

Projective Space Method for Slow Invariant Manifolds of Reactive Systems

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Abstract—One dimensional slow invariant manifolds for dynamical systems arising from modeling isothermal, spatially homogeneous, closed reactive systems are calculated. The technique is based on global analysis of the composition space of the reactive system. The identification of all the system’s finite and infinite critical points plays a major role in calculating the system’s slow invariant manifold. The slow invariant manifolds are constructed by calculating heteroclinic orbits which connect appropriate critical points to the unique stable physical equilibrium point. The technique is applied to small and large detailed kinetics mechanisms.

I. INTRODUCTION

In detailed kinetics models, the presence of a wide range of scales induces a large computational cost when calculations are fully resolved. Because direct numerical simulation (DNS) is not feasible for many practical flows, the main challenge in modeling is to simplify the problem without significant loss of accuracy. One of the major approaches employs lower dimensional manifolds, which are based on a reduction in the composition space dimension.

For spatially homogeneous systems, reaction dynamics are described by a set of ordinary differential equations (ODEs). The solutions of this set of ODEs are represented by trajectories in the species composition space. Each trajectory represents the reactive system’s evolution with time for a specific initial condition. The evolved trajectories seem to quickly be attracted to a special trajectory and stay exponentially close to it until they reach equilibrium in infinite time [1]. The reactive system’s slow modes are the only active ones on this special trajectory. Thus, identifying this slow invariant manifold (SIM) for a reactive system will make it possible to reduce the computational cost by filtering the system’s fast modes. For each reactive system there are SIMs of different dimensions; this work focuses on the construction of only one-dimensional (1-D) SIMs.

Here, 1-D SIMs for unsteady spatially homogeneous mixtures of calorically imperfect ideal gases described by detailed kinetics are calculated. While such construction has been done for small two-dimensional systems [2], the present work offers the first construction of SIMs for realistic detailed kinetics systems of dimension greater than 2-D. The SIM is constructed by a global analysis over the entire composition space. By finding all equilibria and connecting them via heteroclinic orbits, it is easy to identify the system’s actual SIM. Zel’dovich nitric oxide system and a detailed hydrogen-air kinetic system

will be the mechanisms we focus in this paper. The second system is of interest since it is intrinsic to common combustion applications, included in the combustion of all hydrocarbons, and is well-known and widely accepted.

In comparison to other dimension reduction techniques that obtain approximate SIMs, such as the intrinsic low-dimensional manifold (ILDM) [3], the computational singular perturbation (CSP) [4], the invariant constrained equilibrium edge preimage curve method (ICE-PIC) [5], minimal entropy production trajectories (MEPT) [6], and iterative methods [7], the technique presented here identifies the actual SIMs. In the first section, the governing ODEs for closed, isothermal, reactive system are presented. This is followed by a reduction of the ODEs into a system of differential algebraic equations (DAEs) which describes the system’s evolution within the reduced composition space. Following a brief description of how we identify and examine all the system’s finite and infinite equilibria, the numerical method to construct the SIMs is presented. Once the difficult task of identifying all of the equilibria is complete, it is seen that constructing the actual SIMs is easy and computationally efficient. The main results of this study are the construction of the 1-D SIMs for realistic detailed kinetics isothermal reactive systems.

II. MATHEMATICAL MODEL

A. Governing Equations

We consider a mixture of total mass M confined in a volume V containing N gas phase species composed of L atomic elements that undergo J reversible reactions. The evolution of the species with time t is obtained from the following set of ODEs:

$$\frac{dn_i}{dt} = V \sum_{j=1}^J \nu_{ij} r_j, \quad i = 1, \dots, N. \quad (1)$$

Here, the dependent variables are the species’ number of moles n_i . Also, for the j^{th} reaction r_j and ν_{ij} are, respectively, the reaction rate given by the law of mass action and the net stoichiometric matrix. In general, ν_{ij} is a non-square matrix of dimensions $N \times J$, and it is of rank $R \leq (N - L)$; commonly $R = (N - L)$.

