Stochastic Reaction-Diffusion Phenomena in Porous Media with Nonlinear Kinetics: Effects of Quenched Porosity Fluctuations

Ivan L'Heureux*
Department of Physics, University of Ottawa, 150 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada

(Received 10 May 2004; published 28 October 2004)

We study the effects of quenched porosity fluctuations in the presence of nonlinear kinetics in a reaction-diffusion porous system. Adopting a weak-noise approximation and a mean-field assumption, a renormalized equation of motion for the average concentration of a chemical species is obtained. It is characterized by a smaller effective diffusion coefficient and by the presence of supplementary nonlinear reactive terms. Explicit results are given for a Gaussian porosity distribution and for a long-ranged one. Comparisons with simulations in one dimension are presented.

DOI: 10.1103/PhysRevLett.93.180602 PACS numbers: 05.40.–a, 82.33.Ln, 82.56.Lz

An understanding of fluid-phase reaction-diffusion phenomena in porous media is of fundamental importance to a broad range of scientific and engineering disciplines: chemical engineering, soil mechanics, petroleum engineering, groundwater hydrology, and metamorphic or sedimentary aqueous geochemistry, to name only a few nonbiological examples. The standard approach (the method of volume average) to describe the physics of these phenomena is to start from a hydrodynamic description that is valid for a particular phase and to spatially smooth out the resulting equations. This process generates continuum equations that are valid everywhere in the porous media [1] and results, for instance, in a porosity-corrected diffusion coefficient. This standard approach is deterministic and neglects the effect of the quenched porosity fluctuations that characterizes the porous medium. Statistical descriptions of the effects of random heterogeneities in hydrology are available [2]. However, few studies of these effects in the presence of chemical nonlinearities (such as a reaction kinetics that is not zeroth or first order) have been performed [3]. In fact, porosity fluctuations imply that the effective diffusion coefficient is a quantity varying randomly in space. Thus, these fluctuations may generate multiplicative nontrivial noise-induced effects, not dissimilar to those observed in various extended nonlinear systems [4]. For instance, simulations of simple nonlinear reaction kinetics [5] in an artificial diagenetic [6] system have shown that significant differences exist between the dynamics of the average concentration and the results obtained from a purely deterministic description, mostly for fast reaction rates and steep concentration gradients.

In this Letter, we consider a simple reaction-diffusion model describing the mass conservation of a chemical species in a porous medium characterized by time-independent porosity fluctuations (quenched noise). We assume a homogeneous system on the average, so that the average porosity is constant in space. Although the following results can be straightforwardly applied to two and three dimensions, only the one-dimensional situation is treated here. It will be shown that the porosity fluctuations modify the equation of motion for the species concentration (averaged over noise realizations): diffusion is described by an effective (renormalized) coefficient that is smaller than the deterministic one, and three supplementary nonlinear reactive terms that depend on various spatial derivatives of the concentration appear.

We adopt the simplest nonlinear homogeneous reaction kinetics (second order). In general, all transport coefficients and rate coefficients (particularly when heterogeneous reactions are involved) are affected by porosity fluctuations and should be considered as random variables. However, we assume here that porosity fluctuations directly affect only the effective diffusion coefficient, through the tortuosity [1,7] of the porous medium, so that the homogeneous reaction rate coefficient is constant. The mass conservation equation takes the form [7]

$$\frac{\partial c}{\partial t} = \frac{1}{\phi}\frac{\partial}{\partial x}\left(\phi D \frac{\partial c}{\partial x}\right) - kc^2 = D\frac{\partial^2 c}{\partial x^2} + \alpha\frac{\partial c}{\partial x} - kc^2. \tag{1}$$

Here t is time, x is the spatial coordinate, $c(x, t)$ is the concentration (mol/volume liquid phase), ϕ is the (random) porosity, k is the rate coefficient, and $D(\phi) = D_o/\theta^2$ is the effective diffusion corrected by a tortuosity factor $\theta^2(\phi)$, D_o being the molecular diffusion in the fluid phase [1,7]. Finally, $\alpha \equiv \phi^{-1}\partial(\phi D)/\partial x$ describes an effective drift velocity. The porosity fluctuations $\tilde{\phi}$ about the average value $\bar{\phi}$ are assumed to be Gaussian random numbers of zero average, of variance σ^2, and with a spatial correlation $f(|x|)$:

