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

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Thanks:

It is a great pleasure for me to give a talk at this conference. For me this the 3rd MACKIE-2 conference and I hope to profit from it as before by interacting with people whom I do not see as usual mathematical conferences. Many thanks to everybody from the organizing committee!

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These results are obtained in collaboration with C.J. van Duijn and I. S. Pop (TU Eindhoven, The Netherlands), C. Rosier (Université du Littoral, France) and C. Choquet (Marseille).

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Introduction

"*Modèles de dispersion efficace pour des problèmes de Chimie-Transport: Changement d'échelle dans la modélisation du transport réactif en milieux poreux, en présence des nombres caractéristiques dominants.* ”

In many processes arising in chemical engineering it is important to study the diffusion of a solute transported by a fluid flowing through a porous medium. In addition, there are reactions or adsorption occurring at the solid/fluid interfaces.

Examples are chromatographic systems, heterogeneous reactors from chemical and catalytic reaction engineering, the use of surfactants in tertiary oil recovery processes, environmental problems ....

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In many processes arising in chemical engineering it is important to study the diffusion of a solute transported by a fluid flowing through a porous medium. In addition, there are reactions or adsorption occurring at the solid/fluid interfaces.
Examples are chromatographic systems, heterogeneous reactors from chemical and catalytic reaction engineering, the use of surfactants in tertiary oil recovery processes, environmental problems ....
These systems are analyzed in terms of **dispersion equations** for momentum, energy and mass transfer in continua. In fact averaging of the physical first principles should give

us the dispersion coefficients (=**effective coefficients**). Nevertheless, there are difficulties:

Even the simplest models contain the transport terms of the form $\vec{v} \cdot \nabla c$. Since both the velocity and the concentration gradient are oscillatory, in general the average of the product is different from the product of the averages.

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Par example, in Taylor’s dispersion the velocity field contributes, after averaging, to the effective diffusion and one obtains Taylor’s mechanical dispersion term. Presence of the chemical reactions complicates additionally determination of the effective coefficients since they can depend on the reaction term or on the adsorption isotherm in a complicated way. It is fairly complicated to determine this dependance using just **laboratory experiments**.

In order to start with a simple situation, we consider a porous medium comprised of a bundle of capillary tubes. The disadvantage is that a bundle of capillary tubes represents a geometrically oversimplified model of a porous medium. Nevertheless, there is considerable insight to be gained from such analysis.

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We start with a "simple" problem:

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

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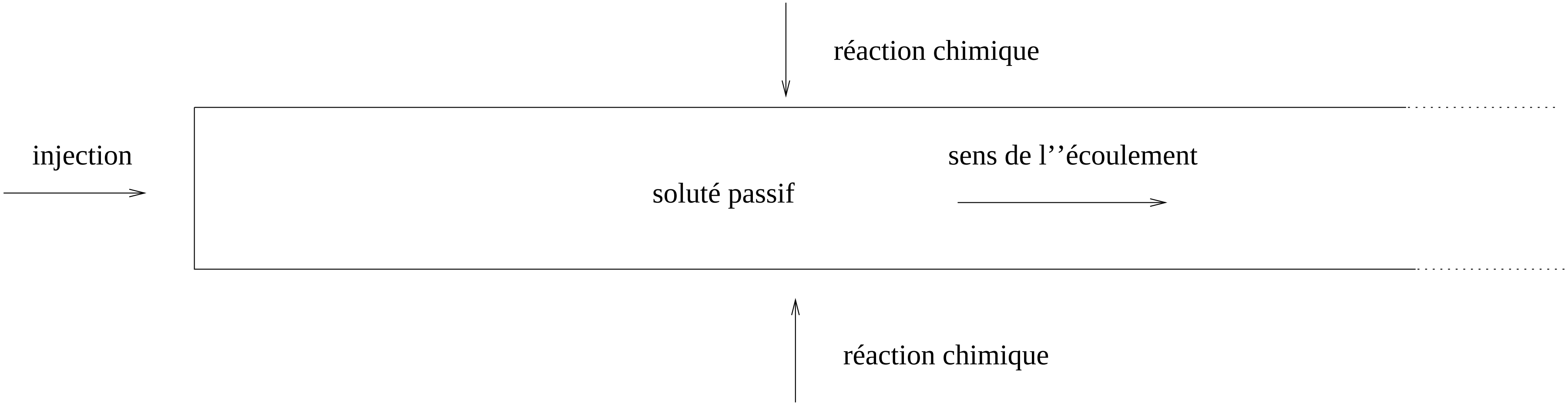

réaction chimique

injection

sens de l''écoulement

soluté passif

réaction chimique

Figure 1: The tube

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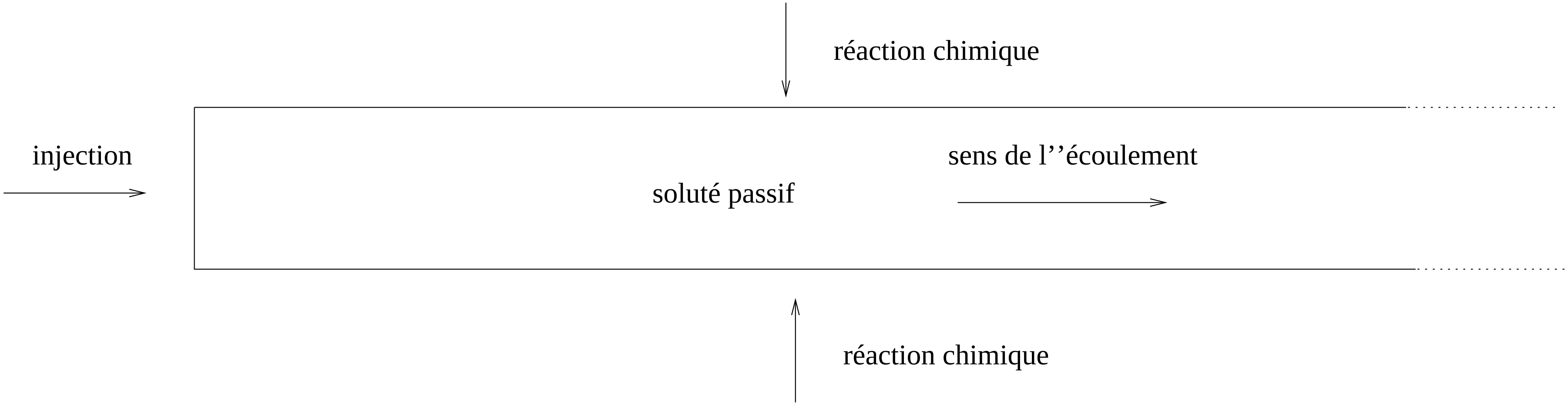

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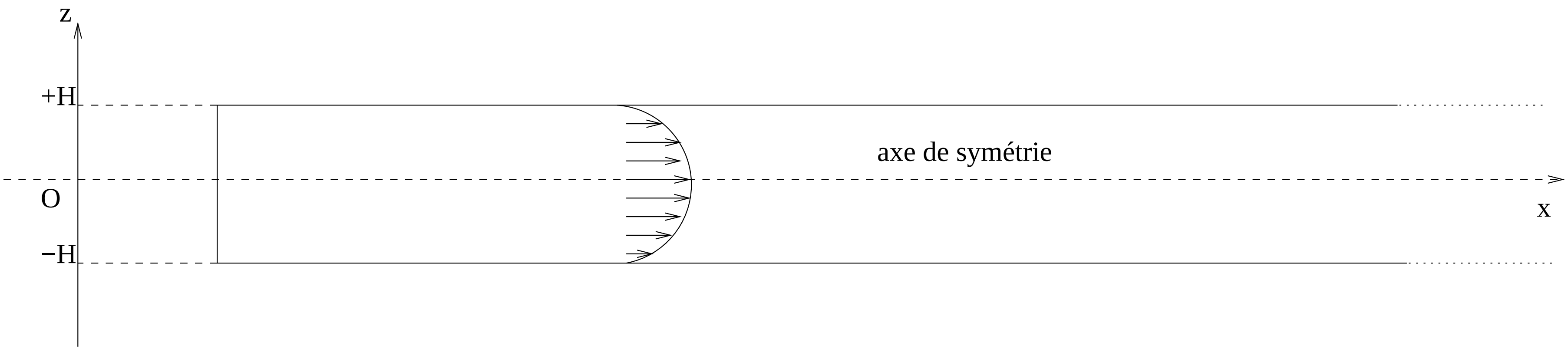
Figure 3: The tube



z

+H

axe de symétrie

O

x

−H

$$\frac{\partial c^*}{\partial t^*} + q(z)\frac{\partial c^*}{\partial x^*} - D^*\Delta_{x^*,z}c^* = 0 \text{ in } I\!R_+ \times (-H,H), \qquad (1)$$

$$\frac{\partial c^*}{\partial t^*} + q(z)\frac{\partial c^*}{\partial x^*} - D^*\Delta_{x^*,z}c^* = 0 \text{ in } \mathbb{R}_+ \times (-H, H), \qquad (3)$$

where $q(z) = Q^*(1-(z/H)^2)$ and Q^* (**velocity**) and D^* (**molecular diffusion**) are positive constants. At the lateral boundaries $z = \pm H$ the first-order chemical reaction with the solute particles is modeled through the following boundary condition :

$$-D^*\partial_{y^*}c^* = K_e\frac{\partial c^*}{\partial t^*} \quad \text{on } \Gamma^*, \qquad (4)$$

where K_e is the linear adsorption equilibrium constant and $\Gamma^* = \{(x^*, y^*) : \, 0 < x^* < +\infty, \, |y^*| = H\}$.

At the inlet boundary, infiltration with a pulse of water containing a solute of concentration c_f^*,
followed by solute-free water is described using the Danckwerts boundary condition

$$-D^*\partial_{x^*}c^* + q(y^*)c^* = \begin{cases} q(y^*)c_f^*, & \text{for } 0 < t^* < t_0^* \\ 0, & \text{for } t > t_0^*. \end{cases} \qquad (5)$$

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".

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Problem involves the following time scales:

T_L **= characteristic longitudinal time scale =**L_R/Q_R

T_T **= characteristic transversal time scale =**H^2/D_R

T_C **= superficial chemical reaction time scale =** $\dfrac{L_R K_e}{HQ_R}$**,**

and the non-dimensional number $\mathbf{Pe} = \dfrac{L_R Q_R}{D_R}$ (Peclet number).

