

Effective Dispersion Equations For Reactive Flows With Dominant Peclet and Damkohler Numbers*

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Abstract: In this paper we study a reactive flow through a capillary tube. The solute particles are transported and diffused by the fluid. At the tube lateral boundary they undergo an adsorption-desorption process. The transport and reaction parameters are such that we have large, dominant Peclet and Damkohler numbers with respect to

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the ratio of characteristic transversal and longitudinal lengths (the small parameter ε). Using the anisotropic singular perturbation technique we derive the effective equations. In the absence of the chemical reactions they coincide with Taylor's dispersion model. The result is compared with the turbulence closure modeling and with the central manifold approach. Furthermore, we present a numerical justification of the model by a direct simulation.

Keywords: Taylor's dispersion, high Peclet number, Damkohler number, anisotropic singular perturbation

1 Introduction

In many processes involving reactive flows different phenomena are present at different order of magnitude. It is fairly common that transport dominates diffusion and that chemical reaction happen at different time scales than convection/diffusion. Such processes are of importance in chemical engineering, pollution studies etc.

In bringing the models to a non-dimensional form, the presence of dominant Peclet and Damkohler numbers in reactive flows is observed. The problems of interest arise in complex geometries like porous media or systems of capillary tubes.

Taylor's dispersion is one of the most well-known examples of the role of transport in dispersing a flow carrying a dissolved solute. The simplest setting for observing it, is the injection of a solute into a slit channel. The solute is transported by Poiseuille's flow. In fact this problem could be studied in three distinct regimes: a) *diffusion-dominated mixing*, b) *Taylor dispersion-mediated mixing* and c) *chaotic advection*.

In the first flow regime, the velocity is small and Peclet's number is of order one or smaller. Molecular diffusion plays the dominant role in solute dispersion. This case is well-understood even for reactive flows (see e.g. [13], [14], [15], [16], [17], [19], [20], [23] and references therein).

If the flow rate is increased so that Peclet's number $\mathbf{Pe} \gg 1$, then there is a time scale at which transversal molecular diffusion smears the contact discontinuity into a plug. In [32], Taylor found an effective long-time axial diffusivity, proportional to the square of the transversal Peclet number and occurring in addition to the molecular diffusivity. After this pioneering work of Taylor, a vaste literature on the subject developed, with over 2000 citations to date. The most notable references are the paper [2] by Aris, where Taylor's intuitive approach was explained through moments expan-

sion and the lecture notes [9], where a probabilistic justification of Taylor’s dispersion is given. In addition to these results, addressing the tube flow with a dominant Peclet number and in the absence of chemical reactions, there is a huge literature on mechanical dispersion for flows through porous media. Since this is not the scope of our paper, we refer to the book [6] for more details about the modeling. For the derivation of Taylor’s dispersion in porous media using formal two-scale expansions, we refer to [3] and the references therein.

In the third regime, we observe the *turbulent mixing*.

Our goal is the study of **reactive flows** through slit channels in the regime of Taylor dispersion-mediated mixing and in this paper we will develop new effective models using the technique of anisotropic singular perturbations.

As already said, Taylor’s effective model contains a contribution in the effective diffusion coefficient, which is proportional to the square of the transversal Peclet number. Frequently this term is *more important than the original molecular diffusion*. After his work, it is called **Taylor’s dispersion coefficient** and it is generally accepted and used in chemical engineering numerical simulations. For the practical applications we refer to the classical paper [30] by Rubin. The mathematical study of the models from [30] was undertaken in [18].

Even with this enormous number of scientific papers on the subject, mathematically rigorous results on the subject are rare. Let us mention just ones aiming towards a rigorous justification of Taylor’s dispersion model and its generalization to reactive flows. We could distinguish them by their approach

- The averaging of the equations over the section leads to an infinite system of equations for the moments. A parallel could be drawn with the turbulence and in the article [25], Paine, Carbonell and Whitaker used an ad-hoc closure approach borrowed from Launder’s ”single point” closure schemes of turbulence modeling, for obtaining an effective model for reactive flows in capillary tubes. We will see that this approach leads to correct general form of the effective equations, but it does not give the effective coefficients. Furthermore, let us remark that it is important to distinguish between the turbulent transport, arising for very high Peclet numbers, and the Taylor dispersion arising for dominant Peclet number, but smaller than some threshold value.
- The central manifold approach of Mercer and Roberts (see the article [22] and the subsequent article [29] by Rosencrans) allowed to calculate

approximations at any order for the original Taylor’s model. Even if the error estimate was not obtained, it gives a very plausible argument for the validity of the effective model. This approach was applied to reactive flows in the article [4] by Balakotaiah and Chang. A number of effective models for different Damkohler numbers was obtained. Some generalizations to reactive flows through porous media are in [21] and the preliminary results on their mathematical justification are in [1] .

- More recent approach using the anisotropic singular perturbation is the article [24] by Mikelić, Devigne and van Duijn. This approach gives the error estimate for the approximation and, consequently, the rigorous justification of the proposed effective models. It uses the strategy introduced by Rubinstein and Mauri in [31] for obtaining the effective models.

We continue by applying the later approach for reactive transport with adsorption-desorption through a capillary tube.

2 Non-dimensional form of the problem and statement of the results

We study the diffusion of the solute particles transported by the Poiseuille velocity profile in a semi-infinite 2D channel. Solute particles are participants in a chemical reaction with the boundary of the channel. They don’t interact between them. The simplest example is described by the following model for the solute concentration c^* :

$$\frac{\partial c^*}{\partial t^*} + q(z) \frac{\partial c^*}{\partial x^*} - D^* \Delta_{x^*,z} c^* = 0 \text{ in } \mathbb{R}_+ \times (-H, H), \quad (1)$$

where $q(z) = Q^*(1 - (z/H)^2)$ and Q^* (**velocity**) and D^* (**molecular diffusion**) are positive constants. At the lateral boundaries $z = \pm H$

$$-D^* \partial_z c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{k}^*(c^* - \hat{c}/K_e) \text{ on } z = \pm H, \quad (2)$$

where \hat{k}^* represents the rate constant for adsorption and K_e the linear adsorption equilibrium constant. \hat{k}^*/K_e is the constant desorption rate.

The natural way of analyzing this problem is to introduce the appropriate scales. They would come from the characteristic concentration \hat{C} , the characteristic length L_R , the characteristic velocity Q_R , the characteristic diffusivity D_R and the characteristic time T_R . The characteristic length L_R coincides in fact with the ” observation distance”. Setting

$$c_F = \frac{c^*}{c_R}, \quad x = \frac{x^*}{L_R}, \quad y = \frac{z}{H}, \quad t = \frac{t^*}{T_R}, \quad Q = \frac{Q^*}{Q_R}, \quad D = \frac{D^*}{D_R},$$

$$k = \frac{\hat{k}^*}{k_R}, \quad c_s = \frac{\hat{c}}{\hat{c}_R}, \quad K = \frac{K_e}{K_{eR}},$$

we obtain the dimensionless equations

$$\frac{\partial c_F}{\partial t} + \frac{Q_R T_R}{L_R} Q (1-y^2) \frac{\partial c_F}{\partial x} - \frac{D_R T_R}{L_R^2} D \frac{\partial^2 c_F}{\partial x^2} - \frac{D_R T_R}{H^2} D \frac{\partial^2 c_F}{\partial y^2} = 0 \quad \text{in } \Omega \quad (3)$$

and

$$-\frac{D D_R}{H} c_R \frac{\partial c_F}{\partial y} = \frac{\hat{c}_R}{T_R} \frac{\partial c_s}{\partial t} = k_R k (c_R c_F - \frac{\hat{c}_R c_s}{K K_{eR}}) \quad \text{at } y = 1, \quad (4)$$

where

$$\Omega = (0, +\infty) \times (-1, 1), \quad \Gamma^+ = (0, +\infty) \times \{1\} \quad \text{and} \quad \Gamma = (0, +\infty) \times \{-1, 1\}. \quad (5)$$

This problem involves the following time scales:

$$T_L = \text{characteristic longitudinal time scale} = L_R / Q_R$$

$$T_T = \text{characteristic transversal time scale} = H^2 / D_R$$

$$T_{DE} = K_{eR} / k_R \quad (\text{characteristic desorption time})$$

$$T_A = \hat{c}_R / (c_R k_R) \quad (\text{characteristic adsorption time})$$

$$T_{react} = \text{superficial chemical reaction time scale} = H / k_R$$

and the following characteristic non-dimensional numbers

$$\mathbf{Pe} = \frac{L_R Q_R}{D_R} \quad (\text{Peclet number}); \quad \mathbf{Da} = \frac{L_R}{T_A Q_R} \quad (\text{Damkohler number})$$

Further we set $\varepsilon = \frac{H}{L_R} \ll 1$ and choose $T_R = T_L$.

Solving the full problem for arbitrary values of coefficients is costly and one would like to find the effective (or averaged) values of the dispersion coefficient and the transport velocity and an effective corresponding 1D parabolic equation for the effective concentration.

We consider the case when $K_{eR} = H$, $T_A \approx T_L \approx T_{DE}$. We choose $Q = \frac{Q^*}{Q_R} = \mathcal{O}(1)$, and

$$\frac{T_T}{T_L} = \frac{H Q_R}{D_R} \varepsilon = \mathcal{O}(\varepsilon^{2-\alpha}) = \varepsilon^2 \mathbf{Pe}.$$

Then the situation from Taylor's article corresponds to the case when $0 \leq \alpha < 2$, i.e. the transversal Peclet number is equal to $(\frac{1}{\varepsilon})^{\alpha-1}$ and $\hat{k}^* = 0$ (no chemistry). It is interesting to remark that in his paper Taylor has $\alpha = 1.6$ and $\alpha = 1.9$.

Our domain is now the infinite strip $Z^+ = \mathbb{R}_+ \times (0, 1)$. Then using the antisymmetry of $c^\varepsilon = c_F$, our equations in their non-dimensional form are

$$\frac{\partial c^\varepsilon}{\partial t} + Q(1-y^2) \frac{\partial c^\varepsilon}{\partial x} = D\varepsilon^\alpha \partial_{xx} c^\varepsilon + D\varepsilon^{\alpha-2} \partial_{yy} c^\varepsilon \quad \text{in } Z^+ \quad (6)$$

$$c^\varepsilon(x, y, 0) = 1, \quad (x, y) \in \mathbb{R}_+ \times (0, 1), \quad (7)$$

$$-D\varepsilon^{\alpha-2} \frac{\partial c^\varepsilon}{\partial y} = \frac{T_A}{T_{DE}} \frac{\partial c_s^\varepsilon}{\partial t} = \frac{T_L}{T_{DE}} k(c^\varepsilon - \frac{T_A}{T_{DE}} c_s^\varepsilon / K)|_{y=1} \quad \text{on } \Gamma^+ \times (0, T) \quad (8)$$

$$\partial_y c^\varepsilon(x, 0, t) = 0, \quad (x, t) \in \mathbb{R}_+ \times (0, T) \quad (9)$$

$$c_s^\varepsilon(0, t) = 0 \quad \text{and} \quad c^\varepsilon(0, y, t) = 0, \quad (y, t) \in (0, 1) \times (0, T). \quad (10)$$

We study the behavior of the solution to (6)-(10), with square integrable gradient in x and y , when $\varepsilon \rightarrow 0$ and try to obtain an **effective problem**.

In the paragraph §3.1 we will give a detailed derivation of the effective equations. Our technique is motivated by the paper [31] by J. Rubinstein and R. Mauri, where the analysis is based on the hierarchy of time scales and a corresponding 2-scale expansion. For $\hat{k}^* = 0$, our approach gives the effective problem from Taylor's paper [32]:

$$\begin{cases} \partial_t c^{Tay} + \frac{2Q}{3} \partial_x c^{Tay} = (\frac{D}{\mathbf{Pe}} + \frac{8}{945} \frac{Q^2 T_T}{D T_L}) \partial_{xx} c^{Tay}, \\ \text{in } \mathbb{R}_+ \times (0, T), \quad c^{Tay}|_{x=0} = 1, \\ c^{Tay}|_{t=0} = 0, \quad \partial_x c^{Tay} \in L^2(\mathbb{R}_+ \times (0, T)), \end{cases} \quad (11)$$

What is known concerning derivation of effective equations? Our approach and calculations performed in §3, gives the following non-dimensional effective equations in $(0, +\infty) \times (0, T)$:

$$\partial_t (c + \frac{T_A}{T_{DE}} c_s) + (\frac{2Q}{3} + \frac{2Qk}{45D} \frac{T_T}{T_{DE}}) \partial_x c - (D\varepsilon^\alpha + \frac{8}{945} \frac{Q^2}{D} \varepsilon^{2-\alpha}) \partial_{xx} c = \frac{2Qk}{45DK} \frac{T_A}{T_{DE}} \frac{T_T}{T_{DE}} \partial_x c_s \quad (12)$$

$$(1 + \frac{k}{3D} \frac{T_T}{T_{DE}}) \partial_t c_s = k \frac{T_L}{T_A} (c + \frac{2Q}{45D} \varepsilon^{2-\alpha} \partial_x c - \frac{T_A}{T_{DE}} c_s / K) \quad (13)$$

The system (12)-(13) could be compared with the corresponding non-dimensional effective equations obtained by Paine, Carbonell and Whitaker in [25].

After substituting the equation (13) at the place of $\partial_t c_s$ in (12), we see that our effective equations (12)-(13) coincide with the effective non-dimensional system (39)-(40), page 1784 from [25]. There is however a notable difference: the system (39)-(40) from [25] contains the parameters A_1 , A_2 , K^* and \mathbf{Sh} which depend nonlocally on c and c_s . Instead we give explicit values of the effective coefficients.

This case can not be compared with the results from [4], since they have a different time scale on the pages 61-73. Nevertheless, a comparison will be possible in the case $K_e = +\infty$.

In its dimensional form our effective problem reads

$$\partial_{t^*}(c^* + \frac{\hat{c}}{H}) + (\frac{2Q^*}{3} + \frac{2Q^*\mathbf{Da}_T}{45})\partial_{x^*}c^* - D^*(1 + \frac{8}{945}\mathbf{Pe}_T^2)\partial_{x^*x^*}c^* = \frac{2Q^*\mathbf{Da}_T}{45K_e}\partial_{x^*}\hat{c} \quad (14)$$

$$(1 + \frac{1}{3}\mathbf{Da}_T)\partial_{t^*}\hat{c} = \hat{k}^*(c^* + \frac{2H\mathbf{Pe}_T}{45}\partial_{x^*}c^* - \frac{\hat{c}}{K_e}) \quad (15)$$

where $\mathbf{Pe}_T = \frac{Q^*H}{D^*}$ is the transversal Peclet number and $\mathbf{Da}_T = \frac{\hat{k}^*H}{D^*}$ is the transversal Damkohler number.

Taking the transversal section mean gives

$$\partial_{t^*}(c^{moy} + \frac{\hat{c}^{moy}}{H}) + \frac{2Q^*}{3}\partial_{x^*}c^{moy} - D^*\partial_{x^*x^*}c^{moy} = 0 \quad (16)$$

$$\partial_{t^*}\hat{c} = \hat{k}^*(c^{moy} - \frac{\hat{c}}{K_e}). \quad (17)$$

We will compare numerically our effective equations (14)-(15) with the system (16)-(17), but we have even stronger arguments in our favor.

Why we prefer our model to other models from the literature? Because we are able to prove the error estimate. They were established in [24] for the particular case when $K_e = +\infty$ (the case of an irreversible, first order, heterogeneous reaction).

