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Fractals and Chaos in Chemical Engineering

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PREFACE

The CFIC 96 Conference (Rome, September 2-5, 1996) is the second meeting on fractals and chaos and their applications in chemical engineering organized by the Italian Research Center on Disordered Systems and Fractals in Chemical Engineering, jointly founded in 1993 by the Departments of Chemical Engineering of the Universities of Cagliari, Genoa and Rome and the Polytechnic Institute of Milan.

The CFIC 96 Conference was attended by over 100 researchers and students from all countries and all research fields. The original goal of organizing a working conference to facilitate the interdisciplinary exchange of ideas and to address the most relevant applications of dynamical and disordered system theory in reaction engineering, chemical physics and catalysis can, with no undue rhetoric, be described as successfully achieved. The very positive and in some cases enthusiastic response of many participants was the best reward for the great organizational effort involved. Special thanks for making it possible to organize this conference go to the entire group of the University of Rome, and to A.R. Giona, A. Adrover and O. Patierno in particular.

This book contains the articles presented at the conference and accepted for publication after a peer-reviewing procedure. These articles are fully representative of the intense and scientifically rich program of the Conference. The articles are divided into different sections representing the main fields of application of fractal and chaos theory in chemical engineering science.

Special thanks go to the members of the Scientific Committee (P.M. Adler, D. Avnir, F. Brouers, M.-O. Coppens, J. Drahos, R. Krishna, R. Lapasin, F. Muzzio, W. Rudzinski, W.A. Schwalm, T. Vicsek) and to the referees for their cooperation in the preparation of this book. The financial support of the CNR (Consiglio Nazionale delle Ricerche, Comitato per la Chimica) is gratefully acknowledged.

Massimiliano Giona and Giuseppe Biardi
Chairmen of CFIC 96 Conference

CONTENTS

Aggregates and Growth Models

Turbulence, Mixing and Spatiotemporal Patterns

Reactor Dynamics and Chaos

Transport, Reaction, Adsorption in Disordered Systems

The influence of spatial correlations on reaction/diffusion and convective transport phenomena

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The article analyzes the influence of the spatial correlation of the pore structure on reaction-diffusion and convective transport phenomena. Two aspects are developed in greater detail: prediction of the permeability of correlated porous structures and the influence of correlations in fluid-solid noncatalytic reactions. A general purpose simulator for fluid-solid reaction in complex geometries is also proposed.

1 Introduction

Random percolation networks are an important tool for modeling transport processes in disordered systems such as porous media, polymers and gels. In the study of percolation models, spatial disorder is usually assumed to be uncorrelated, i.e. the probability of any site being occupied is independent of the occupancy of other sites. However, natural systems exhibit some degree of spatial correlation, and correlated percolation models [1,2] prove to be useful in application to porous media and transport because they mimic the structure of real materials [3] better than the customary uncorrelated percolation schemes.

The generation of correlated percolation lattices can be regarded as an application of the *reconstruction of porous media*. This topic has been extensively studied by Joshi [4], Quiblier [5], Adler et al.[3]. An analytic solution of the inverse reconstruction problem has recently been proposed by Giona and Adrover [6] for isotropic and homogeneous porous media and further extended to the generation of non homogeneous porous matrices with prescribed pore-pore correlation function and position-dependent porosity [7].

The purpose of this article is to analyze the influence of the spatial correlations of the pore network on reaction/diffusion and convective transport phenomena. In particular, we review the main results of the permeability model for correlated porous structures proposed by Adrover and Giona [8] and analyze the influence of the spatial correlation of solid reactant distribution on fluid-solid noncatalytic reactions, presenting an efficient lattice simulator for diffusion and reaction phenomena in the presence of moving boundary conditions.

