Kinetic scheme reduction, attractive invariant manifold and slow/fast dynamical systems

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March 1995

Abstract

An effective reduction method based on geometric singular perturbation and center manifold techniques is proposed. This method eliminates the fast and stable dynamics and gives the equations describing the slow ones. It is coordinate free and extends the well-known quasi-steady-state method classically used for kinetic scheme reduction. This yields directly the slow dynamics even if the differential equations are not in standard two time-scale form (Tikhonov form). Application to combustion kinetics including 13 species and 67 reactions is presented and simulations are given.

1 Introduction

Let us begin with a simple reaction scheme. It involves three chemical species X_1, X_2 and X_3 and three elementary independent reactions :

$$X_1 \xrightarrow{k_1 x_1} X_2, \quad X_2 \xrightarrow{k_2 x_2} X_1, \quad X_1 + X_2 \xrightarrow{\varepsilon k x_1 x_2} X_2 + X_3;$$

the x_i's are compositions of the X_i's; k_1, k_2 and εk are the kinetic constants. The small positive parameter ε indicates here that the third reaction is slow with respect to the first two reactions.

From this reaction scheme, we derive an ordinary differential equation system. It corresponds to the conservation of each species in a closed homogeneous reactor. The species balances are:

$$\begin{aligned} \dot{x}_1 &= -k_1 x_1 + k_2 x_2 - \varepsilon k x_1 x_2 \\ \dot{x}_2 &= k_1 x_1 - k_2 x_2 \\ \dot{x}_3 &= \varepsilon k x_1 x_2. \end{aligned} \qquad (1)$$

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where the dots above the x's indicate differentiation with respect to time. Since x_3 follows from the chemical invariant $\zeta = x_1 + x_2 + x_3$ ($\dot{\zeta} = 0$), we focus on the first two equations of (1).

The quasi-steady-state assumption applied to x_2 leads to the following reduced system

$$\begin{array}{rcl} \dot{x}_1 & = & -k_1 x_1 + k_2 x_2 - \varepsilon k x_1 x_2 \\ 0 & = & k_1 x_1 - k_2 x_2 \end{array} \tag{2}$$

or

$$\dot{x}_1 = -\varepsilon \frac{k k_1}{k_2} (x_1)^2 \tag{3}$$

with

$$x_2 = \frac{k_1}{k_2} x_1. \tag{4}$$

This system does not yield a correct approximation of the slow dynamics for ε small. The reason is the following. From (1), we have $\dfrac{\mathrm{d}(x_1 + x_2)}{\mathrm{d}t} = -\varepsilon k x_1 x_2$. Thus, if equation (4) was valid, one would have

$$(1 + k_1/k_2)\dot{x}_1 = -\varepsilon \frac{k k_1}{k_2} (x_1)^2.$$

This stands in contradiction with equation (3).

Here, the quasi-steady-state method cannot be directly applied. A change of coordinates is required before. Instead of using (x_1, x_2), consider the coordinates

$$(\xi = x_1 + x_2 \ , \ x_2). \tag{5}$$

The first two equations of (1) are transformed to:

$$\begin{array}{rcl} \dot{\xi} & = & -\varepsilon k (\xi - x_2) x_2 \\ \dot{x}_2 & = & k_1 (\xi - x_2) - k_2 x_2. \end{array} \tag{6}$$

Notice that ξ corresponds to an approximate lumping of x_1 and x_2 (for more about lumping, see, e.g. [12, 13, 14]). The application of the quasi-steady-state method to x_2 leads then to the correct approximation,

$$\dot{\xi} = -\varepsilon k (\xi - x_2) x_2, \quad 0 = k_1 (\xi - x_2) - k_2 x_2,$$

that reads, in the original coordinates (x_1, x_2),

$$\left(1 + \frac{k_1}{k_2}\right) \dot{x}_1 = -\varepsilon \frac{k k_1}{k_2} (x_1)^2 \quad \text{with} \quad x_2 = \frac{k_1}{k_2} x_1. \tag{7}$$

The difference with (2) lies only in the coefficient $(1 + k_1/k_2)$ multiplying the derivative of x_1. The algebraic equation, giving x_2 with respect to x_1 remains unchanged. For this simple system, the "good coordinates" (ξ, x_2) are easy to find. In [3, 4], it is explained how to find such linear change of coordinates when the reactions can be separated into fast and slow ones. For more complex systems, such as the combustion system of section 5, this is no more the case: there is no clear decomposition into slow and fast reactions and thus the change of coordinates is probably nonlinear.

In this paper, we propose a reduction method that overcomes the difficulty of finding the coordinate change. The obtained reduced model (equations (8) and (9) of section 2) is directly given in the modeling variables.

A deeper analysis yields the following explanations. The quasi-steady-state method is not coordinate free: it can be applied only to systems written with special coordinates, called Tikhonov coordinates in the sequel (see figure 1 and system (11)). Our extension provides a coordinate free reduction method. This means that no change of coordinates is required. This extension admits a clear and rigorous justification within the theory of perturbations of dynamical systems [1, 10]. More precisely, we use here the theory of singular perturbations [18], its geometric setting due to Fenichel [9], and a special version of the center manifold approximation lemma [5] (see, also, [7, 8], for application of center manifold techniques to reduction of chemical kinetic schemes, in a slightly different context). Another approach to model reduction is proposed in [16]. When the system admits two time-scales, one can prove that this method is equivalent to ours.

The content is the following. In section 2, we describe the practical aspect of our method. The mathematical framework is the object of section 3: we recall the classical Tikhonov form of singularly perturbed systems; we explain the geometric definition of slow/fast systems [9]; the system reduction via invariant manifold techniques is derived on the basis of an approximation lemma that can be found in [5]. Section 4 is devoted to a special class of chemical systems where the two time-scales are due to fast and slow reactions. In section 5, the application of our reduction method to a combustion scheme considered in [16] is presented. For this system, the quasi-steady-state method yields a rather poor approximation.

A preliminary version of this work can be found in [6, 17].

2 The reduction method

For readers not interested in technical developments, we just present here the formulae that are required for applying our reduction method to a dynamical system of the form

$$\dot{x} = v(x) \quad \text{with} \quad x = (x_1, \ldots, x_n), \quad v = (v_1, \ldots, v_n),$$

n being the dimension of x.

Assume that this system admits two time-scales:

- a slow time-scale that can be described by $n_s < n$ variables.
- a fast and (hyperbolically) stable time-scale that can be described by $n_f = n - n_s$ variables.

The integer n_s will be the number of differential equations of the reduced slow system. The integer n_f corresponds to the number of derivatives that are set to 0 in the quasi-steady-state method, i.e., the number of algebraic equations that must be solved.

As in the quasi-steady-state method, we decompose the state $x \in I\!R^n$ into two sets of components, $x = (x_s, x_f)$ of dimension n_s for x_s and n_f for x_f. Similarly, the system is decomposed into two part

$$\dot{x}_s = v_s(x_s, x_f), \quad \dot{x}_f = v_f(x_s, x_f)$$

with $v = (v_s, v_f)$. This decomposition is up to the choice of the user. We give below some guidelines to make this choice. In particular, the eigenvalue structure of the Jacobian matrix $\left(\frac{\partial v_i}{\partial x_j}\right)$ provides an estimation of n_f.

