

Some asymptotic limits of reaction–diffusion systems appearing in reversible chemistry

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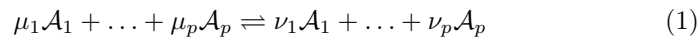
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Abstract This paper concerns reaction–diffusion systems consisting of three or four equations, which come out of reversible chemistry. We introduce different scalings for those systems, which make sense in various situations (species with very different concentrations or very different diffusion rates, chemical reactions with very different rates, etc.). We show how recently introduced mathematical tools allow to prove that the formal asymptotics associated to those scalings indeed hold at the rigorous level.

Keywords Reaction-Diffusion equations · Reversible chemistry · Singular Perturbations

1 Introduction

A generic reversible reaction like



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between chemical species $\mathcal{A}_1, \dots, \mathcal{A}_p$ diffusing in a non-reactive background can be modeled by the reaction-diffusion system

$$\partial_t \tilde{a}_i - \tilde{d}_i \Delta_x \tilde{a}_i = \tilde{\ell}(\mu_i - \nu_i) \tilde{a}_1^{\nu_1} \cdots \tilde{a}_p^{\nu_p} - \tilde{k}(\mu_i - \nu_i) \tilde{a}_1^{\mu_1} \cdots \tilde{a}_p^{\mu_p}, \quad (2)$$

where the r.h.s. of the system expresses the mass action law (cf. for example [10] for a complete presentation of the mass action law). Here \tilde{d}_i is the diffusion rate of the species \mathcal{A}_i , μ_i , and ν_i are the stoichiometric coefficients associated to the chemical reaction (1) and $\tilde{\ell}, \tilde{k}$ are the reaction rates. Finally, the unknowns $\tilde{a}_i := \tilde{a}_i(t, x)$ are the concentrations of the chemical species \mathcal{A}_i at time $t \in \mathbb{R}_+$ and point x .

When the species are confined in a chemical reactor modeled by a domain $\Omega \subset \mathbb{R}^N$, we add to (2) the homogeneous Neumann boundary conditions

$$\nabla_x \tilde{a}_i(t, x) \cdot n(x) = 0, \quad \forall x \in \partial\Omega, \quad t \in \mathbb{R}_+, \quad (3)$$

where $n := n(x)$ is the outward normal vector at point x on the boundary $\partial\Omega$ of the domain Ω .

Finally, we introduce nonnegative initial data

$$\tilde{a}_i(0, x) = \tilde{a}_{i0}(x) \geq 0 \quad (4)$$

for the concentrations (note that eq.(2) preserves nonnegativeness of each concentration in the time evolution).

Recently, reaction-diffusion equations like (2) have attracted a lot of attention from the mathematical community. The difficulties in the mathematical treatment increase according to increment of number of involved species, of dimension N , and of exponents μ_i, ν_i .

Among recent results, let us quote the existence of renormalized solutions for general equations of the form (2) (cf. [9]), and the existence of regular solutions for $p = 4$, $\mu_1 = \mu_3 = 1$, $\nu_2 = \nu_4 = 1$, $\nu_1 = \nu_3 = 0$, $\mu_2 = \mu_4 = 0$, $N = 2$ (cf. [11] and [4]). Among the tools available to treat systems like (2) we shall use in this work the entropy structure related to the reversibility of eq.(2), the duality lemmas introduced in [13], and their refinement described in [4].

This paper is devoted to the study of some singular limits of simple rescaled systems of the form (2) appearing in the study of chemical reactions. Note that this subject has already been investigated, especially in the special case of the so-called QSSA (cf. [1], [3]) in the context of reversible chemistry. Note also that other papers are devoted to the study of such limits in the case of irreversible chemistry ([5], [12]).

In order to explain how the considered singular limits naturally appear, let us introduce new variables and parameters in the following way:

$$\tilde{a}_i(t, x) = A_i a_i(t, x), \quad \tilde{a}_{i0}(x) = A_i a_{i0}(x), \quad \tilde{d}_i = D_i d_i, \quad \tilde{\ell} = L\ell, \quad \tilde{k} = Kk, \quad (5)$$

where $A_i, D_i, L, K > 0$, and a_i, d_i, ℓ, k are of order 1. Then eq.(2) writes

$$\begin{aligned} A_i \partial_t a_i - D_i d_i A_i \Delta_x a_i &= L\ell (\mu_i - \nu_i) A_1^{\nu_1} a_1^{\nu_1} \cdots A_p^{\nu_p} a_p^{\nu_p} \\ &\quad - Kk (\mu_i - \nu_i) A_1^{\mu_1} a_1^{\mu_1} \cdots A_p^{\mu_p} a_p^{\mu_p}, \end{aligned} \quad (6)$$

whereas (3), (4) become

$$\forall x \in \partial\Omega, \quad t \in \mathbb{R}_+, \quad \nabla_x a_i(t, x) \cdot n(x) = 0, \quad a_i(0, x) = a_{i0}(x) \geq 0. \quad (7)$$

Note then that various singular limits can appear depending whether the coefficients A_i, D_i, L, K have the same order of magnitude or not. For example, if one species, say \mathcal{A}_i , corresponds to very small-mass molecules with respect to another species, say \mathcal{A}_j , we expect that $D_i \gg D_j$. If some species, say \mathcal{A}_i , is very unstable (radical, excited state of a given molecule, etc.) and some other \mathcal{A}_j is stable, we expect that $A_i \ll A_j$. Finally (and this sometimes depends on the temperature), we can have reaction rates which are of the same order of magnitude, i.e. $K \approx L$, or of different order of magnitude, $K \ll L$.

