Dynamical Structures in Stochastic Chemical Reaction Systems

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***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 gas-solid 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 two-dimensional 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 ε 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

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

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*

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

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:

$$dX(t) = f(X,Y;\varepsilon) + \mu F(X,Y;\varepsilon)dW(t), \quad (4)$$
$$\varepsilon dY(t) = g(X,Y;\varepsilon) + \sigma\sqrt{\varepsilon}G(X,Y;\varepsilon)dW(t), \quad (5)$$

in which μ^2 and σ^2 measure *(rate of diffusion)^2/the speed of drift* for X and Y respectively, and $W(t)$ denotes the standard Brownian motion. Here the parameters μ, σ and ε 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

$$\dot{x}(t) = -x(t), \quad (6)$$
$$\dot{y}(t) = -\gamma y(t) + \gamma\frac{x(t)}{1+x(t)} - \frac{x(t)}{(1+x(t))^2}, \quad (7)$$

where γ ($1/\gamma$ corresponds to ε) 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 fast-slow system (6) - (7). For the system to make physical sense, we choose multiplicative noise to ensure solutions are non-negative, and obtain the stochastic Davis-Skodje system:

$$dX(t) = -X(t)dt + \mu X(t)dW(t), \quad (8)$$
$$dY(t) = \left(-\gamma Y(t) + \gamma\frac{X(t)}{1+X(t)} - \frac{X(t)}{(1+X(t))^2}\right)dt + \sigma\sqrt{\gamma}Y(t)dW(t). \quad (9)$$

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

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