Then, the reduced system is as follows:

$$\left\{\begin{array}{rcl} \dot{x}_s & = & C(x_s, h_0) \cdot v_s(x_s, h_0) \\ 0 & = & v_f(x_s, h_0) \\ x_f & = & h_0 - \left[\left(\left(\frac{\partial v_f}{\partial x_f}\right)^2 + \frac{\partial v_f}{\partial x_s} \cdot \frac{\partial v_s}{\partial x_f}\right)^{-1} \frac{\partial v_f}{\partial x_s}\right] \cdot v_s(x_s, h_0) \end{array}\right. \tag{8}$$

where the matrix $C(x_s, h_0)$ is given by

$$C = \left(1_{n_s} + \frac{\partial v_s}{\partial x_f}\left(\frac{\partial v_f}{\partial x_f}\right)^{-2} \frac{\partial v_f}{\partial x_s}\right)^{-1} \tag{9}$$

with 1_{n_s} the identity matrix of order n_s. All the partial derivatives are computed at $x = (x_s, h_0)$. Some algebraic manipulations provide another equivalent expression for C that might by preferable in practice:

$$C = 1_{n_s} - \frac{\partial v_s}{\partial x_f}\left(\left(\frac{\partial v_f}{\partial x_f}\right)^2 + \frac{\partial v_f}{\partial x_s}\frac{\partial v_s}{\partial x_f}\right)^{-1} \frac{\partial v_f}{\partial x_s}.$$

Notice that formulae (8), applied to (1) with $x_s = (x_1, x_3)$ and $x_f = x_2$, leads to the correct approximation, the correction factor $(1+k_1/k_2)$ of (7) corresponding then to the matrix C^{-1} (up to terms of order 1 in ε). In fact, the only difference between (8) and the equation resulting from the quasi-steady-state method lies only in the correction matrix C. For systems with $v_s = \varepsilon \tilde{v}_s$, such as system (6) with $x_s = \xi$, then the matrix C is close to 1_{n_s} up to terms of order 1 in ε. In this case, our method coincides, up to terms of order 2 in ε, with the quasi-steady-state one.

In order to avoid the computation and the inversion of the jacobian matrices contained in (8) and (9), it may be useful to approximate (8) via the following differential-algebraic system:

$$\left\{\begin{array}{rcl} \frac{dx_s}{dt} & = & v_s(x_s, x_f) \\ 0 & = & v_f(x_s, h_0) \\ 0 & = & v_f(x_s + \delta v_s(x_s, x_f), h_0 + \delta v_f(x_s, x_f)) \end{array}\right. \tag{10}$$

where δ is a very small parameter and (x_s, h_0, x_f) are the unknown [1]. Such differential-algebraic systems of index 1 can be easily solved numerically via Gear-like schemes and standard codes of public domain, such as DASSL or LSODE/LSODI (see, e.g., [2]).

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[1] Some elementary computation show that if δ ($\neq 0$) is of order 2 in ε at least then the variable x_f in (10) satisfies (14) for $p = 1$.

As far as we know, formulae (8) and its approximation (10) are new and have never been introduced elsewhere in a so simple formulation.

Remark that, for the computation of the reduced slow dynamics, it is not required to exhibit ε as a function of the model parameters. We just need to know that the system admits two time-scales, that the dimension of the fast part is n_f , and that it is asymptotically stable. This point and the simplicity of the formulae constitute the major interest of the method proposed here.

In practice, we have to define n_f (or equivalently $n_s = n - n_f$). Since our reduction method amounts to eliminating fast and stable time scales, we may be guided by two criteria:

1. what is the fastest time scale that cannot be eliminated?
2. the time scales of the reduced model (slow time scales) must be significantly slower than those that have been eliminated.

The answer to the first question is given by the following considerations:

- the kinetic model may be part of a bigger model including for example transport. In this last case, one must keep in the reduced model the time scales that are of the same order of magnitude as those of transport phenomena (and of course the slower ones). We denote by α this typical time constant.
- the time of evolution of the system, T, may be a priori known. In this case, one eliminates those time scales that are significantly faster than T, i.e., time-scales less than or equal to α with $0 \leq \alpha \ll T$.

The characteristic times of the system, $(\tau_i)_{i=1,\ldots,n}$ may be estimated with the help of the eigenvalues of the jacobian $\dfrac{\partial v}{\partial x}$, $(\lambda_i)_{i=1,\ldots,n}$:

$$\tau_i \approx \frac{1}{|Re(\lambda_i)|}.$$

To satisfy the second criterion, one computes the eigenvalues along different trajectories of the system. Then one tries to separate the characteristic times into two groups, $(\tau_1, \tau_2, \ldots, \tau_{n_f})$ and $(\tau_{n_f+1}, \ldots, \tau_n)$, such that:

$$\tau_1 \leq \tau_2 \leq \ldots \leq \tau_{n_f} \ll \alpha \leq \tau_{n_f+1} \leq \ldots \leq \tau_n.$$

The eigenvalues relative to the first group have a large, negative real part: they correspond to fast and stable phenomena. The eigenvalues of the second group correspond to the slow part of the system and thus are close to zero.

After having determined n_f, one has to parametrize the reduced model, i.e. choose a decomposition of x into (x_s, x_f). In view of the algebraic equations of (8), it seems reasonable to choose the x_f variables among those that are at or near quasi-steady-state. A species is in quasi-steady-state when its creation rate is (almost) equal to its destruction rate. This may be evaluated by the ratio:

$$\frac{|\text{creation} - \text{destruction}|}{\text{creation} + \text{destruction}}.$$

The species for which this ratio is small (compared to 1) may be considered as being in quasi-steady-state. This ratio can be numerically calculated along the trajectories of the system. We choose the x_f variables among those for which this ratio is small.

Other procedures for defining n_s and (x_s, x_f) can be used. We just have sketched here a simple one that gives, for the combustion system of section 5, an efficient reduced model of dimension 1. Let us now explain how we have obtained (8) and (9).

3 Geometric singular perturbations

3.1 Model reduction

The following question underlies this paper: what is model reduction ? A possible and reasonable answer to this question for dynamical systems of the form, $\dot{x} = v(x)$, $x \in I\!R^n$, is displayed on figure 2. Reduction can be defined via an *attractive invariant manifold* Σ. A sub-manifold Σ is invariant with respect to the vector field v, if v is tangent to Σ: if a trajectory starts on Σ, it remains on Σ for all time. Σ is called (locally) attractive if any trajectory $t \rightarrow x(t)$ of $\dot{x} = v(x)$ (starting near Σ) tends to Σ as t tends to $+\infty$. In this case, the reduced system corresponds to the restriction of the vector field v to Σ. This restriction is meaningful since Σ is invariant.

It seems then natural to approximate trajectories of the complete system $\dot{x} = v(x)$ by trajectories on Σ. In fact, such an approximation is proved to be valid when, roughly speaking, the dynamics transverse to Σ (the dynamics that are neglected) are faster than the dynamics on Σ (see [1] and [11] for more details on normally hyperbolic invariant manifolds).

Reduction means then *restriction of the dynamics to an invariant attractive manifold* Σ. In practice the equations defining Σ are not known. Only the vector field, v, is explicitly available. The main difficulty is thus to obtain the equations of Σ or, at least, good approximations of them.

3.2 Tikhonov normal form of slow/fast dynamical system

We restrict here the study to a special class of dynamical systems, depending of a small parameter ε and having an attractive invariant manifold Σ_ε. Such systems are characterized by dynamics transverse to Σ_ε which is much faster than the dynamics on Σ_ε. This corresponds to systems having two time-scales: an asymptotically stable and fast one and a slow one (stable or unstable). A first kind of such systems are singularly perturbed systems of the form, called Tikhonov form,

$$\frac{\mathrm{d}x_s}{\mathrm{d}t} = \varepsilon\, v_s(x_s, x_f, \varepsilon), \quad \frac{\mathrm{d}x_f}{\mathrm{d}t} = v_f(x_s, x_f, \varepsilon) \tag{11}$$

where $0 < \varepsilon \ll 1$. Very often, such systems are written with the time-scale $\tau = \varepsilon t$:

$$\frac{dx_s}{d\tau} = v_s(x_s, x_f, \varepsilon), \quad \varepsilon \frac{dx_f}{d\tau} = v_f(x_s, x_f, \varepsilon).$$

The terminology "singular perturbations" comes from the fact that the small parameter ε multiplies the highest derivative (here $dx_f/d\tau$). More details on this classical standpoint can be found, e.g., in [18].

In the sequel we always consider the time-scale t and approximations of trajectories for $t \in [0, 1/\varepsilon]$ and with $\varepsilon > 0$ but close to 0.