In this case the effective non-dimensional problem is

$$\partial_t c + Q(\frac{2}{3} + \frac{4k}{45D}\varepsilon^{2-\alpha})\partial_x c + k(1 - \frac{k}{3D}\varepsilon^{2-\alpha})c = (D\varepsilon^\alpha + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2-\alpha})\partial_{xx}c. \quad (18)$$

Our result could be stated in dimensional form: Let us suppose that $L_R > \max\{D_R/Q_R, Q_R H^2/D_R, H\}$. Then the upscaled dimensional problem cor-

responding to the case $K_e = +\infty$ reads

$$\begin{aligned} \frac{\partial c^{*,eff}}{\partial t^*} + \left(\frac{2}{3} + \frac{4}{45} \mathbf{Da}_T\right) Q^* \frac{\partial c^{*,eff}}{\partial x^*} + \frac{k^*}{H} \left(1 - \frac{1}{3} \mathbf{Da}_T\right) c^{*,eff} = \\ D^* \left(1 + \frac{8}{945} \mathbf{Pe}_T^2\right) \frac{\partial^2 c^{*,eff}}{\partial (x^*)^2}. \end{aligned} \quad (19)$$

Let us now compare the physical concentration c^ε with the effective concentration c . $H(x)$ denotes Heaviside's function.

Theorem 1. *Let c be the unique solution of (18) and let $\Omega_K = (0, K) \times (0, 1)$, $K > 0$. Then we have*

$$\max_{0 \leq t \leq T} t^3 \int_{\Omega_K} |c^\varepsilon(x, y, t) - c(x, t)| \, dx dy \leq C \varepsilon^{2-\alpha} \quad (20)$$

$$\begin{aligned} \left(\int_0^T \int_{\Omega_K} t^6 |\partial_y c^\varepsilon(x, y, t)|^2 \, dx dy dt \right)^{1/2} \leq C (\varepsilon^{2-5\alpha/4} H(1-\alpha) + \\ \varepsilon^{3/2-3\alpha/4} H(\alpha-1)) \end{aligned} \quad (21)$$

$$\begin{aligned} \left(\int_0^T \int_{\Omega_K} t^6 |\partial_x (c^\varepsilon(x, y, t) - c(x, t))|^2 \right)^{1/2} \leq \\ C (\varepsilon^{2-7\alpha/4} H(1-\alpha) + \varepsilon^{3/2-5\alpha/4} H(\alpha-1)). \end{aligned} \quad (22)$$

Furthermore, there exists a linear combination $\mathcal{C}_{cor}(x, y, t, \varepsilon)$ of products between polynomials in y and derivatives of c up to order 3, such that for all $\delta > 0$, we have

$$\begin{aligned} \max_{0 \leq t \leq T} \max_{(x, y) \in \Omega^+} |t^3 (c^\varepsilon(x, y, t) - c(x, t) - \mathcal{C}_{cor}(x, y, t))| \leq \\ \begin{cases} C \varepsilon^{4-7\alpha/2-\delta}, & \text{if } \alpha < 1, \\ C \varepsilon^{3/2-\alpha-\delta}, & \text{if } \alpha \geq 1. \end{cases} \end{aligned} \quad (23)$$

For details of the proof we refer to [24].

If we compare the non-dimensional effective equation (18) with the corresponding equation (57), page 1786, from [25], we find out that they have the same form. Contrary to [25], we have calculated the effective coefficients and we find them independent of the time and of the moments of c .

In the article [4] the surface reactions are much faster and do not correspond to our problem. In order to compare two approaches we will present in the paragraph §3.4 computations with our technique for the time scale chosen in [4] and we will see that one gets identical results. This shows that our approach through the anisotropic singular perturbation reproduces exactly the results obtained using the central manifold technique.

2.1 Statement of the results in case of nonlinear reactions

At sufficiently high concentrations of the transported solute particles, the surface coverage becomes important and nonlinear laws for the rate of adsorption should be used.

Now we study some of nonlinear cases. First, the condition (36) is replaced by

$$-D^* \partial_z c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{\Phi}(c^*) - \hat{k}_d^* \hat{c} \quad \text{on } z = \pm H, \quad (24)$$

where \hat{k}_d^* represents the constant desorption rate. Examples of $\hat{\Phi}$ are

$$\begin{cases} \hat{\Phi}(c) = \frac{k_1^* c}{1 + k_2^* c}, & \text{(Langmuir's adsorption)} ; \\ \hat{\Phi}(c) = k_1^* c^{k_2}, & \text{(Freundlich's adsorption)}. \end{cases} \quad (25)$$

Let us write non-dimensional forms for both nonlinear adsorption laws.

We start with **Langmuir's isotherm**. In this case the adsorption speed is k_1^* , having the characteristic size k_{1R} and $k_1^* = k_{1R} k_1$. For the second parameter we set $k_2^* c_R = k_2$, where k_2 is a dimensionless positive constant. Let $\Phi(u) = k_1 u / (1 + k_2 u)$. The characteristic times linked with the surface reactions are now:

$$T_A = \hat{c}_R / (c_R k_{1R}) \quad (\text{characteristic adsorption time})$$

$$T_{react} = \text{superficial chemical reaction time scale} = H / k_{1R}$$

Then after a short calculation we get the non-dimensional form of (24):

$$-D \varepsilon^{\alpha-2} \frac{\partial c^\varepsilon}{\partial y} = \frac{T_A}{T_{react}} \frac{\partial c_s^\varepsilon}{\partial t} = \frac{T_L}{T_{react}} (\Phi(c^\varepsilon) - k_d^* T_A c_s^\varepsilon)|_{y=1} \quad \text{on } \Gamma^+ \times (0, T) \quad (26)$$

We suppose $T_L \approx T_A \approx 1/k_d^*$ and k_1 and k_2 of order 1.

Next we consider **Freundlich's isotherm**. In this case it makes sense to suppose that $k_1^* = k_1 k_{1R} c_R^{1-k_2}$ and k_1 and k_2 of order 1. Then we get once more (26) but with $\Phi(u) = k_1 u^{k_2}$.

After the calculations from the section §3.2, we find out that the effective

equations in $(0, +\infty) \times (0, T)$:

$$\begin{aligned} \partial_t(c_{FN}^0 + \frac{T_A}{T_{react}}c_{sN}^{eff}) + \frac{2Q}{3}\partial_x(c_{FN}^0 + \frac{1}{15D}\frac{T_T}{T_{react}}\Phi(c_{FN}^0)) = \\ \varepsilon^\alpha(D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)})\partial_{xx}c_{FN}^0 + \frac{2Q}{45D}\frac{T_A T_T k_d^*}{T_{react}}\partial_x c_{sN}^{eff}, \end{aligned} \quad (27)$$

$$\partial_t c_{sN}^{eff} = \frac{T_L}{T_A}(\Phi(c_{FN}^0 + \varepsilon^{2-\alpha}c_{FN}^1|_{y=1}) - k_d^*T_A c_{sN}^0), \quad (28)$$

$$c_{FN}^1|_{y=1} = \frac{2}{45}\frac{Q}{D}\partial_x c_{FN}^0 - \frac{T_A}{3DT_{react}}\partial_t c_{sN}^{eff}, \quad (29)$$

$$c_{FN}^0|_{x=0} = 0, \quad c_{FN}^0|_{t=0} = 1, \quad c_{sN}^{eff}|_{t=0} = c_{s0}. \quad (30)$$

In its dimensional form our effective problem for the volume and surface solute concentrations $\{c_N^*, \hat{c}_N\}$ reads

$$\partial_{t^*}(c_N^* + \frac{\hat{c}_N}{H}) + \partial_{x^*}(\frac{2Q^*}{3}c_N^* + \frac{\mathbf{Pe}_T}{15}\hat{\Phi}(c_N^*)) =$$

$$D^*(1 + \frac{8}{945}\mathbf{Pe}_T^2)\partial_{x^*x^*}c_N^* + \frac{2k_d^*\mathbf{Pe}_T}{45}\partial_{x^*}\hat{c}_N \quad (31)$$

$$\partial_{t^*}\hat{c}_N = \hat{\Phi}(c_N^* + \mathbf{Pe}_T\tilde{c}_N^1) - k_d^*\hat{c}_N \quad (32)$$

$$\tilde{c}_N^1 = \frac{2H}{45}\partial_{x^*}c_N^* - \frac{1}{3}\partial_{t^*}\hat{c}_N, \quad (33)$$

where $\mathbf{Pe}_T = \frac{Q^*H}{D^*}$ is the transversal Peclet number.

Similar to the linear case, taking the mean over the transversal section gives

$$\partial_{t^*}(c_N^{moy} + \frac{\hat{c}_N^{moy}}{H}) + \frac{2Q^*}{3}\partial_{x^*}c_N^{moy} - D^*\partial_{x^*x^*}c_N^{moy} = 0 \quad (34)$$

$$\partial_{t^*}\hat{c}_N = \hat{\Phi}(c_N^{moy}) - k_d^*\hat{c}_N. \quad (35)$$

We point out that for the non-negligible local Peclet number, taking the simple mean over the section does not lead to a good approximation.

2.2 Statement of the results in the case of an infinite adsorption rate

Here we concentrate our attention to the case when the adsorption rate constant \hat{k}^* is infinitely large.

This means that the reaction at channel wall $\Gamma^* = \{(x^*, z) : 0 < x^* < +\infty, |z| = H\}$ is described by the the following flux equation

$$-D^* \partial_z c^* = K_e \frac{\partial c^*}{\partial t^*} \quad \text{on } \Gamma^*, \quad (36)$$

where K_e is, as before, the linear adsorption equilibrium constant. Now we see that (2) is replaced by (36), which corresponds to taking the limit $\hat{k}^* \rightarrow \infty$.

The characteristic times T_A and T_{DE} can not be used any more and we introduce the new characteristic time $T_C = \frac{K_{eR}}{\varepsilon Q_R}$, which has a meaning of the superficial chemical reaction time scale. As before, we set $\varepsilon = \frac{H}{L_R} \ll 1$ and choose $T_R = T_L$.

Introducing the dimensionless numbers into the starting and considering constant initial/boundary conditions yields the problem :

$$\frac{\partial c^\varepsilon}{\partial t} + Q(1 - y^2) \frac{\partial c^\varepsilon}{\partial x} = D\varepsilon^\alpha \frac{\partial^2 c^\varepsilon}{\partial x^2} + D\varepsilon^{\alpha-2} \frac{\partial^2 c^\varepsilon}{\partial y^2} \quad \text{in } \Omega^+ \times (0, T) \quad (37)$$

$$-D\varepsilon^{\alpha-2} \frac{\partial c^\varepsilon}{\partial y} = -D \frac{1}{\varepsilon^2 \mathbf{Pe}} \frac{\partial c^\varepsilon}{\partial y} = \frac{T_C}{T_L} K \frac{\partial c^\varepsilon}{\partial t} \quad \text{on } \Gamma^+ \times (0, T) \quad (38)$$

$$c^\varepsilon(x, y, 0) = 1 \quad \text{for } (x, y) \in \Omega^+, \quad (39)$$

$$c^\varepsilon(0, y, t) = 0 \quad \text{for } (y, t) \in (0, 1) \times (0, T), \quad (40)$$

$$\frac{\partial c^\varepsilon}{\partial y}(x, 0, t) = 0, \quad \text{for } (x, t) \in (0, +\infty) \times (0, T). \quad (41)$$

Further, we suppose that $T_C \approx T_L$.

After the calculations from the subsection §3.3 we find that the effective problem for the concentration $c_K^{*,eff}$ in its dimensional form reads

$$(1 + \mathbf{Da}_K) \frac{\partial c_K^{*,eff}}{\partial t^*} + \frac{2Q^*}{3} \frac{\partial c_K^{*,eff}}{\partial x^*} = D^* \left(1 + \frac{4}{135} \mathbf{Pe}_T^2 \left[\frac{2}{7} + \frac{\mathbf{Da}_K(2 + 7\mathbf{Da}_K)}{(1 + \mathbf{Da}_K)^2} \right] \right) \frac{\partial^2 c_K^{*,eff}}{\partial (x^*)^2}. \quad (42)$$

In (42) $\mathbf{Pe}_T = \frac{Q^* H}{D^*}$ is the transversal Peclet number and $\mathbf{Da}_K = \frac{K_e}{H}$ is the transversal Damkohler number.

The transversal section mean gives

$$(1 + \mathbf{Da}_K) \partial_{t^*} c_K^{moy} + \frac{2Q^*}{3} \partial_{x^*} c_K^{moy} - D^* \partial_{x^* x^*} c_K^{moy} = 0 \quad (43)$$

Once more, for the non-negligible local Peclet and Damkohler numbers, taking the simple mean over the section does not lead to a good approximation and our numerical simulations, presented in the last section, will confirm these theoretical results.

We note the possible similarities of the effective model (42) with Golay's theory as presented in [25]. In the effective dispersion term this theory predicts a rational function of K_e and we confirm it. Nevertheless, there is a difference in particular coefficients.

3 Derivation of the effective models in the non-dimensional form

In this section we will obtain the non-dimensional **effective or upscaled equations** using a two-scale expansion with respect to the **transversal Peclet number** $\varepsilon^{2-\alpha}$. Note that the transversal Peclet number is equal to the ratio between the characteristic transversal time scale and longitudinal time scale. Then we use Fredholm's alternative¹ to obtain the effective equations. However, they do not follow immediately. Direct application of Fredholm's alternative gives hyperbolic equations which are not satisfactory for our model. In order to obtain a better approximation, we use the strategy of Rubinstein and Mauri from [31] and embed the hyperbolic equation to the next order equations. This approach leads to the effective equations containing Taylor's dispersion type terms. Since we are in the presence of chemical reactions, dispersion is not caused only by the important Peclet number, but also by the effects of the chemical reactions, entering through Damkohler's number.

¹Comment for a non-mathematical reader: Fredholm's alternative gives a necessary and sufficient criterium for solvability of an equation, in the critical situation when we are in a spectrum. For linear algebraic system $\mathcal{A}\mathbf{x} = \mathbf{b}$, it says that if 0 is an eigenvalue of the matrix \mathcal{A} , the system has a solution if and only if \mathbf{b} is orthogonal to the eigenvectors of \mathcal{A} that correspond to the eigenvalue 0. Except the last example, that is borrowed from [4], in all examples considered here 0 is a simple eigenvalue. Therefore the corresponding boundary value problem in y -variable admit a solution if and only if the mean of the right hand side with respect with respect to the transversal variable y is equal to the value of the flux at $y = 1$. We refer to the textbooks as [34], for the Fredholm theory for the partial differential equations.

3.1 Full linear model with adsorption-desorption

We start with the problem (6)-(10) and search for c^ε in the form

$$c^\varepsilon = c_F^0(x, t; \varepsilon) + \varepsilon^{2-\alpha} c_F^1(x, y, t) + \varepsilon^{2(2-\alpha)} c_F^2(x, y, t) + \dots \quad (44)$$

$$c_s^\varepsilon = c_s^0(x, t; \varepsilon) + \varepsilon^{2-\alpha} c_s^1(x, y, t) + \varepsilon^{2(2-\alpha)} c_s^2(x, y, t) + \dots \quad (45)$$

After introducing (44) into the equation (6) we get

$$\begin{aligned} \varepsilon^0 \left\{ \partial_t c_F^0 + Q(1-y^2) \partial_x c_F^0 - D \partial_{yy} c_F^1 \right\} + \varepsilon^{2-\alpha} \left\{ \partial_t c_F^1 + Q(1-y^2) \partial_x c_F^1 - \right. \\ \left. D \varepsilon^{2(\alpha-1)} \partial_{xx} c_F^0 - D \varepsilon^\alpha \partial_{xx} c_F^1 - D \partial_{yy} c_F^2 \right\} = \mathcal{O}(\varepsilon^{2(2-\alpha)}) = \mathcal{O}\left(\left(\frac{T_T}{T_L}\right)^2\right). \end{aligned} \quad (46)$$

At the lateral boundary $y = 1$, after introducing (45) into (8) we get:

$$\left(-D \partial_y c_F^1 - \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t}\right) + \varepsilon^{2-\alpha} \left(-D \partial_y c_F^2 - \frac{T_A}{T_{DE}} \frac{\partial c_s^1}{\partial t}\right) + \dots = 0 \quad (47)$$

$$\begin{aligned} \left(\frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} - \frac{T_L}{T_{DE}} k(c_F^0 - \frac{T_A}{T_{DE}} \frac{c_s^0}{K})\right) + \varepsilon^{2-\alpha} \left(\frac{T_A}{T_{DE}} \frac{\partial c_s^1}{\partial t} - \right. \\ \left. \frac{T_L}{T_{react}} k(c_F^1 - \frac{T_A}{T_{DE}} \frac{c_s^1}{K})\right) + \dots = 0 \end{aligned} \quad (48)$$

To satisfy (46)-(48) for every $\varepsilon \in (0, \varepsilon_0)$, all coefficients in front of the powers of $\varepsilon^{2-\alpha}$ should be zero.

