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Explicit Time Integration of the Stiff Chemical Langevin Equation

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Program Overview

- Past work under BES GPCP
  - Detailed kinetic modeling and analysis of hydrocarbon flames
  - Chemical model reduction with Computational Singular Perturbation (CSP) methods
  - Uncertainty quantification in chemical kinetic models
  - Estimation of uncertain kinetic rate constants with missing data
- Present work
  - Stochastic chemical systems
  - Bayesian optimal experimental design
- Today's talk focuses on stochastic chemical systems
  - The chemical Langevin equation (CLE)

Motivation

- The chemical master equation (CME) governs the evolution of chemical systems at molecular scales
  - Discrete Markov system - integer valued molecular counts
- The Chemical Langevin Equation (CLE) is good path-wise approximation for the CME when the # of molecules of each species in the control volume is large enough – continuous Markov system
  (Gillespie JChemPhs 2000,Hildebrand & Mikhailov JPhysChem 1996)
- The CLE is relevant when the number of molecules of each species is small enough so that stochastic effects are non-negligible
  - macroscale deterministic models are inadequate
- Relevant applications:
  - catalysis
    - e.g. noise-induced transitions bet. bistable states – CO:Pt
  - biochemistry

Stochastic Chemical System Formulation

- Consider a chemical system
  - with N species $\mathcal{S}_1, \cdots, \mathcal{S}_N$, and R reactions $\mathcal{R}_1, \ldots, \mathcal{R}_R$.
  - spatially uniform, fixed volume, constant temperature
- $X_i(t)$: # $\mathcal{S}_i$ molecules, time t, and: $\boldsymbol{X}_t := (X_1(t), \cdots, X_N(t))^T$
- Chemical Langevin equation (CLE)

$$\mathrm{d}X_i(t) = \sum_{j=1}^{R} \nu_{ji}\rho_j(\boldsymbol{X}_t)\mathrm{d}t + \sum_{j=1}^{R} \nu_{ji}\sqrt{\rho_j(\boldsymbol{X}_t)}\mathrm{d}W_j(t), \quad i = 1, \cdots, N$$

  - ν_{ji} is the change in X_i caused by one $\mathcal{R}_j$ reaction
  - ρ_j is the propensity function for reaction $\mathcal{R}_j$
  - $W_j(t)$ are statistically independent Brownian motions

We can write the CLE, for convenience, as

$$\boxed{\mathrm{d}\boldsymbol{X}_t = f(\boldsymbol{X}_t)\mathrm{d}t + \textstyle\sum_{j=1}^{R} g_j(\boldsymbol{X}_t)\mathrm{d}W_j(t)}$$

SDE Time Integration

- The time integration of the CLE can employ a range of available time integration schemes for stochastic differential equations (SDEs)
- Consider the Itô SDE

$$\mathrm{d}X_t = f(X_t)\mathrm{d}t + g(X_t)\mathrm{d}W_t$$

- Time integration

$$X_t = X_{t_0} + \int_{t_0}^{t} f(X_s)\mathrm{d}s + \int_{t_0}^{t} g(X_s)\mathrm{d}W_s$$

- Euler-Maruyama (EM) – explicit, order 1 weak convergence

$$Y_{n+1} = Y_n + f_n h_n + g_n \sqrt{h_n}\mathcal{N}_n, \qquad h_n = t_{n+1} - t_n, \quad Y_0 = X_{t_0}$$

  - EM is the simplest explicit SDE time integration

SDE Stiffness

- An SDE is stiff when it exhibits a large range of time scales
- A chemical system with very slow/fast reactions results in a stiff CLE
- Stiffness results in challenges for **explicit** SDE time integrators
  - Stability requires time steps smaller than the fastest time scale
  - However, for accurate time integration, ideally, the optimal time step choice is dictated by the *active* time scale
- One remedy is to use implicit time integration, but can we do better with explicit constructions?
  - This has been done for ODEs using Computational Singular Perturbation (CSP)

    Valorani & Goussis, JCP, 2001
  - We would like to extend this to SDEs, specifically to the CLE
    - Utility for both time integration and analysis

