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Global behavior and asymptotic reduction of a chemical kinetics system with continua of equilibria

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We consider a model chemical kinetics system describing the dynamics of species concentrations taking part is consecutive-competitive reaction in a continuopusly stirred tank reactor. Corresponding dynamical system has a continua of equilibria. Particular equilibrium to which the solution of the system tends depends on the initial conditions. The global behavior of the system and its reductions via the invariant manifold and the boundary function methods are studied.

KEY WORDS: chemical kinetics, dynamical system, invariant manifold, singular perturbations, boundary function method

AMS subject classification: 34D15, 34D35, 37C10

1. Introduction

In this paper we consider a chemical kinetics model describing the dynamics of concentrations of species taking part in the reactions (in a continuously stirred tank reactor) according to the following reaction scheme

$$A + B \xrightarrow{k_1} C, \qquad B + C \xleftrightarrow{k^{\pm}} D. \tag{1.1}$$

This consecutive–competitive reaction sequence appears in several important chemical engineering applications, such as in the reaction of ethylene oxid with water, ammonia and alcohol as well as in halogenation and hydrogenation of organic molecules [1].

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The reaction scheme (1.1) has been considered in [2] under the additional assumption $k^{\pm} \gg 1$, i.e., the second reaction is in a quasi-equilibrium, in order to illustrate the basic idea of the boundary function method in studying the time behavior of the concentrations of species A, B, C and D in a finite time interval.

The chemical kinetics system presented above has continua of equilibria such that the equilibrium to which the system tends as t is going to ∞ depends on the prescribed initial conditions. Such behavior often appears in chemical kinetics models in which conservation relations for some species are observed, and/or for which the initial concentrations of reacting species are not given in exact proportions specified by the reaction kinetics scheme. In the latter case, while some species are completely consumed during characteristic reaction time, others still remain in the system.

Here we present the analysis of one such system. We note, however, that some general approaches discussed in this paper can be used for the analysis of other applied dynamical systems of this type as well. The results of this paper can be summarized as follows. (i) First, we investigate the long-term behavior of (1.1) without any additional conditions about the reaction rate constants. We prove that (1.1) tends to an equilibrium which, indeed, depends on the initial conditions. (ii) Under the assumption that the second reaction is in quasi-equilibrium (i.e., corresponding forward and reverse reactions are fast, the reaction rate constants k^+ and k^- are large, and their ratio k^-/k^+ is moderate) we show the existence of an attracting invariant manifold, and construct an approximation for this invariant manifold. The equilibrium to which the system tends is located on the attracting invariant manifold. (iii) We construct an approximation to the solution of the initial value problem under the quasi-equilibrium assumption using the boundary function method [3–5]. Here, we present an approach based on the reduced model as well as we describe an algorithmic approach applied to the original system which can be implemented. (iv) Finally, we discuss and compare the results obtained for the same original problem using the method of invariant manifolds and the boundary function method.

Before we proceed, let us make several comments on current applications of the model reduction procedures. The reduction of a particular real life applied model is possible when processes observed in the system are characterized by widely varying "physical" scales. These could be different time scales (fast/slow motions), spatial scales (large/small dimensions), etc. While the importance of the asymptotic methods as a tool for explicit calculations has decreased over the past decades due to appearance of fast computers and specialized software, their role in elucidating the underlying dynamics (via qualitative analysis of reduced models), and in determination of model parameters from experiments has become more significant. Often the restrictions on the precision of the measuring devices do not allow the identification of model parameters associated with either very small or very large scales. In such situation, reduced models help

to understand which parameters can be eliminated from the system, and which combinations of parameters are, in principle, identifiable from experiment.

Our discussion of the asymptotic reduction procedure based on the boundary function method approach has the goal to emphasize its features that could make it useful as a part of computerized reduction algorithms. In [6] we presented an algorithm for asymptotic model reduction based on invariant manifold theory. Such algorithms are necessary for the reduction of large systems that appear in chemical engineering [2,7] atmospheric chemistry modeling [8,9], and other areas [10].

2. Mathematical model and its reduced equivalent formulation

Let us keep the notation A, B, C, D for the concentration of the species A, B, C, D, respectively. Then, the corresponding differential equations system describing the behavior of (1.1) has the form

$$\begin{aligned}
\frac{\mathrm{d}A}{\mathrm{d}\bar{t}} &= -k_1 AB, \\
\frac{\mathrm{d}B}{\mathrm{d}\bar{t}} &= -k_1 AB - k^+ BC + k^- D, \\
\frac{\mathrm{d}C}{\mathrm{d}\bar{t}} &= k_1 AB - k^+ BC + k^- D, \\
\frac{\mathrm{d}D}{\mathrm{d}\bar{t}} &= k^+ BC - k^- D,
\end{aligned} \tag{2.1}$$

where we assume that k_1, k^+ and k^- are positive constants. We study the behavior of system (2.1) satisfying the initial condition

$$A(0) = A_0 > 0, \quad B(0) = B_0 > 0, \quad C(0) = C_0 \geqslant 0, \quad D(0) = D_0 \geqslant 0. \tag{2.2}$$

Rescaling $\bar{t}$ by $k_1 \bar{t} = t$ and taking into account that (2.1) has the first integral

$$B(t) + C(t) + 2D(t) = B_0 + C_0 + 2D_0 \tag{2.3}$$

we get from (2.1)

$$\begin{aligned}
\frac{\mathrm{d}A}{\mathrm{d}t} &= -AB, \\
\frac{\mathrm{d}B}{\mathrm{d}t} &= -AB - \frac{k^+}{k_1} BC + \frac{k^-}{2k_1}(B_0 + C_0 + 2D_0 - B - C), \\
\frac{\mathrm{d}C}{\mathrm{d}t} &= AB - \frac{k^+}{k_1} BC + \frac{k^-}{2k_1}(B_0 + C_0 + 2D_0 - B - C).
\end{aligned} \tag{2.4}$$

