full line), and with corrections using the mean velocity over a time step (+), for $D = 0.04$, $\delta x = 0.4$ and $\delta t = 2$.

The conclusion is that for fine discretization the simulations are not affected by overshoot errors. The oscillational behavior of asymptotic coefficients in Fig. 1 and 2, where the discretization was finer than in Fig. 4 ($\delta x = \delta y = 0.1$ and $\delta t = 0.5$) cannot be explained by computation errors and the cause could be the pour stationarity or the periodic behavior of the simulated velocity fields.

5 Path decomposition of macrodispersion coefficient

5.1 Path decomposition method

To analyze the influence of statistical properties of the velocity fields, we develop a method suggested by the discrete nature of computation of the diffusion coefficient.

Let us consider a 2-dimensional space grid with steps $\delta x = \delta y$, and let δt be the time step. Let

$$\mathcal{P}_\alpha^{(S)}(i,j) = \{(i_\alpha(0), j_\alpha(0)), (i_\alpha(1), j_\alpha(1)), \cdots, (i_\alpha(S), j_\alpha(S))\}$$

be *the path* α, starting at (i,j) and containing S successive positions. A point which belong to the path α and corresponds to the s-th position, $0 \leqslant s \leqslant S$, is denoted by

$$\mathcal{P}_\alpha^{(S)}(i,j;s) = (i_\alpha(s), j_\alpha(s)).$$

The initial point for all paths α is $\mathcal{P}_\alpha^{(S)}(i,j;0) = (i,j)$ (fig. 5).

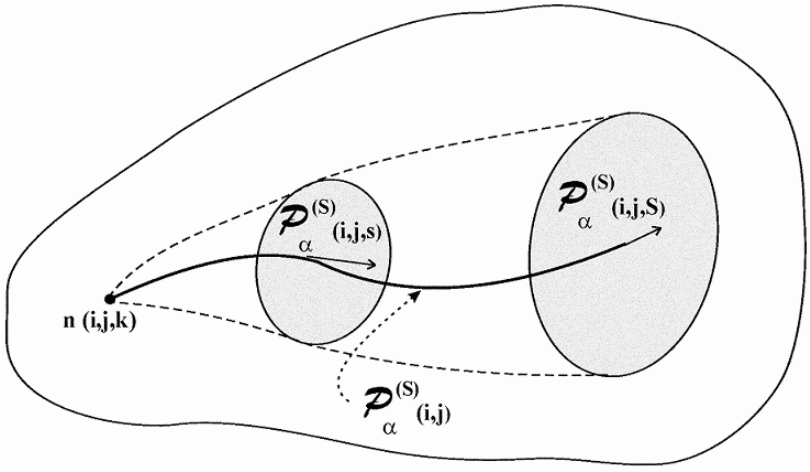
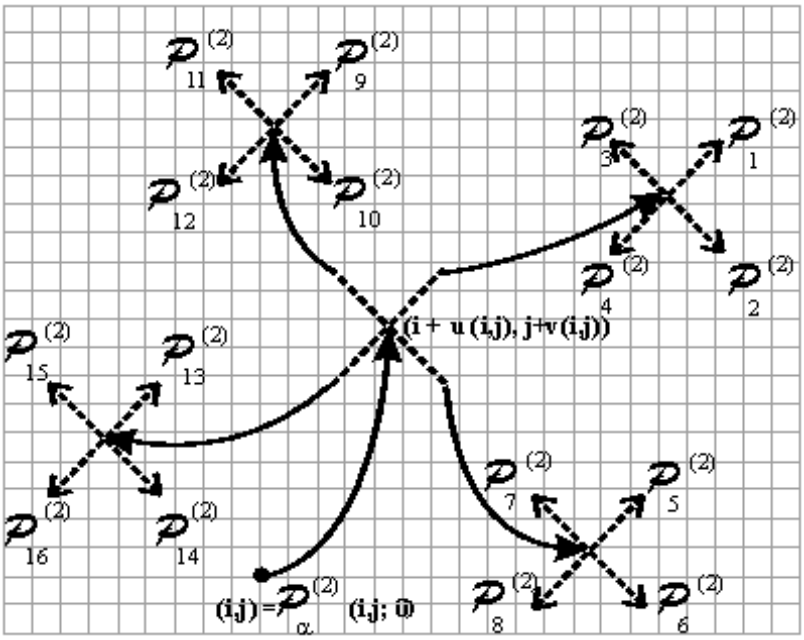


FIG. 5 At each time step k, the n particles spread along paths starting in (i,j).

