Combustion Theory and Modelling

Transport-chemistry coupling in the reduced description of reactive flows

Zhuyin Ren [a]; Stephen B. Pope [a]
[a] Sibley School of Mechanical & Aerospace Engineering, Cornell University, Ithaca, NY, USA

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Transport-chemistry coupling in the reduced description of reactive flows

ZHUYIN REN* and STEPHEN B. POPE

Sibley School of Mechanical & Aerospace Engineering,
Cornell University, Ithaca, NY 14853, USA

The reduced description of inhomogeneous reactive flows by chemistry-based low-dimensional manifolds is complicated by the transport processes present and the consequent transport-chemistry coupling. In this study, we focus on the use of intrinsic low-dimensional manifolds (ILDMs) to describe inhomogeneous reactive flows. In particular we investigate three different approaches which can be used with ILDMs to incorporate the transport-chemistry coupling in the reduced description, namely, the Maas–Pope approach, the 'close-parallel' approach, and the approximate slow invariant manifold (ASIM) approach. For the Maas–Pope approach, we validate its fundamental assumption: that there is a balance between the transport processes and chemical reactions in the fast subspace. We show that even though the Maas–Pope approach makes no attempt to represent the departure of composition from the ILDM, it does adequately incorporate the transport-chemistry coupling in the dynamics of the reduced system. For the 'close-parallel' approach, we demonstrate its use with the ILDM to incorporate the transport-chemistry coupling. This approach is based on the 'close-parallel' assumption that the compositions are on a low-dimensional manifold which is close to and parallel to the ILDM. We show that this assumption implies a balance between the transport processes and chemical reaction in the normal subspace of the ILDM. The application of the ASIM approach in general reactive flows is investigated. We clarify its underlying assumptions and applicability. Also in the regime where the fast chemical time scales are much smaller than the transport time scales, we reformulate the ASIM approach so that explicit governing PDEs are given for the reduced composition. For the reaction–diffusion systems considered, we show that all the three approaches predict the same dynamics of the reduced compositions, i.e. each results in the same evolution equations for the reduced composition variables (to leading order). We also show that all the three approaches are valid only when the fast chemical time scales are much smaller than the transport time scales. Moreover, a simplified ASIM approach is proposed.

Keywords: Close-parallel; Dimension reduction; ILDM; Low-dimensional manifold; Transport-chemistry coupling

1.   Introduction

Many detailed chemical mechanisms describing reactive flows (in combustion, atmospheric science and elsewhere) involve large numbers of chemical species, large numbers of elementary reactions, and widely disparate time scales. For example, the detailed mechanism for the primary reference fuel [1] contains more than 1000 species and more than 4000 elementary reactions that proceed on time scales ranging from nanoseconds to minutes. Consequently,

---

*Corresponding author. E-mail: zr26@cornell.edu

the direct use of detailed chemical mechanisms in numerical calculations of reactive flows is computationally expensive. Therefore there is a well-recognized need to develop methodologies that radically decrease the computational burden imposed by the direct use of detailed mechanisms. Of the several different types of such methodologies, three approaches that are currently particularly fruitful (and which can be used in combination) are: the development of skeletal mechanisms from large detailed mechanisms by the elimination of inconsequential species and reactions [2–4]; storage/retrieval methodologies [5, 6] such as *in situ* adaptive tabulation ISAT [5]; and dimension-reduction techniques [7–49].

Dimension reduction, i.e. the reduced description of reactive flows, is achieved through the use of slow manifolds. The reduced description of inhomogeneous flows is greatly complicated by the transport processes present and the coupling between chemistry and these transport processes. Substantial studies on how and when the transport processes can affect the compositions and the reduced description of reactive flows have been performed in [16, 22, 23, 31–34, 36–49]. Currently, there are two distinct approaches to identifying slow manifolds and providing reduced descriptions. In the first approach, the slow manifold is identified based on the governing PDEs which include convection, diffusion and reaction [38–48]. The transport-chemistry coupling is incorporated in the construction of slow manifolds. For example, in [41], the CSP global approach obtains slow manifolds for reaction–diffusion systems with full account of the combined effects of transport processes and chemical reactions. This is done through transforming the governing PDEs into a set of ODEs by performing finite differencing of the diffusion term in the reaction–diffusion system on a computational grid. In [38, 39], starting from the governing PDEs for inhomogeneous reactive flows, Davis obtains low-dimensional manifolds in the infinite-dimensional function space. In the second approach, the slow manifold is a low-dimensional attracting manifold in the finite-dimensional composition space and is identified solely based on chemical kinetics without accounting for transport processes: we refer to such manifolds as 'chemistry-based'. Chemistry-based manifolds are identified based on homogeneous systems by different existing methods [7–21, 25–30, 33, 34], such as intrinsic low-dimensional manifolds (ILDM) [21], the quasi-steady state assumption (QSSA) [7–10], computational singular perturbation (CSP) [33–35], the method of invariant manifolds [17–19], and the ICE-PIC method [30]. When applying the chemistry-based manifolds for the reduced description of inhomogeneous flows, the transport-chemistry coupling needs to be accounted for appropriately. Moreover the accuracy of this approach depends on the dimensionality of the manifold being sufficiently high that the largest unrepresented chemical timescale is less than transport time scales [32, 41].

In this paper, we focus on studying the use of chemistry-based manifolds, particularly the widely used intrinsic low-dimensional manifold (ILDM) [21], to describe inhomogeneous reactive flows. The ILDM is identified based on the analysis of the Jacobian matrix of chemical reaction source term in a reactive flow. As shown in [16, 24, 28, 45] the ILDM is not strictly invariant, but is so to a good approximation. By definition, a chemistry-based manifold is invariant if the reaction trajectory from any point in the manifold remains in the manifold. (Note that the definition of invariance used pertains to the homogenous system in which the ILDM is identified.) Previous studies [21, 32] show that for typical combustion processes, chemical kinetics have a much wider range of time scales than those of transport processes. It is believed that due to the fast chemical time scales all the compositions in inhomogeneous reactive flows (after an initial transient and far from the boundaries) still lie close to the ILDM (with sufficiently high dimension). The transport processes such as molecular diffusion may tend to draw the composition off the ILDM, whereas the fast chemical processes relax the perturbations back towards the manifold. Hence as shown in [32], in the regime where the fast chemical time scales are much smaller than the transport time scales, the ILDMs (identified based solely on chemical kinetics) can still be employed to describe inhomogeneous

reactive flows, but it is essential to incorporate the transport-chemistry coupling in the reduced description. Here, we investigate different approaches for ILDM to incorporate the transport-chemistry coupling in the reduced description, namely, the Maas–Pope approach [22, 23], the 'close-parallel' approach [14, 31, 32], and the approximate slow invariant manifold (ASIM) approach of Singh *et al*. [45].

In [22, 23], based on time scale arguments, the Maas–Pope approach is proposed for the ILDM to incorporate the coupling in the regime where the fast chemical time scales are much smaller than the transport time scales. The fundamental assumption employed in this approach is that there is a balance between the transport processes and chemical reactions in the fast subspace (identified based on the Jacobian matrix of the reaction source term). The transport-chemistry coupling is incorporated in the reduced description by projecting the transport processes onto the slow subspace. No attempts have been made in [22, 23] to understand and quantify the relation between the departure of compositions from the ILDM and the consequent transport-chemistry coupling. The validity of the approach is tested both in a perfectly stirred flow reactor of CO/H_2/air mixture and in premixed laminar hydrogen and syngas flames. The results from the reduced description are compared with those of the full description. In the present study, for a class of reaction–diffusion systems, we more rigorously quantify the approach's accuracy in the prediction for both the full composition and the dynamics of the reduced composition.

Following the work of Tang and Pope [14], the 'close-parallel' assumption is proposed by Ren *et al*. [31, 32] for general chemistry-based slow manifolds to incorporate the transport-chemistry coupling in the reduced description. The assumption employed is that when the fast chemical time scales are much smaller than the transport time scales, the compositions in inhomogeneous flows lie on a manifold which is close to and parallel to the chemistry-based manifold used in the reduced description. The validity of this assumption is studied in [32]. Previous works [31, 32] show that, with the use of the 'close-parallel' approach, the departure of compositions from the chemistry-based manifold and the consequent transport-chemistry coupling can be obtained and incorporated in the reduced description. In the present study, we demonstrate the use of this assumption for the ILDM to incorporate transport-chemistry coupling.

Following similar ideas to those in the Maas–Pope approach, the approximate slow invariant manifold (ASIM) approach is proposed by Singh *et al*. [45] to provide a reduced description of reactive flows. In the ASIM approach, the full governing equations are projected onto the fast and slow subspaces. By equilibrating the fast dynamics, a set of elliptic PDEs are obtained which describe the infinite-dimensional approximate slow invariant manifold (ASIM) to which the reactive flow system relaxes before reaching steady state. In [45], Singh *et al*. performed a comparison between the Mass–Pope approach and the ASIM approach. However the comparison is focused on the prediction of the full composition instead of the more important quantity: the dynamics of the reduced composition. In the present paper, for a class of reaction–diffusion systems, we more rigorously compare these two approaches in the prediction for both the full composition and the dynamics of the reduced composition. Moreover, by studying reaction–diffusion systems, we also clarify the underlying assumptions and applicability of the ASIM approach.

The contributions of the present paper are to clarify the underlying assumptions and to validate the three different approaches to incorporate transport-chemistry coupling. Moreover, a modified ASIM approach is proposed. For a class of reaction–diffusion model systems, the accuracy of these approaches are quantified and compared. While we use the ILDM in this study, most of the conclusions on coupling issues apply to other dimension reduction approaches too. The outline of the remainder of the paper is as follows. In Section 2, we provide a brief overview of the reduced description of reactive flows using ILDM. In Section 3, we

outline the Maas–Pope approach and validate it in the reaction–diffusion system. In Section 4, we introduce the 'close-parallel' assumption for ILDM to incorporate the transport-chemistry coupling. In Section 5, we briefly outline the ASIM approach: its underlying assumptions and applicability are clarified. Section 6 provides a discussion and conclusions.

2. Reduced description of inhomogeneous reactive flows using ILDM

In this section, we provide a brief overview of the reduced description of reactive flows using ILDM. Then we introduce the class of reaction–diffusion systems employed for this study.

2.1 *General reactive flows*

We consider an inhomogeneous reactive flow, where the pressure p and enthalpy h are taken to be constant and uniform (although the extension to other circumstances is straightforward). The system at time t is then fully described by the full composition $\mathbf{z}(\mathbf{x}, t)$, which varies both in space, $\mathbf{x}$, and time, t. The full composition $\mathbf{z}$ can be taken to be the mass fractions of the n_s species or the specific species moles (mass fractions divided by the corresponding species molecular weights). The system evolves according to the set of n_s PDEs

$$\frac{\partial}{\partial t}\mathbf{z}(\mathbf{x}, t) + \mathbf{C}\{\mathbf{z}(\mathbf{x}, t)\} = \mathbf{D}\{\mathbf{z}(\mathbf{x}, t)\} + \mathbf{S}(\mathbf{z}(\mathbf{x}, t)), \tag{1}$$

where $\mathbf{S}$ denotes the rate of change of the full composition (or net reaction rate) due to chemical reactions. The spatial transport includes the convective contribution $\mathbf{C}$ ($v_i \partial \mathbf{z}/\partial x_i$, where $\mathbf{v}(\mathbf{x}, t)$ is the velocity field) and the diffusive contribution $\mathbf{D}$. In calculations of reactive flows, one simplified model widely used for diffusion is

$$\mathbf{D}\{\mathbf{z}\} = \frac{1}{\rho}\nabla \cdot (\rho\boldsymbol{\Gamma}\nabla\mathbf{z}), \tag{2}$$

where ρ is the mixture density, and $\boldsymbol{\Gamma}$ is a diagonal matrix with the diagonal components $\Gamma_1, \Gamma_2, \ldots, \Gamma_{n_s}$ being the mixture-averaged species diffusivities, which are usually functions of $\mathbf{z}$.