Now we introduce the new variable E by

$$E := C - B. \tag{2.5}$$

Then, we obtain from (2.4)

$$\begin{aligned}
\frac{\mathrm{d}A}{\mathrm{d}t} &= -AB,\\
\frac{\mathrm{d}B}{\mathrm{d}t} &= -AB - \frac{k^+}{k_1}B(E+B) + \frac{k^-}{2k_1}(B_0 + C_0 + 2D_0 - 2B - E),\\
\frac{\mathrm{d}E}{\mathrm{d}t} &= 2AB.
\end{aligned} \tag{2.6}$$

Exploiting the property that (2.6) has the first integral

$$2A(t) + E(t) = 2A_0 + C_0 - B_0, \tag{2.7}$$

we get from (2.6)

$$\begin{aligned}
\frac{\mathrm{d}A}{\mathrm{d}t} &= -AB,\\
\frac{\mathrm{d}B}{\mathrm{d}t} &= -AB - \tfrac{k^+}{k_1}B(B - 2A + 2A_0 + C_0 - B_0) + \tfrac{k^-}{k_1}(B_0 + D_0 - B - A_0 + A).
\end{aligned} \tag{2.8}$$

Thus, the initial value problem (2.1), (2.2) is equivalent to the initial value problem (2.8),

$$A(0) = A_0 > 0, \quad B(0) = B_0 > 0, \tag{2.9}$$

where the right hand side of (2.8) depends on the initial conditions. In the next section we determine the long-time behavior of (2.8), (2.9).

3. Long-time behavior

First we note that system (2.8) has $A = 0$ as an invariant straight line. Thus, the trajectory of (2.8) starting at a point $(\bar{A}, \bar{B})$ with $\bar{A} > 0$ can never reach the region $A < 0$.

Next we investigate the equilibria of (2.8). For convenience we introduce the parameter k by $k := k^-/k^+$. It is easy to verify that the equilibria of (2.8) are located on the coordinate axes $A = 0$ and $B = 0$ and are defined by

$$\begin{gathered}
(A_1 := A_0 - B_0 - D_0,\ B_1 := 0),\\
(A_e := 0,\ B_{e,1} := B_+), \quad (A_e := 0,\ B_{e,2} := B_-),
\end{gathered} \tag{3.1}$$

where

$$B_\pm := \tfrac{1}{2}\Big[-(2A_0 - B_0 + C_0 + k) \pm \sqrt{(2A_0 - B_0 + C_0 + k)^2 - 4k(A_0 - B_0 - D_0)}\Big]. \tag{3.2}$$

From (3.1) to (3.2) we get

Lemma 3.1. For all non-negative A_0 and B_0 system (2.8) has a unique equilibrium (A_*, B_*) in the positive orthant $O_+ := \{(A, B) \in R^2 : A \geqslant 0, B \geqslant 0\}$, where

$$(A_*, B_*) = \begin{cases} (A_1, 0) & \text{for } A_0 \geqslant B_0 + D_0, \\ (0, B_+) & \text{for } A_0 \leqslant B_0 + D_0. \end{cases} \tag{3.3}$$

In what follows we will prove that the trajectory of (2.8) starting at $(A_0, B_0) \in O_+$ has the equilibrium (A_*, B_*) as ω-limit set.

First we note that any straight line $A = \bar{A}, B > 0$ with $0 < \bar{A} \leqslant A_0$ is a straight line without contact which is crossed by the trajectories of (2.8) from right to left for increasing t, and that the straight line $B = B_0 + D_0$ is a line without contact for $0 \leqslant A < A_0$ and such that the trajectories of (2.8) cross this straight line for increasing t from above. Moreover, we can conclude that the trajectory of (2.8) starting at $(A_0, B_0) \in O_+$ will never leave the region $0 < A \leqslant A_0$, $B \leqslant B_0 + D_0$ (see figure 1).

Now we distinguish the cases $A_0 \leqslant B_0 + D_0$ and $A_0 > B_0 + D_0$. In case $A_0 \leqslant B_0 + D_0$, the equilibrium is located on the axis $A = 0$. For $A_0 \leqslant B_0 + D_0$, the axis $B = 0$ is a straight line without contact for $A \geqslant 0$, where all trajectories of (2.8) enter O_+ for increasing t. For $A_0 = B_0 + D_0$, the origin is an equilibrium point, and all trajectories crossing $B = 0$ at a point $(\bar{A}, 0)$ with

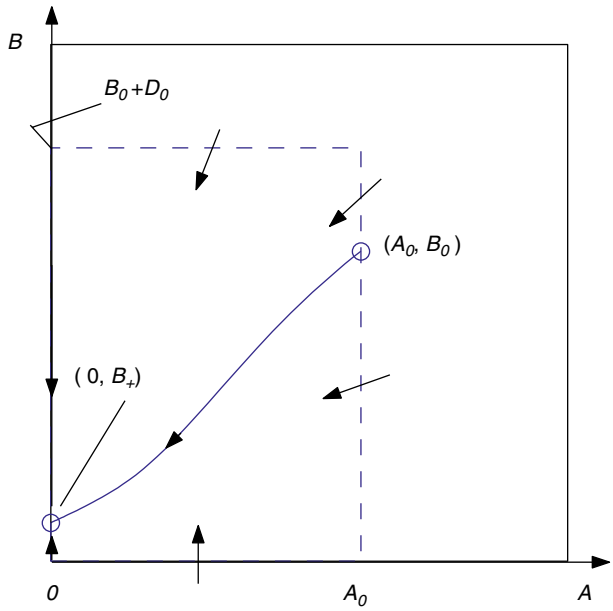

Figure 1.

