**Proceedings of the** 

### Fourth International Workshop on Model Reduction in Reacting Flows

San Francisco, CA, USA June 29-21, 2013 www.modelreduction.net



#### **Location**

Marriott Marquis San Francisco Hotel 55 Fourth Street San Francisco, CA 94103, USA +1-800-228-9290 www.marriott.com/hotels/travel/sfodt-san-francisco-marriott



#### **Scientific Committee**

Dmitris A. Goussis	National Technical University of Athens, Greece
Ulrich Maas	Karlsruhe Institute of Technology, Germany
Fabian Mauss	Brandenburg University of Technology, Germany
Habib N. Najm	Sandia National Laboratories, USA
Samuel Paolucci	University of Notre Dame, USA
Stephen B. Pope	Cornell University, USA
Joseph M. Powers	University of Notre Dame, USA
Mauro Valorani	Sapienza University of Rome, Italy

### **Technical Program**

The workshop 3-day agenda is given below, followed by the extended abstracts, arranged in the same chronological order.

Wednesday, June 19, 2013						
08:30 am	Breakfast Breakfast					
08:50	Welcome					
Session I — Chair: T. Lu						
09:00	Model Reductions with Special CSP Data — S.H. Lam					
09:30	Low-Dimensional Manifolds in Direct Numerical Simulations of Autoigniting Mixing					
	Layers — J. van Oijen, U. Goktolga, P. de Goey					
10:00	Uncertainties in Rate Constants of Important Reactions for Propene Oxidation -					
	S. Burke, H. Curran					
10:30	Break					
11:00	The Slowness of Invariant Manifolds Constructed by Connection of Heteroclinic Orbits					
11.00	— J. Powers, S. Paolucci, J. Mengers					
11:30	Dynamical Structures in Stochastic Chemical Reaction Systems — X. Han, H. Najm					
12:00	Characterizing Reduced-Order Manifolds by Finite-Time Lyapunov Analysis —					
	M. Maggia, K. Mease					
12:30	Lunch					
12:30	Lunch Session II — Chair: H. Curran					
12:30 02:00 pm	Session II — Chair: H. Curran           Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —					
12:30 02:00 pm	Lunch         Session II — Chair: H. Curran         Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —         L. Tosatto, Y. Marzouk					
12:30 02:00 pm 02:30	Lunch         Session II — Chair: H. Curran         Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —         L. Tosatto, Y. Marzouk         A Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa-					
12:30 02:00 pm 02:30	Lunch         Session II — Chair: H. Curran         Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —         L. Tosatto, Y. Marzouk         A Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa-         tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. Pope					
12:30 02:00 pm 02:30 03:00	Lunch         Session II — Chair: H. Curran         Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —         L. Tosatto, Y. Marzouk         A Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementation of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. Pope         A Boundary Value View on the Reverse Trajectory-Based Optimization Approach for					
12:30         02:00 pm         02:30         03:00	Lunch         Session II — Chair: H. Curran         Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —         L. Tosatto, Y. Marzouk         A Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa-         tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. Pope         A Boundary Value View on the Reverse Trajectory-Based Optimization Approach for         Kinetic Model Reduction — D. Lebiedz, J. Unger					
12:30 02:00 pm 02:30 03:00 03:30	Lunch         Session II — Chair: H. Curran         Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —         L. Tosatto, Y. Marzouk         A Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa-         tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. Pope         A Boundary Value View on the Reverse Trajectory-Based Optimization Approach for         Kinetic Model Reduction — D. Lebiedz, J. Unger         Break					
12:30         02:00 pm         02:30         03:00         03:30         04:00	Lunch         Session II — Chair: H. Curran         Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains —         L. Tosatto, Y. Marzouk         A Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa-         tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. Pope         A Boundary Value View on the Reverse Trajectory-Based Optimization Approach for         Kinetic Model Reduction — D. Lebiedz, J. Unger         Break         Reduced Kinetic Mechanism of a Selective Non-Catalytic Process with Urea as Reduc-					
12:30         02:00 pm         02:30         03:00         03:30         04:00	LunchSession II — Chair: H. CurranSimplifying Chemical Kinetic Systems under Uncertainty using Markov Chains — L. Tosatto, Y. MarzoukA Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa- tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. PopeA Boundary Value View on the Reverse Trajectory-Based Optimization Approach for Kinetic Model Reduction — D. Lebiedz, J. UngerBreakReduced Kinetic Mechanism of a Selective Non-Catalytic Process with Urea as Reduc- ing Agent — D. Vasquez, A. Luz Villa, F. Bustamante, C. Tobon					
12:30         02:00 pm         02:30         03:00         03:30         04:30	LunchSession II — Chair: H. CurranSimplifying Chemical Kinetic Systems under Uncertainty using Markov Chains — L. Tosatto, Y. MarzoukA Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa- tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. PopeA Boundary Value View on the Reverse Trajectory-Based Optimization Approach for Kinetic Model Reduction — D. Lebiedz, J. UngerBreakReduced Kinetic Mechanism of a Selective Non-Catalytic Process with Urea as Reduc- ing Agent — D. Vasquez, A. Luz Villa, F. Bustamante, C. TobonMechanism Reduction as a Preconditioning Strategy for Integrating Large Chemical Ki-					
12:30         02:00 pm         02:30         03:00         03:30         04:30	LunchSession II — Chair: H. CurranSimplifying Chemical Kinetic Systems under Uncertainty using Markov Chains — L. Tosatto, Y. MarzoukA Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa- tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. PopeA Boundary Value View on the Reverse Trajectory-Based Optimization Approach for Kinetic Model Reduction — D. Lebiedz, J. UngerBreakReduced Kinetic Mechanism of a Selective Non-Catalytic Process with Urea as Reduc- ing Agent — D. Vasquez, A. Luz Villa, F. Bustamante, C. TobonMechanism Reduction as a Preconditioning Strategy for Integrating Large Chemical Ki- netic Systems — M. McNenly, R. Whitesides, D. Flowers					
12:30         02:00 pm         02:30         03:00         03:30         04:00         04:30         05:00	LunchSession II — Chair: H. CurranSimplifying Chemical Kinetic Systems under Uncertainty using Markov Chains — L. Tosatto, Y. MarzoukA Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementa- tion of Detailed Combustion Chemistry — P. Pepiot, Y. Liang, V. Hiremath, S. PopeA Boundary Value View on the Reverse Trajectory-Based Optimization Approach for Kinetic Model Reduction — D. Lebiedz, J. UngerBreakReduced Kinetic Mechanism of a Selective Non-Catalytic Process with Urea as Reduc- ing Agent — D. Vasquez, A. Luz Villa, F. Bustamante, C. TobonMechanism Reduction as a Preconditioning Strategy for Integrating Large Chemical Ki- netic Systems — M. McNenly, R. Whitesides, D. FlowersPinning Reaction Fronts in a Windy Vortex Array — J. Mahoney, K. Mitchell					

Thursday, June 20, 2013						
08:00 am	08:00 am Breakfast					
Session III — Chair: P. Pepiot						
08:30	A Manifold Learning Approach to Model Reduction in Combustion - E. Chiavazzo,					
	C. Gear, B. Sonday, I. Kevrekidis					
09:00	Chemical Reductions Do Not Necessarily Lead to Computational Reductions -					
	T. Grenga, S. Paolucci, M. Valorani					
09:30	Relaxation Redistribution Method for Model Reduction — M. Kooshkbaghi,					
	C. Frouzakis, E. Chiavazzo, I. Karlin, K. Boulouchos					
10:00	Hydrogen/Air Auto-ignition: Algorithmic Identification of QSSA and PEA -					
	P. Kourdis, D. Goussis					
10:30	Break					
11:00	Active Subspace Identification in Surrogate Modeling - T. Russi, A. Packard,					
	M. Frenklach					
11:30	Global Sensitivity Analysis with Small Sample Sizes — M. Davis, W. Liu					
12:00	A Kinetic Model for Limit Phenomena Prediction Based on Bifurcation Analysis -					
	R. Shan, T. Lu					
12:30	Lunch					
Session IV — Chair: Y. Marzouk						
01:30 pm	Chemistry Guided Reduction of a Multicomponent Reaction Mechanism — L. Seidel,					
	C. Klauer, X. Wang, F. Mauss					
02:00	The GNAT Nonlinear Model-Reduction Method with Application to Large-Scale Tur-					
	bulent Flows — K. Carlberg, C. Farhat, J. Cortial, D. Amsallem					
02:30	Break					
03:00	Challenges for Mechanism Reduction — W. Pitz					
03:30	Fast Solver Techniques for Algebraic Equations Resulting from the Quasi Steady State					
	Approximation — F. Mauss					
04:00	Adjourn					

Friday, June 21, 2013					
08:00 am	08:00 am Breakfast				
Session V — Chair: E. Chiavazzo					
08:30	A Tangential Stretching Rate Index to Analyze Ignition Phenomena — M. Valorani,				
	S. Paolucci, E. Martelli, T. Grenga				
09:00	Reduced Basis Model Reduction for Nonlinear Evolution Equations based on Empirical				
	Operator Interpolation — M. Drohmann, B. Haasdonk, M. Ohlberger				
09:30	Challenges of Reduction for Open Systems — J. Powers, J. Mengers				
10:00	Analysis of Transient Processes in the Context of REDIM - U. Maas, V. Bykov,				
	A. Neagos				
10:30	Break				
11:00	Progress-Variable-Free State-Space Parameterizations for Premixed Combustion -				
	M. Ayoobi, I. Schoegl				
11:30	Analysis and Reduction of Chemical Models under Uncertainty — H. Najm, R. Berry,				
	B. Debusschere				
12:00	Adjourn				

### Model Reductions with Special CSP Data

S. H. Lam\*

\*Princeton University, MAE Department, Princeton, N.J. 08544, U.S.A.

Abstract-Certain reaction-specific CSP data are shown to be especially useful for model reductions.

#### I. STATEMENT OF THE PROBLEM

Consider the following general initial-value problem:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}; \epsilon), \quad \mathbf{y}(t=0) = \tilde{\mathbf{y}}, \tag{1}$$

where both y and g are N-dimensional column vectors, the components of  $\mathbf{g}(\mathbf{y}; \epsilon)$  are given algebraic functions of y, and  $\epsilon$  is a small dimensionless parameter. The y initial value is denoted by  $\tilde{\mathbf{y}}$  and is arbitrary. We are interested in the small  $\epsilon$  case when (1) is known to be *stiff*. We shall show that for general chemical kinetics problems certain reaction-specific data are most useful for doing CSP model reductions, yielding results that are very easy to interpret.

For chemical kinetics problems,  $g(y; \epsilon)$  is usually given in the following form:

$$\mathbf{g}(\mathbf{y};\epsilon) = \sum_{r=1}^{R} \boldsymbol{\alpha}_{r} \Omega^{r}(\mathbf{y};k_{r}), \qquad (2)$$

where the  $\alpha_r$ 's are N-dimensional column vectors, and R is the total number of chemical reactions in the reaction system. The physical dimensions of the elements of  $\alpha_r$ are the same as that of the corresponding elements of y, while the physical dimensions of all the  $\Omega^r(\mathbf{y}; k_r)$ 's are reciprocal time. For each of the r-th reaction, the elements of  $\alpha_r$  are proportional to the *stoichiometric coefficients*,  $\Omega^r(\mathbf{y}; k_r)$  is the *net reaction rate*, and  $k_r$  is the kinetic rate parameter. Usually,  $\Omega^r(\mathbf{y}; k_r)$  is proportional to  $k_r$  and its y dependence is nonlinear. For most real world problems, the  $\alpha_r$ 's dependence on y, if any, is weak, and R is often much bigger than N—so many  $\alpha_r$ 's are linearly dependent. Equation (1) is stiff when M > 0 reactions are much faster than all others. The stiffness of (1) is symbolically represented by the dimensionless parameter  $\epsilon$  in  $\mathbf{g}(\mathbf{y}; \epsilon)$ . In the present paper, we exploit the fact that both  $\alpha_r$  and  $\Omega^r(\mathbf{y}; k_r)$  are reaction-specific entities which are chemically/physically meaningful to knowledgeable investigators.

#### II. THE CSP SIMPLIFIED REDUCED MODEL

When there are M linearly independent fast reactions, CSP [1], [2], [3], [4] introduces a dimensionless  $N \times N$ fast subspace projection matrix  $\mathcal{Q}^{fast}(M)$  as follows:

$$\mathcal{Q}^{fast}(M) \equiv \sum_{m=1}^{M} \mathbf{a}_m \mathbf{b}^m, \qquad (3)$$

where the  $a_m$ 's and the  $b^m$ 's are M pairs of the fast subspace's column and row basis vectors which are linearly independent and have been CSP-refined at least once. They are-by definition-orthonormal to each other:

$$\mathbf{b}^m \odot \mathbf{a}_{m'} = \delta_{m'}^m, \quad m, m' = 1, \dots, M, \tag{4}$$

where  $\odot$  denotes the inner product operator and  $\delta^m_{m'}$  denotes the Kronecker Delta.

CSP provides iterative refinement procedures to find good quality  $\mathbf{a}_m$ 's and  $\mathbf{b}^m$ 's. The right-hand side of (1) is partitioned using a good quality  $\mathcal{Q}^{fast}(M)$ :

$$\mathbf{g}(\mathbf{y};\epsilon) = \mathbf{g}^{fast}(\mathbf{y};\epsilon) + \mathbf{g}^{slow}(\mathbf{y};\epsilon), \quad (5a)$$

$$\int_{ast}^{ast}(\mathbf{y};\epsilon) = O^{fast}(M) \odot \mathbf{g}(\mathbf{y};\epsilon), \quad (5b)$$

$$\mathbf{g}^{fast}(\mathbf{y};\epsilon) \equiv \mathcal{Q}^{fast}(M) \odot \mathbf{g}(\mathbf{y};\epsilon), \qquad (5b)$$

$$\mathbf{g}^{\text{aver}}(\mathbf{y};\epsilon) \equiv (\mathcal{I} - \mathcal{Q}^{\text{funct}}(M)) \odot \mathbf{g}(\mathbf{y};\epsilon), \quad (\mathbf{5c})$$

and  $\mathcal{I}$  is the identify matrix. CSP shows that  $\mathbf{g}^{fast}(\mathbf{y};\epsilon)$ is dominant only during the initial fast transient. After the fast transient is exhausted (assuming the system is stable),  $\mathbf{g}^{fast}(\mathbf{y};\epsilon)$  is  $O(\epsilon)$  in comparison to  $\mathbf{g}^{slow}(\mathbf{y};\epsilon)$ . The CSPderived simplified reduced model and initial condition for the original given problem in the slow epoch are then:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}^{slow}(\mathbf{y}; \epsilon) + O(\epsilon), \qquad (6)$$
$$\mathbf{g}^{fast}(\tilde{\mathbf{y}}^{slow}; \epsilon) = O(\epsilon), \quad \tilde{\mathbf{y}}^{slow} \equiv \mathbf{y}(t = O(\epsilon)).$$

Any solution  $\mathbf{y}(t)$  of the above non-stiff initial-value problem is guaranteed by CSP to automatically stay inside the slow subspace defined by:

$$\mathbf{g}^{fast}(\mathbf{y}(t);\epsilon) = O(\epsilon), \quad t > O(\epsilon).$$
 (7)

The quality of the CSP-derived simplified reduced modelas measured by the smallness of the  $O(\epsilon)$  terms above depends on the quality of the  $\mathbf{a}_m$ 's and  $\mathbf{b}^m$ 's in  $\mathcal{Q}^{fast}(M)$ .

#### III. REACTION-SPECIFIC CSP DATA

Equation (2) clearly associates the column vector  $\alpha_r$  with the r-th reaction. We now associate the following row vector  $\beta^r$  with the *r*-th reaction:

$$\boldsymbol{\beta}^{r} \equiv \tau_{r} \frac{\partial \Omega^{r}(\mathbf{y}; k_{r})}{\partial \mathbf{y}} = \boldsymbol{\beta}^{r}(\mathbf{y}), \quad r = 1, \dots, R, \qquad (8a)$$

where  $\tau_r$ , a most interesting **reaction-specific** entity with time as its physical dimension, is defined by:

$$\tau_r \equiv \frac{1}{\frac{\partial \Omega^r}{\partial \mathbf{y}} \odot \boldsymbol{\alpha}_r} = \tau_r(\mathbf{y}, k_r), \quad r = 1, \dots, R.$$
 (8b)

We next define  $\Gamma_{r'}^r(\mathbf{y})$ , a  $R \times R$  dimensionless matrix, by:

$$\Gamma_{r'}^{r}(\mathbf{y}) = \boldsymbol{\beta}^{r} \odot \boldsymbol{\alpha}_{r'}, \quad r, r' = 1, \dots R.$$
(9)

Equation (8b)—the formula for  $\tau_r(\mathbf{y}, k_r)$ —was obtained by setting the diagonal elements of  $\Gamma_{r'}^r(\mathbf{y})$  to unity. Note that in general  $\Gamma_{r'}^r(\mathbf{y}) \neq 0$  when  $r \neq r'$ , while  $\Gamma_r^r(\mathbf{y}) = 1$  is always honored by definition.

#### IV. EXPLOITATION OF THE CSP DATA

The  $\tau_r(\mathbf{y}, k_r)$  data is most interesting. If the *r*-th reaction is the only reaction in a reaction system, then it is easy to show that  $d\Omega^r/dt = \Omega^r/\tau_r$ . Thus  $|\tau_r(\mathbf{y}, k_r)|$ , with time as its physical dimension, is an *intrinsic time scale* of the *r*-th reaction. The smaller  $|\tau_r(\mathbf{y}, k_r)|$  is, the faster is the intrinsic speed of the *r*-th reaction. Thus we can, at any time *t*, order the *R* reactions in ascending order of their  $|\tau_r(\mathbf{y}(t), k_r)|$ 's so that r = 1 is intrinsically the fastest reaction of them all at that time. Ordering reactions this way is much easier (but less theoretically definitive) than ordering by eigenvalues—which physical dimensions are reciprocal time—of the Jacobian matrix  $\partial \mathbf{g}/\partial \mathbf{y}$  [5].

Mathematically, the stiffness of (1) is caused by a large gap in the values of the  $\tau_r(\mathbf{y}, k_r)$ 's. Such gaps separate the fast and slow reaction subspaces. When the ratio of two successive values of  $\tau_r(\mathbf{y}, k_r)$  is small, this ratio is a credible estimate of the small parameter  $\epsilon$  in  $\mathbf{g}(\mathbf{y}; \epsilon)$ .

For the sake of simplicity, we assume that the set of M fast  $\alpha_1, \ldots, \alpha_M$  so identified are linearly independent, and that all M fast  $\tau_m(\mathbf{y}, k_m)$ 's are negative. In addition, we also assume that the total number of linearly dependent  $\alpha_r$ 's is not very large. The fast subspace is then M-dimensional (with M < N) and stable. It is then *intuitively* obvious that the chemically/physically meaningful  $\alpha_m(\mathbf{y})$ 's are excellent choices for the  $\mathbf{a}_m(\mathbf{y})$ 's:

$$\mathbf{a}_m(\mathbf{y}) = \boldsymbol{\alpha}_m(\mathbf{y}) + O(\epsilon), \quad m = 1, \dots, M.$$
 (10a)

We next choose the  $\mathbf{b}^m$ 's to be some linear combinations of the fast  $\beta^m(\mathbf{y})$ 's:

$$\mathbf{b}^{m}(\mathbf{y}) = \sum_{m'=1}^{M} \Theta_{m'}^{m}(\mathbf{y}) \boldsymbol{\beta}^{m'}(\mathbf{y}) + O(\epsilon), m = 1, ..., M,$$
(10b)

where  $\Theta_{m^{"}}^{m}(\mathbf{y})$ , a  $M \times M$  dimensionless matrix, is determined by imposing  $\mathbf{b}^{m} \odot \mathbf{a}_{m^{"}} = \delta_{m^{"}}^{m}$ :

$$\Theta_{m^{"}}^{m}(\mathbf{y}) = \left(\Gamma_{m}^{m^{"}}(\mathbf{y})\right)^{-1} + O(\epsilon), m, m^{"} = 1, \dots, M.$$
(10c)

Thus  $Q^{fast}(M)$  is found. To validate the choices made in (10b), we perform the so-called *step #1 CSP refinement procedure* on the  $\mathbf{b}^m(\mathbf{y})$ 's as outlined by (6.17a,b) of [3]. Noting that  $d\mathbf{b}^m/dt + \mathbf{b}^m \odot \partial \mathbf{g}/\partial \mathbf{y} = \partial(\mathbf{b}^m \odot \mathbf{g})/\partial \mathbf{y}$ , we rewrite the original iterative refinement formula as follows:

$$\mathbf{b}_{o}^{m}(\mathbf{y}) = \sum_{m'=1}^{M} \tau_{m'}^{m} \frac{\partial}{\partial \mathbf{y}} (\mathbf{b}^{m'}(\mathbf{y}) \odot \mathbf{g}), \ m = 1, \dots, M, \ (11)$$

where  $\tau_{m'}^{m'}(\mathbf{y})$ , a  $M \times M$  matrix, is determined immediately below. It is readily demonstrated that  $\mathbf{b}_{o}^{m}(\mathbf{y}) = \mathbf{b}^{m}(\mathbf{y}) + O(\epsilon)$ . Using (10b) for  $\mathbf{b}^{m}(\mathbf{y})$  on the right-hand side of (11), imposing  $\mathbf{b}_{o}^{m} \odot \mathbf{a}_{m'} = \delta_{m'}^{m}$  and taking advantage of (10c), the leading order approximation for  $\tau_{m'}^{m'}(\mathbf{y})$  is found to be:

$$\tau_{m'}^{m}(\mathbf{y}) = \Theta_{m'}^{m}(\mathbf{y})\tau_{m'}(\mathbf{y}, k_{m'}) + O(\epsilon), \quad m, m' = 1, \dots, M.$$
(12)

The M eigenvalues of  $\tau_{m'}^m(\mathbf{y})$ —all are expected to be  $O(\tau_m)$  and negative—are credible approximations of the time scales of the fast subspace in the small  $\epsilon$  limit.

The wisdom of the intuitive  $\mathbf{a}_m(\mathbf{y})$ 's choices made in (10a) can be similarly validated using the step #2 iterative CSP refinement procedure. See §6.5 of [3].

#### V. The Net value of $\Omega^m(\mathbf{y})$ in the slow epoch

After the fast reactions are exhausted, we know  $\mathbf{b}^m \odot \mathbf{g} = O(\epsilon)$ . Using (10b) for  $\mathbf{b}^m$ , this equation tells us that in the slow epoch  $\Omega^m(\mathbf{y}; k_m) - \Omega^m_\infty(\mathbf{y}) = O(\epsilon)$ , where:

$$\Omega_{\infty}^{m}(\mathbf{y}) \equiv -\sum_{m^{*}=1}^{M} \Theta_{m^{*}}^{m} \sum_{r=M+1}^{R} \Gamma_{r}^{m^{*}} \Omega^{r}(\mathbf{y};k_{r}), \quad (13)$$
$$m = 1, \dots, M.$$

In other words, the forward and reverse reaction rates of the fast reactions are *not* in balance in the slow epoch their *net* values are given approximately by (13). Note that  $\mathbf{g}^{slow}(\mathbf{y}; \epsilon)$  in the slow epoch can also be derived/calculated using the original (2)—*instead* of (5c)—provided the above  $\Omega^m_{\infty}(\mathbf{y})$ 's are used for all the needed  $\Omega^m(\mathbf{y}; k_m)$ 's.

#### VI. CONCLUDING REMARKS

Subroutines for  $\alpha_r(\mathbf{y})$ ,  $\beta^r(\mathbf{y})$ , and  $\tau_r(\mathbf{y}, k_r)$  should be included for every reaction in chemical kinetics databases so that—for any reaction system of interest—credible values of M and  $\epsilon$  can easily be found, and that system data such as  $\Gamma_{r'}^r(\mathbf{y})$ ,  $\Theta_{m'}^m(\mathbf{y})$ ,  $\mathbf{b}^m(\mathbf{y})$ ,  $\mathcal{Q}^{fast}(M)$ ,  $\tau_{m'}^m(\mathbf{y})$ , etc. can be routinely computed when needed. Such CSP data can provide informative answers to questions such as *what roles does the r-th reaction play at time t*? How to deal with large number of linearly dependent  $\alpha_r(\mathbf{y})$ 's will be discussed.

- S. H. Lam, "Singular perturbation for stiff equations using numerical methods," *Recent Advances in the Aerospace Sciences*, Corrado Casci, Ed., Plenum Press, New York and London, 1985, pp.3-20.
- [2] S. H. Lam, "Using CSP to understand complex chemical kinetics," Combust. Sci. and Tech, 89, 1993, pp. 375-404.
- [3] S. H. Lam and D. A. Goussis, "The CSP Method for Simplifying Kinetics," *International Journal of Chemical Kinetics*, 26, 1994, pp. 461-486.
- [4] P. D. Kourdis, R. Steuer and D. A. Goussis, "Physical understanding of complex multiscale biochemical models via algorithmic simplification: Glycolysis in Saccharomyces cerevisiae," *Physica D*, 239, 2010, pp. 1798-1817.
- [5] U. Maas and S. B. Pope, "Simplifying Chemical KineticsL Intrinsic Low-Dimensional Manifolds in Composition Space," *Combust. Flame*, 88, 1992, pp. 239-264.

## Low-Dimensional Manifolds in Direct Numerical Simulations of Autoigniting Mixing Layers

Jeroen van Oijen, Ugur Göktolga, Philip de Goey

Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

*Abstract*—Direct numerical simulation of autoigniting mixing layers are performed to investigate the turbulence chemistry interaction in jet-in-hot-coflow flames. The results of these simulations with a skeletal reaction model are analyzed in composition space. The ignition process appears to follow a low-dimensional manifold that can be parameterized by mixture fraction and a reaction progress variable.

#### I. INTRODUCTION

The focus of this research is on new combustion concepts, which produce energy from current and future fuels, with substantially enhanced efficiency and significantly reduced pollutant emissions. Going by names such as high efficiency combustion and flameless oxidation, these new methods allow the use of recuperated heat in high-temperature processes without the penalty of increased NO<sub>x</sub> emissions, and offer the possibility of substantially homogenizing the temperature field in combustion devices (see, e.g., [1, 2]). In these combustion systems a high degree of preheating of the reactants is coupled with a high degree of dilution. Following [2], we use the term MILD combustion to refer to these systems.

In MILD systems, combustion takes place in the midst of turbulent mixing of the reactants. Since the temperature of the reactants is above that of autoignition, a complex interplay between turbulent mixing, molecular transport and chemical kinetics occurs. In order to reveal the fundamental reaction structures of MILD combustion, high-fidelity numerical simulations are needed in which all scales of turbulent motion are resolved. Combined with detailed chemical reaction models, direct numerical simulation (DNS) is the appropriate tool to investigate these phenomena. The drawback of DNS, conversely, is that it is extremely expensive from a computational point of view.

In the present study, the process of a cold methanehydrogen fuel jet issuing in a hot diluted coflow and the subsequent ignition process is modeled by DNS of autoigniting mixing layers using detailed chemistry and transport models. The conditions are taken to match the experiments of Dally *et al.* [3] as close as possible. The interaction between the ignition chemistry and the developing mixing layer is investigated by analyzing 2D DNS results in composition space. It is investigated whether the ignition process proceeds along a lower-dimensional manifold in composition space, which could be the basis of a reduced chemistry model.

#### II. DNS OF AUTOIGNITING MIXING LAYERS

Igniting temporally evolving mixing layers have been modeled by using DNS. The employed DNS code solves the governing equations in fully compressible form in terms of density  $\rho$ , velocity u, species mass fractions  $Y_{\alpha}$ , and temperature T. The viscosity and conductivity of the mixture are fitted as functions of temperature. The diffusion of species is modeled by using a constant Lewis number approach. The Lewis numbers were determined by fitting the expressions to results of 1D simulations with more detailed transport models. The chemical source terms are computed by using the DRM19 reaction mechanism, which is a reduced reaction set derived from the GRI mechanism and contains 21 species and 84 reversible reactions [4].

The DNS consists of a temporally evolving, nonpremixed, 2D planar jet flame. A layer of fuel in the domain center is surrounded by counterflowing oxidizer. In the streamwise (x) direction, periodic boundary conditions are applied, while in the cross-stream (y) direction, nonreflecting outlet boundaries are used assuming atmospheric pressure at infinity. The fuel is a mixture of methane and hydrogen, equal in volume. The oxidizer consists of air diluted with combustion products and nitrogen. The temperature of the oxidizer is 1300 K. The compositions of the fuel and the oxidizer are chosen to match the conditions of experiment HM1 in Ref. [3]. The stoichiometric mixture fraction for these streams is  $Z_{\rm st} = 6.7 \times 10^{-3}$ . The fuel core width, W, is 2 mm, and the difference in the velocity of the streams,  $\Delta U$ , is 67 m/s. Together with the viscosity  $\nu$  of the fuel stream, this leads to a Reynolds number of 3850, which is in the range of the experiments by Dally et al. [3]. A more detailed description of the code and the simulation setup can be found in Refs. [5,6].

The DNS results of the two-dimensional turbulent mixing layer are presented in Fig. 1. The evolution of  $Y_{\rm H_2}$  and  $Y_{\rm H}$  is shown. The contour plots of H<sub>2</sub> show the growth of the shear layer instability. This instability forms vortical structures which interact and merge. Due to the very small values of  $Z_{\rm st}$ , the stoichiometric isocontours lie at the outside of the mixing layer and appear to enclose the



Fig. 1. Mass fraction of H<sub>2</sub> (left) and H (middle) and T (right) at t = 0.2, 0.3, 0.4 ms (top to bottom). The gray scale varies from 0 to 0.111 and from 0 to  $4.6 \times 10^{-4}$  for H<sub>2</sub> and H, respectively. The red dashed lines represent the stoichiometric mixture fraction  $Z = Z_{\rm st}$ .

turbulent region. As a result, the reaction layers in these flames are only mildly influenced by turbulence.

#### III. LOW-DIMENSIONAL MANIFOLDS

In order to investigate whether the ignition chemistry takes place in a lower-dimensional manifold, the DNS results are analyzed in composition space. Since we are dealing with a non-premixed system, the mixture fraction Zis the principal controlling variable to describe the chemical state. A second parameter is needed to describe the reaction progress. The question is whether this 2D parametrization with the mixture fraction Z and a reaction progress variable  $\mathcal{Y}$  is enough to describe the chemical state in this system with a reasonable accuracy, or whether additional dimensions are needed.

In Fig. 2, the mass fraction of OH is plotted as a function of the progress variable  $\mathcal{Y}$  conditioned at  $Z = Z_{st}$ . The progress variable is a normalized linear combination of reaction products. Since we are mainly interested in the ignition chemistry, logarithmic scales are used in the plot. The scatter from the DNS appears to collaps on a single curve. This indicates that there is a strong correlation between OH and the progress variable and that  $Y_{OH} = f(Z, \mathcal{Y})$  apart from some small deviations. These small deviations can be explained by variations in the scalar dissipation rate along the stoichiometric isocontour. The blue and red curves in Fig. 2 represent the correlations in a homogeneous ignition simulation and in a 1D laminar igniting mixing layer, respectively. In the homogeneous



Fig. 2. Mass fraction of OH as a function of the progress variable conditioned at  $Z = Z_{st}$ . The scatter corresponds to the DNS results at t = 0.24, 0.26, 0.28, 0.30, 0.40 ms from dark to light gray. The red curve corresponds to a 1D laminar igniting mixing layer, and the blue curve corresponds to a homogeneous ignition simulation.

simulation, the scalar dissipation rate is zero, while in the laminar mixing layer it is comparable to that of the DNS (see [6]). In the absence of gradients the OH mass fraction is slightly higher, but the states in the 1D mixing layer agree very well with the DNS results.

When ignition has occurred and a flame has been formed (t > 0.3 ms), the correlation between OH and the progress variable becomes much weaker. In this phase of the combustion process a third dimension seems inevitable, but the ignition chemistry follows a 2D manifold that can be parameterized by mixture fraction and a progress variable. Due to the limited interaction of the turbulence with the reaction layers for the conditions of the flames studied here, this conclusion may not hold for other conditions with much stronger turbulence chemistry interaction. The following steps in this research include the use of this manifold in the DNS and a validation against the detailed results.

#### ACKNOWLEDGMENT

The financial support of the Dutch Technology Foundation STW is gratefully appreciated.

- J. A. Wünning, J. G. Wünning, "Flameless oxidation to reduce thermal NO-formation", *Prog. Energy Combust. Sci.* 23 (1997) 81– 94.
- [2] A. Cavaliere, M. de Joannon, "Mild Combustion", Prog. Energy Combust. Sci. 30 (2004) 329–366.
- [3] B. B. Dally, A. N. Karpetis, R. S. Barlow, "Structure of turbulent non-premixed jet flames in a diluted hot coflow", *Proc. Combust. Inst.* 29 (2002) 1147–1154.
- [4] A. Kazakov, M. Frenklach, Reduced Reaction Sets based on GRI-Mech 1.2.
- [5] R. J. M. Bastiaans, L. M. T. Somers, H. C. de Lange, in: B. J. Geurts (Ed.), Modern Simulation Strategies for Turbulent Flow, R. T. Edwards Publishers, Philadelphia, 2001, pp. 247–261.
- [6] J. A. van Oijen, "Direct numerical simulation of autoigniting mixing layers in MILD combustion", *Proc. Combust. Inst.* 34 (2013) 1163– 1171.

# Uncertainties in rate constants of important reactions for propene oxidation

Sinéad Burke\*, Henry Curran\*

\*Combustion Chemistry Centre/NUI Galway, Galway, Ireland

*Abstract*—A detailed chemical kinetic mechanism has been developed to describe the oxidation of propene over a wide range of experimental conditions in experimental devices including a flow reactor, shock tubes, jet-stirred reactors and in flame studies. The mechanism contains uncertainties in the choice of critical rate constants for certain key reactions, which are discussed, particularly at high pressure.

#### I. INTRODUCTION

Propene is a key intermediate in the combustion of higher alkanes, and thus understanding the kinetics of propene is vitally important in the hierarchical development of the kinetic mechanisms. Propene oxidation can also contribute to soot production (and other pollutant formation). Therefore strategies for mitigating pollutant formation in advanced combustion systems depend on a complete understanding of the oxidation of alkenes such as propene.

Several studies have investigated propene pyrolysis and oxidation at high temperatures experimentally. Burcat and Radhakrishan [1] and Qin *et al.* [2] separately used a shock tube to measure ignition delay times for propene oxidation in shock tubes over a temperature range of 1270–1840 K and at post-shock pressures in the range of 0.95–7.04 atm. Hidaka *et al.* [3] studied the thermal decomposition of propene behind reflected shocks with a temperature range of 1200–1800 K and measured the product distribution.

Davis *et al.* [4] studied the pyrolysis and oxidation of propene in a flow reactor at atmospheric pressure and at temperatures of 1181–1210 K and also measured laminar flame speeds of propene/air mixtures. Other flame speed studies include the study of Jomaas *et al.* [5] at pressures of 1, 2 and 5 atm. Saaed and Stone [6] studied burning velocities of propene-air mixtures at varying temperatures (293 and 425 K) and pressures (0.5, 1.0, 2.0 and 3.5 bar).

