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Analytical approximation for diffusion-reaction processes in rough pores

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Abstract. – The concept of an active zone in Laplacian transport is used to obtain an analytical approximation for the reactive effectiveness of a pore with an arbitrary rough geometry. We show that this approximation is in very good agreement with direct numerical simulations performed over a wide range of diffusion-reaction conditions (*i.e.*, with or without screening effects). In particular, we find that in most practical situations, the effect of roughness is to increase the intrinsic reaction rate by a geometrical factor, namely the ratio between the real and the apparent surface area. We show that this simple geometrical piece of information is sufficient to characterize the reactive effectiveness of a pore, in spite of the complex morphological features it might possess.

The physics of diffusion-reaction phenomena in disordered media has attracted a lot of attention, due to its close connections with major technological subjects like catalysis and waste disposal. Modeling heterogeneous catalytic processes represents a real challenge, mainly due to the limitations of classical pseudo-homogeneous representations [1, 2]. These models only implicitly account for the geometrical features of real pore spaces [3]. Due to *screening effects*, even if the active sites are uniformly distributed in space along the surface, the regions corresponding to fins or extended protrusions will display a higher activity as opposed to the deep parts of fjords which are more difficult to access. The standard modeling approach is to consider the catalyst particle as a homogeneous system where reagents and products can diffuse and react according to an effective diffusion coefficient and an intrinsic reaction mechanism. Although in recent years some effort has been dedicated to the investigation of diffusion and reaction in heterogeneous geometries (*e.g.*, fractals) [4–7], the role played by

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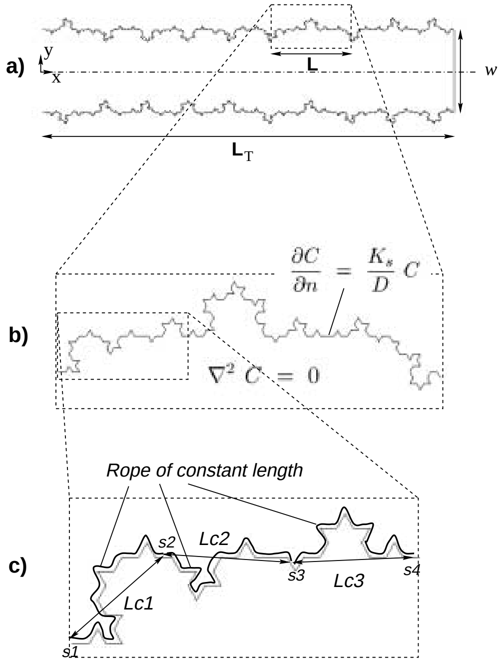

Fig. 1 – (a) Schematic representation of a two-dimensional rough pore. The reactive walls are composed of 10 successive different random Koch curves (RKC) of the third generation. (b) Schematic representation of the wall element. The reactive interface is irregular and the reactant concentration obeys the Laplace equation. A constant concentration C_S is maintained at the source line and the boundary condition at the interface is $\partial C/\partial n = K_s C/D$. (c) Schematic representation of the coarse-graining or finite renormalization procedure used in the "Land Surveyor Method" (LSM). Successive ropes of length Λ determine successive chords of lengths $L_{\mathrm{c}1}$, $L_{\mathrm{c}2}, \ldots$.

the pore shape or the local surface morphology on the overall diffusivity and reactivity of the catalyst remains to be understood.

The notion of *active zone* [8] has been recently applied to elucidate several relevant features of the Laplacian transport to and across irregular interfaces (*e.g.*, electrodes and membranes). We show here that this concept can be used to derive an analytical approximation for the diffusion-reaction activity of pores of arbitrary rough geometry. In a first step, we use a coarse-graining argument to obtain the *effective* reaction rate of an irregular wall element. In the second step, this result is used to calculate the reactive effectiveness of a deep rough pore analytically. Finally, this two-step approach is validated by numerical simulations of the full problem.