CSP Basics

Harvey Lam, Dimitris Goussis, 1980s – present

- Autonomous stiff ODE system $\qquad \dot{\boldsymbol{x}} = \boldsymbol{g}(\boldsymbol{x}), \qquad \boldsymbol{x} \in \mathbb{R}^N$
- Define basis vectors $\boldsymbol{a}_1(x), \dots, \boldsymbol{a}_N(x)$, row vectors $\boldsymbol{b}^1(x), \dots, \boldsymbol{b}^N(x)$
  - with $\boldsymbol{b}^i \boldsymbol{a}_j \equiv \delta_{ij}$
- Expand the RHS in this basis: $\boldsymbol{g}(\boldsymbol{x}) = \sum_{i=1}^N \boldsymbol{a}_i f^i$, with $f^i := \boldsymbol{b}^i \cdot \boldsymbol{g}$

whence:

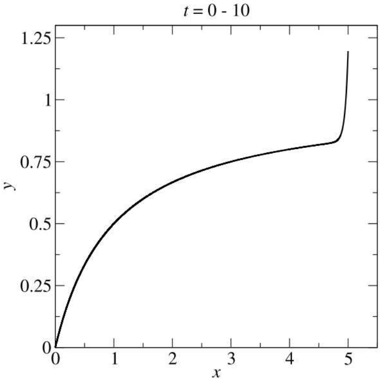
$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} f^1 \\ \vdots \\ f^N \end{bmatrix} = \Lambda(\boldsymbol{x}) \begin{bmatrix} f^1 \\ \vdots \\ f^N \end{bmatrix}$$

$\Lambda \in \mathbb{R}^{N\times N}$, $\Lambda_{ij} = (\frac{\mathrm{d}\boldsymbol{b}^i}{\mathrm{d}t} + \boldsymbol{b}^i J_{\boldsymbol{g}})\boldsymbol{a}_j$, and $J_g = \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}$ is the Jacobian of $\boldsymbol{g}$

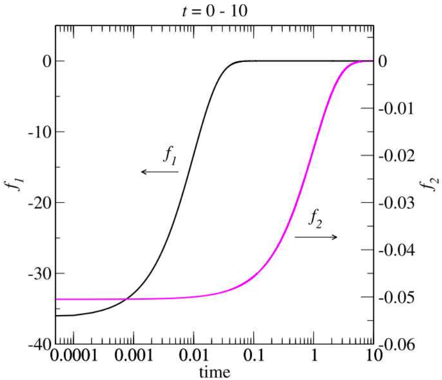
The ideal basis decouples fast and slow processes, *i.e.* diagonalizes Λ

- Eigenvectors of $J_{\boldsymbol{g}}$ are an approximation of the ideal CSP basis
  - Exact for a linear system, where $\mathrm{d}\boldsymbol{b}^i/\mathrm{d}t \equiv 0$, $\forall i$
- Decoupling allows time-scale-informed time integration

CSP Illustration with a Model ODE system



Time evolution of the state vector in the configuration space



Time evolution of CSP (signed) mode amplitudes $f^i, i = 1, 2$

$$\boldsymbol{z} := \begin{bmatrix} y \\ x \end{bmatrix} \text{ \& } \gamma := 1/\epsilon: \qquad \dot{\boldsymbol{z}} = \boldsymbol{g}(\boldsymbol{z}) = \begin{bmatrix} -\gamma y + \dfrac{\gamma x}{1+x} - \dfrac{x}{(1+x)^2} \\ -x \end{bmatrix}$$

(Davis and Skodje, J.Chem.Phys. 1999)

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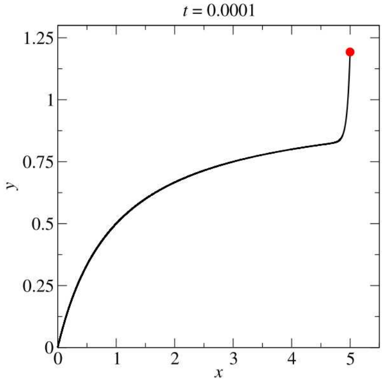

