TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2024 SUMMER SCHOOL ON COMBUSTION

Mechanism Reduction and Computational Flame Diagnostics

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Model Reduction and Computational Flame Diagnostics

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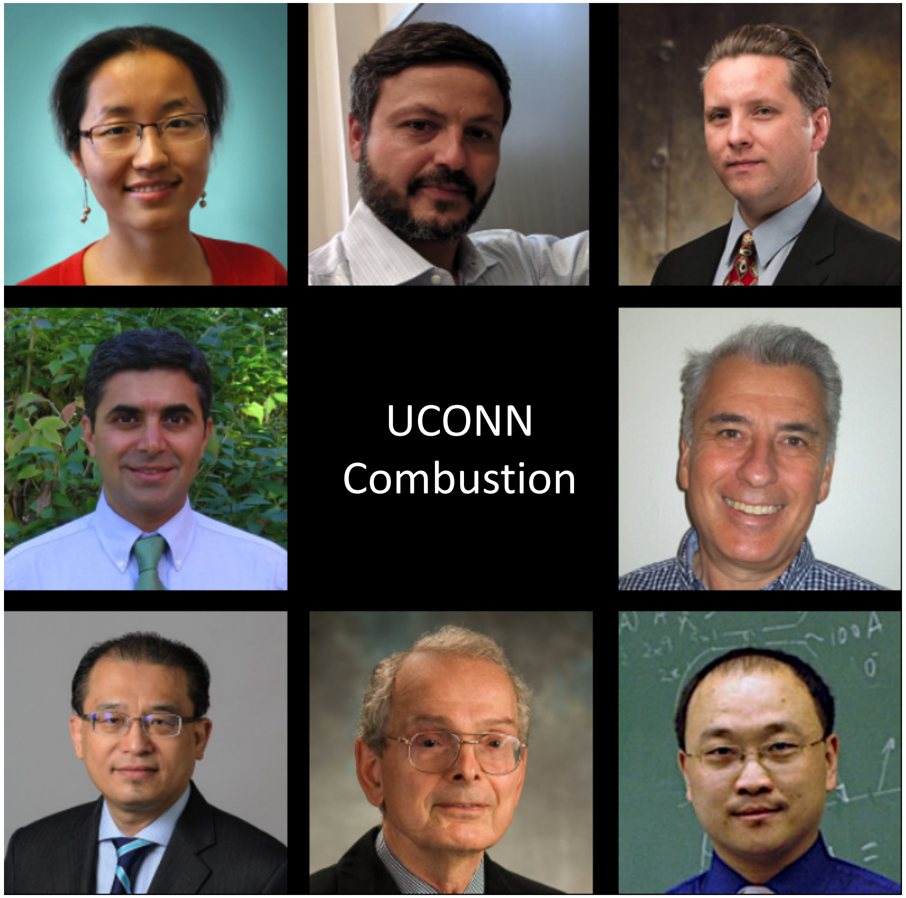
About UCONN



UCONN
Combustion

About UCONN

US Energy Source: Importance of Combustion Energy

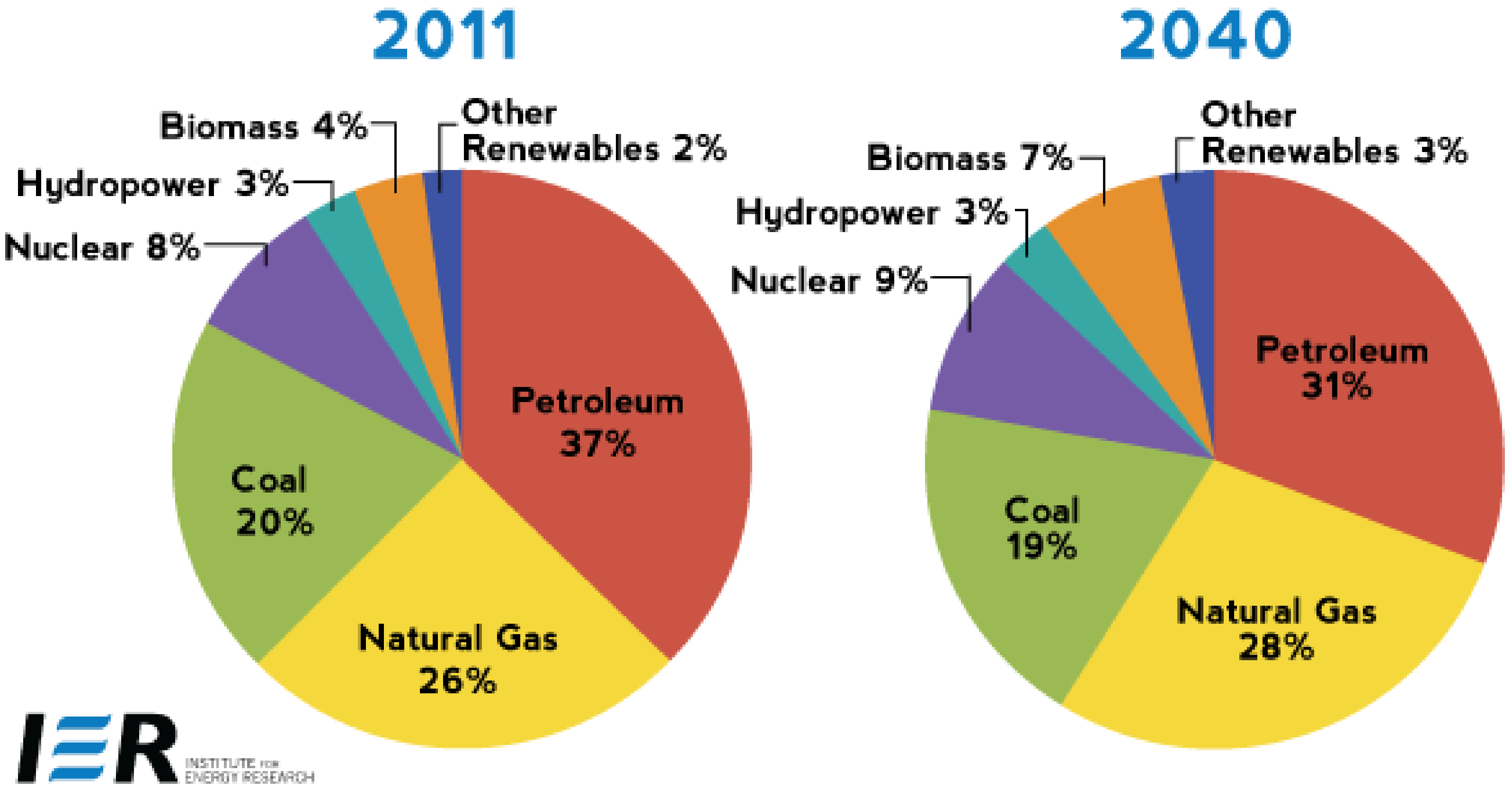
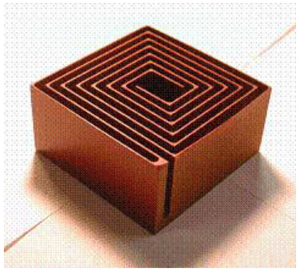


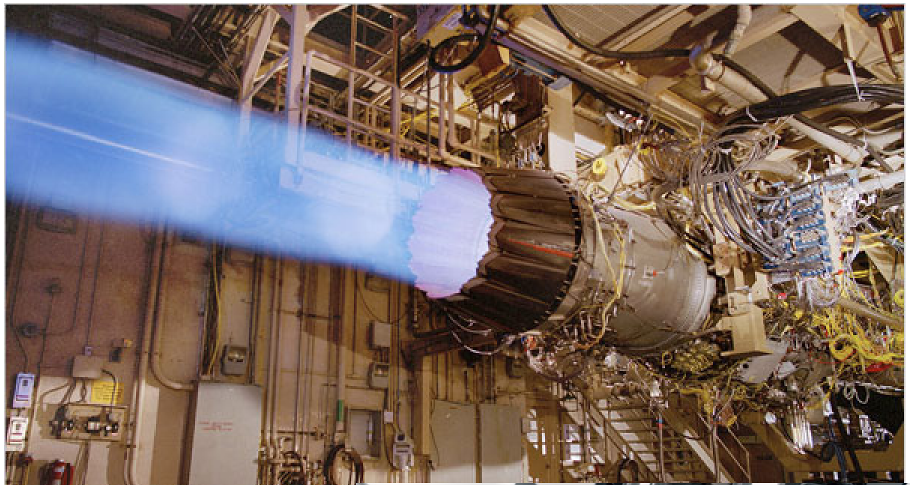
Figure from IER, Data Source: EIA

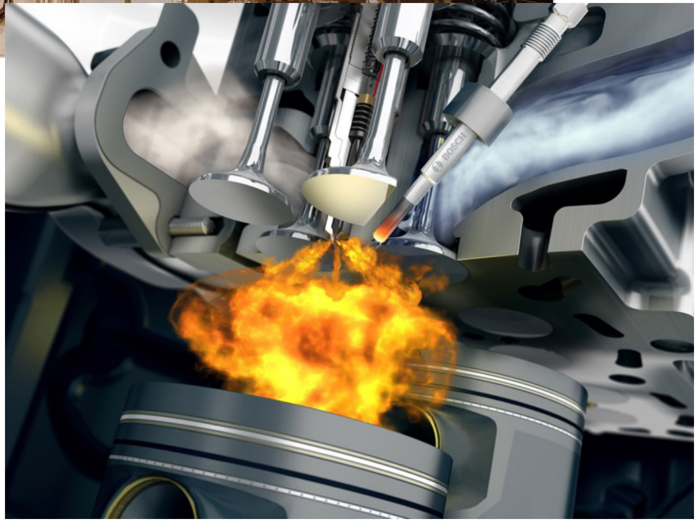
Background on Combustion Applications

Micro-combustors

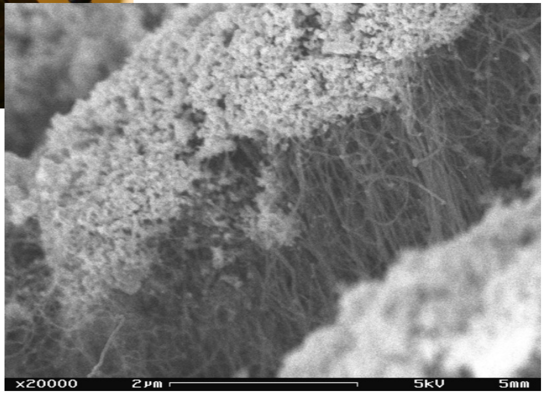


Engines





Material synthesis



Adverse Effects

Fire safety

Emissions

Chemical Equilibrium

The 1st Law for Reacting Systems

- Total energy of a chemically reacting system

$$E = \sum_i E_i$$

subscript i indicate the ith species

- The 1st Law

$$dE = \sum_i N_i de_i + \sum_i e_i dN_i\,,$$

$$de_i = Tds_i - p_i dv_i$$

where e_i is the mole specific energy, $v_i = \frac{1}{n_i} = \frac{V}{N_i}$,

s_i is the mole specific entropy, and $N_i$is the total number of mole, for the ith species

The 2nd Law & Chemical Equilibrium

- The 2nd law of thermodynamics: entropy can not decrease for isolated (closed & adiabatic) systems
- Total entropy of a reacting system

$$S(T, N_i) = \sum_i S_i = \sum_i N_i s_i$$

- Chemical equilibrium is where a reacting system evolves to, given infinitely long time
  - determines total heat release & final compositions etc.
  - Typically needs to be accurately captured by detailed or reduced chemistry
- Entropy reaches maximum in an isolated system at chemical equilibrium

Adiabatic Flame Temperature

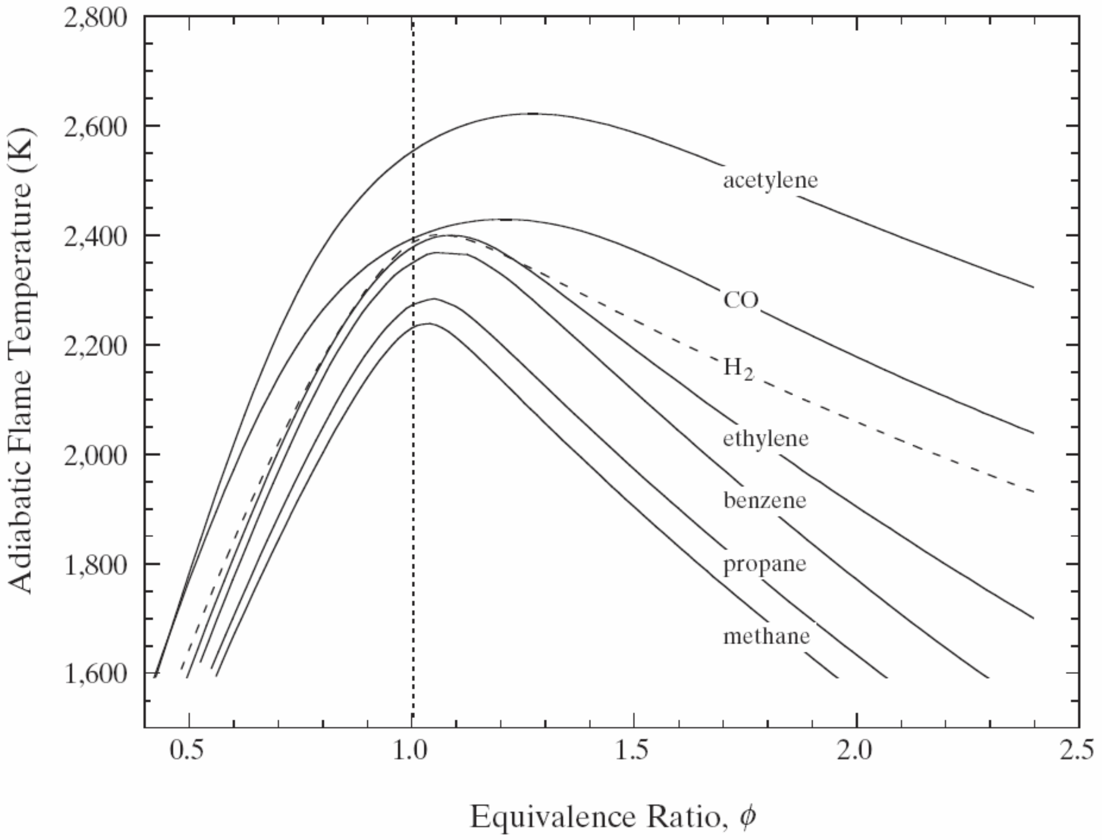


Figure 1.4.3. Adiabatic flame temperature, T_{ad}, as a function of fuel equivalence ratio, ϕ, for several fuel–air mixtures at STP.

(Law, Combustion Physics 2007)

Equations for Chemical Equilibrium (1/3)

- Based on the 1st Law

$$dE = \sum_i N_i(Tds_i - p_i dv_i) + \sum_i e_i dN_i$$

$$= \sum_i N_i T ds_i - \sum_i N_i p_i dv_i + \sum_i e_i dN_i$$

$$= T\sum_i d(N_i s_i) - \sum_i T s_i dN_i - \sum_i p_i d(N_i v_i) + \sum_i p_i v_i dN_i$$

$$+ \sum_i e_i dN_i = TdS - pdV + \sum_i (e_i + p_i v_i - Ts_i) dN_i$$

- i.e.: $dE = TdS - pdV + \sum_i g_i dN_i$
- For an isolated system: $dE = 0, dV = 0$

Equations for Chemical Equilibrium (2/3)

- For an isolated system: $dE = 0, dV = 0,$

$$TdS = -\sum_i g_i dN_i$$

- For a reacting system (for simplicity consider one-step reaction $\sum_i \Delta\nu_i M_i = 0$):
  $dN_i = \Delta\nu_i d\xi$, where ξ is the progress variable

- At chemical equilibrium the total entropy reaches maximum:

$$\frac{dS}{d\xi} = 0$$

- That is

$$\sum_i g_i \Delta\nu_i = 0$$

Equations for Chemical Equilibrium (3/3)

- Governing equations for a one-step reaction at equilibrium

$$\sum_i g_i \Delta\nu_i = 0$$

  - The equation involves only state variables - not dependent on the history of a system – applicable to arbitrary, not only isolated, systems
  - For a multi-step reaction system, each reaction reaches equilibrium at chemical equilibrium (detailed balancing)
  - The maximum number of independent equations: # of species - # of elements

Equilibrium Constant Kp

- When a reaction ($\sum_i \Delta\nu_i M_i = 0$) reaches equilibrium: $\sum_i g_i \Delta\nu_i = 0$
- The mole specific Gibbs free energy can be decomposed to

  $$g_i(p_i, T) = g_i^0(p^0, T) + R_u T ln\left(\frac{p_i}{p^0}\right)$$

  where the superscript 0 denotes the standard state (p = 1atm) quantity

  $$\sum_i \Delta\nu_i \left(g_i^0(p_i^0, T) + R_u T ln\left(\frac{p_i}{p^0}\right)\right) = 0$$

  $$\frac{\sum_i \Delta\nu_i g_i^0}{R_u T} + \ln\left(\prod_{\mathrm{i}} \left(\frac{p_i}{p^0}\right)^{\Delta\nu_i}\right) = 0$$

  $$\prod_{\mathrm{i}} \left(\frac{p_i}{p^0}\right)^{\nu_i} = \exp(-\frac{\sum_i \Delta\nu_i g_i^0}{R_u T})$$

- $K_p(T) \equiv \exp(-\frac{\sum_i \Delta\nu_i g_i^0}{R_u T})$ is the equilibrium constant

Rates of a Reaction in Equilibrium

- For a reaction $\sum \nu_i' M_i = \sum \nu_i'' M_i$
- At equilibrium the forward and reverse rates must be balanced, such that the net rate is zero, $\omega_f = \omega_r$
- The law of mass action

$$\omega_f = k_f \prod c_i^{\nu_i'}$$

$$\omega_r = k_r \prod c_i^{\nu_i''}$$

- At equilibrium $k_f \prod c_i^{\nu_i'} = k_r \prod c_i^{\nu_i''}$

$$\frac{k_f}{k_r} = \frac{\prod c_i^{\nu_i''}}{\prod c_i^{\nu_i'}} = \prod c_i^{\Delta \nu_i}$$

Equilibrium Constant Kc

- Equilibrium equation based on Kp

$$K_p \equiv \exp(-\frac{\sum_i \Delta\nu_i g_i^0}{R_u T})$$

- Equilibrium equation based on Kc

$$Kc = \prod_i c_i^{\Delta\nu_i}$$

- Relating the two equations using ideal gas law ($p_i = c_i R_u T$)

$$K_c = K_p \left(\frac{R_u T}{p^0}\right)^{-\sum_i \Delta\nu_i}$$

- Note that Kp and Kc are functions of temperature only

Chemical Equilibrium of Multiple Reactions

- In equilibrium, the net reaction rate of every reaction is 0: (detailed balancing)
- The equilibrium equation may not be linearly independent for arbitrary number of reactions

$$\ln\left[K_{1,C}(T)\right]=\ln\left[\prod_{i=1}^{K}\left(C_i^{\Delta\nu_{1,i}}\right)\right]=\sum_{i=1}^{K}\Delta\nu_{1,i}\ln(C_i) \qquad \text{(R1)}$$

$$\ln\left[K_{2,C}(T)\right]=\ln\left[\prod_{i=1}^{K}\left(C_i^{\Delta\nu_{2,i}}\right)\right]=\sum_{i=1}^{K}\Delta\nu_{2,i}\ln(C_i) \qquad \text{(R2)}$$

…

$$\ln\left[K_{I,C}(T)\right]=\ln\left[\prod_{i=1}^{K}\left(C_i^{\Delta\nu_{I,i}}\right)\right]=\sum_{i=1}^{K}\Delta\nu_{I,i}\ln(C_i) \qquad \text{(RI)}$$

Linear Dependency of Equilibrium Equations with Multiple Reactions

$$\begin{pmatrix} \Delta\nu_{1,1} & \Delta\nu_{1,2} & \dots & \Delta\nu_{1,K} \\ \Delta\nu_{2,1} & \Delta\nu_{2,2} & \dots & \Delta\nu_{2,K} \\ \dots & & & \dots \\ \Delta\nu_{I,1} & \Delta\nu_{I,2} & \dots & \Delta\nu_{I,K} \end{pmatrix} \begin{pmatrix} \ln(C_1) \\ \ln(C_2) \\ \dots \\ \ln(C_K) \end{pmatrix} = \begin{pmatrix} \ln(K_{1,C}) \\ \ln(K_{2,C}) \\ \dots \\ \ln(K_{I,C}) \end{pmatrix}$$

$$\mathbf{S}^T \equiv \begin{pmatrix} \Delta\nu_{1,1} & \Delta\nu_{1,2} & \dots & \Delta\nu_{1,K} \\ \Delta\nu_{2,1} & \Delta\nu_{2,2} & \dots & \Delta\nu_{2,K} \\ \dots & & & \dots \\ \Delta\nu_{I,1} & \Delta\nu_{I,2} & \dots & \Delta\nu_{I,K} \end{pmatrix}$$

S: The stoichiometric matrix (not entropy) of size K (# of species) by I (# of reactions), each column in S indicates a reaction.

If I>K-M, not all the equations are linearly independent, M is # of elements

Example of the Linear Dependency

Reactions:

$$H_2 + O_2 \rightleftharpoons 2OH$$
$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
$$H_2 \rightleftharpoons 2H$$
$$O_2 \rightleftharpoons 2O$$
$$H + OH \rightleftharpoons H_2 + O$$

$$\mathbf{S}^T = \left[\begin{array}{cccccc} O & H & O_2 & H_2 & OH & H_2O \\ \hline 0 & 0 & -1 & -1 & +2 & 0 \\ 0 & 0 & -1 & -2 & 0 & +2 \\ 0 & +2 & 0 & -1 & 0 & 0 \\ +2 & 0 & -1 & 0 & 0 & 0 \\ +1 & -1 & 0 & +1 & -1 & 0 \end{array}\right]$$

I = 5, K=6, M=2

Linearly independent reactions: K-M = 4

Equations for Chemical Equilibrium for Multi-Reaction Systems

- Variable set: K species + 2 state variables (e.g. T, P)
- Equation set
  - K-M equations for reaction equilibrium:

$$\sum_i g_i \Delta\nu_{ij} = 0, j = 1,2, \dots, K - M$$

  - M equations for element conservation:

$$\sum_k \alpha_{lk} N_k = a_k^0, l = 1, 2, \dots, M,$$

$$\alpha_{lk}: \ the\ \#\ of\ the\ lth\ element\ in\ the\ kth\ species$$

  - Two thermodynamic constraints, e.g.
    - $E = 0, V = V_0$ for isolated systems
    - $T = T_0, p = p_0$ for isothermic & isobaric systems
    - …

Equilibrium Conditions for Other Systems

- Following the same procedure as for isolated systems

$$dE = TdS + pdV + \sum_i g_i dN_i$$

$$dH = TdS + Vdp + \sum_i g_i dN_i$$

$$dA = -SdT - pdV + \sum_i g_i dN_i$$

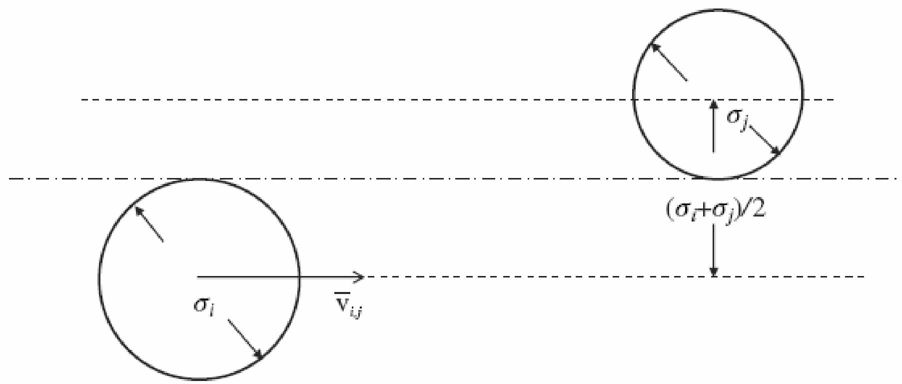
$$dG = -SdT + Vdp + \sum_i g_i dN_i$$

- Equilibrium conditions for example constrained systems
  - $dE = 0\ and\ dV = 0\ (i.e.\ constant\ E\ and\ V){:}\ dS = 0\ (\max S)$
  - $dH = 0\ and\ dp = 0\ (i.e.\ constant\ S\ and\ p){:}\ dS = 0\ (\max S)$
  - $dS = 0\ and\ dV = 0\ (i.e.\ constant\ S\ and\ V){:}\ dE = 0\ (\min E)$
  - $dS = 0\ and\ dp = 0\ (i.e.\ constant\ S\ and\ p){:}\ dH = 0\ (\min H)$
  - $dT = 0\ and\ dV = 0\ (i.e.\ constant\ T\ and\ V){:}\ dA = 0\ (\min A)$
  - $dT = 0\ and\ dp = 0\ (i.e.\ constant\ T\ and\ p){:}\ dG = 0\ (\min G)$

Chemical Kinetics and Transport

Collision Frequency of A & B

- Collision frequency is proportional to
  - Molecular size of A and B, measured by the molecular diameter σ_A and σB. Define $2\sigma_{AB} = \sigma_A + \sigma_B$



  - Concentrations of A and B, measured by the number density (#/volume), $n_{\mathbf{A}}$ and n_B
  - Average velocity of A and B, given by the Maxwell distribution,

$$\overline{V}_{AB} = \sqrt{\frac{8kT}{\pi m_{AB}}}, \quad m_{AB} = \frac{m_A m_B}{m_A + m_B}$$

- Putting them together $Z_{A,B} = n_A n_B \pi \sigma_{AB}{}^2 \overline{V}_{AB} = n_A n_B \pi \sigma_{AB}{}^2 \sqrt{\frac{8kT}{\pi m_{AB}}}$

Activation Energy

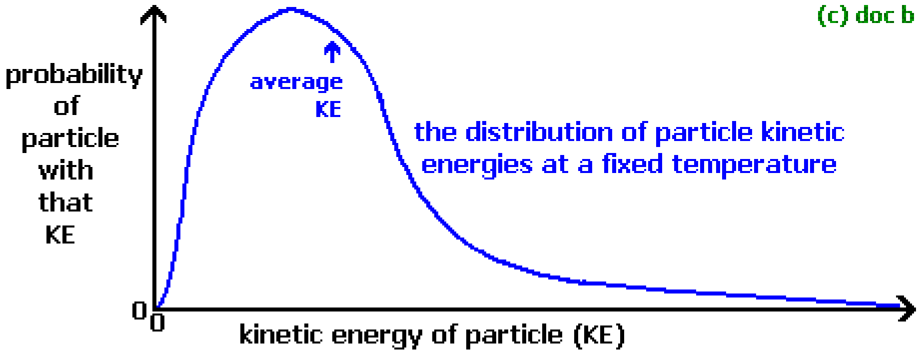
- For a given temperature, the molecules move not in the same speed, but in Maxwell-Boltzmann distribution

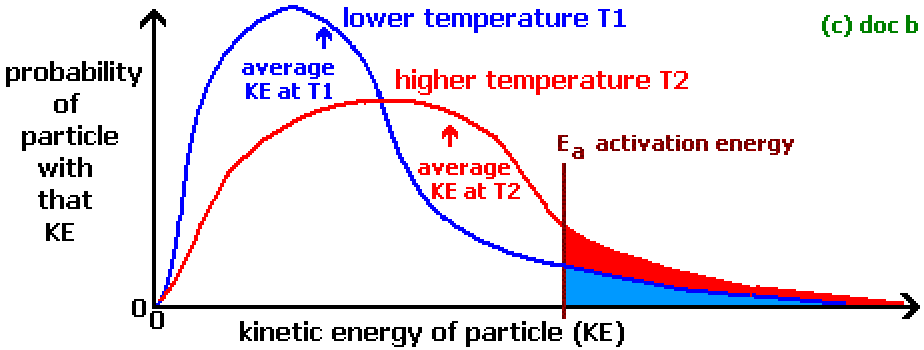
- Only those involving a critical kinetic energies (KE) may result in bond-breaking

- This critical KE is called Activation Energy, E_A

- The fraction *P* of collisions with KE>E_A is given by the M-B-distribution

$$P = \exp\left(\frac{-E_A}{R_u T}\right)$$





From: http://www.docbrown.info/page03/ASA2rates.htm

Elementary Reaction Rate (1/2)

- The reaction rate for A + B -> products:

$$\omega_f = Z_{A,B} P = n_A n_B \pi \sigma_{AB}^{\ 2} \sqrt{\frac{8kT}{\pi m_{AB}}} \exp\left(\frac{-E_A}{R_u T}\right)$$

$n_A \sim c_A, n_B \sim c_B$ where *c* is the mole concentration

$$\omega_f \sim c_A c_B T^{1/2} \exp\left(\frac{-E_A}{R_u T}\right)$$

- The **Arrhenius rate expression**, including the steric factor

$$\omega_f = k_f(T) c_A c_B, \quad k_f(T) = A T^n \exp\left(\frac{-E_A}{R_u T}\right)$$

  - *A* is a constant determined by molecular properties of A and B and the steric factor.
  - *A, n,* E_A together determines $k_f(T)$ of the reaction.

Elementary Reaction Rate (2/2)

- Net reaction rate

$$
\begin{aligned}
\omega &= \omega_f - \omega_r \\
&= k_f(T)\prod_{i=1}^{K} c_i^{\nu_i'} - k_r(T)\prod_{i=1}^{K} c_i^{\nu_i''} = k_f(T)\prod_{i=1}^{K} c_i^{\nu_i'} - \frac{k_f(T)}{K_C}\prod_{i=1}^{K} c_i^{\nu_i''}
\end{aligned}
$$

- Relation with total progress variable of the system, ξ:

$$\frac{d\xi}{dt} = \omega \cdot V$$

- In a closed system

$$\frac{dN_i}{dt} = \Delta\nu_i \frac{d\xi}{dt} = \Delta\nu_i \cdot \omega \cdot V, \quad i = 1,2,\ldots,K$$

One-Step Reaction in a Fixed Volume

- A system with fixed volume V, initially filled with N_A, N_B, N_C, N_D moles of A, B, C, and D, respectively, at temperature T
- Consider reaction: A + 2B = C + D

$$\omega = \omega_f - \omega_r \qquad \omega_f = k_f(T)c_A c_B{}^2 \qquad \omega_r = k_r(T)c_C c_D$$

$$\frac{dN_A}{dt} = \Delta\nu_A \cdot \omega \cdot V \quad \Longrightarrow \quad \frac{dc_A}{dt} = \frac{d\left(N_A/V\right)}{dt} = \frac{dN_A}{Vdt} = \Delta\nu_A \cdot \omega = -\omega$$

- Similarly

$$\frac{dc_B}{dt} = \frac{d\left(N_B/V\right)}{dt} = \frac{dN_B}{Vdt} = \Delta\nu_B \cdot \omega = -2\omega$$

$$\frac{dc_C}{dt} = \frac{d(N_C/V)}{dt} = \frac{dN_C}{Vdt} = \Delta\nu_C \cdot \omega = \omega$$

$$\frac{dc_D}{dt} = \frac{d(N_D/V)}{dt} = \frac{dN_D}{Vdt} = \Delta\nu_D \cdot \omega = \omega$$

Systems with Multiple Reactions

- For a system with the following reactions

  $\nu_{i,1}' M_1 + \nu_{i,2}' M_2 + \ldots + \nu_{i,K}' MK \Leftrightarrow \nu_{i,1}'' M_1 + \nu_{i,2}'' M_2 + \ldots + \nu_{i,K}'' MK \; , i$

- The rate for the ith reaction is:

$$\frac{d\xi_i}{Vdt} = \omega_i = \omega_{if} - \omega_{ir} = k_{if}(T)\prod_{k=1}^{K} c_i^{\nu_{i,k}'} - k_{ir}(T)\prod_{k=1}^{K} c_i^{\nu_{i,k}''}$$

- The rate of change for the kth species

$$\frac{dN_k}{dt} = \sum_{i=1}^{I}\left(\nu_{i,k}\frac{d\xi_i}{dt}\right) = \sum_{i=1}^{I}\left(\nu_{i,k}\omega_i\right)\cdot V$$

- If V is constant

$$\frac{dc_k}{dt} = \frac{dN_k}{Vdt} = \sum_{i=1}^{I}\left(\Delta\nu_{i,k}\omega_i\right)$$

Species Production Rates In Matrix-Vector Form

- For the kth species $\frac{dc_k}{dt} = \sum_{i=1}^{I} \left(\nu_{i,k} \omega_i \right)$ k=1,2, …, K
- In matrix form: $\frac{d\mathbf{c}}{dt} = \mathbf{S} \cdot \boldsymbol{\omega}$

$$\mathbf{c}_{K\times 1} = \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_K \end{pmatrix} \qquad \mathbf{S}_{K\times I} = \begin{pmatrix} \nu_{1,1} & \nu_{2,1} & \dots & \nu_{I,1} \\ \nu_{1,2} & \nu_{2,2} & \dots & \nu_{I,2} \\ \dots & & & \dots \\ \nu_{1,K} & \nu_{2,K} & \dots & \nu_{I,K} \end{pmatrix} \qquad \boldsymbol{\omega}_{I\times 1} = \begin{pmatrix} \omega_1 \\ \omega_2 \\ \dots \\ \omega_I \end{pmatrix}$$

- **S** is the **stoichiometric coefficient matrix**

Example:

(1) $H_2 + O_2 \rightleftharpoons 2OH$

(2) $2H_2 + O_2 \rightleftharpoons 2H_2O$

(3) $H_2 \rightleftharpoons 2H$

(4) $O_2 \rightleftharpoons 2O$

(5) $H + OH \rightleftharpoons H_2 + O$

- Species list:
  - H2, O2, H2O, H, O, OH

$$\mathbf{S}_{6\times 5} = \begin{pmatrix} -1 & -2 & -1 & 0 & 1 \\ -1 & -1 & 0 & -1 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & -1 \\ 0 & 0 & 0 & 2 & 1 \\ 2 & 0 & 0 & 0 & -1 \end{pmatrix}$$

- The reaction rates

$$\omega_1 = \omega_{1f} - \omega_{1r} = k_{1f} c_{H2} c_{O2} - k_{1r} c_{OH}{}^2$$

$$\omega_2 = \omega_{2f} - \omega_{2r} = k_{2f} c_{H2}{}^2 c_{O2} - k_{2r} c_{H2O}{}^2$$

$$\omega_3 = \omega_{3f} - \omega_{3r} = k_{3f} c_{H2} - k_{3r} c_H{}^2$$

$$\omega_4 = \omega_{4f} - \omega_{4r} = k_{4f} c_{O2} - k_{4r} c_O{}^2$$

$$\omega_5 = \omega_{5f} - \omega_{5r} = k_{5f} c_H c_{OH} - k_{5r} c_{H2} c_O$$

$$\frac{d\mathbf{c}}{dt} = \mathbf{S} \cdot \boldsymbol{\omega} = \ldots$$

Chain Reactions

- Radicals are important in determining reaction rates
  - e.g. H radical typically controls the oxidation of hydrogen and hydrocarbon
  - Examples of other important radicals OH, O, HCO (for hydrocarbons)

- Based on the creation/consumption of radicals, an elementary reaction can serve for
  - Chain initiation: creates radicals from major species
    e.g. H2 -> H + H
  - Chain propagation: consumes a radical and generates another
    e.g. OH + H2 -> H2O + H
  - Chain branching: generates more radicals than consumed
    e.g. H + O2 -> OH + O,   O + H2 -> OH + H
  - Chain termination:
    e.g. H + OH -> H2O

Quasi Steady State Assumptions

- Example

$$A \xrightarrow{1} B \xRightarrow{1/\varepsilon} C \qquad \tau_{\text{control}} \sim O(1)$$

  - Destruction much faster than creation
  - B is a QSS species:

$$\frac{dB}{dt} = A - \frac{B}{\varepsilon} \approx 0 \quad \longrightarrow \quad B \approx A\varepsilon$$

  - QSSA is a kinetics controlled problem, that is a fast reaction is waiting for slow reactions in a serial process

Partial Equilibrium Assumptions

- An example:

