



# **Lesson 14: Some comments about Numerics and Mechanism Reduction**

Slides from Prof. Tianfeng Lu

University of Connecticut

Email: [tianfeng.lu@uconn.edu](mailto:tianfeng.lu@uconn.edu)



# Need Detailed Kinetics: not simple!!

## Example: $\text{H}_2\text{-O}_2$ Chemistry

Species:  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , (Major species);  $\text{H}$ ,  $\text{O}$ ,  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$  (Radicals)

### No. Reactions

#### $\text{H}_2\text{-O}_2$ Chain Reactions

- (1)  $\text{H} + \text{O}_2 = \text{O} + \text{OH}$
- (2)  $\text{O} + \text{H}_2 = \text{H} + \text{OH}$
- (3)  $\text{OH} + \text{H}_2 = \text{H} + \text{H}_2\text{O}$
- (4)  $\text{O} + \text{H}_2\text{O} = \text{OH} + \text{OH}$

#### $\text{H}_2\text{-O}_2$ Dissociation/Recombination

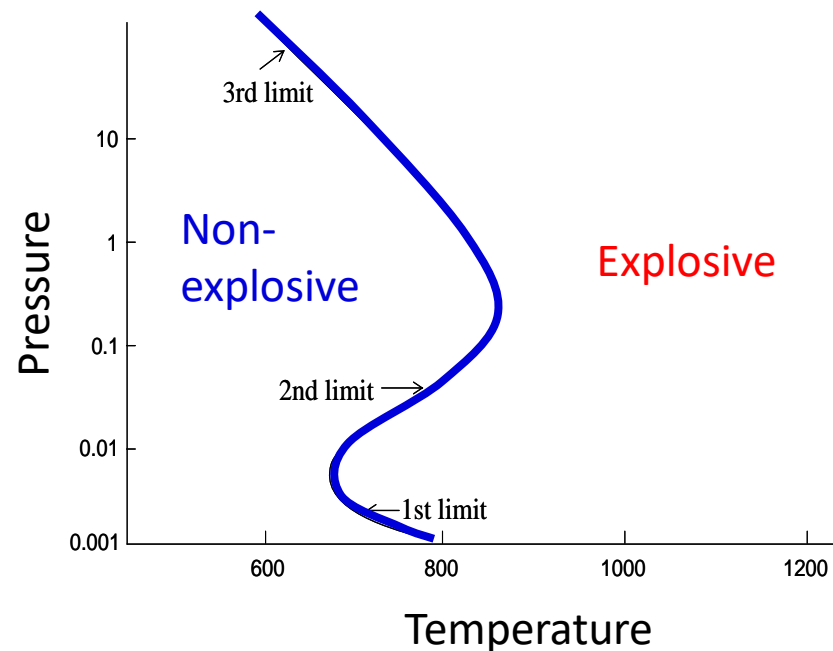
- (5)  $\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$
- (6)  $\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$
- (7)  $\text{O} + \text{H} + \text{M} = \text{OH} + \text{M}$
- (8)  $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$

#### Formation and Consumption of $\text{HO}_2$

- (9)  $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$
- (10)  $\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$
- (11)  $\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$
- (12)  $\text{HO}_2 + \text{O} = \text{OH} + \text{O}_2$
- (13)  $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$

#### Formation and Consumption of $\text{H}_2\text{O}_2$

- (14)  $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$
- (15)  $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$
- (16)  $\text{H}_2\text{O}_2 + \text{H} = \text{H}_2\text{O} + \text{OH}$
- (17)  $\text{H}_2\text{O}_2 + \text{H} = \text{H}_2 + \text{HO}_2$
- (18)  $\text{H}_2\text{O}_2 + \text{O} = \text{OH} + \text{HO}_2$
- (19)  $\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$



