



# *Chemical Model Reduction under Uncertainty*

H. Najm<sup>1</sup>, R.C. Malpica Galassi<sup>2</sup>, and M. Valorani<sup>2</sup>

<sup>1</sup>Sandia National Laboratories  
Livermore, CA

<sup>2</sup>Sapienza University of Rome  
Rome, Italy

SRI-UQ Workshop  
KAUST, KSA  
Jan 5 – 10, 2016

---

*Support:*

*DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, & Biosciences  
Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST)*

*Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin  
Company, for the United States Department of Energy under contract DE-AC04-94-AL85000.*

---

# Outline

- 1 Introduction
- 2 Deterministic Chemical Mechanism Simplification with CSP
- 3 Uncertain Chemical Mechanism Simplification with CSP
- 4 Demonstration on an Uncertain n-butane Mechanism
- 5 Closure

# Uncertainty in Reacting Flow Modeling

- Chemical models involve much empiricism
- Model uncertainties: choice of species and reactions
- Parametric uncertainties:
  - Chemical rate constants
  - Thermodynamic parameters
  - turbulence/subgrid models
  - mass/energy transport and fluid constitutive laws
  - geometry and initial/boundary conditions
- Present focus on parametric uncertainty
  - kinetic rate coefficients

# Uncertainty and Chemical Model Reduction

- Typical ingredients in chemical model reduction
  - A detailed starting chemical kinetic mechanism  $M^*$
  - Operating conditions of interest
  - Quantities of interest (QoIs) desired with specified accuracy

$$\mathcal{E} \equiv \|\Phi - \Phi^*\| < \alpha$$

- Consequences of uncertainty in the detailed model?
  - Errors in QoIs: acceptable over range of uncertainty
  - QoIs are uncertain -  $\Phi(\omega)$  - error measure definition
  - Probabilistic measures of model fidelity

$$\mathcal{E}(\omega) \equiv \|\Phi - \Phi^*\| \quad \Rightarrow \quad \text{Prob}[\mathcal{E} < \alpha] < \epsilon$$

$$\mathcal{E} \equiv \|\mathcal{S}(\Phi) - \mathcal{S}(\Phi^*)\| \quad \Rightarrow \quad \mathcal{E} < \alpha$$

$$\mathcal{E} \equiv \mathcal{D}_{\text{KL}}[p(\Phi), p(\Phi^*)] \quad \Rightarrow \quad \mathcal{E} < \alpha$$

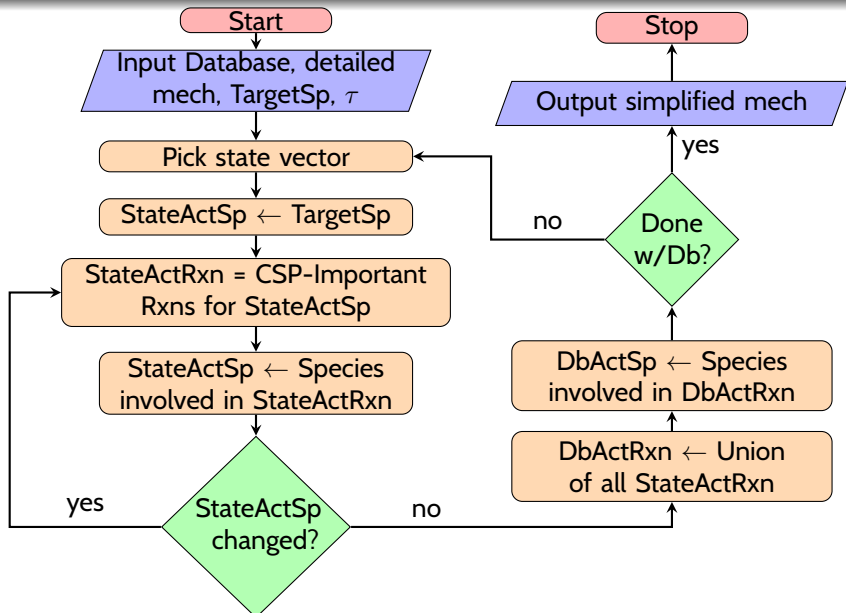
# Model Robustness, Error and Uncertainty

