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LAPLACIAN TRANSPORT TOWARDS PARTIALLY PASSIVATED 2D IRREGULAR INTERFACES: A CONJECTURAL EXTENSION OF THE MAKAROV THEOREM

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Abstract

In several phenomena of practical interest, such as catalyst deactivation, fouling in heat transfer and other systems of technological and scientific relevance, an irregular surface accessed by diffusion can be progressively passivated. In a diffusion limited situation, an interface that works unevenly due to Laplacian screening is simultaneously and unevenly passivated. To study this phenomenon, we describe a process in which the regions of the surface that are initially working, are transformed into passive, reflecting zones. As a consequence, at each step, a new part of the interface becomes active. In turn, this new active zone is passivated, and so on. It is found that the length of the successive active zones remains approximately constant for a prefractal interface. The concept of active zone in Laplacian transport can then be successfully extended to elucidate this *self-limiting* behavior of the passivation process. A conjecture is then proposed which states that, in $D = 2$, the information dimension of the harmonic measure on a fractal supporting a "passivated or reflecting subfractal" (of smaller dimension) is equal to 1. This constitutes an extension of Makarov theorem. From our results, fractal geometry is revealed as a potential candidate to engineer substrate morphologies that are robust to Laplacian passivation.

Keywords: Passivation; Harmonic Measure; Diffusion; Heterogeneous Catalysis.

1. INTRODUCTION

The mathematical concept of harmonic measure, or modulus of the normal derivative of an interface Laplacian field, covers many different phenomena in physics and chemistry. It may, for example, represent the electric charge distribution on a (possibly irregular or fractal) capacitor electrode or the current distribution on an irregular electrode in an electrochemical cell. It also describes the probability density of diffusing particles reaching an irregular interface in the case of a catalyst with an irregular geometry.

In 1985, an important theorem, given by N. Makarov,[1] stated that the information dimension of the harmonic measure on a connected set, would it be fractal or not, is equal to 1 in $D = 2$, where D is the embedding dimension. The physical meaning of this exact result is that the length of the *active zone*, i.e. the zone which receives the majority of the Laplacian flux, should be of the order of the size or diameter of the smallest sphere that surrounds the interface. This result measures how the non-uniform accessibility of the interface to random walkers determines the activity of the system. For example, in catalysis, the efficiency of the interface can be significantly smaller than the one expected from its intrinsic activity because diffusing particles reach preferably the protrusions of the irregular interface. These so-called *screening effects* are responsible for substantial differences in behavior between the deep parts of the interface displaying a lower activity, and its most exposed regions that are highly active. Note that the theorem of Makarov is only valid for Dirichlet boundary condition (BC), where the interface presents no resistance to transport or, equivalently, infinite reactivity or permeability.

Inspired by this result, a coarse-graining method was proposed that permits to extend the consequences of the Makarov theorem to "resistive" interfaces which do not necessarily obey Dirichlet BC's.[2] Through this method, it is possible to determine the flux across an arbitrarily irregular interface from its geometry alone, avoiding the solution of the Laplace problem within a complex boundary domain.

However, a related problem, that arises, for example, in the frame of heterogeneous catalysis, has very important scientific and technological implications. It is the process of catalyst deactivation, where a progressive decrease of the surface activity is observed with time. This is due to the fact that, together with the primary chemical reaction, there is a secondary reaction which gradually "passivates" the surface reactivity of the active zone.

So the following question naturally arises: what comes next? After deactivation, the diffusing particles hitting the now passivated zones are reflected and may eventually reach and react at zones of the surface that have not been passivated yet, but were initially poorly active because of screening. This process is the subject discussed in the present paper. Although the results presented below are obtained in $D = 2$ where Makarov's theorem applies, the concept of active zone still remains in $D = 3$. This work then constitutes a first step towards the understanding of the real ($D = 3$) problem which represents a practical issue of importance since the cost involved in catalyst replacement and process shutdown for the industry due to deactivation can be extremely high, reaching the order of billions of dollars per year.

