Global analysis of chemical kinetic mechanisms

22nd ICDERS, Minsk, July 27-31 2009

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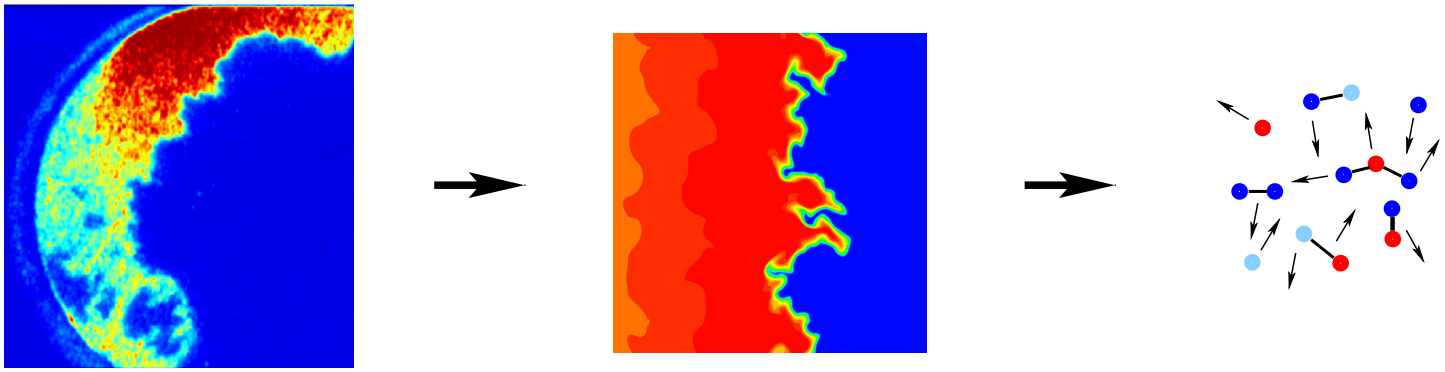


Introduction

- **Aim: Kinetic model formulation ⇔ Model order reduction**

  …the main purpose is mechanism analysis AND reduction of the system dimension…

- **Assumptions:**
  - Detailed model describes the considered phenomenon satisfactorily
  - Parametrical region of the system parameters is given
  - There are significantly different time scales present in the system

- **Result: Automatic model reduction strategy:**

  …in many engineering applications one would be interested to construct an appropriate tool, which has only moderate accuracy, but allows to calculate the reduced model in a very fast, efficient and robust way…

Methods overview

- **Lumping**

  …generated reaction scheme may still contain multiple scales and information about a specific component can be lost…

- **Sensitivity analysis**

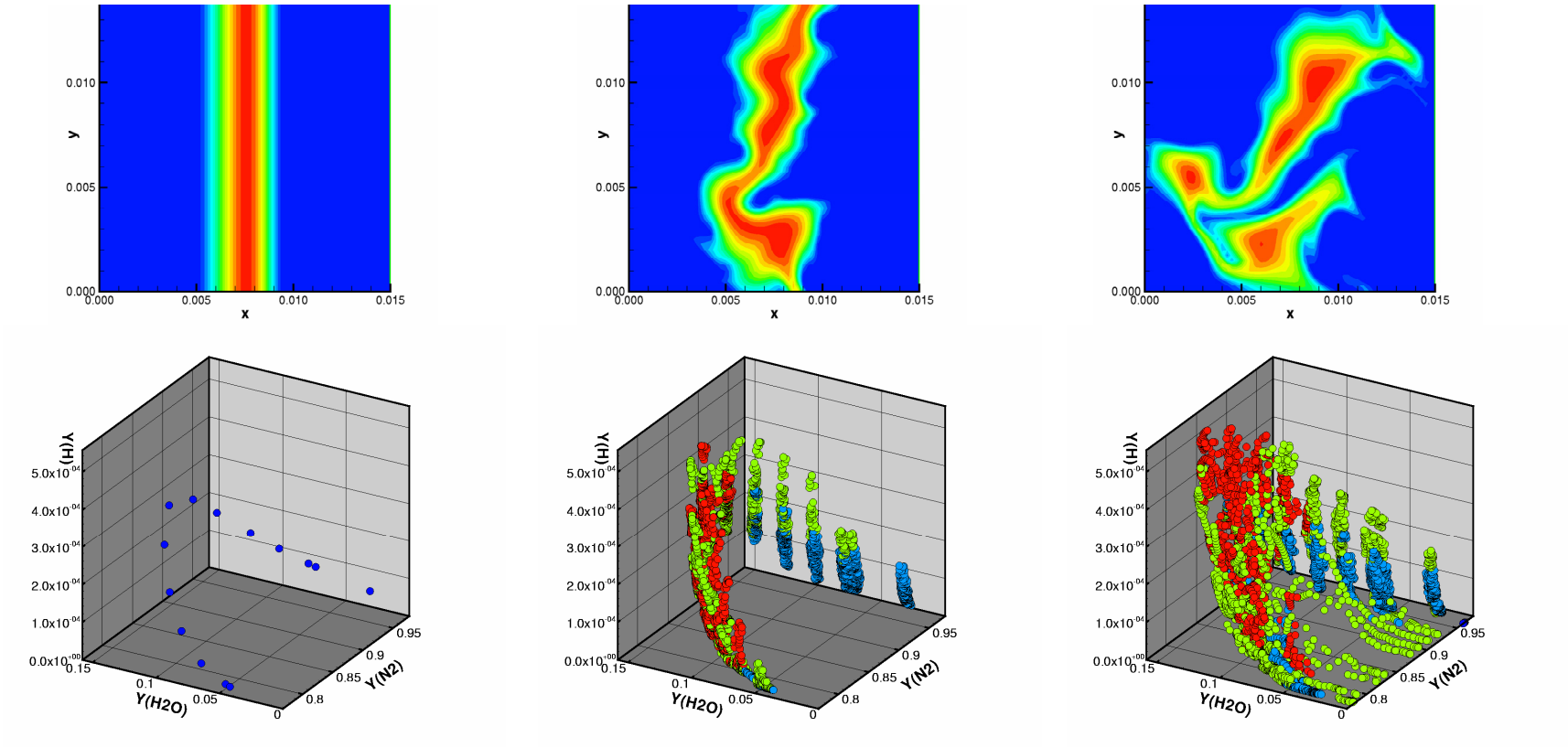
  …is feasible when the complete solution is known, because for given parametric regions it should be used for validation…

