CHAPTER 1

Effective Dispersion Equations for Reactive Flows with Dominant Péclet and Damkohler Numbers

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Abstract

In this chapter 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 Péclet and Damkohler numbers with respect to 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 center manifold approach. Furthermore, we present a numerical justification of the model by a direct simulation.

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 timescales 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 Péclet 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 Péclet 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. Conca et al., 2004, 2003; van Duijn and Knabner, 1997; van Duijn and Pop, 2004; van Duijn et al., 1998; Hornung and Jäger, 1991; Knabner et al., 1995; Mikelić and Primicerio, 2006 and references therein).

If the flow rate is increased so that Péclet number $Pe \gg 1$, then there is a timescale at which transversal molecular diffusion smears the contact discontinuity into a plug. In Taylor (1993), Taylor found an effective long-time axial diffusivity, proportional to the square of the transversal Péclet number and occurring in addition to the molecular diffusivity. After this pioneering work of Taylor, a vast literature on the subject developed, with over 2000 citations to date. The most notable references are the article (Aris, 1956) by Aris, where Taylor's intuitive approach was explained through moments expansion and the lecture notes (Caflisch and Rubinstein, 1984), where a probabilistic justification of Taylor's dispersion is given. In addition to these results, addressing the tube flow with a dominant Péclet 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 (Bear and Verruijt, 1987) for more details about the modeling. For the derivation of Taylor's dispersion in porous media using formal two-scale expansions, we refer to Auriault and Adler (1995) 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 chapter 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 Péclet 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 (Rubin, 1983) by Rubin. The mathematical study of the models from Rubin (1983) was undertaken in Friedman and Knabner (1992).

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 toward 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 Paine et al. (1983), 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 Péclet numbers, and the Taylor dispersion arising for dominant Péclet number, but smaller than some threshold value.
- The center manifold approach of Mercer and Roberts (see the article Mercer and Roberts, 1990 and the subsequent article by Rosencrans, 1997) 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 by Balakotaiah and Chang (1995). A number of effective models for different Damkohler numbers were obtained. Some generalizations to reactive flows through porous media are in Mauri (1991) and the preliminary results on their mathematical justification are in Allaire and Raphael (2007).
- Another approach consisting of the Liapounov–Schmidt reduction coupled with a perturbation argument is developed in the articles Balakotaiah and Chang (2003), Balakotaiah (2004) and Chakraborty and Balakotaiah (2005). It allows developing multi-mode hyperbolic upscaled models.

- Recent approach using the anisotropic singular perturbation is the article by Mikelić et al. (2006). 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 (1986) 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 two-dimensional (2D) channel. Solute particles are participants in a chemical reaction with the boundary of the channel. They do not interact between them. The simplest example is described by the following model for the solute concentration c^*:

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

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

$$-D^*\partial_z c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{k}^*(c^* - \hat{c}/K_{\mathrm{e}}) \qquad \text{on } z = \pm H \tag{2}$$

where $\hat{k}^*$ represents the rate constant for adsorption and K_{e} the linear adsorption equilibrium constant.

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

$$c_{\mathrm{F}} = \frac{c^*}{c_{\mathrm{R}}}, \quad x = \frac{x^*}{L_{\mathrm{R}}}, \quad y = \frac{z}{H}, \quad t = \frac{t^*}{T_{\mathrm{R}}}, \quad Q = \frac{Q^*}{Q_{\mathrm{R}}}, \quad D = \frac{D^*}{D_{\mathrm{R}}},$$

$$k = \frac{\hat{k}^*}{k_{\mathrm{R}}}, \quad c_{\mathrm{s}} = \frac{\hat{c}}{\hat{c}_{\mathrm{R}}}, \quad K = \frac{K_{\mathrm{e}}}{K_{\mathrm{eR}}}$$

we obtain the dimensionless equations

$$\frac{\partial c_{\mathrm{F}}}{\partial t} + \frac{Q_{\mathrm{R}}T_{\mathrm{R}}}{L_{\mathrm{R}}}Q(1-y^2)\frac{\partial c_{\mathrm{F}}}{\partial x} - \frac{D_{\mathrm{R}}T_{\mathrm{R}}}{L_{\mathrm{R}}^2}D\frac{\partial^2 c_{\mathrm{F}}}{\partial x^2} - \frac{D_{\mathrm{R}}T_{\mathrm{R}}}{H^2}D\frac{\partial^2 c_{\mathrm{F}}}{\partial y^2} = 0 \qquad \text{in } \Omega \tag{3}$$

and

$$-\frac{DD_{\mathrm{R}}}{H}c_{\mathrm{R}}\frac{\partial c_{\mathrm{F}}}{\partial y} = \frac{\hat{c}_{\mathrm{R}}}{T_{\mathrm{R}}}\frac{\partial c_{\mathrm{s}}}{\partial t} = k_{\mathrm{R}}k(c_{\mathrm{R}}c_{\mathrm{F}} - \frac{\hat{c}_{\mathrm{R}}c_{\mathrm{s}}}{KK_{\mathrm{eR}}}) \qquad \text{at } y = 1 \tag{4}$$

where

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

This problem involves the following timescales:

T_{L} = characteristic longitudinal timescale = $L_{\mathrm{R}}/Q_{\mathrm{R}}$
T_{T} = characteristic transversal timescale = H^2/D_{R}
$T_{\mathrm{DE}} = K_{\mathrm{eR}}/k_{\mathrm{R}}$ (characteristic desorption time)
$T_{\mathrm{A}} = \hat{c}_{\mathrm{R}}/(c_{\mathrm{R}}k_{\mathrm{R}})$ (characteristic adsorption time)
T_{react} = superficial chemical reaction timescale $= H/k_{\mathrm{R}}$

and the following characteristic non-dimensional numbers

$$Pe = \frac{L_{\mathrm{R}}Q_{\mathrm{R}}}{D_{\mathrm{R}}}(\text{Péclet number});\qquad Da = \frac{L_{\mathrm{R}}}{T_{\mathrm{A}}Q_{\mathrm{R}}}(\text{Damkohler number})$$

Further we set $\varepsilon = H/L_{\mathrm{R}} \ll 1$ and choose $T_{\mathrm{R}} = T_{\mathrm{L}}$.

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 1*D* parabolic equation for the effective concentration.

We consider the case when $K_{\mathrm{eR}} = H$, $T_{\mathrm{A}} \approx T_{\mathrm{L}} \approx T_{\mathrm{DE}}$. We choose $Q = Q^*/Q_{\mathrm{R}} = \mathcal{O}(1)$, and

$$\frac{T_{\mathrm{T}}}{T_{\mathrm{L}}} = \frac{HQ_{\mathrm{R}}}{D_{\mathrm{R}}}\varepsilon = \mathcal{O}(\varepsilon^{2-\alpha}) = \varepsilon^2 Pe$$

Then the situation from Taylor's article corresponds to the case when $0 \leqslant \alpha < 2$, i.e. the transversal Péclet number is equal to $(1/\varepsilon)^{\alpha-1}$ 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 $c^\varepsilon = c_{\mathrm{F}}$, our equations in their non-dimensional form are

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

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

$$-D\varepsilon^{\alpha-2}\frac{\partial c^\varepsilon}{dy} = \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^\varepsilon}{\partial t} = \frac{T_{\mathrm{L}}}{T_{\mathrm{DE}}}k\left(c^\varepsilon - \frac{(T_{\mathrm{A}}/T_{\mathrm{DE}})c_s}{K}\right)\Bigg|_{y=1} \quad on\ \Gamma^+\times(0,T) \tag{8}$$

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

$$c_{\mathrm{s}}^\varepsilon(0,t) = 0 \text{ and } c^\varepsilon(0,y,t) = 0, \qquad (y,t)\in(0,1)\times(0,T) \tag{10}$$

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

In the paragraph from Section 3.1, we will give a detailed derivation of the effective equations. Our technique is motivated by the paper by Rubinstein and Mauri, 1986, where the analysis is based on the hierarchy of timescales and a corresponding two-scale expansion. For $\hat{k}^* = 0$, our approach gives the effective problem from Taylor's (1993) paper :

$$\begin{cases} \partial_t c^{\mathrm{Tay}} + \dfrac{2Q}{3}\partial_x c^{\mathrm{Tay}} = \left(\dfrac{D}{Pe} + \dfrac{8}{945}\dfrac{Q^2}{D}\dfrac{T_{\mathrm{T}}}{T_{\mathrm{L}}}\right)\partial_{xx} c^{\mathrm{Tay}}, \\ \text{in } \mathbb{R}_+ \times (0,T), \qquad c^{\mathrm{Tay}}|_{x=0} = 1, \\ c^{\mathrm{Tay}}|_{t=0} = 0, \qquad \partial_x c^{\mathrm{Tay}} \in L^2(\mathbb{R}_+ \times (0,T)) \end{cases} \tag{11}$$

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

$$\partial_t\left(c + \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}c_{\mathrm{s}}\right) + \left(\frac{2Q}{3} + \frac{2Qk}{45D}\frac{T_{\mathrm{T}}}{T_{\mathrm{DE}}}\right)\partial_x c - \left(D\varepsilon^{\alpha} + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2-\alpha}\right)\partial_{xx} c = \frac{2Qk}{45DK}\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{T_{\mathrm{T}}}{T_{\mathrm{DE}}}\partial_x c_{\mathrm{s}} \tag{12}$$

$$\left(1 + \frac{k}{3D}\frac{T_{\mathrm{T}}}{T_{\mathrm{DE}}}\right)\partial_t c_{\mathrm{s}} = k\frac{T_{\mathrm{L}}}{T_{\mathrm{A}}}\left(c + \frac{2Q}{45D}\varepsilon^{2-\alpha}\partial_x c - \frac{(T_{\mathrm{A}}/T_{\mathrm{DE}})c_s}{K}\right) \tag{13}$$

The system (12)–(13) could be compared with the corresponding non-dimensional effective equations obtained by Paine et al. (1983). After substituting the Equation (13) at the place of $\partial_t c_{\mathrm{s}}$ in Equation (12), we see that our effective Equations (12) and (13) coincide with the effective non-dimensional system (39)–(40), Paine et al. (1983, p. 1784). There is however a notable difference: the system (39)–(40) from Paine et al. (1983) contains the parameters A_1, A_2, K^* and Sh which depend non-locally on c and c_{s}. Instead we give explicit values of the effective coefficients.

This case cannot be compared with the results from Balakotaiah and Chang (1995), since they have a different timescale on the pages 61–73. Nevertheless, a comparison will be possible in the case $K_{\mathrm{e}} = +\infty$.

Balakotaiah and Chakraborty introduce a four-mode hyperbolic model but with non-linear reactions, in three-dimensional geometry and with much bigger Damkohler number (Balakotaiah, 2004; Chakraborty and Balakotaiah, 2005). The effective model cannot be directly compared with our system (12)–(13). Nevertheless, in Section 3.1 we derive a four-mode hyperbolic model, analogous to the models from Balakotaiah (2004) and Chakraborty and Balakotaiah (2005). We show that it is formally equivalent to our model at the order $\mathcal{O}(\varepsilon^{2(2-\alpha)})$. This shows the relationship between the upscaled models developed by Balakotaiah and Chakraborty and our results (Balakotaiah, 2004; Chakraborty and Balakotaiah, 2005).

In its dimensional form our effective problem reads

$$\partial_{t^*}\left(c^* + \frac{\hat{c}}{H}\right) + \left(\frac{2Q^*}{3} + \frac{2Q^* Da_{\mathrm{T}}}{45}\right)\partial_{x^*} c^* - D^*\left(1 + \frac{8}{945}Pe_{\mathrm{T}}^2\right)\partial_{x^* x^*} c^* = \frac{2Q^* Da_{\mathrm{T}}}{45K_{\mathrm{e}}}\partial_{x^*}\hat{c} \tag{14}$$

$$\left(1+\frac{1}{3}Da_{\mathrm{T}}\right)\partial_{t^*}\hat{c}=\hat{k}^*\left(c^*+\frac{2HPe_{\mathrm{T}}}{45}\partial_{x^*}c^*-\frac{\hat{c}}{K_{\mathrm{e}}}\right) \tag{15}$$

where $Pe_{\mathrm{T}}=Q^*H/D^*$ is the transversal Péclet number and $Da_{\mathrm{T}}=\hat{k}^*H/D^*$ the transversal Damkohler number.

Taking the transversal section mean gives

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

$$\partial_{t^*}\hat{c}=\hat{k}^*\left(c^{\mathrm{moy}}-\frac{\hat{c}}{K_{\mathrm{e}}}\right) \tag{17}$$

We will compare numerically our effective Equations (14) and (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 Mikelić et al. (2006) for the particular case when $K_{\mathrm{e}}=+\infty$ (the case of an irreversible, first order, heterogeneous reaction).

In this case the effective non-dimensional problem is

$$\begin{aligned}\partial_t c+Q\left(\frac{2}{3}+\frac{4k}{45D}\varepsilon^{2-\alpha}\right)\partial_x c+k\left(1-\frac{k}{3D}\varepsilon^{2-\alpha}\right)c\\=\left(D\varepsilon^{\alpha}+\frac{8}{945}\frac{Q^2}{D}\varepsilon^{2-\alpha}\right)\partial_{xx}c\end{aligned} \tag{18}$$

Our result could be stated in dimensional form: Let us suppose that $L_{\mathrm{R}}>\max\{D_{\mathrm{R}}/Q_{\mathrm{R}},\ Q_{\mathrm{R}}H^2/D_{\mathrm{R}},\ H\}$. Then the upscaled dimensional problem corresponding to the case $K_{\mathrm{e}}=+\infty$ reads

$$\begin{aligned}\frac{\partial c^{*,\mathrm{eff}}}{\partial t^*}+\left(\frac{2}{3}+\frac{4}{45}Da_{\mathrm{T}}\right)Q^*\frac{\partial c^{*,\mathrm{eff}}}{\partial x^*}+\frac{k^*}{H}\left(1-\frac{1}{3}Da_{\mathrm{T}}\right)c^{*,\mathrm{eff}}\\=D^*\left(1+\frac{8}{945}Pe_{\mathrm{T}}^2\right)\frac{\partial^2c^{*,\mathrm{eff}}}{\partial(x^*)^2}\end{aligned} \tag{19}$$

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

$$\max_{0\le t\le T}t^3\int_{\Omega_K}\left|c^{\varepsilon}(x,y,t)-c(x,t)\right|\,\mathrm{d}x\mathrm{d}y\le C\varepsilon^{2-\alpha} \tag{20}$$

$$\left(\int_0^T\int_{\Omega_K}t^6\left|\partial_y c^{\varepsilon}(x,y,t)\right|^2\mathrm{d}x\mathrm{d}y\mathrm{d}t\right)^{1/2}\le C\left(\varepsilon^{2-5\alpha/4}H(1-\alpha)+\varepsilon^{3/2-3\alpha/4}H(\alpha-1)\right) \tag{21}$$

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

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

$$\max_{0\le t\le T} \max_{(x,y)\in\Omega^+} \left|t^3\left(c^\varepsilon(x,\, y,\, t) - c(x,\, t) - C_{\mathrm{cor}}(x,\, y,\, t)\right)\right| \le \begin{cases} C\varepsilon^{4-7\alpha/2-\delta}, & \text{if } \alpha < 1, \\ C\varepsilon^{(3/2)-\alpha-\delta} & \text{if } \alpha \ge 1 \end{cases} \tag{23}$$

For details of the proof we refer to Mikelić et al. (2006).