In this work, we wish to focus on specific examples which illustrate the mathematical difficulties related to typical choices of the parameters A_i, D_i, L, K .

First we consider the case of equation (2) when $p = 3$ (three species), and $\mu_1 = 1, \mu_2 = \mu_3 = 0; \nu_1 = 0, \nu_2 = \nu_3 = 1$, that is



or



where \mathcal{B} is a species ‘‘in excess’’, that is having a concentration so large that it can be assumed as constant in the evolution (and thus not appearing in the equations).

Then eq.(2) writes

$$\begin{cases} \partial_t \tilde{a}_1 - \tilde{d}_1 \Delta_x \tilde{a}_1 = \tilde{\ell} \tilde{a}_2 \tilde{a}_3 - \tilde{k} \tilde{a}_1, \\ \partial_t \tilde{a}_2 - \tilde{d}_2 \Delta_x \tilde{a}_2 = \tilde{k} \tilde{a}_1 - \tilde{\ell} \tilde{a}_2 \tilde{a}_3, \\ \partial_t \tilde{a}_3 - \tilde{d}_3 \Delta_x \tilde{a}_3 = \tilde{k} \tilde{a}_1 - \tilde{\ell} \tilde{a}_2 \tilde{a}_3, \end{cases} \quad (10)$$

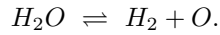
and the choice $A_1 = \varepsilon, A_2 = A_3 = 1, D_1 = D_2 = D_3 = 1, L = 1, K = 1/\varepsilon$ leads to

$$\begin{cases} \varepsilon (\partial_t a_1 - d_1 \Delta_x a_1) = \ell a_2 a_3 - k a_1, \\ \partial_t a_2 - d_2 \Delta_x a_2 = k a_1 - \ell a_2 a_3, \\ \partial_t a_3 - d_3 \Delta_x a_3 = k a_1 - \ell a_2 a_3, \end{cases} \quad (11)$$

whereas the choice $A_1 = \varepsilon, A_2 = A_3 = 1, D_1 = 1/\varepsilon, D_2 = D_3 = 1, L = 1, K = 1/\varepsilon$ leads to

$$\begin{cases} \varepsilon \partial_t a_1 - d_1 \Delta_x a_1 = \ell a_2 a_3 - k a_1, \\ \partial_t a_2 - d_2 \Delta_x a_2 = k a_1 - \ell a_2 a_3, \\ \partial_t a_3 - d_3 \Delta_x a_3 = k a_1 - \ell a_2 a_3. \end{cases} \quad (12)$$

Examples of dissociation/recombination reactions of type (8), leading to the scaled forms (11) are provided, in sufficiently high temperature regime, by the following one



In this reaction, the water, H_2O has a concentration that can be supposed much smaller than those of the other two species since, due to high temperature, the dissociation process is dominant. At the same time and for the same reason the reaction rate Kk can be assumed much larger than the other, $L\ell$, relative to the recombination process. Moreover, since the masses of the involved species are of the same order, it is natural to expect their diffusion rates to be of the same order too, and this corresponds to the scaling leading to system (11).

It is not frequent to find chemical reactions leading to equations of the type of system (12). Nevertheless, it can occur for example when one considers a chemical reaction like (9), when \mathcal{A}_2 and \mathcal{A}_3 have a much bigger mass than \mathcal{A}_1 (a configuration which cannot happen for the chemical reaction (8) because of the conservation of mass).

As a second case, we consider a reversible bimolecular reaction corresponding to $p = 4$ (four species) in equation (2), and $\mu_1 = \mu_3 = 1$, $\mu_2 = \mu_4 = 0$; $\nu_1 = \nu_3 = 0$, $\nu_2 = \nu_4 = 1$, that is



Then eq.(2) re-writes (for $i = 1, \dots, 4$)

$$\partial_t \tilde{a}_i - \tilde{d}_i \Delta_x \tilde{a}_i = (-1)^{i+1} (\tilde{\ell} \tilde{a}_2 \tilde{a}_4 - \tilde{k} \tilde{a}_1 \tilde{a}_3), \quad (14)$$

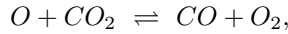
and the choice $A_1 = \varepsilon$, $A_2 = A_3 = A_4 = 1$, $D_1 = D_2 = D_3 = D_4 = 1$, $L = 1$, $K = 1/\varepsilon$ leads to

$$\begin{cases} \varepsilon (\partial_t a_1 - d_1 \Delta_x a_1) = \ell a_2 a_4 - k a_1 a_3, \\ \partial_t a_j - d_j \Delta_x a_j = (-1)^{j+1} (\ell a_2 a_4 - k a_1 a_3), \quad j = 2, 3, 4. \end{cases} \quad (15)$$

Another scaled equation can be obtained in the case of a reaction with two unstable species, say \mathcal{A}_1 , \mathcal{A}_2 . The choice $A_1 = A_2 = \varepsilon$, $A_3 = A_4 = 1$, $D_1 = D_2 = D_3 = D_4 = 1$, $L = K = 1/\varepsilon$ then leads to