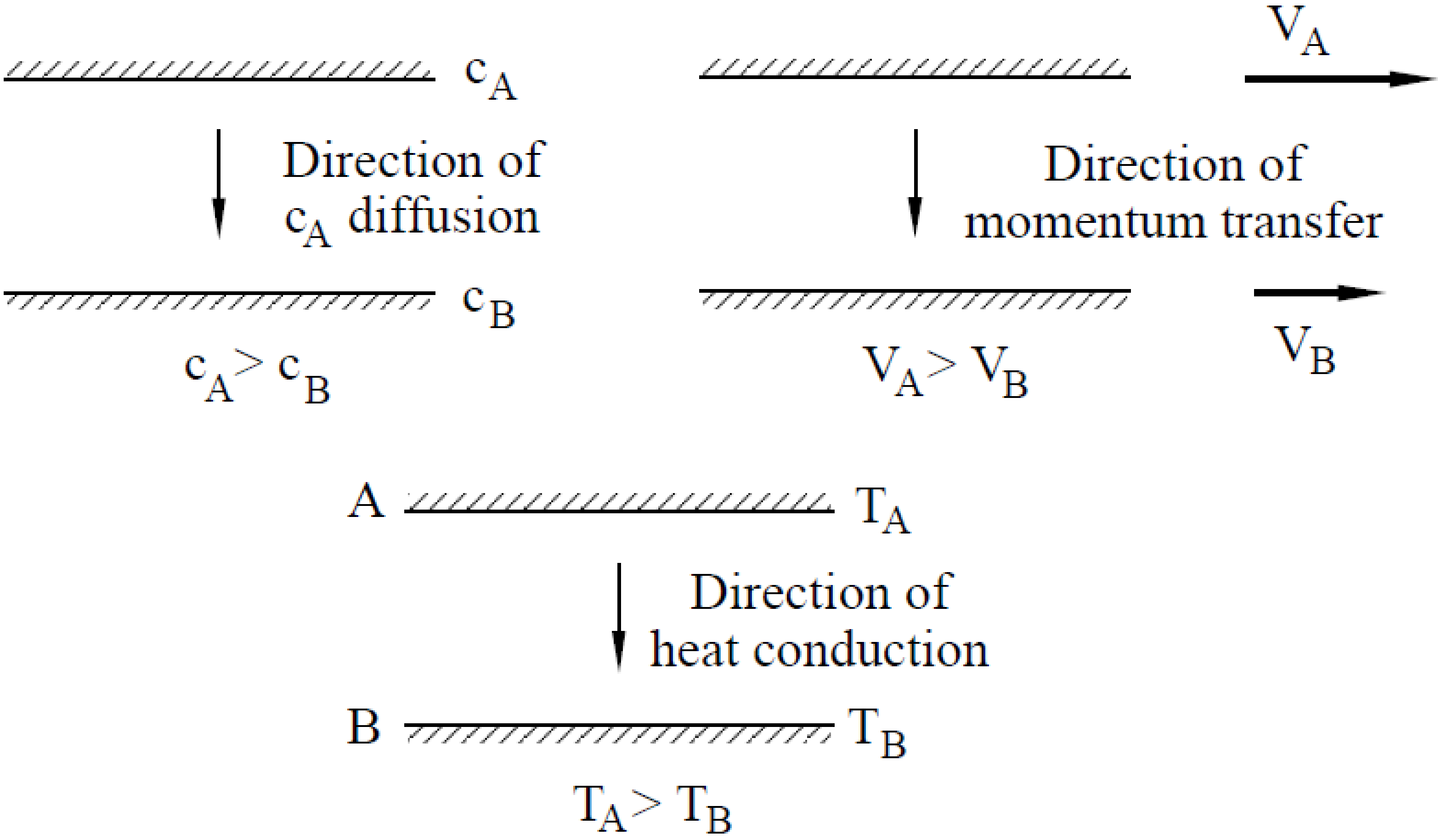
$$A \xrightarrow{1} B \overset{1/\varepsilon}{\Longleftrightarrow} C \qquad \tau_{\text{control}} \sim O(1)$$

  - Forward and backward rates are much faster than the net rate
  - Reaction B↔C is in PE:

$$\frac{B}{\varepsilon} - \frac{C}{\varepsilon} \approx 0 \qquad \longrightarrow \qquad B \approx C$$

  - PEA is intrinsically a chemical equilibrium problem, controlled by thermodynamics

Transport of
Mass, Momentum and Energy



(Law, Combustion Physics, 2006)

Mass, Momentum, and Energy Flux

- The flux of a quantity, Φ, is defined as the amount of Φ across a unit area and unit time:

$$f_{\Phi} = \frac{\Delta\Phi}{A\Delta t}$$

- Intensive quantities: $\phi = \frac{\Phi}{\mathrm{M}}$

$$\phi = Y_i \quad : \quad mass\ of\ \ the\ ith\ species$$

$$\phi = \vec{V} \quad : \quad momentum$$

$$\phi = e \quad : \quad energy$$

Transport Coefficients and Molecular Collisions

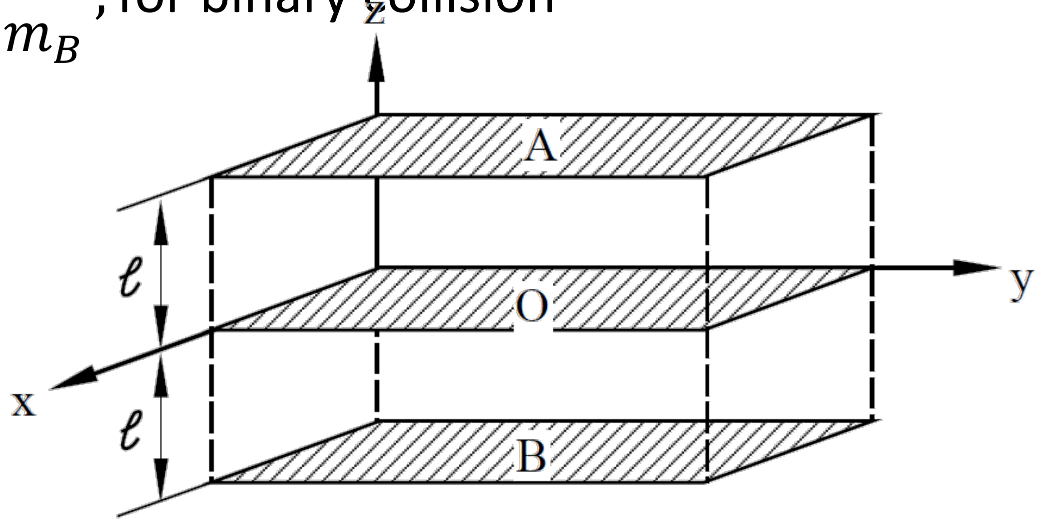
- Flux of ϕ

$$\overrightarrow{f_\Phi} = -\beta_\phi n\bar{V}l\nabla(m\phi) = -\beta_\phi \rho\bar{V}l\nabla\phi$$

$$\bar{V} = \sqrt{\frac{8kT}{\pi m}}$$

$$l = \frac{1}{n\pi\sigma^2}$$

$$\frac{1}{m} = \frac{1}{m_A} + \frac{1}{m_B}, \text{for binary collision}$$



  - n: number density
  - ρ: density
  - l: mean free path
  - β_ϕ: a ϕ-dependent constant

(Law, Combustion Physics, 2007)

Transport Laws

- $\overrightarrow{f_\phi} \sim -f_\phi(T)\,\nabla\phi$
- Fick's Law:

$$\overrightarrow{f_{\mathrm{Y_i}}} = -\rho\beta_{Y_i}\bar{V}l\nabla Y_i = -\rho D_i\nabla Y_i$$

- Newton's Law:

$$\overrightarrow{f_{\mathrm{u}}} = -\rho\beta_u\bar{V}l\nabla u = -\rho\nu\nabla u = -\mu\nabla u$$

- Fourier's Law:

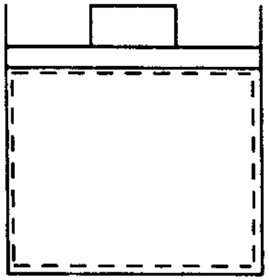
$$\overrightarrow{f_{\mathrm{e}}} = -\rho\beta_e\bar{V}l\nabla e = -\rho\alpha c_v\nabla T = -\lambda\nabla T$$

- In a multicomponent system, the transport coefficients of each species can be approximated as scalars, which are function of all the species concentrations and binary transport coefficients through mixture averaged models

Review of 0-D Reactors

Typical Zero-D Reactors

(a)
Constant-pressure fixed-mass reactor



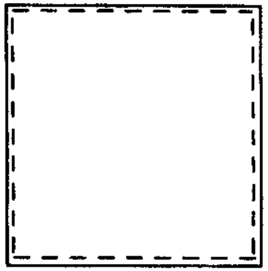
$T = T(t)$

$[X_i] = [X_i](t)$

$V = V(t)$

Perfectly-mixed,
homogeneous reaction

(b)
Constant-volume fixed-mass reactor



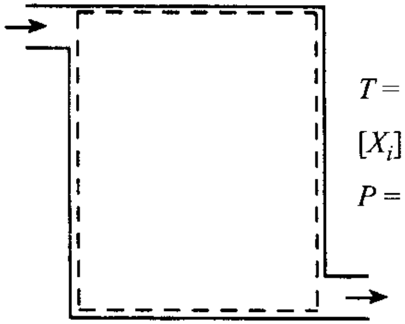
$T = T(t)$

$[X_i] = [X_i](t)$

$P = P(t)$

Perfectly-mixed,
homogeneous reaction

(c)
Well-stirred reactor



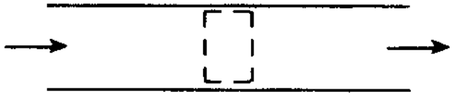
$T = \text{constant}$

$[X_i] = \text{constant}$

$P = \text{constant}$

Steady-state,
steady-flow,
perfectly mixed

(d)
Plug-flow reactor



$T = T(x)$

$[X_i] = [X_i](x)$

$P = P(x)$

$\mathbf{V} = v_x(x)$

Steady-state,
steady-flow,
no axial mixing

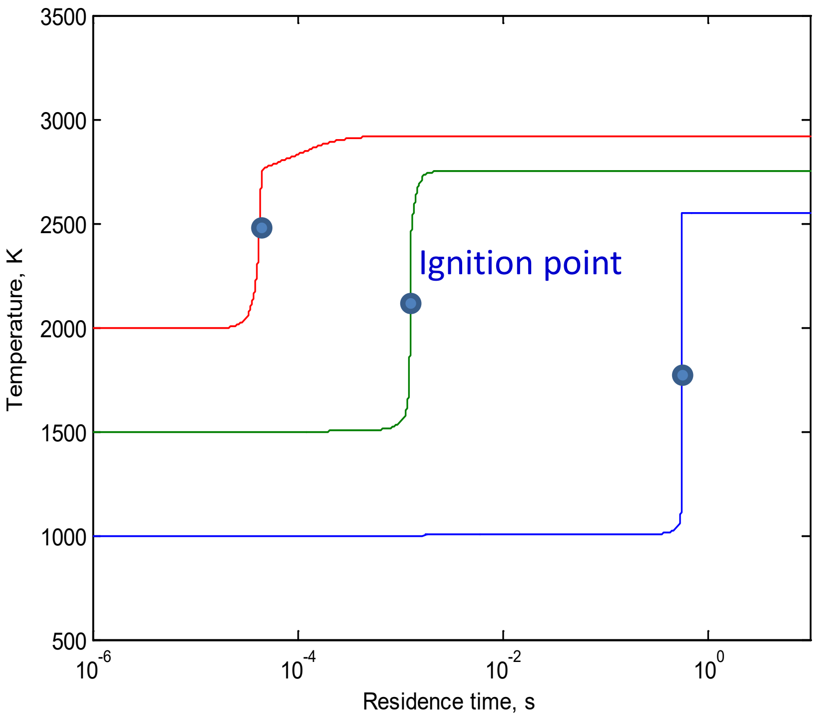
(Turns, 1996)

Auto-Ignition

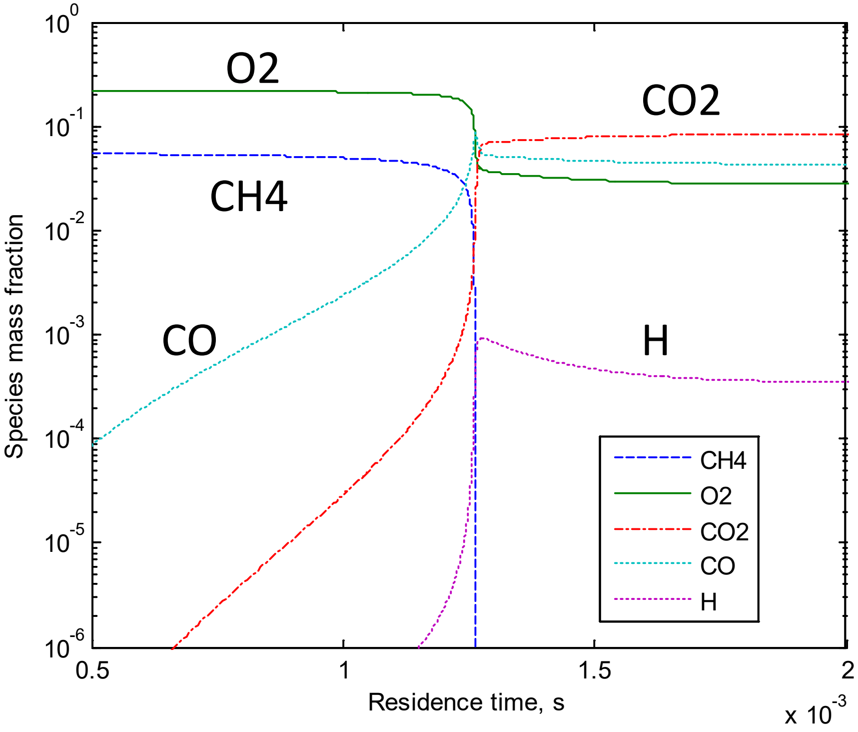
- Approximately spatially homogeneous
- Typically involves radical explosion and thermal runaway
  - Radical explosion is often a quasi linear problem with a positive eigenvalue in the Jacobian, and is typically slow (measured in milliseconds in shock tubes, rapid compression engines etc.)
  - Thermal runaway is typically nonlinear and fast (typically measures in microseconds)
- Ignition delay is considered an important fuel property

Auto-ignition: Small Hydrocarbons

Methane-air, ϕ = 1.0, p = 1 atm

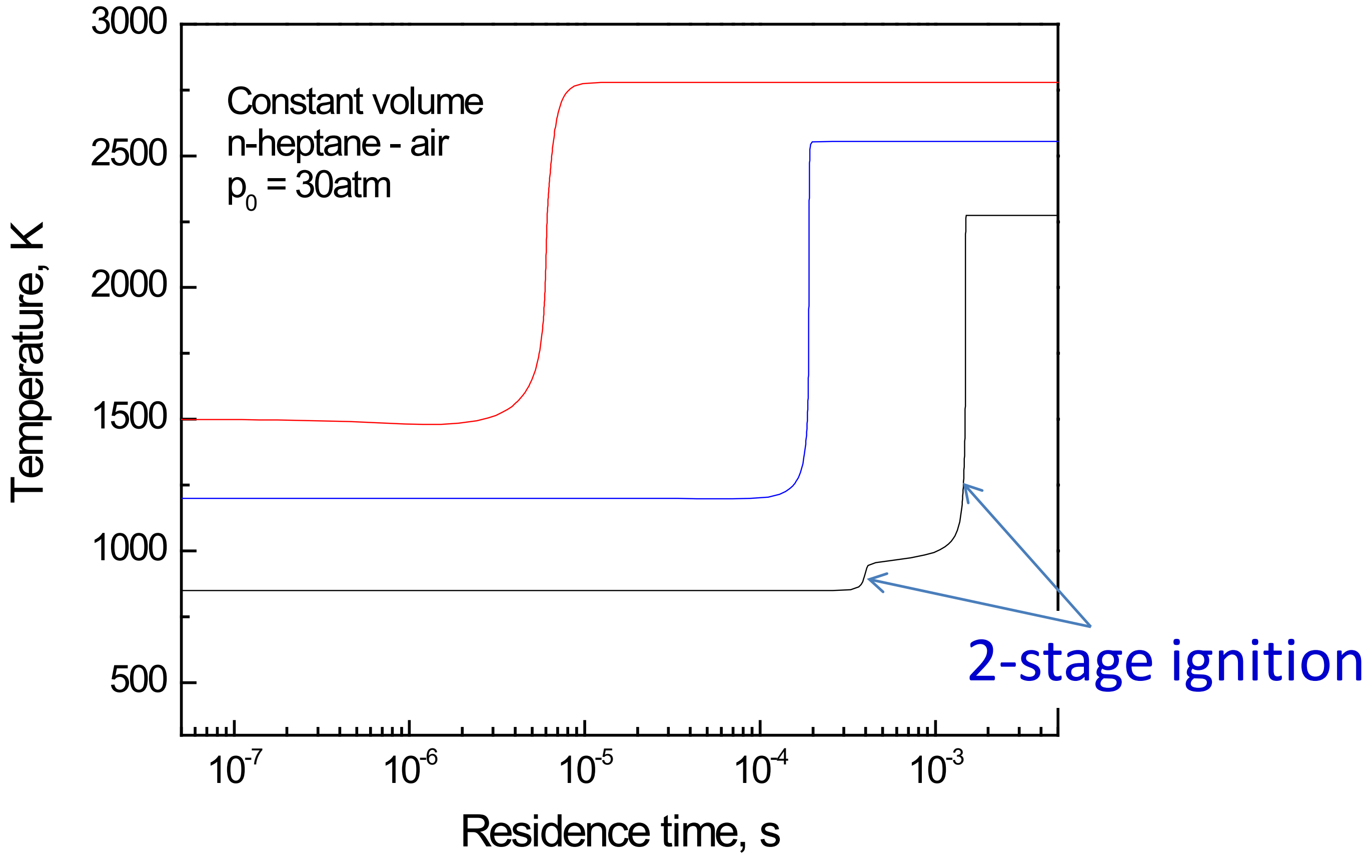


Methane-air,
ϕ = 1.0, p = 1 atm, T0 = 1500K



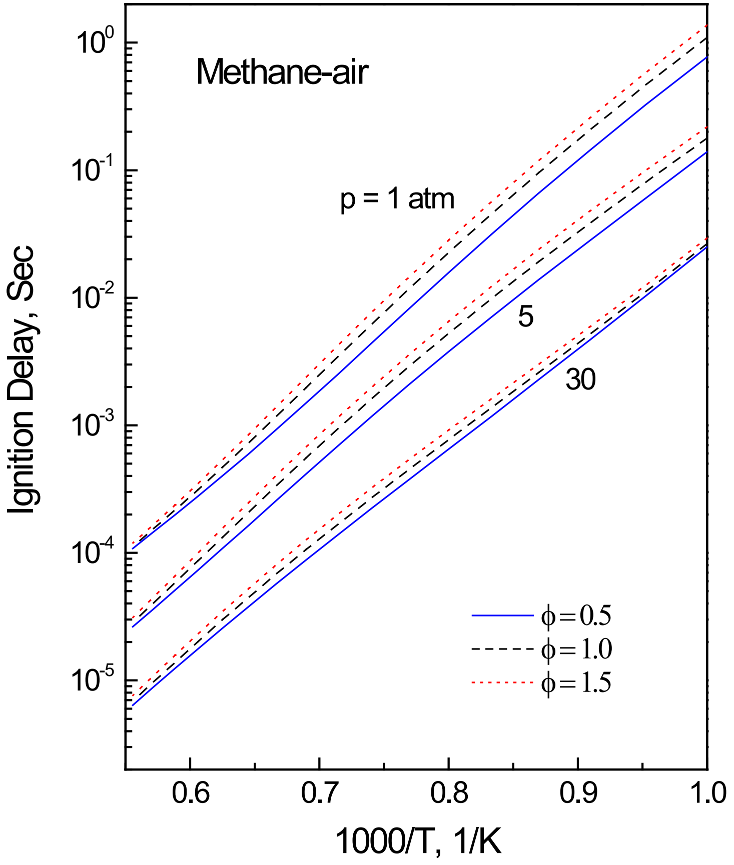
Ignition delay:
the residence time at the ignition point

Auto-ignition: Temperature Profiles for Large Hydrocarbons

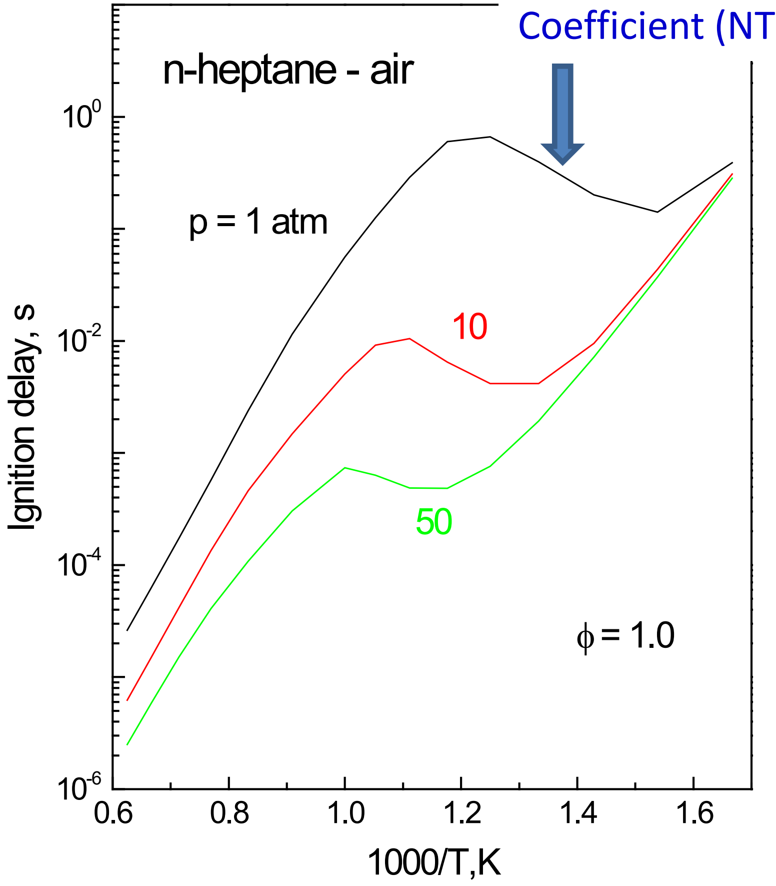


2-stage ignition

Ignition Delay:
Low vs. High Hydrocarbons

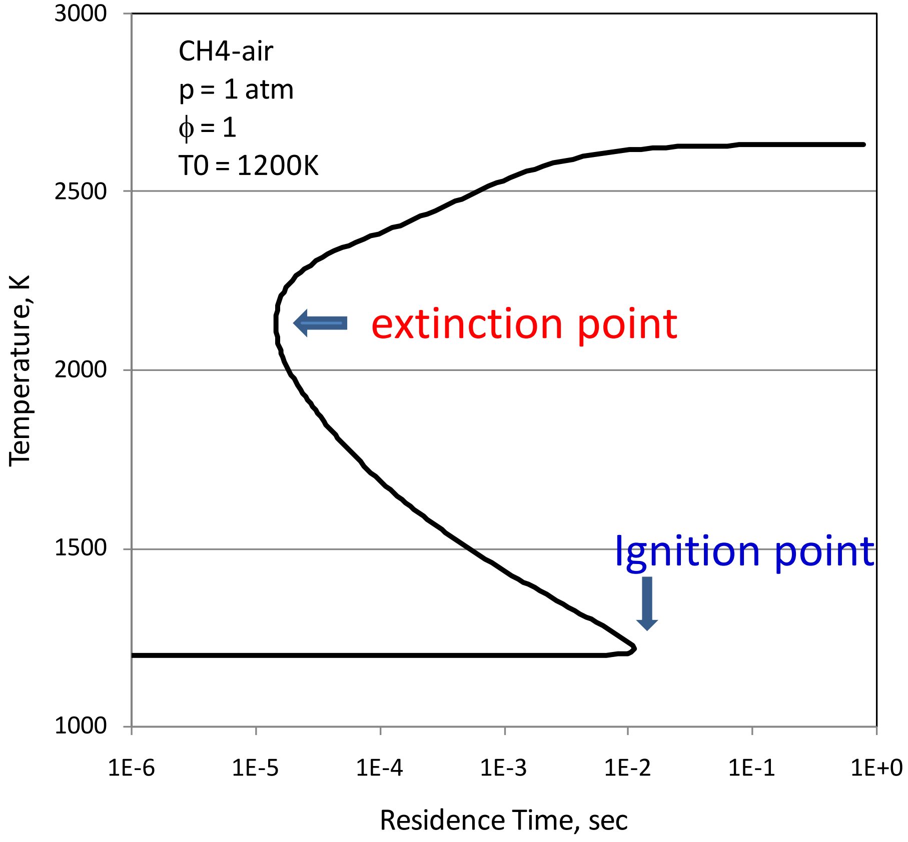


Negative Temperature Coefficient (NTC)



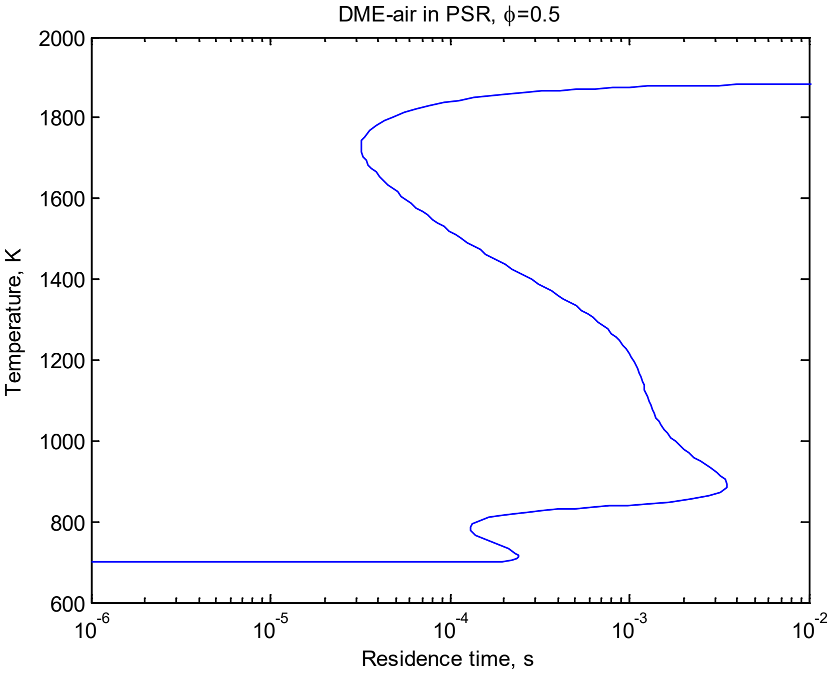
S-Curve of PSR: Steady State Combustion

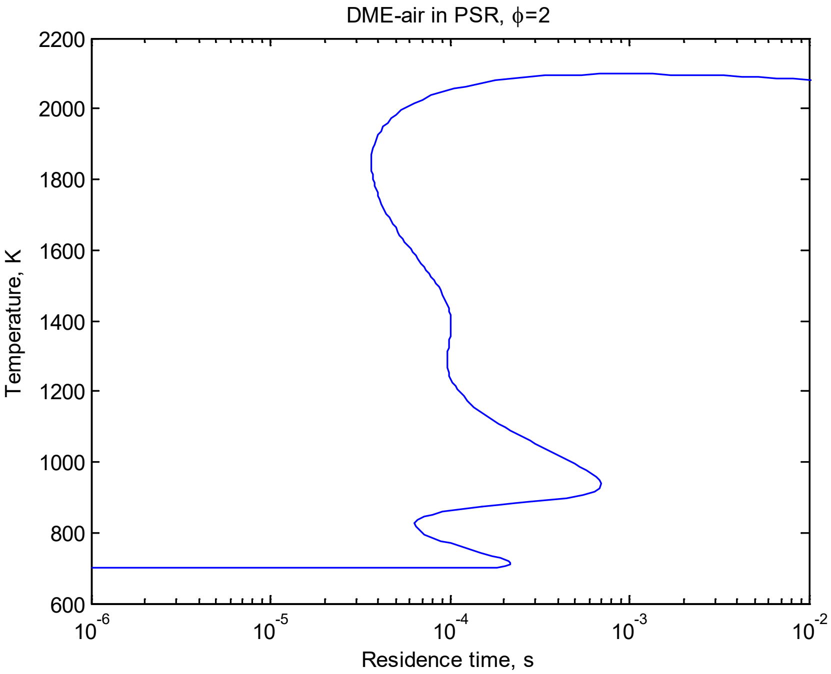
- Approximately spatially homogeneous
- Relevant to flame holding, e.g. with a recirculation zone, in many combustors
- Solution features the S-curve, with turning points being the extinction and ignition points



S-curve with Multiple Turnings

DME-air, p = 30 atm, T_{in}=700K



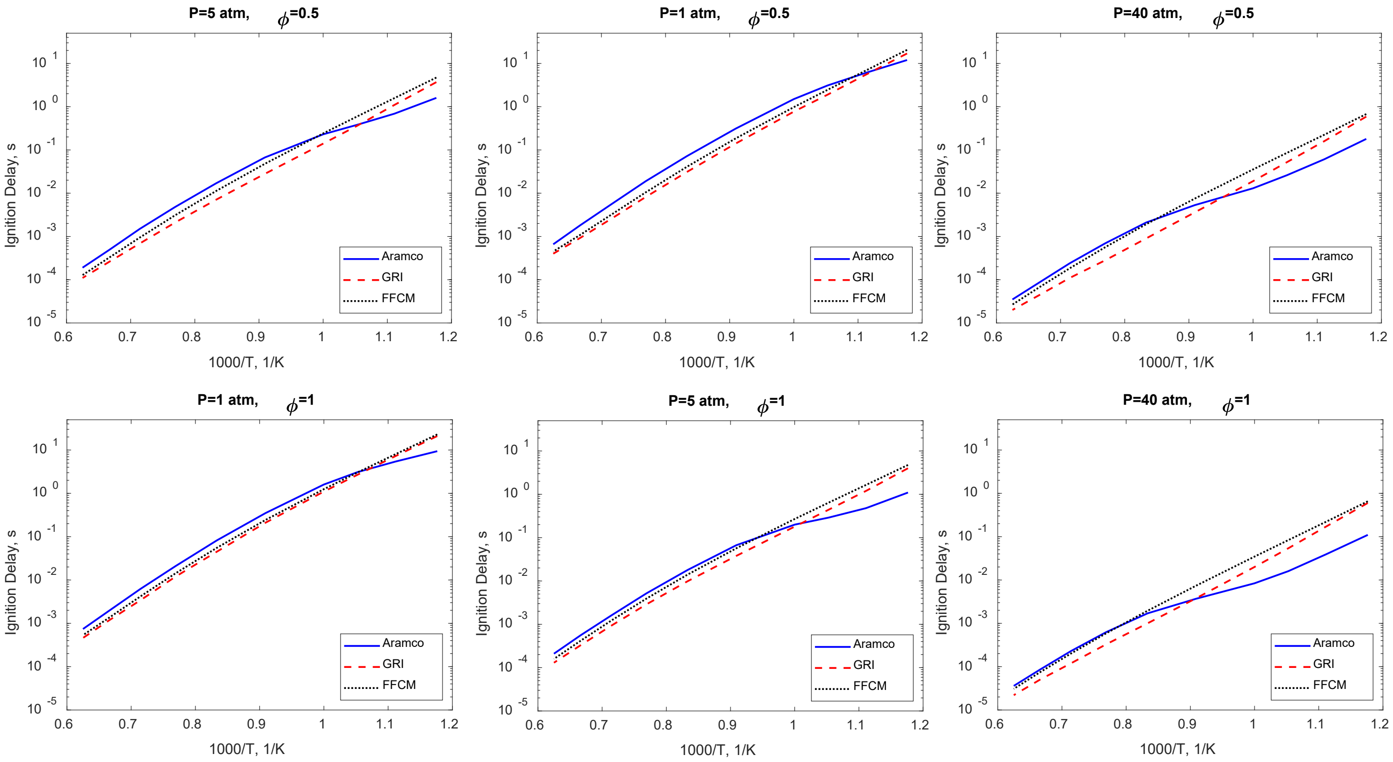


IDT Typically Well Calibrated

$p = 1\ atm$ $p = 5\ atm$ $p = 40\ atm$

$\phi = 0.5$

$\phi = 1$



Aramco v3: 581-species

GRI-v3.0: 53-species

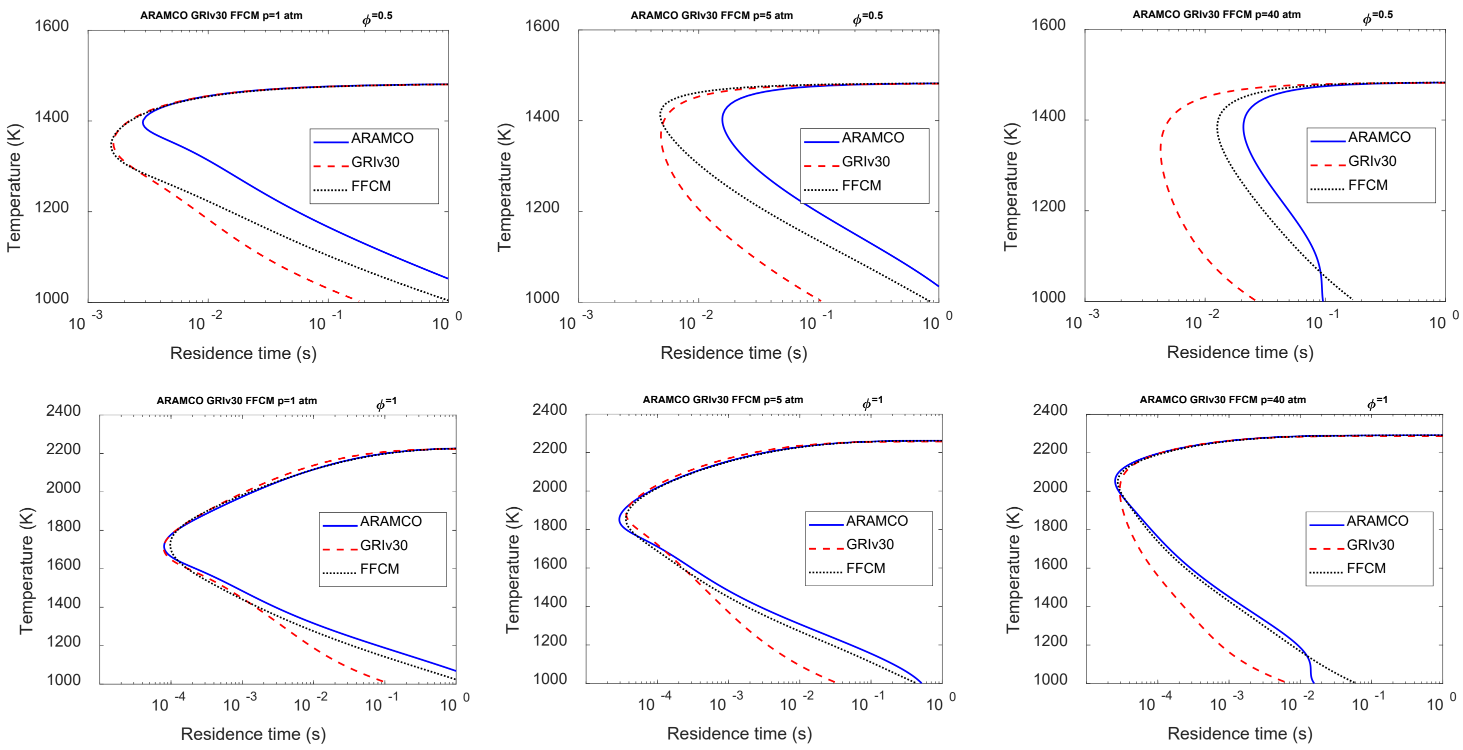
FFCM-1: 38-species

Large Differences in Fast Burning

$p = 1\ atm$ $p = 5\ atm$ $p = 40\ atm$

$\phi = 0.5$

$\phi = 1$



Aramco v3: 581-species

GRI-v3.0: 53-species

FFCM-1: 38-species

Transport Equations

- Continuity

$$\frac{D\rho}{Dt} + \rho\nabla \cdot \vec{V} = 0$$

- Momentum

$$\rho\frac{D\vec{V}}{Dt} = \rho\vec{g} - \nabla p + \nabla \cdot \boldsymbol{\tau}$$

- Species

$$\rho\frac{DY_i}{Dt} = \nabla \cdot (\rho D_i \nabla Y_i) + M_i \omega_i$$

- Energy

$$\rho\frac{De}{Dt} = -\nabla \cdot \vec{q} - p\left(\nabla \cdot \vec{\mathrm{V}}\right) + \boldsymbol{\tau}\colon \nabla\vec{\mathrm{V}}$$