$$\overline{\tilde{\phi}(x)\tilde{\phi}(y)} = \sigma^2 f(|x - y|). \tag{2}$$

Since ϕ is a random variable, so are the effective diffusion and the concentration field. Let an overbar and a tilde (~) over a quantity denote its average value and its fluctuations about the average, respectively. Substituting the expansions $D = \bar{D} + \tilde{D}$, $\alpha = \bar{\alpha} + \tilde{\alpha}$, $c = \bar{c} + \tilde{c}$ in Eq. (1), the dynamics of the average concentration and its fluctuating part are, respectively, given by:

$$\frac{\partial \bar{c}}{\partial t} = \bar{D}\frac{\partial^2 \bar{c}}{\partial x^2} + \overline{\tilde{D}\frac{\partial^2 \tilde{c}}{\partial x^2}} + \bar{\alpha}\frac{\partial \bar{c}}{\partial x} + \overline{\tilde{\alpha}\frac{\partial \tilde{c}}{\partial x}} - k\bar{c}^2 - k\overline{\tilde{c}^2}; \quad (3)$$

$$\frac{\partial \tilde{c}}{\partial t} = \bar{D}\frac{\partial^2 \tilde{c}}{\partial x^2} + \tilde{D}\frac{\partial^2 \bar{c}}{\partial x^2} + \tilde{D}\frac{\partial^2 \tilde{c}}{\partial x^2} - \overline{\tilde{D}\frac{\partial^2 \tilde{c}}{\partial x^2}} + \bar{\alpha}\frac{\partial \tilde{c}}{\partial x} + \tilde{\alpha}\frac{\partial \bar{c}}{\partial x}$$
$$+\tilde{\alpha}\frac{\partial \tilde{c}}{\partial x} - \overline{\tilde{\alpha}\frac{\partial \tilde{c}}{\partial x}} - k\tilde{c}^2 - 2k\bar{c}\,\tilde{c} + k\overline{\tilde{c}^2}. \quad (4)$$

We now assume a *weak-noise regime*, in which the porosity fluctuations are sufficiently small, so that the terms involving noise correlations of higher order than quadratic are neglected. For a homogeneous porous medium, $\bar{\alpha} \cong \overline{\tilde{D}\partial\tilde{\phi}}/\partial x - (\bar{D}/\bar{\phi})\overline{\tilde{\phi}\partial\tilde{\phi}}/\partial x$ is already of second order in the porosity fluctuations. Thus, the term $\bar{\alpha}\partial\tilde{c}/\partial x$ can be dropped from Eq. (4).

We introduce the notation $\xi_1 \equiv \tilde{\alpha}$ and $\xi_2 \equiv \tilde{D}$. Taking the space-Fourier transform and the time-Laplace transform of the average Eq. (3), gives the formal solution for the Fourier-Laplace transform of the average concentration $\bar{c}_{Ks} = \int_0^\infty dt \int dx e^{-iKx-st}\bar{c}(x,t)$:

$$\bar{c}_{Ks} = G_{Ks}^{-1}[\bar{c}_K(0) + \bar{R}_{Ks}] \quad (5)$$

where K is the wave vector and s the Laplace-transform variable. Also, $G_{Ks} = s + \bar{D}K^2$ is the inverse of the bare (i.e. deterministic) diffusive propagator, $\bar{c}_K(0)$ is the Fourier transform of the initial average concentration and $\bar{R}_{Ks}$ denotes the Fourier-Laplace transform of

$$\bar{R} = -k\bar{c}^2 + \bar{\alpha}\frac{\partial \bar{c}}{\partial x} + \sum_{m=1,2}\overline{\xi_m\frac{\partial^m \tilde{c}}{\partial x^m}} - k\overline{\tilde{c}^2}. \quad (6)$$

The first term on the right-hand side of Eq. (6) corresponds to the deterministic nonlinear reactive part, the second term describes a trivial correction to the drift, whereas the last two terms are nontrivial corrections due to the correlations between the porosity fluctuations and the concentration field.