In the reduced description, when the ILDM method [21–23] is employed, the full compositions in the reactive flow are assumed to be on (or close to) an n_r-dimensional intrinsic low-dimensional manifold (where $n_r < n_s$ is specified). The n_r-dimensional ILDM is identified based on the analysis of the Jacobian of the reaction source term, i.e. identified solely based on chemical kinetics without accounting for transport processes. (In other words, the ILDM is identified based on a corresponding homogeneous system.) The Jacobian $\mathbf{J}$ is defined as

$$J_{ij} = \frac{\partial S_i}{\partial z_j}. \tag{3}$$

We assume that the Jacobian can be diagonalized as

$$\mathbf{J} = \mathbf{V}\boldsymbol{\Lambda}\tilde{\mathbf{V}}^T = \begin{bmatrix} \mathbf{V}_s & \mathbf{V}_f \end{bmatrix} \begin{bmatrix} \boldsymbol{\Lambda}_1 & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\Lambda}_2 \end{bmatrix} \begin{bmatrix} \tilde{\mathbf{V}}_s & \tilde{\mathbf{V}}_f \end{bmatrix}^T, \tag{4}$$

where $\mathbf{V}$ is the $n_s \times n_s$ right eigenvector matrix and $\tilde{\mathbf{V}}^T = \mathbf{V}^{-1}$ is the left eigenvector matrix. The diagonal matrices $\boldsymbol{\Lambda}_1$ ($n_r \times n_r$) and $\boldsymbol{\Lambda}_2$ ($n_u \times n_u$ with $n_u \equiv n_s - n_r$), contain the eigenvalues of $\mathbf{J}$ ($\lambda_i, i = 1, 2, \ldots, n_s$), ordered in decreasing value of their real parts. The chemical time
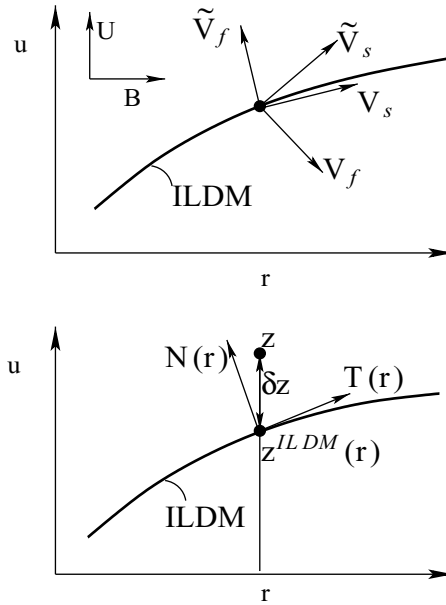
Figure 1. A sketch in the composition space showing the ILDM and the different subspaces spanned by $\mathbf{V}_s$, $\mathbf{V}_f$, $\tilde{\mathbf{V}}_s$ and $\tilde{\mathbf{V}}_f$. Also shown are the tangent subspace span($\mathbf{T(r)}$) and the normal subspace span($\mathbf{N(r)}$) of the ILDM. The composition in reactive flows is expressed as $\mathbf{z} = \mathbf{z}^{\mathrm{ILDM}} + \delta\mathbf{z}$ with $\delta\mathbf{z}$ being in the unrepresented subspace. The axes denote the reduced composition $\mathbf{r}$ (in the subspace span($\mathbf{B}$)) and the unrepresented variables $\mathbf{u}$ (in the subspace span($\mathbf{U}$) = span($\mathbf{B}$)$^{\perp}$).

scales are related to the eigenvalues by $\tau_i \equiv 1/|Re(\lambda_i)|$. (Hence the knowledge of the n_u fast chemical time scales is contained in $\boldsymbol{\Lambda}_2$.) The columns of $\mathbf{V}_s$ ($n_s \times n_r$) span the slow subspace; and the columns of $\mathbf{V}_f$ ($n_s \times n_u$) span the fast subspace. The matrices $\tilde{\mathbf{V}}_s$ and $\tilde{\mathbf{V}}_f$ are of dimension $n_s \times n_r$ and $n_s \times n_u$, respectively. A geometric interpretation of the different subspaces is shown in figure 1. The n_r-dimensional ILDM is defined as the union of all the compositions which satisfy the set of n_u algebraic equations $\tilde{\mathbf{V}}_f^T(\mathbf{z})\mathbf{S}(\mathbf{z}) = 0$, i.e. the manifold is

$$\mathcal{M}^{\mathrm{ILDM}} \equiv \{\mathbf{z} \,|\, \tilde{\mathbf{V}}_f^T(\mathbf{z})\mathbf{S}(\mathbf{z}) = 0\}. \tag{5}$$

(We do not address the difficulty that arises when the eigenvalues λ_{n_r} and λ_{n_r+1} form a complex conjugate pair.) The ILDM can be parameterized by a smaller number n_r of reduced composition variables $\mathbf{r}(\mathbf{x}, t) = \{r_1, r_2, \ldots, r_{n_r}\}$, which can be taken to be the mass fractions (or the specific moles) of some species and linear combinations of the species. One important aspect, not discussed in the paper, is the choice of the parametrization of the ILDM, i.e. the specification of n_r and $\mathbf{r}$. For the purpose of this study, both n_r and $\mathbf{r}$ are user-specified. Some studies on this topic can be found in [21–23, 28].

In general, the reduced composition $\mathbf{r}$ can be expressed as

$$\mathbf{r} = \mathbf{B}^T \mathbf{z}, \tag{6}$$

where $\mathbf{B}$ is an $n_s \times n_r$ constant matrix. For example, if $\mathbf{r}$ consists of specified 'major' species, then each column of $\mathbf{B}$ is a unit vector consisting of a single entry (unity) in the row corresponding to a major species. But more generally, equation (6) allows for linear combinations of species. (In practice, the choice of a constant fixed reduced representation, i.e. constant $\mathbf{B}$ is important for the application of dimension reduction to reactive flows.) Thus the full

n_s-dimensional composition space can be decomposed into an n_r-dimensional represented subspace (spanned by the columns of **B**) and an n_u-dimensional unrepresented subspace (spanned by columns of **U**, with **U** being a constant $n_s \times n_u$ orthogonal matrix spanning span$(\mathbf{B})^{\perp}$). We define the unrepresented variables to be

$$\mathbf{u}(\mathbf{x}, t) = \mathbf{U}^T \mathbf{z}(\mathbf{x}, t). \tag{7}$$

In the inhomogeneous reactive system, the full compositions can be generally expressed as

$$\mathbf{z}(\mathbf{x}, t) = \mathbf{z}^{\text{ILDM}}(\mathbf{r}(\mathbf{x}, t)) + \delta\mathbf{z}(\mathbf{x}, t), \tag{8}$$

where $\mathbf{z}^{\text{ILDM}}(\mathbf{r}(\mathbf{x}, t))$ is the full composition on the ILDM, and $\delta\mathbf{z}(\mathbf{x}, t)$ is the departure from the ILDM. The departure $\delta\mathbf{z}(\mathbf{x}, t)$ is small if the dimensionality of the ILDM is sufficiently high. As shown in [16, 22, 23, 37, 41, 44, 49], departures from the ILDM may be introduced by initial and boundary conditions, transport processes, and the non-invariance of the ILDM. With this representation, the departure is defined to be in the unrepresented subspace, i.e.

$$\delta\mathbf{z} = \mathbf{U}\delta\mathbf{u}, \tag{9}$$

where $\delta\mathbf{u} = \mathbf{U}^T[\mathbf{z}(\mathbf{x}, t) - \mathbf{z}^{\text{ILDM}}(\mathbf{r}(\mathbf{x}, t))]$.

In the reduced description, the reactive system is described in terms of of the reduced composition **r**. The essential task of the reduced description is to derive the evolution equations for the reduced composition variables, which accurately represent the dynamics of the full system. Note that the exact evolution equation for the reduced composition can be obtained by pre-multiplying equation (1) with $\mathbf{B}^T$, i.e.

$$\frac{\partial \mathbf{r}}{\partial t} + v_i \frac{\partial \mathbf{r}}{\partial x_i} = \mathbf{B}^T \mathbf{D}\{\mathbf{z}\} + \mathbf{B}^T \mathbf{S}(\mathbf{z}). \tag{10}$$

In the reduced description, the task is to express the right-hand side of equation (10) ($\mathbf{B}^T \mathbf{D}\{\mathbf{z}\} + \mathbf{B}^T \mathbf{S}(\mathbf{z})$) as a function of **r**. It is known [22, 23, 31–33, 36, 41] that a common practice referred to as the 'first approximation' is in general not valid to derive the evolution equation for **r**. The 'first approximation' assumes that the compositions in a reactive flow lie exactly on the ILDM, i.e.

$$\mathbf{z}(\mathbf{x}, t) = \mathbf{z}^{\text{ILDM}}(\mathbf{r}(\mathbf{x}, t)). \tag{11}$$

Hence the evolution equation for the reduced composition variables according to the 'first approximation' is

$$\frac{\partial \mathbf{r}}{\partial t} + v_i \frac{\partial \mathbf{r}}{\partial x_i} = \mathbf{B}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}(\mathbf{r})\} + \mathbf{B^T S}(\mathbf{z}^{\text{ILDM}}(\mathbf{r})). \tag{12}$$

By completely neglecting the departures from the ILDM, the 'first approximation' completely neglects the transport-chemistry coupling in the reduced description, which is in general not valid.

Hence, when employing ILDM for the reduced description of inhomogeneous reactive flows, it is important to adequately incorporate the transport-chemistry coupling. In the following, by using a class of reaction–diffusion systems, we investigate and compare the Maas–Pope approach, the 'close-parallel' approach, and the ASIM approach to incorporate the transport-chemistry coupling in the reduced description.

2.2 *Reaction–diffusion model system*

In order to investigate and quantify the performance of different approaches, we consider the following class of non-dimensional reaction–diffusion systems (which have been thoroughly

studied in [32]),

$$\frac{\partial z_1}{\partial t} = c\frac{z_2 - f(z_1)}{\varepsilon} + g_1(z_1, z_2) + \nabla \cdot (D_1 \nabla z_1)$$

$$\frac{\partial z_2}{\partial t} = -\frac{z_2 - f(z_1)}{\varepsilon} + g_2(z_1, z_2) + \nabla \cdot (D_2 \nabla z_2), \tag{13}$$

where $\mathbf{z} = [z_1 \quad z_2]^T$ is the full composition, t is a normalized (i.e. non-dimensional) time, $\varepsilon \ll 1$ is a small parameter, c is a non-negative constant (which may be 0, $\mathcal{O}(\varepsilon)$ or $\mathcal{O}(1)$) which describes the coupling between z_1 and the fast chemistry, and D_1 and D_2 (in general dependent on $\mathbf{z}$) are the non-dimensional diffusivities of z_1 and z_2 respectively. In equation (13), $f(z_1)$, $g_1(z_1, z_2)$ and $g_2(z_1, z_2)$ are assumed to be of order one. The chemical reactions have a large linear contribution from the fast chemistry (represented by the terms $c\left[z_2 - f(z_1)\right]/\varepsilon$ and $-\left[z_2 - f(z_1)\right]/\varepsilon$) and another generally nonlinear contribution from the slow chemistry (represented by $g_1(z_1, z_2)$ and $g_2(z_1, z_2)$). As shown below, for the systems considered, the fast chemical time scale is $\mathcal{O}(\varepsilon)$. Let L_1 and L_2 be the characteristic diffusion length scales of z_1 and z_2, respectively. We assume that the fast chemical time scale is much smaller than the diffusion times scales, i.e. $L_1^2/D_1\varepsilon \gg 1$ and $L_2^2/D_2\varepsilon \gg 1$. In this study, the characteristic diffusion length scales are estimated based on the given composition distribution. A more rigorous study on the diffusion time scales is given in [41]. The unsteady reaction–diffusion system (equation 13) is well posed given appropriate boundary and initial conditions. In this study, both the initial and boundary compositions for the governing PDEs are taken to be exactly on the ILDM. As discussed in Section 2.2.2, this simplification allows the boundary and initial conditions for the reduced composition variable in the reduced description to be taken directly from those corresponding conditions in the full description. Hence we can focus on comparing the accuracy of the reduced description by different approaches without the need to consider the difficulties relates to the boundary and initial conditions.