There are several speciation studies in a jet-stirred reactor (JSR) by Dagaut and co-workers [7–9]. The most recent work by Le Cong *et al.* [9] investigated the oxidation of pure propene and its oxidation in the presence of  $CO_2$  and  $H_2O$  at atmospheric pressure over a temperature range of 950–1450 K. The older studies [7], [8] investigated propene oxidation as a function of residence time over the temperature range 900–1200 K in the pressures range of 1–8 atm.

#### A. Model

AramcoMech1.4 contains 315 species and 1804 reactions. It is based on a previously published mechanism which described the oxidation of  $C_1$ – $C_2$  hydrocarbon and oxygenated hydrocarbon species [10]. A brute force sensitivity analysis was carried out to identify the important

reactions for propene oxidation, described below. The recommended rate constants for the important reactions are discussed in the text were carried out using CHEMKIN PRO.

#### B. Sensitivity analysis

In order to highlight the important chemistry involved in propene oxidation a 'brute force' sensitivity analysis was performed Fig. 1. The sensitivity coefficient ( $\sigma$ ) is defined as:  $\sigma = \log(\tau'/\tau'') / (\log 2.0/0.5)$  where  $\tau'$  the ignition delay time calculated with a factor of two increase in *k*, and  $\tau''$  is the ignition delay time calculated with a factor of two decrease in *k*. A negative  $\sigma$  indicates an overall promoting effect on reactivity, and vice versa.



Fig. 1. Brute force sensitivity analysis of  $C_3H_6/air$  shock tube ignition delay time,  $\phi = 1.0$ , p = 1 atm, T = 1250 K.

#### C. Rate consant discussion

 $C_3H_6 + OH \Leftrightarrow Products:$  Fig. 1 shows that the system is sensitive to the branching ratio of the three radicals formed; the production of the resonantly stabilized allyl (3-propenyl) radical inhibits reactivity while the other two channels producing 2-propenyl ( $C_3H_5$ -t) and 1-propenyl ( $C_3H_5$ -s) respectively, lead to an increase in reactivity. We have adopted a rate constant from Vasu *et al.* [11], where the total rate constant was measured in a shock tube but it was not possible to distinguish the three product channels. However, this measurement was in excellent agreement with an abinitio study by Zádor *et al.* [12]. Thus, we utilize the rates recommended by Zádor *et al.* Fig. 2 shows the difference is branching ratio from the old to the current mechanism. A relatively small change in branching ratio (Fig. 2) has a significant effect on model prediction of JSR data (Fig. 3).



Fig. 2 Branching ratio for the reaction  $C_3H_6+OH$  as recommended in a previous version of the mechanism [10] - - - and Zádor *et al.*[12] —

 $C_3H_5-a+HO_2 \Leftrightarrow$  Products: The sensitivity analysis emphasizes the importance of the ally radical and hydroperoxyl system. Goldsmith *et al.* [13] theoretically investigated the kinetics of the allyl + HO<sub>2</sub> reaction, the thermal decomposition of C<sub>3</sub>H<sub>5</sub>OOH, and the uni-molecular reactions of C<sub>3</sub>H<sub>5</sub>O, and we use these calculated values.

 $C_3H_5$ -a+ $O_2 \Leftrightarrow Products$ : This system has been adopted from the study of Bozzelli and Dean [14]. These reactions promote reactivity as they convert the stable allyl radical to more reactive hydroxyl, vinoxy and hydroperoxyl radicals. We believe these reactions require further investigation.

 $C_3H_6 + O_2 \Leftrightarrow Products$ : The reaction of propene with molecular oxygen to give allyl and a hydroperoxyl radical is a very sensitive one, Fig 1. The rate constants for all three channels adopted in this work are estimated values. The activation energies are based on the heat of reaction while the pre-exponential factors are estimated. There appears to be a high level of uncertainty associated with this rate constant especially at higher temperatures. The dotted line in Fig. 3 highlights the effect the Baulch *et al.* [15] recommendation for propene has on the model prediction on propene oxidation in a JSR.



Fig. 3. Propene species profile from a JSR. — current mechanism, -- current mechanism plus  $C_3H_6+O_2$  description from Baulch *et al.*, ... current mechanism plus original branching fraction for  $C_3H_6+OH$ .

#### D. Summary

Despite being the subject of several studies [1-9, 11-14] the oxidation of propene is still not well understood especially at higher pressures. There is scope for further studies into the uncertainties associated with some of the important rate constants; for example the abstraction reaction of propene with molecular oxygen and the relative branching ratios for hydrogen atom abstraction from propene by the hydroxyl radical.

- A. Burcat, and K. Radhakrishnan, "High temperature oxidation of propene", *Combust. Flame*, vol. 60, 1985, pp. 157–169.
- [2] Z. Qin, H. Yang and W. C. Gardiner, "Measurement and modeling of shock-tube ignition delay for propene", *Combust. Flame*, vol. 124, 2001, pp. 246–254.
- [3] Y. Hidaka, T. Nakamura, H. Tanaka, A Jinno, H. Kawano and T. Higashihara, "Shock-tube and modeling study of propene pyrolysis", *Int. J. Chem. Kinet.*, vol. 24, 1992, pp. 761–780.
- [4] S. G. Davis, C. K. Law, and H. Wang, "Propene pyrolysis and oxidation kinetics in a flow reactor and laminar flames", *Combust. Flame*, vol. 119, 1999, pp. 375–399.
- [5] G. Jomaas, X. L. Zheng, D. L. Zhu and C. K. Law, "Experimental determination of counterflow ignition temperatures and laminar flame speeds of C2–C3 hydrocarbons at atmospheric and elevated pressures", *Proc. Combust. Inst.*, vol. 30, 2005, pp. 193–200.
- [6] K. Saeed, and R. Stone, "Laminar burning velocities of propene--air mixtures at elevated temperatures and pressures", J. Energy Inst., vol. 80, 2007, pp. 73–82.
- [7] P. Dagaut, M. Cathonnet and J. C. Boettner, "Experimental study and kinetic modeling of propene oxidation in a jet stirred flow reactor", *J. Phys. Chem.*, vol. 92, 1988, pp. 661–671.
- [8] P. Dagaut, M. Cathonnet and J. C. Boettner, "A kinetic modeling study of propene oxidation in jsr and flame", *Combust. Sci. Technol.*, vol. 83, 1992, pp. 167–185.
- [9] T. Le Cong, E. Bedjanian, and P. Dagaut, "Oxidation of Ethylene and Propene in the Presence of CO<sub>2</sub> and H<sub>2</sub>O: Experimental and Detailed Kinetic Modeling Study", *Combust. Sci. Technol.*, vol. 182, 2010, pp. 333–349.
- [10] W. K. Metcalfe, S. M. Burke, S. S Ahmed and H. J. Curran "A Hierarchical and Comparative Kinetic Modeling Study of C1-C2 Hydrocarbon and Oxygenated Fuels", *Fuel*, in review 2013
- [11] S. S. Vasu, Z. Hong, D. F. Davidson, R. K. Hanson and D. M. Golden "Shock Tube/Laser Absorption Measurements of the Reaction Rates of OH with Ethylene and Propene", *J. Phys. Chem. A.*, vol 144, 2010, pp. 11529–11539
- [12] J. Zádor, A. W. Jasper and J. A. Miller, "The reaction between propene and hydroxyl", *Phys. Chem. Chem. Phys.*, vol 11 2009, pp. 11040–11053
- [13] F. C Goldsmith, S. J. Klippenstein, and W. H. Green, "Theoretical rate coefficients for allyl + HO<sub>2</sub> and allyloxy decomposition", *Proc. Combust. Inst.*, vol. 33, 2011, pp. 273–282.
- [14] J. W. Bozzelli, and A. M. Dean, "Hydrocarbon radical reactions with oxygen: comparison of allyl, formyl, and vinyl to ethyl", J. Phys. Chem. vol. 9, 1997, pp. 4427–4441.
- [15] D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, Th. Just, J. A. Kerr, M. J. Pilling, D. Stocker, J. Troe, W. Tsang, R. W. Walker, and J.Warnatz, "Evaluated Kinetic Data for Combustion Modeling: Supplement II", *J. Phys. Chem. Ref. Data* vol. 34, 2005, pp. 757–1397.

### The Slowness of Invariant Manifolds Constructed by Connection of Heteroclinic Orbits

Joseph M. Powers\*, Samuel Paolucci\*, Joshua D. Mengers<sup>†</sup>

\*University of Notre Dame, Department of Aerospace and Mechanical Engineering, Notre Dame, Indiana, USA <sup>†</sup>US Department of Energy, Geothermal Technologies Office, Washington, DC, USA

*Abstract*— It is demonstrated that a common technique in reaction dynamics for construction of Slow Invariant Manifolds, connection of equilibria by heteroclinic orbits, can fail. While the method is guaranteed to generate an invariant manifold, the local dynamics far from equilibrium may be such that nearby trajectories are in fact carried away from the identified invariant manifold, thus rendering it to be of limited utility in capturing slow dynamics far from equilibrium. An eigenvalue-based method is described to characterize the local behavior of such invariant manifolds.

#### I. INTRODUCTION

Spatially homogeneous chemical reactions are described by dynamical systems of the form

$$\frac{d\mathbf{z}}{dt} = \mathbf{f}(\mathbf{z}), \qquad \mathbf{z}(0) = \mathbf{z}_o, \qquad \mathbf{z}, \mathbf{z}_o, \mathbf{f} \in \mathbb{R}^N.$$
(1)

Here, z is a vector of length N containing the species concentrations, assuming that linear constraints representing element conservation have been removed, t is time, and **f** is a non-linear function of z representing the law of mass action with Arrhenius kinetics.

We take a Slow Invariant Manifold (SIM) to be an invariant manifold (IM) on which slow dynamics are confined and to which nearby trajectories are attracted. The identification of one-dimensional SIMs by constructing heteroclinic orbits connecting equilibria has gained attention since its introduction [1] and extension by others, *e.g.* [2], [3], [4]. The essence of the fundamental hypothesis is illustrated in Fig. 1. That hypothesis is that SIMs may be constructed by 1) identifying equilibria of Eq. (1), *i.e.* points z where f(z) = 0, and 2) connecting by trajectories from appropriate



Fig. 1. Sketch of SIM envisioned as the invariant manifold connecting equilibria.



Fig. 2. Sketch of failure of the method of heteroclinic orbit construction for SIM identification.

non-physical saddle equilibria (those with at most one positive eigenvalue) to the unique physical equilibrium, which is a sink. Near the equilibria, the IM is guaranteed to be attractive; moreover, for many reactive systems the IM appears to be attractive in regions far from equilibrium.

However, nothing in the SIM construction algorithm precludes the scenario sketched in Fig. 2. Certainly, equilibria can be identified and connected via heteroclinic orbits to construct a canonical IM. But for a generic f(z), one has no guarantee that trajectories near the canonical IM are in fact attracted to it. In this study, we summarize analyses and an example given by Mengers [5] for attractiveness criteria for an IM; additional background is to be found in [6].

#### II. SUMMARY OF ANALYSIS

With the local Jacobian  $\mathbf{J} = \partial \mathbf{f} / \partial \mathbf{z}$ , defined throughout the entire phase space, one can analyze  $\mathbf{J}$  in the neighborhood of any IM, such as an IM connecting equilibria. At the physical equilibrium, all of the eigenvalues of  $\mathbf{J}$  are guaranteed to be negative and real, and all nearby points will be drawn to the physical equilibrium. Away from the physical equilibrium, it is possible for some eigenvalues to be positive, and this can lead to certain trajectories being drawn away from an IM. It is well known that tr( $\mathbf{J}$ ) is proportional to the rate of change of a local volume in phase space. However, even if tr( $\mathbf{J}$ ) < 0, the existence of a positive eigenvalue can induce a local repulsion of an individual trajectory from an IM.

It is possible [2], [5] to identify a unit tangent vector to the IM,  $\alpha_t$ , and a set of unit normal vectors,  $\alpha_{ni}$ , i = 1, ..., N - 1. These vectors can be used to identify the tangential and normal stretching rates,  $\sigma_t$  and  $\sigma_{ni}$ :

$$\sigma_t = \boldsymbol{\alpha}_t^T \cdot \mathbf{J}_s \cdot \boldsymbol{\alpha}_t, \ \sigma_{ni} = \boldsymbol{\alpha}_{ni}^T \cdot \mathbf{J}_s \cdot \boldsymbol{\alpha}_{ni}, \ i = 1, \dots, N-1.$$
(2)

Here  $\mathbf{J}_s = (\mathbf{J} + \mathbf{J}^T)/2$ , the symmetric part of  $\mathbf{J}$ . Along the IM,  $\alpha_t$  is uniquely defined, up to its sign. However, there are an infinite set of  $\alpha_{ni}$  when N > 2. Certainly if all possible  $\sigma_{ni} < 0$  and  $\min_i |\sigma_{ni}| \gg |\sigma_t|$ , the IM will be a SIM; however, it is easy to construct cases for which these criteria are not met.

One can pose the following optimization problem to identify the maximum  $\sigma_n$  and its associated  $\alpha_n$ . First, we can recast  $\mathbf{J}_s = \mathbf{Q} \cdot \mathbf{\Lambda} \cdot \mathbf{Q}^T$ , where  $\mathbf{Q}$  is a rotation matrix with normalized eigenvectors of  $\mathbf{J}_s$  in its columns, and  $\mathbf{\Lambda}$  is a diagonal matrix with the eigenvalues of  $\mathbf{J}_s$  on its diagonal. Then we seek  $\alpha_n$  to maximize

$$\sigma_n = (\mathbf{Q}^T \cdot \boldsymbol{\alpha}_n)^T \cdot \boldsymbol{\Lambda} \cdot (\mathbf{Q}^T \cdot \boldsymbol{\alpha}_n), \tag{3}$$

subject to

$$\boldsymbol{\alpha}_n^T \cdot \boldsymbol{\alpha}_n = 1, \qquad \boldsymbol{\alpha}_n^T \cdot \boldsymbol{\alpha}_t = 0.$$
 (4)

Because  $\mathbf{Q}$  and  $\alpha_n$  both have unit norms, it is obvious that  $|\sigma_n| \leq |\lambda_{max}|$ , where  $|\lambda_{max}|$  is the magnitude of the largest eigenvalue of  $\mathbf{J}_s$ .

#### III. EXAMPLE

Consider the system, of the form of Eq. (1), with N = 3:

$$\frac{dz_1}{dt} = \frac{1}{20}(1-z_1^2), \tag{5a}$$

$$\frac{dz_2}{dt} = -2z_2 - \frac{35}{16}z_3 + 2(1-z_1^2)z_3, \quad (5b)$$

$$\frac{dz_3}{dt} = z_2 + z_3. \tag{5c}$$

This system has two finite roots,  $R_1$  at  $\mathbf{z} = (-1, 0, 0)^T$  and  $R_2$  at  $\mathbf{z} = (1, 0, 0)^T$ . The Jacobian  $\mathbf{J}$  has eigenvalues of  $\lambda =$  $\{1/10, -1/4, -3/4\}$  at  $R_1$  and  $\lambda = \{-1/10, -1/4, -3/4\}$ at  $R_2$ . Thus,  $R_1$  is a saddle with one unstable mode, and  $R_2$ is a sink, analogous to a physical equilibrium in a reactive system. There is a canonical IM defined by the heteroclinic orbit that connects  $R_1$  to  $R_2$  along the  $z_2 = z_3 = 0$  axis; however, we find this branch does not attract neighboring trajectories along the entire IM, as is obvious by inspecting Fig. 3, which shows a projection of the IM and nearby trajectories in the  $(z_1, z_3)$  plane. The unit tangent to the canonical IM is  $\alpha_t = (1,0,0)^T$ , yielding a tangential stretching rate of  $\sigma_t = -z_1/10$ . On the canonical IM, we thus find that  $\sigma_t \sim 1/10$  near  $R_1$  and  $\sigma_t \sim -1/10$ near the physical equilibrium  $R_2$ . There exist points all along the canonical IM with  $\sigma_n > 0$ . For example, at z = $(0,0,0)^T$ , the maximum normal stretching rate is  $\sigma_{n,max} =$  $-1/2 + \sqrt{2473}/32 = 1.05$  for  $\alpha_n = (0, -0.132, -0.991)^T$ . Near the physical equilibrium at  $\mathbf{z} = (1, 0, 0)^T$ , one still finds  $\sigma_{n,max} = -1/2 + \sqrt{2665}/32 = 1.11$  for  $\alpha_n =$ 



Fig. 3. Projection of the IM connecting equilibria along with nearby trajectories illustrating the non-attractive regions of the IM.

 $(0, -0.187, 0.982)^T$ , but the real negative eigenvalues of **J** itself render all trajectories to be attracted to the equilibrium. It is likely that non-normality effects [7] need to be further analyzed to better explain the behavior.

#### IV. CONCLUSION

Construction of invariant manifolds via connection of equilibria by heteroclinic orbits offers no guarantee that one has found a slow invariant manifold.

#### ACKNOWLEDGMENTS

The study was originally supported by the National Science Foundation under Grant No. CBET-0650843; partial support was also received in the form of a fellowship from the University of Notre Dame's Department of Applied and Computational Mathematics and Statistics.

- M. J. Davis and R. T. Skodje, 1999, "Geometric investigation of low-dimensional manifolds in systems approaching equilibrium," *J. Chem. Phys.*, 111(3): 859-874.
- [2] F. Creta, A. Adrover, S. Cerbelli, M. Valorani, and M. Giona, 2006, "Slow manifold structure in explosive kinetics. 1. bifurcations of points-at-infinity in prototypical models," *J. Phys. Chem. A*, 110(50): 13447-13462.
- [3] M. Giona, A. Adrover, F. Creta, and M. Valorani, 2006, "Slow manifold structure in explosive kinetics. 2. extension to higher dimension systems," J. Phys. Chem. A, 110: 13463-13474.
- [4] A. N. Al-Khateeb, J. M. Powers, S. Paolucci, A. J. Sommese, J. A. Diller, J. D. Hauenstein, and J. D. Mengers, 2009, "Onedimensional slow invariant manifolds for spatially homogeneous reactive systems," *J. Chem. Phys.*, 131(2): 024118.
- [5] J. D. Mengers, 2012, "Slow invariant manifolds for reaction-diffusion systems," Ph.D. dissertation, University of Notre Dame.
- [6] S. Paolucci, 2013, Continuum Mechanics and Thermodynamics, in preparation.
- [7] D. J. Higham and L. N. Trefethen, 1993, "Stiffness of ODEs," Bit, 33(2): 285-303.

### Dynamical Structures in Stochastic Chemical Reaction Systems

Xiaoying Han\*, and Habib N. Najm<sup>†</sup>

\*Department of Mathematics and Statistics, Auburn University, Auburn, AL 36849, USA <sup>†</sup>Sandia National Laboratories, P.O. Box 969, MS 9051, Livermore, CA 94551, USA

*Abstract*— Motivated by the need for dynamical analysis and model reduction in stiff stochastic chemical systems, we focus on the development of methodologies for analysis of the dynamical structure of singularly-perturbed stochastic dynamical systems. We outline a formulation based on random dynamical systems theory. We demonstrate the analysis for a model two-dimensional stochastic dynamical system built on an underlying deterministic system with a tailored fast-slow structure, and an analytically known slow manifold, employing multiplicative brownian motion noise forcing.

#### I. INTRODUCTION

At a fundamental level, chemical reactions are the result of molecular collisions. Given the random nature of these collisions, the progress of chemical processes at the smallest scales is stochastic, and is adequately described by the Chemical Master Equation (CME) [9]. In a computational setting, the CME can be simulated directly only for systems involving a sufficiently small number of species, and molecule counts. Alternately, the Stochastic Simulation Algorithm (SSA) [6,8] can be used to simulate a jump Markov process, involving integer-valued species molecule counts, with resulting trajectories whose statistics accurately model the CME solution. These stochastic effects are averaged out when system size and molecule counts are at the continuum scale, resulting in the familiar deterministic Ordinary Differential Equation (ODE) system models for chemical systems. An intermediate, mesoscale, regime exists, when molecule counts are large, e.g.  $\mathcal{O}(10^3)$ , but not sufficiently so to make the continuum approximation viable. In this regime, the Fokker-Planck equation can be used to simulate the evolution of the probability density function (PDF) of states, or the Chemical Langevin Equation (CLE) [5] can be used to simulate state trajectories [7]. This regime is frequently encountered in models of reaction processes in biological systems, as well as in models of catalytic reaction processes in the vcinity of micro/nano-scale features at gassolid interfaces.

The mesoscale regime, and particularly the CLE, is the focus of this work. More specifically, we are interested in developing methods for dynamical analysis and model reduction in stiff stochastic chemical systems governed by the CLE. From a dynamical perspective, these systems, as is true for chemical models at all scales, can exhibit a significant degree of stiffness, resulting from the large range of time-scales of the modeled reaction processes [3]. Moreover, the underlying chemical kinetic models can be quite large, involving large numbers of species and reactions. Accordingly, there is a strong need for understanding the dynamical landscape of these systems, and for development of associated robust model reduction strategies. There has been a significant amount of work in this area [1,10,12–14].

In the present work, we describe our work in this area, building on the existing literature. We formulate the stochastic differential equation (SDE) mathematical setting for singularly perturbed stochastic chemical systems, and outline our initial steps towards a random dynamical system (RDS) framework to study the dynamics of these systems. The RDS framework has key advantages as outlined below. We discuss this framework and demonstrate its use for dynamical analysis, and identification of underlying manifolds in a stochastic version of the Davis-Skodje problem [4], where a simple analytical manifold is embedded in a twodimensional model system.

#### II. MATHEMATICAL SETTING

#### A. Singular Perturbation

Consider a system involving two well-separated timescales:

$$\frac{dx}{dt} = f(x, y; \varepsilon), \quad \varepsilon \frac{dy}{dt} = g(x, y; \varepsilon), \tag{1}$$

where  $\varepsilon$  is a small parameter. Since  $\frac{dy}{dt}$  can be much larger than  $\frac{dx}{dt}$ , y is called the *fast variable* and x is called the *slow variable*.

System (1) behaves singularly in the limit  $\varepsilon \to 0$  and the results depend on the way this limit is performed. If we simply set  $\varepsilon = 0$ , it degenerates to the reduced system

$$\frac{dx}{dt} = f(x, y; 0), \quad 0 = g(x, y; 0).$$
 (2)

We assume that there exists a differentiable manifold with equation  $y = y^*(x)$  on which  $g(x, y^*(x); 0) = 0$  for all x. Then  $y = y^*(x)$  is called a *slow manifold* [2], and the dynamics on it are described by the *reduced equation* 

$$\frac{dx}{dt} = f(x, y^*(x); 0).$$
 (3)

For long times, solutions of equations (1) remain in an  $\varepsilon$ -neighborhood of the slow manifold, and are thus well approximated by the reduced equation (3) [11,16].

To study the effect of noise on the slow-fast system (1), we perturb both equations with noise, with different intensities due to different timescales. Since the diffusive nature of Brownian motion causes paths to spread like  $\sqrt{t}$ , we choose the following scaling of the noise intensities:

$$dX(t) = f(X,Y;\varepsilon) + \mu F(X,Y;\varepsilon)dW(t), \quad (4)$$

$$\varepsilon dY(t) = g(X,Y;\varepsilon) + \sigma \sqrt{\varepsilon} G(X,Y;\varepsilon) dW(t),$$
 (5)

in which  $\mu^2$  and  $\sigma^2$  measure (*rate of diffusion*)<sup>2</sup>/*the speed* of *drift* for X and Y respectively, and W(t) denotes the standard Brownian motion. Here the parameters  $\mu$ ,  $\sigma$  and  $\varepsilon$  are considered to be small.

#### B. Methodology

To study the effect of noise on the invariant manifold of a randomly perturbed system, the traditional stochastic approach is to solve the Fokker-Planck equation for stationary solutions. This is usually done numerically by integrating the system forward in time and then finding the time average to obtain the probability density function (PDF). However, such an approach provides only statistical information, not the geometric details of the invariant manifold. We propose, rather, to use the RDS approach to study the geometric behavior of random invariant manifolds of stochastic chemical systems.

One major advantage of the RDS approach is that it is based on path-wise analysis rather than a simple ensemble of realizations. Moreover, the RDS approach is a pullback approach, in which the system runs from a time in the past until the present time, instead of integrating forward in time. By looking at the system in this pullback point of view, the geometric structures associated with the invariant manifold of stochastic systems emerge naturally, as the RDS theory is based on random invariant measures.

#### III. A BENCHMARK MODEL - STOCHASTIC DAVIS-SKODJE SYSTEM

The Davis and Skodje (D-S) model [4,15] consists of a two-dimensional system which models a spatially homogeneous premixed reactor and is given by

$$\dot{x}(t) = -x(t),$$
 (6)

$$\dot{y}(t) = -\gamma y(t) + \gamma \frac{x(t)}{1+x(t)} - \frac{x(t)}{(1+x(t))^2},$$
 (7)

where  $\gamma$   $(1/\gamma$  corresponds to  $\varepsilon$ ) measures the stiffness of the system. The system has one stable equilibrium (0,0) and one stable exact slow manifold  $y^*(x) = \frac{x}{1+x}$ .

Our purpose is to study the effect of noise on the fastslow system (6) - (7). For the system to make physical sense, we choose multiplicative noise to ensure solutions are nonnegative, and obtain the stochastic Davis-Skodje system:

$$dX(t) = -X(t)dt + \mu X(t)dW(t), \qquad (8)$$

$$dY(t) = \left(-\gamma Y(t) + \gamma \frac{X(t)}{1 + X(t)} - \frac{X(t)}{(1 + X(t))^2}\right) dt + \sigma \sqrt{\gamma} Y(t) dW(t).$$
(9)

Since system (6) - (7) has one unique exact slow manifold, we expect that the main effect of the noise terms  $\mu X(t)dW(t)$  and  $\sigma \sqrt{\gamma}Y(t)dW(t)$  is to cause solutions to fluctuate around their deterministic counterpart, and approach to a "random slow manifold" after a certain period of time. We will construct explicitly the random slow manifold of system (8) - (9) by using the random dynamical system approach.

#### **IV. REFERENCES**

- A. Arkin and J. Ross. Statistical construction of chemical reaction mechanisms from measured time series. J. Phys. Chem., 99:970–979, 1995.
- [2] N. Berglund and B. Gentz. Geometric singular perturbation theory for stochastic differential equations. *Journal of Differential Equations*, 191(1):1 – 54, Jun 2003.
- [3] Y. Cao, D. Gillespie, and L. Petzold. Multiscale stochastic simulation algorithm with stochastic partial equilibrium assumption for chemically reacting systems. *Journal of Computational Physics*, 206:395– 411, 2005.
- [4] M.J. Davis and R.T. Skodje. Geometric investigation of lowdimensional manifolds in systems approaching equilibrium. J. Chem. Phys., 111:859–874, 1999.
- [5] D. T. Gillespie. The chemical langevin equation. *Journal of Chemical Physics*, 113(1):297 306, Jul 2000.
- [6] D. T. Gillespie. Approximate accelerated stochastic simulation of chemically reacting systems. *Journal of Chemical Physics*, 115(4):1716 – 33, Jul 2001.
- [7] D. T. Gillespie. The chemical langevin and fokker-planck equations for the reversible isomerization reaction. *Journal of Physical Chemistry A*, 106(20):5063 – 5071, May 2002.
- [8] D.T. Gillespie. Exact Stochastic Simulation of Coupled Chemical Reactions. Journal of Physical Chemistry, 81(25):2340–2361, 1977.
- [9] D.T. Gillespie. A rigorous derivation of the chemical master equation. *Phys. A*, 188:404–425, 1992.
- [10] J Goutsias. Quasiequilibrium approximation of fast reaction kinetics in stochastic biochemical systems. *Journal of Chemical Physics*, 122(18):184102, 2005.
- [11] I.S. Gradstein. Application of a.m. lyapunov's theory of stability to the theroy of differential equations with small coefficients in the derivatives. *Mat. Sbornik N. S.*, 32:263–286, 1953.
- [12] E.L. Haseltine and J.B. Rawlings. On the origins of approximations for stochastic chemical kinetics. *Journal of Chemical Physics*, 123(16):164115–1–16, 2005.
- [13] E.A. Mastny, E.L. Haseltine, and J.B. Rawlings. Two classes of quasi-steady-state model reductions for stochastic kinetics. *Journal* of Chemical Physics, 127(9):094106–1–16, 2007.
- [14] C.V. Rao and A.P. Arkin. Stochastic chemical kinetics and the quasisteady-state assumption: Application to the Gillespie algorithm. J. Chem. Phys., 118(11):4999–5010, 2003.
- [15] S.Singh, J.M.Powers, and S.Paolucci. On slow manifold of chemically reactive systems. J.Chem. Physics, 117:1482–1496, 2002.
- [16] A.N. Tikhonov. Systems of differential equations containing small parameters in the derivatives. *Mat. Sbornik N. S.*, 31:575–586, 1952.

### Characterizing Reduced-Order Manifolds by Finite-Time Lyapunov Analysis

Marco Maggia\*, Kenneth D. Mease\*

\*University of California Irvine / Mechanical and Aerospace Engineering, Irvine, CA, USA

*Abstract*— Finite-time Lyapunov analysis (FTLA) is used to determine reduced-order manifold structures in the flow of nonlinear dynamical systems exhibiting two-timescale behavior. The approach is described and explained in the context of a simple example.

#### I. INTRODUCTION

The purpose of the paper is to present a methodology for diagnosing two-timescale nonlinear behavior and characterizing the associated manifold structure, and to illustrate its use. The methodology is inspired by the intrinsic low-dimensional manifold method (ILDM) [1], but instead of using eigenvalues and eigenvectors, it uses finite-time Lyapunov exponents and vectors. The methodology [2], [3] derives from the asymptotic theory of partially hyperbolic systems [4]. The use of Lyapunov exponents and vectors has also been explored in [5].

#### **II. FINITE-TIME LYAPUNOV ANALYSIS**

The goal of our analysis is to diagnose two-timescale behavior of nonlinear dynamical systems and to determine points on the reduced-order slow manifold. The timescale information is based on the finite-time Lyapunov exponents and vectors (FTLE/Vs). Consider a nonlinear dynamical system  $\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$  with associated tangent linear dynamics  $\dot{\mathbf{v}} = D\mathbf{f}(\mathbf{x})\mathbf{v}$  where  $\mathbf{x}(t) \in \mathbb{R}^n$  and  $\mathbf{v}(t) \in T_{\mathbf{x}}\mathbb{R}^n$ .  $\Phi(t, \mathbf{x})$ denotes the fundamental matrix of the linear dynamics for initial conditions  $\mathbf{x}(0) = \mathbf{x}$  and  $\Phi(0, \mathbf{x}) = I_n$ . The forward and backward FTLEs are given by

$$\mu^{\pm}(T, \mathbf{x}, \mathbf{v}) := (\ln \|\Phi(\pm T, \mathbf{x})\mathbf{v}\|)/T, \tag{1}$$

for propagation time T > 0. The corresponding forward and backward FTLVs,  $\mathbf{l}_i^{\pm}(\pm T, \mathbf{x})$ ,  $i = 1, \ldots, n$ , can be computed by choosing the proper vectors from the singular value decomposition of the transition matrix  $\Phi(\pm T, \mathbf{x})$  [6], [2]. The orthonormal FTLVs define the following subspaces, for  $i = 1, \ldots, n$ :

$$\mathcal{L}_i^+(T, \mathbf{x}) := span\{\mathbf{l}_1^+(T, \mathbf{x}), \dots, \mathbf{l}_i^+(T, \mathbf{x})\},$$

$$\mathcal{L}_i^-(T, \mathbf{x}) := span\{\mathbf{l}_i^-(T, \mathbf{x}), \dots, \mathbf{l}_n^-(T, \mathbf{x})\},$$

$$(2)$$

**Definition [3]:** A set  $\mathcal{X} \subset \mathbb{R}^n$ ,  $n \geq 2$ , is a uniform finitetime two-timescale set for  $\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$ , with fast, slow and convergence time constants  $(\nu^{-1}, \sigma^{-1} \text{ and } \Delta \mu^{-1})$ , if there exist positive integers  $n^s$ ,  $n^c$ ,  $n^u$ , with  $n^s + n^c + n^u = n$ ,  $n^c \geq 1$  and  $n^s + n^u > 0$ , a start time  $t_s$ , a cut-off time  $t_c$ , and an available averaging time  $\overline{T}$  with  $0 \le t_s < t_c \le \overline{T}$  such that the following three properties are satisfied. We use the notation  $\mathcal{T} = (t_s, \overline{T}]$  and  $\mathcal{T}_c = (t_s, t_c]$ .

1) There exist positive constants  $\beta > \alpha > 0$  such that, uniformly on  $\mathcal{T} \times \mathcal{X}$ , the forward and backward Lyapunov spectra are separated by gaps of size  $\Delta \mu = \beta - \alpha$  into  $n^s$ ,  $n^c$  and  $n^u$  dimensional subsets.

2) For each  $\mathbf{x} \in \mathcal{X}$ , there is a continuous splitting of the tangent bundle

$$T_{\mathbf{x}}\mathbb{R}^{n} = \mathcal{E}^{s}(\overline{T}, \mathbf{x}) \oplus \mathcal{E}^{c}(\overline{T}, \mathbf{x}) \oplus \mathcal{E}^{u}(\overline{T}, \mathbf{x}) \quad \text{where} \\ \mathcal{E}^{s} = \mathcal{L}_{n^{s}}^{+}, \ \mathcal{E}^{c} = \mathcal{L}_{n^{s}+n^{c}}^{+} \cap \mathcal{L}_{n^{s}+1}^{-}, \ \mathcal{E}^{u} = \mathcal{L}_{n^{s}+n^{c}+1}^{-}.$$
(3)

3) There exist  $\nu > \sigma > 0$  such that at each  $\mathbf{x} \in \mathcal{X}$  for all  $t \in \mathcal{T}_c$ 

$$\mathbf{v} \in \mathcal{E}^{s}(\overline{T}, \mathbf{x}) \Rightarrow \begin{cases} \|\Phi(-t, \mathbf{x})\mathbf{v}\| \ge e^{\nu t} \|\mathbf{v}\| \\ \|\Phi(t, \mathbf{x})\mathbf{v}\| \le e^{-\nu t} \|\mathbf{v}\| \\ \mathbf{v} \in \mathcal{E}^{c}(\overline{T}, \mathbf{x}) \Rightarrow e^{-\sigma t} \|\mathbf{v}\| \le \|\Phi(\pm t, \mathbf{x})\mathbf{v}\| \le e^{\sigma t} \|\mathbf{v}\| \\ \mathbf{v} \in \mathcal{E}^{u}(\overline{T}, \mathbf{x}) \Rightarrow \begin{cases} \|\Phi(-t, \mathbf{x})\mathbf{v}\| \le e^{-\nu t} \|\mathbf{v}\| \\ \|\Phi(t, \mathbf{x})\mathbf{v}\| \ge e^{\nu t} \|\mathbf{v}\| \\ \|\Phi(t, \mathbf{x})\mathbf{v}\| \ge e^{\nu t} \|\mathbf{v}\| \end{cases}. \end{cases}$$
(4)

Provided that  $\mathcal{X}$  is a uniform finite-time two-timescale set, we can now look for a finite-time  $n^c$ -dimensional slow manifold  $\mathcal{S}(\overline{T})$  such that  $\mathbf{f}(\mathbf{x}) \in \mathcal{E}^c(\overline{T}, \mathbf{x})$  for all  $\mathbf{x} \in \mathcal{S}(\overline{T})$ . The set

$$\{\mathbf{x} \in \mathcal{X} : \langle \mathbf{f}(\mathbf{x}), \mathbf{w} \rangle = 0, \forall \mathbf{w} \in (\mathcal{E}^c(\overline{T}, \mathbf{x}))^{\perp}\}$$
(5)

thus satisfies a necessary condition for a finite-time slow manifold.