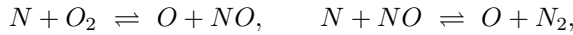
$$\begin{cases} \varepsilon (\partial_t a_i - d_i \Delta_x a_i) = (-1)^{i+1} (\ell a_2 a_4 - k a_1 a_3), \quad i = 1, 2, \\ \partial_t a_i - d_i \Delta_x a_i = (-1)^{i+1} (\ell a_2 a_4 - k a_1 a_3), \quad i = 3, 4. \end{cases} \quad (16)$$

The reaction



appearing in the reactive oxygen-carbon chain, can be cited as example for the scaled form (15). Here, in fact, the atom of oxygen is strongly unstable, which justifies the assumptions that its concentration is much smaller than the others, and that the reaction rate Kk , relative to the encounters O and CO_2 , is much higher than the other rate $L\ell$.

The scaled form (16) can describe, for example, two typical reactions of the oxygen-nitrogen chain, i.e.



in which both atoms N and O are unstable. In both these scalings the diffusion rates are expected to be of the same order since the masses are of the same order.

Note that the asymptotics appearing in (12) leads formally at the limit to a nontrivial system of coupled elliptic and parabolic equations, that is

$$\begin{cases} -d_1 \Delta_x a_1 = \ell a_2 a_3 - k a_1 \\ \partial_t a_j - d_j \Delta_x a_j = k a_1 - \ell a_2 a_3, \quad j = 2, 3, \end{cases} \quad (17)$$

whereas the asymptotics appearing in (11), (15) and (16) lead at the limit to an uncoupled system of standard heat equations, that is, for (11):

$$\partial_t a_j - d_j \Delta_x a_j = 0, \quad j = 2, 3, \quad (18)$$

for (15):

$$\partial_t a_j - d_j \Delta_x a_j = 0, \quad j = 2, 3, 4. \quad (19)$$

and for (16):

$$\partial_t a_j - d_j \Delta_x a_j = 0, \quad j = 3, 4. \quad (20)$$

Our main results show that those formal asymptotics indeed rigorously hold, (with some restriction in the case of (19)) (and sometimes only in dimension $N = 1$ or $N = 2$). More precisely, we obtain the

Proposition 1 *Let $d_1, d_2, d_3 > 0$ be the diffusion rates and $k, \ell > 0$ be the reaction rates. We consider a bounded smooth domain $\Omega \subset \mathbb{R}^N$, together with initial data $\varepsilon a_{10}, a_{20}, a_{30} \in L^2(\Omega)$.*

Then for each $\varepsilon > 0$, there exists a unique smooth (for $t > 0$) solution $a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon$ of (11) with homogeneous Neumann boundary condition and such that $a_1^\varepsilon(0, x) = \varepsilon a_{10}(x)$, $a_j^\varepsilon(0, x) = a_{j0}(x)$, $j = 2, 3$.

Moreover, for all $T > 0$, $a_1^\varepsilon \rightharpoonup a_1$ in $L^1([0, T] \times \Omega)$ weak, $a_j^\varepsilon \rightarrow a_j$ a.e. on $[0, T] \times \Omega$ for $j = 2, 3$ where $k a_1 = \ell a_2 a_3$, and a_2, a_3 is the unique (smooth for $t > 0$) solution of the heat equation (18) with homogeneous Neumann boundary conditions and initial data $a_j(0, x) = a_{j0}(x)$, $j = 2, 3$. \square

Proposition 2 *Let $d_1, d_2, d_3 > 0$ be the diffusion rates and $k, \ell > 0$ be the reaction rates. We consider a bounded smooth domain $\Omega \subset \mathbb{R}^N$ with $N = 1$, together with initial data $\varepsilon a_{10}, a_{20}, a_{30} \in L^2(\Omega)$.*

Then for each $\varepsilon > 0$, there exists a unique smooth (for $t > 0$) solution $a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon$ of (12) with homogeneous Neumann boundary condition and such that $a_1^\varepsilon(0, x) = \varepsilon a_{10}(x)$, $a_j^\varepsilon(0, x) = a_{j0}(x)$, $j = 2, 3$.

Moreover, for all $T > 0$, up to extraction of subsequences, $a_1^\varepsilon \rightharpoonup a_1$ in $L^1([0, T] \times \Omega)$ in the sense of weak measures, $a_j^\varepsilon \rightarrow a_j$ for $j = 2, 3$ and in $L^p([0, T] \times \Omega)$ (strong) for some $p > 2$. Finally, for a.e. $t \in [0, T]$,

$$\int_{\Omega} \ell a_2 a_3 dx = \int_{\Omega} k a_1 dx, \quad (21)$$

and equations (17) (together with the homogeneous Neumann boundary conditions and initial data $a_j(0, x) = a_{j0}(x)$, $j = 2, 3$) hold in the following weak sense:

for all test functions $\varphi_1, \varphi_2, \varphi_3 \in C_c^1([0, T[\times \bar{\Omega})$

$$-d_1 \int_0^T \int_{\Omega} a_1 \Delta_x \varphi_1 \, dx dt = \int_0^T \int_{\Omega} (\ell a_2 a_3 - k a_1) \varphi_1 \, dx dt, \quad (22)$$

$$\begin{aligned} j = 2, 3 : \quad & - \int_{\Omega} a_{j0}(x) \varphi_j(0, x) \, dx - \int_0^T \int_{\Omega} a_j \partial_t \varphi_j \, dx dt \\ & - d_j \int_0^T \int_{\Omega} a_j \Delta_x \varphi_j \, dx dt = \int_0^T \int_{\Omega} (k a_1 - \ell a_2 a_3) \varphi_j \, dx dt. \quad \square \end{aligned} \quad (23)$$

Proposition 3 Let $d_i > 0$ ($i = 1, \dots, 4$) be the diffusion rates and $k, \ell > 0$ be the reaction rates. We consider a bounded smooth domain $\Omega \subset \mathbb{R}^N$, with $N = 1$ or $N = 2$, together with initial data $\varepsilon a_{10}, a_{20}, a_{30}, a_{40} \in L^2(\Omega)$.