Equating the ε^0 terms gives the problem

$$\left\{ \begin{array}{l} -D \partial_{yy} c_F^1 = Q(y^2 - 1/3) \partial_x c_F^0 - (\partial_t c_F^0 + 2Q \partial_x c_F^0/3) \text{ on } (0, 1), \\ -D \partial_y c_F^1 = \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} = \frac{T_L}{T_{DE}} k(c_F^0 - \frac{T_A}{T_{DE}} \frac{c_s^0}{K}) \text{ on } y = 1, \\ \text{and } \partial_y c_F^1 = 0 \text{ on } y = 0, \end{array} \right. \quad (49)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. By Fredholm's alternative, this problem has a solution if and only if

$$\partial_t c_F^0 + 2Q \partial_x c_F^0/3 + \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} = 0 \quad (50)$$

$$\text{and } \frac{\partial c_s^0}{\partial t} = \frac{T_L}{T_A} k(c_F^0 - \frac{T_A}{T_{DE}} \frac{c_s^0}{K}) \quad (51)$$

in $(0, \infty) \times (0, T)$. Unfortunately our initial and boundary data are incompatible and therefore the solution to this hyperbolic equation with a memory

is discontinuous. Since the asymptotic expansion for c^ε involves derivatives of c_F^0 , system (50)- (51) does not suit our needs. In the case $k = 0$, considered in [8], this difficulty was overcome by assuming compatible initial and boundary data. Such an assumption does not always suit the experimental data and we proceed by following an idea from [31]. More precisely, we suppose that expression (50) is of the next order in our asymptotic expansion, i.e. that

$$\partial_t c_F^0 + 2Q\partial_x c_F^0/3 + \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} = \mathcal{O}(\varepsilon^{2-\alpha}) \quad \text{in } (0, +\infty) \times (0, T). \quad (52)$$

This hypothesis will be justified *a posteriori*, after getting an equation for c_F^0 and c_s^0 .

Combining (49) and (50) and using hypothesis (52) gives

$$\left\{ \begin{array}{l} -D\partial_{yy}c_F^1 = -Q(1/3 - y^2)\partial_x c_F^0 + \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} \quad \text{on } (0, 1), \\ -D\partial_y c_F^1 = \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} = \frac{T_L}{T_{DE}} k(c_F^0 - \frac{T_A}{T_{DE}} \frac{c_s^0}{K}) \quad \text{on } y = 1, \\ \text{and } \partial_y c_F^1 = 0 \quad \text{on } y = 0, \end{array} \right. \quad (53)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. Consequently

$$c_F^1(x, y, t) = \frac{Q}{D} \left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180} \right) \partial_x c_F^0 + \frac{1}{D} \left(\frac{1}{6} - \frac{y^2}{2} \right) \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} + A(x, t), \quad (54)$$

where $A(x, t)$ is an arbitrary function.

The problem corresponding to the order $\varepsilon^{2-\alpha}$ is

$$\left\{ \begin{array}{l} -D\partial_{yy}c_F^2 = \varepsilon^\alpha D\partial_{xx}c_F^1 - Q(1 - y^2)\partial_x c_F^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c_F^0 - \\ \partial_t c_F^1 - \varepsilon^{\alpha-2} \left(\partial_t c_F^0 + 2Q\partial_x c_F^0/3 + \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} \right) \quad \text{on } (0, 1), \\ -D\partial_y c_F^2 = \frac{T_A}{T_{DE}} \frac{\partial c_s^1}{\partial t} = \frac{T_L}{T_{DE}} k(c_F^1 - \frac{T_A}{T_{DE}} \frac{c_s^1}{K}) \quad \text{on } y = 1, \\ \text{and } \partial_y c_F^2 = 0 \quad \text{on } y = 0, \end{array} \right. \quad (55)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. Note that in order to have an expression for c_s^1 compatible with (54), when adding an arbitrary function $A(x, t)$ to c_F^1 in (54), we should also add to c_s^1 a function $B(x, t)$ satisfying

$$\partial_t B = \frac{T_L}{T_A} \left(A - \frac{T_A}{T_{DE}} \frac{B}{K} \right). \quad (56)$$

The problem (55) has a solution if and only if

$$\begin{aligned} & \partial_t c_F^0 + 2Q \partial_x c_F^0 / 3 + \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t} + \varepsilon^{2-\alpha} \frac{T_A}{T_{DE}} \frac{\partial c_s^1}{\partial t} + \varepsilon^{2-\alpha} \partial_t \left(\int_0^1 c_F^1 dy \right) - \\ & \varepsilon^\alpha D \partial_{xx} c_F^0 + Q \varepsilon^{2-\alpha} \partial_x \left(\int_0^1 (1-y^2) c_F^1 dy \right) - D \varepsilon^2 \partial_{xx} \left(\int_0^1 c_F^1 dy \right) = 0 \end{aligned} \quad (57)$$

in $(0, +\infty) \times (0, T)$. Note that this is the equation for c_F^0 and c_s^0 . Next let us remark that

$$\int_0^1 c_F^1 dy = A(x, t), \quad (58)$$

$$\int_0^1 (1-y^2) c_F^1 dy = \frac{2}{3} A(x, t) - \frac{Q}{D} \frac{8}{945} \partial_x c_F^0 + \frac{2}{45D} \frac{T_A}{T_{DE}} \frac{\partial c_s^0}{\partial t}, \quad (59)$$

and equation (57) becomes

$$\begin{aligned} & \partial_t \left(c_F^0 + \frac{T_A}{T_{DE}} (c_s^0 + \varepsilon^{2-\alpha} c_s^1) \right) + \frac{2Q}{3} \partial_x c_F^0 - \varepsilon^\alpha \tilde{D} \partial_{xx} c_F^0 = \\ & -\varepsilon^{2-\alpha} \frac{T_A}{T_{DE}} \frac{2Q}{45D} \partial_{xt} c_s^0 - \varepsilon^{2-\alpha} \left\{ \frac{T_A}{T_{DE}} \partial_t B + \partial_t A + \frac{2Q}{3} \partial_x A + D \varepsilon^2 \partial_{xx} A \right\} \end{aligned} \quad (60)$$

in $(0, +\infty) \times (0, T)$, with

$$\tilde{D} = D + \frac{8}{945} \frac{Q^2}{D} \varepsilon^{2(1-\alpha)}. \quad (61)$$

Let

$$\mathcal{L}_1\{A, B\} = \frac{T_A}{T_{DE}} \partial_t B + \partial_t A + \frac{2Q}{3} \partial_x A + D \varepsilon^2 \partial_{xx} A \quad (62)$$

$$\mathcal{L}_2\{A, B\} = \partial_t B - \frac{T_L}{T_A} \left(A - \frac{T_A}{T_{DE}} \frac{B}{K} \right). \quad (63)$$

There is no clear criterium for choosing the functions A and B . Nevertheless, if $\mathcal{L}_1\{A, B\} = \mathcal{O}(\varepsilon^{2-\alpha})$ and $\mathcal{L}_2\{A, B\} = 0$, $\{c_F^0, c_s^0\}$ would change at order $\mathcal{O}(\varepsilon^{2(2-\alpha)})$ and the contribution appears at the next order in the expansion for c^ε . Optimal choice of $\{A, B\}$ could come only from higher order calculations. For simplicity we choose $A = B = 0$. This choice simplifies the equation (60) and the boundary condition at $y = 1$ to the following system

of partial differential equations on $(0, +\infty) \times (0, T)$:

$$\begin{aligned} \partial_t(c_F^0 + \frac{T_A}{T_{DE}}c_s^{eff}) + (\frac{2Q}{3} + \frac{2}{45}\frac{T_T}{T_{DE}}\frac{Qk}{D})\partial_x c_F^0 = \\ \varepsilon^\alpha(D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)})\partial_{xx}c_F^0 + \frac{2}{45}\frac{T_A T_T}{(T_{DE})^2}\frac{Qk}{DK}\partial_x c_s^{eff} \end{aligned} \quad (64)$$

$$(1 + \frac{T_T}{T_{DE}}\frac{k}{3D})\partial_t c_s^{eff} = \frac{T_L k}{T_A}(c_F^0 + \frac{2}{45}\frac{Q}{D}\varepsilon^{2-\alpha}\partial_x c_F^0 - \frac{T_A}{KT_{DE}}c_s^{eff}) \quad (65)$$

where $c_s^{eff} = c_s^0 + \varepsilon^{2-\alpha}c_s^1$.

In fact it is possible to proceed differently, to eliminate $\partial_x c_F^0$ and have the right hand side of the first equation in (53) expressed in terms of $\partial_t c_F^0$ and $\partial_t c_s^{eff}$. In this approach the effective equations are hyperbolic. For more details we refer to [5]. In this paper our goal is to have a generalization of Taylor's dispersion and we search for a parabolic operator for c_F^0 .

3.2 Nonlinear reactions

Now we study some nonlinear surface reactions.

We start with the problem (6)-(10), but with (8) replaced by (26) (i.e. we have a nonlinear adsorption). As before we search for c^ε in the form

$$c^\varepsilon = c_{FN}^0(x, t; \varepsilon) + \varepsilon^{2-\alpha}c_{FN}^1(x, y, t) + \varepsilon^{2(2-\alpha)}c_{FN}^2(x, y, t) + \dots \quad (66)$$

$$c_s^\varepsilon = c_{sN}^0(x, t; \varepsilon) + \varepsilon^{2-\alpha}c_{sN}^1(x, y, t) + \varepsilon^{2(2-\alpha)}c_{sN}^2(x, y, t) + \dots \quad (67)$$

After introducing (66)-(67) into the equation (6) we get once more equation (46). To satisfy it for every $\varepsilon \in (0, \varepsilon_0)$, all coefficients in front of the powers of ε should be zero.

In addition we have the the following equations for the boundary reactions at $y = 1$:

$$(-D\partial_y c_{FN}^1 - \frac{T_A}{T_{react}}\frac{\partial c_{sN}^0}{\partial t}) + \varepsilon^{2-\alpha}(-D\partial_y c_{FN}^2 - \frac{T_A}{T_{react}}\frac{\partial c_{sN}^1}{\partial t}) + \dots = 0 \quad (68)$$

$$\begin{aligned} (\frac{T_A}{T_{react}}\frac{\partial c_{sN}^0}{\partial t} - \frac{T_L}{T_{react}}(\Phi(c_{FN}^0) - k_d^*T_A c_{sN}^0)) + \varepsilon^{2-\alpha}(\frac{T_A}{T_{react}}\frac{\partial c_{sN}^1}{\partial t} - \\ \frac{T_L}{T_{react}}(\Phi'(c_{FN}^0)c_{FN}^1 - k_d^*T_A c_{sN}^1)) + \dots = 0 \end{aligned} \quad (69)$$

As before, the ε^0 terms give the problem

$$\left\{ \begin{array}{l} -D\partial_{yy}c_{FN}^1 = Q(y^2 - 1/3)\partial_x c_{FN}^0 - (\partial_t c_{FN}^0 + 2Q\partial_x c_{FN}^0/3) \text{ on } (0, 1), \\ -D\partial_y c_{FN}^1 = \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t} = \frac{T_L}{T_{react}} (\Phi(c_{FN}^0) - k_d^* T_A c_{sN}^0) \text{ on } y = 1, \\ \text{and } \partial_y c_{FN}^1 = 0 \text{ on } y = 0, \end{array} \right. \quad (70)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. By Fredholm's alternative, this problem has a solution if and only if

$$\partial_t c_{FN}^0 + 2Q\partial_x c_{FN}^0/3 + \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t} = 0 \quad (71)$$

$$\text{and } \frac{\partial c_{sN}^0}{\partial t} = \frac{T_L}{T_{react}} (\Phi(c_{FN}^0) - k_d^* T_A c_{sN}^0) \quad (72)$$

in $(0, \infty) \times (0, T)$. Unfortunately our initial and boundary data are incompatible and therefore the solution to this hyperbolic equation with a memory is discontinuous. Since the asymptotic expansion for c^ε involves derivatives of c_{FN}^0 , system (71)- (72) does not suit our needs and, as in the previous subsection, we proceed by following an idea from [31]. More precisely, we suppose that expression (71) is of the next order in our asymptotic expansion, i.e. that

$$\partial_t c_{FN}^0 + 2Q\partial_x c_{FN}^0/3 + \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t} = \mathcal{O}(\varepsilon^{2-\alpha}) \quad \text{in } (0, +\infty) \times (0, T). \quad (73)$$

This hypothesis will be justified *a posteriori*, after getting an equation for c_{FN}^0 and c_{sN}^0 .

Combining (49) and (71) and using hypothesis (73) gives

$$\left\{ \begin{array}{l} -D\partial_{yy}c_{FN}^1 = -Q(1/3 - y^2)\partial_x c_{FN}^0 + \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t} \text{ on } (0, 1), \\ -D\partial_y c_{FN}^1 = \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t} = \frac{T_L}{T_{react}} (\Phi(c_{FN}^0) - k_d^* T_A c_{sN}^0) \text{ on } y = 1, \\ \text{and } \partial_y c_{FN}^1 = 0 \text{ on } y = 0, \end{array} \right. \quad (74)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. Consequently

$$c_{FN}^1(x, y, t) = \frac{Q}{D} \left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180} \right) \partial_x c_{FN}^0 + \frac{1}{D} \left(\frac{1}{6} - \frac{y^2}{2} \right) \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t} + A_N(x, t), \quad (75)$$

where $A_N(x, t)$ is an arbitrary function.

