About the Quasi Steady State Approximation for a Reaction Diffusion System Describing a Chain of Irreversible Chemical Reactions

F. Conforto

Dipartimento di Matematica e Informatica, Università di Messina
V.le F. Stagno d'Alcontres, 31, 98166 Messina, Italy
E-mail: fiamma@unime.it

L. Desvillettes

CMLA, ENS Cachan, CNRS
61 Av. du Pdt. Wilson, 94235 Cachan Cedex, France
E-mail: desville@cmla.ens-cachan.fr

R. Monaco

DIST (Dipartimento Interateneo di Scienze, Progetto e Politiche del Territorio), Politecnico di Torino
Castello del Valentino, Viale Mattioli 39, 10125 Torino, Italy
E-mail: roberto.monaco@polito.it

Abstract

We present here a rigorous proof of the quasi steady state approximation in the context of a system of reaction-diffusion equations coming out of a typical chain of irreversible chemical reactions.

1 Introduction

The quasi steady state approximation (or QSSA) is a standard procedure in the study of chemical reactions kinetics allowing to eliminate from the equations the evolution of the species having a short time of existence w.r.t. the typical time of reaction of the chain. It consists in neglecting the speed of variation of the unstable species (that is, to replace it by 0). One can find in [15] a detailed description of the QSSA and the assumptions underlying its validity.

This approximation has been studied extensively at the mathematical level in the case when the spatial structure is not taken into account (that is, the chemistry is modeled by ODEs satisfied by the global concentrations of the species), see for instance [15, 2, 8, 14] and the references therein.

Our goal is to study the rigorous validity of the QSSA when the evolution of the species is described by reaction diffusion PDEs (each species having its own diffusion). In order to do so, we intend to use methods based on Lyapounov functionals and duality lemmas. Such a study was performed in [1] and in [5] in the case of a typical system of reversible equations. We wish in this paper to study the possible extensions of those methods in the context of a typical chain of irreversible reactions, where the entropy used in [1] is not available anymore. The analysis that we propose is in fact closer to that of [5] (the results that we provide could probably at least partly be recovered by following the arguments of [5], we propose however slightly different arguments).

Note that the QSSA has also been investigated in [16] in cases when there is a bounded invariant region for the unknowns. Finally the fast reaction asymptotics is another interesting problem for reaction-diffusion PDEs, which shares common features with the QSSA. It has been studied for example in [9, 6] for irreversible reactions, and in [3, 4] for reversible ones.

Here, we are interested in a typical chain of chemical reactions, such as

$$\begin{cases} A+B & \longrightarrow & C+D, \\ D+E & \longrightarrow & A+C, \\ C+E & \longrightarrow & A, \end{cases} \tag{1}$$

or its simpler version

$$\begin{cases} A+B & \longrightarrow & C+D, \\ D+E & \longrightarrow & A+C, \\ C & \longrightarrow & A, \end{cases} \tag{2}$$

We also introduce the corresponding systems of reaction diffusion for unknowns $a := a(t,x) \geq 0$, $b := b(t,x) \geq 0$, $c := c(t,x) \geq 0$, $d := d(t,x) \geq 0$ and $e := e(t,x) \geq 0$, which represent the concentrations at time $t \in \mathbb{R}_+$ and point $x \in \Omega$ (Ω being a bounded smooth open subset of $\mathbb{R}^N$, $N \in \mathbb{N}^*$) of the species A, B, C, D and E.