In this paper we fix the reference time by setting $T_R = T_C = T_L$ and $K = K_e/H = T_C/T_L = \mathcal{O}(1)$. To carry out the analysis we need to compare the dimensionless numbers with respect to ε. For this purpose we set $\mathbf{Pe} = \varepsilon^{-\alpha}$.

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Solving the full problem for arbitrary values of coefficients is costly and practically impossible. Consequently, **one would like to find the effective (or averaged) values of the dispersion coefficient and the transport velocity and an effective corresponding 1D parabolic equation for the effective concentration**. In 1953 G.I. Taylor obtained an explicit effective expression for the enhanced diffusion coefficient and it is called in literature *Taylor's dispersion formula*.

We choose $Q = \frac{Q^*}{Q_R} = \mathcal{O}(1)$, and

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

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

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

$$\frac{\partial c^{\varepsilon}}{\partial t} + Q(1-y^2)\frac{\partial c^{\varepsilon}}{\partial x} = D\varepsilon^{\alpha}\frac{\partial^2 c^{\varepsilon}}{\partial x^2} + D\varepsilon^{\alpha-2}\frac{\partial^2 c^{\varepsilon}}{\partial y^2} \quad \text{in } \Omega^{+}\times(0,T), \tag{6}$$

$$-D\varepsilon^{\alpha-2}\frac{\partial c^{\varepsilon}}{\partial y} = -D\frac{1}{\varepsilon^2 \mathbf{Pe}}\frac{\partial c^{\varepsilon}}{\partial y} = K\frac{\partial c^{\varepsilon}}{\partial t} \quad \text{on } \Gamma^{+}\times(0,T), \tag{7}$$

$$c^{\varepsilon}(x,y,0) = 0 \quad \text{for } (x,y)\in\Omega^{+}, \tag{8}$$

$$(-D\varepsilon^{\alpha}\partial_x c^{\varepsilon} + Q(1-y^2)c^{\varepsilon})_{x=0} = \begin{cases} Q(1-y^2)c_f, & \text{for } 0<t<t_0 \\ 0, & \text{for } t>t_0. \end{cases}, \tag{9}$$

$$\frac{\partial c^{\varepsilon}}{\partial y}(x,0,t) = 0, \quad \text{for } (x,t)\in(0,+\infty)\times(0,T). \tag{10}$$

We study the behavior of the solution to (6) -(10), with square integrable gradient in x and y, when $\varepsilon \to 0$.
In the absence of chemical reactions, the effective problem with Taylor's dispersion coefficient reads:

$$\left\{ \begin{array}{l} \partial_t c^{Tay} + \frac{2Q}{3}\partial_x c^{Tay} = (D\varepsilon^{\alpha} + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2-\alpha})\partial_{xx} c^{Tay}, \\ \text{in } \ I\!\!R_+ \times (0,T), \quad c^{Tay}|_{x=0} = c_f, \\ \ c^{Tay}|_{t=0} = 0, \ \partial_x c^{Tay} \in L^2(I\!\!R_+ \times (0,T)), \end{array} \right. \qquad (11)$$

What is known concerning derivation of (11) ?

◇ For the formal derivation using the **method of moments**, see the paper of Aris from Proc. Roy. Soc. London (1956).

◇ Another approach is in the paper by Lungu and Moffat, J. Engng Math (1982). They used a large time and small wave number expansion, after a Fourier transform, to decipher the asymptotic behaviour.

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◇ " Near rigorous " derivation using the centre manifold theory is due to Mercer and Roberts, SIAM J. Appl. Math. (1990). The initial value problem is studied and the Fourier transform with respect to x is applied. The resulting PDE is written in the form $\dot{u} = \mathcal{A}u + F(u)$, with $u = (k, \hat{c})$. Then the **centre manifold theory** is applied to obtain effective equations at various orders. Since the corresponding centre manifold isn't finite dimensional, the results aren't rigorous.

◇ When the chemistry is added (e.g. having an irreversible, 1st order, chemical reaction with equilibrium at $y = 1$, as we have), then there is a paper by M.A. Paine, R.G. Carbonell and S. Whitaker in Chemical Engineering Science, (1983).Paine et al used the "single-point" closure schemes of turbulence modeling by Launder to obtain a closed model for the averaged concentration. Their effective equations are non-local and the effective coefficients are not determined.

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◇ More recently, there is an approach using the centre manifold theory in the article by Balakotaiah et Chang, Phil. Trans. R. Soc. Lond. A (1995), where they use the ratio between T_T and T_L.

Our technique is motivated by the paper by J. Rubinstein, R. Mauri in SIAM J. Appl. Math. (1986), where the analysis is based on the hierarchy of time scales. In our knowledge the only rigorous result concerning the effective dispersion, in the presence of high Peclet's numbers (and no chemistry), is in the recent paper by A. Bourgeat, M. Jurak and A.L. Piatnitski, in Math. Meth. Appl. Sci. (2003). Their approach is based on the regular solutions for compatible data for the underlying linear transport equation. In the absence of the compatibility, it seems more efficient to use the "Gausslets", than very compatible hyperbolic equations.

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We obtained several **mathematically rigorous** results on Taylor’s dispersion, with and without chemical reactions and I’ll present some of them.

Laplace's transform

The Laplace's transform method is widely used in solving engineering problems. In applications it is usually called the operational calculus or Heaviside's method.

For locally integrable function $f \in L^1_{loc}(\mathbb{R})$ such that $f(t) = 0$ for $t < 0$ and $|f(t)| \leq Ae^{at}$ as $t \to +\infty$, the Laplace transform of f, denoted $\hat{f}$, is defined as

$$\hat{f}(\tau) = \int_0^{+\infty} f(t)e^{-\tau t}\,dt, \quad \tau = \xi + i\,\eta \in \mathbb{C}. \tag{12}$$

It is closely linked with Fourier's transform in $\mathbb{R}$. We note that

$$\hat{f}(\tau) = \mathcal{F}\big(f(t)e^{-\xi t}\big)(-\eta), \quad \xi > a, \tag{13}$$

Laplace 1

where the Fourier's transform of a function $g \in L^1(\mathbb{R})$ is given by

$$\mathcal{F}\big(g(t)\big)(\omega) = \int_{\mathbb{R}} g(t)e^{i\omega t}\,dt, \quad \omega \in \mathbb{R}.$$

It is well-known that $\hat{f}$ defined by (12) is analytic in the half-plane $\{\mathrm{Re}(\tau) = \xi > a\}$ and it tends to zero as $\mathrm{Re}(\tau) \to +\infty$.
For real applications, Laplace's transform of functions is not well-adapted and it is natural to use Laplace's transform of distributions.
Laplace's transform is applier to linear ODEs and PDEs, the transform problem is solved and its solution $\hat{f}$ is calculated.

Laplace 2

Then the important question is how to inverse the Laplace's transform.

We have the sufficient condition by Prüss:

Theorem by Prüss. Let $q : \{\mathrm{Re}(\tau) > 0\} \to X$ be analytic. If there exists a real number $M > 0$ such that $\|\lambda q(\lambda)\|_X \leq M$ and $\|\lambda^2 q'(\lambda)\|_X \leq M$ for $\mathrm{Re}(\lambda) > 0$, then there exists a bounded function $f \in \mathcal{C}(0, +\infty; X)$ such that

$$q(\lambda) = \int_0^{+\infty} f(t) e^{-\lambda t}\, dt.$$

In particular

$q \in \mathcal{C}_w^\infty(\mathbb{R}_+; X)$=$\mathcal{C}_w^\infty(\mathbb{R}_+; X) = \{r \in \mathcal{C}^\infty((0, +\infty); X);\ \|r\|_w = \sup_{n \in \mathbb{N}} \sup_{\lambda > 0} \frac{\lambda^{n+1}}{n!} \Big\| \frac{d^n}{d\lambda^n} r(\lambda) \Big\|_X < +\infty\}.$

A simple mean

This result represents a complicated criterium and we will use a direct approach based on the link to Fourier's transform.

The simplest way to average the problem (6)-(10) is to take the mean value with respect to y. Let $c_0^{eff} = < c^\varepsilon > = \int_0^1 c^\varepsilon \, dy$. Supposing that the mean of the product is the product of the means, which is in general wrong, we get the following problem for the " averaged " concentration $c_0^{eff}(x,t)$:

$$\left\{ \begin{array}{l} (1+K)\dfrac{\partial c_0^{eff}}{\partial t} + \dfrac{2Q}{3}\dfrac{\partial c_0^{eff}}{\partial x} = \varepsilon^\alpha D \dfrac{\partial^2 c_0^{eff}}{\partial x^2} \ \text{ in } I\!R_+ \times (0,T), \\ -D\varepsilon^\alpha \partial_x c_0^{eff} + 2Q c_0^{eff}/3 = 2Q\hat{c}_f/3 \ \text{ in } I\!R_+ \times (0,T), \\ c_0^{eff}|_{t=0} = 0, \ \partial_x c_0^{eff} \in L^2(I\!R_+ \times (0,T)). \end{array} \right. \qquad (14)$$

The problem for Laplace's transform reads:

$$\begin{cases} (1+K)\tau c_0^{L,eff} + \dfrac{2Q}{3}\dfrac{\partial c_0^{L,eff}}{\partial x} = \varepsilon^{\alpha} D \dfrac{\partial^2 c_0^{L,eff}}{\partial x^2} \quad \text{in } (0,+\infty), \\ \\ \partial_x c_0^{L,eff} \in L^2((0,+\infty)), \\ \\ -D\varepsilon^{\alpha}\partial_x c_0^{L,eff} + 2Q c_0^{L,eff}/3 = 2Q\hat{c}_f/3, \qquad \text{for } x = 0. \end{cases} \tag{15}$$

We will call this problem the "**simple closure approximation**". We get

Proposition 2

$$\|\hat{c}^{\varepsilon} - c_0^{L,eff}\|_{L^2(I\!R_+\times(0,1))} \leq \varepsilon^{\beta} \frac{C|\tau||\hat{c}_f|}{1+(\varepsilon^{\alpha}|\tau|)^{1/4}}, \tag{16}$$

$$\|\partial_x(\hat{c}^{\varepsilon} - c_0^{L,eff})\|_{L^2(I\!R_+\times(0,1))} \leq \varepsilon^{\beta-\alpha/2} \frac{C|\tau||\hat{c}_f|}{1+(\varepsilon^{\alpha}|\tau|)^{1/4}}, \tag{17}$$

$$\|\partial_y(\hat{c}^{\varepsilon} - c_0^{L,eff})\|_{L^2(I\!R_+\times(0,1))} \leq \varepsilon^{\beta+1-\alpha/2} \frac{C|\tau||\hat{c}_f|}{1+(\varepsilon^{\alpha}|\tau|)^{1/4}}, \tag{18}$$

where $\beta = 1-\alpha/2$ if $\alpha \geq 1/2$ and $\beta = (1+\alpha)/2$ if $\alpha < 1/2$.

