Mathematical background
for diffusion processes
in natural porous media

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Forword

This report contains the English abstract of the Ph.D. thesis, "On the Connection Between the Microscopic and Macroscopic Modeling of the Thermodynamic Processes", that the author defended at "Simion Stoilow Institute of Mathematics of the Romanian Academy" in December 1998. Passing through general definitions and results from the mathematics of stochastic processes and dynamical systems as tools in nonequilibrium statistical mechanics (Section 2), this work presents a mathematical frame of "stochastic theories" of diffusion in hydrogeological environments and proposes new approaches for both continuous-mathematical and numerical modeling.

The general frame allowing to obtain the connection between Lagrangian and Eulerian descriptions, to introduce Corsin's conjecture and to discuss about asymptotic diffusive behavior is presented in Section 3. One underlines the difference between the genuine diffusion coefficients (3.4) and the effective ones (3.5), the requirement that more than one statistical ensemble should be defined to describe movements in random fields (two in (3.10) and three in (3.13), when both random field and local diffusion are considered) and the non-additivity between the "molecular diffusion" and effective diffusion in absence of molecular diffusion (3.14-15).

The continuous modeling based on space-time coarse grained averages from Section 4 outlines the derivation of Darcy-Buckingham law (4.15) and porosity dependent advection-diffusion equation (4.16). This continuous modeling is also useful in designing random walkers numerical models for diffusion.

The numerical models presented in Section 5 were tested for 1-dimensional diffusion at very small concentrations and model-problem of non-diffusive behavior in stratified aquifers of Matheron and de Marsily. These preliminary results are the basis of a numerical model for diffusion which is being developed in our research group.

This short excursion through the field of irreversibility, continuous modeling and diffusion in random environments is based on the results from the author's work during several stays in the research team "Verhalten von Schadstoffen in geologischen systemen" at Forschungszentrum Jülich. The references list of the report contains their previous results and relevant works for a thorough study of these problems.

Jülich, September 5, 2000   Dr. H. Vereecken

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NICOLAE SUCIU

ON THE CONNECTION BETWEEN THE MICROSCOPIC AND MACROSCOPIC MODELING OF THE THERMODYNAMIC PROCESSES

(The English abstract of the Ph.D. Thesis)

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Bucureşti, 1998

1   Introduction

The goal of statistical mechanics is to derive macroscopic behavior of physical systems from the behavior of their microscopic components [Bălescu, 1975, pp.3, 34]. The specific paradigm is to study not a single physical system but large collections of identical systems, continuously distributed into the 'phases space', called *statistical ensemble*. This is done by means of a density defined on the space of all possible states. It has the meaning of the probability density for the state of the system to correspond to a given point in the state space. The *basic postulate of statistical mechanics* [Bălescu, 1975, p.724] says that the probability density provides a complete description of the system and statistical averages give macroscopic observable values of all physical quantities.

In passing from a microscopic description, by dynamical systems, to a statistical macroscopic one, the *ergodicity problem* occurs: time and statistical averages must be equal in order to have the same observable value of the physical quantity in both descriptions. Moreover, if the statistical description uses the framework of state space then it is isomorphic to the deterministic description [Onicescu, 1977, p.363, Prigogine, 1998]. In this case the irreversible behavior, as described by increasing entropy, cannot be derived [Lasota and Mackey, 1994]. This is referred to as the *Statistical mechanics paradox.*

These difficulties can be removed if the microscopic description uses the framework of stochastic processes, defined by probability measures on the space of trajectories of the microscopic constituents [Doob, 1953, chap.2]. The nondegenerate case is that one when through a given point passes a whole set of trajectories, and not only one trajectory as it is the case of dynamical systems. Stochastic processes also could be mathematical models for statistical ensemble of Gibbs and Boltzmann, "a concept consisting of many physical systems with different initial conditions" [Boltzmann, 1981, p.204]. The probabilities on the state space are obtained by projections of probabilities defined on the space of trajectories. There exists a nontrivial class of Markov processes (including diffusion processes) which are ergodic and allow the derivation of the entropy law. In this general approach micoscopic dynamics does not explicitly occur. As a consequence, no 'correspondence principle' can be used (for instance, one cannot find the Newtonian mechanics as a limiting case).

The attempt of the 'Bruxelles school' [Misra et al., 1979, Prigogine, 1980, 1999] to obtain "a probabilistic reformulation of microscopic dynamics" yields representations of irreversible Markov processes by dynamical systems into measure spaces. But this abstract dynamics is not explicit, no equations of motion of physical particles are proposed, and correspondence principle is not yet established. This could be a reason for the dominant pragmatic attitude based on the remark that for many particle systems or for systems with sensible dependence on initial conditions deterministic predictions are inoperative. "A paradigmatic jump" or "a change of philosophy by supply of new concepts and probabilistic predictions" is claimed [Lebowitz, 1999, Parisi, 1999, Ruelle, 1999].

Despite of its foundation difficulties, statistical mechanics successfully solved many practical problems by using supplementary hypotheses. Among them, the thermodynamics of systems close to equilibrium gives good predictions for transport coefficients by Green-Kubo formulas and fluctuation-dissipation theorems [Bălescu, 1975]. In order to achieve these, the microscopic description is proposed by Langevin type equations (generalizing Newton law up to a perturbed dynamical system). The corresponding continuous description is obtained as Fokker-Planck equations for probability densities. A frequently used complementary approach is the numerical procedure called the 'molecular dynamics'. According to this, the

behavior of physical systems is obtained through the simulation of the movement of a large number of particles followed by space-time averages yielding a continuous description [Koplik and Banavar, 1995].

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The Ph.D. thesis discusses a few questions on theoretical foundation of statistical mechanics, argues for a new method in continuous modeling of corpuscular physical systems and proposes a molecular dynamics type numerical approach for diffusion processes.

$\Diamond$ Section 2 contains a general presentation of both stochastic processes and measure dynamical systems as random functions in the Doob sense. Deterministic processes are shown to be degenerated Markov processes. It is found that the 'strongly ergodic' Markov processes, as defined by Gardiner [1983], describe irreversible thermodynamic behavior. Their representation as measure dynamical systems in spaces of trajectories could reformulate the Misra-Prigogine-Courbage theory of irreversibility.

$\Diamond$ In the Section 3 diffusion processes are defined and equivalence between Fokker-Planck and Langevin equations is presented. Starting with the Langevin-like equation for the molecules motion, the Gibbs thermodynamic relation between free energy, entropy and temperature is derived. The transport coefficients are obtained as Green-Kubo formulas. Some definitions and results from the theory of diffusion in random fields are formulated and used to model turbulent diffusion and transport processes in porous media.

$\Diamond$ Section 4 proposes a new macroscopic continuous model for discrete systems, based on [Vamoş et al., 1996a,b]. If physical quantities associated with particles can be described by piece-wise analytical functions then, coarse grained space-time averages give a.e. continuous fields verifying identities similar to balance equations from mechanics of continua. Throughout continuous fields and macroscopic balance equations are obtained by averaging over the statistical ensemble. The correspondence with classical results of Kirkwood [1967] is obtained for small space-time scales. In addition, it is shown that from the requirement that the concentration balance be a diffusion-like equation, a microscopic criterion for irreversibility is obtained. This could be useful in numerical simulations and experimental data analysis. As an illustration, a continuous model of transport processes in porous media, the derivation of Darcy law and porosity dependent transport equations are presented.