The problem corresponding to the order $\varepsilon^{2-\alpha}$ is

$$\left\{ \begin{array}{l} -D\partial_{yy}c_{FN}^2 = \varepsilon^\alpha D\partial_{xx}c_{FN}^1 - Q(1-y^2)\partial_x c_{FN}^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c_{FN}^0 - \\ \partial_t c_{FN}^1 - \varepsilon^{\alpha-2}(\partial_t c_{FN}^0 + 2Q\partial_x c_{FN}^0/3 + \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t}) \quad \text{on } (0, 1), \\ -D\partial_y c_{FN}^2 = \frac{T_A}{T_{react}} \frac{\partial c_{sN}^1}{\partial t} = \frac{T_L}{T_{react}} (\Phi'(c_{FN}^0)c_{FN}^1 - k_d^* T_A c_{sN}^1) \quad \text{on } y = 1, \\ \text{and } \partial_y c_{FN}^2 = 0 \quad \text{on } y = 0, \end{array} \right. \quad (76)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. Note that in order to have an expression for c_{sN}^1 that is compatible with (75), when adding an arbitrary function $A_N(x, t)$ to c_{FN}^1 in (54), we should also add to c_{sN}^1 a function $B_N(x, t)$ satisfying

$$\partial_t B_N = \frac{T_L}{T_A} (\Phi(A_N) - k_d^* T_A B_N). \quad (77)$$

The problem (76) has a solution if and only if

$$\begin{aligned} \partial_t c_{FN}^0 + 2Q\partial_x c_{FN}^0/3 + \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t} + \varepsilon^{2-\alpha} \frac{T_A}{T_{react}} \frac{\partial c_{sN}^1}{\partial t} + \varepsilon^{2-\alpha} \partial_t \left(\int_0^1 c_{FN}^1 dy \right) - \\ \varepsilon^\alpha D\partial_{xx}c_{FN}^0 + Q\varepsilon^{2-\alpha} \partial_x \left(\int_0^1 (1-y^2)c_{FN}^1 dy \right) - D\varepsilon^2 \partial_{xx} \left(\int_0^1 c_{FN}^1 dy \right) = 0 \end{aligned} \quad (78)$$

in $(0, +\infty) \times (0, T)$.² Note that this is the equation for c_{FN}^0 and c_{sN}^0 . Next let us remark that

$$\int_0^1 c_{FN}^1 dy = A_N(x, t), \quad (79)$$

$$\int_0^1 (1-y^2)c_{FN}^1 dy = \frac{2}{3}A_N(x, t) - \frac{Q}{D} \frac{8}{945} \partial_x c_{FN}^0 + \frac{2}{45D} \frac{T_A}{T_{react}} \frac{\partial c_{sN}^0}{\partial t}, \quad (80)$$

²Note that Freundlich's adsorption non-linearity is not differentiable since in most applications $0 < k_2 < 1$. Nevertheless at the end we will get expressions which do not involve derivative of Φ . Hence in manipulations we can use a smooth regularization of Φ . Clearly, a lacking smoothness of Φ would deteriorate precision of the approximation.

and equation (78) becomes

$$\begin{aligned} & \partial_t \left(c_{FN}^0 + \frac{T_A}{T_{react}} (c_{sN}^0 + \varepsilon^{2-\alpha} c_{sN}^1) \right) + \frac{2Q}{3} \partial_x c_{FN}^0 - \varepsilon^\alpha \tilde{D} \partial_{xx} c_{FN}^0 = \\ & -\varepsilon^{2-\alpha} \frac{T_A}{T_{react}} \frac{2Q}{45D} \partial_{xt} c_{sN}^0 - \varepsilon^{2-\alpha} \left\{ \frac{T_A}{T_{react}} \partial_t B_N + \partial_t A_N + \frac{2Q}{3} \partial_x A_N + D \varepsilon^2 \partial_{xx} A_N \right\} \end{aligned} \quad (81)$$

in $(0, +\infty) \times (0, T)$, with

$$\tilde{D} = D + \frac{8}{945} \frac{Q^2}{D} \varepsilon^{2(1-\alpha)}. \quad (82)$$

Let

$$\mathcal{L}_1\{A, B\} = \frac{T_A}{T_{react}} \partial_t B + \partial_t A + \frac{2Q}{3} \partial_x A + D \varepsilon^2 \partial_{xx} A \quad (83)$$

$$\mathcal{L}_2\{A, B\} = \partial_t B - \frac{T_L}{T_A} (\Phi(A) - k_d^* T_A B). \quad (84)$$

There is no clear criterium for choosing the functions A_N and B_N . With the same arguing as in §3.1 we choose $A_N = B_N = 0$. This choice simplifies (81). The next simplification is to eliminate the term $\partial_{xt} c_{sN}^0$ using (72), i.e.

$\frac{\partial c_{sN}^0}{\partial t} = \frac{T_L}{T_{react}} (\Phi(c_{FN}^0) - k_d^* T_A c_{sN}^0)$. Then

$$\varepsilon^{2-\alpha} \frac{T_A}{T_{react}} \frac{2Q}{45D} \partial_{xt} c_{sN}^0 = \frac{2Q}{45D} \frac{T_T}{T_{react}} \partial_x \Phi(c_{FN}^0) + \frac{2Q}{45D} \frac{T_T T_A k_d^*}{T_{react}} \partial_x c_{sN}^0 \quad (85)$$

and equation (81) reads

$$\begin{aligned} & \partial_t \left(c_{FN}^0 + \frac{T_A}{T_{react}} c_{sN}^{eff} \right) + \frac{2Q}{3} \partial_x \left(c_{FN}^0 + \frac{1}{15D} \frac{T_T}{T_{react}} \Phi(c_{FN}^0) \right) = \\ & \varepsilon^\alpha \left(D + \frac{8}{945} \frac{Q^2}{D} \varepsilon^{2(1-\alpha)} \right) \partial_{xx} c_{FN}^0 + \frac{2Q}{45D} \frac{T_A T_T k_d^*}{T_{react}} \partial_x c_{sN}^{eff} \text{ in } (0, +\infty) \times (0, T), \end{aligned} \quad (86)$$

where $c_{sN}^{eff} = c_s^0 + \varepsilon^{2-\alpha} c_s^1$. Next, after putting together the expansions for the ordinary differential equations from (74)-(76) for surface concentration at $y = 1$, we obtain

$$\partial_t c_{sN}^{eff} = \frac{T_L k}{T_A} (\Phi(c_{FN}^0 + \varepsilon^{2-\alpha} c_{FN}^1|_{y=1}) - k_d^* T_A c_{sN}^0) \quad (87)$$

$$c_{FN}^1|_{y=1} = \frac{2}{45} \frac{Q}{D} \partial_x c_{FN}^0 - \frac{T_A}{3DT_{react}} \partial_t c_{sN}^{eff} \quad (88)$$

in $(0, +\infty) \times (0, T)$

The effective problem is now

$$\begin{aligned}
& \partial_t(c_{FN}^0 + \frac{T_A}{T_{react}}c_{sN}^{eff}) + \frac{2Q}{3}\partial_x(c_{FN}^0 + \frac{1}{15D}\frac{T_T}{T_{react}}\Phi(c_{FN}^0)) = \\
& \varepsilon^\alpha(D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)})\partial_{xx}c_{FN}^0 + \frac{2Q}{45D}\frac{T_A T_T k_d^*}{T_{react}}\partial_x c_{sN}^{eff} \text{ in } (0, +\infty) \times (0, T), \\
& \partial_t c_{sN}^{eff} = \frac{T_L k}{T_A}(\Phi(c_{FN}^0 + \varepsilon^{2-\alpha}c_{FN}^1|_{y=1}) - k_d^* T_A c_{sN}^0) \text{ in } (0, +\infty) \times (0, T), \\
& c_{FN}^1|_{y=1} = \frac{2}{45}\frac{Q}{D}\partial_x c_{FN}^0 - \frac{T_A}{3DT_{react}}\partial_t c_{sN}^{eff} \text{ in } (0, +\infty) \times (0, T), \\
& c_{FN}^0|_{x=0} = 0, c_{FN}^0|_{t=0} = 1, c_{sN}^{eff}|_{t=0} = c_{s0}, \partial_x c \in L^2((0, +\infty) \times (0, T)).
\end{aligned} \tag{89}$$

3.3 Infinite adsorption rate

We start with the equations (37)-(38) and search for c^ε in the form

$$c^\varepsilon = c_K^0(x, t; \varepsilon) + \varepsilon^{2-\alpha}c_K^1(x, y, t) + \varepsilon^{2(2-\alpha)}c_K^2(x, y, t) + \dots \tag{90}$$

After introducing (44) into the equation (37) we get

$$\begin{aligned}
& \varepsilon^0 \left\{ \partial_t c_K^0 + Q(1-y^2)\partial_x c_K^0 - D\partial_{yy}c_K^1 \right\} + \varepsilon^{\alpha-2} \left\{ \partial_t c_K^1 + \right. \\
& \left. Q(1-y^2)\partial_x c_K^1 - D\varepsilon^{2(\alpha-1)}\partial_{xx}c_K^0 - D\varepsilon^\alpha\partial_{xx}c_K^1 - D\partial_{yy}c_K^2 \right\} = \mathcal{O}(\varepsilon^{2(2-\alpha)})
\end{aligned} \tag{91}$$

In order to have (91) for every $\varepsilon \in (0, \varepsilon_0)$, all coefficients in front of the powers of ε should be zero.

The problem corresponding to the order ε^0 is

$$\begin{cases} -D\partial_{yy}c_K^1 = -Q(1/3 - y^2)\partial_x c_K^0 - (\partial_t c_K^0 + 2Q\partial_x c_K^0/3) & \text{on } (0, 1), \\ \partial_y c_K^1 = 0 & \text{on } y = 0 \text{ and } -D\partial_y c_K^1 = K\frac{T_C}{T_L}\partial_t c_K^0 & \text{on } y = 1 \end{cases} \tag{92}$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. By the Fredholm's alternative, the problem (92) has a solution if and only if

$$(1 + K\frac{T_C}{T_L})\partial_t c_K^0 + 2Q\partial_x c_K^0/3 = 0 \quad \text{in } (0, L) \times (0, T). \tag{93}$$

Unfortunately our initial and boundary data are incompatible and the hyperbolic equation (93) has a discontinuous solution. Since the asymptotic

expansion for c^ε involves derivatives of c_K^0 , the equation (93) doesn't suit our needs. As before, we proceed by following an idea from [31] and suppose that

$$(1 + K \frac{T_C}{T_L}) \partial_t c_K^0 + 2Q \partial_x c_K^0 / 3 = \mathcal{O}(\varepsilon^{2-\alpha}) \quad \text{in } (0, +\infty) \times (0, T). \quad (94)$$

The hypothesis (94) will be justified *a posteriori*, after getting an equation for c_K^0 .

Hence (92) reduces to

$$\begin{cases} -D \partial_{yy} c_K^1 = -Q(1/3 - y^2) \partial_x c_K^0 + K \frac{T_C}{T_L} \partial_t c_K^0 & \text{on } (0, 1), \\ \partial_y c_K^1 = 0 & \text{on } y = 0 \quad \text{and} \quad -D \partial_y c_K^1 = K \frac{T_C}{T_L} \partial_t c_K^0 & \text{on } y = 1 \end{cases} \quad (95)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$, and we have

$$c_K^1(x, y, t) = \frac{Q}{D} \left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180} \right) \partial_x c_K^0 + \frac{K T_C}{D T_L} \left(\frac{1}{6} - \frac{y^2}{2} \right) \partial_t c_K^0 + C_{0K}(x, t), \quad (96)$$

where C_{0K} is an arbitrary function.

Let us go to the next order. Then we have

$$\begin{cases} -D \partial_{yy} c_K^2 = -Q(1 - y^2) \partial_x c_K^1 + D \varepsilon^{2(\alpha-1)} \partial_{xx} c_K^0 - \partial_t c_K^1 + \\ D \varepsilon^\alpha \partial_{xx} c_K^1 - \varepsilon^{\alpha-2} \left((1 + K \frac{T_C}{T_L}) \partial_t c_K^0 + 2Q \partial_x c_K^0 / 3 \right) & \text{on } (0, 1), \\ \partial_y c_K^2 = 0 & \text{on } y = 0 \quad \text{and} \quad -D \partial_y c_K^2 = K \frac{T_C}{T_L} \partial_t c_K^1 & \text{on } y = 1 \end{cases} \quad (97)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. The problem (97) has a solution if and only if

$$\begin{aligned} & \partial_t c_K^0 + 2Q \partial_x c_K^0 / 3 + K \frac{T_C}{T_L} (\partial_t c_K^0 + \varepsilon^{2-\alpha} \partial_t c_K^1|_{y=1}) + \varepsilon^{2-\alpha} \partial_t \left(\int_0^1 c_K^1 dy \right) - \\ & \varepsilon^\alpha D \partial_{xx} c_K^0 + Q \varepsilon^{2-\alpha} \partial_x \left(\int_0^1 (1 - y^2) c_K^1 dy \right) = D \varepsilon^2 \partial_{xx} \left(\int_0^1 c_K^1 dy \right) \\ & \text{in } (0, +\infty) \times (0, T). \end{aligned} \quad (98)$$

(98) is the equation for c_K^0 . Next let us remark that

$$\int_0^1 c_K^1 dy = C_{0K}(x, t), \quad (99)$$

$$\int_0^1 (1-y^2)c_K^1 dy = \frac{2}{3}C_{0K}(x, t) - \frac{Q}{D} \frac{8}{945} \partial_x c_K^0 + \frac{2K}{45D} \frac{T_C}{T_L} \frac{\partial c_K^0}{\partial t}, \quad (100)$$

$$\frac{\partial c_K^1}{\partial t} \Big|_{y=1} = \frac{2Q}{45D} \partial_{xt} c_K^0 - \frac{K}{3D} \frac{T_C}{T_L} \partial_{tt} c_K^0 + \partial_t C_{0K}. \quad (101)$$

In order to get a parabolic equation for c_K^0 we choose C_{0K} such that $\partial_{tt} c_K^0$ and $\partial_{xt} c_K^0$ do not appear in the effective equation.³ Then C_{0K} is of the form $C_{0K} = a \partial_{tt} c_K^0 + b \partial_{xt} c_K^0$ and after a short calculation we find that

$$C_{0K}(x, t) = \frac{1}{3D} \left(\frac{T_C}{T_L} \right)^2 \frac{K^2}{1 + KT_C/T_L} \partial_t c_K^0 - \frac{2Q}{45D} \frac{T_C}{T_L} \frac{K(2 + 7KT_C/T_L)}{(1 + KT_C/T_L)^2} \partial_x c_K^0. \quad (102)$$

Now c_K^1 takes the form

$$c_K^1(x, y, t) = \frac{Q}{D} \left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180} - \frac{2Q}{45D} \frac{T_C}{T_L} \frac{K(2 + 7KT_C/T_L)}{(1 + KT_C/T_L)^2} \right) \partial_x c_K^0 + \frac{K}{D} \frac{T_C}{T_L} \left(\frac{1}{6} + \frac{1}{3} \frac{T_C}{T_L} \frac{K}{1 + KT_C/T_L} - \frac{y^2}{2} \right) \partial_t c_K^0. \quad (103)$$

For $\alpha \geq 1$, $2 \geq 2(2 - \alpha)$ and we are allowed to drop the term of order $\mathcal{O}(\varepsilon^2)$. Now the equation (98) becomes

$$(1 + KT_C/T_L) \partial_t c_K^0 + \frac{2Q}{3} \partial_x c_K^0 = \varepsilon^\alpha \tilde{D} \partial_{xx} c_K^0 \quad \text{in } (0, +\infty) \times (0, T). \quad (104)$$

with

$$\tilde{D} = D + \frac{8}{945} \frac{Q^2}{D} \varepsilon^{2(1-\alpha)} + \frac{4Q^2}{135D} \frac{T_C}{T_L} \frac{K(2 + 7KT_C/T_L)}{(1 + KT_C/T_L)^2} \varepsilon^{2(1-\alpha)} \quad (105)$$

³Note that this strategy differs from the approach in the previous section, and the current effective equations can not be obtained as a limit $\tilde{k}^* \rightarrow 0$ of the effective equations obtained before. Nevertheless they are of the same order.

Now the problem (97) becomes

$$\left\{ \begin{array}{l}
-D\partial_{yy}c_K^2 = -\frac{Q^2}{D}\partial_{xx}c_K^0\left\{\frac{8}{945} + (1-y^2)\left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180}\right)\right\} + \\
\partial_{xt}c_K^0\frac{Q\tilde{K}}{D}\left\{\frac{2}{45} - (1-y^2)\left(\frac{1}{6} - \frac{y^2}{2}\right)\right\} + \frac{2Q\tilde{K}}{45D}\left(1 + \frac{\tilde{K}(7\tilde{K}+2)}{(1+\tilde{K})^2}\right)\partial_{xt}c_K^0 \\
-\left(\frac{\tilde{K}^2}{3D} - \frac{\tilde{K}^3}{3D(1+\tilde{K})}\right)\partial_{tt}c_K^0 - \left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180}\right)\partial_{xt}c_K^0\frac{Q}{D} + \\
\frac{Q\tilde{K}\left(\frac{1}{3} - y^2\right)}{D(1+\tilde{K})}\left(Q\partial_{xx}c_K^0\frac{7\tilde{K}+2}{1+\tilde{K}} - \frac{\tilde{K}}{3}\partial_{xt}c_K^0\right) - \left(\frac{1}{6} - \frac{y^2}{2}\right)\partial_{tt}c_K^0\frac{\tilde{K}}{D}\} \\
\text{on } (0,1), \quad \partial_y c_K^2 = 0 \text{ on } y=0 \quad \text{and on } y=1 \\
-D\partial_y c_K^2 = \frac{2\tilde{K}Q}{45D}\left(1 + \frac{\tilde{K}(7\tilde{K}+2)}{(1+\tilde{K})^2}\right)\partial_{xt}c_K^0 - \frac{\tilde{K}^2}{3D}\left(1 - \frac{\tilde{K}}{1+\tilde{K}}\right)\partial_{tt}c_K^0.
\end{array} \right. \quad (106)$$

where $\tilde{K} = KT_C/T_L$.