If we compare the non-dimensional effective equation (18) with the corresponding equation (57), from Paine et al. (1983, p. 1786), we find out that they have the same form. Contrary to Paine et al. (1983), we have calculated the effective coefficients and we find them independent of the time and of the moments of c.

In the article Balakotaiah and Chang (1995) 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 from Section 3.4 computations with our technique for the timescale chosen in Balakotaiah and Chang (1995) 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 center manifold technique.

2.1 Statement of the results in the case of non-linear reactions

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

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

$$-D^*\partial_z c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{\Phi}\left(c^*\right) - \hat{k}_{\mathrm{d}}^*\hat{c} \;\text{ on } z = \pm H \tag{24}$$

where $\hat{k}_{\mathrm{d}}^*$ represents the constant desorption rate. For simplicity we suppose $\hat{\Phi}(0) = 0$. Examples of $\hat{\Phi}$ are

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

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

We start with *Langmuir's isotherm*. In this case the adsorption speed is k_1^*, having the characteristic size $k_{1\mathrm{R}}$ and $k_1^* = k_{1\mathrm{R}} k_1$. For the second parameter we set $k_2^* c_{\mathrm{R}} = k_2$, 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:

$$T_{\mathrm{A}} = \hat{c}_{\mathrm{R}}/(c_{\mathrm{R}} k_{1\mathrm{R}}) \text{ (characteristic adsorption time)}$$

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

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

$$-D\varepsilon^{\alpha-2}\frac{\partial c^{\varepsilon}}{\partial y} = \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c_{\mathrm{s}}^{\varepsilon}}{\partial t} = \frac{T_{\mathrm{L}}}{T_{\mathrm{react}}}\left(\Phi(c^{\varepsilon}) - k_{\mathrm{d}}^{*} T_{\mathrm{A}} c_{\mathrm{s}}^{\varepsilon}\right)\Big|_{y=1} \text{ on } \Gamma^{+}\times(0,T) \tag{26}$$

We suppose $T_{\mathrm{L}} \approx T_{\mathrm{A}} \approx 1/k_{\mathrm{d}}^{*}$ and k_1 and k_2 of order 1.

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

After the calculations from Section 3.2, we find out that the effective equations in $(0,+\infty)\times(0,T)$:

$$\begin{aligned}
&\partial_t\left(c_{\mathrm{FN}}^{0} + \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}} c_{\mathrm{sN}}^{\mathrm{eff}}\right) + \frac{2Q}{3}\partial_x\left(c_{\mathrm{FN}}^{0} + \frac{1}{15D}\frac{T_{\mathrm{T}}}{T_{\mathrm{react}}}\Phi\left(c_{\mathrm{FN}}^{0}\right)\right) \\
&= \varepsilon^{\alpha}\left(D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)}\right)\partial_{xx}c_{\mathrm{FN}}^{0} + \frac{2Q}{45D}\frac{T_{\mathrm{A}}T_{\mathrm{T}}k_{\mathrm{d}}^{*}}{T_{\mathrm{react}}}\partial_x c_{\mathrm{sN}}^{\mathrm{eff}}
\end{aligned} \tag{27}$$

$$\partial_t c_{\mathrm{sN}}^{\mathrm{eff}} = \frac{T_{\mathrm{L}}}{T_{\mathrm{A}}}\left(\Phi\left(c_{\mathrm{FN}}^{0} + \varepsilon^{2-\alpha}c_{\mathrm{FN}}^{1}\big|_{y=1}\right) - k_{\mathrm{d}}^{*}T_{\mathrm{A}}c_{\mathrm{sN}}^{0}\right) \tag{28}$$

$$c_{\mathrm{FN}}^{1}\big|_{y=1} = \frac{2}{45}\frac{Q}{D}\partial_x c_{\mathrm{FN}}^{0} - \frac{T_{\mathrm{A}}}{3DT_{\mathrm{react}}}\partial_t c_{\mathrm{sN}}^{\mathrm{eff}} \tag{29}$$

$$c_{\mathrm{FN}}^{0}\big|_{x=0} = 0, \qquad c_{\mathrm{FN}}^{0}\big|_{t=0} = 1, \qquad c_{\mathrm{sN}}^{\mathrm{eff}}\big|_{t=0} = c_{\mathrm{s0}} \tag{30}$$

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

$$\begin{aligned}
&\partial_{t^*}\left(c_{\mathrm{N}}^{*} + \frac{\hat{c}_{\mathrm{N}}}{H}\right) + \partial_{x^*}\left(\frac{2Q^*}{3}c_{\mathrm{N}}^{*} + \frac{Pe_{\mathrm{T}}}{15}\hat{\Phi}\left(c_{\mathrm{N}}^{*}\right)\right) \\
&\qquad = D^*\left(1 + \frac{8}{945}Pe_{\mathrm{T}}^2\right)\partial_{x^*x^*}c_{\mathrm{N}}^{*} + \frac{2k_{\mathrm{d}}^{*}Pe_{\mathrm{T}}}{45}\partial_{x^*}\hat{c}_{\mathrm{N}}
\end{aligned} \tag{31}$$

$$\partial_{t^*}\hat{c}_{\mathrm{N}} = \hat{\Phi}\left(c_{\mathrm{N}}^{*} + Pe_{\mathrm{T}}\tilde{c}_{\mathrm{N}}^{1}\right) - k_{\mathrm{d}}^{*}\hat{c}_{\mathrm{N}} \tag{32}$$

$$\tilde{c}_{\mathrm{N}}^{1} = \frac{2H}{45}\partial_{x^*}c_{\mathrm{N}}^{*} - \frac{1}{3}\partial_{t^*}\hat{c}_{\mathrm{N}} \tag{33}$$

where $Pe_{\mathrm{T}} = Q^*H/D^*$ is the transversal Péclet number.

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

$$\partial_{t^*}\left(c_{\mathrm{N}}^{\mathrm{moy}} + \frac{\hat{c}_{\mathrm{N}}^{\mathrm{moy}}}{H}\right) + \frac{2Q^*}{3}\partial_{x^*}c_{\mathrm{N}}^{\mathrm{moy}} - D^*\partial_{x^*x^*}c_{\mathrm{N}}^{\mathrm{moy}} = 0 \tag{34}$$

$$\partial_{t^*}\hat{c}_{\mathrm{N}} = \hat{\Phi}\left(c_{\mathrm{N}}^{\mathrm{moy}}\right) - k_{\mathrm{d}}^{*}\hat{c}_{\mathrm{N}} \tag{35}$$

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

Here also we could propose four-mode models in the sense of Balakotaiah (2004) and Chakraborty and Balakotaiah (2005).

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 following flux equation

$$-D^* \partial_z c^* = K_\mathrm{e} \frac{\partial c^*}{\partial t^*} \quad \text{on } \Gamma^* \tag{36}$$

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

The characteristic times T_A and T_DE cannot be used anymore and we introduce the new characteristic time $T_\mathrm{C} = K_\mathrm{eR}/\varepsilon Q_\mathrm{R}$, which has a meaning of the superficial chemical reaction timescale. As before, we set $\varepsilon = H/L_\mathrm{R} \ll 1$ and choose $T_\mathrm{R} = T_\mathrm{L}$.

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

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

$$-D\varepsilon^{\alpha-2}\frac{\partial c^\varepsilon}{\partial y} = -D\frac{1}{\varepsilon^2 Pe}\frac{\partial c^\varepsilon}{\partial y} = \frac{T_\mathrm{C}}{T_\mathrm{L}} K \frac{\partial c^\varepsilon}{\partial t} \quad \text{on } \Gamma^+ \times (0,T) \tag{38}$$

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

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

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

Further, we suppose that $T_\mathrm{C} \approx T_\mathrm{L}$.

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

$$\begin{aligned}&(1+Da_K)\frac{\partial c_K^{*,\mathrm{eff}}}{\partial t^*} + \frac{2Q^*}{3}\frac{\partial c_K^{*,\mathrm{eff}}}{\partial x^*}\\ &= D^*\left(1 + \frac{4}{135}Pe_\mathrm{T}^2\left[\frac{2}{7} + \frac{Da_K(2+7Da_K)}{(1+Da_K)^2}\right]\right)\frac{\partial^2 c_K^{*,\mathrm{eff}}}{\partial (x^*)^2}\end{aligned} \tag{42}$$

In Equation (42) $Pe_\mathrm{T} = Q^* H/D^*$ is the transversal Péclet number and $Da_K = K_\mathrm{e}/H$ is the transversal Damkohler number.

The transversal section mean gives

$$(1 + Da_K)\partial_{t^*} c_K^{\mathrm{moy}} + \frac{2Q^*}{3} \partial_{x^*} c_K^{\mathrm{moy}} - D^* \partial_{x^* x^*} c_K^{\mathrm{moy}} = 0 \tag{43}$$

Once more, for the non-negligible local Péclet 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. For an error estimate analogous to Theorem 1, we refer to the articles Mikelić and Rosier (2007) and Choquet and Mikelić (2008).

We note the possible similarities of the effective model (42) with Golay's theory as presented in Paine et al. (1983). 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 Péclet number* $\varepsilon^{2-\alpha}$. Note that the transversal Péclet number is equal to the ratio between the characteristic transversal timescale and longitudinal timescale. Then we use Fredholm's alternative[1] 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. To obtain a better approximation, we use the strategy from Rubinstein and Mauri (1986) 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 Péclet number, but also by the effects of the chemical reactions, entering through Damkohler number.

3.1 Full linear model with adsorption–desorption

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

$$c^\varepsilon = c_{\mathrm{F}}^0(x, t; \varepsilon) + \varepsilon^{2-\alpha} c_{\mathrm{F}}^1(x, y, t) + \varepsilon^{2(2-\alpha)} c_{\mathrm{F}}^2(x, y, t) + \cdots \tag{44}$$

$$c_{\mathrm{s}}^\varepsilon = c_{\mathrm{s}}^0(x, t; \varepsilon) + \varepsilon^{2-\alpha} c_{\mathrm{s}}^1(x, y, t) + \varepsilon^{2(2-\alpha)} c_{\mathrm{s}}^2(x, y, t) + \cdots \tag{45}$$

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[1] Comment for a non-mathematical reader: Fredholm's alternative gives a necessary and sufficient criteria for solvability of an equation, in the critical situation when we are in a spectrum. For linear algebraic system $A\mathbf{x} = \mathbf{b}$, it says that if 0 is an eigenvalue of the matrix A, the system has a solution if and only if $\mathbf{b}$ is orthogonal to the eigenvectors of A that correspond to the eigenvalue 0. Except the last example, that is borrowed from Balakotaiah and Chang (1995), in all examples considered here 0 is a simple eigenvalue. Therefore the corresponding boundary value problem in y-variable admits a solution if and only if the mean of the right-hand side with respect to the transversal variable y is equal to the value of the flux at $y = 1$. We refer to the textbooks as Wloka (1987), for the Fredholm theory the partial differential equations.

After introducing Equation (44) into Equation (6) we get

$$\begin{aligned}&\varepsilon^0\{\partial_t c_{\mathrm{F}}^0 + Q(1-y^2)\partial_x c_{\mathrm{F}}^0 - D\partial_{yy}c_{\mathrm{F}}^1\} + \varepsilon^{2-\alpha}\{\partial_t c_{\mathrm{F}}^1 + Q(1-y^2)\partial_x c_{\mathrm{F}}^1 \\ &\quad -D\varepsilon^{2(\alpha-1)}\partial_{xx}c_{\mathrm{F}}^0 - D\varepsilon^{\alpha}\partial_{xx}c_{\mathrm{F}}^1 - D\partial_{yy}c_{\mathrm{F}}^2\} = \mathcal{O}\left(\varepsilon^{2(2-\alpha)}\right) = \mathcal{O}\left(\left(\frac{T_{\mathrm{T}}}{T_{\mathrm{L}}}\right)^2\right)\end{aligned} \tag{46}$$

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

$$\left(-D\partial_y c_{\mathrm{F}}^1 - \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^0}{\partial t}\right) + \varepsilon^{2-\alpha}\left(-D\partial_y c_{\mathrm{F}}^2 - \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^1}{\partial t}\right) + \cdots = 0 \tag{47}$$

$$\begin{aligned}&\left(\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^0}{\partial t} - \frac{T_{\mathrm{L}}}{T_{\mathrm{DE}}}k\left(c_{\mathrm{F}}^0 - \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{c_{\mathrm{s}}^0}{K}\right)\right) \\ &\quad + \varepsilon^{2-\alpha}\left(\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^1}{\partial t} - \frac{T_{\mathrm{L}}}{T_{\mathrm{react}}}k\left(c_{\mathrm{F}}^1 - \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{c_{\mathrm{s}}^1}{K}\right)\right) + \cdots = 0\end{aligned} \tag{48}$$

To satisfy Equations (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

$$\begin{cases} -D\partial_{yy}c_{\mathrm{F}}^1 = Q\left(y^2 - \dfrac{1}{3}\right)\partial_x c_{\mathrm{F}}^0 - \left(\partial_t c_{\mathrm{F}}^0 + \dfrac{2Q\partial_x c_{\mathrm{F}}^0}{3}\right) \text{ on } (0,1), \\ -D\partial_y c_{\mathrm{F}}^1 = \dfrac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\dfrac{\partial c_{\mathrm{s}}^0}{\partial t} = \dfrac{T_{\mathrm{L}}}{T_{\mathrm{DE}}}k\left(c_{\mathrm{F}}^0 - \dfrac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\dfrac{c_{\mathrm{s}}^0}{K}\right) \text{ on } y=1 \\ \text{and } \partial_y c_{\mathrm{F}}^1 = 0 \text{ on } y = 0 \end{cases} \tag{49}$$

