A Mathematical Proof in Nanocatalysis: Better Homogenized Results in the Diffusion of a Chemical Reactant Through Critically Small Reactive Particles

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Abstract We consider a reaction-diffusion in which the reaction takes place on the boundary of the reactive particles. In this sense the particles can be thought of as a catalysts that produce a change in the ambient concentration w_ε of a reactive element. It is known that depending on the size of the particles with respect to their periodic repetition there are different homogeneous behaviors. In particular, there is a case in which the kind of nonlinear reaction kinetics changes and becomes more smooth. This case can be linked with the strange behaviors that arise with the use of nanoparticles. In this paper we show that concentrations of a catalyst are always higher when nanoparticles are applied.

1 Introduction

We consider a reaction-diffusion problem in which the reaction takes place on the boundary of the inclusions. In this sense the inclusions can be though as a catalysts that produce as change in the ambient concentration w_ε of a reactive element. This is standardly modeled as

$$\begin{cases} -\Delta w_\varepsilon = 0 & \Omega_\varepsilon, \\ \partial_\nu w_\varepsilon + \varepsilon^{-\gamma} g(w_\varepsilon) = 0 & S_\varepsilon, \\ w_\varepsilon = 1 & \partial\Omega, \end{cases} \tag{1}$$

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where g is a nondecreasing function such that $g(0) = 0$, Ω_ε is a perforated domain, $\partial\Omega_\varepsilon = S_\varepsilon \cup \partial\Omega$. R. Aris defined (see, e.g., [1]) the effectiveness of a reactor Ω as

$$\eta_\varepsilon = \frac{1}{|S_\varepsilon|} \int_{S_\varepsilon} g(w_\varepsilon) dx. \tag{2}$$

In the case where the particles are large (in a sense that would be precised later), the problem can be though homogenous, as $\Omega_\varepsilon \to \Omega$ then $w_\varepsilon \to w$ (in a sense that would be precised later), where the homogenized problem results

$$\begin{cases} -\Delta w + A g(w) = 0 & \Omega, \\ w = 1 & \partial\Omega, \end{cases} \tag{3}$$

for a certain constant A. In this setting Aris defined the effectiveness for the homogenized problem as

$$\eta = \frac{1}{|\Omega|} \int_{\Omega} g(w) dx. \tag{4}$$

This kind of problems, when g is not Lipschitz, has been shown to develop, in some cases, a region of positive measure $\{x \in \Omega : u(x) = 0\}$. This region, which is sometimes known as a dead core, has been studied in [2, 5].

Nonetheless, when the holes are of a sufficiently small size with respect to their repetition, the behaviour of the limit changes and becomes

$$\begin{cases} -\Delta w + B h(w) = 0 & \Omega, \\ w = 1 & \partial\Omega, \end{cases} \tag{5}$$

and h is a new nonlinearity, which we will introduce later, and $B > 0$ is a constant.

This change in behaviour, which is related to the pioneering paper [3], will be linked to new surprising properties that arise with the use of nanoparticles (see [11]). In this setting, the correct definition for the effectiveness of the limit problem is unclear.

The aim of this paper is to show that homogenized problem is more effective in the case associated with nanoparticles than the other cases. It represents a mathematical proof of some experimental facts in the literature.

2 Statement of Results

Let Ω be a bounded domain in $\mathbb{R}^n$, $n \geq 2$, with a smooth boundary $\partial\Omega$ and let $Y = (-1/2, 1/2)^n$. Denote by $G_0 = B_1(0)$ the unit ball centered at the origin. For $\delta > 0$ and $\varepsilon > 0$ we define $\delta B = \{x \,|\, \delta^{-1}x \in B\}$ and $\widetilde{\Omega}_\varepsilon = \{x \in \Omega | \rho(x, \partial\Omega) > 2\varepsilon\}$. Let

$$a_\varepsilon = C_0 \varepsilon^\alpha, \tag{6}$$

where $\alpha > 1$ and C_0 is a given positive number. Define

$$G_\varepsilon = \bigcup_{j \in \Upsilon_\varepsilon} (a_\varepsilon G_0 + \varepsilon j) = \bigcup_{j \in \Upsilon_\varepsilon} G_\varepsilon^j,$$

where $\Upsilon_\varepsilon = \{j \in \mathbb{Z}^n : (a_\varepsilon G_0 + \varepsilon j) \cap \overline{\widetilde{\Omega}}_\varepsilon \neq \emptyset\}$, $|\Upsilon_\varepsilon| \cong d\varepsilon^{-n}$, $d = const > 0$, $\mathbb{Z}^n$ is the set of vectors z with integer coordinates. The reference cell is represented by Fig. 1.