Rather than using eigenvectors of  $D\mathbf{f}(\mathbf{x})$  as in the ILDM method [1], or direction information from a neighboring manifold [7], we use the appropriate Lyapunov vectors to form the basis for the orthogonal complement of  $\mathcal{E}^{c}(\overline{T}, \mathbf{x})$ 

$$(\mathcal{E}^{c}(T,\mathbf{x}))^{\perp} = span\{\mathbf{l}_{1}^{-}(T,\mathbf{x}),\dots,\mathbf{l}_{n^{s}}^{-}(T,\mathbf{x}), \\,\mathbf{l}_{n^{s}+n^{c}+1}^{+}(T,\mathbf{x}),\dots,\mathbf{l}_{n}^{+}(T,\mathbf{x})\}.$$
(6)

We assume that the manifold can locally be parametrized by a subset of  $n^c$  of the *n* system coordinates and represented as a graph. The  $n^c$  independent variables are chosen such that their coordinate axes are not parallel to any directions in  $(\mathcal{E}^c)^{\perp}$  and the remaining  $n - n^c$  are found by solving the orthogonality conditions in (5).

#### A. Example - 4D Hamiltonian System

Consider the following Hamiltonian system which arises from the first-order necessary conditions of an optimal control problem

$$\dot{x}_{1} = x_{2}, \dot{x}_{2} = -\left(cx_{2} + k_{1}x_{1} + k_{2}x_{1}^{3} + \lambda_{2}/m\right)/m, \dot{\lambda}_{1} = \lambda_{2}\left(k_{1} + 3k_{2}x_{1}^{2}\right)/m, \dot{\lambda}_{2} = -\lambda_{1} + c\lambda_{2}/m.$$

$$(7)$$

We consider (7) in the form  $\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$  with  $\mathbf{x} =$  $[x_1, x_2, \lambda_1, \lambda_2]^T \in \mathbb{R}^4$  and **f** defined appropriately. For small values of m, the system can be expected to evolve on two disparate timescales. For the numerical results we use m = 0.5,  $k_1 = 1$ ,  $k_2 = 0.01$ , and  $c = 4\sqrt{k_1 m}$ . FTLA is applied in a region  $\mathcal{X}$ , chosen such that the ILDM method is applicable yet the slow manifold curvature is large enough that the ILDM method produces noticeable error. We present results for five points that are representative of all the points in  $\mathcal{X}$ . Figure 1 shows the forward and backward Lyapunov exponents for the five points as functions of the averaging time T. With  $n^s = n^u = 1$ ,  $n^c = 2, \ \alpha = 0.5, \ \beta = 5.6, \ \Delta \mu = 5.1, \ \sigma = 0.7,$  $\nu = 5.2, t_s = 0$  and  $t_c = \overline{T} = 0.5$ , the conditions, for a uniform two-timescale set resolvable over 2.6 convergence time constants, are satisfied.



Fig. 1. Superposition of backward and forward FTLEs for points in  $\mathcal{X}$ . Note that only segments of the y-axis are shown to highlight the central FTLEs.

Computing Slow Manifold Points Using FTLA: The slow subspace  $\mathcal{E}^c(\overline{T}, \mathbf{x})$  and its orthogonal complement have dimension  $n^c = n - n^c = 2$  and can be written as

$$\begin{array}{lll} \mathcal{E}^{c}(\overline{T}, \mathbf{x}) &= \mathcal{L}_{3}^{+}(\overline{T}, \mathbf{x}) \cap \mathcal{L}_{2}^{-}(\overline{T}, \mathbf{x}) \\ (\mathcal{E}^{c}(\overline{T}, \mathbf{x}))^{\perp} &= span\{\mathbf{l}_{1}^{-}(\overline{T}, \mathbf{x}), \mathbf{l}_{4}^{+}(\overline{T}, \mathbf{x})\}. \end{array}$$

$$(8)$$

We use  $(x_1, \lambda_1)$  as the independent coordinates and compute the  $(x_2, \lambda_2)$  coordinates for the graph of S(T) by solving the orthogonality conditions in (5). Because the exact location of the slow manifold is not known, we use



Fig. 2. Projection onto the  $\lambda_1$ - $x_2$  plane of the forward and backward propagations from initial points on the slow manifold (circles).

the following consistency check to assess accuracy. The estimated slow manifold points  $\hat{\mathbf{x}}_j$  are propagated backward and forward in time to  $\phi(t^{\pm}, \hat{\mathbf{x}}_j)$ . Then for each of the end points, we fix the independent variables,  $x_1$  and  $\lambda_1$ , and use FTLA to recompute the dependent variables,  $x_2$  and  $\lambda_2$  for the slow manifold point estimate. The degree of consistency between the propagated estimates and re-estimated values of the dependent variables is an indication of accuracy. The same procedure is performed for the ILDM estimates.

Fig. 2, showing points and trajectories projected onto the  $\lambda_1$ - $x_2$  plane, indicates that FTLA is more consistent than the ILDM method. Although the initial ILDM points (red circles) appear close to the initial FTLA points, the high degree of inconsistency at the end points indicates greater inaccuracy.

- U. Maas and S. B. Pope, "Simplifying chemical kinetics: intrinsic low-dimensional manifolds in composition space", Combustion and Flame 88 (1992) 239–264.
- [2] K. D. Mease, S. Bharadwaj, and S. Iravanchy, "Timescale analysis for nonlinear dynamical systems", J. Guidance, Control and Dynamics 26 (2003) 318-330.
- [3] K. D. Mease, U. Topcu, E. Aykutlug, M. Maggia, "Characterizing two-timescale nonlinear dynamics using finite-time Lyapunov exponents and vectors, Characterizing Two-Timescale Nonlinear Dynamics Using Finite-Time Lyapunov Exponents and Vectors", arXiv:0807.0239 [math.DS], 2012. [eprint]
- [4] B. Hasselblatt and Y. B. Pesin, "Partially Hyperbolic Dynamical Systems", in B. Hasselblatt and A. Katok (Eds.), Handbook of Dynamical Systems, Vol. 1B, Elsevier, New York, 2005.
- [5] A. Adrover, F. Creta, M. Giona, M. Valorani and V. Vitacolonna, "Natural tangent dynamics with recurrent biorthonormalizations: A geometric computational approach to dynamical systems exhibiting slow manifolds and periodic/chaotic limit sets", Physica D 213(2) (2006) 121 – 146.
- [6] L. Dieci and E. S. Van Vleck, "Lyapunov spectral intervals: theory and computation", SIAM J. Numerical Analysis 40(2) (2002) 516– 542.
- [7] B. Rasmussen and L. Dieci, "A geometrical method for the approximation of invariant tori", J. Computational and Applied Mathematics 216 (2008) 388–412.

### Simplifying Chemical Kinetic Systems under Uncertainty using Markov Chains

Luca Tosatto<sup>\*</sup> and Youssef Marzouk<sup>\*</sup> \*Massachusetts Institute of Technology, Cambridge, MA USA

*Abstract*— We describe a novel method to obtain skeletal reduction of chemical mechanisms. The reduction method maps the system of equations that describe the evolution of the chemical mixture into a set of memoryless Markov processes, one for each chemical element. Each Markov process "tracks" an atom through its chemical evolution, i.e., each state in the Markov process corresponds to a chemical species and the transition probability between two states models the probability that an atom is transfered between molecules. We show that this methodology provides an inexpensive estimate of the species elimination error in stirred reactor problems.

#### I. INTRODUCTION

In the last decade, the sizes of chemical mechanisms used in combustion modeling have grown by orders of magnitude [1], increasing from 20–30 species for methane combustion to more than 1000 in some recent detailed mechanisms [2]. For this reason, the numerical solution of multidimensional reacting flow still constitutes a great challenge that approaches the limit of the world's largest computational facilities [3].

A way to bridge the gap between computational fluid dynamics and complex chemistry is to replace the full set of chemical species and reactions by a simpler one. The new smaller model is optimized for a given problem and can thus generate results of the same accuracy at a much smaller computational cost.

We focus our attention on *skeletal reduction*, i.e., on the elimination of unimportant species from the mechanism. A number of techniques are available in the literature to perform this simplification: sensitivity analysis [4], CSP simplification [5], directed relation graph (DRG) reduction [6], which evolved into an array of derived techniques [7], [8], [9], path flux analysis [10], and error minimization [11].

All these methods can be subdivided in two groups:

- Intrusive methods, which extract information from the detailed mechanism and use this information to estimate the error generated by the elimination of species;
- Inspective methods, which directly test a set of candidate reduced mechanisms and thus generate the skeletal mechanism in a trial-and-error fashion.

The inspective approach typically results in a much smaller skeletal mechanism but is more computationally expensive. Furthermore, there is a link between intrusive and inspective methods; the error estimate provided by an intrusive method can be used to "guide" an inspective method in the adaptive generation of a skeletal mechanism. For example, the DRG (intrusive) method naturally evolved to the DRGASA (inspective) method.

The present contribution shows that Markov processes can be used to generate a computationally inexpensive estimate of the elimination error.

#### II. DEFINITION OF THE MARKOV PROCESSES

We consider stirred reactor problem, i.e., a nonequilibrium steady-state chemical mixture, defined by a vector of mass fractions  $Y_i$ , i = 1, ..., N and a temperature T. The steady-state condition is provided by a set of reactions  $\mathcal{R}$  characterized by the reaction rates  $r_{\alpha}$ ,  $\alpha =$ 1, ..., M and a stoichiometric matrix  $\nu_{i\alpha}$ . Furthermore, we consider the set of chemical elements  $\mathcal{E}$  (for a typical combustion problem,  $\mathcal{E}$  includes hydrogen, nitrogen, oxygen and carbon) and the composition matrix  $n_{iK}$ , whose entries represent the number of atoms of element K in molecule i.

In a stirred reactor, the mass fraction vector is calculated as the steady-state condition of a stiff system of differential equations, which is computationally expensive to solve. For this reason, we introduce an alternative probabilistic representation of the problem, in which atoms are tracked while they move from one chemical species to another. In particular, a Markov process will be defined for each of the chemical elements.

Any given atom of element K can be part of one of the molecules in set S (or at least any molecule for which the composition matrix entry  $n_{iK} > 0$ ). Thus we can say that an atom of type K can assume different *states* in S. Chemical reactions can cause a change of state of the atom since molecule *i* could be "transformed" into a different chemical species, which we will indicate with index *j*. Without resorting to molecular simulations—i.e., in the continuous regime of large species populations, typical for gas-phase combustion—it is possible to compute the probability that atom K will transition from *i* to *j*.

Elementary probability theory suggests that the probability of an  $i \rightarrow j$  transfer for atom K is given by the sum over all reactions of the probability that reaction  $\alpha$  occurs and that this reaction transfers the atom

$$\mathbb{P}(K; i \to j) = \sum_{\alpha} \mathbb{P}(K \text{ transferred} | \text{reaction } \alpha)$$
$$\mathbb{P}(\text{reaction } \alpha)$$

This probability can be calculated from the reaction rates;

$$P_{i \to j}^{K} = \sum_{\alpha \in \mathcal{R}(i)} \frac{n_{Kj} \nu_{\alpha j}^{-}}{\sum_{\ell \in R_{\alpha}} n_{K\ell} \nu_{\alpha \ell}^{-}} \frac{r_{\alpha}^{+}}{\sum_{\beta \in \mathcal{R}(i)} r_{\beta}} \quad , \quad (1)$$

where  $\mathcal{R}(i)$  is the set of reactions that involve species i and  $P_{i \to j}^{K}$  is a compact notation for  $\mathbb{P}(K; i \to j)$ .

#### III. THE ERROR ESTIMATE

In order to obtain an elimination error estimate from (1), we introduce the hypothesis that the chemical process under investigation is qualitatively modeled by a one-step irreversible global reaction. This means that there are a set of species—the global products (typically CO<sub>2</sub> and H<sub>2</sub>O)—whose transition probabilities are well approximated by  $P_{i\rightarrow j}^{K} = \delta_{ij}$  and that act as *absorbing states* in the Markov process. Conversely, the global reactants provide initial conditions, meaning that we postulate that the initial distribution of the Markov process concentrates the probability of each atom K on the global reactants. Under this approximation the transition probability (1) models the evolution of microstates from reactants to products.

For a given set  $S_r \subset S$  of potentially unimportant species that could be removed, we define the error estimate as

$$E(\mathcal{S}_r) = \mathbb{P}(\text{reaching } \mathcal{S}_r \text{ before a global product}), \quad (2)$$

which can be efficiently calculated from the transition probability (1).

#### **IV. RESULTS**

We consider a stirred reactor with an inlet temperature of 300K, in which a stoichiometric mixture of methane and oxygen is injected along with 90% nitrogen (by mass). The quantity of interest (QoI) in our study is the extinction timescale; to compute this QoI, we perform a continuation solution, progressively reducing the residence time in the reactor until extinction occurs. Starting from the 53-species GRI mechanism [12] we randomly generate skeletal reduced mechanisms of size 47 to 25. Each mechanism is tested and the error estimate (2) is calculated along with the true error in extinction time. Figure 1 shows that the error estimate correlates very well with the elimination error.

#### V. CONCLUSION

A novel intrusive approach to skeletal reduction has been presented, which relies on a Markov process description of the chemical state to estimate the error associated with the elimination of a set of species. The error estimate correlates very well with the actual elimination error. Thus it can be used to guide intrusive skeletal reduction algorithms.



Fig. 1. Scatter plot of error estimates and the true elimination errors for different reduced mechanisms, showing strong correlation.

#### ACKNOWLEDGMENT

This research is supported in part by BP through the BP-MIT Energy Conversion Program, and by the US Department of Energy, Office of Advanced Scientific Computing Research (ASCR) under grant DE-SC0003564.

- T. Lu, C. K. Law, Toward accommodating realistic fuel chemistry in large-scale computations, Progress in Energy and Combustion Science 35 (2009) 192–215.
- [2] C. K. Westbrook, W. J. Pitz, O. Herbinet, H. J. Curran, E. J. Silke, A comprehensive detailed chemical kinetic reaction mechanism for combustion of *n*-alkane hydrocarbons from *n*-octane to *n*-hexadecane, Combustion and Flame 156 (2009) 181–199.
- [3] D. O. Lignell, J. H. Chen, P. J. Smith, Three-dimensional direct numerical simulation of soot formation and transport in a temporally evolving nonpremixed ethylene jet flame, Combustion and Flame 155 (1–2) (2008) 316–333.
- [4] Y. Reuven, M. D. Smooke, H. Rabitz, Sensitivity analysis of boundary value problems – application to nonlinear reaction diffusion systems, Journal of Compututational Physics 64 (1986) 27–55.
- [5] M. Valorani, F. Creta, D. A. Goussis, J. C. Lee, H. N. Najm, An automatic procedure for the simplification of chemical kinetic mechanisms based on CSP, Combustion and Flame 146 (1–2) (2006) 29–51.
- [6] T. Lu, C. K. Law, A directed relation graph method for mechanism reduction, Proceedings of the Combustion Institute 30 (2005) 1333– 1341.
- [7] Z. Luo, T. Lu, M. J. Maciaszek, S. Som, D. E. Longman, A reduced mechanism for high-temperature oxidation of biodiesel surrogates, Energy & Fuels 24 (2010) 6283–6293.
- [8] P. Pepiot-Desjardins, H. Pitsch, An efficient error-propagation-based reduction method for large chemical kinetic mechanisms, Combustion and Flame 154 (2008) 67–81.
- [9] X. Zheng, T. Lu, C. Law, Experimental counterflow ignition temperatures and reaction mechanisms of 1,3-butadiene, Proceedings of the Combustion Institute 31 (1) (2007) 367–375.
- [10] W. Sun, Z. Chen, X. Gou, Y. Ju, A path flux analysis method for the reduction of detailed chemical kinetic mechanisms, Combustion and Flame 157 (7) (2010) 1298–1307.
- [11] T. Nagy, T. Turányi, Reduction of very large reaction mechanisms using methods based on simulation error minimization, Combustion and Flame 156 (2009) 417–428.
- [12] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Golderberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner Jr., V. V. Lissianski, Z. Qin, GRI version 3.0, available online at: http://www.me.berkeley.edu/gri\_mech (1999).

## A Combined Adaptive Chemistry and Tabulation Strategy for the Efficient Implementation of Detailed Combustion Chemistry

Perrine Pepiot<sup>\*</sup>, Youwen Liang<sup>\*</sup>, Varun Hiremath<sup>†</sup>, Stephen B. Pope<sup>\*</sup>

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

<sup>†</sup>CD-adapco, Lebanon, NH, USA

Abstract-Significant progress is being made in the development of detailed chemical kinetic mechanisms for transportation fuels and their surrogates, leading to models involving up to several thousands molecular species. A major challenge is to make use of this chemical knowledge in turbulent combustion models, which most often become intractable if more than tens of species are considered. In this work, we propose a novel adaptive chemistry strategy specifically designed for LES/particle PDF simulations of non-premixed turbulent flames with the following key properties: (i) the composition space is partitioned a priori into a user-specified number of regions, over which suitable reduced chemical representations and chemical models are identified; (ii) the computational particles in the LES/PDF simulations carry only the variables present in the reduced representations; and (iii) the region a given particle belongs to is identified using a low-dimensional binary tree search algorithm, thereby keeping the run-time overhead associated with the adaptive approach to a minimum. An overview of the adaptive strategy is first presented, with details being provided for the major components of the algorithm. The adaptive treatment of the chemistry is then implemented within the ISAT/RCCE framework validated previously by Hiremath et al. [Hiremath, Ren & Pope, Combust. Flame, 2011]. A proof-of-concept of the combined adaptive chemistry and tabulation strategy is presented for the simpler partially stirred reactor (PaSR) with pair-wise mixing configuration. Preliminary results indicate that compared to results based on a single reduced representation for all particles, the adaptive methodology provides similar accuracy at a lower overall computational cost.

#### I. INTRODUCTION

The understanding of chemical kinetics for hydrocarbon fuel combustion has exploded over the past two decades, leading to the development of ever growing detailed kinetic schemes for a wide range of molecular species relevant to hydrocarbon combustion [1]. With more accurate rate rules and improved mechanistic considerations, some of the latest published mechanisms are approaching  $10^4$  species and as many reactions [2]. However, these advances in chemical kinetics and detailed model development have to be integrated with Computational Fluid Dynamics (CFD) tools to fully realize their potential in terms of improved understanding and optimization of practical combustion devices. The real challenge then is to maximize the level of chemical detail that can be afforded in CFD. One strategy to address this challenge was recently proposed by Hiremath et al. using a combination of dimension reduction and tabulation [3] and applied to the simulation of turbulent flames. Such techniques greatly increase the level of description of the chemistry that can be used, allowing, for example, the use of about 40 species in large-eddy simulation/probability density function (LES/PDF) calculations. However, significant further gains are clearly needed to handle the chemical complexities of real fuels, which can be attained through the development of adaptive chemistry methodologies, in which (ideally), in different regions of the flow, the smallest possible reduced mechanism is used as required by the local chemical activity and thermodynamic state. Several adaptive chemistry approaches have been proposed recently in the literature (e.g. [4], [5], [6], [7], [8], [9]), generally yielding quite promising results.

In this work, we propose an adaptive strategy to handle large chemical mechanisms tailored for LES/PDF simulations of non-premixed combustion, with the following constraints: the framework should be compatible and work synergistically with existing LES/PDF implementations (*e.g.*[10]), the overhead cost associated with the adaptive treatment of the chemistry should be small, and only reduced representations should be used to evolve the composition of the particles. In the following, a overview of the adaptive methodology is provided, and the integration of the adaptive algorithm within the ISAT/RCCE framework of Hiremath *et al.* [3] is discussed.

#### II. ADAPTIVE CHEMISTRY METHODOLOGY

We consider a detailed chemical mechanism involving a set of species  $\Phi^D$ , of cardinality  $n_D$ , and we denote the mass fraction of the species by the  $n_D$ -vector **Y**. We consider the case of constant-pressure combustion, so that the thermochemical state of the fluid is fully characterized by **Y** and the temperature *T*. In the LES/PDF calculation, the fluid within the turbulent flow field is represented by a large number of particles. At time *t*, the *n*th particle has a composition  $\mathbf{C}^{(n)}(t) = \{\mathbf{Y}^{(n)}(t), T^{(n)}(t)\}$ . The simulation marches in time in uniform time steps  $\Delta t$ . While the particles move in physical space due to the resolved flow and the unresolved turbulence, the particle compositions change due to just two processes: reaction and mixing. We call reaction mapping over a time step  $\Delta t$  the evolution from  $\mathbf{C}^{(n)}(t)$  to  $\mathbf{C}^{(n)}(t + \Delta t)$  due to reaction. In this context, our approach to adaptive chemistry is decomposed into a pre-processing step to define the reduced chemistry framework *prior to* the flame simulations, and a procedure to dynamically assign the appropriate reduced representation and model to each of the particles *during* the flame simulation. More specifically, the strategy consists of the following components:

#### A. Pre-processing of the chemical kinetics

The pre-processing uses the detailed kinetic model in simpler Partially Stirred Reactor calculations, whose conditions are representative of the turbulent flame simulation to be performed, to generate a large database of detailed test compositions. This database is used for:

- 1) **Partitioning:** Suitably partition the composition space into a number of regions, the  $J^{th}$  one being denoted by  $R_J$ , using a cutting-plane method.
- 2) **Reduction:** For each region  $R_J$ , develop an accurate reduced chemical model  $M_J$ , in which the composition has a reduced representation  $\mathbf{c}_J = \{\mathbf{y}_J, T_J\}$ . The reduced mass fraction vector  $\mathbf{y}_J$  is of size  $n_{R,J} \ll n_D$ . This is accomplished using the Directed Relation Graph with Error Propagation reduction technique [11].

The partition then is stored as a binary tree, associated with a set of reduced models, one for each leaf of the tree, and a set of cutting planes, one for each node of the tree.

#### B. Adaptive approach in flame simulation

In the LES/PDF computations, the particle composition located in region  $R_J$  carries the reduced composition  $\mathbf{c}_J^{(n)}(t) = {\mathbf{y}_J^{(n)}(t), T_J}$  instead of  $\mathbf{C}^{(n)}(t)$ , and this composition is advanced during the reaction sub-step using the reduced model  $M_J$ . This requires two main procedures:

- Conversion: Convert a particle composition from reduced representation J to reduced representation L as the particle moves across regions. A simple merge of the representations, followed by normalization is used here to get the new mass fraction vector.
- Classification: An efficient binary tree search based on a well-chosen small set of species is used to determine the region a given particle belongs to based on its reduced representation.

#### **III. PRELIMINARY RESULTS**

The adaptive strategy is tested using PaSR calculations for non-premixed propane/air and a detailed mechanism containing 115 species [12]. The composition space is partitioned into 20 regions based on a detailed sample database of  $10^4$  compositions. The evolution of the particle compositions are then compared to the detailed solution for different levels of reductions, and shown in Fig. 1. The errors obtained when using a single reduced representation and single reduced model for all particles are also shown. While only basic algorithms for all components involved in the adaptive approach have been implemented, these results indicate that the adaptive methodology provides similar accuracy at a lower overall computational cost compared to single model approaches.



Fig. 1. Evolution of the overall error in a propane/air PaSR calculation between detailed representation, a 43-species (green) and a 34-species (blue) *single* reduced representations, and adaptive representations with an average of 30 (black) and 34 (red) species.

#### IV. INTEGRATION WITH ISAT/RCCE

The integration within the framework of Hiremath *et al.* follows in a straightforward manner. The size of the reduced representations are further decreased by introducing RCCE to complement species elimination provided by DRGEP, while for the reaction fractional step in flame simulation, separate ISAT tables are used for each region, reducing significantly the time to build the tables and accelerating the retrieval of reaction mappings.

#### ACKNOWLEDGMENT

This work is supported by the Department of Energy under the grant DE-FG02-90ER14128.

- [1] T. Lu and C. K. Law. Prog. Energy Comb. Sci., 35:192 215, 2009.
- [2] O. Herbinet, W. J. Pitz, and C. K. Westbrook. Comb. Flame, 154:507– 528, 2008.
- [3] V. Hiremath, Z. Ren, and S. B. Pope. Comb. Flame, 158:2113, 2011.
- [4] L. Liang, J. G. Stevens, and J. T. Farrell. Proc. Comb. Inst., 32(1):527–534, 2009.
- [5] F. Contino, H. Jeanmart, T. Lucchini, and G. D'Errico. Proc. Comb. Inst., 33(2):3057–3064, 2011.
- [6] L. Tosatto, B. A. V. Bennett, and M. D. Smooke. Comb. Flame, 158(5):820–835, 2011.
- [7] T. Løvas, S. Navarro-Martinez, and S. Rigopoulos. Proc. Comb. Inst., 33(1):1339–1346, 2011.
- [8] B. J. Debusschere, Y. M. Marzouk, H. N. Najm, B. Rhoads, D. A. Goussis, and M. Valorani. *Comb. Th. Mod.*, 16(1):173–198, 2012.
- [9] I. Banerjee and M. Ierapetritou. Comb. Flame, 144(3):619-633, 2006.
- [10] V. Hiremath, S.R. Lantz, H. Wang, S.B. Pope. Proc. Comb. Inst., 34:205–215, 2013.
- [11] P. Pepiot and H. Pitsch. Comb. Flame, 154(1-2):67-81, 2008.
- [12] H.J. Curran, T.M. Jayaweera, and W.J. Pitz. WSS Meeting of the Comb. Inst., 2004.

## A Boundary Value View on the Reverse Trajectory-Based Optimization Approach for Kinetic Model Reduction

Dirk Lebiedz\*, Jonas Unger\*

\*Department of Numerical Mathematics, Ulm University, Germany

*Abstract*— Chemical combustion models in terms of ordinary differential equations correspond to finite dimensional dissipative dynamical systems involving a multiple time scale structure. A slow mode-description of the full model for dimension reduction purposes is achieved via computation of slow manifolds which can be identified in these reaction systems. We discuss basic analytical components of model reduction by means of a linear test model and present a boundary value problem bundling ideas of many model reduction approaches.

#### I. INTRODUCTION

Chemically reacting flows comprise an interplay between convective and diffusive species transport and chemical reaction processes involving a large number of chemical species and reactions. Together with the stiffness of the kinetic model equation with time scales ranging from nanoseconds to seconds, simulation of chemically reacting flows (for instance in combustion processes) is often nearly impossible in reasonable time. This calls for complexity reduction and multi-scale approaches.

Most of those model and complexity reduction techniques exploit the time scale separation of the model solution into fast and slow modes by approximating the large time scale system dynamics via eliminating the fast relaxing modes by enslaving them to the slow ones. This results in invariant manifolds of slow motion (SIMs) possessing the property of attracting system solution trajectories. The process of mapping a subset of the chemical species of the full model onto the full species composition by determining a point on a SIM is provided by an implicitly defined function. This *species reconstruction technique* is used by many model reduction approaches for SIM identification.

In this talk we discuss basic analytical issues of model reduction by means of a linear test model and present, why a (reverse) trajectory-based optimization approach suggested by Lebiedz [3] identifies SIMs exactly for an infinite time horizon [7] yielding the formulation of a boundary value problem.

#### II. LINEAR TEST MODEL: ANALYTICAL TREATMENT

For simplicity we consider a two-dimensional linear ODE test model, representing chemical combustion model equation:

$$\partial_t z_1(t) = \left(-1 - \frac{\gamma}{2}\right) z_1(t) + \frac{\gamma}{2} z_2(t) \tag{1a}$$

$$\partial_t z_2(t) = \frac{\gamma}{2} z_1(t) + \left(-1 - \frac{\gamma}{2}\right) z_2(t), \quad \gamma > 0, \qquad (1b)$$

with  $\gamma \in \mathbb{R}$ ,  $t \in \mathbb{R}$ ,  $z_1, z_2 \in C^{\infty}(\mathbb{R}, \mathbb{R})$ , and analytical solution

$$z_1(t) = c_1 e^{-t} + c_2 e^{(-1-\gamma)t}$$
(2a)

$$z_2(t) = c_1 e^{-t} - c_2 e^{(-1-\gamma)t}, \quad c_1, c_2 \in \mathbb{R}$$
 (2b)

with  $c_i$ , i = 1, 2 being integration constants, to be determined by setting initial values. Due to the availability of explicit formula for the SIM, this model is well suited for analytical treatment. This formula is achieved by eliminating the fast modes (here implying setting  $c_2$  equal to zero) yielding  $z_1 \equiv z_2$  being the SIM. Subsituting this into (1) results in the following reduced model equation:

$$z_1(t) = z_2(t) \tag{3a}$$

$$\partial_t z_2(t) = -z_2(t) \tag{3b}$$

with analytical solution  $z_1(t) = z_2(t) = c_1 e^{-t}$  being equivalent to the solution of the full model (2) without fast modes  $(c_2 = 0)$ .

Finding an additional criterion that automatically eliminates the fast modes without knowing the analytical solution of the underlying ODE model equations is the main challenge of model reduction approaches.

#### III. SLOW MANIFOLD COMPUTATION

#### A. Boundary Value Problem

In dissipative ODE systems where it holds that

$$d(z(t_0), \text{SIM}) > d(z(t_*), \text{SIM})$$
(4)

with  $t_0 < t_*$ ,  $d(\cdot, \cdot) \in C^{\infty}(\mathbb{R}^n \times \mathbb{R}^n, \mathbb{R})$  being the distance function, and  $z(t_*)$  meaning  $z(t_*) = z(t_* - t_0, z(t_0))$  (i.e. the solution of the initial value problem  $\partial_t z(t) = S(z(t))$ ,  $z(t_0) = z^{t_0}$  evaluated after a time period of  $t_* - t_0$ ), the point of interest (POI)  $z(t_*)$  identifies a SIM exactly for  $t_* - t_0 = \infty$ and  $d(z(t_0), \text{SIM}) \in \mathbb{R}$ :

$$d(z(t_*), \text{SIM}) = 0.$$
 (5)

Having this in mind, the following general formulation of a boundary value problem for SIM computation is presented:

$$\partial_t z(t) = S(z(t)) \tag{6a}$$

$$z_j(t_*) = z_j^{t_*}, \ j \in I_{\text{fixed}}, \ t_* \in \mathbb{R}$$
(6b)

$$z_j(t_0) = K_j, \ j \notin I_{\text{fixed}}, \ K_j = \text{const.} \land \ |K_j| \neq \infty \ \forall j \notin I_{\text{fixed}}$$
  
(6c)

with  $t_0 < t_*$  in the reverse mode formulation [7], [8]. Here, (6a) describes the system dynamics, (6b) the fixation of those variables that parameterize the SIM at time  $t = t_*$ , and  $I_{\text{fixed}}$  denotes the index set containing those reaction progress variables. For globally attractive systems the choice of K is without significance to achieve  $\lim_{t_0\to-\infty} z(t_*) \in SIM$ , whereas in realistic chemical processes the choice of K plays a significant role caused by additional physical constraints restricting the area where the ODE model is defined and thus,  $t_0$  can only be chosen as small as possible. This idea of using a boundary value method for slow manifold computation is also found in [2], [9], [10] for example. Exact SIM identification by using this reverse boundary value problem with an infinite time horizon is confirmed by analytical and numerical tests applying the linear model (1) (see [8]).

#### B. Trajectory-Based Optimization Approach and Zero-Derivative Principle

For a 'good choice' of K we use the derivative idea from the Zero-Derivative Principle (ZDP) [1], [11] (POI is closer to SIM with higher derivatives) and relate it to the trajectory-based optimization approach [3], [4], [5], [6], [7] leading to the following formulation of a model reduction technique combining both the boundary value idea from above and the derivative idea of the ZDP:

$$\min_{z(t)} \left\| \partial_t^m z(t) \right\|_2^2 \Big|_{t=t_0}, \quad m \in \mathbb{N}$$
(7a)

subject to

$$\partial_t z(t) = S(z(t)) \tag{7b}$$

$$0 = g(z(t_*)), \quad t_* \in \mathbb{R}$$
(7c)

$$z_i(t_*) = z_i^{t_*}, \quad j \in I_{\text{fixed}} \tag{7d}$$

with  $g \in C^{\infty}(\mathbb{R}^n, \mathbb{R}^b)$  containing possible additional constraints (for instance chemical element mass conservation relations) and can be omitted for the linear test model above. In this formulation *K* improves with higher *m* yielding

$$\lim z(t_*) \in \text{SIM} \tag{8a}$$

$$\lim_{t_0 \to -\infty} z(t_*) \in \text{SIM.}$$
(8b)

Both analytical and numerical computations confirm these results.

In numerical implementations for realistic combustion processes difficulties arise from choosing m > 2. The kinetic

ODE model is only defined on a polyhedron in phase space based on additional constraints entering the optimization problem such that  $t_0$  cannot get arbitrarily small. Thus, for a good SIM approximation in realistic models two issues have to be addressed:

- choosing *m* as large as possible.
- choosing  $t_0$  as small as possible.

#### C. How to Treat Constraints in Realistic Kinetic Models

Since the POI improves with smaller  $t_0$ , the aim is a minimal feasible choice of  $t_0$ . We address this issue via analytical treatment for the linear model (1).

Solving (7) with (1) analytically provides analytical formula for the integration constants from (2)  $\hat{c}_1$  and  $\hat{c}_2$  dependent on  $t_0$  which are substituted into  $z_1 = z_1(\hat{c}_1, \hat{c}_2)$  and  $z_2 = z_2(\hat{c}_1, \hat{c}_2)$  for solving the following optimization problem yielding the minimal  $t_0$  that is feasible

m

$$in t_0$$
(9a)

subject to

$$z_1(\hat{c}_1, \hat{c}_2) \ge 0$$
 (9b)

$$z_2(\hat{c}_1, \hat{c}_2) \ge 0 \tag{9c}$$

$$z_1(c_1, c_2) \le n_1 z_2(c_1, c_2) + b_1 \tag{9d}$$

$$z_1(\hat{c}_1, \hat{c}_2) \le n_2 z_2(\hat{c}_1, \hat{c}_2) + b_2 \tag{9e}$$

with (9b)–(9e) being the additional constraints entering the model reduction above as function g. Solving (9) with different choices of the constants results in a minimal feasible choice of  $t_0$ .