Corollary 3. Let $c_f \in \mathcal{D}(0,T)$ and let c_0^{eff} be such that $\hat{c}_0^{eff} = c_0^{L,eff}$. Let β be defined as in Proposition 2. Then we have

$$\|c^\varepsilon - c_0^{eff}\|_{\mathcal{C}(\mathbb{R}_+;L^2(\Omega^+))} \leq C\varepsilon^\beta.$$

Next let $c_f \in W^{1,\infty}(\mathbb{R}_+)$ with compact support in $[0,+\infty)$, such that $c_f(0) \neq 0$. Then for $1 < r < +\infty$, we have

$$\|c^\varepsilon - c_0^{eff}\|_{L^r(\mathbb{R}_+;L^2(\Omega^+))} \leq \begin{cases} C\varepsilon^{1-\alpha/2-\alpha\delta}, & 2 > \alpha \geq 1/2,\ 0 < \delta < 1/ \\ C\varepsilon^{(1+\alpha)/2}, & 1/2 > \alpha \geq 0. \end{cases}$$

Presence of the contact discontinuity due to $c_f(0) \neq 0$ diminishes precision.
For details see

[A1] C. Choquet, A. Mikelić : Laplace transform approach to the rigorous upscaling of the infinite adsorption rate reactive flow under dominant Peclet number through a pore, accepted for publication in *Applicable Analysis*, 2008.

Furthermore, the case of $c_f = 1$ on $(0, T)$ is covered by Corollary 3, since it could be extended to a Lipschitz function on $\mathbb{R}_+$, with compact support in $[0, +\infty)$.

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IS THERE A BETTER APPROXIMATION ?

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IS THERE A BETTER APPROXIMATION ?
Paine et al propose the following effective model

$$\begin{cases} \partial_t c^{Pai} + Q\big(\frac{2}{3} + A_1\big)\partial_x c^{Pai} + C_2 c^{Pai} = K^* \partial_{xx} c^{Pai}, \\ \text{in } \mathbb{R}_+ \times (0,T),\ \partial_x c^{Pai} \in L^2(\mathbb{R}_+ \times (0,T)) \\ c^{Pai}|_{x=0} = c_f,\ c^{Pai}|_{t=0} = 1, \end{cases} \tag{20}$$

where A_1 depends on the zeroth order moments of c^{Pai} and qc^{Pai} and K^* depends on the zero, first and second order moments of the same quantities and Peclet's number.
This is a non-local problem, hence difficult solve. Even worse: it was derived using an **AD HOC** closure assumption.
We performed a different derivation of the effective model.
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The model we got is the following:

$$(EFF)$$

$$\begin{cases} \partial_t c + \frac{2Q}{3(1+K)} \partial_x c = \tilde{D} \varepsilon^\alpha \frac{\partial_{xx} c}{1+K} \text{ in } (0,+\infty) \times (0,T), \\ -D\varepsilon^\alpha \partial_x c|_{x=0} + \frac{2Q}{3}(c|_{x=0} - c_f \chi_{t<t_0}) = 0, \\ \partial_x c \in L^2((0,+\infty) \times (0,T)),\ c|_{t=0} = 0, \end{cases}$$

where

$$\tilde{D} = D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2-2\alpha} + \frac{4Q^2}{135D}\frac{K(7K+2)}{(1+K)^2}\varepsilon^{2-2\alpha}. \qquad (21)$$

Our result could be restated in dimensional form:

Theorem 4 Let us suppose that $L_R > \max\{D_R/Q_R, Q_R H^2/D_R, H\}$. Then the upscaled *dimensional* approximation for (1) reads

$$(1+K)\frac{\partial c^{*,eff}}{\partial t^*} + \frac{2}{3}Q^*\frac{\partial c^{*,eff}}{\partial x^*} = D^*\Big(1 + (\frac{8}{945} + \frac{4}{135}\frac{K(7K+2)}{(1+K)^2})\mathbf{Pe}_T^2\Big) \qquad (22)$$

where $\mathbf{Pe}_T = \dfrac{Q^* H}{D^*}$ is the transversal Peclet number and $K = K_e/H$ is the transversal Damkohler number.

Why our model is better than other models from the literature?

For simplicity, we compare only the physical concentration c^ε with c.

Theorem 5 Let $\alpha \geq 1$ and let $c_f \in C_0^\infty(0,T)$. Let c be given by (EFF). Then we have

$$\|c^\varepsilon - c\|_{\mathcal{C}([0,T];L^2(\Omega^+))} \leq C\varepsilon^{2-\alpha}, \tag{23}$$

$$\|\partial_y c^\varepsilon\|_{\mathcal{C}([0,T];L^2(\Omega^+))} \leq C\varepsilon^{3-3\alpha/2}, \tag{24}$$

$$\|\partial_x\big(c^\varepsilon - c\big)\|_{\mathcal{C}([0,T];L^2(\Omega^+))} \leq C\varepsilon^{2-3\alpha/2}. \tag{25}$$

For ill-prepared data we have following more precise result:

Let

$$c_1^{L,eff}(x,y;\varepsilon) = c_0(x;\varepsilon) + \varepsilon^{2-\alpha}\frac{Q}{D}\Big(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180} - \frac{2}{45}\frac{K(7K+2)}{(1+K)^2}$$

$$\cdot\partial_x c_0(x;\varepsilon) + \varepsilon^{2-\alpha}\frac{K}{D}\Big(\frac{1}{6} + \frac{K}{3(1+K)} - \frac{y^2}{2}\Big)\tau c_0(x;\varepsilon) \qquad (26)$$

where $c_0 \in H^1(\Omega^+)$ is the solution of the following effective problem

$$\left\{ \begin{array}{l} (1+K)\tau c_0 + \frac{2Q}{3}\partial_x c_0 - \varepsilon^\alpha \tilde{D}\partial_{xx}^2 c_0 = 0 \,\text{in}\, (0,+\infty), \\ -D\varepsilon^\alpha \partial_x c_0 + \frac{2Q}{3} c_0 = \frac{2Q}{3}\hat{c}_f \text{ for } x = 0, \end{array} \right. \qquad (27)$$

Then we have

Proposition 6

$$\|(\hat{c}^{\varepsilon} - c_1^{L,eff})(\tau)\|_{L^2(\mathbb{R}_+\times(0,1))} \leq C\varepsilon^{2-\alpha}\frac{|\tau^2 c_f|}{1+(\varepsilon^{\alpha}|\tau|)^{1/4}}, \qquad (28)$$

$$\|\partial_x(\hat{c}^{\varepsilon} - c_1^{L,eff})\|_{L^2(\mathbb{R}_+\times(0,1))} \leq C\varepsilon^{2-3\alpha/2}\frac{|\tau^2 c_f|}{1+(\varepsilon^{\alpha}|\tau|)^{1/4}}, \qquad (29)$$

Corollary 7. Let $c_f \in C_0^{\infty}(0,T)$ and let c_0^{eff} be such that $\hat{c}_0^{eff} = c_0^{L,eff}$. Let β be defined as in Proposition 6. Then we have

$$\|c^{\varepsilon} - c_0^{eff}\|_{C(\mathbb{R}_+;L^2(\Omega^+))} \leq C\varepsilon^{2-\alpha}.$$

Next let $c_f \in W^{1,\infty}(\mathbb{R}_+)$ with compact support in $[0,+\infty)$, such that $c_f(0) \neq 0$. Then for $1 < r < +\infty$, we have

$$\| \int_0^t (c^\varepsilon - c_0^{eff})\, dt \|_{L^r(\mathbb{R}_+;L^2(\Omega^+))} \le C\varepsilon^{2-\alpha-\alpha\delta},\ 0 < \delta < 1/4,\ r(1-\delta)$$

These results are more precise than previous from the article

[A2] A. Mikelić , C. Rosier : Rigorous upscaling of the infinite adsorption rate reactive flow under dominant Peclet number through a pore, *Ann Univ Ferrara*,Vol. 53 (2007), p. 333–359. obtained by a different technique.

Next we present the formal derivation of the upscaled equation, which can be found in

[A3] C.J. van Duijn, A. Mikelić, I. S. Pop, C. Rosier : Effective Dispersion Equations For Reactive Flows With Dominant Peclet and Damkohler Numbers, accepted for publication in *Advances in Chemical Engineering* , 2008.

Formal expansion

The estimate obtained when we took the simple mean value, isn't satisfactory. At the other hand, it is known that the Taylor dispersion model gives a very good 1D approximation. With this motivation we briefly explain how to obtain formally the higher precision effective models and notably the variant of Taylor's dispersion formula, by the 2-scale asymptotic expansion.

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The estimate obtained when we took the simple mean value, isn’t satisfactory. At the other hand, it is known that the Taylor dispersion model gives a very good 1D approximation. With this motivation we briefly explain how to obtain formally the higher precision effective models and notably the variant of Taylor’s dispersion formula, by the 2-scale asymptotic expansion.

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

$$c^\varepsilon = c^0(x,t;\varepsilon) + \varepsilon^{2-\alpha} c^1(x,y,t) + \varepsilon^{2(2-\alpha)} c^2(x,y,t) + \dots \quad (31)$$

After introducing (30) into the equation (6) we get

$$\varepsilon^0\Big\{\partial_t c^0 + Q(1-y^2)\partial_x c^0 - D\varepsilon^{\alpha-1}\partial_{yy}c^1\Big\}+$$
$$\varepsilon^{2-\alpha}\Big\{\partial_t c^1 + Q(1-y^2)\partial_x c^1 - D\varepsilon^{\alpha-1}\partial_{xx}c^0 -$$
$$D\varepsilon^{\alpha-1}\partial_{yy}c^2\Big\} = \mathcal{O}(\varepsilon^{2(2-\alpha)}) \qquad (32)$$

In order to have (32) for every $0 < \varepsilon < \varepsilon_0$, all coefficients in front of the powers of ε should be zero.

$$\varepsilon^{0}\Big\{\partial_t c^0 + Q(1-y^2)\partial_x c^0 - D\varepsilon^{\alpha-1}\partial_{yy}c^1\Big\}+$$
$$\varepsilon^{2-\alpha}\Big\{\partial_t c^1 + Q(1-y^2)\partial_x c^1 - D\varepsilon^{\alpha-1}\partial_{xx}c^0 -$$
$$D\varepsilon^{\alpha-1}\partial_{yy}c^2\Big\} = \mathcal{O}\big(\varepsilon^{2(2-\alpha)}\big) \qquad (34)$$

In order to have (32) for every $0 < \varepsilon < \varepsilon_0$, all coefficients in front of the powers of ε should be zero.