- **Time-scale analysis: CSP, ILDM, MIM, RCCE, QSSA, PE ..**

  …slow system dynamics is found while fast processes and their influence on reduced dynamics are neglected…

- **How can the information of detailed models be condensed to yield reduced models?**

Multi-scales phenomena: modeling

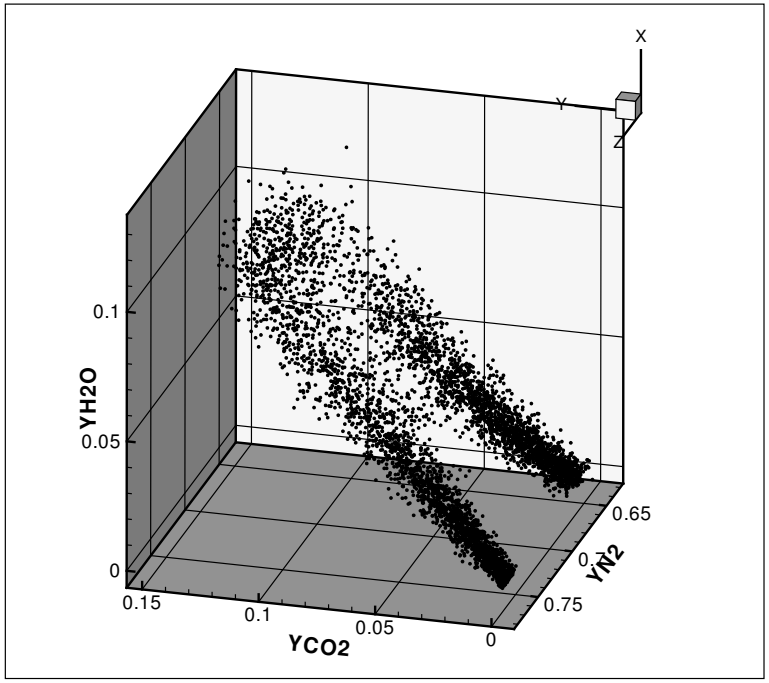


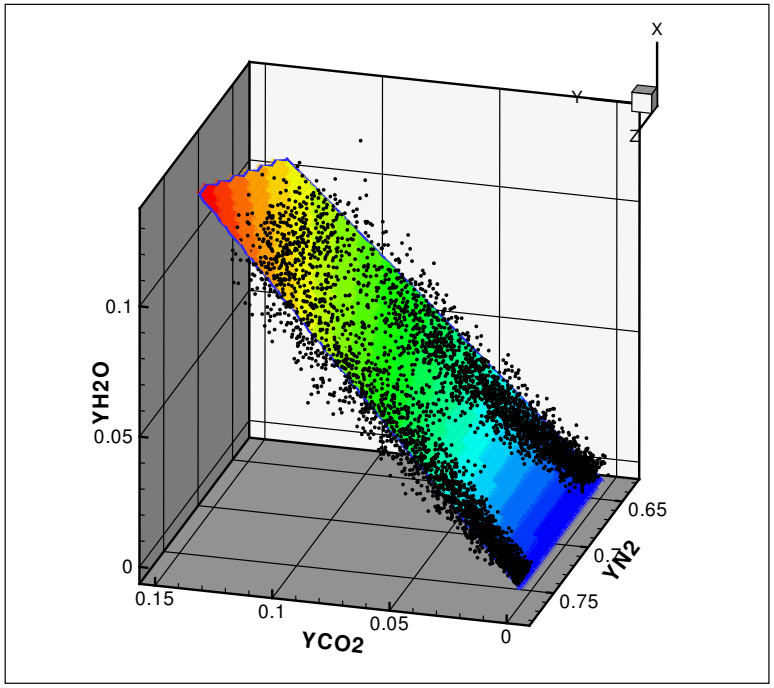
Maas & Thévenin 1998

- **DNS of a turbulent non-premixed hydrogen flame**
- **Only a small subspace is actually accessed**
- **In addition the accessed space is confined to low-dimensional manifolds**
- **Chemistry and transport cause the existence of low-dimensional attractors**