2.2.1 ILDM for the reaction–diffusion system.

For the reaction–diffusion system considered, the Jacobian matrix of the reaction source term is

$$\mathbf{J} = \frac{1}{\varepsilon}\begin{bmatrix} -cf' & c \\ f' & -1 \end{bmatrix} + \mathcal{O}(1), \tag{14}$$

where $f'(z_1) \equiv df(z_1)/dz_1$. The eigenvalue associate with the fast chemical time scale is $-(1 + cf')/\varepsilon + \mathcal{O}(1)$. (The function $f(z_1)$ is specified such that $(1 + cf')$ is positive and hence there are slow attracting manifolds in the system.) Hence the fast chemical time scale is $\mathcal{O}(\varepsilon)$. Based on the Jacobian matrix, the slow and fast invariant subspaces are

$$\begin{bmatrix} \mathbf{V}_s & \mathbf{V}_f \end{bmatrix} = \begin{bmatrix} 1 & -c \\ f' & 1 \end{bmatrix} + \mathcal{O}(\varepsilon), \tag{15}$$

and

$$\begin{bmatrix} \tilde{\mathbf{V}}_s & \tilde{\mathbf{V}}_f \end{bmatrix} = \frac{1}{1 + cf'}\begin{bmatrix} 1 & -f' \\ c & 1 \end{bmatrix} + \mathcal{O}(\varepsilon). \tag{16}$$

When applying the ILDM method to the reaction–diffusion system, z_1 is chosen as the reduced composition variable and used to parameterize the ILDM. We assume the composition on the ILDM to have the following perturbation series expression

$$z_2^{\text{ILDM}} = f(z_1) + \varepsilon f_1(z_1) + o(\varepsilon), \tag{17}$$

with $\lim_{\varepsilon \to 0} o(\varepsilon)/\varepsilon = 0$. Substituting the expression for **S** and equations (16) and (17) into equation (5), we obtain

$$\begin{bmatrix} -f' \\ 1 \end{bmatrix}^T \begin{bmatrix} cf_1 + g_1(z_1, f(z_1)) \\ -f_1 + g_2(z_1, f(z_1)) \end{bmatrix} + o(\varepsilon)/\varepsilon = 0, \tag{18}$$

and hence

$$f_1 = \frac{g_2(z_1, f(z_1)) - f'g_1(z_1, f(z_1))}{1 + cf'}. \tag{19}$$

Thus the ILDM is given by

$$z_2^{\text{ILDM}} = f(z_1) + \varepsilon \frac{g_2(z_1, f(z_1)) - f'g_1(z_1, f(z_1))}{1 + cf'} + o(\varepsilon). \tag{20}$$

From equation (20), it is easy to verify that, to $o(\varepsilon)$, the ILDM is invariant for the corresponding homogeneous system, i.e. for $z_2 = z_2^{\text{ILDM}}(z_1)$

$$\frac{dz_2}{dt} = \left(\frac{dz_2^{\text{ILDM}}}{dz_1}\right)\frac{dz_1}{dt} + o(\varepsilon)/\varepsilon. \tag{21}$$

2.2.2 Reduced description of the reaction–diffusion system. The class of reaction–diffusion systems (equation (13)) is thoroughly studied in [32]. In the reduced description, if z_1 is chosen as the reduced composition variable, then by perturbation analysis, it is shown that (after the initial transient and far away from the boundaries) the composition is given by

$$z_2 = f(z_1) + \varepsilon \frac{g_2(z_1, f(z_1)) - f'g_1(z_1, f(z_1))}{1 + cf'}$$
$$+ \varepsilon \frac{f''D_1\nabla z_1 \cdot \nabla z_1}{1 + cf'} + \varepsilon \frac{\nabla \cdot (f'[D_2 - D_1]\nabla z_1)}{1 + cf'} + o(\varepsilon), \tag{22}$$

and the evolution equation for z_1 is given by

$$\frac{\partial z_1}{\partial t} = g_1(z_1, f(z_1)) + \nabla \cdot (D_1\nabla z_1) + c\frac{g_2(z_1, f(z_1)) - f'g_1(z_1, f(z_1))}{1 + cf'}$$
$$+ c\frac{f''D_1\nabla z_1 \cdot \nabla z_1}{1 + cf'} + c\frac{\nabla \cdot (f'[D_2 - D_1]\nabla z_1)}{1 + cf'} + o(\varepsilon)/\varepsilon, \tag{23}$$

where $f'(z_1) \equiv df(z_1)/dz_1$ and $f'' \equiv d^2f/dz_1^2$. (Note that $f''/(1 + f'^2)^{\frac{1}{2}}$ is the curvature of the ILDM to a good approximation, see equation (20).) The last two terms in equations (22) and (23) are in general nontrivial and arise when transport processes are present. Therefore they represent the chemistry-transport coupling. More specifically as identified in [32], they represent the effects of the 'dissipation-curvature' and 'differential diffusion' on the composition and evolution of the reduced composition variable. These two terms arise, respectively: if the manifold is curved and there is non-zero molecular diffusion; and if the diffusivities of the species differ. The difference between equation (20) and equation (22) reveals that the compositions in the reaction–diffusion system are perturbed from the ILDM by $\mathcal{O}(\varepsilon)$ due to molecular diffusion.

The reduced description of the unsteady reaction–diffusion system (e.g. equation (23)) is well posed given the appropriate boundary and initial conditions on z_1. In this study, the boundary and initial conditions for the reduced composition variable in the reduced description are taken directly from those corresponding conditions in the full description. This simplification

follows from the fact that, in this study, both the initial and boundary compositions are taken to be exactly on the ILDM. When the boundary and initial compositions are not exactly on the ILDM, thin boundary layers of compositions form close to the boundaries [37, 41]. Inside these boundary layers, the compositions are not within $\mathcal{O}(\varepsilon)$ of the ILDM; whereas far away from the boundaries, after the initial transient, the compositions are close to the manifold. The evolution equation equation (23) for the reduced composition variable is accurate to describe the long-term composition dynamics away from the boundaries. However, the boundary and initial conditions for the reduced description require a more thorough study, which is not undertaken in this paper. A rigorous derivation of the reduced description of reactive flows within the boundary layers has recently been given by Lam [37].

In the following, we validate the Maas–Pope approach, the 'close-parallel' assumption and the ASIM approach by comparing their predictions with the reduced description (equations (22) and (23)).

3. The Maas–Pope approach

In the Maas–Pope approach [22, 23], the transport processes such as convection and molecular diffusion are viewed as small disturbances to the chemical reaction system. This is valid only when the fast chemical time scales are much smaller than the transport time scales. These perturbations are decomposed in the local eigenvector basis, i.e. in two part, one describing the rate of change in the slow subspace, and the other describing the rate of change in the fast subspace. Hence equation (1) is decomposed as

$$\frac{\partial}{\partial t}\mathbf{z}(\mathbf{x}, t) = \left(\mathbf{V}_s \tilde{\mathbf{V}}_s^T + \mathbf{V}_f \tilde{\mathbf{V}}_f^T\right)(-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\} + \mathbf{S}(\mathbf{z})). \tag{24}$$

In the regime where the fast chemical time scales are much smaller than the transport times scales, Maas and Pope assume that the components of the reaction and transport processes in the fast subspace have a minor effect on the reactive system, i.e.

$$\mathbf{V}_f \tilde{\mathbf{V}}_f^T(-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\} + \mathbf{S}(\mathbf{z})) = 0, \tag{25}$$

whereas the components in the slow subspace instead directly affect the movement, i.e.

$$\frac{\partial}{\partial t}\mathbf{z}(\mathbf{x}, t) = \mathbf{V}_s \tilde{\mathbf{V}}_s^T (-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\} + \mathbf{S}(\mathbf{z})). \tag{26}$$

In other words, after the initial transient, in the fast subspace the transport processes balance the net reaction rate. By pre-multiplying equation (26) with $\mathbf{B}^T$, the evolution equation for the reduced composition is obtained as

$$\frac{\partial \mathbf{r}}{\partial t} = \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T (-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\} + \mathbf{S}(\mathbf{z})). \tag{27}$$

Hence in the reduced description, the transport-chemistry coupling is accounted for by projecting the transport processes locally onto the slow subspace. Maas and Pope argue that the right-hand side of equation (27) can be well approximated based on the ILDM and the evolution equation for the reduced composition is (with $\mathbf{V}_s \tilde{\mathbf{V}}_s^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}) = \mathbf{S}(\mathbf{z}^{\text{ILDM}})$)

$$\frac{\partial \mathbf{r}}{\partial t} + \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T v_i \frac{\partial \mathbf{z}^{\text{ILDM}}}{\partial x_i} = \mathbf{B}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}(\mathbf{r})) + \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}(\mathbf{r})\}. \tag{28}$$

As far as the full composition is concerned, without attempting to represent the composition departure from the ILDM due to molecular diffusion, Maas and Pope argue that the

compositions in the reactive flow is well approximated by

$$\mathbf{z}(\mathbf{x}, t) \approx \mathbf{z}^{\text{ILDM}}(\mathbf{r}(\mathbf{x}, t)). \tag{29}$$

In short, following the assumption (equation (25)) that there exists a balance between the transport processes and chemical reaction in the fast subspace, the Maas–Pope approach predicts that the dynamics of the reduced composition are given by equation (28). Given the reduced composition, it also predicts that the full composition (or the unrepresented composition) in the reactive flow could be well approximated by equation (29), i.e. by the composition on the ILDM.

3.1 *Validation of the Maas–Pope approach in reaction–diffusion system*

When applying the ILDM to the reaction–diffusion systems considered (equation (13)), given the reduced composition, the Maas–Pope approach predicts the unrepresented composition by equation (20). Hence there is an error (of order $\mathcal{O}(\varepsilon)$) in the prediction (see equations (20) and (22)) because the Maas–Pope approach does not attempt to account for the small departure of composition from the ILDM caused by molecular diffusion. However as far as the dynamics of the reduced composition is concerned, it is easy to verify (by substituting equations (15), (16) and (20) into equation (28)) that the approach gives the same evolution equation (to leading order) for the reduced composition as the perturbation analysis (equation (23)).

For demonstration, we consider one particular case in the class of models. In this case $f(z_1) = z_1/(1+z_1)$, $g_1(z_1, z_2) = -z_1$, $g_2(z_1, z_2) = -z_1/(1+z_1)^2$ and $c = 1$. Similar models have been investigated in [26, 41, 45]. The length of the physical domain is set to be $L = 1$ over $0 \leq x \leq 1$. The boundary conditions are on the ILDM with $z_1(t, x = 0) = 0$ and $z_1(t, x = 1) = 1$. Initially, $z_1(t = 0, x)$ is linear in x. The corresponding boundary and initial conditions for z_2 are determined from equation (5) so that the full compositions are on the ILDM. The governing PDEs such as equation (13) are discretized in space with central finite differences over a mesh consisting of 201 equally spaced nodes, and integrated in time using a stiff ODE integrator. Substantial efforts were made to ensure that the results are numerically accurate.