The problem corresponding to the order ε^0 is

$$\left\{\begin{array}{l} -D\partial_{yy}c^1 = -Q(1/3-y^2)\partial_x c^0 - \\ \big(\partial_t c^0 + 2Q\partial_x c^0/3\big) \;\text{ on }\; (0,1), \\ \partial_y c^1|_{y=0} = 0,\; -D\partial_y c^1|_{y=1} = K\partial_t c^0. \end{array}\right. \qquad (35)$$

for every $(x,t) \in (0,+\infty) \times (0,T)$. By Fredholm's alternative, the problem (33) has a solution if and only if

$$(1+K)\partial_t c^0 + 2Q\partial_x c^0/3 = 0 \quad \text{in } (0,L) \times (0,T). \tag{36}$$

Unfortunately our initial and boundary data are incompatible and the hyperbolic equation (36) has a discontinuous solution. Since the asymptotic expansion for c^ε involves derivatives of c^0, the equation (36) doesn't suit our needs.

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In the article by Bourgeat et al the difficulty was overcome by supposing compatible initial and boundary data. We proceed by following an idea by Rubinstein and Mauri and suppose that

$$(1+K)\partial_t c^0 + 2Q\partial_x c^0/3 = \mathcal{O}(\varepsilon^{2-\alpha}) \quad \text{in} \ (0,+\infty) \times (0,T). \qquad (39)$$

The hypothesis (37) will be justified *a posteriori*, after getting an equation for c^0. Hence (33) reduces to

$$\begin{cases} -D\partial_{yy}c^1 = -Q(1/3 - y^2)\partial_x c^0 + K\partial_t c^0 \text{ on } (0,1), \\ \partial_y c^1|_{y=0} = 0, \ -D\partial_y c^1|_{y=1} = K\partial_t c^0, \end{cases} \tag{40}$$

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

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$$\begin{cases} -D\partial_{yy}c^1 = -Q(1/3 - y^2)\partial_x c^0 + K\partial_t c^0 \text{ on } (0,1), \\ \partial_y c^1|_{y=0} = 0, \; -D\partial_y c^1|_{y=1} = K\partial_t c^0, \end{cases} \tag{42}$$

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

$$c^1(x,y,t) = \frac{Q}{D}\left(\frac{y^2}{6} - \frac{y^4}{12}\right)\partial_x c^0 + \frac{K}{D}\left(\frac{1}{6} - \frac{y^2}{2}\right)\partial_t c^0 + C_0(x,t), \tag{43}$$

where C_0 is an arbitrary function.

Let us go to the next order. Then we have

$$\begin{cases} -D\partial_{yy}c^2 = -Q(1-y^2)\partial_x c^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c^0 - \\ \partial_t c^1 + D\varepsilon^{\alpha}\partial_{xx}c^1 - \varepsilon^{\alpha-2}\big((1+K)\partial_t c^0 + 2Q\partial_x c^0/3 \\ \big) \text{ on } (0,1),\ \partial_y c^2|_{y=0} = 0 \text{ and} \\ -D\partial_y c^2|_{y=1} = K\partial_t c^1|_{y=1} \end{cases} \tag{44}$$

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

Let us go to the next order. Then we have

$$\left\{\begin{array}{l} -D\partial_{yy}c^2 = -Q(1-y^2)\partial_x c^1 + D\varepsilon^{2(\alpha-1)}\partial_{xx}c^0 - \\ \partial_t c^1 + D\varepsilon^{\alpha}\partial_{xx}c^1 - \varepsilon^{\alpha-2}\Big((1+K)\partial_t c^0 + 2Q\partial_x c^0/3 \\ \Big) \text{ on } (0,1),\ \partial_y c^2|_{y=0} = 0 \text{ and} \\ -D\partial_y c^2|_{y=1} = K\partial_t c^1|_{y=1} \end{array}\right. \qquad (45)$$

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

The problem (44) has a solution if and only if

$$\partial_t c^0 + 2Q\partial_x c^0/3 + K(\partial_t c^0 + \varepsilon^{2-\alpha}\partial_t c^1|_{y=1}) -$$

$$D\varepsilon^2\partial_{xx}(\int_0^1 c^1 dy) + \varepsilon^{2-\alpha}\partial_t(\int_0^1 c^1\ dy) - \varepsilon^{\alpha} D\partial_{xx}c^0 +$$

$$\varepsilon^{2-\alpha} Q \partial_x \Big(\int_0^1 (1-y^2) c^1 \, dy \Big) = 0 \ \text{ in } \ (0,+\infty) \times (0,T). \tag{46}$$

(46) is the equation for c^0 . Next let us remark that

$$\int_0^1 c^1 \, dy = C_0(x,t), \tag{47}$$

$$\int_0^1 (1-y^2) c^1 \, dy = \frac{2}{3} C_0(x,t) - \frac{Q}{D} \frac{8}{945} \partial_x c^0 + \frac{2K}{45D} \frac{\partial c^0}{\partial t}, \tag{48}$$

$$\frac{\partial c^1}{\partial t}\Big|_{y=1} = \frac{2Q}{45D} \partial_{xt} c^0 - \frac{K}{3D} \partial_{tt} c^0 + \partial_t C_0. \tag{49}$$

In order to get a parabolic equation for c^0_K we choose C_{0K} such that $\partial_{tt}c^0_K$ and $\partial_{xt}c^0_K$ do not appear in the effective equation.

Then C_0 is of the form $C_0 = a\partial_t c^0 + b\partial_x c^0$ and after a short calculation we find that

$$C_0(x,t) = \frac{1}{3D}\frac{K^2}{1+K}\partial_t c^0 - \frac{2Q}{45D}\frac{K(2+7K)}{(1+K)}\partial_x c^0. \qquad (50)$$

Now c^1 takes the form

$$c^1(x,y,t) = \frac{Q}{D}(\frac{y^2}{6} - \frac{y^4}{12} - \frac{7}{180} - \frac{2}{45}\frac{K(2+7K)}{(1+K)}\partial_x c^0 +$$

$$\frac{K}{D}(\frac{1}{6} + \frac{1}{3}\frac{K}{1+K} - \frac{y^2}{2})\partial_t c^0. \qquad (51)$$

For $\alpha \geq 1$, $2 \geq 2(2-\alpha)$ and we are allowed to drop the term of order $\mathcal{O}(\varepsilon^2)$. Now the equation (46) becomes

$$(1+K)\partial_t c^0 + \frac{2Q}{3}\partial_x c^0 = \varepsilon^\alpha \tilde{D}\partial_{xx}c^0 \quad \text{in } (0,+\infty)\times(0,T). \tag{52}$$

with

$$\tilde{D} = D + \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)} + \frac{4Q^2}{135D}\frac{K(2+7K)}{(1+K)^2}\varepsilon^{2(1-\alpha)} \tag{53}$$

Using the energy arguments, we prove Proposition 6 and Corollary 7. The estimate would be normally of order $\mathcal{O}(\varepsilon^{2(2-\alpha)})$, but presence of the boundary layer at $x=0$ reduces our precision to $\mathcal{O}(\varepsilon^{2-\alpha})$

Proofs through the combination of Laplace’s transform and anisotropic energy arguments in [A1], are much simpler than the corresponding ones in [A2] or in the original article [A4] A. Mikelić, V. Devigne, C.J. van Duijn, Rigorous upscaling of the reactive flow through a pore, under dominant Peclet and Damkohler numbers, *SIAM J. Math. Anal.*, Vol. 38, Issue 4 (2006), p. 1262-1287,
where the reactions were given by

$$D^* \partial_z c^* + k^* c^* = 0 \quad \text{on } z = \pm H, \tag{54}$$

Numerical comp. 1

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

Table 1: A. Parameter values for the longest time example of Taylor.

Numerical comp. 2

For the direct numerical solution of 2D problem we use the package **FreeFem++** by O. Pironneau, F. Hecht and A. Le Hyaric.

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:

$$\frac{\partial c}{\partial t} + (\vec{q}.\nabla)c = D\varepsilon^{\alpha}\partial_{xx}c + D\varepsilon^{\alpha-2}\partial_{yy}c = f(x,y,t) \qquad (55)$$

  Let c^m be an approximation for the solution c at a time $m\delta t$.

Numerical comp. 3

- Then the one step backward convection scheme by the method of characteristics reads as follows:

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

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

we start with

CASE A: time of flow: $t^* = 11220$ sec

Numerical comp. 4

We solve

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

$$\partial_{t^*} c^{Tay} + \frac{2Q^*}{3} \partial_{x^*} c^{Tay} = D^* (1 + \frac{8}{945} \mathbf{Pe}_T^2) \partial_{x^* x^*} c^{Tay} \text{ for } x, t > 0 \tag{56}$$

$$c^{Tay}|_{x=0} = 1 \text{ and } c^{Tay}|_{t=0} = 0. \tag{57}$$

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

Numerical comp. 5

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

$$\partial_{t^*} c^{moy} + \frac{2Q^*}{3}\partial_{x^*} c^{moy} - D^*\partial_{x^*x^*} c^{moy} = 0 \text{ in } (0,+\infty)\times(0,T) \tag{58}$$

with initial/boundary conditions (57). On the figures its solution is denoted by (moyenne).

On the figure we show the comparison between concentration from Taylor's paper (taylor), from the original problem (pbreel) and the simple average (moyenne) at $t = 11220$ sec.