Multi-scales Phenomena: experiment

- **Methane-air diffusion flame**





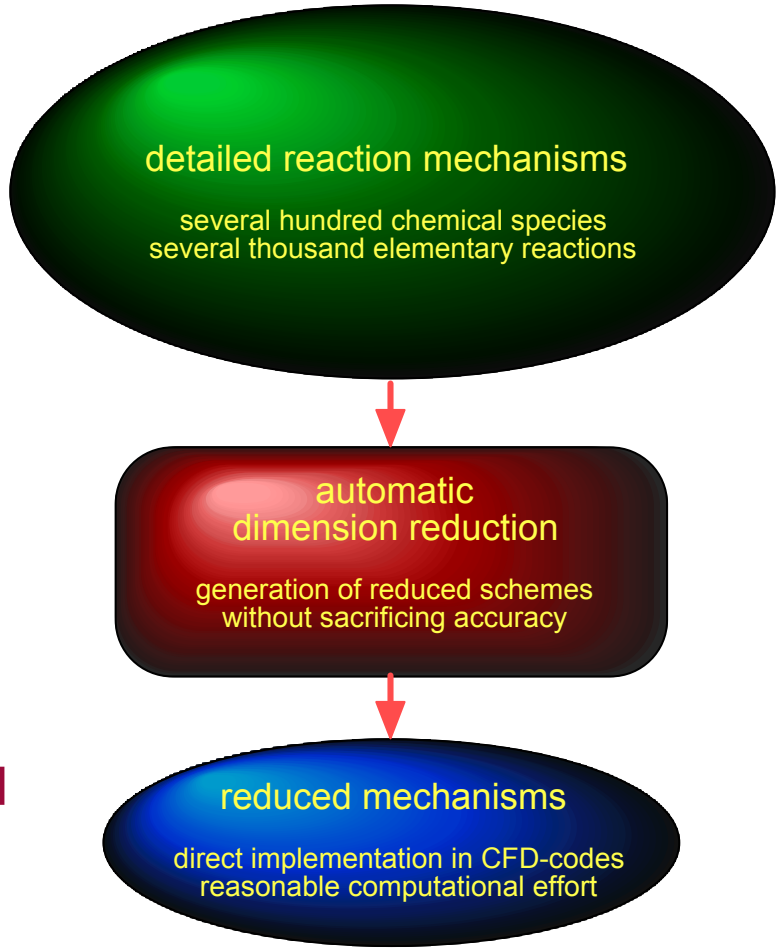
R. Schießl – ITT, Karlsruhe (TH)

R. Barlow und J. Frank - www.ca.sandia.gov/TNF

Model Analysis and Reduction

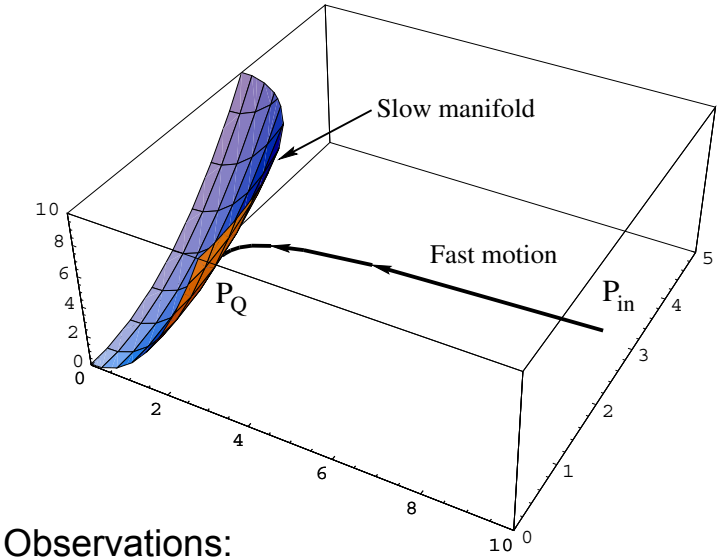
Fundamental questions:

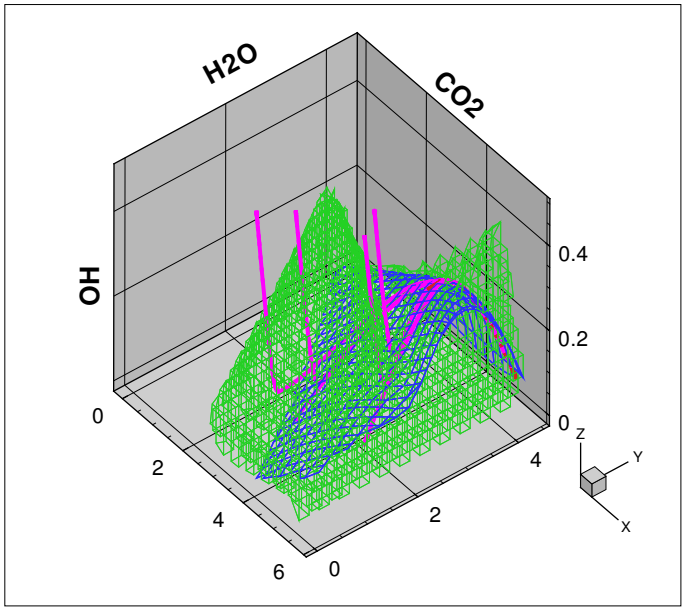
- **How much detail is needed for the description of the chemical kinetics?**
- **Does the chemical kinetics exhibit a hierarchical structure?**
- **IF YES: Is it possible to obtain an a-priori information about system's hierarchy and use it for modelling and mechanism analysis?**



Model reduction by decomposition

- …multi-scale phenomena…





- Observations:
  - **the system accesses only a small domain of the state space**
  - **it is relaxed along low dimensional manifolds onto a low dimensional manifold**

- Idea: Reduce the dimension of the system by using “fast” / “slow” invariant manifolds!

