

# MODEL REDUCTION FOR REACTION-CONVECTION PROCESSES WITH FAST AND SLOW REACTIONS

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## Abstract

This paper addresses the derivation of a non-stiff PDE model for convection-reaction processes where the presence of large reaction rates induces stiffness. The slow dynamics are shown to be modeled by a singular partial differential algebraic system (PDAE) for which an equivalent PDE system is derived. The method is illustrated in a simple example.

## 1 Introduction

Transport reaction processes often exhibit stiff dynamics due to physical and chemical phenomena occurring on different characteristic time and length scales. Here we focus on tubular reactors where the co-existence of fast and slow reactions induces stiffness. Hence, numerical simulations of such systems are computationally expensive. Moreover, a direct application of distributed control methods may lead to ill-conditioned controllers because the effect of small measurement or modeling errors might be amplified. Thus, there is a need for techniques to derive non-stiff models that capture the essential dynamical features of the slow dynamics.

Whereas the model reduction of chemical reaction systems has attracted a lot of attention for spatially homogeneous systems (see the review in [9]), very few efforts have been devoted to the study of similar spatially inhomogeneous problems. Research has focused both on analytical and computational approaches. Asymptotic methods have proved to be analytically challenging; therefore, they are adequate only for small and simple problems. The computational singular perturbation approach developed for stiff ordinary differential equations has been extended to reaction diffusion equations to provide a method to identify slow and fast subspaces [3]. However, this approach is computationally intensive, as the vectors spanning those subspaces rely on the eigenvalues of the Jacobian of the source term and, therefore, depend on time and position.

Here we consider non-isothermal plug flow reactors with fast and slow reactions. These reaction-convection processes give rise to first order hyperbolic partial differential equations (PDEs). Because all the variables present temporal and spatial boundary layers, there is no clear distinction between fast and slow variables. Asymptotic methods are therefore not appropriate since the absence of separation between fast and slow

variables renders difficult the identification of the unknowns likely to reach quasi steady behavior.

By combining the method of characteristics and singular perturbation arguments, we present a systematic framework to obtain a partial differential algebraic equation (PDAE) formulation of the slow dynamics after a fast boundary layer in space and time. We identify the constraints that are to be satisfied in the slow dynamics, and obtain an explicit non-stiff PDE model of the slow (dominant) dynamics. As an illustration, the analysis framework is applied to a simple chemical reaction system exhibiting stiffness due to fast and slow reactions. We derive a non-stiff PDE model using the proposed methodology, and, show how the reduced order model compares well to the full model.

## 2 Modeling

### 2.1 The stiff PDE model

Consider a PFR where the following  $R$  reactions involving  $S$  species take place

$$\sum_{j=1}^S \nu_{ij} A_j = 0 \quad i = 1, \dots, R \quad (1)$$

where  $A_j$  denotes the species  $j$  and  $\nu_{ij}$  denotes the stoichiometric coefficient of the species  $j$  in the reaction  $i$ . The material and energy balances describing the evolution of the species compositions and temperature take the form

$$\begin{aligned} \frac{\partial C_j}{\partial t} &= -\bar{V} \frac{\partial C_j}{\partial z} + \sum_{i=1}^R \nu_{ij} r_i \quad j = 1, \dots, S \\ \frac{\partial T}{\partial t} &= -\bar{V} \frac{\partial T}{\partial z} - \frac{1}{\rho C_p} \sum_{i=1}^R \Delta H_i r_i + \frac{UA}{\rho C_p \bar{V}} (T^h - T) \end{aligned} \quad (2)$$

with  $C_j(t=0, z) = f_j(z)$  as initial conditions and  $C_j(t, z=0) = g_j(t)$  as feed data for  $j = 1, \dots, S$ , where  $t$  denotes time,  $z$  denotes the position with respect to the entrance of the reactor,  $C_j$  denotes the molar concentration of species  $j$ ,  $T$  denotes the temperature,  $\bar{V}$  is the axial velocity of the reacting mixture,  $\rho$  the density of the reacting mixture,  $C_p$  the mass heat capacity of the mixture,  $U$  the heat transfer coefficient,  $A$  the area of heat transfer,  $V$  the volume of the reactor,  $T^h$  the temperature of the heat-transfer medium,  $\Delta H_i$  is the heat of reaction (with the usual convention of  $\Delta H_i < 0$  for an exothermic reaction), and  $r_i$  is the reaction rate of the reaction  $i$  (in moles per unit of time per unit volume). This model can be written in matrix