For the chain (1), it writes

$$\partial_t a - d_1\, \Delta_x a = -k_1\, a\, b + k_2\, d\, e + k_3\, c\, e, \tag{3}$$

$$\partial_t b - d_2\, \Delta_x b = -k_1\, a\, b, \tag{4}$$

$$\partial_t c - d_3\, \Delta_x c = k_1\, a\, b + k_2\, d\, e - k_3\, c\, e, \tag{5}$$

$$\partial_t d - d_4\, \Delta_x d = k_1\, a\, b - k_2\, d\, e, \tag{6}$$

$$\partial_t e - d_5\, \Delta_x e = -k_2\, d\, e - k_3\, c\, e, \tag{7}$$

together with Neumann boundary conditions (for all $x \in \partial\Omega$)

$$\nabla_x a \cdot n(x) = 0, \quad \nabla_x b \cdot n(x) = 0, \quad \nabla_x c \cdot n(x) = 0, \quad \nabla_x d \cdot n(x) = 0, \quad \nabla_x e \cdot n(x) = 0, \tag{8}$$

and initial data

$$a(0,\cdot) = a_{in}, \quad b(0,\cdot) = b_{in}, \quad c(0,\cdot) = c_{in}, \quad d(0,\cdot) = d_{in}, \quad e(0,\cdot) = e_{in}. \tag{9}$$

The parameters $d_1, .., d_5$ are the diffusion rates of the species $A, .., E$, and $k_1, .., k_3$ are the rates of the three reactions in the chain.

In the simpler chain (2), we get

$$\partial_t a - d_1 \, \Delta_x a = -k_1 \, a \, b + k_2 \, d \, e + k_3 \, c, \tag{10}$$

$$\partial_t b - d_2 \, \Delta_x b = -k_1 \, a \, b, \tag{11}$$

$$\partial_t c - d_3 \, \Delta_x c = k_1 \, a \, b + k_2 \, d \, e - k_3 \, c, \tag{12}$$

$$\partial_t d - d_4 \, \Delta_x d = k_1 \, a \, b - k_2 \, d \, e, \tag{13}$$

$$\partial_t e - d_5 \, \Delta_x e = -k_2 \, d \, e - k_3 \, c, \tag{14}$$

still with boundary and initial conditions (8), (9).

If we now suppose that C is unstable (w.r.t. other species). This amounts to assume that $k_3 >> k_1, k_2$, so that we take the notation $k_3 = 1/\varepsilon$. The QSSA predicts that (in the limit $\varepsilon \to 0$) the concentration c should be of order ε, provided that $c_{in}(x) = 0$ for all $x \in \Omega$ (so that no initial layer appears). In order to state a rigorous result of convergence, we introduce explicitly the dependence of the concentrations w.r.t. ε, and get for the chain (1):

$$\partial_t a_\varepsilon - d_1 \, \Delta_x a_\varepsilon = -k_1 \, a_\varepsilon \, b_\varepsilon + k_2 \, d_\varepsilon \, e_\varepsilon + \frac{k_3}{\varepsilon} \, c_\varepsilon \, e_\varepsilon, \tag{15}$$

$$\partial_t b_\varepsilon - d_2 \, \Delta_x b_\varepsilon = -k_1 \, a_\varepsilon \, b_\varepsilon, \tag{16}$$

$$\partial_t c_\varepsilon - d_3 \, \Delta_x c_\varepsilon = k_1 \, a_\varepsilon \, b_\varepsilon + k_2 \, d_\varepsilon \, e_\varepsilon - \frac{k_3}{\varepsilon} \, c_\varepsilon \, e_\varepsilon, \tag{17}$$

$$\partial_t d_\varepsilon - d_4 \, \Delta_x d_\varepsilon = k_1 \, a_\varepsilon \, b_\varepsilon - k_2 \, d_\varepsilon \, e_\varepsilon, \tag{18}$$

$$\partial_t e_\varepsilon - d_5 \, \Delta_x e_\varepsilon = -k_2 \, d_\varepsilon \, e_\varepsilon - \frac{k_3}{\varepsilon} \, c_\varepsilon \, e_\varepsilon, \tag{19}$$

together with Neumann boundary conditions (for all $x \in \partial\Omega$)

$$\nabla_x a_\varepsilon \cdot n(x) = 0, \quad \nabla_x b_\varepsilon \cdot n(x) = 0, \quad \nabla_x c_\varepsilon \cdot n(x) = 0, \quad \nabla_x d_\varepsilon \cdot n(x) = 0, \quad \nabla_x e_\varepsilon \cdot n(x) = 0, \tag{20}$$

and initial data

$$a_\varepsilon(0, \cdot) = a_{in}, \quad b_\varepsilon(0, \cdot) = b_{in}, \quad c_\varepsilon(0, \cdot) = 0, \quad d_\varepsilon(0, \cdot) = d_{in}, \quad e_\varepsilon(0, \cdot) = e_{in}. \tag{21}$$

