

# Diffusion Correction to Slow Invariant Manifolds in a Short Length Scale Limit

Joshua D. Mengers\*, Joseph M. Powers\*

\*University of Notre Dame, Aerospace and Mechanical Engineering, Notre Dame, IN, USA

**Abstract**—Slow Invariant Manifolds (SIM) are calculated for isothermal closed reaction-diffusion systems as a model reduction technique. Diffusion effects are examined using a Galerkin projection that rigorously accounts for the coupling of reaction and diffusion processes. This method reduces the infinite dimensional dynamical system by projecting it on a low dimensional approximate inertial manifold. A robust method of constructing a one-dimensional SIM by calculating equilibria and then integrating heteroclinic orbits is discussed. A diffusion-coupling of length and time scales is shown. Examples are demonstrated on a physical reaction mechanism.

## I. INTRODUCTION

Reactive flow problems display a disparity in physical scales, which manifests itself as stiffness in numerical computations. Reaction mechanisms induce multiple time scales, while diffusion couples these time scales to length scales. The full range of spatial and temporal scales must be resolved for a verifiable simulation. Model reduction offers an ability to reduce the range of scales while maintaining consistency with the physical model. The reviews of Griffiths [1] and Lu and Law [2] describe various model reduction techniques; however, most of the methods address only reaction mechanisms. Research that extends model reduction to systems with diffusion often only examines a limit of long length scales.

This research considers the extension of Slow Invariant Manifolds (SIM) to systems with diffusion in the limit of small length scales. The SIM is a unique trajectory of the dynamical system that efficiently describes the long time dynamics of the system's evolution. Davis and Skodje [3] and Al-Khateeb et al. [4] describe the calculation of a one-dimensional SIM by integrating a heteroclinic orbit between the system's physical and non-physical equilibrium points.

The SIM is extended to systems with diffusion by modeling spatial variations using a Galerkin projection. This reduces the governing partial differential equations (PDEs) into an approximate inertial manifold (AIM) system of ordinary differential equations (ODEs) in a technique described by Robinson [5]. A subset of the ODEs includes the spatially homogeneous system. These ODEs are then evaluated to identify the SIM.

## II. MODEL

We model a system of detailed reaction kinetics of  $N$  species reacting in  $J$  reactions with diffusion in one spatial dimension. The key assumptions in our model include: ideal gas, negligible advection, isochoric, and a

single constant mass diffusivity. Our governing species evolution equation is

$$\rho \frac{\partial Y_i}{\partial t} + \frac{\partial j_i^m}{\partial x} = M_i \dot{\omega}_i, \quad \text{for } i \in [1, N], \quad (1)$$

where  $Y_i \in \mathbb{R}^N$  is a vector of mass fractions,  $j_i^m \in \mathbb{R}^N$  is a vector of diffusive mass fluxes,  $\dot{\omega}_i \in \mathbb{R}^N$  is the reaction source term,  $M_i$  is the molecular mass of species  $i$ , and  $\rho$  is the constant density. The spatial domain,  $x \in [0, \ell]$ , has homogeneous Neumann boundary conditions at  $x = 0$  and  $x = \ell$ . The constitutive equation for the diffusive mass flux is

$$j_i^m = -\rho \mathcal{D} \frac{\partial Y_i}{\partial x}, \quad (2)$$

where  $\mathcal{D}$  is constant mass diffusivity.

This set of PDEs has  $L$  algebraic constraints, which can be integrated from (1) as a result of stoichiometric balance; this requires initial spatially homogeneous distributions of the constrained values that are not perturbed by the boundary conditions. Let us now use these constraints to transform variables into a set of reduced variables,

$$z_i \equiv \frac{Y_i}{M_i} \quad \text{for } i \in [1, N - L], \quad (3)$$

which are governed by the PDEs

$$\frac{\partial z_i}{\partial t} = \frac{\dot{\omega}_i}{\rho} + \mathcal{D} \frac{\partial^2 z_i}{\partial x^2}, \quad \text{for } i \in [1, N - L]. \quad (4)$$