Numerical comp. 6

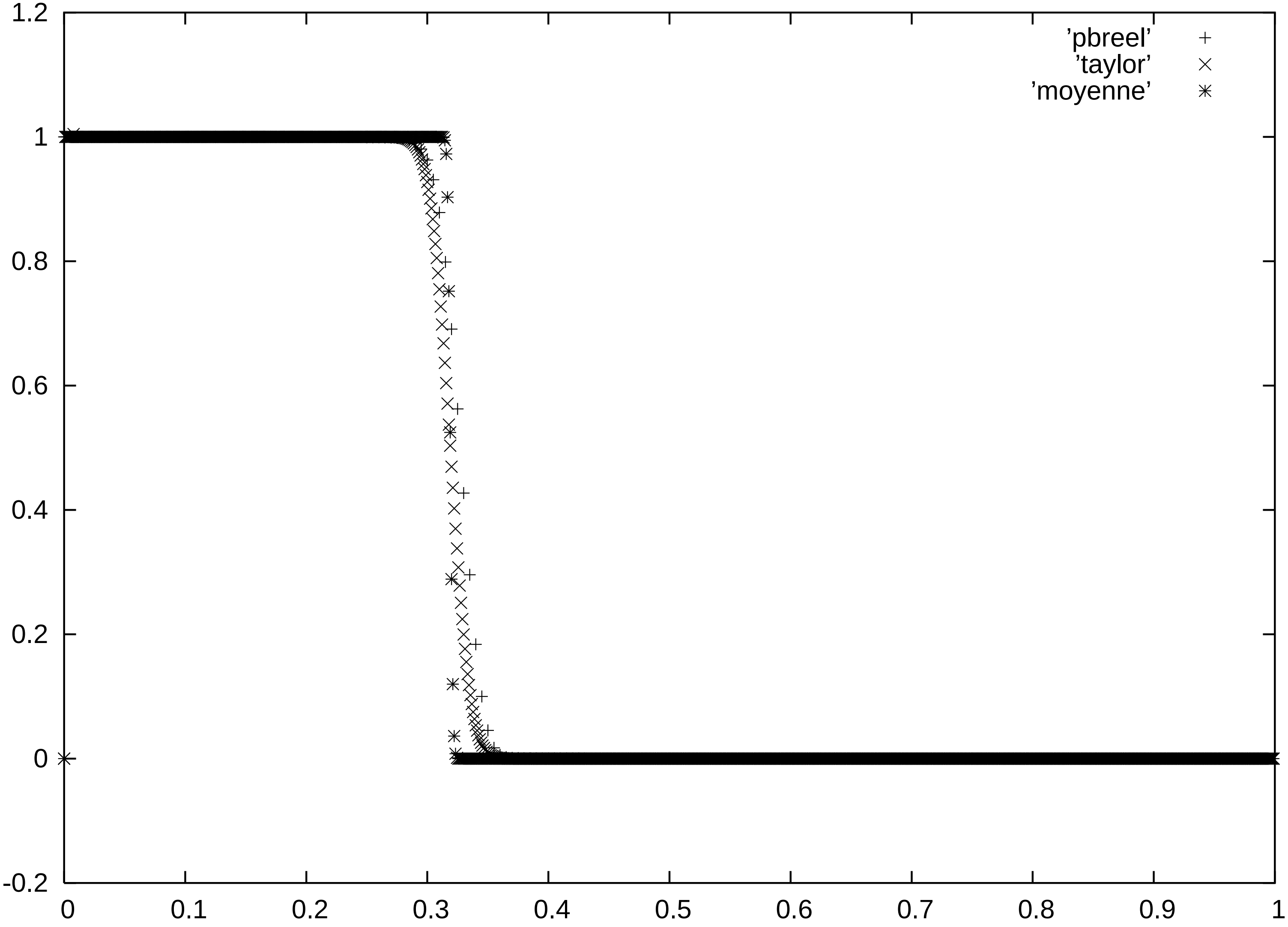

Figure 5: Comparison between concentrations at $t = 11220$ sec.

Numerical comp. 7

Note that in the absence of the chemical reactions we can solve the problems (56)-(57), respectively (58) - (57) explicitly. With $\bar{Q} = \frac{2Q^*}{3}$ and $\bar{D} = D^*(1 + \frac{8}{945}\mathbf{Pe}_T^2)$, the solution for (56)-(57) reads

$$c^{Tay}(x,t) = 1 - \frac{1}{\sqrt{\pi}}\Big[\exp\{\frac{\bar{Q}x}{\bar{D}}\}\int_{(x+\bar{Q}t)/(2\sqrt{\bar{D}t})}^{\infty} e^{-\eta^2}\,d\eta + \int_{(x-\bar{Q}t)/(2\sqrt{\bar{D}t})}^{\infty} e^{-\eta^2}\,d\eta\Big] \tag{59}$$

For the problem (58),(57), everything is analogous.

CASE B: time of flow $t^* = 240$ sec.

Numerical comp. 8

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

Table 2: B. Parameter values for the characteristic time 240 seconds from Taylor's paper

Numerical comparison (C. Rosier) 9

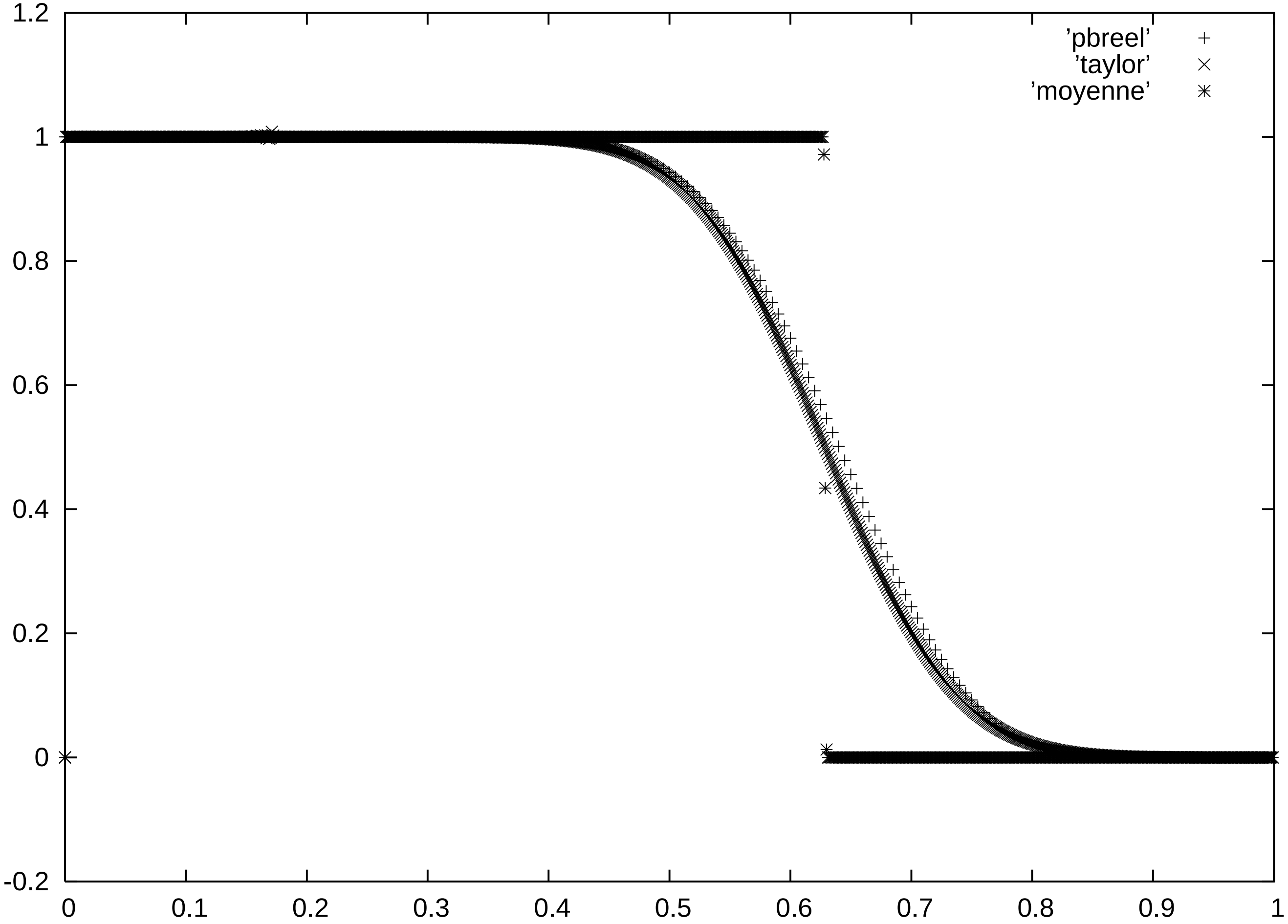

Figure 6: Case B: 2nd case from Taylor's paper. Comparison between the solutions at $t^* = 240$ sec.

Numerical comp. 10

On the Figure the comparison between concentration from Taylor’s paper, from the original problem and the simple average at $t = 240$ sec.

Surface reaction 1

Now we study the case of the linear surface adsorption-desorption reaction. Then the condition (2) is replaced by

$$-D^*\partial_{y^*}c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{k}^*(c^* - \hat{c}/K_e) \quad \text{on } z = \pm H, \tag{60}$$

where $\hat{k}^*$ represents the rate constant for adsorption and K_e the linear adsorption equilibrium constant. We note here presence of 3 new characteristic times: $T_{DE} = K_{eR}/k_R$ (characteristic desorption time), $T_A = \hat{c}_R/(c_R k_R)$ (characteristic adsorption time) and $T_{react} = H/k_R$ (superficial chemical reaction time scale). We consider the case when $K_{eR} = H$, $T_A = T_L = T_{DE}$. In non- dimensional form, (60) reads

Surface reaction 2

$$-D\varepsilon^{\alpha-2}\frac{\partial c^\varepsilon}{\partial y} = \frac{T_A}{T_{DE}}\frac{\partial c_s^\varepsilon}{\partial t} = \frac{T_L}{T_{DE}}k(c^\varepsilon - \frac{T_A}{T_{DE}}c_s^\varepsilon/K)|_{y=1} \text{ on } \Gamma^+ \times (0, T \tag{61}$$

The effective problem is now

$(EFF22)$

$$\begin{cases} \partial_t(c + \frac{T_A}{T_{DE}}c_s) + (\frac{2Q}{3} + \frac{2Qk}{45D}\frac{T_T}{T_{DE}})\partial_x c - (D\varepsilon^\alpha + \\ \\ \frac{8}{945}\frac{Q^2}{D}\varepsilon^{2-\alpha})\partial_{xx}c = \frac{2Qk}{45DK}\frac{T_A}{T_{DE}}\frac{T_T}{T_{DE}}\partial_x c_s \text{ in } (0, +\infty) \times (0, T) \\ \\ (1 + \frac{k}{3D}\frac{T_T}{T_{DE}})\partial_t c_s = k\frac{T_L}{T_A}(c + \frac{2Q}{45D}\varepsilon^{2-\alpha}\partial_x c - \frac{T_A}{T_{DE}}c_s/K) \\ \text{ in } (0, +\infty) \times (0, T) \end{cases}$$

Dimensional form

The effective problem in its dimensional form is

(DIM)

$$\begin{cases} \partial_{t^*}\left(c^* + \frac{\hat{c}}{H}\right) + \left(\frac{2Q^*}{3} + \frac{2Q^*\mathbf{Da}_T}{45}\right)\partial_{x^*}c^* - D^*\Big(1+ \\ \frac{8}{945}\mathbf{Pe}_T^2\Big)\partial_{x^*x^*}c^* = \frac{2Q^*\mathbf{Da}_T}{45K_e}\partial_{x^*}\hat{c} \text{ in } (0,+\infty)\times(0,T) \\ \left(1+\frac{1}{3}\mathbf{Da}_T\right)\partial_{t^*}\hat{c} = \hat{k}^*\left(c^* + \frac{2H\mathbf{Pe}_T}{45}\partial_{x^*}c^* - \frac{\hat{c}}{K_e}\right) \\ \text{ in } (0,+\infty)\times(0,T) \\ c|_{x=0} = 0,\ c|_{t=0} = 1,\ \partial_x c \in L^2((0,+\infty)\times(0,T)). \end{cases}$$

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

CASE A2: time of flow: $t^* = 100$ sec

Our scaling impose $\hat{k}^* = \varepsilon Q^*$ and $K_e = H$. This gives $\mathbf{Da}_T = \varepsilon \mathbf{Pe}_T$. Now the system to solve is (DIM) and we should compare between the solutions to (1), (60) with the initial/boundary conditions (**??**), $\hat{c}|_{t=0} = 0$ and (DIM) and the problem obtained by taking the simple mean, with the same initial/boundary conditions.