Figure 2 validates the fundamental assumption in the Maas–Pope approach: that there is a balance between the transport processes and chemical reactions in the fast subspace (see
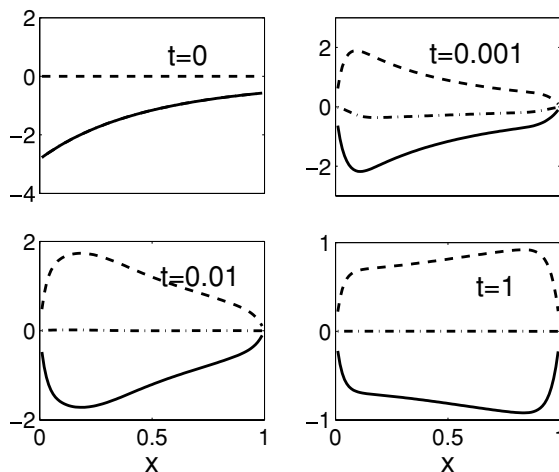

Figure 2. The balance at different times of rate of change (dash-dotted line), molecular diffusion (solid line) and reaction (dashed line) in the fast subspace from the full model (13) with $\varepsilon = 0.001$, $D_1 = 1$ and $D_2 = 2$.
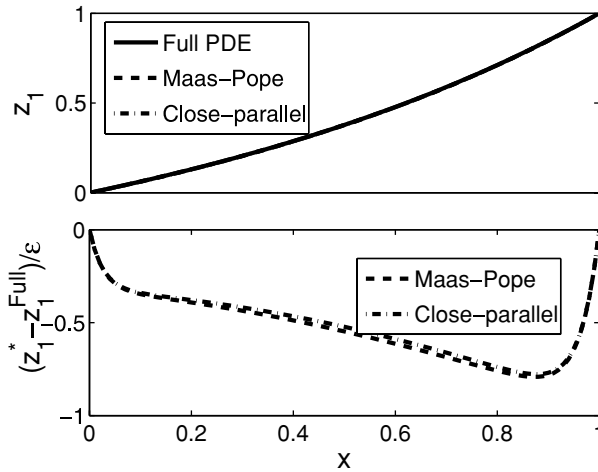
Figure 3. Distribution of z_1 (unnormalized and normalized) from the full model, reduced description by the Maas–Pope approach, and reduced description by the 'close-parallel' assumption at $t = 1$ with $\varepsilon = 0.001$, $D_1 = 1$ and $D_2 = 2$. In the upper figure, the three lines are indistinguishable. In the lower figure, z_1^{Full} denotes the results from the full model and z_1^* denotes the results using the Maas–Pope (dashed line) and the 'close-parallel' assumption (dot-dashed line).

equation (25)). The figure shows the components of the rate of change, molecular diffusion and reaction in the fast subspace for the reaction–diffusion system. As may be seen, after the initial transient ($t \approx 0.001$), over the whole physical domain molecular diffusion balances the net reaction rate.

Figure 3 shows the steady-state distribution of the reduced composition z_1 from both the full description and reduced descriptions. In figure 4, the dynamics of the reduced composition are studied by comparing the evolution of z_1 at the center location ($x = 1/2$). As may be seen, as far as the reduced composition is concerned, the reduced description given by the Maas–Pope
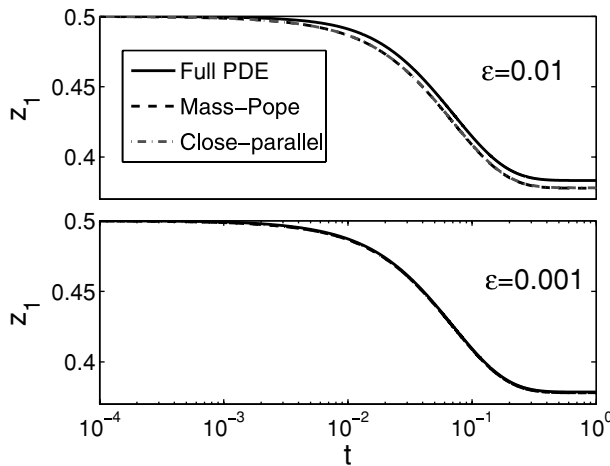

Figure 4. Evolution of z_1 at $x = \frac{1}{2}$ from the full model, reduced description by the Maas–Pope approach, and the reduced description by the 'close-parallel' assumption with $D_1 = 1$ and $D_2 = 2$. In the upper figure, the results from the Maas–Pope and 'close-parallel' assumption are indistinguishable. In the lower figure, the three lines are indistinguishable.
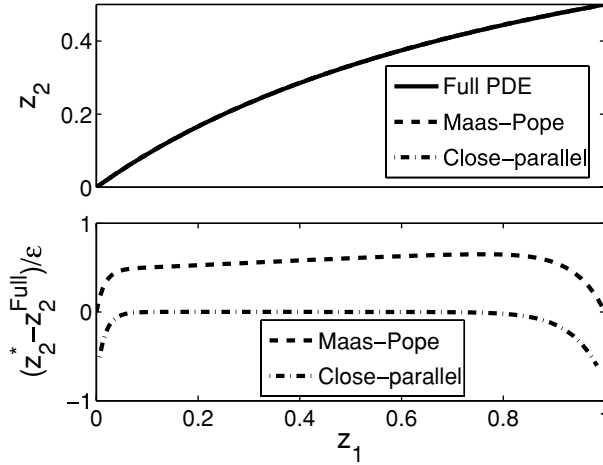
Figure 5.   The steady state distribution of z_2 (unnormalized and normalized) against z_1 from the full model, the reduced description by the Maas–Pope approach, and the reduced description by the 'close-parallel' assumption with $\varepsilon = 0.001$, $D_1 = 1$ and $D_2 = 2$. In the figure, z_1^{Full} denotes the results from the full model and z_1^* denotes the results using the Maas–Pope (dashed line) and the 'close-parallel' assumption (dot-dashed line).

approach agrees well with the full description. The error in the reduced composition is of order ε. As shown in figure 4, the accuracy of the Maas–Pope approach dramatically increases with the decease of ε.

As mentioned, the Maas–Pope approach does not account for the transport effect on the compositions. As a consequence, in the composition space, given the reduced composition, the Maas–Pope approach's prediction for unrepresented compositions has an error of order ε as shown in figure 5.

3.2 *Comments on convection*

As shown, the exact evolution equation for the reduced composition, equation (10), is obtained by pre-multiplying equation (1) with $\mathbf{B}^T$. This equation follows from equation (1) without any assumption or approximation. By comparing equation (28) with equation (10), we see that any accurate reduced description should not project the convection process onto the slow subspace (even though the projection of convection most likely incurs a negligible error as can be shown for simple systems). Hence when applying ILDM to inhomogeneous reactive flows, the Maas–Pope approach for the evolution of the reduced composition can be improved as

$$\frac{\partial \mathbf{r}}{\partial t} + v_i \frac{\partial \mathbf{r}}{\partial x_i} = \mathbf{B}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}(\mathbf{r})) + \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}(\mathbf{r})\}, \tag{30}$$

i.e. only the molecular diffusion process is projected onto the slow subspace.

It is worth mentioning briefly the effect and role of convection in the reduced description. As previously observed [23, 32, 49], convection alone does not pull compositions off the ILDM and in fact it does not even change the composition of a fluid particle. Hence convection does not have a direct effect on the composition; nor, as may be seen from equation (30), does it have a direct effect on the evolution of the reduced composition. However, convection can have significant indirect effects both on the composition and the reduced description. Convection manifests its effect through the diffusion process by changing the gradients of composition

field. In a reactive flow, the enhanced diffusion caused by convection may further pull the compositions off the ILDM and therefore enhance the transport-chemistry coupling.

4. 'Close-parallel' assumption for the ILDM method

The 'close-parallel' assumption was first employed by Tang and Pope [14] to provide a more accurate projection for homogeneous systems in the rate-controlled constrained equilibrium method [11, 12]. In [31, 32], the 'close-parallel' assumption is extended to incorporate the transport-chemistry coupling when chemistry-based slow manifolds are used to provide reduced descriptions of inhomogeneous reactive flows. Here, we demonstrate the use of the 'close-parallel' assumption for the ILDM to incorporate the transport-chemistry coupling. In the assumption, compositions in an inhomogeneous reactive flow are assumed to be on a low-dimensional manifold which is close to and parallel to the ILDM. This assumption is valid only when the fast chemical time scales are much smaller than the transport time scales. The departure $\delta \mathbf{z}$ ($= \mathbf{U} \delta \mathbf{u}$) from the ILDM can be obtained by considering the balance equation in the normal subspace of the ILDM. For given $\mathbf{r}$, we denote by $\mathbf{T}(\mathbf{r})$ an $n_s \times n_r$ orthogonal matrix spanning the tangent subspace of the ILDM at $\mathbf{z}^{\text{ILDM}}(\mathbf{r})$, and similarly $\mathbf{N}(\mathbf{r})$ is an $n_s \times n_u$ orthogonal matrix spanning the normal subspace. Hence, $\mathbf{N}^T \mathbf{T} = \mathbf{0}$, $\mathbf{N}^T \mathbf{N} = \mathbf{I}_{n_u \times n_u}$, $\mathbf{T}^T \mathbf{T} = \mathbf{I}_{n_r \times n_r}$, and $\mathbf{N}\mathbf{N}^T + \mathbf{T}\mathbf{T}^T = \mathbf{I}_{n_s \times n_s}$. As sketched in figure 1, in general, the subspace span($\mathbf{T}$) does not coincide with the subspace span($\mathbf{V}_s$) due to the non-invariance of the ILDM. However, when the ILDM is highly attractive, the angle between span($\mathbf{T}$) and span($\mathbf{V}_s$) is likely to be small. For the model system (13), as shown in Section 4.1, the tangent and normal subspaces are readily known. Moreover, to a good approximation, $\mathbf{T}$ and $\mathbf{V}_s$ span the same direction (see equations (46) and (15)), so do $\mathbf{N}$ and $\tilde{\mathbf{V}}_f$ (see equations (47) and (16)).

Considering the balance of the governing PDEs (equation (1)) in the normal subspace, with $\mathbf{z} = \mathbf{z}^{\text{ILDM}} + \delta \mathbf{z}$, we have

$$\mathbf{N}^T(\mathbf{r}) \frac{\partial(\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z})}{\partial t} + \mathbf{N}^T(\mathbf{r}) v_i \frac{\partial(\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z})}{\partial x_i}$$
$$= \mathbf{N}^T(\mathbf{r})\mathbf{D}\{\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z}\} + \mathbf{N}^T(\mathbf{r})\mathbf{S}(\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z}). \quad (31)$$

Following the close-parallel assumption, we have the following approximations

$$\mathbf{N}^T(\mathbf{r}) \frac{\partial \delta \mathbf{z}}{\partial t} \approx 0, \quad (32)$$

and

$$\mathbf{N}^T(\mathbf{r}) v_i \frac{\partial \delta \mathbf{z}}{\partial x_i} \approx 0. \quad (33)$$

(Note that $\mathbf{N}^T \partial \mathbf{z}^{\text{ILDM}}/\partial t$ and $\mathbf{N}^T v_i \partial \mathbf{z}^{\text{ILDM}}/\partial x_i$ are exactly zero.) Hence equation (31) can be simplified to

$$0 \approx \mathbf{N}^T(\mathbf{r})\mathbf{D}\{\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z}\} + \mathbf{N}^T(\mathbf{r})\mathbf{S}(\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z}). \quad (34)$$

Note that the terms on the right-hand side of equation (34) are the components of molecular diffusion and chemical reactions in the normal subspace, respectively. Hence equation (34) implies a balance between the molecular diffusion and chemical reaction in the normal subspace of the ILDM.