Assume that the fast part is hyperbolically stable, i.e., that the sub-system $\dot{x}_f = v_f(x_s, x_f, \varepsilon)$ with x_s fixed, admits (locally) an equilibrium with characteristic exponents (eigenvalues of $\frac{\partial v_f}{\partial x_f}$ at this equilibrium) having a strictly negative real part. Then the slow approximation is obtained by the quasi-steady-state method [18]:

$$\left\{ \begin{array}{rcl} \dot{x}_s & = & \varepsilon v_s(x_s, x_f, \varepsilon) \\ 0 & = & v_f(x_s, x_f, \varepsilon). \end{array} \right.$$

The algebraic equations, $v_f = 0$, correspond here to an approximation up to terms of order 1 in ε, of Σ_ε equations. These coordinates (x_s, x_f) where the quasi-steady-state method applies, and where the vector field v is quasi-vertical (see figure 1) are clearly very specific.

3.3 Geometric setting

Since we are interested in developing a reduction method that avoids changing coordinates, we need a coordinate-free point of view. The geometric definition of singularly perturbed systems due to Fenichel [9] is as follows.

Consider the dynamical system

$$\dot{x} = v(x, \varepsilon), \quad x \in I\!R^n, \quad 0 \le \varepsilon \ll 1. \tag{12}$$

This system is said to have two time-scales, a fast and asymptotically stable one and a slow one, if, and only if, the following two assumptions are satisfied [9]:

A1 for $\varepsilon = 0$, (12) admits an equilibrium manifold of dimension n_s, $0 < n_s < n$, denoted by Σ_0.

A2 for all $x_0 \in \Sigma_0$, the Jacobian matrix, $\left.\frac{\partial v}{\partial x}\right|_{(x_0,0)}$ admits $n_f = n - n_s$ eigenvalues with a strictly negative real part (the eigenvalues are counted with their multiplicities).

This definition is illustrated in figure 3. Assumption **A1** implies that the velocity $v(x, \varepsilon)$ is large everywhere excepted for x in a neighborhood of Σ_0 where v is small and of order 1 in ε.

A1 and **A2** imply that, for $x_0 \in \Sigma_0$, the kernel, $E_0^c(x_0)$, of the linear operator $\left.\frac{\partial v}{\partial x}\right|_{(x_0,0)}$ coincides with the tangent space of Σ_0 at x_0. The linear space $E_0^s(x_0)$ corresponding to the eigenvalues with real negative part satisfies:

$$E_0^s(x_0) \oplus E_0^c(x_0) = I\!R^n.$$

The trajectories of the perturbed system are captured by a trapping region around Σ_0 and enter with a direction nearly parallel to $E_0^s(x_0)$.

In [9][part of theorem 9.1], Fenichel proves the following result. It asserts, for ε small enough, the existence of a slow invariant attractive manifold Σ_ε for the perturbed system (12).

Theorem 1 (Fenichel (1979)) *Consider (12) satisfying **A1** and **A2**. Then, for every open and bounded subset Ω_0 of Σ_0, there exists an open neighborhood V_0 of Ω_0 in $I\!R^n$, such that, for ε positive and small enough, the perturbed system (12) admits an attractive invariant submanifold Σ_ε contained in V_0 and close to Σ_0.*

We are interested in approximations, up to terms of order 1 in ε, of slow trajectories for $t \in [0, 1/\varepsilon]$. Thus we need an approximation up to terms of order 2 for the slow dynamics ($\varepsilon^2 \times (1/\varepsilon) = \varepsilon$). This means that an approximation, up to terms of order 2 in ε, of Σ_ε equations is needed.

3.4 Approximation of Σ_ε

Proposition 1 *Consider (12) satisfying **A1** and **A2**. Take $x_0 \in \Sigma_0$. Then locally around x_0, there exists a partition of the state x into two groups of components, $x = (x_s, x_f)$, with* $\dim(x_s) = n_s$ *and* $\dim(x_f) = n_f$, *such that the projection of Σ_ε on the x_s-coordinates is a local diffeomorphism around x_0. The equations defining Σ_ε around x_0 admits the following approximation:*

$$\begin{aligned} x_f &= h_0(x_s,\varepsilon) + O(\varepsilon) \\ x_f &= h_0(x_s,\varepsilon) \\ &\quad - \left[\left(\left(\frac{\partial v_f}{\partial x_f} \right)^2 + \frac{\partial v_f}{\partial x_s} \cdot \frac{\partial v_s}{\partial x_f} \right)^{-1} \left. \frac{\partial v_f}{\partial x_s} \right|_{(x_1, h_0(x_s,\varepsilon),\varepsilon)} \right] \cdot v_s(x_s, h_0(x_s,\varepsilon),\varepsilon) + O(\varepsilon^2) \end{aligned} \tag{13}$$

where h_0 is solution of $v_f(x_s, h_0(x_s,\varepsilon),\varepsilon) = 0$.

In some generic sense, that can be easily defined, almost every partition of x in (x_s, x_f) is admissible for (13). But in practice, the coordinates x_s must be chosen such that the projection of Σ_ε onto the x_s-space is as well conditioned as possible.

Proof By the approximation lemma of invariant manifold, and its version for two-time scale systems [5, theorem 5, page 32], the equation $x_f = h_p(x_s,\varepsilon)$ is an approximation up to term of order $p+1$ in ε of Σ_ε equations, if they satisfied the following equation stating the invariance of Σ_ε:

$$v_f(x_s, h_p(x_s,\varepsilon),\varepsilon) = \left.\frac{\partial h_p}{\partial x_s}\right|_{(x_s,\varepsilon)} v_s(x_s, h_p(x_s,\varepsilon),\varepsilon) + O(\varepsilon^{p+1}). \tag{14}$$

Since $v_f(x_s, h_0(x_s,\varepsilon),\varepsilon) = 0$ and $v_s(x_s, h_0(x_s,\varepsilon),\varepsilon) = O(\varepsilon)$, $x_f = h_0(x_s,\varepsilon)$ is an approximation up to terms of order 1 in ε.

Set $h_1 = h_0 + \varepsilon p_1$ where p_1 is a smooth function of x_s that will be adjusted in order to verify (14) with $p = 1$. We have

$$v_f(x_s, h_0(x_s,\varepsilon) + \varepsilon p_1,\varepsilon) = \varepsilon \left.\frac{\partial v_f}{\partial x_f}\right|_{(x_s,h_0(x_s,\varepsilon),\varepsilon)} p_1 + O(\varepsilon^2)$$

since $v_f(x_s, h_0(x_s,\varepsilon),\varepsilon) = 0$. We also have

$$\left.\frac{\partial(h_0+\varepsilon p_1)}{\partial x_s}\right|_{(x_s,\varepsilon)} v_s(x_s, h_0(x_s,\varepsilon)+\varepsilon p_1,\varepsilon) = \left.\frac{\partial h_0}{\partial x_s}\right|_{(x_s,\varepsilon)} v_s(x_s, h_0(x_s,\varepsilon)+\varepsilon p_1,\varepsilon) + O(\varepsilon^2)$$

with

$$v_s(x_s, h_0(x_s,\varepsilon)+\varepsilon p_1,\varepsilon) = v_s(x_s, h_0(x_s,\varepsilon),\varepsilon) + \varepsilon \left.\frac{\partial v_s}{\partial x_f}\right|_{(x_s,h_0(x_s,\varepsilon),\varepsilon)} p_1 + O(\varepsilon^2).$$

Using

$$\frac{\partial h_0}{\partial x_s} = -\left(\frac{\partial v_f}{\partial x_f}\right)^{-1} \frac{\partial v_f}{\partial x_s},$$

we obtain (13). The matrix

$$\left(\frac{\partial v_f}{\partial x_f}\right)^2 + \frac{\partial v_f}{\partial x_s}\cdot\frac{\partial v_s}{\partial x_f}$$

is invertible: this results from **A1**, **A2** and from some elementary calculations. ■

The reduced slow model (8) comes from (13) and

$$v_s(x_s, h_0+\varepsilon p_1,\varepsilon) = v_s(x_s,h_0,\varepsilon) + \left.\frac{\partial v_s}{\partial x_f}\right|_{(x_s,h_0,\varepsilon)} \varepsilon p_1 + O(\varepsilon^2).$$

Notice that approximation (8) applied to a system already in Tikhonov normal form yields an approximation of the dynamics on Σ_ε, up to terms of order 3 in ε (use (13) and replace v_s in (13) by εv_s for systems like (11)).