We apply a Galerkin projection to (4), reducing it to an approximate inertial manifold (AIM) [5]. To accomplish this, we assume a spectral decomposition of

$$z_i(x, t) = \sum_{m=0}^{\infty} z_{i,m}(t) \phi_m(x), \quad \text{for } i \in [1, N - L], \quad (5)$$

where  $z_{i,m}(t)$  is the  $m^{\text{th}}$  time-dependent amplitude associated with species  $i$ , and  $\phi_m(x)$  are the corresponding basis functions. Notice that this projection is only in the reduced variables; the algebraic constraints, which remain constant in space, govern the evolution of the remaining variables. We choose  $\phi_m$  as the eigenfunctions of the diffusion operator,  $\partial^2/\partial x^2 \phi_m = \mu_m \phi_m$ , that match the boundary conditions, which gives us the complete basis

$$\phi_m = \cos\left(\frac{m\pi x}{\ell}\right), \quad \text{for } m \in [0, \infty). \quad (6)$$

These basis functions are orthogonal, and their eigenvalues are real, given by  $\mu_m = -(m\pi/\ell)^2$ . By substituting (5) into (4) and taking the inner product with each basis

function,  $\phi_m$ , we obtain an infinite system of ODEs for the evolution of the amplitudes

$$\frac{dz_{i,m}}{dt} = \frac{\langle \phi_m, \dot{\omega}_i(\sum_{n=0}^{\infty} z_{i,n}\phi_n) / \rho \rangle}{\langle \phi_m, \phi_m \rangle} - \mu_m \mathcal{D}z_{i,m},$$

for  $i \in [1, N-L]$  and  $m \in [0, \infty)$ . (7)

For our choice of basis functions,  $\langle \phi_m, \phi_m \rangle = \ell$  for  $m = 0$  and  $\langle \phi_m, \phi_m \rangle = \ell/2$  for  $m \geq 1$ . For small  $\ell$  and  $m \geq 1$ , the diffusion term dominates the reaction term, which makes the  $m \geq 1$  amplitudes decay rapidly.

We can reduce the infinite system of ODEs in (7) by truncating the system at a sufficiently large  $M$ ; this results in the system of  $(M+1)(N-L)$  ODEs,

$$\frac{dz_{i,m}}{dt} = \frac{\dot{\omega}_{i,m}}{\rho} - \frac{m^2 \pi^2 \mathcal{D}}{\ell^2} z_{i,m}, \quad \text{for } i \in [1, N-L]$$

and  $m \in [0, M]$ , (8)

where  $\dot{\omega}_{i,m}$  is the reaction term recovered from the inner product in (7). This term can be obtained analytically for isothermal reactions with our choice of simple basis functions. In some cases a truncation at  $M = 0$  is appropriate, in which case (7) reduces to a spatially homogeneous system,

$$\frac{dz_i}{dt} = \frac{\dot{\omega}_i}{\rho}, \quad \text{for } i \in [1, N-L]. \quad (9)$$

This is a reasonable truncation if there are no spatial variations in the initial conditions or in the limit where  $\ell \rightarrow 0$ . For the infinitesimal length scale case, the diffusion term will dominate the reaction term making diffusion infinitely fast; any spatial inhomogeneities will rapidly equilibrate, and we recover a spatially homogeneous system.

### III. REACTION MECHANISM

We evaluate the Zel'dovich mechanism of  $NO$  production identical to the system studied by Al-Khateeb et al. [4] (see Table I). This system has  $N = 5$  species and

TABLE I  
THE ZEL'DOVICH MECHANISM FOR  $NO$  PRODUCTION.

$j$	Reaction	$a_j$ [mol/(cm s K)]	$\beta_j$	$E_j$ [cal/mol]
1	$N + NO \rightleftharpoons N_2 + O$	$2.107 \times 10^{13}$	0.00	0.0
2	$N + O_2 \rightleftharpoons NO + O$	$5.839 \times 10^9$	1.01	6196

$J = 2$  reactions. The system is taken to be isothermal at  $T = 4000$  K, isochoric at  $V = 1000$  cm<sup>3</sup>, and has constant algebraic constraints which are uniform in space and correspond to each of the five species having initial conditions of  $10^{-3}$  mol. Conservation of atomic elements yields two algebraic constraints, while a third algebraic constraint, conservation of molecules, is obtained since the system is comprised of exclusively bimolecular reactions. This leaves  $L = 3$  species constraints that allow the system to be simplified to  $N - L = 2$  reduced variables; we choose to evaluate the specific moles of  $NO$  and  $N$  as  $z_1$  and  $z_2$ , respectively. The evolution of the three remaining species  $N_2$ ,  $O$ , and  $O_2$ , are coupled to the evolution of  $z_1$  and  $z_2$  by the algebraic constraints.