Then for each $\varepsilon > 0$, there exists a unique smooth (for $t > 0$) solution $a_1^\varepsilon, \dots, a_4^\varepsilon$ of (15) with homogeneous Neumann boundary condition and such that $a_1^\varepsilon(0, x) = \varepsilon a_{10}(x)$, $a_j^\varepsilon(0, x) = a_{j0}(x)$, $j = 2, 3, 4$.

Moreover, for all $T > 0$, there exists $g \in L^1([0, T] \times \Omega)$ such that $a_1^\varepsilon a_3^\varepsilon \rightharpoonup g$ in $L^1([0, T] \times \Omega)$ weak, $a_j^\varepsilon \rightarrow a_j$ for $j = 2, 3, 4$, and in $L^p([0, T] \times \Omega)$ (strong) for some $p > 2$. Then, for $j = 2, 3, 4$,

$$\partial_t a_j - d_j \Delta_x a_j = (-1)^{j+1} (\ell a_2 a_4 - k g) \quad (24)$$

in the sense of distributions, or more precisely in the following weak sense: for all test functions $\varphi_2, \varphi_3, \varphi_4 \in C_c^1([0, T[\times \Omega)$, and $j = 2, 3, 4$,

$$\begin{aligned} & - \int_{\Omega} a_{j0}(x) \varphi_j(0, x) \, dx - \int_0^T \int_{\Omega} a_j \partial_t \varphi_j \, dx dt \\ & - d_j \int_0^T \int_{\Omega} a_j \Delta_x \varphi_j \, dx dt = \int_0^T \int_{\Omega} (-1)^{j+1} (\ell a_2 a_4 - k g) \, dx dt. \end{aligned} \quad (25)$$

Finally,

$$a_3 (\partial_t - d_1 \Delta_x)^{-1} (\ell a_2 a_4 - k g) = 0, \quad (26)$$

where $(\partial_t - d_1 \Delta_x)^{-1}$ is the reciprocal of the heat operator on $[0, T] \times \Omega$ with homogeneous Neumann boundary conditions and zero initial datum. \square

Proposition 4 Let $d_i > 0$ ($i = 1, \dots, 4$) be diffusion rates and $k, \ell > 0$ be reaction rates. We consider a bounded smooth domain Ω , and initial data $\varepsilon a_{10}, \varepsilon a_{20}, a_{30}, a_{40}$ in $L^2(\Omega)$.

Then for each $\varepsilon > 0$, there exists a weak (for $t > 0$) solution $a_1^\varepsilon, \dots, a_4^\varepsilon$ of (16) with homogeneous Neumann boundary conditions and such that $a_i^\varepsilon(0, x) =$

$a_{i0}(x)$ when $i = 3, 4$, and $a_i^\varepsilon(0, x) = \varepsilon a_{i0}(x)$ when $i = 1, 2$. This solution is smooth when $N = 1$ or $N = 2$.

Moreover, for some $p > 2$, $a_i^\varepsilon \rightarrow a_i$ in $L^p([0, T] \times \Omega)$ (strong) when $i = 3, 4$, and $a_i^\varepsilon \rightharpoonup a_i$ in $L^p([0, T] \times \Omega)$ weak when $i = 1, 2$, where $a_i \in L^p([0, T] \times \Omega)$.

Finally,

$$\ell a_2 a_4 = k a_1 a_3, \quad \partial_t (a_1 + a_2) - \Delta_x (d_1 a_1 + d_2 a_2) = 0, \quad (27)$$

$$\partial_t a_3 - d_3 \Delta_x a_3 = 0, \quad \partial_t a_4 - d_4 \Delta_x a_4 = 0. \quad \square \quad (28)$$

As explained in the beginning of the introduction, these four propositions are consequences of the entropy structure of the equations, and of (revised versions of) duality lemmas. There are therefore some common points in the proof with previous works on connected subjects like [1], [3], [5]. One of the novelties is the use of the most recent refinements in the duality lemmas, enabling to obtain L^p estimates with $p > 2$ rather than L^2 estimates (cf. [4]). Proposition 1 and Proposition 2 are straightforward results stating that the formal asymptotics indeed rigorously holds. On the other hand, Proposition 3 is much more involved: according to (26), on all open sets where $a_3 \neq 0$, one has $\ell a_2 a_4 = k g$ and one recovers the formal asymptotics. It does not seem however easy to show that $a_3 \neq 0$ on $[0, T] \times \Omega$. Note that a similar difficulty appeared also in [5].