If we choose c^2 such that $\int_0^1 c^2 dy = 0$, then

$$\begin{aligned}
c^2(x, y, t) = & -\frac{Q^2}{D^2}\partial_{xx}c_K^0\left(\frac{281}{453600} + \frac{23}{1512}y^2 - \frac{37}{2160}y^4 + \frac{1}{120}y^6 - \frac{1}{672}y^8\right) \\
& + \frac{Q}{D^2}\partial_{xt}c_K^0\left(\frac{31}{7560} - \frac{7}{360}y^2 + \frac{y^4}{72} - \frac{y^6}{360}\right) - \frac{Q}{D^2}\left(-\frac{y^4}{12} + \frac{y^2}{6} - \frac{7}{180}\right) \\
& \left(Q\partial_{xx}c_K^0\frac{\tilde{K}(7\tilde{K}+2)}{(1+\tilde{K})^2} - \frac{\tilde{K}^2}{3(1+\tilde{K})}\partial_{xt}c_K^0\right) + \frac{Q\tilde{K}}{D^2}\partial_{xt}c_K^0\left(\frac{y^6}{60} - \frac{y^4}{18} + \frac{11y^2}{180} - \frac{11}{810}\right) \\
& + \frac{\tilde{K}}{2D^2}\partial_{tt}c_K^0\left(-\frac{y^4}{12} + \frac{y^2}{6} - \frac{7}{180}\right) + \left(\frac{\tilde{K}Q}{45D^2} + \frac{Q\tilde{K}}{45D^2}\frac{\tilde{K}(7\tilde{K}+2)}{(1+\tilde{K})^2}\right)\partial_{xt}c_K^0 - \left(\frac{\tilde{K}^2}{6D^2} - \frac{\tilde{K}^3}{6D^2(1+\tilde{K})}\right)\partial_{tt}c_K^0\left(\frac{1}{3} - y^2\right) \quad (107)
\end{aligned}$$

3.4 Irreversible very fast 1st order reaction

The goal of this subsection is to compare our approach with the central manifold technique from [4]. We study the 2D variant of the model from [4], pages 58-61, and we keep the molecular diffusion. Then the corresponding

analogue of the problem (6)-(10), with $K = +\infty$, is

$$\frac{\partial c^\varepsilon}{\partial t} + Q(1-y^2)\frac{\partial c^\varepsilon}{\partial x} = D\varepsilon^\alpha \frac{\partial^2 c^\varepsilon}{\partial x^2} + D\varepsilon^{\alpha-2} \frac{\partial^2 c^\varepsilon}{\partial y^2} \quad (108)$$

$$-D\varepsilon^{\alpha-2} \frac{\partial c^\varepsilon}{\partial y} \Big|_{y=1} = k\varepsilon^{\alpha-2} c^\varepsilon \Big|_{y=1} \quad \text{and} \quad \frac{\partial c^\varepsilon}{\partial y} \Big|_{y=0} = 0. \quad (109)$$

Due to a very fast reactions, we expect fast decay of the solution in time. We search for c^ε in the form

$$c^\varepsilon = e^{-\lambda_0 \varepsilon^{\alpha-2} t} (c^0(x, t; \varepsilon) \psi_0(y) + \varepsilon^{2-\alpha} c^1 + \varepsilon^{2(2-\alpha)} c^2 + \dots) + \mathcal{O}(e^{-\lambda_1 \varepsilon^{\alpha-2} t}). \quad (110)$$

After introducing (110) into the equation (108) we get

$$\begin{aligned} & \varepsilon^{\alpha-2} \left\{ -\lambda_0 c^0 \psi_0 - D \partial_{yy} \psi_0 c^0 \right\} + \varepsilon^0 \left\{ \psi_0(y) (\partial_t c^0 + Q(1-y^2) \partial_x c^0) - \right. \\ & D \partial_{yy} c^1 - \lambda_0 c^1 \left. \right\} + \varepsilon^{2-\alpha} \left\{ \partial_t c^1 + Q(1-y^2) \partial_x c^1 - D \varepsilon^{2(\alpha-1)} \partial_{xx} c^0 \psi_0(y) - \right. \\ & \left. D \varepsilon^\alpha \partial_{xx} c^1 - D \partial_{yy} c^2 - \lambda_0 c^2 \right\} = \mathcal{O}(\varepsilon^{2(2-\alpha)}) = \mathcal{O}\left(\left(\frac{T_T}{T_L}\right)^2\right). \end{aligned} \quad (111)$$

To satisfy (111) for every $\varepsilon \in (0, \varepsilon_0)$, all coefficients in front of the powers of ε should be zero.

The problem corresponding to the order $\varepsilon^{\alpha-2}$ is

$$\begin{cases} -D \partial_{yy} \psi_0 = \lambda_0 \psi_0 & \text{on } (0, 1), \\ \partial_y \psi_0 = 0 & \text{on } y = 0 \quad \text{and} \quad -D \partial_y \psi_0 = k \psi_0 & \text{on } y = 1, \end{cases} \quad (112)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. This spectral problem⁴ has an one dimensional proper space, spanned by $\psi_0(y) = \sqrt{2} \cos(\sqrt{\frac{\lambda_0}{D}} y)$, where the eigenvalue λ_0 is the first positive root of the equation $\sqrt{\frac{\lambda_0}{D}} \tan(\sqrt{\frac{\lambda_0}{D}}) = \frac{k}{D}$.

Next, the ε^0 problem reads

$$\begin{cases} -D \partial_{yy} c^1 - \lambda_0 c^1 = -\psi_0(y) (Q(1-y^2) \partial_x c^0 + \partial_t c^0) & \text{on } (0, 1), \\ \partial_y c^1 = 0 & \text{on } y = 0 \quad \text{and} \quad -D \partial_y c^1 = k c^1 & \text{on } y = 1, \end{cases} \quad (113)$$

By Fredholm's alternative, this problem has a solution if and only if

$$\partial_t c^0 + Q \left(\int_0^1 \psi_0^2(y) (1-y^2) dy \right) \partial_x c^0 = 0 \quad (114)$$

⁴References for spectral problems for partial differential equations are e.g. [33] and [34]

in $(0, \infty) \times (0, T)$. As before, our initial and boundary data are incompatible and therefore the solution to this linear transport equation does not suit our needs. We proceed by using again the idea in [31] and suppose that expression (114) is of the next order in our asymptotic expansion:

$$\psi(y)(\partial_t c^0 + Q(\int_0^1 \psi_0^2(y)(1-y^2) dy)\partial_x c^0) = \mathcal{O}(\varepsilon^{2-\alpha}) \quad \text{in } (0, +\infty) \times (0, T), \quad (115)$$

and justify it *a posteriori*, after getting an equation for c^0 . Following [4] we set $\alpha_{00} = \int_0^1 \psi_0^2(y)(1-y^2) dy$.

Combining (113) and (114) and using hypothesis (115) leads us to consider

$$\begin{cases} -D\partial_{yy}c^1 - \lambda_0c^1 = -Q\psi_0(y)((1-y^2) - \alpha_{00})\partial_x c^0 & \text{on } (0, 1), \\ -D\partial_y c^1 = kc^1 & \text{on } y = 1, \quad \text{and } \partial_y c^1 = 0 & \text{on } y = 0, \end{cases} \quad (116)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. Consequently

$$c^1(x, y, t) = Q\partial_x c^0 q_0(y) + \psi_0(y)A(x, t), \quad (117)$$

where A is arbitrary and q_0 is the solution for (116) with $Q\partial_x c$ replaced by 1, such that $\int_0^1 \psi_0(y)q_0(y) dy = 0$.

The problem corresponding to the order $\varepsilon^{2-\alpha}$ is

$$\begin{cases} -D\partial_{yy}c^2 - \lambda_0c^2 = -\partial_t c^1 - Q(1-y^2)\partial_x c^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c^0\psi_0(y) \\ + \varepsilon^\alpha D\partial_{xx}c^1 - \varepsilon^{\alpha-2}\psi_0(y)(\partial_t c^0 + Q\alpha_{00}\partial_x c^0) & \text{on } (0, 1), \\ -D\partial_y c^2 = kc^2 & \text{on } y = 1 \quad \text{and } \partial_y c^2 = 0 & \text{on } y = 0, \end{cases} \quad (118)$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. This problem has a solution if and only if

$$\partial_t c^0 + Q\alpha_{00}\partial_x c^0 - (\varepsilon^\alpha D - Q^2(\int_0^1 \psi_0(y)q_0(y)(1-y^2) dy))\partial_{xx}c^0 = 0 \quad (119)$$

in $(0, +\infty) \times (0, T)$. We note that the arbitrary function A enters into (119) as $\partial_t A + Q\alpha_{00}\partial_x A$ and this term is of higher order for reasonable choice of A . We take $A = 0$.

Next, we note that, through Hilbert-Schmidt expansion⁵, q_0 is given by

$$q_0(y) = -\sum_{k=1}^{+\infty} \frac{\alpha_{0k}\psi_k(y)}{\lambda_k - \lambda_0}, \quad (120)$$

⁵For an elementary presentation of the Hilbert-Schmidt expansion see [33]

where $\{\lambda_k, \psi_k\}_{k \geq 0}$ is the orthonormal basis defined by the spectral problem (112). Now we see that

$$\int_0^1 \psi_0(y) q_0(y) (1 - y^2) dy = - \sum_{k=1}^{+\infty} \frac{\alpha_{0k}^2}{\lambda_k - \lambda_0}$$

and Taylor's contribution to the effective diffusion coefficient is strictly positive. We note that this result confirms the calculations from [4], pages 58-61. Since

$$\lambda_0 = \frac{T_L}{T_{react}} k \psi_0(1),$$

in the limit when $T_{react} \gg T_T$ we obtain the effective equation (18). In fact our calculations indicate the relationship between the central manifold approach and approach using Bloch's waves (see the recent paper [1], by G. Allaire and A.-L. Raphael).

4 Numerical Tests

For carrying out the numerical tests we have chosen the data from the original paper by Taylor [32]. Analogous data are taken in the presence of chemistry.

The representative case considered in [32] is his case **(B)**, where the longitudinal transport time L/u_0 is much bigger than the transversal diffusive time a^2/D . The problem of a diffusive transport of a solute was studied experimentally and analytically. Two basically different cases were subjected to experimental verification in Taylor's paper:

Case (B1) Solute of mass M concentrated at a point $x = 0$ at time $t = 0$.

The effective concentration is given by

$$C_m(x, t) = \frac{M}{2a^2 \sqrt{\pi^3 kt}} \exp\{-(x - u_0 t/2)^2 / (4kt)\} \quad (121)$$

Case (B2) Dissolved material of uniform concentration C_0 enters the pipe at $x = 0$, starting at time $t = 0$. Initially, the concentration of the solvent was zero.

Clearly, it is Taylor's case **(B2)** which is well suited for the numerical simulations and it dictates the choice of the initial/boundary value conditions:

$$c^*|_{x^*=0} = c_R \quad \text{and} \quad c^*|_{t^*=0} = 0. \quad (122)$$

In the presence of the boundary concentration \hat{c} we choose the following initial condition

$$\hat{c}|_{t^*=0} = 0. \quad (123)$$

Originally this problem is formulated in a semi-infinite channel. In our numerical computations we have considered a finite one of length $2L_R$. At the outflow we have imposed a homogeneous Neumann boundary condition

$$\partial_{x^*} c^*|_{x^*=2L_R} = 0. \quad (124)$$

In a similar fashion, taking a homogeneous Neumann condition in the z^* direction along the x^* axis $z^* = 0$, the anti-symmetry of the concentrations allows considering only the upper half of the channel.

In each of the cases we will solve the **full physical problem** numerically. Its section average will be compared with the solution the proposed effective one dimensional model with Taylor's dispersion. Finally, if one makes the unjustified hypothesis that the average of a product is equal to the product of averages, averaging over sections gives an one dimensional model which we call the "simple mean". We will make a comparison with the solution of that problem as well.

Numerical solution of the full physical problem is costly, due to dominant Peclet and Damkohler numbers. We solve it using two independent methods.

<i>PARAMETERS</i>	<i>VALUES</i>
Width of the slit : H	$2.635 \cdot 10^{-4}$ m,
Characteristic length : L_R	0.319 m
$\varepsilon = H/L_R$	$0.826 \cdot 10^{-3}$
characteristic velocity: Q^*	$4.2647 \cdot 10^{-5}$ m/sec
diffusion coefficient: D^*	$1.436 \cdot 10^{-10}$ m ² /sec,
longitudinal Peclet number: $\mathbf{Pe} = \frac{L_R Q^*}{D^*} =$	$0.94738 \cdot 10^5$
$\alpha = \log \mathbf{Pe} / \log(1/\varepsilon) =$	1.614172
transversal Peclet number: $\mathbf{Pe}_T = \frac{H Q^*}{D^*} =$	$0.7825358 \cdot 10^2$

Table 1: Case A. Parameter values for the longest time example ($t^* = 11220$ sec) from Taylor's paper.

In the first approach we use the package **FreeFem++** by Pironneau, Hecht and Le Hyaric. For more information we refer to [26]. For the problem (6)-(10) the method of characteristics from [27] is used. We present a very short description of the method:

- Discretization in time :

The first order operator is discretized using the method of characteristics. More precisely, the equation (6) is written as:

$$\frac{\partial c}{\partial t} + (\vec{q} \cdot \nabla)c = D\varepsilon^\alpha \partial_{xx}c + D\varepsilon^{\alpha-2} \partial_{yy}c = f(x, y, t) \quad (125)$$

Let c^m be an approximation for the solution c at a time $m\delta t$. Then the one step backward convection scheme by the method of characteristics reads as follows:

$$\frac{1}{\delta t}(c^{m+1}(x, y) - c^m(x - q(y)\delta t, y)) = f^m(x, y)$$

- Space discretization:

One of the characteristics of our problem is the presence of a smeared front. In order to track it correctly, the Lagrange P1 finite elements, with adaptive mesh, are used. The mesh is adapted in the neighborhood of front after every 10 time steps.

Second method consists of a straightforward discretization method: first order (Euler) explicit in time and finite differences in space. Both the time step and the grid size are kept constant and satisfying the *CFL* condition to ensure the stability of the calculations. To deal with the transport part we have considered the minmod slope limiting method based on the first order upwind flux and the higher order Richtmyer scheme (see, for example [28], Chapter 14). We call this method (**SlopeLimit**).

A similar procedure is considered for the upscaled, one dimensional problems, obtained either by our approach or by taking the simple mean. It is refined in the situations when we have explicit formulas for the solution, using the direct numerical evaluation of the error function erf.

4.1 Examples from Taylor's article (no chemistry)

First let us note that in Taylor's article [32] the problem is axially symmetric with zero flux at the lateral boundary. The solute is transported by Poiseuille's velocity.

For simplicity we will consider the flow through the two-dimensional slit $\Omega^* = (0, +\infty) \times (0, H)$. In order to have a two dimensional problem equivalent to the case (B) from Taylor's article, we reformulate the characteristic velocity and the radius. Obviously we have

$$Q^* = \frac{3}{4}u_0, \quad H = a\sqrt{\frac{35}{32}}. \quad (126)$$

Then we start with

4.1.1 CASE A: 1st example from Taylor's paper with the time of flow: $t^* = 11220$ sec

x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$ (SlopeLimit)	$\frac{1}{H} \int_0^H c^* dz$ (FreeFem++)
0	1	1	1	1
0.3	0.930	0.968	0.97	0.945
0.308	0.805	0.863	0.888	0.885
0.313	0.685	0.725	0.775	0.844
0.314	0.659	0.695	0.75	0.821
0.317	0.571	0.588	0.665	0.69
0.324	0.359	0.329	0.439	0.58
0.3255	0.317	0.279	0.39	0.5625
0.33	0.206	0.155	0.256	0.427
0.3365	0.094	0.05	0.115	0.2957
0.337	0.088	0.048	0.107	0.2677
0.3385	0.070	0.035	0.085	0.2398
0.34	0.057	0.025	0.067	0.1839
0.344	0.029	0.009	0.033	0.0993
0.3475	0.016	0.003	0.016	0.04544

Table 2: Comparison between the concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the Case A at the time $t^* = 11220$ sec.