4 Chemical systems with slow and fast reactions

In this section we consider the case of kinetic systems where the reactions can be split into one group of slow reactions and one group of fast reactions. The reduction of such systems has been studied in [3, 4]. We show here that the reduced models deduced from their calculations and the reduced model obtained from (8) coincide, up to terms of order 2 in ε.

Consider the reaction system

$$\dot{x} = A\, v(x,\varepsilon) \tag{15}$$

where x is the vector of concentrations, A is the stoichiometric matrix, $v(x)$ is the vector of the chemical rates and ε is a small number ($0 < \varepsilon \ll 1$). Assume that v can be split into $v = (\varepsilon\tilde{v}_s, \tilde{v}_f)$, where $\varepsilon\tilde{v}_s$ (resp. $\tilde{v}_f$) is the vector of the chemical rates of the slow (resp. fast) reactions. System (15) can be rewritten as

$$\dot{x} = A_s\, \varepsilon\tilde{v}_s(x) + A_f\, \tilde{v}_f(x). \tag{16}$$

Let A_{ff} be a square sub-matrix of A_f such that its rank is equal to the rank of A_f. Let

$$A_f = \begin{pmatrix} A_{sf} \\ A_{ff} \end{pmatrix}$$

and

$$A_s = \begin{pmatrix} A_{ss} \\ A_{fs} \end{pmatrix}.$$

Then (15) reads

$$\begin{array}{rcl} \dot{x}_s & = & A_{ss}\ \varepsilon\tilde{v}_s(x_s,x_f) + A_{sf}\ \tilde{v}_f(x_s,x_f) \\ \dot{x}_f & = & A_{fs}\ \varepsilon\tilde{v}_s(x_s,x_f) + A_{ff}\ \tilde{v}_f(x_s,x_f) \end{array} \tag{17}$$

The change of coordinates

$$(x_s,x_f) \mapsto (\xi = x_s - A_{sf}(A_{ff})^{-1}x_f\ ,\ x_f).$$

leads to a quasi-vertical vector field. It yields the following Tikhonov form:

$$\begin{array}{rcl} \dot{\xi} & = & (A_{ss} - A_{sf}(A_{ff})^{-1}A_{fs})\ \varepsilon\tilde{v}_s \\ \dot{x}_f & = & A_{fs}\varepsilon\tilde{v}_s + A_{ff}\tilde{v}_f. \end{array}$$

Assuming that eigenvalues of $A_{ff}\dfrac{\partial\tilde{v}_f}{\partial x_f}$ have strictly negative real parts, then the quasi-steady-state method can be applied and leads to the following slow system

$$\begin{array}{rcl} \dot{\xi} & = & (A_{ss} - A_{sf}(A_{ff})^{-1}A_{fs})\ \varepsilon\tilde{v}_s \\ 0 & = & A_{fs}\ \varepsilon\tilde{v}_s + A_{ff}\ \tilde{v}_f. \end{array}$$

Pulling back into the original coordinates (x_s,x_f) yields:

$$\begin{array}{rcl} \dot{x}_s & = & \left[1_{n_s} - A_{ss}(A_{ff})^{-1}\left(\dfrac{\partial v_f}{\partial x_f}\right)^{-1}\dfrac{\partial v_f}{\partial x_s}\right]\ (A_{ss} - A_{sf}(A_{ff})^{-1}A_{fs})\ \varepsilon\tilde{v}_s \\ 0 & = & A_{fs}\ \varepsilon\tilde{v}_s(x_s,x_f) + A_{ff}\ \tilde{v}_f(x_s,x_f). \end{array}$$

This approximation differs from (8) only via terms of order 2 in ε: at order 1 in ε both approximations coincide.

The main feature of (8) in this case relies on the following point: one does not need to know precisely the decomposition between slow and fast kinetics. This can be an advantage if one is only interested in the slow dynamics. Notice that, even if the two time-scale structure is not due to fast and slow kinetics, formulae (8) are still valid.

If, as displayed on figure 4, we are also interested by the fast dynamics, the situation is different. In this case, we would like to describe how and where trajectories starting far from the slow attractive manifold Σ_ε are catched by Σ_ε. The quantity $\xi = x_s - A_{sf}(A_{ff})^{-1}x_f$ plays an important role here: it is a quasi-invariant during the fast transient, before arriving near Σ_ε. As displayed on figure 4, the trajectory of (17) with initial condition (x_s^0, x_f^0), becomes close, after a time interval of length of order 1, to the trajectory of the slow system (8) starting at the same time 0 with initial conditions $(\bar{x}_s^0, \bar{x}_f^0)$ solution of

$$\bar{x}_s^0 - A_{sf}(A_{ff})^{-1}\bar{x}_f^0 = x_s^0 - A_{sf}(A_{ff})^{-1}x_f^0, \quad v_f(\bar{x}_s^0, \bar{x}_f^0, \varepsilon) = 0.$$

The above formulae give the initial conditions $(\bar{x}_s^0, \bar{x}_f^0)$ of the slow sub-system from the ones of the complete system (x_s^0, x_f^0).

5 Case-study

In this section, we apply the above reduction method to the CO/H_2/air combustion system also considered in [16]. 13 chemical species are present: N_2, CO, H_2, O_2, H_2O, CO_2, OH, H, O, HO_2, CHO, H_2O_2, CH_2O. 67 reactions are taken into account. Their list is given in table 1. Notice that N_2 is inert. The system will be supposed closed, isobaric and adiabatic. It is modelized by a system of differential equations whose dimension is 9 (the system is isobaric, adiabatic, and four atomic invariants are present: C, H, N and O).

The determination of n_f and of the partition (x_s, x_f) is based on a sample trajectory starting at $t = 0$ from the initial conditions given in table 2. This corresponds to the beginning of the explosive phase that lasts about $T = 10^{-2}$ s.

The eigenvalues at different times along this trajectory are given in table 3 (they have been sorted in increasing order). All eigenvalues, except one at the beginning of the trajectory, are real and negative. For the reduction purpose, one may notice that the eighth and the ninth eigenvalues are well separated for $t > \alpha$ (where $\alpha \approx 2\ 10^{-4} \ll T$): the ratio of the latter to the former (when both are negative) ranges from 2 to more than 200 for $t \in [\alpha, T]$. This indicates that we should be able to build a 1-dimensional reduced model. Thus $n_f = 8$ and $n_s = 1$.

The ratios

$$\frac{|\text{creation} - \text{destruction}|}{\text{creation} + \text{destruction}}.$$

at different times along this trajectory are given in table 4 (they have been sorted in increasing order). The ratio for N_2 is not given since this species is neither created nor destructed. Since the largest ratios corresponds to CO_2 (or CO), we can set x_s to the mass fraction of CO_2 (or CO as well).

The simulations of figures 5, 6, 7, 8, 9, 10 compare three models

1. the complete model of dimension 9 (solid line).
2. the 1-dimensional reduced slow model resulting from formulae (8), with $n_s = 1$ and $x_s =$CO$_2$.
3. the 1-dimensional quasi-steady-state model

$$\begin{aligned} \dot{x_s} &= v_s(x_s, x_f) \qquad (18) \\ 0 &= v_f(x_s, x_f) \qquad (19) \end{aligned}$$

   with $n_s = 1$ and $x_s =$CO$_2$.

In these simulations, the starting value of $x_s =$CO$_2$ remains unchanged between the three models. For $x_s =$CO$_2$, we take as initial value, 0.16, corresponding to the point of the sample trajectory reached at $t = \alpha = 2\ 10^{-4}$ s.

For the reduced models, the initial conditions are entirely specified by $x_s =$CO$_2$, the remaining variables x_f result from algebraic equations. Since these equations are different for the two reduced models, the starting value for x_f may be different even if the initial value of $x_s =$CO$_2$ is the same (see tables 5 and 6).