In the case of the simpler chain (2), eq. (15) – (19) are replaced by

$$\partial_t a_\varepsilon - d_1 \, \Delta_x a_\varepsilon = -k_1 \, a_\varepsilon \, b_\varepsilon + k_2 \, d_\varepsilon \, e_\varepsilon + \frac{k_3}{\varepsilon} \, c_\varepsilon, \tag{22}$$

$$\partial_t b_\varepsilon - d_2 \, \Delta_x b_\varepsilon = -k_1 \, a_\varepsilon \, b_\varepsilon, \tag{23}$$

$$\partial_t c_\varepsilon - d_3\,\Delta_x c_\varepsilon = k_1\,a_\varepsilon\,b_\varepsilon + k_2\,d_\varepsilon\,e_\varepsilon - \frac{k_3}{\varepsilon}\,c_\varepsilon, \tag{24}$$

$$\partial_t d_\varepsilon - d_4\,\Delta_x d_\varepsilon = k_1\,a_\varepsilon\,b_\varepsilon - k_2\,d_\varepsilon\,e_\varepsilon, \tag{25}$$

$$\partial_t e_\varepsilon - d_5\,\Delta_x e_\varepsilon = -k_2\,d_\varepsilon\,e_\varepsilon - \frac{k_3}{\varepsilon}\,c_\varepsilon, \tag{26}$$

while the initial and boundary conditions (20) and (21) are left unchanged.

We start by stating a Theorem which shows that the QSSA is indeed rigorously justified in the case of the simplified system (22) – (26).

Theorem 1: Let Ω be a smooth (C^2), bounded and connected open subset of $\mathbb{R}^N$ ($N \in \mathbb{N}^*$), let $d_1, .., d_5 > 0$, $k_1, .., k_3 > 0$, and let a_{in},..,e_{in} be initial data in $C^2(\overline{\Omega}, \mathbb{R}_+)$, compatible with the Neumann boundary condition (20). Then, for any $\varepsilon > 0$, there exists a unique global strong ($C^2(\mathbb{R}_+ \times \overline{\Omega}; \mathbb{R}_+)$) solution $(a_\varepsilon, .., e_\varepsilon)$ to the system (22) – (26) with initial and boundary conditions (20) and (21). Moreover, this solution $(a_\varepsilon, .., e_\varepsilon)$ converges in $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+ \times \Omega)$ strong towards $(a, b, 0, d, e)$, where (a, b, d, e) is the unique global strong ($C^2(\mathbb{R}_+ \times \overline{\Omega}; \mathbb{R}_+)$) solution of the following limit system:

$$\partial_t a - d_1 \Delta_x a = 2\,k_2\,d\,e, \tag{27}$$

$$\partial_t b - d_2\,\Delta_x b = -k_1\,a\,b, \tag{28}$$

$$\partial_t d - d_4\,\Delta_x d = k_1\,a\,b - k_2\,d\,e, \tag{29}$$

$$\partial_t e - d_5 \Delta_x e = -2\,k_2\,d\,e - k_1\,a\,b, \tag{30}$$

together with initial and boundary conditions (20) and (21) [except those for c].

As expected in the QSSA framework, c_ε converges to 0 (that is, the unstable species has a very small concentration). Moreover, the limit system is closed thanks to the convergence towards 0 of the variation of c_ε, that is $k_1\,a_\varepsilon\,b_\varepsilon + k_2\,d_\varepsilon\,e_\varepsilon - \frac{k_3}{\varepsilon}\,c_\varepsilon \to 0$.