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 $t^* = 100, t^* = 211$ and $t^* = 350$ sec sec, is shown on the Figures 7, 8 and 9.

Test 1

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

Test 2

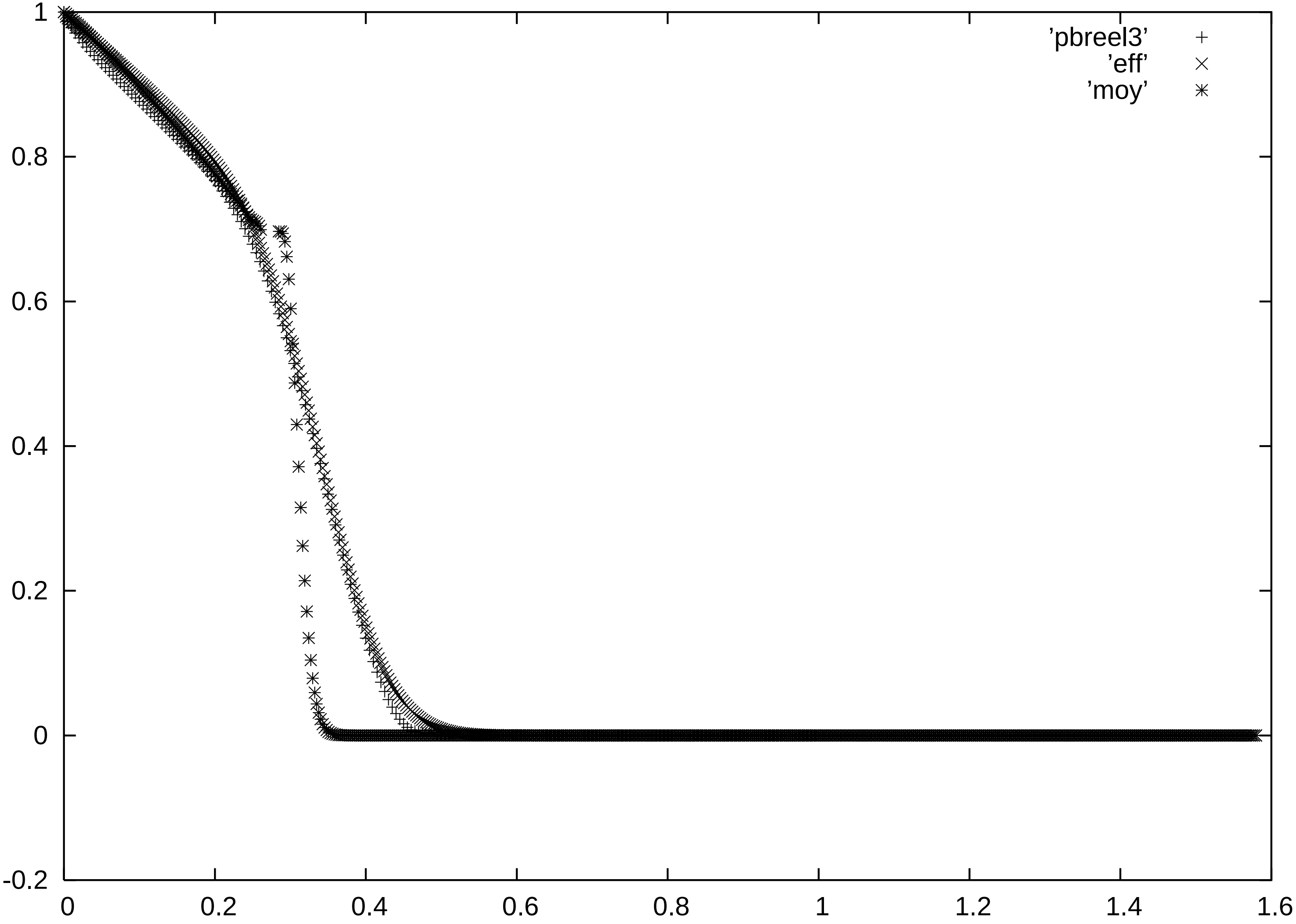

Figure 7: Comparison between the volume concentrations at time $t^* = 100$ sec.

Test 2

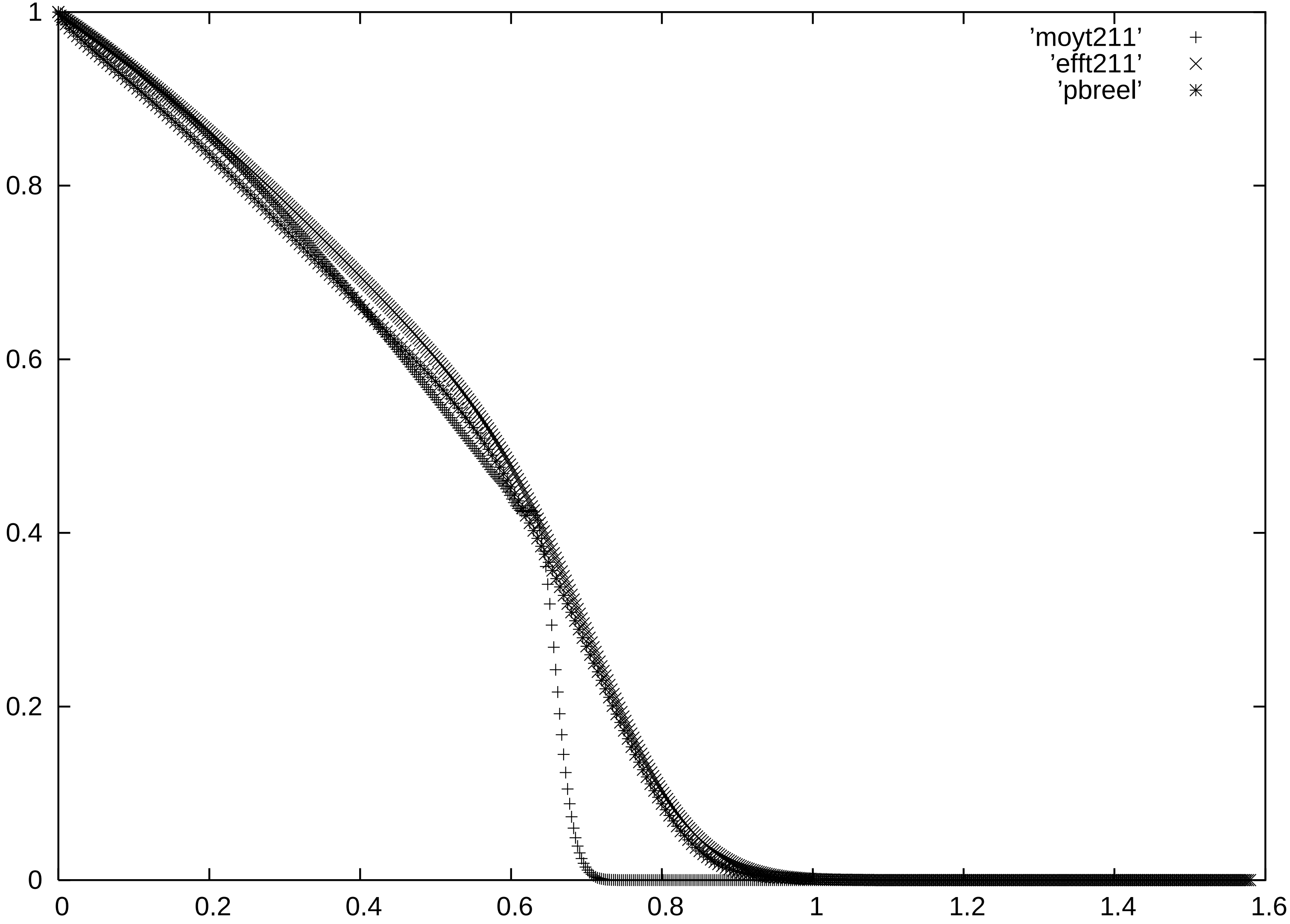

Figure 8: Comparison between the volume concentrations at time $t^* = 211$ sec.