For figures 5, 6, 7 (resp. figures 8, 9, 10), the initial condition (x_s, x_f) of the complete model coincides with the starting values of the reduced slow model (resp. quasi-steady-state model) given in table 5 (resp. table 6). These choices of initial conditions for the complete model admit the following explanation: reduction is a restriction to an attractive invariant manifold. So the comparison between the reduced models and the complete one is meaningful only for trajectories starting near this manifold.

When the initial condition of the complete model coincides with those of the reduced slow one, the trajectories remain very close. This is no more true for the quasi-steady-state model.

Concluding remarks

The reduction method presented here can be applied to any dynamical system having two time-scales (a slow one and a fast asymptotically stable one). As described in [15], this method can be adapted for deriving slow control models where time derivatives of the control appear in the slow equation even if they are not present in the modeling equations. Notice that the explicit value of ε is not required for computing the reduced slow system (8). This tends to indicate that such approximation techniques can be extended to more general systems than two time-scales ones, and, in particular, to systems admitting a normally hyperbolic and attractive invariant manifold [11].

Acknowledgments

The results presented here have been motivated by active discussions with Jean Lévine, especially during the Geometrical Colloquium in Moscow, May 93. This work benefits also of

several discussions with Alain Bamberger, Zakia Benjelloun, Pierre Galtier, Anne Jaecker, Willy Nastoll and Arnaud Trouvé from I.F.P.

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List of Tables

			k_0	β	E_a
$O_2 + H$	$\longrightarrow$	$OH + O$	$2.00\,10^{14}$	0.00	16791.
$OH + O$	$\longrightarrow$	$O_2 + H$	$1.47\,10^{13}$	0.00	502.
$H_2 + O$	$\longrightarrow$	$OH + H$	$5.06\,10^{4}$	2.67	6282.
$OH + H$	$\longrightarrow$	$H_2 + O$	$2.24\,10^{4}$	2.67	4395.
$H_2 + OH$	$\longrightarrow$	$H_2O + H$	$1.00\,10^{8}$	1.60	3296.
$H_2O + H$	$\longrightarrow$	$H_2 + OH$	$4.46\,10^{8}$	1.60	18415.
$OH + OH$	$\longrightarrow$	$H_2O + O$	$1.50\,10^{9}$	1.14	96.
$H_2O + O$	$\longrightarrow$	$OH + OH$	$1.51\,10^{10}$	1.14	17101.
$H + H + M$	$\longrightarrow$	$H_2 + M$	$1.80\,10^{18}$	−1.00	0.
$H_2 + M$	$\longrightarrow$	$H + H + M$	$6.98\,10^{18}$	−1.00	104137.
$H + OH + M$	$\longrightarrow$	$H_2O + M$	$2.20\,10^{22}$	−2.00	0.
$H_2O + M$	$\longrightarrow$	$H + OH + M$	$3.80\,10^{23}$	−2.00	119280.
$O + O + M$	$\longrightarrow$	$O_2 + M$	$2.90\,10^{17}$	−1.00	0.
$O_2 + M$	$\longrightarrow$	$O + O + M$	$6.78\,10^{18}$	−1.00	118563.
$H + O_2 + M$	$\longrightarrow$	$HO_2 + M$	$2.30\,10^{18}$	−0.80	0.
$HO_2 + M$	$\longrightarrow$	$H + O_2 + M$	$2.66\,10^{18}$	−0.80	49250.
$HO_2 + H$	$\longrightarrow$	$OH + OH$	$1.50\,10^{14}$	0.00	1003.
$OH + OH$	$\longrightarrow$	$HO_2 + H$	$1.63\,10^{13}$	0.00	37738.
$HO_2 + H$	$\longrightarrow$	$H_2 + O_2$	$2.50\,10^{13}$	0.00	693.
$H_2 + O_2$	$\longrightarrow$	$HO_2 + H$	$8.39\,10^{13}$	0.00	55603.
$HO_2 + H$	$\longrightarrow$	$H_2O + O$	$3.00\,10^{13}$	0.00	1720.
$H_2O + O$	$\longrightarrow$	$HO_2 + H$	$3.29\,10^{13}$	0.00	55460.
$HO_2 + O$	$\longrightarrow$	$OH + O_2$	$1.80\,10^{13}$	0.00	−406.
$OH + O_2$	$\longrightarrow$	$HO_2 + O$	$2.67\,10^{13}$	0.00	52618.
$HO_2 + OH$	$\longrightarrow$	$H_2O + O_2$	$6.00\,10^{13}$	0.00	0.
$H_2O + O_2$	$\longrightarrow$	$HO_2 + OH$	$8.97\,10^{14}$	0.00	70030.
$HO_2 + HO_2$	$\longrightarrow$	$H_2O_2 + O_2$	$2.50\,10^{11}$	0.00	−1242.
$OH + OH + M$	$\longrightarrow$	$H_2O_2 + M$	$3.25\,10^{22}$	−2.00	0.
$H_2O_2 + M$	$\longrightarrow$	$OH + OH + M$	$2.11\,10^{24}$	−2.00	49393.
$H_2O_2 + H$	$\longrightarrow$	$H_2 + HO_2$	$1.70\,10^{12}$	0.00	3750.
$H_2 + HO_2$	$\longrightarrow$	$H_2O_2 + H$	$9.35\,10^{11}$	0.00	21783.
$H_2O_2 + H$	$\longrightarrow$	$H_2O + OH$	$1.00\,10^{13}$	0.00	3583.
$H_2O + OH$	$\longrightarrow$	$H_2O_2 + H$	$2.66\,10^{12}$	0.00	73469.
$H_2O_2 + O$	$\longrightarrow$	$OH + HO_2$	$2.80\,10^{13}$	0.00	6401.
$OH + HO_2$	$\longrightarrow$	$H_2O_2 + O$	$6.80\,10^{12}$	0.00	22547.
$H_2O_2 + OH$	$\longrightarrow$	$H_2O + HO_2$	$5.40\,10^{12}$	0.00	1003.
$H_2O + HO_2$	$\longrightarrow$	$H_2O_2 + OH$	$1.32\,10^{13}$	0.00	34155.

Table 1: reaction list (mass action law and kinetics constant given by $k = k_0 T^{\beta} \exp(-E_a/RT)$).

			k_0	β	E_a
$CO + OH$	$\longrightarrow$	$CO_2 + H$	$4.40\,10^{6}$	1.50	−740.
$CO_2 + H$	$\longrightarrow$	$CO + OH$	$6.12\,10^{8}$	1.50	22475.
$CO + HO_2$	$\longrightarrow$	$CO_2 + OH$	$1.50\,10^{14}$	0.00	23574.
$CO_2 + OH$	$\longrightarrow$	$CO + HO_2$	$2.27\,10^{15}$	0.00	83524.
$CO + O + M$	$\longrightarrow$	$CO_2 + M$	$7.10\,10^{13}$	0.00	−4538.
$CO_2 + M$	$\longrightarrow$	$CO + O + M$	$1.69\,10^{16}$	0.00	120952.
$CO + O_2$	$\longrightarrow$	$CO_2 + O$	$2.50\,10^{12}$	0.00	47769.
$CO_2 + O$	$\longrightarrow$	$CO + O_2$	$2.55\,10^{13}$	0.00	54696.
$HCO + M$	$\longrightarrow$	$CO + H + M$	$7.10\,10^{14}$	0.00	16791.
$CO + H + M$	$\longrightarrow$	$HCO + M$	$1.07\,10^{15}$	0.00	2054.
$HCO + H$	$\longrightarrow$	$CO + H_2$	$2.00\,10^{14}$	0.00	0.
$CO + H_2$	$\longrightarrow$	$HCO + H$	$1.17\,10^{15}$	0.00	89424.
$HCO + O$	$\longrightarrow$	$CO + OH$	$3.00\,10^{13}$	0.00	0.
$CO + OH$	$\longrightarrow$	$HCO + O$	$7.72\,10^{13}$	0.00	87537.
$HCO + O$	$\longrightarrow$	$CO_2 + H$	$3.00\,10^{13}$	0.00	0.
$CO_2 + H$	$\longrightarrow$	$HCO + O$	$1.07\,10^{16}$	0.00	110753.
$HCO + OH$	$\longrightarrow$	$CO + H_2O$	$1.00\,10^{14}$	0.00	0.
$CO + H_2O$	$\longrightarrow$	$HCO + OH$	$2.60\,10^{15}$	0.00	104543.
$HCO + O_2$	$\longrightarrow$	$CO + HO_2$	$3.00\,10^{12}$	0.00	0.
$CO + HO_2$	$\longrightarrow$	$HCO + O_2$	$5.21\,10^{12}$	0.00	34513.
$CH_2O + M$	$\longrightarrow$	$HCO + H + M$	$1.40\,10^{17}$	0.00	76431.
$HCO + H + M$	$\longrightarrow$	$CH_2O + M$	$2.62\,10^{15}$	0.00	−13566.
$CH_2O + H$	$\longrightarrow$	$HCO + H_2$	$2.50\,10^{13}$	0.00	3989.
$HCO + H_2$	$\longrightarrow$	$CH_2O + H$	$1.82\,10^{12}$	0.00	18152.
$CH_2O + O$	$\longrightarrow$	$HCO + OH$	$3.50\,10^{13}$	0.00	3487.
$HCO + OH$	$\longrightarrow$	$CH_2O + O$	$1.12\,10^{12}$	0.00	15764.
$CH_2O + OH$	$\longrightarrow$	$HCO + H_2O$	$3.00\,10^{13}$	0.00	1194.
$HCO + H_2O$	$\longrightarrow$	$CH_2O + OH$	$9.71\,10^{12}$	0.00	30477.
$CH_2O + HO_2$	$\longrightarrow$	$HCO + H_2O_2$	$1.00\,10^{12}$	0.00	8001.
$HCO + H_2O_2$	$\longrightarrow$	$CH_2O + HO_2$	$1.32\,10^{11}$	0.00	4132.