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

$$\partial_t c_{\mathrm{F}}^0 + \frac{2Q\partial_x c_{\mathrm{F}}^0}{3} + \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^0}{\partial t} = 0 \tag{50}$$

$$\text{and } \frac{\partial c_{\mathrm{s}}^0}{\partial t} = \frac{T_{\mathrm{L}}}{T_{\mathrm{A}}}k\left(c_{\mathrm{F}}^0 - \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{c_{\mathrm{s}}^0}{K}\right) \tag{51}$$

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 Bourgeat et al. (2003), 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 Rubinstein and Mauri (1986). More precisely, we suppose that expression (50) is of the next order in our asymptotic expansion, i.e.

$$\partial_t c_{\mathrm{F}}^0 + \frac{2Q\partial_x c_{\mathrm{F}}^0}{3} + \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^0}{\partial t} = \mathcal{O}(\varepsilon^{2-\alpha}) \qquad \text{in } (0, +\infty) \times (0, T) \tag{52}$$

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

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

$$\begin{cases} -D\partial_{yy}c_{\mathrm{F}}^1 = -Q\left(\dfrac{1}{3}-y^2\right)\partial_x c_{\mathrm{F}}^0 + \dfrac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\dfrac{\partial c_{\mathrm{s}}^0}{\partial \mathrm{t}} \ \text{ on } (0,1), \\ -D\partial_y c_{\mathrm{F}}^1 = \dfrac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\dfrac{\partial c_{\mathrm{s}}^0}{\partial t} = \dfrac{T_{\mathrm{L}}}{T_{\mathrm{DE}}}k\left(c_{\mathrm{F}}^0 - \dfrac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\dfrac{c_{\mathrm{s}}^0}{K}\right) \ \text{ on } y=1, \\ \text{and } \partial_y c_{\mathrm{F}}^1 = 0 \ \text{ on } y=0 \end{cases} \tag{53}$$

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

$$c_{\mathrm{F}}^1(x,y,t) = \frac{Q}{D}\left(\frac{y^2}{6}-\frac{y^4}{12}-\frac{7}{180}\right)\partial_x c_{\mathrm{F}}^0 + \frac{1}{D}\left(\frac{1}{6}-\frac{y^2}{2}\right)\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^0}{\partial t} + A(x,\ t) \tag{54}$$

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

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

$$\begin{cases} -D\partial_{yy}c_{\mathrm{F}}^2 = \varepsilon^\alpha D\partial_{xx}c_{\mathrm{F}}^1 - Q(1-y^2)\partial_x c_{\mathrm{F}}^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c_{\mathrm{F}}^0 \\ \quad -\partial_t c_{\mathrm{F}}^1 - \varepsilon^{\alpha-2}\left(\partial_t c_{\mathrm{F}}^0 + \dfrac{2Q\partial_x c_{\mathrm{F}}^0}{3} + \dfrac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\dfrac{\partial c_{\mathrm{s}}^0}{\partial t}\right) \ \text{ on } (0,1), \\ -D\partial_y c_{\mathrm{F}}^2 = \dfrac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\dfrac{\partial c_{\mathrm{s}}^1}{\partial t} = \dfrac{T_{\mathrm{L}}}{T_{\mathrm{DE}}}k\left(c_{\mathrm{F}}^1 - \dfrac{T_{\mathrm{A}}}{\mathrm{T}_{\mathrm{DE}}}\dfrac{c_{\mathrm{s}}^1}{K}\right) \ \text{ on } y=1 \\ \qquad \text{and } \partial_y c_{\mathrm{F}}^2 = 0 \ \text{ on } y=0 \end{cases} \tag{55}$$

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

$$\partial_t B = \frac{T_{\mathrm{L}}k}{T_{\mathrm{A}}}\left(A - \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{B}{K}\right) \tag{56}$$

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

$$\begin{aligned} &\partial_t c_{\mathrm{F}}^0 + \frac{2Q\partial_x c_{\mathrm{F}}^0}{3} + \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^0}{\partial t} + \varepsilon^{2-\alpha}\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^1}{\partial t} + \varepsilon^{2-\alpha}\partial_t\left(\int_0^1 c_{\mathrm{F}}^1\,\mathrm{d}y\right) \\ &-\varepsilon^\alpha D\partial_{xx}c_{\mathrm{F}}^0 + Q\varepsilon^{2-\alpha}\partial_x\left(\int_0^1 (1-y^2)c_{\mathrm{F}}^1\,\mathrm{d}y\right) \\ &-D\varepsilon^2\partial_{xx}\left(\int_0^1 c_{\mathrm{F}}^1\,\mathrm{d}y\right) = 0 \end{aligned} \tag{57}$$

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

$$\int_0^1 c_{\mathrm{F}}^1\,\mathrm{d}y = A(x,t) \tag{58}$$

$$\int_0^1 (1-y^2)\, c_{\mathrm{F}}^1\,\mathrm{d}y = \frac{2}{3}A(x,t) - \frac{Q}{D}\frac{8}{945}\partial_x c_{\mathrm{F}}^0 + \frac{2}{45D}\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^0}{\partial t} \tag{59}$$

and Equation (57) becomes

$$\partial_t\left(c_{\mathrm{F}}^0 + \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\left(c_{\mathrm{s}}^0 + \varepsilon^{2-\alpha}c_{\mathrm{s}}^1\right)\right) + \frac{2Q}{3}\partial_x c_{\mathrm{F}}^0 - \varepsilon^\alpha \tilde{D}\partial_{xx}c_{\mathrm{F}}^0$$
$$= -\varepsilon^{2-\alpha}\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{2Q}{45D}\partial_{xt}c_{\mathrm{s}}^0 - \varepsilon^{2-\alpha}\left\{\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\partial_t B + \partial_t A + \frac{2Q}{3}\partial_x A - \mathrm{D}\varepsilon^\alpha\partial_{xx}A\right\} \tag{60}$$

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

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

Let

$$\mathscr{L}_1\{A,B\} = \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\partial_t B + \partial_t A + \frac{2Q}{3}\partial_x A - \mathrm{D}\varepsilon^\alpha\partial_{xx}A \tag{62}$$

$$\mathscr{L}_2\{A,B\} = \partial_t B - \frac{T_{\mathrm{L}}}{T_{\mathrm{A}}}\left(A - \frac{\mathrm{T_A}}{T_{\mathrm{DE}}}\frac{B}{K}\right) \tag{63}$$

There is no clear criterion for choosing the functions A and B. Nevertheless, if $\mathscr{L}_2\{A,B\}=0$, it is possible to introduce the change of unknown functions $c_{\mathrm{F}}^0 \to c_{\mathrm{F}}^0 + \varepsilon^{2-\alpha}A$ and $c_{\mathrm{s}}^1 \to c_{\mathrm{s}}^1 + B$. Then Equation (60) differs only by the term $\varepsilon^{2(2-\alpha)}(2Q/45D)\partial_{xt}B$ from its variant with $A=B=0$. Hence $\{c_{\mathrm{F}}^0, c_{\mathrm{s}}^0 + \varepsilon^{2-\alpha}c_{\mathrm{s}}^1\}$ 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 Equation (60) and the boundary condition at $y=1$ to the following system of partial differential equations on $(0,+\infty)\times(0,T)$:

$$\partial_t\left(c_{\mathrm{F}}^0 + \frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}c_{\mathrm{s}}^{\mathrm{eff}}\right) + \left(\frac{2Q}{3} + \frac{2}{45}\frac{T_{\mathrm{T}}}{T_{\mathrm{DE}}}\frac{Qk}{D}\right)\partial_x c_{\mathrm{F}}^0$$
$$= \varepsilon^\alpha\left(D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)}\right)\partial_{xx}c_{\mathrm{F}}^0 + \frac{2}{45}\frac{T_{\mathrm{A}}T_{\mathrm{T}}}{(T_{\mathrm{DE}})^2}\frac{Qk}{DK}\partial_x c_{\mathrm{s}}^{\mathrm{eff}} \tag{64}$$

$$\left(1 + \frac{T_{\mathrm{T}}}{T_{\mathrm{DE}}}\frac{k}{3D}\right)\partial_t c_{\mathrm{s}}^{\mathrm{eff}} = \frac{T_{\mathrm{L}}k}{T_{\mathrm{A}}}\left(c_{\mathrm{F}}^0 + \frac{2}{45}\frac{Q}{D}\varepsilon^{2-\alpha}\partial_x c_{\mathrm{F}}^0 - \frac{T_{\mathrm{A}}}{KT_{\mathrm{DE}}}c_{\mathrm{s}}^{\mathrm{eff}}\right) \tag{65}$$

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

In fact it is possible to proceed differently and to "hyperbolize" the effective model. Following Balakotaiah and Chang (2003), Balakotaiah (2004) and Chakraborty and Balakotaiah (2005) we set

$$C_{\mathrm{m}}(x,t) = \int_0^1 (1-y^2)(c_{\mathrm{F}}^0 + \varepsilon^{2-\alpha}c_{\mathrm{F}}^1)\,\mathrm{d}y = \frac{2}{3}c_{\mathrm{F}}^0(x,t) + \varepsilon^{2-\alpha}\int_0^1 (1-y^2)c_{\mathrm{F}}^1\,\mathrm{d}y \tag{66}$$

(the mixing-cup concentration)

$$C_{\mathrm{w}}(x,t) = c_{\mathrm{F}}^0(x,t) + \varepsilon^{2-\alpha}c_{\mathrm{F}}^1(x,1,t) \tag{67}$$

(the effective solute concentration at the wall)

Then if $1<\alpha<2$ we can drop the axial diffusion term $\varepsilon^{\alpha}\tilde{D}\partial_{xx}c_{\mathrm{F}}^{0}$ and write Equation (57) in the form

$$\frac{\partial c_{\mathrm{F}}^{0}}{\partial t}+Q\frac{\partial C_{\mathrm{m}}}{\partial x}+\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^{\mathrm{eff}}}{\partial t}=0 \tag{68}$$

Next we have

$$\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\frac{\partial c_{\mathrm{s}}^{\mathrm{eff}}}{\partial t}=-\frac{\partial c_{\mathrm{F}}^{0}}{\partial t}-\frac{2Q}{3}\frac{\partial C_{\mathrm{F}}^{0}}{\partial x}+\mathcal{O}(\varepsilon^{2(2-\alpha)}) \tag{69}$$

and after replacing $\partial_t c_{\mathrm{s}}^{0}$ by the right hand side of Equation (69) we get

$$c_{\mathrm{F}}^{1}(x,y,t)=\frac{Q}{D}\left(\frac{y^{2}}{2}-\frac{y^{4}}{12}-\frac{3}{20}\right)\partial_x c_{\mathrm{F}}^{0}-\frac{1}{D}\left(\frac{1}{6}-\frac{y^{2}}{2}\right)\partial_t c_{\mathrm{F}}^{0} \tag{70}$$

$$\int_{0}^{1}(1-y^{2})c_{\mathrm{F}}^{1}\,dy=-\frac{Q}{D}\frac{4}{105}\partial_x c_{\mathrm{F}}^{0}-\frac{2}{45D}\partial_t c_{\mathrm{F}}^{0} \tag{71}$$

$$C_{\mathrm{m}}(x,t)=\frac{2}{3}c_{\mathrm{F}}^{0}(x,t)-\frac{1}{D}\varepsilon^{2-\alpha}\left\{\frac{4Q}{105}\partial_x c_{\mathrm{F}}^{0}+\frac{2}{45}\partial_t c_{\mathrm{F}}^{0}\right\} \tag{72}$$

$$C_{\mathrm{w}}(x,t)=c_{\mathrm{F}}^{0}(x,t)+\frac{1}{D}\varepsilon^{2-\alpha}\left\{\frac{4Q}{15}\partial_x c_{\mathrm{F}}^{0}+\frac{1}{3}\partial_t c_{\mathrm{F}}^{0}\right\} \tag{73}$$

Equation (65) now reads

$$\frac{T_{\mathrm{A}}}{T_{\mathrm{DE}}}\partial_t c_{\mathrm{s}}^{\mathrm{eff}}=\frac{T_{\mathrm{L}}k}{T_{\mathrm{DE}}}\left(C_{\mathrm{w}}-\frac{T_{A}}{KT_{\mathrm{DE}}}c_{\mathrm{s}}^{\mathrm{eff}}\right) \tag{74}$$

The system (68), (74), (72) and (73) is analogous to the four-mode hyperbolic model (60)–(63), from Balakotaiah (2004, p. 324) and to the four-mode model (90)–(93), from Chakraborty and Balakotaiah (2005, p. 233).

In this chapter our goal is to have a generalization of Taylor's dispersion and we search for a parabolic operator for c_{F}^{0}.

3.2 Non-linear reactions

Now we study some non-linear surface reactions.