The evolution along a path of length S of particles undergoing a diffusion with coefficient D, $D = (\delta x)^2 d^2/(2\delta t)$, in a single realization of a random field, $\mathbf{V} = (V_1, V_2)$, $V_1 = u\delta x/\delta t$, $V_2 = v\delta x/\delta t$ is described by

$$i_\alpha(s+1) = i_\alpha(s) + u(\mathcal{P}_\alpha^{(S)}(i,j;s)) \pm d$$
$$j_\alpha(s+1) = j_\alpha(s) + v(\mathcal{P}_\alpha^{(S)}(i,j;s)) \pm d.$$

Hence for given S, there are 4^S paths and the values of α are $\alpha = 1, 2, \cdots, 4^S$ (fig. 6).



.

FIG. 6 Paths of length $S = 2$ starting from the point (i, j).

In the following we describe the computation of the longitudinal effective coefficient using the "path decomposition" approach. The longitudinal variance of particles displacements, σ_{11}^2, is given, in dimensionless form, by

$$\frac{1}{(\delta x)^2}\sigma_{11}^2(k\delta t) = \frac{1}{N}\sum_{i,j} i^2 n(i,j,k) - \left[\frac{1}{N}\sum_{i,j} i\ n(i,j,k)\right]^2, \tag{5.1}$$

where $n(i, j, k)$ is the number of particles in (i, j) at time k and $N = \sum_{i,j} n(i, j, k)$ is the total number of particles. The variation of the variance (5.1) between two successive time steps, using the previously introduced path notations, is given by

$$\frac{1}{(\delta x)^2}\left[\sigma_{11}^2((k+S+1)\delta t) - \sigma_{11}^2((k+S)\delta t)\right] = d^2 + R_{uu}(k;S) + 2\sum_{s=0}^{S-1} R_{uu}(k;s) + \mathcal{M}(k;S) + \epsilon(k,S). \tag{5.2}$$

The correlation of longitudinal velocity components u, in points corresponding to the position s and the end S of paths starting in all points (i, j) contained in the plume area, is defined by:

$$R_{uu}(k;s) = \frac{1}{4^S N}\sum_{\alpha=1}^{4^S}\sum_{i,j} u(\mathcal{P}_\alpha^{(S)}(i,j;s))u(\mathcal{P}_\alpha^{(S)}(i,j;S))n(i,j,k) - \overline{u(\mathcal{P}^{(S)}(k,s))}\ \overline{u(\mathcal{P}^{(S)}(k,S))},$$

with the average (over paths and grid points) velocity,

$$\overline{u(\mathcal{P}^{(S)}(k,s))} = \frac{1}{4^S N}\sum_{\alpha=1}^{4^S}\sum_{i,j} u(\mathcal{P}_\alpha^{(S)}(i,j;s))n(i,j,k) = \frac{1}{4^S}\sum_{\alpha=1}^{4^S}\overline{u(\mathcal{P}_\alpha^{(S)}(k,s))},$$

where

$$\overline{u(\mathcal{P}_\alpha^{(S)}(k,s))} = \frac{1}{N}\sum_{i,j} u(\mathcal{P}_\alpha^{(S)}(i,j;s))n(i,j,k)$$

is a space averaged velocity.

The correlation of velocities at the path's ends, S,

$$R_{uu}(k;S) = \frac{1}{4^S N}\sum_{\alpha=1}^{4^S}\sum_{i,j}\left[u(\mathcal{P}_\alpha^{(S)}(i,j;S))\right]^2 n(i,j,k) - \left[\overline{u(\mathcal{P}^{(S)}(S))}\right]^2, \tag{5.3}$$

is the corresponding velocity variance.