#### References

- C.W. GEAR, T.J. KAPER, I.G. KEVREKIDIS, AND A. ZAGARIS, Projecting to a slow manifold: Singularly perturbed systems and legacy codes, SIAM J. Appl. Dyn. Syst., 4 (2005), pp. 711–732.
- [2] J. GUCKENHEIMER AND C. KUEHN, Computing slow manifolds of saddle type, SIAM J. Appl. Dyn. Syst., 8 (2009), pp. 854–879.
- [3] D. LEBIEDZ, Computing minimal entropy production trajectories: An approach to model reduction in chemical kinetics, J. Chem. Phys., 120 (2004), pp. 6890–6897.
- [4] D. LEBIEDZ, V. REINHARDT, AND J. SIEHR, Minimal curvature trajectories: Riemannian geometry concepts for model reduction in chemical kinetics, J. Comp. Phys., 229 (2010), pp. 6512–6533.
- [5] D. LEBIEDZ, Entropy-related extremum principles for model reduction of dynamical systems, Entropy, 12 (2010), pp. 706–719.
- [6] D. LEBIEDZ, V. REINHARDT, J. SIEHR, AND J. UNGER, Geometric criteria for model reduction in chemical kinetics via optimization of trajectories, in Coping with Complexity: Model Reduction and Data Analysis, A. N. Gorban, D. Roosepp, eds., Springer, 2011, pp. 241– 252.
- [7] D. LEBIEDZ, J. SIEHR, AND J. UNGER, A variational principle for computing slow invariant manifolds in dissipative dynamical systems, SIAM J. Sci. Comput., 33 (2011), pp. 703–720.
- [8] D. LEBIEDZ AND J. UNGER, A boundary value view on trajectory-based slow manifold approximation in kinetic models with spectral gap, In preparation.
- [9] Z. REN AND S.B. POPE, Species reconstruction using pre-image curves, in Proc. Comb. Inst., 30 (2005), pp. 1293–1300.
- [10] Z. REN, S.B. POPE, A. VLADIMIRSKY, AND J.M. GUCKENHEIMER, The invariant constrained equilibrium edge preimage curve method for the dimension reduction of chemical kinetics, J. Chem. Phys., 124 (2006), p. 114111.
- [11] A. ZAGARIS, C.W. GEAR, T.J. KAPER, AND Y.G. KEVREKIDIS, Analysis of the accuracy and convergence of equation-free projection to a slow manifold, ESAIM: Math. Model. Num., 43 (2009), pp. 757–784.

# Reduced Kinetic Mechanism of a Selective Non-Catalytic Process with Urea as Reducing Agent

Diana M. Vásquez<sup>a</sup>, Aída Luz Villa<sup>b</sup>, Felipe Bustamante<sup>c</sup>, Carlos M. Tobón<sup>d</sup>

<sup>a,b,c,d</sup>Universidad de Antioquia, Chemical Engineering Department, Environmental Catalysis Research Group,Medellin-Colombia.

Abstract-A detailed kinetic mechanism consisting of 116 reactions and 26 species was obtained based on the NOxOUT mechanism proposed by Rota and the mechanism developed by Miller et al. The kinetic mechanism proposed in this contribution is suggested as a model of SNCR process using urea as reducing agent. The mechanism was validated with experimental data reported by Gentemann and Caton for various CO concentrations; good agreement of the detailed model with experimental data was obtained. The detailed mechanism was reduced to 44 reactions and 23 species. Agreement between the detailed and reduced kinetic mechanisms was good for the range of conditions of SNCR studied. The new reduced mechanism has been incorporated into CFD simulation in order to validate, the reduced reaction mechanism compares well the seven-step mechanism reported by Nguyen.

#### I. INTRODUCTION

The rapid industrialization has had a significant negative effect on air quality. Therefore, more stricte mission standards have fostered the development of technologies for control of emissions. Among them, selective non-catalytic reduction (SNCR) is a cost-effective post-combustion technology for controlling emissions of nitrogen oxides (NOx). SNCR consists in the controlled injection of a reducing agent, such as ammonia or urea, into the flue gas. Use of urea has been widely accepted due to its easier and safer handling. The relatively narrow temperature window over which significant NOx reduction can be attained depends on parameters such as composition of the flue gas (NOx, CO,  $H_2O$  and  $O_2$ ), and reductant/NO molar ratio (or NSR) [1, 2].

Computational Fluid Dynamics (CFD) techniques have been used to simulate SNCR processes in order to gain a better understanding of the process as well as to obtain the best operating conditions. However, CFD simulations can be easily overwhelmed because kinetic models may involve hundreds of species and reactions[3].Moreover, coupling of turbulence and heat transfer phenomena with the detailed chemistry is very demanding on computer time and memory. Several authors have reported various reduced kinetic models for NOx reduction [3–6]; these models have been widely adopted in CFD modeling.

The main objectives of this work are: (1) to develop a detailed mechanism based on kinetic mechanism reported in the literature and validate it with experimental data for

SNCR process, (2) to reduce the detailed kinetic mechanism, and (3) compare the results of the reduced kinetic mechanism and of the detailed kinetic mechanism (4) evaluate its performance in CFD simulations.

#### II. DEVELOPMENT OF THE DETAILED MECHANISM

The detailed mechanism was based on the mechanism of Miller and Bowman [7] for NOx reduction using  $NH_3$ , and the mechanism of Rota et al.[8] with urea, ammonia and isocyanic acid as reducing agents some elementary reactions related to SNCR process were chosen from the Miller and Rota mechanisms.

Kinetic mechanism of 116 reactions and 26 species was determined. The results of the model were compared with experimental data (Table 1) reported by Gentemann[9], using four different CO concentrations..

TABLE I. EXPERIMENTAL CONDITIONS OF GENTEMANN REPORT FOR SNCR PROCESS WITH UREA [9]

Experimental conditions					
Temperature range	800-1300 K	Nitric oxide	330		
Residence time	1.3-2.1 sec	Urea	0-900 ppm		
Total reactor flow	1100 sccm	Oxygen	5%		
ID reactor	1.8 cm	Carbon monoxide	0,100,600,90 0 ppm		
Length	30.48 cm	Nitrogen	Balance		



Figure 1. Nitric oxide reduction as a function of reactor temperature for 0 ppm carbon monoxide and for 5% oxygen.



Figure 2. Nitric oxide reduction as a function of reactor temperature for 100 ppm carbon monoxide and for 5% oxygen.

As presented in the above Figures 1 and 2, the simulated data of NO reduction using the detailed mechanism show good agreement, both qualitatively and quantitatively, with the experimental data of Gentemann[9].

#### III. DEVELOPMENT OF REDUCED MECHANISM

A new reduced chemical kinetic model was developed through a sensitivity analysis of the detailed mechanism. The reduced mechanism includes 44 reactions and 23 species. Deviation between results of the detailed and reduced kinetic mechanisms was very small for the concentration of the more important species. For instance, a low Residual Square Sum (RSS) value and a high Determination Coefficient ( $r^2$ ) of 0.98 were obtained when comparing the two mechanisms (see Figures 3 and 4).



Figure 3. Comparison between detailed kinetic mechanism and reduced kinetic mechanism in NO reduction



Figure 4.Carbon monoxide concentration as a function of the temperature using detailed kinetic mechanism and reduced kinetic mechanism

The reduced kinetic mechanism was incorporated into a CFD model without excessive computational load into the simulation (less than two times that of a reduced mechanism with 7 reactions and 13 species). The reduced reaction mechanism compares well a seven-step mechanism for an isothermal reactor at 940°C, Figure 5.



Figure 5. Comparison of simulations results using mechanism reported by Nguyen and mechanism proposed in this work. Inlet conditions: 400ppm NO,  $5\% v/v H_2O$ ,  $12\% v/v O_2$  and balance N<sub>2</sub>.

#### **ACKNOWLEDGMENTS**

This work was supported by the Universidad de Antioquia, SUMICOL and Colciencias through Project 1115-454-25886.

- [1] T. D. B. Nguyen, Y.-I. Lim, S.-J. Kim, W.-H. Eom, and K.-S. Yoo, "Experiment and Computational Fluid Dynamics (CFD) Simulation of Urea-Based Selective Noncatalytic Reduction (SNCR) in a Pilot-Scale Flow Reactor," *Energy & Fuels*, vol. 22, no. 6, pp. 3864–3876, Nov. 2008.
- [2] J. Bin Lee and S. D. Kim, "Kinetics of NOx reduction by Urea solution in a pilot sacle reactor,1996".
- [3] Y. Lv, Z. Wang, J. Zhou, and K. Cen, "Reduced Mechanism for Hybrid NO x Control Process," *Energy & Fuels*, vol. 23, no. 12, pp. 5920–5928, Dec. 2009.
- [4] M. A. Cremer, C. J. Montgomery, D. H. Wang, M. P. Heap, R. E. International, and S. L. City, "Development and implementation of reduced chemistry for CFD modeling of Selective Non-Catalytic Reduction," no. 801.
- [5] H. Xu, L. D. Smoot, and S. C. Hill, "A Reduced Kinetic Model for NOx Reduction by Advanced Reburning"pp. 1278–1289, 1998.
- [6] F. Perini, J. L. Brakora, R. D. Reitz, and G. Cantore, "Development of reduced and optimized reaction mechanisms based on genetic algorithms and element flux analysis," *Combustion and Flame*, vol. 159, no. 1, pp. 103–119, Jan. 2012.
- [7] J. A. Miller and C. T. Bowman, "Kinetic modeling of the reduction of nitric oxide in combustion products by isocyanic acid," *International Journal of Chemical Kinetics*, vol. 23, no. 4, pp. 289–313, Apr. 1991.
- [8] R. Rota, D. Antos, É. F. Zanoelo, and M. Morbidelli, "Experimental and modeling analysis of the NOXOUT process," *Chemical Engineering Science*, vol. 57, no. 1, pp. 27–38, Jan. 2002.
- [9] A. M. G. Gentemann, "Flow reactor experiments on the selective non-catalytic removal (SNCR) of nitric oxide using a urea-water solution," pp. 1–6.

## Mechanism Reduction as a Preconditioning Strategy for Integrating Large Chemical Kinetic Systems

Matthew J. McNenly<sup>\*</sup>, Russell A. Whitesides<sup>\*</sup> and Daniel L. Flowers<sup>\*</sup>

\* Lawrence Livermore National Laboratory, Computational Engineering Division, Livermore, CA, United States

*Abstract*— Mechanism reduction techniques are used to develop a class of adaptive preconditioners for integrating the ordinary differential equations (ODE) associated with large chemical kinetic mechanisms. The new adaptive preconditioners reduce the computational cost by several orders of magnitude relative to traditional dense solution methods for a detailed 2-methylnonadecane mechanism ( $C_{20}H_{42}$  with 7172 species).

#### I. INTRODUCTION

Preconditioners are sought to increase the convergence rate of the iterative linear system solver embedded within the implicit ODE solver. In particular, the linear system solver is used for every iteration of the Newton-Raphson nonlinear solver, which computes the chemical state at future timesteps in the implicit discretization of the ODEs [1]. A good preconditioning matrix for ODE solvers is one that captures the dominant behavior of the system evolution, but is significantly easier to solve than the complete system [2].

The Jacobian matrices associated with the ODEs of reduced mechanisms are thus ideal candidates for use as preconditioners. A preconditioner need only serve as an approximation to the true ODE system, which is then improved by the iterative linear and non-linear solvers to achieve the same solution as direct methods (to within a user-specified accuracy). This means that the reduced mechanism selected for the preconditioner can be smaller and lower in fidelity than the standard approach to global mechanism reduction. Further, the reduced mechanism must only be accurate for the chemical state over the duration of an individual timestep, which means even greater reduction is possible by allowing the preconditioning mechanism to adapt. This feature, referred to as adaptive preconditioning, allows the integration of detailed chemical kinetic mechanisms to occur at a cost

comparable to methods using on-the-fly mechanism reduction without any loss of accuracy.

#### II. APPROACH

A number of adaptive preconditioners are tested using several different reduction heuristics. The simplest reduction technique is based on removing reactions that have a slow characteristic timescale relative to the integrator timestep. To filter out the slow reactions in the preconditioner matrix P, a threshold operation is applied to the Jacobian matrix B of the backward differentiation formulas (BDF) for the stiff ODE integrator. Specifically,

$$P_{ij} = \begin{cases} B_{ij} & \text{if } i = j \text{ or } |B_{ij}| > \eta \\ 0 & \text{otherwise,} \end{cases}$$
(1)

where  $\eta$  is a nondimensional, user-specified threshold. A more complete description of the approach to reducing the mechanism in this preconditioner is found in [3].

Other preconditioners are also tested as part of this investigation, but none have been found so far to produce a measurably faster method than the simple reaction filtering approach in (1). As a consequence, the computational timings for these other preconditioners are not discussed in detail. The filter metrics for these other preconditioners include: (i) the species coupling frequency normalized by the destruction rate (i.e., row-normalization); (ii) the species coupling frequency normalized by the perturbation species destruction rate (i.e., column normalization); (iii) the maximum and minimum of metrics (i) and (ii); and (iv) the species coupling metric used in the technique in [4] for mechanism reduction via directed relational graph with error propagation (DRG-EP) analysis. It is interesting to note that filtering by the DRG-EP metric offers large reductions in the preconditioner size near equilibrium. However, the performance is not consistent over the range of conditions tested due to convergence problems. Further investigation is necessary to apply this more sophisticated preconditioner in a manner that is able to systematically avoid the non-linear convergence errors currently observed.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contact DE-AC52-07NA27344. The authors gratefully acknowledge the support of Gurpreet Singh, the Advanced Combustion Engines Program Leader for the U.S. Department of Energy Vehicle Technologies Office.



Fig. 1. Comparison of the computational cost between the new adaptive preconditioner approach (blue solid circles) and the traditional ODE solver using dense matrix methods (red empty squares).

#### III. TEST CASES

The average computation times are compared between two approaches for integrating a constant volume, homogenous reactor model. The first approach is based on the traditional stiff-ODE solver methods first used in chemical kinetics. This approach is still found in some multi-dimensional computational fluid dynamics codes (e.g. KIVA-MZ [5]). The second approach is based on the adaptive preconditioner (1) using the optimized integrator and sparse matrix settings developed in [6].

A total of ten different mechanisms are tested ranging in size from hydrogen (10 species [7]) to 2-methylnonadecane (7172 species [8]). The initial compositions are a stoichiometric mixture of fuel and idealized air (79% N<sub>2</sub> and 21% O<sub>2</sub>) at an initial pressure of 20 atmospheres. Between eight and twenty-five initial temperatures are tested ranging from 650 to 1450 Kelvin for each mechanism. The evolution of each mixture composition is simulated for one second of physical time, and only those initial conditions leading to auto-ignition are included in the average computation time reported. A more complete description of the test cases is found in [3] along with a full reference list and optimum threshold values  $\eta$  found for each mechanism.

#### **IV. RESULTS**

The average computation time is obtained for each approach using a single thread of an Intel Xeon E5620 processor (2.4 GHz clock speed with 1.33 GHz DDR3 ECC RAM). The timing results are shown in Fig. 1. For the largest mechanism tested (2-methylnonadecane, 7172 species), the adaptive preconditioner has an average solution time of 32 seconds compared to 10<sup>5</sup> seconds (more

than one day) for the traditional approach, which represents three orders of magnitude of computational speedup. It is important to stress that while the mechanism is effectively reduced at each timestep by the filtering operation for the preconditioner (1), the mechanism governing the ODE system is unchanged. Consequently, the ignition delay times, temperatures and major species mass fractions (greater than  $10^{-6}$ ) obtained through the two approaches agree to a minimum of six decimal places for the userspecified relative tolerance of  $10^{-8}$ . The mass fractions of trace species (between  $10^{-12}$  and  $10^{-6}$ ) are found to agree to within four decimal places. The computational speedup shown in Fig. 1 therefore occurs with no practical loss in accuracy.

For the smaller mechanisms, hydrogen (10 species) and methane (53 species) the Jacobian matrix is sufficiently dense that the adaptive preconditioner is comparable to the traditional approach. In fact, for the hydrogen mechanism the dense approach is approximately two times faster. To avoid this penalty, a metastrategy can be developed that combines the two approaches and automatically selects the best method based on mechanism size or through automatic tuning when the mechanism information is first read into the simulation.

- A. C. Hindmarsh and R. Serban, User Documentation for CVODE v2.6.0, Technical Report UCRL-SM-208108, Lawrence Livermore National Laboratory, May 2009.
- [2] L. N. Trefethen and D. Bau III, *Numerical Linear Algebra*, Philadelphia: SIAM, 1997, pp. 313–319.
- [3] M. J. McNenly, R. A. Whitesides, and D. L. Flowers, "Adaptive preconditioning strategies for integrating large kinetic mechanisms," 8<sup>th</sup> US Nat. Combust. Meet., no. 070RK-0377, Park City, UT, 2013.
- [4] P. Pepiot-Desjardins and H. Pitsch, "An efficient error-propagationbased reduction method for large chemical kinetic mechanisms," *Combust. Flame*, vol. 154, pp. 67–81, 2008.
- [5] A. Babajimopoulos, D. N. Assanis, D. L. Flowers, S. M. Aceves, and R. P. Hessel, "A fully coupled computational fluid dynamics and multi-zone model with detailed chemical kinetics for the simulation of premixed charge compression ignition engines," *Int. J. Engine Res.*, vol. 6, pp. 497–512, 2005.
- [6] R. A. Whitesides, M. J. McNenly and D. L. Flowers, "Optimizing time integration of chemical-kinetic networks for speed and accuracy," 8<sup>th</sup> US Nat. Combust. Meet., no. 070RK-0363, Park City, UT, 2013.
- [7] M. O'Connaire, H. J. Curran, J. M. Simmie, W. J. Pitz, and C. K. Westbrook, "A comprehensive modeling study of hydrogen oxidation," *Int. J. Chem. Kinet.*, vol. 36, pp. 603–622, 2004.
- [8] S. M. Sarathy et al., "Comprehensive chemical kinetic modeling of the oxidation of 2-methylalkanes from C7 to C20," *Combust. Flame*, vol. 158, pp. 2338–2357, 2011.

### Pinning Reaction Fronts in a Windy Vortex Array

John Mahoney\*, Kevin Mitchell\*

\*University of California, Merced/School of Natural Sciences, Merced, USA

Abstract—Previous experiments on the **Belousov-**Zhabotinsky reaction in a vortex array fluid flow demonstrated the existence of "frozen fronts"-nontrivial and stable spatial patterns-upon the addition of an external "wind". While certain aspects of these patterns could be explained, a more complete theory was lacking. Invariant manifolds are key geometric structures in the phase space of passive fluid flows. These manifolds have been used to analyze passive transport, e.g. in vortex arrays. Recent work has developed the analogous invariant manifolds relevant for front propagation in fluid flows-burning invariant manifolds (BIMs). These studies have focused on BIMs as local barriers. That is, the BIM has a finite physically relevant length which is eventually circumnavigated by impinging fronts. Here we show that BIMs can also form global barriers (which cannot be circumnavigated) and that these are exactly the frozen fronts originally observed in experiments.

#### I. INTRODUCTION

We are generally interested in systems that combine the dynamics of front propagation with an underlying flow. The front propagation aspect could model the progress of a combustion reaction, a phase transition, or an infectious disease. The front is assumed to clearly divide fluid into "burned" and "unburned" regions. This propagation occurs in a medium that is itself moving in a fluid-like way, and propagation occurs normal to the local front tangent and with a constant speed in the comoving frame.

#### **II. FROZEN FRONTS**

We are motivated by the experimental results in [1] that demonstrated these frozen fronts. In these experiments, the front propagation dynamics was supplied by the rutheniumcatalyzed excitable Belousov-Zhabotinsky (BZ) reaction. This autocatalytic reaction can be triggered by inserting a silver wire into the reagents. The flow used was a linear array of alternating vortices generated in a thin fluid using magnetohydrodynamic forcing. Furthermore, a "wind" was applied to this flow in order to counter the progress of the reaction front. In this way one may generate "frozen fronts". These frozen fronts are locally stable and persist over relatively long time scales. It can be seen that their appearance and shape bear some relation to the flow in which they exist, but this relation was not yet entirely clear.

#### **III. INVARIANT MANIFOLDS**

Invariant manifolds are fundamental geometric objects that are important for understanding passive transport in



Fig. 1. (a) Reaction is pulled around by each vortex and then burns through the separatrix to proceed into the adjacent vortex (not pinned). (b) Sufficient wind to the left produces stable state. (Fig. 2 reproduced from [1])

fluid flows [2]. These manifolds are defined for some flow map  $\phi$ . This can be representative of either a timeindependent or time-periodic flow. The stable (unstable) manifold is the set of points that converge to a fixed point under iteration of  $\phi$  ( $\phi^{-1}$ ). These manifolds divide classes of trajectories which will diverge (have converged).

#### **IV. BURNING INVARIANT MANIFOLDS**

From the theoretical perspective, we may recast a PDE approach to reaction propagation in flows as an ODE for individual front elements. A front element's position evolves according to the underlying flow, and also propagation in the direction of the unit normal at the constant speed  $v_0$ . The orientation of the front element is treated accordingly.

$$\mathbf{r} = \mathbf{u} + v_0 \mathbf{\hat{n}}$$
  
$$\dot{\theta} = -\hat{\mathbf{n}}_i \mathbf{u}_{i,j} \hat{\mathbf{g}}_j$$
(1)

In analysis of these equations, we find that as  $v_0$  increases from 0, the invariant manifolds of this augmented system split off of the passive invariant manifolds in either direction. Furthermore, these manifolds are oppositely oriented (recall that they exist in  $xy\theta$  space).

It is a primary result of recent work that these new *burning invariant manifolds* (BIMs) are *one-sided* barriers to front propagation in fluid flows [3], [4], [5]. Fronts are bounded by them on one side, but pass through from the other.

Unlike passive invariant manifolds, BIMs have cusps and self-intersections (when projected into the xy-plane). A



Fig. 2. Reaction from left (green) bounded by BIM, but wraps around at cusp.



Fig. 3. BIM (red) spans the channel—type 1 pinning. Reaction region (green) converges to BIM and does not pass. Another BIM span related by symmetry (blue).

cusp plays a particularly important role, as it marks the end of the physically relevant portion of the BIM. Fronts bounded by a BIM will spread along it until they reach the cusp where they wrap around and fill in from the other side. In this way, BIMs are often only local boundaries (Fig. 2).

#### V. ONSET OF PINNING

The main result of this work is to show that BIMs may also be *global* boundaries, and that these boundaries are exactly the frozen fronts observed in [1]. By adding a finite amount of wind, a new cusp is created near the top of the channel. We can understand this cusp formation as passage of the BIM through a heteroclinic connection. A little more wind causes this cusp to meet the channel wall forming a complete span across the channel. This spanning BIM is a *global* barrier. Reactions to the left will converge upon this barrier, but not pass through (Fig. 3). We refer to this particular type of front pinning as "type-1".

#### VI. PINNING TYPES

The BIM theory of pinning also predicts other topologically distinct pinning types, many of which have been realized experimentally. We illustrate two other types here.

*Type 2:* Increasing the wind causes the BIM to sweep backward along the channel wall, eventually creating another cusp (Fig. 4). It may appear that pinning is lost because a front converging to this BIM will wrap around this cusp. However, the front would soon meet another BIM emerging from the opposite channel wall that prevents further progress. While neither of these BIMs alone forms a



Fig. 4. Blue BIM has been swept back far enough to create another cusp, and then lifts from the channel wall. Reaction (green) converges to blue BIM, wraps around cusp, but is then blocked by red BIM. Only together the two BIMs form a span.



Fig. 5. Experimental realization of type 2 pinning. Time increases upward.

global barrier, together they form a composite pinning front. *Type 3:* Increasing the wind further, this cusp reenters the channel wall and each BIM is again a complete span across the channel. The difference is that these BIMs intersect (whereas in type-1 they do not). This means that in addition to observing one or the other BIM as a pinning front, we may observe their union as a third pinning front.

*More complex pinning front topologies:* Previous studies [1] found the same phenomenon in flows with a number of vortices arranged in a disordered 2D pattern. This analysis on BIMs now explains these more complex pinning as multiple BIMs (no one of which is a span) "sewn" together by hiding each cusp behind the adjacent BIM.

#### ACKNOWLEDGMENTS

The authors wish to thank Tom Solomon, Carleen Boyer, Maya Narajan and John Li.

- M. E. Schwartz and T. H. Solomon. Chemical reaction fronts in ordered and disordered cellular flows with opposing winds. *Phys. Rev. Lett.*, 100:028302, Jan 2008.
- [2] S. Wiggins. Chaotic Transport in Dynamical Systems. Springer-Verlag, New York, 1992.
- [3] John Mahoney, Dylan Bargteil, Mark Kingsbury, Kevin Mitchell, and Tom Solomon. Invariant barriers to reactive front propagation in fluid flows. *Euro. Phys. Lett.*, 98:44005, 2012.
- [4] Kevin A. Mitchell and John Mahoney. Invariant manifolds and the geometry of front propagation in fluid flows. *Chaos*, 22, 2012.
- [5] Dylan Bargteil and Tom Solomon. Barriers to front propagation in ordered and disordered vortex flows. *Chaos*, 22, 2012.

### A manifold learning approach to model reduction in combustion

Eliodoro Chiavazzo<sup>‡</sup>\*, C. William Gear\*, Benjamin E. Sonday\*, Ioannis G. Kevrekidis<sup>\*†</sup> \*Princeton University/Department of Chemical and Biological Engineering, Princeton, NJ, USA <sup>†</sup>Princeton University/Program in Applied and Computational Mathematics, Princeton, NJ, USA <sup>‡</sup>Politecnico di Torino/Energy Department, Torino, Italy

Abstract—We use a relatively recent nonlinear manifold learning technique (diffusion maps) to parameterize low dimensional attracting manifolds arising in the description of detailed chemical kinetics mechanisms. With no *a priori* knowledge about the shape and dimension of the manifold, such an approach provides a way of solving a reduced (and less stiff) set of equations in terms of automatically detected slow variables. Advantages as well as disadvantages of the approach are discussed.

#### I. INTRODUCTION

The solution of detailed models for chemical kinetics (either ODE or discretized PDE) often poses severe numerical difficulties mainly due to two aspects: First, the number of degrees of freedom is large; second, the dynamics is characterized by disparate time scales. As a result, reactive flow solvers with detailed chemistry often become intractable even for large clusters of CPUs, especially when dealing with direct numerical simulation (DNS) of turbulent combustion problems. This has motivated the development of several approaches for reducing the complexity of such kinetics models, by expressing them in terms of only a few slow variables. However, there are no generally applicable recipes for selecting a good global parameterization of the reduced model, and the choice of slow variables often relies upon intuition and experience. Clearly, a more systematic approach in this respect would be highly desirable. In this work, we follow a fully automated approach where the lowdimensional attracting manifold is identified, parametrized and a consistent reduced model constructed. The key step is the parameterization, which is obtained by learning the slow manifold through diffusion maps (DMAPs).

#### **II. DIFFUSION MAPS**

The diffusion maps approach has recently emerged as a powerful tool in data analysis [1], [2], [3]. The basic aim is to provide a nonlinear extension of the Principal Component Analysis (PCA) in order to construct a low-dimensional embedding for a given set of M points  $(X_1,...,X_M)$  in a high-dimensional space, if such an embedding exists. To this end, a distance  $d_{ij}$  between a pair of states  $(X_i$  and  $X_j)$  is needed. Based on  $d_{ij}$ , a pairwise affinity function can be established such that  $W_{ij} = W_{ji} \ge 0$ , with the heat kernel being a popular option:

$$W_{ij} = \exp\left[-\left(\frac{d_{ij}}{\varepsilon}\right)^2\right].$$
 (1)

Although, for data in  $\Re^N$ , an obvious choice for  $d_{ij}$  is the standard Euclidean distance, this is not always the best option. For instance, a weighted Euclidean norm may be necessary when the different coordinates of a generic point  $X_i$  are characterized by disparate orders of magnitude. This is indeed the case encountered in many combustion problems, where data are likely points in concentration space and major species (i.e. reactants and products) arise in much higher concentrations compared to minor species (i.e. radicals). The notion of locality is introduced through the model parameter  $\varepsilon$  which defines the width of a small neighborhood, where the chosen distance d can be assumed as a good measure of proximity. Based on the symmetric matrix  $W = \{W_{ij}\}$ , a diagonal matrix  $D = \{D_{ii}\}$  can be defined such that:  $D_{ii} = \sum_{k=1}^{M} W_{ik}$ . Following the DMAPs approach, if the initial data points are located on a low dimensional manifold with dimension k, a gap appears between k nontrivial eigenvalues of the Markov matrix  $K = D^{-1}W$  and the remaining ones. Moreover, the components in the corresponding k eigenvectors establish a projection of the high-dimensional points  $(X_1,...,X_M)$  into a k-dimensional space.

#### **III. APPLICATION TO COMBUSTION**

We will demonstrate the feasibility of constructing reduced kinetics models for combustion applications, by extracting the slow dynamics on a manifold globally parameterized by diffusion maps. To this end, preliminary results are shown for a homogeneous reactive mixture of hydrogen and air at stoichiometric proportions under fixed total enthalpy (H = 300[kJ/kg]) and pressure (P = 1[bar]). Time evolution of the chemical species follows the Li mechanism [4], and can be generally formulated as follows:

$$\frac{d\vec{y}}{dt} = \vec{f}\left(\vec{y}\right),\tag{2}$$

with  $\vec{y}$  representing the state in terms of mass fractions of the nine participating chemical components ( $H_2$ ,  $N_2$ , H, O, OH,  $O_2$ ,  $H_2O$ ,  $HO_2$ ,  $H_2O_2$ ). Equations (2) are further complemented by an implicit algebraic equation for temperature, stipulating the constancy of total enthalpy.

The first step of the proposed method requires the identification of the low-dimensional attracting manifold. While many possible constructions have been suggested in the literature (see, e.g., [5], [6], [7], [8]) here, in the spirit of the *equation free* framework [9], [10], we assume that only the rates  $\vec{f}(\vec{y})$  are accessible and do not rely upon any prior knowledge about a good parameterization of the manifold.

For data collection, Eqs. (2) are integrated starting from a rich enough set of random states within the admissible phase-space (convex polytope defined by elemental conservation constraints and concentration positivity) and, after sufficient time to approach a neighborhood of the manifold, samples are collected from each trajectory. As a result, a set of points  $\{X_i, i = 1, ..., M\}$  in  $\Re^N$  (hopefully dense enough within the region of interest) becomes available for defining the manifold.

As a second step, the diffusion maps approach is performed as outlined in Section II. Due to a disparity of the magnitudes of species concentrations,  $d_{ij}$  is taken as the Euclidean distance between properly rescaled points  $\tilde{X}_i$ and  $\tilde{X}_j$ , with  $\tilde{X}_i = RX_i$  using the fixed diagonal matrix  $R = \{R_{kk}\}, R_{kk} = 1/max(X(k))$ . Here, max(X(k))represents the largest k-th coordinate among all sample points, whereas the parameter  $\varepsilon$  in (1) can be chosen as a multiple of the quantity:  $\max_j \min_{i \neq j} d_{ij}$  [11], [12], [13]. An example is shown in Fig. 1. Finally, as a third step, following [13], [14], the reduced model of (2) can be constructed as follows:

$$\frac{d\vec{L}}{dt} = \frac{\partial \vec{\psi} \left( \vec{\psi}^{-1} \left( \vec{L} \right) \right)}{\partial \vec{y}} \vec{f} \left( \vec{\psi}^{-1} \left( \vec{L} \right) \right), \qquad (3)$$

where  $\vec{L}$  denotes the reduced state, while  $\vec{\psi}$  and  $\vec{\psi}^{-1}$  represent the *restriction* and *lifting* operators. Clearly, obtaining these operators, for example through Nyström extension [15] and various interpolation approaches, is a crucial step in our model reduction method.

#### IV. CONCLUSION

In this work, we provide evidence that the diffusion maps technique is a useful tool for systematically extracting a global parameterization of low-dimensional manifolds arising in combustion problems, while less stiff reduced systems can be expressed in terms of the slow variables parametrizing these manifolds as identified by the process.

#### ACKNOWLEDGMENT

E.C. acknowledges partial support of the Fulbright commission and the Italian Ministry of Research (FIRB grant



Fig. 1. Homogeneous reactive mixture of hydrogen and air at stoichiometric proportions with fixed enthalpy (H = 300[kJ/kg]) and pressure (P = 1[bar]). Two dimensional DMAPs parameterization of 1095 points as provided by the two nontrivial leading eigenvectors  $\phi_1$  and  $\phi_2$  of the Markov matrix K. Colors represent mass fractions, while black filled circle and black diamond represent the fresh mixture condition and equilibrium state, respectively.

RBFR10VZUG). I.G.K. and C.W.G. gratefully acknowledge partial support by the US DOE.

- R. Coifman, S. Lafon, A. Lee, M. Maggioni, B. Nadler, F. Warner and S. Zucker, *PNAS*, vol. 102, pp. 7426, 2005.
- [2] R. Coifman, S. Lafon, A. Lee, M. Maggioni, B. Nadler, F. Warner and S. Zucker, *PNAS*, vol. 102, pp. 7432, 2005.
- [3] R. Coifman, S. Lafon, Appl. Comput. Harmon. Anal., vol. 21, pp. 5-30, 2006.
- [4] J. Li, Z. Zhao, A. Kazakov and F. L. Dryer, *Int. J. Chem. Kinet.*, vol. 36, pp. 566-575, 2004.
- [5] U. Maas and S. Pope, Combust. Flame, vol. 88, pp. 239-264, 1992.
- [6] U. Maas and D. Goussis, in *Turbulent Combustion Modeling*, vol. 95, T. Echekki and E. Mastorakos, Eds. Springer, 2011, pp. 193–220.
- [7] E. Chiavazzo and I.V. Karlin, *Phys. Rev. E*, vol. 83: 036706, 2011.
- [8] E. Chiavazzo, J. Comp. Phys., vol. 23, pp. 1751-1765, 2012.
- [9] I. G. Kevrekidis, C. W. Gear, J. M. Hyman, P. G. Kevrekidis, O. Runborg and C. Theodoropoulos, *Comm. Math. Sci.* vol. 1, pp. 715-762, 2003.
- [10] I. G. Kevrekidis, C. W. Gear and G. Hummer, AIChE Journal, vol. 50, pp. 1346-1355, 2004.
- [11] C. W. Gear, Parameterization of non-linear manifolds, http://www.princeton.edu/~wgear/.
- [12] M. A. Rohrdanz, W. Zheng, M. Maggioni, C. Clementi, J. Chem. Phys. vol. 134: 124116, 2011.
- [13] B. E. Sonday, C. W. Gear, A. Singer and I. G. Kevrekidis, Solving differential equations by model reduction on learned manifolds *Preprint*, 2013.
- [14] B. E. Sonday, PhD thesis, Princeton University, 2011.
- [15] E. J. Nyström, Commentationes Physico-Mathematicae vol. 4, pp. 1-52, 1928.

## Chemical Reductions Do Not Necessarily Lead to Computational Reductions

T. Grenga,\* S. Paolucci,\* M. Valorani,<sup>†</sup>

\*University of Notre Dame, Aerospace and Mechanical Engineering Department, Notre Dame, IN, USA <sup>†</sup>Sapienza University of Rome, Mechanical and Aerospace Engineering Department, Rome, Italy

Abstract— The comparison of solutions of the shock-ignition of a hydrogen bubble in air using detailed and reduced chemical mechanisms is presented. The reduced chemical kinetics mechanism with 9 species and 12 irreversible reactions is obtained using the *G-Scheme*. The test shows that the simulation becomes computationally more expensive using the reduced mechanism.