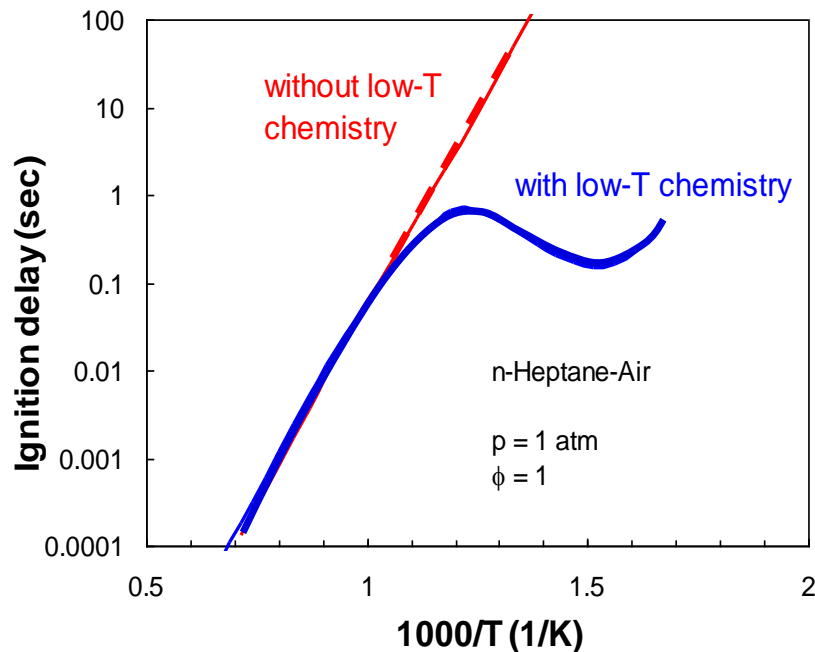
Detailed chemistry are crucial for:  
Ignition, extinction, instabilities ...



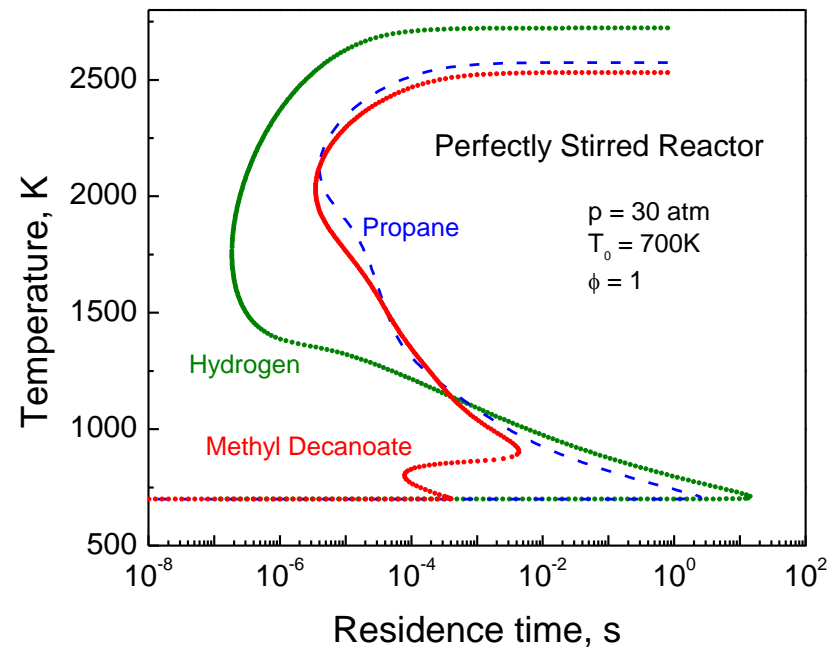
# Need Realistic Chemistry for Each Fuel and Reaction Condition

- Fuel chemistry substantially affects flame dynamics
- Accurate chemical kinetics needed to **predict** flame behaviors

Ex1: Negative Temperature Coefficients (NTC)