The term

$$\mathcal{M}(k;S) = \frac{2}{4^S N}\sum_{\alpha=1}^{4^S}\sum_{i,j}(i - i_{CM}(k))u(\mathcal{P}_\alpha^{(S)}(i,j;S))n(i,j,k),$$

is an average momentum of velocity with respect to the center of mass, where

$$i_{CM}(k) = \frac{1}{N}\sum_{i,j} i\ n(i,j,k)$$

is the i component of the center of mass.

The term

$$\epsilon(k,S) = \frac{d}{4^S}\sum_{\alpha=1}^{4^S}(-1)^{a_\alpha} b_\alpha \overline{u(\mathcal{P}_\alpha^{(S)}(S))},$$

where a_α and b_α are constants, is a sum of terms with approximately equal absolute values but with opposite signs.

In the case $S = 1$, using the path points corresponding to the first iteration in fig. 6, these quantities become:

$$R_{uu}(k;1) = \frac{1}{4N}\sum_{i,j}\left\{\left[u(\mathcal{P}_1^{(1)}(i,j;1))\right]^2 + \left[u(\mathcal{P}_2^{(1)}(i,j;1))\right]^2 + \left[u(\mathcal{P}_3^{(1)}(i,j;1))\right]^2 + \left[u(\mathcal{P}_4^{(1)}(i,j;1))\right]^2\right\} n(i,j,k) - \left[\overline{u(\mathcal{P}^{(1)}(1))}\right]^2,$$

$$\mathcal{M}(k;1) = \frac{2}{4N}\sum_{i,j}(i - i_{CM}(k))\ \left[u(\mathcal{P}_1^{(1)}(i,j;1)) + u(\mathcal{P}_2^{(1)}(i,j;1)) + u(\mathcal{P}_3^{(1)}(i,j;1)) + u(\mathcal{P}_4^{(1)}(i,j;1))\right] n(i,j,k),$$

$$\epsilon(k,1) = \frac{d}{4N}\left[\overline{u(\mathcal{P}_1^{(1)}(1))} + \overline{u(\mathcal{P}_2^{(1)}(1))} - \overline{u(\mathcal{P}_3^{(1)}(1))} - \overline{u(\mathcal{P}_4^{(1)}(1))}\right].$$

Writing the successive terms (5.2), for $k = 0, \cdots, T-1$,

$$\begin{aligned}
\tfrac{1}{(\delta x)^2}\left[\sigma_{11}^2((S+1)\delta t) - \sigma_{11}^2(S\delta t)\right] = \quad & d^2 + R_{uu}(0;S) + 2\sum_{s=0}^{S-1} R_{uu}(0;s) + \mathcal{M}(0;S) \\
& +\epsilon(0,S) \\
\tfrac{1}{(\delta x)^2}\left[\sigma_{11}^2((1+S+1)\delta t) - \sigma_{11}^2((1+S)\delta t)\right] = \quad & d^2 + R_{uu}(1;S) + 2\sum_{s=0}^{S-1} R_{uu}(1;s) + \mathcal{M}(1;S) \\
& +\epsilon(1,S) \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\tfrac{1}{(\delta x)^2}\left[\sigma_{11}^2((T+S+1)\delta t) - \sigma_{11}^2((T+S)\delta t)\right] = \quad & d^2 + R_{uu}(T;S) + 2\sum_{s=0}^{S-1} R_{uu}(T;s) + \mathcal{M}(T;S) \\
& +\epsilon(T,S),
\end{aligned}$$

summing over k and multiplying by $(\delta x)^2/[2(T+S)\delta t]$, we obtain

$$\begin{aligned}
\frac{\sigma_{11}^2((T+S+1)\delta t)}{2(T+S)\delta t} =& \frac{\sigma_{11}^2(S\delta t)}{2(T+S)\delta t} + \frac{(\delta x)^2 d^2}{2(T+S)\delta t}T + \frac{(\delta x)^2}{2(T+S)\delta t}\sum_{k=0}^{T-1} R_{uu}(k;S) \\
&+ 2\sum_{s=0}^{S-1}\frac{(\delta x)^2}{2(T+S)\delta t}\sum_{k=0}^{T-1} R_{uu}(k;s) + \frac{(\delta x)^2}{2(T+S)\delta t}\sum_{k=0}^{T-1}\mathcal{M}(k;S) \\
&+ \frac{(\delta x)^2}{2(T+S)\delta t}\sum_{k=0}^{T-1}\epsilon(k,S).
\end{aligned} \tag{5.4}$$