In the case of the full system, the QSSA can only be partially proven, in the sense that instead of getting $c = 0$ in the limit, we only get $c\,e = 0$.

We end up in fact with the following Theorem:

Theorem 2: Let Ω be a smooth (C^2), bounded and connected open subset of $\mathbb{R}^N$ ($N \in \mathbb{N}^*$), let $d_1, .., d_5 > 0$, $k_1, .., k_3 > 0$, and let a_{in},..,e_{in} be initial data in $C^2(\overline{\Omega}, \mathbb{R}_+)$, compatible with the Neumann boundary condition (20). Then, for any $\varepsilon > 0$, there exists a unique global strong ($C^2(\mathbb{R}_+ \times \overline{\Omega}; \mathbb{R}_+)$) solution $(a_\varepsilon, .., e_\varepsilon)$ to the system (15) – (19) with initial and boundary conditions (20) and (21). Moreover, this solution $(a_\varepsilon, .., e_\varepsilon)$ converges up to extraction of a subsequence in $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+ \times \Omega)$ strong towards (a, b, c, d, e), where (a, b, c, d, e) is a global weak solution of the following limit system:

$$\partial_t(a + c) - \Delta_x(d_1\,a + d_3\,c) = 2\,k_2\,d\,e, \tag{31}$$

$$\partial_t b - d_2\,\Delta_x b = -k_1\,a\,b, \tag{32}$$

$$c\,e = 0, \tag{33}$$

$$\partial_t d - d_4\,\Delta_x d = k_1\,a\,b - k_2\,d\,e, \tag{34}$$

$$\partial_t (e-c) - \Delta_x (d_5\,e - d_3\,c) = -2\,k_2\,d\,e - k_1\,a\,b. \tag{35}$$

together with initial and boundary conditions (20) and (21) [except those for c].

Note that if we knew that $c = 0$ in the above system, we would be able to conclude that the convergence of the whole sequence holds, since there would be uniqueness of a (weak) solution of the system. This identity seems however difficult to prove without extra assumptions. As can be seen, the QSSA is not completely proven in this case (more precisely, it is proven only in the regions where $e \neq 0$: no information about those regions is available unfortunately).

Note also that in the above theorems, we made no effort to give optimal conditions on the initial data (part of the conclusions would hold even in if the initial data were only continuous, or even belonged to some well chosen L^p space. Also the convergences (of a_ε towards a, etc.) are shown to hold a.e., but part of them in fact hold in (well chosen) Sobolev spaces.

Finally we did not try here to study the case when the unstable species has a non zero initial datum. In that case, an initial layer should appear, which needs a specific treatment (cf. [5]).

The rest of this paper is devoted to the Proof of Theorem 1 (section 2) and Theorem 2 (section 3).

2 Proof of the Theorem for the simplified model

We begin here the

Proof of Theorem 1: Let us first briefly recall how (for any $\varepsilon > 0$), existence and uniqueness of a strong (smooth, nonnegative) solution to system (22) - (26) can be obtained. First, local (in time) solutions are proven to exist thanks to an iterative method like in [10].

Then, this solution is shown to be global (in time) thanks to a continuation process using *a priori* estimates. We recall here the necessary estimates. First, thanks to the maximum principle, it is clear that (for all $t \geq 0$ such that the solution exists)

$$0 \leq e_\varepsilon(t,x) \leq ||e_{in}||_{L^\infty(\Omega)}, \qquad 0 \leq b_\varepsilon(t,x) \leq ||b_{in}||_{L^\infty(\Omega)}. \tag{36}$$