form as

$$\frac{\partial}{\partial t} \begin{bmatrix} C_1 \\ \vdots \\ C_j \\ \vdots \\ C_S \\ T \end{bmatrix} = -\bar{V} \frac{\partial}{\partial z} \begin{bmatrix} C_1 \\ \vdots \\ C_j \\ \vdots \\ C_S \\ T \end{bmatrix} + \begin{bmatrix} 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \\ T^h - T \end{bmatrix} \frac{UA}{\rho C_p \bar{V}} \quad (3)$$

$$+ \begin{bmatrix} \nu_{11} & \dots & \nu_{i1} & \dots & \nu_{R1} \\ \vdots & & \vdots & & \vdots \\ \nu_{1j} & \dots & \nu_{ij} & \dots & \nu_{Rj} \\ \vdots & & \vdots & & \vdots \\ \nu_{1S} & \dots & \nu_{iS} & \dots & \nu_{RS} \\ \frac{-\Delta H_1}{\rho C_p} & \dots & \frac{-\Delta H_i}{\rho C_p} & \dots & \frac{-\Delta H_R}{\rho C_p} \end{bmatrix} \begin{bmatrix} r_1 \\ \vdots \\ r_i \\ \vdots \\ r_R \end{bmatrix}$$

or in the following general form

$$\frac{\partial x}{\partial t} = -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}(x)r(x) \quad (4)$$

where  $x = [C_1, \dots, C_S, T]^T \in \mathcal{X} \subset \mathbb{R}^n$  is the vector of state variables of dimension  $n = S + 1$ ,  $\mathcal{V}(x)$  is a  $(n \times R)$  'generalized' stoichiometric matrix,  $r(x)$  denotes a  $R$ -dimensional reaction rate vector, and  $g(x)$  denotes the  $n$ -dimensional vector associated with heat transfer. Typically, the reaction rate  $r_i$  is expressed as  $r_i(x) = k_i(T)\bar{r}_i(C)$ , where  $C = [C_1, \dots, C_S]^T$  is the vector of concentrations and  $k_i(T)$  is the reaction rate constant.

It is assumed that, in the temperature range of interest,  $p$  fast reactions have been identified; without loss of generality, we consider that the reactions  $i = 1, \dots, R - p$  are slow and the reactions  $i = R - p + 1, \dots, R$  are fast. More specifically, the reaction rate of the  $(R - p + 1)^{th}$  reaction evaluated at some nominal temperature  $T^0$  and denoted  $k^* = k_{R-p+1}(T^0)$  is assumed to be a large parameter such that the reaction rates of the first  $R - p$  reactions are of much smaller order of magnitude than  $k^*$ , and the reaction rates of the remaining  $p$  reactions are of the same order of magnitude as  $k^*$ . Following this classification of slow and fast reactions, Eq. 3 takes the form

$$\frac{\partial}{\partial t} \begin{bmatrix} C_1 \\ \vdots \\ C_j \\ \vdots \\ C_S \\ T \end{bmatrix} = -\bar{V} \frac{\partial}{\partial z} \begin{bmatrix} C_1 \\ \vdots \\ C_j \\ \vdots \\ C_S \\ T \end{bmatrix} + \begin{bmatrix} 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \\ T^h - T \end{bmatrix} \frac{UA}{\rho C_p \bar{V}}$$

$$+ \begin{bmatrix} \nu_{11} & \dots & \nu_{(R-p)1} \\ \vdots & & \vdots \\ \nu_{1S} & \dots & \nu_{(R-p)S} \\ \frac{-\Delta H_1}{\rho C_p} & \dots & \frac{-\Delta H_{R-p}}{\rho C_p} \end{bmatrix} \begin{bmatrix} r_1 \\ \vdots \\ r_{R-p} \end{bmatrix}$$

$$+ \begin{bmatrix} \nu_{(R-p+1)1} & \dots & \nu_{R1} \\ \vdots & & \vdots \\ \frac{\nu_{(R-p+1)S}}{\rho C_p} & \dots & \frac{\nu_{RS}}{\rho C_p} \\ \frac{-\Delta H_{R-p+1}}{\rho C_p} & \dots & \frac{-\Delta H_R}{\rho C_p} \end{bmatrix} \begin{bmatrix} r_{R-p+1} \\ \vdots \\ r_R \end{bmatrix} \quad (5)$$

or in general form

$$\frac{\partial x}{\partial t} = -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \mathcal{V}_f(x)r_f(x) \quad (6)$$

where the subscripts  $s$  and  $f$  denote the generalized stoichiometric matrices and the reaction rate vectors for the slow and the fast reactions, respectively.