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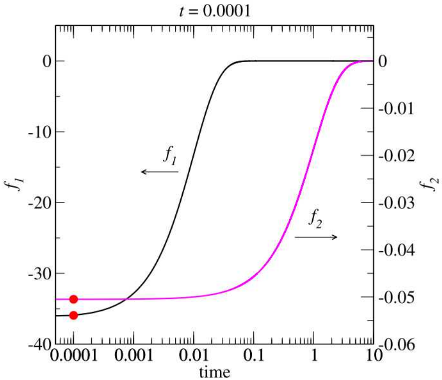

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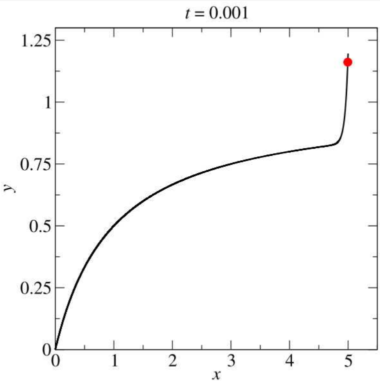

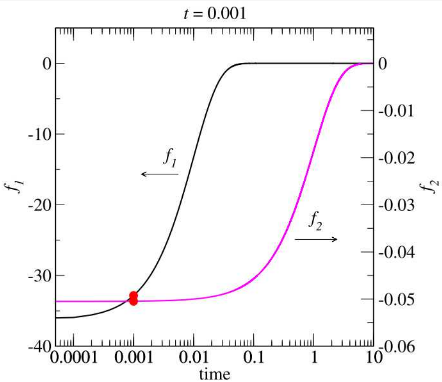

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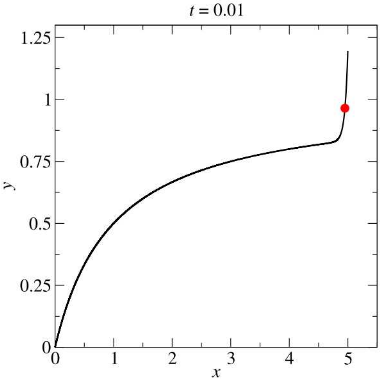

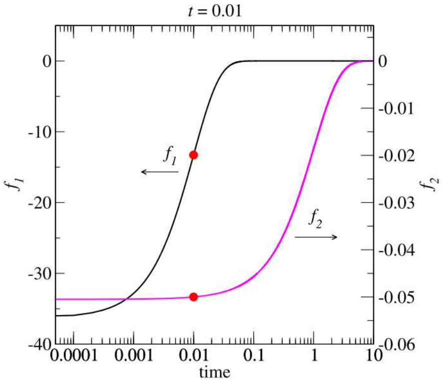

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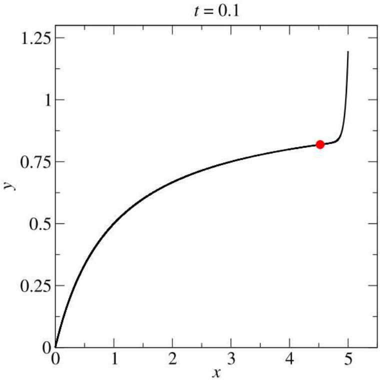

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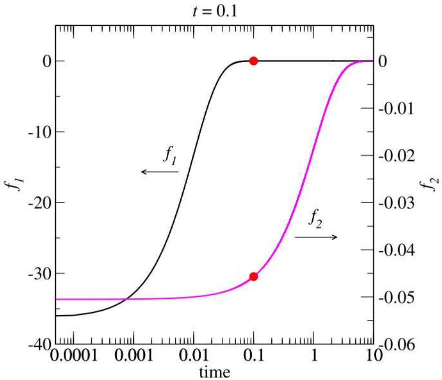