#### I. INTRODUCTION

Detailed and reliable numerical simulations of compressible reactive flows are particularly challenging because of their strong multiscale characteristics. Chemical, diffusive and viscous phenomena occur on molecular scales. Thus, spatial scales span five orders of magnitude for the simulation of a device having the size of the order of centimeters.

In this work we use the *p*arallel Wavelet Adaptive Multiscale Representation (pWAMR) method [1], [2] for controlling the grid adaptivity based on magnitudes of wavelet amplitudes. The amplitude of the wavelet transform provides a direct measure of the local error at each associated collocation point. Applying a threshold and omitting those points with small amplitudes, a dynamically adaptive sparse grid is generated.

The numbers of species and reactions included in a chemical mechanism are other factors that lead to an increase in computational cost. The use of a reduced mechanism can help in reducing the computational cost at the sacrifice of introducing a small inaccuracy in the solution. We use a reduction method based on the *G-Scheme* [3]. The methodology proposed [4] identifies the most important reactions in the process using an objective index.

We perform the numerical simulation of a shock impacting a hydrogen bubble.

#### II. TEST CASE DESCRIPTION

The pWAMR method is used to solve the same problem proposed by Billet *et al.* [6]. The domain is two-dimensional with height of 0.75 cm and length of 5 cm. The ambient gas is air, represented by a  $78N_2 : 22O_2$  mixture in mole fraction. A hydrogen bubble of radius  $r_0 = 0.28$  cm is centered at x = 0.8 cm. A Mach 2 shock is located at x =0.4656 cm. The unshocked gas has a uniform pressure of 1 atm and temperature of 1000 K. The post-shock state has a pressure of 4.41 atm, temperature of 1559 K, and velocity of 798 m/s. The left boundary is a supersonic inflow with the post-shock conditions prescribed, and top and bottom boundaries are symmetry planes.

The problem is modeled using the reactive Navier-Stokes equations for a multicomponent gas mixture. It includes the evolution equations for species' partial density. The production rate for the species for the kinetic mechanism considered is evaluated using Chemkin. The constitutive relations include detailed multi-component diffusion, Sorét and Dufour effects and state dependent transport properties. The pWAMR method is implemented as a method of lines algorithm. Here we use a standard 4th/5th-order Runge-Kutta-Fehlberg scheme to integrate the equations.

#### III. G-Scheme REDUCTION METHOD

A separate analysis using the G-Scheme is performed to obtain the reduced chemical kinetics mechanism. The ODEs representing just the chemical reactions constitute a multi-scale system. The G-Scheme is a time accurate computational tool that exploits, adaptively, opportunities for reduction of a multi-scale system in order to integrate only a non-stiff subset of equations. The space is decomposed in 4 subspaces according to the time scale of each mode: the active subspace  $\mathbb{A}$  contains all the active scales, the subspaces  $\mathbb{H}$  has all scales slower than the active ones, while faster scales are in the subspaces  $\mathbb{T}$ , and the invariant subspace  $\mathbb{E}$  contains the invariant modes. Only the active subspace is numerically integrated using a time step of the order of the time scale of the fastest mode in this subspace. The contributions of the slow and fast subspaces are evaluated using a asymptotic approximations.

The standard CSP Participation Index [5] provides a nondimensional measure of the contribution of the *k*-th reaction to the *i*-th mode at the state x. In the *G*-Scheme we modify it to define the Participation Index of the *k*-th reaction relative to the dynamics of the subspace<sup>1</sup> s:

$$\widehat{\mathscr{P}}_{k}^{s}(\mathbf{x}) = \frac{\sum_{i=N_{s,b}}^{N_{s,e}} C_{k}^{i}(\mathbf{x}) r^{k}(\mathbf{x})}{\sum_{i=N_{s,b}}^{N_{s,e}} \sum_{k'=1}^{\mathbb{R}} |C_{k'}^{i}(\mathbf{x}) r^{k'}(\mathbf{x})|}, \qquad (1)$$

<sup>1</sup>The index s = h/a/t identifies one of the four subspaces as follows: h for  $\mathbb{H}$ , a for  $\mathbb{A}$ , and t for  $\mathbb{T}$ .

where  $C_k^i = \mathbf{b}^i(\mathbf{x}) \cdot \mathbf{S}_k$ ,  $\mathbf{b}^i$  is the contravariant basis vector, and  $\mathbf{S}_k$  the stoichiometric vector. Note that  $0 < P_k^i(\mathbf{x}) < 1$ . The CSP Participation Index provides a non-dimensional measure of the contribution of the the k-th reaction to the *i*-th mode at the state  $\mathbf{x}$  normalized by the contribution of all reactions at the state  $\mathbf{x}$ . In contrast, equation (1) provides a measure of the contribution of the k-th reaction to the subspace s normalized by the contribution of all reactions in the same subspace. In other words, it provides a criterium to identify if the k-th reaction is *active*, *slow*, *fast*, or as *negligible* if it doesn't have a relevant value in any subspace. The concept of an *important reaction* is not an inherent property of the reaction but a function of the local state.

We can rank the reactions according to the maximum value of  $\widehat{\mathscr{P}}_k^s$  in the time interval considered as follows:

$$\overline{\mathscr{P}}_{k}^{s} = \max_{t_{b} < t < t_{e}} \left( |\widehat{\mathscr{P}}_{k}^{s}(\mathbf{x})| \right).$$
(2)

Equation (2) provides a value that summarizes all the information given by (1). By identifying the maximum value of the participation index calculated for any reaction along the process, we obtain an objective measure of the importance of the reaction for the analyzed problem.

Based on (2), we can create a very simple iterative procedure to obtain a simplified mechanism that satisfies an objective criteria defined by the analyst. In this study we choose the error in the equilibrium temperature and ignition time as criteria, defined as:

$$err_T = \frac{T_{f,s} - T_{f,c}}{T_{f,c}}$$
 and  $err_t = \frac{t_{e,s} - t_{e,c}}{t_{e,c}}$ , (3)

where  $T_{f,s}$  and  $T_{f,c}$  are the equilibrium temperatures for the simplified and complete mechanism respectively, while  $t_{e,s}$  and  $t_{e,c}$  are the ignition times for the simplified and complete mechanism respectively. Then the algorithm finds iteratively the threshold value of ParticipationIndex giving the smallest mechanism that satisfies a user-defined value for these error criteria. In this study we have used  $err_T =$  $err_t = 0.02$ .

The simplified mechanism found contains 16 irreversible reactions. In comparing it with the full mechanism, it yields a maximum error of 1.76% for the equilibrium temperature and 1.27% for the ignition time in the range of initial temperature, pressure and mixture ratio of  $T_i = 700 - 1500 K$ ,  $p_i = 0.5 - 100 atm$ , and  $\phi = 0.5 - 2$ .

#### IV. RESULTS

We perform the numerical simulation of a shock impacting a hydrogen bubble. Since the bubble is less dense than the surrounding air, large bubble distortions result and reactions start on the deformed bubble surface.

The mechanisms used for the test both have 9 species; the detailed one includes 19 reversible elementary reactions



Fig. 1. Comparison of the umber of grid point required for the simulation using the complete and the reduced mechanism.

while the reduced one 16 irreversible reactions. The solutions obtained in both cases are very accurate and do not show any sensible difference.

Most interestingly, Fig. 1 shows that the number of grid points used in the simulation with the reduced mechanism is *larger* than in the one with the detailed mechanism. The average number of grid points with the detailed mechanism is 164,369, while it increases to 182,635 when using the reduced mechanism.

The test shows that the simulation becomes computationally more expensive using the reduced mechanism. For a small mechanism, like hydrogen/air with 9 species, it is not possible to reduce the number of species without introducing a relatively large error. The present computational study shows that just a reduction in the number of reactions does not necessarily produce a significant saving in the computational cost.

We observe that a larger number of points at the finest scale is necessary to solve the problem with the same accuracy. We note that the finest resolution required by the solutions is below 1  $\mu$ m for both detailed and reduced mechanisms. An explanation of this increase based on analysis of the solution, with particular attention to the species involved in the deleted reactions, will be discussed.

- S. Paolucci, Z. Zikoski and D. Wirasaet, WAMR: An Adaptive Wavelet Method for the Simulation of Compressible Reactive Flow. Part I. Accuracy and Efficiency of Algorithm, Journal of Computational Physics, Submitted.
- [2] S. Paolucci, Z. Zikoski and T. Grenga, WAMR: An Adaptive Wavelet Method for the Simulation of Compressible Reactive Flow. Part II. The Parallel Algorithm, Journal of Computational Physics, Submitted.
- [3] M. Valorani and S. Paolucci, *The G-Scheme: A framework for multi-scale adaptive model reduction*, Journal of Computational Physics, vol. 228 (13), 2009, pp. 4665-4701.
- [4] T. Grenga, S. Paolucci and M. Valorani, A G-Scheme based simplification and analysis methodology, in preparation.
- [5] D.A.Goussis and S.H.Lam, A Study of Homogeneous Methanol Oxidation Kinetic Using CSP, Proc. Comb. Inst., vol. 24, 1992, pp. 113-120.
- [6] G. Billet, V. Giovangigli and G. de Gassowski, *Impact of Volume Viscosity on a Shock-Hydrogen-Bubble Interaction*, Combustion Theory and Modelling, vol. 12, 2008, pp. 221–248.

# Relaxation Redistribution Method for model reduction

Mahdi Kooshkbaghi\*, Christos E. Frouzakis\*, Eliodoro Chiavazzo<sup>†‡</sup>, Ilya V. Karlin\*, Konstantinos Boulouchos\* \*ETH Zurich, Aerothermochemistry and Combustion Systems Laboratory, Zurich CH-8092, Switzerland <sup>†</sup>Politecnico di Torino, Energy Department, Corso Duca degli Abruzzi 24, 10129 Torino, Italy <sup>‡</sup>Princeton University, Department of Chemical and Biological Engineering, Princeton, NJ, USA

Abstract— The Relaxation Redistribution Method (RRM) is based on the notion of slow invariant manifold (SIM) and is applied for constructing a simplified model of detailed multiscale combustion phenomena. The RRM procedure can be regarded as an efficient and stable scheme for solving the film equation of dynamics, where a discrete set of points is gradually relaxed towards the slow invariant manifold (SIM). Here, the global realization of the RRM algorithm is briefly reviewed and used for auto-ignition and adiabatic premixed laminar flame of a homogeneous hydrogen-air ideal gas mixture.

#### I. INTRODUCTION

The detailed reaction mechanisms of practical fuels contain hundreds of species participating in hundreds to thousands of elementary chemical reactions. In addition to the large number of variables that need to be accounted for, disparate time scales introduce stiffness and increase the computational cost of numerical computations. On the other hand, time scales associated with transport phenomena cover a narrower range of typically slower time scales. When the coupling of flow phenomena and chemical kinetics is of interest, changes due to the fastest time scales can be assumed to be equilibrated. Model reduction can then be employed to reduce the computational cost by extracting only the important slow system dynamics [1], [2], [3].

The *Relaxation Redistribution Method* (RRM) was recently proposed as an efficient technique to construct low dimensional manifolds of any dimensions [4]. RRM consists of an algorithm for refining an initial guess (initial grid) till convergence within a neighborhood of the SIM is achieved, by mimicking the film equation of dynamics. Here, the initial manifold is immersed into a phase space and the motion of trajectories along the manifold is subtracted from the whole dynamics by a simple redistribution of the grid points in the reduced space. Moreover, in its local realization, stability of the RRM refinements provide a natural criterion for finding the minimal dimension of a reduced model [4].

Here, the global realization of RRM is shortly reviewed and applied for homogeneous auto-ignition and a laminar premixed hydrogen flame.

#### II. FILM EQUATION OF DYNAMICS AND RRM

The detailed (microscopic) dynamics of an autonomous system in terms of the state N(t) in a phase space S (say  $n_s$ -dimensional) is given by,

$$\frac{d\mathbf{N}}{dt} = f(\mathbf{N}). \tag{1}$$

A subspace  $U \subset S$  is a positively invariant manifold for the system (1) if every trajectory starting on U at time  $t_0$ remains on U for any  $t > t_0$ . Therefore,  $\mathbf{N}(t_0) \subset U$  implies  $\mathbf{N}(t) \subset U$  for  $t > t_0$ .

The components of the state vector typically evolve at different time scales. Because of such time scale disparity, the trajectories of (1) starting from arbitrary initial conditions are typically quickly attracted to a lower dimensional manifold, where motions continue at a slower rate towards the steady state (or equilibrium  $\mathbf{N}^{eq}$  with  $f(\mathbf{N}^{eq}) = 0$ ). This positively invariant manifold is the *slow invariant manifold*, (SIM), and its construction can be based on the definition of fast and slow sub-spaces within *S* [3].

Accordingly, neglecting the initial fast evolution of the detailed system, the long-time dynamics can be described by a smaller number of macroscopic variables, which are to be used to *uniquely* parametrize the SIM. The macroscopic variables  $\boldsymbol{\xi}$  belong to the  $n_d$ -dimensional space  $\boldsymbol{\Xi}$ , with  $n_d < n_s$ , and offer a possible representation for a coarse description of (1). In other words, for an arbitrary state  $\mathbf{N}^{SIM}$  located on the low-dimensional manifold, we can write  $W = \mathbf{N}^{SIM}(\boldsymbol{\xi})$ , where W is a (1-1) map from the parameter space  $\boldsymbol{\Xi}$  into the phase-space S.

The evolution rate of the state N, f(N), can be decomposed into a component along the tangent space of W,  $T_W$ , and its complement in a transversal direction,

$$f(\mathbf{N}(\boldsymbol{\xi})) = f(\mathbf{N}(\boldsymbol{\xi}))_{\parallel_{T_W}} + f(\mathbf{N}(\boldsymbol{\xi}))_{\perp_{T_W}}, \qquad (2)$$

The components are defined as

$$f(\mathbf{N}(\boldsymbol{\xi}))_{\parallel_{T_W}} = \mathbf{P}f(\mathbf{N}(\boldsymbol{\xi}))$$
(3)

$$f(\mathbf{N}(\boldsymbol{\xi}))_{\perp_{T_W}} = \Delta = (\mathbf{I} - \mathbf{P})f(\mathbf{N}(\boldsymbol{\xi})).$$
(4)

 $\Delta$  is the *defect of invariance* where I and P are  $n_s \times n_s$  identity matrix and projector operator, respectively.



Fig. 1. Relaxation and Redistribution algorithm; The effect of slow motions is neutralized via redistribution.

By definition, W is a positively invariant manifold if the state does not leave it during the subsequent system evolution. Hence, relaxation will happen only along the tangent space and the normal component should be zero,

$$\Delta = 0 \qquad \boldsymbol{\xi} \in \boldsymbol{\Xi}. \tag{5}$$

Equation (5) is the differential equation which is known as *invariance condition* [3]. In the *Method of Invariant Manifold* (MIM), the slow invariant manifold is the stable solution of the film extension of dynamics,  $\frac{dN(\boldsymbol{\xi})}{dt} = \Delta$ . This is the evolutionary equation guiding an initial mapping  $N(\boldsymbol{\xi})$  towards  $N^{SIM}(\boldsymbol{\xi})$ . A detailed explanation of MIM algorithm and the choice of the projector **P** can be found in [5], [6].

The states located on an initial grid relax according to (1) with  $f(\mathbf{N}^{ini}(\boldsymbol{\xi}))$ . After some time, all grid points move towards the SIM and the volume of the initial manifold shrinks due to the concurrent action of slow motions. In the RRM though, the latter effect is neutralized by redistributing the points of the relaxed grid after each time step [4]. As sketched in Fig. 1, relaxed grid (open circles) are located at different positions on the slow space  $\Xi$  with respect to their initial positions (black circles). Clearly, even after a short relaxation the density of the grid points tends to increase near the equilibrium, with a drastic change of the grid spacing in  $\Xi$ . To prevent this, a redistribution step is applied to bring the grid points back to their previous  $\xi$ values. Such a step requires interpolation between the inner relaxed states and extrapolation for boundary grid points. The converged solution is the manifold containing all the states for which further relaxations move the states only along the manifold. In order to keep the computational effort low, here we focus on manifolds with a dimension up to three. We should however remind that low dimensional SIM are usually appropriate within some neighborhood of the phase space around the equilibrium point, leaving open the problem of how to extend it further to cover the states all the way to the fresh mixture condition [7].

On the other hand, in the original RRM method, extrapolations during the redistribution step at the SIM boundaries may sometimes result in physically meaningless values for compositions (e.g. negative concentrations). In this work, to prevent such a problem, we suggest a possible approximate solution as follows. Global 2D or 3D initial manifolds are constructed (see RCCE construction below) and their boundaries subsequently fixed during the refinement process. In other words, the RRM is applied just on the interior grid points till convergence. Based on our experience, the resulting manifold practically coincides with the SIM for the part of the phase space for which low dimensional SIM exists, whereas it provides with a convenient extension for regions far from equilibrium.

#### III. RESULTS

The global RRM method is applied to homogeneous H<sub>2</sub>/air mixtures. The detailed kinetics scheme includes  $n_s = 9$  species and 21 reactions [8]. The popular *Rate-Controlled Constrained-Equilibrium* (RCCE) linear constraints (see e.g. [9]) are used for manifold parameterization, such as the total number of moles ( $\xi_1$ ), moles of active valences ( $\xi_2$ ) and moles of free oxygen ( $\xi_3$ ).

The initial mole numbers of the species are given based on stoichiometric values,  $N_{\rm H_2} = 1.0$ ,  $N_{\rm O_2} = 0.5$  and  $N_{\rm N_2} = 1.881$ . The rest of the species are assigned chemically insignificant positive initial values to ensure a strictly positive composition [10]. The initial guess for the manifold (initial grid) is constructed on  $\Xi$  as much extent as possible to contain both projected locations of initial and equilibrium points. The initialization is done based on constrained minimization of thermodynamic potentials utilizing the CEQ FORTRAN package library [11].

The grid points which are located on the boundaries are fixed and global RRM procedure applied for interior grid. The SHEPPACK FORTRAN package is used for interpolation [12]. The RCCE and RRM manifold are shown in Fig. 2 while the sample trajectory is plotted for comparison. The temporal evolution of the temperature and species mass fractions are presented in Fig. 3. Good agreement is found with the detailed description for the temperature and major reactants as well as the radicals in large concentration. Far away from equilibrium, the RCCE manifold results in strongly underpredicted HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> concentrations.

At the Workshop, results will be presented for the test case of a laminar premixed hydrogen flame.

#### IV. CONCLUSION

An algorithm for constructing the globally generated manifold is proposed based on the relaxation and redistribution method. The accuracy of the method has been assessed through the auto-ignition and laminar premixed flame of homogeneous  $H_2/air$  from the initial mixture far from equilibrium. The proposed method shows the improvements for ignition delay and capturing the radicals with respect to the popular low dimensional RCCE method.



Fig. 2. RCCE and RRM manifold with the detailed system trajectory.  $\xi_1$  is the number of total moles and  $\xi_2$  is the moles of free valence.



Fig. 3. Temporal evolution of species and temperature found by 3-dimensional RCCE and RRM manifolds for stoichiometric H<sub>2</sub>/air with  $T_0 = 1000$  K

#### V. ACKNOWLEDGMENTS

This work is supported by Swiss National Foundation under Project number 137771. I.V. Karlin thanks support of ERC Advanced Grant ELBM. E. Chiavazzo acknowledges support of the Fulbright commission.

- U. Maas and S.B. Pope. Simplifying chemical kinetics: intrinsic low-dimensional manifolds in composition space. *Combustion and Flame*, 88(3):239–264, 1992.
- [2] SH Lam and DA Goussis. The csp method for simplifying kinetics. International Journal of Chemical Kinetics, 26(4):461–486, 2004.
- [3] A.N. Gorban and I.V. Karlin. *Invariant manifolds for physical and chemical kinetics*, volume 660. Springer, 2005.
- [4] E. Chiavazzo and I. Karlin. Adaptive simplification of complex multiscale systems. *Physical Review E*, 83(3):036706, 2011.
- [5] E. Chiavazzo, A.N. Gorban, and I.V. Karlin. Comparison of invariant manifolds for model reduction in chemical kinetics. *Commun. Comput. Phys*, 2(5):964–992, 2007.
- [6] E. Chiavazzo, I.V. Karlin, C.E. Frouzakis, and K. Boulouchos. Method of invariant grid for model reduction of hydrogen combustion. *Proceedings of the Combustion Institute*, 32(1):519–526, 2009.
- [7] V. Bykov and U. Maas. Extension of the ildm method to the domain of slow chemistry. *Proceedings of the Combustion Institute*, 31(1):465–472, 2007.
- [8] J. Li, Z. Zhao, A. Kazakov, and F.L. Dryer. An updated comprehensive kinetic model of hydrogen combustion. *International journal of chemical kinetics*, 36(10):566–575, 2004.

- [9] R. Law, M. Metghalchi, and J.C. Keck. Rate-controlled constrained equilibrium calculation of ignition delay times in hydrogen-oxygen mixtures. In *Symposium (International) on Combustion*, volume 22, pages 1705–1713. Elsevier, 1989.
- [10] Q. Tang and S.B. Pope. A more accurate projection in the ratecontrolled constrained-equilibrium method for dimension reduction of combustion chemistry. *Combustion Theory and Modelling*, 8(2):255–279, 2004.
- [11] S.B. Pope. The computation of constrained and unconstrained equilibrium compositions of ideal gas mixtures using gibbs function continuation. FDA03-02, Cornell University, http://eccentric. mae. cornell. edu/~ pope/Reports/CEQ\_FDA. pdf, 2003.
- [12] W.I. Thacker, J. Zhang, L.T. Watson, J.B. Birch, M.A. Iyer, and M.W. Berry. Algorithm 905: Sheppack: modified shepard algorithm for interpolation of scattered multivariate data. ACM Transactions on Mathematical Software (TOMS), 37(3):34, 2010.

### Hydrogen/Air Auto-ignition: Algorithmic Identification of QSSA and PEA

Panayotis D. Kourdis\*, Dimitris A. Goussis<sup>†</sup>

\*Department of Mechanical and Civil Engineering, California Institute of Technology, Pasadena, USA <sup>†</sup>School of Applied Mathematics and Physical Sciences, National Technical University of Athens, Zografou, Greece

*Abstract*—Algorithmic criteria for the applicability of the Quasi Steady State and Partial Equilibrium approximations are presented and verified in the context of the hydrogen/air auto-ignition.

#### I. INTRODUCTION

The classical approach in model reduction involves the introduction of the *Quasi Steady State* (QSSA) and the *Partial Equilibrium* (PEA) approximations. Although both approximations have been devised and used for quite a long time, it was only until very recently when their applicability and connection was thorough investigated in [1] in the context of the *CSP method* [2]. Here, the criteria established in [1] for the applicability of QSSA and PEA are presented in a new form and are validated in the case of the Hydrogen/Air autoignition.

#### **II. STATEMENT OF THE PROBLEM**

The evolution of a homogeneous ideal gas mixture where K reversible reactions occur simultaneously among N reacting chemical species obeys the (N + 1)-dim. system of autonomous ODEs:

$$\frac{d}{dt} \begin{bmatrix} \mathbf{y} \\ T \end{bmatrix} = \begin{bmatrix} \mathbf{S} \\ \mathbf{Q}(\mathbf{y}, T) \end{bmatrix} \mathbf{R}(\mathbf{y}, T) \equiv \mathbf{g}(\mathbf{y}, T)$$
(1)

where  $\mathbf{y}, \mathbf{g} \in \mathbb{R}^N$  and  $\mathbf{y}$  contains the variables relating to the N species (e.g., mass fractions), T is the temperature,  $\mathbf{R} \in \mathbb{R}^K$  contains the reaction rates,  $\mathbf{S} \in \mathbb{R}^{N \times K}$  is the constant stoichiometric matrix and  $\mathbf{Q} \in \mathbb{R}^{1 \times K}$  is a row vector depending on the thermodynamic properties of the mixture. We assume that a (N + 1 - M)-dim. normally hyperbolic slow invariant manifold  $\Omega \subset \mathbb{R}^{N+1}$  develops in phase space as the result of the exhaustion of M fast dissipative time scales  $\tau_i, (i = 1, \dots, M)$ .

Casting (1) in CSP form yields:

$$\frac{d}{dt} \begin{bmatrix} \mathbf{y} \\ T \end{bmatrix} = \mathbf{a}_r(\mathbf{y}, T) \mathbf{f}^r(\mathbf{y}, T) + \mathbf{a}_s(\mathbf{y}, T) \mathbf{f}^s(\mathbf{y}, T)$$
(2)

where the M basis vectors in  $\mathbf{a}_r$  and the (N+1-M) basis vectors in  $\mathbf{a}_s$  span the fast and slow subspaces of the tangent space at the point  $\mathbf{y} \in \Omega$  and  $\mathbf{f}^r$ ,  $\mathbf{f}^s$  are the corresponding fast and slow amplitudes in these subspaces. Moreover, Eq. (1) simplifies to the differential-algebraic system:

$$\mathbf{f}^{r}(\mathbf{y},T) \approx 0$$
  $\frac{d}{dt} \begin{bmatrix} \mathbf{y} \\ T \end{bmatrix} \approx \mathbf{a}_{s}(\mathbf{y},T)\mathbf{f}^{s}(\mathbf{y},T)$  (3)

where the symbol " $\approx$ " is indicative of the accuracy by which the fast and slow subspaces are spanned by the basis vectors in  $\mathbf{a}_r$  and  $\mathbf{a}_s$ . Starting from an initial guess,  $\mathbf{a}_r^0$  and  $\mathbf{a}_s^0$ , CSP provides refined fast and slow basis vectors that produce stable (i.e., non stiff) and of increasing accuracy reduced models.

#### III. CRITERIA FOR VALID QSSA AND PEA

In order to produce a reduced model for Eq. (1) on the basis of QSSA or PEA, M fast variables, say  $\mathbf{y}^r$ , and M fast reactions, say  $\mathbf{R}^r$ , must be selected. Under such a choice it was shown in [1] that QSSA and PEA produce specific approximations of the fast and slow subspaces of  $\Omega$  and that QSSA is a limiting case of PEA. This formulation enables for comparison with the CSP basis vectors and the introduction of the following criteria for the applicability of QSSA and PEA:

#### A. Stability

The criterion that guarantees stability of the reduced model constructed with QSSA or PEA can be expressed as:

$$\left[\mathbf{D}_{\mathbf{n}_{r}}(\tilde{\mathbf{f}}^{s})\right] \left[\mathbf{D}_{\mathbf{n}_{r}}(\mathbf{g}^{r})\right]^{-1} = \mathcal{O}(\epsilon)$$
(4)

where,  $\varepsilon$  denotes the fast/slow time scale gap,  $\mathbf{D}_{\mathbf{n}_r}[\bullet]$  denotes the directional derivate along the axis of the fast variables,  $\tilde{\mathbf{f}}^s$  are the slow amplitudes of the QSSA/PEA reduced model and  $\mathbf{g}^r$  is the part of the vector field  $\mathbf{g}$  that corresponds to  $\mathbf{y}^r$ .

#### B. Accuracy

The criterion that guarantees leading-order accuracy of the reduced model constructed by the PEA can be expressed as:

$$\left[\mathbf{D}_{\mathbf{n}_{r}}(\mathbf{g}^{r})\right]^{-1}\left[\mathbf{D}_{\tilde{\mathbf{a}}_{s}}(\mathbf{g}^{r})\right] = \mathcal{O}(\epsilon)$$
(5)

where  $\mathbf{D}_{\tilde{\mathbf{a}}_s}[\bullet]$  denotes the directional derivate along the PEA slow basis vectors  $\tilde{\mathbf{a}}_s = [-\mathbf{V}_s^r, \mathbf{I}_s^s]^T$ , where  $\mathbf{V}_s^r =$ 



Fig. 1. Top: the evolution of the species mass fractions and of the temperature. Bottom: the evolution of the time scales.

 $\begin{pmatrix} \frac{\partial \mathbf{R}^r}{\partial \mathbf{y}^r} \end{pmatrix}^{-1} \begin{pmatrix} \frac{\partial \mathbf{R}^r}{\partial \mathbf{y}^s} \end{pmatrix}, \mathbf{I}_s^s \text{ is the } (N+1-M) \times (N+1-M) - dim. identity matrix and <math>\mathbf{y}^s$  represents the N+1-M variables in  $\mathbf{y}$  that do not belong in  $\mathbf{y}^r$  [1]. Moreover, if:

$$\mathbf{V}_s^r = \mathcal{O}(\epsilon) \tag{6}$$

the PEA reduces to the QSSA, so that the QSSA provides leading-order accuracy as well.

#### IV. HYDROGEN-AIR AUTO-IGNITION

To examine the validity of the above criteria, the autoignition of a homogeneous hydrogen-air mixture under constant volume is considered [3]. The chemical kinetic mechanism consists of 21 reversible reactions among 8 reacting and one inert (nitrogen) species [4]. Considering a stoichiometric mixture ( $\phi = 1$ ) with initial temperature  $T_0 = 1100 K$  and pressure  $P_0 = 2.0 bar$ , Fig. 1 displays the corresponding evolution of the species mass fraction, temperature and time scales.

Before the ignition of the mixture, the two fastest time scales are dissipative followed by an explosive one. The time scale gap between the fast dissipative time scales and the explosive one is  $\epsilon = \mathcal{O}(0.10)$ . CSP analysis identifies OH and O as the fast variables for the two fast CSP modes and  $H_2 + OH \leftrightarrow H_2O + H$  and  $H_2 + O \leftrightarrow OH + H$ as the two fast reactions, respectively. This information is sufficient for calculating the quantities in Eqs. (4), (5) and (6) presented in Fig. 2. It is demonstrated that Eqs. (4) and (6) hold but Eq. (5) fails. This implies that the QSSA/PEA reduced models will not provide leading-order accuracy, which is verified by the computed relative errors shown in



Fig. 2. The evolution of the quantities in Eqs. (4), (5) and (6).



Fig. 3. The relative errors for the reduced models constructed by the PEA (top row) or QSSA (bottom row) approximation.

Fig. 3. Note, that both reduced models produce the same relative errors due to the negligible value of  $\mathbf{V}_s^r$ .

At the Workshop a detailed analysis and validation of the criteria for the validity of QSSA/PEA will be presented.

ACKNOWLEDGEMENTS: The work of DAG was supported by the Operational Program Education and Lifelong Learning of the National Strategic Reference Framework (NSRF)- Research Funding Program: "Aristeia" 2012-2015.

- D. A. Goussis. Quasi steady state and partial equilibrium approximations: Their relation and their validity. *Combustion Theory and Modelling*, 16(5), 2012.
- [2] S. H. Lam and D. A. Goussis. CSP method for simplifying kinetics. *International Journal of Chemical Kinetics*, 26(4): 461–486, 1994.
- [3] P. D. Kourdis. Asymptotic studies of stiff dynamical systems; construction and analysis of reduced systems in biology and combustion. *PhD Thesis, NTUA, Greece*, 2012.
- [4] P. Saxena and F. A. Williams. Testing a small detailed chemical-kinetic mechanism for the combustion of hydrogen and carbon monoxide. *Combustion and Flame*, 145(1-2):316– 323, 2006.

## Active Subspace Identification in Surrogate Modeling

Trent Russi<sup>\*</sup>, Andrew Packard<sup>†</sup>, Michael Frenklach<sup>†</sup> \*Rentrak Corporation, Portland OR <sup>†</sup>Mechanical Engineering, UC Berkeley

*Abstract*— Many applications and analysis techniques in science and engineering use simulation as a means for gauging a system's behavior. In coarse designs, simulation provides a qualitative look at system attributes. Much denser simulation might be required for more quantitative assessments. However, in advanced simulation techniques with complex models, each simulation can take hours or days. Processes with many variables require many simulation runs to adequately cover the space of responses. In this case, even if each simulation only takes a few minutes, the total simulation time can grow exponentially.

Surrogate modeling is the technique of creating an algebraic approximation to the simulation's map from parameters to response. The resulting *response surface* or *surrogate model* is much more efficient to evaluate than the original simulation and can provide much insight into the behavior of the original system [7]. The best form for a surrogate model depends on the application. They are formed with various methods such as standard regression, support vector machines [12], and kriging methods [8]. Data Collaboration techniques [3] use quadratic and rational-quadratic surrogate models to calculate outer bounds to various optimization objectives such as the consistency measures and response prediction.

One of the major problems facing surrogate modeling occurs when long simulation time is required to adequately sample the model response. To fit a surrogate model, many simulation runs are often required. The number of simulations can depend on the form of the surrogate (e.g., the number of basis functions) and the dimension of the parameter vector. For example, with a quadratic surrogate, the number of basis functions (monomials with a degree of at most 2) increases quadratically with the number of parameters.

This talk describes a technique for discovering the possible dependence of the response to a lower-dimensional active subspace of the parameters. If such an active subspace were known, the amount of simulation required to make a surrogate would depend on the subspace dimension rather than the original full dimension. The procedure determines if the gradient of the function is confined to a subspace, from which the active subspace can be identified.

Subspace dependence is not a new concept. However, the focus of many studies is on searching for a subspace dependence of the multivariate output of a function or of the evolving state vector of a set of coupled ODEs [1], [5], [6]. Some works use local subspace dependence to preserve neighborhood relationships and fit low-dimensional nonlinear manifolds to the data [2], [4], [11]. High-dimensional model representations (HDMRs, [9], [10]) build up a surrogate model by iteratively fitting along every coordinate-aligned subspace starting with the 0-dimensional subspace.

The talk will outline the procedure and derivation, and

a simple complexity analysis. We illustrate the method's behavior on a wide variety of problems, including hydrogen and methane combustion models.

- Zhaojun Bai. Krylov subspace techniques for reduced-order modeling of large-scale dynamical systems. *Applied Numerical Mathematics*, 43:9–4, 2002.
- [2] David L. Donoho and Carrie Grimes. Hessian eigenmaps: Locally linear embedding techniques for high-dimensional data. In *Proceed*ings of the National Academy of Sciences of the United States of America, volume 100, pages 5591–5596, 2003.
- [3] Ryan Patrick Feeley. Fighting the Curse of Dimensionality: A method for model validation and uncertainty propagation for complex simulation models. PhD thesis, University of California, Berkeley, CA, 2008.
- [4] Baskar Ganapathysubramanian and Nicholas Zabaras. Modelling diffusion in random heterogeneous media: data-driven models, stochastic collocation and the variational multi-scale method. *Journal of Computational Physics*, 226:326–353, 2007.
- [5] Eric James Grimme. Krylov Projection Methods for Model Reduction. PhD thesis, University of Illinois, Urbana Champaign, IL, 1997.
- [6] Sanjay Lall, Jerrold E. Marsden, and Sonja Glavaski. A subspace approach to balanced truncation for model reduction of nonlinear control systems. *International Journal of Robust and Nonlinear Control*, 12(6):519–535, 2002.
- [7] Raymond H. Myers and Douglas C. Montgomery. Response Surface Methodology: Process and Product Optimization Using Designed Experiments. Wiley, 2002.
- [8] M.A. Oliver and R. Webster. Kriging: a method of interpolation for geographical information systems. *International Journal of Geographical Information Science*, 4(3):313–332, 1990.
- [9] Herschel Rabitz and Ömer F. Alış. General foundations of highdimensional model representations. *Journal of Mathematrical Chemistry*, 425:197–233, 1999.
- [10] Herschel Rabitz, Ömer F. Alış, Jeffrey Shorter, and Kyurhee Shim. Efficient input-output model representations. *Computer Physics Communications*, 117:11–20, 1999.
- [11] Sam T. Roweis and Lawrence K. Saul. Nonlinear dimensionality reduction by locally linear embedding. *Science*, 290:2320–2326, 2000.
- [12] A.J. Smola and B. Schölkopf. A tutorial on support vector regression. *Statistics and Computing*, 14:199–222, 2004.