2 Generation of correlated percolation lattices

Let us consider a thin section of a porous medium as a two-dimensional image $\mathcal{I}$, and let $\mathcal{P}$ be the pore space, described by its characteristic function $\chi_{\mathcal{P}}(\mathbf{x})$, such that $\chi_{\mathcal{P}}(\mathbf{x}) = 1$ if $\mathbf{x} \in \mathcal{P}$ and $\chi_{\mathcal{P}}(\mathbf{x}) = 0$ elsewhere.

The porosity ε is given by $\varepsilon =< \chi_{\mathcal{P}}(\mathbf{x}) >$, and the normalized pore-pore correlation function by

$$C_{2\chi}(\mathbf{x}) = \frac{\langle(\chi_{\mathcal{P}}(\mathbf{y}) - \varepsilon)(\chi_{\mathcal{P}}(\mathbf{y}+\mathbf{x}) - \varepsilon)\rangle}{\varepsilon - \varepsilon^2} \,. \tag{1}$$

On the assumption of isotropy, $C_{2\chi}(\mathbf{x})$ is solely a function of $x = |\mathbf{x}|$ and a generic cross section of the material is representative of the entire three-dimensional structure. The goal of the reconstruction of porous media is to generate stochastic lattice models with the same porosity and the same pore-pore correlation function as the original image. The methods developed to solve the reconstruction problem [6] can be applied to generate percolation models with correlations by assuming a given functional expression for the pore-pore correlation function and by letting the porosity vary.

Let us define the set of basis processes $\{\mathcal{Y}(\mathbf{x}, \lambda)\}$ by convoluting a system of Gaussian uncorrelated processes $\xi_\lambda(\mathbf{x})$ (with zero mean and unit variance) with a Gaussian kernel,

$$\mathcal{Y}(\mathbf{x}, \lambda) = \int_{E^d} a(\mathbf{u}, \lambda)\xi_\lambda(\mathbf{u}+\mathbf{x})d\mathbf{u} = \left(\frac{4\lambda}{\pi}\right)^{d/4} \int_{E^d} \mathrm{e}^{-2\lambda u^2}\xi_\lambda(\mathbf{u}+\mathbf{x})d\mathbf{u} \,, \tag{2}$$

where E^d is the Euclidean d-dimensional space, $E^d = \{\mathbf{x} \mid -\infty < x_i < \infty \,, (i = 1, .., d)\}$. Each basis process $\mathcal{Y}(\mathbf{x}, \lambda)$ is still Gaussian with zero mean and unit variance but exhibits a Gaussian decay of the correlation function [a] $C_{2\mathcal{Y}}(x, \lambda) = \mathrm{e}^{-\lambda x^2}$.

We can expand a generic Gaussian process $\mathcal{Y}(\mathbf{x})$ as the linear superposition[6,8] of a continuous and a discrete spectrum of basis process $\{\mathcal{Y}(\mathbf{x}, \lambda)\}$

$$\mathcal{Y}(\mathbf{x}) = \int_0^\infty \widehat{p}(\lambda)\mathcal{Y}(\mathbf{x}, \lambda)d\lambda + \sum_{i=1}^{N_{loc}} \sqrt{\alpha_i}\mathcal{Y}(\mathbf{x}, \lambda_i) \,, \tag{3}$$

which admits the correlation function

$$C_{2\mathcal{Y}}(x) = \int_0^\infty \widehat{\pi}(\lambda)\mathrm{e}^{-\lambda x^2}d\lambda + \sum_{i=1}^{N_{loc}} \alpha_i \mathrm{e}^{-\lambda_i x^2} \,, \tag{4}$$

[a] The basis processes $\{\mathcal{Y}(\mathbf{x}, \lambda)\}$ for different λ are uncorrelated with one another, i.e. $< \mathcal{Y}(\mathbf{x}, \lambda_1)\mathcal{Y}(\mathbf{x}', \lambda_2) >= 0$ for $\lambda_1 \neq \lambda_2$.

where N_{loc} is the number of discrete (localized) Gaussian contributions and $\widehat{\pi}(\lambda) = \widehat{p}^2(\lambda)$.