In equation (34), since $\mathbf{D}$ depends on derivatives of $\mathbf{z}$, and since by assumption $\mathbf{z}$ is close to and parallel to $\mathbf{z}^{\text{ILDM}}$, the diffusion process is not sensitive to the perturbations and the

indicated approximation is

$$\mathbf{D}\{\mathbf{z}^{\text{ILDM}} + \delta\mathbf{z}\} \approx \mathbf{D}\{\mathbf{z}^{\text{ILDM}}\}. \tag{35}$$

For chemical reaction, however, small perturbations off the ILDM may result in significant changes in the reaction rate due to fast processes in the chemical kinetics. The assumption that $\mathbf{z}$ is close to $\mathbf{z}^{\text{ILDM}}$ implies that $\delta\mathbf{z}$ is small, and hence the last term on the right-hand side of equation (34) can be well approximated by

$$\mathbf{S}(\mathbf{z}^{\text{ILDM}} + \delta\mathbf{z}) \approx \mathbf{S}(\mathbf{z}^{\text{ILDM}}) + \mathbf{J}\delta\mathbf{z}, \tag{36}$$

where $J_{ij} \equiv \partial S_i / \partial z_j |_{\mathbf{z}=\mathbf{z}^{\text{ILDM}}}$ is the Jacobian matrix. Hence, with the 'close-parallel' assumption, equation (34) can be simplified as

$$0 \approx \mathbf{N}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}\} + \mathbf{N}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}) + \mathbf{N}^T \mathbf{J}(\mathbf{z}^{\text{ILDM}})\delta\mathbf{z}. \tag{37}$$

The term $\mathbf{N}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}})$ is generally nonzero due to the fact that the ILDM is not exactly invariant. (But it may be negligible compared with other terms in equation 37 as shown in the reaction–diffusion systems.) With $\delta\mathbf{z} = \mathbf{U}\delta\mathbf{u}$ (see equation 9), from equation (37) we obtain

$$\delta\mathbf{u} = -(\mathbf{N}^T \mathbf{J}(\mathbf{z}^{\text{ILDM}})\mathbf{U})^{-1} \left[\mathbf{N}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}\} + \mathbf{N}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}) \right]. \tag{38}$$

As may be seen from equation (38), based on the 'close-parallel' assumption, the compositions in the inhomogeneous reactive flows are pulled off the ILDM due to the molecular diffusion and the non-invariance of the ILDM. And the compositions are given by

$$\mathbf{z} = \mathbf{z}^{\text{ILDM}}(\mathbf{r}) - \mathbf{U}(\mathbf{N}^T \mathbf{J}(\mathbf{z}^{\text{ILDM}})\mathbf{U})^{-1} \left[\mathbf{N}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}\} + \mathbf{N}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}) \right]. \tag{39}$$

With equations (38) and (39), the evolution equations for the reduced composition variables can be obtained as following. Recall that the exact evolution equation (10) for the reduced composition can be obtained by pre-multiplying equation (1) with $\mathbf{B}^T$. With $\mathbf{z} = \mathbf{z}^{\text{ILDM}} + \delta\mathbf{z} = \mathbf{z}^{\text{ILDM}} + \mathbf{U}\delta\mathbf{u}$, equation (10) can be written as

$$\frac{\partial \mathbf{r}}{\partial t} + v_i \frac{\partial \mathbf{r}}{\partial x_i} = \mathbf{B}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}(\mathbf{r}) + \mathbf{U}\delta\mathbf{u}\} + \mathbf{B}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}(\mathbf{r}) + \mathbf{U}\delta\mathbf{u}). \tag{40}$$

With the 'close-parallel' assumption, equation (40) can be simplified as

$$\frac{\partial \mathbf{r}}{\partial t} + v_i \frac{\partial \mathbf{r}}{\partial x_i} = \mathbf{B}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}(\mathbf{r})\} + \mathbf{B}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}(\mathbf{r})) + \mathbf{B}^T \mathbf{J}\mathbf{U}\delta\mathbf{u}. \tag{41}$$

With the perturbation given by equation (38), the evolution equations for the reduced composition $\mathbf{r}$ are

$$\frac{\partial \mathbf{r}}{\partial t} + v_i \frac{\partial \mathbf{r}}{\partial x_i} = \mathbf{B}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}(\mathbf{r})\} + \mathbf{B}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}(\mathbf{r})) + \mathbf{H}^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}\} + \mathbf{H}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}) \tag{42}$$

where $\mathbf{H}^T \equiv -\mathbf{B}^T \mathbf{J}\mathbf{U}(\mathbf{N}^T \mathbf{J}\mathbf{U})^{-1}\mathbf{N}^T$ is an $n_r \times n_s$ matrix. Equation (42) differs from equation (12) by the last two additional terms, which represent the transport-chemistry coupling and non-invariance effect. Hence as shown in equation (39) and (42), the compositions in general inhomogeneous reactive flows are pulled off the ILDM by molecular diffusion and the non-invariance of the ILDM, and correspondingly, these perturbations introduce coupling terms in the evolution equation of the reduced composition. (As shown in [32], the molecular diffusion affects the composition and reduced description through 'dissipation curvature' and 'differential diffusion' effects.) For the reaction–diffusion model system, as is shown in Section 4.1, the non-invariance effect is negligible since the ILDM is invariant to $o(\varepsilon)$.

It is worth exploring more about the transport-chemistry coupling terms which arise. Assume that the Jacobian can be decomposed as in equation (4). When the ILDM is highly attractive,

to a good approximation, $\mathbf{N}$ and $\tilde{\mathbf{V}}_f$ span the same subspace. (Compare $\mathbf{N}$ given by equation 47 and $\tilde{\mathbf{V}}_f$ given by equation (16) in the model system (13).) Hence, the coupling terms can be approximated by

$$
\begin{aligned}
\mathbf{H}^T(\mathbf{D}\{\mathbf{z}^{\mathrm{ILDM}}\} + \mathbf{S}(\mathbf{z}^{\mathrm{ILDM}})) &\approx -\mathbf{B}^T\mathbf{V}_f(\tilde{\mathbf{V}}_f^T\mathbf{V}_f)^{-1}\mathbf{N}^T(\mathbf{D}\{\mathbf{z}^{\mathrm{ILDM}}\} + \mathbf{S}(\mathbf{z}^{\mathrm{ILDM}})) \\
&\quad -\mathbf{B}^T\mathbf{V}_s\boldsymbol{\Lambda}_1\tilde{\mathbf{V}}_s^T\mathbf{U}(\tilde{\mathbf{V}}_f^T\mathbf{U})^{-1}\boldsymbol{\Lambda}_2^{-1}(\tilde{\mathbf{V}}_f^T\mathbf{V}_f)^{-1}\mathbf{N}^T(\mathbf{D}\{\mathbf{z}^{\mathrm{ILDM}}\} + \mathbf{S}(\mathbf{z}^{\mathrm{ILDM}})) \\
&\approx -\mathbf{B}^T\mathbf{V}_f(\tilde{\mathbf{V}}_f^T\mathbf{V}_f)^{-1}\mathbf{N}^T(\mathbf{D}\{\mathbf{z}^{\mathrm{ILDM}}\} + \mathbf{S}(\mathbf{z}^{\mathrm{ILDM}})),
\end{aligned}
\tag{43}
$$

where the second step follows from the observation that the second term on the right-hand side involves the ratio of eigenvalues which is small. According to equation (43), the transport-chemistry coupling is in general not negligible. One exception is when the represented subspace (spanned by $\mathbf{B}$) is chosen to be perpendicular to the fast directions spanned by $\mathbf{V}_f$. Since the fast directions $\mathbf{V}_f$ vary with position in composition space, for a fixed reduced representation with constant $\mathbf{B}$, the best that can practically be achieved is a choice of $\mathbf{B}$ which minimizes the principal angles between span($\mathbf{B}$) and span($\mathbf{V}_f$) for compositions in the region of the slow manifold where the transport-chemistry coupling is significant. In practice, without a prior knowledge of $\mathbf{V}_f$, the pragmatical choice of constant $\mathbf{B}$ in general introduces non-negligible transport-chemistry coupling in the reduced description. Moreover, the matrix $\mathbf{N}^T\mathbf{JU}$ in the definition of the matrix $\mathbf{H}$ is invertible as long as the represented subspace is not aligned with the subspace spanned by $\tilde{\mathbf{V}}_f$ (i.e. $\mathbf{U}$ is not perpendicular to $\tilde{\mathbf{V}}_f$), which is the case for a reasonable parametrization of the ILDM.

We also note that equation (42) can be rewritten as

$$
\frac{\partial \mathbf{r}}{\partial t} + v_i\frac{\partial \mathbf{r}}{\partial x_i} = \mathbf{B}^T\mathbf{P}(\mathbf{S}(\mathbf{z}^{\mathrm{ILDM}}(\mathbf{r})) + \mathbf{D}\{\mathbf{z}^{\mathrm{ILDM}}(\mathbf{r})\}),
\tag{44}
$$

where the $n_s \times n_s$ matrix $\mathbf{P}$

$$
\mathbf{P} \equiv \mathbf{TT}^T + (\mathbf{N} - \mathbf{JU}[\mathbf{N}^T\mathbf{JU}]^{-1})\mathbf{N}^T,
\tag{45}
$$

represents a particular projection onto the tangent subspace of the ILDM (since $\mathbf{N}^T\mathbf{P} = 0$, $\mathbf{PT} = \mathbf{T}$). The matrix $\mathbf{P}$ serves the similar functionality as $\mathbf{V}_s\tilde{\mathbf{V}}_s^T$ in the Maas–Pope approach (see equation (28)). Hence, as far as the dynamics of the reduced composition are concerned, by following the close-parallel assumption, a particular projection can be identified to obtain the accurate reduced description when a constant reduced representation (constant $\mathbf{B}$) is employed to describe a reactive flow. The projection matrix $\mathbf{P}$ involves only the information about the manifold and the reduced representation (requiring no transport information). As shown in [32], the 'close-parallel' approximation can be applied to both homogeneous and inhomogeneous reactive flows to obtain an accurate reduced description.

4.1 *Validation of the 'close-parallel' approximation in reaction–diffusion systems*

For the reaction–diffusion systems considered, the unit tangent vector of the ILDM (derived based on equation (20)) is

$$
\mathbf{T} = \frac{1}{\sqrt{1 + f'^2}}\begin{bmatrix} 1 + \mathcal{O}(\varepsilon) \\ f'(z_1) + \mathcal{O}(\varepsilon) \end{bmatrix},
\tag{46}
$$

and the normal unit vector is

$$\mathbf{N} = \frac{1}{\sqrt{1 + f'^2}} \begin{bmatrix} -f'(z_1) + \mathcal{O}(\varepsilon) \\ 1 + \mathcal{O}(\varepsilon) \end{bmatrix}. \tag{47}$$

Recall that $\mathbf{B} = [1 \quad 0]^T$, $\mathbf{U} = [0 \quad 1]^T$, the Jacobian is given by equation (14), and the composition on the ILDM is given by equation (20). Substituting the above expressions into equation (38), we obtain

$$\delta z_2 = \varepsilon \frac{f'' D_1 \nabla z_1 \cdot \nabla z_1}{1 + cf'} + \varepsilon \frac{\nabla \cdot (f'[D_2 - D_1] \nabla z_1)}{1 + cf'} + o(\varepsilon). \tag{48}$$

Note that the non-invariance of the ILDM $\mathbf{N}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}})$ only pulls the compositions off the ILDM by of order $o(\varepsilon)$, and hence the non-invariance effect is negligible compared with the molecular diffusion effect on the composition. This is consistent with the findings in [16], in which by asymptotic expansion, it is shown that the ILDM manifold agrees with the slow invariant manifold up to and including terms of $\mathcal{O}(\varepsilon)$ as is evident from equation (20). For general reactive systems, it is not clear whether the non-invariance effect is negligible or not compared with the diffusion effect. Nevertheless, both the non-invariance effect and diffusion effects have been included in the 'close-parallel' assumption (see equations (39) and (42)).

Hence for the reaction–diffusion systems, the 'close-parallel' approximation predicts the compositions by equation (48) which is the same as the perturbation analysis result to leading order (see equation (22)). By substituting equation (48) into equation (13), it is easy to verify that the evolution equation for z_1 given by the 'close-parallel' approximation is the same as the perturbation analysis results and the Maas–Pope prediction (equation (23)) (to leading order in ε).

As mentioned above, the 'close-parallel' assumption implies a balance between molecular diffusion and chemical reaction in the normal subspace of ILDM (see equation (34)). For the reaction–diffusion system, this balance is easy to demonstrate. (For the model system, the angle between the fast subspace and normal space is $\mathcal{O}(\varepsilon)$. Therefore, the balance in the normal subspace is similar to the balance in the fast subspace, see figure 2.) As may be seen from figures 3 and 4, as far as the reduced composition is concerned, the 'close-parallel' assumption achieves the same accuracy as the Maas–Pope approach. However, in the composition space, as shown in figure 5, given the reduced composition, the 'close-parallel' assumption gives a more accurate prediction for the unrepresented composition because it incorporates the transport effect on the composition. (The deterioration close to the boundaries is due to the effect of boundary conditions.)