Define $Y_\varepsilon^j = \varepsilon Y + \varepsilon j$, where $j \in \Upsilon_\varepsilon$ and note that $\overline{G}_\varepsilon^j \subset \overline{Y}_\varepsilon^j$ and center of the ball G_ε^j coincides with the center of the cube Y_ε^j. Our "microscopic domain" is defined as

$$\Omega_\varepsilon = \Omega \setminus \overline{G_\varepsilon}, \qquad S_\varepsilon = \partial G_\varepsilon, \qquad \partial\Omega_\varepsilon = \partial\Omega \cup S_\varepsilon,$$

which can be represented as in Fig. 2.

We define the space $W^{1,p}(\Omega_\varepsilon, \partial\Omega)$ be the completion, with respect to the norm of $W^{1,p}(\Omega_\varepsilon)$, of the set of infinitely differentiable functions in $\overline{\Omega}_\varepsilon$ equal to zero in a neighborhood of $\partial\Omega$.

We are interest in understating the comparison of the limits of (1) when $\alpha \in (1, \frac{n}{n-2})$ and $\alpha = \frac{n}{n-2}$, which are known as the subcritical and critical cases in homogenization. The case $\alpha = 1$ was studied in [4]. In order to do this, we consider

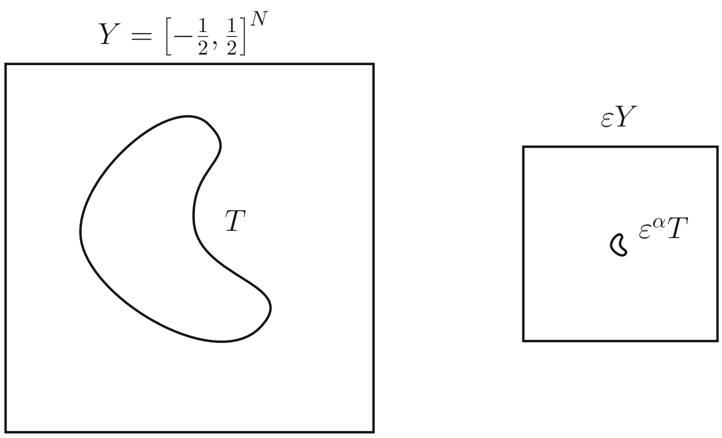

Fig. 1 The reference cell Y and the scalings by ε and ε^α, for $\alpha > 1$. Notice that, for $\alpha > 1$, $\varepsilon^\alpha T$ (for a general particle shaped as T) becomes smaller relative to εY, which scales as the repetition. In our case T will be a ball $B_1(0)$