Before performing a similar operation on the fluctuating Eq. (4), we use a *mean-field approximation* for the term $-2k\bar{c}\,\tilde{c}$. We assume that the average concentration in that term is replaced by its value averaged over a large space domain L and time interval T: $\bar{c}(x,t) \to \int_0^T dt \int c(x,t)dx/LT \equiv g$.The formal solution of the Fourier-Laplace transform of the fluctuating concentration $\tilde{c}_{Ks}$ is thus given by

$$\tilde{c}_{Ks} = \hat{G}_{Ks}^{-1}\tilde{R}_{Ks} \quad (7)$$

where $\hat{G}_{Ks} = G_{Ks} + 2kg$ and $\tilde{R}_{Ks}$ is the Fourier-Laplace transform of

$$\tilde{R} = \tilde{D}\frac{\partial^2 \bar{c}}{\partial x^2} + \tilde{D}\frac{\partial^2 \tilde{c}}{\partial x^2} - \overline{\tilde{D}\frac{\partial^2 \tilde{c}}{\partial x^2}} + \tilde{\alpha}\frac{\partial \bar{c}}{\partial x} + \tilde{\alpha}\frac{\partial \tilde{c}}{\partial x} - \overline{\tilde{\alpha}\frac{\partial \tilde{c}}{\partial x}}$$
$$-k\tilde{c}^2 + k\overline{\tilde{c}^2}. \quad (8)$$

In the space-time domain, the fluctuating concentration is then given by the convolution integral:

$$\tilde{c}(x,t) = \int_0^t \int dt' dx' \hat{G}^{-1}(x-x', t-t')\tilde{R}(x', t')$$
$$\equiv \hat{G}^{-1}_{x-x',t-t'} * \tilde{R}_{x',t'}. \quad (9)$$

The third term on the right-hand side of Eq. (6) is obtained by multiplying appropriate spatial derivatives of the fluctuating concentration Eq. (9) by the fluctuating transport term $\xi_m(x)$, taking the average over the realizations and dropping the third order terms in the porosity fluctuations. This procedure gives

$$\overline{\xi_m(x)\frac{\partial^m \tilde{c}}{\partial x^m}} = \sum_{n=1,2}\frac{\partial^m \hat{G}^{-1}_{x-y,t-t'}}{\partial x^m} * \overline{\xi_m(x)\xi_n(y)}\frac{\partial^n \bar{c}(y)}{\partial y^n}. \quad (10)$$

Similarly, the fourth term on the right-hand side of Eq. (6) is given by multiplying the fluctuating concentration Eq. (9) by $\tilde{c}(x,t)$ and taking the average over the realizations. Up to second order in $\tilde{\phi}$, this results in

$$\overline{\tilde{c}(x)\tilde{c}(x)} = \sum_{m,n=1,2}\hat{G}^{-1}_{x-y,t-t'} * G^{-1}_{x-z,t-t''}$$
$$* \overline{\xi_m(y)\xi_n(z)}\frac{\partial^m \bar{c}(y)}{\partial y^m}\frac{\partial^n \bar{c}(z)}{\partial z^n}. \quad (11)$$

Taking the Fourier-Laplace transform of Eqs. (10) and (11) and substituting in Eq. (5) finally give

$$\bar{c}_{Ks} = G_{Ks}^{-1}\bar{c}_K(0) + G_{Ks}^{-1}\left(\bar{\alpha}\frac{\partial \bar{c}}{\partial x}\right)_{Ks} + G_{Ks}^{-1}V_{Ks}\bar{c}_{Ks}$$
$$- G_{Ks}^{-1}\iint \frac{dP}{2\pi}\frac{ds'}{2\pi i}k^*_{KPss'}\bar{c}_{Ps'}\bar{c}_{K-Ps-s'} \quad (12)$$

where

$$V_{Ks} = \sum_{m,n=1,2}\int \frac{dQ}{2\pi}\hat{G}^{-1}_{K-Qs}\overline{\xi_{Qm}\xi_{-Qn}}[i(K-Q)]^m(iK)^n$$
$$\equiv \sum_{m,n=1,2} V_{KS,mn}, \quad (13)$$

$$k^*_{KPss'} = k + \sum_{m,n=1,2} k \int \frac{dQ}{2\pi}\hat{G}^{-1}_{K-P-Qs-s'}\hat{G}^{-1}_{P+Qs'}$$
$$\times \overline{\xi_{Qm}\xi_{-Qn}}[i(K-P)]^m(iP)^n$$
$$\equiv k + \sum_{m,n=1,2} k_{mn}. \quad (14)$$

P and Q are dummy wave-vector labels. Rewriting Eq. (12) in the form

$$\bar{c}_{Ks} = (G_{KS} - V_{KS})^{-1}\left[\bar{c}_K(0) + \left(\bar{\alpha}\frac{\partial \bar{c}}{\partial x}\right)_{Ks}\right] - (G_{KS} - V_{KS})^{-1}\int \frac{dP}{2\pi}\frac{ds'}{2\pi i} k^{*}_{KPss'}\bar{c}_{Ps'}\bar{c}_{K-Ps-s'}, \quad (15)$$

it is seen that the term V_{Ks} corresponds to a renormalized transport coefficient, whereas $k^{*}_{KPss'}$describes the renormalization of the rate coefficient by the porosity fluctuations. Note that the factors $[i(K-Q)]^m(iK)^n$ in $k^{*}_{KPss'}$ will give rise to fluctuation-induced reactive corrections that are quadratic in the *derivatives* of the average concentration field.