4.2 *Discussion*

The Maas–Pope approach and the 'close-parallel' assumption for the ILDM to incorporate the transport-chemistry coupling are similar in several aspects. The Maas–Pope approach assumes a balance between the transport processes and chemical reaction in the fast subspace (equation (25)). In contrast, the 'close-parallel' assumption implies a balance between the transport processes and chemical reaction in the normal subspace of the ILDM. For the reaction–diffusion systems considered, the angle between the fast subspace and normal subspace is small ($\mathcal{O}(\varepsilon)$). Moreover, the formulations of the reduced description from the two approaches are similar. The reduced description is given by a set of PDEs for the reduced composition variables, in which the terms arising can be evaluated on the ILDM. On the boundaries, only the reduced composition needs to be provided.
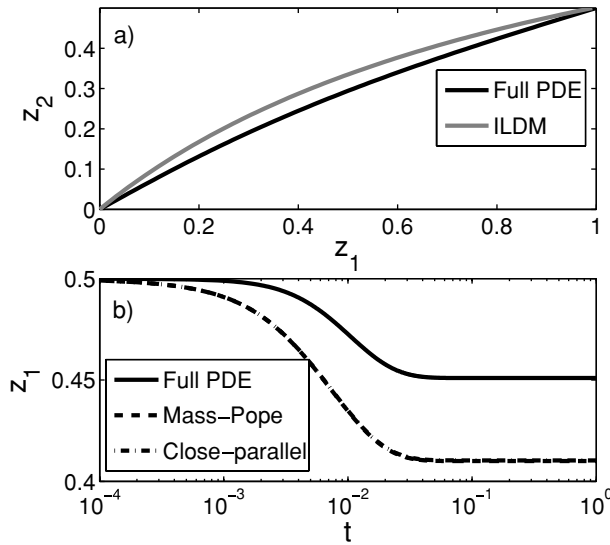
Figure 6. (a) Steady state distribution of compositions in the composition space from the full model with $\varepsilon = 0.01$, $D_1 = 10$ and $D_2 = 20$. Also shown is the calculated ILDM. (b) Evolution of z_1 at $x = \frac{1}{2}$ from the full model, the reduced description by the Maas–Pope approach, and the reduced description by the 'close-parallel' assumption with $\varepsilon = 0.01$, $D_1 = 10$ and $D_2 = 20$.

Even though the Maas–Pope approach makes no attempt to represent the departure of composition from the ILDM (by neglecting the molecular diffusion effect on the compositions), it does incorporate the transport-chemistry coupling in the dynamics of the reduced system. For the reaction–diffusion systems, as shown, the reduced description given by Maas–Pope approach accurately represents the full system even though the prediction for composition has an error of $\mathcal{O}(\varepsilon)$. In contrast, the 'close-parallel' assumption accurately incorporates the effects of molecular diffusion both on the composition and on the dynamics of the reduced composition.

Both approaches are supposed to be valid only when the fast chemical time scales are much smaller than the transport time scales. When the transport time scales are comparable to the fast chemical time scales, the accuracy of both these approaches decreases. As shown in figure 6, when we increase the diffusivities of the compositions, in the composition space, the full compositions are far away from the ILDM. The reduced description results obtained from both approaches are significantly different from the full PDE solution. (For the case shown, $L^2/(D_1\varepsilon) = 10$ and $L^2/(D_2\varepsilon) = 5$.)

5. Infinite-dimensional approximate slow invariant manifold (ASIM)

In [45], Singh *et al.* proposed the ASIM approach, an extension of the ILDM method, for the reduced description of reactive flows with transport processes. The reduced model equations are obtained by equilibrating the fast dynamics of a system and resolving only the slow dynamics of the same system in order to reduce computational costs. In the following, after briefly outlining this approach, we clarify its underlying assumption. We also show that in the regime where fast chemical time scales are much smaller than the transport time scales, the ASIM approach gives the same accurate description of the reduced compositions as the Maas–Pope approach and the close-parallel assumption.

In the ASIM approach, the full model equations (1) are projected onto the slow and fast invariant subspaces based on the reaction source terms, i.e.

$$\tilde{\mathbf{V}}_s^T \frac{\partial \mathbf{z}}{\partial t} + \tilde{\mathbf{V}}_s^T \mathbf{C}\{\mathbf{z}\} = \tilde{\mathbf{V}}_s^T \mathbf{D}\{\mathbf{z}\} + \tilde{\mathbf{V}}_s^T \mathbf{S}(\mathbf{z}), \tag{49}$$

and

$$\tilde{\mathbf{V}}_f^T \frac{\partial \mathbf{z}}{\partial t} + \tilde{\mathbf{V}}_f^T \mathbf{C}\{\mathbf{z}\} = \tilde{\mathbf{V}}_f^T \mathbf{D}\{\mathbf{z}\} + \tilde{\mathbf{V}}_f^T \mathbf{S}(\mathbf{z}). \tag{50}$$

In the regime where transport processes occur on time scales which are slower than reaction time scales of order $1/|Re(\lambda_{n_r+1})|$, i.e. all the fast chemical time scales, Singh *et al.* assume that in the fast subspace the components of the transient and transport processes are negligible, i.e.

$$0 = \tilde{\mathbf{V}}_f^T \mathbf{S}(\mathbf{z}). \tag{51}$$

(Note that λ_{n_r+1} is the $(n_r + 1)$-th eigenvalue of the Jacobian $\mathbf{J}$ and the eigenvalues are ordered in decreasing value of their real parts.) Hence, the slow dynamics of the system (1) can be approximated by equation (49) and equation (51). On the other hand, in the regime where the transport time scales overlap with fast chemical time scales, i.e. the convection and diffusion processes occur on time scales of order $1/|Re(\lambda_p)|$ for $n_r < p < n_s$ and slower, Singh *et al.* assume the following balance

$$0 = \tilde{\mathbf{V}}_{fs} \mathbf{S}(\mathbf{z}) + \tilde{\mathbf{V}}_{fs}(-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\})$$
$$0 = \tilde{\mathbf{V}}_{ff} \mathbf{S}(\mathbf{z}), \tag{52}$$

where $\tilde{\mathbf{V}}_{fs}$ ($n_s \times (p - n_r)$)) and $\tilde{\mathbf{V}}_{ff}$ ($n_s \times (n_s - p)$)) are components of the matrix $\tilde{\mathbf{V}}_f$, i.e.

$$\tilde{\mathbf{V}}_f = \begin{bmatrix} \tilde{\mathbf{V}}_{fs} & \tilde{\mathbf{V}}_{ff} \end{bmatrix}. \tag{53}$$

Hence the slow dynamics for equation (1) is approximated by equation (49) and equation (52). The authors also argue that in general reactive flows, the transport time scales are not known a priori and so, for convenience, equation (49) and equation (52) can be used to represent the dynamics of the full system (equation 1) in both regimes.

Equation (52) represents the infinite-dimensional approximate slow invariant manifold (ASIM) on which the slow dynamics occur once all fast time scale processes have equilibrated. Equations (49) and (52) correspond to a system of differential algebraic equations which have to be solved in physical space together with the prescribed boundary conditions.

As may be seen, the formulation of the reduced description by the ASIM approach is different from those by the Maas–Pope and 'close-parallel' approaches. In the ASIM approach, the reduced description is given by the set of PDEs (49) supplemented by the differential algebraic equations (52). The ASIM approach makes no clear distinction between the reduced compositions and unrepresented compositions. On the boundaries, the full composition is provided, and therefore the boundary conditions are satisfied even for arbitrary full composition at the boundaries. During the calculation, all the equations have to be solved together and it is in general computationally expensive. In contrast, in the Maas–Pope and 'close-parallel' approaches, the reduced description is given by a set of PDEs for the reduced composition variables (see equations (28) and (44)), in which the terms arising are evaluated on the ILDM. On the boundaries, only the reduced composition needs to be provided. When the full composition on the boundaries is on the low-dimensional manifold, the boundary conditions for the

reduced composition can be taken directly from the corresponding full composition at boundaries. For arbitrary full composition at the boundaries, a rigorous derivation of the boundary conditions for the reduced description is given by Lam [37]. Given the reduced composition, the ILDM point can either be retrieved from a pre-tabulated table containing the manifold information, or it can be obtained through a local computation using equation (5). In the local computation of the manifold, no spatial information is needed.

5.1 *Investigation of the ASIM assumptions*

In the regime where the fast chemical time scales are much smaller than the diffusion time scales, according to ASIM, the components of the transient and transport processes in the fast subspace are negligible (see equation (51)); but we can see from figure 2 that, for the reaction–diffusion system considered, in fact the component of the molecular diffusion in the fast subspace is not negligible (of order one). In the fast subspace, after the initial transient, molecular diffusion and reaction (both of order one) balances each other. Hence the physically sound assumption should be

$$0 = \tilde{\mathbf{V}}_f^T(-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\} + \mathbf{S}(\mathbf{z})), \tag{54}$$

instead of equation (51). Note that this assumption (54) is exactly the one used in the Maas–Pope approach, see equation (25). However, the functionality of these equations in these two approaches is different. In the Maas–Pope approach, equation (25) is only used to derive the governing equations for the reduced composition, and does not need to be solved in the reduced description. In the Maas–Pope approach, the full composition (or unrepresented composition) is given by equation (29). In contrast, in the ASIM approach, equation (54), which defines the infinite-dimensional approximate slow invariant manifold (ASIM), has to be solved both to give a reduced description and to predict the full composition.

In the regime where the convection and diffusion time scales overlap with the fast chemical time scales, according to ASIM, the component of the transient process in the fast subspace is negligible (see equation (52)). Here we designed the following case to test this assumption by studying the balance of different processes in the fast subspace. For this particular case in the class of models, we specify $f(z_1) = z_1/(1+z_1)$, $g_1(z_1, z_2) = -z_1$, $g_2(z_1, z_2) = -z_1/(1+z_1)^2$ and $c = 1$. The length of the physical domain is set to be $L = 1$ over $0 \leq x \leq 1$. (These are the same setting as those in Section 3.1.) The boundary conditions are set to be periodic. The initial conditions are on the ILDM with $z_1(t = 0, x) = 1 - \cos(2\pi x)$. The corresponding initial conditions for z_2 are determined from equation (5) so that the full compositions are on the ILDM.

Figure 7 shows the distribution of z_1 and z_2 from the full model in physical space at discrete times with $\varepsilon = 0.01$ and $D_1 = D_2 = 1$. The diffusion length scale can be roughly estimated from figure 7, which is of order $L/4 = 0.25$. Hence the characteristic diffusion time scale estimated based on the diffusion length scale and the diffusivities is of order 0.06, which is comparable to the fast chemical time scale (which is of order 0.01). In figure 8, we show the balance of rate of change, molecular diffusion and reaction in the fast subspace from the full model. One clear piece of information from the figure is that the component of the rate of change in the fast subspace is not negligible compared to other processes. Hence the assumption (54) is questionable in the regime where the convection and diffusion time scales overlap with fast chemical time scales. Note that the fast and slow subspace decomposition used depends only on the chemistry. One possible solution proposed by Singh *et al.* [45] is to perform the fast and slow subspace decomposition with account for the transport effects.
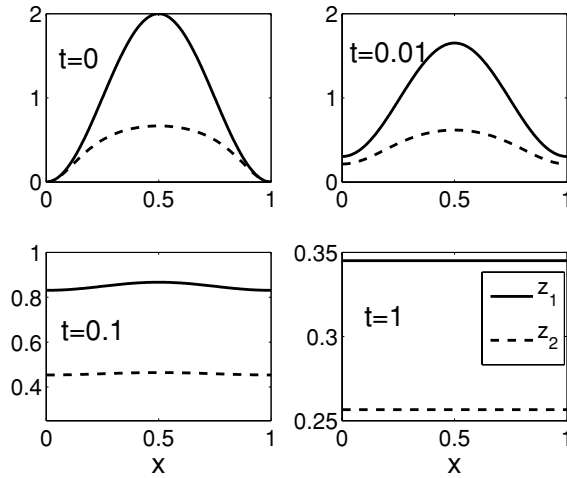
Figure 7. The distribution of z_1 and z_2 from the full model in physical space at discrete times with $\varepsilon = 0.01$, $D_1 = D_2 = 1$ and periodic boundary conditions. The initial conditions are on the ILDM with $z_1(t = 0, x) = 1 - \cos(2\pi x)$ (see Section 5.1 for details).