Since each term of the vector  $r_f(x)$  corresponds to a fast reaction rate which is expressed as the product of a large term ( $k_i$  is of  $O(k^*)$ ) and a small term ( $\bar{r}_i(C)$  is of  $O(1/k^*)$ ), the dynamic system in Eq. 6 exhibits stiffness. In order to isolate the stiffness to a single parameter, the large parameter  $k^*$  is extracted from the reaction rate for the fast reactions, so that

$$r_f(x) = k^* \text{diag} \left[ \frac{k_i}{k^*} \right] \bar{r}_f(C) \quad i = R - p + 1, \dots, R$$

By defining the  $(R - p) \times (R - p)$  diagonal matrix  $K_f(T) = \text{diag}[k_i/k^*]$ , and the small parameter  $\epsilon = 1/k^*$ , the system dynamics is described by the following PDE system with a small parameter

$$\frac{\partial x}{\partial t} = -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \frac{1}{\epsilon} \mathcal{V}_f(x)K_f(T)\bar{r}_f(C) \quad (7)$$

Without loss of generality, it is assumed that the matrix  $\mathcal{V}_f(x)$  has full column rank, i.e. the assumption of stoichiometric linear independence of the fast reactions holds [12]. If the column rank of  $\mathcal{V}_f(x)$  is  $p' < p$ , it is possible to construct a  $n \times p'$  matrix  $\mathcal{V}'_f(x)$  with the  $p'$  linearly independent columns, and a modified  $p' \times 1$  reaction rate vector  $\bar{r}'_f(x)$  is then defined, so that Eq. 7 is written

$$\frac{\partial x}{\partial t} = -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \frac{1}{\epsilon} \mathcal{V}'_f(x)\bar{r}'_f(x) \quad (8)$$

where

$$\bar{r}'_f(x) = \left[ [\mathcal{V}'_f(x)]^T [\mathcal{V}'_f(x)] \right]^{-1} [\mathcal{V}'_f(x)]^T [\mathcal{V}_f(x)] K_f(T)\bar{r}_f(C) \quad (9)$$

It is also assumed that the Jacobian of the vector  $\bar{r}'_f(x)$  with respect to  $x$  is full row rank [12]. Indeed, if the row rank of  $\partial \bar{r}'_f(x)/\partial x$  is  $p^* < p'$ , then there exists a  $p' \times p'$  invertible matrix  $E(x)$  such that the  $p' - p^*$  last rows of  $\bar{r}^*_f(x) = E(x)\bar{r}'_f(x)$  are equal to 0, and such that  $\bar{r}^*_f(x)$  has a full row rank Jacobian. Then, the system in Eq. 8 can be written

$$\frac{\partial x}{\partial t} = -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \frac{1}{\epsilon} \mathcal{V}^*_f(x)\bar{r}^*_f(x) \quad (10)$$

where  $\mathcal{V}^*_f(x) = \mathcal{V}'_f(x)E(x)^{-1}$  has full column rank. This assumption can be viewed as "kinetic" linear independence of the fast reactions.

Moreover, the vector  $\bar{r}_f^*(x)$  can be written as

$$\bar{r}_f^*(x) = \begin{bmatrix} \bar{r}_f^{*1}(x) \\ 0 \end{bmatrix} \quad (11)$$

where  $\bar{r}_f^{*1}(x)$  is a  $p^*$ -dimensional vector. Similarly, the matrix  $\mathcal{V}_f^*(x)$  can be decomposed as

$$\mathcal{V}_f^*(x) = [ \mathcal{V}_f^{*1}(x) \quad \mathcal{V}_f^{*2}(x) ] \quad (12)$$

where  $\mathcal{V}_f^{*1}(x)$  is a  $n \times p^*$  matrix, and  $\mathcal{V}_f^{*2}(x)$  is a  $n \times (p' - p^*)$  matrix. By using the decomposition introduced in Eq. 11 and Eq. 12, the system in Eq. 10 is equivalent to the following system