2. THE DIFFUSION CELL

The question that we try to solve is illustrated in Fig. 1. We consider a two-dimensional cell where mass is transported by diffusion through a fluid, from a source line of length L towards an irregular interface of perimeter L_p but with the same diameter L. In the bulk of the cell, the transport of mass obeys Fick's law, $\mathbf{q}(\mathbf{r}) \equiv -D\boldsymbol{\nabla}C$, where $\mathbf{q}$ represents the mass flux vector field, $C(\mathbf{r})$ is the local concentration at position $\mathbf{r}$ and D is the (molecular) diffusion coefficient. Under steady state conditions, the concentration field satisfies Laplace equation,

$$\nabla^2 C = 0\,. \tag{1}$$

At the source line, a constant concentration C_S is imposed as the boundary condition, whereas the lateral walls of the access space between the source and the interface are considered to be perfectly nonabsorbing. In the initial, non-passivated, regime (top part of Fig. 1), the boundary condition is Dirichlet everywhere (i.e. $C = 0$). In that situation the active zones are in the most prominent regions of the geometry. They are shown in red in the

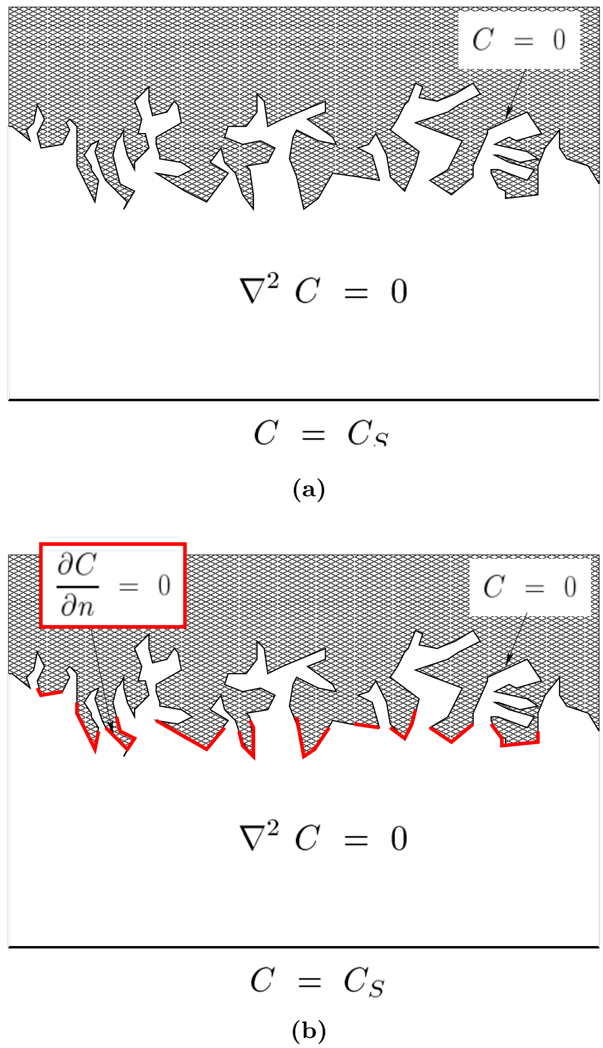

Fig. 1 Schematic representation of the diffusion cell subjected to passivation. The reactive interface is irregular, the reactant concentration obeys the Laplace equation and a constant concentration C_S is maintained at the source line. The passivation mechanism adopted will dictate the type of BC at a given subset of the interface, and for a given iteration of the process. **(a)** At the beginning, the entire interface follows Dirichlet's BC (i.e. $C = 0$). **(b)** Only the most exposed zones (shown in red), however, receive the quasi totality of the flux. After passivation, these same regions are deactivated (i.e. they obey Neumann's BC, $\partial C/\partial n = 0$) and the zone of high activity moves deeper into the irregular geometry. The Makarov theorem states that the cumulative length of the red regions is of the order of the system size.

bottom part of Fig. 1. The question to be solved is the following: if now these same zones are passivated (i.e. the BC at these zones becomes purely Neumann: $\partial C/\partial n = 0$), what is the new active zone? It will be shown in the following section that the length of the new active zone is approximately the same as the length of the first active zone. Even more, this remains true if we iterate the process up to the point where the entire interface is passive. We first discuss the simple case of a smooth pore, and then apply the same procedure to a prefractal interface.