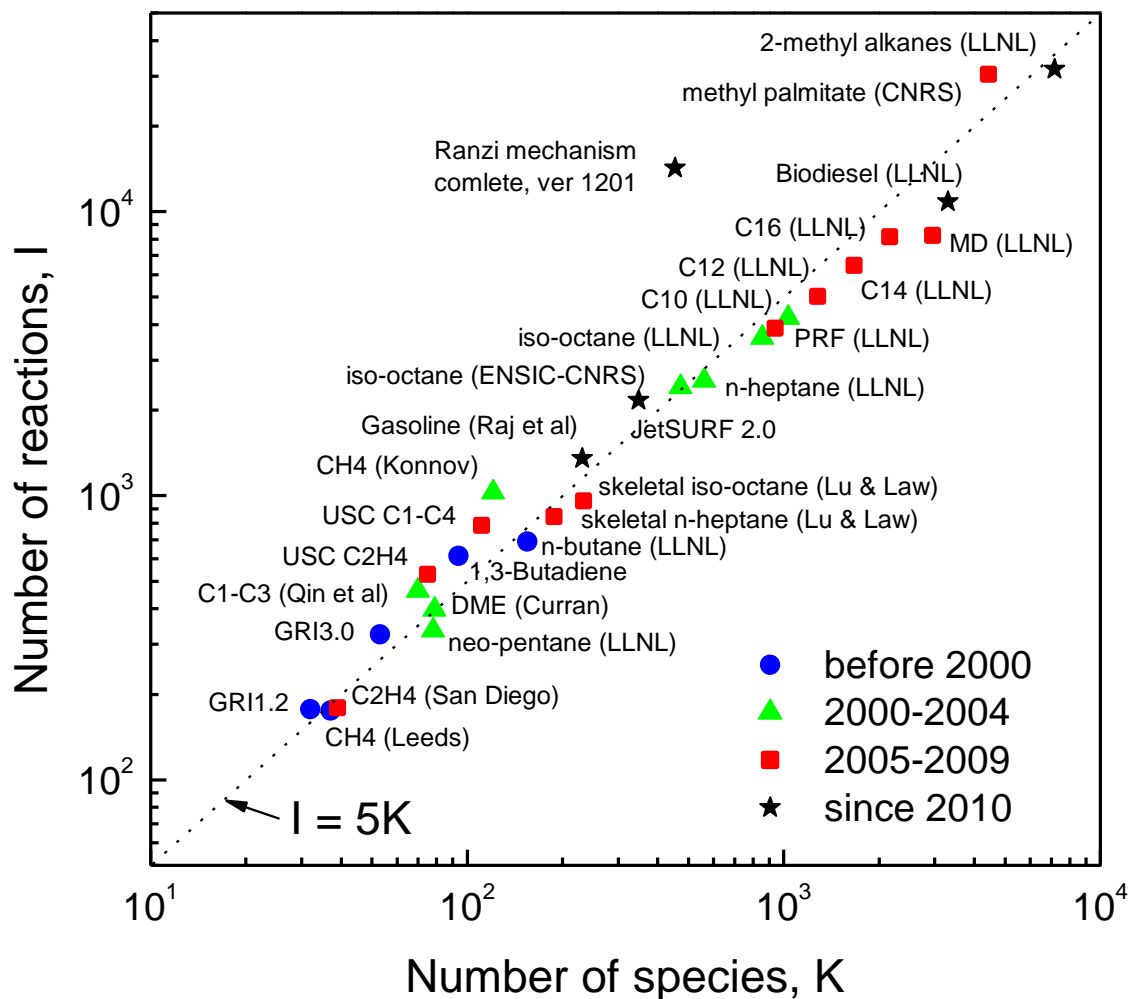


Ex2: Combustion "S"-curves





# Scaling of Detailed Chemistry



(Lu & Law, PECS 2009)

- Detailed mechanisms are large
- Transportation fuels:  
 $\sim 10^3$  species  
 $\sim 10^4$  reactions
- Flame simulations with detailed chemistry are time-consuming or unaffordable
- The excessive output data renders it difficult to identify the controlling physicochemical processes



# Identification of Important Pathways

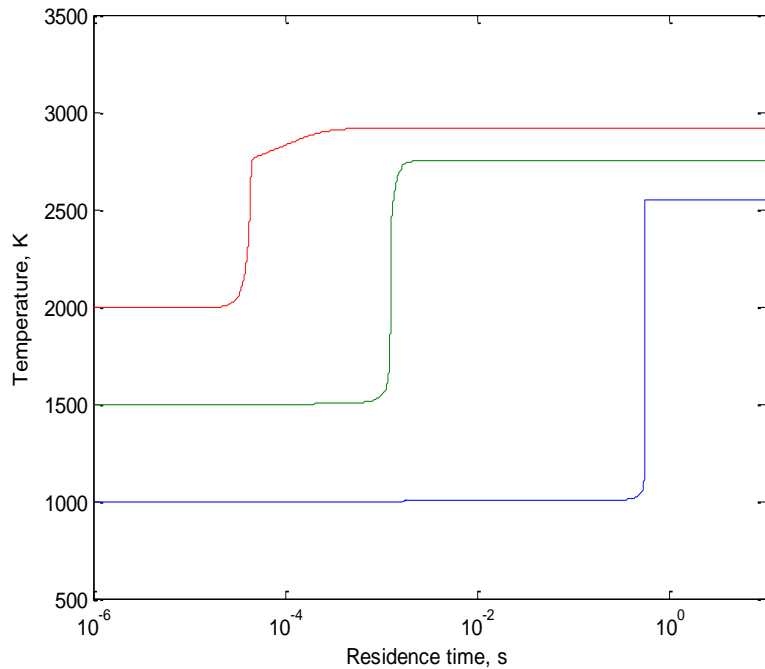
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- Reaction rates are determined by temperature and species concentrations (T, C), i.e. local reaction states
- Different reaction pathways are controlling at different reaction conditions. So model that works well at one reaction condition can be very wrong at some other condition.
- Any mechanism reduction is specific to a target set of reaction conditions, and also user's error tolerances
  - Important reactions cannot be identified without concentration information (e.g. fuel rich is really different from fuel lean!)
  - Reaction state sampling from representative reactors is required for reduction. Finding a good model is an iterative process.
- Reactors for reaction state sampling
  - Auto-ignition
  - Perfectly stirred reactors (PSR)
  - 1-D laminar flames
  - Turbulent flames?