$$\begin{aligned} \frac{\partial x}{\partial t} &= -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \frac{1}{\epsilon} \mathcal{V}_f^*(x) \bar{r}_f^*(x) \\ &= -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) \\ &\quad + \frac{1}{\epsilon} [ \mathcal{V}_f^{*1}(x) \quad \mathcal{V}_f^{*2}(x) ] \begin{bmatrix} \bar{r}_f^{*1}(x) \\ 0 \end{bmatrix} \\ &= -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \frac{1}{\epsilon} \mathcal{V}_f^{*1}(x) \bar{r}_f^{*1}(x) \end{aligned} \quad (13)$$

where  $\mathcal{V}_f^{*1}(x)$  has full column rank, and  $\bar{r}_f^{*1}(x)$  has a full row rank Jacobian.

In what follows, for simplicity, the prime and asterisk superscripts are dropped and the system in Eq. 13 is expressed as

$$\frac{\partial x}{\partial t} = -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \frac{1}{\epsilon} \mathcal{V}_f(x) \bar{r}_f(x) \quad (14)$$

where stoichiometric and kinetic linear independencies are assumed to hold. The hyperbolic equations of Eq. 14 are stiff in the sense that all the equations contain the large parameter  $(1/\epsilon)$ . There is no clear distinction between the fast and the slow variables; all the variables exhibit boundary layers both in time and in position.

## 2.2 The method of characteristics

The fundamental strategy in the method of characteristics is to find a substitution which transforms the given PDE into one in which all but one of the variables can be treated as parameters in the sense that they can be held constant temporarily, which effectively reduces the PDE into an ODE system. This approach has been used in combination with sliding mode techniques for controller design of single quasi-linear first order hyperbolic PDEs [11,4].

Hyperbolic PDE systems of the form of Eq. 14 are easily amenable to the method of characteristics. We review some results as they are discussed in [8,10]. Let's consider the following quasi-linear first order PDE

$$a(z, t, u) \frac{\partial u}{\partial t} + b(z, t, u) \frac{\partial u}{\partial z} = c(z, t, u) \quad (15)$$

where  $u$  is the dependent variable while  $z, t$  are the independent variables, and  $a, b, c$  are given functions of  $z, t, u$  which are

continuously differentiable and satisfy the condition  $a^2 + b^2 \neq 0$ . Suppose that the solution surface  $u = u(z, t)$  has been determined, then Eq. 15 implies that the two vectors  $(a, b, c)^T$  and  $(u_t, u_z, -1)^T$  are orthogonal. Thus, the PDE in Eq. 15 can be interpreted geometrically as imposing the requirement that any solution surface  $u = u(z, t)$  through a point  $B(z, t, u)$  must be tangent to  $(a, b, c)^T$ . It then follows that

$$\frac{dt}{a} = \frac{dz}{b} = \frac{du}{c} \quad (16)$$

at the point  $B$ . Eq. 16 defines a direction field in the  $(z, t, u)$ -space and its integral curves are called the characteristic curves of the PDE in Eq. 15. The projections of those curves onto the  $(z, t)$  plane are referred to as the characteristics. If we introduce a parameter  $s$  running along the characteristic curves, Eq. 16 can be written as

$$\frac{dt}{a} = \frac{dz}{b} = \frac{du}{c} = ds \quad (17)$$

Integration of this system yields  $F(z, t, u) = C_1$  and  $G(z, t, u) = C_2$ , so that the general solution of Eq. 15 is an arbitrary function of  $F$  and  $G$ . If 'initial data' (namely, initial conditions and feed data) are provided, then a unique solution is obtained, provided that these initial data do not lie on a characteristic curve. For multiple PDEs described by the system

$$\begin{aligned} a_i(z, t, u_1, \dots, u_n) \frac{\partial u_i}{\partial t} \\ + b_i(z, t, u_1, \dots, u_n) \frac{\partial u_i}{\partial z} = c_i(z, t, u_1, \dots, u_n) \end{aligned}$$

for  $i = 1, \dots, n$ , this method is easily extended when  $a_1 = \dots = a_n = a$  and  $b_1 = \dots = b_n = b$ ; in this case, the slopes of the characteristics onto the plane  $(z, t)$  for each equation are equal (the common slope is  $a/b$ ), so that a unique parameter  $s$  can be introduced.