$\bar{A} > 0$, enter O^+ for increasing t. Hence, for $A_0 \leqslant B_0 + D_0$, the rectangular domain $R_0 := \{(A, B) \in R^2 : 0 \leqslant A \leqslant A_0, 0 \leqslant B \leqslant B_0 + D_0\}$ is positively invariant and contains no limit cycle and no separatrix loop. Therefore, according to the Poincare–Bendixson theory, the trajectory of (2.8) starting at $(A_0, B_0) \in O_+$ tends for $t \to +\infty$ to the equilibrium $(0, B_+)$ (see figure 1).

In case $A_0 > B_0 + D_0$, $(A_0 - B_0 - D_0, 0)$ is the unique equilibrium of (2.8) in O_+. In what follows we consider the triangular domain $\mathcal{T}$ bounded by the straight lines $B = 0$, $A = A_0$ and $B = A + B_0 + D_0 - A_0$. If we differentiate $B - A$ along system (2.8) and consider this derivative at the straight line $B = A + B_0 + D_0 - A_0$ we get

$$\frac{\mathrm{d}(B - A)}{\mathrm{d}t} = -B\frac{k^+}{k_1}(-A + A_0 + D_0 + C_0) < 0. \tag{3.4}$$

Thus, we can conclude that $\mathcal{T}$ is positively invariant and that the trajectory of (2.8) starting at (A_0, B_0) has $(A_0 - B_0 - D_0, 0)$ as ω-limit set (see figure 2). Summarizing our investigations we have

Theorem. The solution of the initial value problem (2.1), (2.2) exist for all $t > 0$ and tends for $t \to \infty$ to the equilibrium point of (A_*, B_*), defined in (3.3).

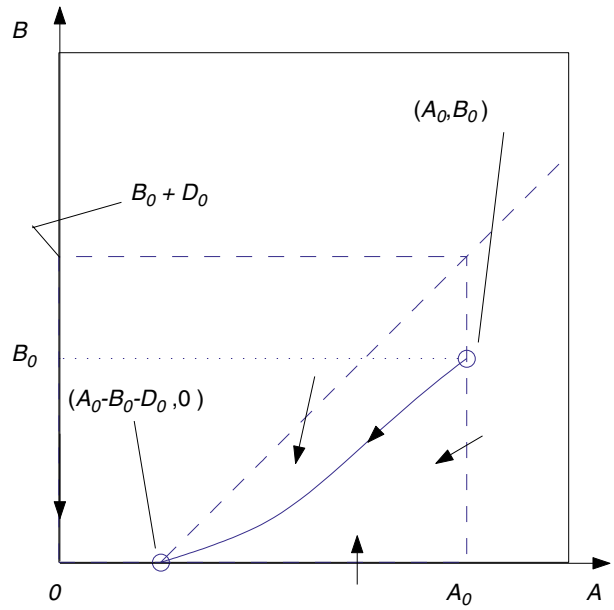

Figure 2.

4. The case of fast reversible reaction

In what follows we assume

$$(A) \qquad \frac{k^+}{k_1} = \frac{1}{\varepsilon} \gg 1, \qquad \text{and} \quad k = \frac{k^-}{k^+}, \tag{4.1}$$

that is, the second reaction in (1.1) is in quasi-equilibrium. From (2.8) and (4.1) we obtain

$$\begin{aligned} \frac{\mathrm{d}A}{\mathrm{d}t} &= -AB, \\ \varepsilon \frac{\mathrm{d}B}{\mathrm{d}t} &= -\varepsilon AB - B(B - 2A + 2A_0 + C_0 - B_0) + k(B_0 + D_0 - B - A_0 + A). \end{aligned} \tag{4.2}$$

Since ε is a small positive parameter system, (4.2) represents a singularly perturbed system. Our goal is to study the solution of (4.2) satisfying the initial condition (2.9), where we distinguish the problems,

1. Long-time behavior of the solution of (4.2), satisfying $A(0) = A_0 > 0$, $B(0) = B_0 > 0$ (see (2.9)).
2. Approximation of the initial value problem (4.2), (2.9) on the finite interval $[0, T]$.

4.1. *Long-time behavior of the solution of (4.2),(2.9)*

To study the long-time behavior of the solution of (4.2), (2.9) we apply the method of invariant manifolds, i.e., we want to prove the existence of an invariant manifold to system (4.2) of the form

$$B = h(A, \varepsilon),$$

which is exponentially attracting. To this end, we study the equilibria of the associated equation

$$\frac{\mathrm{d}B}{\mathrm{d}\sigma} = f(B) = -B(B-2A+2A_0+C_0-B_0) + k(B_0 + D_0 - B - A_0 + A). \tag{4.3}$$

Any equilibrium of (4.3) is defined by

$$\begin{aligned} B = B_\pm(A) = \tfrac{1}{2}\Big[&- (2A_0 + C_0 - B_0 - 2A + k) \\ &\pm \sqrt{(2A_0 + C_0 - B_0 - 2A + k)^2 - 4k(A_0 - A - B_0 - D_0)}\Big]. \end{aligned} \tag{4.4}$$

Under the assumption

$$A_0 - A - B_0 - D_0 \leqslant 0,$$

which is equivalent to

$$A \geqslant A_0 - B_0 - D_0, \tag{4.5}$$

only the branch $B = B_+(A),\ A \geqslant \max(0, A_0 - B_0 - D_0)$, is located in the positive orthant (see figure 3). We note that the graph of $B = B_+(A)$ intersects the A-axis at the point $A_0 - B_0 - D_0$.
In case

$$A_0 - A - B_0 - D_0 \geqslant 0$$

it is easy to check that there is no equilibrium of (4.3) in the positive orthant.