- Robustness: A reduced model developed based on a given database should not learn "too much" from the data
  - Reduced models based on different training/test data subsets should not vary "much"
- Optimally, requirements on reduced model error should be made in light of uncertainty in detailed model predictions
  - There is little point in insisting on error bounds much smaller than uncertainty in the reference data
- Measures of reduced model fidelity can include accurate prediction of
  - the nominal reference solution
  - uncertainty in specific observables

# Deterministic Chemical ODE System Analysis

- Computational Singular Perturbation (CSP) analysis
- Jacobian eigenvalues provide first-order estimates of the time-scales of system dynamics:  $\tau_i \sim 1/\lambda_i$
- Jacobian eigenvectors provide first-order estimates of the vectors that span the fast/slow tangent spaces
- With chosen thresholds, have  $M$  “fast” modes
  - $M$  algebraic constraints define a slow manifold
  - Fast processes constrain the system to the manifold
  - System evolves with slow processes along the manifold
- CSP Importance indices provide estimates of “importance” of a given reaction to a given species in each of the fast/slow subspaces

# A CSP-based Mechanism Simplification Algorithm



# Reduction Strategy under Uncertainty

- Deterministic strategy:
  - Given
    - Detailed starting chemical model  $M^*$ , with parameters  $\lambda$
    - Solution database  $D$  of state vectors generated with  $M^*(\lambda)$
    - Quantities of interest  $Q$  - mole fractions of target species
    - Specified thresholds  $\tau$  on CSP Importance Indices
  - Discover a simplified model  $M(M^*(\lambda), D, Q, \tau) := M(\lambda)$
- Probabilistic strategy:
  - Given uncertainty in  $\lambda$ , we model this parameter vector as a random vector with a given joint density  $p(\lambda)$ .
  - As a result, the resulting model structure  $M(\lambda)$  is a random object, with a probability for any given  $M$ , denoted by  $P(M)$ .
  - Each  $M \in \mathcal{M}$  is defined by a network of species/reactions
  - The set  $\mathcal{M}$  is not easy to work with



# Convenient coordinates on model space

- Given the starting detailed model  $M^*$ , any simplified model  $M$  is uniquely defined by the set of retained reactions
  - Retained species are those involved in retained reactions
- Set of elementary reactions in  $M^*$ :  $\mathcal{R}_{M^*} = \{R_1, \dots, R_K\}$
- Define the bit vector  $\alpha = (\alpha_1, \dots, \alpha_K) \in \{0, 1\}^K$
- A model  $M$  is specified by  $\alpha(M)$  where, for  $r = 1, \dots, K$ ,

$$\alpha_r(M) = \begin{cases} 1 & \text{if } R_r \in \mathcal{R}_M \\ 0 & \text{otherwise} \end{cases}$$

clearly:  $\alpha(M^*) = (1, \dots, 1)$

- Thus, given  $M^*$ , we have the mapping:  $\lambda \rightarrow \alpha(\lambda)$

# Uncertain Simplified Model Specification

- For uncertain  $\lambda$ :  $p(\lambda) \rightarrow P(\alpha) \equiv P_\alpha$
- Clearly,  $P_\alpha \geq 0$ , and  $\sum_\alpha P_\alpha = 1$
- Illustrative example:  $M^*: \mathbf{A} \begin{matrix} \xrightarrow{1} \\ \xleftarrow{2} \end{matrix} \mathbf{B}$ 
  - $K = 2$ , such that  $\alpha = (\alpha_1, \alpha_2)$
  - Set of possible values of  $\alpha$ :  $\{(1, 1), (1, 0), (0, 1), (0, 0)\}$
  - Set of possible models  $M$ :  $\{M_{(1,1)}, M_{(1,0)}, M_{(0,1)}, M_{(0,0)}\}$
  - Uncertain simplified model specification:

$$\{P_{(1,1)}, P_{(1,0)}, P_{(0,1)}, P_{(0,0)}\}$$

where  $P_{(i,j)} \equiv P(\alpha = (i, j))$

# Uncertain Reduction Strategy - 1

- Generate  $N$  random samples of  $\lambda$  from  $p(\lambda)$
- For each  $\lambda^i, i = 1, \dots, N$ 
  - Analyze resulting  $M^*(\lambda^i)$  for ignition - range of  $(T, P, \Phi)$  ICs
  - Get simplified model  $M^i(\mathcal{S}^i, \mathcal{R}^i)$
  - Evaluate  $\alpha^i = \alpha(M^i)$ :

$$\alpha_k^i = \begin{cases} 1 & \text{for } R_k \in \mathcal{R}_{M^i} \\ 0 & \text{otherwise} \end{cases} \quad k = 1, \dots, K$$

- Estimate Model probabilities:  $P_\alpha = \frac{1}{N} \sum_{i=1}^N \delta_{\alpha, \alpha^i}$
- Marginal reaction probabilities:

$$P_{\alpha_k} = \frac{1}{N} \sum_{i=1}^N \delta_{\alpha_k, \alpha_k^i}, \quad k = 1, \dots, K$$

# Uncertain Reduction Strategy - 2

- Marginal reaction inclusion probability

$$P_k := P_{\{\alpha_k=1\}} = \frac{1}{N} \sum_{i=1}^N \alpha_k^i, \quad k = 1, \dots, K$$

- Include reaction  $k$  if:

$$P_k > \theta$$

- Resulting model  $M_{\tau, \theta}(\lambda)$  is the CSP-simplified model given
  - the starting detailed model  $M^*(\lambda)$
  - the database of solution state vectors
  - the CSP Importance Index tolerance  $\tau$
  - for  $\lambda \sim p(\lambda)$

with marginal reaction inclusion probability  $> \theta$

# Computational Considerations

- Efficient Tchem based thermochemistry
  - In-memory manipulation of Arrhenius parameters
  - Fast evaluation of source term and analytical Jacobian
  - <http://www.sandia.gov/tchem>
  - Contact: C. Safta: [csafta@sandia.gov](mailto:csafta@sandia.gov)
- Fast cvode based stiff time integration
  - <http://computation.llnl.gov/casc/sundials>
- Efficient CSPTk analysis and reduction
  - Minimal I/O
  - On-demand/as-needed evaluation of Importance Indices
  - Contact: M. Valorani: [mauro.valorani@uniroma1.it](mailto:mauro.valorani@uniroma1.it)
- In-memory statistics of random trajectories and associated analysis

# Demo on n-butane ignition

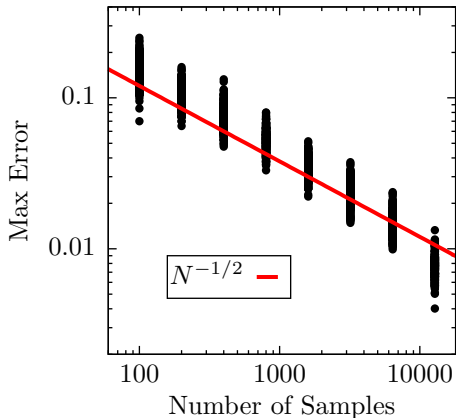
- Detailed chemical mechanism for n-butane/air combustion, with specified uncertainty factors in the pre-exponentials  
E. Hebrard, A.S. Tomlin, R. Bounaceur, F. Battin-Leclerc, Proc. Comb. Inst. **35**(1):607-616, 2015.
- $N = 1111$  reactions
- Temperature-dependent uncertainty factors
  - Mechanism specificities ( $f_r, g_r$ ) for each reaction  $r$
  - Uncertainty factor:  $\ln A = \ln A_{\text{nom}} \pm \ln F$

$$F_r(T) = f_r \exp \left( \left| g_r \left( \frac{1}{T} - \frac{1}{300} \right) \right| \right)$$