$\Diamond$ On the basis of the results from the Section 4, the Section 5 develops a molecular dynamics type numerical model for diffusion. Continuous fields are derived by coarse grained averages over the trajectories of a system of random walkers evolving in a grid. The space-time scale and the number of particles needed for a given precision is obtained, numerical and analytical solutions are compared and the microscopic irreversibility criterion is tested. Moreover, a two-dimension simulation of diffusion in a random field is performed to test the method by comparing its results with the features of the model of Matheron and de Marsily [1980].

2 Dynamical Systems and Stochastic Processes

Statistical mechanics description for a physical system consisting of N particles is given by systems of ordinary differential equations (Newton law or Hamiltonian system)

$$\frac{dy}{dt} = V(y), \; y \in Y, \; Y \subseteq \mathbb{R}^{6N}, \; V \in \mathcal{C}^1(Y), \tag{2.1}$$

If there is a unique solution of the Cauchy problem (2.1), $y(0) = y_0$, for $\forall t \in \mathbb{R}$, then $S_t(y_0) = y(t, y_0)$ defines a *differentiable dynamical system*, $\{S_t\}_{t \in \mathbb{R}}$, generated by the vectors field V. Moreover, the dynamical system preserves the Lebesgue measure, μ, defined on the Borel σ-algebra $\mathcal{B}$, i.e. $\mu(B) = \mu(S_{-t}B)$, $\forall \; B \in \mathcal{B}$. It follows that $\{S_t\}_{t \in \mathbb{R}}$ is a *group of automorphisms* in the measure space $(Y, \mathcal{B}, \mu)$ (*state space*). Then, with the microscopic description (2.1) one associates the **continuous macroscopic description** given by the Frobenius-Perron unitary group [Cornfeld et al., 1982, pp.26,48],

$$\{U_t\}_{t \in \mathbb{R}}, \; U_t : L^1(Y) \longmapsto L^1(Y), \; (U_t f)(y) = f(S_{-t}(y)). \tag{2.2}$$

Let p_0 be the density of the measure P, absolutely continuous with respect to μ, $P(B) = \int_B p_0(y) dy$, $\forall \; B \in \mathcal{B}$. The evolution of $p(y, t) = U_t p_0(y)$ is described by the *Liouville equation*,

$$\frac{\partial p}{\partial t} + \sum_{k=1}^{6N} \frac{\partial}{\partial y_k}(pV_k) = 0. \tag{2.3}$$

The projection of p on $\mathbb{R}^3$ is a concentration and from (2.3) one derives the continuity equation.

Densities described by (2.2-3) conserve the Gibbs entropy $S(t) = -\int p(y, t) \ln p(y, t) dy$ = *const*. Thus, differentiable dynamical systems preserving a measure in the state space cannot be used as models for thermodynamic irreversibility [Gardiner, 1983, pp.61-62, Lasota and Mackey, 1994, chap.9].

Let $\Lambda \subseteq \mathbb{R}$ be a set of parameters, $(\Omega, \mathcal{A}, P)$ be a measure space with probability measure and let $(Y, \mathcal{B})$ be a measurable space A. *stochastic process* is defined as a random variable

$$\boldsymbol{\eta} : \Omega \longmapsto Y^\Lambda, \; \boldsymbol{\eta}(\omega) = y^\omega, \; y^\omega \in Y^\Lambda, \; \forall \; \omega \in \Omega. \tag{2.4}$$

The function $y^\omega : \Lambda \longmapsto Y$, is a *trajectory* and its values, $y^\omega(\lambda) = y_\lambda$, are points in the state space Y. If $\mathcal{B}^\Lambda$ is a σ-algebra in Y^Λ, then $P_{\boldsymbol{\eta}}(C) = P(\{\boldsymbol{\eta} \in C\})$, $\forall C \in \mathcal{B}^\Lambda$, define the *distribution* of the process (2.4) and the space of trajectories becomes a probability space, $(Y^\Lambda, \mathcal{B}^\Lambda, P_{\boldsymbol{\eta}})$, called *phase space*. Uniquely up to an isomorphism, phase space defines the *stochastic process in the sense of Doob.* [Doob, 1953, Iosifescu and Tăutu, 1973].

When the microscopic description is performed by means of *stationary Markov processes* (i.e. the state after a time interval τ does not depend on the previous states), the continuous description can be obtained using semigroups of *kernel type Markov operators*, $\{K_\tau\}_{\tau \geq 0}$, defined by

$$K_\tau f(y) = \int_Y p(y, \tau \mid y_0) f(y_0) dy_0, \; \forall \; f \in L^1(Y), \tag{2.5}$$

where $p(. \mid .)$ is the density of *transition probability*.

The existence of the limit

$$p(y_1, t_1 - t_2 \mid y_2) \longrightarrow p_s(y_1), \text{ for } t_1 - t_2 \longrightarrow \infty, \tag{2.6}$$

ensure the *strong ergodicity* [Gardiner, 1983, Sect.3.7.3]. With a strongly ergodic process one associates a non-stationary process through the 'preparation of an initial state' [Gardiner, 1983, p.60, van Kampen, 1981, p.92]

$$p(y, t) = p(y, t - t_0 \mid y_0) \text{ and } p(y, t \mid y', t') = p(y, t - t' \mid y'), \ \forall \ t, t' > t_0, \tag{2.7}$$

for fixed t_0. These processes are also referred to as *homogeneous processes*. Their important property is the existence of the limit $p(y, t) \to p_s(y)$ as $t \to \infty$ (or $t_0 \to -\infty$), which, when used in (2.5), implies

$$\|K_t p - p_s\|_{L^1} \to 0, \text{ for } t \to \infty. \tag{2.8}$$

The semigroups endowed with the property (2.8) are just the 'strong Markov' [Misra et al., 1979] or 'irreversible' [Antoniou and Gustafson, 1993] semigoups. For these semigroups the Gibbs entropy (and any convex functional of p) monotonically increases up to a maximum value corresponding to the equilibrium state, i.e. they satisfy the second law of thermodynamics.

From (2.2) and (2.5) it follows that the Frobenius-Perron operators are Markov operators with a singular transition probability (between states lying on the same trajectory): $p(y, t \mid y_0) = \delta(y - S_t(y_0))$. This is the reason the dynamical systems are presented as degenerated Markov processes [Misra et al., 1979]. The following proposition was proved.

Proposition 2.3: *If the dynamical system $\{S_t\}_{t \in \mathbb{R}}$ preserves a measure P in the states space, $P(B) = P(S_{-t}B)$, $\forall \ B \in \mathcal{B}$, then it generates a stochastic process in the sense of Doob, $\boldsymbol{\eta}$, and the corresponding state and phase spaces are isomorphic: $(Y, \mathcal{B}, P) \sim (Y^{\mathbb{R}}, \mathcal{B}^{\mathbb{R}}, P_{\boldsymbol{\eta}})$.* □

A stationary Markov process can be represented as a dynamical system in the space of its trajectories. By the Kolmogorov theorem [Iosifescu and Tăutu, 1973], the measure $P_{\boldsymbol{\eta}}$ is completely defined by the measure of the *cylindrical sets* from $\mathcal{B}^{\mathbb{R}}$, defined as $C_{n+1} = \{y^\omega(t_0) \in B_0, \cdots, y^\omega(t_n) \in B_n \mid B_0, \cdots, B_n \in \mathcal{B}\}$, $t_0 < \cdots < t_n$. For Markov processes this reads

$$P_{\boldsymbol{\eta}}(C_{n+1}) = \int_{B_0} p(y_0, t_0) dy_0 \int_{B_1} p(y_1, t_1 \mid y_0, t_0) dy_1 \cdots \int_{B_1} p(y_n, t_n \mid y_{n-1}, t_{n-1}) dy_n,$$

and the because the process is stationary,

$$P_{\boldsymbol{\eta}}(C_{n+1}) = P_{\boldsymbol{\eta}}(\Sigma_\tau(C_{n+1})) = P_{\boldsymbol{\eta}}(\Sigma_{-\tau}(C_{n+1})).$$