In the next step we investigate the stability of the equilibria belonging to the branch $B_+(A)$ for $A \geqslant A_0 - B_0 - D_0$. For this purpose we determine the sign of f'_B at $B = B_+(A)$. From (4.3) and (4.4) we get

$$f'_B(B_+(A)) = -\sqrt{(2A_0 + C_0 - B_0 - 2A + k)^2 - 4k(A_0 - A - B_0 - D_0)}.$$

The expression $2A_0+C_0-B_0-2A+k$ vanishes only for $A = A_0+(1/2)(C_0-B_0+k)$, and for this value of A we have $A_0-A-B_0-D_0 = (-1/2)(C_0 + B_0 + k) - D_0 < 0$.

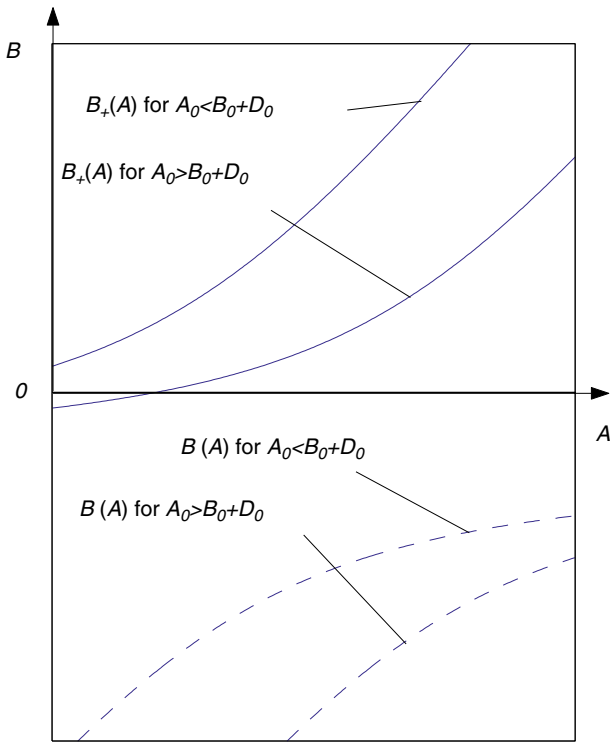

Figure 3.

Consequently, we can conclude $f'_B(B_+(A)) < 0$, that is, the equilibria are asymptotically stable. According to a general theorem on the existence of invariant manifolds in singularly perturbed systems [11] we have the following result.

Lemma 4.1. For sufficiently small ε, system (4.2) has an invariant manifold of the type

$$\mathcal{M}_\varepsilon := \{(A, B) \in R^2 : B = h(A, \varepsilon) = B_+(A) + O(\varepsilon)\}.$$

On the manifold $\mathcal{M}_\varepsilon$ system (4.2) reads

$$\frac{\mathrm{d}A}{\mathrm{d}t} = Ah(A, \varepsilon) = AB_+(A) + O(\varepsilon). \tag{4.6}$$

If we suppose $A_0 > B_0 + D_0$ then, for sufficiently small ε, $h(A, \varepsilon)$ has a positive root A_1 near $A_0 - B_0 - D_0$, and h is positive (negative) for $A < A_1$ ($A > A_1$) (see curve $B_+(A)$ for $A_0 > B_0 + D_0$ in figure 3). Thus, the trajectory of (4.6) starting at A_0 has A_1 as ω -limit point. In case $A_0 < B_0 + D_0$, the function $h(A, \varepsilon)$ is positive for $A > 0$, and we can conclude that the trajectory tends to $A = 0$ as t tends to infinity (see curve $B_+(A)$ for $A_0 < B_0 + D_0$ in figure 3). Consequently, we have got the same results about the long-time behavior of system (2.8) as in Lemma 3.1.

In section 4.2 we look for an approximation of the solution of the initial value problem (4.2), (2.9) on $(0, T)$.

4.2. Approximation of the solution of the initial value problem

We study the initial value problem (2.1), (2.2) assuming that the reversible reaction is fast, that is, under the assumption (A). In that case, after rescaling of time introduced in section 2 and with ε defined by (4.1) the original system can be re-written in the form

$$\begin{aligned}
\frac{\mathrm{d}A}{\mathrm{d}t} &= -AB, \\
\varepsilon\frac{\mathrm{d}B}{\mathrm{d}t} &= -\varepsilon AB - BC + kD, \\
\varepsilon\frac{\mathrm{d}C}{\mathrm{d}t} &= \varepsilon AB - BC + kD, \\
\varepsilon\frac{\mathrm{d}D}{\mathrm{d}t} &= BC - kD.
\end{aligned} \tag{4.7}$$

We supply (4.7) with the initial conditions (2.2) and investigate this initial value problem by means of the *boundary function method* (see [5]) in order to get a uniform asymptotic approximation of the solution on the interval $[0, T]$. In what

follows, we restrict ourselves to construction of the leading order approximation of the solution. According to this method, we seek asymptotic expansions of the unknown functions in the form

$$Z(t, \varepsilon) = \sum_{i=0}^{\infty} \varepsilon^i (\bar{Z}_i(t) + \Pi_i Z(\tau)), \tag{4.8}$$

where Z stands for A, B, C and D. Here, $\bar{E}_i(t), i = 0, 1, \ldots,$ are the regular parts of the asymptotic expansions describing the "slow" dynamics of the solution; $\Pi_i E(\tau), i = 0, 1, \ldots,$ are the, so-called, boundary functions important in a vicinity of the initial time $t = 0$, and $\tau = t/\varepsilon$ is the stretched variable. All the boundary functions have to decay exponentially to zero as the stretched variable $\tau \to \infty$.