For systems of the form in Eq. 14, since all the PDEs have the same velocity, a unique parameter  $\bar{s}$  is required to obtain the characteristic differential equations

$$dt = \frac{dz}{\bar{V}} = \frac{dx_i}{\left[ \mathcal{V}_s(x)r_s(x) + g(x) + \frac{1}{\epsilon} \mathcal{V}_f(x) \bar{r}_f(x) \right]_i} = d\bar{s} \quad (18)$$

for  $i = 1, \dots, n$ , where  $x_i$  denotes the  $i$ th component of the variable  $x$ , and  $[\mathcal{V}_s(x)r_s(x) + g(x) + (1/\epsilon)\mathcal{V}_f(x)\bar{r}_f(x)]_i$  the  $i$ th component of the vector  $[\mathcal{V}_s(x)r_s(x) + g(x) + (1/\epsilon)\mathcal{V}_f(x)\bar{r}_f(x)]$ . Thus, the characteristics in the  $(z, t)$  plane are straight lines of slope  $1/\bar{V}$ . The characteristic passing through the origin delimits two regions: when  $z > \bar{V}t$ , the information carried along the characteristics corresponds to the initial conditions (i.e.,  $t = 0$ ), whereas when  $z < \bar{V}t$  the solution is influenced by the feed data (i.e.,  $z = 0$ ). An expression for the state variable  $x$  can be obtained in terms of  $\bar{s}$  along the characteristics

such that

$$\begin{aligned}\frac{dx}{d\bar{s}} &= \frac{\partial x}{\partial t} \frac{dt}{d\bar{s}} + \frac{\partial x}{\partial z} \frac{dz}{d\bar{s}} \\ &= 1 \frac{\partial x}{\partial t} + \bar{V} \frac{\partial x}{\partial z} \\ &= \frac{Dx}{Dt}\end{aligned}\quad (19)$$

Eq. 19 implies that considering the ordinary differential equation for  $x$  along the characteristics is equivalent to taking the total derivative. Note that this approach of taking the derivative following the motion is equivalent to modeling the plug flow reactor as the limit of a succession of continuously stirred tank reactors. Along the characteristics, Eq. 14 is rewritten

$$\frac{dx}{d\bar{s}} = \frac{Dx}{Dt} = g(x) + \mathcal{V}_s(x)r_s(x) + \frac{1}{\epsilon}\mathcal{V}_f(x)\bar{r}_f(x) \quad (20)$$

This formulation proves useful to derive the dynamics of the original system in the fast and slow time scales.

### 3 Model reduction

#### 3.1 Fast dynamics

Let us now consider the fast dynamics of Eq. 14. Since all the components of the vector  $x$  present boundary layers both in time and in position, it seems natural to consider the derivation of these fast dynamics in the framework of the characteristics. Along the characteristics, the PDE system of Eq. 14 is transformed into the ODE system of Eq. 20, which allows us to apply methods developed for stiff ODEs [5,12]. We define a stretched fast time scale  $\tau = t/\epsilon$ , so that the system of Eq. 20 takes the form

$$\frac{Dx}{D\tau} = \epsilon g(x) + \epsilon \mathcal{V}_s(x)r_s(x) + \mathcal{V}_f(x)\bar{r}_f(x)$$

In the limit  $\epsilon \rightarrow 0$ , the description of the fast dynamics of the system is obtained

$$\frac{Dx}{D\tau} = \mathcal{V}_f(x)\bar{r}_f(x) \quad (21)$$

Since the matrix  $\mathcal{V}_f(x)$  has full column rank, the  $(n-p)$  quasi-steady-state constraints that are to be satisfied point-wise and time-wise are

$$0 = \bar{r}_f(x) \quad (22)$$

These constraints imply reaction equilibrium for fast reversible reactions and complete conversion for irreversible reactions.