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

$$c^{\varepsilon}=c_{\mathrm{FN}}^{0}(x,t;\varepsilon)+\varepsilon^{2-\alpha}c_{\mathrm{FN}}^{1}(x,y,t)+\varepsilon^{2(2-\alpha)}c_{\mathrm{FN}}^{2}(x,y,t)+\dots \tag{75}$$

$$c_{\mathrm{s}}^{\varepsilon}=c_{\mathrm{sN}}^{0}(x,t;\varepsilon)+\varepsilon^{2-\alpha}c_{\mathrm{sN}}^{1}(x,y,t)+\varepsilon^{2(2-\alpha)}c_{\mathrm{sN}}^{2}(x,y,t)+\dots \tag{76}$$

After introducing Equations (75)–(76) into 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 following equations for the boundary reactions at $y=1$:

$$\left(-D\partial_y c^1_{\mathrm{FN}} - \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t}\right) + \varepsilon^{2-\alpha}\left(-D\partial_y c^2_{\mathrm{FN}} - \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^1_{\mathrm{sN}}}{\partial t}\right) + \cdots = 0 \tag{77}$$

$$\begin{aligned}&\left(\frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} - \frac{T_{\mathrm{L}}}{T_{\mathrm{react}}}\left(\Phi(c^0_{\mathrm{FN}}) - k^*_{\mathrm{d}}T_{\mathrm{A}}c^0_{\mathrm{sN}}\right)\right)\\ &+\varepsilon^{2-\alpha}\left(\frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^1_{\mathrm{sN}}}{\partial t} - \frac{T_{\mathrm{L}}}{T_{\mathrm{react}}}\left(\Phi'(c^0_{\mathrm{FN}})c^1_{\mathrm{FN}} - k^*_{\mathrm{d}}T_{\mathrm{A}}c^1_{\mathrm{sN}}\right)\right) + \cdots = 0\end{aligned} \tag{78}$$

As before, the ε^0 terms give the problem

$$\begin{cases} -D\partial_{yy}c^1_{\mathrm{FN}} = Q\left(y^2 - \frac{1}{3}\right)\partial_x c^0_{\mathrm{FN}} - \left(\partial_t c^0_{\mathrm{FN}} + \frac{2Q\partial_x c^0_{\mathrm{FN}}}{3}\right) \text{ on } (0,1),\\ -D\partial_y c^1_{\mathrm{FN}} = \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} = \frac{T_{\mathrm{L}}}{T_{\mathrm{react}}}\left(\Phi(c^0_{\mathrm{FN}}) - k^*_{\mathrm{d}}T_{\mathrm{A}}c^0_{\mathrm{sN}}\right) \text{ on } y=1,\\ \text{and } \partial_y c^1_{\mathrm{FN}} = 0 \text{ on } y=0 \end{cases} \tag{79}$$

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

$$\partial_t c^0_{\mathrm{FN}} + \frac{2Q\partial_x c^0_{\mathrm{FN}}}{3} + \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} = 0 \tag{80}$$

$$\text{and } \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} = \frac{T_{\mathrm{L}}}{T_{\mathrm{react}}}\left(\Phi(c^0_{\mathrm{FN}}) - k^*_{\mathrm{d}}T_{\mathrm{A}}c^0_{\mathrm{sN}}\right) \tag{81}$$

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^0_{FN}, system (80)–(81) does not suit our needs and, as in the previous subsection, we proceed by following an idea from Rubinstein and Mauri (1986). More precisely, we suppose that expression (80) is of the next order in our asymptotic expansion, i.e.

$$\partial_t c^0_{\mathrm{FN}} + \frac{2Q\partial_x c^0_{\mathrm{FN}}}{3} + \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} = \mathcal{O}(\varepsilon^{2-\alpha}) \text{ in } (0,+\infty) \times (0,T) \tag{82}$$

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

Combining (49) and (80) and using hypothesis (82) gives

$$\begin{cases} -D\partial_{yy}c^1_{\mathrm{FN}} = -Q\left(\frac{1}{3} - y^2\right)\partial_x c^0_{\mathrm{FN}} + \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} \text{ on } (0,1),\\ -D\partial_y c^1_{\mathrm{FN}} = \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} = \frac{T_{\mathrm{L}}}{T_{\mathrm{react}}}\left(\Phi(c^0_{\mathrm{FN}}) - k^*_{\mathrm{d}}T_{\mathrm{A}}c^0_{\mathrm{sN}}\right) \text{ on } y=1\\ \text{and } \partial_y c^1_{\mathrm{FN}} = 0 \text{ on } y=0 \end{cases} \tag{83}$$

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

$$c^1_{\mathrm{FN}}(x,y,t) = \frac{Q}{D}\left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180}\right)\partial_x c^0_{\mathrm{FN}} + \frac{1}{D}\left(\frac{1}{6} - \frac{y^2}{2}\right)\frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} + A_{\mathrm{N}}(x,t) \tag{84}$$

where $A_{\mathrm{N}}(x,t)$ is an arbitrary function.

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

$$\begin{cases} -D\partial_{yy}c^2_{\mathrm{FN}} = \varepsilon^{\alpha} D\partial_{xx}c^1_{\mathrm{FN}} - Q(1-y^2)\partial_x c^1_{\mathrm{FN}} + D\varepsilon^{2(\alpha-1)}\partial_{xx}c^0_{\mathrm{FN}} \\ \quad -\partial_t c^1_{\mathrm{FN}} - \varepsilon^{\alpha-2}\left(\partial_t c^0_{\mathrm{FN}} + \dfrac{2Q\partial_x c^0_{\mathrm{FN}}}{3} + \dfrac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\dfrac{\partial c^0_{\mathrm{sN}}}{\partial t}\right) \text{ on } (0,1), \\ -D\partial_y c^2_{\mathrm{FN}} = \dfrac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\dfrac{\partial c^1_{\mathrm{sN}}}{\partial t} = \dfrac{T_{\mathrm{L}}}{T_{\mathrm{react}}}\left(\Phi'(c^0_{\mathrm{FN}})c^1_{\mathrm{FN}} - k^*_{\mathrm{d}} T_{\mathrm{A}} c^1_{\mathrm{sN}}\right) \text{ on } y=1, \\ \text{and } \partial_y c^2_{\mathrm{FN}} = 0 \text{ on } y = 0 \end{cases} \tag{85}$$

for every $(x,\ t) \in (0,\ +\infty) \times (0,\ T)$. Note that in order to have an expression for c^1_{sN} that is compatible with Equation (84), when adding an arbitrary function $A_{\mathrm{N}}(x,t)$ to c^1_{FN} in Equation (54), we should also add to c^1_{sN} a function $B_{\mathrm{N}}(x,t)$ satisfying

$$\partial_t B_{\mathrm{N}} = \frac{T_{\mathrm{L}}}{T_{\mathrm{A}}}\left(\Phi(A_{\mathrm{N}}) - k^*_{\mathrm{d}} T_{\mathrm{A}} B_{\mathrm{N}}\right) \tag{86}$$

The problem (85) has a solution if and only if

$$\partial_t c^0_{\mathrm{FN}} + \frac{2Q\partial_x c^0_{\mathrm{FN}}}{3} + \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} + \varepsilon^{2-\alpha}\frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^1_{\mathrm{sN}}}{\partial t} + \varepsilon^{2-\alpha}\partial_t\left(\int_0^1 c^1_{\mathrm{FN}}\,\mathrm{d}y\right)$$
$$-\varepsilon^{\alpha} D\partial_{xx}c^0_{\mathrm{FN}} + Q\varepsilon^{2-\alpha}\partial_x\left(\int_0^1 (1-y^2)c^1_{\mathrm{FN}}\,\mathrm{d}y\right) - D\varepsilon^2\partial_{xx}\left(\int_0^1 c^1_{\mathrm{FN}}\,\mathrm{d}y\right) = 0 \tag{87}$$

in $(0,+\infty) \times (0,T)$.[2] Note that this is the equation for c^0_{FN} and c^0_{sN}.

Next let us remark that

$$\int_0^1 c^1_{\mathrm{FN}}\,\mathrm{d}y = A_{\mathrm{N}}(x,\ t) \tag{88}$$

$$\int_0^1 (1-y^2)\, c^1_{\mathrm{FN}}\,\mathrm{d}y = \frac{2}{3}A_{\mathrm{N}}(x,t) - \frac{Q}{D}\frac{8}{945}\partial_x c^0_{\mathrm{FN}} + \frac{2}{45D}\frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{\partial c^0_{\mathrm{sN}}}{\partial t} \tag{89}$$

and Equation (87) becomes

$$\begin{aligned} &\partial_t\left(c^0_{\mathrm{FN}} + \frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\left(c^0_{\mathrm{sN}} + \varepsilon^{2-\alpha}c^1_{\mathrm{sN}}\right)\right) + \frac{2Q}{3}\partial_x c^0_{\mathrm{FN}} - \varepsilon^{\alpha}\tilde{D}\partial_{xx}c^0_{\mathrm{FN}} \\ &\quad = -\varepsilon^{2-\alpha}\frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\frac{2Q}{45D}\partial_{xt}c^0_{\mathrm{sN}} \\ &\qquad - \varepsilon^{2-\alpha}\left\{\frac{T_{\mathrm{A}}}{T_{\mathrm{react}}}\partial_t B_{\mathrm{N}} + \partial_t A_{\mathrm{N}} + \frac{2Q}{3}\partial_x A_{\mathrm{N}} - D\varepsilon^{\alpha}\partial_{xx}A_{\mathrm{N}}\right\} \end{aligned} \tag{90}$$

---

[2] Note 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.

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

$$\tilde{D} = D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)} \tag{91}$$

Let

$$\mathscr{L}_1\{A, B\} = \frac{T_\mathrm{A}}{T_\mathrm{react}}\partial_t B + \partial_t A + \frac{2Q}{3}\partial_x A - D\varepsilon^\alpha \partial_{xx} A \tag{92}$$

$$\mathscr{L}_2\{A, B\} = \partial_t B - \frac{T_\mathrm{L}}{T_\mathrm{A}}(\Phi(A) - k_\mathrm{d}^* T_\mathrm{A} B) \tag{93}$$

There is no clear criterion for choosing the functions A_N and B_N. With the same arguing as in Section 3.1 we choose $A_\mathrm{N} = B_\mathrm{N} = 0$. This choice simplifies (90). The next simplification is to eliminate the term $\partial_{xt} c_\mathrm{sN}^0$ using Equation (81), i.e. $\frac{T_\mathrm{A}}{T_\mathrm{react}}\frac{\partial c_\mathrm{sN}^0}{\partial t} = \frac{T_\mathrm{L}}{T_\mathrm{react}}\left(\Phi(c_\mathrm{FN}^0) - k_\mathrm{d}^* T_\mathrm{A} c_\mathrm{sN}^0\right)$. Then

$$\varepsilon^{2-\alpha}\frac{T_\mathrm{A}}{T_\mathrm{react}}\frac{2Q}{45D}\partial_{xt} c_\mathrm{sN}^0 = \frac{2Q}{45D}\frac{T_\mathrm{T}}{T_\mathrm{react}}\partial_x \Phi(c_\mathrm{FN}^0) - \frac{2Q}{45D}\frac{T_\mathrm{T} T_\mathrm{A} k_\mathrm{d}^*}{T_\mathrm{react}}\partial_x c_\mathrm{sN}^0 \tag{94}$$

and Equation (90) reads

$$\begin{aligned} &\partial_t\left(c_\mathrm{FN}^0 + \frac{T_\mathrm{A}}{T_\mathrm{react}} c_\mathrm{sN}^\mathrm{eff}\right) + \frac{2Q}{3}\partial_x\left(c_\mathrm{FN}^0 + \frac{1}{15D}\frac{T_\mathrm{T}}{T_\mathrm{react}}\Phi(c_\mathrm{FN}^0)\right) \\ &= \varepsilon^\alpha\left(D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)}\right)\partial_{xx} c_\mathrm{FN}^0 \\ &+ \frac{2Q}{45D}\frac{T_\mathrm{A} T_\mathrm{T} k_\mathrm{d}^*}{T_\mathrm{react}}\partial_x c_\mathrm{sN}^\mathrm{eff} \ \text{ in } (0, +\infty) \times (0, T) \end{aligned} \tag{95}$$

where $c_\mathrm{sN}^\mathrm{eff} = c_\mathrm{s}^0 + \varepsilon^{2-\alpha} c_\mathrm{s}^1$. Next, after putting together the expansions for the ordinary differential equations from Equations (83)–(85) for surface concentration at $y = 1$, we obtain

$$\partial_t c_\mathrm{sN}^\mathrm{eff} = \frac{T_\mathrm{L}}{T_\mathrm{A}}\left(\Phi\left(c_\mathrm{FN}^0 + \varepsilon^{2-a} c_\mathrm{FN}^1|_{y=1}\right) - k_\mathrm{d}^* T_\mathrm{A} c_\mathrm{sN}^\mathrm{eff}\right) \tag{96}$$

$$c_\mathrm{FN}^1|_{y=1} = \frac{2}{45}\frac{Q}{D}\partial_x c_\mathrm{FN}^0 - \frac{T_\mathrm{A}}{3DT_\mathrm{react}}\partial_t c_\mathrm{sN}^\mathrm{eff} \tag{97}$$

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

The effective problem is now

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

$$c^1_{\mathrm{FN}}|_{y=1} = \frac{2}{45}\frac{Q}{D}\partial_x c^0_{\mathrm{FN}} - \frac{T_{\mathrm{A}}}{3DT_{\mathrm{react}}}\partial_t c^{\mathrm{eff}}_{\mathrm{sN}} \text{ in } (0,+\infty)\times(0,T),$$
$$c^0_{\mathrm{FN}}|_{x=0} = 0,\ c^0_{\mathrm{FN}}|_{t=0} = 1,\ c^{\mathrm{eff}}_{\mathrm{sN}}|_{t=0} = c_{s0},\ \partial_x c \in L^2((0,+\infty)\times(0,T)) \tag{98}$$

3.3 Infinite adsorption rate

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

$$c^\varepsilon = c^0_K(x,t;\varepsilon) + \varepsilon^{2-\alpha}c^1_K(x,y,t) + \varepsilon^{2(2-\alpha)}c^2_K(x,y,t) + \dots \tag{99}$$

After introducing (44) into Equation (37) we get

$$\varepsilon^0\{\partial_t c^0_K + Q(1-y^2)\partial_x c^0_K - D\partial_{yy}c^1_K\} + \varepsilon^{\alpha-2}\{\partial_t c^1_K + Q(1-y^2)\partial_x c^1_K - D\varepsilon^{2(\alpha-1)}\partial_{xx}c^0_K - D\varepsilon^\alpha\partial_{xx}c^1_K - D\partial_{yy}c^2_K\} = \mathcal{O}(\varepsilon^{2(2-\alpha)}) \tag{100}$$

In order to have Equation (100) 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

$$\begin{cases} -D\partial_{yy}c^1_K = -Q\left(\frac{1}{3} - y^2\right)\partial_x c^0_K - \left(\partial_t c^0_K + \frac{2Q\partial_x c^0_K}{3}\right) \text{ on } (0,1), \\ \partial_y c^1_K = 0 \text{ on } y=0 \text{ and } -D\partial_y c^1_K = K\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\partial_t c^0_K \text{ on } y=1 \end{cases} \tag{101}$$

for every $(x,t)\in(0,+\infty)\times(0,T)$. By the Fredholm's alternative, the problem (101) has a solution if and only if

$$\left(1 + K\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\right)\partial_t c^0_K + \frac{2Q\partial_x c^0_K}{3} = 0 \text{ in } (0,\ L)\times(0,\ T) \tag{102}$$

Unfortunately our initial and boundary data are incompatible and the hyperbolic Equation (102) has a discontinuous solution. Since the asymptotic expansion for c^ε involves derivatives of c^0_{K}, Equation (102) does not suit our needs. As before, we proceed by following an idea from Rubinstein and Mauri (1986) and suppose that

$$\left(1 + K\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\right)\partial_t c^0_K + \frac{2Q\partial_x c^0_K}{3} = \mathcal{O}(\varepsilon^{2-\alpha}) \text{ in } (0,+\infty)\times(0,T) \tag{103}$$

The hypothesis (103) will be justified *a posteriori*, after getting an equation for c^0_{K}.