Observing that

$$\partial_t (a_\varepsilon + c_\varepsilon + 2\,e_\varepsilon) - \Delta_x (d_1\,a_\varepsilon + d_3\,c_\varepsilon + 2\,d_5\,e_\varepsilon) = -2\,\frac{k_3}{\varepsilon}\,c_\varepsilon\,e_\varepsilon \leq 0,$$

and

$$\partial_t (b_\varepsilon + d_\varepsilon) - \Delta_x (d_2\,b_\varepsilon + d_4\,d_\varepsilon) = -k_2\,d_\varepsilon\,e_\varepsilon \leq 0,$$

we see using the duality method (cf. [12], [11]) that (for any $T > 0$ such that the solution exists)

$$||a_\varepsilon||_{L^2([0,T]\times\Omega)} \le C_T, \qquad ||c_\varepsilon||_{L^2([0,T]\times\Omega)} \le C_T, \qquad ||d_\varepsilon||_{L^2([0,T]\times\Omega)} \le C_T,$$

where $C_T > 0$ does not depend on ε (in fact it only depends on the L^2 bounds of the initial data a_{in}, b_{in}, d_{in}, e_{in}, and of the the diffusion rates $d_1, .., d_5 > 0$). It would even be possible to replace L^2 in the estimates above by $L^{2+\delta}$ for some $\delta > 0$ using the arguments of [7], but we shall show in the sequel that an even better estimate holds.

Indeed, a more careful examination of the duality method shows that (cf. [13])

$$||d_\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T \tag{37}$$

for all $p \neq \infty$. Also, as a consequence

$$||d_\varepsilon\, e_\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T. \tag{38}$$

Then, writing

$$\partial_t(a_\varepsilon + e_\varepsilon) - \Delta_x(d_1\, a_\varepsilon + d_5\, e_\varepsilon) = -k_1\, a_\varepsilon\, b_\varepsilon \le 0,$$

and using again the duality arguments of [13], we end up with

$$||a_\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T \tag{39}$$

for all $p \neq \infty$. Finally, observing that

$$\partial_t(a_\varepsilon + c_\varepsilon) - \Delta_x(d_1\, a_\varepsilon + d_3\, c_\varepsilon) = 2\, k_2\, d_\varepsilon\, e_\varepsilon,$$

and using estimate (38) together with (one last time) the duality arguments of [13], we see that

$$||c_\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T \tag{40}$$

for all $p \neq \infty$. Note that all those estimates are independent on $\varepsilon > 0$.

As a consequence of the previous estimates (the second inequality having already been stated in (38),

$$||a_\varepsilon\, b_\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T, \qquad ||d_\varepsilon\, e_\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T, \tag{41}$$

and

$$||c_\varepsilon/\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T/\varepsilon, \tag{42}$$

so that thanks to the properties of the heat equation, and eq. (22) - (26),

$$||a_\varepsilon, b_\varepsilon, c_\varepsilon, d_\varepsilon, e_\varepsilon||_{L^\infty([0,T]\times\Omega)} \le C_{T,\varepsilon}. \tag{43}$$

According to [10], existence (for a given $\varepsilon > 0$) of a global (locally bounded) solution to system (22) - (26) holds. Then, the smoothness of this solution is a direct consequence of bootstraps arguments using the heat kernel properties, and uniqueness also holds (cf. also [10]).

We now turn to the proof of the QSSA. Note that estimates (43) cannot be used since the constant appearing there is not ε-independent, whereas estimates (36) – (40) are available since they are ε-independent.

We observe that integrating eq. (26) over $[0,T]\times\Omega$,

$$\int_\Omega e_\varepsilon(T,x)\,dx + \frac{k_3}{\varepsilon}\int_0^T\int_\Omega c_\varepsilon(t,x)\;dxdt \le \int_\Omega e_{in}(x)\,dx.$$

In other words,

$$||c_\varepsilon/\varepsilon||_{L^1([0,T]\times\Omega)} \le C_T. \tag{44}$$

which, together with estimate (40), entails the convergence towards 0 of c_ε in $\cap_{p\in[1,+\infty[}L^p_{loc}(\mathbb{R}_+\times\Omega)$ strong.