As shown in fig. 1, we consider the steady-state diffusion transport of reactant A in a single slit-shaped pore of nominal length L_T (x-direction). The two reactive walls of this pore are rough surfaces of thickness b (z-direction) separated by a distance w (y-direction). By definition, they are generated through the translation along the z-direction of two lines made by the connection of several elementary irregular interfaces. In the example shown in fig. 1(a), the walls of the pore have a fractal geometry of a 3-generation random Koch curve (RKC) [9,10]. From a source at the pore entrance, molecules of species A diffuse into the pore through a neutral solvent to react at the walls according to a first-order kinetics, $A \rightarrow A^\star$.

The first step, namely, to find an effective reaction rate for an irregular wall element, can be achieved through the use of the *Land Surveyor Method* (LSM) [8,11,12]. We briefly recall the principle of this method focusing on a typical finite region of the pore (fig. 1). This subset can be approximately treated as a diffusion-reaction cell where reagent species A diffuse from a source line of length L towards an irregular reactive interface of perimeter L_p and thickness b (see fig. 1(b)). In the bulk of this cell, the flux $\vec{J}(\vec{r})$ of species A obeys Fick's law, $\vec{J}(\vec{r}) \equiv -D\vec{\nabla}C$, where $C(\vec{r})$ is the local concentration and D is the molecular diffusion coefficient. Under steady-state conditions, the concentration field of the reactant species satisfies the Laplace equation $\nabla^2 C = 0$. For the boundary conditions, we assume a constant concentration of A equal to C_S at the source line. At the reactive interface, the depletion rate of A follows $J_n \equiv -K_s C$, where K_s is the *intrinsic* reaction rate constant. Due to mass conservation, the local reaction flux must be equal to the diffusive flux reaching the active interface from the bulk. As a consequence, the boundary condition at this point can be written as

$$\frac{\partial C}{\partial n} = \frac{K_s}{D}\, C\,. \tag{1}$$

This introduces a finite-length scale $\Lambda \equiv D/K_s$ into the problem. Thus, in order to understand diffusion-reaction, one has to solve the Laplace equation with the boundary condition (1) on the walls. This is an unsolved mathematical problem. In contrast, the problem of the Dirichlet boundary condition ($C = 0$) on irregular surfaces has been thoroughly studied, specially for the case of two-dimensional systems. An important theorem proposed by Makarov [13] has been used to describe the properties of the current distribution on irregular electrodes (*e.g.*, fractal electrodes) [8]. This theorem states that *the information dimension of the harmonic measure on a singly connected electrode in* $d = 2$ *is exactly equal to* 1. In terms of activity, this means that, whatever the shape of the interface, the size L_{act} of the region where most of the reaction takes place is of the order of the overall size (or diameter) L of the cell under a dilation transformation. When applied to the diffusion-reaction cell shown in fig. 1(b), Makarov's theorem has a simple but general consequence: the screening effect due to geometrical irregularities of the reactive interface can be characterized in terms of the ratio [8]

$$S \equiv L_p/L\,. \tag{2}$$

Because the active length of the interface is of the order of the system size, $L_{\text{act}} \approx L$, then $L_{\text{act}} \approx L_p/S$ and the factor S can be considered as the "screening factor" of the Dirichlet-Laplacian field. This result cannot be applied as such to a real diffusion-reaction cell because the boundary condition on the reacting interface is not $C = 0$, but rather $\partial C/\partial n = C/\Lambda$. To account for this more realistic boundary condition, we use the Land Surveyor Method. In this method, one switches from the real geometry obeying the real boundary condition to a coarse-grained geometry obeying the Dirichlet boundary condition, where the coarse-graining depends on Λ. The size of the active zone of the reactive interface can then be obtained from the screening factor of that new geometry.