3. THE PASSIVATION PROCESS

One should recall that the notion of active zone is a powerful, but drastic simplification of the problem. It is based on the strongly uneven distribution of the harmonic measure on the interface. The passivation, being a consequence of the local activity, will then occur first on the most active fraction of the interface. To characterize quantitatively this process, one has to find the regions of the interface that receives the highest fluxes and constitute a large, but not total, p-fraction of the total flux. (The total flux corresponding to $p = 1$ is supported by the entire interface.) Here we will consider the cumulative lengths of the zones that receive the fraction $p = 0.8$ or 0.9 of the total flux.

For a given interface geometry and passivation step, the solution of the Laplacian problem Eq. (1) for the concentration field C inside the diffusion cell is obtained after numerical discretization. A structured mesh comprising quadrilateral elements is generated and the solution is calculated by means of the finite-difference technique. From the solution C at a given passivation step, we compute each local mass flux ϕ_i crossing the non-passivated elements i of the interface as well as the total flux penetrating the system Φ.

Starting from a non-passivated interface, we select the wall elements that have the higher mass fluxes ϕ_i, and for which the sum constitutes a large fixed fraction p of the total flux Φ. We change the BC's on these selected elements from Dirichlet's type, $C = 0$, to Neumann's type, $\partial C/\partial n = 0$. These operations constitute the first iteration.

One then starts the second iteration: the concentration field and the local fluxes in the remaining potentially active parts of the interface (those that are still Dirichlet) are recalculated. A new active zone is determined by selection of the same large fraction p of the total activity. It is then passivated and so on. At each iteration step it, we count the number of elements $L_{it}(p)$ that support the highest fluxes and totalize a given fraction p of the entire flux. This is what we call the active zone length at stage it. If it keeps constant as a function of it, the cumulative passivated zone should be a linear function of it until the entire interface becomes passivated. This is what is found approximately for a prefractal interface and very precisely for a single smooth pore.

During this process, the total flux in the system slowly decreases. Since we restrict ourselves here to the study of the effects of passivation on the evolution of the active surface, we renormalize the local fluxes at each iteration of the passivation process. This corresponds to the definition of the information dimension which is computed from the *normalized* measure distribution. The complex dynamics of the total flux, which is certainly a subject of practical interest, is discussed elsewhere in a more realistic diffusion-reaction model.[3]

3.1. Sequential Passivation of a Smooth Pore

We first apply the passivation scheme proposed here to the case of a finite straight pore, as shown schematically in Fig. 2. In this case, the flux in the starting (non-passivated) configuration decreases monotonically from the entrance to the deeper parts of the pore. Practically, we suppose that there exists a small passive zone at the pore entrance in order to suppress the local divergences linked to non-realistic discontinuities between the source and the absorbing wall at the entrance corners. Due to symmetry, the amount L_{it} that receives the fraction p of the entire flux corresponds to the sum of the lengths of two identical parallel wall subsets at the pore inlet. As shown in Fig. 3, the length L_{it} that supports a fraction p increases rapidly with p and saturates at a value close to the pore entry diameter L. For example, a length $L_{it} = L$ is found to support around 90% of the total flux in accordance with our practical interpretation of Makarov's result. The amount L_{it} of the interface which is passivated at each iteration of the process should remain essentially *constant* for a given value of the fraction p. In other words, the passivation process can be described as a simple sequence of translations of the pore inlet in the axis direction by a distance $L_{it}/2$, as schematized in Fig. 2. The cumulative passivated length

$$S_{it} = \sum_{j=1}^{it} L_j$$

for $p = 0.9$ is shown in Fig. 4 for a pore of diameter 30 and depth 185 (total perimeter 400). The cumulative passivated length saturates at the pore perimeter. The inset in the figure shows that