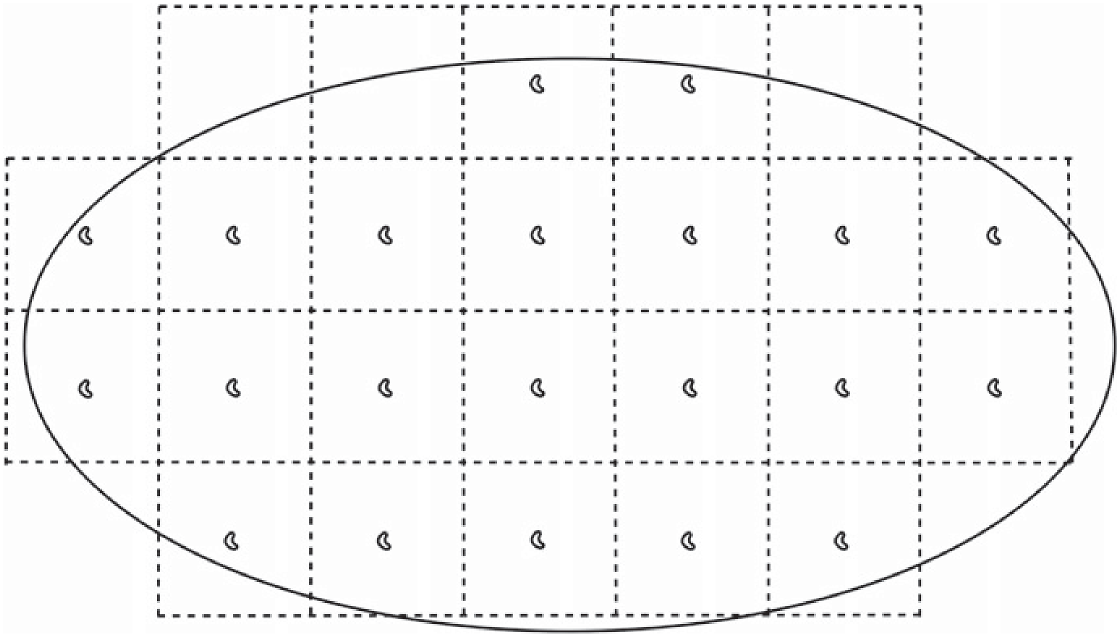

Fig. 2 The fixed bed reactor, i.e., the domain Ω_ε

the change in variable $u = 1 - w$, $\sigma(u) = g(1) - g(1-u)$ we have

$$\begin{cases} -\Delta u_\varepsilon = 0 & \Omega_\varepsilon, \\ \partial_\nu u_\varepsilon + \varepsilon^{-\gamma}\sigma(u_\varepsilon) = \varepsilon^{-\gamma} g(1) & S_\varepsilon, \\ u_\varepsilon = 0 & \partial\Omega. \end{cases} \tag{7}$$

The direct study of the family of solutions $(u_\varepsilon)_{\varepsilon>0}$ is difficult, since they are not defined in the same domain. We consider a family of linear extension operators (see [10])

$$P_\varepsilon : \{u \in H^1(\Omega_\varepsilon) : u = 0, \partial\Omega\} \to H_0^1(\Omega) \tag{8}$$

such that

$$\|\nabla P_\varepsilon u\|_{L^2(\Omega)} \le \|\nabla u\|_{L^2(\Omega_\varepsilon)}. \tag{9}$$

We define the different possible limits u:

- If $\alpha \in \left(1, \frac{n}{n-2}\right)$ then $u = u_{\text{non-crit}}$, which for $A = C_0^{n-1}\omega_n$ satisfies

$$\begin{cases} -\Delta u_{\text{non-crit}} + A\sigma(u_{\text{non-crit}}) = Ag(1) & \Omega, \\ u_{\text{non-crit}} = 0 & \partial\Omega. \end{cases} \tag{10}$$

- If $\alpha = \frac{n}{n-2}$ then $u = u_{\text{crit}}$, which for $B = (n-2)C_0^{n-2}\omega_n = \frac{n-2}{C_0}A$ satisfies

$$\begin{cases} -\Delta u_{\text{crit}} + BH(u_{\text{crit}}) = 0 & \Omega, \\ u_{\text{crit}} = 0 & \partial\Omega, \end{cases} \tag{11}$$

where H is the solution of the functional equation

$$\frac{n-2}{C_0}H(s) = \sigma(s - H(s)) - g(1). \tag{12}$$

We will start by indicating that, in the sense of maximal monotone graphs, in the particular case of $\sigma(u) = g(1) - g(1-u)$ one has

Lemma 1 *Let σ be a maximal monotone graph, then the solution H of (12) is given by*

$$H(u) = -\left(g^{-1}\left(\frac{n-2}{C_0}\cdot\right) + Id\right)^{-1}(1-u). \tag{13}$$

Hence $H(u) \le 0$ for every $u \in [0,1]$.

Remark 1 Notice that, in particular, in Eq. (5) we have

$$h(w) = \left(g^{-1}\left(\frac{n-2}{C_0}\cdot\right) + Id\right)^{-1}(w) \tag{14}$$

which is a nondecreasing function such that $h(0) = 0$.

Lemma 2 *Let σ be a bounded maximal monotone graph of $[0,1] \times \mathbb{R}$, then H is non-expansive in $[0,1]$ (and hence Lipschitz continuous).*

Proof If $\sigma \in \mathscr{C}^1([0,1])$, differentiating (12) with respect to s we derive

$$H'(s) = \frac{\sigma'(s-H(s))}{\frac{n-2}{C_0} + \sigma'(s-H(s))} \in (0,1). \tag{15}$$

Hence,

$$|H(t) - H(s)| \le |t-s| \tag{16}$$

for all $t, s \in [0,1]$. If σ is a maximal monotone graph, let $\sigma_\delta \in \mathscr{C}^1([0,1])$ be an approximation in the sense of maximal monotone graphs $\sigma_\delta \to \sigma$. In particular, $H_\delta \to H$ pointwise, and hence

$$|H(t) - H(s)| \le |t-s| \tag{17}$$

which concludes the proof. □

We have the following homogenization result.