Then, thanks to estimates (36), (37) and (39), we see that up to the extraction of a subsequence, $a_\varepsilon \rightharpoonup a$, $d_\varepsilon \rightharpoonup d$ in $\cap_{p\in[1,+\infty[}L^p_{loc}(\mathbb{R}_+\times\Omega)$ weak (where a, d are some elements of $\cap_{p\in[1,+\infty[}L^p_{loc}(\mathbb{R}_+\times\Omega)$), and $b_\varepsilon \rightharpoonup b$, $e_\varepsilon \rightharpoonup e$ in $L^\infty(\mathbb{R}_+\times\Omega)$ weak (where b, e are some elements of $L^\infty(\mathbb{R}_+\times\Omega)$).

Using estimate (44) together with (41) and eq. (22) - (26), and remembering the compactness properties of the heat equation, we see that the convergences above also hold for a.e. t, x, and therefore in $\cap_{p\in[1,+\infty[}L^p_{loc}(\mathbb{R}_+\times\Omega)$ strong.

As a consequence, the sequence $a_\varepsilon\,b_\varepsilon$ converges (up to extraction of a subsequence) towards $a\,b$ in $\cap_{p\in[1,+\infty[}L^p_{loc}(\mathbb{R}_+\times\Omega)$ and the sequence $d_\varepsilon\,e_\varepsilon$ converges (up to extraction of a subsequence) towards $d\,e$ in $\cap_{p\in[1,+\infty[}L^p_{loc}(\mathbb{R}_+\times\Omega)$.

We can therefore pass to the limit in the sense of distributions (more precisely, with test functions taken in $C^\infty_c(\mathbb{R}_+\times\overline{\Omega})$)) in eq. (23) and (25) and get eq. (28) and (29) in the sense of distributions (more precisely, those equations are satisfied in the weak sense including the boundary condition (8) [for b and d] and the initial data (9) [for b and d]; this means once again that the test functions are taken in $C^\infty_c(\mathbb{R}_+\times\overline{\Omega})$).

We then write the result of the sum of eq. (22) and eq. (24) on one hand, and the result of the difference between eq. (26) and eq. (24) on the other hand:

$$\partial_t(a_\varepsilon + c_\varepsilon) - \Delta_x(d_1\,a_\varepsilon + d_3\,c_\varepsilon) = 2\,k_2\,d_\varepsilon\,e_\varepsilon, \tag{45}$$

$$\partial_t(e_\varepsilon - c_\varepsilon) - \Delta_x(d_5\,e_\varepsilon - d_3\,c_\varepsilon) = -2\,k_2\,d_\varepsilon\,e_\varepsilon - k_1\,a_\varepsilon\,b_\varepsilon. \tag{46}$$

We can also pass to the limit in this equation in the sense of distributions (once again, more precisely, with test functions taken in $C^\infty_c(\mathbb{R}_+\times\overline{\Omega})$), and get eq. (27) and (30) in the sense of distributions (more precisely, those equations are satisfied in the weak sense including the boundary condition (8) [for a and e] and the initial data (9) [for a and e]; this means once again that the test functions are taken in $C^\infty_c(\mathbb{R}_+\times\overline{\Omega})$).

In this way, we end up with a weak solution of the limit system (27) – (30) together with initial and boundary conditions (20) and (21) [except those for c]. According to the method described in [10] for example, we know that this solution is the unique strong (smooth, nonnegative) solution of the system, so that the whole family $a_\varepsilon, b_\varepsilon, c_\varepsilon, d_\varepsilon, e_\varepsilon$ (and not just a subsequence) converges towards $a, b, 0, d, e$.

This concludes the Proof of Theorem 1. $\square$

3 Proof of the Theorem for the complete model

We begin here the

Proof of Theorem 2: We observe that estimates (36) – (41) still hold for the (local in time) solution of system (15) - (19), the proof being identical to the one of the previous section.