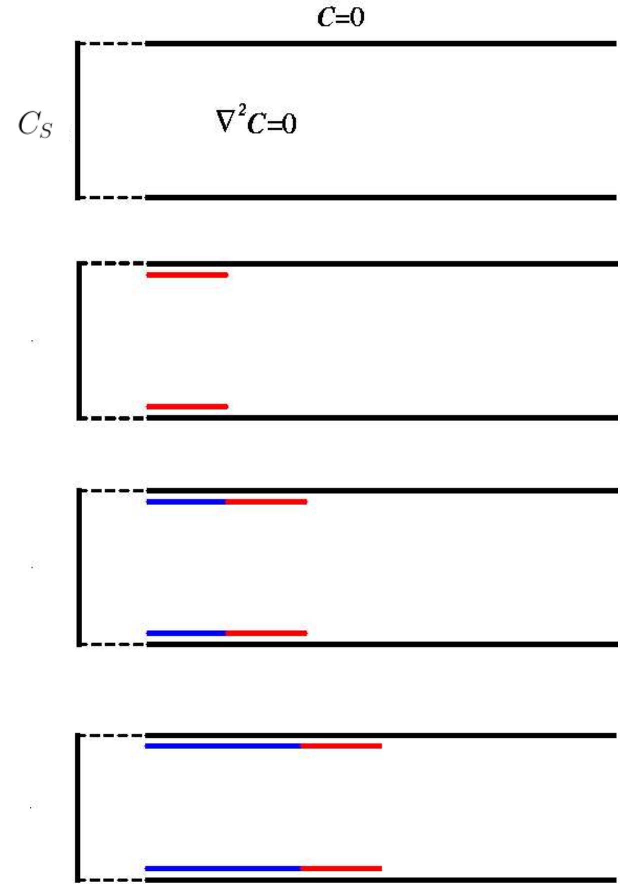

Fig. 2 Schematic diagram of the passivation process applied to a smooth pore. The amount of the interface $L_{it}(p)$ which is passivated (shown in red) at each iteration of the process remains constant. It is of the order of half the entrance diameter L. The passivation process follows as a simple sequence of translations of the pore inlet by the same passivated distance (shown in blue) $L_{it}(p)/2$.

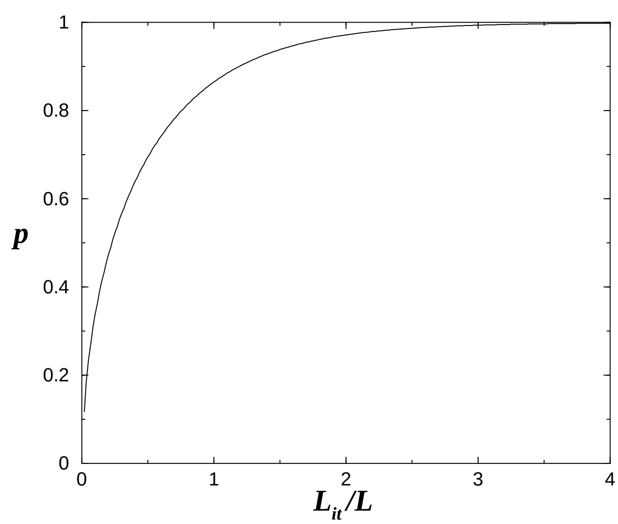

Fig. 3 Dependence of the fraction p of the total flux on the ratio L_{it}/L for the case of a smooth pore.