5.2 *Simplification of the ASIM approach*

Following the above discussion, in the regime where the fast chemical time scales are much smaller than those of transport processes, the appropriate governing equations for the ASIM approach are

$$\tilde{\mathbf{V}}_s^T \frac{\partial \mathbf{z}}{\partial t} + \tilde{\mathbf{V}}_s^T \mathbf{C}\{\mathbf{z}\} = \tilde{\mathbf{V}}_s^T \mathbf{D}\{\mathbf{z}\} + \tilde{\mathbf{V}}_s^T \mathbf{S}(\mathbf{z}),$$

$$0 = \tilde{\mathbf{V}}_f^T(-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\} + \mathbf{S}(\mathbf{z})). \tag{55}$$

This set of partial differential equations is computationally expensive to solve. Here following similar techniques in the 'close-parallel' approach, we propose the following simplification.
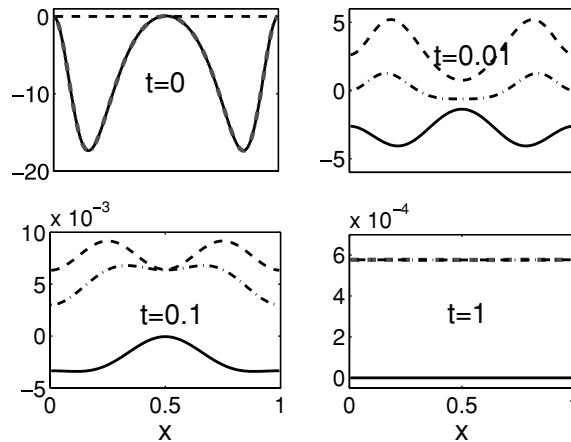

Figure 8. The balance of rate of change (dash-dotted line), molecular diffusion (solid line) and reaction (dashed line) in the fast subspace from the full model (13) with $\varepsilon = 0.01$, $D_1 = D_2 = 1$, and periodic boundary conditions. The initial conditions are on the ILDM with $z_1(t = 0, x) = 1 - \cos(2\pi x)$ (see Section 5.1 for details).

Notice that the assumption (54) in the ASIM approach implies $\tilde{\mathbf{V}}_f \partial \mathbf{z}/\partial t = 0$. With this relation, by pre-multiplying the first equation in (55) with $\mathbf{B}^T$, equation (55) can be rewritten as

$$\frac{\partial \mathbf{r}}{\partial t} + \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T \mathbf{C}\{\mathbf{z}\} = \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T \mathbf{D}\{\mathbf{z}\} + \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T \mathbf{S}(\mathbf{z}),$$

$$0 = \tilde{\mathbf{V}}_f^T(-\mathbf{C}\{\mathbf{z}\} + \mathbf{D}\{\mathbf{z}\} + \mathbf{S}(\mathbf{z})). \tag{56}$$

Notice that by making this transformation, we make a clear distinction between the reduced compositions and unrepresented compositions.

Following the fact that in this regime considered, the compositions in the reactive flows depart only slightly from the ILDM, the second equation in equation (56) can be rewritten as

$$0 = \tilde{\mathbf{V}}_f^T(-\mathbf{C}\{\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z}\} + \mathbf{D}\{\mathbf{z}^{\text{ILDM}} + \delta \mathbf{z}\} + \mathbf{S}(\mathbf{z}^{\text{ILDM}}) + \mathbf{J}(\mathbf{z}^{\text{ILDM}})\delta \mathbf{z}), \tag{57}$$

where $\delta \mathbf{z}$ is in the unrepresented subspace, i.e. $\delta \mathbf{z} = \mathbf{U}\delta \mathbf{u}$. By manipulating equation (57), and neglecting the negligible terms, the modified ASIM predicts the departure from the ILDM as

$$\delta \mathbf{u} = -\left(\tilde{\mathbf{V}}_f^T \mathbf{J}(\mathbf{z}^{\text{ILDM}})\mathbf{U}\right)^{-1}\left(-\tilde{\mathbf{V}}_f^T \mathbf{C}\{\mathbf{z}^{\text{ILDM}}\} + \tilde{\mathbf{V}}_f^T \mathbf{D}\{\mathbf{z}^{\text{ILDM}}\}\right), \tag{58}$$

where $\tilde{\mathbf{V}}_f^T \mathbf{C}\{\mathbf{z}^{\text{ILDM}}\}$ is generally negligible (cf. the close-parallel approach in equation (38)).

With the perturbation given by equation (58) and $\mathbf{V}_s \tilde{\mathbf{V}}_s^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}) = \mathbf{S}(\mathbf{z}^{\text{ILDM}})$, for the modified ASIM approach, we obtain the following set of PDEs for the reduced compositions

$$\frac{\partial \mathbf{r}}{\partial t} + \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T (\mathbf{I} + \mathbf{P}^A)\mathbf{C}\{\mathbf{z}^{\text{ILDM}}\} = \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T (\mathbf{I} + \mathbf{P}^A)\mathbf{D}\{\mathbf{z}^{\text{ILDM}}\} + \mathbf{B}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}), \tag{59}$$

where $\mathbf{P}^A = -\mathbf{J}\mathbf{U}(\tilde{\mathbf{V}}_f^T \mathbf{J}\mathbf{U})^{-1}\tilde{\mathbf{V}}_f^T$. Following the same argument as in Section 3.2, the convection process does not require any projection, therefore equation (59) can be improved as

$$\frac{\partial \mathbf{r}}{\partial t} + v_i \frac{\partial \mathbf{r}}{\partial x} = \mathbf{B}^T \mathbf{V}_s \tilde{\mathbf{V}}_s^T (\mathbf{I} + \mathbf{P}^A)\mathbf{D}\{\mathbf{z}^{\text{ILDM}}\} + \mathbf{B}^T \mathbf{S}(\mathbf{z}^{\text{ILDM}}). \tag{60}$$

As shown, the original ASIM approach (equation (55)) can be modified and simplified to equation (60). Similar to the Maas–Pope and 'close-parallel' approaches, in the modified ASIM approach, the reduced description is given by a set of PDEs for the reduced composition variables equation (60), in which the terms arising are evaluated on the ILDM. On the boundaries, only the reduced composition needs to be provided. The modified ASIM approach incorporates the transport effects on both the compositions and the dynamics of the reduced compositions. It predict the composition off the ILDM by equation (58) and the dynamics of the reduced compositions by equation (60). It is easy to verify that when applied to the reaction–diffusion system, the composition for z_2 and the evolution equation for z_1 given by the modified ASIM approach (58) and (60) are identical (to leading order) to the 'close-parallel' assumption.

Figure 9 compares the predictions of z_1 by the full model and different reduced descriptions. The computations are for $\varepsilon = 0.001$, $D_1 = 1$ and $D_2 = 2$. The fast chemical time scale (and the initial transient time) is of order 0.001. As may be seen, all of the four reduced descriptions, the Maas–Pope approach, the 'close-parallel' approach, the ASIM approach, and the modified ASIM approach, achieve the same accuracy: all have an error (of order ε) in the prediction for the dynamics of the reduced composition. For the case considered, it finally reaches steady state. Inevitably, when approaching steady state, the accuracy in the ASIM approach increases because the steady-state solution from the ASIM approach is identical to the full system. However, this does not justify that the ASIM approach is more accurate than other approaches. As may be seen from the figure, after the initial transient ($t \approx 0.001$), for a wide
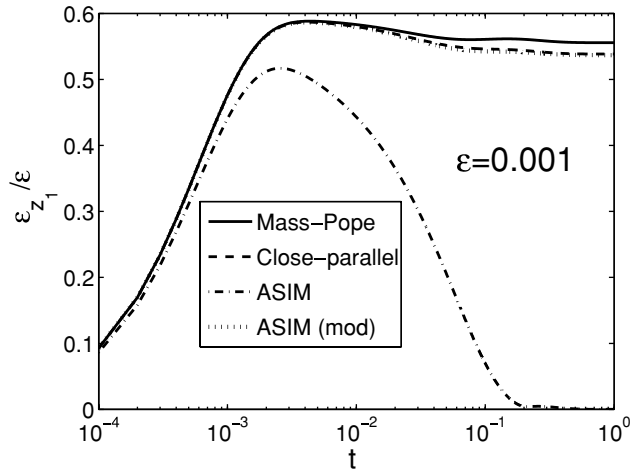
Figure 9. Normalized errors in the predictions for the reduced composition variable z_1 by different approaches. The error $\varepsilon_{z_1}(t)$ is defined to be the square root of $\frac{1}{L}\int_0^L (z_1^*(x,t) - z_1^{\text{Full}}(x,t))^2 dx$, where L is the length of physical domain, z_1^{Full} denotes the results from the full model, and z_1^* denotes the results by the different approaches. Model parameters are $\varepsilon = 0.001$, $D_1 = 1$ and $D_2 = 2$.

range of time (from about $t = 0.0001$ to $t = 0.1$) where the dynamics are interested, the ASIM approach has an error of order ε.

Figure 10 compares the predictions of unrepresented composition z_2 against z_1 in the composition space at discrete times. As may be seen, after the initial transient, away from the boundaries, the 'close-parallel' approach, the ASIM approach and the modified ASIM approach give more accurate predictions for the unrepresented composition than the Maas–Pope approach
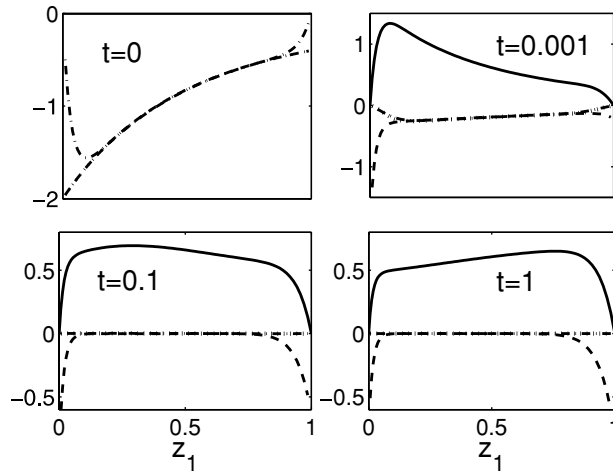

Figure 10. Given z_1, the predictions of normalized z_2 (i.e. $(z_2^* - z_2^{\text{Full}})/\varepsilon$) against z_1 in the composition space at discrete times by the Maas–Pope approach (29) (solid line), the 'close-parallel' assumption (39) (dashed line), the ASIM approach (54) (dot-dashed line), and the modified ASIM approach (58) (dotted line). In the normalization, z_1^{Full} denotes the results from the full model and z_1^* denotes the results by the different approaches. Model parameters are $\varepsilon = 0.001$, $D_1 = 1$ and $D_2 = 2$. In the figure, the ASIM approach (dot-dashed line) and the modified ASIM approach (dotted line) are indistinguishable.

because they incorporates the transport effect on the composition whereas the Maas–Pope approach does not. The deterioration of the 'close-parallel' approach close to the boundaries is due to the effect of boundary conditions.

6. Conclusion

In this study, we investigate three different approaches for the chemistry-based manifold, the ILDM to incorporate the transport-chemistry coupling in the reduced description of inhomogeneous reactive flows, namely, the Maas–Pope approach [22, 23], the 'close-parallel' approach [31, 32] and the ASIM approach [45]. Moreover, a modified ASIM approach is proposed.

Both the Maas–Pope approach and the 'close-parallel' approach explicitly use the reduced composition variables **r** to represent the reactive system. The reduced description is given by the set of PDEs for the reduced composition variables, in which the terms arising can be evaluated on the ILDM. On the boundaries, only the reduced composition needs to be provided. When the full composition on the boundaries is on the low-dimensional manifold, the boundary conditions for the reduced composition can be taken directly from the corresponding full composition at boundaries. For arbitrary full composition at the boundaries, a rigorous derivation of the boundary conditions for the reduced description is given by Lam [37]. For the Maas–Pope approach, we validate its fundamental assumption: that there is a balance between the transport processes and chemical reactions in the fast subspace. We show that even though the Maas–Pope approach makes no attempt to represent the composition departure from the ILDM (by neglecting the molecular diffusion effect on the compositions), it does incorporate the transport-chemistry coupling in the dynamics of the reduced system. For the 'close-parallel' approach, we demonstrate its use for the ILDM method to incorporate the transport-chemistry coupling. In the ILDM context, this approach assumes the compositions in an inhomogeneous reactive flow are on a low-dimensional manifold which is close to and parallel to the ILDM. We demonstrate the implied balance between the transport processes and chemical reactions in the normal subspace of the ILDM.