### Global Sensitivity Analysis with Small Sample Sizes

Michael J. Davis\* and Wei Liu\*

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439

*Abstract*—Methods for doing global sensitivity analysis with small sample sizes are discussed. Two changes are made to our previous algorithm. Rather than an HDMR expansion, we use a full polynomial response surface, but limit the number of interaction terms we include. This reduces the sample size by approximately a factor of five. Further reductions are obtained by using sparse regression techniques to find the regression coefficients, particularly the sparse group lasso.

#### I. INTRODUCTION

Chemical kinetic models of combustion processes consist of hundreds or thousands of reactions describing the chemistry of dozens to hundreds of chemical species [1]. Even for the most studied chemical reactions the rate coefficients are not known with a great deal of precision, and in many cases most of the rate coefficients are estimated [2]. The well-known uncertainty of rate coefficients has led to extensive use of sensitivity analysis. Traditionally sensitivity analysis has been carried out in a local and linear fashion, generated from information near the estimated rate coefficient [3]. If the rate coefficient is sufficiently different from the nominal value the local sensitivity may be an inaccurate estimation of the role of the uncertainty of the rate coefficient in the uncertainty of the target. Global sensitivity analysis ([4] and [5]) samples the full range of uncertainty of all the reactions at once, so that nonlinearities and correlations may be described.

We present here work [6] on using the sparsity of the sensitivity indices to significantly reduce the sample size needed to get a ranking of the sensitivity of reactions in a chemical model. Using sparse techniques, the sample sizes can be much smaller than the number of reactions and thus can require less computational effort than linear one-at-atime methods that are often used for ignition delays.

#### II. RESULTS AND DISCUSSION

In order to used sparse regression techniques, the response surface for the ignition target studied here is written in a form [6] that differs from the HDMR expansion we typically have used (for example, Ref. 7):

$$\begin{aligned} \tau^{(1)}(\{u_i\}) &= \sum_{i=1}^{m} \sum_{k=0}^{n} a_{ik} u_i^k \\ \tau^{(2)}(\{u_i\}) &= \sum_{i=1}^{m} \sum_{k=1}^{n} a_{ik} u_i^k + \sum_{j=1}^{p} \sum_{s=1}^{n-1} \sum_{\substack{k+r \le s \\ k,r > 0}} b_{jkr} u_{v(j,1)}^k u_{v(j,2)}^r , \end{aligned}$$
(1a)

where m refers to the number of reactions and n refers to the order of the expansion. It is straightforward to generate sensitivity indices  $(S_i,s)$  using expansions like those in Eq. (1a) [6]. Equation (1b) uses the information from the fit in Eq (1a): p is a number determined from the expansion in Eq. (1a). Only reactions in Eq. (1a) whose sensitivity indices are above a threshold are used in the second set of terms in Eq. (1b). The value of p is generally less than 200 in our calculations. We typically use thresholds of  $S_i = 0.005$  or  $S_i = 0.01$ . The indices "v(j,1)" and "v(j,2)" in Eq. (1b) refer to a pair of reactions that are used in the interaction term based on their  $S_i$ 's. It is straightforward to use Eq. (1a) to extract  $S_i$ 's. Extraction of  $S_i$ 's from Eq. (1b) requires integration, done analytically for the polynomial expansions.

Results for butanol ignition are presented in the middle panel of Fig. 1, generated using the expansions in Eqs. (1a) and (1b). Comparison of this plot and the one above it demonstrates that good results can be obtained with the expansion in Eqs. (1a) and (1b) with much smaller sample sizes. The sample size of 7,000 used for Eqs. (1a) and (1b) is a significant improvement over the previous sample size of 50,000 (top panel of Fig. 1). We have used an HDMR expansion in many studies and found that convergence was achieved much more rapidly for the large S<sub>i</sub>'s than for small S<sub>i</sub>'s. The slowness of the convergence is a manifestation of a phenomenon called "overfitting" [8], which is alleviated to a significant extent by the expansion in Eqs. (1a) and (1b). The reduction of effort is achieved using ordinary least squares regression for the fits in Eqs. (1a) and (1b). Even further reductions can be found by starting from Eqs. (1a) and (1b) and taking into account the sparseness of the results - most sensitivity coefficients are very small. The additional reduction is achieved by using sparse regression techniques [8].

The savings from sparse regression results from the fact that typically the uncertainty of only a few reactions contribute significantly to the uncertainty in a given target. The sparse regression techniques take advantage of this without any prior knowledge about which reactions contribute. This is accomplished by adding a "penalty" term to the usual error function for least squares fits:

$$E(\mathbf{c}) = \frac{1}{2} \sum_{k=1}^{M} \left( t_{k} - \sum_{i=1}^{L} c_{j} g_{j}(\mathbf{u}_{k}) \right)^{2} + \lambda \sum_{j=1}^{L} |c_{j}|, \qquad (2)$$

where  $t_k$  refers to the ignition delay time for the k<sup>th</sup> sample run. The specific algorithm we use is described in the upcoming paper [6].

The expansion described in Eq. (2) is referred to as the LASSO [8]. The penalty term serves two purposes, it



Fig. 1. The top and middle panels show results for butanol ignition with the old algorithm and new algorithm, respectively. The bottom panel shows a calculation using sparse regression.

#### **Butanol Selection (Ignition)**

Rxn	No	S <sub>i</sub>	Rank	400	800	1200
NC4H9OH+HO2 = C4H8OH-1+H2O2	1353	0.403	1	1	1	1
H2O2+O2 = HO2+HO2 (dupl.)	14	0.158	2	2	2	2
H2O2(+M) = OH+OH(+M)	16	0.116	3	3	3	3
NC4H9OH+HO2 = C4H8OH-3+H2O2	1351	0.055	4	4	4	4
NC4H9OH+HO2 = C4H8OH-2+H2O2	1352	0.032	5	5	5	5
C2H5+HO2 = C2H5O+OH	171	0.0290	6	6	7	7
H2O2+O2 = HO2+HO2 (dupl.)	15	0.0287	7	7	6	6
NC4H9OH+HO2 = C4H8OH-4+H2O2	1350	0.018	8	8	8	8
NC4H9OH+HO2 = C4H8OH-4+H2O2	1329	0.011	9	9	9	9

#### Columns 3 and 4: OLS, n = 7000

Fig. 2. Reaction Selection for n-Butanol ignition is shown.

"regularizes" the solution, reducing overfitting, but more importantly, for our purposes, it selects coefficients, resulting in many coefficients that are zero for specific values of  $\lambda$ . There are a number of ways of picking good values of  $\lambda$  [8], and typically we use cross-validation or an empirical rule we discerned from a number of applications. Equation (2) is a simplification of the procedure used in Ref. [6], the sparse group lasso [9], which recognizes the grouping of expansion coefficients based on individual reactions. There is an additional adjustable parameter,  $\alpha$ , set to 0.5 here (it can range from 0.0 to 1.0).

The results of applying the previously described algorithm is presented in the bottom panel of Fig. 1, which demonstrates that we can obtain good agreement between ordinary least squares and sparse techniques, with much smaller sample sizes. Figure 2 has a detailed comparison for all sensitivity coefficients greater than 0.01 (1% of the variance). The comparisons are made for three sample sizes in the sparse case: 400, 800, and 1200. Numbers in red indicate the reactions than are mis-ordered and it can be observed that this only occurs for a single pair which have very close sensitivity coefficients in the much larger ordinary least squares calculation (7000 samples).

#### ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U.S. Department of Energy, under contract number DE-AC02-06CH11357.

- C. K. Westbrook, Y. Mizobuchi, T. J. Poinsot, P. J. Smith, J. Warnatz,, "Computational Combustion", *Proc. Combust. Inst.* 30, 125-157 (2005).
- [2] H. J. Curran, P. Gaffuri, W. J. Pitz, and C. K. Westbrook, "A Comprehensive Modeling Study of n-Heptane Oxidation" *Combustion and Flame* 114, 149-177 (1998).
- [3] J. Zador, I. G. Zseley, and T. Turanyi, "Local and global uncertainty analysis of complex chemical kinetic systems", *Reliab. Eng. Syst. Saf.* 91, 1232-1240 (2006).
- [4] A. Saltelli, M. Ratto, T. Andres, F. Campolongo, J. Cariboni, D. Gatelli, M. Sasana, and S. Tarantola, *Global Sensitivity Analysis*. *The Primer*; John Wiley & Sons: Hoboken NJ (2008).
- [5] A. S. Tomlin and T. Ziehn, "The Use of Global Sensitivity Methods for the Analysis, Evaluation and Improvement of Complex Modelling Systems" in *Coping with Complexity: Model Reduction and Data Analysis*; A. N. Gorban and D. Roose, Eds.; Springer; Berlin, (2010), p. 9.
- [6] M. J. Davis and W. Liu, "Global Sensitivity Analysis with Small Sample Sizes", to be submitted.
- [7] R. T. Skodje, A. S. Tomlin, S. J. Klippenstein, L. B. Harding, and M. J. Davis, "Theoretical Validation of Chemical Kinetic Mechanisms: Combustion of Methanol", *J. Phys. Chem. A* 114, 8286-8301 (2010).
- [8] T. Hastie, R. Tibshirani, and J. Friedman, *Elements of Statistical Learning: Data Mining, Inference, and Prediction*, Second Edition, Springer (2009).
- [9] N. Simon, J. Friedman, T. Hastie, and R. Tibshirani, "A Sparse Group Lasso", *Journal of Computational and Graphical Statistics*, to be published.

### A Kinetic Model for Limit Phenomena Prediction Based on Bifurcation Analysis

Ruiqin Shan and Tianfeng Lu Department of Mechanical Engineering University of Connecticut, Storrs, CT 06269-3139, USA

A bifurcation analysis was employed to construct a compact kinetic model to predict limit flame phenomena in steady state perfectly stirred reactors (PSR), including ignition, extinction and onset of flame instabilities. The method is demonstrated with dimethyl ether (DME)/air mixtures that involve the negative temperature coefficient (NTC) chemistry and thus showing cool flames in PSR. A Bifurcation Index (BI) is defined to quantify the contribution of each reaction to the limit phenomena. Reactions with large BI are selected and tuned to obtain a kinetic model that can accurately reproduce the bifurcation states obtained by the full mechanism.

#### I. INTRODUCTION

Limit flame phenomena, such as ignition, extinction and onset of flame instabilities are important for combustion applications. In a steady state system, ignition and extinction were typically believed to be associated with the turning points on the *S*-curves<sup>[1]</sup>. Such limit phenomena are induced by the competition between finite rate chemistry and the mixing processes. Therefore, accurate prediction of the limit phenomena requires realistic chemistry that is typically nonlinear, stiff and large, and thus computational expensive <sup>[2]</sup>. In the present study, a method based on bifurcation analysis was developed to construct efficient kinetic models that can accurately mimic the detailed mechanisms to predict limit flame phenomena.

A turning point on canonical S-curves is associated with a singular Jacobian matrix <sup>[3]</sup>, where changes in flame stability can occur. However, with detailed chemical kinetics, such as that of dimethyl ether (DME), the S-curve can be complex and involve multiple criticalities <sup>[4]</sup>. Furthermore, it was found using flame stability analysis that extinction of DME/air flames in steady state PSR may occur prior to reaching the turning points primarily due to the competition between different reaction pathways<sup>[5]</sup>. In such cases flame stability analysis is needed to rigorously detect the limit phenomena rather than simply depending on the turning points on the S-curves. In a recent study on chemical explosive mode analysis (CEMA) [6], it was further shown that the limit phenomena in PSR is primarily induced by the competition between chemical explosive modes (CEM) and the mixing processes. As such, the species and reactions controlling the CEM can be similar to those controlling the limit phenomena.

In the present study, the controlling reactions for the limit phenomena are identified using a bifurcation index, defined in analogous to the participation index (BI) in computational singular perturbation (CSP)<sup>[7]</sup> and CEMA. Important reactions are selected based on their BI values to form a compact skeletal mechanism. The A-factors of reaction with large BI values are tuned to obtain S-curves that are mostly identical to those by the detailed mechanism.

#### II. METHODOLOGY

The governing equations of a homogeneous combustion system, e.g. an unsteady PSR, can be represented by a set of ordinary differential equation (ODE):

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}), \qquad (1)$$

where **y** is the vector of dependent variables,  $\boldsymbol{\omega}$  is the chemical source term, and **s** is the mixing term. The time evolution of a small perturbation,  $\delta \mathbf{y}$ , induced to the steady state solution can be approximated with the following linear ODE:

$$\frac{d\delta \mathbf{y}}{dt} \approx \mathbf{J}_{\mathbf{g}} \cdot \delta \mathbf{y}, \ \delta \mathbf{y} = \delta \mathbf{y}_0 \text{ at } t = 0, \quad (2)$$

where  $J_g$  is the Jacobian evaluated with the steady state solution  $y_s$ . Note that  $J_g$  consists of two components, which are attributed to the chemical source term and the mixing term, respectively.

$$\mathbf{J}_{\mathbf{g}} = \frac{\partial \mathbf{g}}{\partial \mathbf{y}} = \mathbf{J}_{\omega} + \mathbf{J}_{s}, \ \mathbf{J}_{\omega} = \frac{\partial \boldsymbol{\omega}}{\partial \mathbf{y}}, \ \mathbf{J}_{s} = \frac{\partial \mathbf{s}}{\partial \mathbf{y}} \quad (3)$$

The eigenvalue  $\lambda_1$  of  $\mathbf{J}_{\mathbf{g}}$  with the largest real part determines the absolute stability of the system, and a bifurcation point with  $\operatorname{Re}(\lambda_1) = 0$  separates a stable branch from an unstable branch on the *S*-curve, where "Re()" denotes the real part of a complex number. Note that, the Jacobian  $\mathbf{J}_{\mathbf{g}}$  is singular at the turning points of an *S*-curve, i.e.  $\lambda_i = 0$ . The turning points nevertheless may not necessarily indicate changes in flame stability if  $i \neq 1$ . In such cases, ignition and extinction of the system may occur at Hopf bifurcation points located away from the turning points <sup>[5]</sup>. At a bifurcation point, where  $\text{Re}(\lambda_1) = 0$ , the eigenvalue can be decomposed as

$$\operatorname{Re}(\lambda_{1}) = \sum_{r=1}^{I+1} \operatorname{Re}(\lambda_{r}) = 0, \ \lambda_{r} = \mathbf{b}_{1} \cdot \mathbf{J}_{r} \cdot \mathbf{a}_{1}$$
$$\mathbf{J}_{\omega} = \sum_{r=1}^{I} \mathbf{J}_{r}, \ \mathbf{J}_{s} = \mathbf{J}_{I+1}$$
(4)

where  $\mathbf{J}_r$  is the contribution of the  $r^{\text{th}}$  reaction to the chemical Jacobian, *I* is the total number of reactions, and  $\mathbf{b}_1$  and  $\mathbf{a}_1$  are the left and right eigenvectors of  $\mathbf{J}_g$ , respectively, associated with  $\lambda_1$ . The bifurcation index (BI) of the  $r^{\text{th}}$  reaction is defined as

$$BI^{r} = \frac{\operatorname{Re}(\lambda_{r})}{\max |\operatorname{Re}(\lambda_{r})|_{r=1,l+1}}.$$
 (5)

The value of BI<sup>*r*</sup> therefore indicates the normalized contribution from the *r*<sup>th</sup> reaction or the mixing process to the zero-crossing of  $\text{Re}(\lambda_1)$  at a bifurcation point.

#### III. RESULTS

Fig. 1 shows the temperature profile, i.e. the *S*-curve, for a rich DME/air mixture calculated with a detailed mechanism with 55 species and 290 reactions <sup>[8]</sup>. Three stable branches (solid lines), the strong flames branch, the cool flames branch, and the no-flame branch, respectively, were observed in the top-down order, with  $E_{2b}$ ,  $E_{1b}$ ,  $I_{2b}$ , and  $I_{1b}$  being the extinction of strong flames, extinction of cool flames, ignition of strong flames, and ignition of cool flames, respectively.



Fig. 1: An S-curve of a rich DME/air in PSR. Solid line:  $\operatorname{Re}(\lambda_1) \leq 0$ , Dashed line:  $\operatorname{Re}(\lambda_1) > 0$ .

The important reactions for the ignition and extinction states shown in Fig. 1 are identified using the BI values defined in Eq. (5), as shown in Fig. 2 for the extinction of the strong flames at  $E_{2b}$ '. A skeletal mechanism was formed by selecting the 103 reactions with non-negligible BI values (BI > 0.01) from the detailed mechanism. The A-factors of a small group of reactions with large BI values at all the six bifurcation points in Fig. 1 are tuned such that the bifurcation points predicted by the tuned mechanism almost

exactly match those predicted by the detailed mechanism as shown in Fig. 3.



Fig. 2: Reactions with large BI values at strong flames extinction state,  $E_{2b}$ '.



Fig. 3: The *S*-curves predicted by detailed, skeletal and tuned mechanisms for DME/air, respectively.

#### ACKNOWLEDGMENT

This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, under Grant DE-SC0008622.

- C.K. Law, *Combustion physics* (New York: Cambridge University Press, 2006).
- T.F. Lu, and C.K. Law, Progress in Energy and Combustion Science, 35 (2009), 192-215.
- R. Seydel, Practical bifurcation and stability analysis. 3rd edn, Interdisciplinary applied mathematics (New York: Springer Verlag, 2010), pp. xvii, 483 p.
- W. Liu, C.K. Law, and T.F. Lu, International Journal of Chemical Kinetics, 41 (2009), 764-776.
- 5. R. Shan, and T. Lu, Combustion and Flame, 159 (2012), 2069-2076.
- R. Shan, C.S. Yoo, J.H. Chen, and T. Lu, *Combustion and Flame*, 159 (2012), 3119-3127.
- 7. S.H. Lam, Combustion Science and Technology, 89 (1993), 375-404.
- Z. Zhao, M. Chaos, A. Kazakov, and F.L. Dryer, *International Journal of Chemical Kinetics*, 40 (2008), 1-18.

### Chemistry Guided Reduction of an Multicomponent Reaction Mechanism

Lars Seidel\*, Christian Klauer<sup>†</sup>, Xiaoxiao Wang\*, Fabian Mauss\*

\*Brandenburg University of Technology / Thermodynamics and Thermal Process Engineering , Cottbus, Germany <sup>†</sup>Lund Combustion Engineering AB, Lund, Sweden

#### I. INTRODUCTION

The development in computational fluid dynamics and turbulence chemistry interaction modeling in recent years allows for the usage of detailed chemical information for the analyses and optimization of combustion devices. The latest development shows a trend in engineering to replace single component with multi-component reference fuels. This causes reaction mechanisms of increasing sizes, and thereby an increasing demand in mechanism reduction or tabulation techniques.

Mechanism reduction can be performed through lumping, species removal, and quasi steady state or partial equilibrium assumptions. Species removal is frequently performed through directed relation graphs. In [1] we introduced a directed relation graph which used fuel molecules, oxidizer molecules, and sensitive species as seed. Relation graphs were calculated for each atomic flux in the reductionoxidation system. A reaction sensitivity analysis was performed and the relation graph was initialized for each species by the weighted sensitivity coefficients of all reactions in which the species appeared as reactant. The sensitivity analysis thereby allowed setting targets of the reduced reaction mechanism. Multistep error propagation was calculated from an iterative procedure, which resulted in species weights, which sorted the species according their necessity to be part of the targeted reduced reaction mechanism. We introduced this method as necessity analysis. In [5] we applied the necessity analysis to develop skeleton mechanisms for n-heptane for the full temperature regime and for the high temperature regime only.

Directed relation graph methods cannot reduce mechanisms efficiently which consist of a high number of parallel pathways, with almost equal fluxes. Unfortunately this feature is found in all oxidation mechanisms for larger hydrocarbons. Such mechanisms can be efficiently simplified through chemical lumping, which we applied in [2] as a prestage of the necessity analysis applied in [5]. We introduced a simple rule for the lumping procedure: species of equal size, with the same distance between the same functional groups found at the same carbon classes (primary, secondary, or tertiary carbon) can be lumped. Concentrations of these species are assumed to be equal. This rule allowed to apply chemical lumping during the automated generation of reaction mechanisms [3], [4].

In [1] we assumed that it is necessary to develop reduced reaction mechanisms over the full range of initial conditions, and to define the final set of necessary species by all species with necessity in at least one point of the parameter range. In [5] we identified critical chemical conditions, which are representative for the full parameter range. Since then we apply the method for the critical conditions only, and verify the mechanism thereafter for the full parameter range. Chemistry Guided Reduction (CGR) reduces the development time needed to find an optimum reduced reaction mechanism.

Each reaction in a reaction mechanism has a sensitivity on the performance of the total reaction mechanism. It is not possible to just add submechanisms for different fuel molecules without side effects on the performance of the mechanism for the individual fuel molecules. Each combination of fuel molecules makes a correction of some reaction rate coefficients necessary. In mechanism development these corrections can be performed through automated optimization procedures. On the other hand, the performance of the mechanism will be influenced, if a submechanism for a unused fuel molecule is removed from the reaction mechanism. Again automated optimization can be used to readjust the mechanism. When applying necessity analysis for species removal it is found, that a large number of species can be removed with almost no change of the performance of the reaction mechanism. Species with medium scaled necessity values influence results of the mechanism, and readjustment is necessary if further simplification of the reaction mechanism is wanted. In this presentation we perform CGR for a complex blend of fuel molecules, and demonstrate the performance of strongly simplified chemical systems for low and high temperature combustion.

#### II. THE DETAILED REACTION MECHANISM

The detailed reaction mechanism consists of 477 species and 4228 reactions. It consists of two larger alkanes: nheptane and iso-octane. Those reaction models are generated as described in [2] via an semi automatic procedure [4]. The aromatic content is modelled by toluene as described in [6]. All three submechanisms are based on the same C1-C4 chemistry [7] which was extended by a submechanism for ethanol oxidation.

Calculations for all fuel molecules (n-heptane, iso-octane, toluene and ethanol) show good agreement with the experimental values [8].

#### III. REDUCTION PROCEDURE

1) Horizontal lumping: The technique of horizontal lumping is applied for the submechanisms for n-heptane and iso-octane [2]. Lumping reduced the mechanism to a size of 400 species and 3988 reactions.

2) Species removal based on necessity analysis: To efficiently remove species with the lowest importance a series of steps were taken. First a set of different constant volume reactors and freely propagating flames is calculated including necessity analysis [1]. The selection of the reactors follow the ideas from [2]. In a second step the probability for species removal is weighted by its necessity value. Species are selected randomly, respectively to their probability for removal. Finally the accuracy of the model and the numerical stiffness is controlled. If the targets of the mechanism are meat the species removal is accepted and the procedure is repeated. Targets can be species concentrations or global parameter such as ignition delay time or laminar flame speed. A skeletal mechanism was generated with 290 species and 3026 reactions. The accuracy of the mechanism after each species removal is compared to the necessity value, which demonstrates the performance of the method.

3) Reaction removal based on sensitivity analysis: A further reduction can be achieved be removing single reactions. To identify those reactions a sensitivity analysis towards various targets such as species, ignition delay time and / or laminar flame speeds is used. The sensitivy coefficient over all cases are normalised and a probability to be removed is assigned to each reaction. This probability density function is used to efficiently decide which reaction to remove while keeping a certain randomness.

4) Species removal and reoptimization: The reduction technique explained before reduced the mechanism to the smallest set of species and reactions within the given accuracy limits. Each further reduction leads to a reaction mechanism which cannot predict the targets of the mechanism with the demanded accuarcy. Nevertheless further reduction is possible when reoptimisation of the Arrhenius coefficients is applied. We apply a genetic optimisation algorithm. The final mechanism for the four component gasoline reference fuel has a size of 205 species and 1460 reactions. The meachnism can be further reduced by the help of time scale analysis or tabulation techniques.

#### **IV.** CONCLUSIONS

The reduction techniques explained above were applied and the reduced mechanisms is validated against the detailed reaction mechanism. For the laminar flame speed



Fig. 1. Simulated ignition delay time for n-heptane at stocheometric conditions. light grey p=3 bar, grey p=27.25 bar, dark grey p=51.5 bar and black p=100 bar. The rectangles represents the lumped mechanism. The line represents the skeletal mechanism after species removal.

no deviation was observed for the lumped and skeletal mechanisms. Fig. 1 shows that the final mechanism predicts accurately ignition delay times for a wide range of pressures and temperatures. Such mechanisms can be direct input to combustion simulation, or input to further mechanism reduction based on time scale analysis.

All calculations were performed using DARSv2.08.30.

- Soyhan, H., Mauss, F. and Sorusbay, C., Chemical Kinetic Modelling of Combustion in Internal Combustion Engines using Reduced Chemistry, Combust. Sci. Technol., Vol. 174 (11-2), 73-91, 2002
- [2] Ahmed, S.S., Mauss, F., Morac, G. and Zeuch, T., A Comprehensive and Compact n-Heptane Oxidation Model Derived Using Chemical Lumping, Phys. Chem. Chem. Phys., 9, 11071126, 2007
- [3] Morac, G., Blurock, E.S., and Mauss, F., Automatic Generation of a Detailed Mechanism for the Oxidation of n-Decane, Combust. Sci. Tech., 178, 10-11, pp. 2025-2038, 2006
- [4] Hilbig, M., Seidel, L., Wang, X., Mauss, F. Zeuch, T., "Computer Aided Detailed Mechanism Generation for Large Hydrocarbons: n-Decane" 23rd ICDERS July 2429, 2011 Irvine, USA
- [5] Zeuch, T., Moreac, G., Ahmed, S.S., and Mauss, F., A Comprehensive Skeleton Mechanism for the Oxidation of n-heptane Generated by Chemistry Guided Reduction, Combust. Flame, 155, 651674, 2008
- [6] S. S. Ahmed, F. Mauss, T. Zeuch: The Generation of a Compact n-Heptane / Toluene Reaction Mechanism Using the Chemistry Guided Reduction (CGR) Technique, Z. Phys. Chem. 223 (2009) 551-563.
- [7] Schenk, M., Leon, L., Moshammer, K., Osswald, P., Zeuch, T., Seidel, L., Mauss, F., Kohse-Höinghaus, K., "Detailed mass spectrometric and modeling study of isomeric butene flames", Combust. Flame, 2013
- [8] Leon, L., Mauss, F., Moreac, G., Seidel, L., Zeuch, T., "A comprehensive mechanism for fuel mixtures including oxygenated species", ECM, 2011

# The GNAT nonlinear model-reduction method with application to large-scale turbulent flows

Kevin Carlberg<sup>\*</sup>, Charbel Farhat<sup>†</sup>, Julien Cortial<sup>\*</sup>, David Amsallem<sup>†</sup> \*Sandia National Laboratories, Livermore, CA, USA <sup>†</sup>Stanford University, Stanford, CA, USA

Abstract— The Gauss-Newton with approximated tensors (GNAT) method is a nonlinear model-reduction method recently proposed in Ref. [1]. In contrast to proper orthogonal decomposition (POD)–Galerkin, GNAT employs discrete-optimal approximations: the solution computed at each time step minimizes an error measure with respect to the full-order-model solution. This leads to improved stability and accuracy over POD–Galerkin for many problems.

Here, we describe recent developments in the GNAT methodology. First, we present global state-space error bounds. Next, we introduce a 'sample mesh' concept that enables an efficient, distributed implementation of GNAT in finite-volume-based CFD codes. Finally, we demonstrate GNAT's performance on an unsteady, compressible, turbulent flow problem with over 17 million unknowns.

#### I. PROBLEM FORMULATION

Consider the ODE resulting from semi-discretizing the conservation form of the compressible Navier-Stokes equations (with turbulence model) by a finite volume method with specified boundary conditions:

$$\frac{dw}{dt} = F(w(t), t; \mu)$$

$$w(0) = w^{0}(\mu).$$
(1)

Here,  $w \in \mathbb{R}^N$  denotes the state (i.e., the vector of conserved fluid variables) with N 'large',  $w^0$  denotes the parameterized initial condition, and  $\mu$  denotes the vector of inputs, e.g., shape parameters. Our goal is to rapidly solve (1) for arbitrary values of  $\mu$ .

#### II. GNAT OVERVIEW

GNAT introduces approximations after ODE (1) has been discretized in time. This enables the method to achieve *discrete optimality*: it minimizes a measure of the error between the computed state and the state fullorder-model state at each time step.

#### A. Full-order model

Assuming that Eq. (1) is solved by an implicit linear multi-step integrator, the algebraic system of nonlinear equations arising at a given time step for given inputs  $\mu$  can be written as

$$R(w) = 0, (2)$$

where we have omitted the time index and inputparameter dependence for notational simplicity.

#### B. GNAT projection

GNAT reduces the dimension of Eq. (2) via projection: it computes a solution of the form  $\tilde{w} = w^0 + \Phi_w w_r$ , where  $\Phi_w \in \mathbb{R}^{N \times n_w}$  is a reduced basis of dimension  $n_w \ll N$  computed by POD, for example.

Substituting  $w \leftarrow \tilde{w}$  in Eq. (2) yields  $R(w^0 + \Phi_w w_r) = 0$ , which is an overdetermined system of N nonlinear equations in  $n_w$  unknowns. Rather than solve  $\Phi_w^T R(w^0 + \Phi_w w_r) = 0$  like Galerkin methods, GNAT computes  $\tilde{w}$  as the solution to the minimization problem

$$\underset{\bar{w}\in w^{0}+\operatorname{range}(\Phi_{w})}{\operatorname{minimize}} \|R(\bar{w})\|_{2}$$
(3)

using the Gauss–Newton method. Thus, GNAT delivers a solution that is *discrete optimal at each time step*: the solution minimizes the discrete residual associated with the full-order model over the trial subspace. In contrast, Galerkin methods generally do not exhibit discrete optimality [1].

#### C. GNAT complexity reduction

Although the dimension of the trial subspace is small, the computational cost of solving nonlinear leastsquares problem (3) scales with N, because  $R : \mathbb{R}^N \to \mathbb{R}^N$ . To address this bottleneck, GNAT employs gappy POD [3] to approximate the discrete residual:

$$\ddot{R} = \Phi_R \left[ Z \Phi_R \right]^+ Z R. \tag{4}$$

Here,  $\Phi_R \in \mathbb{R}^{N \times n_R}$  with  $n_R \ll N$  defines a POD basis for the residual, Z is a sampling matrix consisting of  $n_i \ll N$  selected rows of the identity matrix, and the + superscript denotes the Moore–Penrose pseudoinverse. This approximation is also discrete optimal, as

$$\tilde{R} = \arg \min_{x \in \operatorname{range}(\Phi_R)} \|ZR - Zx\|_2$$
(5)

Substituting  $R \leftarrow \tilde{R}$  in (3) yields the GNAT model defined at each time step:

$$\min_{\bar{w} \in w^0 + \operatorname{range}(\Phi_w)} \|\Phi_R \left[ Z \Phi_R \right]^+ Z R(\bar{w}) \|_2.$$
 (6)

See Refs. [1], [2] for more information on the construction of the reduced bases and sampling matrix.

#### III. ERROR BOUNDS

The following proposition (proved in Ref. [2]) provides global state-space error bounds for the GNAT solution and highlight the merit of GNAT's design.

Proposition 3.1: Assume  $f : (w,t;\mu) \mapsto w - \Delta t F(w,t;\mu)$  satisfies the following inverse Lipschitz continuity condition for inputs  $\mu$  and  $n = 1, \ldots, n_t$ :

$$\frac{\|f(w,t^{n};\mu) - f(y,t^{n};\mu)\|}{\|w - y\|} \ge \varepsilon > 0.$$
(7)

Further assume that the backward-Euler scheme is employed and computes states  $w^n$ ,  $n = 1, ..., n_t$  satisfying

$$||R^n(w^{n+1};\mu)|| \le \epsilon_{\text{Newton}}.$$
(8)

Then, for any sequence of states  $\tilde{w}^n$ ,  $n = 0, \ldots, n_t$  satisfying  $\tilde{w}^0 = w^0$ , a global error bound for the state at time step n is

$$\|w^{n} - \tilde{w}^{n}\| \le \sum_{k=1}^{n} a^{k} b_{n-k}.$$
(9)

Here,

$$a \equiv \sup_{n \in \{1,...,n_t\}} \sup_{w \neq y} \frac{\|w - y\|}{\|f(w, t^n; \mu) - f(y, t^n; \mu)\|}$$
  
$$b_n \equiv \epsilon_{\text{Newton}} + \|\Phi_R [Z\Phi_R]^+ Z\bar{R}^n(\tilde{w}^{n+1}; \mu)\| + \|(I - \Phi_R [Z\Phi_R]^+ Z)\bar{R}^n(\tilde{w}^{n+1}; \mu)\|$$

 $\bar{R}^n(w;\mu) = w - \tilde{w}^n - \Delta t F(w,t^n;\mu).$ 

Note that GNAT minimizes one component of this error bound (compare the definition of  $b_n$  with Eq. (6)).

#### **IV. SAMPLE-MESH IMPLEMENTATION**

The 'sample mesh' concept enables a distributed, computationally efficient implementation of the GNAT method in finite-volume-based CFD codes. The main idea is to extract only the subset of the mesh required to compute the sampled residual ZR (see Eq. (6)); all other parts of the mesh are not needed by GNAT and are omitted from online computations.

#### V. EXAMPLE: AHMED-BODY WAKE FLOW

We assess GNAT's performance on a benchmark problem in the automotive industry: the Ahmed body. The full-order model corresponds to an unsteady Navier–Stokes simulation with a DES turbulence model and wall function. The finite-volume discretization leads to N = 17,342,604. The implicit three-point BDF scheme defines the time discretization.

Figure 2 compares the pressure contours computed by both the full-order model and GNAT. The GNAT

solution incurs a time-averaged error in the drag coefficient of only 0.68%, yet consumes only 0.23% of the computational resources of the full-order model (in walltime  $\times$  cores). This savings is mainly attributable to the decrease in cores from 512 to 4 enabled by the sample-mesh implementation.



Fig. 1 Sample mesh (red) allows GNAT to run on 4 cores, as only 0.59% of nodes are loaded into memory.