The invertible map $\Sigma_\tau : Y^{\mathbb{R}} \longmapsto Y^{\mathbb{R}}$, $\Sigma_\tau(y_t) = y_{t+\tau}$, (translation along the trajectories of the Markov process) preserves the measure $P_{\boldsymbol{\eta}}$. Thus, $\{\Sigma_\tau\}_{\tau \in \mathbb{R}}$ is a *group of Markov automorphisms* [Cornfeld et al. 1982, p.188] defined in probability space $(Y^{\mathbb{R}}, \mathcal{B}^{\mathbb{R}}, P_{\boldsymbol{\eta}})$.

The **"Misra-Prigogine-Courbage Theory"** attempts to get thermodynamic irreversibility, by strong Markov semigroup, starting with deterministic descriptions given by dynamical systems [Misra et al., 1979]. A intertwining relation $K_t \Phi = \Phi U_t$, between the strong Markov

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semigroup, $\{K_t\}_{t\geq 0}$, and the restriction for $t \geq 0$ of a unitary group, $\{U_t\}_{t\in\mathbb{R}}$, is derived in order to performe a change from deterministic to probabilistic description. When the mapping Φ between the corresponding L^2 spaces is invertible a 'nounitary equivalence' is established and if Φ is only surjective one gets a 'coarse-graining projection'.

The physical relevance of the formalism was formulated by Antoniou and Gustafson [1993] as a possibility that "experimentally observed Markov semigroups, such as chemical reactions and diffusion, can be *lifted to a unitary superdynamics*". The result was presented in terms of the unitary dilations.

Following the definition given by Sz.-Nagy and Foiaş [1970, pp.10, 31], the group $\{U_\tau\}_{\tau\in\mathbb{R}}$, defined in the Hilbert space $L^2(Y^\mathbb{R})$, is the *unitary dilation* of the semigroup $\{K_\tau\}_{\tau\geq 0}$, defined in Hilbert space $L^2(Y)$, if the relation $K_\tau = \mathrm{Pr}\,U_\tau$ holds for $\tau \geq 0$, where Pr is the orthogonal projection of $L^2(Y^\mathbb{R})$ on $L^2(Y)$. It was proved that the continuous groups of contractions can be dilated up to a minimal continuous group, uniquely defined up to an isomorphism [Sz.-Nagy and Foiaş, 1970, Theorem 8.1 p.31, p.146]. The result includes the class of Markov operators (they are isometric, thus contractions). In order to preserve the meaning of probability, it is also necessary that dilations preserve positivity. By using the theorem of Rokhlin on the natural extension of exact dynamical systems, Antoniou and Gustafson [1993] proved that the Markov semigroup induced by an 'exact' dynamical system can be dilated up to a unitary group associated with a 'K system'. In [Antoniou and Gustafson, 1997, Antoniou et al., 1998] the extension of probabilities measures was used to obtain the dilation for constant preserving Markov semigroups ($K_\tau 1 = 1$).

Proposition 2.5:

1) *The adjoint Markov semigroups $\{K_\tau^*\}_{\tau\geq 0}$ corresponding to a stationary Markov process possess positive dilations to unitary groups;*

2) *For strongly ergodic and constant preserving Markov semigroups, both $\{K_\tau^*\}_{\tau\geq 0}$ and $\{K_\tau\}_{\tau\geq 0}$ possess positive dilations to a unitary group, $\{U_\tau\}_{\tau\geq 0}$, induced by K-systems. In addition, there is an invertible mapping $\Phi : L^2(Y^\mathbb{R}) \longmapsto L^2(Y)$, $(\Phi f)(y) = \int_\Omega f(y^\omega)\delta(y - \eta(t,\omega))P(d\omega)$ for which the intertwining relation $K_\tau\Phi = \Phi U_\tau$ holds for $t \geqslant 0$.* $\square$

Proposition 2.5 states that the 'change of representation' from [Misra et al., 1979] can formally be obtained by representing genuine irreversible processes as dynamical systems into the space of trajectories.

3 Continuous Modeling by Diffusion Processes

Diffusion processes. A Markov process with trajectories in the measurable space $(Y,\mathcal{B})$, $Y \subseteq \mathbb{R}^3$ 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

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

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

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

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

$$\partial_t p(x,t \mid x_0, t_0) = -\nabla[Ap(x,t \mid x_0, t_0)] + \nabla^2[\tilde{B}(x,t)p(x,t \mid x_0, t_0)], \qquad (3.1)$$

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

$$p(x,t \mid x_0, t_0) = [4\pi D(t - t_0)]^{-\frac{1}{2}} \exp[(x - x_0)^2 / 4D(t - t_0)]. \qquad (3.2)$$

The corresponding Fokker-Planck equation becomes the *diffusion equation* $\partial_t p = D\partial_x^2 p$. More generally, if the average is $x_0 + u(t - t_0)$, the *advection-diffusion equation* $\partial_t p + u\partial_x p = D\partial_x^2 p$ is obtained.

Theorem 3.1 [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 $\tilde{B}$ is a.e. positively defined, then the solutions of Fokker-Planck equation (3.1) are attracted by the stationary solution p_s: $\|p(x,t) - p_s(x)\|_{L^1(Y)} \longrightarrow 0$, as $t \to \infty$.* $\square$

Theorem 3.1 give the *sufficient conditions* for the existence of the strong ergodicity property (2.8). A corollary is the *asymptotic stability property* [Lasota and Mackey, 1985, p.176] of the Markov semigroup (2.5): $K_t p \longrightarrow p_s$, for $t \longrightarrow \infty$, $\forall\ p_s$, $K_t p_s = p_s$, for all solutions p of (3.1).

The Wiener process is the Gaussian with the transition probabilities given by (3.2), $D = 0.5$, starting from $x_0 = 0$ at $t_0 = 0$. The representation as a two variables function, $w(t,\omega)$, $w : [0,\infty] \times \Omega \longmapsto Y$, allows the introduction of *Itô stochastic differential equation*

$$dx(t) = a(x(t),t)dt + \tilde{b}(x(t),t)dw(t). \qquad (3.3)$$

If for every fixed ω there exists a unique solution of (3.4), $x(t) = X(w(t,\omega), x_0, t_0) = X(t,\omega, x_0, t_0)$, which satisfies the initial condition $x_0 = x(t_0)$, then the time function $x(t)$ is the trajectory of a stochastic process $\chi : \Omega \times Y \longmapsto Y^{[0,\infty]}$, defined in the Cartesian product space $\Omega \times Y$. If the coefficients of (3.3) are related to those of (3.1) by $A(x,t) = a(x,t)$, and $\tilde{B}(x,t) = \frac{1}{2}\tilde{b}\tilde{b}^{\mathrm{T}}(x,t)$, then the probability density of the process χ obeys the Fokker-Planck equation [Gardiner, 1983, chap.4].