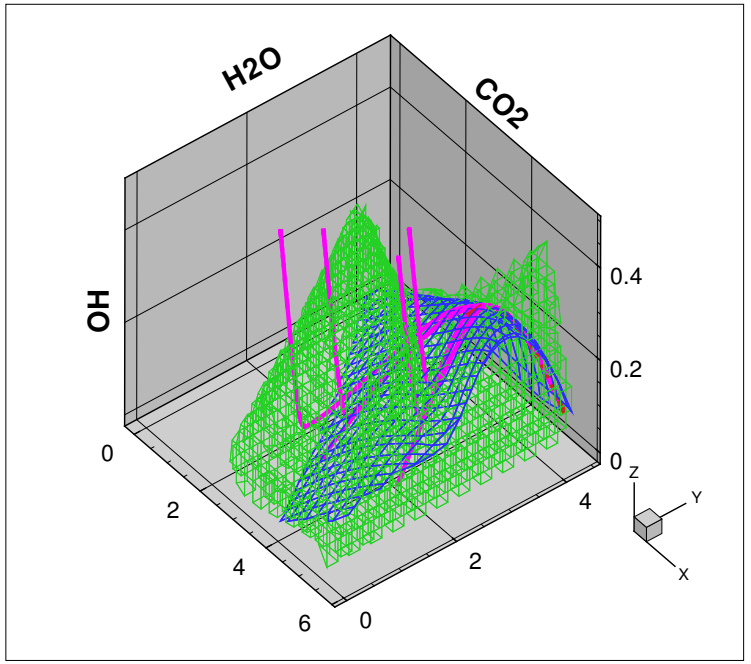
Global analysis - Reduced spaces

- **Pure homogenous ODE system**

$$\frac{d\psi}{dt} = F(\psi) \quad \Rightarrow \quad M = \{\psi : \Phi(\psi) = 0\}$$

$$M = \{\psi(\theta) : \Phi(\psi(\theta)) = 0\}$$

$$\dim(\theta) << \dim(\psi)$$



$CO\text{-}H_2\text{-}O_2$ homogeneous system

- The developed method defines the equation of the low-dimensional manifolds that describe accurately the system behavior in the state space!

- Reference: Bykov, Maas, Z. Phys. Chem., 223 (2009)

Global Quasi-linearization (GQL)

- **In a fixed domain we approximate the vector field by a linear map:**

$$T : \psi_i \mapsto \Phi(\psi_i)$$

$$\Phi^* = \begin{bmatrix} \Phi(\psi_1) \dots & \Phi(\psi_n) \\ \dots & \dots \dots \\ | & | \end{bmatrix}, \Psi = \begin{bmatrix} \psi_1 \dots & \psi_n \\ \dots & \dots \dots \\ | & | \end{bmatrix} \Rightarrow \boxed{T = \Phi^* \Psi^{-1}}$$

- **Invariant subspaces gives the decomposed form and manifolds equations:**

$$T = (Z_s \; Z_f) \begin{pmatrix} N_s & 0 \\ 0 & N_f \end{pmatrix} \begin{pmatrix} \tilde{Z}_s \\ \tilde{Z}_f \end{pmatrix} \rightarrow \varepsilon = \left(\frac{|\lambda_{m_s+1}(T)|}{|\lambda_{m_s}(T)|} \right)^{-1} \rightarrow \begin{cases} \Phi_s : \tilde{Z}_f F(\psi) = 0 \\ \\ \Phi_f : \tilde{Z}_s \psi = \tilde{Z}_s \psi_0 \end{cases}$$

"Global Quasi Linearization (GQL) for the automatic reduction of chemical kinetics"
by Bykov, Gol'dshtein, Maas, 2007

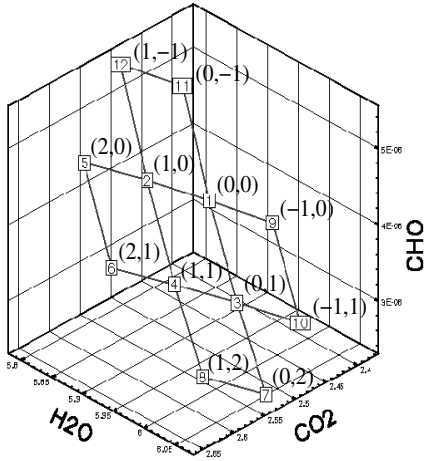
Generalized Coordinates

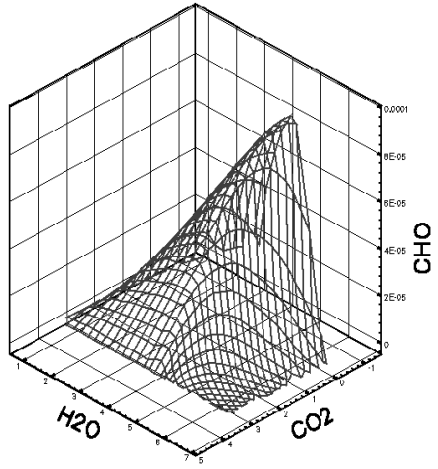
- **Manifold is parameterized and tabulated by indices of mesh points**

at any grid point we tabulate the state space with tangent subspace defined in this point:

$$M = \{\psi = \psi(\theta) : \Phi(\psi(\theta)) \equiv 0\}$$

$$\psi(\theta_0), \quad \psi_\theta(\theta_0)$$





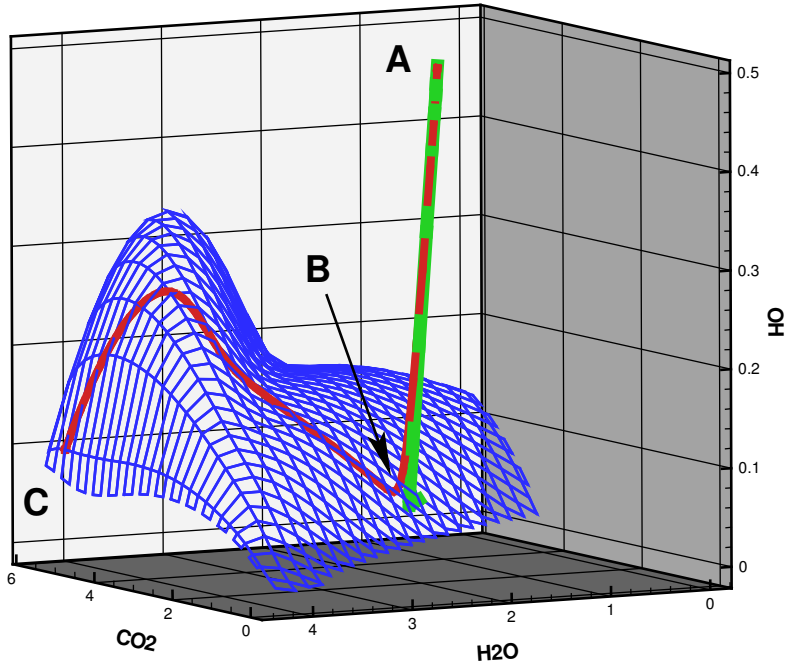
then, the system can be projected on the manifold by using normal subspace

$$\frac{\partial \theta}{\partial t} = S(\theta), \quad S(\theta) = \psi_\theta^+(\theta) F(\psi(\theta))$$