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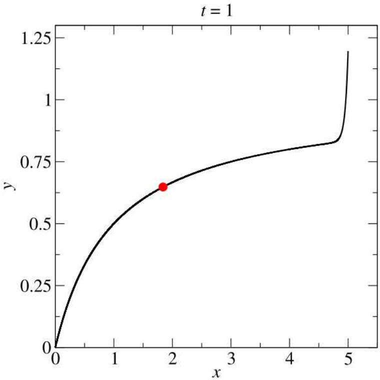

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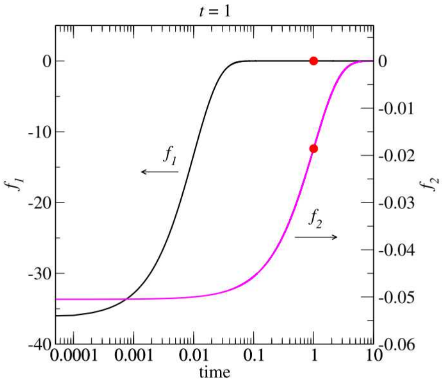

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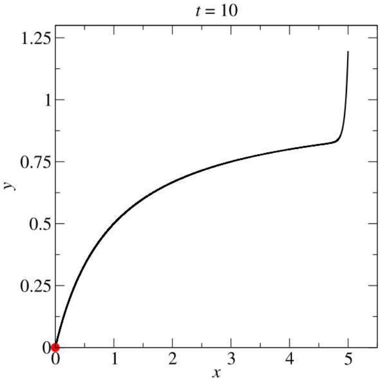

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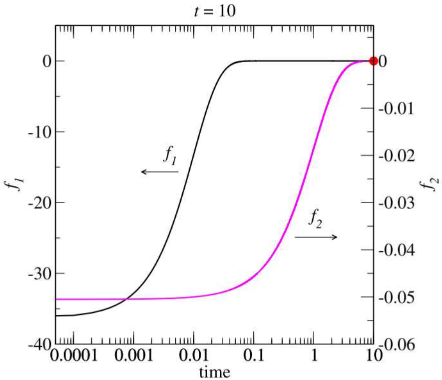

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(Davis and Skodje, J.Chem.Phys. 1999)

CSP Decomposition and Time Integration

ODE: $$\dot{\boldsymbol{x}} = \boldsymbol{g}(\boldsymbol{x}), \qquad \boldsymbol{x} \in \mathbb{R}^N$$

Evaluate eigensolution for Jacobian matrix $J_{\boldsymbol{g}}$, and sort the eigenmodes

$$\lambda_1, \cdots, \lambda_N \qquad \text{with } |\lambda_i| \geq |\lambda_{i+1}|$$

with time scales $\tau_i = 1/|\lambda_i|$ and $\tau_i \leq \tau_{i+1}$

$$\boldsymbol{g} \;=\; \sum_{i=1}^{N} \boldsymbol{a}_i f^i = \underbrace{\boldsymbol{a}_1 f^1 + \cdots + \boldsymbol{a}_M f^M}_{\boldsymbol{g}_{\text{fast}} \approx 0} \;+\; \underbrace{\boldsymbol{a}_{M+1} f^{M+1} + \cdots + \boldsymbol{a}_N f^N}_{\boldsymbol{g}_{\text{slow}}}$$

Explicit integration in time

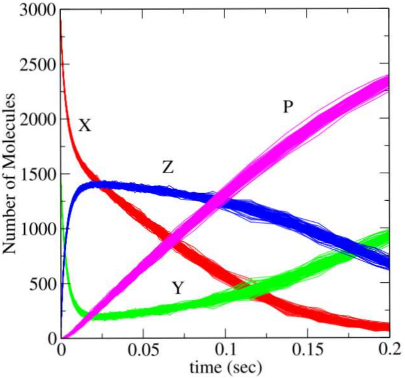
$$\boldsymbol{x}^{n+1} = \boldsymbol{x}^n + \sum_{i=1}^{M} \int_{t_n}^{t_{n+1}} \boldsymbol{a}_i f^i \mathrm{d}t + \sum_{i=M+1}^{N} \boldsymbol{a}_i f^i \Delta t$$