The entire spectrum $\pi(\lambda)$ of λ encompassing both the continuous and the discrete part is given by $\pi(\lambda) = \widehat{\pi}(\lambda) + \sum_{i=1}^{N_{loc}} \alpha_i \delta(\lambda - \lambda_i)$.

The transformation from the $\mathcal{Y}$-process to the binary (pore/pore matrix, 0/1) porous structure with a given value of the porosity ε is given by a nonlinear filter [3,6] $\mathcal{G}$ depending on the Gaussian distribution function $F_{\mathcal{Y}}$ of $\mathcal{Y}$ and on the assigned porosity ε.

For each point $\mathbf{x}$, the characteristic function of the generated (0/1) porous structure $\chi_{\mathcal{P}}(\mathbf{x})$ is given by

$$\chi_{\mathcal{P}}(\mathbf{x}) = \mathcal{G}(\mathcal{Y}(\mathbf{x}), \varepsilon) = \begin{cases} 1 & F_{\mathcal{Y}}(\mathcal{Y}(\mathbf{x})) < \varepsilon \\ 0 & F_{\mathcal{Y}}(\mathcal{Y}(\mathbf{x})) > \varepsilon \, . \end{cases} \tag{5}$$

Eq. (5) ensures statistically that the generated porous medium admits the porosity ε, while the correlation function $C_{2\chi}(x)$ is related to the corresponding correlation function $C_{2\mathcal{Y}}(x)$ through the relation [3,6]

$$C_{2\chi}(x) = \int_{-\infty}^{\infty} dy_1 \int_{-\infty}^{\infty} dy_2 \left[\frac{(\mathcal{G}(y_1, \varepsilon) - \varepsilon)(\mathcal{G}(y_2, \varepsilon) - \varepsilon)}{\varepsilon - \varepsilon^2} \right] p(y_1, y_2, C_{2\mathcal{Y}}(x)) \, , \tag{6}$$

where $p(y_1, y_2, C_{2\mathcal{Y}}(x))$ is a bivariate Gaussian p.d.f. with correlation coefficient $C_{2\mathcal{Y}}(x)$.

In order to generate a lattice structure possessing a specified porosity and a given functional expression of $C_{2\chi}(x)$, for every $C_{2\chi}(x)$, the corresponding value of $C_{2\mathcal{Y}}(x)$ is evaluated through eq. (6). From the knowledge of $C_{2\mathcal{Y}}(x)$, the weight function $\pi(\lambda)$ can be evaluated numerically or analytically (where possible) from eq. (4).

It should be observed that, on the condition that $C_{2\mathcal{Y}}(x) \geq 0$, and putting $z = x^2$, $\widetilde{C}_{2\mathcal{Y}}(z) = C_{2\mathcal{Y}}(x)$,

$$\widetilde{C}_{2\mathcal{Y}}(z) = \int_0^{\infty} \pi(\lambda) \mathrm{e}^{-\lambda z} d\lambda \, , \tag{7}$$

it follows that $\pi(\lambda)$ is the inverse Laplace transform of the analytic continuation on the complex plane $\widetilde{C}^{(p)}_{2\mathcal{Y}}(z)$ of the correlation function of the $\mathcal{Y}(\mathbf{x})$ process [b] $\widetilde{C}_{2\mathcal{Y}}(z)$. In all those cases in which closed-form solutions for the inverse Laplace transform of $\widetilde{C}^{(p)}_{2\mathcal{Y}}(z)$ cannot be obtained, the weight function $\pi(\lambda)$ should be obtained numerically.

[b] The analytic continuation $\widetilde{C}^{(p)}_{2\mathcal{Y}}(z)$ of $\widetilde{C}_{2\mathcal{Y}}(z)$ valid for all complex z (whose restriction to real z coincides with $\widetilde{C}_{2\mathcal{Y}}(z)$) can be achieved by considering rational approximations (Padé approximants) or by means of other methods such as orthogonal polynomial expansion [6].