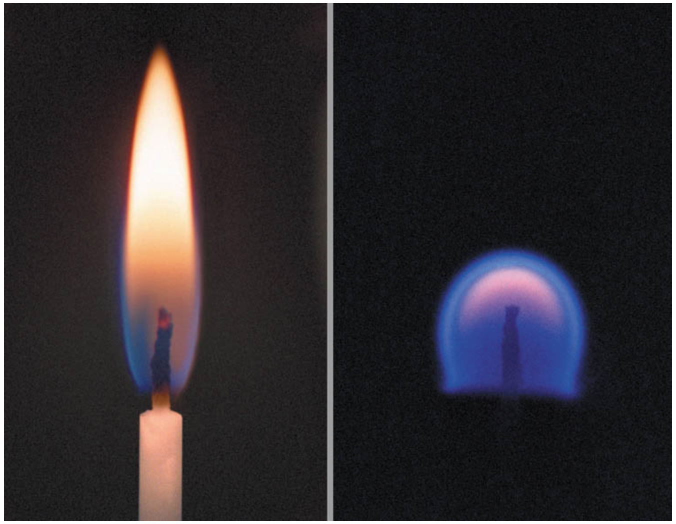
- Equation of state

$$p = \rho RT$$

Review of 1-D Flames

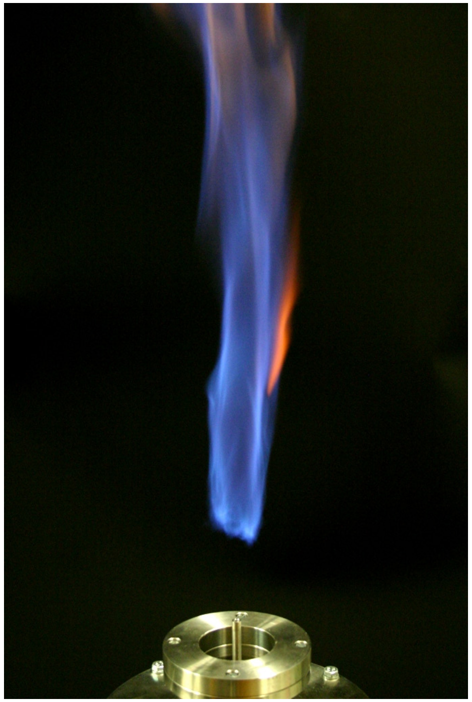
1-D Non-Premixed Flames

Candle flames

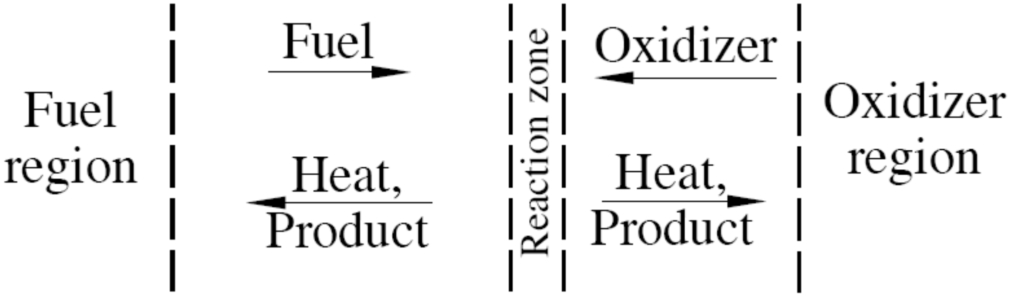


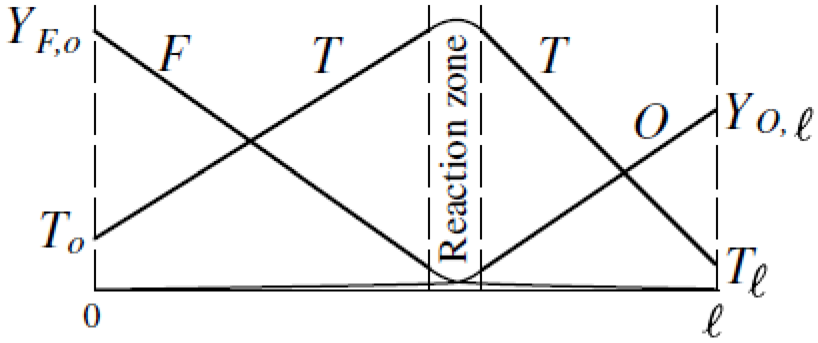
A turbulent
non-premixed jet flame
unpiloted

A lifted turbulent jet flame

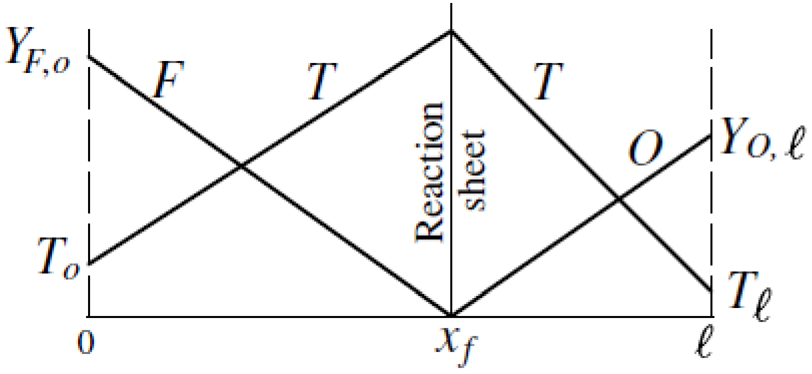


The Chambered Flame





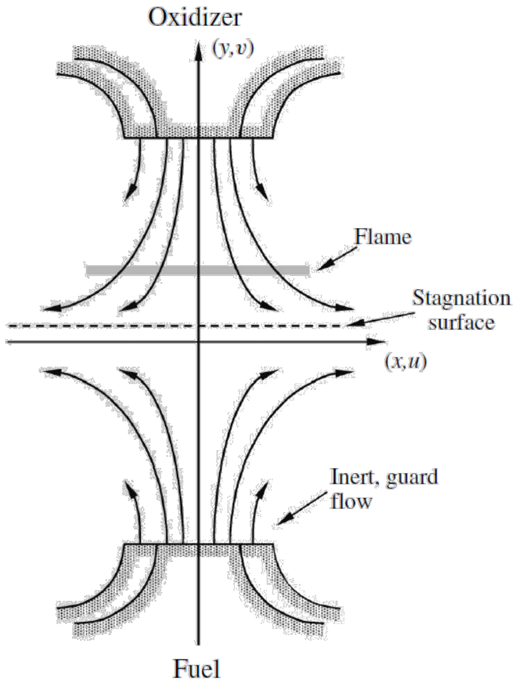
With finite-rate chemistry

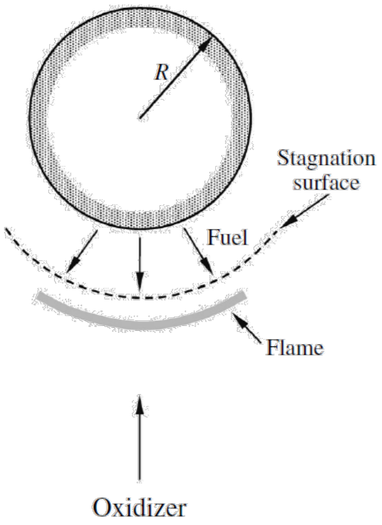


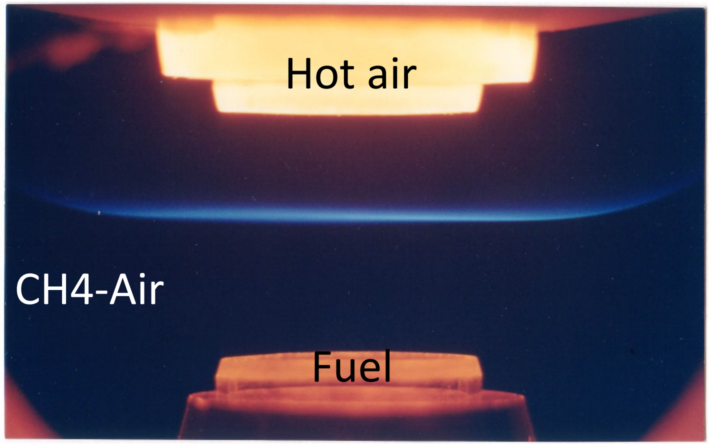
With fast chemistry – flamesheet approximation

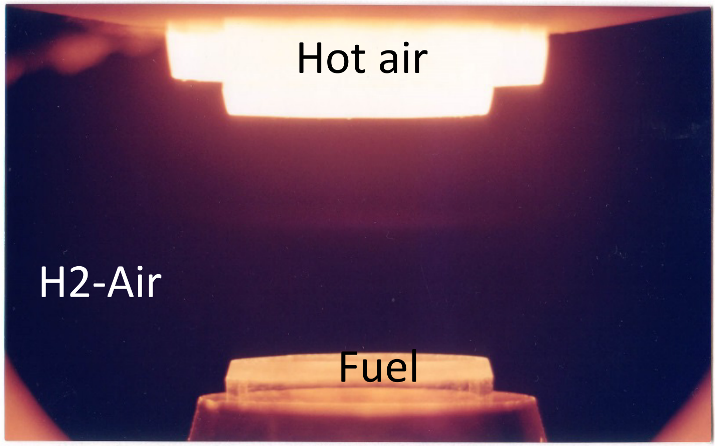
(Combustion Physics, Law 2006)

Non-premixed Counterflow Flames

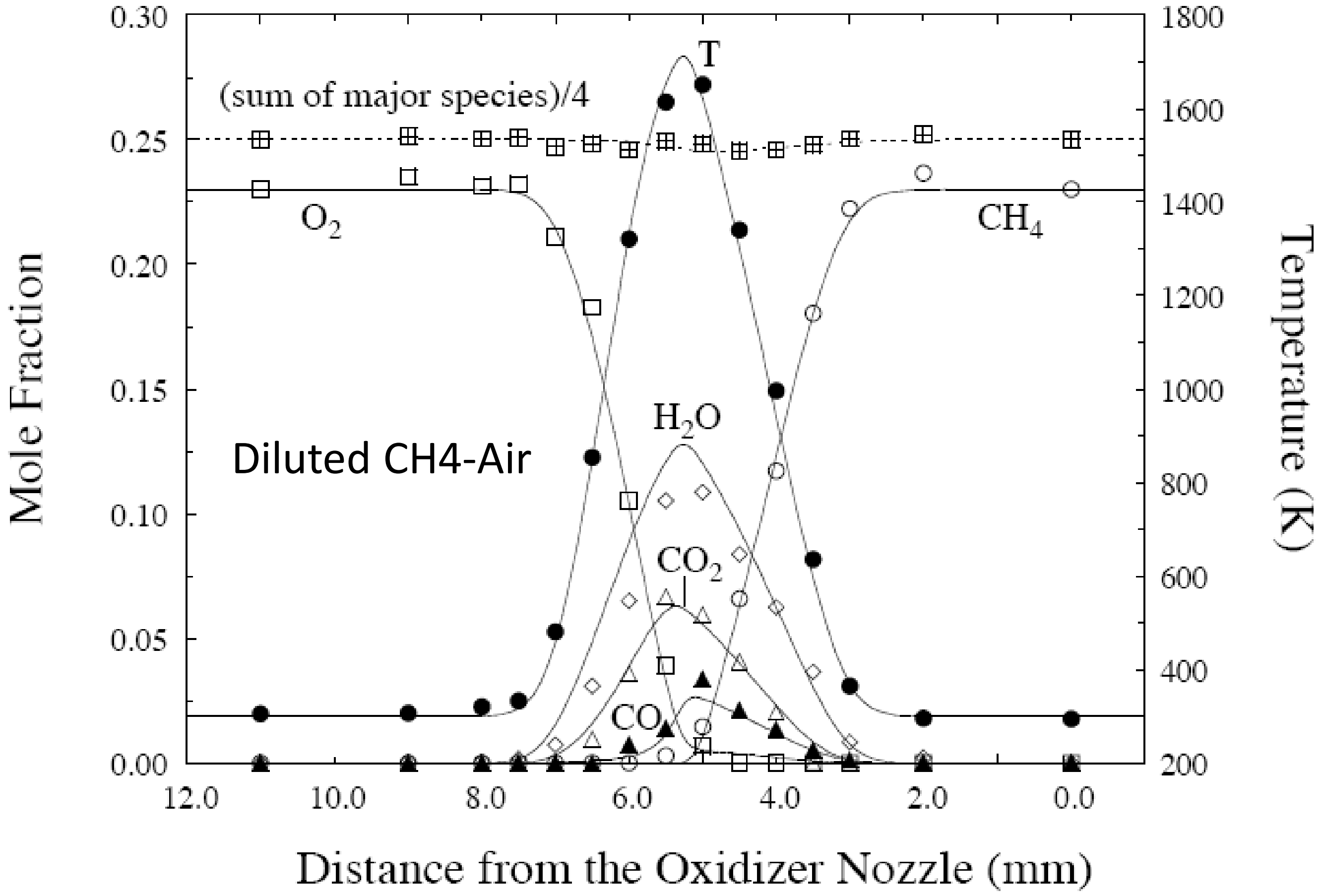






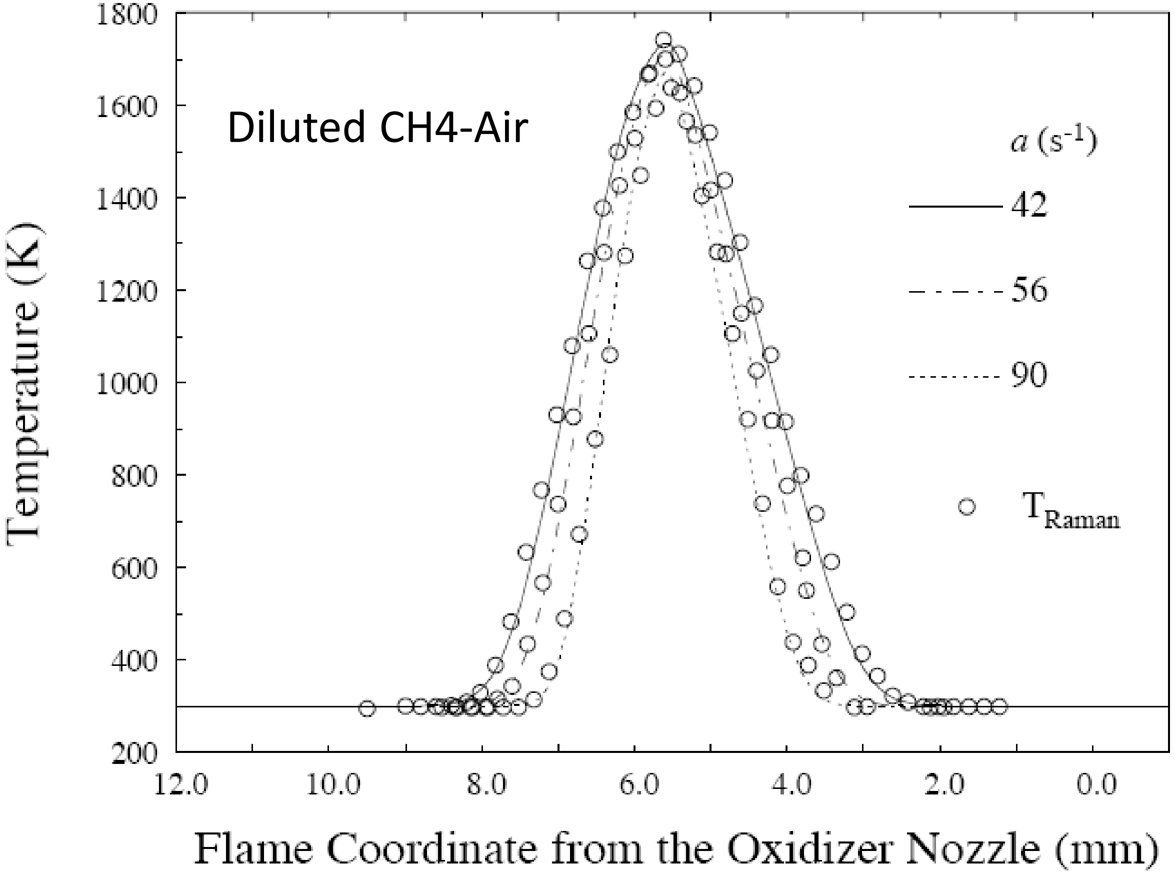


Structure of Counterflow Non-premixed Flames



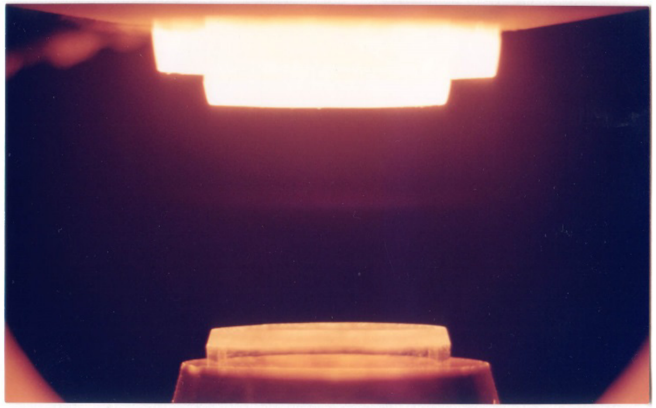
(Combustion Physics, Law 2006)

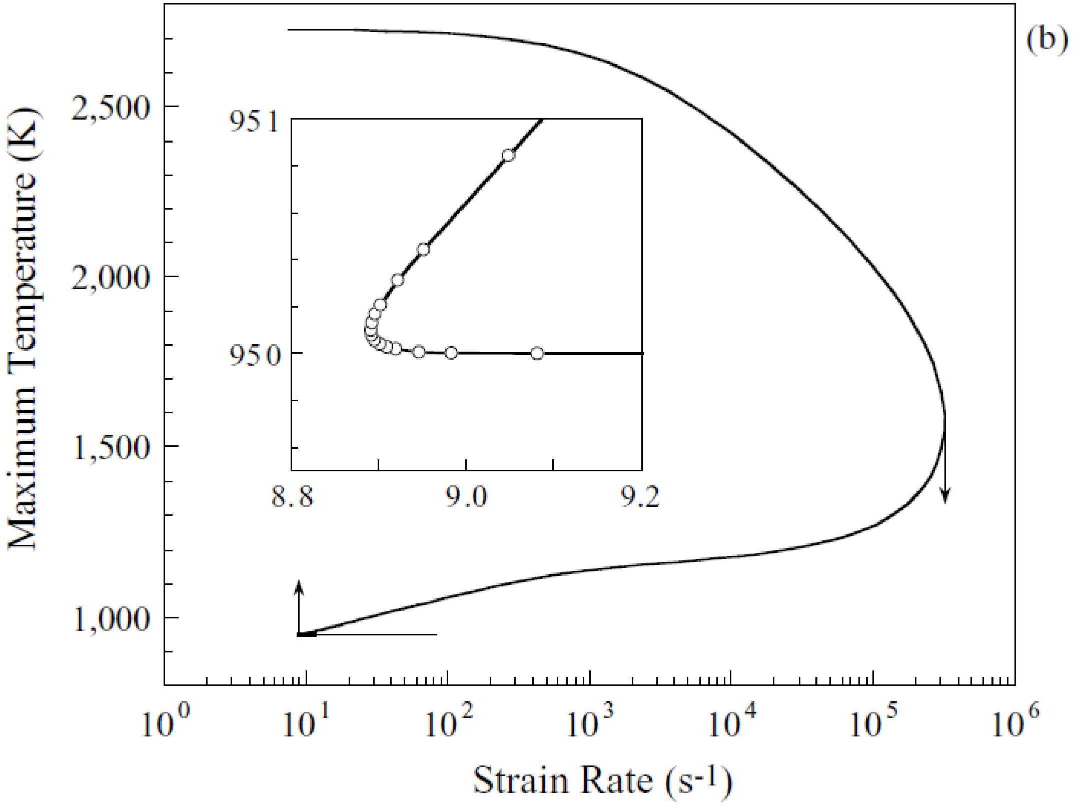
Effect of Strain Rate on Counterflow Non-premixed Flames



(Combustion Physics, Law 2006)

S-Curve for Counterflow Flames



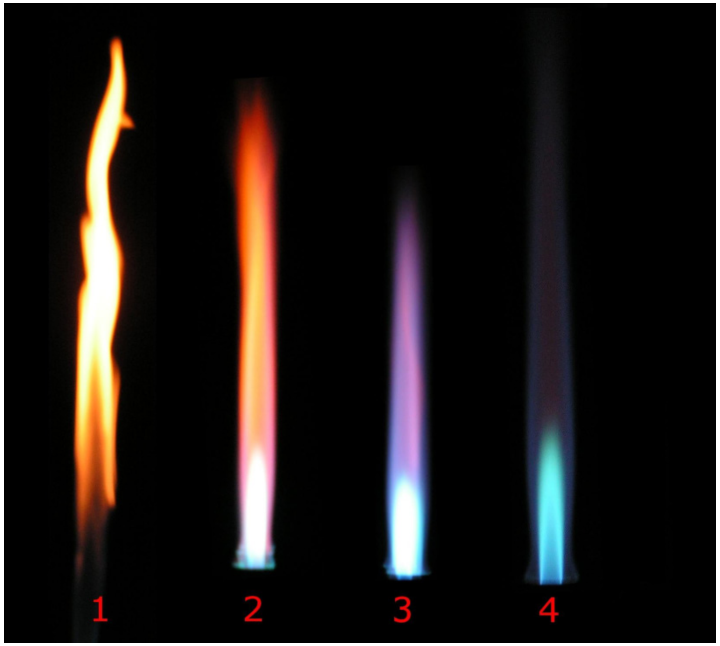


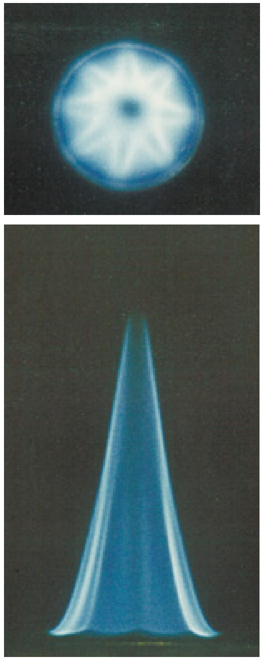
(Combustion Physics, Law 2006)

1-D Premixed Flames

Bunsen Flames

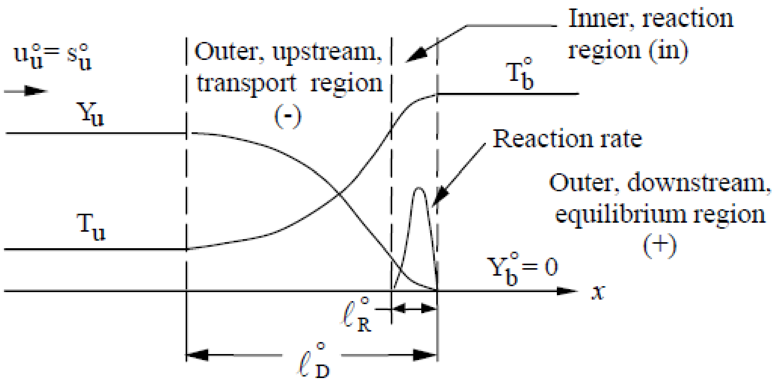
Diffusion flame ← → Premixed flame



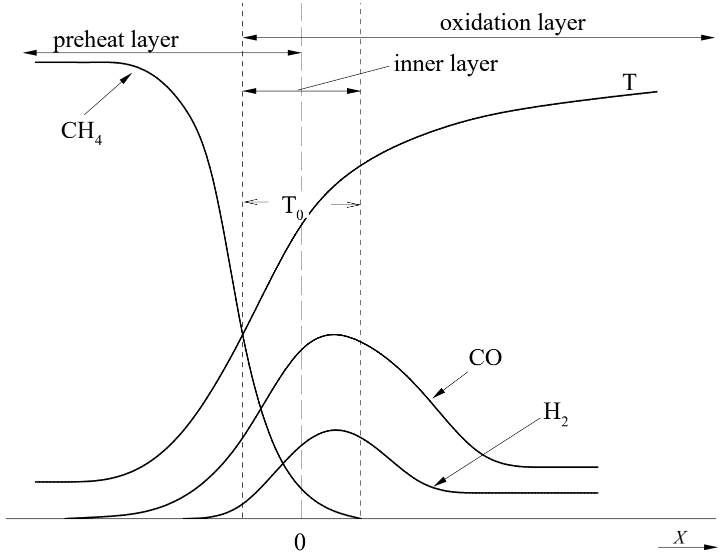


Gas stove flame

Premixed Flame Structures



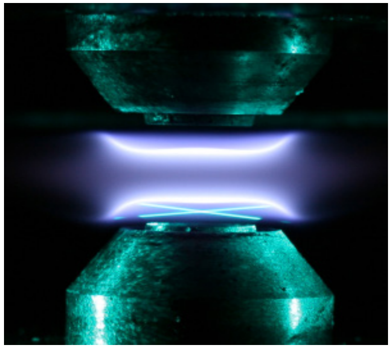
(c)



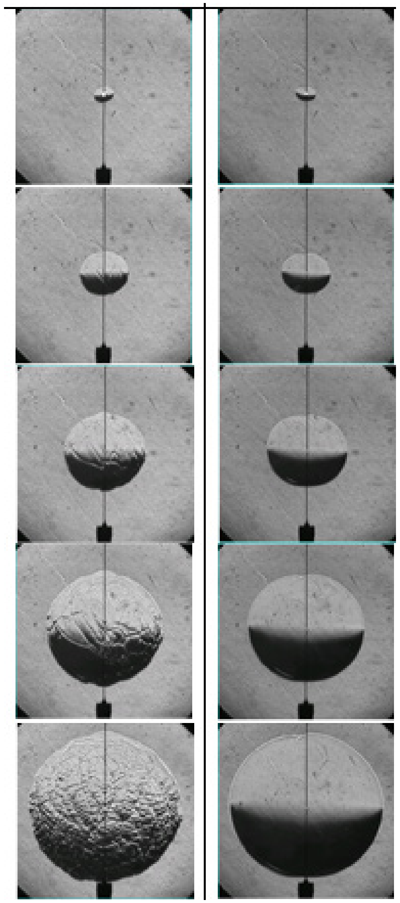
(Combustion Physics, Law 2006)

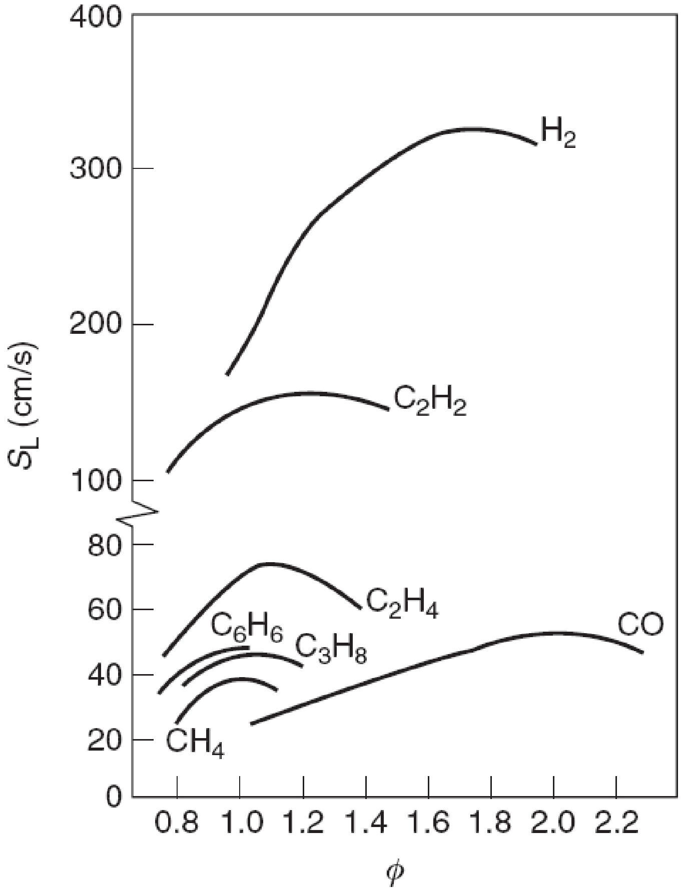
Lab Flames to
Measure Flame Structures and Speeds

Counterflow



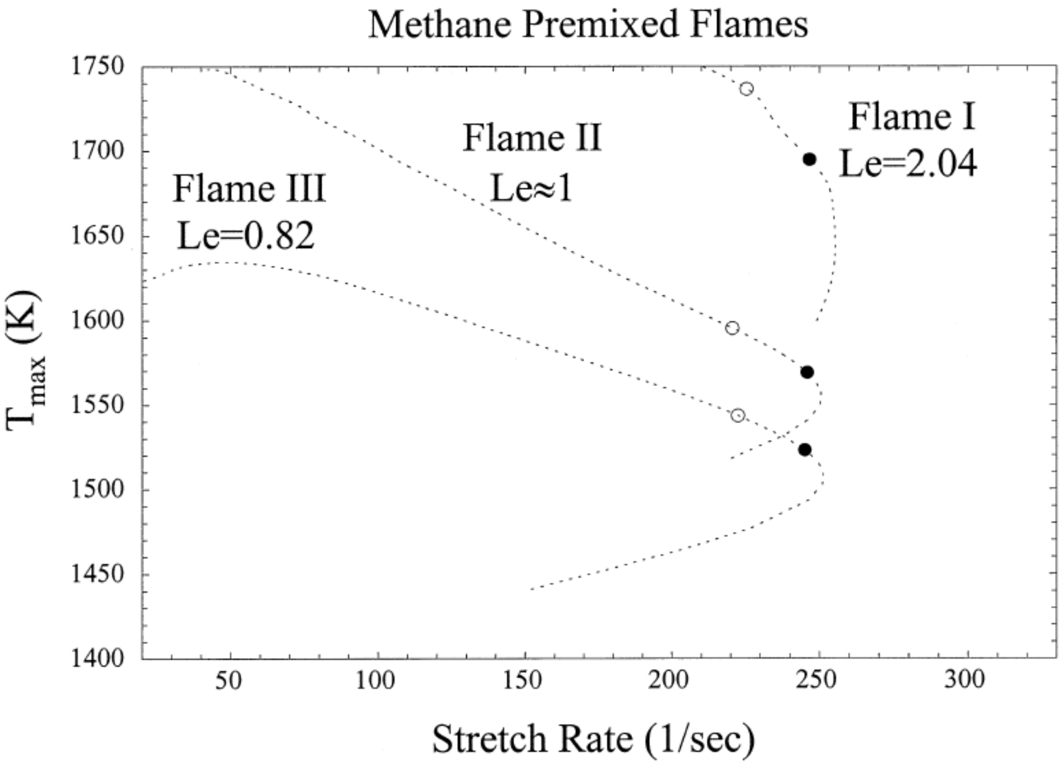
Spherical flames





(Glassman & Yetter, Combustion, 4th ed)

S-curves for Premixed Flames



S-curve of various methane-air premixed flames
(Sung & Law CNF 2000)

Model Reduction and Computational Flame Diagnostics

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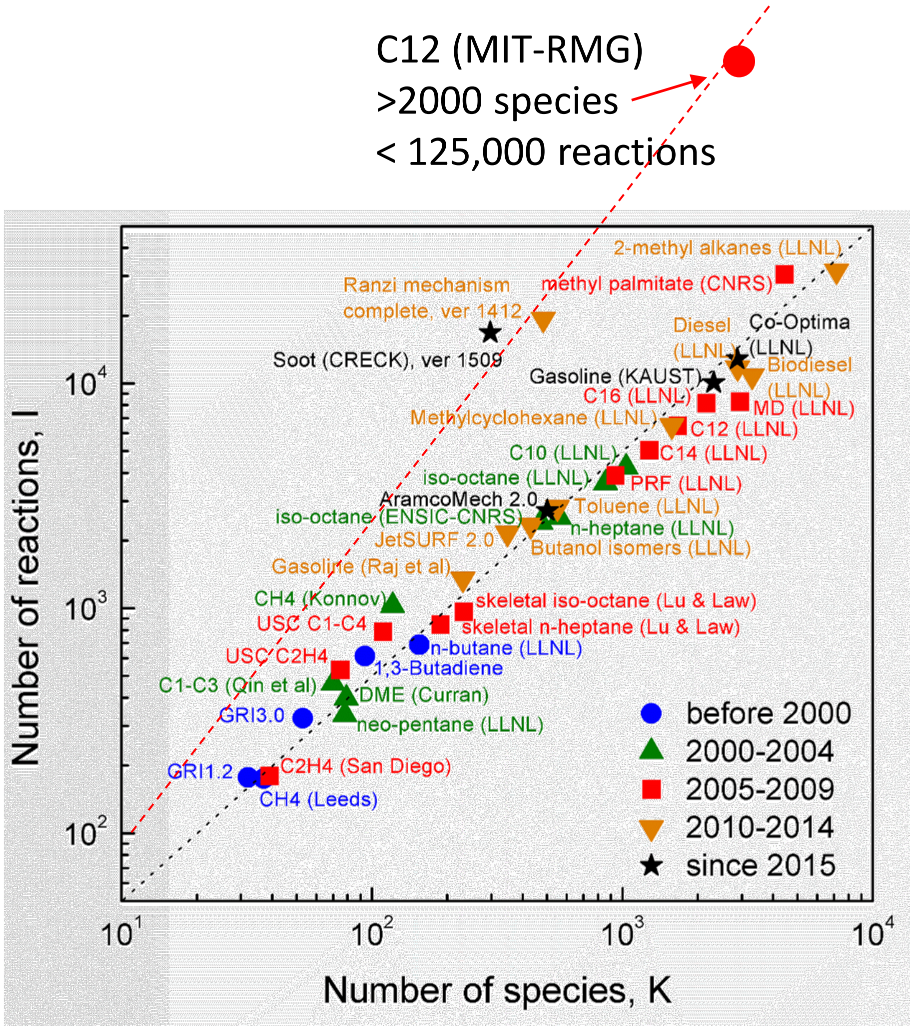
Tsinghua-Princeton-CI
2024 Summer School on Combustion
July 7-13, 2024

Size of Detailed Chemistry



C12 (MIT-RMG)
>2000 species
< 125,000 reactions

(Lu & Law, PECS 2009)

- Detailed mechanisms are large
- Transportation fuels: ~10^3 species,
  ~10^4 reactions
- Flame simulations with detailed chemistry are time-consuming or unaffordable

Approaches for Mechanism Reduction

- 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)
  - …
- Other methods
  - Tabulation, e.g. in situ adaptive tabulation
  - Optimization
  - Solver techniques
  - …

Reduced Mechanisms

- Necessary for possible/faster simulations
  - Smaller size (species & reactions)
  - Reduced stiffness
- Crucial for improving detailed mechanisms
  - Identification/update of the controlling components
  - Understand the couplings

- Challenges
  - Complex couplings
  - Massive information

Starting Point of Mechanism reduction: CPU Cost Analysis

- For each integration step:
  - Chemical source term
  - Diffusion term
  - Jacobian evaluation/manipulation

- Size of integration step affected by stiffness

Integration of Stiff ODEs

$$\frac{d\boldsymbol{Y}}{dt} = g(\boldsymbol{Y})$$

$$\frac{\boldsymbol{Y}^{n+1} - \boldsymbol{Y}^{n}}{h} = g(\boldsymbol{Y}^{n+1})$$

$$F(\boldsymbol{Y}^{n+1}) = \boldsymbol{Y}^{n+1} - hg(\boldsymbol{Y}^{n+1}) - \boldsymbol{Y}^{n} = 0$$

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

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

Time Complexity of Typical Combustion Simulations

- Time complexity of major components:
  - Chemistry: ~ $I \sim 5K$
  - Jacobian (brute force): ~ $KI \sim 5K^2$
  - Diffusion (mixture average): ~ $K^2/2$
- Implicit solvers (Jacobian, chemistry, diffusion)
  - $t_{imp} \sim KI + I + K^2/2 \sim 10K^2 + 10K + K^2$
- Explicit solvers (chemistry, diffusion)
  - $t_{exp} \sim I + K^2/2 \sim 10K + K^2$

- Jacobian is the most expensive component in many applications

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

y: vector of variables,
e.g. species concentration

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

$$\mathbf{J} = \begin{bmatrix} \frac{dg_1}{dy_1} & \frac{dg_1}{dy_2} & \cdots & \frac{dg_1}{dy_n} \\ \frac{dg_2}{dy_1} & \frac{dg_2}{dy_2} & \cdots & \frac{dg_2}{dy_n} \\ \cdots & & & \\ \frac{dg_n}{dy_1} & \frac{dg_n}{dy_2} & \cdots & \frac{dg_n}{dy_n} \end{bmatrix}$$

  - Newton solvers (e.g. PREMIX)
  - Implicit integration solvers (most CFD codes for unsteady flow with detailed chemistry) (why implicit?)