Note that in all asymptotics, we selected initial data in such a way that no initial layer are produced for a_2, a_3, a_4 , whereas an initial layer will be produced for a_1 (the initial datum for a_1 is lost in the limiting equations). In the case in which ε appears in front of the diffusion of a_1 ((11) and (16)), a boundary layer also appears for this concentration.

This paper is structured as follows: in Section 2 we prove Proposition 1 and Proposition 2 (that is the case in which three species are involved in the chemical reaction). Then, we study the case of four species in Section 3. Finally, Section 4 is devoted to the discussion of possible extensions of these results.

2 Proofs of the propositions related to the three-species case

We begin with the

Proof of Proposition 1: We first write the equation for the evolution of the (local) entropy

$$\begin{aligned} H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon) &:= \varepsilon a_1^\varepsilon \ln(\varepsilon a_1^\varepsilon) - \varepsilon a_1^\varepsilon \ln\left(\varepsilon e \frac{\ell}{k}\right) + \varepsilon \frac{\ell}{k} \\ &+ \sum_{i=2}^3 (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon + 1) \geq 0. \end{aligned} \quad (29)$$

A simple computation shows that

$$\begin{aligned} \partial_t H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon) - \Delta_x \left\{ d_1 \left[\varepsilon a_1^\varepsilon \ln(\varepsilon a_1^\varepsilon) - \varepsilon a_1^\varepsilon \ln\left(\varepsilon e \frac{\ell}{k}\right) + \varepsilon \frac{\ell}{k} \right] \right. \\ \left. + \sum_{i=2}^3 d_i (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon + 1) \right\} \\ + \varepsilon d_1 \frac{|\nabla_x a_1^\varepsilon|^2}{a_1^\varepsilon} + \sum_{i=2}^3 d_i \frac{|\nabla_x a_i^\varepsilon|^2}{a_i^\varepsilon} \\ + (k a_1^\varepsilon - \ell a_2^\varepsilon a_3^\varepsilon) [\ln(k a_1^\varepsilon) - \ln(\ell a_2^\varepsilon a_3^\varepsilon)] = 0. \end{aligned} \quad (30)$$

As a first consequence, integrating this identity on Ω , we see that the following *a priori* bound holds:

$$\int_0^T \int_\Omega (k a_1^\varepsilon - \ell a_2^\varepsilon a_3^\varepsilon) [\ln(k a_1^\varepsilon) - \ln(\ell a_2^\varepsilon a_3^\varepsilon)] dx dt \leq C_T. \quad (31)$$

Then, rewriting identity (30) as

$$\partial_t H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon) - \Delta_x [M^\varepsilon H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon)] \leq 0, \quad (32)$$

with

$$M^\varepsilon := \frac{d_1 \left[\varepsilon a_1^\varepsilon \ln(\varepsilon a_1^\varepsilon) - \varepsilon a_1^\varepsilon \ln\left(\varepsilon e \frac{\ell}{k}\right) + \varepsilon \frac{\ell}{k} \right] + \sum_{i=2}^3 d_i (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon + 1)}{\varepsilon a_1^\varepsilon \ln(\varepsilon a_1^\varepsilon) - \varepsilon a_1^\varepsilon \ln\left(\varepsilon e \frac{\ell}{k}\right) + \varepsilon \frac{\ell}{k} + \sum_{i=2}^3 (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon + 1)}, \quad (33)$$

we can use the duality lemma of [13] and get that

$$\int_0^T \int_\Omega M^\varepsilon |H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon)|^2 dx dt \leq C_T, \quad (34)$$

so that $a_2^\varepsilon, a_3^\varepsilon$ are bounded in $L^2(\ln L)^2([0, T] \times \Omega)$. Note that this argument is also quite close to the computations of [6].

Then, $a_2^\varepsilon a_3^\varepsilon$ is bounded in $L \ln L([0, T] \times \Omega)$ and, thanks to a classical argument developed for example in [8], estimate (31) implies that a_1^ε is weakly compact in $L^1([0, T] \times \Omega)$.

We can therefore extract subsequences (still denoted by ε) such that

$$a_1^\varepsilon \rightharpoonup a_1, \quad a_2^\varepsilon \rightharpoonup a_2, \quad a_3^\varepsilon \rightharpoonup a_3,$$

where a_1 lies in $L^1([0, T] \times \Omega)$, a_2, a_3 lie in $L^2([0, T] \times \Omega)$, and the convergences hold respectively in $L^1([0, T] \times \Omega)$ weak for the first one, and in $L^2([0, T] \times \Omega)$ weak for the second and third one.

Since $\partial_t a_2^\varepsilon - d_2 \Delta_x a_2^\varepsilon$ and $\partial_t a_3^\varepsilon - d_3 \Delta_x a_3^\varepsilon$ are bounded in $L^1([0, T] \times \Omega)$, the sequences a_2^ε and a_3^ε are in fact converging respectively to a_2 and a_3 a.e., so

that (since a_2^ε , and a_3^ε are bounded in $L^2(\ln L)^2([0, T] \times \Omega)$), $a_2^\varepsilon a_3^\varepsilon$ converges in $L^1([0, T] \times \Omega)$ strong to $a_2 a_3$. We now can pass to the limit in system (11), and end up with (18) together with the chemical equilibrium identity $\ell a_2 a_3 = k a_1$. This concludes the proof of Proposition 1. \square