4.3. *Construction of the leading order approximation for simplified equivalent system*

As we have demonstrated above, the initial value problems (4.7), (2.2) and (4.2), (2.9) are equivalent. Therefore, we apply the boundary function method first to (4.2), (2.9).

In the first step we determine the boundary function $\Pi_0 A(\tau)$. For this purpose we substitute (4.8) into (4.2), (2.9) and equate the terms multiplying ε^{-1} in both sides. We get

$$\frac{\mathrm{d}\Pi A_0}{\mathrm{d}\tau} = 0.$$

Since $\Pi A_0(t)$ must decay to zero for increasing τ we get

$$\Pi A_0(t) \equiv 0. \tag{4.9}$$

Next, we determine the regular part $\bar{A}_0(t)$. From the relations that represent initial conditions in the leading order approximation,

$$\begin{aligned} \bar{A}_0(0) + \Pi_0 A(0) &= A_0, \\ \bar{B}_0(0) + \Pi_0 B(0) &= B_0, \end{aligned} \tag{4.10}$$

and from (4.9) we get $\bar{A}_0(0) = A_0$.

Since the slow dynamics of (4.2) is determined by the scalar differential equation (4.6), $\bar{A}_0(t)$ is determined by the initial value problem

$$\frac{\mathrm{d}\bar{A}_0}{\mathrm{d}t} = \bar{A}_0 B_+(\bar{A}_0), \qquad \bar{A}_0(0) = A_0, \tag{4.11}$$

where $B_+(A)$ is defined by

$$B_+(A) = \tfrac{1}{2}\Big[-(2A_0 + C_0 - B_0 - 2A + k) + \sqrt{(2A_0 + C_0 - B_0 - 2A + k)^2 - 4k(A_0 - A - B_0 - D_0)}\Big]. \tag{4.12}$$

The regular part $\bar{B}_0(t)$ is determined by

$$\bar{B}_0(t) = B_+(\bar{A}_0(t)). \tag{4.13}$$

Finally, we determine the boundary layer function $\Pi_0 B(\tau)$. We obtain for it the differential equation

$$\begin{aligned}\frac{d\Pi_0 B(\tau)}{d\tau} &= -(2\bar{B}_0(0) + C_0 - B_0 + k)\Pi_0 B(\tau) - (\Pi_0 B(\tau))^2 \\ &= -(2B_+(A_0) + C_0 - B_0 + k)\Pi_0 B(\tau) - (\Pi_0 B(\tau))^2\end{aligned} \tag{4.14}$$

with initial condition $\Pi_0 B(0) = B_0 - B_+(A_0)$.

For our choice of approximation to the "slow manifold" (given by (4.12)) it can be shown that the differential equation (4.14) for the boundary function $\Pi_0 B(\tau)$ has a solution that decays exponentially to zero as $\tau \to \infty$ (see additional discussion of that in section 4.4). The justification of the leading order asymptotics follows immediately from the results for singularly perturbed systems of Tikhonov's type (see, e.g., [5]).

4.4. The general approach description

We start with the original model formulation, and we apply the reduction procedure directly to (4.7), (2.2) without making preliminary simplifications and eliminations of terms/equations from the system. We present the asymptotic reduction procedure as a set of steps that can be implemented in a computerized symbolic reduction algorithm. The justification of the procedure for a general case can be found in [4, 5]. In what follows, whenever we use the phrases like "result can be found symbolically", we mean that the result can be obtained with the help of some symbolic computer software (e.g., MAPLE). Also, along with explanation of theoretical steps of the procedure, we will mention the practical (simpler) steps that can be undertaken to obtain the same "theoretical" result.

The uniform (on a time domain of interest) asymptotic approximation of the solution of (4.7), (2.2) can be obtained by truncating (4.8).

Let us briefly describe the steps of construction of the leading order approximation. First, we need to substitute (4.8) into (4.7), (2.2) and equate the terms multiplying like powers of ε in both sides of the resulting equations separately for regular and boundary functions. Practically, to obtain the equations for regular functions only, one can substitute the regular series (e.g., first three terms) into the equations (4.7), and set $\varepsilon = 0$.

For the regular functions in the leading order we obtain:

$$\begin{aligned} \frac{\mathrm{d}\bar{A}_0}{\mathrm{d}t} &= -\bar{A}_0\bar{B}_0, \\ 0 &= -\bar{B}_0\bar{C}_0 + k\bar{D}_0. \end{aligned} \tag{4.15}$$

In fact, (4.15) contains three identical algebraic equations, and here we only write out one of them. Thus, we arrive at a system of two equations involving four unknown variables. From the second (algebraic) equation of (4.15) we cannot find $\bar{B}_0$, $\bar{C}_0$, $\bar{D}_0$ uniquely. Instead, we can derive a family of solutions (that is, express one of the unknowns, e.g., $\bar{D}_0$, in terms of the remaining two). Two additional equations are needed to define all the regular functions in the leading order in the next step of the asymptotic algorithm. Such situation is often referred to in the literature as the *critical case* or *singular singularly perturbed problem*.

Practically, we do not need to resolve the algebraic equation in (4.15). Instead, let us show how we can check the fact that three algebraic equations in the leading order approximation are identical. We construct the Jacobian matrix (only for the equations without derivatives in the right-hand side of (4.15)).

$$J = \begin{pmatrix} -\bar{C}_0 & -\bar{B}_0 & k \\ -\bar{C}_0 & -\bar{B}_0 & k \\ \bar{C}_0 & \bar{B}_0 & -k \end{pmatrix}. \tag{4.16}$$

The rank of this matrix (rank=1), as well as the eigenvalues ($\lambda_{1,2} = 0$, $\lambda_3 = -\bar{C}_0 - \bar{B}_0 - k$) can be easily computed symbolically. Thus, we determine that we, indeed, have only one equation instead of three.