Hence Equation (101) reduces to

$$\begin{cases} -D\partial_{yy}c^1_K = -Q\left(\frac{1}{3} - y^2\right)\partial_x c^0_K + K\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\partial_t c^0_K \text{ on } (0,1) \\ \partial_y c^1_K = 0 \text{ on } y=0 \text{ and } -D\partial_y c^1_K = K\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\partial_t c^0_K \text{ on } y=1 \end{cases} \tag{104}$$

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

$$c^1_K(x,y,t) = \frac{Q}{D}\left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180}\right)\partial_x c^0_K + \frac{K}{D}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\left(\frac{1}{6} - \frac{y^2}{2}\right)\partial_t c^0_K + C_{0K}(x,t) \tag{105}$$

where C_{0K} is an arbitrary function.

Let us go to the next order. Then we have

$$\begin{cases} -D\partial_{yy}c_K^2 = -Q(1-y^2)\partial_x c_K^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c_K^0 - \partial_t c_K^1 \\ \quad +D\varepsilon^{\alpha}\partial_{xx}c_K^1 - \varepsilon^{\alpha-2}\left(\left(1+K\dfrac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\right)\partial_t c_K^0 + \dfrac{2Q\partial_x c_K^0}{3}\right) \text{ on } (0,1), \\ \partial_y c_K^2 = 0 \text{ on } y=0 \text{ and } -D\partial_y c_K^2 = K\dfrac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\partial_t c_K^1 \text{ on } y=1 \end{cases} \tag{106}$$

for every $(x,\ t)\in(0,\ +\infty)\times(0,\ T)$. The problem (106) has a solution if and only if

$$\begin{aligned} &\partial_t c_K^0 + \frac{2Q\partial_x c_K^0}{3} + K\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\left(\partial_t c_K^0 + \varepsilon^{2-\alpha}\partial_t c_K^1|_{y=1}\right) + \varepsilon^{2-\alpha}\partial_t\left(\int_0^1 c_K^1\,\mathrm{d}y\right) \\ &\quad - \varepsilon^{\alpha}D\partial_{xx}c_K^0 + Q\varepsilon^{2-\alpha}\partial_x\left(\int_0^1 (1-y^2)\,c_K^1\,\mathrm{d}y\right) \\ &\quad = D\varepsilon^2\partial_{xx}\left(\int_0^1 c_K^1\,\mathrm{d}y\right) \text{ in } (0,+\infty)\times(0,T) \end{aligned} \tag{107}$$

Equation (107) is the equation for c_K^0. Next let us remark that

$$\int_0^1 c_K^1\,\mathrm{d}y = C_{0K}(x,t) \tag{108}$$

$$\int_0^1 (1-y^2)\,c_K^1\,\mathrm{d}y = \frac{2}{3}C_{0K}(x,t) - \frac{Q}{D}\frac{8}{945}\partial_x c_K^0 + \frac{2K}{45D}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\frac{\partial c_K^0}{\partial t} \tag{109}$$

$$\left.\frac{\partial c_K^1}{\partial t}\right|_{y=1} = \frac{2Q}{45D}\partial_{xt}c_K^0 - \frac{K}{3D}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\partial_{tt}c_K^0 + \partial_t C_{0K} \tag{110}$$

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 $C_{0K} = a\partial_t c_K^0 + b\partial_x c_K^0$ and after a short calculation we find that

$$C_{0K}(x,t) = \frac{1}{3D}\left(\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\right)^2\frac{K^2}{1+KT_{\mathrm{C}}/T_{\mathrm{L}}}\partial_t c_K^0 - \frac{2Q}{45D}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\frac{K(2+7KT_{\mathrm{C}}/T_{\mathrm{L}})}{(1+KT_{\mathrm{C}}/T_{\mathrm{L}})^2}\partial_x c_K^0 \tag{111}$$

Now c_K^1 takes the form

$$\begin{aligned} c_K^1(x,y,t) = {}& \frac{Q}{D}\left(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180} - \frac{2}{45}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\frac{K\left(2+7KT_{\mathrm{C}}/T_{\mathrm{L}}\right)}{\left(1+KT_{\mathrm{C}}/T_{\mathrm{L}}\right)^2}\right)\partial_x c_K^0 \\ & + \frac{K}{D}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\left(\frac{1}{6} + \frac{1}{3}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\frac{K}{1+KT_{\mathrm{C}}/T_{\mathrm{L}}} - \frac{y^2}{2}\right)\partial_t c_K^0 \end{aligned} \tag{112}$$

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

For $\alpha \geqslant 1$, $2 \geqslant 2(2-\alpha)$ and we are allowed to drop the term of order $\mathcal{O}(\varepsilon^2)$. Now the Equation (107) becomes

$$\left(1+\frac{KT_{\mathrm{C}}}{T_{\mathrm{L}}}\right)\partial_t c_K^0+\frac{2Q}{3}\partial_x c_K^0=\varepsilon^{\alpha}\tilde{D}\partial_{xx}c_K^0 \ \text{ in } \ (0,+\infty)\times(0,T) \tag{113}$$

with

$$\tilde{D}=D+\frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)}+\frac{4Q^2}{135D}\frac{T_{\mathrm{C}}}{T_{\mathrm{L}}}\frac{K\left(2+7KT_{\mathrm{C}}/T_{\mathrm{L}}\right)}{\left(1+KT_{\mathrm{C}}/T_{\mathrm{L}}\right)^2}\varepsilon^{2(1-\alpha)} \tag{114}$$

Now the problem (106) becomes

$$\left\{\begin{array}{l}
-D\partial_{yy}c_K^2=-\dfrac{Q^2}{D}\partial_{xx}c_K^0\left\{\dfrac{8}{945}+(1-y^2)\left(\dfrac{y^2}{6}-\dfrac{y^4}{12}-\dfrac{7}{180}\right)\right\}\\
+\partial_{xt}c_K^0\dfrac{Q\tilde{K}}{D}\left\{\dfrac{2}{45}-(1-y^2)\left(\dfrac{1}{6}-\dfrac{y^2}{2}\right)\right\}+\dfrac{2Q\tilde{K}}{45D}\left(1-\dfrac{\tilde{K}(7\tilde{K}+2)}{\left(1+\tilde{K}\right)^2}\right)\partial_{xt}c_K^0\\
-\left(\dfrac{\tilde{K}^2}{3D}-\dfrac{\tilde{K}^3}{3D(1+\tilde{K})}\right)\partial_{tt}c_K^0-\left(\dfrac{y^2}{6}-\dfrac{y^4}{12}-\dfrac{7}{180}\right)\partial_{xt}c_K^0\dfrac{Q}{D}\\
+\dfrac{Q\tilde{K}\left(\dfrac{1}{3}-y^2\right)}{D(1+\tilde{K})}\left(\dfrac{2Q}{45}\partial_{xx}c_K^0\dfrac{7\tilde{K}+2}{1+\tilde{K}}-\dfrac{\tilde{K}}{3}\partial_{xt}c_K^0\right)-\left(\dfrac{1}{6}-\dfrac{y^2}{2}\right)\partial_{tt}c_K^0\dfrac{\tilde{K}}{D}\}\\
\text{on } \ (0,1), \ \ \partial_y c_K^2=0 \ \text{ on } \ y=0 \ \text{ and } \ \text{on } \ y=1\\
-\mathrm{D}\partial_y c_K^2=\dfrac{2\tilde{K}Q}{45D}\left(1-\dfrac{\tilde{K}(7\tilde{K}+2)}{\left(1+\tilde{K}\right)^2}\right)\partial_{xt}c_K^0-\dfrac{\tilde{K}^2}{3D}\left(1-\dfrac{\tilde{K}}{1+\tilde{K}}\right)\partial_{tt}c_K^0
\end{array}\right. \tag{115}$$

where $\tilde{K}=KT_{\mathrm{C}}/T_{\mathrm{L}}$.

If we choose c^2 such that $\int_0^1 c^2\mathrm{d}y=0$, then

$$\begin{aligned}
c^2(x,y,t)=&-\frac{Q^2}{D^2}\partial_{xx}c_K^0\left(\frac{281}{453600}+\frac{23}{1512}y^2-\frac{37}{2160}y^4+\frac{1}{120}y^6-\frac{1}{672}y^8\right)\\
&+\frac{Q}{D^2}\partial_{xt}c_K^0\left(\frac{31}{7560}-\frac{7}{360}y^2+\frac{y^4}{72}-\frac{y^6}{360}\right)\\
&-\frac{Q}{D^2}\left(-\frac{y^4}{12}+\frac{y^2}{6}-\frac{7}{180}\right)\left(\frac{2Q}{45}\partial_{xx}c_K^0\frac{\tilde{K}(7\tilde{K}+2)}{\left(1+\tilde{K}\right)^2}-\frac{\tilde{K}^2}{3(1+\tilde{K})}\partial_{xt}c_K^0\right)\\
&+\frac{Q\tilde{K}}{D^2}\partial_{xt}c_K^0\left(\frac{y^6}{60}-\frac{y^4}{18}+\frac{11y^2}{180}-\frac{11}{945}\right)+\frac{\tilde{K}}{2D^2}\partial_{tt}c_K^0\left(-\frac{y^4}{12}+\frac{y^2}{6}-\frac{7}{180}\right)\\
&-\left(\left(\frac{\tilde{K}Q}{45D^2}+\frac{Q\tilde{K}}{45D^2}\frac{\tilde{K}(7\tilde{K}+2)}{(1+\tilde{K})^2}\right)\partial_{xt}c_K^0\right.\\
&\left.-\left(\frac{\tilde{K}^2}{6D^2}-\frac{\tilde{K}^3}{6D^2(1+\tilde{K})}\right)\partial_{tt}c_K^0\right)\left(\frac{1}{3}-y^2\right)
\end{aligned} \tag{116}$$

3.4 An irreversible very fast first order reaction

The goal of this subsection is to compare our approach with the center manifold technique from Balakotaiah and Chang (1995). We study the 2D variant of the model from Balakotaiah and Chang (1995, pp. 58–61), and we keep the molecular diffusion. Then the corresponding analog of the problem (6)–(10), with $K = +\infty$, is

$$\frac{\partial c^\varepsilon}{\partial t} + Q\big(1 - y^2\big)\frac{\partial c^\varepsilon}{\partial x} = D\varepsilon^\alpha \frac{\partial^2 c^\varepsilon}{\partial x^2} + D\varepsilon^{\alpha-2}\frac{\partial^2 c^\varepsilon}{\partial y^2} \tag{117}$$

$$-D\varepsilon^{\alpha-2}\left.\frac{\partial c^\varepsilon}{\partial x}\right|_{y=1} = k\varepsilon^{\alpha-2}c^\varepsilon\big|_{y=1} \text{ and } \left.\frac{\partial c^{\,\varepsilon}}{\partial y}\right|_{y=0} = 0 \tag{118}$$

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

$$c^\varepsilon = \mathrm{e}^{-\lambda_0\varepsilon^{\alpha-2}t}\big(c^0(x,t;\varepsilon)\psi_0(y) + \varepsilon^{2-\alpha}c^1 + \varepsilon^{2(2-\alpha)}c^2 + \ldots\big) + \mathcal{O}(\mathrm{e}^{-\lambda_1\varepsilon^{\alpha-2}t}) \tag{119}$$

After introducing Equation (119) into Equation (117) we get

$$\begin{aligned}
&\varepsilon^{\alpha-2}\big\{-\lambda_0 c^0\psi_0 - D\partial_{yy}\psi_0 c^0\big\} + \varepsilon^0\big\{\psi_0(y)\big(\partial_t c^0 + Q(1-y^2)\partial_x c^0\big)\\
&\quad -D\partial_{yy}c^1 - \lambda_0 c^1\big\} + \varepsilon^{2-\alpha}\{\partial_t c^1 + Q(1-y^2)\partial_x c^1\\
&\quad - D\varepsilon^{2(\alpha-1)}\partial_{xx}c^0\psi_0(y) - D\varepsilon^\alpha\partial_{xx}c^1 - D\partial_{yy}c^2 - \lambda_0 c^2\}\\
&\quad = \mathcal{O}(\varepsilon^{2(2-\alpha)}) = \mathcal{O}\left(\left(\frac{T_\mathrm{T}}{T_\mathrm{L}}\right)^2\right)
\end{aligned} \tag{120}$$

To satisfy Equation (120) 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

$$\begin{cases} -D\partial_{yy}\psi_0 = \lambda_0\psi_0 \text{ on } (0,1),\\ \partial_y\psi_0 = 0 \text{ on } y = 0 \text{ and } -D\partial_y\psi_0 = k\psi_0 \text{ on } y = 1 \end{cases} \tag{121}$$

for every $(x, t) \in (0, +\infty) \times (0, T)$. This spectral problem[4] has one-dimensional (1D) proper space, spanned by $\psi_0(y) = \sqrt{2}\cos(\sqrt{\lambda_0/D}y)$, where the eigenvalue λ_0 is the first positive root of the equation $\sqrt{\lambda_0/D}\ \tan(\sqrt{\lambda_0/D}) = k/D$.

Next, the ε^0 problem reads

$$\begin{cases} -D\partial_{yy}c^1 - \lambda_0 c^1 = -\psi_0(y)\big(Q(1-y^2)\partial_x c^0 + \partial_t c^0\big) \text{ on } (0,1),\\ \partial_y c^1 = 0 \text{ on } y = 0 \text{ and } -\mathrm{D}\partial_y c^1 = kc^1 \text{ on } y = 1 \end{cases} \tag{122}$$

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

$$\partial_t c^0 + Q\left(\int_0^1 \psi_0^2(y)(1-y^2)\,\mathrm{d}y\right)\partial_x c^0 = 0 \tag{123}$$

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.

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[4] References for spectral problems for partial differential equations are e.g. Vladimirov (1996) and Wloka (1987).

We proceed by using again the idea in Rubinstein and Mauri (1986) and suppose that expression (123) is of the next order in our asymptotic expansion:

$$\psi(y)\left(\partial_t c^0 + Q\left(\int_0^1 \psi_0^2(y)(1-y^2)\,\mathrm{d}y\right)\partial_x c^0\right) = \mathcal{O}(\varepsilon^{2-\alpha}) \text{ in } (0,+\infty)\times(0,T) \tag{124}$$

and justify it *a posteriori*, after getting an equation for c^0. Following Balakotaiah and Chang (1995) we set $\alpha_{00} = \int_0^1 \psi_0^2(y)(1-y^2)\,\mathrm{d}y$.

