

# Construction of Random Low-dimensional Manifolds for Stochastic Chemical Reaction Systems with Stiffness

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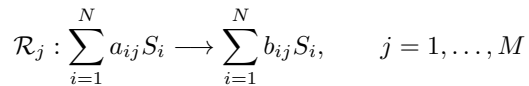
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**Abstract**—The research on reduction methods is driven by the complexity of chemical reaction systems, to seek simplified systems involving a smaller set of species and reactions that can approximate the original detailed systems in the prediction of specific quantities of interest. The existence of such reduced systems frequently hinges on the existence of a lower-dimensional, attracting, and invariant manifold characterizing long-term dynamics. The Computational Singular Perturbation (CSP) method provides a general framework for analysis and reduction of chemical reaction systems. In this work we propose an algorithm based on the theory of stochastic singular perturbation, that can be applied to stochastic reaction systems with stiffness, to obtain their random low-dimensional manifolds.

## I. INTRODUCTION

Consider a well-stirred, thermally equilibrated mixture consisting of  $N$  chemical species  $\{S_i\}_{i=1,\dots,N}$ , which interact through  $M$  chemical reaction channels



where  $a_{ij}, b_{ij} \geq 0$  are the stoichiometry coefficients. Arranging the stoichiometry coefficients into an  $N \times M$  matrix gives the stoichiometric matrix  $\Gamma = (\gamma_{ij})_{i=1,\dots,N, j=1,\dots,M}$ . Denote by  $x_i(t)$  the concentration of species  $S_i$  in the system at any time  $t$ , and  $\mathbf{x} = (x_1, x_2, \dots, x_N)^T$  the state vector. Then reaction rate equations (RREs) describing chemical kinetics at the continuum level are:

$$\frac{d\mathbf{x}}{dt} = \Gamma \cdot \mathbf{R}(\mathbf{x}) := \mathcal{G}(\mathbf{x}), \quad (1)$$

where  $\mathbf{R}(\mathbf{x}) = (R_1(\mathbf{x}), \dots, R_M(\mathbf{x}))^T$ , and  $R_j(\mathbf{x})$ ,  $j = 1, \dots, M$  is the rate of progress of the  $j$ th reaction.

When there are two classes of variables, e.g.,  $m$  fast species and  $n$  slow species\*, the vector field  $\mathcal{G}$  can be cast in the following form:

$$\mathcal{G} = \begin{pmatrix} \varepsilon g_1 \\ g_2 \end{pmatrix} = \begin{pmatrix} I_m & 0 \\ 0 & I_n \end{pmatrix} \begin{pmatrix} \varepsilon g_1 \\ g_2 \end{pmatrix}, \quad (2)$$

\*A species is declared fast/slow if its time evolution is dominated by the fast/slow processes.

where  $\varepsilon$  is a small parameter that characterizes the spectral gap of the vector field,  $I_m$  and  $I_n$  are the identity matrices in  $\mathbb{R}^m$  and  $\mathbb{R}^n$ , respectively. The theory of geometric singular perturbation (GSP) provides a framework to analyze fast-slow ODE systems such as (2) and gives an abstract description of the slow manifold  $\mathcal{M}_\varepsilon$  (if it exists) for  $\varepsilon$  sufficiently small.

The traditional stoichiometric matrix used in (1) is physically meaningful, but not unique. In fact, one can always decompose the  $N$ -dimensional vector  $\mathcal{G}$  into  $N$  additive components or modes. The CSP method [3,4,6–8] seeks a “good” basis for the vector field  $\mathcal{G}$ , by which the fast and slow dynamics are decoupled. This object is achieved by deriving the evolution equations for the fast and slow modes and updating the basis iteratively. After each iteration, CSP identifies an approximation to the slow manifold  $\mathcal{M}_\varepsilon$  by GSP theory along with an approximation of the reduced dynamics on the slow manifold.

Chemical reactions are stochastic in principle. The ODE system (1) is physically meaningful only when the system size is at continuum/macroscale, where stochastic effects are averaged out. When particle counts are large, e.g.,  $\mathcal{O}(10^3)$ , but not sufficiently so to make the continuum approximation viable, the chemical Langevin equation (CLE) can be used to simulate the state dynamics [2]. The theory of stochastic geometric singular perturbation can be used to analyze general fast-slow stochastic differential equations, providing an abstract description of the random slow manifold if it exists [1]. By using the theory of random dynamical systems, a geometric description of the random slow manifold can be constructed for particular classes of fast-slow CLEs with a simplified structure of the noise [5]. These results provide the theoretical foundation for developing an algorithm analogous to the CSP, which we name CSSP (computational stochastic singular perturbation), that can approximate the random slow manifold and the reduced dynamics on the manifold, for stochastic chemical reactions systems described by CLEs. The foundations of the CSSP method are highlighted briefly in the following.

## II. MATHEMATICAL FORMULATION

### A. CSP for RREs

Given a set of  $N$  linearly independent column basis vectors  $\mathbf{a}_i$ ,  $i = 1, \dots, N$ , The vector field  $\mathcal{G}$  can be represented as

$$\mathcal{G}(\mathbf{x}) = \sum_{i=1}^N \mathbf{a}_i g_i(\mathbf{x}), \quad (3)$$

where  $g_i$  is the amplitude of the  $i$ -th mode given by  $g_i(\mathbf{x}) := \mathbf{b}_i \odot \mathcal{G}$ , where  $\odot$  denotes the dot product, and  $\mathbf{b}_i$  is the set of row vectors which are the inverses of  $\mathbf{a}_i$  satisfying

$$\mathbf{b}_i \odot \mathbf{a}_j = \delta_{ij}, \quad i, j = 1, \dots, N \quad (4)$$