In the large time limit, $T \gg S$, the left side of (5.4) is the discrete form of definition (2.48) for effective diffusion coefficients. The first term in the right side of (5.4) vanishes and the second term tends to the local diffusion coefficient D, when (3.7) is used. Thus, for large times, (5.4) gives the discrete effective diffusion coefficient as a sum of influences of Lagrangian correlation computed as averages over all trajectories of length S, staring in all points inside the solute plume, of the velocity momentum $\mathcal{M}$, and a residual term ϵ:

$$D_{eff} = D + \lim_{T\longrightarrow\infty}\frac{(\delta x)^2}{2(T+S)\delta t}\sum_{k=0}^{T-1}\left[R_{uu}(k;S) + 2\sum_{s=0}^{S-1} R_{uu}(k;s) + \mathcal{M}(k;S) + \epsilon(k,S)\right]. \tag{5.5}$$

To simplify the notations, we denoted the longitudinal effective coefficient D_{11}^{eff} by D_{eff}. In a condensed form, the relation (5.5) can be written as

$$D_{eff} = D + D_{eff}(S) + 2\sum_{s=0}^{S-1} D_{eff}(s) + \mathcal{M}_{eff}(S) + \epsilon_{eff}(S), \tag{5.6}$$

which we call *path decomposition of discrete effective diffusion coefficient*. If the contribution of the last two terms in (5.6) is negligible, then the relation (5.5) looks like a discrete form of the effective diffusion coefficient (2.87) defined in analytical Lagrangian model of diffusion in random fields,

$$D_{eff} = D + \lim_{T\longrightarrow\infty}\int_0^T R_{uu}(t)dt.$$

For a perfectly uncorrelated velocity field, the last three terms in (5.6) should vanish. To prove that, we write the analytic longitudinal Lagrangian correlation in single realization as

$R_{L11}(s,s') = \sigma^2_{V_1}\delta(s-s')$, where $\sigma^2_{V_1}$ is the longitudinal velocity variance. Because R_{L11} is stationary and even function of $\tau = s - s'$, the "Taylor formula" can be used for (2.69) and the variance of displacements, of form (2.83), becomes

$$\sigma^2_{11}(t) = 2Dt + 2\sigma^2_{V_1}\int_0^t (t-\tau)\delta(\tau)d\tau.$$

Using the definition (2.48), we obtain the effective coefficient

$$D_{eff} = \frac{1}{2}\lim_{t\longrightarrow\infty}\frac{\sigma^2_{11}(t)}{t} = D + \sigma^2_{V_1}\int_0^\infty \delta(\tau)d\tau - \sigma^2_{V_1}\lim_{t\longrightarrow\infty}\frac{1}{t}\left[\int_0^t \tau\delta(\tau)d\tau\right] = D + \dddot{\sigma}^2_{V_1}, \qquad (5.7)$$

where $\dddot{\sigma}^2_{V_1}$ is the value of $\sigma^2_{V_1}$ multiplied by time dimension, due to the integration. Thus the macrodispersion coefficient for diffusion in uncorrelated random velocity fields is the sum between the local diffusion coefficient and the velocity variance (multiplied by the physical dimension of time).

5.2 A case study

To verify the path decomposition method, we first consider the case of uncorrelated fields. A weakly correlated field was produced with the same procedure as in section 4, when a small correlation length of $\ln K$, $\lambda = 0.01$, was used in Kraichnan generator. The terms of path decomposition of D_{eff}, for $S = 3$ and $T = 100$ days are presented in Fig. 7. The asymptotic value is reached after cca. 40 days, the sum of first three terms from the right side of (5.6) is very closed to the asymptotic value and, the term $D_{eff}(3)$, accounting for the influence of the velocity variance (5.3), has significant influence on final value of D_{eff}. The results are thus in agreement with theoretical prediction given by (5.7).