System projection and decomposition

$$\mathrm{Pr}_{TM} = Z_f \tilde{Z}_f$$

$$\begin{cases} \dfrac{d\psi}{dt} = Z_f \tilde{Z}_f F(\psi) \\ \tilde{Z}_s \psi = \tilde{Z}_s \psi_0 \end{cases}$$



$$\mathrm{Pr}_{TM^{\perp}} = Z_s \tilde{Z}_s$$

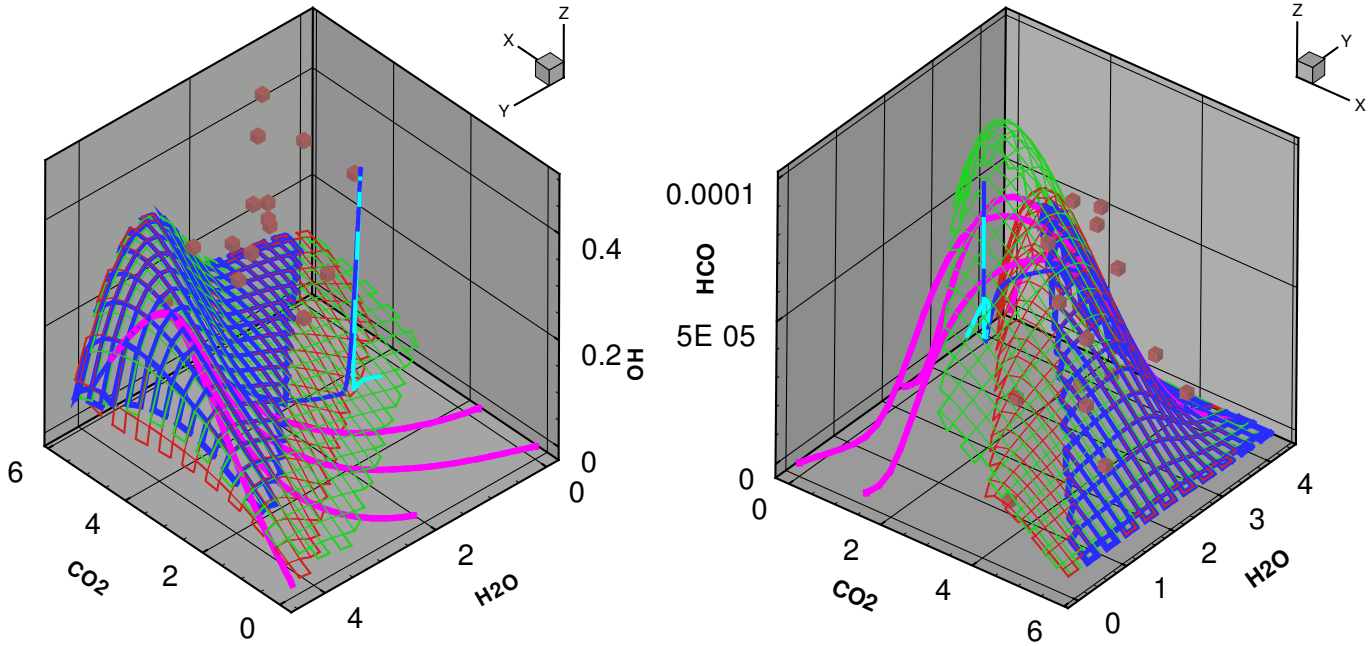
$$\begin{cases} \dfrac{d\psi}{dt} = Z_s \tilde{Z}_s F(\psi) \\ \tilde{Z}_f F(\psi) = 0 \end{cases}$$

- **Original coordinates can be used by the method due to available projections operators!**

- Reference: Bykov, Gol'dshtein, Maas, CTM, 12 (2), 389 – 405 (2008)

Stability analysis and high order approximations

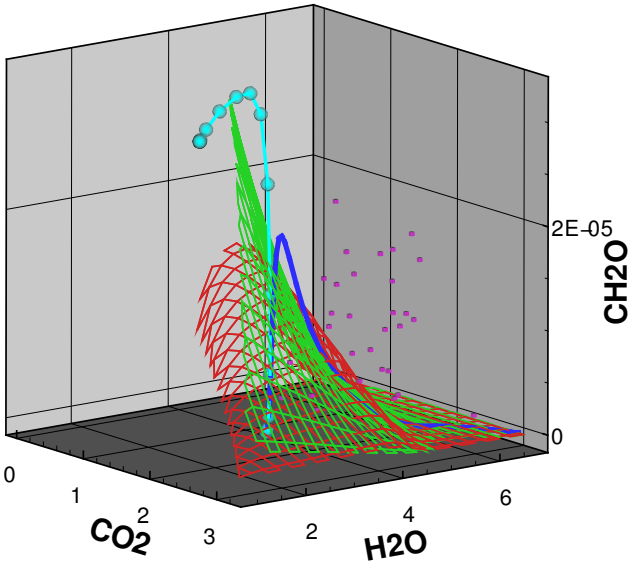
$$M_1 = \left\{\psi : \widetilde{Z}_f \, D_\psi F(\psi) F(\psi) = 0\right\}, \quad \mathrm{Re}\left(\lambda\left(\widetilde{Z}_f \, D_\psi F(\psi) Z_f\right)\right) < 0$$