**Fig. 2** Surface-pressure contours at t = 0.1 s

#### ACKNOWLEDGMENTS

We acknowledge partial support by the Motor Sports Division of the Toyota Motor Corporation under Agreement Number 48737, and partial support by the Army Research Laboratory through the Army High Performance Computing Research Center under Cooperative Agreement W911NF-07-2-0027. The first author also acknowledges partial support by the NSF Graduate Fellowship, the NDSEG Fellowship, and an appointment to the Sandia National Laboratories Truman Fellowship in National Security Science and Engineering. The Truman Fellowship is sponsored by Sandia Corporation (a wholly owned subsidiary of Lockheed Martin Corporation) as Operator of Sandia National Laboratories under its U.S. Department of Energy Contract No. DE-AC04-94AL85000. The content of this publication does not necessarily reflect the position or policy of any of these institutions, and no official endorsement should be inferred.

- K. Carlberg, C. Bou-Mosleh, and C. Farhat. Efficient non-linear model reduction via a least-squares Petrov–Galerkin projection and compressive tensor approximations. *International Journal for Numerical Methods in Engineering*, 86(2):155–181, April 2011.
- [2] K. Carlberg, C. Farhat, J. Cortial, and D. Amsallem. The GNAT method for nonlinear model reduction: effective implementation and application to computational fluid dynamics and turbulent flows. *Journal of Computational Physics*, in press, doi:10.1016/j.jcp.2013.02.028, 2013.
- [3] R. Everson and L. Sirovich. Karhunen–Loève procedure for gappy data. *Journal of the Optical Society of America A*, 12(8):1657–1664, 1995.

### Challenges for mechanism reduction

#### William J. Pitz

#### Lawrence Livermore National Laboratory/Chemical Sciences Division, Livermore, USA

*Abstract*—Detailed chemical kinetic mechanisms are becoming increasingly complex. They are growing in the number species and reactions due to large size of components in practical fuels. They also are growing due to the need to develop surrogate fuel models that contain many fuel components. Additionally, these models have to reproduce complex chemical and physical behavior important for combustion in practical devices. These requirements represent severe challenges to mechanism reduction needed for CFD codes.

#### I. INTRODUCTION

Much progress has been made in mechanism reduction. It is now routine to reduce detailed chemical kinetic mechanisms for hydrocarbons (e.g. methane, propane, nheptane) that are valid for ignition from low to high temperatures [1].

However, detailed chemical kinetic mechanisms are becoming increasingly complex. The number species and reactions in mechanisms are growing because of the need to address components in practical fuels that have a large number of atoms. A recent chemical kinetic model for a series of n-alkanes and iso-alkanes from LLNL contains 7200 species and 31400 reactions [2]. They also are growing due to the requirements to develop mechanisms for not just a single fuel component, but multiple fuel components to represent practical fuels like gasoline and diesel fuels. In a recent publication on surrogate fuels for diesel, a 8-component surrogate fuel for diesel is proposed to simulate multiple characteristics of real diesel fuels including composition, ignition behavior, vaporization, and density [3]. The corresponding chemical kinetic mechanism for this surrogate will also be huge because of the large number of components and their large size having 9 - 21 carbon atoms each in each component. These mechanisms must to be severely reduced in size to accommodate the needs of computational fluid dynamic (CFD) codes in combustion.

#### II. COMPLEX BEHAVIOR TO BE SIMULATED

#### A. Complex chemical behavior of fuels

One of challenges of developing reduced mechanisms is ensuring that they can reproduce the complex chemical behavior of real fuels. The simulation of low temperature behavior is important because low temperature combustion controls ignition in diesel and homogeneous charge compression ignition (HCCI) engines. Fig. 1 shows the complex behavior of ignition delay in a rapid compression machine that simulates ignition at internal combustion (IC) engine conditions. The ignition delay increases as the temperature increases in the so-called negative temperature coefficient (NTC) region. It is essential for detailed and reduced models to simulate this behavior to accurately model ignition in engines.

The NTC behavior is also observed in species concentrations as the temperature is increased. Fig. 2 has experimental and computed results from the LLNL model [4] in a jet stirred reactor for stoichiometric mixtures of n-heptane. Reduced models for IC engine applications need to be able to reproduce this behavior to provide accurate predictions.



Fig. 1. Measured and computed ignition delay times for stoichiometric mixtures of methyl cyclohexane [5].



Fig. 2 Measured and computed fuel concentration for temperatures over the NTC region in a jet stirred reactor for stoichiometric n-heptane [6].

The capability to predict soot emissions from combustion devices is also essential. The formation of soot precursors is an important step in many soot models used in CFD engine simulation codes. Detailed and reduced mechanisms should be able to accurately simulate the formation and consumption of important soot precursors like benzene. Fig. 3 shows a comparison of the computed and measured benzene concentrations in a low-pressure flame using the LLNL methyl cyclohexane (MCH) mechanism [7].

Detailed and reduced models should reproduce the chemical behavior of target fuels that often contain hundreds of components. In the case of diesel fuel, Mueller et al. [3] proposed that components in the surrogate mixture model

should represent the molecular structure characteristics of 11 different carbon types and match their relative proportion in the target fuel as well has possible. In this case, this required the inclusion of 8 different fuel components that represented the chemical classes of n-alkanes, iso-alkanes, cycloalkanes, 1-ring aromatics, 2-ring aromatics, and naphtho-aromatics. The inclusion of all these fuel components makes the development of a highly reduced models challenging.

Biofuels present an additional challenge because they have further molecular structures that need to be included in detailed and reduced models. When they are mixed with conventional fuels, the models must include all the molecular structures required for hydrocarbons as well as that of the biofuel. Additionally, biofuels are often saturated (i.e. include double bonds). Three of the five types of methyl esters in most biodiesels have double bonds in the carbon chain, and these three components are present in the highest concentration [8]. These double bonds allow addition of radicals to the double bond, an additional reaction class to be included in the model. Also, the presence of double bonds in a carbon chain on a methyl ester allow the formation of resonantly stabilized radicals that are longlived and need to be additionally considered in detailed and reduced models.

#### B. Complex physical behavior of fuels

Not only does the chemical behavior of fuels need to be simulated, but physical behavior is well. In the case of fuel vaporization, additional fuel components should be included to model the distillation properties of the fuel. In a reacting fuel spray, low boiling point components will evaporate prior to high boiling point components. The lighter nalkanes that vaporize first ignite more slowly than the higher molecular components that vaporize readily at higher temperatures. To be able to include this effect in a surrogate fuel model, additional components in the same chemical class (e.g. n-alkanes) need to be included that span the boiling point range of fuel.



Fig. 3 Measured and computed benzene concentrations in a low pressure MCH flame for stoichiometric and rich mixtures [7].

#### **III.** DISCUSSION

To simulate the behavior real fuels, the chemical and physical behavior of the fuel must be taken into account. The molecular structures present in real fuels need to be included in the detailed and reduced models, and chemical behavior such as low temperature chemistry needs to be accurately represented. In order to predict soot emissions, the production and consumption of soot precursor species should be modeled accurately. In addition to the chemical properties, the surrogate mixture model should be able to simulate the physical properties such as the vaporization characteristics of the target fuel. This is particularly important for diesel and biodiesel fuels which contain high boiling point components so that some relatively low boiling point species will evaporate in a reacting spray before other higher boiling point compounds. Including all these fuel components and representing these complex behaviors in a reduced model is challenging. These reduced models are used in multidimensional CFD codes that have many submodels which compete for computer resources. The requirements of surrogate fuel models with more than 10 components means that the mechanisms must be highly reduced to limit the impact of the chemistry solver requirements on the overall reacting flow simulation. This severe reduction of the detailed models makes it difficult to simulate the complex chemical behavior of the real surrogate fuel. Currently, the reduced models for surrogate fuels with many components are partially reduced "by hand" rather than in a fully automatic way because of the severe reduction requirements. One of the challenges of mechanism reduction is to fully automate this reduction process.

#### ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

#### References

[1] T. F. Lu and C. K. Law, "Toward accommodating realistic fuel chemistry in large-scale computations," *Progress in Energy and Combustion Science* 35 (2) (2009) 192-215.

[2] S. M. Sarathy, C. K. Westbrook, M. Mehl, W. J. Pitz, C. Togbe, P. Dagaut, H. Wang, M. A. Oehlschlaeger, U. Niemann, K. Seshadri, P. S. Veloo, C. Ji, F. N. Egolfopoulos and T. Lu, "Comprehensive chemical kinetic modeling of the oxidation of 2-methylalkanes from C7 to C20," *Combust. Flame* 158 (12) (2011) 2338-2357.

[3] C. J. Mueller, W. J. Cannella, T. J. Bruno, B. Bunting, H. D. Dettman, J. A. Franz, M. L. Huber, M. Natarajan, W. J. Pitz, M. A. Ratcliff and K. Wright, "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," *Energy & Fuels* 26 (6) (2012) 3284–3303.

[4] W. J. Pitz, C. K. Westbrook, M. Mehl, H. J. Curran and S. M. Sarathy, "LLNL Chemical Kinetic Mechanisms," https://www-pls.llnl.gov/?url=science\_and\_technology-chemistry-combustion, 2013.

[5] B. W. Weber, W. J. Pitz, C. J. Sung, M. Mehl, E. J. Silke and A. C. Davis, "Experiments and Modeling of the Autoignition of Methyl-Cyclohexane at High Pressure," *8th Annual U.S. National Combustion Meeting*, Park City, Utah, 2013.

[6] O. Herbinet, B. Husson, Z. Serinyel, M. Cord, V. Warth, R. Fournet, P.-A. Glaude, B. Sirjean, F. Battin-Leclerc, Z. Wang, M. Xie, Z. Cheng and F. Qi, "Experimental and modeling investigation of the lowtemperature oxidation of n-heptane," *Combust. Flame* 159 (12) (2012) 3455-3471.

[7] W. J. Pitz, S. S. Skeen, M. Mehl, N. Hansen and E. J. Silke, "Chemical kinetic modeling of low pressure methylcyclohexane flames," *7th Annual U.S. National Combustion Meeting*, Park City, UT, 2013.

[8] C. K. Westbrook, C. V. Naik, O. Herbinet, W. J. Pitz, M. Mehl, S. M. Sarathy and H. J. Curran, "Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels," *Combust. Flame* 158 (4) (2011) 742-755.

# Fast solver techniques for algebraic equations resulting from the Quasi Steady State Approximation

#### Fabian Mauss\*

\*Brandenburg University of Technology / Thermodynamics and Thermal Process Engineering, Cottbus, Germany

#### I. INTRODUCTION

In this abstract we discuss strategies for efficient solving ordinary differential equations together with non-linear algebraic equations. This set of equations is typical for kinetic system for which a high number of quasi steady state species have been defined. There are two possible strategies which can be applied with regular chemistry solvers. 1) operater splitting methods, and 2) nested solver technolgies. For operator splitting techniques there is no high demand on the speed of the solver for the set of algebraic equations. Each timestep will be calculated faster compared to original problem, since the size of each problem is reduced, and the stiffness of the unsteady problem is reduced, since the timescales have been clearly seperated. However operator splitting techniques are not fully implicit, and a reduction of the timestep size is necessary. This decreases the performance of the reduced chemical mechanism. Nested solver strategies are fully implicit, and do not experience the problem of limited timestep sizes. However there is a high demand on the speed and accuarcy of the algebraic solver.

In most chemistry software implicit Newton solvers are applied. Just in the field of DNS explicit Runge Kutta solvers are found. For the latter the application of operator splitting method is the method of choice, since the explicit Runge Kutta solver will not experience further restrictions in time step size from the application of operator splitting methods. For Newton methods applied for the outer solver the inner solver for the set of algebraic equations will be called for each species once, during the build of the Jacobian matrix applied by the outer solver. There is further one call of the inner solver for each iteration step of the outer solver. Hence the calls of the inner solver are an order of magnitude higher than calls of the outer solver, which explains the high demand in speed on the inner solver. In addition a high accuracy of the inner solver is needed to calculate the Jacobian of the outer solver with the accuracy needed for convergence.

In the presentation we compare two solution methods with each other: 1) fixpoint iteration, and 2) a highly optimized Newton solver. The shortcoming of method 1) is that the convergence of the method is not guaranteed. In case of divergence other methods need to be applied to find a solution. One possibility is a random pertuabation of the initial guess, which is successful for most applications. The shortcoming of method 2) is the high CPU demand for the build of the inner solver. To reach a faster solution we developed a sparse matrix method, for which the sparsity is optimized by simply ordering the list of chemical species. We further use the fact, which the sparsity pattern of the Jacobian matrix is only dependent on the chemical species, which are chosen to be in steady state. This allows performing the Gaussian elimination in a preprocessing step, before starting the calculation of the physical problem. This behavior is independent on the complexity of the physical system. Beyond the huge speed up, that can be reached through chemical lumping, and species elimination, the QSSA resulted in a further 40% gain in CPU time. This advantage is of interest for many complex CFD applications. The accuracy of the resulting mechanism is very high. In the following this technique is further discussed. In the presentation we compare the different solution techniques with each other.

#### II. THE NUMERICAL METHOD

The numerical method for the system of DAE is a combination of two numerical methods, one for the system of ODE and one for the system of NAE, the latter representing the QSS species. The numerical method for the system of ODE is a predictor-corrector method, where the predictor is based on Gears backward differencing scheme and the corrector is a damped Newton method. The system of NAE is solved by a modified Newton method.

The Newton solver for the system of ODE (in the following called the outer solver), is iterated until convergence for each time step. An inner loop for the system of NAE (in the following called the inner solver) is iterated until convergence, for each evaluation of the chemical source terms. This solver is called several times while solving the system of DAE. The inner solver must be very accurate to allow an accurate prediction of the Jacobian, needed for the outer solver. In the past we tested fix point solver, since they are highly efficient. However, it was found that this solver combination was not robust. In this work a Newton solver is chosen as an inner solver. The computational cost of the Newton solver scales roughly as n square if the decomposed Jacobian is reused for many iteration steps. The inner Newton solver must be optimized for computational cost, to gain a speed up by the total procedure. The modifications of the inner Newton solver that lead to a total speed up of the solver combination are explained in the following sections.

1) The optimisation of the inner solver: A modified Newton solver was chosen as an inner solver because of the high accuracy demands on the solution from the NAE. This implies that a Jacobian matrix must be calculated followed by a Gaussian elimination. The back substitution and the update of the source-vector must be called at each iteration step of the inner solver. The CPU time of the inner solver can therefore be decreased considerably by optimizing the building of the Jacobian, the Gaussian elimination, the back substitution and the update of the source vector. The sparsity pattern of the Jacobian of the inner solver is constant in time, since the chemical reaction scheme is invariant. The values of the matrix elements depend on the concentrations of the non-steady state species. The constant sparsity pattern implies that all operations made on the Jacobian will involve the same matrix elements of the Jacobian. Hence, every operation involved in the entire Gaussian elimination and the back substitution can be automatically written as source code in a preprocessing step. A highly optimized sparse matrix solver is generated. Only the non-zero elements of the Jacobian are used in the Gaussian elimination and backsubstitution. The CPU-time needed for this solver is proportional to the number of operations in the automatically written source code. The sparsity pattern of the Jacobian, and thereby the number of operations in the inner solver, is strongly dependent on the order of the QSS species in the concentration vector. In order to find the optimum order of the QSS species vector, which corresponds to the minimum number of operations in the inner solver, the Metropolis algorithm is employed. The Metropolis algorithm accepts or declines the new QSS species vector, which is generated by a random shuffle of the QSS species order. The procedure is outlined as follows:

Initialize the concentration vector for the inner solver Initialize the fictive temperature  $\theta$ 

Repeat until terminating condition is fulfilled

- 1) Change the places of two randomly chosen species in the concentration vector.
- 2) Create new Jacobian and perform Gaussian elimination.
- Calculate the Sum Of Operations (SOP) in the Gaussian elimination and back substitution of the solver for the algebraic equations.
- 4) Calculate the SOP, based on the new and old concentration vector.
- 5) If the SOP is less than zero accept the new concentra-

tion vector. Otherwise accept the new concentrationvector with probability:

$$P\left(SOP,\theta\right) = exp\left(-\frac{SOP}{\theta}\right)$$

#### 6) Decrease $\theta$

The initial value of  $\theta$  and the function used in order to decrease  $\theta$  can be optimized for each case. In this work we used a predefined number of iterations as termination condition. The Metropolis algorithm allows leaving areas of local minima, and converging towards deeper local minima. With some probability it is accepting SOP i, 0. This algorithm does not guarantee that the global minimum is found, but in most cases a deep enough local minimum, corresponding to a very low number of operations in the inner solver, is found. Hence, the total CPU time needed for the integration of the system of DAE at high reduction levels will be reduced. It should be noted that the final value of SOP does not necessary correspond to the deepest minima. For this reason, the QSS concentration vector which corresponds to the deepest minima during the entire optimization procedure is saved instead in this work. The optimized Jabian matrix results in 317 non-zero elements after Gaussian elimination, while the original matrix resulted in 452 non-zero elements. We also calculated the worst sorting for the steady state species, which resulted in 923 non-zero elements. This is a factor 3 larger, than the optimum sorting. In Figure 1 we show the calculated speed up of the program as a function of the number of QSS species. The maximum speed up is 40% at 52 steady state species, this is about half of the total number of species. Considering a quadratic decrease of the CPU time with the number of species, a 75% speed up would have been expected. However, this would assume that the steady state species solver works at no CPU cost.



Fig. 1. Normalized CPU time as a function of the number of QSS species. The figure shows the reference case T = 900 K,  $\phi = 1.0$ , p = 40 bar.

### A Tangential Stretching Rate Index to analyze Ignition Phenomena

M. Valorani<sup>\*</sup>, S. Paolucci<sup>†</sup>, E. Martelli<sup>‡</sup>, T. Grenga<sup>†</sup> \*Sapienza University of Rome, Rome, Italy <sup>†</sup>University of Notre Dame, South Bend, Indiana <sup>‡</sup>Second University of Naples, Caserta, Italy

*Abstract*—We introduce an index to analyze numerical datasets simulating ignition in reactive systems. The index is obtained by combining the concepts of stretching rate in dynamical systems with the CSP method, and is validated with reference to a planar model of branched-chain reactions and to a test case involving hydro-carbon oxidation kinetics.

#### I. INTRODUCTION

Ignition of hydrocarbon fuels is controlled by branched chain-reactions and its complexities increase with the length/size of the fuel molecule. A time scale analysis of auto-ignition in spatially homogeneous systems, carried out by either the Computational Singular Perturbation (CSP) Method [1], [2] or Chemical Explosive Mode Analysis (CEMA) [3], pointed out that a distinguishing feature of the explosive behavior is the the emergence of positive eigenvalues during both chain-branching and thermal ignition. To explore details of ignition with the simplest possible model, we consider a planar (2D) model: an isothermal branched-chain explosion model proposed by Williams. We analyzed Williams' model by means of (i) the local tangential stretching rate (TSR) [4], and (ii) a normalized index measuring the relative contribution of each mode to TSR. We first present the theory for the TSR and its validation with reference to Williams' model and the propane/air system.

#### **II. TANGENTIAL STRETCHING RATE: THEORY**

The point dynamics of a chemical kinetic system is described by a set of ODEs  $\frac{d\mathbf{z}}{dt} = \mathbf{g}(\mathbf{z}), \ \mathbf{z}(0) = \mathbf{z}_0, \ \mathbf{z} \in \mathbb{R}^N$ . The state vector  $\mathbf{z}$  stands for the species concentration vector,  $\mathbf{g}(\mathbf{z}) = S\mathbf{r}(\mathbf{z})$  the species reaction rate vector, S the stoichiometric coefficients matrix,  $\mathbf{r}(\mathbf{z})$  the net reaction rates vector, and  $\mathbf{z}_0$  the initial concentrations vector. Consider a scaled measure  $\mathbf{v}(t)$  of the difference between two trajectories emanating from two nearby initial conditions,  $\mathbf{z}_1$ , and  $\mathbf{z}_2$ . The vector dynamics of  $\mathbf{v}(t) := \lim_{|\mathbf{\varepsilon}| \to \mathbf{0}} (\mathbf{z}_2(t) - \mathbf{z}_1(t))/|\mathbf{\varepsilon}|$ , is described by the set of ODEs:

$$\frac{d\mathbf{v}}{dt} = J_{\mathbf{g}}(\mathbf{z})\,\mathbf{v}, \qquad \mathbf{v}(0) = \mathbf{1},\tag{1}$$

where  $J_{\mathbf{g}} := \partial \mathbf{g}(\mathbf{z}) / \partial \mathbf{z}$  is the Jacobian matrix of  $\mathbf{g}$ , and  $\mathbf{1}$  is a unit vector at  $\mathbf{z}_0$  taken along any direction. The time

evolution of the norm  $v = \sqrt{\mathbf{v}^T \cdot \mathbf{v}}$  obeys the ODE:

$$\frac{dv}{dt} = \left(\frac{\mathbf{v}^T \cdot J_{\mathbf{g}} \cdot \mathbf{v}}{v^2}\right) v, \qquad v(0) = 1.$$
(2)

The rate at which v grows/shrinks is governed by the (local) rate of stretching of the dynamics,  $\omega_{\tilde{\mathbf{u}}}$ , evaluated along the direction identified by the unit vector  $\tilde{\mathbf{u}} := \mathbf{v}/v$  and defined as:

$$\omega_{\tilde{\mathbf{u}}} := \tilde{\mathbf{u}}^T \cdot J_{\mathbf{g}} \cdot \tilde{\mathbf{u}}. \tag{3}$$

We introduced the TSR by setting  $\tilde{\tau} := \mathbf{g}/\mathbf{g}$ , with  $\mathbf{g} = |\mathbf{g}|$ , and N-1 normal stretching rates. Defining the unit normal vector as  $\tilde{\mathbf{n}}(\mathbf{z}) = {\tilde{\tau}_2(\mathbf{z}), -\tilde{\tau}_1(\mathbf{z})}$ , we have

$$\omega_{\tilde{\tau}} := \tilde{\boldsymbol{\tau}}^T \cdot J_{\mathbf{g}} \cdot \tilde{\boldsymbol{\tau}}, \qquad \omega_{\tilde{\mathbf{n}}} := \tilde{\mathbf{n}}^T \cdot J_{\mathbf{g}} \cdot \tilde{\mathbf{n}}.$$
(4)

Now:  $J_{\mathbf{g}} = A\Lambda B$ , with left and right normalized eigenvector matrices  $A = \{\mathbf{a}_j\}_{j=1,N}$  and  $B = \{\mathbf{b}^i\}_{i=1,N}$ , and eigenvalue matrix  $\Lambda = \{\lambda_j^i\}_{i,j=1,N}$ . The unit vector  $\tilde{\tau}$  can be rewritten after projecting the vector field over the right eigenvector basis as  $\tilde{\tau} = \frac{\mathbf{g}}{\mathbf{g}} = \frac{1}{\mathbf{g}} \sum_{i=1}^{N} \mathbf{a}_i f^i$ , with  $f^i := \mathbf{b}^i \cdot \mathbf{g}$ , and  $\mathbf{g} = \sum_{i=1}^{N} \mathbf{a}_i f^i$ . We now have

$$\omega_{\tilde{\tau}} = \tilde{\tau}^T \cdot J_{\mathbf{g}} \cdot \tilde{\tau} = \frac{1}{g^2} \left( \mathbf{g}^T A \Lambda B \, \mathbf{g} \right) = \frac{\mathbf{g}^T}{g^2} \sum_{i=1}^N \mathbf{a}_i \lambda_i \left( \mathbf{b}^i \cdot \mathbf{g} \right)$$
$$= \frac{\mathbf{g}^T}{g^2} \sum_{i=1}^N \mathbf{a}_i \lambda_i f^i = \frac{1}{g^2} \sum_{i=1}^N \left( \mathbf{g}^T \cdot \mathbf{a}_i \right) \lambda_i f^i = \sum_{i=1}^N W_i \, \lambda_i,$$
(5)

where  $\omega_{\tilde{\tau}}$  is the weighted average of the eigenvalues with weights that depend on the normalized mode amplitudes and on the degree of co-linearity of the eigenvectors  $\mathbf{a}_i$  with respect to the vector field  $\mathbf{g}$ .

#### III. TEST CASES

#### A. Williams' Model

Williams' model [5] consists of a system of three irreversible isothermal branched-chain reactions:  $R \rightarrow C$  (init),  $R+C \rightarrow \alpha C+P$  (prop),  $C \rightarrow P$  (term), where R=reactants, C=intermediates, P=products. After normalization, the evolution of R (x<sub>1</sub>) and P (x<sub>2</sub>) is described by:

$$\mathbf{x}_1' = -\mathbf{x}_1 - \mathbf{x}_1 \mathbf{x}_2$$



Fig. 1. Williams' model:  $\tilde{\omega}_{\tilde{\tau}}$  (brown),  $\tilde{\omega}_{\tilde{\mathbf{n}}}$  (green) and the real part of eigenvalues  $\lambda_1$  (red),  $\lambda_2$  (blue).

$$\epsilon x_2' = \mathbf{x}_1 + (\alpha - 1)\mathbf{x}_1\mathbf{x}_2 - \gamma \mathbf{x}_2,$$
  
$$\gamma x_3' = \gamma \mathbf{x}_2 + \mathbf{x}_1\mathbf{x}_2,$$
  
$$(\mathbf{x}_1(0), \mathbf{x}_2(0), \mathbf{x}_3(0)) = (1, 0, 0).$$

Figure 1 compares the evolution of the tangential (brown) and normal (green) stretching rates with respect to variations of the real parts of the eigenvalues. We observe that  $\omega_{\tilde{\tau}}$ follows the fast eigenvalue (positive (blue) in the first phase, negative (red) in the last phase) up to time t = 0.2. In the interval t = 0.2–0.45, the two stretching rates switch between the eigenvalues, so that after t = 0.45,  $\omega_{\tilde{\tau}}$  follows the slow eigenvalue (blue). The opposite trend is followed by the normal rate. The striking finding is that  $\omega_{\tilde{\tau}}$  undergoes a smooth transition from the fast to the slow scale occurring in the time range t = 0.2 - 0.4. and in so doing it tracks the controlling time scale at all times, independently of any user-defined error threshold.

#### B. Propane/Air Curran Mechanism

We analyze (Fig. 2) the branched-chain/thermal, adiabatic isochoric, auto-ignition of propane/air oxidation (Curran mechanism [6]) with the TSR, for initial conditions p=1 atm, T=1000K, and a stoichiometric mixture. After a short transient,  $\omega_{\tilde{\tau}}$  becomes coincident with  $\lambda_{a+}$ ; a bit sooner than the merging of the two positive eigenvalue,  $\omega_{\tilde{\tau}}$ departs from  $\lambda_{a+}$ . In fact,  $\omega_{\tilde{\tau}}$  begins to sense the "most energetic" dissipative scales until equilibrium, when it becomes coincident with one particular negative eigenvalue. Next, we define a Participation Index of the *i*-th mode to the TSR as:  $P_i^{\omega_{\tilde{\tau}}} = W_i |\lambda_i| / \sum_{j=1}^N |W_j| \lambda_i ||$ . Modes with a large  $P_i^{\omega_{\tilde{\tau}}}$  contribute the most to the development of the most energy containing time scale and form the active sub-space. Figure 3 shows the modes mostly contributing to the active sub-space for the propane/air mechanism  $(P_i^{\omega_{\tilde{\tau}}} > 10^{-2})$ . It can be noted that at sample #170 of Fig. 2, only two modes (one with an eigenvalue with negative real part and the other with an eigenvalue with positive real part), are above the selected tolerance. We can also apply the CSP criterion [7] to find the number of exhausted modes M.



Fig. 2. TSR analysis for propane; eigenvalues with positive real parts (black ); first non-exhausted mode (blue);  $\omega_{\tilde{\tau}}$  (red), modes in active subspace (green).



Fig. 3. Participation Index and first non-exhausted mode for different tolerances for sample #170 (see Fig. 2).

The picture shows that, the modes just slower than the first non-exhausted mode, M+1, do not contribute much to  $\omega_{\tilde{\tau}}$ .

#### **IV. CONCLUSIONS**

The Tangential Stretching Rate concept is a proper characteristic chemical time scale. It is the most relevant during both the explosive and relaxation regimes, is intrinsic to the dynamics, and, as such, it can be identified without the need of ad-hoc assumptions.

- [1] Kazakov, et al., J. Phys. Chem. A (2006), 110 (21), 7003-7009.
- [2] D. Diamantis, D. Kyritsis, and D.A. Goussis, (2009) 2<sup>nd</sup> Int. Workshop on Model Reduction in Reacting Flows, Notre Dame.
- [3] R. Shan, C. S. Yoo, J. H. Chen, T.Lu, Combustion and Flame 159 (2012) 31193127
- [4] A. Adrover, et al., J.Comput. Phys. (2007), 225 (2), 1442-1471.
- [5] F.A. Williams, Combustion Theory, 2<sup>nd</sup> edn, pp. 570-573.
- [6] H. Curran, et al., Combust. Flame, 114 (1998), 149-177.
- [7] M. Valorani, H. N. Najm, D.A. Goussis , Combust. Flame, 134 (2003), 35–53.

# Reduced Basis Model Reduction for Nonlinear Evolution Equations based on Empirical Operator Interpolation

Martin Drohmann<sup>\*</sup>, Bernard Haasdonk<sup>†</sup>, Mario Ohlberger <sup>‡</sup> \*Sandia National Laboratories, Livermore, CA, USA <sup>†</sup>Institute for Applied Analysis and Numerical Simulation, Stuttgart, Germany <sup>‡</sup>Institute for Computational and Applied Mathematics, Münster, Germany

*Abstract*— Many important problems from chemistry, physics or biology are modeled by nonlinear partial differential equations. Often, e.g. in the context of inverse problems, optimization or uncertainty quantification, the numerical models need to be evaluated for many different parameter values. As numerical simulations consume a huge amount of computational power, *many-query* applications are still infeasible to deal with.

The reduced basis can be a remedy for such situations. It features an automatic procedure to generate projection based reduced order models equipped with reliable error bounds, which are efficiently computable. The latter allows to control the accuracy to an extent that matches the reliability of the underlying high dimensional discretization.

In this presentation, we present a variant of this method that can be applied to a variety of nonlinear evolution equations. Numerical examples are provided for various partial differential equations from the field of computational fluid dynamics.

#### I. INTRODUCTION

The reduced basis method is a means to deal with *many-query* or *real-time* applications based on simulations of partial differential equations. The idea is to let the experimenter choose a parametrization of the problem that restricts the manifold of possible solutions S to those that are "interesting" to the application. Then, the essential characteristics of this manifold can be extracted as basis functions of a low dimensional *reduced basis space*. The generating algorithms depend on few solutions of a high-dimensional model, but give rise to efficient and still reliable reduced models. Reference [4] provides a good overview of the machinery with a focus on linear problems.

For nonlinear problems, it is not sufficient to approximate the solution manifold S by a linear space. Supplementary, the nonlinear behaviour of the system needs to be "learnt" and approximated by the so-called *empirical operator interpolation* method.

In this presentation, we want to focus on nonlinear parametrized evolution equations of the form

$$\partial_t u(\boldsymbol{\mu}; t) + \mathcal{L}(\boldsymbol{\mu}) u(\boldsymbol{\mu}; t) = 0, \qquad u(\boldsymbol{\mu}; 0) = u_0(\boldsymbol{\mu}) \quad (1)$$

TABLE I
EXEMPLARY RUN-TIME COMPARISON.

Ν	М	ø-run-time[s]	max. error	offline time[h]
H = 7200	_	90.01	0.00	0
42	72	4.44	$1.73 \cdot 10^{-3}$	0.54
83	144	6.04	$5.74 \cdot 10^{-5}$	1.09
125	216	8.37	$7.30 \cdot 10^{-6}$	1.55
167	288	11.92	$7.63 \cdot 10^{-7}$	2.08
208	360	15.08	$2.31 \cdot 10^{-7}$	2.69
233	402	16.48	$1.55 \cdot 10^{-7}$	3.27

defined on a regular domain  $\Omega$ , and supplemented with adequate boundary conditions. Here,  $\mu$  denotes a vector of parameters, controlling e.g. material constants, the domain geometry, boundary or initial conditions. For the numerical model, we want to focus on finite volume discretizations by an Euler scheme of the form

$$\left(\mathrm{Id} + \Delta t \mathcal{L}_{h}^{I}(\boldsymbol{\mu})\right) u_{h}^{k+1}(\boldsymbol{\mu}) = \left(\mathrm{Id} - \Delta t \mathcal{L}_{h}^{E}(\boldsymbol{\mu})\right) u_{h}^{k}(\boldsymbol{\mu}),$$
(2)

where the operator  $\mathcal{L}$  is decomposed into implicit and explicit computations. After the generation of a suitable reduced basis and empirical interpolants for the operators, all parameter independent parts can be reduced by a projection onto the reduced basis space. This allows to compute (2) with low computational complexity.

Table I shows time gains and accuracy results from one of our experiments with a nonlinear diffusion problem. Compared to the high dimensional problem, the time gain factor is in the range of 8-20 depending on the size of reduced basis N and the number of interpolation points M.

In the following, we want to dwell shortly into the concepts of basis construction, empirical operator interpolation and a posteriori error estimation.

#### **II. GREEDY BASIS CONSTRUCTION**

If the experimenter defines the parameter vector  $\mu$  and can choose very tight constraints on the possible set of vectors  $\mathcal{M}$ , he gets a rather small response surface of interesting solutions  $S := \{u_h(\mu) | \mu \in \mathcal{M}\}$ . Then, we can assume that a low-dimensional reduced basis exists spanning a linear space that (almost) comprises this manifold.

The theoretical measure for the suitability of the manifold S is given by the Kolmogorov N-width of this manifold.

$$d_N(\mathcal{S}) := \inf_{\substack{\mathcal{V} \\ \dim(\mathcal{V})=N}} \sup_{v_h \in \mathcal{S}} \min_{u_h \in \mathcal{V}} \|v_h - u_h\|_{\mathcal{W}_h}.$$
 (3)

Though not explicitly computable, [3] made the following observation: If the Kolmogorov N-width converges to zero with growing N at polynomial or exponential speed, we can construct sequences of reduced basis spaces that follow this convergence. This is achieved by iterative extension with a "greedy" algorithm: Given a reduced basis space of dimension N, a new basis vector can be defined by

$$\phi_{N+1} = \arg\min_{u_h(\boldsymbol{\mu}) \in \mathcal{S}} \left\| u_h(\boldsymbol{\mu}) - u_{\text{red}}(\boldsymbol{\mu}) \right\|, \qquad (4)$$

where the reduced solutions  $u_{red}(\mu)$  are computed with a low-dimensional reduced basis version of (2). Instead of computing the true error, however, we want to use a posteriori error estimates that can be efficiently computed. This allows to search the manifold S for a larger set of new potential reduced basis functions.

#### **III. EMPIRICAL OPERATOR INTERPOLATION**

The concept applied here, is based on the empirical interpolation method (EIM) [2]. The method empirically learns about interpolation points and ansatz functions for the solutions of interest. This gives rise to interpolations

$$\mathcal{I}_M[\mathcal{L}_h]v_h = (\mathcal{L}_h v_h) |_{X_M} \Xi_M^t \approx \mathcal{L}_h v_h.$$
(5)

Here  $\Xi_M$  denotes a matrix of interpolation ansatz functions, and  $(v)_{X_M}$  refers to the vector of function evaluations  $(v(x_1), \ldots, v(x_M))$  at interpolation points  $X_M := \{x_1, \ldots, x_M\}$ . In order to efficiently compute the operator evaluations at these interpolation points, the operator needs to fulfill some sparsity properties. This, however, is usually true for numerical schemes.