3 Permeability of correlated percolation lattices

In section 2 we have shown that a generic correlated porous structure can be generated by means of the linear superposition of basis processes $\{\mathcal{Y}(\mathbf{x},\lambda)\}$ possessing a Gaussian decay in the correlation function $C_{2\mathcal{Y}}(x)$. Henceforth we shall refer to these structures as Gaussian correlated percolation lattices.

In ref. [8] an analogous superposition principle is applied to predict transport properties, and specifically permeability. Starting from the study of the permeability of random lattices generated by an elementary basis process $\mathcal{Y}(\mathbf{x},\lambda)$, an equation can be derived for the permeability of random structures generated by the superposition of the basis processes $\{\mathcal{Y}(\mathbf{x},\lambda)\}$.

For 2-d lattice structures, the Carman-Kozeny equation [9] for permeability attains the form

$$\frac{K}{a^2} = \frac{N^4}{k_{koz}} \frac{\varepsilon^3}{(w_p/a)^2} , \tag{8}$$

where N is the lattice size expressed in lattice units, a the unit lattice site length, and w_p/a the dimensionless wetted perimeter.

For Gaussian correlated percolation lattices, the dimensionless wetted perimeter w_p/a behaves as $w_p/a \sim N^2\sqrt{1-\varepsilon}(a\sqrt{\lambda_1})$, and the Carman-Kozeny equation attains the form

$$\frac{K}{a^2} = \frac{1}{k_\lambda} \frac{\varepsilon^3}{(1-\varepsilon)(\lambda_1 a^2)} , \tag{9}$$

in which k_λ is a modified Kozeny constant.

Figure 1 shows the comparison of the theoretical curve eq. (9) and the Lattice Boltzmann Equation (LBE) [10] simulation results [c] for the permeability K/a^2 as a function of $\varepsilon^3/((1-\varepsilon)\lambda_1 a^2)$ for many different exponentially correlated lattice structures with $0.70 \leq \varepsilon \leq 0.90$ and $0.01 \leq \lambda_1 a^2 \leq 0.20$. This figure clearly shows that the Carman-Kozeny relation expressed as a function of λ_1, eq. (9), is well verified by exponentially correlated percolation lattices far from criticality with a unique value of the modified Kozeny constant $k_\lambda = 13.5 \pm 0.3$.

In order to develop a predictive model for the permeability of random correlated lattice structures, eq. (9) should be generalized for arbitrary structures possessing a discrete and/or continuous spectrum $\pi(\lambda)$, eq. (4).

[c] Lattice Gas Automata (LGA) and the Lattice Boltzmann Equation (LBE) have been developed as an alternative method to direct simulation and to spectral techniques for solving the partial differential equations of fluid mechanics and transport. The ease with which arbitrary complex boundary conditions are handled by the LBE approach prompts its use to tackle a great variety of problems related to the physics and fluid dynamics of disordered and fractal media.

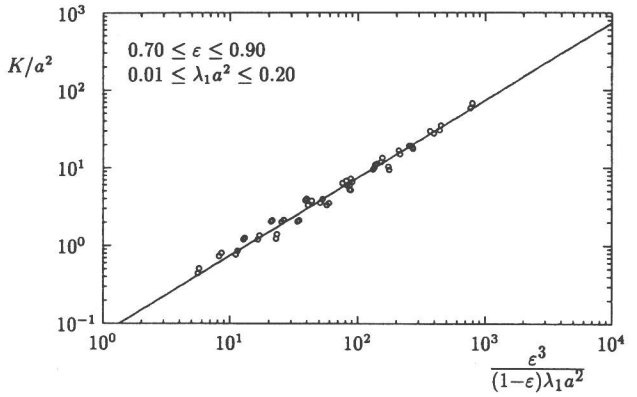

Figure 1: LBE simulation results for the permeability K/a^2 of two different sets of 200 x 200 exponentially correlated percolation lattices ($0.01 \leq \lambda_1 a^2 \leq 0.20$) far from criticality ($0.70 \leq \varepsilon \leq 0.90$). The continuous line corresponds to eq. (9) with a least square fitted value of the modified Kozeny constant $k_\lambda = 13.5$.