B. Reduced System

Equation (1), defines an N -dimensional composition space. The dimensionality of this space is reduced to R

as a consequence of the conservation of elements, and any additional constraints that can possibly arise. The elements constraints are enforced by

$$\sum_{i=1}^N \phi_{li} n_i = \sum_{i=1}^N \phi_{li} n_i^*, \quad l = 1, \dots, L, \quad (2)$$

where ϕ_{li} is the element index matrix and quantities with superscript (*) are at the initial state. Here, the n_i 's are linearly dependent composition variables, which implies that (2) is underconstrained and solutions of the following form

$$n_i = n_i^* + M \sum_{k=1}^R \mathcal{D}_{ik} z_k, \quad i = 1, \dots, N, \quad (3)$$

can be found. Here, z_k is a reduced composition variable, which physically represents the number of moles of species k in M . \mathcal{D}_{ik} is a dimensionless constant matrix of size $N \times R$ and has full rank R . Each column vector of \mathcal{D}_{ik} is linearly independent of the remaining column vectors. However, \mathcal{D}_{ik} is not unique, and it can be constructed in several ways.

As a result, the reactive system described by (1) is recast as an autonomous standard dynamical system of the form

$$\frac{dz}{dt} = \mathbf{f}(\mathbf{z}), \quad \mathbf{z} \in \mathbb{R}^R, \quad (4)$$

where \mathbf{f} is a set of R non-linear coupled polynomials of degree d connected with a given reaction mechanism. From a geometric point of view, \mathbf{z} is a vector in the Euclidian composition space \mathbb{R}^R . Thus, reactive system solutions are trajectories that move on the reduced composition space \mathbb{R}^R , which is a subspace of the full composition space \mathbb{R}^N . Full details are given by [8].

III. METHODOLOGY

A. Equilibria

The proposed construction method of a reactive system's SIM is based on identifying all the equilibria of (4). In general, the set of equilibria of such a function is complex, and contains finite and infinite equilibria [9]. Moreover, the equilibria can be positive dimensional continua [10]. In this work, only the system's real isolated finite and infinite equilibria are considered.

To obtain the dynamical system's finite equilibria, we find all the \mathbf{z}^e that satisfy $\mathbf{f}(\mathbf{z}^e) = \mathbf{0}$. One of the finite equilibria is of special interest; it is the unique critical point located inside the physically accessible domain [11].

The next step is to identify the system's infinite equilibria. To do so, the projective space method is employed [10]. This technique maps the infinite critical points onto the finite domain, and is realized by the following relations

$$Z_k = \frac{1}{z_k}, \quad k \in \{1, \dots, R\}, \quad (5)$$

$$Z_i = \frac{z_i}{z_k}, \quad i \neq k, \quad i = 1, \dots, R, \quad (6)$$

where z_k is any arbitrarily selected dependent variable, and \mathbf{Z} are the state variables in the projective space.

By employing the projective space mapping, the original dynamical system is recast in the following form

$$\frac{d\mathbf{Z}}{d\tau} = \mathbf{F}(\mathbf{Z}), \quad \mathbf{Z} \in \mathbb{R}^R, \quad (7)$$

where \mathbf{F} is a set of R non-linear functions that correspond to the non-linear functions \mathbf{f} in the projective space, and τ is the transformed time in the projective space which is related to t by the following relation, $dt/d\tau = (Z_k)^{d-1}$. The finite equilibria of the resulting dynamical system, \mathbf{Z}^e that satisfy $\mathbf{F}(\mathbf{Z}^e) = \mathbf{0}$, represent the infinite equilibria of the original system (4).

Next, the dynamic behavior of the system in the neighborhood of each finite and infinite equilibrium is investigated by employing standard linearization techniques. The stability of each critical point is determined by examining the eigenvalue spectrum of its local Jacobian and the corresponding eigenvectors. At the physical equilibrium point, the eigenvector associated with the smallest eigenvalue represents the systems slowest mode.