Here we are in absence of the chemistry i.e. $k_R = 0$. We solve

1. The 2D problem (1), (2), (122). It is solved using the FreeFM++ package and with (SlopeLimit). On the images the solution is denoted (pbreel).
2. The effective problem

$$\partial_{t^*} c^{Tay} + \frac{2Q^*}{3} \partial_{x^*} c^{Tay} = D^* \left(1 + \frac{8}{945} \mathbf{P} \mathbf{e}_T^2\right) \partial_{x^* x^*} c^{Tay} \quad \text{for } x, t > 0, \quad (127)$$

$$c^{Tay}|_{x=0} = 1 \quad \text{and} \quad c^{Tay}|_{t=0} = 0. \quad (128)$$

On the images its solution is denoted by (taylor).

3. The problem obtained by taking the simple mean over the vertical section:

$$\partial_{t^*} c^{moy} + \frac{2Q^*}{3} \partial_{x^*} c^{moy} - D^* \partial_{x^* x^*} c^{moy} = 0 \quad \text{in } (0, +\infty) \times (0, T) \quad (129)$$

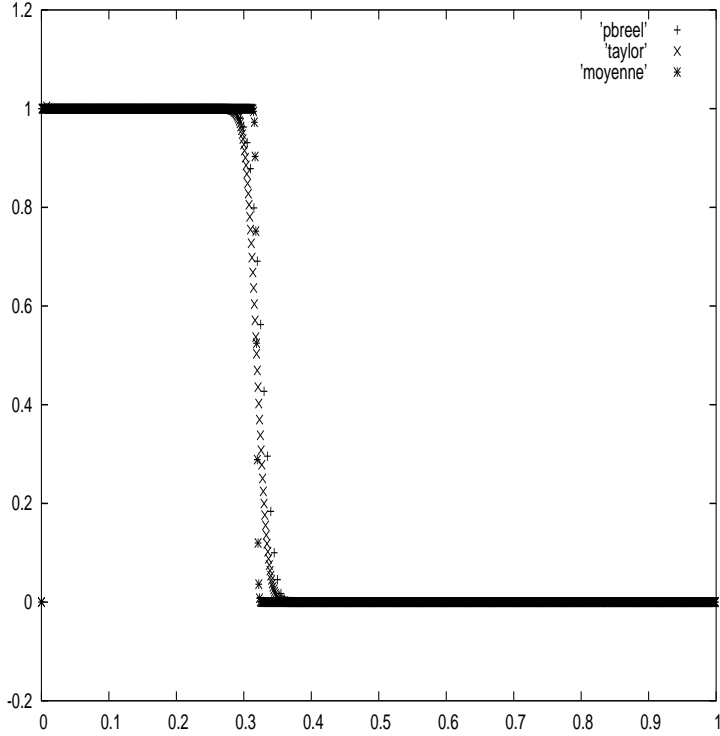


Figure 1: Comparison between concentration from Taylor's paper (taylor), from the original problem (pbreel) and the simple average (moyenne) at $t = 11220$ sec.

with initial/boundary conditions (128). On the images its solution is denoted by (moyenne).

We note that Table 2 is analogous to Table 2, page 196 from Taylor's article [32].

Note that in the absence of the chemical reactions we can solve explicitly the problems (127)-(128), respectively (129) - (128). With $\bar{Q} = \frac{2Q^*}{3}$ and $\bar{D} = D^*(1 + \frac{8}{945} \mathbf{P} \mathbf{e}_T^2)$, the solution for (127)-(128) reads

$$c^{Tay}(x, t) = 1 - \frac{1}{\sqrt{\pi}} \left[\exp\left\{\frac{\bar{Q}x}{\bar{D}}\right\} \int_{(x+\bar{Q}t)/(2\sqrt{\bar{D}t})}^{\infty} e^{-\eta^2} d\eta + \int_{(x-\bar{Q}t)/(2\sqrt{\bar{D}t})}^{\infty} e^{-\eta^2} d\eta \right] \quad (130)$$

For the problem (129),(128), everything is analogous.

4.1.2 CASE B: 2nd example from Taylor’s paper with the time of flow: $t^* = 240$ sec

<i>PARAMETERS</i>	<i>VALUES</i>
Width of the slit : H	$2.635 \cdot 10^{-4}$ m,
Characteristic length : L_R	0.632 m
$\varepsilon = H/L_R$	$0.41693 \cdot 10^{-3}$
characteristic velocity: Q^*	$0.393 \cdot 10^{-2}$ m/sec
diffusion coefficient: D^*	$0.6 \cdot 10^{-9}$ m ² /sec,
longitudinal Peclet number: $\mathbf{Pe} = \frac{L_R Q^*}{D^*} =$	$4.1396 \cdot 10^6$
$\alpha = \log \mathbf{Pe} / \log(1/\varepsilon) =$	1.95769
transversal Peclet number: $\mathbf{Pe}_T = \frac{H Q^*}{D^*} =$	$1.72592 \cdot 10^3$

Table 3: Case B. Parameter values for the characteristic time 240 seconds for the 2nd example from Taylor’s paper

We solve the same equations as in §4.1.1. Since α is very close to the threshold value $\alpha^* = 2$, the difference between the solution to the effective equation obtained by taking the simple mean, at one side, and the solutions to the original problem and to our upscaled equation, are spectacular. Our model approximates fairly well the physical solution even without adding the correctors.

Since no chemistry is considered here, an explicit solution can be given in this case as well and it is given by (130). The results are presented in Table 4 and Figure 2. Figures 1 and 2 show clearly the advantage of the upscaled model over the model obtained by taking the simple mean over the vertical section. Presence of the important enhanced diffusion is very important for numerical schemes. Note that in the case considered in §4.1.2, the transversal Peclet number is 10 times larger then in the case §4.1.1, explaining the difference in the quality of the approximation.

4.2 Examples with the linear surface adsorption-desorption reactions

In the case of the full two-dimensional problem with linear surface adsorption-desorption reactions(1), (2), (122), (123), we present two tests.

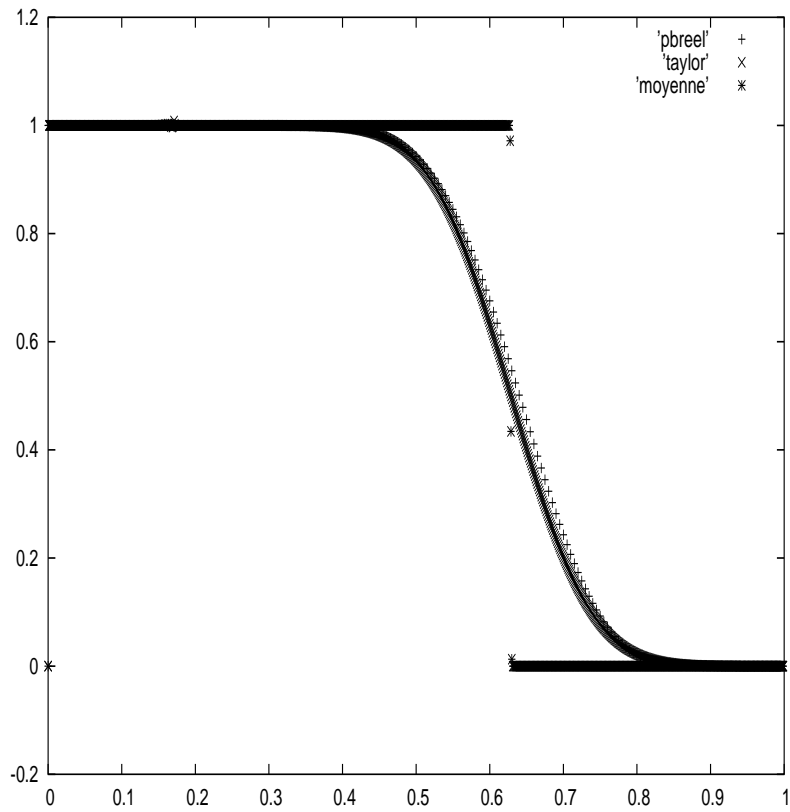


Figure 2: Case B: 2nd case from Taylor's paper. Comparison between the solution for the original problem (pbreel), the solution to the upscaled problem (taylor) and the solution for the problem obtained by taking a simple section average (moyenne) at $t^* = 240$ sec.

x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$ (SlopeLimit)	$\frac{1}{H} \int_0^H c^* dz$ (FreeFem++)
0	1	1	1	1
0.45	0.986	1	0.99	0.98438
0.537	0.876	1	0.89	0.942785
0.58	0.741	0.993	0.758	0.751335
0.605	0.636	0.882	0.65	0.675492
0.638	0.484	0.327	0.49	0.501282
0.667	0.351	0.033	0.348	0.456008
0.68	0.296	0.007	0.288	0.323355
0.711	0.182	0.	0.166	0.20671
0.74	0.106	0.	0.086	0.116112
0.75	0.086	0.	0.065	0.0926387
0.76	0.069	0.	0.049	0.0723552
0.77	0.055	0.	0.035	0.0549984
0.795	0.029	0.	0.014	0.0407674
0.804	0.023	0.	0.009	0.0201409

Table 4: Comparison between the concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the Case B, corresponding to the 2nd example from Taylor's paper, at the time $t^* = 240$ sec.

4.2.1 Linear surface adsorption-desorption reactions. Case A2 with the times of flow: $t^* = 100, t^* = 211$ and $t^* = 350$ sec

This first case is with slightly modified data of the Case A from §4.1.1. We just modify the width of the channel, the diffusivity and choose a shorter time of the flow.

We note that our scaling impose $\hat{k}^* = \varepsilon Q^*$ and $K_e = H$. This gives $\mathbf{Da}_T = \varepsilon \mathbf{Pe}_T$. Now the system to solve is (14)-(15):

$$\begin{aligned} \partial_{t^*} \left(c^* + \frac{\hat{c}}{H} \right) + \left(\frac{2Q^*}{3} + \frac{2Q^* \mathbf{Da}_T}{45} \right) \partial_{x^*} c^* - D^* \left(1 + \frac{8}{945} \mathbf{Pe}_T^2 \right) \partial_{x^* x^*} c^* = \\ \frac{2Q^* \mathbf{Da}_T}{45 K_e} \partial_{x^*} \hat{c} \\ \left(1 + \frac{1}{3} \mathbf{Da}_T \right) \partial_{t^*} \hat{c} = \hat{k}^* \left(c^* + \frac{2H \mathbf{Pe}_T}{45} \partial_{x^*} c^* - \frac{\hat{c}}{K_e} \right) \end{aligned}$$

and no explicit solution is known. We should compare between the solutions to (1)-(2) with the initial/boundary conditions (128), $\hat{c}|_{t=0} = 0$ (giving us all together (pbreel3)) and (14)-(15) (giving us (eff)) and (16)-(17) (giving us (moy)), with the same initial/boundary conditions.

The results are shown on the Tables 6, 7 and 8 and on the Figures 3, 4 and 5.

<i>PARAMETERS</i>	<i>VALUES</i>
Width of the slit : H	$0.5 \cdot 10^{-2}$ m,
Characteristic length : L_R	0.632 m
$\varepsilon = H/L_R$	$0.7911 \cdot 10^{-2}$
characteristic velocity: Q^*	$0.3 \cdot 10^{-2}$ m/sec
diffusion coefficient: D^*	$0.2 \cdot 10^{-6}$ m ² /sec,
longitudinal Peclet number: $\mathbf{Pe} = \frac{L_R Q^*}{D^*} =$	$9.48 \cdot 10^3$
$\alpha = \log \mathbf{Pe} / \log(1/\varepsilon) =$	1.670972
transversal Peclet number: $\mathbf{Pe}_T = \frac{H Q^*}{D^*} =$	75
characteristic reaction velocity: $\hat{k}^* = \varepsilon Q^* =$	$0.237 \cdot 10^{-4}$ m/sec
transversal Damkohler number: $\mathbf{Da}_T = \varepsilon \frac{H Q^*}{D^*} =$	0.5933

Table 5: Full linear surface adsorption-desorption problem: parameter values at the case A2: diffusive transport with surface reaction

Note that the solution to the problem obtained by taking the simple section average develops a physically incorrect contact discontinuity. Also our upscaled problem gives a good approximation for the original two-dimensional problem, which is not the case with the simple mean.

Adding correctors would get us even closer to the solution for the two-dimensional problem.

Figures 3, 4 and 5 show the simulation by FreeFm++ in the case §4.2.1. Advantage of our approach is again fairly clear and the errors of the model obtained by taking a simple mean persist in time.

4.2.2 Linear surface adsorption-desorption reactions. Case B2 with the times of flow: $t^* = 240$ sec

In this case we consider the data of Case B, §4.1.2, as are given in Table 3. The results are shown in Figure 6.

4.3 An example with the 1st order irreversible surface reaction

In this situation we take $K = \frac{K_e}{H} \rightarrow +\infty$. The equation (1) does not change but the boundary condition (2) becomes

$$-D^* \partial_z c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{k}^* c^* \quad \text{on } z = \pm H, \quad (131)$$

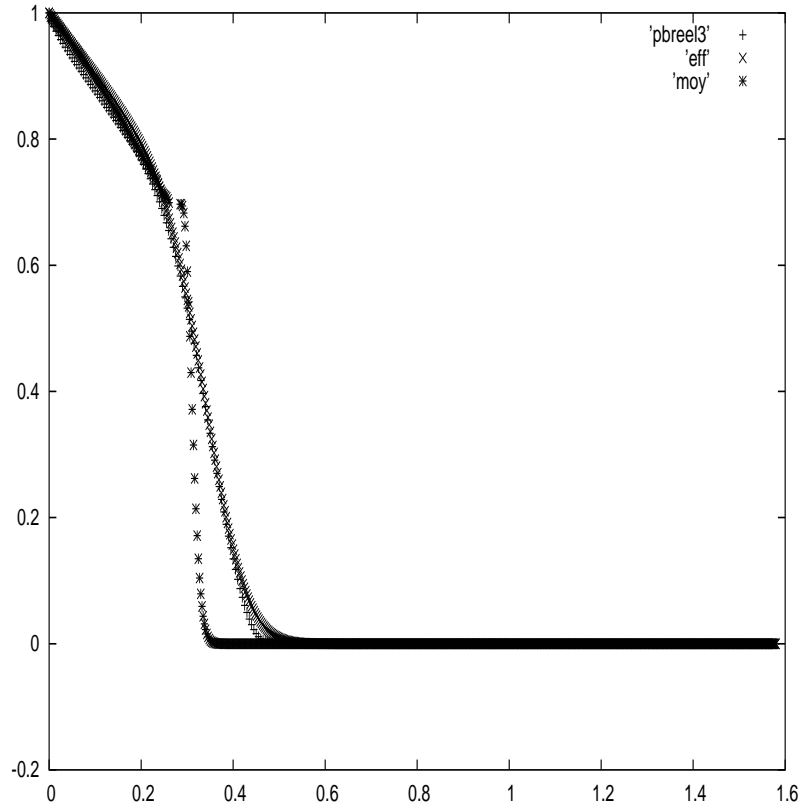


Figure 3: Comparison between the volume concentrations c^{Tay} , $\frac{1}{H} \int_0^H c^* dz$ and c^{moy} for the linear surface adsorption-desorption reactions, Case A2, obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at time $t^* = 100$ sec.