The description realized by the Fokker-Planck equation (probability densities as space-time functions) performs the *Eulerian statistics* and the description which uses the trajectories of fictitious particles, by Itô equation, gives *Lagrangian statistics* [Avellaneda et al., 1991]. In Lagrangian statistics the definition $iii)$ of the diffusion coefficients becomes

$$B_{ij}(x,t) = \frac{1}{2}\frac{d}{ds}(\tilde{\sigma}^2)_{ij}(t + s; x, t)\mid_{s=0}, \qquad (3.4)$$

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).

When the solutions of (3.3) cannot be associated with a Fokker-Planck equation then it is still possible to look for the existence of the *effective diffusion coefficients*

$$D_{ij}^* = \lim_{t\to\infty}\frac{1}{2}\frac{d}{dt}(\tilde{\sigma}^2)_{ij}(t), \qquad (3.5)$$

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If the limit (3.5) is finite one says that *the process behaves asymptotically diffusive.*

Equilibrium thermodynamics. Let the physical system consisting of a single particle, the mass of which is m and its movement is governed by Newton law perturbed with a white noise force,

$$\frac{dx}{dt} = v, \quad \frac{dv}{dt} = -\gamma v + \sqrt{2D}\zeta, \tag{3.6}$$

where $(x, y) \in \mathbb{R}^2$, $D > 0$ and $dw(t) = \zeta(t)\,dt$. The model (3.6) is frequently used to describe a system of particles in contact with a 'booster' (a thermometer and a thermostat) [Bianucci et al., 1995]). The second equation (3.6) is the *Langevin equation* and its solutions are the trajectories of an *Ornstein-Uhlenbeck process.* The transition probability density is a Gausssian endowed with strong ergodicity property (2.6)

$$p(v, t - t_0 \mid v_0) \xrightarrow[t - t_0 \to \infty]{} p_s(v) = \left[\frac{2\pi D}{\gamma}\right]^{-\frac{1}{2}} \exp\left[-\frac{v^2}{\frac{2D}{\gamma}}\right], \tag{3.7}$$

[Gardiner, 1983, Sect.3.8.4].

The Boltzmann-Gibbs *entropy* is $S(t) = -k_B \int_{\mathbb{R}} p(v, t) \ln p(v, t) dv$, where k_B is the Boltzmann constant. A process starting from a nonequilibrium state (2.7) reaches the equilibrium (3.7) with the maximum entropy

$$S^e = k_B \ln Z + \frac{k_B}{\beta}[M(v^2)]^e, \tag{3.8}$$

where

$$\beta = \frac{2D}{\gamma}, \quad Z = \int_{\mathbb{R}} \exp(-v^2/\beta) = \sqrt{\frac{2\pi D}{\gamma}}, \text{and } [M(v^2)]^e = \int_{\mathbb{R}} v^2 p_s(v) dv = \frac{D}{\gamma}.$$

Thus the second law of thermodynamics holds. The *internal energy* is defined by $U = \frac{1}{2}m[M(v^2)]^e$, the temperature is $T = (\frac{2k_B}{\beta m})^{-1}$ and $F = -k_B T \ln Z$ defines the *free energy.* Then (3.8) becomes *the Gibbs relation,* from the equilibrium thermodynamics, $F = U - TS^e$. Also one obtains $\frac{1}{2}m[M(v^2)]^e = \frac{1}{2}k_B T$, which is a form of the *energy equipartition* theorem. Since the internal energy is constant, $U = mD/2\gamma$, p_s gives the maximum entropy of an insulated system, i.e. p_s is the *density* of the *canonical ensemble* [Mackey, 1989].

Fluctuation-dissipation Theorem. For each velocity realization, the first equation (3.6) provides a trajectory of the particle $x(t) = \int_{t_0}^t v(t')dt'$. The average over the velocity ensemble yields the displacements variance

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

The effective diffusion coefficient (3.5) has the finite value $D^* = D/\gamma^2$. Using the correlation computed at the equilibrium state, $\{M[v(t')v(t'')]\}^e$, D^* becomes

$$D^* = \lim_{t \to \infty} \int_{t_0}^t \{M[v(t')v(t)]\}^e dt'. \tag{3.9}$$

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Thus, a *Green-Kubo relation* [Bălescu, 1975, Sect.21.2, Evans and Morriss, 1990, chap.4] takes place for the transport coefficient. The process derived from (3.6) illustrates the approach of *fluctuation-dissipation theorems*. The perturbations in (3.6) can be described more realistically by the finite correlation noise, characterized by the *correlation time* τ_c,

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

In the white noise case, the correlation time becomes $\tau_c = 1/\gamma$. Generally, a finite correlation time is a necessary condition for an asymptotic diffusive behavior.

Movements in random fields. Let $\vartheta : \Omega \longmapsto Y_V^\Lambda$, $Y_V \subseteq \mathbb{R}^3$, $\Lambda \subseteq \mathbb{R}^3$, be a random field, with a space range of parameters. If for every fixed $\omega \in \Omega$ the sample $V^{(\omega)}$, $V^{(\omega)} : \Lambda \longmapsto Y_V$, is a nonsingular vector field, then it generates the differentiable dynamical system $\{S_t^{(\omega)}\}_{t \in \mathbb{R}}$, whose trajectories in $Y_x \subseteq \mathbb{R}^3$, $x^{(\omega)}(t; x_0, t_0) = S_{t-t_0}^{(\omega)}(x_0) = X(t, \omega, x_0, t_0)$, are solutions of the differentiable system

$$\frac{dx^{(\omega)}}{dt} = V^{(\omega)}(x^{(\omega)}). \tag{3.10}$$

The relation (3.10) may represent the description of a 'fluid particle', as in continuum mechanics, or even of a real particle. The random field V describes the action of the neighboring particles (the 'booster'). 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 concentration field for noninteracting systems of particles, $p \equiv c$.

The model of the previous statistical ensemble is the stochastic process $\chi : \Omega \times Y_x \longmapsto Y_x^\mathbb{R}$, where, for fixed $\omega \in \Omega$ and $x_0 \in Y_x$, $\chi(\omega, x_0) = x^{(\omega, x_0)}$ is a trajectory of the dynamical system $\{S_t^{(\omega)}\}_{t \in \mathbb{R}}$. Using Lagrangian statistics and averaging over the random velocities realizations, the coefficients from (3.1) are obtained in the form $\tilde{B}(x_0, t_0) = \tilde{0}$ and $A(x, t) = \overline{V}(x, t)$, where $\overline{V}(x, t) = M_\Omega[V(t, \omega, x_0, t_0)]$ is the average over velocities realizations. Thus, the Fokker-Planck equation takes the form $\partial_t c(x, t) + \nabla_x(\overline{V}(x, t)c(x, t)) = 0$, which is just the average over velocities of the Liouville equation associated with 'sample-system' (3.10). Since the movement of the particele is described by the dynamical system generated by the mean field $\overline{V}$, a *mean field property* [see Avellaneda and Majda, 1991] was proved. Since the coefficients $\tilde{B}$ defined by local time derivative (3,4) vanish, there is no local diffusion.