For the regular functions of the first order we obtain:

$$\begin{aligned} \frac{\mathrm{d}\bar{A}_1}{\mathrm{d}t} &= -\bar{A}_1\bar{B}_0 - \bar{A}_0\bar{B}_1, \\ \frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t} + \bar{A}_0\bar{B}_0 &= -\bar{B}_1\bar{C}_0 - \bar{B}_0\bar{C}_1 + k\bar{D}_1, \\ \frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t} - \bar{A}_0\bar{B}_0 &= -\bar{B}_1\bar{C}_0 - \bar{B}_0\bar{C}_1 + k\bar{D}_1, \\ \frac{\mathrm{d}\bar{D}_0}{\mathrm{d}t} &= \bar{B}_1\bar{C}_0 + \bar{B}_0\bar{C}_1 - k\bar{D}_1. \end{aligned} \tag{4.17}$$

In the last three equations of (4.17) all the terms that do not contain functions of the first order approximation have been moved to the left-hand sides. Comparing the right-hand sides of the last three equations in (4.17) we can easily see that for the second and the third equations they are the same, and they are equal to the negative of the right hand side of the fourth equation. Thus, the left-hand sides of these equations must also satisfy the corresponding relations (i.e., the left-hand sides of the second and the third equations must be equal to

each other and to the left hand side of the fourth equation multiplied by -1). These are the solvability conditions for the linear system of three algebraic equations for $\bar{B}_1$, $\bar{C}_1$, $\bar{D}_1$. In practical terms, the way to derive these solvability conditions using symbolic manipulator can be described as follows. The matrix of the mentioned above algebraic system is J given by (4.16). For the non-homogeneous linear system to be solvable, the non-homogeneity vector must be orthogonal to linearly independent eigenvectors corresponding to zero eigenvalues of J. These eigenvectors are

$$v_1 = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \qquad \text{and} \qquad v_2 = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}. \tag{4.18}$$

If we denote the non-homogeneity vector by F, i.e., $F=(\mathrm{d}\bar{B}_0/\mathrm{d}t + \bar{A}_0\bar{B}_0, \mathrm{d}\bar{C}_0/\mathrm{d}t - \bar{A}_0\bar{B}_0, \mathrm{d}\bar{D}_0/\mathrm{d}t)$, from orthogonality conditions, $(v_i \cdot F) = 0$, we obtain the following pair of equations:

$$\begin{aligned} &\frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t} + \bar{A}_0\bar{B}_0 + \frac{\mathrm{d}\bar{D}_0}{\mathrm{d}t} = 0, \\ &\frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t} - \bar{A}_0\bar{B}_0 + \frac{\mathrm{d}\bar{D}_0}{\mathrm{d}t} = 0. \end{aligned} \tag{4.19}$$

The system consisting of (4.15), (4.19) contains four equations for four unknown functions $\bar{A}_0$, $\bar{B}_0$, $\bar{C}_0$, $\bar{D}_0$. Let us show how the constraint $\bar{B}_0\bar{C}_0 - k\bar{D}_0 = 0$ defining the approximation to the slow manifold can be eliminated from the system. We note that this constraint can be differentiated (symbolically) to produce

$$\frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t}\bar{C}_0 + \frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t}\bar{B}_0 - k\frac{\mathrm{d}\bar{D}_0}{\mathrm{d}t} = 0. \tag{4.20}$$

It can be easily seen that (4.19), (4.20) is a non-homogeneous system of linear equations for $\mathrm{d}\bar{B}_0/\mathrm{d}t$, $\mathrm{d}\bar{C}_0/\mathrm{d}t$, and $\mathrm{d}\bar{D}_0/\mathrm{d}t$, that can be easily resolved symbolically. Practically, to reduce the number of variables one of them may be eliminated from the system. For example, it follows from (4.19), (4.20) that

$$\begin{aligned} &k\frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t} + k\bar{A}_0\bar{B}_0 + \frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t}\bar{C}_0 + \frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t}\bar{B}_0 = 0, \\ &k\frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t} - k\bar{A}_0\bar{B}_0 + \frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t}\bar{C}_0 + \frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t}\bar{B}_0 = 0. \end{aligned} \tag{4.21}$$

Next, system (4.21) may be resolved with respect to $\mathrm{d}\bar{B}_0/\mathrm{d}t$ and $\mathrm{d}\bar{C}_0/\mathrm{d}t$.

$$\frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t} = -\frac{\bar{A}_0\bar{B}_0(k + 2\bar{B}_0)}{k + \bar{C}_0 + \bar{B}_0},$$

$$\frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t} = \frac{\bar{A}_0\bar{B}_0(k+2\bar{C}_0)}{k+\bar{C}_0+\bar{B}_0}. \tag{4.22}$$

So, we now have to solve the system consisting of the first equation of (4.15) and two equations of (4.22). The function $\bar{D}_0$ can either be found from the second equation of (4.15), or by solving the differential equation (4.20), after substituting there (4.22), with corresponding condition.