- For now, we employ a temperature-independent  $F_r$ :

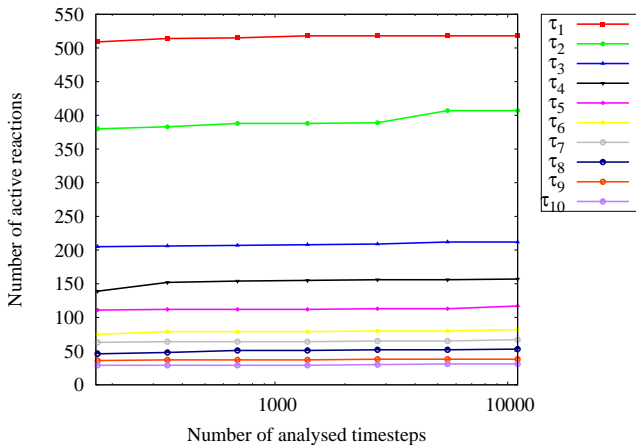
$$F_r := F_r(T)|_{T=1500 \text{ K}}$$

# Convergence with number of MC samples



- Self-convergence of max error in  $P_\alpha$  with # of MC samples
- Expected slope of  $1/\sqrt{N}$  in ensemble mean error

# Convergence with number of sampled trajectory steps

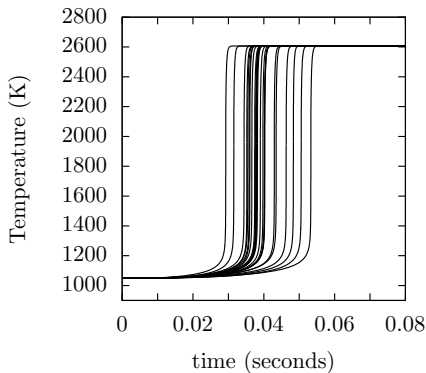


- Somewhat weak dependence on the number of sampled points in each trajectory



# Sampled ignition trajectories – detailed mechanism

- Significant uncertainty in ignition time
- Large range of state-variable uncertainty vs time
  - fast ignition transient
- Examine trajectory errors and uncertainty in an alternate progress-variable phase space
  - Entropic phase space



# Normalized entropy progress variable

- Define the entropy progress variable:

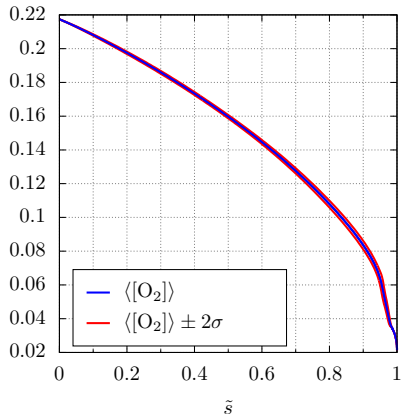
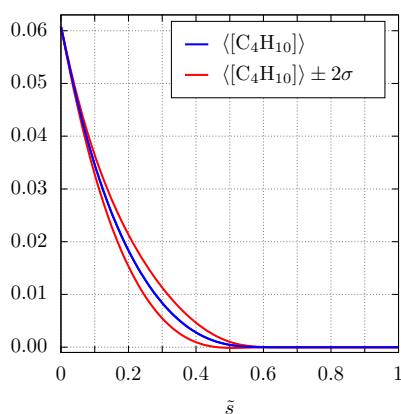
$$\hat{s}(t) = \int_0^t |\mathbf{d}s|$$