For the ASIM approach, by studying reaction–diffusion systems, we clarify the underlying assumptions and the applicability of the ASIM approach. In the regime where the fast chemical time scale is much smaller than the diffusion time scale, the correct balance in the fast subspace is between the transport processes and reaction (as assumed in the Maas–Pope approach). An improved set of PDEs are then proposed. The applicability of the ASIM in the regime where the convection and diffusion time scales overlap with the fast chemical time scales is examined. It is shown that the transient process in the fast subspace is not negligible compared to other processes as it is assumed to be in the ASIM approach. The ASIM approach is different from the Maas–Pope approach and the 'close-parallel' approach in the sense that it makes no clear distinction between the reduced compositions and unrepresented compositions and the formulation of the reduced description is given by the set of PDEs supplemented by the differential algebraic equations. The application of the ASIM approach in general reactive flows are computationally expensive. In this study, in the regime where the fast chemical time scale is much smaller than the transport time scale, we proposed a simplification for the ASIM approach so that explicit governing PDEs are formulated for the reduced composition.

For the reaction–diffusion systems, as shown here, the Mass-Pope approach yields a consistent approximation for both the dynamics of the reduced composition z_1 and the unrepresented composition z_2, i.e. in each the error is $\mathcal{O}(\varepsilon)$. The error of $\mathcal{O}(\varepsilon)$ in z_2 is caused by neglecting the molecular diffusion effect on the compositions. In contrast, the 'close-parallel' assumption, the ASIM approach, and the modified ASIM approach incorporate the effects of molecular diffusion both on the composition and on the dynamics of the reduced composition. Consequently,

given the reduced composition, these approaches are more accurate in the composition prediction (with an error of $o(\varepsilon)$) compared with the Maas–Pope approach. As far as the dynamics of the reduced composition are concerned, the 'close-parallel' assumption, the ASIM approach, and the modified ASIM approach give the same evolution equation (to leading order) as the Maas–Pope approach. All the approaches are valid only when the fast chemical time scales are much smaller than the transport time scales. When the transport time scales are comparable to the fast chemical time scales, the accuracy of all these approaches decreases.

In the reduced description, all the approaches project physical processes locally back onto the chemistry-based manifold. We regard the 'close-parallel' assumption to be the best approach to use. It is simple, and it provides a continuous projection (unlike the Maas–Pope approach and the ASIM approach) if the manifold is sufficiently smooth. Both the Maas–Pope approach and the ASIM approach are based on the slow and fast invariant subspaces, which are locally identified in the composition space based on the local Jacobian matrix. Even though the Jacobian of the reaction rates varies continuously in the composition space, these invariant subspaces do not. Discontinuities occur when the n_r-th and $(n_r + 1)$-th eigenvalues form a complex conjugate pair or cross.

Acknowledgments

References

[1] Curran, H.J., Gaffuri, P., Pitz, W.J. and Westbrook, C.K., 2002, A comprehensive modeling study of iso-octane oxidation. *Combustion and Flame*, **129**, 253–280.
[2] Lu, T. and Law, C.K., 2005, A directed relation graph method for mechanism reduction. *Proceedings of the Combustion Institute*, **30**, 1333–1341.
[3] Pepiot, P. and Pitsch, H., 2005, Systematic reduction of large chemical mechanisms. Paper presented at the 4th Joint Meeting of the US Sections of the Combustion Institute, Philadelphia, PA, March 21–23.
[4] Valorani, M., Creta, F., Donato, F., Najm, H.N., and Goussis, D.A., 2006, Model simplification and diagnostics of hydrocarbon oxidation based on CSP. Paper presented at the 11th International Conference on Numerical Combustion, Granada, Spain, April 23–26.
[5] Pope, S.B., 1997, Computationally efficient implementation of combustion chemistry using *in situ* adaptive tabulation. *Combustion Theory and Modelling*, **1**, 41–63.
[6] Tonse, S.R., Moriarty, N.W., Brown, N.J. and Frenklach, M., 1999, PRISM: piecewise reusable implementation of solution mapping. an economical strategy for chemical kinetics. *Israel Journal of Chemistry*, **39**, 97–106.
[7] Bodenstein, M. and Lind, S.C., 1906, Geschwindigkeit der Bildung des Bromwasserstoffs aus seinen Elementen. *Zeitschrift fr Physikalische Chemie*, **57**, 168–175.
[8] Smooke, M.D. (Ed.), 1991. *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane–Air Flames*, Vol. 384 (Berlin: Springer).
[9] Chen, J-Y., 1988, A general procedure for constructing reduced reaction mechanisms with given independent relation. *Combustion Science and Technology*, **57**, 89–94.
[10] Ren, Z. and Pope, S.B., 2004, Entropy production and element conservation in the quasi-steady-state approximation. *Combustion and Flame*, **137**, 251–254.
[11] Keck, J.C. and Gillespie, D., 1971, Rate-controlled partial equilibrium method for treating reacting gas-mixtures. *Combustion and Flame*, **17**, 237–241.
[12] Keck, J.C., 1990, Rate-controlled constrained equilibrium theory of chemical reactions in complex systems. *Progress in Energy and Combustion Science*, **16**, 125–154.
[13] Tang, Q. and Pope, S.B., 2002, Implementation of combustion chemistry by *in situ* adaptive tabu lation of rate-controlled constrained equilibrium manifolds. *Proceedings of the Combustion Institute*, **29**, 1411–1417.
[14] Tang, Q. and Pope, S.B., 2004, A more accurate projection in the rate-controlled constrained-equilibrium method for dimension reduction of combustion chemistry. *Combustion Theory and Modelling*, **8**, 255–279.
[15] Gear, C.W., Kaper, T.J., Kevrekidis, I.G. and Zagaris, A., 2005, Projecting to a slow manifold: singularly perturbed systems and legacy codes. *SIAM Journal on Applied Dynamical Systems*, **4**, 711–732.
[16] Kaper, H.G. and Kaper, T.J., 2002, Asymptotic analysis of two reduction methods for systems of chemical reactions. *Physica D*, **165**, 66–93.
[17] Gorban, A.N. and Karlin, I.V., 2003, Method of invariant manifold for chemical kinetics. *Chemical Engineering Science*, **58**, 4751–4768.

[18] Gorban, A.N. and Karlin, I.V., 1994, Method of invariant manifolds and regularization of acoustic spectra. *Transport Theory and Statistical Physics*, **23**, 559–632.

[19] Gorban, A.N. and Karlin, I.V., 1992, Thermodynamic parameterization *Physica A*, **190**, 393–404.

[20] Roussel, M.R. and Fraser, S.J., 1993, Global analysis of enzyme inhibition kinetics. *Journal of Physical Chemistry*, **97**, 8316–8327.

[21] Maas, U. and Pope, S.B., 1992, Simplifying chemical kinetics: intrinsic low-dimensional manifolds in composition space. *Combustion and Flame*, **88**, 239–264.

[22] Maas, U. and Pope, S.B., 1992, Implementation of simplified chemical kinetics based on intrinsic low-dimensional manifolds. *Proceedings of the Combustion Institute*, **24**, 103–112.

[23] Maas, U. and Pope, S.B., 1994, Laminar flame calculations using simplified chemical kinetics based on intrinsic low-dimensional manifolds. *Proceedings of the Combustion Institute*, **25**, 1349–1356.

[24] Rhodes, C., Morari, M. and Wiggins, S., 1999, Identification of low order manifolds: validating the algorithm of Maas and Pope. *Chaos*, **9**, 108–123

[25] Pope, S.B. and Maas, U., 1993, Simplifying chemical kinetics: Trajectory-generated low-dimensional manifolds, FDA 93-11, Cornell University.

[26] Davis, M.J. and Skodje, R.T., 1999, Geometric investigation of low-dimensional manifolds in systems approaching equilibrium. *Journal of Chemical Physics*, **111**, 859–874.

[27] Skodje, R.T. and Davis, M.J., 2001, Geometrical simplification of complex kinetic system. *Journal of Physical Chemistry A*, **105**, 10356–10365.

[28] Ren, Z. and Pope, S.B., 2006, The geometry of reaction trajectories and attracting manifolds in composition space. *Combustion Theory and Modelling*, **10**, 361–388.

[29] Ren, Z. and Pope, S.B., 2005, Species reconstruction using pre-image curves. *Proceedings of the Combustion Institute*, **30**, 1293–1300.

[30] Ren, Z., Pope, S.B., Vladimirsky, A. and Guckenheimer, J.M., 2006, The invariant constrained equilibrium edge preimage curve method for the dimension reduction of chemical kinetics. *Journal of Chemical Physics*, **124**, Art. no. 114111.

[31] Ren, Z., Pope, S.B., Vladimirsky, A. and Guckenheimer, J.M., 2007, Application of the ICE-PIC method for the dimension reduction of chemical kinetics coupled with transport. *Proceedings of the Combustion Institute*, **31**, 473–481.

[32] Ren, Z. and Pope, S.B., 2006, The use of slow manifolds in reactive flows. *Combustion and Flame*, **147**, 243–261.

[33] Lam, S.H., 1993, Using CSP to understand complex chemical kinetics. *Combustion Science and Technology*, **89**, 375–404.

[34] Lam, S.H. and Goussis, D.A., 1994, The CSP method for simplifying kinetics. *International Journal of Chemical Kinetics*, **26**, 461–486.

[35] Lu, T., Ju, Y. and Law, C.K., 2001, Complex CSP for chemistry reduction and analysis. *Combustion and Flame*, **126**, 1445–1455.

[36] Lam, S.H., 1992, The effect of fast chemical reactions on mass diffusion. Report T1953-MAE, Princeton University.

[37] Lam, S.H., 2006, Reduced chemistry-diffusion coupling. Paper presented at the 11th International Conference on Numerical Combustion, Granada, Spain, April 23-26. Also, Combustion Science and Technology, in press.

[38] Davis, M.J., 2006, Low-dimensional manifolds in reaction–diffusion equations. 1. Fundamental aspects. *Journal of Physical Chemistry A*, **110**, 5235–5256.

[39] Davis, M.J., 2006, Low-dimensional manifolds in reaction–diffusion equations. 2. Numerical analysis and method development. *Journal of Physical Chemistry A*, **110**, 5257–5272.

[40] Hadjinicolaou, M. and Goussis, D.A., 1999, Asymptotic solution of stiff PDEs with the CSP method: the reaction diffusion equation. *SIAM Journal on Scientifc Computing*, **20**, 781–810.

[41] Goussis, D.A., Valorani, M., Creta, F. and Najm, H.N., 2005, Reactive and reactive-diffusive time scales in stiff reaction–diffusion systems. *Progress in Computational Fluid Dynamics*, **5**, 316–326.

[42] Goussis, D.A. and Valorani, M., 2006, An efficient iterative algorithm for the approximation of the fast and slow dynamics of stiff systems. *Journal of Computational Physics*, **214**, 316–346.

[43] Valorani, M., Goussis, D.A., Creta, F. and Najm, H.N., 2005, Higher order corrections in the approximation of low-dimensional manifolds and the construction of simplified problems with the CSP. *Journal of Computational Physics*, **209**, 754–786.

[44] Yannacopoulos, A.N., Tomlin, A.S., Brindley, J., Merkin, J.H. and Pilling, M.J., 1995, The use of algebraic sets in the approximation of inertial manifolds and lumping in chemical kinetic systems. *Physica D*, **83**, 421–449.

[45] Singh, S., Powers, J.M. and Paolucci, S., 2002, On slow manifolds of chemically reactive systems. *Journal of Chemical Physics*, **117**, 1482–1496.

[46] Bongers, H., van Oijen, J.A. and de Goey, L.P.H., 2002, Intrinsic low-dimensional manifold method extended with diffusion. *Proceedings of the Combustion Institute*, **29**, 1371–1378.

[47] van Oijen, J.A. and de Goey, L.P.H., 2000, Modelling of premixed laminar flames using flamelet-generated manifolds. *Combustion Science and Technology*, **161**, 113–137.

[48] Girimaji, S.S. and Brau, C., 2002, Composition-space behavior of diffusion-reaction systems. *Theoretical and Computational Fluid Dynamics*, **17**, 171–188.

[49] Pope, S.B., 2004, Accessed compositions in turbulent reactive flows. *Flow, Turbulence and Combustion*, **72**(2–4), 219–243.