Table 1: reaction list (mass action law and kinetics constant given by $k = k_0 T^{\beta} \exp(-E_a/RT)$) (continued).

CO	0.21	CO_2	0.11	CH_2O	$1.4\,10^{-7}$	N_2	0.55
H_2	$4.9\,10^{-4}$	OH	$3.7\,10^{-5}$	H	$6.0\,10^{-6}$	temp	1076 K
O_2	0.12	HO_2	$5.9\,10^{-5}$	O	$1.4\,10^{-4}$		
H_2O	$4.5\,10^{-3}$	H_2O_2	$7.5\,10^{-6}$	HCO	$2.3\,10^{-7}$		

Table 2: initial conditions of the complete system for the sample trajectory (mass fractions, temperature).

	$t = 0\,\mathrm{s}$	$t = 10^{-4}\,\mathrm{s}$	$t = 2\,10^{-4}\,\mathrm{s}$	$t = 3\,10^{-4}\,\mathrm{s}$	$t = 5\,10^{-4}\,\mathrm{s}$	$t = 10^{-3}\,\mathrm{s}$	$t = 10^{-2}\,\mathrm{s}$
1	$-7.0\,10^{6}$	$-9.6\,10^{6}$	$-1.9\,10^{7}$	$-4.4\,10^{7}$	$-6.1\,10^{7}$	$-7.3\,10^{7}$	$-9.8\,10^{7}$
2	$-9.1\,10^{5}$	$-1.2\,10^{6}$	$-4.1\,10^{6}$	$-1.2\,10^{7}$	$-8.4\,10^{6}$	$-1.9\,10^{7}$	$-5.4\,10^{7}$
3	$-4.2\,10^{5}$	$-1.2\,10^{6}$	$-1.7\,10^{6}$	$-3.0\,10^{6}$	$-8.0\,10^{6}$	$-4.6\,10^{6}$	$-2.4\,10^{6}$
4	$-1.2\,10^{5}$	$-1.5\,10^{5}$	$-6.8\,10^{5}$	$-2.1\,10^{6}$	$-3.0\,10^{6}$	$-2.6\,10^{6}$	$-2.3\,10^{6}$
5	$-3.9\,10^{4}$	$-1.4\,10^{5}$	$-2.6\,10^{5}$	$-1.6\,10^{6}$	$-1.9\,10^{6}$	$-1.2\,10^{6}$	$-8.8\,10^{5}$
6	$-1.2\,10^{4}$	$-4.7\,10^{4}$	$-1.6\,10^{5}$	$-5.5\,10^{5}$	$-1.0\,10^{6}$	$-1.1\,10^{6}$	$-5.4\,10^{5}$
7	$-8.8\,10^{3}$	$-1.8\,10^{4}$	$-5.4\,10^{4}$	$-2.2\,10^{5}$	$-4.3\,10^{5}$	$-4.3\,10^{5}$	$-2.6\,10^{5}$
8	$-1.2\,10^{3}$	$-6.3\,10^{3}$	$-2.7\,10^{4}$	$-2.6\,10^{4}$	$-6.0\,10^{4}$	$-7.4\,10^{4}$	$-6.8\,10^{4}$
9	$1.3\,10^{4}$	$1.5\,10^{4}$	$1.1\,10^{4}$	$-5.6\,10^{3}$	$-4.7\,10^{3}$	$-1.6\,10^{3}$	$-2.5\,10^{2}$

Table 3: eigenvalues of the CO/H_2/air system at different times along the sample trajectory.

	$t = 0\,\mathrm{s}$	$t = 10^{-4}\,\mathrm{s}$	$t = 2\,10^{-4}\,\mathrm{s}$	$t = 3\,10^{-4}\,\mathrm{s}$	$t = 5\,10^{-4}\,\mathrm{s}$	$t = 10^{-3}\,\mathrm{s}$	$t = 10^{-2}\,\mathrm{s}$
HCO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2O_2	0.51	0.00	0.00	0.01	0.78	0.00	0.00
CH_2O	0.08	0.00	0.00	0.00	0.01	0.00	0.00
H	0.01	0.02	0.01	0.00	0.00	0.00	0.00
H_2O	0.93	0.82	0.01	0.05	0.00	0.00	0.00
O	0.08	0.09	0.05	0.01	0.00	0.00	0.00
H_2	0.74	0.70	0.16	0.00	0.00	0.00	0.00
O_2	0.58	0.45	0.18	0.04	0.00	0.00	0.00
CO	0.91	0.91	0.87	0.44	0.03	0.01	0.00
CO_2	0.99	0.99	0.93	0.46	0.03	0.01	0.00

Table 4: creation/destruction ratios of the CO/H_2/air system at different times along the sample trajectory.

CO	0.18	CO_2	0.16	CH_2O	$2.6\,10^{-8}$	N_2	0.55
H_2	$1.6\,10^{-5}$	OH	$2.7\,10^{-4}$	H	$3.3\,10^{-5}$	temp	1297 K
O_2	0.10	HO_2	$2.4\,10^{-5}$	O	$1.9\,10^{-5}$		
H_2O	$8.4\,10^{-3}$	H_2O_2	$1.6\,10^{-6}$	HCO	$3.7\,10^{-7}$		

Table 5: initial conditions for the reduced slow model (mass fractions, temperature).

CO	0.18	CO_2	0.16	CH_2O	$1.2\,10^{-7}$	N_2	0.55
H_2	$4.2\,10^{-5}$	OH	$4.5\,10^{-4}$	H	$1.0\,10^{-4}$	temp	1297 K
O_2	0.10	HO_2	$3.0\,10^{-5}$	O	$3.8\,10^{-3}$		
H_2O	$7.5\,10^{-3}$	H_2O_2	$3.3\,10^{-6}$	HCO	$9.2\,10^{-7}$		

Table 6: initial conditions for the quasi-steady-state model (mass fractions, temperature).

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Figure 1: the velocity field is quasi-vertical for systems in Tikhonov normal form (11).

Figure 2: an attractive invariant manifold Σ for $\dot{x} = v(x)$.

Figure 3: the geometric definition of singularly perturbed systems due to Fenichel [9].

Figure 4: for system (17), fast transients are along $x_s - A_{sf}(A_{ff})^{-1}x_s$ =constant.