By considering that the correlation function of a lattice structure generated as a linear superposition of the basis processes $\{\mathcal{Y}(\mathbf{x}, \lambda)\}$ is a linear superposition of the correlation functions $C_{2\mathcal{Y}}(x, \lambda)$, it is natural to extend eq. (9) in the form

$$\frac{K}{a^2} = \frac{1}{k_\lambda} \frac{\varepsilon^3}{(1-\varepsilon)(< \lambda > a^2)} , \tag{10}$$

where $< \lambda >$ is the average of λ, with respect to the spectrum $\pi(\lambda)$

$$< \lambda >= \int_0^\infty \lambda \pi(\lambda) d\lambda = \int_0^\infty \lambda \widehat{\pi}(\lambda) d\lambda + \sum_{i=1}^{N_{loc}} \alpha_i \lambda_i . \tag{11}$$

and k_λ is the same modified Kozeny constant estimated in the previous section for exponentially correlated structures.

Eqs. (10) and (11) enable us to predict the permeability of generic 2-d porous structures from their structural data. From the knowledge of the experimental $C_{2\chi}(x)$ and of ε, we calculate $\widetilde{C}_{2\mathcal{Y}}(z)$ by using eq.(6) and then estimate $\pi(\lambda)$ numerically as the inverse Laplace transform of the analytic continuation on the complex plane of $\widetilde{C}_{2\mathcal{Y}}(z)$.

Once ε, $\pi(\lambda)$ and consequently $< \lambda >$ are known, we calculate K/a^2 from eq. (10) with the same value of the modified Kozeny constant k_λ estimated from the analysis of exponentially correlated percolation lattices.

To validate the model, we predict the permeability of deterministic and stochastic fractal structures at different iterations in the construction process,

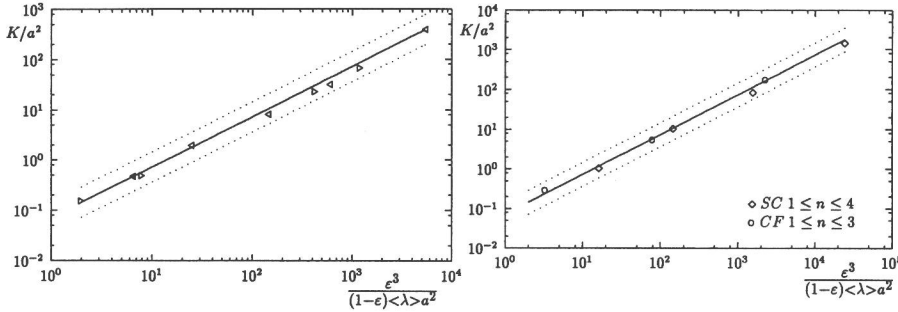

Figure 2: LBE simulation results for the permeability K/a^2 vs $\varepsilon^3/((1-\varepsilon)(<\lambda>a^2))$ for probabilistic and stochastic fractal structures at different iterative construction stages: a) two different realizations of a fractal percolation lattice ($b = 2$, $p = 0.90$, $N = 256$) for $3 \le n \le 7$; b) Sierpinsky Carpet ($1 \le n \le 4$) and Chess Fractal ($1 \le n \le 3$). The continuous line is the model, eq.(11). Dotted lines correspond to an error of factor two, i.e. an error bounded between $K_{model}/2 \le K \le 2K_{model}$.

and compare the model predictions with LBE simulation results. The stochastic structures considered are fractal percolation lattices [11]. The deterministic fractal structures are the Sierpinski Carpet (SC) and the Chess Fractal (CF) [8], specifically designed since, unlike the Sierpinski carpet, it does not exhibit straight channels. A fractal percolation lattice is a random fractal generated by means of an iterative procedure. The square lattice $\mathcal{E}_o = N \times N$ is divided into b^2 squares of side N/b (in lattice units). A subset of these squares is selected to form $\mathcal{E}_1$ in such a way that each square has the independent probability p of being chosen as a square of $\mathcal{E}_2$. The iterative procedure continues so that $\mathcal{E}_n$ is a random collection of squares of side $\delta_n = N/b^n$ (in lattice units).