Test 2

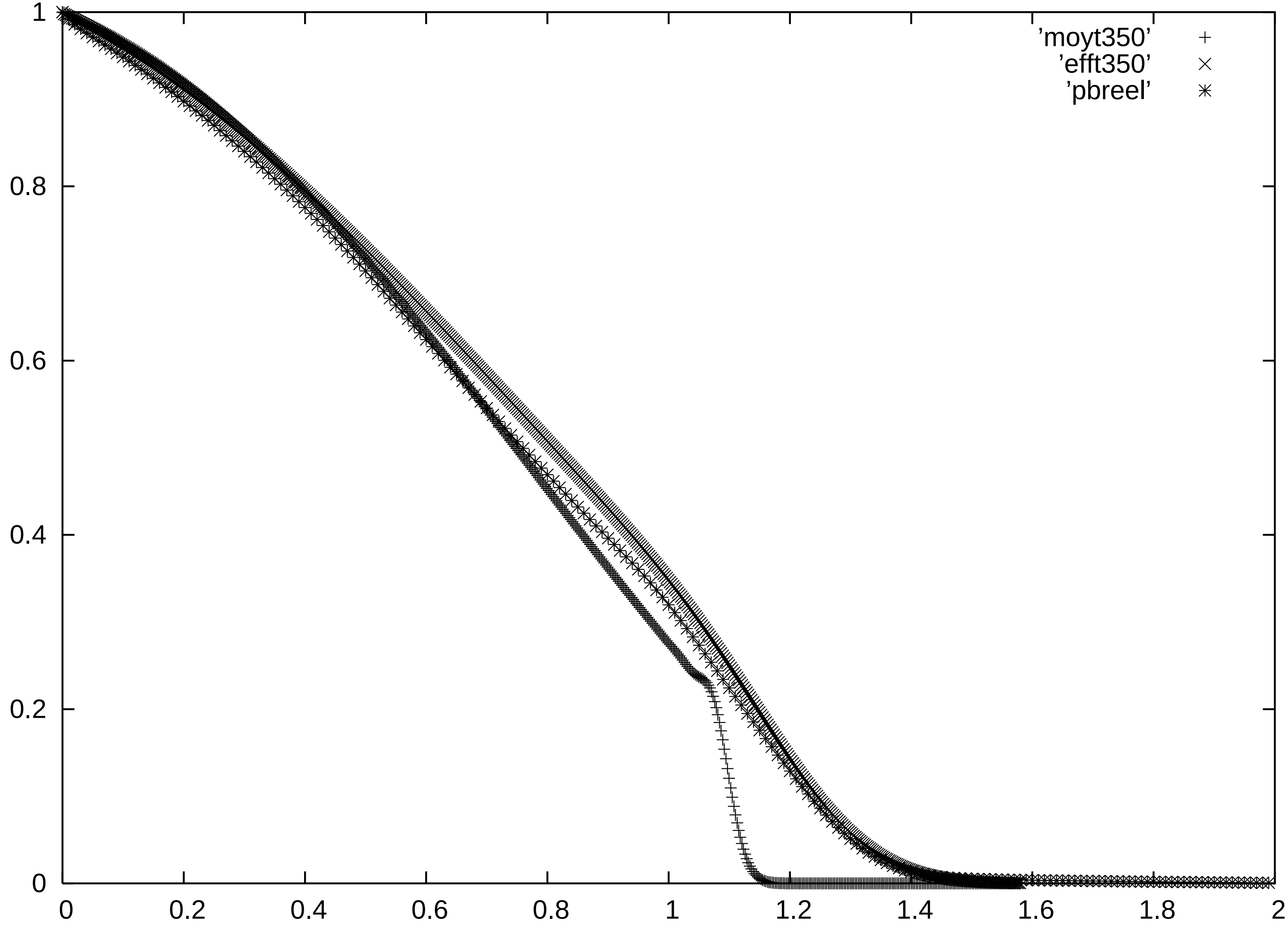

Figure 9: Comparison between the volume concentrations at time $t^* = 350$ sec.

the Nonlinear Problem

Now we study some nonlinear cases. Then the condition (2) is replaced by

$$-D^*\partial_{y^*}c^* = \frac{\partial \hat{c}}{\partial t^*} = \hat{\Phi}(c^*) - \hat{k}_d^* \hat{c} \quad \text{on } z = \pm H, \tag{62}$$

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

$$\hat{\Phi}(c) = \frac{k_1 c}{1 + k_2 c} \quad (\text{Langmuir}) \ ; \quad \hat{\Phi}(c) = k_1 c^{k_2} \quad (\text{Freundlich}). \tag{63}$$

Characteristic times are now $T_A = \hat{c}_R/(c_R k_{1R})$ (characteristic adsorption time) and $T_{react} = H/k_{1R}$ (superficial chemical reaction time scale).

Nonlinear problem 1

In non- dimensional form, (62) reads

$$-D\varepsilon^{\alpha-2}\frac{\partial c^{\varepsilon}}{\partial y}=\frac{T_A}{T_{react}}\frac{\partial c_s^{\varepsilon}}{\partial t}=\frac{T_L}{T_{react}}(\Phi(c^{\varepsilon})-k_d^{*}T_A c_s^{\varepsilon})|_{y=1} \text{ on } \Gamma^{+}\times(0, \tag{64}$$

The effective problem is now

$$\partial_t\Big(c^0_{FN}+\frac{T_A}{T_{react}}c^{eff}_{sN}\Big)+\frac{2Q}{3}\partial_x\Big(c^0_{FN}+\frac{1}{15D}\frac{T_T}{T_{react}}\Phi(c^0_{FN})\Big)=$$

$$\varepsilon^{\alpha}\Big(D+\frac{8}{945}\frac{Q^2}{D}\varepsilon^{2(1-\alpha)}\Big)\partial_{xx}c^0_{FN}+\frac{2Q}{45D}\frac{T_A T_T k_d^{*}}{T_{react}}\partial_x c^{eff}_{sN}, \tag{65}$$

$$\partial_t c^{eff}_{sN}=\frac{T_L}{T_A}\Big(\Phi(c^0_{FN}+\varepsilon^{2-\alpha}c^1_{FN}|_{y=1})-k_d^{*}T_A c^0_{sN}\Big), \tag{66}$$

$$c^1_{FN}|_{y=1}=\frac{2}{45}\frac{Q}{D}\partial_x c^0_{FN}-\frac{T_A}{3DT_{react}}\partial_t c^{eff}_{sN}, \tag{67}$$

Nonlinear problem 1a

$$c^0_{FN}|_{x=0} = 0, \quad c^0_{FN}|_{t=0} = 1, \quad c^{eff}_{SN}|_{t=0} = c_{s0}. \tag{68}$$

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

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

$$D^*(1 + \frac{8}{945}\mathbf{Pe}^2_T)\partial_{x^*x^*}c^*_N + \frac{2k^*_d\mathbf{Pe}_T}{45}\partial_{x^*}\hat{c}_N \tag{69}$$

$$\partial_{t^*}\hat{c}_N = \hat{\Phi}(c^*_N + \mathbf{Pe}_T\tilde{c}^1_N) - k^*_d\hat{c}_N \tag{70}$$

$$\tilde{c}^1_N = \frac{2H}{45}\partial_{x^*}c^*_N - \frac{1}{3}\partial_{t^*}\hat{c}_N, \tag{71}$$

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

Nonlinear problem 1b

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

$$\partial_{t^*}\left(c_N^{moy} + \frac{\hat{c}_N^{moy}}{H}\right) + \frac{2Q^*}{3}\partial_{x^*} c_N^{moy} - D^* \partial_{x^* x^*} c_N^{moy} = 0 \qquad (72)$$

$$\partial_{t^*} \hat{c}_N = \hat{\Phi}(c_N^{moy}) - k_d^* \hat{c}_N. \qquad (73)$$

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

For more details one could consult the article

[P] C.J. van Duijn, Andro Mikelić, I. S. Pop, Carole Rosier: Effective Dispersion Equations For Reactive Flows With Dominant Peclet and Damkohler Numbers, to appear in "Advances in Chemical Engineering", 2008.

Infinite adsorption rate

Here we concentrate our attention to the case when the adsorption rate constant $\hat{k}^*$ is infinitely large.
This means that the reaction at channel wall $\Gamma^* = \{(x^*, z) :\ 0 < x^* < +\infty,\ |z| = H\}$ is described by the the following flux equation

$$-D^* \partial_z c^* = K_e \frac{\partial c^*}{\partial t^*} \quad \text{on } \Gamma^*, \tag{74}$$

where K_e is, as before, the linear adsorption equilibrium constant. Now we see that (60) is replaced by (74), which corresponds to taking the limit $\hat{k}^* \to \infty$.
The characteristic times T_A and T_{DE} can not be used any more and we introduce the new characteristic time $T_C = \dfrac{K_{eR}}{\varepsilon Q_R}$, which has a meaning of the superficial chemical

reaction time scale. As before, we set $\varepsilon = \frac{H}{L_R} << 1$ and choose $T_R = T_L$. Introducing the dimensionless numbers into the starting and considering constant initial/boundary conditions yields the problem :

$$\frac{\partial c^\varepsilon}{\partial t} + Q(1-y^2)\frac{\partial c^\varepsilon}{\partial x} = D\varepsilon^\alpha \frac{\partial^2 c^\varepsilon}{\partial x^2} + D\varepsilon^{\alpha-2}\frac{\partial^2 c^\varepsilon}{\partial y^2} \quad \text{in } \Omega^+ \times (0,T) \tag{75}$$

$$-D\varepsilon^{\alpha-2}\frac{\partial c^\varepsilon}{\partial y} = -D\frac{1}{\varepsilon^2 \mathbf{Pe}}\frac{\partial c^\varepsilon}{\partial y} = \frac{T_C}{T_L}K\frac{\partial c^\varepsilon}{\partial t} \quad \text{on } \Gamma^+ \times (0,T) \tag{76}$$

$$c^\varepsilon(x,y,0) = 1 \quad \text{for } (x,y) \in \Omega^+, \tag{77}$$

$$c^\varepsilon(0,y,t) = 0 \quad \text{for } (y,t) \in (0,1) \times (0,T), \tag{78}$$

Further, we suppose that $T_C \approx T_L$. After the same calculations as before, we find that the effective problem for the concentration $c_K^{*,eff}$ in its dimensional form reads

$$(1+\mathbf{Da}_K)\frac{\partial c_K^{*,eff}}{\partial t^*}+\frac{2Q^*}{3}\frac{\partial c_K^{*,eff}}{\partial x^*}=$$

$$D^*\Big(1+\frac{4}{135}\mathbf{Pe}_T^2\big[\frac{2}{7}+\frac{\mathbf{Da}_K(2+7\mathbf{Da}_K)}{(1+\mathbf{Da}_K)^2}\big]\Big)\frac{\partial^2 c_K^{*,eff}}{\partial (x^*)^2}. \qquad (79)$$

In (79) $\mathbf{Pe}_T = \frac{Q^* H}{D^*}$ is the transversal Peclet number and $\mathbf{Da}_K = \frac{K_e}{H}$ is the transversal Damkohler number.

Numerical experiments

The transversal section mean gives

$$(1+\mathbf{Da}_K)\partial_{t^*} c_K^{moy} + \frac{2Q^*}{3}\partial_{x^*} c_K^{moy} - D^*\partial_{x^*x^*} c_K^{moy} = 0 \qquad (80)$$

We present the numerical solution of the equation (79) with the initial/boundary data

$$c_K^{*,eff}|_{x^*=0} = 0 \text{ and } c_K^{*,eff}|_{t^*=0} = 1. \qquad (81)$$

Parameters are shown on the Table 4.