Proof of Proposition 2: The entropy computation gives in this case (with H defined by (29)),

$$\begin{aligned} \partial_t H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon) - \Delta_x \left\{ d_1 \left[a_1^\varepsilon \ln(\varepsilon a_1^\varepsilon) - a_1^\varepsilon \ln\left(\varepsilon e \frac{\ell}{k}\right) + \frac{\ell}{k} \right] \right. \\ \left. + \sum_{i=2}^3 d_i (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon + 1) \right\} + \sum_{i=1}^3 d_i \frac{|\nabla_x a_i^\varepsilon|^2}{a_i^\varepsilon} \\ + (k a_1^\varepsilon - \ell a_2^\varepsilon a_3^\varepsilon) [\ln(k a_1^\varepsilon) - \ln(\ell a_2^\varepsilon a_3^\varepsilon)] = 0. \end{aligned} \quad (35)$$

Then, estimate (31) still holds, and moreover

$$\sup_{t \in [0, T]} \int_{\Omega} \sum_{i=2}^3 (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon + 1) dx \leq C_T, \quad (36)$$

$$\int_0^T \int_{\Omega} \sum_{i=1}^3 \frac{|\nabla_x a_i^\varepsilon|^2}{a_i^\varepsilon} dx dt \leq C_T. \quad (37)$$

Since the dimension of space is 1, estimates (36) and (37) are sufficient to show, thanks to a standard Sobolev embedding and an easy interpolation, that a_i^ε is a bounded sequence in $L^2([0, T] \times \Omega)$ for $i = 2, 3$. Using estimate (31) and the standard inequality

$$(x - y)(\ln x - \ln y) \geq C |\sqrt{x} - \sqrt{y}|^2,$$

we see that

$$\begin{aligned} \int_0^T \int_{\Omega} k a_1^\varepsilon dx dt \leq 2 \int_0^T \int_{\Omega} \left| \sqrt{k a_1^\varepsilon} - \sqrt{\ell a_2^\varepsilon a_3^\varepsilon} \right|^2 dx dt + 2 \int_0^T \int_{\Omega} \ell a_2^\varepsilon a_3^\varepsilon dx dt \\ \leq C_T, \end{aligned}$$

so that a_1^ε is a bounded sequence in $L^1([0, T] \times \Omega)$.

Then we can extract subsequences (still denoted by ε) such that

$$a_1^\varepsilon \rightharpoonup a_1, \quad a_2^\varepsilon \rightharpoonup a_2, \quad a_3^\varepsilon \rightharpoonup a_3,$$

where a_1 lies in $M^1([0, T] \times \Omega)$ (set of bounded measures), a_2, a_3 lie in $L^2([0, T] \times \Omega)$, and the convergences hold respectively in the sense of weak measures for the first one, and in $L^2([0, T] \times \Omega)$ strong for the second and third ones.

Since $\partial_t a_2^\varepsilon - d_2 \Delta_x a_2^\varepsilon$ and $\partial_t a_3^\varepsilon - d_3 \Delta_x a_3^\varepsilon$ are bounded in $L^1([0, T] \times \Omega)$, the sequences a_2^ε and a_3^ε are in fact converging respectively to a_2 and a_3 a.e. Thanks to the assumption on the dimension, we also know that the properties

of the heat kernel ensure that a_i^ε is a bounded sequence in $L^{3-\delta}([0, T] \times \Omega)$ for $i = 2, 3$, and $\delta \in]0, 1]$. As a consequence, $a_2^\varepsilon a_3^\varepsilon$ converges in $L^1([0, T] \times \Omega)$ strong to $a_2 a_3$.

The passage to the limit is then slightly different from the one of Proposition 1. We start by integrating the first equation of (12) on Ω and get that

$$\varepsilon \partial_t \int_{\Omega} a_1^\varepsilon dx = \int_{\Omega} (\ell a_2^\varepsilon a_3^\varepsilon - k a_1^\varepsilon) dx.$$

Passing to the limit in this equation, we end up with (21). Finally, (17) can be recovered by a direct passage to the limit in the weak form of (12). This concludes the proof of Proposition 2. \square

3 Proofs of the propositions related to the four-species case

Proof of Proposition 3: We first write the evolution of the (local) entropy

$$\begin{aligned} H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon, a_4^\varepsilon) &:= \varepsilon a_1^\varepsilon \ln(\varepsilon a_1^\varepsilon) - \varepsilon a_1^\varepsilon \ln\left(\varepsilon \frac{\ell}{k}\right) + \frac{\varepsilon \ell}{e k} \\ &+ \sum_{i=2}^4 (a_i^\varepsilon \ln a_i^\varepsilon + e^{-1}) \geq 0. \end{aligned} \quad (38)$$

The computation leads to

$$\begin{aligned} \partial_t H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon, a_4^\varepsilon) - \Delta_x \left\{ d_1 \left[\varepsilon a_1^\varepsilon \ln(\varepsilon a_1^\varepsilon) - \varepsilon a_1^\varepsilon \ln\left(\varepsilon \frac{\ell}{k}\right) + \frac{\varepsilon \ell}{e k} \right] \right. \\ \left. + \sum_{i=2}^4 d_i (a_i^\varepsilon \ln a_i^\varepsilon + e^{-1}) \right\} \\ + \varepsilon d_1 \frac{|\nabla_x a_1^\varepsilon|^2}{a_1^\varepsilon} + \sum_{i=2}^4 d_i \frac{|\nabla_x a_i^\varepsilon|^2}{a_i^\varepsilon} \\ + (k a_1^\varepsilon a_3^\varepsilon - \ell a_2^\varepsilon a_4^\varepsilon) [\ln(k a_1^\varepsilon a_3^\varepsilon) - \ln(\ell a_2^\varepsilon a_4^\varepsilon)] = 0. \end{aligned} \quad (39)$$