Combining Equations (122) and (123) and using hypothesis (124) leads us to consider

$$\begin{cases} -D\partial_{yy}c^1 - \lambda_0 c^1 = -Q\psi_0(y)\big((1-y^2)-\alpha_{00}\big)\partial_x c^0 \text{ on } (0,1), \\ -D\partial_y c^1 = kc^1 \text{ on } y=1, \text{ and } \partial_y c^1 = 0 \text{ on } y=0 \end{cases} \tag{125}$$

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

$$c^1(x,y,t) = Q\partial_x c^0 q_0(y) + \psi_0(y)A(x,t) \tag{126}$$

where A is arbitrary and q_0 is the solution for Equation (125) with $Q\partial_x c$ replaced by 1, such that $\int_0^1 \psi_0(y)q_0(y)\,\mathrm{d}y = 0$.

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

$$\begin{cases} -D\partial_{yy}c^2 - \lambda_0 c^2 = -\partial_t c^1 - Q(1-y^2)\partial_x c^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c^0\psi_0(y) \\ +\varepsilon^{\alpha}D\partial_{xx}c^1 - \varepsilon^{\alpha-2}\psi_0(y)\big(\partial_t c^0 + Q\alpha_{00}\partial_x c^0\big) \text{ on } (0,1), \\ -D\partial_y c^2 = kc^2 \text{ on } y=1 \text{ and } \partial_y c^2 = 0 \text{ on } y=0 \end{cases} \tag{127}$$

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

$$\partial_t c^0 + Q\alpha_{00}\partial_x c^0 - \left(\varepsilon^{\alpha}D - Q^2\left(\int_0^1 \psi_0(y)q_0(y)\,(1-y^2)\,\mathrm{d}y\right)\right)\partial_{xx}c^0 = 0 \tag{128}$$

in $(0, +\infty)\times(0, T)$. We note that the arbitrary function A enters into Equation (128) 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 expansion,[5] q_0 is given by

$$q_0(y) = -\sum_{k=1}^{+\infty} \frac{\alpha_{0k}\psi_k(y)}{\lambda_k - \lambda_0} \tag{129}$$

where $\{\lambda_k, \psi_k\}_{k\geq 0}$ is the orthonormal basis defined by the spectral problem (121). Now we see that

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

and Taylor's contribution to the effective diffusion coefficient is strictly positive. We note that this result confirms the calculations from Balakotaiah and

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[5] For an elementary presentation of the Hilbert–Schmidt expansion see Vladimirov (1996).

Chang (1995, pp. 58–61). Since

$$\lambda_0 = \frac{T_{\rm L}}{T_{\rm react}} k\psi_0(1)$$

in the limit when $T_{\rm react} \gg T_{\rm T}$ we obtain the effective Equation (18). In fact our calculations indicate the relationship between the center manifold approach and approach using Bloch's waves and a factorization principle for the two-scale convergence (see the recent papers by Allaire and Raphael, 2006, 2007).

4. NUMERICAL TESTS

For carrying out the numerical tests we have chosen the data from the original paper by Taylor (1993). Analogous data are taken in the presence of chemistry.

The representative case considered in Taylor (1993) 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

$$C_{\rm m}(x,t) = \frac{M}{2a^2\sqrt{\pi^3 kt}} \exp\left\{ -\frac{(x - u_0 t/2)^2}{4kt} \right\} \tag{130}$$

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:

$$c^*|_{x^*=0} = c_{\rm R} \text{ and } c^*|_{t^*=0} = 0 \tag{131}$$

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

$$\hat{c}|_{t^*=0} = 0 \tag{132}$$

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

$$\partial_{x^*} c^*|_{x^*=2L_{\rm R}} = 0 \tag{133}$$

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 1D 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 a 1D 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 Péclet and Damkohler numbers. We solve it using two independent methods.

In the first approach we use the package *FreeFem++* by Pironneau, Hecht and Le Hyaric. For more information we refer to http://www.freefem.org/ff++/. For the problem (6)–(10) the method of characteristics from Pironneau (1988) 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:

  $$\frac{\partial c}{\partial t} + (\vec{q}.\nabla)c = D\varepsilon^{\alpha}\partial_{xx}c + D\varepsilon^{\alpha-2}\partial_{yy}c = f(x,y,t) \tag{134}$$

  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:

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

- Space discretization:

  One of the characteristics of our problem is the presence of a smeared front. 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 Courant Friedrichs Lewy (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, e.g. Quarteroni and Valli, 1994, Chapter 14). We call this method *SlopeLimit*.

A similar procedure is considered for the upscaled, 1D 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 (Taylor, 1993) the problem is axially symmetric with zero flux at the lateral boundary. The solute is transported by Poiseuille velocity.

For simplicity we will consider the flow through the 2D slit $\Omega^* = (0, +\infty) \times (0, H)$. To have a 2D problem equivalent to the case (B) from Taylor's article, we reformulate the characteristic velocity and the radius. Obviously we have

$$Q^* = \frac{3}{4} u_0, \qquad H = a\sqrt{\frac{35}{32}} \tag{135}$$

Then we start with

4.1.1 CASE A: First example from Taylor's paper with the time of flow: $t^* = 11,220$ s

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

1. The 2D problem (1), (2), (131). It is solved using the FreeFem++ package and with (SlopeLimit). On the images the solution is denoted (pbreel).
2. The effective problem

$$\partial_{t^*} c^{\text{Tay}} + \frac{2Q^*}{3} \partial_{x^*} c^{\text{Tay}} = D^* \left(1 + \frac{8}{945} Pe_{\text{T}}^2\right) \partial_{x^* x^*} c^{\text{Tay}} \text{ for } x, t > 0 \tag{136}$$

$$c^{\text{Tay}}|_{x=0} = 1 \text{ and } c^{\text{Tay}}|_{t=0} = 0 \tag{137}$$

   On the images its solution is denoted by (taylor).
3. The problem obtained by taking the simple mean over the vertical section:

$$\partial_{t^*} c^{\text{moy}} + \frac{2Q^*}{3} \partial_{x^*} c^{\text{moy}} - D^* \partial_{x^* x^*} c^{\text{moy}} = 0 \text{ in } (0, +\infty) \times (0, T) \tag{138}$$

   with initial/boundary conditions (137). On the images its solution is denoted by (moyenne).

   Parameter values are at Table 1.

We note that Table 2 is analogous to Table 2, page 196 from Taylor's (1993) article.

Note that in the absence of the chemical reactions we can solve explicitly the problems (136)–(137), respectively (138)–(137). With $\bar{Q} = 2Q^*/3$ and

Table 1 Case A. Parameter values for the longest time example ($t^* = 11{,}220$ s) from Taylor's paper

Parameters	Values
Width of the slit: H	2.635×10^{-4} m
Characteristic length: L_R	0.319 m
$\varepsilon = H/L_R$	0.826×10^{-3}
Characteristic velocity: Q^*	4.2647×10^{-5} m/s
Diffusion coefficient: D^*	1.436×10^{-10} m^2/s
Longitudinal Péclet number: $Pe = L_R Q^*/D^* =$	0.94738×10^5
$\alpha = \log Pe/\log(1/\varepsilon) =$	1.614172
Transversal Péclet number: $Pe_T = HQ^*/D^* =$	0.7825358×10^2

Table 2 Comparison between the concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^*\,\mathrm{d}z$ for the Case A at the time $t^* = 11{,}220\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$ (SlopeLimit)	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$ (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

$\bar{D} = D^*(1 + (8/945)\,Pe_{\mathrm{T}}^2)$, the solution for (136)–(137) reads

$$c^{\mathrm{Tay}}(x,t) = 1 - \frac{1}{\sqrt{\pi}}\left[\exp\left\{\frac{\bar{Q}x}{\bar{D}}\right\}\int_{(x+\bar{Q}t)/(2\sqrt{\bar{D}t})}^{\infty} \mathrm{e}^{-\eta^2}\mathrm{d}\eta + \int_{(x-\bar{Q}t)/(2\sqrt{\bar{D}t})}^{\infty} \mathrm{e}^{-\eta^2}\mathrm{d}\eta\right] \tag{139}$$

For the problems (138) and (137), everything is analogous.

4.1.2 CASE B: second example from Taylor's paper with the time of flow: $t^* = 240\,\mathrm{s}$

We solve the same equations as in Section 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 with the physical solution even without adding the correctors (Table 4). Parameters are given at Table 3.

Since no chemistry is considered here, an explicit solution can be given in this case as well and it is given by Equation (139). 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 Section 4.1.2, the transversal Péclet number is 10 times larger than in the case from Section 4.1.1, explaining the difference in the quality of the approximation.

Table 3 Case B. Parameter values for the characteristic time 240 s for the second example from Taylor's paper

Parameters	Values
Width of the slit: H	$2.635 \times 10^{-4}\,\mathrm{m}$
Characteristic length: L_R	$0.632\,\mathrm{m}$
$\varepsilon = H/L_\mathrm{R}$	0.41693×10^{-3}
Characteristic velocity: Q^*	$0.393 \times 10^{-2}\,\mathrm{m/s}$
Diffusion coefficient: D^*	$0.6 \times 10^{-9}\,\mathrm{m^2/s}$
Longitudinal Péclet number: $Pe = L_\mathrm{R} Q^*/D^* =$	4.1396×10^{6}
$\alpha = \log Pe/ \log (1/\varepsilon) =$	1.95769
Transversal Péclet number: $Pe_\mathrm{T} = HQ^*/D^* =$	1.72592×10^{3}

Table 4 Comparison between the concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^* dz$ for the Case B, corresponding to the second example from Taylor's paper, at the time $t^* = 240\,\mathrm{s}$

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

4.2 Examples with the linear surface adsorption–desorption reactions

In the case of the full 2D problem with linear surface adsorption–desorption reactions (1), (2), (131) and (132), we present two tests.

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

This first case is with slighty modified data of the Case A from Section 4.1.1. We just modify the width of the channel, the diffusivity and choose a shorter time of the flow (Table 5).

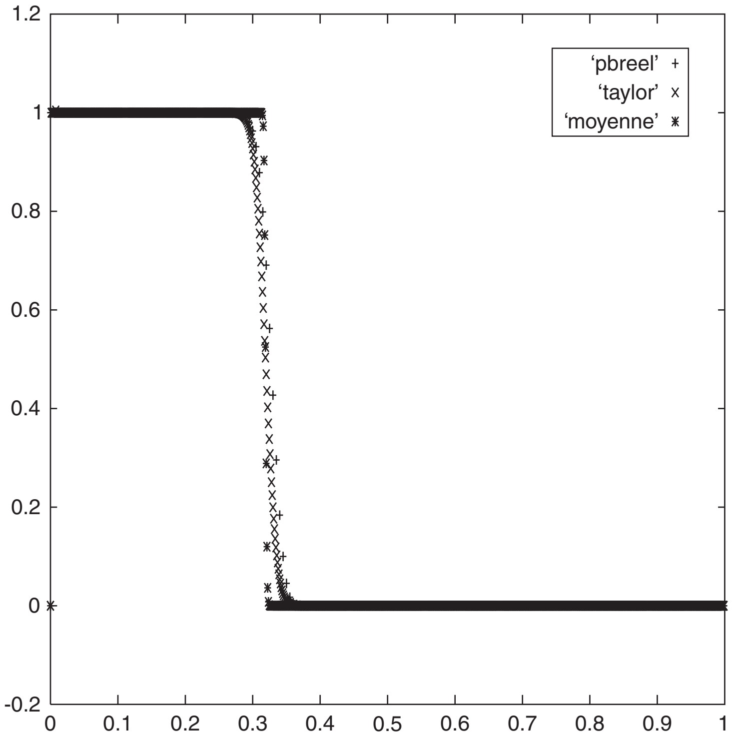

Figure 1 Comparison between concentration from Taylor's paper (taylor), from the original problem (pbreel) and the simple average (moyenne) at $t = 11{,}220$ s.

We note that our scaling impose $\hat{k}^* = \varepsilon Q^*$ and $K_\mathrm{e} = H$. This gives $Da_\mathrm{T} = \varepsilon Pe_\mathrm{T}$. Now the system to solve is Equations (14) and (15):

$$\partial_{t^*}\left(c^* + \frac{\hat{c}}{H}\right) + \left(\frac{2Q^*}{3} + \frac{2Q^* Da_\mathrm{T}}{45}\right)\partial_{x^*} c^* \\ - D^*\left(1 + \frac{8}{945} Pe_\mathrm{T}^2\right)\partial_{x^* x^*} c^* = \frac{2Q^* Da_\mathrm{T}}{45 K_\mathrm{e}} \partial_{x^*}\hat{c}$$

$$\left(1 + \frac{1}{3} Da_\mathrm{T}\right)\partial_{t^*}\hat{c} = \hat{k}^*\left(c^* + \frac{2HPe_\mathrm{T}}{45}\partial_{x^*} c^* - \frac{\hat{c}}{K_\mathrm{e}}\right)$$

and no explicit solution is known. We should compare between the solutions to (1)–(2) with the initial/boundary conditions (137), $\hat{c}|_{t=0} = 0$ (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.

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 2D problem, which is not the case with the simple mean.

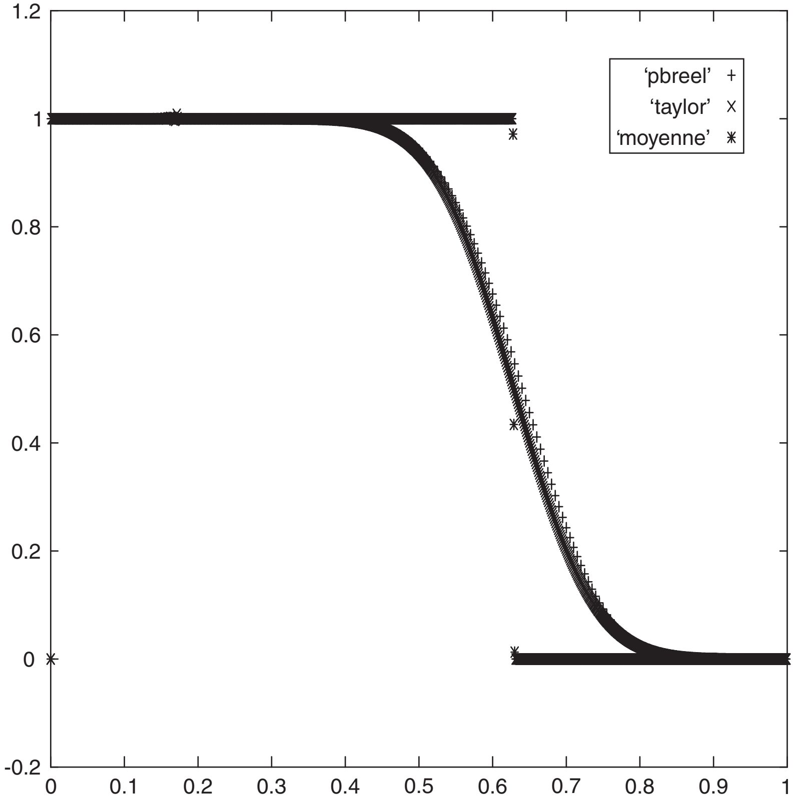

Figure 2 Case B: second case from Taylor's paper. Comparison between the solution for the original problem (pbreel), the solution to the upscaled problem (taylor) and the solution for the problem obtained by taking a simple section average (moyenne) at $t^* = 240\,\text{s}$.