#### 3.2 Slow dynamics

We now consider the derivation of the slow dynamics of the system of Eq. 14. Note that, in the slow time scale, the constraints  $\bar{r}_f(x) = 0$  must be satisfied. Moreover, in the limit  $\epsilon \rightarrow 0$ , the term  $(1/\epsilon)(\bar{r}_f(x) = 0)$  becomes indeterminate. Let  $r = \lim_{\epsilon \rightarrow 0}[\bar{r}_f(x)]/\epsilon$  be the vector of indeterminate, yet finite,

reaction rates of the independent fast reactions in the slow time scale. Then, the slow dynamics of the system in Eq. 14 are described by the following system

$$\begin{aligned}\frac{\partial x}{\partial t} &= -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) + \mathcal{V}_f(x)r \\ 0 &= \bar{r}_f(x)\end{aligned}\quad (23)$$

Thus, the slow dynamics of the reaction-convection system are modeled by a singular PDAE system: the algebraic variables  $r$  are implicitly specified by the constraints, which implies that these constraints are to be differentiated in order to obtain an expression for  $r$ . Note that, along the characteristics, Eq. 23 yields

$$\begin{aligned}\frac{Dx}{Dt} &= g(x) + \mathcal{V}_s(x)r_s(x) + \mathcal{V}_f(x)r \\ 0 &= \bar{r}_f(x)\end{aligned}\quad (24)$$

This implies that, along the characteristics, the slow dynamics of the system are modeled by a DAE system.

The following proposition gives a PDE representation of the PDAE system of Eq. 23.

**Proposition** Consider the PDAE system of Eq. 23; then a PDE representation is given by the system:

$$\begin{aligned}\frac{\partial x}{\partial t} &= -\bar{V} \frac{\partial x}{\partial z} + g(x) + \mathcal{V}_s(x)r_s(x) \\ &\quad - \mathcal{V}_f(x) \left[ \underline{\underline{L}}_{\mathcal{V}_f(x)} \bar{r}_f(x) \right]^{-1} \cdot \underline{\underline{L}}_h \bar{r}_f(x) \\ 0 &= \bar{r}_f(x)\end{aligned}\quad (25)$$

with  $h(x) = \mathcal{V}_s(x)r_s(x) + g(x)$ ,

$$\underline{\underline{L}}_h \bar{r}_f(x) = \begin{bmatrix} L_h \bar{r}_{f_1} \\ \vdots \\ L_h \bar{r}_{f_p} \end{bmatrix}$$

where  $L_h \bar{r}_{f_i}$  is the standard Lie derivative of the  $i$ th component of  $\bar{r}_f(x)$  with respect to  $h(x)$ , and

$$\underline{\underline{L}}_{\mathcal{V}_f(x)} \bar{r}_f(x) = [ \underline{\underline{L}}_{\mathcal{V}_{f_1}} \bar{r}_f \quad \dots \quad \underline{\underline{L}}_{\mathcal{V}_{f_p}} \bar{r}_f ]$$

where  $\mathcal{V}_{f_i}$  is the  $i$ th column of  $\mathcal{V}_f(x)$ .

**Proof** Since the constraints are to be satisfied both in time and in space, we consider their total derivative (or equivalently, we consider the DAE system obtained along the characteristics and differentiate with respect to the parameter running along the characteristics)

$$\begin{aligned}0 &= \frac{D\bar{r}_f(x)}{Dt} = \frac{\partial \bar{r}_f(x)}{\partial t} + \bar{V} \frac{\partial \bar{r}_f(x)}{\partial z} \\ &= \frac{\partial \bar{r}_f(x)}{\partial x} \frac{\partial x}{\partial t} + \bar{V} \frac{\partial \bar{r}_f(x)}{\partial x} \frac{\partial x}{\partial z} = \frac{\partial \bar{r}_f(x)}{\partial x} \left[ \frac{\partial x}{\partial t} + \bar{V} \frac{\partial x}{\partial z} \right] \\ &= \frac{\partial \bar{r}_f(x)}{\partial x} \frac{Dx}{Dt}\end{aligned}\quad (26)$$

where  $\frac{\partial \bar{r}_f}{\partial x}$  is the Jacobian of the vector  $\bar{r}_f$  with respect to  $x = [C_1, \dots, C_S, T]^T$ .