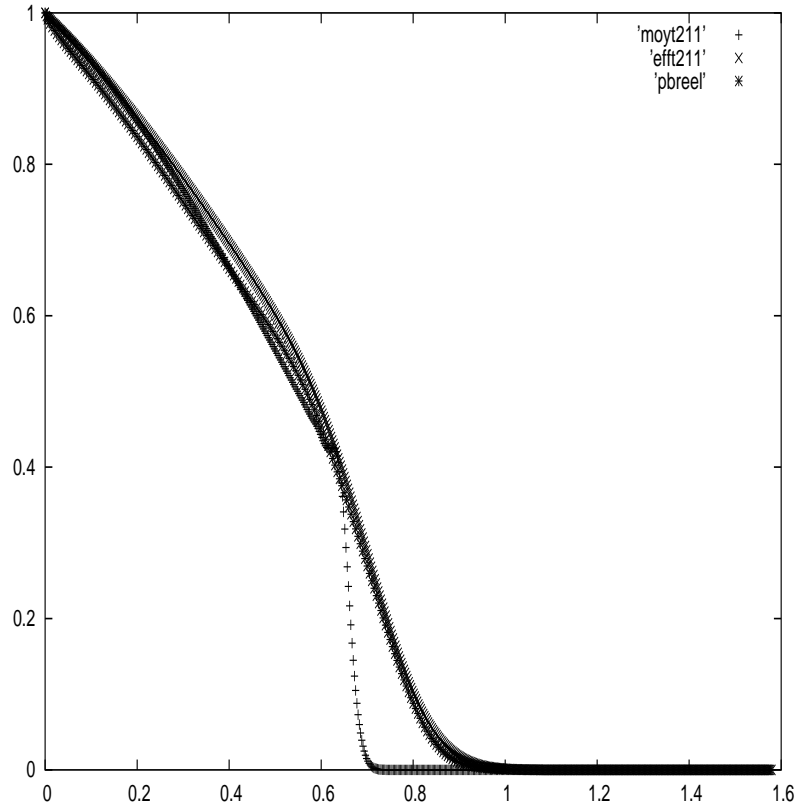


Figure 4: Comparison between the volume concentrations c^{Tay} , $\frac{1}{H} \int_0^H c^* dz$ and c^{moy} for the linear surface adsorption-desorption reactions, Case A2, obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at time $t^* = 211$ sec.

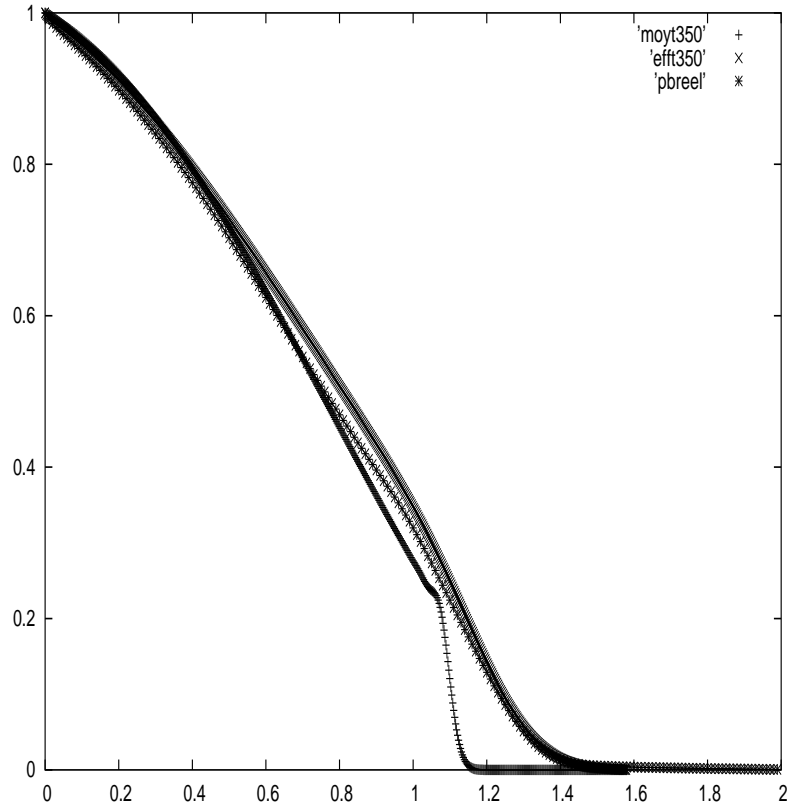


Figure 5: Comparison between the volume concentrations c^{Tay} , $\frac{1}{H} \int_0^H c^* dz$ and c^{moy} for the linear surface adsorption-desorption reactions, Case A2, obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbrel3) and the concentration coming from the simple average (moy) at time $t^* = 350$ sec.

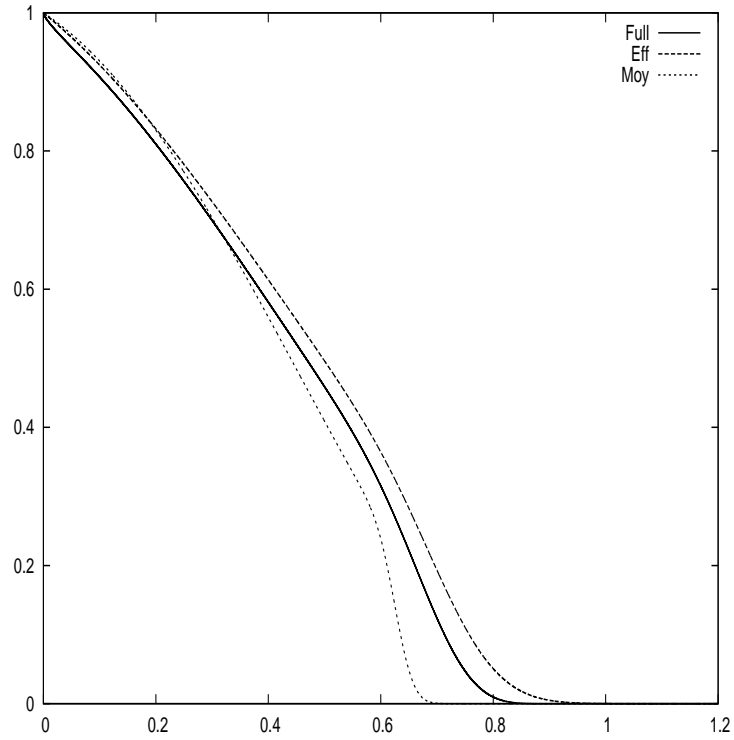


Figure 6: Volume concentrations (linear surface adsorption-desorption reactions, Case B2) : Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (Full) and the concentration coming from the simple average (moy) at $t = 240$ sec.

x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	1	1	1
0.01	0.98669465	0.990034274	0.97837
0.05	0.950946235	0.950663125	0.92873
0.1	0.903593771	0.896561247	0.876323
0.2	0.79700151	0.776023352	0.7669
0.225	0.759276074	0.745201145	0.728739
0.25	0.715756063	0.71148785	0.678978
0.275	0.65174438	0.696567508	0.613898
0.29	0.603878726	0.693955625	0.566586
0.3	0.567950276	0.590067563	0.532094
0.31	0.539037927	0.371543232	0.495586
0.32	0.498188037	0.213820021	0.457112
0.35	0.377225997	0.00495647031	0.333673
0.4	0.172223512	2.41496286E-07	0.134612
0.45	0.0591622065	3.07462138E-13	0.0160686

Table 6: Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the linear surface adsorption-desorption reactions, Case A2, at the time $t^* = 100$ sec.

The system (14)-(15) becomes

$$\left\{ \begin{array}{l} \partial_{t^*} c^* + \left(\frac{2Q^*}{3} + \frac{4Q^* \mathbf{Da}_T}{45} \right) \partial_{x^*} c^* + \\ \frac{\hat{k}^*}{H} \left(1 - \frac{\mathbf{Da}_T}{3} \right) c^* - D^* \left(1 + \frac{8}{945} \mathbf{Pe}_T^2 \right) \partial_{x^* x^*} c^* = 0 \\ \text{in } (0, +\infty) \times (0, T) \end{array} \right. \quad (132)$$

and the equation corresponding to a simple mean reads

$$\left\{ \begin{array}{l} \partial_{t^*} c^{moy} + \frac{2Q^*}{3} \partial_{x^*} c^{moy} + \frac{\hat{k}^*}{H} c^{moy} - D^* \partial_{x^* x^*} c^{moy} = 0 \\ \text{in } (0, +\infty) \times (0, T) \end{array} \right. \quad (133)$$

We impose $\hat{k}^* = Q^*/400$.

For this particular reactive flow, the problem (132) has an explicit solution for the following initial/boundary data:

$$c^*|_{x^*=0} = 0 \quad \text{and} \quad c^*|_{t^*=0} = 1. \quad (134)$$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	1	1	1
0.01	0.989694187	0.994090699	0.986112
0.05	0.967015027	0.971961203	0.952705
0.1	0.934075267	0.936547842	0.91569
0.2	0.861407801	0.857677963	0.836403
0.3	0.781074907	0.765463212	0.750173
0.4	0.694746658	0.662811744	0.662342
0.5	0.600404621	0.553304147	0.574491
0.55	0.544239838	0.497265165	0.521332
0.6	0.474489299	0.438951289	0.452928
0.65	0.386694802	0.318097632	0.366176
0.7	0.284796763	0.0115430139	0.269368
0.75	0.183421956	1.67295192E-05	0.172172
0.8	0.100489679	3.46962941E-09	0.088037
0.9	0.017165388	1.93051599E-19	0.00981583

Table 7: Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the linear surface adsorption-desorption reactions, Case A2, at the time $t^* = 211$ sec.

It reads

$$c^*(x^*, t^*) = e^{-k_1 t^*} \left(1 - \frac{1}{\sqrt{\pi}} \left[e^{\frac{2Q_1 x^*}{3D_1}} \int_{\frac{x+2t^*Q_1/3}{2\sqrt{D_1 t^*}}}^{+\infty} e^{-\eta^2} d\eta + \int_{\frac{x-2t^*Q_1/3}{2\sqrt{D_1 t^*}}}^{+\infty} e^{-\eta^2} d\eta \right] \right) \quad (135)$$

where $k_1 = \frac{\hat{k}^*}{H} (1 - \frac{\mathbf{Da}_T}{3})$, $Q_1 = Q^* (1 + \frac{2\mathbf{Da}_T}{15})$ and $D_1 = D^* (1 + \frac{8}{945} \mathbf{Pe}_T^2)$.

For the problem (133) we also impose the initial/boundary condition (134) and c^{moy} is given by the formula (135) as well, but with $k_1 = \frac{\hat{k}^*}{H}$, $Q_1 = Q^*$ and $D_1 = D^*$.

The data are given in Table 9, whereas the results are shown in Tables 10, 11 and 12 and in Figures 7, 8 and 9, corresponding to the times $t^* = 50, 70$ and 100 sec.

We see that the solution to the problem obtained by taking a simple mean over the vertical section has incorrect amplitude.

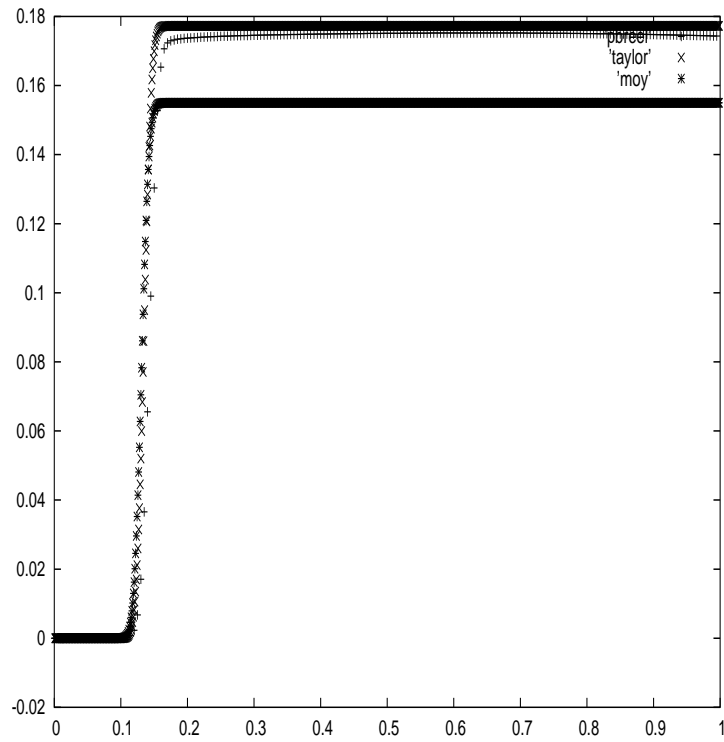


Figure 7: Case of the 1st order irreversible surface reaction ($K = +\infty$): Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbree13) and the concentration coming from the simple average (moy) at $t = 50$ sec.

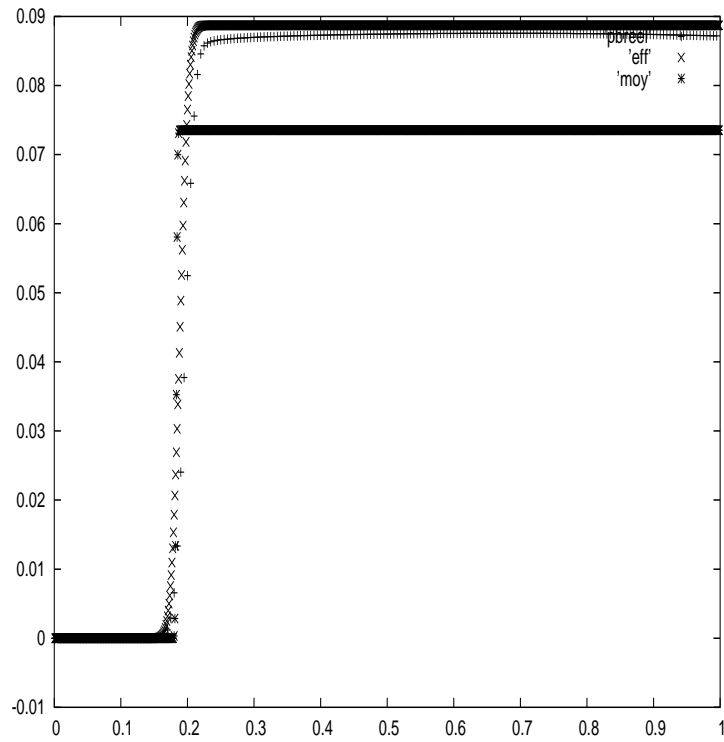


Figure 8: Case of the 1st order irreversible surface reaction ($K = +\infty$): Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel) and the concentration coming from the simple average (moy) at $t = 70$ sec.

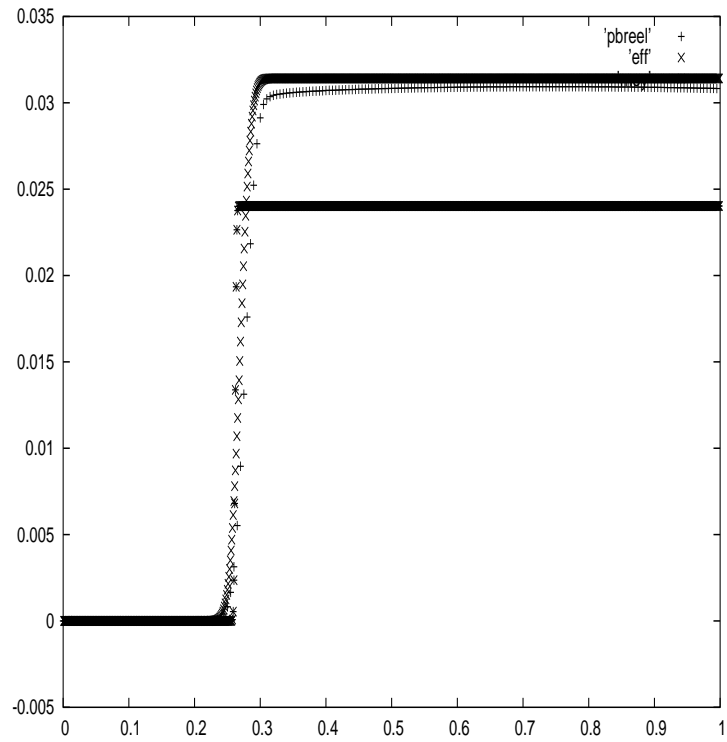


Figure 9: Case of the 1st order irreversible surface reaction ($K = +\infty$): Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel) and the concentration coming from the simple average (moy) at $t = 100$ sec.

x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	1	1	1
0.1	0.95909192	0.965613038	0.9484
0.2	0.911441678	0.919474858	0.897755
0.4	0.794454955	0.793564942	0.775743
0.6	0.657701569	0.631584001	0.624061
0.7	0.583632368	0.542316066	0.545435
0.8	0.508150772	0.453470264	0.469133
0.9	0.431290446	0.363040727	0.39611
1.	0.34825939	0.276213033	0.319716
1.05	0.298816871	0.237173717	0.273235
1.1	0.247412008	0.109554202	0.224233
1.15	0.19336287	0.00589796516	0.175742
1.2	0.140469463	3.17192071E-05	0.128868
1.3	0.058066265	5.57849169E-12	0.0512471
1.4	0.0152972824	4.65348193E-21	0.0131282

Table 8: Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the linear surface adsorption-desorption reactions, Case A2, at the time $t^* = 350$ sec.