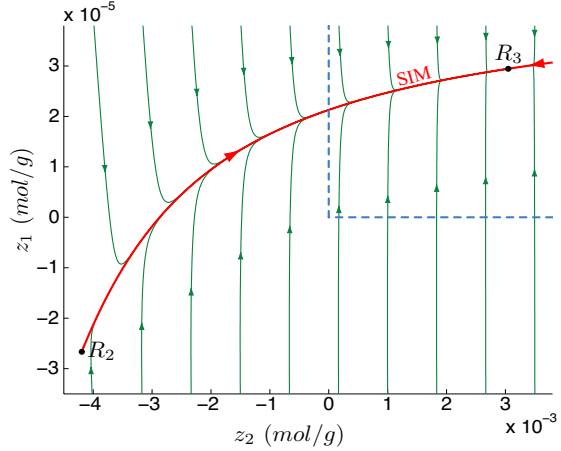


Fig. 1. One branch of the SIM in a spatially homogeneous system.

### IV. RESULTS AND DISCUSSION

We first examine the spatially homogeneous limit, corresponding to truncation at  $M = 0$ . To calculate the SIM, we find the system's equilibria via an algebraic method and use a local linear analysis to characterize these equilibria as sources, saddles, or sinks. The SIM is found by integrating a heteroclinic orbit from a non-physical saddle to the physical sink. Each branch of the SIM emerges from a non-physical saddle equilibria along its only unstable eigenvector and approaches the physical equilibrium sink along the eigenvector associated with its slowest stable, least negative, eigenvalue. One branch of the SIM is shown in Fig. 1 which connects the non-physical saddle,  $R_2$ , to the physical equilibrium,  $R_3$ . This figure also indicates the boundary of the physical domain, where all species concentrations are positive, represented as a blue dashed line. The green lines are various trajectories that display why the SIM is important as a reduction technique; as the trajectories evolve in time, the amplitudes associated with their fast time scales decay quickly, and the trajectories become exponentially close to the SIM in a finite amount of time.

We now include diffusion correction terms, which increase the number of eigenvalues in the local linear analysis by a factor of  $M + 1$ ,

$$\lambda_{i,m} = \lambda_i - \frac{m^2 \pi^2 \mathcal{D}}{\ell^2}, \quad \text{for } i \in [1, N-L],$$

and  $m \in [0, M]$ , (10)

where  $\lambda_i$  are the spatially homogeneous eigenvalues. Defining time scales as the reciprocal of these eigenvalues and truncating at  $M = 1$ , we plot the time scales of the first correction for diffusion in Fig. 2 as a function of length scale. These time scales are defined in the local linear region about the physical equilibrium,  $R_3$ . In the limit of  $\ell \rightarrow 0$ , diffusion becomes infinitely fast, all spatial variations will instantaneously diffuse, and the system behaves spatially homogeneous. For small finite length

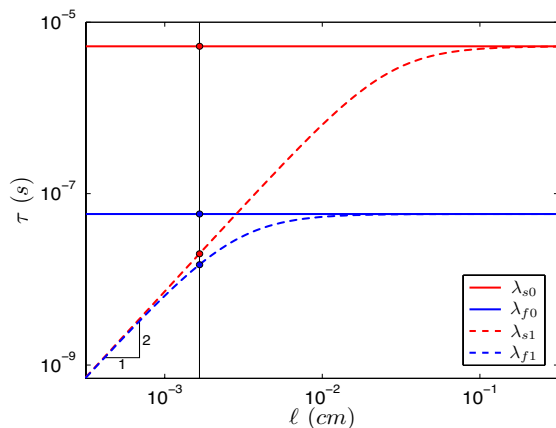


Fig. 2. Time scales of the  $M = 1$  reaction-diffusion system as a function of length scale.

scales the first correction for diffusion adequately resolves spatial variations; for systems with longer length scales the truncation at  $M = 1$  does not sufficiently resolve the dynamics. To fully resolve systems with long length, additional modes must be considered.

We now examine a diffusion correction in the short length scale limit for the Zel'dovich mechanism. In Fig. 3 we see a projection of the four dimensional phase space for this problem with a length scale  $\ell = 16.6 \mu\text{m}$ , where  $D = 14 \text{ cm}^2/\text{s}$  is approximated from an average of the ordinary multicomponent diffusion coefficients in the CHEMKIN TRANSPORT database [6]. The vertical axis shows the  $z_{1,1}$  concentration, while the horizontal axes show the two spatially homogeneous concentrations;  $z_{2,1}$  is not depicted in this figure, but decays in a similar fashion to  $z_{1,1}$  for our choice of  $\tau_D$ . The projection of this system into the  $z_{1,0}$ - $z_{2,0}$  plane is nearly identical to Fig. 1. Fig. 3 shows two equilibria:  $R_3$ , the physical equilibrium sink, and  $R_2$ , a non-physical saddle equilibrium with one positive eigenvalue. Both of these equilibria exist in the spatially homogeneous subspace of the system ( $z_{i,m} = 0$