B. Construction Method

We start the process of SIM construction by generating a heteroclinic orbit from the finite equilibrium which has the least positive eigenvalue. Then, we check whether the generated orbit approaches the the physical equilibrium point in the direction of its slowest mode. After that, another orbit is generated starting from the finite equilibrium which has the second lowest positive eigenvalue. If the two generated orbits approach the the physical equilibrium point in the direction of its slowest mode, then these are the SIM's two branches. Otherwise, we generate a new heteroclinic orbit from the finite equilibrium which has the third lowest eigenvalue, and so on. After checking all finite equilibria, we follow the same procedure with the infinite equilibria. During this procedure, any time we obtain two heteroclinic orbits that approach the physical equilibrium point in the direction of its slowest mode, there is no need to consider the remaining equilibria.

C. Computational Method

The kinetic rates and the thermodynamic properties are calculated using the public domain edition of the Chemkin package [12]. The typical computational time to construct a 1-D SIM is less than one minute on a 2.16 GHz MacPro machine. All the calculations have been performed to high precision. However, all the listed results are rounded to three significant digits. Integers indicate that the reported numbers are exact. Also, Bertini [13], a C-code based on homotopy continuation, is used to obtain the system's equilibria to any desired accuracy. Lastly, all trajectories are obtained by numerical integration of the species evolution equations using a computationally inexpensive explicit fourth-order Runge-Kutta scheme.

IV. RESULTS

A. Zel'dovich mechanism

In this section, the strategy to construct a 1-D SIM is illustrated using a simple but realistic reactive system;

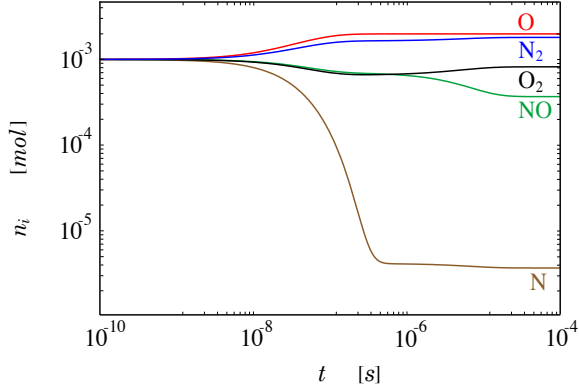


Fig. 1. The time evolution of species for the Zel'dovich model problem.

the Zel'dovich mechanism of nitric oxide formation. This mechanism contains $N = 5$ species, $L = 2$ elements, and $J = 2$ reversible reactions, and the kinetic data have been adopted from Baulch *et al.* [14]. A special case in which the system is isochoric will be considered, and the assigned mixture temperature and volume are $T = 4000 \text{ K}$ and $V = 10^3 \text{ cm}^3$, respectively. For convenience, the assigned initial number of moles of all species are $n_i^* = 10^{-3} \text{ mol}$, where $i = \{1, 2, 3, 4, 5\}$ corresponds to the species $\{NO, N, O, O_2, N_2\}$, respectively. The multi-scale nature of this system is clearly shown in Fig. 1, where the full dynamics of the evolution of the species are presented.

In this system, the total number of moles remain constant, as a consequence of the fact that the kinetics mechanism includes only bimolecular reactions. Consequently, one algebraic constraint, in addition to element conservation, exists in the system. Thus, this model problem is described in the $R = 2$ dimensional reactive composition space [8],

$$\frac{dz}{dt} = \dot{\mathbf{w}} \equiv \mathbf{f}(\mathbf{z}), \quad \{\mathbf{z}, \dot{\mathbf{w}}\} \in \mathbb{R}^R, \quad (8)$$

where

$$\dot{w}_k = \frac{1}{\rho} \sum_{j=1}^R \left[\left(\sum_{i=1}^N \mathcal{D}_{ik} \mathcal{D}_{ij} \right)^{-1} \left(\sum_{i=1}^N \mathcal{D}_{ij} \dot{\omega}_i \right) \right], \quad (9)$$

and $d = 2$.