Amplitudes of fast exhausted modes decay exponentially, thus:

$$\boxed{\boldsymbol{x}^{n+1} = \boldsymbol{x}^n + \sum_{i=1}^{M} \boldsymbol{a}_i^n f_n^i \tau_i^n (1 - e^{-\Delta t/\tau_i^n}) + \sum_{i=M+1}^{N} \boldsymbol{a}_i^n f_n^i \Delta t}$$

CLE Stiffness and Dynamical Response

- A stiff CLE exhibits stochastic manifolds
- Basins of attraction defined by partial mean-equilibration of fast drift processes
  - Meaningful for drift processes that are faster than diffusive time-scales
- Focus on eigenstructure of the **drift** term
- Address decay and exhaustion of drift processes in the mean



Michaelis-Menten CLE system

CSP Applied to the CLE

(Han, Valorani, Najm, J. Chem. Phys. 2019)

- CLE

$$\boldsymbol{X}_{t+\mathrm{d}t} = \boldsymbol{X}_t + \boldsymbol{f}(\boldsymbol{X}_t)\mathrm{d}t + \sum_{j=1}^{R} \boldsymbol{g}_j(\boldsymbol{X}_t)\mathrm{d}W_j(t),$$

- Introduce the CSP basis $\{\boldsymbol{\alpha}_i, \boldsymbol{\beta}^i\}$, $i = 1, \ldots, N$, with $\boldsymbol{\beta}^i \cdot \boldsymbol{\alpha}_i = \delta_{ij}$, $\forall i$
- The (signed) mode amplitudes for the drift term are

$$\xi^i(\boldsymbol{X}) = \boldsymbol{\beta}^i(\boldsymbol{X}) \cdot \boldsymbol{f}(\boldsymbol{X})$$

- Using the stochastic chain rule, with some algebra, we have

$$\boxed{\mathrm{d}\boldsymbol{\xi} = \Lambda\boldsymbol{\xi}\mathrm{d}t + \boldsymbol{\varphi}\mathrm{d}t + \Gamma\mathrm{d}\boldsymbol{W}(t)}$$

where

$$\begin{array}{ll} \Lambda \in \mathbb{R}^{N\times N} & \Lambda_{ij} = \left(\frac{\mathrm{d}\boldsymbol{\beta}^i}{\mathrm{d}t} + \boldsymbol{\beta}^i J_{\boldsymbol{f}}\right)\boldsymbol{\alpha}_j \\ \boldsymbol{\varphi} \in \mathbb{R}^N & \boldsymbol{\varphi}_i = \sum_{r=1}^N \beta_r^i \sum_{k,l=1}^N \sum_{j,m=1}^R \nu_{jk}\nu_{jl}\nu_{mr} \frac{\partial^2 \rho_m}{\partial X_k \partial X_l}\rho_j \\ \Gamma \in \mathbb{R}^{N\times R} & \Gamma_{ij} = \sum_{r=1}^N \beta_r^i \sigma_{rj} \end{array}$$

Linearization of the SDE for the Modes

- We use this SDE, linearized, to motivate the use of the eigenvectors of $J_{\boldsymbol{f}}$ as CSP basis vectors, as done for the ODE case
- A linearized analysis gives

$$\mathrm{d}\boldsymbol{\xi} = \Lambda\boldsymbol{\xi}\mathrm{d}t + \Gamma\mathrm{d}\boldsymbol{W}(t), \qquad \text{with } \Lambda_{ij} = \boldsymbol{\beta}^i J_{\boldsymbol{f}}\boldsymbol{\alpha}_j$$

- Choosing α, β as the right/left eigenvectors of $J_{\boldsymbol{f}}$ diagonalizes Λ, and decouples the time evolution of the **mean** modes
  - for modes with eigenvalues with different real parts
- For the nonlinear CLE, as opposed to a general SDE,
  - Magnitudes of components of φ are small relative to those of Λ
  - The use of the linearized approximation is viable