Note that the initial values for the regular functions $\bar{A}_0(0)$, $\bar{B}_0(0)$, $\bar{C}_0(0)$, and $\bar{D}_0(0)$ are not known yet. These initial values must belong to the approximation of the manifold given by the second equation of (4.15). To find them we need to consider problems for the boundary functions in the leading order approximation. For them we can write,

$$\begin{aligned}
\frac{\mathrm{d}\Pi_0 A}{\mathrm{d}\tau} &= 0,\\
\frac{\mathrm{d}\Pi_0 B}{\mathrm{d}\tau} &= -\bar{C}_0(0)\Pi_0 B - \bar{B}_0(0)\Pi_0 C - \Pi_0 B\Pi_0 C + k\Pi_0 D,\\
\frac{\mathrm{d}\Pi_0 C}{\mathrm{d}\tau} &= -\bar{C}_0(0)\Pi_0 B - \bar{B}_0(0)\Pi_0 C - \Pi_0 B\Pi_0 C + k\Pi_0 D,\\
\frac{\mathrm{d}\Pi_0 D}{\mathrm{d}\tau} &= \bar{C}_0(0)\Pi_0 B + \bar{B}_0(0)\Pi_0 C + \Pi_0 B\Pi_0 C - k\Pi_0 D.
\end{aligned} \tag{4.23}$$

Practically, the equations for boundary functions can be found by making substitution (4.8) into the original system, multiplying the first equation by ε, changing the variable in the derivatives, setting $\varepsilon = 0$, dropping all the terms in the remaining expressions that do not contain any boundary functions, and finally, substituting for the regular functions their initial values (symbolically).

The boundary functions $\Pi_0 A(\tau)$, $\Pi_0 B(\tau)$, $\Pi_0 C(\tau)$, and $\Pi_0 D(\tau)$ together with the regular functions in the leading order approximation must satisfy the initial conditions,

$$\begin{aligned}
\bar{A}_0(0) + \Pi_0 A(0) &= A_0,\\
\bar{B}_0(0) + \Pi_0 B(0) &= B_0,\\
\bar{C}_0(0) + \Pi_0 C(0) &= C_0,\\
\bar{D}_0(0) + \Pi_0 D(0) &= D_0.
\end{aligned} \tag{4.24}$$

Also, the boundary functions must satisfy the conditions: $\Pi_0 A(\tau) \to 0$ for $\tau \to \infty$, etc. From (4.23), (4.24) and conditions at $\tau \to \infty$ it follows that

$$\begin{aligned}
&\Pi_0 A(\tau) \equiv 0,\\
&\Pi_0 B(\tau) = \Pi_0 C(\tau) = -\Pi_0 D(\tau).
\end{aligned} \tag{4.25}$$

Practically, the above relations between $\Pi_0 B(\tau)$, $\Pi_0 C(\tau)$, and $\Pi_0 D(\tau)$ can be obtained as follows. We note that the linear part in the last three equations of (4.23) is nothing but the Jacobian matrix (4.16) evaluated at $t = 0$. Since only

one eigenvalue (λ_3) of J corresponds to decaying solutions (under certain conditions), with corresponding eigenvector $v_3 = (1, 1, -1)^T$ giving the direction of the decay in the phase space, the Π-functions vector consisting of $\Pi_0 B$, $\Pi_0 C$, and $\Pi_0 D$ must decay in the same direction. This means that the components of Π-functions vector must be proportional to v_3, from which (4.25) immediately follows.

Substituting (4.25) into (4.24) and using $\bar{D}_0(0) = \bar{B}_0(0)\bar{C}_0(0)$ (which follows from (4.15)), we obtain

$$\begin{aligned} \bar{A}_0(0) &= A_0, \\ \bar{B}_0(0) + \Pi_0 B(0) &= B_0, \\ \bar{C}_0(0) + \Pi_0 B(0) &= C_0, \\ \bar{B}_0(0)\bar{C}_0(0) - k\Pi_0 B(0) &= kD_0. \end{aligned} \tag{4.26}$$

The first relation in (4.26) is the initial condition for $\bar{A}_0$. From the remaining three equations we can find $\bar{B}_0(0)$, $\bar{C}_0(0)$, and $\Pi_0 B(0)$. Indeed, subtracting the third equation of (4.26) from the second, we have

$$\bar{B}_0(0) - \bar{C}_0(0) = B_0 - C_0. \tag{4.27}$$

Adding the second, multiplied by k, and the fourth equations of (4.26), we obtain

$$k\bar{B}_0(0) + \bar{B}_0(0)\bar{C}_0(0) = k(B_0 + D_0). \tag{4.28}$$

Eliminating $\bar{C}_0(0)$ from the above two expressions, we arrive at a quadratic equation for $\bar{B}_0(0)$,

$$\bar{B}_0^2(0) + (C_0 - B_0 + k)\bar{B}_0(0) - k(B_0 + D_0) = 0.$$

This equation has two solutions of which we choose the positive one.

$$\bar{B}_0(0) = \frac{1}{2}\left(B_0 - C_0 - k + \sqrt{(B_0 - C_0 - k)^2 + 4k(B_0 + D_0)}\right). \tag{4.29}$$

The reason for such choice can be explained by the condition that the zero steady state of the differential system for boundary functions must be stable. For the Π-functions to decay to zero the eigenvalue $\lambda_3 = -\bar{C}_0(0) - \bar{B}_0(0) - k$ must be negative. If we choose $\bar{B}_0(0) < 0$, then it will follow from (4.28) that

$$\bar{B}_0(0)(k + \bar{C}_0(0)) = k(B_0 + D_0) > 0,$$

and so, we must also have $k + \bar{C}_0(0) < 0$. But then λ_3 will become positive and the boundary functions will not decay to zero!

In practical terms, the positive root $\bar{B}_0(0)$ can be chosen directly from "physical" considerations: if small parameter tends to zero we have immediate transition of the solution of the original problem from a given initial condition

to the initial condition lying on slow manifold, and since concentrations must be positive (or, at least, non-negative), $\bar{B}_0(0)$ must also be positive (non-negative $\bar{B}_0(0)$ is also possible only with the choice of plus sign in (4.29)).