Theorem 1 ([12]) *Let $\alpha > 1$, $\gamma = \alpha(n-1)-n$, $\sigma \in \mathscr{C}^1(\mathbb{R})$ be such that $\sigma(0) = 0$,*

$$0 < k_1 \le \sigma'(s) \le k_2, \tag{18}$$

and let u_ε be the weak solution of (7). Then, the extension $P_\varepsilon u_\varepsilon$ converge as $\varepsilon \to 0$

$$P_\varepsilon u_\varepsilon \to \begin{cases} u_{non\text{-}crit} & \text{if } \alpha \in \left(1, \frac{n}{n-2}\right), \\ u_{crit} & \text{if } \alpha = \frac{n}{n-2}, \end{cases} \tag{19}$$

strongly in $W_0^{1,p}(\Omega)$ for $1 \le p < 2$ and weakly in $H_0^1(\Omega)$.

Since, in our case $0 \le u_\varepsilon \le 1$ then we can have a simple corollary:

Corollary 1 *Let $\sigma \in \mathscr{C}([0,1])$, nondecreasing and such that $\sigma(0) = 0$, then (19) holds weakly in $H_0^1(\Omega)$.*

Proof Applying the estimates in [9] we check that $(P_\varepsilon u_\varepsilon)$ is bounded in $H_0^1(\Omega)$, hence there exists a limit $\hat{u}$ such that, up to a subsequence, $P_\varepsilon u_\varepsilon \to \hat{u}$ strongly in L^2.

Let σ_δ be such that it satisfies Theorem 1 and $\sigma_\delta \to \sigma$ in $\mathscr{C}([0,1])$ as $\delta \to 0$. Let $u_{\varepsilon,\delta}$ the solution of (7) with σ_δ. We can check, again with estimates in [9] that

$$\|u_\varepsilon - u_{\varepsilon,\delta}\|_{L^2(\Omega^\varepsilon)} \le C\|\sigma - \sigma_\delta\|_{\mathscr{C}([0,1])}. \tag{20}$$

Passing to the limit as $\varepsilon \to 0$

$$\|\hat{u} - u_\delta\|_{L^2(\Omega)} \le C\|\sigma - \sigma_\delta\|_{\mathscr{C}([0,1])}. \tag{21}$$

On the other hand, applying the theory of maximal monotones graphs, it is easy to check that H_δ the solution of (12) with σ_δ satisfies $H_\delta \to H$ in the sense of maximal monotone graphs. In both cases, $u_\delta \to u$ in L^2 where u is the solution of the problem with H or σ. Therefore $u_\varepsilon \to u$ weakly as $\varepsilon \to 0$. □

It is known already (see [7]) that, for the non critical cases the effectiveness behaves as expected

$$\eta_\varepsilon \to \eta, \qquad \text{as } \varepsilon \to 0. \tag{22}$$

However, in the noncritical case the reaction kinetics changes. Therefore it is not clear whether it is natural to define the effectiveness in the usual way. Nonetheless, we can give a pointwise comparison inequality. Let u_{crit} and $u_{\text{non-crit}}$ be the solutions of (11) and (10):

Theorem 2 *Let $\sigma \in \mathscr{C}([0,1])$ be such that $\sigma(0) = 0$. Then*

$$u_{crit} \le u_{non\text{-}crit}. \tag{23}$$

Proof Since $H(s) \leq 0$ we have that

$$BH(s) = (n-2)C_0^{n-2}\omega_n H(s) = C_0^{n-1}\omega_n \frac{n-2}{C_0} H(u) \tag{24}$$

$$= C_0^{n-1}\omega_n \left(\sigma(s - H(s)) - g(1)\right) = A\left(\sigma(s - H(s)) - g(1)\right) \tag{25}$$

$$\geq A\left(\sigma(s) - g(1)\right). \tag{26}$$

Therefore, applying the comparison principle, $u_{\text{crit}} \leq u_{\text{non-crit}}$. □

Remark 2 Therefore, if $g \in \mathscr{C}([0,1])$, the concentration w in the critical case is always larger than in the non critical cases

$$w_{\text{crit}} \geq w_{\text{non-crit}}. \tag{27}$$

Hence, we get a pointwise better reaction.

Remark 3 The basic convergence result given in Theorem 1 has been proved in many different cases. In particular, for non smooth σ in the form of a root or a Heaviside function and nonlinear diffusion in the form of a p-Laplacian see [6]. The case of Signorini type boundary conditions can be found in [8].

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