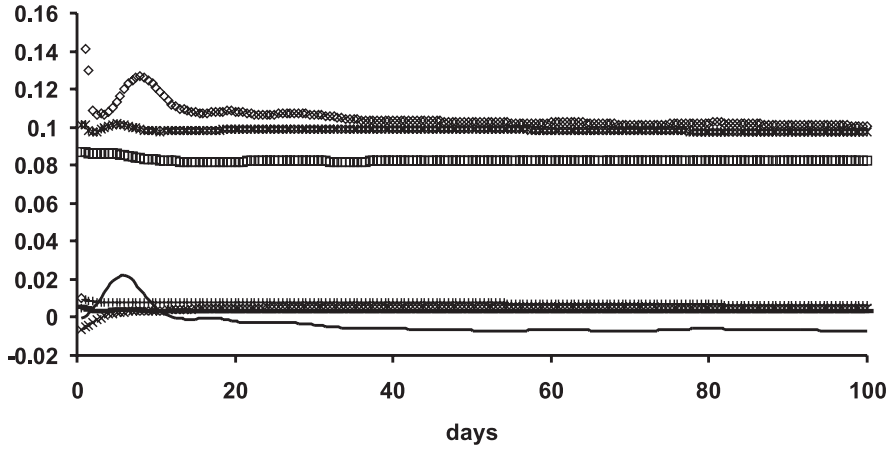


FIG. 7 D_{eff} and its components, for weakly correlated velocities and $S = 3$: D_{eff} ($\diamond$), $[D + D_{eff}(3) + 2\sum_{s=0}^{2} D_{eff}(s)]$ ($*$), $D_{eff}(3)$ ($\square$), $D_{eff}(2)$ ($+$), $D_{eff}(1)$ ($\times$), $D_{eff}(0)$ ($-$), $\mathcal{M}_{eff}(3)$ (full line).

In the following, we use the path decomposition method to analyze the oscillatory behavior of macrodispersion coefficient in simulations presented in Section 4.1. The terms of path decomposition, for $S = 3$ and $T = 100$ days, of D_{eff} were computed for the same exponential correlated field as that used in simulations from Fig. 1.

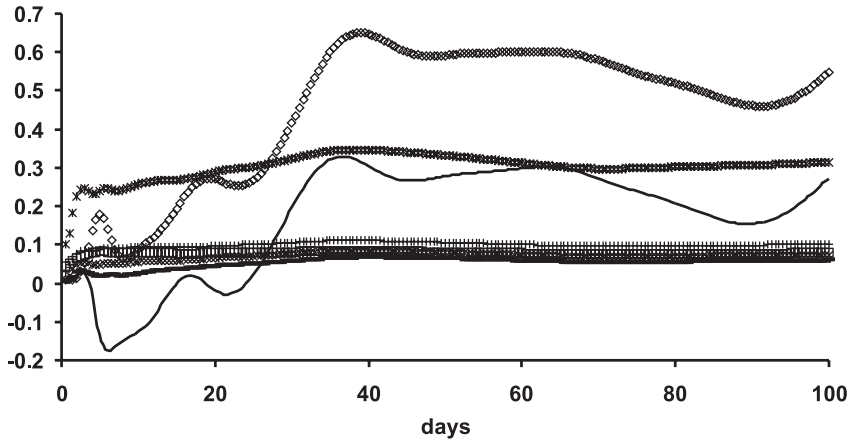


FIG. 8 D_{eff} and its components, for correlated velocities and $S = 3$: D_{eff} ($\diamond$), $[D + D_{eff}(3) + 2\sum_{s=0}^{2} D_{eff}(s)]$ ($*$), $D_{eff}(3)$ ($\square$), $D_{eff}(2)$ ($+$), $D_{eff}(1)$ ($\times$), $D_{eff}(0)$ ($-$), $\mathcal{M}_{eff}(3)$ (full line).