By equilibrating the right hand side of (8) and using Bertini to obtain all \mathbf{z}^e that satisfy $\mathbf{f}(\mathbf{z}^e) = \mathbf{0}$, we find the following finite isolated equilibria,

$$\begin{aligned} R_1 &\equiv (\mathbf{z}^e) = (-1.78 \times 10^{-5}, -1.67 \times 10^{-2}) \text{ mol/g}, \\ R_2 &\equiv (\mathbf{z}^e) = (-4.20 \times 10^{-3}, -2.66 \times 10^{-5}) \text{ mol/g}, \\ R_3 &\equiv (\mathbf{z}^e) = (3.05 \times 10^{-3}, 2.94 \times 10^{-5}) \text{ mol/g}, \end{aligned}$$

where the rest of the species are recast using (3). It is clear that R_1 and R_2 are non-physical equilibria, while R_3 is the reactive systems unique physical equilibrium point.

The dynamical behavior analysis within the neighborhood of each critical point reveals that R_1 is a source, R_2 is saddle with one unstable mode, and R_3 is a sink.

In addition to the systems finite equilibria, (8) has three infinite equilibria. They are obtained using the projective space method, in which we select $k = 1$ arbitrarily. These equilibria are:

$$\begin{aligned} I_1 &\equiv (\mathbf{Z}^e) = (0, 0), \\ I_2 &\equiv (\mathbf{Z}^e) = (0, 1.01), \\ I_3 &\equiv (\mathbf{Z}^e) = (0, 2.60), \end{aligned}$$

The dynamical behavior analysis within the neighborhood of each critical point reveals that I_2 is a source, I_3 is a saddle with one positive eigenvalue, and I_1 is a non-hyperbolic critical point. Using the normal form theory [9], it is found that I_1 is a saddle-node, which consists of two hyperbolic sectors, one parabolic sector, and three separatrices. Only one of these separatrices is unstable.

Now, following our 1-D SIM construction procedure, these three points are ordered as follows: R_2, I_1, I_3 . So, starting from the unstable direction of R_2 , (8) are numerically integrated to generate a heteroclinic orbit. This orbit approaches R_3 along its slowest mode. So, the generated orbit represents the first branch of the 1-D SIM. Then, starting from the unstable direction of I_1 , another heteroclinic orbit is numerically generated. Also, this orbit approaches R_3 along its slowest mode. So, it represents the second and last branch of the reactive systems 1-D SIM. Subsequently, there is no need to check the third critical point, I_3 . In Fig. 2, part of the systems finite phase space and the SIM are presented. The attractiveness of the SIM is revealed by visually examining the relaxation of several trajectories onto it.

B. Detailed Hydrogen-Air Mechanism

In this section, the 1-D SIM for a detailed kinetics hydrogen-air reactive system is constructed using the previously discussed technique. The reaction mechanism used is extracted from Miller *et al.* [15], and consists of $J = 19$ reversible reactions that describe how $N = 9$ species composed of $L = 3$ elements react. The

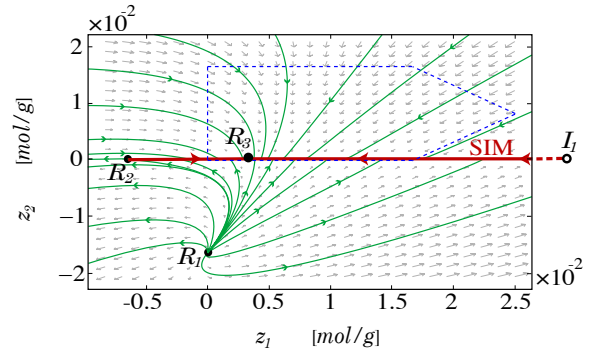


Fig. 2. A region of the finite phase space for the Zel'dovich mechanism. The solid dots represent finite critical points, the open circle represents an infinite critical point, the arrows indicate the flow direction, and the dashed simplex represents the physically accessible domain of the system. The SIM is illustrated as a thick line, the thin lines represent trajectories, and R_3 represents the system's physical equilibrium state.