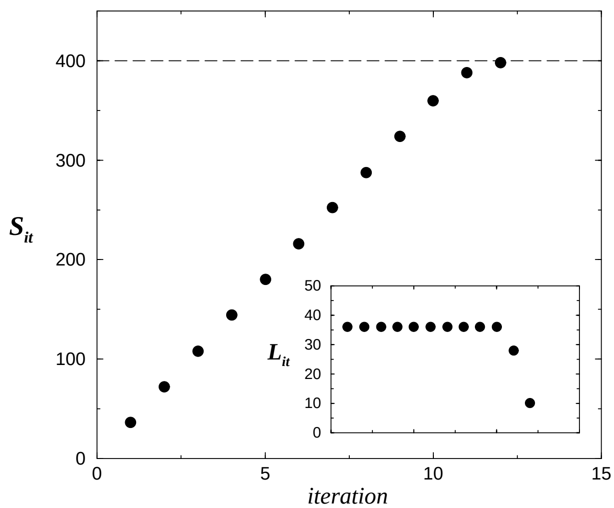

Fig. 4 Dependence of the cumulative amount passivated S_{it} at each step *it* of the process for the case of a smooth pore of width $L = 30$ and perimeter $L_p = 400$. The inset shows the corresponding sequences for L_{it}.

the active length is constant during the passivation process.

This result is not surprising from the theoretical point of view since the passivation amounts to translate sequentially the source inside the pore. It is however interesting from a qualitative point of view as it indicates that random walkers are essentially absorbed from the source within an angle of order $\pi/2$ or within a depth of the order of the lateral width. This corresponds qualitatively to Makarov's result. This means also that essentially all particles are colliding with the pore walls in a distance of the order of the pore width. During passivation, the diffusing particles which are emitted by the source may have two different destinies. Either they diffuse without hitting the pore walls or they hit the passivated regions and are reflected. However, the fraction of particles of the first type is very small so that the absorption (and the consequent passivation) is due to particles which have collided with the passivated walls many times. Even if the passivated region is large, only the deepest part of it will act as a source, constituting now a *deep* source. The very fact that the absorption is in that sense "local" is qualitatively general and is confirmed by the study of the prefractal interface.

3.2. Sequential Passivation of a Prefractal Interface

We now turn to the investigation of the passivation process applied to an irregular interface. The square Koch tree is utilized here as a paradigmatic geometry, but we expect our results to be valid for other complex structures.

In the left part of Fig. 5a we show the iso-concentration lines calculated numerically for a fully active (not yet passivated) interface. After selecting and passivating the most active elements, the concentration field and the local fluxes in the remaining possibly active parts of the interface are recalculated and a new iteration of the passivation process takes place. We proceed with these calculations up to the point where the entire interface becomes inactive (passivated). Figures 5b to f show the effect of sequential passivation on the concentration field C after 1, 3, 5, 7 and 9 iterations of the passivation process, respectively. The results displayed in Figs. 5a to f clearly indicate that the part of the interface receiving most of the flux is gradually moving to the deeper regions of the cell as the passivation develops. In the right part of Figs. 5a–f, we show how the fractal interface becomes progressively passivated for the corresponding iterations.

In Fig. 6, we show the evolution during the passivation process of the cumulative variable S_{it} for $p = 0.8$ and 0.9. Remarkably, S_{it} displays the same linear increase as the smooth pore from the beginning of the passivation process. This behavior persists till a crossover to a saturation regime corresponding to the complete deactivation of the system. The inset of Fig. 6 shows the variation of L_{it} at each iteration for the same geometries and p values. In the fractal case, we observe that the active length, defined above as the support of the p-fraction of the activity, exhibit fluctuations but keeps the same order of magnitude till the entire interface is passivated. Note that for $p = 0.8$ and 0.9 respectively, the length of the successive active zones are approximately 60 and 100. They are of the order of the interface diameter (equal to $3^4 = 81$). This corresponds to Makarov's result, even though the reflecting region increases at each iteration step.

Although expected for regular interfaces (e.g. for the pore geometry), the observed regime of constant passivation length is a non-trivial result for a complex fractal structure. One can understand this behavior by using the concept of active zone. As illustrated by the case of the smooth pore, each fragment of the active zone, *whatever its size*, will find after passivation a nearby absorbing (and active) region of essentially the *same size*. This is why the active zone, although fragmented on a prefractal, exhibits an approximately constant length.