In order to illustrate the evaluation of the integrals in Eqs. (13) and (14), we choose the diffusive term $m = n = 2$. Then, $\overline{\xi_{Q2}\xi_{-Q2}} = \overline{\tilde{D}_Q\tilde{D}_{-Q}} = D'\sigma^2 f_Q$where $D' = d\bar{D}/d\bar{\phi}$ and f_Q is the Fourier transform of the correlation defined in Eq. (2). We consider two types of correlation functions. The first case exhibits Gaussian statistics characterized by a correlation length λ, for which $f(x) = \exp(-x^2/2\lambda^2)$ and $f_Q = \sqrt{2\pi}\lambda \times \exp(-Q^2\lambda^2/2)$. The second one is a long-ranged correlation characterized by the roughness exponent $\beta (0 < \beta < 1)$, for which [8] $f(|x|) = x_o^{\beta}/(x_o^2 + x^2)^{\beta/2}$ and $f_Q = 2^{(3-\beta)/2}\sqrt{\pi}x_o(|q|x_o)^{(\beta-1)/2}K_{(1-\beta)/2}(|q|x_o)/\Gamma(\beta/2)$. Here, x_o is a small cutoff distance, so that $f \sim |x|^{-\beta}$ for $x \gg x_o$, Γ is the gamma function and $K_a(x)$ is the modified Bessel function of order a. All integrals over wave vectors in Eqs. (13) and (14) converge (this is true in two and three dimensions as well). Since we are interested in long time and large spatial scale behavior, we use a conventional approximation [9] and set $s = s' = 0$ and $K = P = 0$ in the Q-dependent terms of the integrands. The results are

$$V_{Ks,22} = \frac{D'^2\sigma^2}{\bar{D}}K^2 G_1(A); \qquad k_{22} = \frac{D'^2\sigma^2 k}{\bar{D}^2}(K-P)^2P^2F_1(A) \quad (16)$$

where A, $G_1(A)$ and $F_1(A)$ are defined in Table I for the two cases considered.

In terms of the space-time domain, Eq. (16) implies that the effects of the porosity fluctuations on the dynamics of the average concentration can be interpreted as a renormalization of the diffusion coefficient to a lower effective value D_{eff} (since $G_1 > 0$), and the generation of a reactive term that depends on the square of the second spatial derivative of the concentration.

It is straightforward to estimate the integrals in Eqs. (13) and (14) for the other terms contributing to the sum over m and n. Collecting all terms, the new conservation equation for the average concentration finally takes the form

$$\frac{\partial \bar{c}}{\partial t} = D_{\text{eff}}\frac{\partial^2 \bar{c}}{\partial x^2} + \bar{\alpha}\frac{\partial \bar{c}}{\partial x} - k\bar{c}^2 - (k_1 + k_3)\left(\frac{\partial^2 \bar{c}}{\partial x^2}\right)^2 - k_2\left(\frac{\partial \bar{c}}{\partial x}\right)^2 + k_3\frac{\partial^3 \bar{c}}{\partial x^3}\frac{\partial \bar{c}}{\partial x} \quad (17)$$

where

$$D_{\text{eff}} = \bar{D} - \frac{D'^2\sigma^2}{\bar{D}}G_1(A) - \frac{(D' + \bar{D}/\bar{\phi})(2D' + \bar{D}/\bar{\phi})\sigma^2}{\bar{D}}G_2(A);$$

$$k_1 = k\frac{D'^2\sigma^2}{\bar{D}^2}F_1(A); \qquad k_2 = k\frac{(D' + \bar{D}/\bar{\phi})^2\sigma^2}{\bar{D}^2}F_2(A);$$

$$k_3 = k\frac{D'(D' + \bar{D}/\bar{\phi})\sigma^2}{\bar{D}^2}F_3(A). \quad (18)$$

The other functions $G_2(A)$ and $F_{2,3}(A)$ are found in Table I. Equations (17) and (18) constitute the central results of this contribution.