In order to check the asymptotic diffusive behavior, one uses the *Lagrangian correlation* of the velocity field

$$\tilde{R}_L(s, s'; x_0, t_0) = M_\Omega[V(s, \omega, x_0, t_0)V(s', \omega, x_0, t_0)]$$
$$- M_\Omega[V(s, \omega, x_0, t_0)]M_\Omega[V(s', \omega, x_0, t_0)].$$

The displacements variance reads

$$\tilde{\sigma}^2(t; x_0, t_0) = \int_{t_0}^{t} ds \int_{t_0}^{t} \tilde{R}_L(s, s'; x_0, t_0) ds'.$$

According to (3.5), the asymptotic diffusive behavior takes place if there exist finite effective coefficients

$$\tilde{D}^* = \lim_{t \to \infty} \frac{1}{2} \frac{d}{dt} \tilde{\sigma}^2(t; x_0, t_0) = \lim_{t \to \infty} \int_{t_0}^{t} \tilde{R}_L(s, s'; x_0, t_0) ds'. \tag{3.11}$$

If (3.11) holds, *one asserts* that the concentration can be approximated by a diffusion equation, $\partial_t c(x, t) = \tilde{D}^* \nabla^2 c(x, t)$. This is the 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, Avellaneda and Majda, 1991]. One remarks that while the existence of derivatives (3.4) determines the Fokker-Planck equation, the existence of the limit (3.11) does not ensure the existence of the diffusion equation as asymptotic approximation.

Since the velocity measurements are performed at fixed space points, the *Eulerian correlation* $\tilde{R}_E(x, x') = M_\Omega[vv' - \overline{V}(x)\overline{V}(x')]$ should be used. In the hypothesis that the average over Ω, used in the definition of $\tilde{R}_L$, factorizes (*the Corsin conjecture*, [Saffman, 1969]), one obtains a relation between the two correlations,

$$\tilde{R}_L(s, s'; x_0, t_0) = \int_{Y_x} \int_{Y_x} dx dx' p(x, s; x', s' \mid x_0, t_0) \tilde{R}_E(x, x'), \tag{3.12}$$

where $p(x, s; x', s' \mid x_0, t_0)$ is the probability density of the process χ starting from (x_0, t_0).

Turbulent diffusion and transport processes in porous media. Sometimes at *local scales* the transport processes in natural porous media are well described by an Itô stochastic equation but at larger, *global scales,* the experimental derived coefficients present an apparent increase as compared to the local ones. This is the so-called 'scale effect' [Saffman, 1969, Fried, 1975]. The explanation could be the heterogeneity of the aquifer properties and implicitly of the flow velocity. As stochastic model for two-scale problem one uses a *Brownian motion in a random 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 let the Wiener process be $\mathbf{w} : \Omega_w \longmapsto Y_w^{[0,\infty]}$, $Y_w \subseteq \mathbb{R}^3$. For every fixed $\omega_V \in \Omega_V$ one considers the Itô equation

$$dx^{(\omega_V)}(t) = V(x^{(\omega_V)}(t), \omega_V) dt + \left(\tfrac{2}{3}D\right)^{\frac{1}{2}} dw(t). \tag{3.13}$$

If there is a unique solution of (3.13), for every trajectory of $\mathbf{w}$ and sample of $\boldsymbol{\vartheta}$, $x^{(\omega_V, \omega_w)}(t) = X(t, \omega_w, \omega_V, x_0, t_0)$, in 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 χ, in the direct product probability space, $\chi : \Omega_V \times \Omega_w \times Y \longmapsto Y^{[0,\infty]}$, $Y \subseteq \mathbb{R}^3$. If $\tilde{R}_L$ decreases to zero fast enough as $t \to \infty$, then the process χ behaves asymptotically diffusive and, from (3.5) it follows

$$\tilde{D}^* = D\tilde{1} + \lim_{t \to \infty} \frac{1}{2} \frac{d}{dt} \int_{t_0}^{t} ds \int_{t_0}^{t} ds' \tilde{R}_L(s, s'; x_0, t_0). \tag{3.14}$$

The effective coefficients (3.14) *are not the sum* of molecular diffusion coefficient D and those of movement in random field (3.11). Moreover the Brownian motion enhances diffusive behavior [Suciu et al., 1996].

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The model of Matheron and de Marsily. The stratified aquifer model of Matheron and de Marsily [1980] describes the movement of a particle by a 2-dimensional Brownian motion, of coefficients D_L and D_T, on which one superposes a horizontal random field function only on transversal coordinate, $V(z, \omega_V)$,

$$dx^{(\omega_V)}(t) = V(z(t), \omega_V)dt + D_L dw(t),$$
$$dz(t) = D_T dw(t),$$

Since the averages over Ω_V and Ω_w factorize, the connection between Lagrangian and Eulerian correlations (3.12) holds without using a 'Corsin conjecture', and the variance of the longitudinal displacements becomes

$$\sigma_x^2(z_0, t_0) = 2D_L(t - t_0) + \int_{t_0}^{t} ds \int_{t_0}^{t} ds' \int_{\mathbb{R}} \int_{\mathbb{R}} dz dz' p(z, s; z', s' \mid z_0, t_0; D_T) R_E(z, z'). \quad (3.15)$$

The main feature of the model is that for Gaussian correlated fields, $R_E \sim e^{-z}$, the variance behaves as $\sigma_x^2 \sim t^{3/2}$ at all times. This property is often used to check the validity of the numerical models of diffusion in random fields [Avellaneda and Majda, 1991].

4 Continuous Macroscopic Modeling Through Space-Time and Stochastic Averages

Continuous description through coarse grained averages. If a microscopic description in terms of piece-wise analytic functions, assigned to the particles of the system, is available, there exists a macroscopic description given by a.e. continuous fields [Vamoş et al., 1996a,b].

For instance, let N be the number of molecules of a mechanical system and let the microscopic *kinematical description* be performed by the analytic time functions $\varphi_i : I \longmapsto \mathbb{R}$, $I = [0, T] \subset \mathbb{R}$ $(1 \leq i \leq N)$. Special φ_i functions are the positions $x_{\alpha i}$ and velocities $\xi_{\alpha i}$, $\alpha = 1, 2, 3$. The *space-time coarse grained average* of a physical quantity φ is the function $\langle \varphi \rangle : \mathbb{R}^3 \times (\tau, T - \tau) \longmapsto \mathbb{R}$,

$$\langle \varphi \rangle(\mathbf{r}, t) = \frac{1}{2\tau \mathcal{V}} \sum_{i=1}^{N} \int_{t-\tau}^{t+\tau} \varphi_i(t') H^+(a^2 - (\mathbf{r}_i(t') - \mathbf{r})^2) dt' \quad (4.1)$$

where $\tau < T/2$ and a are real positive arbitrary parameters, $\mathcal{V} = 4\pi a^3/3$ is the volume of the sphere $S(\mathbf{r}, a)$ and H^+ the left continuous Heaviside function. The average (4.1) characterizes the distribution of the quantity φ in a neighborhood of the point $(\mathbf{r}, t)$. The properies of coarse grained averages are given by the following propositions.

Proposition 4.1: *The Coarse grained average $\langle \varphi \rangle(\mathbf{r}, t)$ possesses continuous partial derivatives a.e. in $\mathbb{R}^3 \times (\tau, T - \tau)$.* □

Proposition 4.2: *The Coarse grained average $\langle \varphi \rangle$ satisfies the identity*

$$\partial_t \langle \varphi \rangle + \partial_\alpha \langle \varphi \xi_\alpha \rangle = \langle \frac{d}{dt} \varphi \rangle. \quad \square \quad (4.2)$$

The identity (4.2) describes the balance of microscopic quantities φ, into a sphere and time interval describing an imaginary measurement. Therefore (4.2) is a kind of microscopic balance equation.