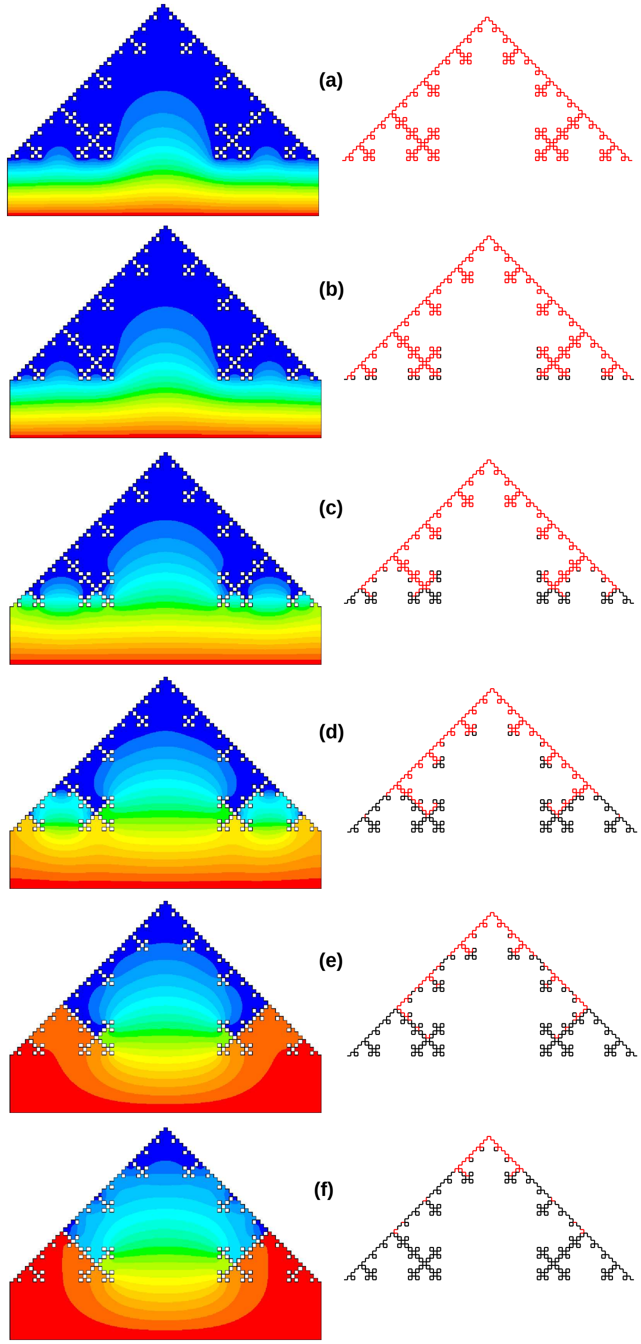

Fig. 5 Iterative passivation of a fourth generation prefractal quadratic Koch curve of dimension Log 5/Log 3. In this case the diameter L and perimeter L_p are respectively equal to 81 and 625 in terms of the smaller cut-off. On the left, the contour plots of the concentration of diffusing species at different iterations of the passivation process: **(a)** starting configuration, **(b)** $it = 1$, **(c)** 3, **(d)** 5, **(e)** 7, and **(f)** 9. The concentration decreases from red to blue. On the right, the corresponding fractal interfaces with non-passivated (shown in red) and passivated (shown in black) wall elements.