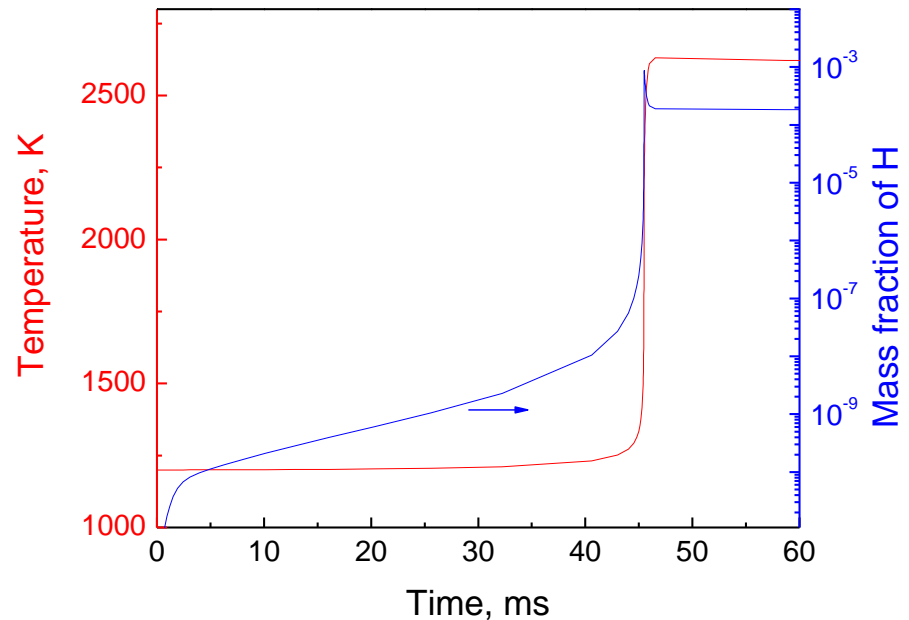


# Sampling from Auto-ignition

Methane-air,  $\phi = 1.0$ ,  $p = 1$  atm



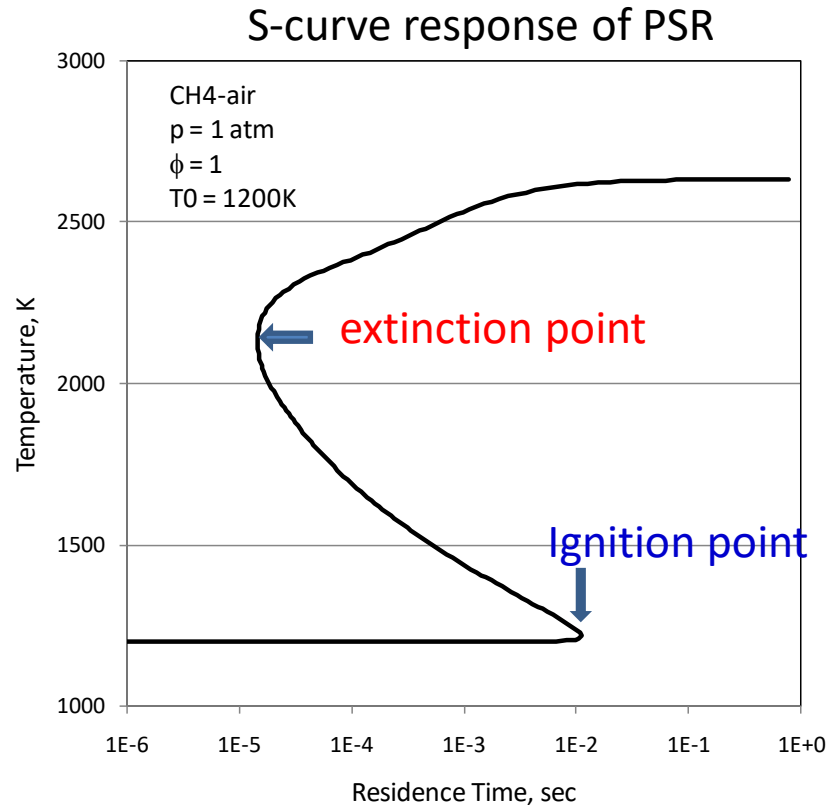
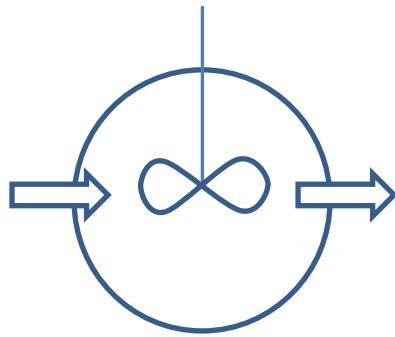
Methane-air,  
 $\phi = 1.0$ ,  $p = 1$  atm,  $T_0 = 1200$  K