Everywhere continuous fields and balance equations. One considers the microscopic model of the N particles system given by a stochastic process, defined in the probability space $(\Omega, \mathcal{A}, P)$,

$$\boldsymbol{\eta} : \Omega \longmapsto Y^I, \text{ where } Y = \mathbb{R}^{6N}, \, I \subseteq \mathbb{R}, \text{and}$$
$$\eta(t,\omega) = (\mathbf{r}_1(t,\omega), ..., \mathbf{r}_N(t,\omega), \boldsymbol{\xi}_1(t,\omega), \cdots, \boldsymbol{\xi}_N(t,\omega)), \tag{4.3}$$

where Y is the state space of positions and velocities and Y^I is the function space of trajectories. A *dynamical description* is performed by using the set of functions $f_i(\mathbf{r}_1, ..., \boldsymbol{\xi}_N, t)$, $1 \leq i \leq N$, defined on the state space. Statistical mechanics defines the value of the continuous field at $(\mathbf{r}, t)$,

$$F(\mathbf{r}, t) = M_\Omega[\sum_{i=1}^{N} f_i(\mathbf{r}_1(t,\omega), ..., \mathbf{r}_{i-1}(t,\omega), \mathbf{r}, \mathbf{r}_{i+1}(t,\omega), \cdots, \boldsymbol{\xi}_N(t,\omega), t)\delta(\mathbf{r} - \mathbf{r}_i(t,\omega))], \tag{4.4}$$

as the stochastic average over the contributions f_i of all particles [Kirkwood, 1967]. For $f_i \equiv 1$, (4.4) defines the concentration field $c(\mathbf{r}, t)$.

For a fixed sample ω, the kinematical description $\varphi_i(t)$, $1 \leq i \leq N$, can be obtained by using the trajectories of the stochastic process $\boldsymbol{\eta}$

$$\varphi_i(t) = \varphi_i(\mathbf{r}_1(t,\omega), ..., \mathbf{r}_N(t,\omega), \boldsymbol{\xi}_1(t,\omega), \cdots, \boldsymbol{\xi}_N(t,\omega), t). \tag{4.5}$$

If the (4.5) are at least piece-wise analytical functions, then the average (4.1) has the properties given by Propositions 4.1 and 4.2.

Proposition 4.3: *The average over the realizations of the process $\boldsymbol{\eta}$ of the coarse grained average (4.1) is equal to the space-time average of the continuous field, F_φ, defined by (4.4),*

$$M_\Omega[\langle\varphi\rangle](\mathbf{r}, t; a, \tau) = \frac{1}{2\tau\mathcal{V}} \int_{t-\tau}^{t+\tau} dt' \int_{S(\mathbf{r},a)} F_\varphi(\mathbf{r}', t')d\mathbf{r}', \tag{4.6}$$

and satisfies the identity

$$\partial_t M_\Omega[\langle\varphi\rangle] + \partial_\alpha M_\Omega[\langle\varphi\xi_\alpha\rangle] = M_\Omega[\langle\frac{d}{dt}\varphi\rangle]. \; \square \tag{4.7}$$

The continuous fields (4.4) of classical statistical mechanics are the limit as a and $\tau \longrightarrow 0$ of the averages (4.6): $M_\Omega[\langle\varphi\rangle](\mathbf{r}, t; a, \tau) \longrightarrow F(\mathbf{r}, t)$.

For $\varphi_i \equiv 1$, $1 \leq i \leq N$, (4.6) gives the concentration $c(\mathbf{r}, t) = M_\Omega[\langle 1\rangle](\mathbf{r}, t)$. A 'hydrodynamic' average of quantities φ is the continuous field $\bar{\varphi}(\mathbf{r}, t) = M_\Omega[\langle\varphi\rangle](\mathbf{r}, t)/c(\mathbf{r}, t)$. Defining the α component of the *Eulerian velocity field*, $u_\alpha(\mathbf{r}, t) = \bar{\xi}_\alpha(\mathbf{r}, t)$, the identity (4.7) takes the usual form of balance equations [Müller, 1985],

$$\partial_t(c \, \bar{\varphi}) + \partial_\alpha(c \, \bar{\varphi}u_\alpha) + \partial_\alpha(\overline{c\varphi(\xi_\alpha - u_\alpha)}) = c \, \overline{\frac{d}{dt}\varphi}. \tag{4.8}$$

Thus, if the stochastic model (4.3) of the physical system allow the construction of suitable kinematic descriptions (4.5), the Proposition 4.3 ensures the existence of smooth continuous fields (4.6) and balance equations (4.8).

The balance of the concentration is described by the continuity equation, obtained from (4.8) for $\varphi_i \equiv 1$:

$$\partial_t c + \partial_\alpha(c u_\alpha) = 0. \tag{4.9}$$

Using $u_\alpha = \overline{dx_\alpha/dt}$ and (4.7), for $\varphi = x_\alpha$, (4.9) becomes

$$\partial_t c + \partial_\alpha(c v_\alpha) = \partial_\alpha \partial_\beta(c \, D_{\alpha\beta}), \tag{4.10}$$

where

$$v_\alpha(\mathbf{r}, t) = \partial_t \overline{x_\alpha}(\mathbf{r}, t) + u_\beta \partial_\beta \overline{x_\alpha}(\mathbf{r}, t), \tag{4.11}$$

is the α component of the *Lagrangian velocity field* $\mathbf{v}$, and

$$D_{\alpha\beta}(\mathbf{r}, t) = \overline{x_\alpha}(\mathbf{r}, t)u_\beta(\mathbf{r}, t) - \overline{x_\alpha \xi_\beta}(\mathbf{r}, t), \tag{4.12}$$

is the *diffusion tensor*.

Proposition 4.4: *If the diffusion tensor (4.12) is positively defined, then the concentration balance is described by the diffusion equation (4.10).* $\square$

The positivity of coefficients (4.12) is a *microscopic criterion of irreversibility* useful to test the diffusive behavior of systems for which the requirements of Proposition 4.3 are fulfilled.

Continuous modeling of transport processes in porous media. Consider a consolidated porous media as a mixing of solid matrix molecules and those of fluid components filling it. To each molecular species one associates the volumes $\mathcal{V}^m$, respectively $\mathcal{V}^{c^1}, \mathcal{V}^{c^2}, \cdots$ and molecular masses $\mathcal{M}^m$, respectively $\mathcal{M}^{c^1}, \mathcal{M}^{c^2}, \cdots$. The corresponding coarse grained averages (4.1) define a.e. continuous fields. Let τ be a time scale much more large than molecular vibrations scale and a space scale a, $(\mathcal{V}^m)^{\frac{1}{3}} \ll a \ll d_p$, where d_p is the pores dimension. For these, (4.6) gives $M_\Omega[\langle \mathcal{M}^m \rangle] \sim F_{\mathcal{M}^m}$. For the solid matrix $F_{\mathcal{M}^m} = \rho^m$, where ρ^m is the mean density of the solid material. Thus $1^m(\mathbf{r}) \sim F_{\mathcal{M}^m}/\rho^m$ is a first asymptotic approximation of the *characteristic function* of the solid matrix domain. The function $1^m(\mathbf{r})$ is continuous except at the points of the surface of the solid matrix, which have a zero Lebesgue measure in $\mathbb{R}^3$, thus it is Riemann integrable. At much more large scales, $a \gg d_p$, one defines the *local porosity* as volume ratio of pores space and sphere $S(\mathbf{r}, t)$, $\Theta(\mathbf{r}, t) = \frac{1}{\mathcal{V}} \int_{\mathbb{R}^3} (1 - 1^m(\mathbf{r}'))H^+(a^2 - (\mathbf{r}' - \mathbf{r})^2)d\mathbf{r}'$. The continuous and positive function Θ corresponds to the local porosity introduced by Hilfer [1991]. The volume ratios of the components satisfy the equality $\Theta^m + \Theta^{c^1} + \Theta^{c^2} + \cdots = 1$ ('the hypothesis that the mixture does not contain void space' [Bowen, 1984, p.67]).