where  $\delta_{ij}$  is the Kronecker delta. Differentiating (1) with respect to time gives

$$\frac{d\mathcal{G}}{dt} = J \odot \mathcal{G}, \quad (5)$$

where  $J = \frac{\partial \mathcal{G}}{\partial \mathbf{x}}$  is the Jacobian matrix of  $\mathcal{G}$  with respect to  $\mathbf{x}$ . Taking the inner product of  $\mathbf{b}_i$  with (5) results in

$$\frac{dg_i}{dt} = \sum_j^N \Lambda_j^i g_j, \quad i = 1, \dots, N \quad (6)$$

$$\Lambda_j^i = \left( \frac{d\mathbf{b}_i}{dt} + \mathbf{b}_i \odot J \right) \odot \mathbf{a}_j, \quad i, j = 1, \dots, N. \quad (7)$$

CSP starts from a trial set of ordered basis, and generates a new refined set of basis vectors, using a two-step refinement procedure. The choice of the trial set is not unique. A natural choice is the eigenvectors of  $J$ , as these form the ideal basis vectors<sup>†</sup> for linear problems. CSP does not aim to find the ideal basis vectors, but rather to compute eigenvectors and produce a block diagonal  $\Lambda_j^i$  when converged [6,8]. Nevertheless the basis vectors provide critical information to CSP algorithms.

In our work we will first formulate the ideal basis vectors and the initial trial for general chemical Langevin equations. We will also develop an algorithm to derive computationally simplified models for stochastic chemical reaction systems.

### B. CSSP formulation for CLEs

Consider a chemical Langevin equation of the general form

$$d\mathbf{X} = \mathcal{G}(\mathbf{X})dt + \mathbf{G}(\mathbf{X})dW(t), \quad (8)$$

where  $\mathbf{X} = (X_1, X_2, \dots, X_N)^T$  is a stochastic process,  $W(t)$  denotes a  $K$ -dimensional standard Brownian motion, and  $\mathbf{G}$  is an  $N \times K$  matrix-valued function. Our goal is to compute the reduced (stochastic) reaction system, that has lower dimension than (8) but approximates select features of (8) qualitatively and quantitatively.

<sup>†</sup>A set of basis vectors  $\mathbf{a}_i(t)$  is said to be *ideal* if (i) the inverse row vectors  $\mathbf{b}_i(t)$  can be accurately computed from (4) for all time interval of interest, (ii)  $\Gamma_j^i(t)$  is diagonal, and (iii) the diagonal elements of  $\Gamma_j^i(t)$  are ordered in descending magnitudes.

Similar to (3), we represent  $\mathcal{G}$  in (8) as

$$\mathcal{G}(\mathbf{X}) = \sum_{i=1}^N \alpha_i g_i(\mathbf{X}).$$

However, the amplitude of the  $i$ -th mode,  $g_i$  now evolves according to stochastic differential equations instead of ordinary differential equations:

$$dg_i = \sum_{j=1}^N \left( \left( \frac{d\mathbf{b}_i}{dt} + \mathbf{b}_i \odot J \right) \odot \mathbf{a}_j \right) g_j + b_i \odot J \odot \mathbf{G}(\mathbf{X})dW(t).$$

We will choose the trial set of ordered basis vectors at each time  $t$  to be the eigen-vectors of  $J(t)$ . The refinement will be done by following the same procedure as in CSP, i.e., fast row and slow column vectors, followed by slow row and fast column vectors, if necessary. However, the number of exhausted modes will be obtained in a drastically different way. This is due to the stochasticity of functions  $g_i$ . Simply requiring the contribution of fast modes to  $\mathcal{G}$  to be negligible is no longer valid, as fast oscillations caused by stochastic effects still exist, even on the slow manifold. We will develop an *exhaustion criterion* for CSSP, based on the theory of geometric singular perturbation for stochastic differential equations [1], and will illustrate the scheme.

## III. ACKNOWLEDGMENT

HNN acknowledges the support of the U.S. Department of Energy, Office of Basic Energy Sciences, 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.

## IV. REFERENCES

- [1] N. Berglund and B. Gentz. Geometric singular perturbation theory for stochastic differential equations. *Journal of Differential Equations*, 191(1):1 – 54, Jun 2003.
- [2] D. T. Gillespie. The chemical langevin equation. *Journal of Chemical Physics*, 113(1):297 – 306, Jul 2000.
- [3] D.A. Goussis and S.H. Lam. A study of homogeneous methanol oxidation kinetic using csp. *Proc. Comb. Inst.*, 24:113–120, 1992.
- [4] D.A. Goussis, S.H. Lam, and P.A. Gnoffo. Reduced and simplified chemical kinetics for air dissociation using computational singular perturbation. In *28th AIAA Aerospace Sciences Meeting*, number AIAA Paper 90-0644, Reno, NV, 1990.
- [5] X. Han and H. Najm. Dynamical structures in stochastic chemical reaction systems. *SIAM J. Appl. Dyn. Sys.*, 13:1033–1351, 2014.
- [6] S.H. Lam. Using CSP to Understand Complex Chemical Kinetics. *Combustion Science and Technology*, 89:375–404, 1993.
- [7] S.H. Lam and D.A. Goussis. Understanding complex chemical kinetics with computational singular perturbation. *Proc. Comb. Inst.*, 22:931–941, 1988.
- [8] S.H. Lam and D.A. Goussis. Conventional Asymptotics and Computational Singular Perturbation for Simplified Kinetics Modelling. In M.O. Smooke, editor, *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, number 384 in Springer Lecture Notes, chapter 10, pages 227–242. Springer Verlag, 1991.