The result presented in Fig. 8 shows that the correlation terms, $D+D_{eff}(3)+2\sum_{s=0}^{2} D_{eff}(s)$, have smooth variations but their influence is not yet decisive for the behavior of the effective diffusion coefficient. The momentum term $\mathcal{M}_{eff}(3)$ is also significant and it has the same oscillatory behavior as the effective coefficient. To understand the meaning of the momentum term we compared D_{eff} and $\mathcal{M}_{eff}$ with the mean velocity of the center of mass, V_{cm}. Fig. 9 shows that the numerically generated random field is not stationary and the oscillations of the effective diffusion coefficient are generated by the oscillations of the center of mass.

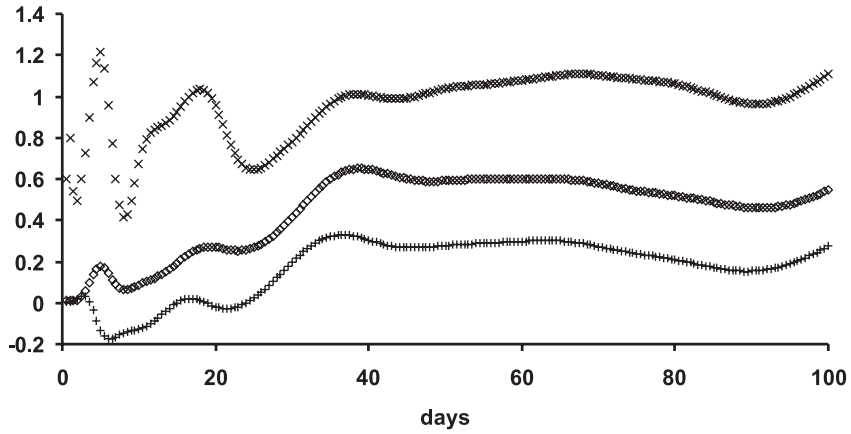


FIG. 9 D_{eff} ($\diamond$) and $\mathcal{M}_{eff}(3)$ ($+$) compared with the mean velocity of the center of mass, V_{cm} ($\times$).

6 Conclusions

In this Report we presented an analytic Lagrangian theory and a numerical model for "macrodispersion" in heterogeneous aquifers. The first conclusion is that the development of a rigorous analytic theory is a hard task, which requires a serious mathematical background, mainly in the theory of measure and random processes, while the physical description of the macrodispersion can be clearly formulated as a numerical model.

The Lagrangian approach can be build using the definitions and properties of random variables, Markov processes and diffusion processes (a minimal background is presented in Sections 2.1, 2.2 and 2.3). To obtain the Lagrangian description of diffusion in random velocity fields we made two hypotheses, presented in Section 2.4.1. These assume the nonsingularity of the velocity field (*H1*) and the continuity as space function of all realizations (*H2*). Although sometimes they sound unrealistic, these hypotheses are not new, we only made them explicitly. An analysis of the original paper of Taylor [1921] shows that the same hypotheses were implicitly used to obtain a diffusive behavior from "continuous movements".

When effective diffusion coefficients are computed, the correct formula is that defining the self-averaging property and asymptotic diffusive behavior, $D_{eff} = \lim_{t\to\infty} \sigma^2(t)/(2t)$, and not the formula as the limit of half of time derivative of displacement variance (Section 2.3.4). The last formula can be used in analytic computations (as we did in Sections 2.3.5 and 2.4.2) but it was shown that it causes oscillations of the effective coefficient in numerical applications [Schwarze et al. 2001].

The asymptotic diffusive behavior described by a Green-Kubo formula, for a particle with velocity governed by a Langevin equation (Section 2.3.5) is an illustration of thermodynamic irreversibility. In this case there were no supplementary hypotheses, as *H1)* and *H2*), because the velocity was not a random field but a stochastic process with strong properties which induce diffusive behavior. Thus, this model problem for thermodynamic irreversibility is easier than macrodispersion problem and has a rigorous solution.

We did not use the Fourier transform in derivation of the basic formula, giving the effective diffusion coefficient as function of Lagrangian correlation. Fourier transform requires supplementary mathematical restrictions and makes unclear the relation between the Lagrangian and Eulerian correlations. Also, no stationarity of the random field or "Lagrangian stationarity" were assumed.