Furthermore, these considerations suggest a conjectural extension of the Makarov theorem to partially passivated interfaces. This conjecture predicts that,

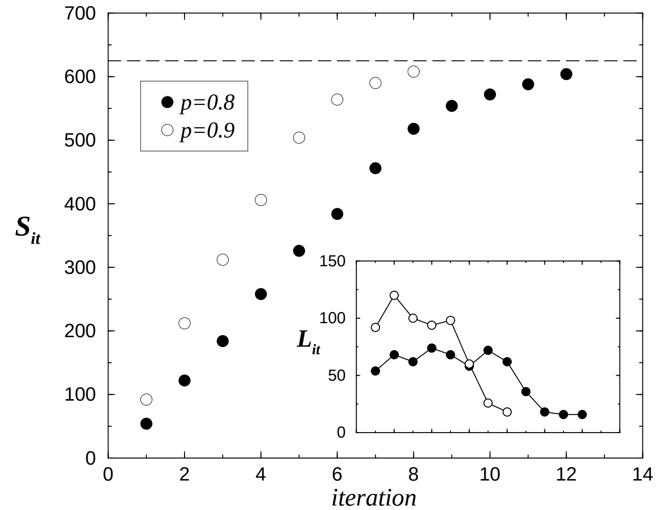

Fig. 6 Dependence of the cumulative passivated length S_{it} at each step it of the process for different values of p. The dashed line corresponds to the interface perimeter $L_p = 625$. The inset shows the corresponding sequences for L_{it}. L_{it} remains approximately constant during the process, up to complete passivation which occurs after 8 and 5 iterations for $p = 0.8$ and 0.9, respectively.

as long as the non-passivated part of the interface is sufficiently larger than L, the transport at the irregular interface should take place on an *active zone* L_{ac} whose length remains of the order of the system diameter L.

4. DISCUSSION AND CONCLUSIONS

Transport due to Laplacian fields towards irregular surfaces is a very common phenomenon in nature with important scientific and technological applications, including heat transfer, electrochemical transport, heterogeneous catalysis, and gas exchange from air to blood during the respiration process. In the case of heterogeneous catalysis, for example, the typical scenario at the microscopic scale is a cell where the reagent species have to be transported by diffusion through the bulk of a fluid to reach an active catalytic surface and be consumed according to a given reaction mechanism.[4,5] The influence of the surface morphology on the efficiency of the catalyst certainly plays an important role on this process and has already been the subject of interest in some previous studies.[6–8]

Concerning catalyst deactivation, the dynamical characteristics of this phenomenon should therefore be considered in the design of the diffusion-reaction system as well as in the process operation and optimization strategies.[9,10] At the level of the catalyst pellet, the role played by the geometry of the pore space on the dynamics of the deactivation process has been the focus of some previous studies.[11–14] In a recent work, the dynamics of deactivation through parallel fouling of an irregular catalytic interface operating under diffusion-limited conditions has been investigated.[3] For the particular case of a first-order reaction, a general analytical approach has been developed that confirms that, even for a *partially* absorbing surface, the active length in a progressively deactivated smooth pore remains constant as a function of time.

We now discuss what can be inferred from our results when the order of fractality increases towards the realization of this same problem on a mathematical fractal. When the generation of the prefractal increases, the ratio L/L_p of the primary active length to the perimeter decreases to 0. In that sense the active zone is more and more diluted. In this situation, the passivation of that zone will also correspond to a gradually smaller fraction of the surface. In the case of a mathematical fractal, the active length represents an infitesimal fraction of the total perimeter. As a consequence, the modification of the activity in this fraction of the interface will not dramatically alter the trajectories of the incoming particles as they will explore by reflection nearby regions which are Dirichlet and have a mass infinite as compared to that of the former active zone which is now Neumann.

This will also be the case for a (mathematical) fractal F' with dimension D'_f supported by our initial fractal F with dimension D_f, provided that D'_f is strictly smaller than D_f. So our conjecture is based on the fact that, if $D'_f < D_f$, F' is infinitely "diluted" in F. Consequently, diffusing particles can finally find Dirichlet regions in any vicinity of the passivated zone. The conjectural extension of Makarov's theorem can then be written as: "The information dimension of the harmonic measure on a fractal with dimension D_f supporting a fractal with dimension D'_f strictly smaller than D_f which is Neumann is equal to 1."

The possible extension of such studies to the passivation of irregular interfaces in $D = 3$ would clearly have important consequences.

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