An Example of Large Scale Simulation: Direct Numerical Simulation (DNS)

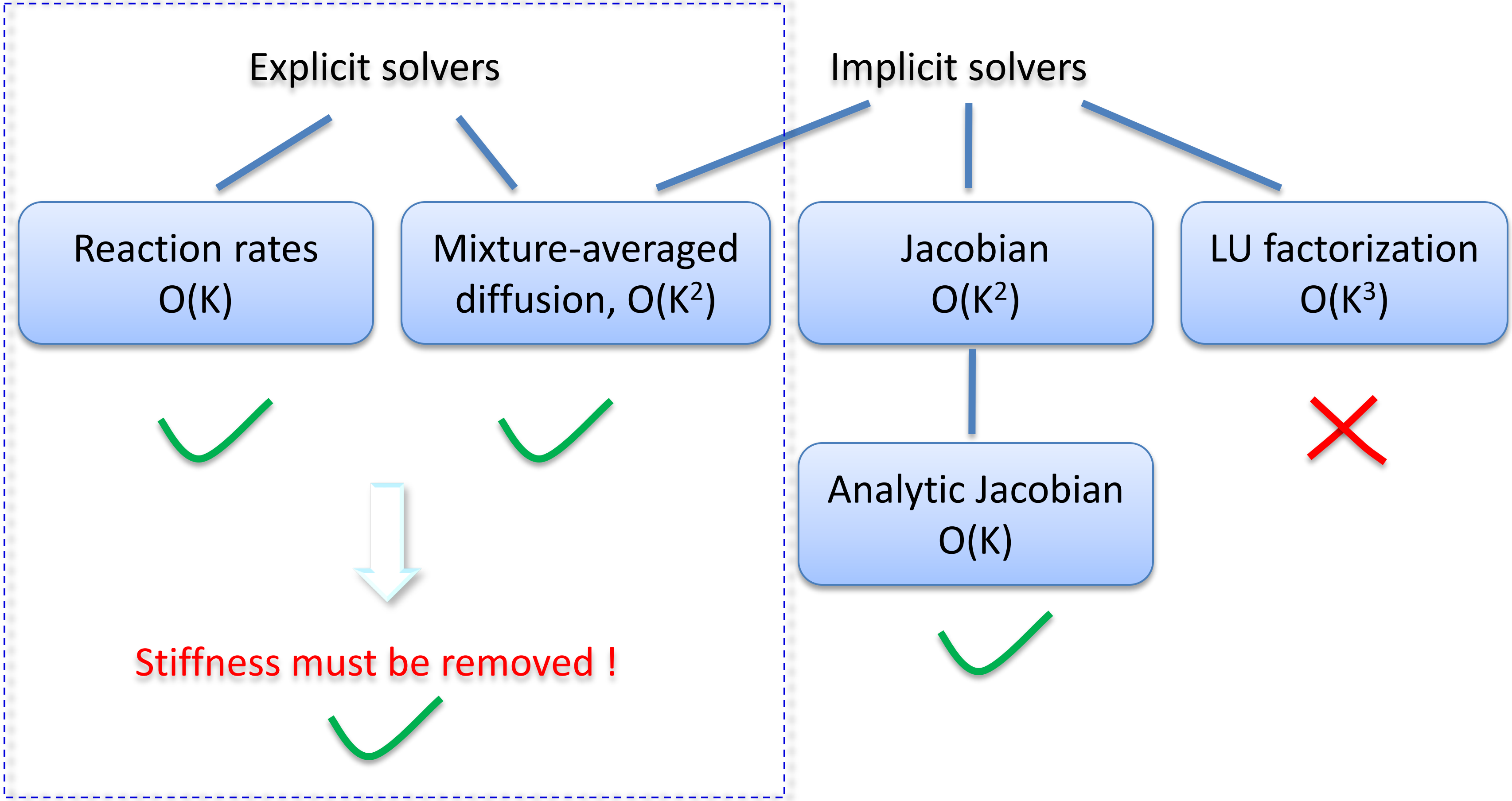
- Solve NS-equation without any turbulence model

- High fidelity
  - Subgrid models for LES & others
  - Numerical experiments

- High cost
  - Turbulence: cost ~ Re^3
    - Need to resolve Kolmogorov scales
  - Chemistry: cost ~ $(K, K^2, \text{or } K^3)$?
    - Large number of variables (species), K
    - Chemical stiffness
  - Overall: ~ Re^3 X $(K, K^2, \text{or } K^3$?)

Selection of Solver for Large Fuels

Overall cost ~ $Re^3 \times O(K, K^2, \text{or } K^3?)$



Explicit solvers

Implicit solvers

Reaction rates
$O(K)$

✓

Mixture-averaged
diffusion, $O(K^2)$

✓

Jacobian
$O(K^2)$

Analytic Jacobian
$O(K)$

✓

LU factorization
$O(K^3)$

✗

Stiffness must be removed !

✓

I. Reduction in Mechanism Size

- Reduction of species (quadratic speedup)
  - Less number of equations (~K)
  - Smaller diffusion matrix, (~K^2)
  - Faster evaluation/manipulation of Jacobian:
    Time complexity of Jacobian ~ K^2

- Reduction of reactions (linear speedup)

Approaches for Skeletal Reduction

- Throwing away redundant species/reactions
  - Brute force
  - Sensitivity analysis: Hwang, Rabitz, Turanyi, …
  - Detailed reduction: Wang & Frenklach
  - Principal component analysis (PCA): Turanyi *et. al.*
  - Computational singular perturbation (CSP): Lam & Gousis
  - **Directed relation graph (DRG)** Lu & Law

Skeletal Reduction with Directed Relation Graph (DRG) (Lu & Law 2005)

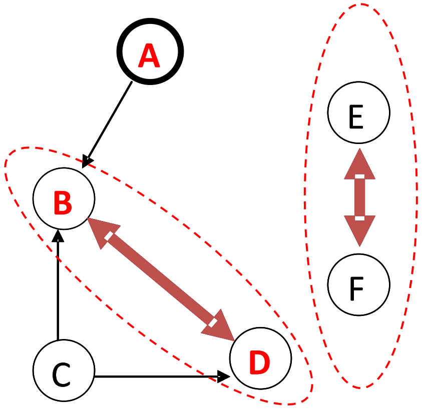
- Targeted at rigorously reducing extremely large mechanisms
- Starts with pair-wise reduction errors (Luo et al, 2010)

$$r_{AB} \equiv \frac{\max_i\left(\left|\nu_{A,i}\omega_i\delta_{Bi}\right|\right)}{\max_i\left(\left|\nu_{A,i}\omega_i\right|\right)} \qquad \delta_{Bi} = \begin{cases} 1, & \text{If reaction i involves species B} \\ 0, & \text{otherwise} \end{cases}$$

$\nu_{A,i}$: stoichiometric coefficient of *A in the* i^{th} *reaction*

ω_i: net reaction rate of the i^{th} reaction

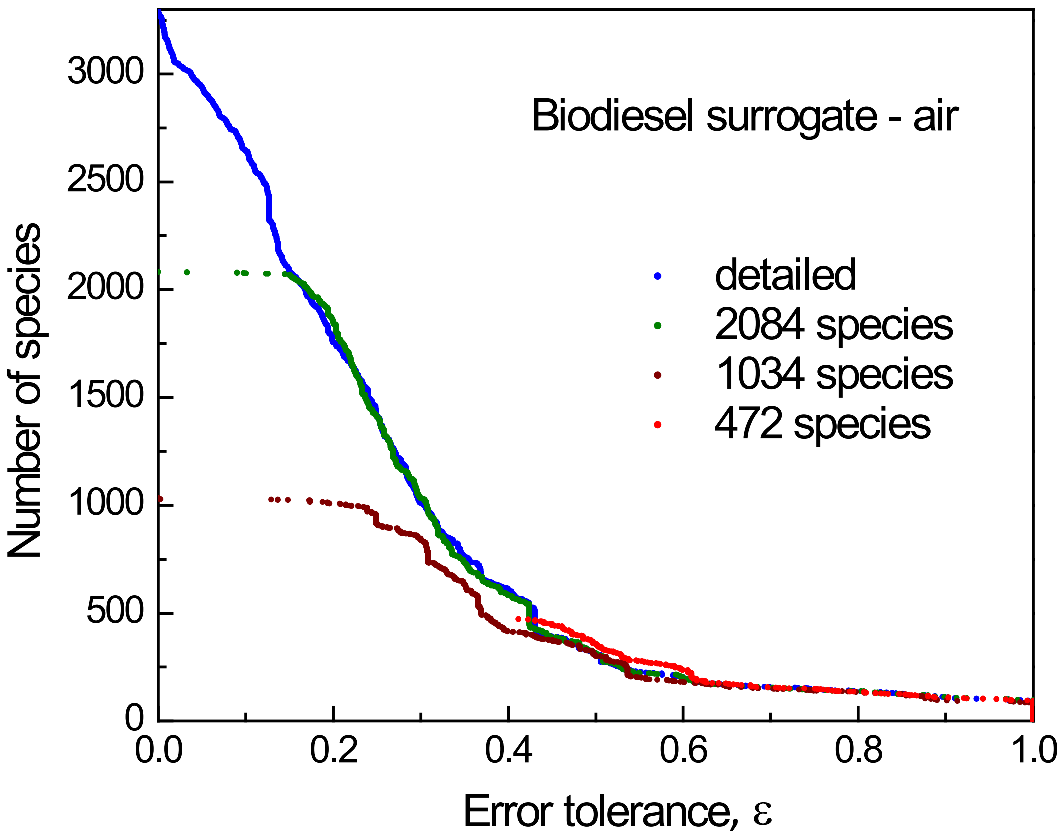
- Construction of DRG
  - Vertex: species (*A*, *B*, *C*, …)
  - Edges: species dependence, $r_{AB} > \varepsilon$
  - Starting vertices: target species
    e.g. H, fuel, oxidizer, product, a pollutant, …



- Graph search: revised depth-first search (RDFS) (Lu & Law, CNF 2006)

Reduction Curves of DRG

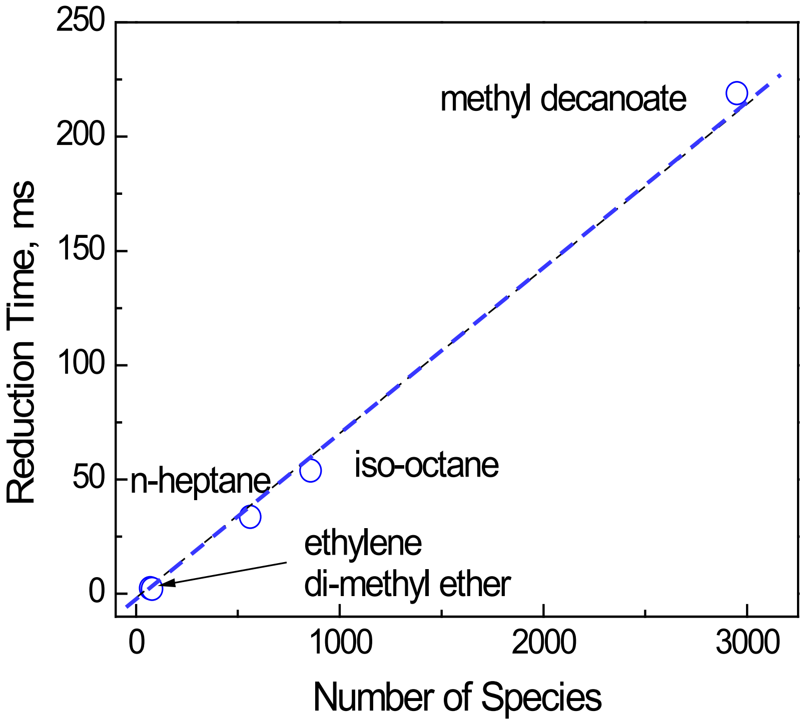
Biodiesel (MD+MD9D+C7) – Air



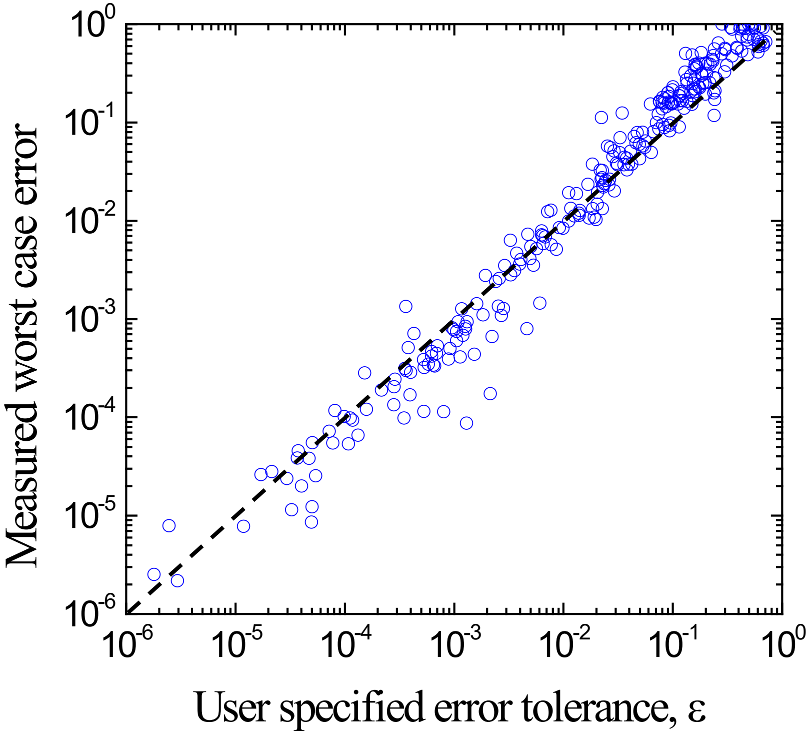
- Detailed mechanism (LLNL 2010):
  - 3329 species
  - 10,806 reactions
- Skeletal Mechanism
  - 472 species
  - 2337 reactions
- Error $\varepsilon/(1+\varepsilon)$: ~30% (worst case)
- Parameter range:
  - p: 1-100 atm
  - ϕ: 0.5 - 2.0
  - Ignition & extinction
  - T_0 >1000K for ignition

Efficiency and Error Control of DRG

- Linear reduction time
  i.e. reduction time ~ # of species



- A priori error control
  Worse-case measured error ~ ε



- Most suitable for
  - The first reduction step for extremely large mechanisms
  - Dynamic adaptive chemistry (DAC)

Other DRG-Based Methods

- DRG with error propagation (DRGEP),
  (Pepiot-Desjardins & Pitsch 2008; Liang et al, 2009; Shi et al 2010)
- Path flux analysis (PFA): (Sun et al, 2009)
- Transport flux based DRG (on-the-fly reduction): (Tosatto et al, 2011)
- DRG with expert knowledge (DRGX): (Lu et al, 2011)

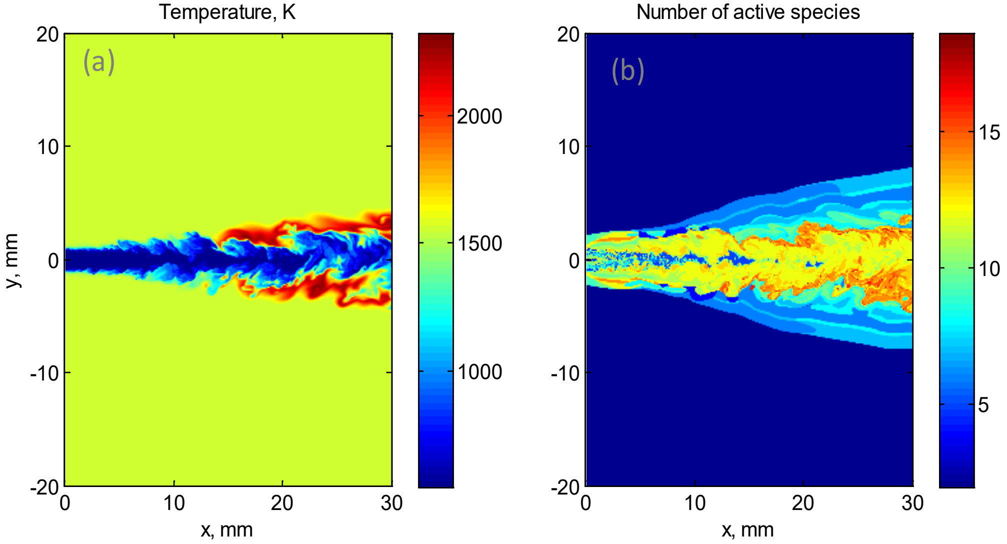
- DRG aided sensitivity analysis (DRGASA),
  (Zheng et al, 2007; Sankaran et al 2007)
- DRGEP with sensitivity analysis (DRGEPSA): (Niemeyer et al 2010)

- Dynamic adaptive chemistry (DAC) with DRG or DRGEP
  (Liang et al 2009; Yang et al 2013)

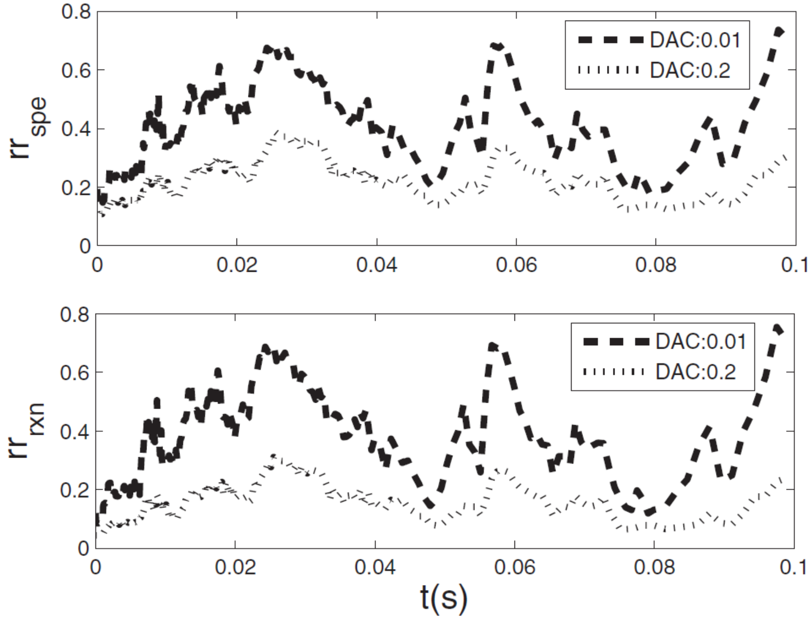
On-the-fly Reduction with
Dynamic Adaptive Chemistry (DAC)

- Number of active species varies dramatically spatially and temporally
- DRG-based methods feature low overhead for DAC (Long et al, 2009)
- Compatible with in situ adaptive tabulation (ISAT) (Pope, CST 1997)

A lifted ethylene jet flame
(Yoo et al, PCI 2011)



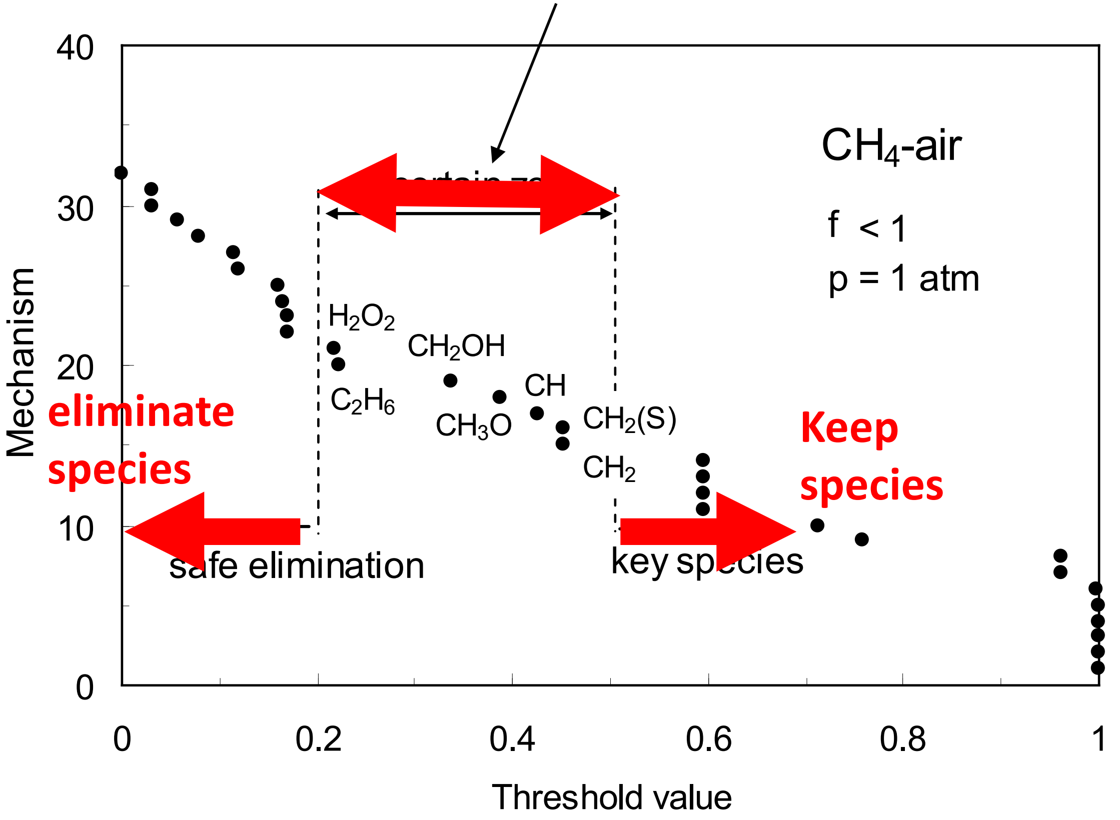
PaSR of non-premixed CH4/Air
(Yang et al, CTM 2013)



DRG Aided Sensitivity Analysis (DRGASA)

Uncertain zone for DRG

Do sensitivity analysis



eliminate species

Keep species

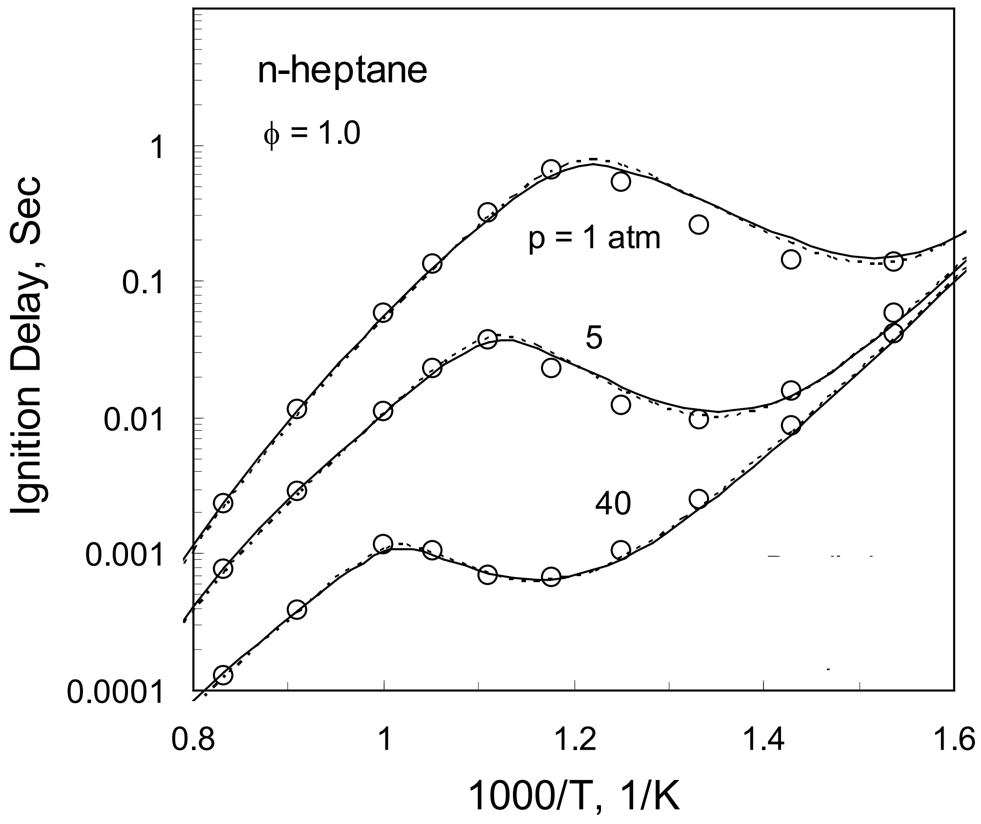
DRGASA

- The number of species for sensitivity analysis is minimized
- Resulting skeletal mechanism is minimal
- Reduction time > DRG
  - DRG ~ ms - s
  - DRGASA ~ hours - days

Example Skeletal Mechanism by DRG+DRGASA

- Detailed
  - 561 species
  - 2539 reactions
- DRG
  - 188 species
  - 939 reactions
- DRGASA
  - 78 species
  - 317 reactions

n-heptane (LLNL)



II: Timescale based Reduction

- Stiffness: large difference in time scales
  - Majors species: typically with controlling time scale
  - Radicals (e.g. OH, HCO, CH2, …): extremely short time scales

- Highly stiff ODEs
  - Implicit solver with small steps
  - Explicit solvers with Jacobian
  - All with high simulation cost

Approaches for Time Scale Reduction

- Quasi steady state (QSS) & Partial equilibrium (PE) assumption
- Rate-controlled constrained equilibrium (RCCE)
- Intrinsic low dimensional manifold (ILDM)
- Computational singular perturbation (CSP)
- …

General Approaches: ILDM & CSP

- The ODEs: $$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y})$$

y: vector of variables,
e.g. species concentration

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

J is time dependent in general

- Basis change: $$\mathbf{f} = \mathbf{B}\cdot\mathbf{g}$$

f: modes,
B: basis vectors,
is time dependent in general

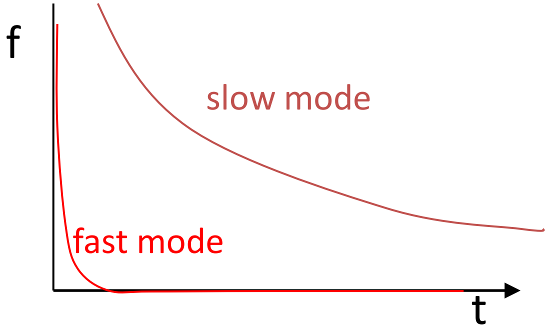
$$\boxed{\frac{d\mathbf{f}}{dt} = \mathbf{\Lambda}\cdot\mathbf{f},}\quad \mathbf{\Lambda} = (\frac{d\mathbf{B}}{dt} + \mathbf{B}\cdot\mathbf{J})\cdot\mathbf{A},\quad \mathbf{A} = \mathbf{B}^{-1}$$

Intrinsic Low Dimensional Manifold (ILDM)

- Assuming constant **J** (local linear model)
- Diagonal (or triangular) $\mathbf{\Lambda}$ can be obtained by eigenvalue decomposition (or Shur decomposition)
- Rates in the directions of the eigenvalues associated with the fast odes vanish in transient time

$$\frac{d\mathbf{f}}{dt} = \mathbf{\Lambda}\cdot\mathbf{f}, \quad \mathbf{\Lambda} = \mathbf{V}^{-1}\cdot\mathbf{J}\cdot\mathbf{V}$$

$$\frac{df_i}{dt} = \lambda_i f_i$$ Time scale of mode: $$\tau_i = 1/\left|\lambda_i\right|$$



$f_i \to 0$ If λ_i is large negative number

Computational Singular Perturbation (CSP)

- **J** is time dependent
- In general, Λ can not be diagonalized
- CSP refinement
  - Find a set of basis vectors **A** and **B**, such that Λ is block-diagonal
  - Eigenvalues of Λ_f are all large negative numbers

$$\mathbf{\Lambda} = (\boxed{\frac{d\mathbf{B}}{dt}} + \mathbf{B} \cdot \mathbf{J}) \cdot \mathbf{A}$$

$$\mathbf{\Lambda} = \begin{bmatrix} \mathbf{\Lambda}_f & \\ & \mathbf{\Lambda}_s \end{bmatrix}$$

$$\mathbf{f} = \begin{pmatrix} \mathbf{f}_{fast} \\ \mathbf{f}_{slow} \end{pmatrix} = \begin{pmatrix} \mathbf{B}_{fast} \\ \mathbf{B}_{slow} \end{pmatrix} \cdot \mathbf{g}$$

$\mathbf{f}_{\mathrm{fast}} \to 0$ in transient time

Comments on CSP

- Advantage: fast processes handled universally

- Time consuming
  - Jacobian evaluation
  - Eigenvalue decomposition or CSP refinement

- Coupling of fast species is typically sparse
  - Classical approaches of QSS and PE can be more efficient

Quasi Steady State Assumptions

- Example

$$A \xrightarrow{1} B \xRightarrow{1/\varepsilon} C \qquad \tau_{\text{control}} \sim O(1)$$

  - Destruction much faster than creation
  - B is a QSS species:

$$\frac{dB}{dt} = A - \frac{B}{\varepsilon} \approx 0 \longrightarrow B \approx A\varepsilon$$

  - Question:
    - How to identify QSS species?

Partial Equilibrium Assumptions

- An example:

$$A \xrightarrow{1} B \xleftrightarrow{1/\varepsilon} C \qquad \tau_{\text{control}} \sim O(1)$$

  - Forward and backward rates are much faster than the net rate
  - Reaction B↔C is in PE:

$$\frac{B}{\varepsilon} - \frac{C}{\varepsilon} \approx 0 \qquad \longrightarrow \qquad B \approx C$$

  - Question: How to apply PE assumptions?

Properties of QSS & PE

QSS Species	**PE involved species**
Concentration ~ O(ε)	O(1)
Can hide from governing equations	Has to be retained in governing equations
Can be directly applied back for rate computation	Should not be directly applied back for rate computation
Both are fast to apply	

QSS and PE species need to be treated differently

Identification of QSS Species

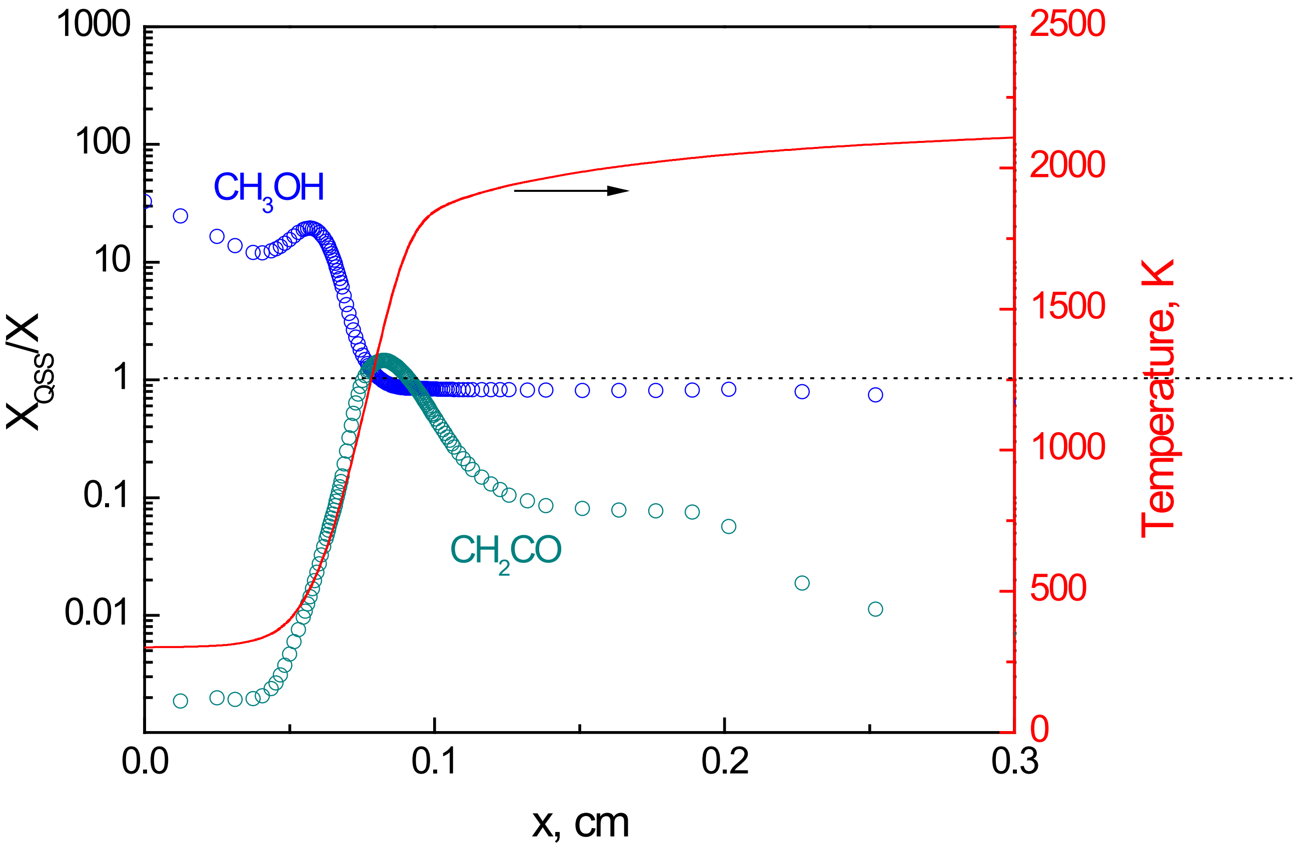
- Conventional criteria
  - Low concentrations
  - Small normalized net production rates
  - Short lifetime (or diagonal elements of Jacobian) $\tau_i = 1/J_{i,i} = 1\Big/\frac{dg_i}{dy_i}$
- These are only necessary conditions for QSSA
- Example:

$$F + R_1 \rightarrow P + R_1 \qquad k_{1f} = 1/\varepsilon$$

$$F \rightarrow R_1 \qquad k_{2f} = \varepsilon$$

$$R_1 \Leftrightarrow R_2 \qquad k_{3f} = k_{3r} = 1/\varepsilon$$

Error Induced by Bad QSSA



Selection of QSS Species

- A criterion based on fast-slow separation (CSP, ILDM, or eigenvalue decomposition)

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

$$\mathbf{f} = \mathbf{B}\cdot\mathbf{g}, \qquad \frac{d\mathbf{f}}{dt} = \mathbf{\Lambda}\cdot\mathbf{f}, \qquad \mathbf{\Lambda} = (\frac{d\mathbf{B}}{dt} + \mathbf{B}\cdot\mathbf{J})\cdot\mathbf{A}, \quad \mathbf{A} = \mathbf{B}^{-1}$$

$$\mathbf{\Lambda} = \begin{pmatrix} \mathbf{\Lambda}_{fast} & \\ & \mathbf{\Lambda}_{slow} \end{pmatrix}, \qquad \mathbf{A} = \begin{pmatrix} \mathbf{A}_{fast} & \mathbf{A}_{slow} \end{pmatrix}, \qquad \mathbf{B} = \begin{pmatrix} \mathbf{B}_{fast} \\ \mathbf{B}_{slow} \end{pmatrix}$$

$$\mathbf{Q} = \mathbf{A}_{slow}\mathbf{B}_{slow}$$

Necessary & sufficient condition:

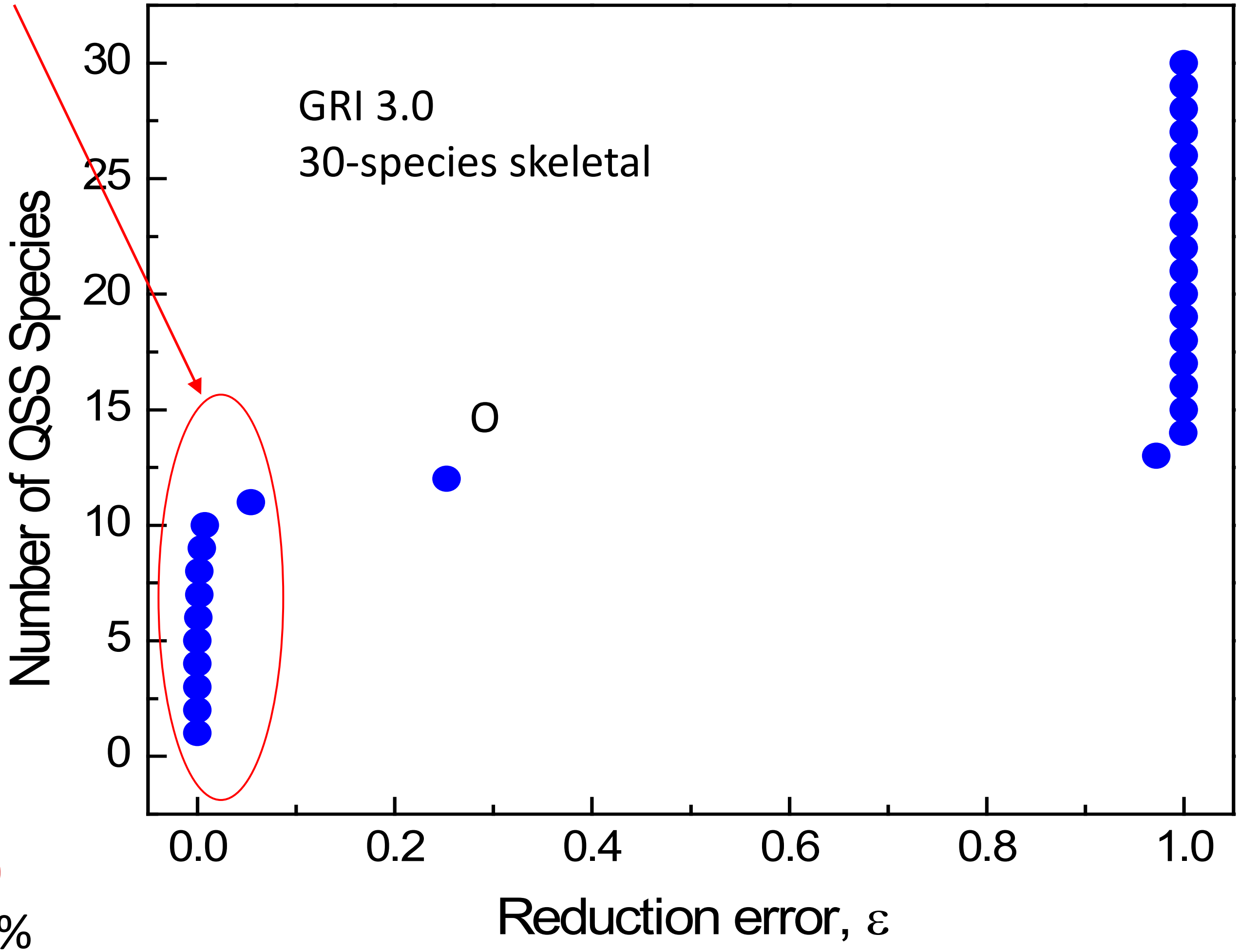
$\mathbf{Q}_{i,i} < \varepsilon \quad \longleftrightarrow \quad$ Species *i* is in QSS

ε: relative induced error

Selection of QSS Species (CH4)

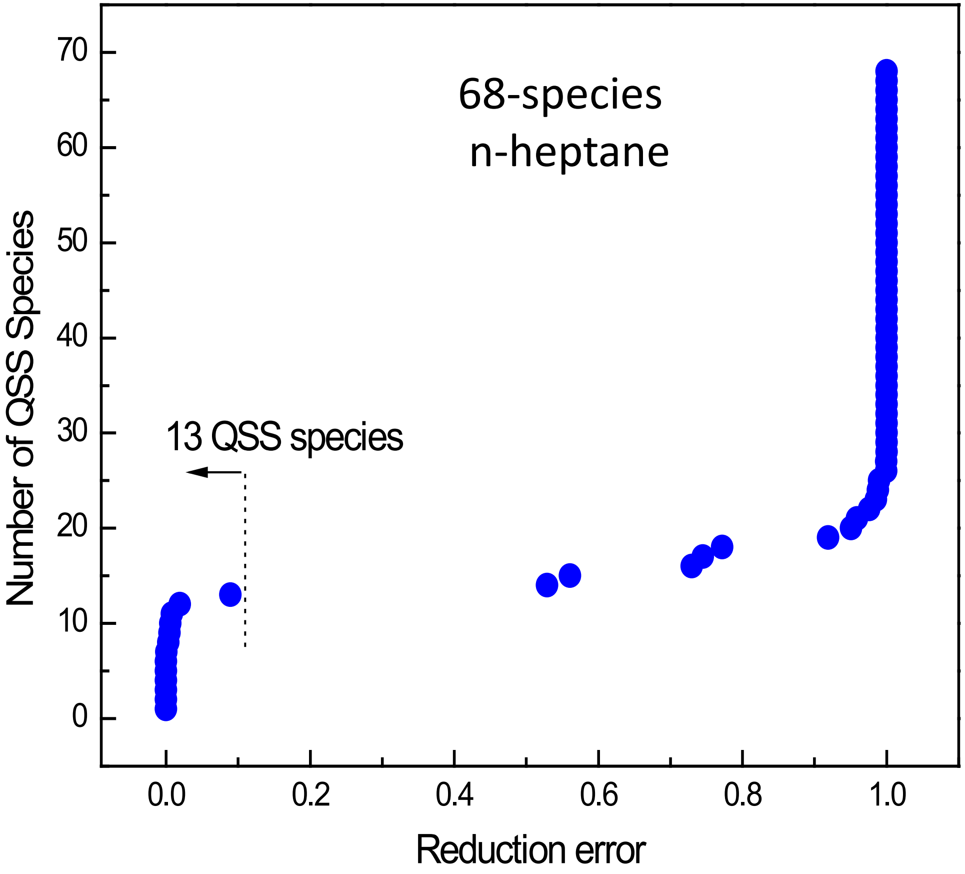
11 QSS species:

HCCO
CH_2
C_2H_5
C_2H_3
CH_3O
HCO
CH
$CH_2(S)$
CH_2OH
C
CH_2CHO



Reduced:
15-step (19 species)
Reduction error: 13%

Selection of QSS Species (heptane)



Reduced: 55 species (51-step)

Next Step: Solving QSS Equations

$$\frac{d\mathbf{y}_{QSS}}{dt} = \mathbf{g}_{QSS}(\mathbf{y}_{\mathbf{QSS}};\mathbf{y}_{major}, p, T) = \mathbf{0}$$

- Traditional approach: algebraic iterations
  - Slow convergence (inefficiency)
  - Divergence (crashes, …)

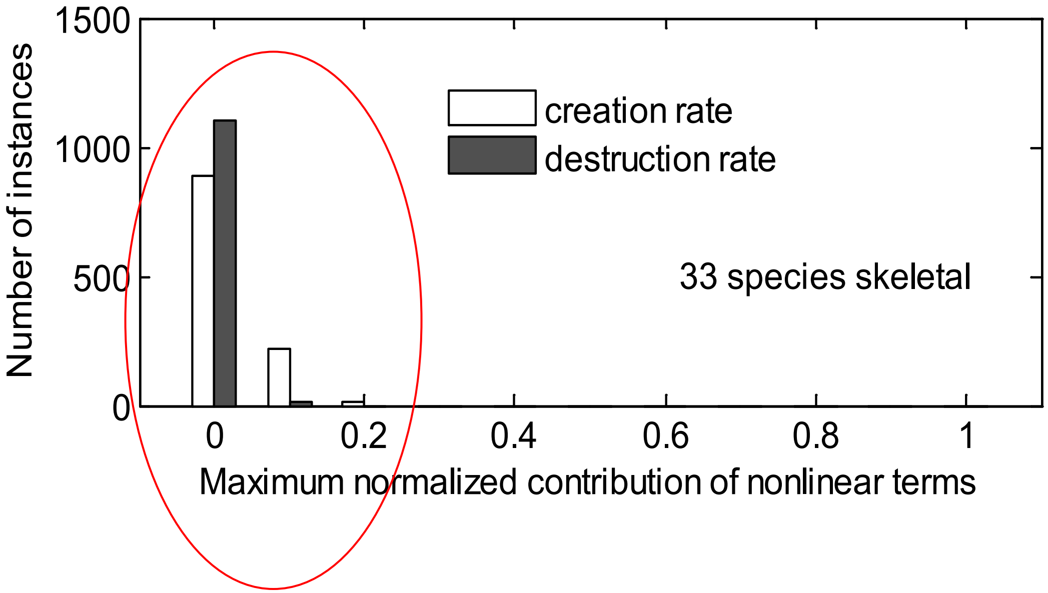
- New approach: analytic solution
  1. Linearization
  2. Solving linearized QSSA with graph theory

Linearized QSSA (LQSSA)

- QSS species are in low concentrations, say $O(\varepsilon)$
- Reactions with more than one QSS reactant are mostly unimportant; reaction rate: $O(\varepsilon^2)$

Example: ethylene

>1000 sampled instances, 12 QSS Species



Analytic Solution of LQSSA

Equation LQSSA:

$$D_i x_i = \sum_{k \neq i} C_{ik} x_k + C_{i0} \qquad D_i > 0,\ C_{ik} \geq 0,\ C_{i0} \geq 0$$

Destruction rate

Creation Rate involving other QSS species

Creation Rate involving major species

Standard form:

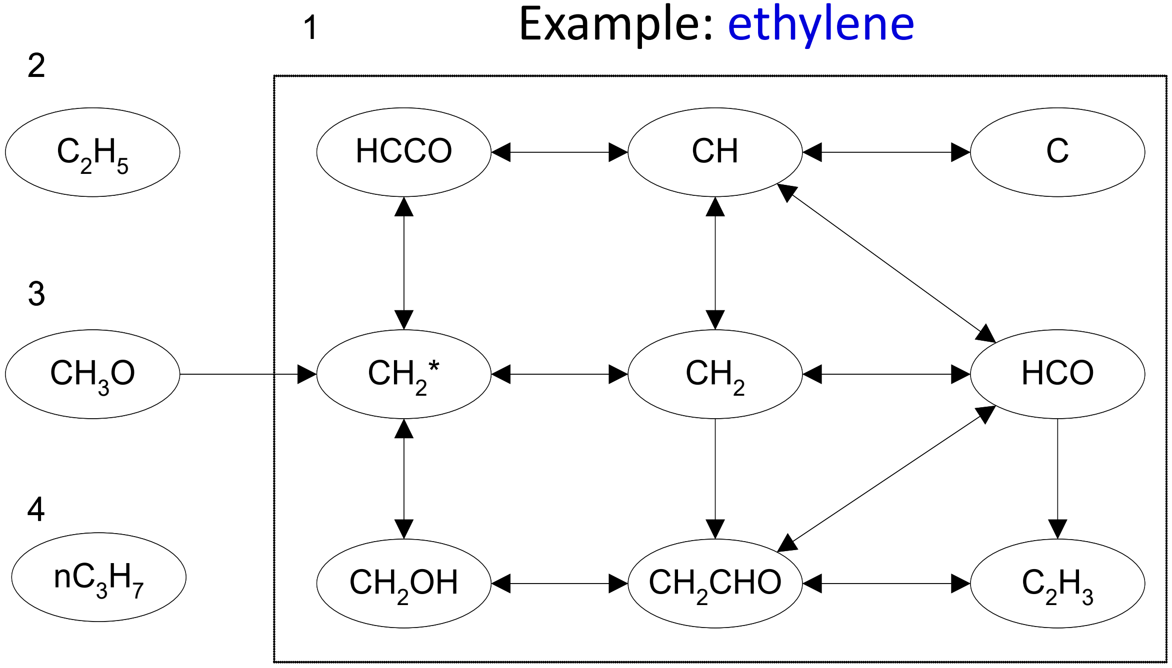
$$x_i = \sum_{j \neq i} A_{ij} x_j + A_{i0} \qquad \boxed{A_{ij} \geq 0,\ A_{i0} \geq 0}$$

- Gaussian elimination ~ N^3
- The coefficient matrix **A** is sparse

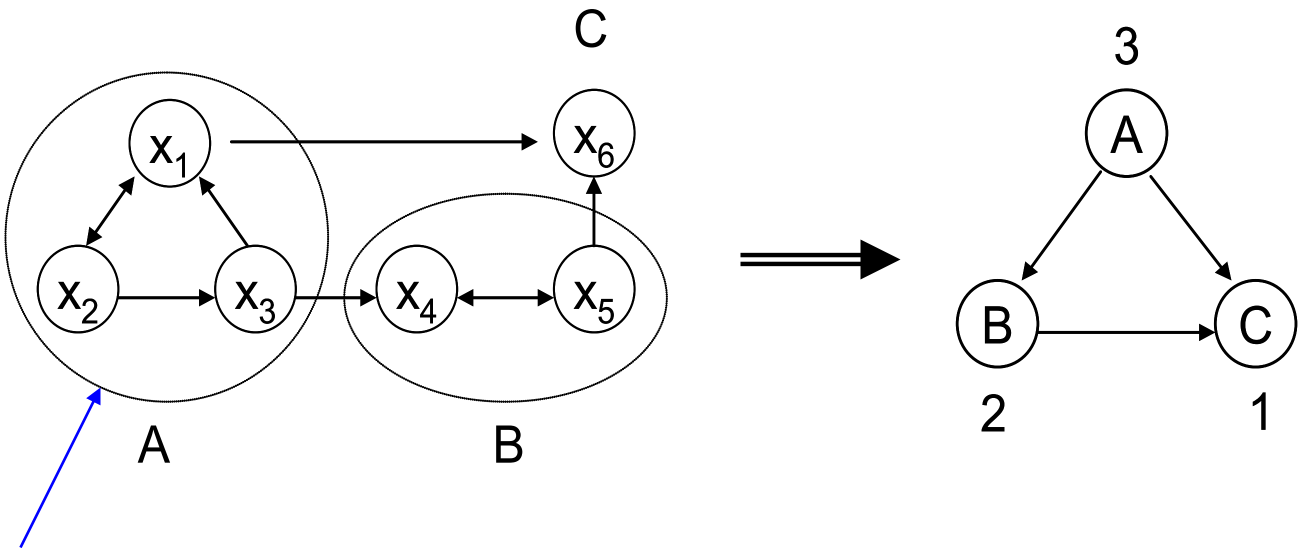
QSS Graph (QSSG)

- Each vertex is a QSS species
- $x_i \rightarrow x_j \;\; iff \, \mathrm{A_{ij}}{>}0, \quad x_i = \sum_{j \neq i} A_{ij} x_j + A_{i0}$

Example: ethylene



Decouple Species Groups by Topological Sort



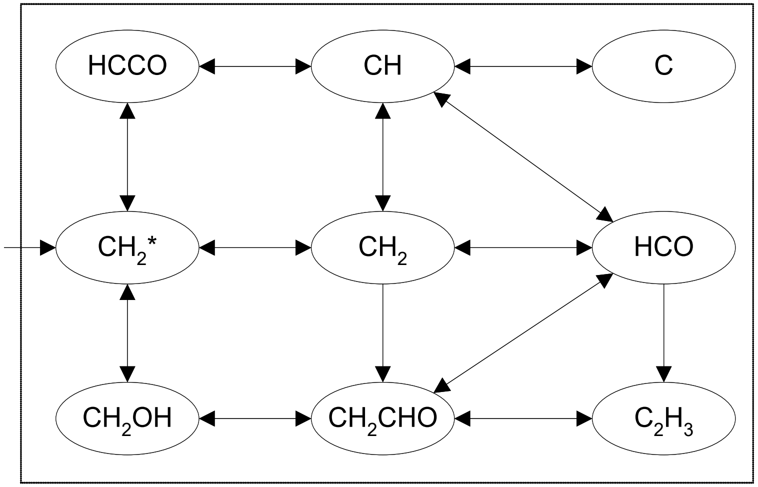
Strongly connected component (SCC): coupled with cyclic path

Identification of SCC:
Depth-First Search for G and G^T

- Treat SCC as composite vertex
- Acyclic graph obtained by topological sort
- Species groups can be solved explicitly in topological order

Solving Implicit Kernels

- Paper & pencil: eliminate the most isolated variables first



- Systematic: a spectral method

$$\mathbf{c} = \mathbf{L} \cdot \mathbf{c}$$

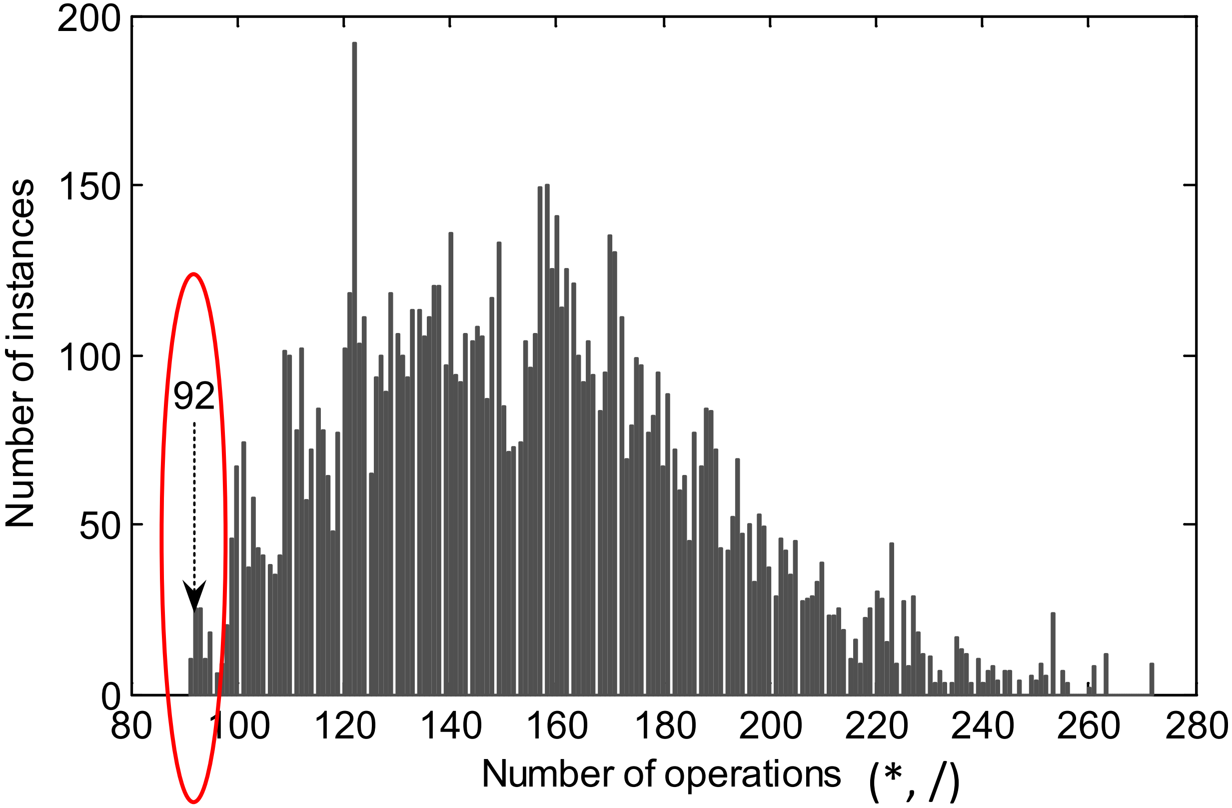
$$\mathbf{c} = (c_1, c_2, \ldots, c_M)^T$$

$$L_{ij} = E_{ij} / \sum_{k=1}^{M} E_{kj}$$

c: Expansion cost vector,
L: Averaging operator
E: the adjacency matrix

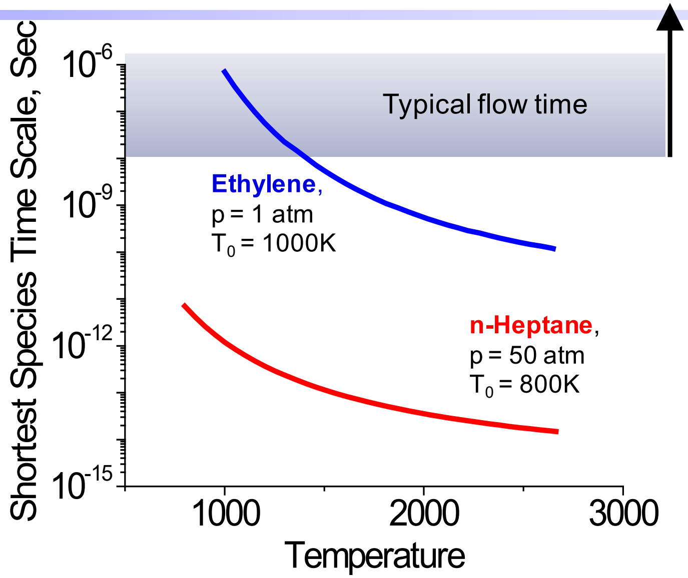
Efficiency of the Analytic Solution

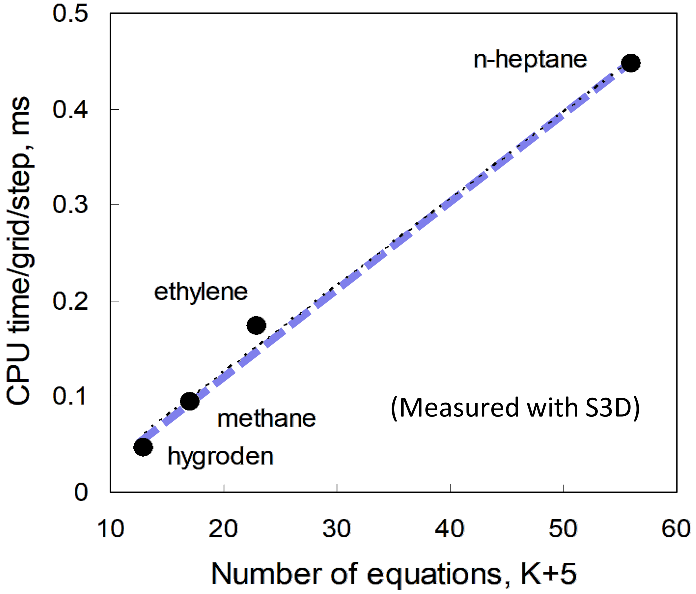
Ethylene/air, 9-species SCC,
10000 random sequences



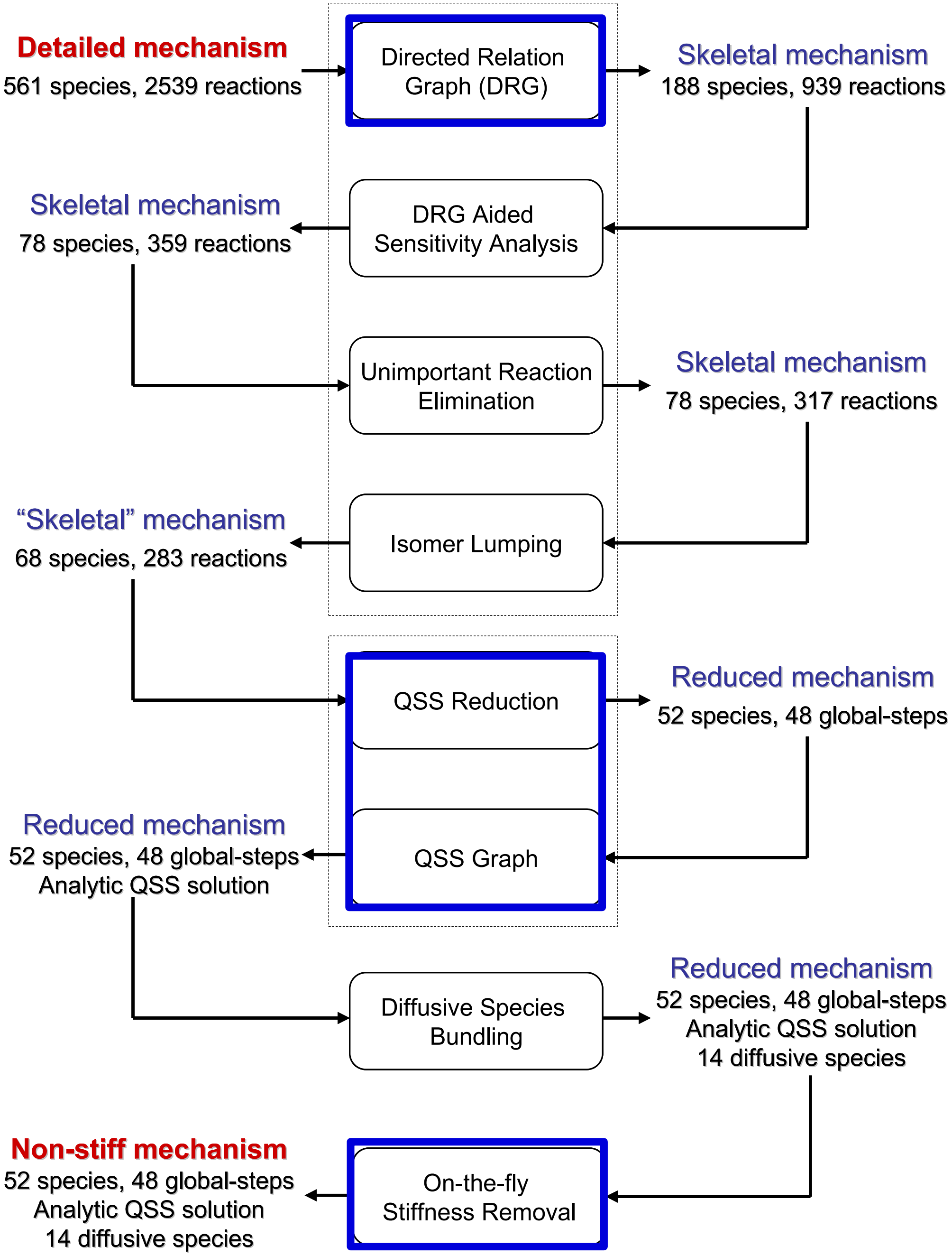
Dynamic Chemical Stiffness Removal (DCSR) (Lu et al, CNF 2009)

- Mechanisms are still stiff after skeletal reduction & global QSSA
- Implicit solvers needed for stiff chemistry
  - Cost in evaluation of Jacobian ~ O(K^2)
  - Cost in factorization of Jacobian ~ 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: ~ O(K)**





Reduction Flow Chart



Detailed mechanism
561 species, 2539 reactions

Directed Relation Graph (DRG)

Skeletal mechanism
188 species, 939 reactions

DRG Aided Sensitivity Analysis

Skeletal mechanism
78 species, 359 reactions

Unimportant Reaction Elimination

Skeletal mechanism
78 species, 317 reactions

Isomer Lumping

“Skeletal” mechanism
68 species, 283 reactions

QSS Reduction

Reduced mechanism
52 species, 48 global-steps

QSS Graph

Reduced mechanism
52 species, 48 global-steps
Analytic QSS solution

Diffusive Species Bundling

Reduced mechanism
52 species, 48 global-steps
Analytic QSS solution
14 diffusive species

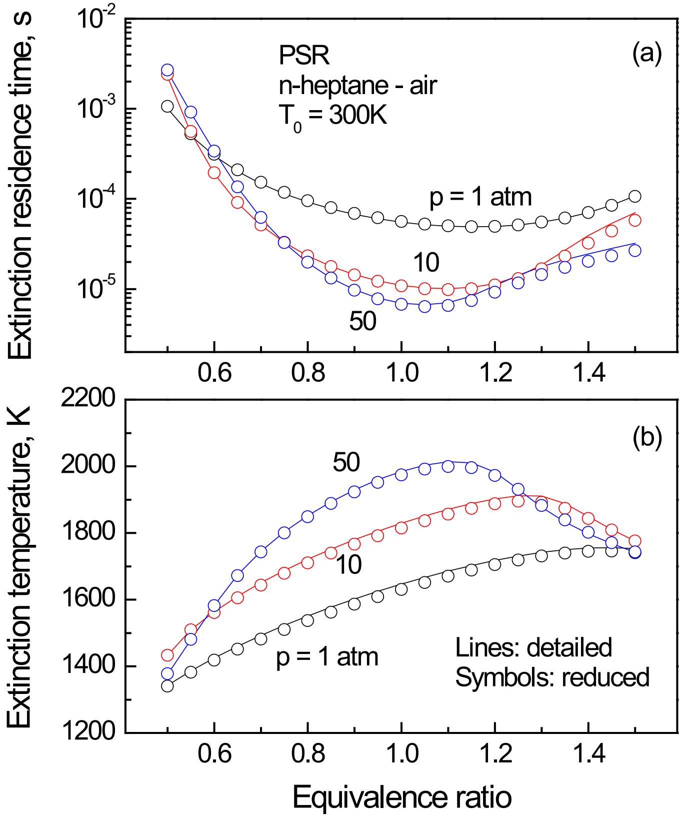
On-the-fly Stiffness Removal

Non-stiff mechanism
52 species, 48 global-steps
Analytic QSS solution
14 diffusive species

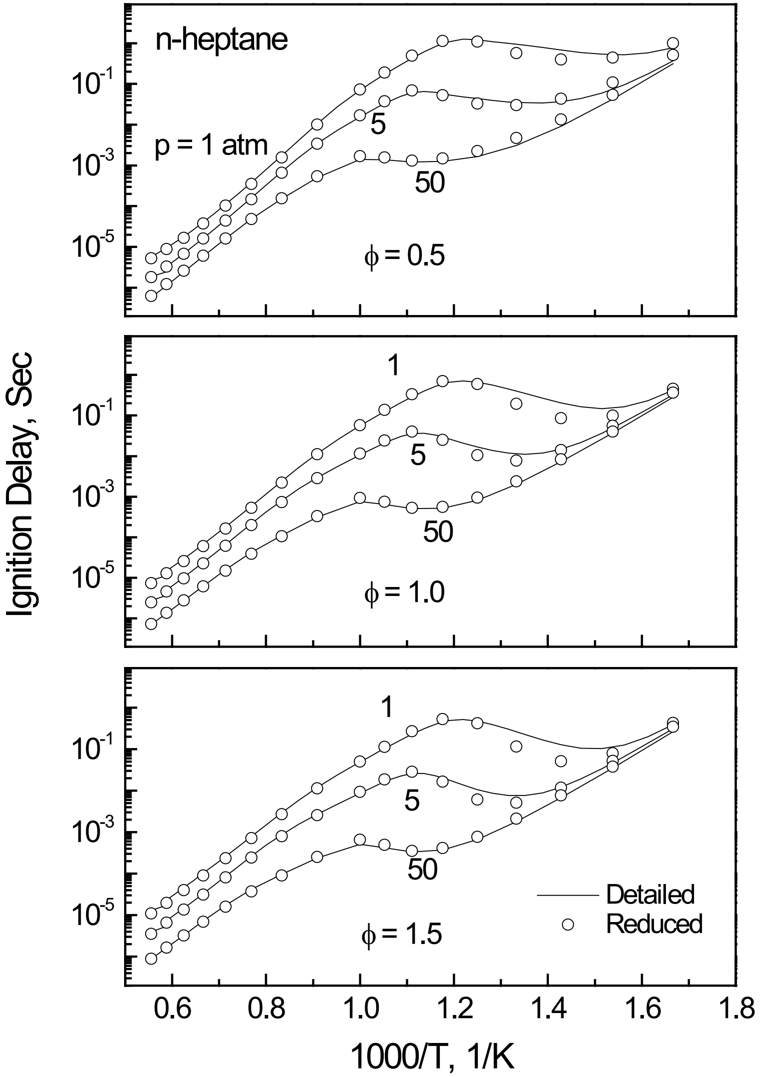
Accuracy of Reduced Mechanisms: $n\text{-}C_7H_{16}$ (1/2)

- Detailed (LLNL): 561 species
- Reduced: 58 species

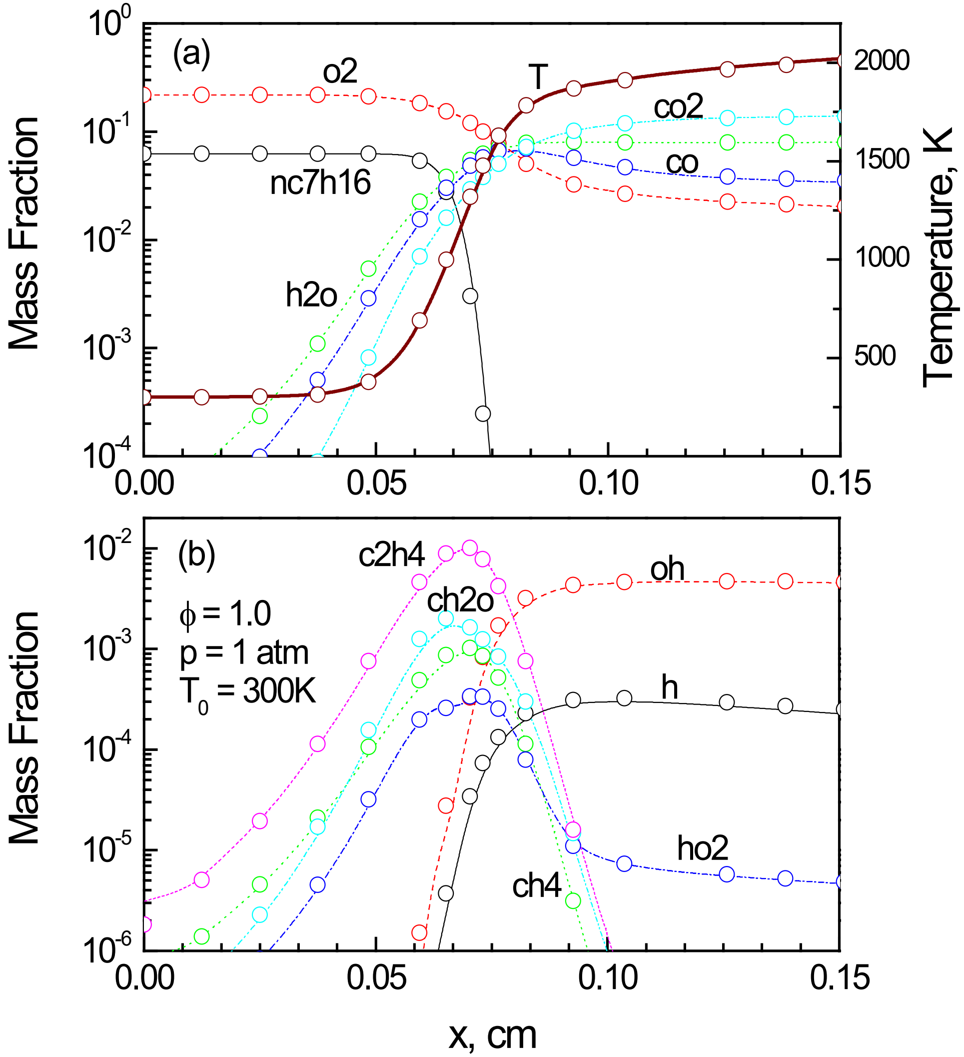
Perfectly Stirred Reactor



Auto-ignition



Accuracy of Reduced Mechanisms: n-C_7H_{16} (2/2)


Premixed Flame Structure

Other reduced mechanisms
(All suitable for DNS)

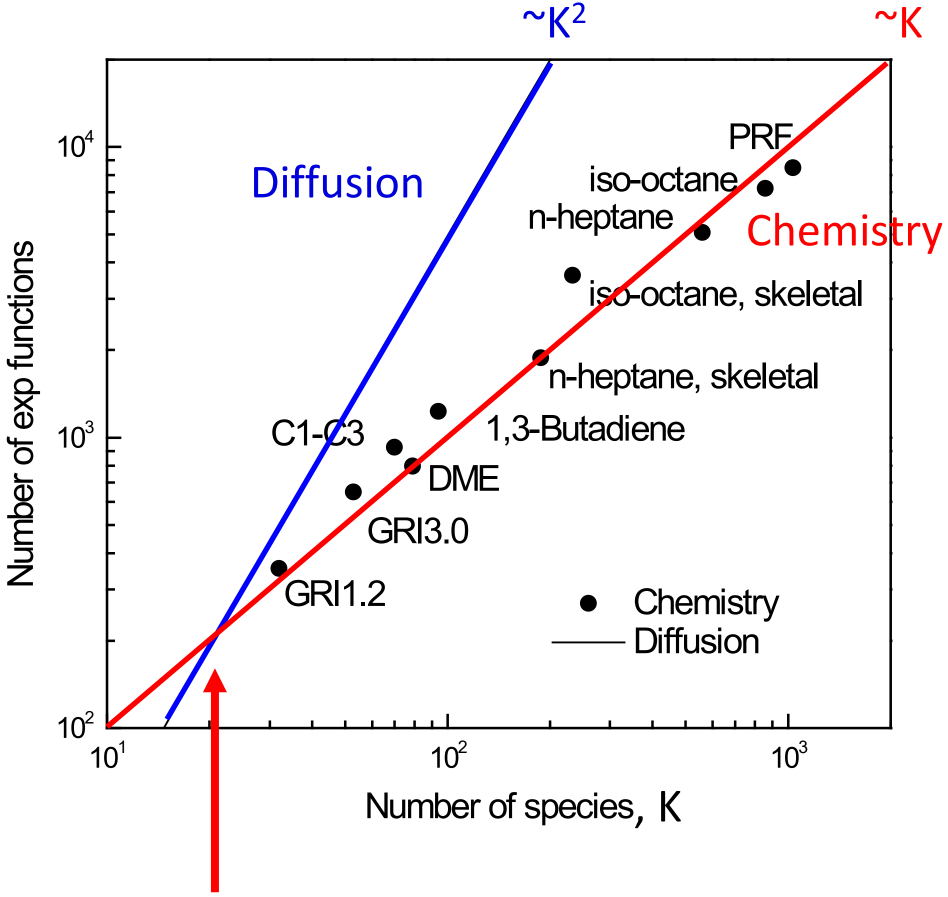
- CH_4 (GRI3.0): 19 species
- C_2H_4 (USC Mech II): 22 species
- DME (Zhao et al): 30 species
- nC_7H_{16} (LLNL): 58 species
- Biodiesel (LLNL): 73 species
- …