#### IV. A POSTERIORI ERROR ESTIMATES

From our discussion about the greedy algorithms to construct the reduced basis space, it follows that efficiently computable error estimates are crucial ingredients for reduced basis methods. In this presentation, we obtain bounds  $\eta_{N,M,M'}^k(\boldsymbol{\mu})$ , such that

$$\left\|u_{h}^{k}(\boldsymbol{\mu}) - u_{\text{red}}^{k}(\boldsymbol{\mu})\right\| \leq \eta_{N,M,M'}^{k}(\boldsymbol{\mu}).$$
(6)

The subscripts of the error refer to the dimension N of the reduced basis space, the number of interpolation points M, and a further parameter M' controlling the accuracy of the computed error induced by the empirical operator interpolation.

Figure 1 shows convergence results of a greedy algorithm with different a posteriori error estimates, proving their suitability for this problem.



Fig. 1. Comparison of estimated error decrease during basis generation with basis generation algorithm. Different error indicators are used in order to select the worst approximated trajectories.

#### ACKNOWLEDGMENT

The first author is supported by Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

- M. Drohmann, B. Haasdonk, and M. Ohlberger. Reduced basis approximation for nonlinear parametrized evolution equations based on empirical operator interpolation. *SIAM J. Sci Comp*, 34:A937– A969, 2012.
- [2] M. Barrault, Y. Maday, N.C. Nguyen, and A.T. Patera. An 'empirical interpolation' method: application to efficient reduced-basis discretization of partial differential equations. C. R. Math. Acad. Sci. Paris Series I, 339:667–672, 2004.
- [3] P. Binev, A. Cohen, W. Dahmen, R. DeVore, G. Petrova, and P. Wojtaszczyk. Convergence rates for greedy algorithms in reduced basis methods. *SIAM J. Math. Anal.*, 43(3):1457–1472, 2011.
- [4] A.T. Patera and G. Rozza. Reduced Basis Approximation and a Posteriori Error Estimation for Parametrized Partial Differential Equations. MIT, 2007. Version 1.0, Copyright MIT 2006-2007, to appear in (tentative rubric) MIT Pappalardo Graduate Monographs in Mechanical Engineering.

### Challenges of Reduction for Open Systems

Joseph M. Powers\*, Joshua D. Mengers<sup>†</sup>

\*University of Notre Dame, Department of Aerospace and Mechanical Engineering, Notre Dame, Indiana, USA <sup>†</sup>US Department of Energy, Geothermal Technologies Office, Washington, DC, USA

*Abstract*—Open spatially homogeneous reactive systems may possess multiple physical equilibria and display limit cycle behavior. It is demonstrated for two systems, i) a simple Gray-Scott model, and ii) a detailed hydrogen-air model, that the existence of multiple physical equilibria and limit cycles introduces challenges for the use of manifold methods as a reduction technique. In particular, detailed understanding of boundaries of basins of attraction is likely required in order for any reduction to maintain fidelity to the full model.

#### I. INTRODUCTION

It is well known that open spatially homogeneous reactive systems may possess multiple physical equilbria and exhibit limit cycle behavior. Any stable physical equilbria, as well as any stable limit cycle, will also possess a basin of attraction, whose boundaries are difficult to discern without fully exploring a multi-dimensional phase space. It is also the case that many reduction methods rely upon projecting an arbitrary point in phase space onto a lower dimension manifold. One common method for identifying such manifolds which are one-dimensional is to connect equilbria with heteroclinic orbits and examine their ability to attract nearby orbits via calculation of normal stretching rates [1]. Those that are attractive are known as Slow Invariant Manifolds (SIMs). However, it must be recognized that naïve projection, uninformed by knowledge of the basins of attraction, from an arbitrary point onto a lower dimensional manifold runs the risk of projecting onto the wrong manifold. For cases in which there are multiple candidate SIMs, even less is clear, including how to define a basin of attraction for a SIM.

In this study, we summarize two such cases whose full exposition, including literature review, model equations, and numerical parameter values, is given by Mengers [2]. Those two cases are i) a simple Gray-Scott model, widely used to study pattern formation dynamics, and ii) a detailed kinetics model for hydrogen-air combustion.

#### II. GRAY-SCOTT

The Gray-Scott model has two irreversible reactions in three species, U, V, and P:  $U + 2V \rightarrow 3V$ ,  $V \rightarrow P$ . The spatially homogenous version is

$$\frac{dY_U}{dt} = -Y_U Y_V^2 + \mathsf{F}(1 - Y_U), \tag{1}$$

$$\frac{dY_V}{dt} = Y_U Y_V^2 - (\mathsf{F} + \mathsf{k}) Y_V.$$
(2)

Here Y represents mass fraction, t time, with F > 0 and k > 0 as parameters. One real finite root,  $R_1 : (Y_U, Y_V) = (1,0)$ , is guaranteed to be a sink. The character of the other two roots depends on F and k. When  $F = 9.16 \times 10^{-3}$  and  $k = 3.1 \times 10^{-2}$ , three real positive finite roots,  $R_1$ ,  $R_2$ , and  $R_3$ , are found, plotted in Fig. 1a.



Fig. 1. Naïve projection onto a reduced manifold in the Gray-Scott system

The sink at  $R_1$  has heteroclinic connections with the saddle at  $R_2$  as well as the point at infinity at  $I_2$ . There is also a spiral source at  $R_3$ . Surrounding  $R_3$  is an invariant manifold comprising a stable limit cycle, whose basin of attraction is shaded. Figure 1a depicts an initial condition within the basin of attraction of the limit cycle, denoted with a "+." Many reduction algorithms would project this point onto the manifold emanating from  $I_2$ , which leads ultimately to  $R_1$ . This induces large error, as the actual trajectory is led to the limit cycle surrounding  $R_3$ . Figure 1b depicts the evolution of  $Y_U$  and  $Y_V$  from "+" for its actual limit cycle behavior and that obtained upon naïve projection to the wrong reduced manifold.

#### III. HYDROGEN-AIR

We next employ a 9 species, 20 reaction hydrogen-air mechanism with a species ordering of  $\{O_2, H_2, H_2O, N_2, OH, H, O, HO_2, H_2O_2\}$  in an isothermal, isochoric simulation of combustion with fresh mixture inflow balanced by exhaust. The system has 3 algebraic constraints; therefore, we can confine attention to species  $i = \{1, 2, 3, 5, 6, 7\}$ . We identify 97 real finite equilibria. Of these, 3 have positive concentrations for all 9 species, making them physical, and 13 have one positive eigenvalue, making them candidates for connection to the physical roots. For the physical equilibria,  $R_4$  has all negative real eigenvalues and thus is a sink;  $R_{69}$  has one positive real eigenvalue, making it a candidate for connecting to other equilibria; and  $R_1$  has four negative real eigenvalues and one complex conjugate pair of eigenvalues with positive real part, making it a saddle. The long time dynamics of systems with initial conditions in the neighborhood of  $R_1$  exhibit limit cycle behavior.

We integrate with initial conditions perturbed along  $R_{69}$ 's unstable eigenvector in either direction. In one direction, the trajectory approaches  $R_4$  along its slowest eigenvector; this is a branch of the SIM. In the other direction, the trajectory collapses onto the limit cycle. These trajectories are shown in a projection of phase space in Fig. 2. Here  $z_i$  is the specific mole number of species *i*.



Fig. 2. The limit cycle and a SIM branch in the hydrogen-air mechanism.

Two time evolutions are shown in Fig. 3, where from nearly identical initial conditions, the top and bottom display relaxation to  $R_4$  and the stable limit cycle, respectively. Thus,  $R_{69}$  lies on the boundary of the basin of attraction between the limit cycle and  $R_4$ . We can identify other branches of the SIM by examining the heteroclinic orbits from other candidate equilibria. We find four additional branches, emanating from  $R_9$ ,  $R_{17}$ ,  $R_{30}$ , and  $R_{53}$ , respectively. A projection of these branches' approach to the physical equilibrium sink,  $R_4$ , is shown in Fig. 4. To evaluate the attractiveness of these branches, we calculate the normal stretching ratio along each manifold. We find that all five normal stretching ratios remain negative along the entire length of both the  $R_{69}$  and  $R_{53}$  branches. Thus, both are candidates for a SIM, rendering it also useful to construct a basin of attraction for each, not done here. We find there are positive stretching ratios in multiple normal directions for a large portion of the branches near  $R_9$ ,  $R_{17}$ , and  $R_{30}$ . This indicates nearby trajectories may diverge, an undesirable trait for a reduction.

#### IV. CONCLUSION

These results raise concerns about the heteroclinic orbit SIM construction technique for open systems in the absence



Fig. 3. Evolutions of hydrogen-air system from near  $R_{69}$ .



Fig. 4. Multiple branches of the SIM in the hydrogen-air mechanism.

of knowledge about the basins of attraction, which are difficult to obtain in practice.

#### **ACKNOWLEDGMENTS**

The study was originally supported by the National Science Foundation under Grant No. CBET-0650843; partial support was also received in the form of a fellowship from the University of Notre Dame's Department of Applied and Computational Mathematics and Statistics.

- A. Adrover, F. Creta, M. Giona, and M. Valorani, "Stretching-based diagnostics and reduction of chemical kinetic models with diffusion," *Journal of Computational Physics* 225(2): 1442-1471.
- [2] J. D. Mengers, 2012, "Slow invariant manifolds for reaction-diffusion systems," Ph.D. dissertation, University of Notre Dame.

# Analysis of transient processes in the context of REDIM

Ulrich Maas<sup>\*</sup>, Viatcheslav Bykov<sup>\*</sup>, Alexander Neagos<sup>\*</sup>

\* Karlsruher Institut für Technologie (KIT) / Institut für Technische Thermodynamik, Karlsruhe, Germany

Abstract— The method of reaction-diffusion manifolds (REDIM) has been shown to be a very efficient model reduction tool for reacting flows. The method is based on attracting low-dimensional manifolds defined in the composition space of a reacting flow system. The reduced kinetic mechanism is constructed as a table of a slow manifold mesh in the system composition space. This work discusses the ability of the method to describe transient behavior of a combustion system. In order to access this property of the reduced model two types of system dynamics are investigated with respect to the tangential and normal subspaces of the system slow manifold. This is accomplished by a local analysis of the eigenvalues of the chemical source term (projecting the Jacobian onto the tangential and normal subspace of the manifold) and by comparison of the detailed and reduced system behavior. Counter-flow diffusion flames of nitrogendiluted Hydrogen-Air are used to illustrate the results.

#### I. INTRODUCTION

In order to fully describe reacting flows mathematically a set of conservation equations for the  $(n = n_s + 2)$ -dimensional state vector  $\psi = (h, p, w_1 / M_1, ..., w_{n_s} / M_{n_s})$  has to be considered [1]. However, accurate models of chemical kinetics become not treatable in a reasonable time even by up to date soft- and hardware facilities due to the models complexity. Thus, the interest in automatic approaches that reduce the dimension and complexity of the system without quantitative loss of the accuracy has increased over the last decade. The assumption about the existence of so-called attractive low dimensional manifolds takes a central role in developing modern model reduction schemes [2-7].

The method of reaction-diffusion manifolds (REDIM) [7-11] is one of such approaches that allow us both to obtain a simplified description (model) of the chemical kinetics and to account for the influence of the molecular transport onto the reduced model. Similarly to other approaches, the main idea behind the REDIM is that the states of the detailed systems solution profiles  $\psi = \psi(x,t)$  during the transient motion of the system are completely confined to a  $low(m_s)$ dimensional subset of the state space. Thus, to describe the transient evolution, whenever the subset is known, less parameters would be needed -  $m_s << n$ . The manifold accounts for the fact that the reacting system states are tend to the states in the composition space where the fastest chemical processes are relaxed (similar to the main assumption of the ILDM method [2, 7]), moderate ones are strongly coupled with the transport, while relatively slow

chemical processes are governed by strong molecular transport processes [8].

It has been shown in previous works that the REDIM approach is able to represent stationary solutions of 1D laminar and turbulent flames [8-11]. This work represents a discussion of properties of the method which describe its ability to capture transient motions such as extinction or reignition [11].

#### II. REDIM

The method is searching for an approximate of an invariant manifold of relatively slow system motions  $M = \{\psi = \psi(\theta), \theta \in R^{m_s}\}$ . Here  $\theta$  is a parameterization of the manifold. An approximation to the invariant manifold is obtained as the stationary solution of a multi-dimensional parabolic system of partial differential equations [7]. In this way the system itself adapts to the states which optimally suits to capture the above mentioned structure of the decomposition of motions. In order to make use of it, the REDIM is tabulated in the form  $\psi = \psi(\theta)$ . Solving the conservation equations for the parameters  $\theta$  yields the time dependent states within the manifold [7, 10, 11].

#### III. ANALYSIS

In order to verify the REDIM method and to address the transient system behavior a state space analysis of a 1D counter-flow diffusion flame has to be considered at first. Then, after a local analysis of the systems source term a comparison of the stationary and non-stationary system solution profiles of the detailed and reduced systems is carried out.

#### A. Tangential motions

The invariance condition of the REDIM postulates that the dynamics of the detailed system will at any time be tangential to the REDIM. However, if the system solution profile is perturbed and the system states leave the manifold it has to be addressed for a secure use of the reduced model. In this case the time scales of physical transport coupled with the time scales of chemical reaction lie beyond the band width of time scales covered by the two parameters  $\theta$ . Suppose that there is a detailed stationary solution attached to the REDIM. In case of strong perturbations the transport processes will cause the detailed profile to leave the REDIM while moving to another stationary state where it is attached again to the REDIM. If the perturbations are strong enough



Fig 1. Contour lines represent real parts of the eigenvalues of the Jacobian of the transformed reaction source term of the system calculated on the 2D REDIM (all projections are in specific mole numbers). The transient solution of the detailed system is shown by black lines, solutions of the reduced model are white lines shown on the 2D REDIM, the red line shows a perturbed initial solution [11].

they can lead to extinction (or to another quasi-stable regime).

The question is how accurately the REDIM can capture the tangential part (i.e. the projection onto the tangential subspace) of these transient motions as well as the conditions which lead to extinction. In order to investigate the stability properties of the reduced model the local Jacobian  $\frac{\partial F}{\partial \Psi}$  of the chemical source term is reformulated in terms of a basis of the composition space containing the vectors  $\Psi_{\theta}$  [11]. The magnitude of the eigenvalues of the transformed Jacobian gives information about the transient behavior (see Fig. 1 (a), (b)).

#### B. Motions normal to the manifold

The attractiveness of the REDIM is justified by the decoupling of the fast chemical processes. It is assumed that whatever perturbations are the system relaxes fast towards M and the balance between diffusion and reaction is established. To confirm this assumption the local Jacobian of the chemical source term is reformulated in terms of a basis of the composition space containing the vectors  $\Psi_{\theta}^{\perp}$  where the vector  $\Psi_{\theta}^{\perp}$  is transversal to the tangential subspace of the manifold. As illustrated by the contour plot in Fig. 1 (c), where the real parts of the smallest in magnitude eigenvalue is shown, the eigenvalues of the transformed Jacobian are strictly negative and large in magnitude. Therefore, if perturbations cause the profile to leave the REDIM, the chemical processes will force the profile to move back onto the manifold. The relaxation time can be roughly estimated by the smallest eigenvalue of the projected source term.

#### **IV. CONCLUSIONS**

The ability to describe the transient (non-stationary) behavior of a reacting flow system by the REDIM method of model reduction was discussed. By analyzing the eigenvalues of the reformulated local Jacobian of the chemical source term in terms of a new basis of the tangential bundle it could be shown that the REDIM can capture both stable and unstable chemical modes that are coupled to the transport. Moreover, it could be shown, that strong negative eigenvalues of the Jacobian in terms of a basis containing vectors transversal to the tangential subspace substantiate the invariance assumption. It was shown how this procedure can be used to prove that the REDIM adequately captures the decomposition and the coupling of physical transport with chemical reaction for the case of transient dynamics.

#### ACKNOWLEDGMENT

Funding by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

#### References

- J. Warnatz, U. Maas and R.W. Dibble, *Combustion*, 4th ed. Springer-Verlag, New York, 2006.
- [2] U. Maas, S. B. Pope, "Simplifying chemical kinetics: Intrinsic lowdimensional manifolds in composition space", *Comb. Flame*, 88, pp. 239, 1992.
- [3] S.H. Lam, D. M. Goussis, "The CSP method for simplifying kinetics", *International Journal of Chemical Kinetics*, 26, pp. 461, 1994.
- [4] J.A. van Oijen, L.P.H. de Goey "Modeling of premixed laminar flames using the flamelet generated manifold method", *Combustion Science and Technology*, 161, pp.113, 2000.
- [5] T. Løvås "Model Reduction Techniques for Chemical Mechanisms" in *Chemical Kinetics*, Vivek Patel, Ed. InTech, pp. 79, 2012.
- [6] A. N. Gorban, I. V. Karlin IV and A. Y. Zinovyev, "Constructive methods of invariant manifolds for kinetic problems", *Physics Reports*, 396, pp. 197, 2004.
- [7] V. Bykov and U. Maas, "The extension of the ILDM concept to reaction-diffusion manifolds", *Combustion Theory and Modelling*, 11(6), pp. 839, 2007.
- [8] V. Bykov, U. Maas, "Problem Adapted Reduced Models Based on Reaction-Diffusion Manifolds (REDIMs)", Proc. Combust. Inst., 32(1), pp. 561, 2009.
- [9] D. B. Roekaerts, B. N. Merci, U. Maas, "Elimination of fast modes in the coupled process of chemistry and diffusion in turbulent nonpremixed flames: an application of the REDIM approach", *Int. Journal for Multiscale Comp. Eng.*, 7(6), pp. 487, 2009.
- [10] V. Bykov, U. Maas, "The extension of the reaction/diffusion manifold concept to systems with detailed transport models", *Proc. Combust. Inst.*, 33, pp. 1253, 2011.
- [11] V. Bykov, A. Neagos, U. Maas, "On transient behavior of nonpremixed counter-flow diffusion flames within the REDIM based model reduction concept", *Proc. Combust. Inst.*, 34, pp. 197, 2013.

### Progress-Variable-Free State-Space Parameterizations for Premixed Combustion

Mohsen Ayoobi, Ingmar Schoegl

Louisiana State University, Mechanical & Industrial Engineering, Baton Rouge, LA, USA.

*Abstract*—Key features of the flame structure remain unchanged throughout the lean and ultra-lean premixed regime, where peak temperatures are a natural parameter. As estimates for peak temperatures can be calculated from local states and transport processes, future expansions to arbitrary reacting flows are envisioned.

#### I. INTRODUCTION

In state-space modeling with reduced-order chemistry, results of detailed 1D simulations are used to span a manifold in which properties are tabulated based on a small set of parameters. As the resulting chemistry tabulation uses information obtained from detailed reaction mechanisms, full chemistry is implicit to simulation results. A main concern of this approach is a suitable parameterization, and various definitions of parameters and associated manifolds have been proposed in available literature, e.g. Intrinsic Low Dimensional Manifolds (ILDM), various flamelet based approaches (FPV, FGM, MFM, ...), and, more recently, Principal Component Analysis (PCA).



Fig. 1. Contours of constant laminar burning flux  $\dot{m}_L$  and adiabatic flame temperature  $T_{\rm ad}$  as a function of  $T_{\rm in}$  and  $\Phi$  based on 696 adiabatic flame simulations for lean CH<sub>4</sub>/air mixtures (using CANTERA/GRI-Mech 3.0).

#### II. METHODOLOGY

In any state-space modeling approach, the main concern is whether the controlling chemistry manifold captures flame characteristics over a broad range of mixture stoichiometries and reactant temperatures. For the present study, a large number of lean premixed  $CH_4$ /air simulations is used to investigate combustion characteristics (Fig. 1). For each simulation, the flame structure is analyzed in terms of species concentrations, net species production rates and heat release. Following a precursor study [2], characteristic temperatures within the inner layer of the flame sheet are defined by minima/maxima of function values, and their first and second derivatives with respect to axial position.

Characteristic temperatures within the flame structure represent *descriptive* information. In order to identify a suitable *minimal* parameterization, the information is plotted in terms of rudimentary parameters that define flame simulations: inlet conditions are specified by (normalized) equivalence ratio  $\Phi$  and reactant temperature  $T_{in}$ , whereas laminar burning flux  $\dot{m}_L$  and adiabatic flame temperature  $T_{ad}$  represent simulation results. Once a suitable parameterization is identified, PCA reveals whether characteristics are valid for a range of similar conditions.

The analysis of the flame structure is based on  $CH_4/air$  flames that are both adiabatic and one-dimensional. In the context of arbitrary reacting flows, parameters defining a manifold may not be available locally, and thus require estimates based on *local* mass fractions, temperature and associated transport processes.

#### **III. RESULTS AND DISCUSSION**

Figure 1 shows 696 test cases where inlet conditions  $(\Phi, T_{in})$  follow a pseudo-random Sobol sequence; contours represent simulation results, i.e.  $\dot{m}_L$  and  $T_{\rm ad}$ . For all test cases, characteristic temperatures  $T_{i,j}^{\star}$  are obtained via post-processing of detailed flame structures. Characteristic temperatures for heat release are presented in Figure 2, where insets display  $T_{i,j}^{\star}(\dot{H})$  as a function of  $\Phi$ ,  $T_{\rm in}$ ,  $\dot{m}_L$ and  $T_{\rm ad}$ , respectively. Results illustrate that inlet conditions are ill-suited for a universal parameterization, despite the fact that they constitute the most *convenient* parameterization. In comparison, a parameterization based on  $\dot{m}_L$ shows a good collapse of the initial curvature of the heat release,  $T_{2,0}^{\star}(H)$ , which is attributed to a transition from the convection-diffusion dominated preheating layer to the reaction-diffusion dominated active reaction zone. A parameterization based on  $T_{\rm ad}$  results in an almost perfect collapse of  $T_{i,j}^{\star}(H)$ , which is a strong indication for  $T_{ad}$ being the single-most important parameter characterizing processes within the active reaction zone.

The collapse of characteristic temperatures  $T_{i,j}^{\star}$  for comparable  $T_{ad}$  indicates that, except for a scaling factor, species production rates and heat release follow almost



Fig. 2. Comparison of different parameterizations for characteristic temperatures for heat release  $\dot{H}$ , calculated for 696 test cases (Fig. 1). From left to right, parameterizations use normalized equivalence ratio  $\Phi$ , inlet temperature  $T_{\rm in}$ , mass burning rate  $\dot{m}_L$ , and adiabatic flame temperature  $T_{\rm ad}$ .



Fig. 3. Principal Component Analysis (PCA): comparison of simulated and recovered heat release  $\dot{H}$ . Principal components (PC's) are calculated for same test case as well as multiple simulations with comparable  $T_{\rm ad}$ .

identical progressions. This result implies that a reduced manifold for a description of chemical kinetics can be obtained, where source terms are tabulated based on two parameters: (i) the local temperature T, which captures the position relative to  $T_{i,j}^{\star}$ , and (ii) the adiabatic temperature  $T_{\rm ad}$  of the flame simulation. Figure 3 compares simulated heat release to heat release recovered from PCA as a function of local temperature. It is evident that  $\dot{H}$  is successfully recovered from PC's obtained for multiple test cases with comparable  $T_{\rm ad}$ , which illustrates the collapse of chemistry characteristics onto a reduced manifold.

PCA results corroborate that net species production rates and heat release collapse based on  $T_{\rm ad}$ , and thus are governed by a reduced manifold for source terms in suitable transport equations. Since  $T_{\rm ad}$  is a non-local characteristic of the local thermo-chemical state, the proposed parameterization required estimates if applied to arbitrary flow fields. In order to obtain accurate estimates for  $T_{\rm ad}$ , conservation equations for energy and atomic species are integrated along an adiabatic stream tube extending from local conditions to a virtual state far downstream of the flame. Thermodynamic equilibrium yields  $\hat{T}_{\rm ad}$  based on estimates for  $T_{\rm in}$  and reactant composition are obtained in a similar fashion [1]. Figure 4 demonstrates that accurate estimates  $\hat{T}_{\rm ad}$  are recovered from



Fig. 4. Estimates for adiabatic temperatures  $\hat{T}_{ad}$  based on local temperature T and species concentration  $X_k$ , as well as fluxes of heat  $\mathbf{q}$ , molecular species  $\mathbf{j}_k$ , and atomic species  $\mathbf{j}_{\alpha}$  [1].

the local thermo-chemical state, where the consideration of associated transport processes is essential.

#### **IV. CONCLUSIONS**

A parameterization based on peak temperatures  $T_{\rm ad}$  produces an almost perfect collapse of flame characteristics, implying that  $T_{\rm ad}$  is a natural parameter for the generation of reduced manifolds for reaction chemistry. In contrast to most other descriptions of manifolds for premixed flames, the current work does not require the definition of a progress variable. Instead, the relative position within the flame is characterized by the local temperature T and an estimate  $\hat{T}_{\rm ad}$ . It is noted that the procedure applies to arbitrary reacting flows, where corresponding (virtual) 1D premixed flames are obtained by calculating  $\hat{T}_{\rm ad}$  from the local thermo-chemical state and associated transport processes.

#### ACKNOWLEDGMENT

The authors thank for support provided by the LaSPACE program (contract NASA/LEQSF(2010-2015)-LaSPACE).

- M. Ayoobi and I. Schoegl. Behavior of preheated premixed flames at lean conditions. In *Joint Meeting of the U.S. Sections of the Combustion Institute*, 2013.
- [2] J. Gibson, M. Ayoobi, and I. Schoegl. Behavior of preheated premixed flames at rich conditions. *Proc. Combust. Inst.*, 34:997–1005, 2013.

## Analysis and Reduction of Chemical Models under Uncertainty

Habib N. Najm<sup>\*</sup>, Robert D. Berry<sup>†</sup>, and Bert J. Debusschere<sup>\*</sup> <sup>\*</sup>Sandia National Laboratories, Livermore, CA <sup>†</sup>Climate Corporation, San Francisco, CA

*Abstract*— We discuss the motivation, utility, and challenges associated with analysis and reduction of chemical models under uncertainty. We outline a mathematical formulation for this area of study, focusing on a probabilistic uncertainty framework and dynamical analysis/reduction methods for ordinary differential equation systems. We highlight our recent progress in this area, and discuss opportunities and challenges going forward.

#### I. INTRODUCTION

Detailed chemical kinetic models for hydrocarbon fuels are typically complex, involving a large number of reactions and species. These elementary-step kinetic models are constructed to include chemical reaction pathways and intermediate/radical species that are judged to be important/relevant. Typically, each reaction involves at least 3 parameters, being the Arrhenius rate expression coefficients. These parameters are either measured experimentally, estimated from *ab-initio* quantum computations, or derived using rate rules from other rate coefficients. In any of these scenarios, these rate parameters are known only to within a certain degree of uncertainty. Broadly speaking, chemical kinetic models are characterized by degrees of both model and parametric uncertainty. In the present discussion, we focus primarily on parametric uncertainty.

Given the above, there is a need for chemical model analysis and reduction strategies to take these uncertainties into account, beside the need to accomodate a broad range of state values and operating conditions. This argument is driven by both accuracy and efficiency considerations. From an accuracy perspective, it is of interest to ensure that conclusions regarding the acceptable performance of a given reduced model are valid over the range of uncertainty in the parameters of the starting detailed model. Just like a reduced model is evaluated against the detailed model over a range of states, this ought to also span a degree of uncertainty in detailed model parameters. In principle, this translates to a higher computational cost in the analysis/reduction strategy. However, it can also translate to considerable savings if/when the choice of reduced model accuracy thresholds is informed by the degree of uncertainty in the detailed model parameters. It does not make sense to insist on reduced model accuracy requirements that are significantly tighter than the uncertainty in the detailed model predictions. The

model reduction error budget ought to take both sources of error into account.

These observations motivate the development of model analysis/reduction methods that take uncertainties into account. In the present context, we give a brief outline of first steps along the path towards this goal, with a particular focus on dynamical analysis methods, specifically computational singular perturbation (CSP), relying on eignanalysis of the Jacobian of the chemical source term under parametric uncertainty.

#### II. FORMULATION

We consider chemical reaction processes in a spatially homogeneous mixture, where the time evolution of the system state vector is described by a system of ordinary differential equations (ODEs). In the deterministic context, one can employ a number of available strategies for model analysis and reduction. We consider specifically CSP analysis and associated model reduction strategies. This method has been used to provide a range of feasible simplified chemical models with roughly monotonous variation of error relative to a given detailed model [6,10,11].

Further, we employ a probabilistic uncertainty quantification (UQ) framework, where we represent uncertain quantities as random variables. We rely on spectral polynomial chaos (PC) representations of random variables [3,5]. Forward propagation of uncertainty in this context can be done using sampling-based non-intrusive methods [5]. This involves evaluation of the deterministic model for a set of parameter values, and assembling the resulting predictions and analysis results to arrive at uncertain outputs of interest. While this is certainly viable, it can be severely taxed by the curse of dimensionality when there is a large number of uncertain parameters. This is particularly true when eigenanalysis is required for CSP analysis with each sample. In the present context, we focus on intrusive PC UQ methods [2,5], where the uncertain/random chemical ODE system is transformed via Galerkin projection into a deterministic ODE system for the spectral PC expansion (PCE) coefficients of the uncertain system state. In this context, a single solution of this (larger) ODE system (system size grows with both dimensionality and order) suffices to provide the full uncertain solution picture.

Extending model analysis/reduction to the uncertain ODE context has received some attention in recent literuare. In [4], small parametric perturbations were considered in the Proper Orthogonal Decomposition (POD) context. Sonday *et al.* [9] studied the eigenstructure of the Galerkin ODE system Jacobian of model uncertain/random ODE systems. Salloum *et al.* [8] provided a joint CSP-UQ study of a model uncertain ODE system with approximate characterization of the eigenstructure of the Galerkin ODE system Jacobian.

#### III. STOCHASTIC EIGENVALUE PROBLEM

In [1,9], we established a number of facts regarding the eigenstructure of the Galerkin ODE system Jacobian and its relationship to the statistics of eigenvalues/eigenvectors, hence dynamics, of the original random ODE system. Results indicate that, in the limit of infinite PC order, the eigenvalues of the Galerkin system tend to the distribution of eigenvalues of the original system. Further, for finite order, these two representations of the uncertain eigenvalues are close, and convergence with PC order, in the sense of measures, can be observed. Moreover, we outlined a constructive strategy for the eigenvectors of the Galerkin system Jacobian, that approximates that of the sampled eigenvectors of the original system. Accordingly, it is clear that there is a path towards learning the dynamical landscape of an uncertain chemical system by analysis of the eigenstructure of the corresponding Galerkin Jacobian.

#### IV. CSP ANALYSIS OF UNCERTAIN ODES

Given the above, we now have the beginnings of a strategy towards CSP analysis of uncertain chemical ODEs, and associated model reduction strategies. Further work is required to extend the various elements of the deterministic analysis/reduction method to the stochastic setting. Thus, while we have means of evaluating the random system eigenstructure, we need to establish robust methods for analyzing the random CSP vectors/co-vectors and associated modal expansion, to arrive at meaningful characterizations of uncertain low-dimensional manifold structure, fast and slow subspaces, classification of major/minor/radical spsecies, and importance and participation indices. We note for example, that uncertainty in fast processes can translate into uncertainty in slow manifold structure, while uncertainty in slow processes would primarily influence the evolution of the system along a deterministic manifold. Further, uncertain/random CSP Indices have to be compared to each other, and to specified thresholds, employing statistical measures of distance. Similarly, in the model reduction context, comparisons between model predictions, and estimates of error measures, have to rely on probabilistic analogues to the original deterministic procedures.

From another perspective, the Galerkin-projected ODE system, whose purpose is to allow the exploration of the dynamics of the original uncertain ODE system, is itself

a candidate for CSP analysis and model reduction, in order to facilitate its time-integration. Given high-order and dimensionality, this system can become quite large and computationally expensive to solve/analyze. Its time integration is challenging, both from accuracy and stability viewpoints [7,12]. Accordingly, there are opportunities for using CSP, or other dynamical analysis methods, along with associated model reduction strategies, in this context.

#### V. ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy (DOE), Office of Advanced Scientific Computing Research (ASCR), Applied Mathematics program, and by the DOE Office of Basic Energy Sciences (BES) Division of Chemical Sciences, Geosciences, and Biosciences. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94-AL85000.

#### VI. REFERENCES

- R.D. Berry, H.N. Najm, and B.J. Debusschere. private communication, 2013.
- [2] B.J. Debusschere, H.N. Najm, P.P. Pébay, O.M. Knio, R.G. Ghanem, and O.P. Le Maître. Numerical challenges in the use of polynomial chaos representations for stochastic processes. *SIAM J. Sci. Comp.*, 26(2):698–719, 2004.
- [3] R.G. Ghanem and P.D. Spanos. Stochastic Finite Elements: A Spectral Approach. Springer Verlag, New York, 1991.
- [4] Chris Homescu, Linda R. Petzold, and Radu Serban. Error estimation for reduced-order models of dynamical systems. *SIAM Review*, 49(2):277–299, 2007.
- [5] H.N. Najm. Uncertainty Quantification and Polynomial Chaos Techniques in Computational Fluid Dynamics. *Annual Review of Fluid Mechanics*, 41(1):35–52, 2009.
- [6] J. Prager, H.N. Najm, M. Valorani, and D. Goussis. Structure of n-Heptane/Air Triple Flames in Partially-Premixed Mixing Layers. *Combustion and Flame*, 158:2128–2144, 2011.
- [7] M.T. Reagan, H.N. Najm, B.J. Debusschere, O.P. Le Maître, O.M. Knio, and R.G. Ghanem. Spectral stochastic uncertainty quantification in chemical systems. *Combustion Theory & Modeling*, 8:607– 632, 2004.
- [8] M. Salloum, A. Alexanderian, O.P. Le Maître, H.N. Najm, and O.M. Knio. Simplified CSP Analysis of a Stiff Stochastic ODE System. *Computer Methods in Applied Mechanics and Engineering*, 217-220:121–138, 2012.
- [9] B.E. Sonday, R.D. Berry, H.N. Najm, and B.J. Debusschere. Eigenvalues of the Jacobian of a Galerkin-Projected Uncertain ODE System. *SIAM J. Sci. Comp.*, 33:1212–1233, 2011.
- [10] M. Valorani, F. Creta, F. Donato, H.N. Najm, and D.A. Goussis. Skeletal Mechanism Generation and Analysis for *n*-heptane with CSP. *Proc. Comb. Inst.*, 31:483–490, 2007.
- [11] M. Valorani, F. Creta, D.A. Goussis, J.C. Lee, and H.N. Najm. Chemical Kinetics Simplification via CSP. *Combustion and Flame*, 146:29–51, 2006.
- [12] X. Wan and G. E. Karniadakis. An adaptive multi-element generalized polynomial chaos method for stochastic differential equations. *J. Comput. Phys.*, 209:617–642, 2005.