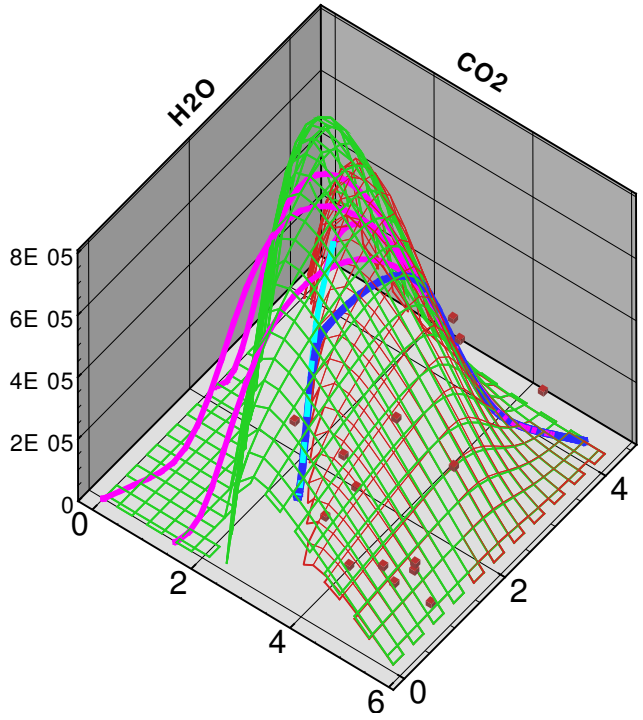
- **The properties of the system on the manifolds are available due to the explicit form of the equation!**

State space analysis

$$\begin{cases} \dfrac{d\psi}{dt} = Z_f \tilde{Z}_f F(\psi) \\ \tilde{Z}_s \psi = \tilde{Z}_s \psi_0 \end{cases}$$

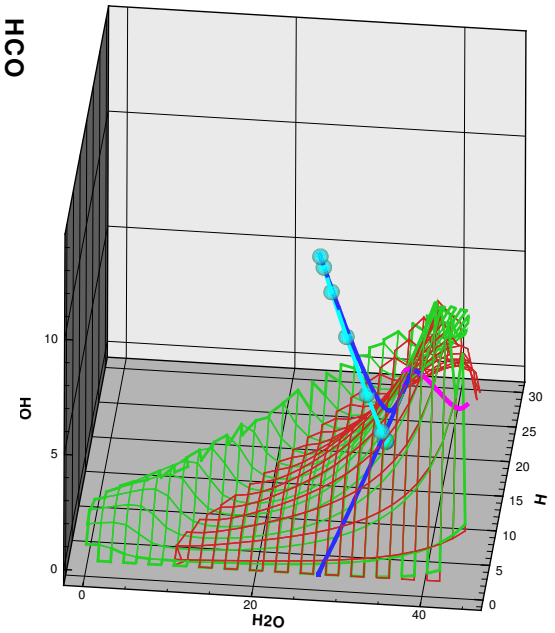


Projection of the state space of the Methane/Air system (n = 36)



Projection of the state space of the $CO\text{-}H_2\text{-}O_2$ system (n = 15)

$$\begin{cases} \dfrac{d\psi}{dt} = Z_s \tilde{Z}_s F(\psi) \\ \tilde{Z}_f F(\psi) = 0 \end{cases}$$



Hydrogen/Oxygen system (n = 10)

Toy problem – Lindemann model (1927)

- **Lindemann established the mechanism for uni-molecular reactions by introducing a third body M:**

$$? \quad A \rightarrow P \quad ?$$

$$\begin{cases} \dfrac{d[A]}{dt} = -k_1^+[A][M] + k_1^-[M][A^*] \\ \dfrac{d[A^*]}{dt} = k_1^+[A][M] - k_1^-[M][A^*] - k_2^+[A^*] \\ \dfrac{d[P]}{dt} = k_2^+[A^*] \end{cases}$$

$$A + M \rightleftarrows A^* + M$$

$$A^* \rightarrow P$$

… rate limiting second step …

$$k_1^+ = k_1^-$$

$$\varepsilon = k_2^+ / k_1^+ << 1$$

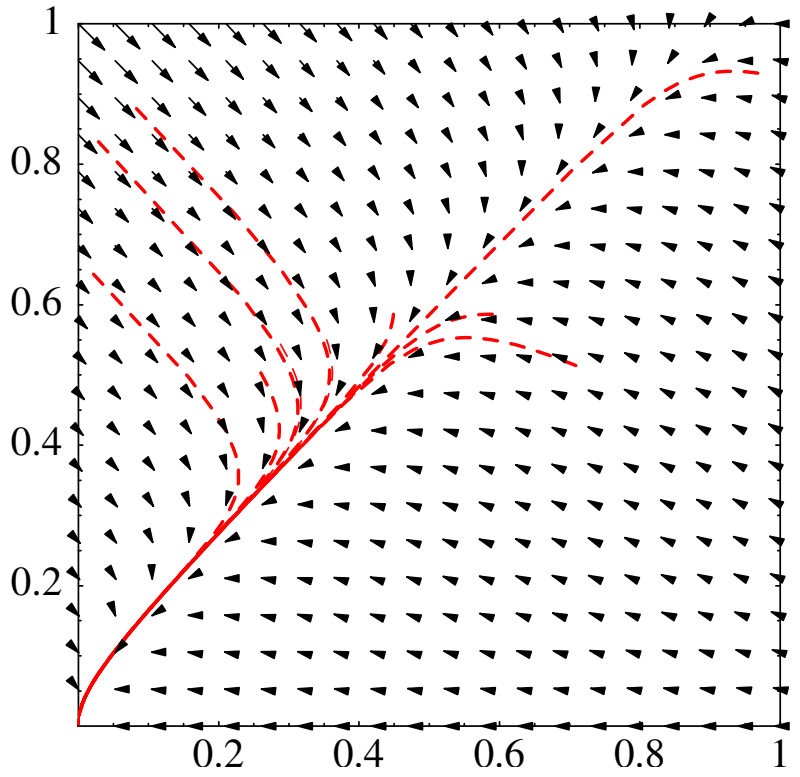
$$\begin{cases} \dfrac{dx}{d\tau} = \dfrac{1}{\varepsilon} y(y-x) - x \\ \dfrac{dy}{d\tau} = -\dfrac{1}{\varepsilon} y(y-x) \end{cases}$$