The Lagrangian approach becomes more useful when the Lagrangian correlation can be related to the Eulerian correlation. This relation can be obtained using the Corsin conjecture or approximations enabling the factorization of averages over the realizations of the velocity field (Section 2.4.2). The stratified aquifer model of Matheron and de Marsily (Section 2.4.4) do not need approximations or Corsin conjecture and give exact results for both diffusive and superdiffusive behavior, as function of Eulerian correlation. Another example where the Eulerian statistics can be introduced without approximations is the computation of mean and variance of travel time in unsaturated soils, presented in Section 2.4.5.

The existence of asymptotic diffusive behavior do not proves the correctness of the use of an effective diffusion equation (Section 2.4.2). When one asserts the existence of the effective diffusion equation, its predictive power for single realization is conditioned by the equality of the effective coefficient computed for the diffusion process in the given realization of the random field with the coefficient computed as average over realizations. This is possible when the Lagrangian velocity correlation, average over realizations, is closed to the corresponding correlation in a given realization, computed as space average over the solute plume weighted

with the time-dependent distribution of concentration (Section 2.4.3).

The numerical model, presented in this Report, is a direct description of the conceptual model of macrodispersion and not a numerical simulation of the stochastic process of diffusion in random fields from the Lagrangian theory. In fact, the simulation of the movement of N random walkers in realizations of a numerically generated random field is a discrete stochastic process represented on the computer, not necessarily based on a mathematical model. This approach has the advantage that it is not concerned with mathematical difficulties related to the formulation of the Lagrangian theory. Some authors also try to avoid these difficulties when they present the "the Lagrangian framework as the limit of the particle tracking procedure" [Vanderborght, 2001, Dagan and Fiori, 1997].

The asymptotic behavior was obtained in single realizations of the random field, when the movement of 10^{10} particles was simulated with the GRW algorithm (Section 4.1). Unlike the methods which simulate individual trajectories, GRW spreads all the particles lying in a grid node, on the directions of diffusive and advective movements, by the use of a single numerical procedure at each time step. This saves computing time and memory and allows the simulation of very large number of particles (Section 3.2).

It was shown that the overshoot errors do not influence the result when ten grid steps per correlation length of logarithm of hydraulic conductivity were used. For coarser grids, the GRW algorithm provides correction technics, presented in Section 4.2.

The effective diffusion coefficients computed in single realizations are close to the theoretical values but present numerical oscillations. Because the use of overshoot corrections shows that the oscillations are not caused by numerical errors in simulations of transport, it was necessary to analyze the accuracy of numerical generated random field.

The path decomposition introduced for the first time in this Report (Section 5.1) is an expression of the numeric effective diffusion coefficient as function of correlations along the trajectories staring in all points inside the solute plume, developed for several time iterations, and of quantities $\mathcal{M}$ and ϵ, which describe the statistical properties of a given realization. In the large time limit, the path decomposition can be interpreted as a discrete form of the effective diffusion coefficient from the Lagrangian theory but it can not be derived from the analytic formula because it depends on particular features of simulation with GRW.

The analysis of its statistical structure with the path decomposition method, shows that the random field obtained with the Kraichnan generator, in first approximation, has an oscillating mean velocity which causes the oscillations of the effective diffusion coefficient (Section 5.2). The result illustrates the utility of this method in case analyses and in evaluation of random field generators.

Further work should continue the present one in several directions:

- the study of numerical errors caused by overshooting, with the methods used this Report and using a new approach, where the velocity will be represented in computer by real numbers, and not by integer discrete values as it is in present;

- the path decomposition analysis of fields produced by different methods (Kraichnan generated hydraulic conductivities and discrete velocity field calculated by FD integration of Darcy law, turning band method, spectral decomposition method, a.s.o.);

- simulation of diffusion in a large collection of realizations, with the most convenient methods for overshooting corrections and random field generator, will be used to study the mean and variance of concentration field, the mean and the variance of the effective diffusion coefficient and the validity of a large scale description of the solute transport by an effective diffusion equation.

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