More reduced mechanisms:
http://www.engr.uconn.edu/~tlu

Binary Integer Programming for Mixture-Averaged Diffusion Reduction

Diffusion Reduction

- Diffusion term: Time cost ~ K^2, (quadratic speedup, but for diffusion term only)



the crossing point: K~20

Mixture Average Model

$$\rho \frac{DY_i}{Dt} = -\nabla \cdot (\rho_i \mathbf{V}_i) + w_i$$

Mixture average model:

$$\mathbf{V}_i = \overline{D}_i \frac{\nabla X_i}{X_i}$$

$$\overline{D}_i \approx (1 - Y_i) / \sum_{j \neq i} \frac{X_j}{D_{i,j}}$$

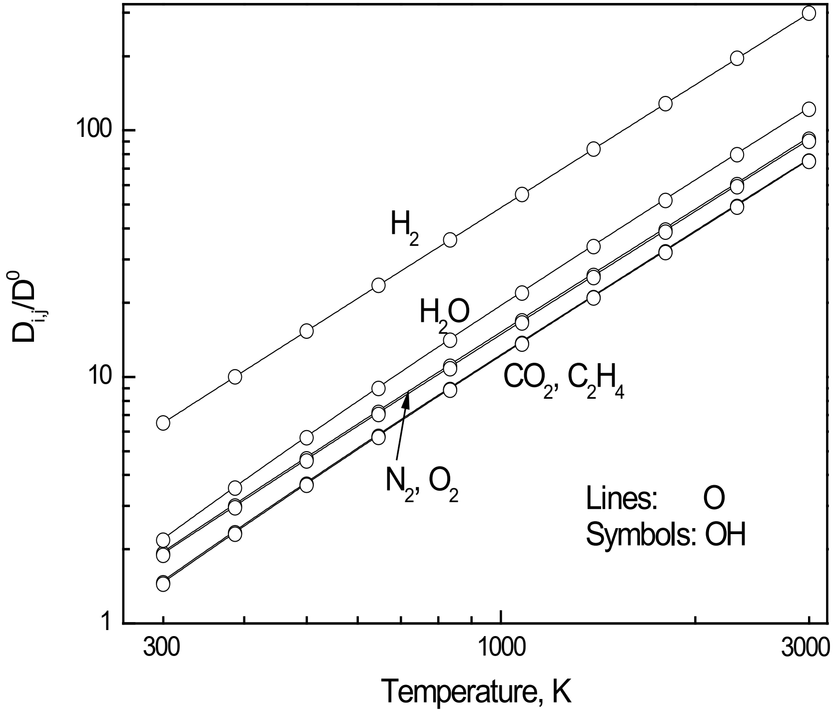
$$\boxed{pD_{i,j} \approx \exp\left(\sum_{n=0}^{N} a_{n,i,j} (\ln T)^n \right)}$$

- Number of exp() ~ K^2
- Exact formulation of $D_{i,j}$ is complicated
- Typically interpolated with polynomials inside exp()

Similarity in Species Diffusivities

- Many species have similar diffusivities

Example: O and OH



- Species with similar diffusivities can be lumped, their diffusivities evaluated as a group

Quantification of
Similarity in Species Diffusivities

- Many species have similar molecular properties
  - Molecular Weight
  - Cross section parameters
  - Molecular structure

- How different are species *i* and *j* to everyone else:

$$\varepsilon_{i,j} = \max_{\substack{k=1,\ldots,K \\ T_{\min}<T<T_{\max}}} \left| \ln\left(\frac{D_{i,k}}{D_{j,k}} \right) \right|$$

Formulation of
Diffusive Species Bundling

- Strategy: divide species to least numbers of group for given threshold error
- A Binary Integer Programming problem
- x_i = 1: representative species
  0: group member

$$\text{Minimize: } \sum_{i=1}^{K} x_i$$

$$\text{Subject to: } \sum_{j=1}^{K} A_{i,j} x_j \geq 1 \,,\; i = 1,\, 2, \ldots, K$$

$$x_i \in \{0, 1\} \,,\; i = 1, 2, \ldots, K$$

User specified error tolerance

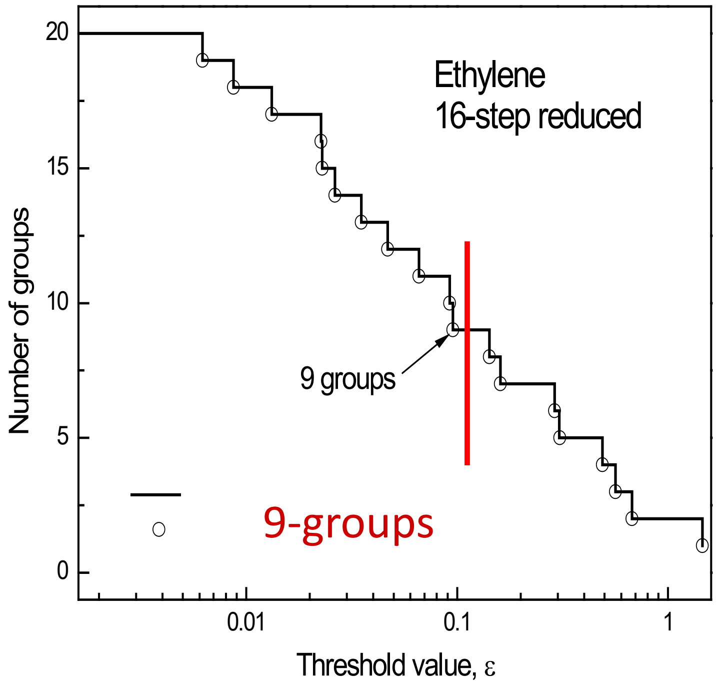
$$A_{i,j} = \begin{cases} 1, & \text{if } \varepsilon_{i,j} < \varepsilon \\ 0, & \text{otherwise} \end{cases}$$

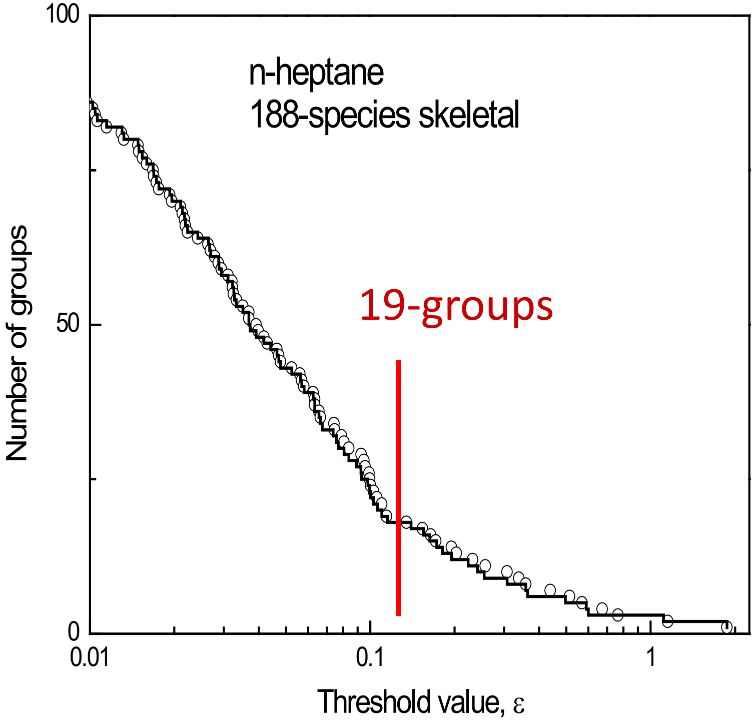
$$\varepsilon_{i,j} = \max_{\substack{k=1,\ldots,K \\ T_{\min} < T < T_{\max}}} \left| \ln\left(\frac{D_{i,k}}{D_{j,k}} \right) \right|$$

Reduction Curve

Ethylene, 20 species

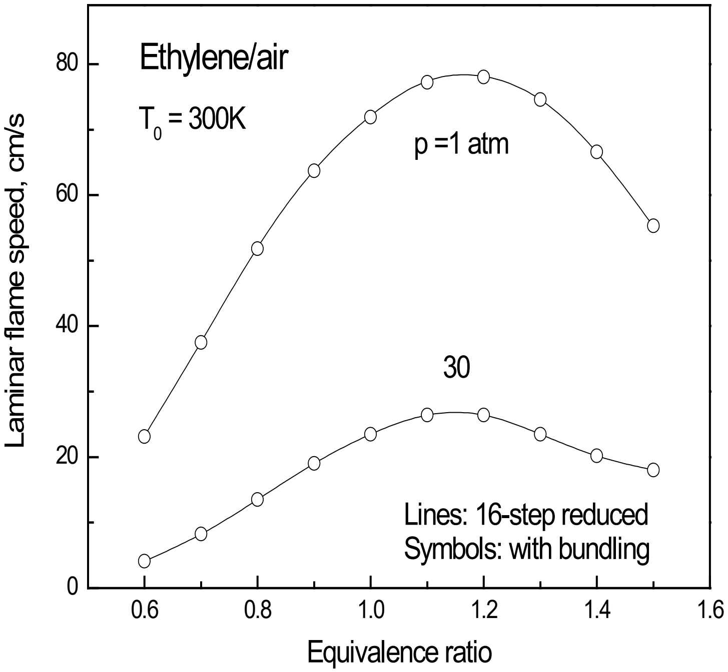
Heptane, 188 species

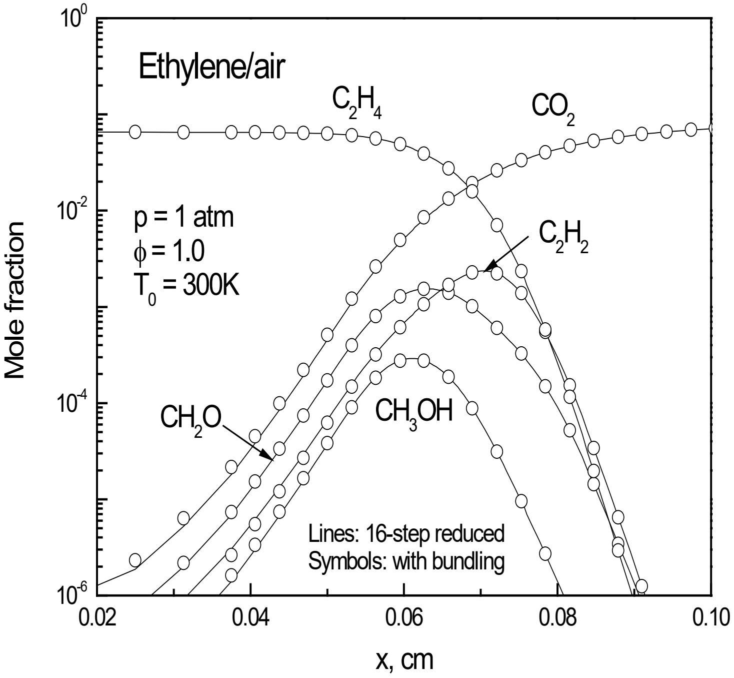




Validation - Ethylene

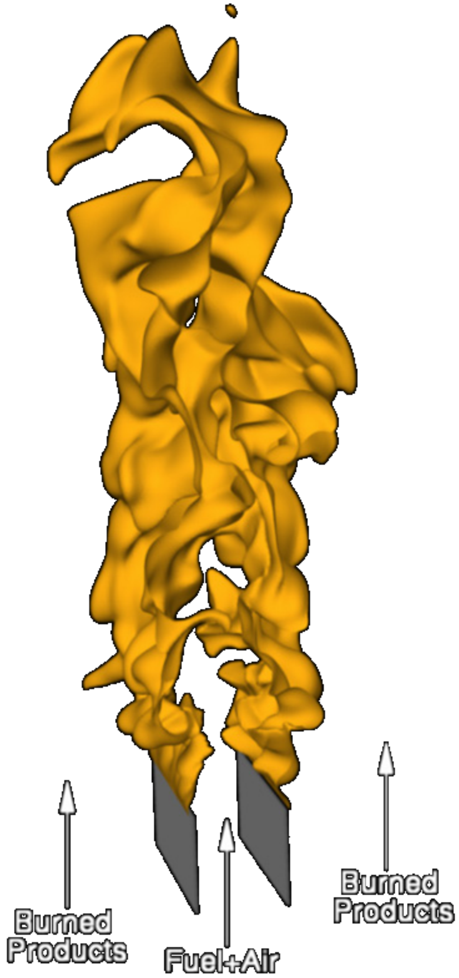
16-step: 20 species
With bundling: 9-groups





DNS of A Turbulent Bunsen Flame

- 3-D premixed Bunsen flame
- CH_4-air (lean): 13 species reduced (detailed: GRI1.2)
- Re: 800
- Grids: 50 million
- Time steps: 1.3 million
- CPU hours: 2.5 million (50Tflops Cray)

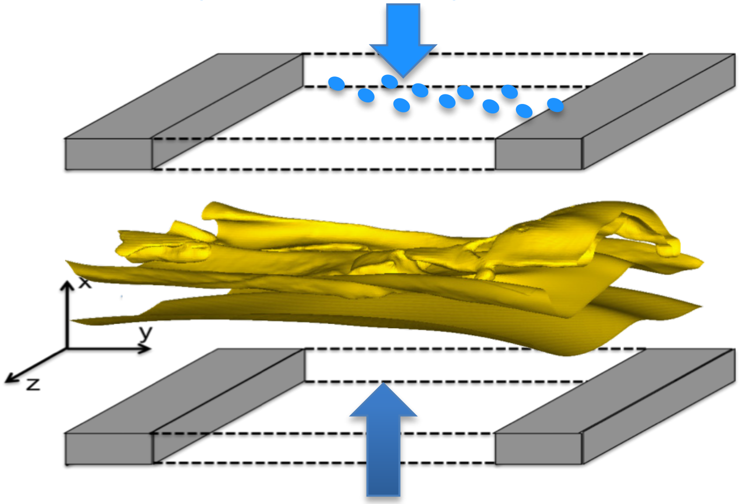


Sankaran et al, PCI 2007

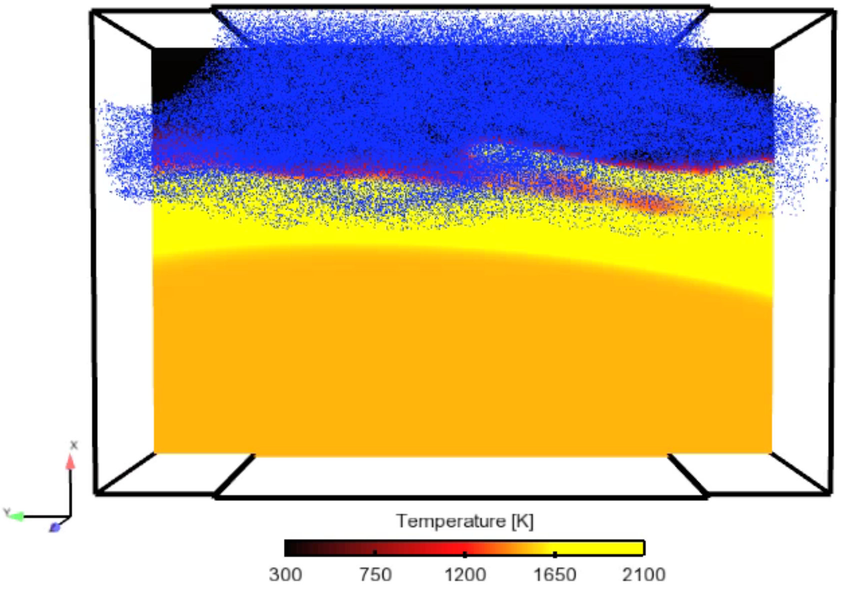
DNS of a Spray Combustion

- DNS configuration (Vie et al, PCI 2015)
  Global strain rate $a = 600\ 1/s$, injection of turbulence
  - Fuel: n-Dodecane (24 species reduced, based on JetSurf)
  - Consider: gaseous fuel, mono-dispersed spray with D={20,40,80}µm

Spray injection in turbulent air stream
$T_l=T_g=300K$, $V_l=V_g=1m/s$, $Re_t=50$

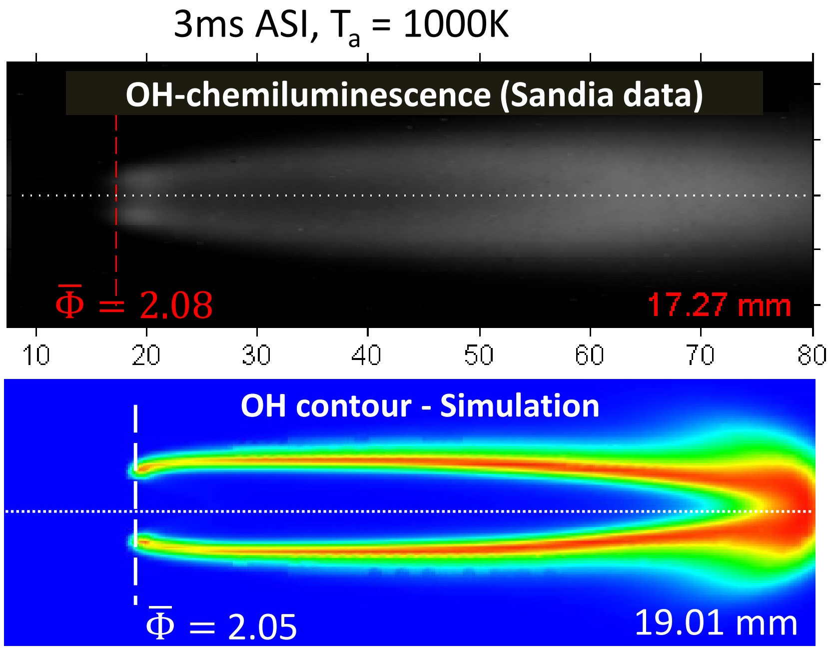


Laminar hot air-stream
$T_g=1500K$ and $V_g=5m/s$



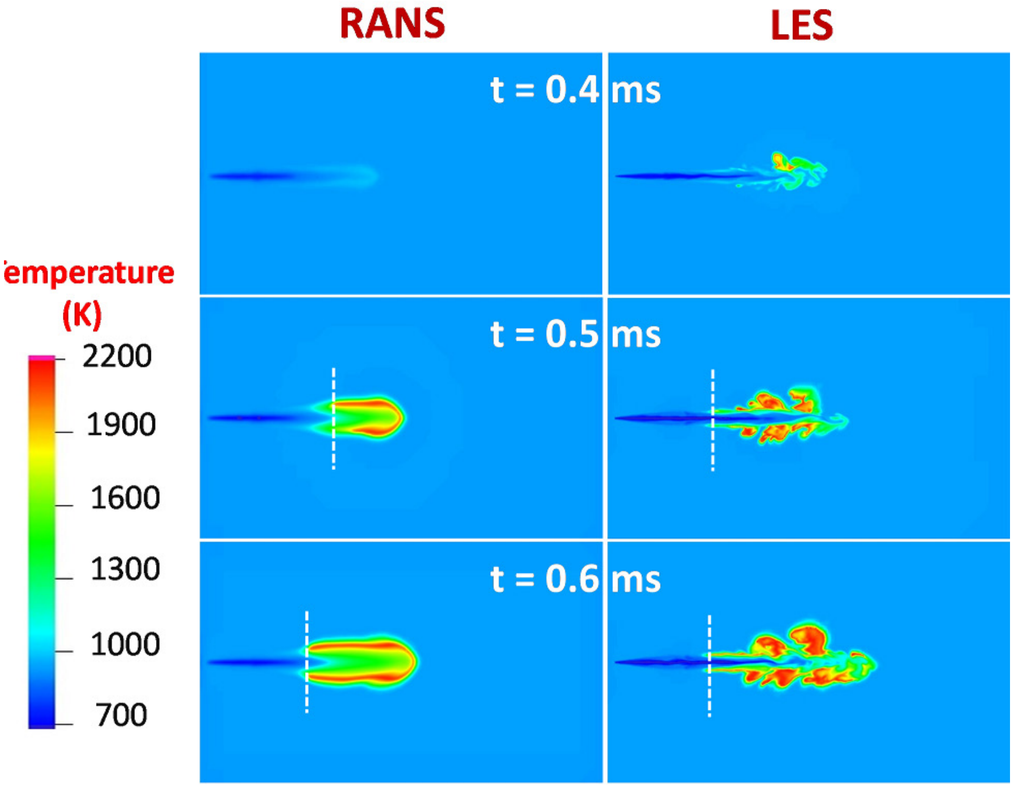
Sample Simulations:
A Lifted Biodiesel Jet Flame (RANS, LES)

- Lifted biodiesel jet flame at diesel engine conditions
- Detailed (LLNL): 3329 species, 10806 reactions
- 115-species skeletal mechanism with low-T chemistry
- Surrogate: MD+MD9D+C7



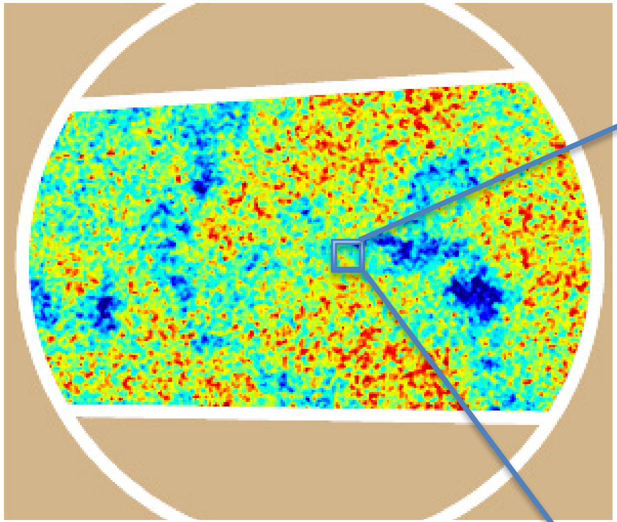
Luo et al, Fuel 2012

Experiment: Pickett et al



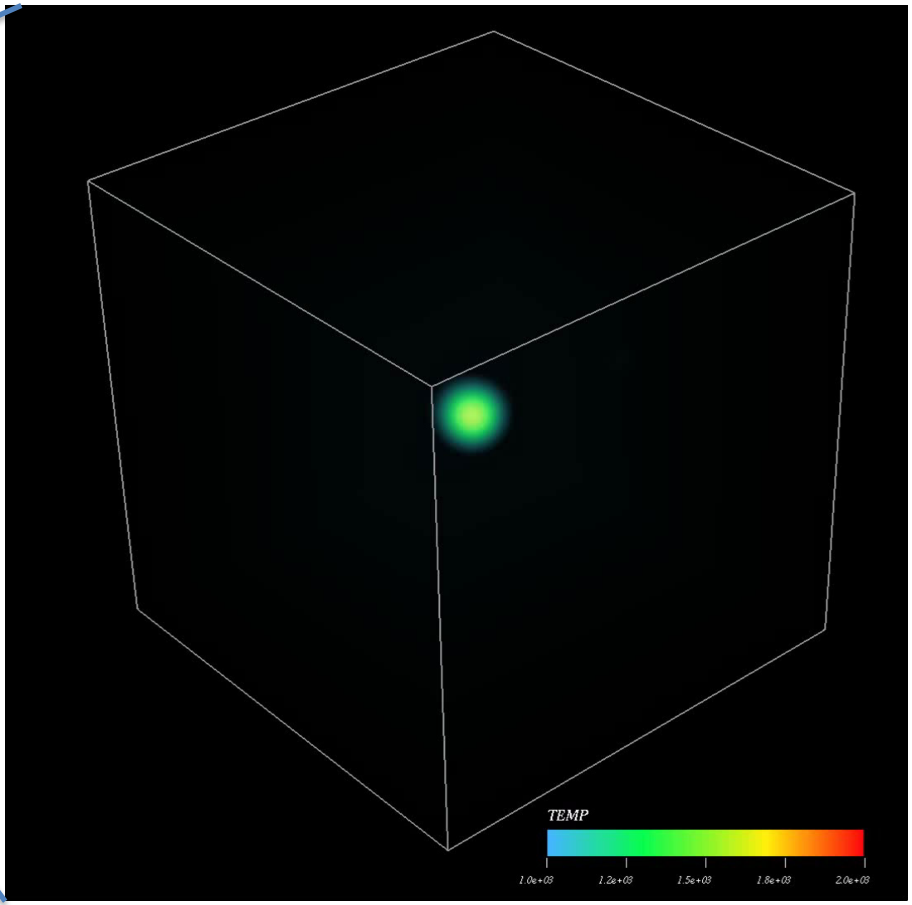
Som et al, JERT 2012

Spark Assisted Compression Ignition (SACI) of Ethanol/Air (DNS)



PLIF based temperature map at 355° CA
mid plane of combustion chamber.
(Dec & Hwang, SAE 2009)

28-species reduced mechanism
(Detailed: 145 species,
Mittal et al, CNF 2014)
$\phi = 0.4$, p = 45 atm
$T_{mean} = 924$ K, $T_{rms} = 25$ K
$U_{rms} = 0.6$m/s, $L_{11} = 0.72$ mm
L = 3.0mm, in 5μm grids



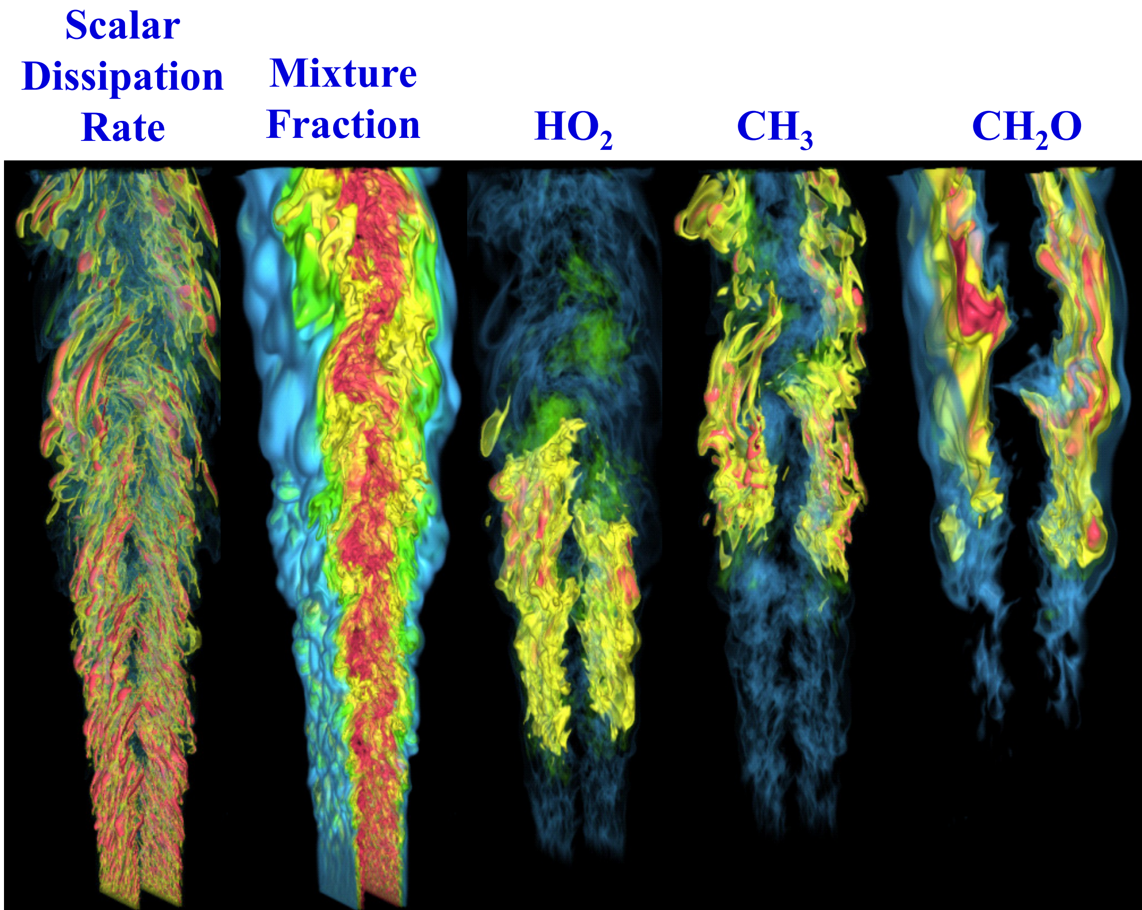
(Bhagatwala et al, CNF 2014)

CEMA for a Lifted Ethylene Jet Flame into Heated Coflowing Air (DNS)

- 3-D lifted ethylene jet flame (Yoo et al, PCI, 2011)
- 22-species, non-stiff (from USC Mech II)
- Re = 10,000
- 1.3 billion grid points
- 14 million CPU hours

- **240 TB output data**
- Difficult to save
- Difficult to transfer
- Difficult to use

- **Systematic methods needed to extract salient information**



Scalar Dissipation Rate

Mixture Fraction

HO_2

CH_3

CH_2O

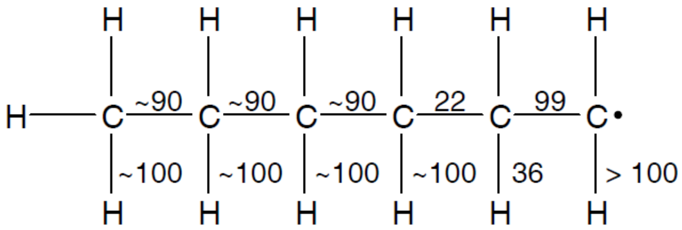
DNS by C. S. Yoo

Volume rendering by H. Yu at Sandia

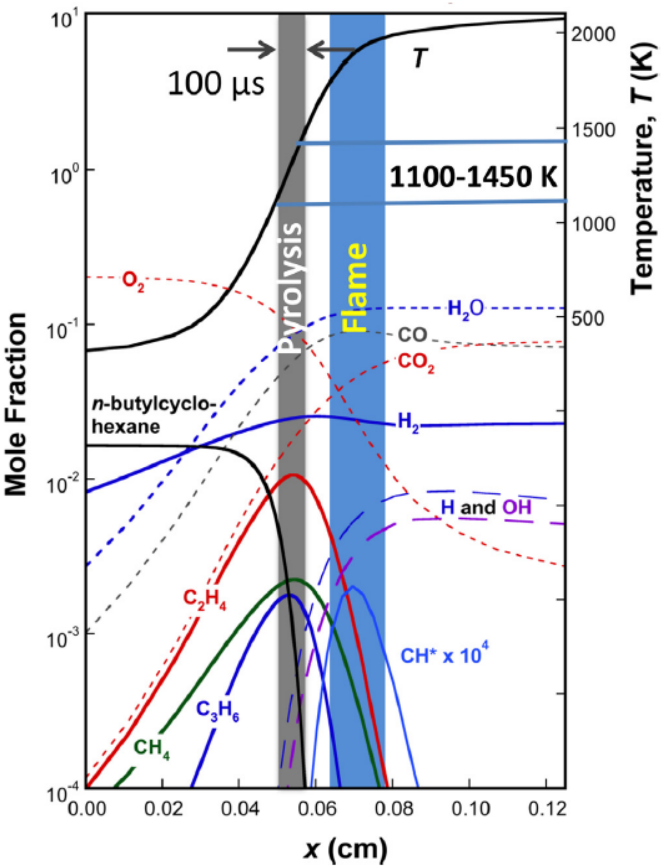
HyChem Models for Real Fuels

Background:
Beta Scission & Decoupled Fuel Cracking and Flame Zones

Beta-scission



(Law, Combustion Physics 2010)

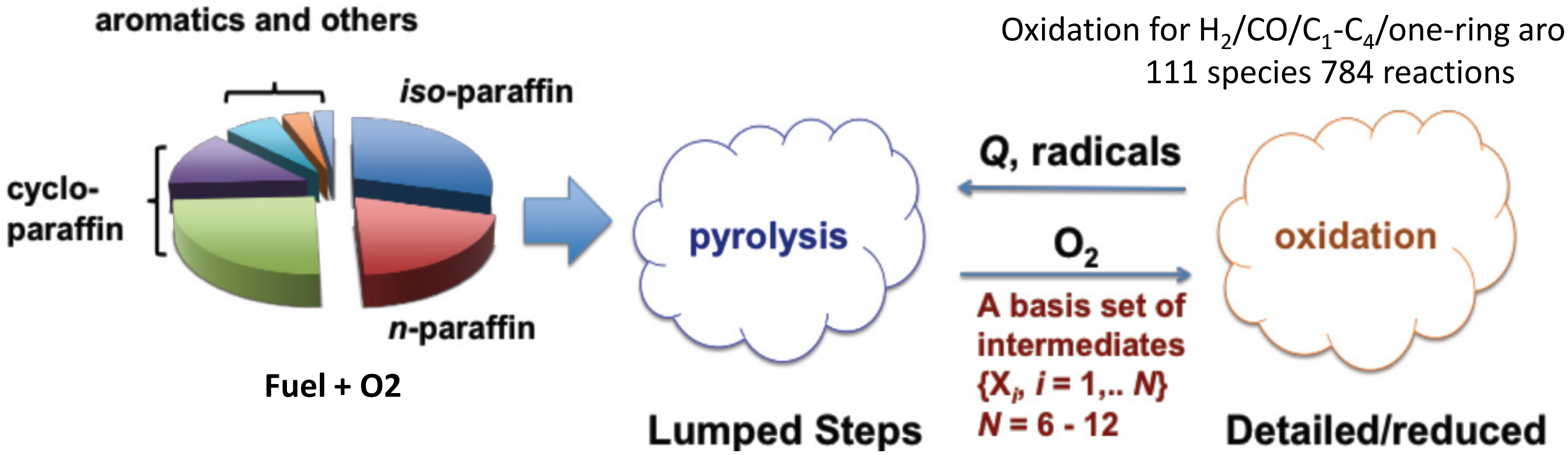


Structure of a 1-D premixed flame of n-butylcyclohexane-air at inlet temperature of 298 K, atmospheric pressure and equivalence ratio of 1.2, calculated using JetSurF 2.0. Figure adapted from (Wang, Xu et al. 2018)

Background:
The HyChem Approach

Foundational fuel chemistry

USC Mech II
Oxidation for H_2/CO/C_1-C_4/one-ring aromatics
111 species 784 reactions



Fuel + O2

(Xu et al., CNF 2018)

Formulation of the Fuel Cracking Steps

- Semi-global reaction steps (Xu et al., CNF 2018)

Type 1: C-C fission like reaction

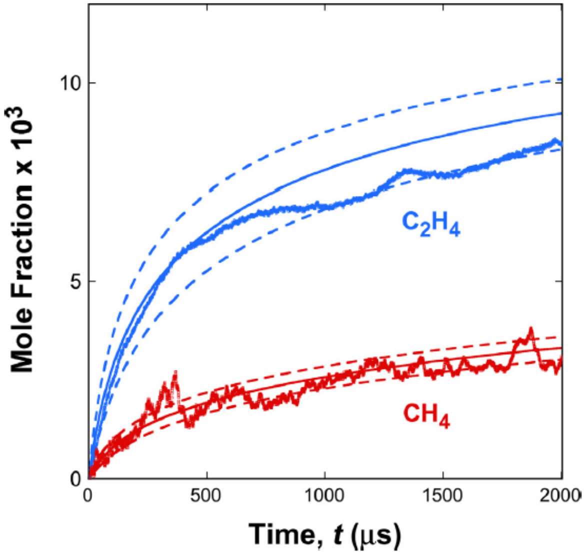
$$C_mH_n \rightarrow e_d(C_2H_4 + \lambda_3 C_3H_6 + \lambda_{4i}\,iC_4H_8 + \lambda_{4n}\,1\text{-}C_4H_8) + b_d[\chi\, C_6H_6 + (1-\chi)\, C_7H_8] + \alpha H + (2-\alpha)CH_3$$

Type II: H-abstraction followed by fuel radical breakdown

$$C_mH_n + R \rightarrow RH + \gamma\, CH_4 + e_a(C_2H_4 + \lambda_3 C_3H_6 + \lambda_{4i}\,iC_4H_8 + \lambda_{4n}\,1\text{-}C_4H_8) + b_a[\chi\, C_6H_6 + (1-\chi)\, C_7H_8] + \beta H + (1-\beta)\, CH_3$$

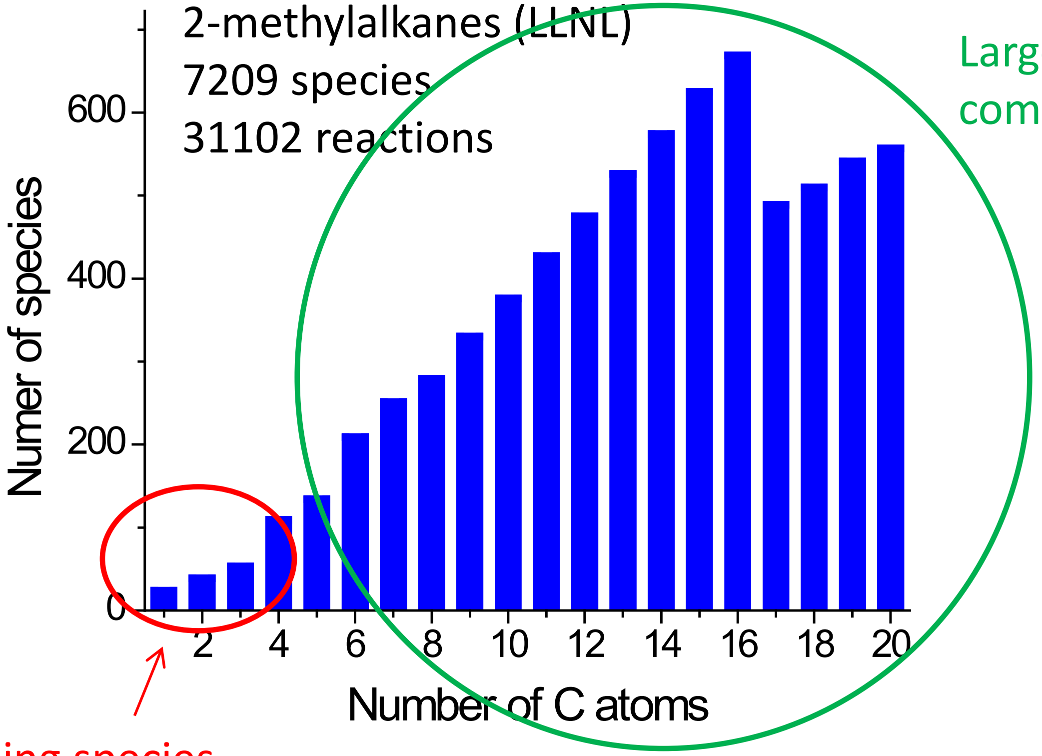
where R is H, CH_3, O, OH, O_2, and HO_2

- Determination of the stoichiometric coefficients
  - Element conservation
  - Branching ratios determined from experimental measurements



Typical time histories of C_2H_4 and CH_4 measured and simulated from thermal decomposition of 0.73 % (mol) A2 fuel in argon in shock tube at $T_5 = 1196$ K and $p_5 = 12.5$ atm. The dashed lines are simulations bracketing the ±15 K temperature uncertainty. Figure adapted from (Wang, Xu et al. 2018).