The system has a small parameter thus a conventional Singularly Perturbed System (SPS) Method can be efficiently implemented for system analysis!

State space – Lindemann model

- **(x,y) state space of the Lindemann model**

$$\begin{cases} \dfrac{dx}{d\tau} = \dfrac{1}{\varepsilon} y(y-x) - x \\ \dfrac{dy}{d\tau} = -\dfrac{1}{\varepsilon} y(y-x) \end{cases}$$

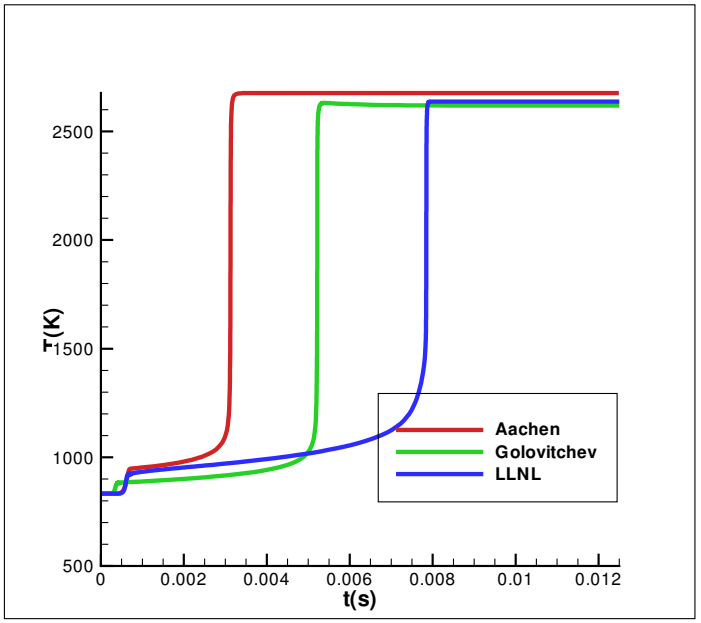


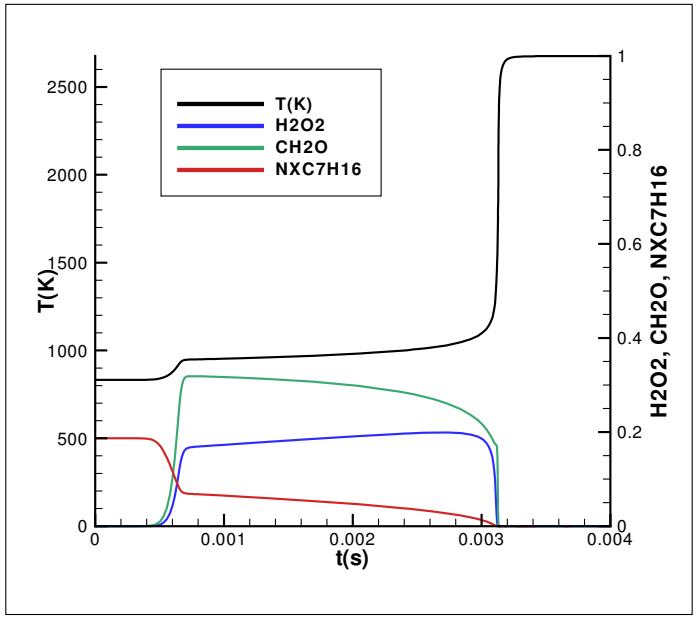
Vector field, epsilon = 0.2

The slow/fast manifolds (slow/fast motions) are developed in the state space!