Consider a region i along the reactive interface with perimeter $L_{pi} = s_{i+1} - s_i$, where s is the curvilinear coordinate along the interface. It has a reactive conductance $G_i = [bK_s]L_{pi}$. The access conductance to reach this surface is $G_{\text{acc}} \approx bD$. Depending on the size of the region i, there exist two situations: $G_i < G_{\text{acc}}$ or $G_{\text{acc}} < G_i$. If L_{pi} is small, $G_i < G_{\text{acc}}$ and the flux is limited by G_i. If L_{pi} is large enough, the flux is limited by the access conductance. In the latter situation we are, in a first approximation, back to the case of a Laplacian field with Dirichlet boundary condition (*i.e.*, $C = 0$). The new geometry is defined through the identity $G_i = G_{\text{acc}}$, which means that the curvilinear distance L_{pi} along the reactive surface is equal to Λ. From its definition, a coarse-grained region can be considered as acting uniformly. If we performed the coarse-graining on a larger scale, the flux would no longer be uniform within a macrosite and, therefore, we would not be able to identify the size of the active zone. The size of a grain, L_c, is the distance in real space (or the chord length) between s_1 and s_2. We then shift from the real geometry to the coarse-grained geometry which is made of successive chords $L_{c1} = L_c(s_0, s_1)$, $L_{c2} = L_c(s_1, s_2)$, ... (see fig. 1(c)).

If we now observe that the perimeter of the coarse-grained interface is $L_{p,\mathrm{cg}} = L_{c1} + L_{c2} + ... = N\langle L_c\rangle$, where $\langle L_c\rangle$ is the average chord length, the screening factor of the coarse-grained geometry is $S_{\mathrm{cg}} = N\langle L_c\rangle/L$. In this way, the effective conductance of the interface can be written as $G_{\mathrm{eff}} = bL_pK_s/S_{\mathrm{cg}}$. By definition, since each chord corresponds to a perimeter Λ, we can write $L_p = N\Lambda$ and then express the equivalent "element" conductance of the reactive interface as [12]

$$G_{\mathrm{eff}} = bD\,\frac{L}{\langle L_c\rangle}\,. \tag{3}$$

This result expresses how the conductance of a typical wall element should depend on the diffusivity of the reagent species in the bulk phase and the average chord length corresponding to a perimeter Λ. The geometry enters through the local relation between a perimeter Λ and its associated chord length. At this point, we can then define from (3) an *effective* reaction rate for the interface as

$$K_{\mathrm{eff}} = D/\langle L_c\rangle\,. \tag{4}$$

This result is general. It provides a very good approximation of the behavior of arbitrary wall geometries as long as the wall itself does not contain too deep pores (as discussed in [12], a deep pore is characterized by an aspect ratio larger than several units). In the particular case where the wall irregularity can be described by a fractal geometry, the chord length $\langle L_c\rangle$ of a self-similar interface with dimension D_f, size L and lower cut-off length scale ℓ can be expressed approximately as

$$\langle L_c\rangle = \begin{cases} \Lambda\,, & \text{if} \quad \Lambda \ll \ell\,, \\ \ell(\Lambda/\ell)^{\frac{1}{D_f}}\,, & \text{if} \quad \ell < \Lambda < L_p\,, \\ \Lambda/S\,, & \text{if} \quad \Lambda \gg L_p\,. \end{cases} \tag{5}$$

Note that in the case where $\Lambda \gg L_p$, eq. (4) becomes

$$K_{\mathrm{eff}} = SK_s\,. \tag{6}$$

This exact relation provides a very simple expression for the effect of the roughness on the effective reaction rate.

In the second step, the LSM result (4) is used to compute the overall activity of the rough pore by considering it as a smooth pore with an effective reactivity. Thus, writing this reactivity of the coarse-grained wall in terms of K_{eff}, it is possible to describe by mass conservation the phenomenon of diffusion and surface reaction over the entire pore using the following differential equation:

$$\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} = 0\,,$$

with boundary conditions

$$C(0,y) = C_S\,, \qquad \frac{\partial C}{\partial x}(L_T, y) = 0\,, \qquad \frac{\partial C}{\partial y}(x, 0) = 0$$