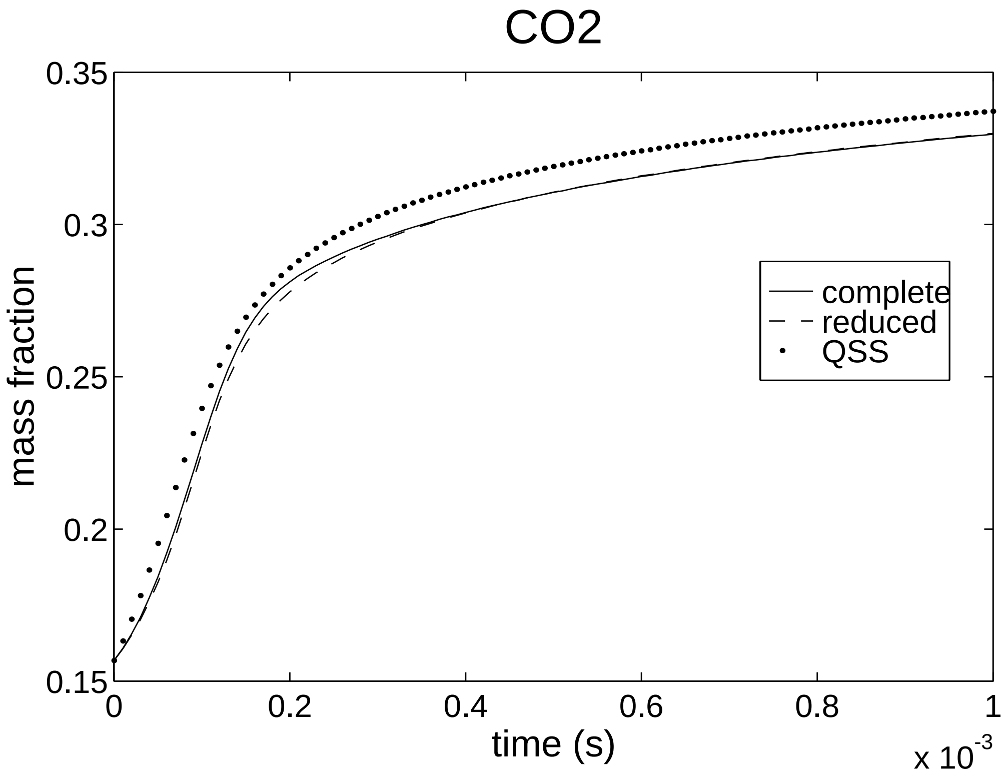

Figure 5: mass fraction of CO_2 calculated by the complete model and the 1-dimensional reduced models (the initial condition of the complete model is the same as that of the reduced model).

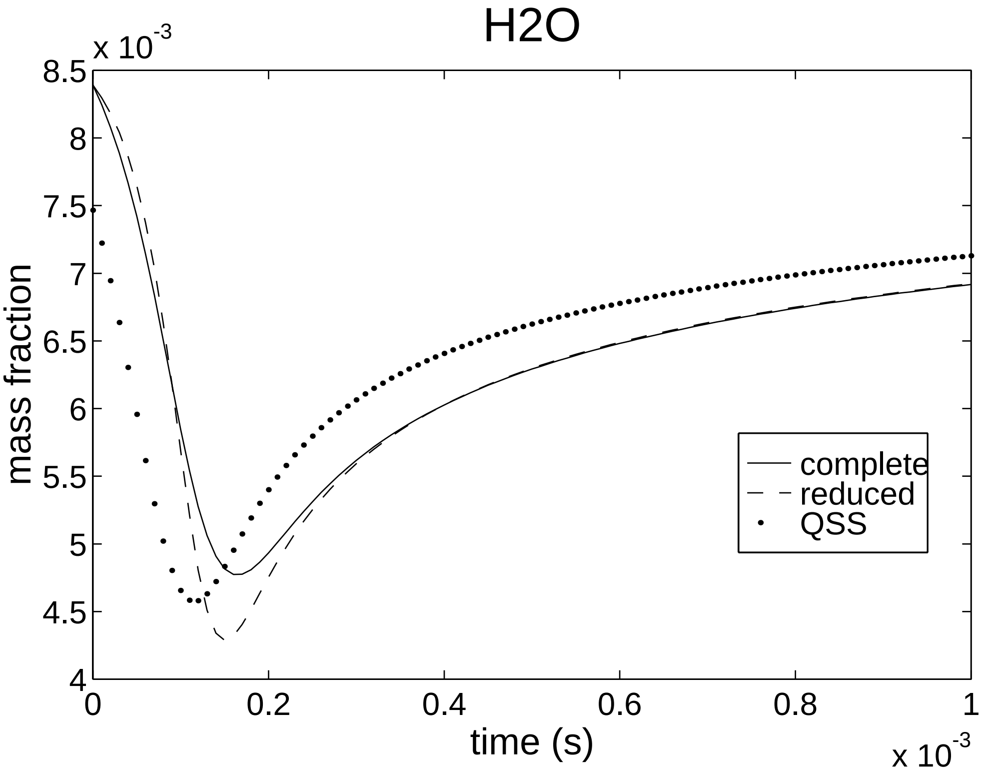

Figure 6: mass fraction of H_2O calculated by the complete model and the 1-dimensional reduced models (the initial condition of the complete model is the same as that of the reduced model).

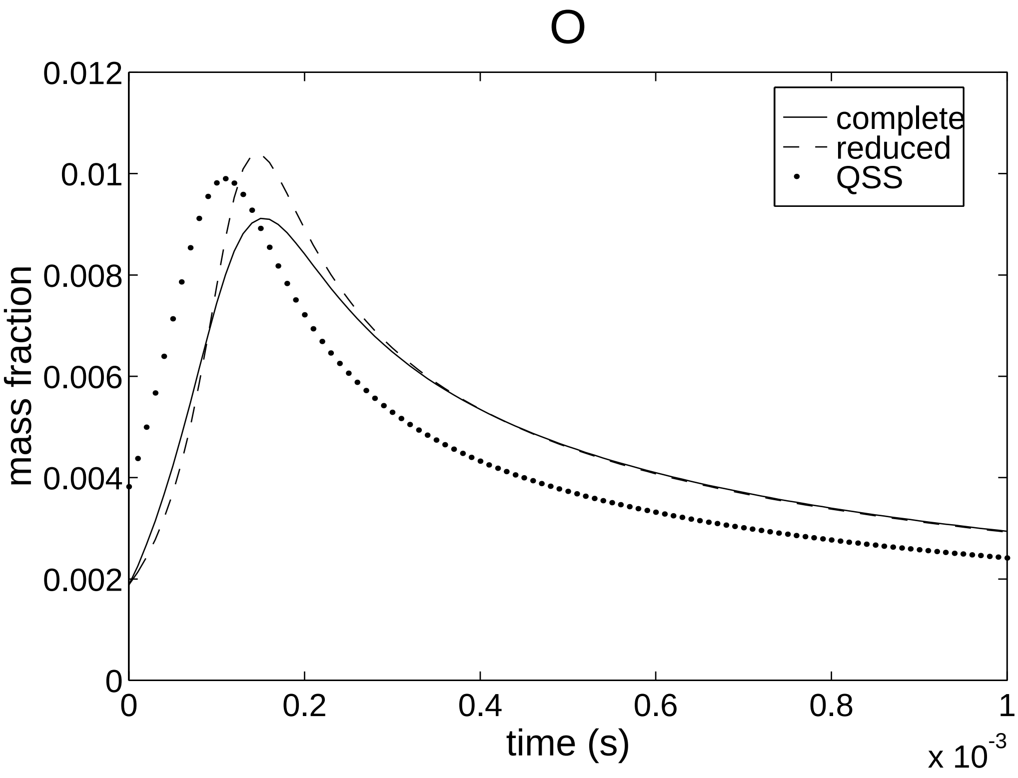

Figure 7: mass fraction of O calculated by the complete model and the 1-dimensional reduced models (the initial condition of the complete model is the same as that of the reduced model).