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

Table 4: Parameter values in the case of an infinite adsorp-

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

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

The simulations are from [P] C.J. van Duijn, A. Mikelić, I. S. Pop, C. Rosier: Effective Dispersion Equations For Reactive Flows With Dominant Peclet and Damkohler Numbers,to appear in *Advances in Chemical Engineering*, 2008.

and the error estimate in the articles [A1] and

[A2] A. Mikelić , C. Rosier : Rigorous upscaling of the infinite adsorption rate reactive flow under dominant Peclet number through a pore, *Ann Univ Ferrara*,Vol. 53 (2007), p. 333–359.

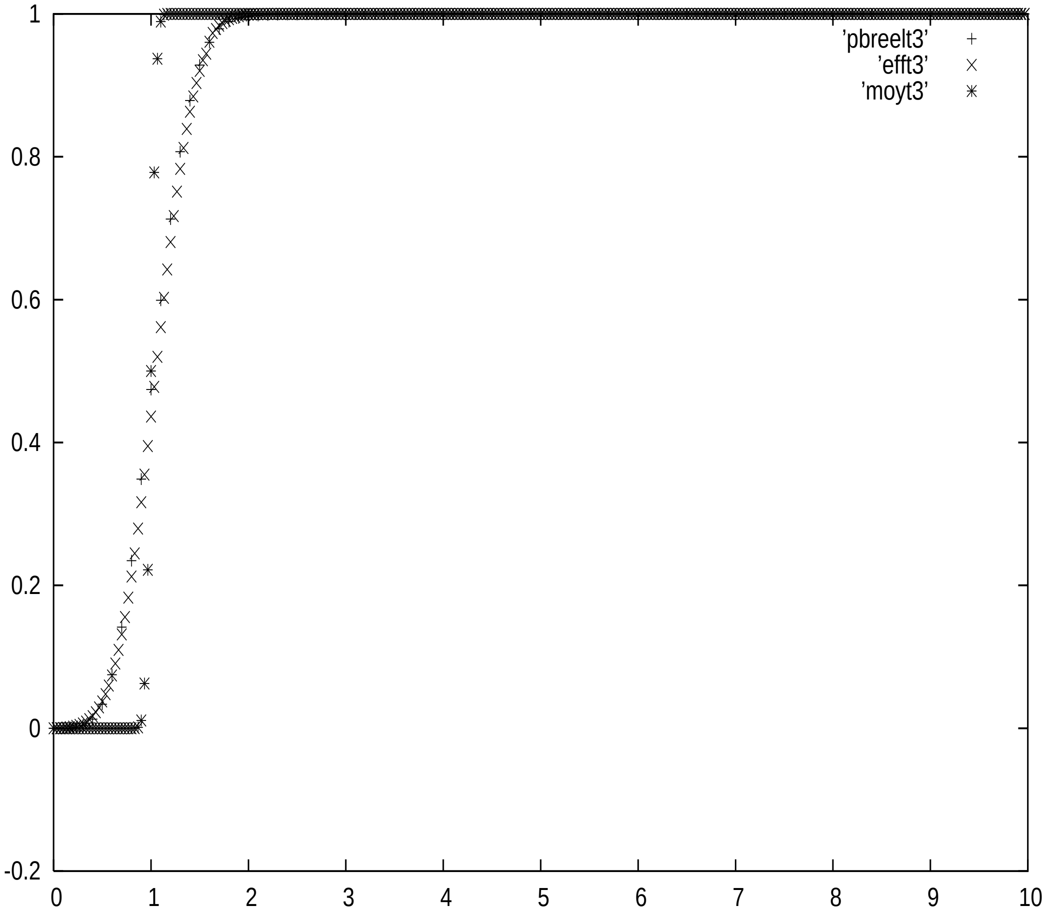

Figure 10: Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentrations at $t = 863$ sec.

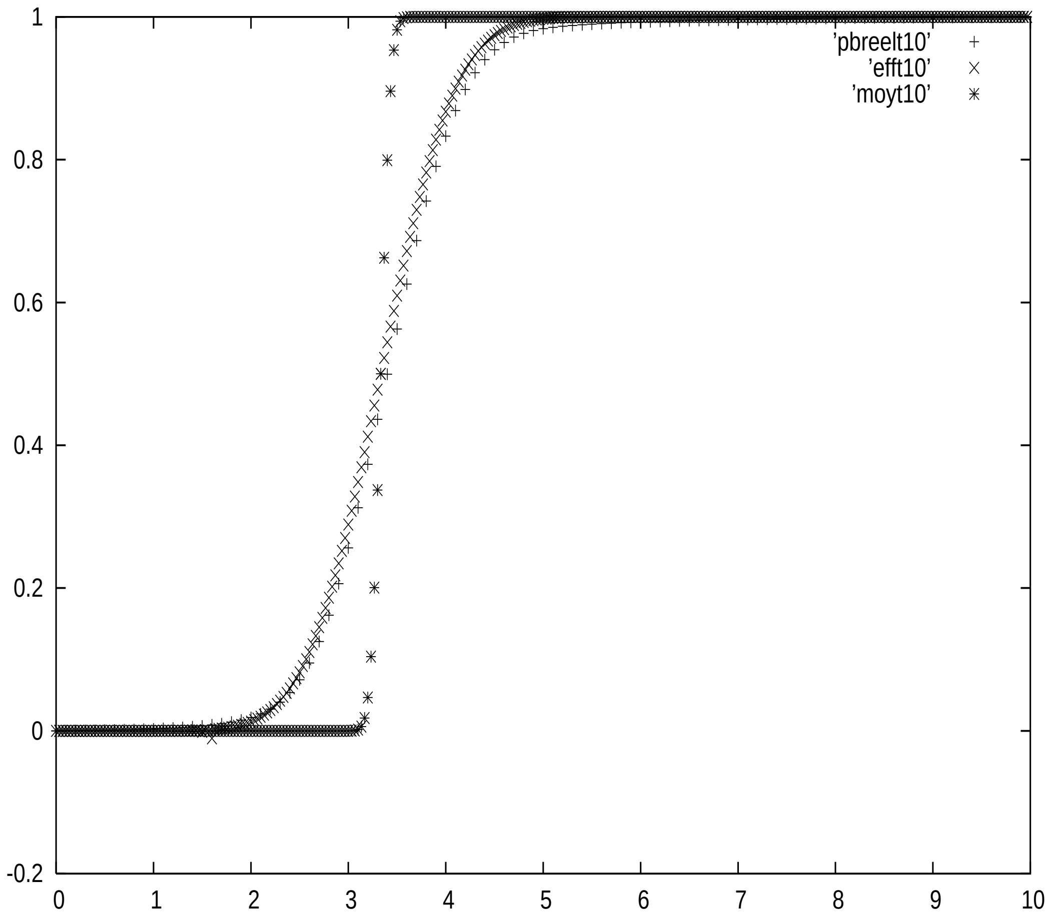

Figure 11: Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentrations at $t = 2877$ sec.

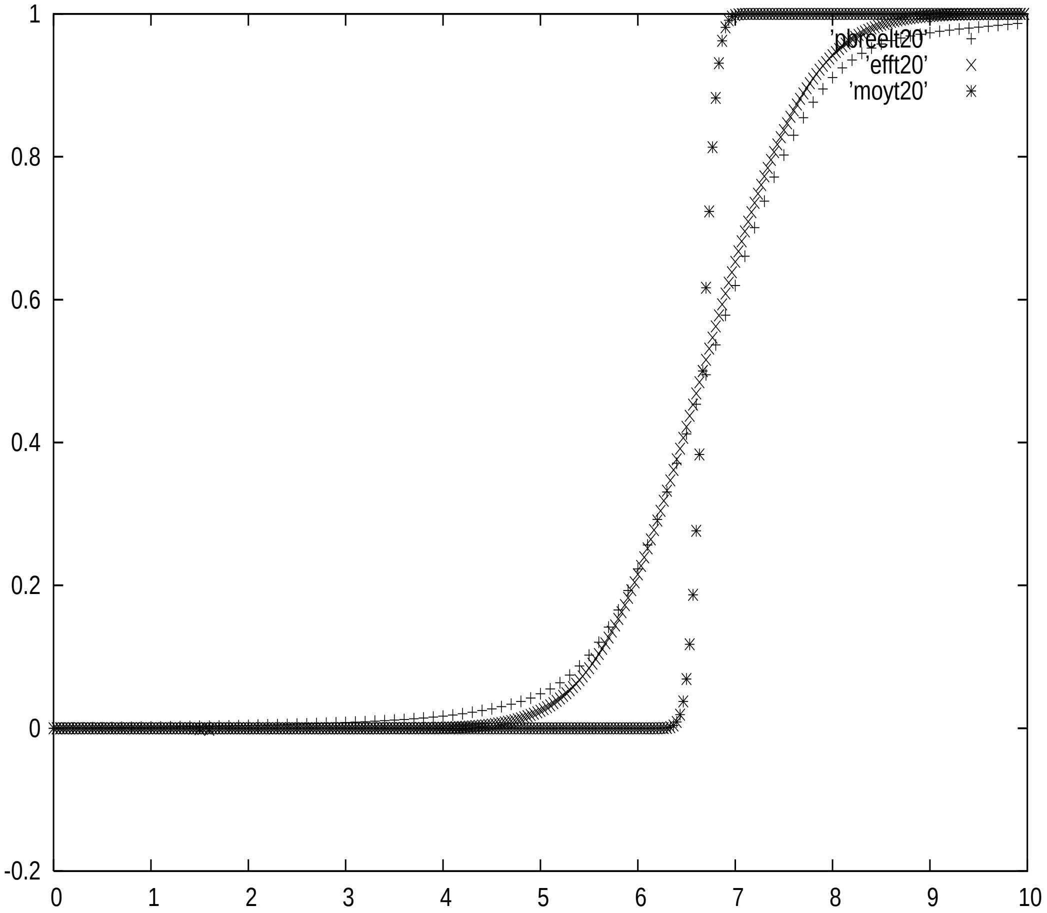

Figure 12: Case of an infinite adsorption rate $\hat{k}^* = +\infty$: Comparison between concentrations at $t = 5755$ sec.

Perspectives:

PERSPECTIVES:

- Getting the effective equation for more complicated chemistry
- Hyperbolic models? Camacho, Cas Berentsen ....
- Generalization to realistic porous media
- Advantages of the homogenization approach over direct simulations of stiff anisotropic multidimensional convection/diffusion are obvious