- Auto-ignition typically involves radical explosion and thermal runaway stages
- The radical explosion is slow (in milliseconds), and typically dominates ignition delay time
- Thermal runaway is typically much faster (in microseconds)
- Radical explosion stage can be bypassed in (laminar and turbulent) flames for fast burning
- Sample reaction states from auto-ignition are representative for ignition chemistry, important for compression ignition engines, detonation waves etc.



# Sampling from PSR



- PSR and other continuous flow reactors feature S-curve responses
- The turning points are corresponding to extinction and ignition states
- The extinction state is determined by how fast chemistry can be
- The states from the upper and middle branches are representative to flame chemistry, important for spark ignition engines, jet engines, flame holding etc.



# Numerical Solution of Multi-Dimensional Flows

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- Transport equations of reactive scalars

$$\frac{DY}{Dt} = \frac{\partial Y}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{Y} = \dot{\omega} + \nabla \cdot (\rho \mathbf{D} \nabla \mathbf{Y}) + \dots$$

$\mathbf{Y}$ : vector of dependent variables, e.g. T and species concentrations

$\mathbf{V}$ : velocity,  $\dot{\omega}_\phi$ : chemical source term,  $D_\phi$ : diffusivity

- Discretization

- Time derivative is typically approximated by finite difference involving the current and future values
- The gradient and divergence operators are typically approximated with linear functions involving multiple neighboring cells
- Subgrid modeling is needed if nontrivial structures are present within a single grid/cell, e.g. in large eddy simulations (LES)
- No subgrid models are needed if the structure of  $\phi$  is fully resolved by the mesh grid, e.g. in direct numerical simulations (DNS)





# Limiting Factors for Solving the Reactive Scalars

- Considering the time integration of a stiff reacting system

$$\frac{dY}{dt} = \mathbf{g}(Y) = \mathbf{C}(Y) + \mathbf{D}(Y) + \boldsymbol{\omega}(Y)$$

$\mathbf{C}(Y)$ : convection term;  $\mathbf{D}(Y)$ : diffusion term;  $\boldsymbol{\omega}(Y)$ : reaction term

- The  $Y$  vector includes all the variables (T, species concentrations) on all the grid points:
  - Total number of variables to be solved: (# of mesh) × (# of species + 5)
  - Typically too large to solve with fully implicit methods, limited by evaluation, storage and factorization of the Jacobian
  - Fully explicit solvers have to use small time steps, limited by the shortest of
    - Convective timescale,  $\Delta/V$  for incompressible flows, and  $\Delta/a$  for compressible flows – the CFL condition ( $\Delta$ : grid size,  $a$ : speed of sound)
    - Diffusion timescale,  $\Delta^2/D$
    - The shortest species timescale
  - Solution of transport (diffusion and convection) is frequently decoupled from solution of chemistry in practical CFD, e.g. in the splitting schemes



# The Strang Splitting Scheme

- Spatially discretized governing equations

$$\frac{d\Phi}{dt} = \mathcal{S}(\Phi) + \mathcal{T}(\Phi), \quad \mathcal{S}: \text{chemical}, \mathcal{T}: \text{transport}$$