Proposed CSP-CLE time integration strategy

- Integrate the drift term using CSP – at every time step:
  - Evaluate eigendecomposition of $J_{\boldsymbol{f}} = \partial \boldsymbol{f} / \partial \boldsymbol{x}$, and sort them

$$\lambda_1, \cdots, \lambda_N \qquad \text{with } |\lambda_i| \geq |\lambda_{i+1}|$$

  with time scales $\tau_i = 1/|\lambda_i|$ and $\tau_i \leq \tau_{i+1}$

$$\boldsymbol{f} = \sum_{i=1}^{N} \boldsymbol{\alpha}_i \xi^i = \underbrace{\boldsymbol{\alpha}_1 \xi^1 + \cdots + \boldsymbol{\alpha}_M \xi^M}_{\boldsymbol{f}_{\text{fast}}} + \underbrace{\boldsymbol{\alpha}_{M+1} \xi^{M+1} + \cdots + \boldsymbol{\alpha}_N \xi^N}_{\boldsymbol{f}_{\text{slow}}}$$

  - Identify fast/slow subspaces, **determine** M
    - Main challenge: define quantitative measure of **exhaustion**
  - Model fast drift processes: exponential decay to $\boldsymbol{f}$-manifold
  - Integrate slow drift processes using EM
- Integrate diffusion term using EM

(can be similarly applied to other explicit SDE integration schemes)

CLE-CSP Time Integration

Path-wise CLE Difference equations, with $\boldsymbol{X}_t^\omega := \boldsymbol{X}(t, \boldsymbol{\eta}^\omega)$

$$\boldsymbol{X}_{t+\mathrm{d}t}^\omega = \boldsymbol{X}_t^\omega + \boldsymbol{f}(\boldsymbol{X}_t^\omega)\mathrm{d}t + \boldsymbol{g}((\boldsymbol{X}_t^\omega, \boldsymbol{\eta}^\omega)\sqrt{\mathrm{d}t}.$$

Thus the CSP time integration is as follows,

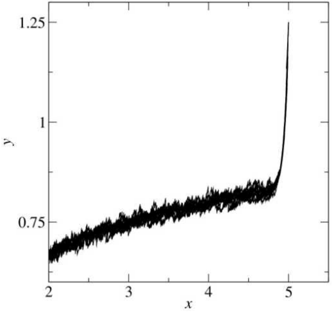
$$\begin{aligned}\boldsymbol{X}_{t+\Delta t}^\omega = \boldsymbol{X}_t^\omega \quad & + \quad \sum_{i=1}^{M} \xi^i(\boldsymbol{X}_t^\omega)\boldsymbol{\alpha}_i(\boldsymbol{X}_t^\omega)\, \tau_i(\boldsymbol{X}_t^\omega)(1 - e^{-\Delta t/\tau_i(\boldsymbol{X}_t^\omega)}) \\ & + \sum_{i=M+1}^{N} \xi^i(\boldsymbol{X}_t^\omega)\boldsymbol{\alpha}_i(\boldsymbol{X}_t^\omega)\, \Delta t \\ & + \quad \boldsymbol{g}((\boldsymbol{X}_t^\omega, \boldsymbol{\eta}^\omega)\, \sqrt{\Delta t}\end{aligned}$$

CLE-CSP – Determination of M

The determination of M in an ODE setting is as follows:

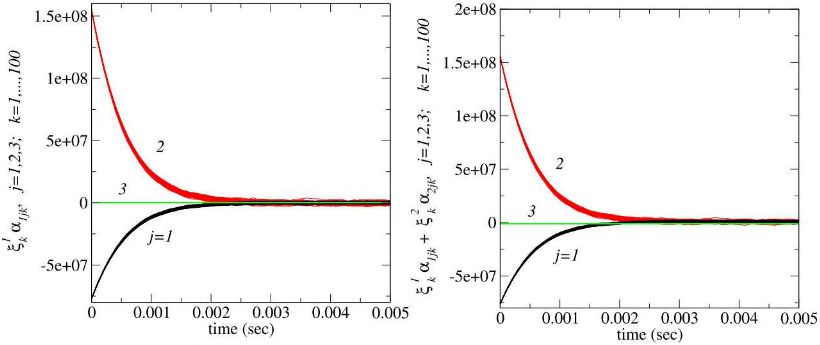
$$M = \max m \quad \text{s.t.} \quad \tau_{m+1} \left| \sum_{i=1}^{m} \boldsymbol{a}_i f^i \right| < \epsilon_r \boldsymbol{x} + \epsilon_a \mathbf{1}$$