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

Parameters	Values
Width of the slit: H	$0.5 \times 10^{-2}\,\text{m}$
Characteristic length: L_R	$0.632\,\text{m}$
$\varepsilon = H/L_\text{R}$	0.7911×10^{-2}
Characteristic velocity: Q^*	$0.3 \times 10^{-2}\,\text{m/s}$
Diffusion coefficient: D^*	$0.2 \times 10^{-6}\,\text{m}^2/\text{s}$
Longitudinal Péclet number: $Pe = L_\text{R}Q^*/D^* =$	9.48×10^3
$\alpha = \log Pe/\log(1/\varepsilon) =$	1.670972
Transversal Peclet number: $\mathbf{Pe}_T = HQ^*/D^* =$	75
Characteristic reaction velocity: $\hat{k}^* = \varepsilon Q^* =$	$0.237 \times 10^{-4}\,\text{m/s}$
Transversal Damkohler number: $Da_\text{T} = \varepsilon(HQ^*/D^*) =$	0.5933

Table 6 Comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^*\,\mathrm{d}z$ for the linear surface adsorption–desorption reactions, Case A2, at the time $t^* = 100\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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 7 Comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^*\,\mathrm{d}z$ for the linear surface adsorption–desorption reactions, Case A2, at the time $t^* = 211\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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 8 Comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^*\,\mathrm{d}z$ for the linear surface adsorption–desorption reactions, Case A2, at the time $t^* = 350\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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

Adding correctors would get us even closer to the solution for the 2D problem.

Figures 3, 4 and 5 show the simulation by FreeFm++ in the case from Section 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: $t^* = 240$ s

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

4.3 An example with the first order irreversible surface reaction

In this situation we take $K = K_{\mathrm{e}}/H \to +\infty$. Equation (1) does not change but the boundary condition (2) becomes

$$-D^*\partial_z c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{k}^* c^* \quad \text{on} \ z = \pm H \tag{140}$$

The system (14)–(15) becomes

$$\begin{cases} \partial_{t^*} c^* + \left(\dfrac{2Q^*}{3} + \dfrac{4Q^* Da_{\mathrm{T}}}{45}\right)\partial_{x^*} c^* \\ \quad + \dfrac{\hat{k}^*}{H}\left(1 - \dfrac{Da_{\mathrm{T}}}{3}\right)c^* - D^*\left(1 + \dfrac{8}{945} Pe_{\mathrm{T}}^2\right)\partial_{x^*x^*} c^* = 0 \\ \text{in } (0, +\infty) \times (0, T) \end{cases} \tag{141}$$

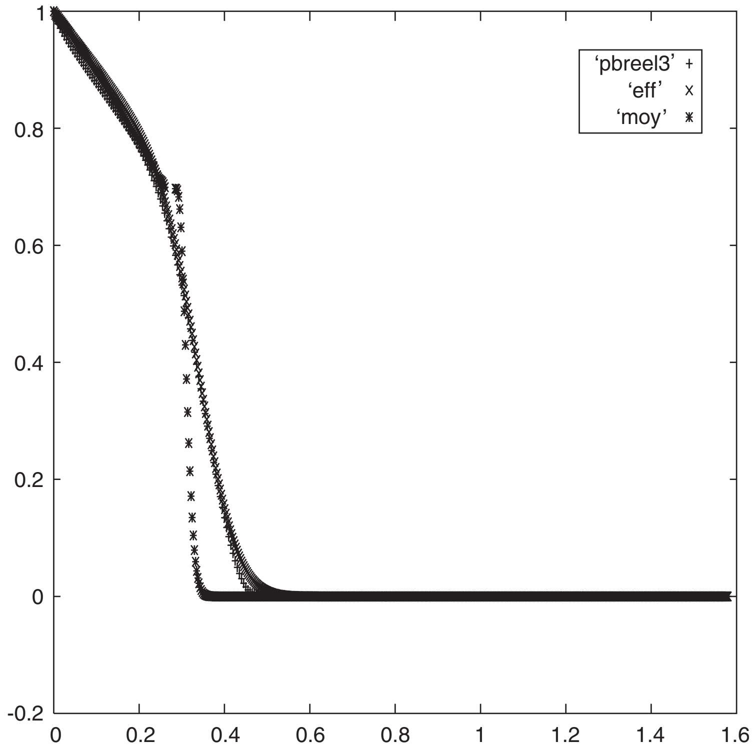

Figure 3 Comparison between the volume concentrations c^{Tay}, $(1/H)\int_0^H c^* \mathrm{d}z$ and c^{moy} for the linear surface adsorption–desorption reactions, Case A2, obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the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

and the equation corresponding to a simple mean reads

$$\begin{cases} \partial_{t^*} c^{\mathrm{moy}} + \dfrac{2Q^*}{3} \partial_{x^*} c^{\mathrm{moy}} + \dfrac{\hat{k}}{H} c^{\mathrm{moy}} - D^* \partial_{x^*x^*} c^{\mathrm{moy}} = 0 \\ \text{in } (0, +\infty) \times (0, T) \end{cases} \tag{142}$$

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

For this particular reactive flow, the problem (141) has an explicit solution for the following initial/boundary data:

$$c^*|_{x^*=0} = 0 \ \text{ and } \ c^*|_{t^*=0} = 1 \tag{143}$$

It reads

$$c^*(x^*, t^*) = \mathrm{e}^{-k_1 t^*} \left(1 - \frac{1}{\sqrt{\pi}} \left[\mathrm{e}^{\frac{2Q_1 x^*}{3D_1}} \int_{\frac{x + 2t^* Q_1/3}{2\sqrt{D_1 t^*}}}^{+\infty} \mathrm{e}^{-\eta^2}\, \mathrm{d}\eta + \int_{\frac{x - 2t^* Q_1/3}{2\sqrt{D_1 t^*}}}^{+\infty} \mathrm{e}^{-\eta^2}\, \mathrm{d}\eta \right] \right) \tag{144}$$

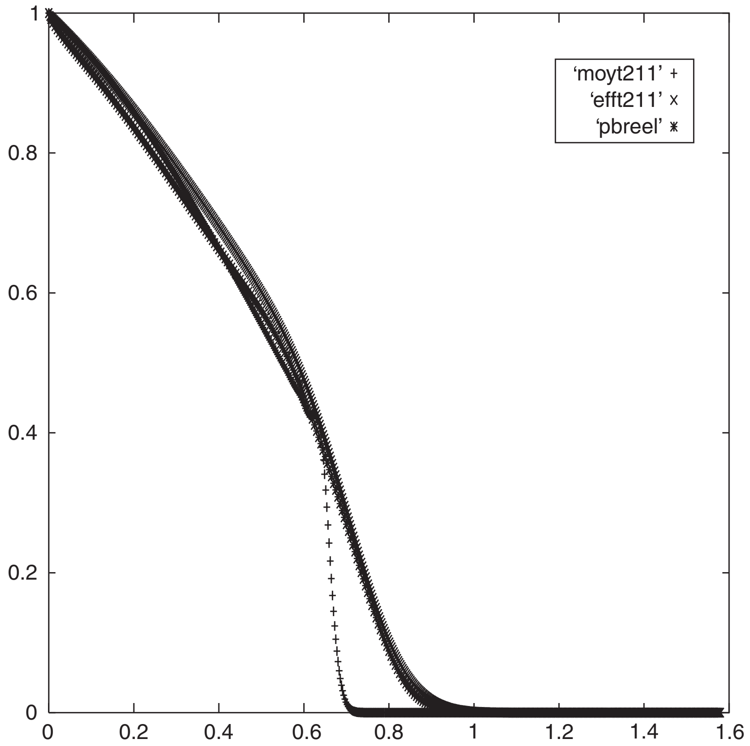

Figure 4 Comparison between the volume concentrations c^{Tay}, $(1/H)\int_0^H c^*\,\mathrm{d}z$ and c^{moy} for the linear surface adsorption–desorption reactions, Case A2, obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and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

where

$$k_1 = \frac{\hat{k}^*}{H}\left(1 - \frac{Da_{\mathrm{T}}}{3}\right), \qquad Q_1 = Q^*\left(1 + \frac{2Da_{\mathrm{T}}}{15}\right) \text{ and } D_1 = D^*\left(1 + \frac{8}{945}\,Pe_{\mathrm{T}}^2\right)$$

For problem (142) we also impose the initial/boundary condition (143) and c^{moy} is given by the formula (144) as well, but with $k_1 = \hat{k}^*/H$, $Q_1 = Q^*$ 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 $100\,\mathrm{s}$.

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

4.4 Numerical experiments in the case of an infinite adsorption rate

In this subsection we solve Equation (42)

$$(1 + Da_K)\frac{\partial c_K^{*,\mathrm{eff}}}{\partial t^*} + \frac{2Q^*}{3}\frac{\partial c_K^{*,\mathrm{eff}}}{\partial x^*} = D^*\left(1 + \frac{4}{135}Pe_{\mathrm{T}}^2\left[\frac{2}{7} + \frac{Da_K(2 + 7Da_K)}{(1 + Da_K)^2}\right]\right)\frac{\partial^2 c_K^{*,\mathrm{eff}}}{\partial (x^*)^2}$$

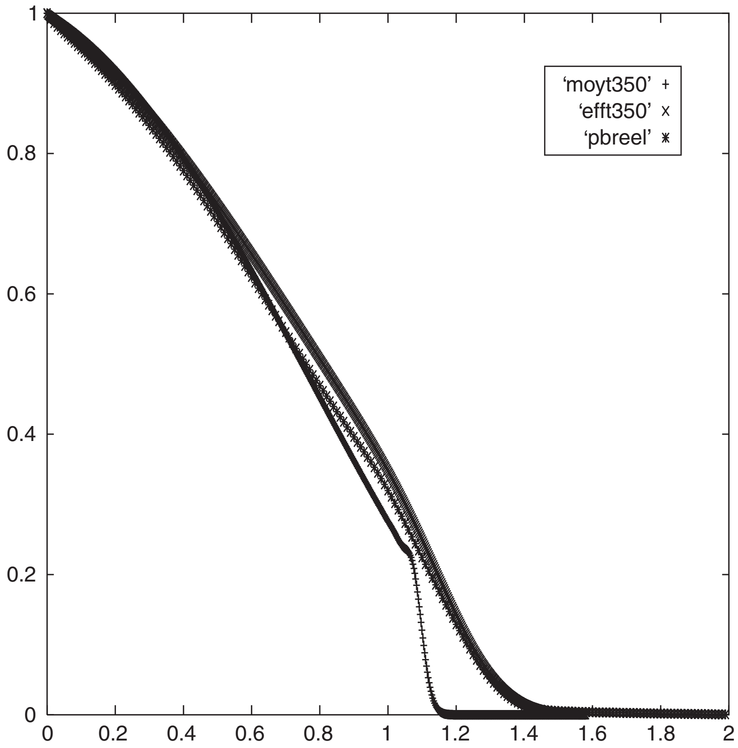

Figure 5 Comparison between the volume concentrations c^{Tay}, $(1/H)\int_0^H c^*\,dz$ and c^{moy} for the linear surface adsorption–desorption reactions, Case A2, obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at time $t^* = 350$ s.

with the initial/boundary data

$$c_K^{*,\mathrm{eff}}|_{x^*=0} = 0 \text{ and } c_K^{*,\mathrm{eff}}|_{t^*=0} = 1 \tag{145}$$

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 $t^* = 863$, 2,877 and 5,755 s.

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.