- Chemistry and transport substeps:

$$\begin{aligned} \frac{d\Phi}{dt} &= \mathcal{S}(\Phi^{(1)}), & \Phi^{(1)}(x, 0) &= \Phi(x, t_n) \text{ on } [t_n, t_n + \Delta t/2] \\ \frac{d\Phi}{dt} &= \mathcal{T}(\Phi^{(2)}), & \Phi^{(2)}(x, 0) &= \Phi^{(1)}(x, \Delta t/2) \text{ on } [t_n, t_n + \Delta t] \\ \frac{d\Phi}{dt} &= \mathcal{S}(\Phi^{(3)}), & \Phi^{(3)}(x, 0) &= \Phi^{(2)}(x, \Delta t) \text{ on } [t_n + \Delta t/2, t_n + \Delta t] \end{aligned}$$

- Transport is relatively linear and has highly structured Jacobian, with weak coupling between species. Special solvers take advantage.
- Chemistry is highly nonlinear and typically solved implicitly. Chemistry terms are Local, so each mesh volume can be solved independently (e.g. **in parallel**)
- Splitting schemes introduce numerical errors and sometimes numerical instabilities. Each splitting scheme has different pros and cons. See e.g. Speth et al. *SIAM J. Numerical Analysis* 51, 3084 (2013)



# ODE Form of the Chemistry Equations

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- Considering the time integration of a stiff reacting system

$$\frac{d\mathbf{Y}}{dt} = \mathbf{g}(\mathbf{Y}) \quad \mathbf{y}: \text{vector of dependent variables, e.g. T and species concentrations}$$

$$\frac{\mathbf{Y}^{n+1} - \mathbf{Y}^n}{h} \approx \mathbf{g}(\mathbf{Y}^{n+1})$$

$$\mathbf{F}(\mathbf{Y}^{n+1}) = \mathbf{Y}^{n+1} - h\mathbf{g}(\mathbf{Y}^{n+1}) - \mathbf{Y}^n = 0$$

$$0 = F(\mathbf{Y}^{n+1}) \approx \frac{\partial F}{\partial \mathbf{Y}} (\mathbf{Y}^{n+1} - \mathbf{Y}^n) + F(\bar{\mathbf{Y}})$$

$$\mathbf{J}(\mathbf{Y}^{n+1} - \mathbf{Y}^n) + F(\mathbf{Y}^n) = 0$$

- Each implicit integration step involves
  - Evaluation of the source terms
  - Jacobian evaluation and factorization, solving linear equations



# The Time Complexity of Chemistry Solvers

- Time complexity of major components:
  - **Chemistry**:  $\sim I \sim 5K$  (I: # of reactions, K: # of species)
  - **Chemistry Jacobian** (brute force):  $\sim KI \sim 5K^2$
  - **Diffusion** (mixture average):  $\sim K^2/2$
- Reducing K and I is an obvious approach to accelerate combustion simulations – mechanism reduction
- Implicit solvers (Jacobian, chemistry, diffusion)
  - Time steps typically limited by the CFL condition
  - $t_{\text{imp}} \sim KI + I + K^2/2 \sim 10K^2 + 10K + K^2$
  - Most effective acceleration approaches: analytic Jacobian, sparse Jacobian techniques, reduced diffusion models
- Explicit solvers (chemistry, diffusion)
  - Time steps limited by the shortest chemical timescale
  - $t_{\text{exp}} \sim I + K^2/2 \sim 10K + K^2$
  - Most effective acceleration approaches: chemical stiffness removal, reduced diffusion models



# The Chemical Jacobian

- Needed in Newton solvers for steady state systems (e.g. PREMIX), and implicit integration solvers
- **Jacobian evaluation and factorization is the most expensive step in many combustion simulations**