stoichiometric hydrogen-air mixture is initially at $p = 10^7$ dyne/cm² and the chosen mixture temperature is $T = 1500$ K. The full dynamics of the species evolution is presented in Fig. 3. Here, the dependent variables are $\{z_{H_2}, z_{O_2}, z_H, z_O, z_{OH}, z_{H_2O}\}$, which correspond to $\{z_1, z_2, z_3, z_4, z_5, z_6\}$, respectively.

Using the procedure discussed earlier, 326 finite and infinite equilibria are found. One of these critical points represents the physical equilibrium state. This point is

$$R_{19} \equiv (\mathbf{z}^e) = (1.98 \times 10^{-6}, 9.00 \times 10^{-7}, 1.72 \times 10^{-9}, 2.67 \times 10^{-10}, 3.66 \times 10^{-7}, 1.44 \times 10^{-2}) \text{ mol/g.}$$

Then, the dynamical character of each of the real finite and infinite critical points is determined. It is found that among them there are only 14 critical points which have eigenvalue spectra that contain only one unstable direction. All of these 14 equilibria are finite. Finally by examining all trajectories that emanate from these 14 equilibria, only two of them are connected with R_{19} along its slowest mode via heteroclinic orbits. These two critical points are R_{74} and R_{79} . Fig. 4 shows a 3-D projection of the 1-D SIM embedded inside the 6-D reduced composition space. Since only the slow modes are present on the SIM, this 1-D manifold is the best description of the system's slowest dynamics.

V. CONCLUSION

Actual 1-D SIMs for closed, spatially homogenous, isothermal, reactive systems described by detailed kinetics are obtained. The construction method is based on a geometrical approach that relies upon finding and examining the dynamical behavior of all the system's critical points. It has been shown that the construction of the 1-D SIMs are algorithmically easy and computationally efficient. The resulting procedure provides a useful tool to significantly reduce the computational cost associated with modeling reactive systems.

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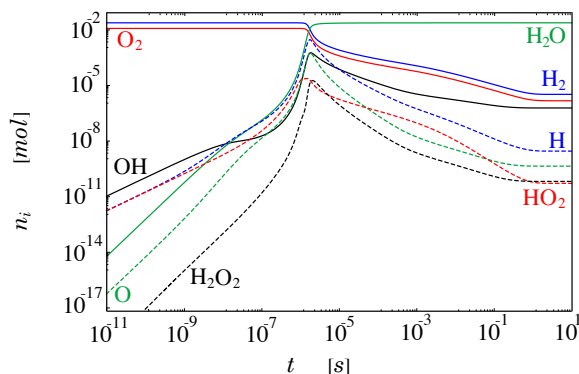


Fig. 3. The time evolution of species for the $H_2 - Air$ reactive system.

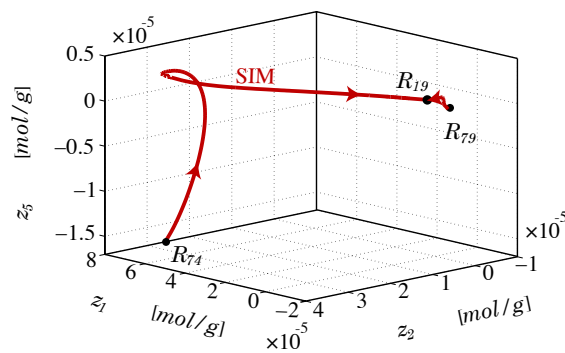


Fig. 4. The 1-D SIM for the detailed $H_2 - Air$ mechanism.

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