This iterative procedure, which depends on the parameters p and b, defines a random fractal $\mathcal{F}_{p,b} = \cap_{n=0}^{\infty}\mathcal{E}_n$ with fractal dimension $D = \log(b^2p)/\log(b)$.

The deterministic fractals analyzed are generated by means of a similar but deterministic iterative procedure. The square lattice $\mathcal{E}_o = N \times N$ is divided into b^2 squares of side N/b. A set of $(b^2 - l^2)$ of these squares is selected to form $\mathcal{E}_1$. The iterative procedure continues so that $\mathcal{E}_n$ is a collection of squares of side $\delta_n = N/b^n$.

For all the lattice structures generated by means of an iterative procedure, the evaluation of $< \lambda >$ should take into account the fact that at each iteration there exists a well-defined minimum dissipation lengthscale controlling the viscous effects at the solid boundary. This minimum dissipation length corre-

sponds to the lattice side $\delta_n = N/b^n$ of the smallest box at the iteration n. The existence of such a lengthscale implies that there exists a limiting value λ_c of λ, $a^2\lambda_c = 4/\delta_n^2$, such that all the values of $\lambda > \lambda_c$ are not related to viscous transport phenomena.

Consequently, eq. (11) should be reformulated as

$$< \lambda >= \frac{\int_0^{\lambda_c} \lambda \widehat{\pi}(\lambda) d\lambda + \sum_{i=1}^{\overline{N}_{loc}} \alpha_i \lambda_i}{\int_0^{\lambda_c} \widehat{\pi}(\lambda) d\lambda + \sum_{i=1}^{\overline{N}_{loc}} \alpha_i} , \tag{12}$$

$\overline{N}_{loc}$ being the number of localized Gaussian contributions with $\lambda_i \leq \lambda_c$.

Figures 2 a)-b) show the excellent agreement between the theoretical curve eq. (10) and the LBE simulation results of permeability for (a) two realizations of fractal percolation lattices ($b = 2$, $p = 0.90$, $N = 256$) and (b) the two deterministic fractals SC ($b = 3$, $l = 1$, $D = \log(8)/\log(3)$, $N = 243$) and CF ($b = 4$, $l = 2$, $D = \log(12)/\log(4)$, $N = 256$), at different iteration stages. The value of k_λ is the same obtained from the analysis of exponentially correlated percolation lattices, $k_\lambda = 13.5$.

Although the model has been derived from the Carman-Kozeny equation applied to exponentially correlated percolation lattices, its range of application and quantitative prediction capabilities are greater than the Carman-Kozeny model. Without any fitting parameters, the model predicts with great accuracy the permeability of highly diluted exponentially correlated percolation lattices ($0.93 \leq \varepsilon \leq 0.995$) and also the permeability of a 2-d square array of cylinders throughout the entire range of the solid fraction c, including the range of c in which the Carman equation fails, i.e. for very concentrated and very diluted arrays.

4 Fluid-solid noncatalytic reactions

The literature on gas-solid noncatalytic reactions [12] usually considers two distinct phenomenologies: (a) the particle is initially non-porous and the solid reactant is distributed in an inert matrix; fluid diffuses through the product layer and reaction occurs at a moving boundary; (b) the particle is initially porous and reaction occurs in a distibuted way throughout the entire pore-space. For both phenomenologies, many authors have analyzed the influence of the spatial distribution of solid reactant [13,14,15] on the conversion vs time curves, regardless of the spatial correlation properties. We study the influence of the spatial correlation of the solid reactant on fluid-solid non-catalytic reactions, focusing on initially non-porous particles with an assigned solid reactant distribution function.