- Stochastic noise renders this test ineffectual for the CLE
- The mode amplitudes ξ^i for any sample-path do not decay to zero
- Choosing an arbitrary threshold is unreliable
- A reliable approach involves utilization of sample-path statistics



Model 3-Species System – Mode Contributions

100 samples



$\xi^1 \boldsymbol{\alpha}_1$ $\qquad$ $\xi^1 \boldsymbol{\alpha}_1 + \xi^2 \boldsymbol{\alpha}_2$

- Noise leads to challenging exhaustion detection problem
- Need a robust means of selecting thresholds
- Ensure that the absolute value of the sums is “small”

Model 3-Species System – Mode Contributions

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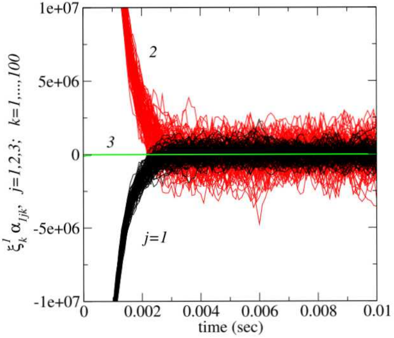

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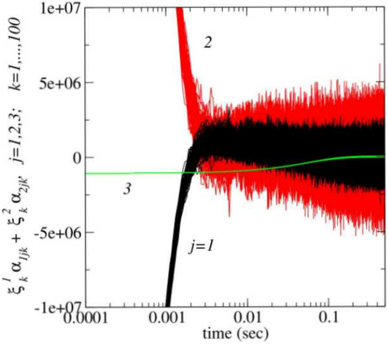

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- Noise leads to challenging exhaustion detection problem
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A Reliable M-Detection Strategy

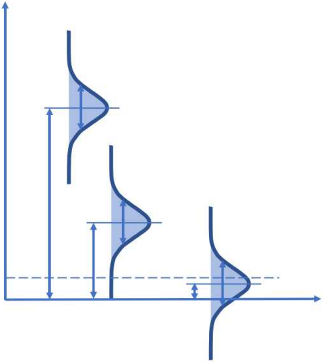
- Run K samples concurrently
- Examine statistics of $\mathfrak{S}_m = \left| \sum_{i=1}^{m} \xi^i \boldsymbol{\alpha}_i \right|$
- Define the $\mathfrak{S}_m$ K-sample mean and standard deviations μ_{mK}, σ_{mK}
- Declare a set of m decaying modes exhausted when $\mu_{mK} < \sigma_{mK}$
- Also ensure that the drift time scale of the fastest slow mode ("active" mode) is faster than the fastest diffusion time scale

$M = \max m \in [1, N]$

such that

$$\mu_{mK} < \beta\, \sigma_{mK}$$

$$\max_k \tau_{m+1,k} < \gamma \min_k \tau_{1,k}^{J_g}$$

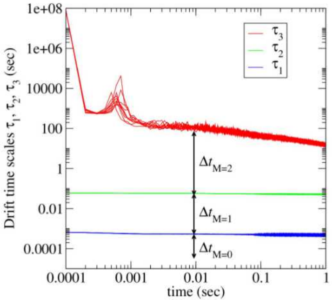


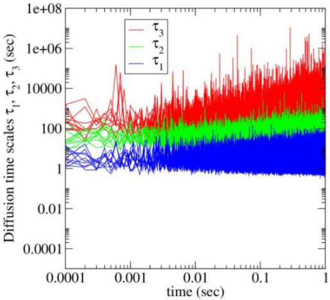
We use $\beta = 5, \gamma = 0.5$

Choice of time step

- Integrate all K samples synchronously in time, same Δt for all

$$\Delta t^* < \min_k \tau_{1,k} \quad \text{for} \quad M = 0$$
$$\Delta t^* \in [\max_k \tau_{M,k}, \min_k \tau_{M+1,k}] \quad \text{for} \quad M > 0$$