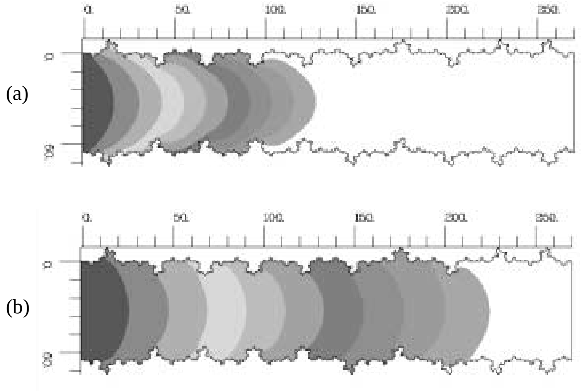

Fig. 2 – Contour plot of the steady-state concentration of reactant penetrating a rough pore. The relevant sizes of the pore are $w = 2L$ and $L_T = 10L$. In (a) $\Lambda/\ell = 10$ while in (b) $\Lambda/\ell = 100$. The contour plots have been computed from direct numerical simulation using the finite-elements technique. The change in the grey scale corresponds to a factor of 2 in concentration.

and

$$\frac{\partial C}{\partial y}(x, \pm w/2) + \frac{K_{\mathrm{eff}}}{D} C(x, \pm w/2) = 0\,. \tag{7}$$

The boundary condition $\frac{\partial C}{\partial y}(x,0) = 0$ corresponds to the assumption that the pore is symmetric with respect to $y = 0$. As in heterogeneous catalysis studies, the effect of reaction-diffusion process is measured by an effectiveness factor [2]:

$$\eta \equiv \frac{\Phi}{\Phi_{\mathrm{max}}}\quad , \tag{8}$$

where Φ is the mass flux penetrating the system:

$$\Phi = 2b \int_0^{w/2} \left[-D \frac{\partial C}{\partial x}(0, y) \right] \mathrm{d}y\,, \tag{9}$$

and $\Phi_{\mathrm{max}} = 2DbL_T S C_S/\Lambda$ is the mass flux in the absence of diffusion limitations. From the analytic solution of eqs. (7) and using definition (8), we obtain the following expression for the reactive effectiveness of a two-dimensional rough pore [14]:

$$\eta = \frac{2\Lambda}{\langle L_{\mathrm{c}} \rangle L_T S} \sum_{n=1}^{\infty} \frac{\tan(\alpha_n w/2) \tanh(\alpha_n L_T)}{[(\alpha_n^2 + \langle L_{\mathrm{c}} \rangle^{-2}) w/2 + \langle L_{\mathrm{c}} \rangle^{-1}]}\,, \tag{10}$$

where α_n is the n-th root of the eigenvalue equation, $\alpha_n \tan(\alpha_n w/2) = \langle L_{\mathrm{c}} \rangle^{-1}$ for $n = 1,\ 2,\ 3,\ \ldots$.

In order to check the validity of eqs. (5) and (10), we numerically calculate the solution of the two-dimensional Laplacian transport in a rough pore geometry whose active walls are composed of several elementary RKC interfaces ($D_f = \log 4/\log 3$). This task is performed here through discretization with unstructured meshes by means of the finite-elements technique [15]. Due to computational limitations, we restrict our simulations to reactive pore

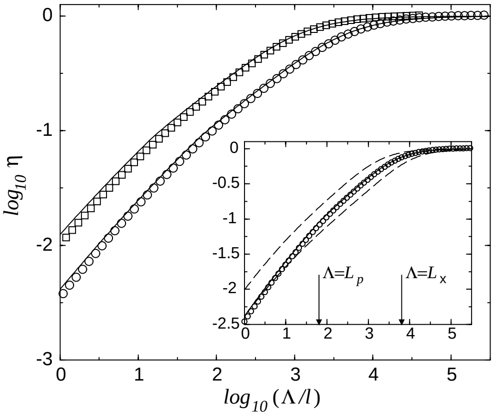

Fig. 3 – Dependence of the effectiveness factor η on Λ/ℓ. The symbols correspond to η values calculated from direct numerical simulation of reactive rough pores whose walls are made of RKCs of second (squares) and third (circles) generation. The thick solid lines correspond to the analytical approximations from eqs. (5) and (10). For comparison with a 3-generations RKC pore, the inset shows two curves corresponding to the effectiveness behavior of smooth pores (dashed lines) with lengths L_T (top) and $L_T S$ (bottom). The arrows point to the crossovers $\Lambda = L_p$ and $\Lambda = L_\times$.