Integrating this identity on Ω , we see that the following *a priori* bound holds

$$\int_0^T \int_{\Omega} (k a_1^\varepsilon a_3^\varepsilon - \ell a_2^\varepsilon a_4^\varepsilon) [\ln(k a_1^\varepsilon a_3^\varepsilon) - \ln(\ell a_2^\varepsilon a_4^\varepsilon)] dx dt \leq C_T. \quad (40)$$

We now add the second and third equations of (15) on one hand, and the third and fourth equations of (15) on the other hand. We see that

$$\partial_t (a_2^\varepsilon + a_3^\varepsilon) - \Delta_x (d_2 a_2^\varepsilon + d_3 a_3^\varepsilon) = 0, \quad (41)$$

$$\partial_t (a_4^\varepsilon + a_3^\varepsilon) - \Delta_x (d_4 a_4^\varepsilon + d_3 a_3^\varepsilon) = 0. \quad (42)$$

Using the improved duality lemma of [4], we get, for some $\delta > 0$, the information that the sequences a_i^ε , for $i = 2, 3, 4$, are bounded in $L^{2+\delta}([0, T] \times \Omega)$.

Then, $a_2^\varepsilon a_4^\varepsilon$ is bounded in $L^{1+\delta/2}([0, T] \times \Omega)$, and (thanks to estimate (40)), $a_1^\varepsilon a_3^\varepsilon$ is weakly compact in $L^1([0, T] \times \Omega)$.

We can therefore extract subsequences (still denoted by ε) such that

$$a_1^\varepsilon a_3^\varepsilon \rightharpoonup g, \quad a_2^\varepsilon \rightharpoonup a_2, \quad a_3^\varepsilon \rightharpoonup a_3, \quad a_4^\varepsilon \rightharpoonup a_4,$$

where g lies in $L^1([0, T] \times \Omega)$, a_2, a_3, a_4 lie in $L^{2+\delta}([0, T] \times \Omega)$, and the convergences hold respectively in $L^1([0, T] \times \Omega)$ weak for the first one, and in $L^{2+\delta}([0, T] \times \Omega)$ weak for the second, third and fourth one.

Since $\partial_t a_i^\varepsilon - d_i \Delta_x a_i^\varepsilon$ are bounded in $L^1([0, T] \times \Omega)$ for $i = 2, 3, 4$, the sequences a_i^ε are in fact converging to a_i a.e. for $i = 2, 3, 4$, and then also in $L^{2+\delta-\zeta}([0, T] \times \Omega)$ strong for all $\zeta \in]0, \delta]$. Then (since $a_2^\varepsilon, a_4^\varepsilon$ are bounded in $L^{2+\delta}([0, T] \times \Omega)$), $a_2^\varepsilon a_4^\varepsilon$ converges in $L^{1+\delta/2-\zeta/2}([0, T] \times \Omega)$ strong to $a_2 a_4$ for all $\zeta \in]0, \delta]$.

We now can pass to the limit in the three last equations of system (15), and end up with (16) (or, more precisely, (25)).

We then introduce the semigroup of the heat equation $e^{d_1 t \Delta_x}$ on Ω with homogeneous Neumann boundary condition (and diffusion rate d_1). Rewriting the first equation of system (15) as

$$\varepsilon a_1^\varepsilon(t, x) = \varepsilon e^{d_1 t \Delta_x} a_1^\varepsilon(0, x) + \int_0^t e^{d_1(t-s) \Delta_x} (a_2^\varepsilon a_4^\varepsilon - a_1^\varepsilon a_3^\varepsilon)(s, x) ds,$$

and multiplying by $a_3^\varepsilon(t, x)$, we see that

$$\begin{aligned} \varepsilon a_1^\varepsilon(t, x) a_3^\varepsilon(t, x) &= \varepsilon a_3^\varepsilon(t, x) e^{d_1 t \Delta_x} a_1^\varepsilon(0, x) \\ &\quad + a_3^\varepsilon(t, x) \int_0^t e^{d_1(t-s) \Delta_x} (a_2^\varepsilon a_4^\varepsilon - a_1^\varepsilon a_3^\varepsilon)(s, x) ds. \end{aligned} \quad (43)$$

Remembering that $a_1^\varepsilon a_3^\varepsilon$ is weakly compact in $L^1([0, T] \times \Omega)$, we see that the l.h.s. of (43) tends to 0. Then, we recall that $(\partial_t - d_1 \Delta_x)^{-1}$ (the operator consisting in solving the heat equation with homogeneous Neumann condition and initial datum 0) transforms continuously $L^1([0, T] \times \Omega)$ in $L^{1+2/N-\zeta}([0, T] \times \Omega)$ when Ω is a smooth subset of \mathbb{R}^N and $\zeta \in]0, 2/N]$ (cf. [4] for example) As a consequence, we see that $\int_0^t e^{d_1(t-s) \Delta_x} (a_2^\varepsilon a_4^\varepsilon - a_1^\varepsilon a_3^\varepsilon) ds$ converges towards $\int_0^t e^{d_1(t-s) \Delta_x} (a_2 a_4 - a_1 a_3) ds$ in $L^{1+2/N-\zeta}([0, T] \times \Omega)$. Finally, since a_3^ε is converging to a_3 in $L^{2+\delta-\zeta}([0, T] \times \Omega)$ strong for all $\zeta \in]0, \delta]$, we see that we can pass to the limit in the r.h.s. of (43) when $N \leq 2$ and end up with (26). This ends the proof of Proposition 3. \square