For known $\bar{B}_0(0)$, the initial condition for $\bar{C}_0$ can be easily found from (4.27),

$$\bar{C}_0(0) = \bar{B}_0(0) - B_0 + C_0. \tag{4.30}$$

Now the system for regular functions in the leading order approximation consisting of differential equation for $\bar{A}_0$ (from (4.15)), and two differential equations (4.22) for $\bar{B}_0$ and $\bar{C}_0$, with corresponding initial conditions given by the first relation in (4.26), and relations (4.29), (4.30), can be solved numerically.

In section 5, we discuss implications of the above analysis from the viewpoint of practical use of the constructed asymptotic approximations, and compare the results produced by the method of invariant manifolds and the boundary function method.

5. Discussion

Let us re-write the problems for the leading order approximation of the solution of the original problem in the limit as $\varepsilon \to 0$. "Physically", this means that we are looking at our original chemical kinetics system under the assumption that the second, reversible, reaction characterized by reaction rate constants k^+ (for forward reaction) and k^- (for reverse reaction) occurs instantaneously, while the ratio $k = k^-/k^+$ stays bounded of order $O(1)$. The limiting problem for simplified equivalent system has the form (compare with (4.11)),

$$\begin{aligned}
\frac{\mathrm{d}\bar{A}_0}{\mathrm{d}t} &= -\bar{A}_0 B_+(\bar{A}_0) \\
&= -\frac{1}{2}\bar{A}_0\Big[-(2A_0 + C_0 - B_0 - 2\bar{A}_0 + k) \\
&\qquad + \sqrt{(2A_0 + C_0 - B_0 - 2\bar{A}_0 + k)^2 - 4k(A_0 - \bar{A}_0 - B_0 - D_0)}\Big], \qquad (5.31)\\
\bar{A}_0(0) &= A_0.
\end{aligned}$$

Limiting system that was produced by the general approach procedure consists of equations

$$\frac{\mathrm{d}\bar{A}_0}{\mathrm{d}t} = -\bar{A}_0\bar{B}_0, \qquad \frac{\mathrm{d}\bar{B}_0}{\mathrm{d}t} = -\frac{\bar{A}_0\bar{B}_0(k + 2\bar{B}_0)}{k + \bar{C}_0 + \bar{B}_0}, \qquad \frac{\mathrm{d}\bar{C}_0}{\mathrm{d}t} = \frac{\bar{A}_0\bar{B}_0(k + 2\bar{C}_0)}{k + \bar{C}_0 + \bar{B}_0}, \tag{5.32}$$

with condition $\bar{A}_0(0) = A_0$, and conditions (4.29) and (4.30) for $\bar{B}_0$ and $\bar{C}_0$, respectively.

Comparing the two limiting problems we note that both require some additional analysis to completely define their behavior at $t \to \infty$. Such analysis was performed previously in sections 3 and 4.1. The two approximate problems presented above are equivalent in the following sense. When the solution $\bar{A}_0$ of (5.31) is known, the approximations for $\bar{B}_0$ and $\bar{C}_0$ could be found from (4.12) and (2.5), (2.7), respectively. These approximations will be equal to solutions $\bar{A}_0$, $\bar{B}_0$ and $\bar{C}_0$ of (5.32) defined for corresponding initial conditions that represent an orthogonal projection of the original conditions on the approximation to slow manifold $\bar{D}_0 = \bar{B}_0\bar{C}_0/k$. Indeed, we can immediately see that substitution of $\bar{A}_0(0) = A_0$ into the expression (4.12) for B^+ produces condition (4.29) for $\bar{B}_0$. On the other hand, the first integrals that were used in obtaining the simplification for the original system can also be constructed for (5.32). For example, it follows from (5.32) that $2\mathrm{d}\bar{A}_0/\mathrm{d}t + \mathrm{d}\bar{C}_0/\mathrm{d}t - \mathrm{d}\bar{B}_0/\mathrm{d}t = 0$, and thus, by virtue of (4.27), $2\bar{A}_0(t) + \bar{C}_0(t) - \bar{B}_0(t) = 2A_0 + C_0 - B_0$, which is exactly the leading order approximation for (2.7).

Let us also comment on the stability properties of the boundary functions constructed for both systems. We note that after substituting (4.25) into (4.23) describing the boundary function system in the general approach case, we immediately arrive at equation (4.14) for the simplified problem case. It is important to mention that the choice of correct projection of the boundary condition onto the slow manifold (see (4.29)) that guaranteed the asymptotic stability of the zero solution for the boundary functions in the general case also justifies mathematically the "physical" choice of the B^+ manifold made earlier for simplified problem (there the choice was made to guarantee that the values of concentrations in the system remain non-negative). Naturally, for such choice of the slow manifold, the zero solution of equation (4.14) for the Π-function is also asymptotically stable.

Note that in both reduced problems only one parameter, k, is present. From the viewpoint of applications, the identification of this parameter will usually be the most important problem in which the asymptotic reductions constructed above are used. Currently, from the numerical analysis viewpoint, for available numerical software and fast computers, obtaining the solution of the original problem (2.1), (2.2) is as easy as obtaining the solution of either one of the limiting problems. However, to solve the original problem all the parameter values in the model must be specified, and this cannot always be done! Both presented reduced models allow us to eliminate the "small" parameter dependence (this parameter usually cannot be robustly identified during the solution of inverse problems of parameter identification), and keep only the "moderate" parameter (which can be identified from experimental data). While in the case of reduction of previously simplified problem only one differential equation must be solved, some amount of work must be done "by hand" (identification and calculation of first integrals, etc.) to arrive at the final limiting problem. For more complex systems the amount of such preliminary work may increase dramatically, and the

steps of the simplification algorithm, which are necessarily problem dependent, cannot be easily quantified for including them into a symbolic system reduction algorithm. The general approach that we have presented, on the other hand, is designed to minimize the amount of preliminary simplification work and is, thus, more suitable for its inclusion as a part of the reduction algorithm in symbolic reduction programs.

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