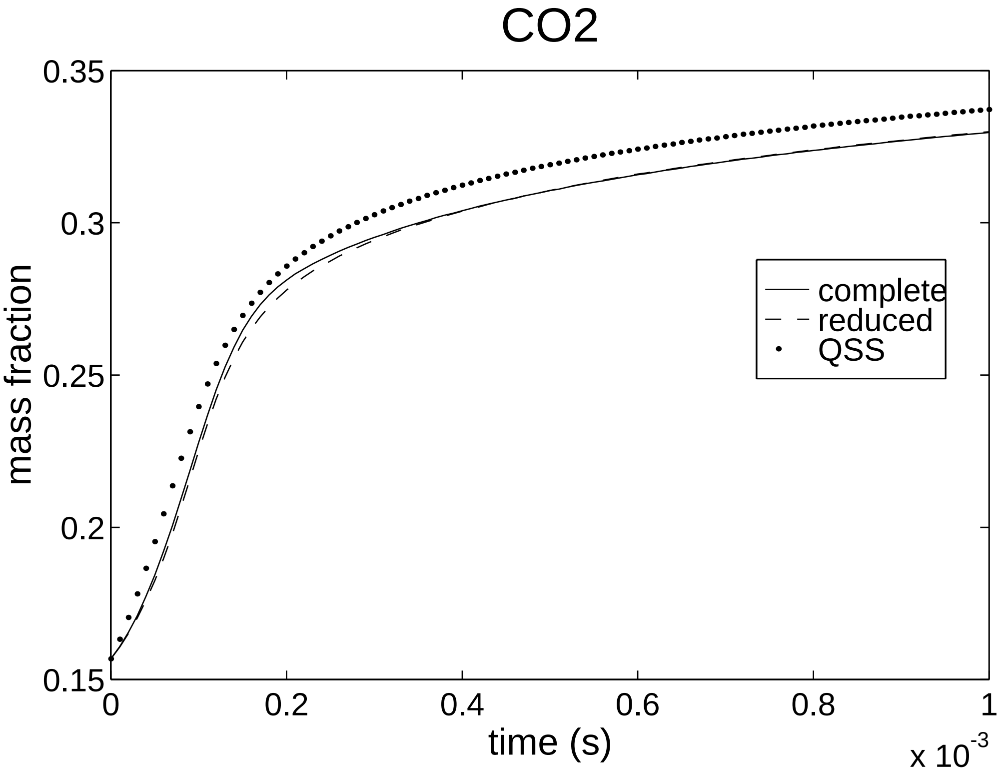

Figure 8: mass fraction of CO_2 calculated by the complete model and the 1-dimensional reduced models (the initial condition of the complete model is the same as that of the quasi-steady-state model).

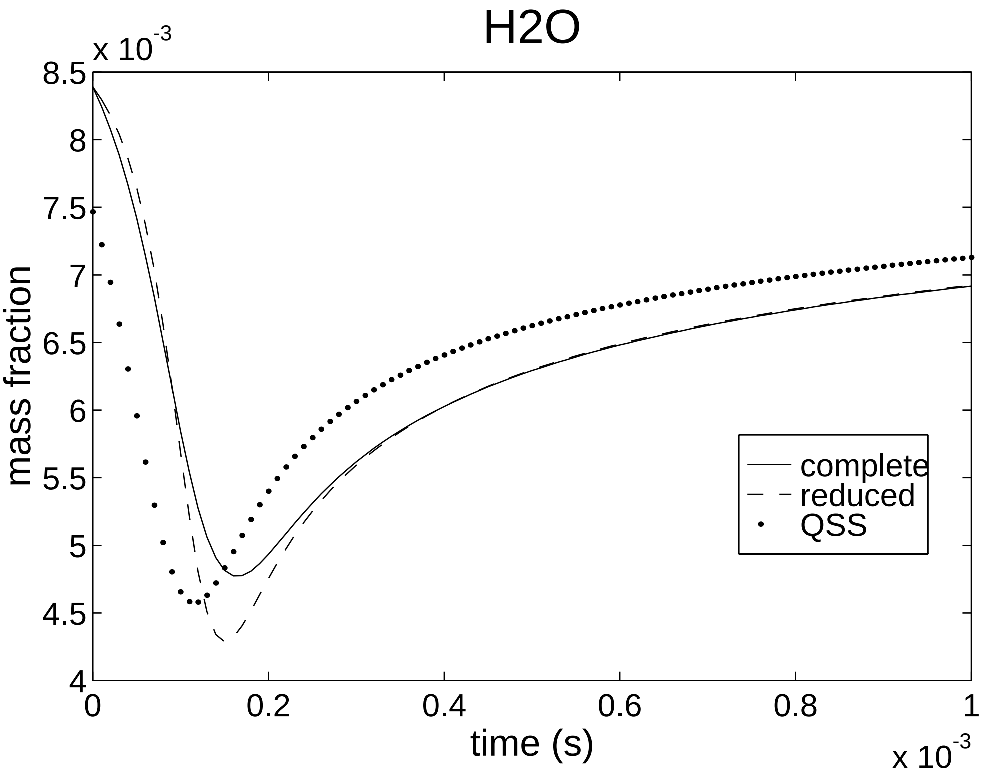

Figure 9: mass fraction of H_2O calculated by the complete model and the 1-dimensional reduced models (the initial condition of the complete model is the same as that of the quasi-steady-state model).

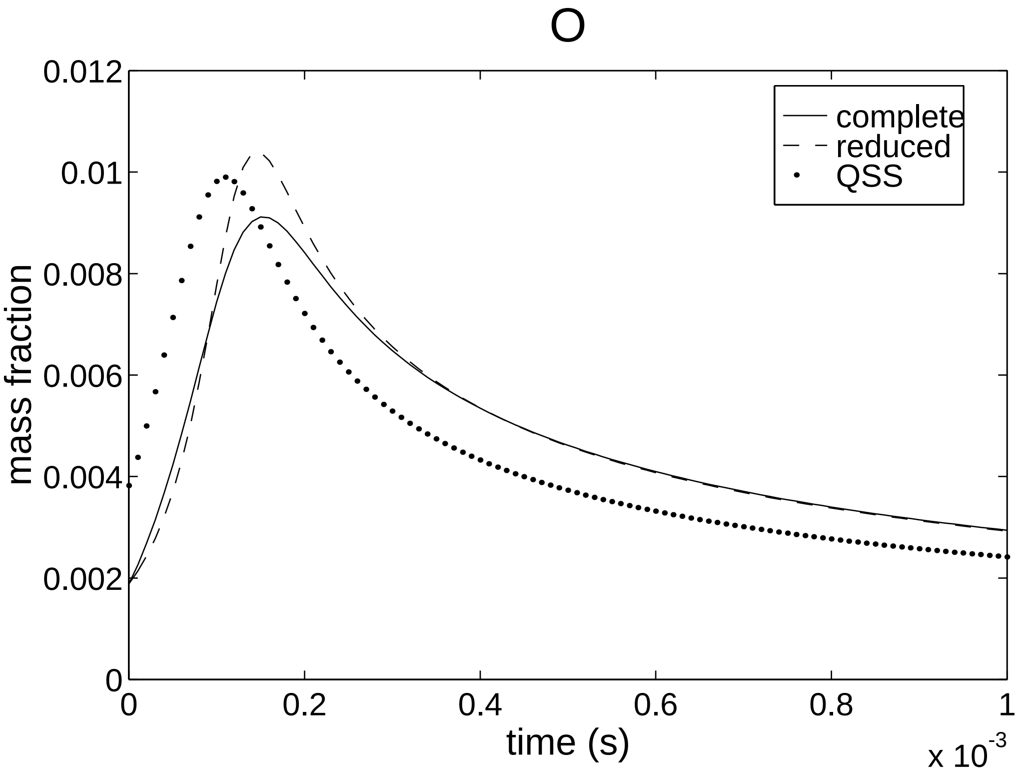

Figure 10: mass fraction of O calculated by the complete model and the 1-dimensional reduced models (the initial condition of the complete model is the same as that of the quasi-steady-state model).