Extent of Species Reduction by HyChem



Large molecules almost completely removed

controlling species at high-T

Reduced A2/C1 Mixture Model

Parameter ranges

ϕ = 0.5 - 1.5

p^0 = 0.5 - 30 atm

T_0 = 1000 - 1600 K for ignition delay

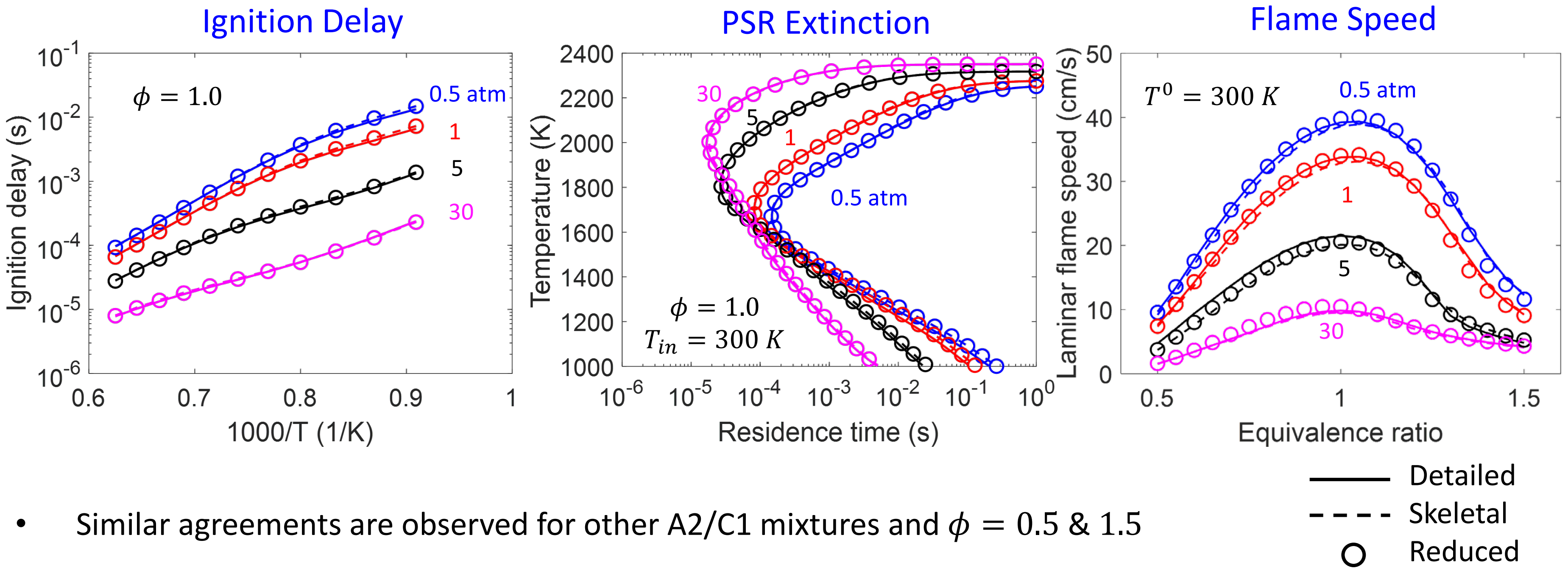
T_{in} = 300 K for PSR extinction

A2 in the A2/C1 mixture = 0%, 20%, 50%, 80%, and 100% in mole

Reduction summary

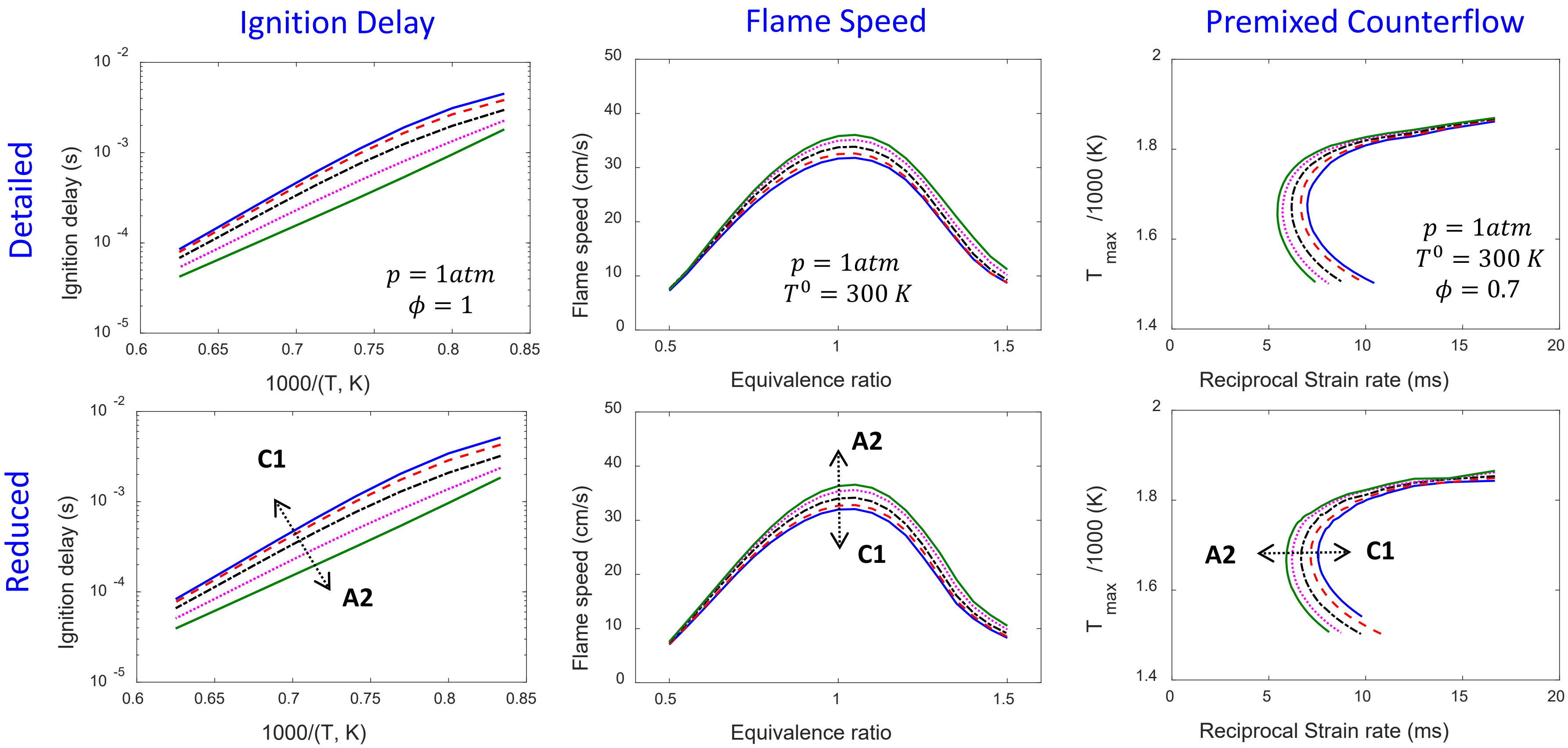
Cat A2/C1	Detailed	Skeletal	Reduced
# of Species	120	51	39

Selected validations (50% of A2 in A2/C1 mixture)



- Similar agreements are observed for other A2/C1 mixtures and $\phi = 0.5\ \&\ 1.5$

Dilution Sensitivities in Reduced Models



- Dilution sensitivities of global parameters are well captured by reduced models

Reduced Models with NTC

Parameter ranges

ϕ = 0.5 - 1.5

p^0 = 0.5 - 30 atm

T_0 = 700 - 1600 K for ignition delay

T_{in} = 300 K for PSR extinction

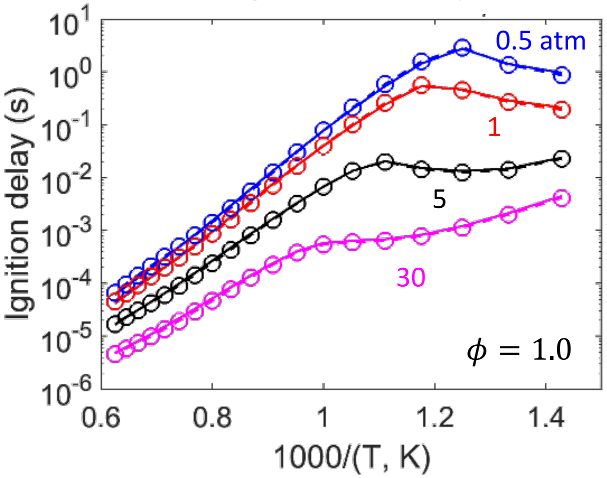
Reduction summary

Cat A2/A2a/A3	Detailed	Skeletal	Reduced
# of Species	125	48/47/50	34/35/36

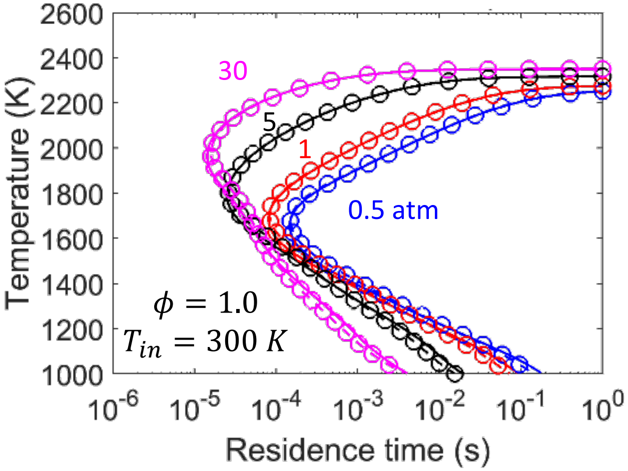
Cat A2	HyChem v2 **(w/o NTC)**	HyChem v2.5 **(w/ NTC)**
# of Species	31	34

Selected validations (Cat A2)

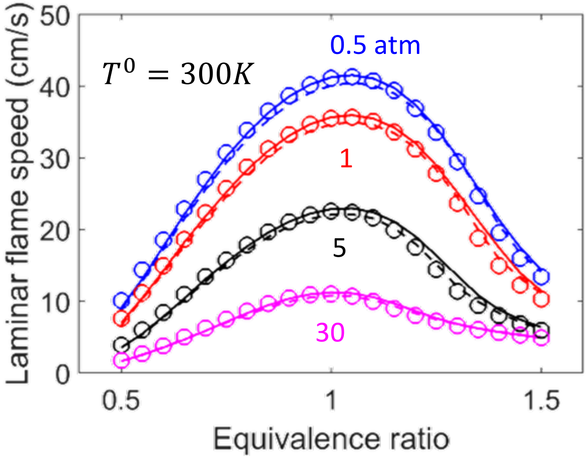
Ignition Delay



PSR Extinction



Flame Speed



- Reduced HyChem w/ NTC has only 3 species more than w/o NTC model
- Similar agreements are observed for A2a/A3 models and $\phi = 0.5\ \&\ 1.5$

—— Detailed
– – – – Skeletal
○ Reduced

Detailed & Reduced HyChem Models for Real Jet Fuels

		Detailed	**Skeletal**	**Reduced**
		Number of species		
Cat A1/A2/A3		119	41	31
Cat C1			34	26
Cat C5			41	31
Cat A2/C1 mixture		120	51	39
Cat A2 / A2a / A3 (w/ NTC)		125	48 / 47 / 50	34 / 35 / 36
Cat A2	with NO	201	71	51
Cat C1			66	45
Cat C4			70	49
RP2-1			70	57
RP2-2			65	47
Cat A2/C1 mixtures		202	81	58
Cat A2 with KAUST PAH		210	79	62

HyChem Models (also has Shell Gasoline fuels) available at:
https://web.stanford.edu/group/haiwanglab/HyChem/pages/download.html

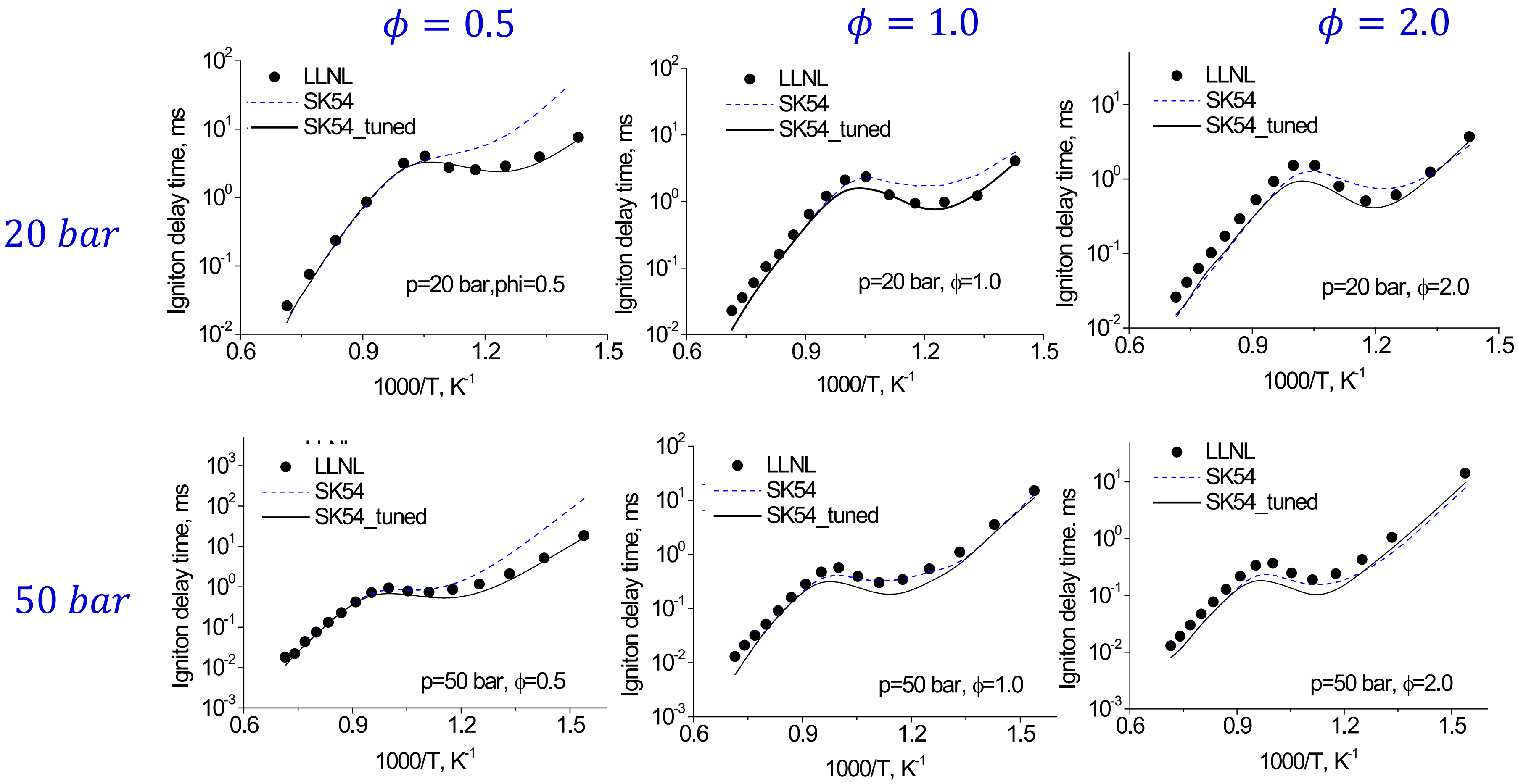
Model/Mechanism Tuning

A Reduced Model for n-Dodecane with Lumped NTC Chemistry (Yao et al., Fuel 2017)

- C_0-C_4 core chemistry
  - A high-T skeletal model based on JetSurf
  - 32 species, 191 reactions
- C_5-C_{12} sub-mechanism
  - Starting model: (You et al, PCI 2009)
  - Skeletal sub-model: 18 species, 60 reactions
- Low-T sub-mechanism
  - Semi-global scheme (4 species, 18 lumped reactions) (Bikas & Peters, CNF 2001)
    $C_{12}H_{25}O_2$, $C_{12}OOH$, $O_2C_{12}H_{24}OOH$, $OC_{12}H_{23}OOH$
  - Rate parameters need tuning
- Final models (Yao et al., US Meeting 2015):
  - Skeletal: 54-species, 269 reactions
  - Reduced: 37 species

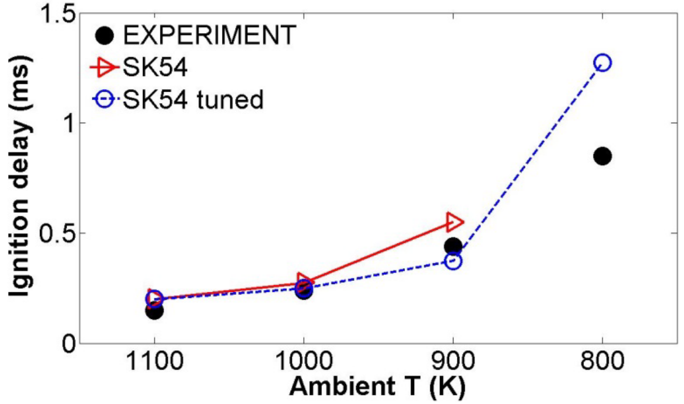
Tuning Against the LLNL Mechanism

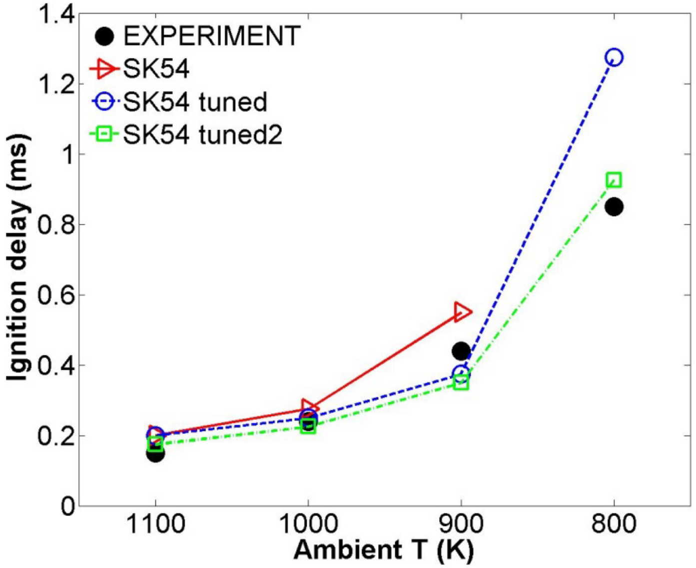
- Rate parameter tuning (where experimental data not available)
  - Low-T steps tuned against LLNL mechanism (Westbrook et al, CNF 2009)
  - High-T reactions unchanged



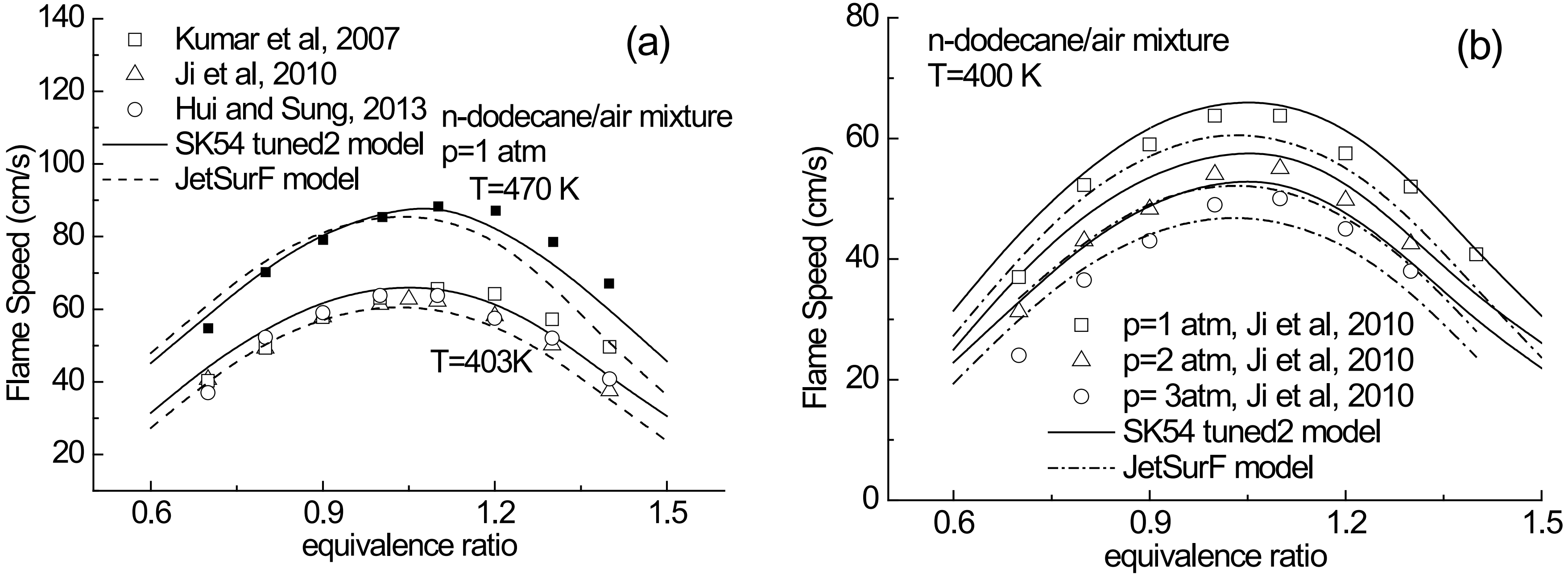
Tuning Based on ECN Data

- Experimental data from ECN (Spray A, lifted n-dodecane jet flame)
- CFD at ANL: RANS (CONVERGE)
  - First-stage ignition occurs in lean mixture
  - Second-stage ignition occurs first in rich mixture
  - ~25% longer Ignition delay at 800K
- Tuning against experiments
  - Based on ignition sensitivity analysis
  - Reactions only with high sensitivities for 800 K tuned down by ~25%
  - Final mechanism: “SK54_tuned2”





Laminar Flame Speed



- Overall good agreement with experimental data
- High-T flame behaviors inherited from USC-Mech II (flame speed, extinction, high-T ignition delay …), unaffected by the tuning

On the Tuning of Over-Reduced Models (1/2)

- It is a widely adopted approach to obtain over-reduced models and then tune the rate parameters to fit a target dataset (ignition delay, flame speed etc.): the extreme case is the one- or a few-step semi-global models
- The tuning of rate parameters against experimental data is a common practice in detailed mechanism compilation
- There are severe over-fitting issues in tuning complex models with many parameters
- Consider a comprehensive model with a set of M model parameters, $\boldsymbol{x} = \binom{\boldsymbol{y}}{\boldsymbol{z}}$, that can accurately describe a set of N (N can be larger than M) targets (ignition delay, flame speed, extinction properties etc.,

$$\boldsymbol{g}(\boldsymbol{y}, \boldsymbol{z}; \dots) = \boldsymbol{0}$$

$$\boldsymbol{h}(\boldsymbol{y}, \boldsymbol{z}; \dots) = \boldsymbol{0}$$

Let an over-reduced model be denoted by a modified subset of parameters, $\boldsymbol{z}$, and the tuning be performed on the remaining subset of parameters, $\boldsymbol{y}$, to fit a selected subset of targets, **g**

$$\boldsymbol{g}(\boldsymbol{y} + \boldsymbol{y}', \boldsymbol{z} + \boldsymbol{z}') = 0$$

On the Tuning of Over-Reduced Models (2/2)

- For simplicity, assume that the changes in model parameters are small perturbations

$$\boldsymbol{g}(\boldsymbol{y}+\boldsymbol{y}',\boldsymbol{z}+\boldsymbol{z}') \approx \boldsymbol{g}(\boldsymbol{y},\boldsymbol{z}) + \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{y}}\boldsymbol{y}' + \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{z}}\boldsymbol{z}' = \mathbf{J}_{11}\boldsymbol{y}' + \mathbf{J}_{12}\boldsymbol{z}' = 0$$

Local sensitivity

- The solution of the optimization is

$$\boldsymbol{y}' = -\left(\mathbf{J}_{11}^{\mathrm{T}}\mathbf{J}_{11}\right)^{-1}\mathbf{J}_{11}^{\mathrm{T}}\mathbf{J}_{12}\boldsymbol{z}', \qquad \mathbf{J} = \frac{\partial\begin{pmatrix}\boldsymbol{g}\\ \boldsymbol{h}\end{pmatrix}}{\partial(\boldsymbol{y},\boldsymbol{z})} = \begin{bmatrix}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{y}} & \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{z}}\\ \frac{\partial \boldsymbol{h}}{\partial \boldsymbol{y}} & \frac{\partial \boldsymbol{h}}{\partial \boldsymbol{z}}\end{bmatrix} = \begin{bmatrix}\mathbf{J}_{11} & \mathbf{J}_{12}\\ \mathbf{J}_{21} & \mathbf{J}_{22}\end{bmatrix}$$

- Let $\boldsymbol{h}$ denote the targets (flame blow out behaviors, flame responses in turbulent environments etc.) not included in the optimization processes

$$\boldsymbol{h}(\boldsymbol{y}+\boldsymbol{y}',\boldsymbol{z}+\boldsymbol{z}') \approx \boldsymbol{h}(\boldsymbol{y},\boldsymbol{z}) + \mathbf{J}_{21}\boldsymbol{y}' + \mathbf{J}_{22}\boldsymbol{z}' = \left[-\mathbf{J}_{21}\left(\mathbf{J}_{11}^{\mathrm{T}}\mathbf{J}_{11}\right)^{-1}\mathbf{J}_{11}^{\mathrm{T}}\mathbf{J}_{12} + \mathbf{J}_{22}\right]\boldsymbol{z}'$$

- Hopefully $\boldsymbol{h}(\boldsymbol{y}+\boldsymbol{y}',\boldsymbol{z}+\boldsymbol{z}') = \mathbf{0}$?

$$\mathbf{J}_{22} = \mathbf{J}_{21}\left(\mathbf{J}_{11}^{\mathrm{T}}\mathbf{J}_{11}\right)^{-1}\mathbf{J}_{11}^{\mathrm{T}}\mathbf{J}_{12} = \mathbf{A}\mathbf{J}_{12}$$

Strategies to Avoid Overfitting

- Avoid over-reduction/tuning if possible
- Try not to tune models with too many knobs
- Use more validation targets (experimental & numerical)
- Use training/test/validation sets
- …

Advanced Chemistry Solvers and Combustor Modeling

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Tsinghua-Princeton-CI
2024 Summer School on Combustion
July 7-13, 2024

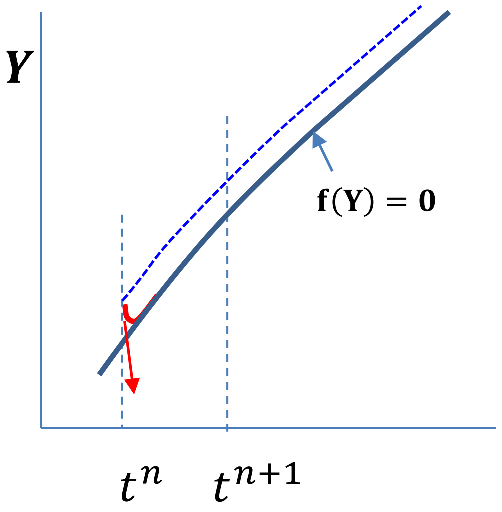
Chemical Stiffness

- Governing equations for general reacting flows

$$\frac{d\mathbf{Y}}{dt} = \frac{\mathbf{f}(\mathbf{Y})}{\boldsymbol{\varepsilon}} + \mathbf{s}(\mathbf{Y}) = \mathbf{g}(\mathbf{Y})$$

- “Slow manifold” of a stiff problem

$$\mathbf{f}(\mathbf{Y}) = \boldsymbol{\varepsilon}\left[\frac{d\mathbf{Y}}{dt} - \mathbf{s}(\mathbf{Y})\right] \approx \mathbf{0}$$



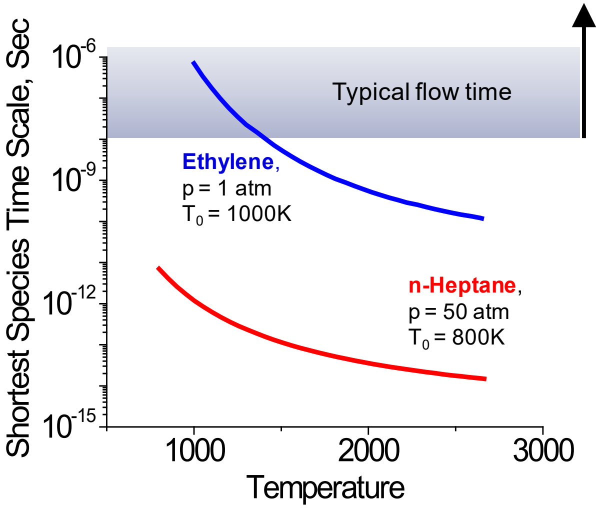
- Failure of explicit solvers

$$\frac{\mathbf{Y}^{n+1} - \mathbf{Y}^{n}}{\Delta t} = \mathbf{g}(\mathbf{Y}^{n}), \qquad \mathbf{Y}^{n+1} = \mathbf{g}(\mathbf{Y}^{n})\Delta t + \mathbf{Y}^{n}$$

- Implicit solver required

$$\frac{\mathbf{Y}^{n+1} - \mathbf{Y}^{n}}{\Delta t} = \mathbf{g}(\mathbf{Y}^{n+1}),$$

$$\mathbf{H}(\mathbf{Y}^{n+1}) = \mathbf{g}(\mathbf{Y}^{n+1})\Delta t + \mathbf{Y}^{n} - \mathbf{Y}^{n+1} = \mathbf{0}$$



The Newton Iteration

- Implicit chemistry solvers eventually solves nonlinear equations:

$$\boldsymbol{h}(\boldsymbol{Y}) = \mathbf{g}(\mathbf{Y}) + \cdots \;=\; \mathbf{0}, \qquad \mathbf{g}\text{: chemical source term}$$

- Newton iterations typically required to find $\mathbf{g}(\mathbf{Y_0}) + \cdots = \mathbf{0}$

$$\mathbf{g}(\mathbf{Y}) = \mathbf{g}(\mathbf{Y_0}) + \cdots + \mathbf{J} \cdot (\mathbf{Y} - \mathbf{Y_0}),$$

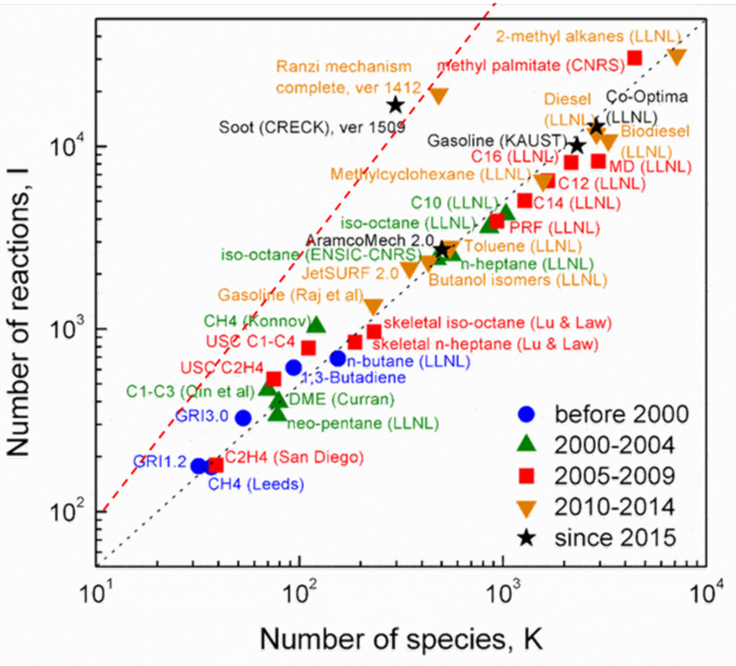
$$\mathbf{J} = \frac{\partial \mathbf{g}}{\partial \mathbf{Y}} \text{ is the Jacoiban}$$

$$\mathbf{Y_0} = \mathbf{Y} - \mathbf{J}^{-1} \cdot \mathbf{g}(\mathbf{Y})$$

The Jacobian

- Jacobian evaluation and factorization/inversion is often the most expensive step in combustion simulations

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



- Jacobian evaluation through numerical perturbation: $\sim O(K \times I) \sim O(K^2)$

- Jacobian factorization/inversion: $\sim O(K^3)$

Statistically $I \sim 5K$

Time Complexity of Implicit Solvers

- Time complexity of major components:
  - Chemistry: $\sim O(I)$
  - Jacobian evaluation (numerical): $\sim O(KI)$; factorization $\sim O(K^3)$
  - Diffusion (mixture average): $\sim O(\frac{1}{2}K^2)$

- 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
  - $t_{imp} \sim O(KI, K^3, I, \frac{1}{2}K^2)$