By taking into account the expression of the total derivative for the state variables vector  $x$ , the total derivative of the constraints takes the form

$$0 = \underline{L}_h \bar{r}_f(x) + \underline{L}_{\mathcal{V}_f(x)} \bar{r}_f(x) r \quad (27)$$

Note that we can write the  $p \times p$  coefficient matrix for the algebraic variable  $r$  as the product of the two following matrices

$$\underline{L}_{\mathcal{V}_f(x)} \bar{r}_f(x) = \frac{\partial \bar{r}_f(x)}{\partial x} \mathcal{V}_f(x)$$

Since both stoichiometric linear independence and kinetic linear independence hold, the first matrix in the above product has full row rank, and the second one has full column rank, which implies that  $\underline{L}_{\mathcal{V}_f(x)} \bar{r}_f(x)$  is an invertible matrix, so that an expression for the algebraic variable is obtained

$$r = - \left[ \underline{L}_{\mathcal{V}_f(x)} \bar{r}_f(x) \right]^{-1} \underline{L}_h \bar{r}_f(x) \quad (28)$$

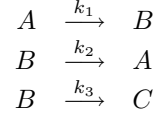
Direct substitution of the previous expression into Eq. 23 yields Eq. 25, thus completing the proof.

**Remark** Note that the PDAE system modeling the slow dynamics can be considered as a 'hidden' DAE system, since, along the characteristics, the system of Eq. 23 takes the form of the DAE system of Eq. 24. This idea allows us to extend the notion of index developed for DAE systems to PDAE systems of the form of Eq. 23. Several notions of indexes have already been introduced for PDAEs, most of them for numerical solution purposes. In [1,6], the authors defined perturbation, spatial and time indexes for parabolic PDAEs, which enabled them to obtain convergence theorems for specific numerical approximation methods. By generalizing these concepts to hyperbolic linear PDAEs with linear time-dependent DAE boundary conditions, Gunther and Wagner [2] proved that the index of the approximate DAE depends on the method adopted to discretize the PDAE. In a more general framework where the PDAEs are then viewed as abstract Cauchy problems in any direction in the independent variable space, Martinson and Barton [7] generalized the notion of differential time index introduced for DAEs to PDAEs to estimate an upper bound for the number of boundary conditions needed to obtain a well-posed problem. For PDAEs of the form of Eq. 23, we showed that an expression for the algebraic variable  $r$  can be obtained from the total derivative of the constraints. So, the index of the DAE system of Eq. 24 is equal to two. If we define the index for a PDAE of the form of Eq. 23 as the number of total differentiations needed in order to obtain an equivalent PDE, then the index of this PDAE system is equal to two.

## 4 Example

Let us apply the preceding modeling procedure to a simple example. We consider a reaction system consisting of the follow-

ing three reactions in an isothermal plug flow reactor



where  $A, B$ , and  $C$  represent three different species. The reaction rates for these reactions are given by  $r_1 = k_1 C_A$ ,  $r_2 = k_2 C_B$  and  $r_3 = k_3 C_C$  respectively. The values of the reaction rate constants are  $k_1 = 110$ ,  $k_2 = 100$ ,  $k_3 = 10$ , and the velocity is  $\bar{V} = 2$ , in consistent units.

Since  $k_1 \gg k_3$  and  $k_2 \gg k_3$ , the first and the second reactions are much faster than the third reaction. Defining the small parameter  $\epsilon = 1/k^* = 1/k_1$ , the dynamic model can be expressed in the matrix form of Eq. 7

$$\begin{aligned} \frac{\partial}{\partial t} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} &= -\bar{V} \frac{\partial}{\partial z} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} + \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} r_3 \\ &+ \frac{1}{\epsilon} \begin{bmatrix} -1 & 1 \\ 1 & -1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} k'_1 & 0 \\ 0 & k'_2 \end{bmatrix} \begin{bmatrix} \bar{r}_1 \\ \bar{r}_2 \end{bmatrix} \end{aligned}$$

where  $k'_1 = (k_1/k^*)$ ,  $k'_2 = (k_2/k^*)$ ,  $\bar{r}_1 = C_A$  and  $\bar{r}_2 = C_B$ .

The  $3 \times 2$  matrix  $\mathcal{V}_f(x)$  is clearly of rank 1. Thus, we select the first column as the new stoichiometric matrix  $\mathcal{V}'_f(x) = [-1 \ 1 \ 0]^T$ , so that the modified reaction rate is

$$\bar{r}'_f(x) = \frac{1}{k^*} [k_1 \bar{r}_1 - k_2 \bar{r}_2] = \frac{k_1}{k^*} \left[ \bar{r}_1 - \frac{\bar{r}_2}{\kappa} \right]$$

where  $\kappa = \frac{k_1}{k_2}$  represents the equilibrium constant for the fast reversible reaction  $A \rightleftharpoons B$ . It is easily checked that the Jacobian of the vector  $\bar{r}'_f(x)$  has full row rank, so that the dynamic model is expressed in the form of Eq. 14

$$\begin{aligned} \frac{\partial}{\partial t} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} &= -\bar{V} \frac{\partial}{\partial z} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} + \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} r_3 \\ &+ \frac{1}{\epsilon} \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix} \frac{k_1}{k^*} \left[ \bar{r}_1 - \frac{\bar{r}_2}{\kappa} \right] \end{aligned} \quad (29)$$