5. CONCLUSIONS AND PERSPECTIVES

In this chapter we have justified by direct numerical simulation the effective (or upscaled) equations obtained using the techniques of anisotropic singular

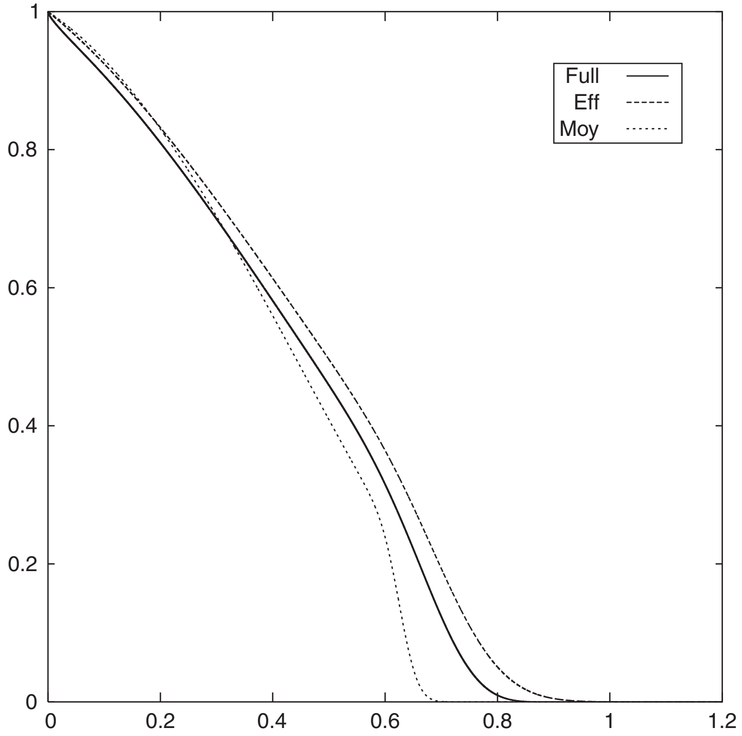

Figure 6 Volume concentrations (linear surface adsorption–desorption reactions, Case B2): Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (full) and the concentration coming from the simple average (moy)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

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

Parameters	Values
Width of the slit: H	$2.635 \times 10^{-4}\,\mathrm{m}$
Characteristic length: L_R	$0.632\,\mathrm{m}$
$\varepsilon = H/L_R$	0.41693×10^{-3}
Characteristic velocity: Q^*	$0.393 \times 10^{-2}\,\mathrm{m/s}$
Diffusion coefficient: D^*	$1.2 \times 10^{-8}\,\mathrm{m^2/s}$
Longitudinal Péclet number: $Pe = L_R Q^*/D^* =$	2.0698×10^5
$\alpha = \log Pe/\log(1/\varepsilon) =$	1.572789
transversal Péclet number: $Pe_T = HQ^*/D^* =$	86.296

Table 10 Case of the first order irreversible surface reaction ($K = +\infty$): comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\ \int_0^H c^*\,\mathrm{d}z$ at the time $t^* = 50\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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 11 Case of the first order irreversible surface reaction ($K = +\infty$): comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\ \int_0^H c^*\,\mathrm{d}z$ at the time $t^* = 70\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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 12 Case of the first order irreversible surface reaction ($K = +\infty$): comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^* \, dz$ at the time $t^* = 100$ s

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^* \mathrm{d}z$
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

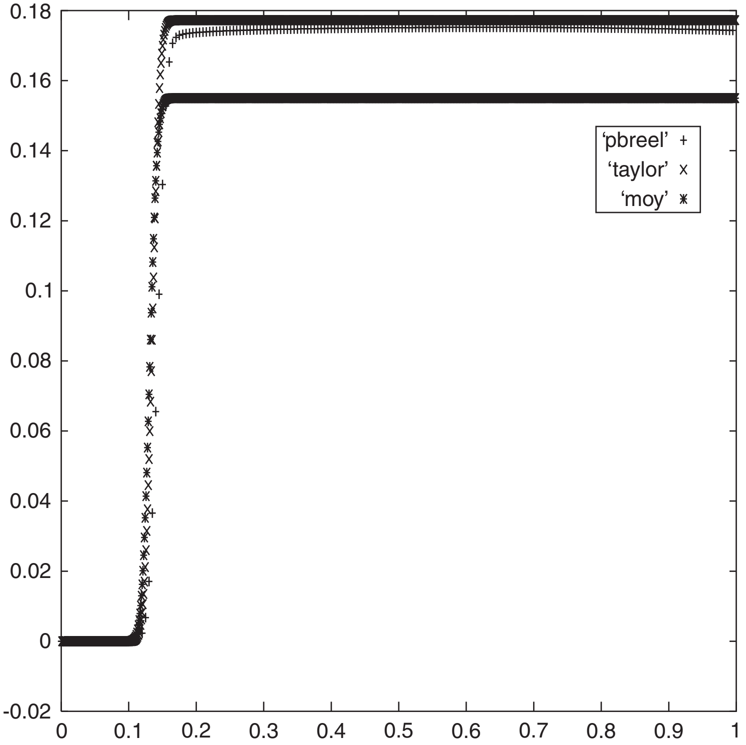

Figure 7 Case of the first order irreversible surface reaction ($K = +\infty$): Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at $t = 50$ s.

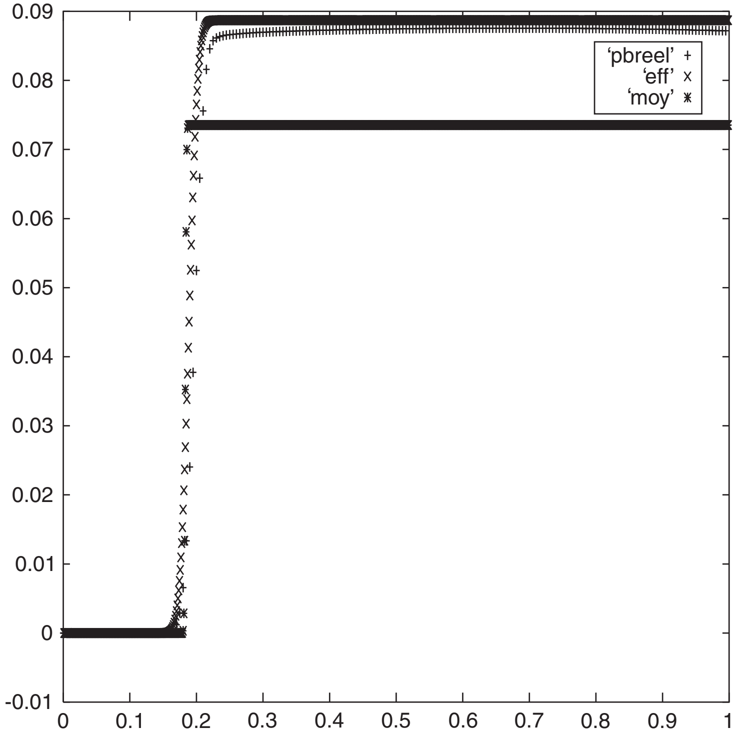

Figure 8 Case of the first order irreversible surface reaction ($K = +\infty$): Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel) and the concentration coming from the simple average (moy) at $t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

perturbation for the partial differential equations describing reactive flows through a slit under dominant Péclet and Damkohler numbers.

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

Nevertheless, there is the possibility of obtaining hyperbolic models, at same order of precision, $\mathcal{O}(\varepsilon^{2(2-\alpha)})$. We note that such models where derived by Balakotaiah and Chang (2003) for a number of practical situations. In several articles, Balakotaiah et al. used the Liapounov–Schmidt reduction coupled with perturbation, to develop multi-mode models, which exhibit hyperbolic behavior (Balakotaiah, 2004; Chakraborty and Balakotaiah, 2005). Our comparison calculation from Section 3.1 shows that formally multi-mode models are of the same order as our parabolic effective equations. This was already argued in Balakotaiah and Chang (2003). It would be interesting to calculate the error estimate for the multi-mode hyperbolic models, introduced

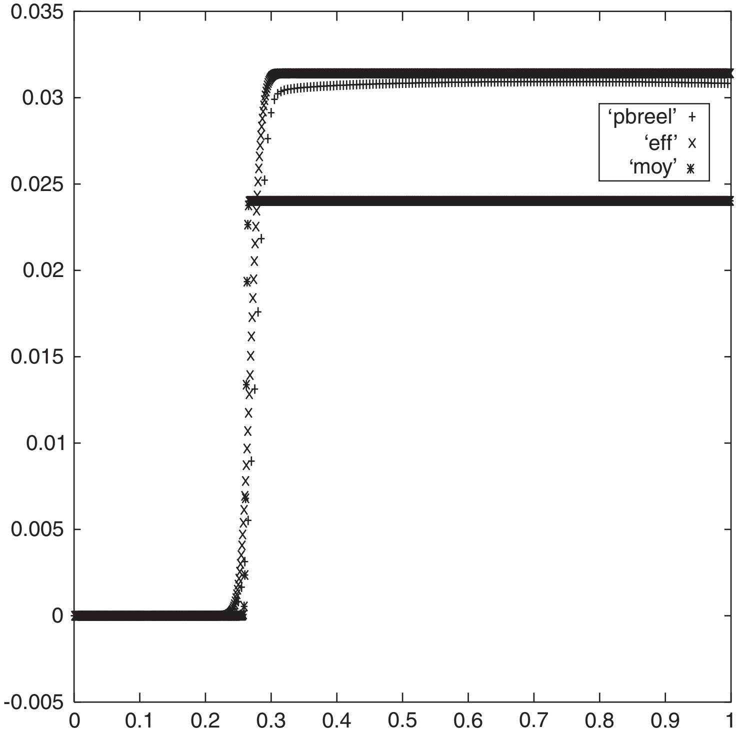

Figure 9 Case of the first order irreversible surface reaction ($K = +\infty$): Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel) and the concentration coming from the simple average (moy) at $t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

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

Parameters	Values
Width of the slit: H	5×10^{-3} m
Characteristic length: L_R	0.8632 m
$\varepsilon = H/L_R$	5.7924001×10^{-3}
Characteristic velocity: Q^*	0.3×10^{-3} m/s
Diffusion coefficient: D^*	$2 \times 10^{-7}\,\mathrm{m}^2/\mathrm{s}$
Longitudinal Péclet number: $Pe_T = L_R Q^*/D^* =$	1.2948×10^5
$\alpha = \log Pe/\log(1/\varepsilon) =$	1.83815052
Transversal Péclet number: $Pe_T = HQ^*/D^* =$	75
Transversal Damkohler number: $Da_T = K_e/H =$	1

Table 14 Comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^*\,\mathrm{d}z$ for the case of an infinite adsorption rate $\hat{k}^* = +\infty$ at the time $t^* = 863\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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 15 Comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^*\,\mathrm{d}z$ for the case of an infinite adsorption rate $\hat{k}^* = +\infty$ at the time $t^* = 2{,}877\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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 16 Comparison between the volume concentrations c^{Tay}, c^{moy} and $(1/H)\int_0^H c^*\,\mathrm{d}z$ for the case of an infinite adsorption rate $\hat{k}^* = +\infty$ at the time $t^* = 5{,}755\,\mathrm{s}$

x^*	c^{Tay}	c^{moy}	$\frac{1}{H}\int_0^H c^*\mathrm{d}z$
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

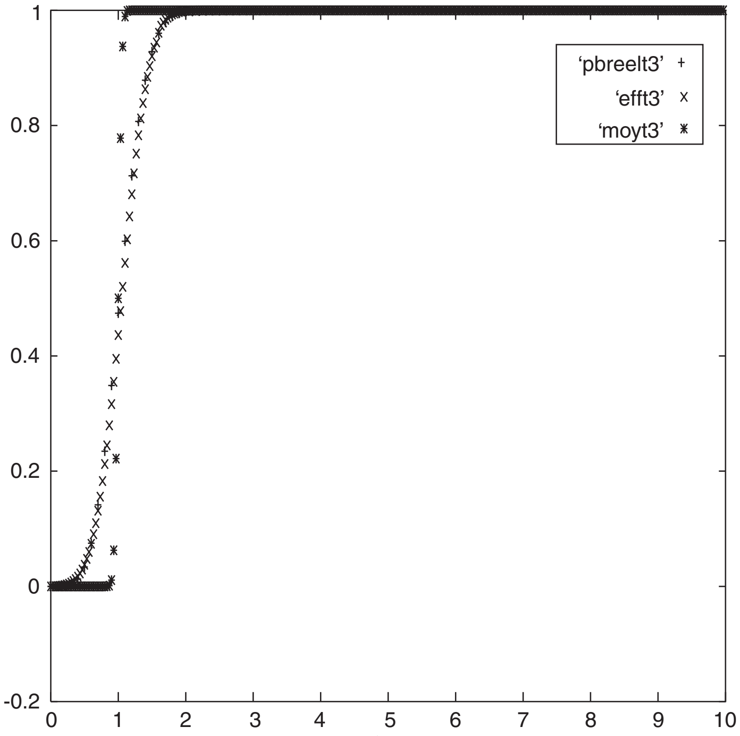

Figure 10 Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at $t = 863\,\mathrm{s}$.

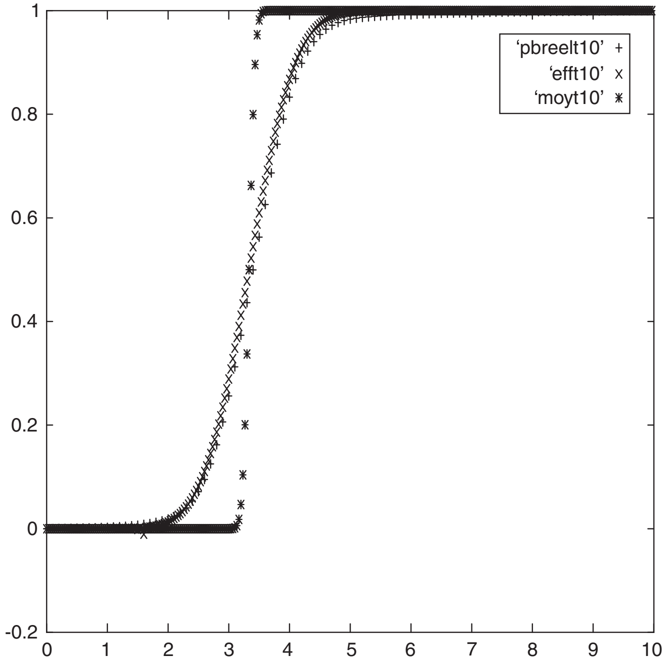

Figure 11 Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at $t = 2{,}877$ s.

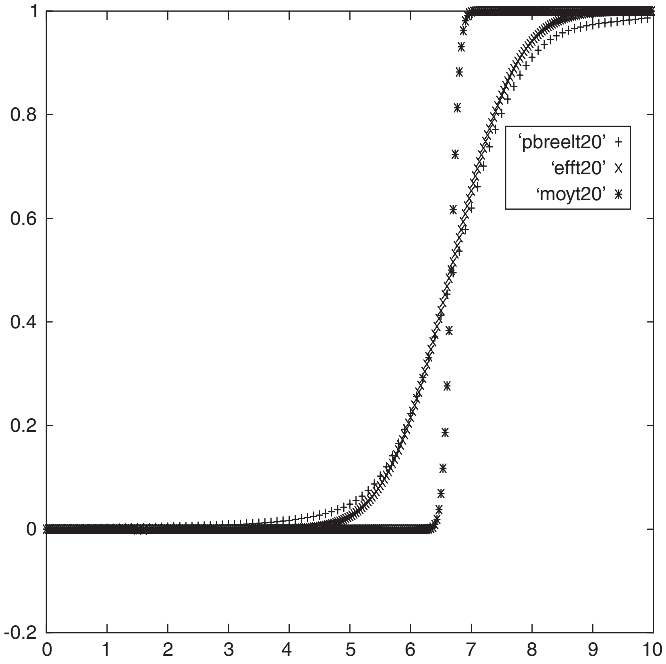

Figure 12 Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentration obtained using our effective problem (eff), average of the section of the concentration from the original problem (pbreel3) and the concentration coming from the simple average (moy) at $t = 5{,}755$ s.

by Balakotaiah et al., and to compare the approximations on mathematically rigorous way.

Furthermore, there is approach by Camacho using a viewepoint of Irreversible Thermodynamics and leading to the Telegraph equation. For more details we refer to Camacho (1993a, b, c) and to the doctoral thesis Berentsen (2003). We plan to address this subject in the near future and extend our result in this direction.

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