Proof of Proposition 4: We first write the evolution of the (local) entropy

$$\begin{aligned} H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon, a_4^\varepsilon) &:= \sum_{i=1}^2 [\varepsilon a_i^\varepsilon \ln(\varepsilon a_i^\varepsilon) - \varepsilon a_i^\varepsilon \ln(\varepsilon a_i) + 1] \\ &\quad + a_3^\varepsilon \ln a_3^\varepsilon - a_3^\varepsilon + 1 \\ &\quad + a_4^\varepsilon \ln a_4^\varepsilon - \left[1 + \ln\left(\frac{k}{\ell}\right) \right] a_4^\varepsilon + \frac{k}{\ell} \geq 0. \end{aligned} \quad (44)$$

The computation of its time derivative leads to

$$\begin{aligned}
\partial_t H(a_1^\varepsilon, a_2^\varepsilon, a_3^\varepsilon, a_4^\varepsilon) - \Delta_x \left\{ \sum_{i=1}^2 d_i [\varepsilon a_i^\varepsilon \ln(\varepsilon a_i^\varepsilon) - \varepsilon a_i^\varepsilon + 1] \right. \\
+ d_3 (a_3^\varepsilon \ln a_3^\varepsilon - a_3^\varepsilon + 1) \\
+ d_4 \left[a_4^\varepsilon \ln a_4^\varepsilon - \left[1 + \ln\left(\frac{k}{\ell}\right) \right] a_4^\varepsilon + \frac{k}{\ell} \right] \left. \right\} \\
+ \varepsilon \sum_{i=1}^2 d_i \frac{|\nabla_x a_i^\varepsilon|^2}{a_i^\varepsilon} + \sum_{i=3}^4 d_i \frac{|\nabla_x a_i^\varepsilon|^2}{a_i^\varepsilon} \\
+ \varepsilon (ka_1^\varepsilon a_3^\varepsilon - \ell a_2^\varepsilon a_4^\varepsilon) [\ln(ka_1^\varepsilon a_3^\varepsilon) - \ln(\ell a_2^\varepsilon a_4^\varepsilon)] = 0. \quad (45)
\end{aligned}$$

We now add the first and second equations of (16) on one hand, and the third and fourth equations of (16) on the other hand. We see that

$$\partial_t (a_1^\varepsilon + a_2^\varepsilon) - \Delta_x (d_1 a_1^\varepsilon + d_2 a_2^\varepsilon) = 0, \quad (46)$$

$$\partial_t (a_3^\varepsilon + a_4^\varepsilon) - \Delta_x (d_3 a_3^\varepsilon + d_4 a_4^\varepsilon) = 0. \quad (47)$$

Using the improved duality lemma of [4], we get, for some $\delta > 0$, the information that the sequences a_i^ε , for $i = 1, \dots, 4$, are bounded in $L^{2+\delta}([0, T] \times \Omega)$.

We can therefore extract subsequences (still denoted by ε) such that

$$a_i^\varepsilon \rightharpoonup a_i, \quad i = 1, \dots, 4,$$

where a_i lie in $L^{2+\delta}([0, T] \times \Omega)$, and the convergences hold in $L^{2+\delta}([0, T] \times \Omega)$ weak.

Since $\partial_t a_i^\varepsilon - d_i \Delta_x a_i^\varepsilon$ is bounded in $L^{1+\delta/2}([0, T] \times \Omega)$ for $i = 3, 4$, the sequences a_i^ε are in fact converging to a_i a.e. (for $i = 3, 4$), and so in $L^2([0, T] \times \Omega)$ strong. As a consequence, $a_1^\varepsilon a_3^\varepsilon$ (respectively $a_2^\varepsilon a_4^\varepsilon$) converges weakly towards $a_1 a_3$ (respectively $a_2 a_4$) in $L^1([0, T] \times \Omega)$.

Passing to the limit (in the sense of distributions) in the first equation of (16), we see that $\ell a_2 a_4 = k a_1 a_3$. Adding the two first equations of (16) and passing to the limit, we also see that the second part of (27) holds. Finally, passing to the limit in the third and fourth equation of (16), we get (28). This ends the proof of Proposition 4. \square

4 Concluding remarks

This work faces some typical asymptotic problems appearing in PDEs describing diffusion and reversible reactions.

The main aim of this paper is to highlight the strength of the methods for parabolic equations, based on the entropy structure, and on duality lemmas, which yield rigorous proofs of convergence in the asymptotics.

We restricted ourselves here to cases which are sufficiently simple to be treated by already established methods.

Future developments will concern more complex chemical processes naturally appearing in the applications in the context of networks of reactions, in which also non reversible chemical processes may arise. In fact, although for networks of reactions, many works exist in the context of ODEs, still not so many are available when reaction-diffusion systems are concerned. We refer to [7] and the references therein for a precise description of the existing theory.

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