We used an ODE solver to integrate the ODE system obtained along the characteristics for the PDE system of Eq. 29 where, for simplicity, the initial conditions and the feed data are taken to be identical:  $f_A(z) = g_A(t) = 10$ ,  $f_B(z) = g_B(t) = 16$ ,  $f_C(z) = g_C(t) = 0$  in the appropriate units. The concentration profiles show that the concentrations of the three species exhibit boundary layers both in time and in space.

By multiplying Eq. 29 by  $\epsilon$  and considering the limit  $\epsilon \rightarrow 0$ , the quasi-steady-state constraints are obtained

$$0 = \bar{r}_1 - \frac{\bar{r}_2}{\kappa}$$

which implies that the fast reversible reaction is at equilibrium everywhere along the reactor.

In the limit  $\epsilon \rightarrow 0$ , the algebraic variable  $r$  is defined

$$r = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \frac{k_1}{k^*} \left[ \bar{r}_1 - \frac{\bar{r}_2}{\kappa} \right]$$

so that the slow dynamics are described by the following system

$$\begin{aligned} \frac{\partial}{\partial t} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} &= -\bar{V} \frac{\partial}{\partial z} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} + \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} r_3 + \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix} r \\ 0 &= \bar{r}_1 - \frac{\bar{r}_2}{\kappa} \end{aligned}$$

An expression of the algebraic variable can be easily obtained from the total derivative of the constraints

$$r = -\frac{k_2 \cdot k_3}{k_1 + k_2} C_B = -\frac{k_1 \cdot k_3}{k_1 + k_2} C_A$$

so that the slow dynamics are modeled by the following non-stiff PDE system

$$\begin{aligned} \frac{\partial}{\partial t} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} &= -\bar{V} \frac{\partial}{\partial z} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} + \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} r_3 \\ &\quad - \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix} \frac{k_2 \cdot k_3}{k_1 + k_2} C_B \end{aligned} \quad (30)$$

where  $[C_A \ C_B \ C_C]^T \in \mathcal{M} = \{x \in \mathcal{X} : 0 = \bar{r}_f(x)\}$ .

Figure 1 and 2 show the concentration profiles for the species A at position  $z = 3$  and at time  $t = 3$ , respectively. Similar plots can be obtained for the species B and C. It can be observed that the two models are in excellent agreement.

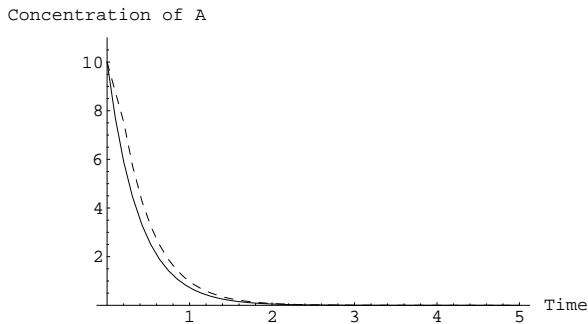


Figure 1: Concentration profile for A for the original system (dashed) and the reduced-order system (solid) at  $z=3$

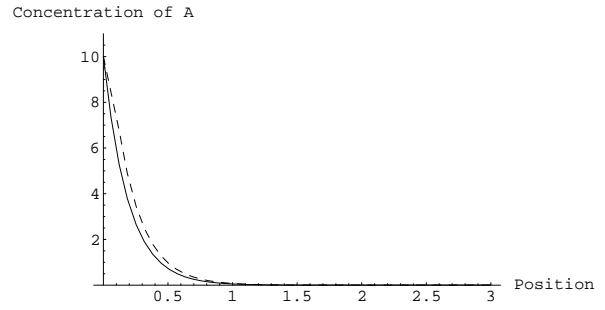


Figure 2: Concentration profile for A for the original system (dashed) and the reduced-order system (solid) at  $t=3$

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