- Given any quantity of interest  $\phi(t, \cdot)$
- And, time trajectory  $(t_k, \phi(t_k, \cdot))$ ,  $k = 1, \dots, K$
- Re-parametrize the trajectory using a normalized entropy:

$$\tilde{s}(t) = \frac{\hat{s}(t)}{\hat{s}(t_{\text{final}})}$$

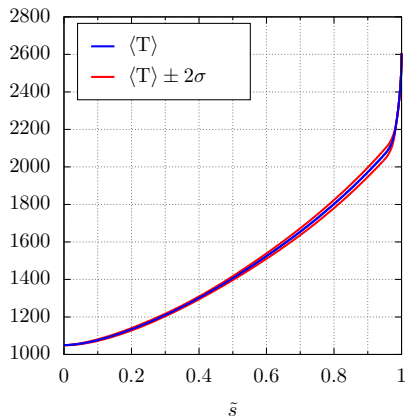
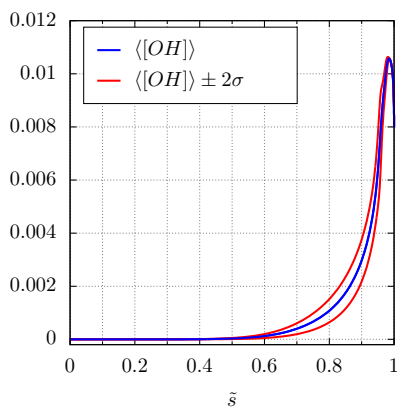
- Thus,  $\phi(\mathfrak{s}, \cdot) := \phi(t_{\mathfrak{s}}, \cdot)$  where  $t_{\mathfrak{s}} = t(\mathfrak{s}) := \{t \mid \tilde{s}(t) = \mathfrak{s}\}$
- Compare solutions in the  $(\mathfrak{s}, \phi)$  phase space
  - Trajectories  $(\mathfrak{s}_k, \phi(\mathfrak{s}_k, \cdot))$ ,  $k = 1, \dots, K$

# Uncertain trajectories in the entropy phase space



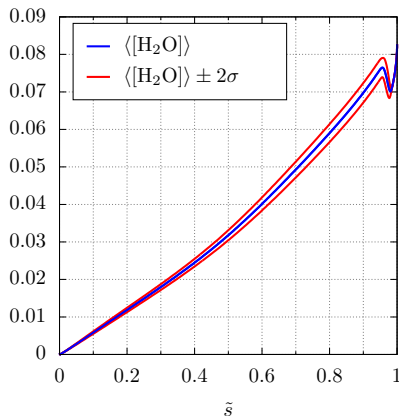
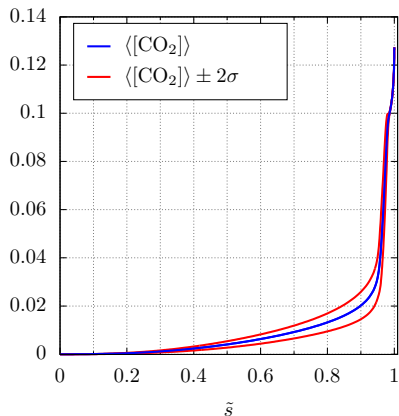
- Mean and Mean  $\pm 2\sigma$  trajectories for select state variables
- No uncertainty at equilibrium
  - Rate parameters, not thermodynamic properties, are uncertain
- Coefficient of variation can be large when the mean is low