We now replace estimate (42) by

$$||c_\varepsilon\, e_\varepsilon/\varepsilon||_{L^p([0,T]\times\Omega)} \le C_T/\varepsilon, \tag{47}$$

so that thanks to the properties of the heat equation, and eq. (15) - (19), estimates (43) hold. Using then the results of [10], existence (for a given $\varepsilon > 0$) of a global in time (locally bounded) solution to system (15) - (19) holds. We recall that the smoothness of this solution is a direct consequence of bootstraps arguments using the heat kernel properties, and that uniqueness also holds (cf. also [10]).

We now investigate the validity of the QSSA for this chain reaction. We integrate eq. (19) over $[0,T]\times\Omega$, and end up with

$$\int_\Omega e_\varepsilon(T,x)\,dx + \frac{k_3}{\varepsilon}\int_0^T\int_\Omega c_\varepsilon(t,x)\,e_\varepsilon(t,x)\,dxdt \le \int_\Omega e_{in}(x)\,dx.$$

Then,

$$||c_\varepsilon\, e_\varepsilon/\varepsilon||_{L^1([0,T]\times\Omega)} \le C_T, \tag{48}$$

which, together with estimates (36) and (40), entails the convergence towards 0 of $c_\varepsilon\, e_\varepsilon$ in $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+\times\Omega)$ strong.

Using as in the previous section estimates (36) – (39), but also (40), we see that up to the extraction of a subsequence, $a_\varepsilon \rightharpoonup a$, $c_\varepsilon \rightharpoonup c$, $d_\varepsilon \rightharpoonup d$ in $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+\times\Omega)$ weak (where a, c, d are some elements of $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+\times\Omega)$), and $b_\varepsilon \rightharpoonup b$, $e_\varepsilon \rightharpoonup e$ in $L^\infty(\mathbb{R}_+\times\Omega)$ weak (where b, e are some elements of $L^\infty(\mathbb{R}_+\times\Omega)$).

Using now estimate (48) together with (41) and eq. (15) - (19), and remembering the compactness properties of the heat equation, we see that the convergences above also hold for a.e. t, x, and therefore in $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+\times\Omega)$ strong. As in the previous section, we therefore see that the sequence $a_\varepsilon\, b_\varepsilon$ converges (up to extraction of a subsequence) towards $a\, b$ in $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+ \times \Omega)$ and that the sequence $d_\varepsilon\, e_\varepsilon$ converges (up to extraction of a subsequence) towards $d\, e$ in $\cap_{p\in[1,+\infty[} L^p_{loc}(\mathbb{R}_+ \times \Omega)$.

We now pass to the limit in the system (15) - (19). Using estimate (48) and Fatou's lemma, we first see that $c\, e = 0$, so that (33) holds.

We can also pass to the limit in the sense of distributions (more precisely, with test functions taken in $C^\infty_c(\mathbb{R}_+ \times \overline{\Omega})$)) in eq. (16) and (18) and get eq. (32) and (34) in the sense of distributions (more precisely, those equations are satisfied in the weak sense including the boundary condition (8) [for b and d] and the initial data (9) [for b and d]; this means once again that the test functions are taken in $C^\infty_c(\mathbb{R}_+ \times \overline{\Omega})$).

We then write the result of the sum of eq. (15) and eq. (17) on one hand, and the result of the difference between eq. (19) and eq. (17) on the other hand:

$$\partial_t(a_\varepsilon + c_\varepsilon) - \Delta_x(d_1\, a_\varepsilon + d_3\, c_\varepsilon) = 2\, k_2\, d_\varepsilon\, e_\varepsilon, \tag{49}$$

$$\partial_t(e_\varepsilon - c_\varepsilon) - \Delta_x(d_5\, e_\varepsilon - d_3\, c_\varepsilon) = -2\, k_2\, d_\varepsilon\, e_\varepsilon - k_1\, a_\varepsilon\, b_\varepsilon. \tag{50}$$

We can also pass to the limit in these equations in the sense of distributions (once again, more precisely, with test functions taken in $C^\infty_c(\mathbb{R}_+ \times \overline{\Omega})$), and get eq. (31) and (35) in the sense of distributions (more precisely, those equations are satisfied in the weak sense including the boundary condition (8) [for a and e] and the initial data (9) [for a and e]; this means once again that the test functions are taken in $C^\infty_c(\mathbb{R}_+ \times \overline{\Omega})$).