In this approach, *the volume fraction of the c* component can be defined by using (4.6) as $\theta^c = \mathcal{V}^c M_\Omega[\langle 1 \rangle] = \mathcal{V}^c c_a^c$, where c_a^c is an apparent concentration, and (4.7) becomes a continuity equation

$$\partial_t \theta^c + \partial_\alpha(u_\alpha^c \theta^c) = 0. \tag{4.13}$$

From Proposition 4.4 it follows that (4.13) is equivalent to the advection-diffusion equation

$$\partial_t \theta^c + \partial_\alpha (v_\alpha^c \theta^c) = \partial_\alpha \partial_\beta (K_{\alpha\beta} \; \theta^c), \tag{4.14}$$

if the tensor $K_{\alpha\beta}(\mathbf{r}, t) = \overline{x_\alpha^c u_\beta^c} - \overline{x_\alpha^c \xi_\beta^c}$ is positively defined. Form (4.13-14), the flux density of volume fraction θ_α^c is

$$J_\alpha = \theta^c(u_\alpha^c - v_\alpha^c) = -\partial_\beta (K_{\alpha\beta} \; \theta^c). \tag{4.15}$$

If θ^c represents the 'water content of an aquifer' then $\mathbf{u}_f = (\mathbf{u}^c - \mathbf{v}^c)\theta^c$ defines the *filtration velocity* and (4.15) becomes the *Darcy-Buckingham law*, for volumetric density of water flux through porous media [Sposito, 1986]. For instance, in a saturated aquifer, under the free surface level f, $\theta^c = \Theta$ and (4.15) take the usual form of Darcy law [Bowen, 1984], $J = -\tilde{K} \nabla f$.

The actual concentration of the substance represented by the component c, corresponding to that derived from a water sample, is $c(\mathbf{r}, t) = c_a^c(\mathbf{r}, t)/\Theta(\mathbf{r})$. Divided by the constant $\mathcal{V}^c$, the equation (4.16) becomes the porosity dependent advection-diffusion equation

$$\Theta \partial_t c + \partial_\alpha (v_\alpha^c c \Theta) = \partial_\alpha \partial_\beta (K_{\alpha\beta} \; c \Theta). \tag{4.16}$$

If the tensor (4.12) is positively defined, then Darcy's law and advection-diffusion equations are adequate models to the space-time scale (a, τ) and no 'scale effect' occur [Suciu et al., 1998a,b]. This outline of continuous modeling can be extended to unconsolidated porous media, if the motion of solid matrix molecules is considered.

5 Numerical Modeling of Diffusion by Systems of Random Walkers

Cellular automata numerical algorithm. Cellular automata simulate the behavior of complex systems by simple rules applied to transform a finite set of states assigned to each node or cell of a space grid [Gaylord and Nishidate, 1996]. 'Random walkers' cellular automata can be used in molecular dynamics simulation and, due to the independence of 'walkers', are suitable for parallel computing and Monte-Carlo algorithms [Nishidate et al., 1996]. Diffusion processes can also be described by 'infinite dimensional cellular automata', if the states are the (infinity countable) numbers of particles at nodes (cells) and the rules are given by 'unbiased random walk', sometimes with superposed complex random advection fields [Vamoş et al. 1998, 2000].

Let N be a system of unbiased random walkers in the 1-dimensional grid $\{x_k = k\delta x \mid -m \leq k \leq m\}$: the i-th particle starting at t from k, at $t + \delta t$ lies either in $k - 1$ or $k + 1$ with the probability 1/2. If there are no 'staying states', the total number n_k of particles in k at $t + \delta t$ is the sum of particles coming from $k + 1$, n'_{k+1}, and those from $k - 1$, n''_{k-1},

$$n_k(t + \delta t) = n'_{k+1} + n''_{k-1} = \frac{1}{2}(n_{k-1} + n_{k+1}) - \delta n_{k+1} + \delta n_{k-1}, \tag{5.1}$$

where $\delta n_k = \frac{1}{2}n_k - n'_k = n''_k - \frac{1}{2}n_k$ are negligeable terms for large enough n_k (when, by 'large numbers law', $n'_k/n_k = n''_k/n_k \longrightarrow 1/2$). If the concentration c is a smooth function of $x \in \mathbb{R}$

and $t \in \mathbb{R}_+$, then $n_k \simeq c(x, t)\delta x$ and, with $c(x, t + \delta t) = [c(x - \delta x, t) + c(x + \delta x, t)]/2$, (5.1) becomes the explicit finite differences scheme for diffusion equation

$$\frac{c(x, t + \delta t) - c(x, t)}{\delta t} = \frac{\delta x^2}{2\delta t} \frac{c(x + \delta x, t) - 2c(x, t) + c(x - \delta x, t)}{\delta x^2},$$

with a diffusion coefficient $D = \delta x^2/2\delta t$. This corresponds to the maximum value of the von Neumann condition of stability, $D\delta t/\delta x^2 = 1/2$ [Crank, 1975]. Also, for Dirac initial condition and infinite domain, the convergence is of order δx: the numerical solution approaches the Gaussian one as $\delta x \longrightarrow 0$ [Gardiner, 1983].

Comparing (5.1) with the solution p, (3.2), of diffusion for $D = 0.5$, one estimates the precision of the simulation through the 'index'

$$I(t) = \sum_{k=-m}^{m} \left| \frac{n_k}{N} - p(x_k, t)\delta x \right|.$$

TABLE 1
Maximum and minimum I values for different grid dimensions

	$N = 10^3$	$N = 10^4$	$N = 10^5$	$N = 10^6$
$m = 10$	0,062	0,031	0,022	0,024
	0,102	0,112	0,106	0,104
$m = 20$	0,027	0,024	0,010	0,013
	0,133	0,052	0,013	0,017
$m = 30$	0,053	0,019	0,009	0,003
	0,129	0,038	0,015	0,007
$m = 40$	0,062	0,028	0,008	0,003
	0,137	0,039	0,015	0,005

Coarse grained space-time average. Similarly to 'molecular dynamics' [Koplik and Banavar, 1995], the space time averages improve the smoothness of simulated fields. Moreover, numerical modeling benefits of special properties of averages (4.1) [Vamoş and Suciu, 1996].

If the i-th particle is introduced into the grid at t_i^+ and it gets out at t_i^-, then the velocity $\xi_i = \dot{x}_i : [t_i^+, t_i^-] \longmapsto \{-\delta x/\delta t, \delta x/\delta t\}$ (a jump function) and the position $x_i : [t_i^+, t_i^-] \longmapsto [x_{-m}, x_m] \subset \mathbb{R}$ (discontinuous when particle's velocity change the sign), are both piece-wise analytical. From Proposition 4.3 an a.e. continuous description exists, given by

$$\partial_t \langle 1 \rangle (x, t) + \partial_x \langle \xi \rangle (x, t) = g(x, t),$$

where the function $g(x, t)$ describes the variation of particles number [Vamoş et al. 1997a].