4.4 Numerical experiments in the case of an infinite adsorption rate

In this subsection we solve the equation (42)

$$(1 + \mathbf{Da}_K) \frac{\partial c_K^{*,eff}}{\partial t^*} + \frac{2Q^*}{3} \frac{\partial c_K^{*,eff}}{\partial x^*} = D^* \left(1 + \frac{4}{135} \mathbf{Pe}_T^2 \left[\frac{2}{7} + \frac{\mathbf{Da}_K (2 + 7\mathbf{Da}_K)}{(1 + \mathbf{Da}_K)^2} \right] \right) \frac{\partial^2 c_K^{*,eff}}{\partial (x^*)^2}.$$

with the initial/boundary data

$$c_K^{*,eff}|_{x^*=0} = 0 \quad \text{and} \quad c_K^{*,eff}|_{t^*=0} = 1. \quad (136)$$

Parameters are shown on the Table 13.

Results are shown at Tables 14, 15 and 16 and on corresponding Figures 10, 11 and 12, at times $t^* = 863, 2877$ and 5755 sec.

Once more the model obtained by the simple averaging over vertical section gives an approximation which is not good and which gets worse during time evolution.

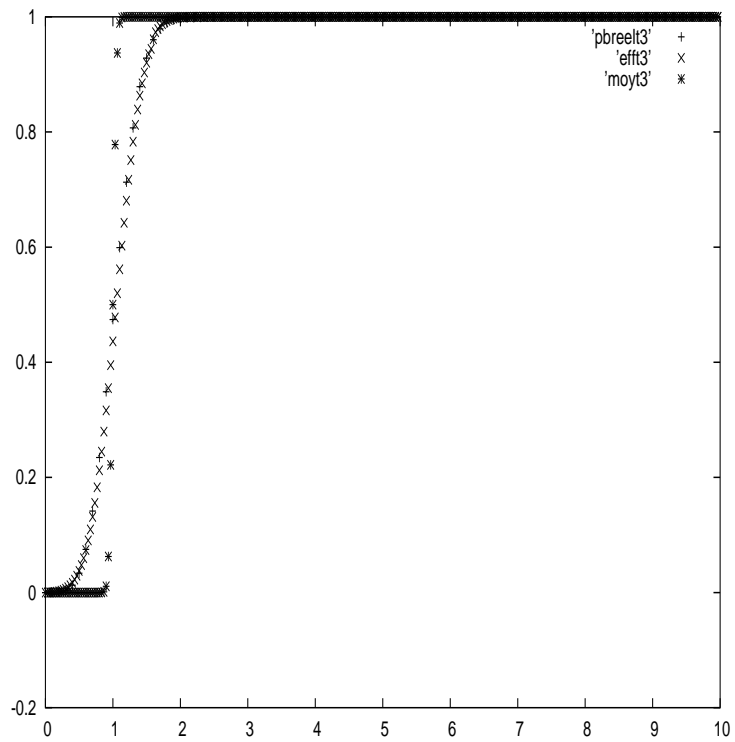


Figure 10: Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at $t = 863$ sec.

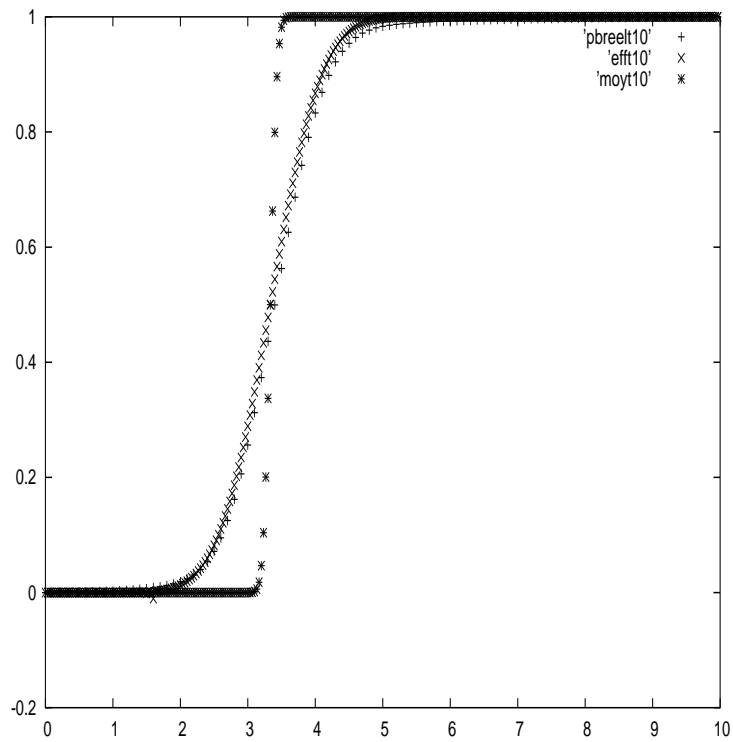


Figure 11: Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at $t = 2877$ sec.

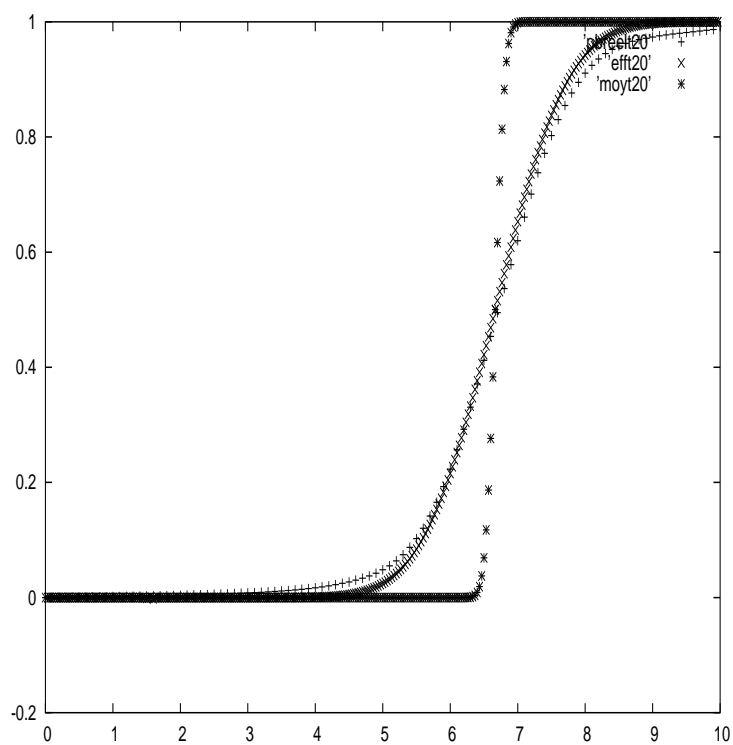


Figure 12: Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbree13) and the concentration coming from the simple average (moy) at $t = 5755$ sec.

PARAMETERS	VALUES
Width of the slit : H	$2.635 \cdot 10^{-4}$ m,
Characteristic length : L_R	0.632 m
$\varepsilon = H/L_R$	$0.41693 \cdot 10^{-3}$
characteristic velocity: Q^*	$0.393 \cdot 10^{-2}$ m/sec
diffusion coefficient: D^*	$1.2 \cdot 10^{-8}$ m ² /sec,
longitudinal Peclet number: $\mathbf{Pe} = \frac{L_R Q^*}{D^*} =$	$2.0698 \cdot 10^5$
$\alpha = \log \mathbf{Pe} / \log(1/\varepsilon) =$	1.572789
transversal Peclet number: $\mathbf{Pe}_T = \frac{H Q^*}{D^*} =$	86,296

Table 9: Parameter values in the case of the 1st order irreversible surface reaction ($K = +\infty$)

5 Conclusions and perspectives

In this article we have justified by direct numerical simulation the effective (or upscaled) equations obtained using the techniques of anisotropic singular perturbation for the partial differential equations describing reactive flows through a slit under dominant Peclet and Damkohler numbers.

In order to have a good comparaison with classical Taylor's paper we were forcing our models to be parabolic, when it was possible.

Nevertheless, the possibility of obtaining hyperbolic models, at same order of precision, is left open. We note that such models where derived by Balakotaiah and Chang in [5] for a number of practical situations. Furthermore, there is approach by Camacho using a viewpoint of Irreversible Thermodynamics and leading to the Telegraph equation. For more details we refer to [10], [11], [12] and to the doctoral thesis [7]. We plan to address this subject in the near future and extend our results in this direction.

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x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	0	0	0
0.1	1.37300401E-17	2.17207153E-17	5.17763e-05
0.11	0.000418590074	1.04498908E-16	0.00231391
0.13	0.0519752326	0.0280014326	0.0170583
0.14	0.128440421	0.155000571	0.0655227
0.145	0.153338539	0.155000571	0.0990472
0.15	0.169945407	0.155000571	0.130369
0.155	0.175667748	0.155000571	0.152722
0.16	0.176884544	0.155000571	0.165339
0.165	0.177199575	0.155000571	0.170635
0.17	0.177233822	0.155000571	0.172341
0.18	0.177238982	0.155000571	0.173227
0.19	0.177239004	0.155000571	0.173531
0.2	0.177239004	0.155000571	0.173718
0.3	0.177239004	0.155000571	0.174536

Table 10: *Case of the 1st order irreversible surface reaction ($K = +\infty$): Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ at the time $t^* = 50$ sec.*

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x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	0	0	0
0.1	4.86944849E-17	3.51572972E-18	4.27436e-06
0.16	0.000252862511	1.27275794E-17	0.000184936
0.18	0.0178727814	0.0003202901	0.00657295
0.185	0.0303102565	0.0699896992	0.0133435
0.19	0.0488626237	0.0735303344	0.0240309
0.195	0.0630697107	0.0735303475	0.0377344
0.2	0.0765167157	0.0735303475	0.0524721
0.205	0.0830143704	0.0735303475	0.0658466
0.21	0.0869467435	0.0735303475	0.0755906
0.215	0.0881363431	0.0735303475	0.081589
0.22	0.0885999673	0.0735303475	0.0845812
0.3	0.0887121329	0.0735303475	0.0869702
0.6	0.0887121329	0.0735303475	0.0875448

Table 11: *Case of the 1st order irreversible surface reaction ($K = +\infty$) : Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ at the time $t^* = 70$ sec.*

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x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	0	0	0
0.1	7.40437514E-18	1.14872338E-18	9.51673e-07
0.2	3.20048527E-10	4.15858702E-18	1.22748e-05
0.24	0.000270157055	4.15858702E-18	0.000189098
0.26	0.00693874586	0.00236291078	0.00313599
0.28	0.025151632	0.0240251771	0.0175925
0.285	0.0278139146	0.0240251771	0.021842
0.29	0.0298614239	0.0240251771	0.0252274
0.295	0.0307142265	0.0240251771	0.0276271
0.3	0.0311937104	0.0240251771	0.0291264
0.31	0.0313963959	0.0240251771	0.0302246
0.32	0.0314129272	0.0240251771	0.0304318
0.35	0.0314136645	0.0240251771	0.030591
0.36	0.0314136645	0.0240251771	0.0306213
0.5	0.0314136645	0.0240251771	0.0308346

Table 12: *Case of the 1st order irreversible surface reaction ($K = +\infty$): Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ at the time $t^* = 100$ sec.*

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<i>PARAMETERS</i>	<i>VALUES</i>
Width of the slit : H	$5 \cdot 10^{-3}$ m,
Characteristic length : L_R	0.8632 m
$\varepsilon = H/L_R$	$5.7924001 \cdot 10^{-3}$
characteristic velocity: Q^*	$0.3 \cdot 10^{-3}$ m/sec
diffusion coefficient: D^*	$2 \cdot 10^{-7}$ m ² /sec,
longitudinal Peclet number: $\mathbf{Pe} = \frac{L_R Q^*}{D^*} =$	$1.2948 \cdot 10^5$
$\alpha = \log \mathbf{Pe} / \log(1/\varepsilon) =$	1.83815052
transversal Peclet number: $\mathbf{Pe}_T = \frac{H Q^*}{D^*} =$	75
transversal Damkohler number: $\mathbf{Da}_T = \frac{K_\varepsilon}{H} =$	1

Table 13: Parameter values in the case of an infinite adsorption rate $\hat{k}^* = +\infty$

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x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	0	0	0
0.1	0.000476974507	1.48207153E-17	0.00019277
0.3	0.00665410189	2.36823908E-16	0.00402643
0.4	0.0169799929	4.65358482E-16	0.0127379
0.6	0.0739152145	1.9895652E-15	0.074789
0.8	0.212484001	2.14373031E-06	0.23459
1.0	0.436195692	0.5	0.474176
1.1	0.561624158	0.989232525	0.59902
1.3	0.783030278	1.	0.807166
1.5	0.920190592	1.	0.928339
1.7	0.983578518	1.	0.979062
1.9	0.996962548	1.	0.994446
2.	0.998850322	1	0.99675
3.	0.99999	1.	0.99969
4.	1.	1.	0.999917

Table 14: Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the case of an infinite adsorption rate ($\hat{k}^* = +\infty$) at the time $t^* = 863$ sec.

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x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	0	0	0
1.	2.15685873E-05	1.10453096E-16	0.00264385
2.	0.0129950594	5.15917604E-16	0.0186693
2.3	0.0422251119	6.74184016E-16	0.0401594
2.6	0.110382208	7.66476726E-16	0.095134
2.9	0.234665783	2.44409991E-08	0.205974
3.	0.288903773	1.35588449E-05	0.256387
3.2	0.411909396	0.0466182486	0.373383
3.4	0.544317915	0.799344896	0.499505
3.6	0.671938419	0.999606221	0.625723
3.8	0.782076721	0.999999998	0.742053
4.	0.867184442	1.	0.832967
4.3	0.94674831	1.	0.921783
5.	0.997306633	1.	0.983445
6.	0.99999576	1.	0.992814

Table 15: Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the case of an infinite adsorption rate ($\hat{k}^* = +\infty$) at the time $t^* = 2877$ sec.

x^*	c^{Tay}	c^{moy}	$\frac{1}{H} \int_0^H c^* dz$
0	0	0	0
5.	0.0245430842	7.99463577E-16	0.0481293
5.5	0.0841804114	2.05329898E-15	0.102444
6.	0.21560078	1.47268882E-09	0.223168
6.3	0.332534457	0.000549169915	0.330783
6.6	0.468630165	0.276435631	0.453472
6.8	0.562546008	0.882371619	0.536562
7.	0.653050221	0.998497928	0.619671
7.2	0.735557754	0.999998971	0.700753
7.4	0.806714035	1.	0.771646
7.6	0.864767429	1.	0.830057
7.8	0.909573473	1.	0.876335
8.	0.942287957	1.	0.910953
8.5	0.984791852	1.	0.957911
9.	0.997065201	1.	0.973686

Table 16: Comparison between the volume concentrations c^{Tay} , c^{moy} and $\frac{1}{H} \int_0^H c^* dz$ for the case of an infinite adsorption rate ($\hat{k}^* = +\infty$) at the time $t^* = 5755$ sec.