In this way, we end up with a weak solution of the limit system (31) – (35) together with initial and boundary conditions (20) and (21) [except those for c]. Note however that we have no information on the smoothness of the solutions to system (31) – (35) since it is not written under the standard parabolic form. We also do not know if uniqueness holds for this system, so that we cannot prove that the whole family $a_\varepsilon, b_\varepsilon, c_\varepsilon, d_\varepsilon, e_\varepsilon$ converges towards a, b, c, d, e.

This concludes the Proof of Theorem 2. □

References

[1] M. Bisi, F. Conforto, L. Desvillettes, "Quasi–steady–state approximation for reaction–diffusion equations", *Bull. Inst. Acad. Sin. (N.S.)* **2** (2007), n.4, 823–850.

[2] A. Blouza, F. Coquel, F. Hamel, "Reduction of linear kinetic systems with multiple scales", *Combust. Theory Modelling* **4** (2000), 339–362.

[3] D. Bothe, "Instantaneous limits of reversible chemical reactions in presence of macroscopic convection", *J. Differential Equations* **193** (2003), 27–48.

[4] D. Bothe, D. Hilhorst, "A reaction–diffusion system with fast reversible reaction", *J. Math. Anal. Appl.* **286** (2003), 125–135.

[5] D. Bothe, M. Pierre "Quasi–steady–state approximation for a reaction–diffusion system with fast intermediate", *J. Math. Anal. Appl.* **368** (2010), n.1, 120–132.

[6] D. Bothe, M. Pierre "The instantaneous limit for reaction–diffusion systems with a fast irreversible reaction", *Discrete Contin. Dyn. Syst. Ser. S* **5** (2012), n.1, 49–59.

[7] J. A. Canizo, L. Desvillettes, K. Fellner, "Improved duality estimates and applications to reaction-diffusion equations", Preprint n. 2013-07 of CMLA, ENS Cachan. Accepted for publication in Commun. Partial Differential Equations.

[8] G.M. Come, "Radical reaction mechanisms. Mathematical theory", *J. Phys. Chem.* **81** (1977), 2560–2563.

[9] D. Hilhorst, R. Van Der Hout, L.A. Peletier, "Nonlinear diffusion in the presence of fast reaction", *Nonlinear Anal.* **41** (2000), 803–823.

[10] L. Desvillettes, "About Entropy Methods for Reaction-Diffusion Equations", *Rivista di Matematica della Università di Parma.* **7**, n.7, (2007), 81–123.

[11] R. H. Martin, M. Pierre, "Nonlinear reaction-diffusion systems", *Math. Sci. and Engrg.* **185** (1992), 363-398.

[12] M. Pierre, D. Schmitt, "Blowup in reaction-diffusion systems with dissipation of mass", *SIAM Rev.* **42** (2000), n.1, 93–106.

[13] P. Quittner, Ph. Souplet, Superlinear parabolic problems. Blow-up, global existence and steady states, Birkhauser Advanced Texts, 2007.

[14] Z. Ren, S.B. Pope, "Entropy production and element conservation in the quasi–steady–state approximation", *Combustion and Flame* **137** (2004), 251–254.

[15] L.A. Segel, M. Slemrod, "The quasi–steady–state assumption: a case study in perturbation", *SIAM Review* **31** (1989), 446–477.

[16] A.N. Yannacopoulos, A.S. Tomlin, J. Brindley, J.H. Merkin, M.J. Pilling, "Error propagation in approximations to reaction–diffusion–advection–equations", *Phys. Letters A* **223** (1996), 82–90.