For $2a = \delta x$ and $\tau \ll \delta t/2T$, the concentration estimation is given by $\langle 1 \rangle (x_k, t_l) = c(x_k, t_l)$ and the estimation for particles' flux, by $\langle \xi \rangle (x_k + \delta x/2, t_l + \delta t/2) = J(x_k, t_l)$. By using the coarse grained averages the needed number of particles reduces without loose in accuracy, and, consequently, a smaller computation time is needed.

Numerical model for diffusion at small concentrations. The average (4.1) is the sum of individual contributions $\langle 1 \rangle_i$ of all the N particles: $\langle 1 \rangle = \sum_{i=1}^{N} \langle 1 \rangle_i$. The definition

(4.6) provides the smooth concentration field c as an average over trajectories of all particles starting at the origin and reaching the grid's extremities: $c \simeq M[\langle 1 \rangle] = N \cdot M[\langle 1 \rangle_i]$. The standard deviation is $\sigma = \sqrt{N}\sigma_i$ and the relative error is $\sigma/M[\langle 1 \rangle]$. For fixed error and confiance level, relations can be derived between the number of particles N, time scale 2τ and space scale a. For example, Table 3 presents the results for a stationary diffusion (a constant number of particles is introduced into the origin of the grid at each time step and particles reaching the extremities are removed). For $N \simeq 10^7$, $a = 0.125\delta x$ and relative error 0.01 at confiance level 0.995, the Table 3 presents the time scale 2τ, in $10^5 \delta t$ units, for different number $\mathcal{N}$ of samples, used to compute $M[\langle 1 \rangle_i]$ and σ_i, and grid positions x.

TABLE 3

	$\mathcal{N}=100$	$\mathcal{N}=200$	$\mathcal{N}=400$	$\mathcal{N}=800$	$\mathcal{N}=1600$	$\mathcal{N}=3200$
$x=0,0$	4,31	4,98	4,74	4,96	4,83	4,71
$x=0,1$	4,84	5,39	5,17	5,36	5,11	5,02
$x=0,2$	5,47	6,11	5,90	6,09	5,76	5,65
$x=0,3$	5,98	6,99	6,75	6,90	6,47	6,43
$x=0,4$	6,85	8,13	7,87	7,95	7,50	7,53
$x=0,5$	8,22	9,37	9,12	9,28	9,05	9,11
$x=0,6$	10,9	11,2	11,1	11,4	11,4	11,5
$x=0,7$	15,3	15,0	14,9	15,3	15,2	15,2
$x=0,8$	22,0	22,3	22,5	22,9	22,2	22,1
$x=0,9$	46,0	44,3	44,3	45,1	43,6	44,0

Table 4 presents the time scale in $10^5 \delta t$ units, for different x and a, and fixed $\mathcal{N} = 200$.

TABLE 4.

	$a=\delta x/8$	$a=\delta x/4$	$a=\delta x/2$	$a=\delta x$	$a=2\delta x$	$a=4\delta x$	$a=8\delta x$
$x=0,000$	4,98	4,98	4,98	4,98	2,59	1,45	0,95
$x=0,025$	10,1	10,1	6,24	4,16	2,40	1,41	0,95
$x=0,050$	10,1	10,1	10,1	3,91	2,36	1,40	0,95
$x=0,075$	10,1	10,1	6,64	4,29	2,46	1,43	0,95
$x=0,100$	5,39	5,39	5,39	5,39	2,74	1,49	0,96

The simulations performed at very small concentrations verified the Fick law with arbitrary small deviations if the space-tine scale is large enough [Vamoş et al., 1997b]. Also, using a variable step grid, so that diffusion coefficients where $D(\{k < 0\}) = 0.05$ and $D(\{k > 0\}) = 5.0$, one obtains good numerical estimates for the diffusion coefficient (4.12) [Vamoş et al. 1998a,b].

Diffusion in random field. The model of Matheron and de Marsily. Similarly with the 1-dimensional case, a random walkers cellular automaton was considered in 2-dimensional grid $\{x_k = k\delta x, y_l = l\delta y \; ; \; -m \leq k, l \leq m\}$ [Vamoş et al. 2000]. A horizontal random advection, constant in each layer, and Gaussian correlated on the transverse direction, $R_E \sim e^{-(l\delta y)^2}$, was superposed over the unbiased random walk. Numerical computation reveals a good agreement with the 3/2 law of Matheron and de Marsily [1980]:

$$\sigma_x^2(t) = 0.30 \; t^{1.53}.$$

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Effective diffusion coefficients were estimated through $D_x = \sigma_x^2(t)/2t$ and $D_y = \sigma_y^2(t)/2t$. The curves presented in the picture below also agree with the model: $D_y \simeq const.$ and $D_x \simeq const. \cdot t^{\frac{1}{2}}$.
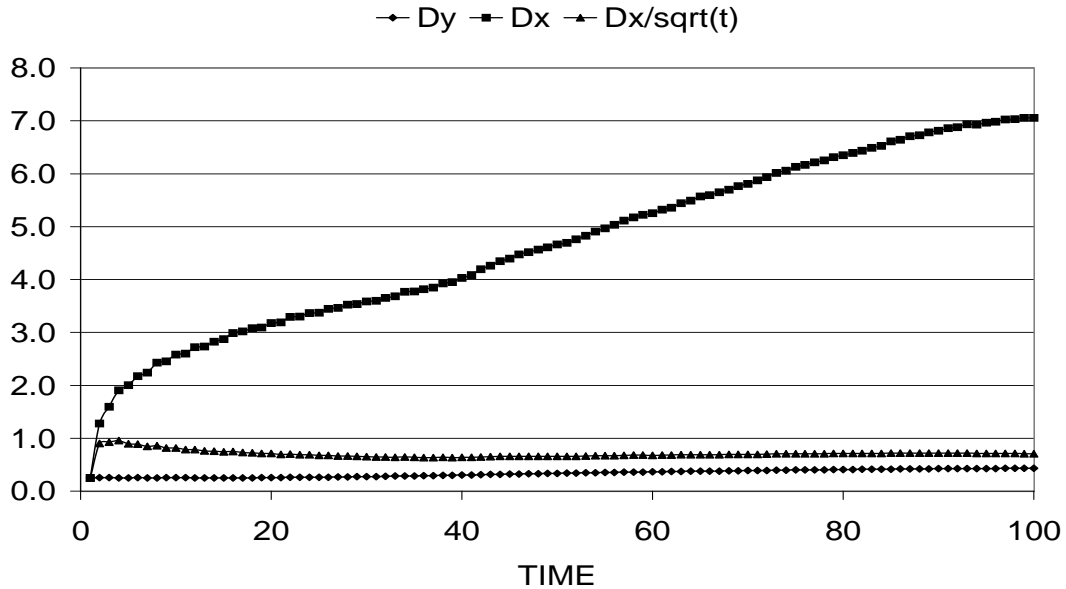
This is a validity test for the algorithm. If the values of the advection velocities and diffusion coefficients are associated with an advection-diffusion equation, i.e. the advection velocity equals the drift coefficient from the Fokker-Planck equation (3.1) and the local time derivatives of σ_x^2 and σ_y^2 give finite diffusion coefficients (3.4), then the coarse-grained averaged concentration, defined by (4.1) as $c \simeq \langle 1 \rangle$, gives the numerical solution of the partial derivatives equation. Such models can be further used to study more complex cases of diffusion in random environment, where no analogies between a Langevin (3.3) and Fokker-Planck (3.1) equations are possible. In these cases, the mathematical model for diffusion process is no longer a differential equation, for which one looks for numerical solutions, but it is just the random walkers numerical model, as a computer code.

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