walls made of RKC curves of 2 and 3 generations. In figs. 2(a) and (b), we show the concentration fields in a typical reactive rough pore constructed with 3-generations RKC walls and calculated at $\Lambda/\ell = 10$ and 100, respectively.

The results displayed in fig. 3 show that the LSM predictions for the effectiveness are in excellent agreement with numerical simulations of the complete diffusion-reaction equations in both 2- and 3-generations RKC pores and over the whole range of relevant η variability, namely, for $\Lambda > \ell$ [16]. It is illustrative to compare the results obtained for a rough pore with the classical behavior of reactive, but flat pores. In the inset of fig. 3, we show the logarithmic curves of η *vs.* Λ/ℓ calculated for a rough pore (3-generations RKC) and for the corresponding smooth pores with lengths L_T and $L_T S$. The large discrepancy which can be observed among the behaviors of rough and flat pores clearly indicates the important role played by the geometry of the reactive interfaces. Finally, one should note that, in the limit of negligible resistance to pore diffusion, the effectiveness approaches asymptotically its maximum, $\eta = 1$. If the pore is very deep ($L_T \gg w$), the one-dimensional approximation of eq. (7) allows one to estimate the crossover for this saturation regime as $\Lambda = L_\times \equiv 2{L_T}^2 S/w$. This prediction is also in good agreement with the numerical simulations (see the inset of fig. 3).

In summary, the work presented here provides clear evidence that the effect of pore space morphology on the global efficiency of a diffusion-reaction system is not only relevant, but should govern the reactivity of irregular interfaces under diffusion limitations. In particular, it is found that, contrary to the classical description [1, 2], the effect of an arbitrary rough geometry is to modify the reaction rate and *not* the effective diffusion coefficient. Note that the analytical approximation derived here and validated through direct numerical simulations relies solely on the knowledge of simple geometrical characteristics. It provides accurate predictions for the effectiveness of rough pores over a wide range of diffusion-reaction conditions. For all practical situations where the reactant penetration in the pore is significant, one can use the simple model of a smooth pore with an effective reactivity K_{eff} to describe the efficiency of a rough pore. Remarkably, K_{eff} is the product of the intrinsic reactivity by the simple factor S which is the ratio between the real and the apparent surface area of the pore and can be experimentally quantified (*e.g.*, by electron microscopy and/or small-angle X-ray scattering). It is noteworthy that the reactive efficiency of rough pores is governed by the screening factor S alone, regardless of underlying geometrical details. Indeed, it has been shown recently that random and deterministic fractal interfaces with the same fractal dimension display the same transport properties [10]. We expect these results to be valid for real diffusion-reaction systems such as porous catalysts.

Another result of potential application from this study is the significant difference one can detect by comparing the effectiveness behavior of a pore with smooth active walls and a given nominal length and a pore with the same nominal length, but with rough catalytic surfaces. We argue that this, among other factors like the complex structure of the pore space in real catalyst grains, could contribute to the significant discrepancies previously found between experimental measurements and the standard theoretical approach using effective diffusion coefficients [17].

Finally, since the Land Surveyor Method has also been successfully applied to the response of non-linear irregular electrodes [18], it could possibly be used to study higher-order reactions in rough pores. Therefore, we believe that the LSM approximation in combination with the modeling techniques presented here can be useful and general tools to provide interesting guidelines for the relevant design problem of a suitable catalyst structure for a given reactive system.

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