In order to illustrate the effects of porosity fluctuations, direct numerical simulations have been performed on a spatial domain of size L partitioned by a uniform grid of step Δx. For simplicity, it is sufficient to omit the drift term in Eq. (1), so that only G_1 and F_1 are nonzero in Eq. (18). Scaling the porosity variance adequately, an explicit tortuosity function is thus not needed. To fix the ideas, the boundary conditions $c(0,t) = c_o$ and $\partial c/\partial x(L,t) = 0$ have been chosen. Spatially random diffusion distributions with the proper correlation have been constructed [3] by generating Gaussian random numbers of zero mean and appropriate variance in Fourier space and using a fast Fourier transform algorithm [10]. The reaction-diffusion Eq. (1) was solved numerically for each noise realization, and the results averaged over

TABLE I. Definitions of terms appearing in Eq. (18) for the Gaussian correlation and the long-ranged correlation cases. $p(\beta)$ denotes $\Gamma(\frac{\beta}{2})\Gamma(\frac{\beta+1}{2})\sin(\pi\beta)$.

Term	Gaussian correlation	Long-ranged correlation (up to order A)
A	$(\lambda^2 kg/\bar{D})^{1/2}$	$(2{x_o}^2 kg/\bar{D})^{1/2}$
G_1	$1 - \sqrt{\pi}A\exp(A^2)[1 - \text{erf}(A)]$	$1 - 2^{1-\beta}\pi^{3/2}A^{\beta}/p(\beta)$
G_2	$1 + 2A^2 - 2\sqrt{\pi}Ae^{A^2}(1 + A^2)[1 - \text{erf}(A)]$	$1 - 2^{1-\beta}\pi^{3/2}(1+\beta)A^{\beta}/p(\beta)$
F_1	$\lambda\sqrt{\pi}(\bar{D}/kg)^{3/2}\{e^{A^2}(2A^2 - 1)[\text{erf}(A) - 1] + 2A/\sqrt{\pi}\}/8$	$\pi^{3/2}(\bar{D}/kg)^2(2-\beta)A^{\beta}/2^{\beta+2}p(\beta)$
F_2	$\lambda\sqrt{\pi}(\bar{D}/kg)^{1/2}\{e^{A^2}(2A^2 + 1)[1 - \text{erf}(A)] - 2A/\sqrt{\pi}\}/4$	$\pi^{3/2}(\bar{D}/kg)\beta A^{\beta}/2^{\beta+1}p(\beta)$
F_3	$\lambda\sqrt{\pi}(\bar{D}/kg)^{3/2}\{2A(1 + 2A^2)/\sqrt{\pi} + e^{A^2}(1 - 4A^2 - 4A^4)[1 - \text{erf}(A)]\}/8$	$\pi^{3/2}(\bar{D}/kg)^2\beta(2-\beta)A^{\beta}/2^{\beta+2}p(\beta)$

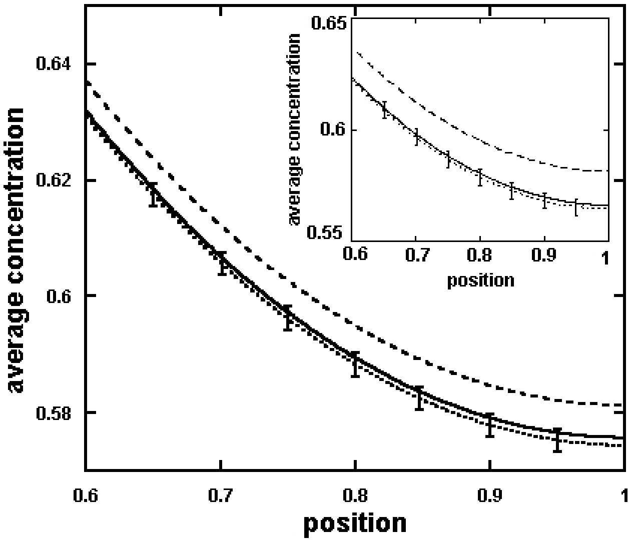

FIG. 1. Dimensionless steady-state average concentration profiles for a long-ranged correlation case: $g = 0.705$, $\beta = 0.5$, $x_o/L = 0.1$, $D'^2\sigma^2/\bar{D}^2 = 0.05$ and $\bar{D}/kc_oL^2 = 0.5$. The concentration is scaled by its boundary condition c_o at $x = 0$ and position x by the size L of the domain. Only the part $x > 0.6$ is shown. Upper dashed line: numerical solution of the deterministic version of Eq. (1) (with $\bar{\alpha} = 0$ and $\bar{c}$ replacing c). Continuous curve: numerical solution of Eq. (17) (with $\bar{\alpha} = G_2 = F_2 = F_3 = 0$). Lower dotted line: averages of ten sets of direct simulation results differing by their initial seed. For the simulations, the number of discrete spatial nodes was 1024 and each set was averaged over 200 realizations. The inset shows similar curves for a Gaussian correlation case: $g = 0.709$, $\lambda/L = 0.2$, $D'^2\sigma^2/\bar{D}^2 = 0.1$, and $\bar{D}/kc_oL^2 = 0.5$.