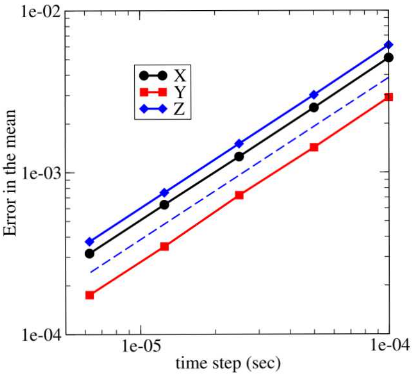


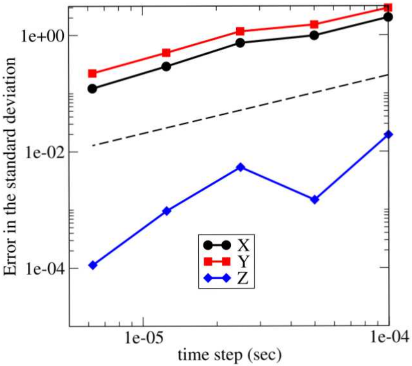


- Reduce impact of large sudden increase in Δt; enforce

$$\Delta t_n = \min(\Delta t^*, 2\Delta t_{n-1})$$

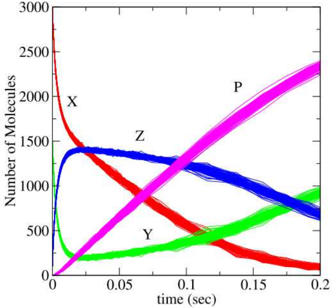
CLE time integration with CSP – Error convergence

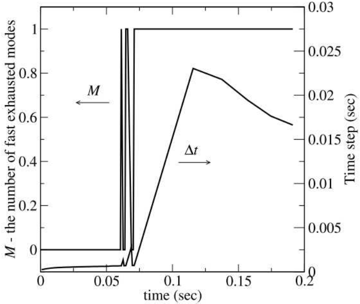




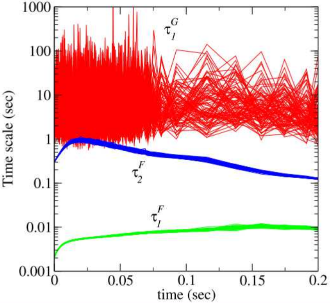
- Convergence is with respect to small-Δt computations with EM
- First order weak-convergence of EM is retained
  - for both the mean and standard deviation

Michaelis-Menten system CLE





- M goes up to a maximum of 1
- Limited by diffusion time scales
- Noise in M-selection induced by the noisy sample-based $\tau_{\min}^{g}$



Computational Performance

Computational savings of large explicit time steps have to be balanced against the costs of Jacobian eigensolves

- Our current EM implementation is 1.5$\times$ faster than CSP integration

Potential remedies to improve computational performance include:

- Resolving the diffusion-induced upper limit on Δt, thus allowing larger time step computations
- Reusing the computed eigendecomposition of the Jacobian over some number of time steps
  - Reuse enabled 2–5$\times$ speedup in a similar (ODE) integrator for systems with up to 561 species and 2538 reactions (Valorani *et al.*, 2018)
- Exploring eigensolvers that can
  - make efficient use of a good initial guess
  - compute only the fastest $M + 1$ eigenmodes

Closure

- We demonstrated the utility of CSP for enabling large time step explicit integration of stiff CLEs
- We retain the weak convergence rate of the explicit integrator in both mean and standard deviation
- Numerous directions for future work are feasible
  - Develop adequate modeling of fast diffusional processes
  - Reduce eigendecomposition costs
    - reuse, good initial guess, partial eigensolve
  - Development of treatment for multiple manifolds and switching between basins of attraction

Collaborators

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