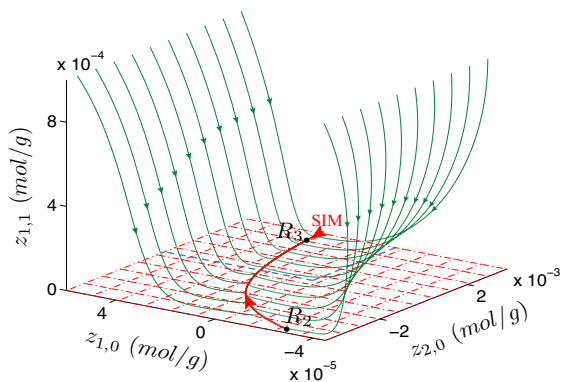


Fig. 3. SIM branch with one mode of diffusion correction.

for all  $i$  and  $m \geq 1$ ), and therefore are identical to  $R_2$  and  $R_3$  in Fig. 1. The additional eigenvalues at each equilibria are more negative than their analogous spatially homogeneous eigenvalues; therefore, for this length scale the branch of the SIM between  $R_2$  and  $R_3$  remains in the spatially homogeneous subspace of the system and is the same spatially homogeneous SIM shown in Fig. 1.

## V. CONCLUSIONS

We have successfully identified a diffusion-corrected SIM for the limit of short length scales. When  $\ell$  is below a critical length scale where the diffusion has a time scale that is the same order as the slowest reaction time scale, the effects of diffusion on a reactive system are minimal. In this limit the SIM remains spatially homogeneous. When lengths are at or above this critical length, diffusion plays a more important role. Our choice of  $\ell$  shorter than the critical length scale allowed us to maintain spatial resolution with a truncation at  $M = 1$ . For large  $\ell$ , the fundamental modes are dominated by reaction, and in these modes diffusion evolves on slower scales than reaction. To fully resolve the system in this case, additional modes must be included until the highest frequency mode is diffusion-dominant.

This technique also provides a framework for future research to evaluate how to best account for coupling of reaction and diffusion processes. It provides a good basis for examining the amount of this coupling, by identifying the diffusion-modulation of reaction eigenvalues. The method also has the ability to identify the slow dynamics of a reaction-diffusion system. When identified, the slow dynamics provide an ideal basis for reduction. This technique can be extended to capture a larger number of spatial modes, allowing this method to be applied to globally analyze systems of longer characteristic lengths.

## ACKNOWLEDGMENT

The authors recognize the support of the National Science Foundation (NSF) under Grant No. CBET-0650843. J. D. Mengers also recognizes the support from the University of Notre Dame Department of Applied and Computational Mathematics and Statistics fellowship.

## REFERENCES

- [1] Griffith, J. F., "Reduced kinetic-models and their application to practical combustion systems," *Progress in Energy and Combustion Science*, Vol. 21, No. 1, 1995, pp. 25-107.
- [2] Lu, T. F. and Law, C. K., "Toward accommodating realistic fuel chemistry in large-scale computations," *Progress in Energy and Combustion Science*, Vol. 35, No. 2, 2009, pp. 192-215.
- [3] Davis, M. J. and Skodje, R. T., "Geometric investigation of low-dimensional manifolds in systems approaching equilibrium," *Journal of Chemical Physics*, Vol. 111, No. 3, 1999, pp. 859-874.
- [4] Al-Khateeb, A. N., Powers, J. M., Paolucci, S., Sommes, A. J., Diller, J. A., Hauenstein, J. D., and Mengers, J. D., "One-dimensional manifolds for spatially homogenous systems," *Journal of Chemical Physics*, Vol. 131, No. 2, 2009, pp. 024118.
- [5] Robinson, J., *Infinite-Dimensional Dynamical Systems: From Basic Concepts to Actual Calculations*, Cambridge University Press, Cambridge, U.K., 2001, pp. 197-198, 371.
- [6] Kee, R. J., Dixon, L. G., Warnatz, J., Coltrin, M. E., and Miller, J. A., "A Fortran computer code package for the evaluation of gas-phase multicomponent transport properties," Report No. SAND86-8246, Sandia National Laboratories, 1991.