many realizations. The results can then be compared with the direct numerical solution of Eq. (17) on one hand (for which the mean-field concentration g is easily found self-consistently) and with the solution of the deterministic equation (Eq. (1) with c replaced by $\bar{c}$) on the other hand. Figure 1 compares these various solutions in the steady-state situation and for an example of the long-ranged correlation case ($\beta = 0.5$) and for a Gaussian correlation case (inset). Notwithstanding a small overestimate, it is seen that the solution of Eq. (17) is consistent with the direct simulations and is significantly different from the deterministic solution (although the deviation from the latter is not large). The cases $\beta = 0.75$ and 0.25 with $D'^2\sigma^2/\bar{D}^2 = 0.05$ are in similar agreement with Eq. (17) (not illustrated).

In conclusion, we have analyzed the effects of quenched porosity fluctuations inherent to any porous media on the nonlinear reaction-diffusion dynamics of the concentration of a chemical species. We have used a weak-noise approximation and a mean-field approximation, whereby the average concentration is replaced by a constant in the renormalized inverse propagator $\hat{G}_{Ks}$. These porosity fluctuations generate multiplicative time-independent random terms in the equation of motion via the porosity dependence of the effective diffusion coefficient. Besides a trivial noise-induced drift term [The term proportional to $\bar{\alpha}$ in Eq. (17)] the noise decreases the effective diffusion coefficient and generates supplementary nonlinear reactive terms that depend on first, second and third order spatial derivatives of the concentration. These features are found both for the short-ranged porosity correlation case and the long-ranged one. In the framework of the approximations used here, these effects are quantitatively relatively small, so that the use of a deterministic equation of motion does not lead to dramatic differences in chemical engineering or geochemical applications. However, they illustrate yet another nontrivial manifestation of noise in nonlinear spatially extended systems. In the future, it will be interesting to investigate the effects of porosity fluctuations in a system where many chemical species are nonlinearly coupled, such as in realistic diagenetic models. It will also be useful to investigate other important types of reactive nonlinearities (e.g., Monod kinetics) or heterogeneous reactions (such as nonlinear adsorption reactions [6]) for which the porosity dependence of the rate coefficients may be important.

This work was funded by a grant from the Natural Sciences and Engineering Research Council of Canada. I wish to thank Christof Meile for helpful discussions.

---

*Electronic address: ilheureu@physics.uottawa.ca

[1] Y. Bachmat and J. Bear, Transp. Porous Media **1**, 213 (1986); **1**, 241 (1986); S. Whitaker, *The Method of Volume Averaging* (Kluwer, Dordrecht, 1999).

[2] See, e.g., L.W. Gelhar, *Stochastic Subsurface Hydrology* (Prentice Hall, Englewood Cliffs, 1993); M. Sahimi, Comput. Geosci. **26**, 877 (2000); M. Saadatfar and M. Sahimi, Phys. Rev. E **65**, 036116 (2002).

[3] Examples may be found in *Nonlinear Dynamics and Control in Process Engineering—Recent Advances*, edited by G. Continillo, S. Crescitelli, and M. Giona (Springer, Milano, 2002).

[4] J. García-Ojalvo and J. M. Sancho, *Noise in Spatially Extended Systems* (Springer, New York, 1999).

[5] C. Meile, P. Van Cappellen, and K. Tuncay, in Abstracts of the American Society of Limnology and Oceanography Meeting, Honolulu, February 2004 (unpublished).

[6] Diagenesis refers to the ensemble of transport and biogeochemical processes that take place in sediments.

[7] B. P. Boudreau, *Diagenetic Models and Their Implementation* (Springer, Berlin, 1997).

[8] H. A. Makse, S. Havlin, M. Schwartz, and H. E. Stanley, Phys. Rev. E **53**, 5445 (1996).

[9] See, e.g., D. Forster, *Hydrodynamics Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin-Cummings, Reading, Massachusetts, 1977.

[10] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran* (Cambridge University Press, Cambridge, England, 1992).