# Uncertain trajectories in the entropy phase space



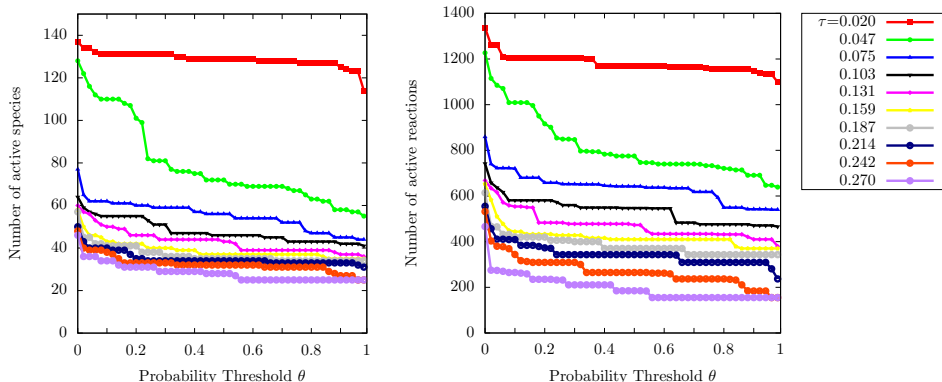
- Mean and Mean  $\pm 2\sigma$  trajectories for select state variables
- No uncertainty at equilibrium
  - Rate parameters, not thermodynamic properties, are uncertain
- Coefficient of variation can be large when the mean is low

# Uncertain trajectories in the entropy phase space



- Mean and Mean  $\pm 2\sigma$  trajectories for select state variables
- No uncertainty at equilibrium
  - Rate parameters, not thermodynamic properties, are uncertain
- Coefficient of variation can be large when the mean is low

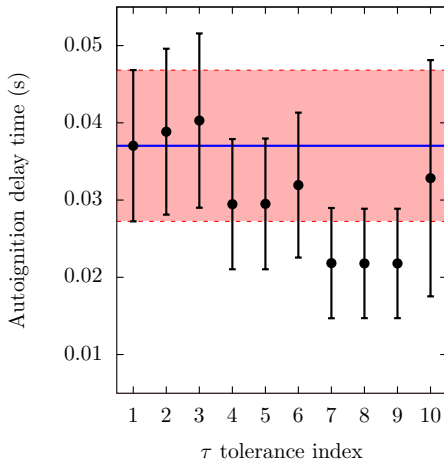
# # of active reactions/species varies inversely with $(\tau, \theta)$



- Number of active reactions/species goes down monotonically with:
  - increasing threshold  $\theta$  on  $P_k$
  - increasing Importance Index threshold  $\tau$

# Error in Uncertain Ignition time prediction

- Detailed model:  $t_{\text{ign}}^d(\lambda)$
- Simplified model:  
 $t_{\text{ign}}(\lambda, \tau, \theta = 0.3)$
- Global trend towards
  - lower  $t_{\text{ign}}$
  - larger  $t_{\text{ign}}$ -error
 with increasing  $\tau$
- Non-monotonous local behavior



# A posteriori error estimation

For any quantity of interest  $\phi(\mathfrak{s}, \cdot)$ , define the trajectory error norm over time steps  $t_k : k = 1, \dots, K$ , with  $\mathfrak{s}_k = \tilde{s}(t_k)$ ,

$$\mathcal{E}_{\phi}^{p,w} = \frac{\|\phi - \phi_d\|_{p,w}}{\|\phi_d\|_{p,w}} = \frac{\left( \frac{1}{K} \sum_{k=1}^K w_k |\phi(\mathfrak{s}_k, \cdot) - \phi_d(\mathfrak{s}_k, \cdot)|^p \right)^{1/p}}{\left( \frac{1}{K} \sum_{k=1}^K w_k |\phi_d(\mathfrak{s}_k, \cdot)|^p \right)^{1/p}}$$

where

$\phi_d$  refers to the detailed model

$w_k = w(\mathfrak{s}_k)$  is a weight function e.g.  $w_k = 1$  or  $w_k = 1/\sigma_d(\mathfrak{s}_k)$



# A posteriori error estimation

Example quantities of interest for trajectory error estimation

- A per-trajectory error that is random

$$\phi(\mathfrak{s}, \lambda) := X_i(\mathfrak{s}, \lambda) \quad \Rightarrow \quad \mathcal{E}_{X_i}^{p,w}(\lambda; \tau, \theta)$$