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y})$$

$\mathbf{y}$ : vector of variables, e.g. species concentration

$$\frac{d\mathbf{g}}{dt} = \mathbf{J} \cdot \mathbf{g}(\mathbf{y}),$$

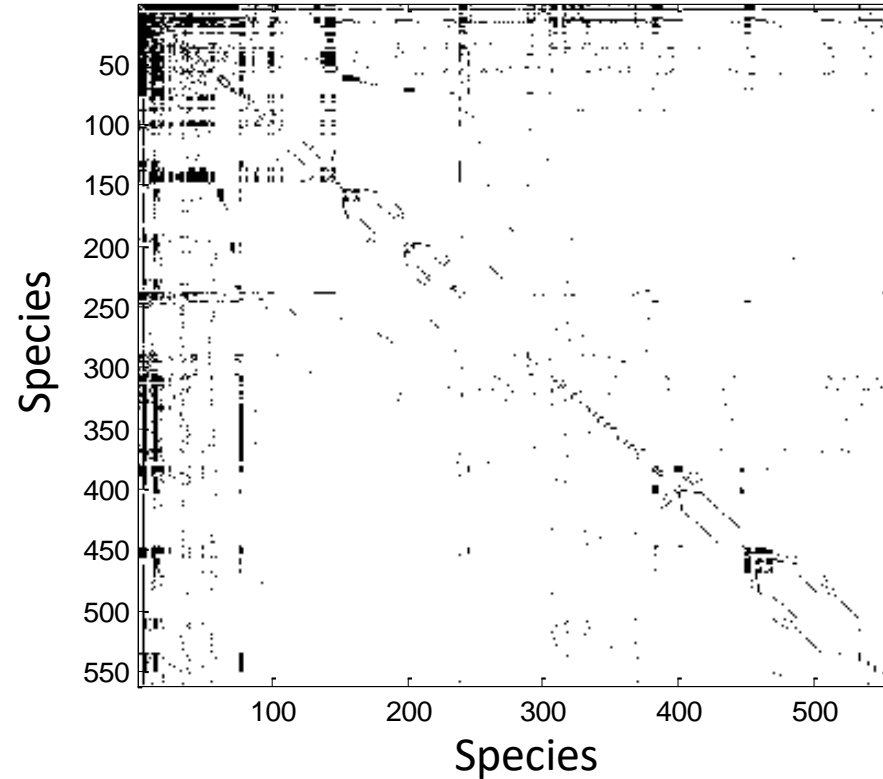
$$\mathbf{J} = \frac{d\mathbf{g}}{d\mathbf{y}}$$

$$\mathbf{J} = \begin{bmatrix} \frac{\partial g_1}{\partial y_1} & \frac{\partial g_1}{\partial y_2} & \dots & \frac{\partial g_1}{\partial y_n} \\ \frac{\partial g_2}{\partial y_1} & \frac{\partial g_2}{\partial y_2} & \dots & \frac{\partial g_2}{\partial y_n} \\ \dots & \dots & \dots & \dots \\ \frac{\partial g_n}{\partial y_1} & \frac{\partial g_n}{\partial y_2} & \dots & \frac{\partial g_n}{\partial y_n} \end{bmatrix}$$