Auto-ignition problem

- **n-heptane combustion system**



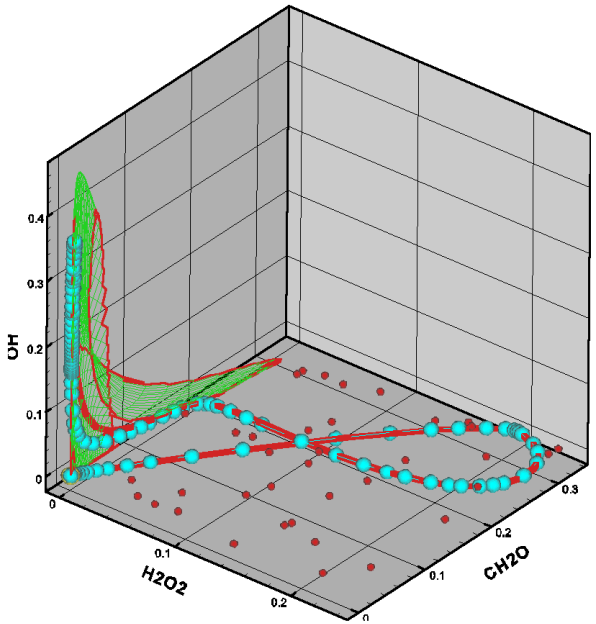


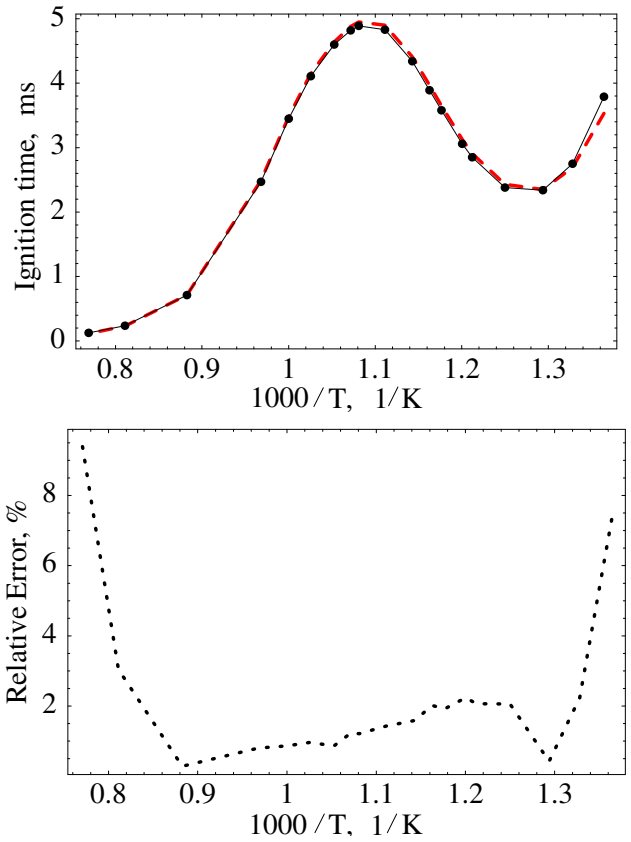
- LLNL – n = 159
- Golovitchev – n = 56
- Peters (Aachen) – n = 37

Typical time histories

GQL for the ignition problem

- red curve: detailed solution
- green mesh: 2D GQL manifold
- red cubes: reference set
- spheres: reduced solution





Temperature dependence of the ignition delay time.
circles: reduced model (m_s = 14)
red dashed curve: detailed model (n = 37)

Summary

The suggested method of the mechanism hierarchy analysis allows at the same time

- **Check the system hierarchy!**
- **Estimate the reduced dimensions!**
- **Approximate the reduced manifolds!**
- **Decompose the system!**

Acknowledgments:

- Financial support by the Deutsche Forschungsgemeinschaft SFB 606 and SPP 1276 is gratefully acknowledged.

Thank you for your attention!

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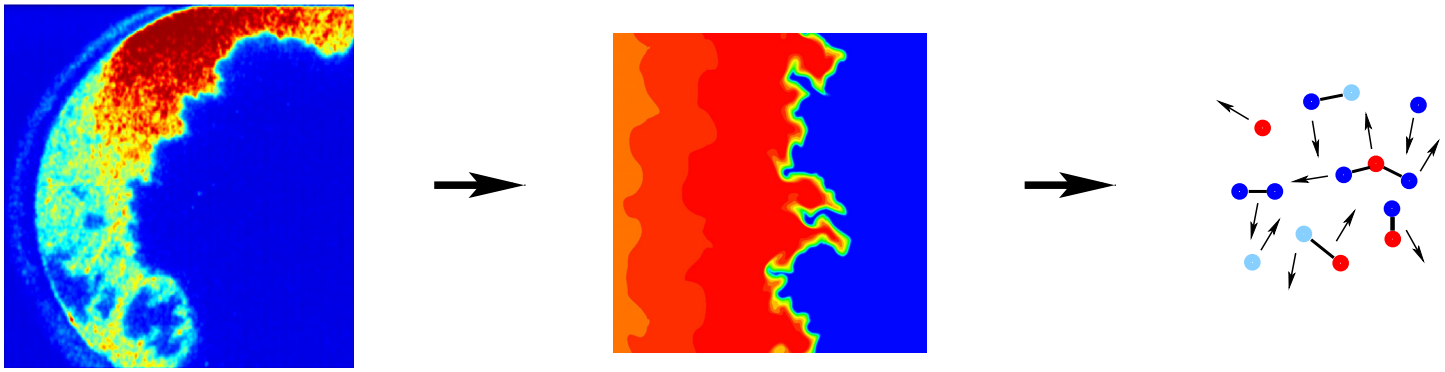
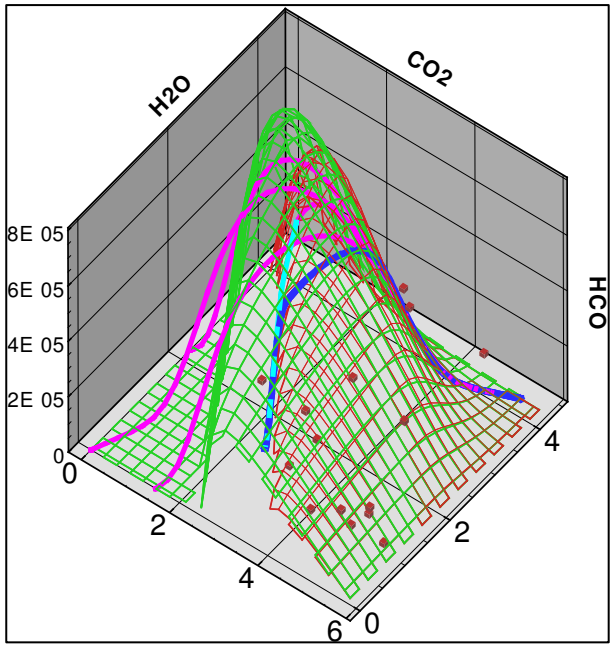


Coupling with transport - REDIM

- **Projection onto different spaces of species mole numbers**



Projection of the state space of the CO-H_2-O_2 system - laminar reaction wave

- **Stationary solutions for different fresh mixtures having the same element composition and enthalpy!**