- An error in the mean of uncertain trajectories

$$\phi(\mathfrak{s}) := \mu_i(\mathfrak{s}) = \mathbf{E}_\lambda[X_i(\mathfrak{s}, \lambda)] \quad \Rightarrow \quad \mathcal{E}_{\mu_i}^{p,w}(\tau, \theta)$$

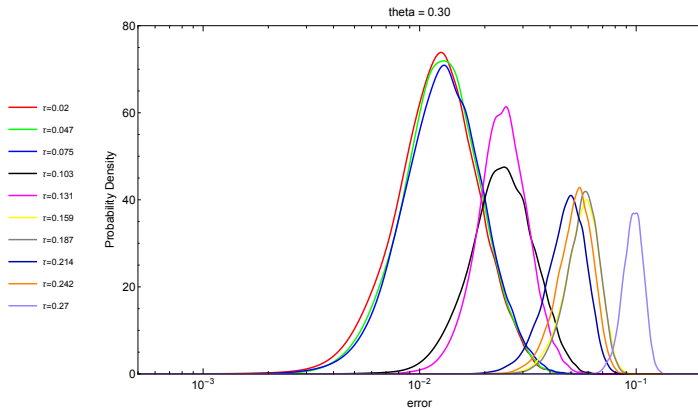
- An error in the standard deviation of uncertain trajectories

$$\phi(\mathfrak{s}) := \sigma_i(\mathfrak{s}) = (\mathbf{V}_\lambda[X_i(\mathfrak{s}, \lambda)])^{1/2} \quad \Rightarrow \quad \mathcal{E}_{\sigma_i}^{p,w}(\tau, \theta)$$

## Trajectory error statistics

$$p = 2, w = 1$$

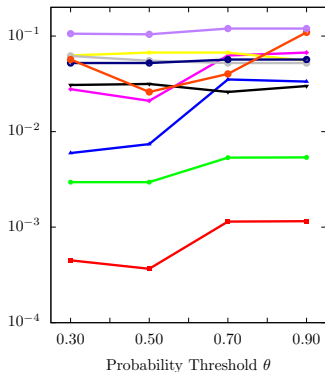
- PDF of trajectory error, averaged over target species,  $\theta = 0.30$



- PDF generally shifts towards larger errors with increasing  $\tau$
- Generally non-monotonic trend with variation in  $(\tau, \theta)$

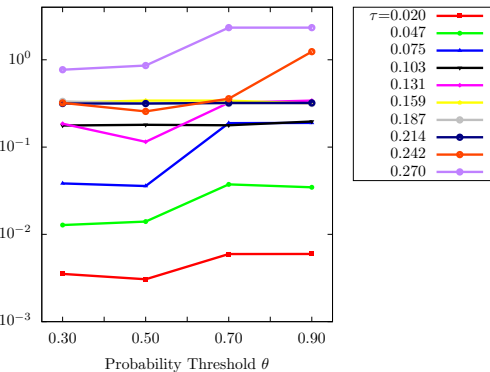
# Error in mean & stdv, avg on target species; $p = 2, w = 1$

$L_2$  Unweighted Error on Target Species Averages



Mean

$L_2$  Unweighted Error on Target Species Std Devs



Standard Deviation

- Non-monotonic trend towards higher error with increasing  $\tau, \theta$
- Trend is more evident at low  $\tau$

# Closure

- We presented a probabilistic framework for analysis and reduction of chemical models under uncertainty
- The construction employs the target problem and the deterministic analysis/reduction strategy as a black box
- We employ a convenient indexing of models
- We use *a posteriori* error norms for entropic phase space trajectories
- We demonstrated the construction with an uncertain n-butane mechanism
  - Monotonic trend towards smaller/simpler mechanisms with increasing  $(\tau, \theta)$  tolerances
  - Occasional non-monotonic behavior in *a posteriori* errors
    - consistent with deterministic CSP simplification