# Sparse Species Couplings in Detailed Chemistry



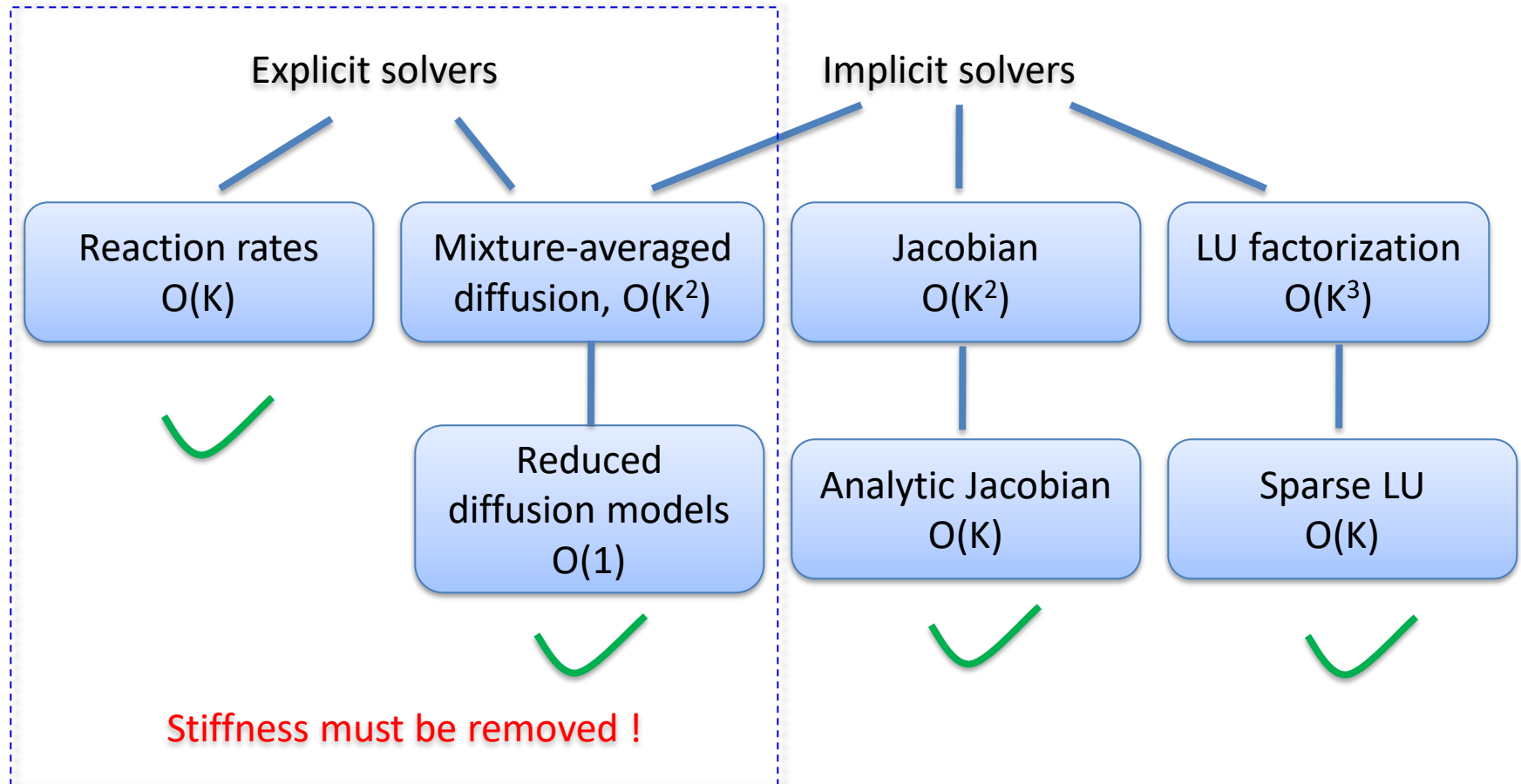
n-heptane  
(LLNL, 561 species)



Black pixel: a pair of directly coupled species,  
appearing together in any reaction



# Advanced Chemistry Solvers



- Both implicit and explicit solvers can achieve linear scaling, i.e.  $O(K)$ , for computational cost. But  $K$  is so large! Often need to remove species to make it practical to solve the reacting flow simulation: **Model Reduction**



# Many Approaches for Mechanism Reduction

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- Skeletal reduction
  - Sensitivity analysis
  - Principal component analysis
  - Graph based methods, e.g. direct relation graph (DRG)
- Timescale based reduction
  - Quasi steady state approximations (QSSA)
  - Partial equilibrium approximations
  - Rate controlled constrained equilibrium
  - Intrinsic low dimensional manifold (ILDM)
  - Computational singular perturbation (CSP)
  - ...
- HyChem
- Other methods
  - Tabulation, e.g. in situ adaptive tabulation
  - Optimization
  - Solver techniques
  - ...





# Usually don't know the error introduced by model reduction

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- There have been several attempts to try to control the errors introduced by model reduction.
- In special cases one can derive error bounds, e.g. see papers by Oluwole.
- Ultimately, we need a way to adaptively change the model reduction as we solve the reacting flow simulation, to have automatic error control.
  - This is not routine today. Tricky to re-introduce species that were previously eliminated
- Several ways to adapt either the model structure, or which species in the model are being integrated, see e.g. Gao et al., *Combust. Flame* 2015; Xu et al., *Combust. Flame* 2016



# Dynamic Chemical Stiffness Removal (DCSR) (Lu et al, CNF 2009)

- Mechanisms are still stiff after skeletal reduction & global QSSA
- Implicit solvers needed for stiff chemistry
  - Cost in evaluation of Jacobian  $\sim O(K^2)$
  - Cost in factorization of Jacobian  $\sim O(K^3)$
- Idea of DCSR
  - Chemical stiffness induced by fast reactions
  - Fast reactions results in either QSSA or PEA, Classified *a priori* Analytically solved on-the-fly
- Explicit solver can be used after DCSR
  - Time step limited by CFL condition
  - Cost of DNS:  $\sim O(K)$
- Typically applicable to compressible flows with time steps  $< \sim 20$  ns