Explicit Solvers with Dynamic Stiffness Removal

Time Complexity of Explicit Solvers

- Time complexity of major components:
  - Chemistry: $\sim O(I)$
  - Jacobian evaluation (numerical): $\sim O(KI)$; factorization $\sim O(K^3)$
  - Diffusion (mixture average): $\sim O(\frac{1}{2}K^2)$
- Explicit solvers (chemistry, diffusion)
  - Time steps limited by
    the shortest chemical timescale
  - $t_{exp} \sim O(I, \frac{1}{2}K^2)$

Idea of Chemical Stiffness Removal

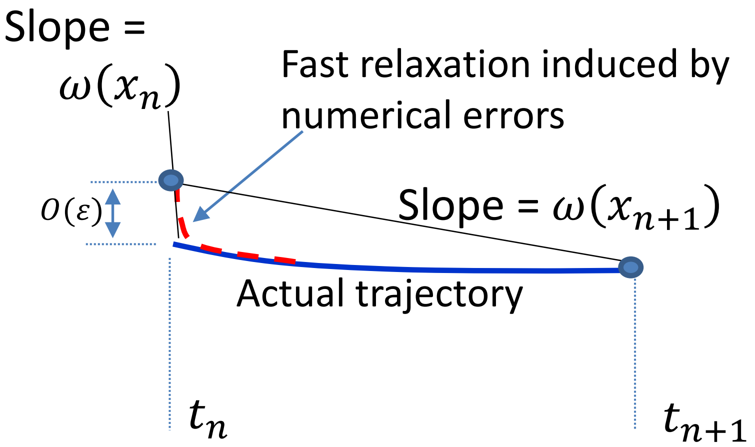
- An example of stiff problem

$$C \rightarrow x \xRightarrow{k=1/\varepsilon} P$$

  - x: a radical
  - C: diffusion + chemical formation
  - Consumption rate of x: $D = kx = x/\varepsilon$
- Governing equation for species x:

$$\frac{Dx}{Dt} = \omega = -D + C = -\frac{x}{\varepsilon} + C$$

  - $x \approx \varepsilon\left(C - \frac{Dx}{Dt}\right) = O(\varepsilon)$
  - $\frac{Dx}{Dt} = O(\varepsilon)$
  - $x = \varepsilon C + O(\varepsilon^2)$
- The trajectory of fast species can be analytically predicted



- Obtaining the correct slope:

$$x^0 \equiv \varepsilon C = x_{n+1} + O(\varepsilon^2)$$

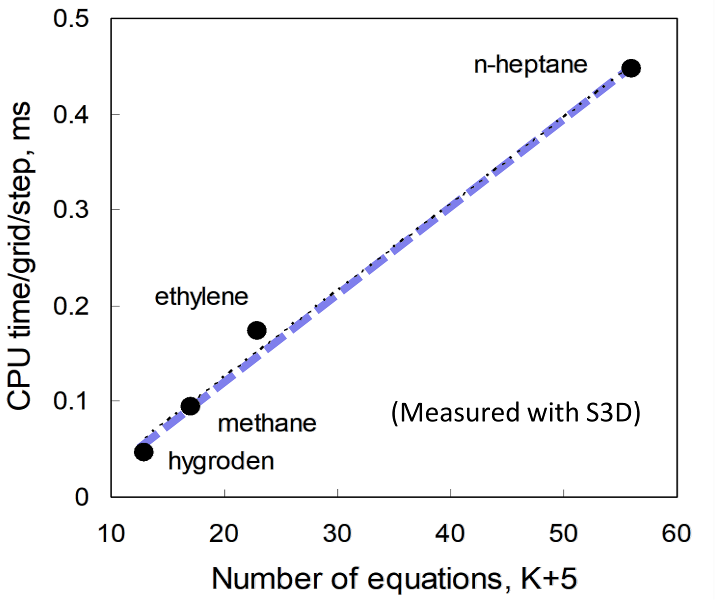
$$x^1 \equiv \varepsilon\left(C + \frac{x_n - x^0}{h}\right)$$

c_k^1 is used to obtain the correct slope:

$$\omega(x^1) = -\frac{x^1}{\varepsilon} + C = \frac{x^0 - x_n}{h} \approx \frac{x_{n+1} - x_n}{h}$$

Dynamic Chemical Stiffness Removal

- Typically applicable to compressible flows with time steps < ~20 ns
- Can use iterations to extend to >~100ns (Xu & Lu, US Meeting 2017)
- Explicit integration can be used with DCSR
  - Time step limited by CFL condition
  - Cost ~ O(K)



(Measured with S3D)

An Iterative Uncoupled QSS (IU-QSS) Method

(Xu & Lu, US Meeting 2017)

- For kth iteration, $\tau_{i,k}, C_{i,k}$ are calculated from $c_{i,k}^1$, then

$$c_i^0 = \tau_{i,k} C_{i,k}$$

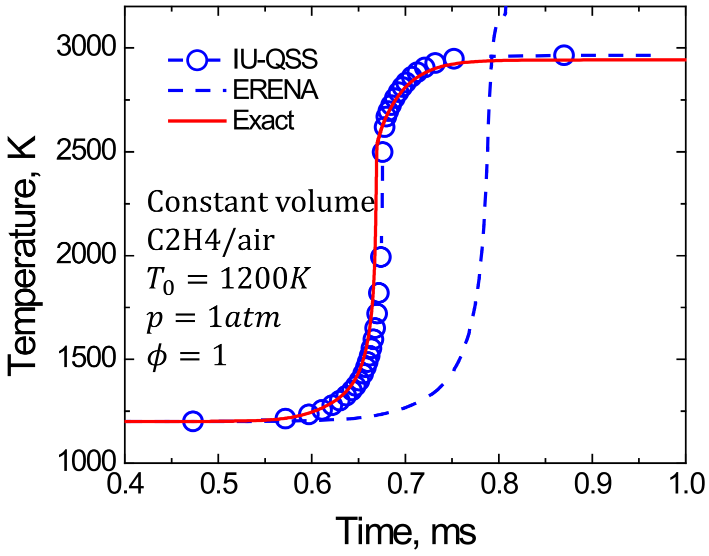
$$c_{i,k+1}^1 = \tau_{i,k} \left(C_{i,k} + \frac{c_i - c_i^0}{h} \right)$$

- If not converged, $c_{i,k}^1 = c_{i,k+1}^1$, repeat above procedure, until it converges

- Adaptive time step control to improve robustness
  - If the convergence is not achieved within a maximum iteration number (max_iter) specified by the user (e.g., 5), step size is reduced

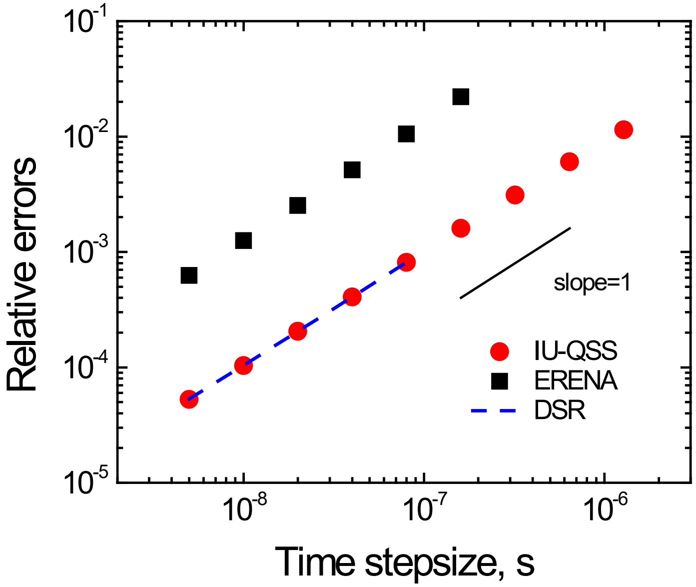
Accuracy & Stability Range

Temperature for auto-ignition



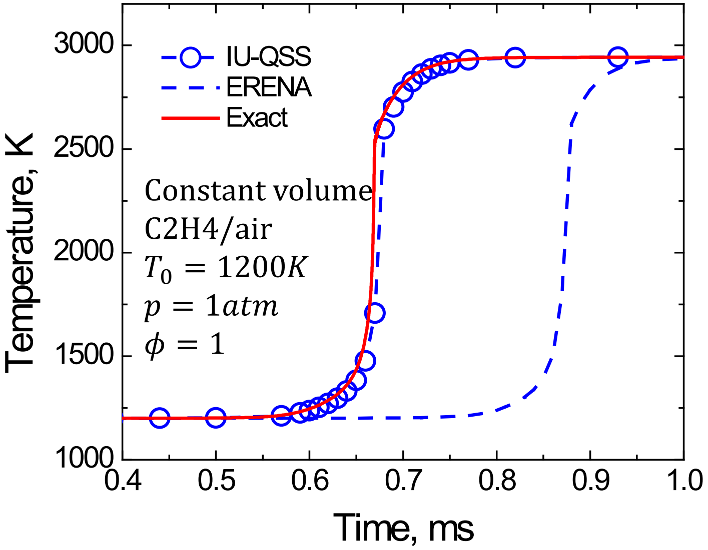
$\Delta t = 10^{-6}s$

Error in ignition delay vs. Stepsize

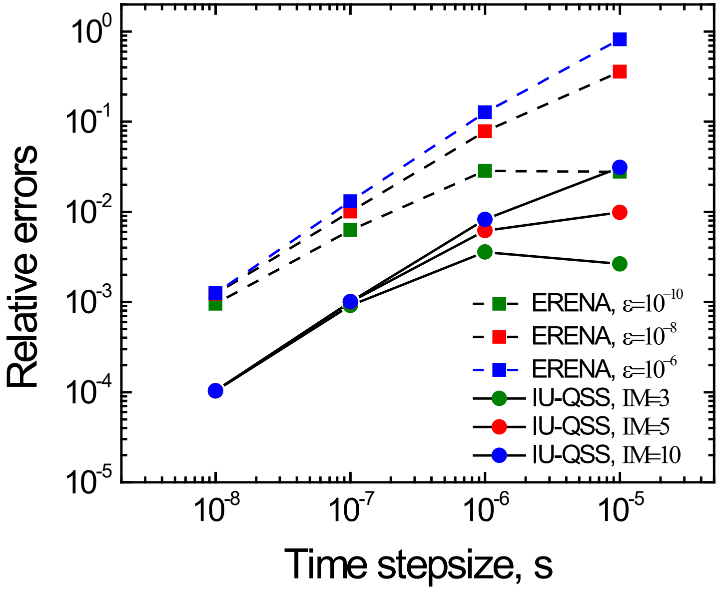


- DCSR shows first order accuracy
- Iterative DCSR extends the stability range to $1\mu s$, suitable for most practical CFD simulations

Performance with Adaptive Timestepping



$$\Delta t_{base} = 10^{-5}s$$



- Both robust for large timesteps
- IU-QSS is more accuracy than ERENA

Semi-Implicit Solvers

The Strang Splitting Scheme

- Spatially discretized governing equations

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

- Chemistry and transport substeps:

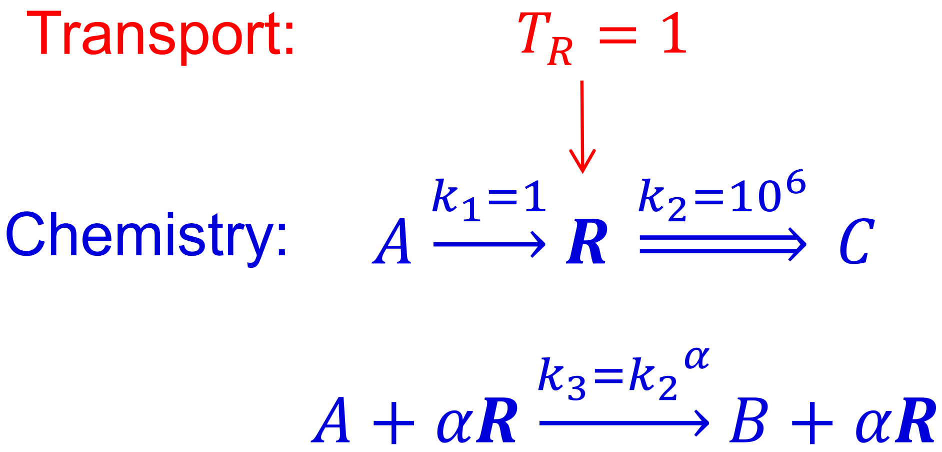
$$\frac{d\boldsymbol{\Phi}}{dt} = \boldsymbol{S}\left(\boldsymbol{\Phi}^{(1)}\right), \quad \boldsymbol{\Phi}^{(1)}(x,0) = \boldsymbol{\Phi}(x,t_n)\ on[t_n, t_n + \Delta t/2\,]$$

$$\frac{d\boldsymbol{\Phi}}{dt} = \boldsymbol{T}\left(\boldsymbol{\Phi}^{(2)}\right), \quad \boldsymbol{\Phi}^{(2)}(x,0) = \boldsymbol{\Phi}^{(1)}(x,\Delta t/2\,)\ on\ [t_n, t_n + \Delta t]$$

$$\frac{d\boldsymbol{\Phi}}{dt} = \boldsymbol{S}\left(\boldsymbol{\Phi}^{(3)}\right), \quad \boldsymbol{\Phi}^{(3)}(x,0) = \boldsymbol{\Phi}^{(2)}(x,\Delta t)\ on[t_n + \Delta t/2\,, t_n + \Delta t\,]$$

- Could the splitting incur major problems?

A Toy Problem



Transport: $T_R = 1$

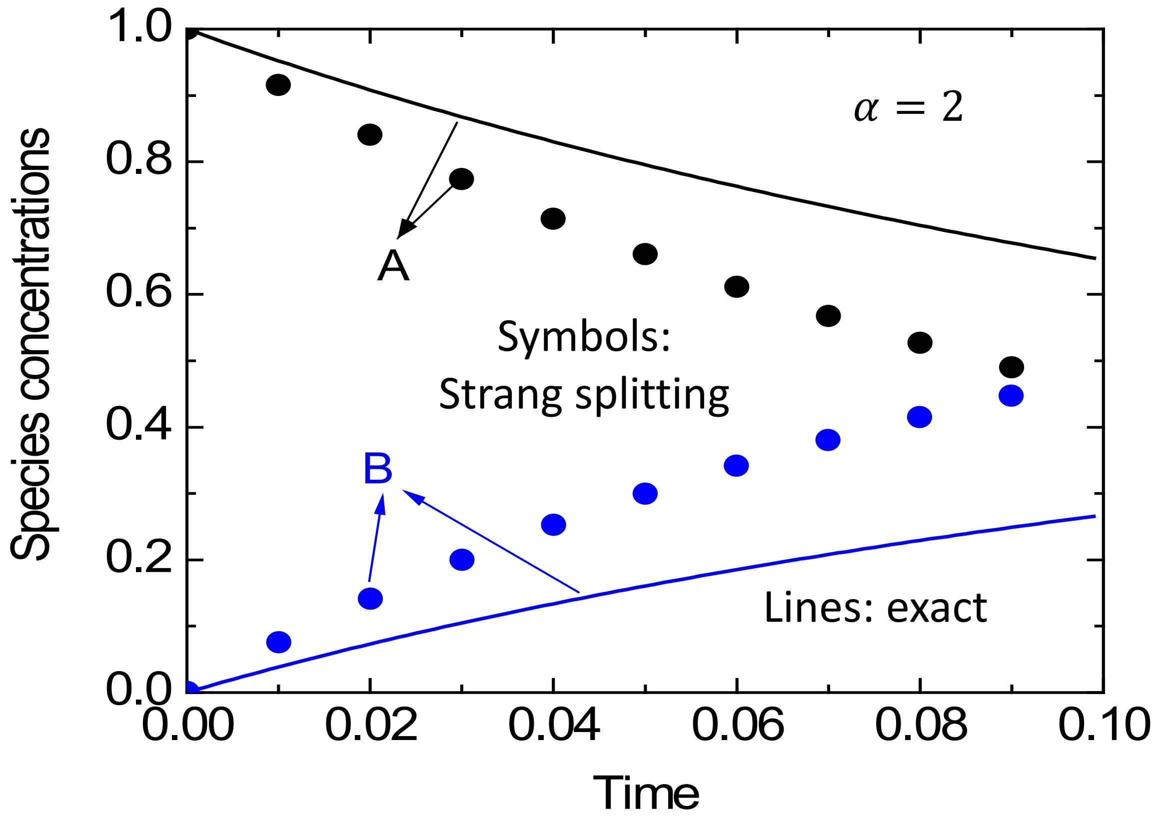
Chemistry: $A \xrightarrow{k_1=1} \boldsymbol{R} \overset{k_2=10^6}{\Longrightarrow} C$

$$A + \alpha \boldsymbol{R} \xrightarrow{k_3={k_2}^{\alpha}} B + \alpha \boldsymbol{R}$$

Radical ***R:***

- Timescale: $\tau = {k_2}^{-1} = 10^{-6} \rightarrow$ stiffness
- In quasi steady state (QSS): $\omega_2 \approx (\omega_1 + T_R)$
- Transport source (T_R) ~ chemical formation rate (ω_1)
- R is catalytic for the main path (R_3)
- $\alpha \neq 1$ induces nonlinearity

O(1) Errors in Strang-Splitting



- Sufficiently small splitting time step: $\Delta t = 10^{-5}$
- Fully-explicit integration applicable at $\Delta t = 10^{-6}$

Mechanism of the Error:
Erroneous Radical Concentrations

- $\boldsymbol{R}$ is in QSS:

  $$\omega_2 = k_2 R \;\approx\; \omega_1 + T_R = k_1 A + T_R$$

  consumption rate　　　　production rate

- Correct concentration:

  $$R^+ \approx \frac{k_1 A + T_R}{k_2}$$

- Excluding transport:

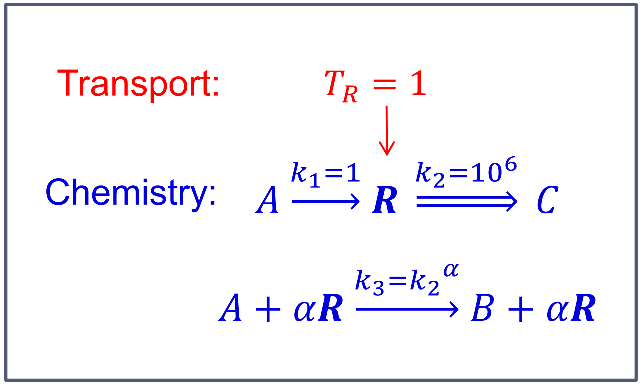
  $$R^- \approx \frac{k_1 A}{k_2} < R^+$$

- Error source:

  Splitting chemical & transport

  → incorrect radical pool level

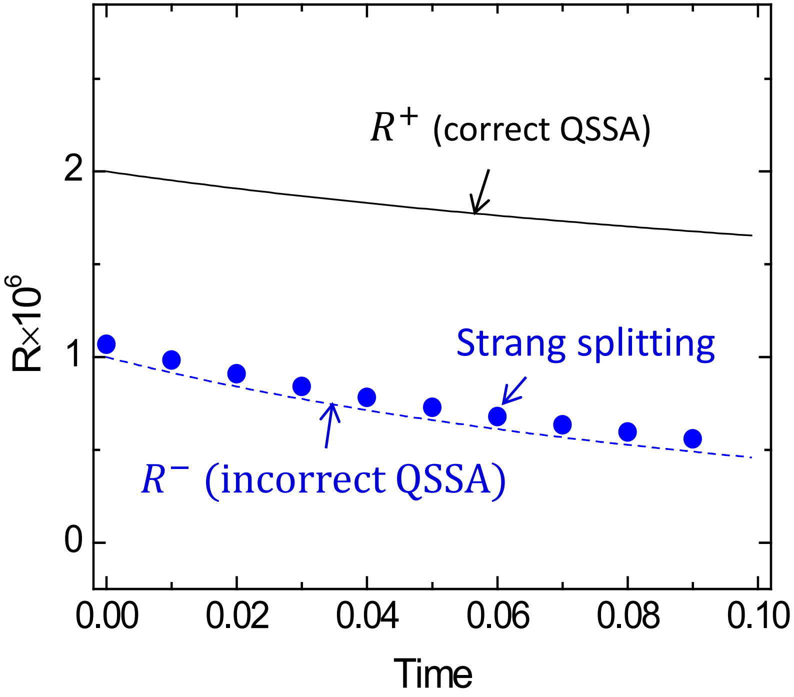
  → incorrect reactivity



Transport: $T_R = 1$

Chemistry: $A \xrightarrow{k_1=1} \boldsymbol{R} \xRightarrow{k_2=10^6} C$

$$A + \alpha \boldsymbol{R} \xrightarrow{k_3={k_2}^{\alpha}} B + \alpha \boldsymbol{R}$$



Development of Advanced Chemistry Solvers: Dynamic Adaptive Hybrid Integration (AHI)

- Governing equations

$$\frac{d\mathbf{\Phi}}{dt} = \boldsymbol{S}(\mathbf{\Phi}) + \boldsymbol{T}(\mathbf{\Phi}),$$ ***S***: chemical source, ***T***: transport

- Integrate chemistry and transport together
  - Fast chemistry treated implicitly
  - Slow chemistry & transport treated explicitly (cost comparable to splitting schemes)
  - Fast species & reactions identified by a CSP criterion (Lam CNF 2013)
  - A 1^{st} $order$ scheme constructed (Gao et al, CNF 2015)

$$\frac{d}{dt}\begin{bmatrix}\mathbf{\Phi}_f \\ \mathbf{\Phi}_s\end{bmatrix} = \boldsymbol{S}_f + \mathbf{g}_s$$

$$\boldsymbol{S}_f = \sum_{i=1}^{m} \boldsymbol{\nu}_i \Omega_i \,, \qquad \mathbf{g}_s = \sum_{i=m+1}^{n_r} \boldsymbol{\nu}_i \Omega_i + \boldsymbol{T}$$

Fast chemistry

Slow chemistry & transport

Separation of Fast & Slow Chemistry

- Timescale of a reaction (Lam, CNF 2013)

$$\tau_i \equiv |\mathbf{J}_i \cdot \boldsymbol{\nu}_i|^{-1},\ \mathbf{J}_i = \frac{\partial \Omega_i}{\partial \boldsymbol{c}} = \left[\frac{\partial \Omega_i}{\partial c_1}\ \frac{\partial \Omega_i}{\partial c_2} \cdots \frac{\partial \Omega_i}{\partial c_k} \cdots \frac{\partial \Omega_i}{\partial c_{n_s}}\right]$$

$\mathbf{J}_i$: Jacobian of reaction rate Ω_i, $\boldsymbol{\nu}_i$: stoichiometric coefficients

- Criterion for a fast reaction (*i*)

$\tau_i < \tau_c, \quad \tau_c$: typically the integration time step

- Criterion for a fast species (*k*)

$$\left|\frac{\partial \Omega_i}{\partial c_k}\right|^{-1} < \tau_c\ ,\ any\ i$$

- A first-order AHI scheme

$$\frac{1}{h}\begin{bmatrix} \boldsymbol{\Phi}_f^{\mathrm{n}+1} - \boldsymbol{\Phi}_f^{\mathrm{n}} \\ \boldsymbol{\Phi}_s^{\mathrm{n}+1} - \boldsymbol{\Phi}_s^{\mathrm{n}} \end{bmatrix} = \boldsymbol{S}_f(\boldsymbol{\Phi}_f^{\mathrm{n}+1}, \boldsymbol{\Phi}_s^{\mathrm{n}}) + \mathbf{g}_s(\boldsymbol{\Phi}_f^{\mathrm{n}}, \boldsymbol{\Phi}_s^{\mathrm{n}})$$

n: the nth integration step, h: time step size

A Second Order AHI Scheme (AHI2)

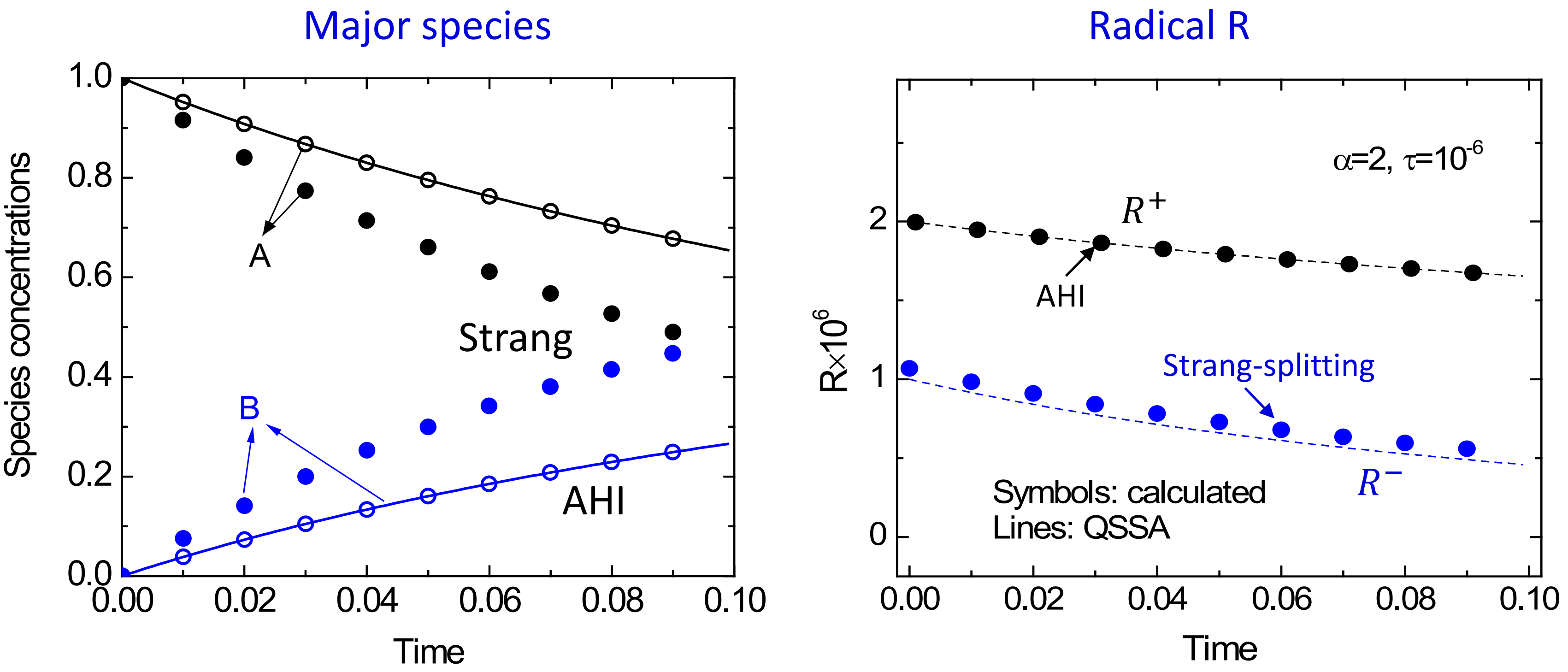
(Wu et al., CNF 2020)

$$\begin{pmatrix} \boldsymbol{\phi}_f^{mid} - \boldsymbol{\phi}_f^n \\ \boldsymbol{\phi}_s^{mid} - \boldsymbol{\phi}_s^n \end{pmatrix} = \frac{h}{2} \begin{pmatrix} \boldsymbol{F}_f\left(\boldsymbol{\phi}_f^{mid}, \boldsymbol{\phi}_s^n\right) + \boldsymbol{S}_f\left(\boldsymbol{\phi}_f^n, \boldsymbol{\phi}_s^n\right) \\ \boldsymbol{F}_s\left(\boldsymbol{\phi}_f^{mid}, \boldsymbol{\phi}_s^n\right) + \boldsymbol{S}_s\left(\boldsymbol{\phi}_f^n, \boldsymbol{\phi}_s^n\right) \end{pmatrix}$$

$$\boldsymbol{\phi}_s^{n+\frac{1}{2}} - \boldsymbol{\phi}_s^n = \frac{h}{2}\left(\boldsymbol{F}_s\left(\boldsymbol{\phi}_f^n, \boldsymbol{\phi}_s^n\right) + \boldsymbol{S}_s\left(\boldsymbol{\phi}_f^{mid}, \boldsymbol{\phi}_s^{mid}\right)\right)$$

$$\begin{pmatrix} \boldsymbol{\phi}_f^{n+1} - \boldsymbol{\phi}_f^n \\ \boldsymbol{\phi}_s^{n+1} - \boldsymbol{\phi}_s^n \end{pmatrix} = \frac{h}{2} \begin{pmatrix} \boldsymbol{F}_f\left(\boldsymbol{\phi}_f^{n+1}, \boldsymbol{\phi}_s^{n+\frac{1}{2}}\right) + \boldsymbol{F}_f\left(\boldsymbol{\phi}_f^n, \boldsymbol{\phi}_s^{n+\frac{1}{2}}\right) \\ \boldsymbol{F}_s\left(\boldsymbol{\phi}_f^{n+1}, \boldsymbol{\phi}_s^{n+\frac{1}{2}}\right) + \boldsymbol{F}_s\left(\boldsymbol{\phi}_f^n, \boldsymbol{\phi}_s^{n+\frac{1}{2}}\right) \end{pmatrix} + h \begin{pmatrix} \boldsymbol{S}_f\left(\boldsymbol{\phi}_f^{mid}, \boldsymbol{\phi}_s^{mid}\right) \\ \boldsymbol{S}_s\left(\boldsymbol{\phi}_f^{mid}, \boldsymbol{\phi}_s^{mid}\right) \end{pmatrix}$$

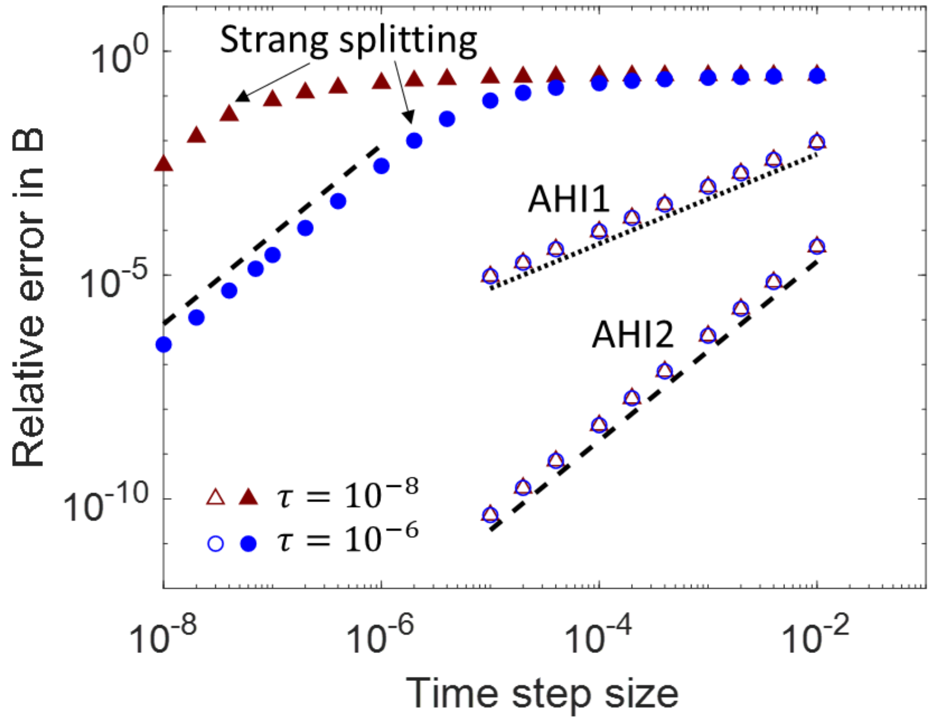
Comparison with Strang-Splitting



$$\Delta t = 10^{-5}$$

- Strang-Splitting: $\mathrm{O}(1)$ errors in every species
- AHI: errors suppressed

Comparison with Strang Splitting: Accuracy for a Toy Problem



$$T_R = 1$$

$$A \xrightarrow{k_1} R \overset{k_2}{\Longrightarrow} C$$

$$A + \alpha R \xrightarrow{k_3} B + \alpha R$$

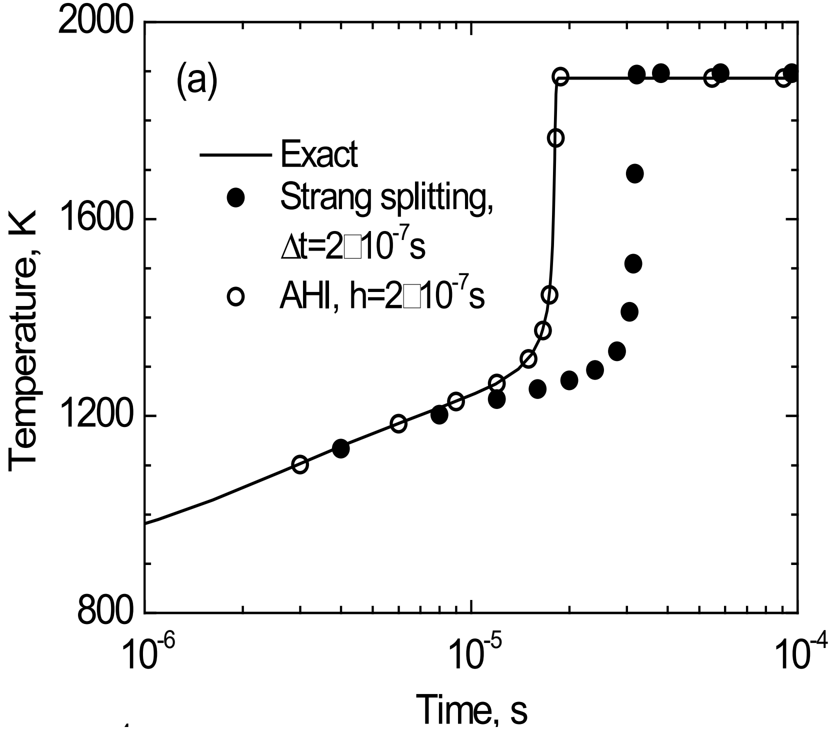
Timescale of R:
$\tau = k_2^{-1} = 10^{-6}$

- Strang splitting: time step $\sim O(\tau)$ to show 2^{nd} *order* behavior
- AHI: error significantly smaller and independent of τ

(Wu et al. CNF 2020)

AHI vs. Splitting for H_2/Air

Force Ignition of H_2/air in PSR



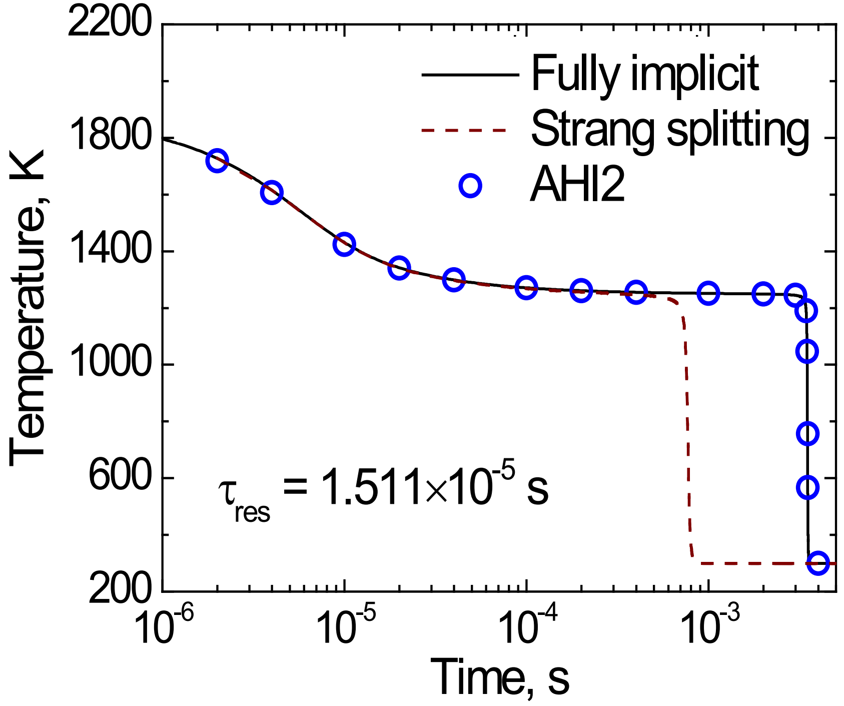
2% H at inlet stream (mole)

$$p = 80\ atm, T_0 = Tin = 875K,\ \phi = 0.3$$

$$\Delta t = 2 \times 10^{-7}\ s$$

(Gao et al., CNF 2015)

Extinction of H_2/air in PSR



Initial condition perturbed from the extinction turning point

$$p = 1\ atm, T_{in} = 300K, \phi = 1$$

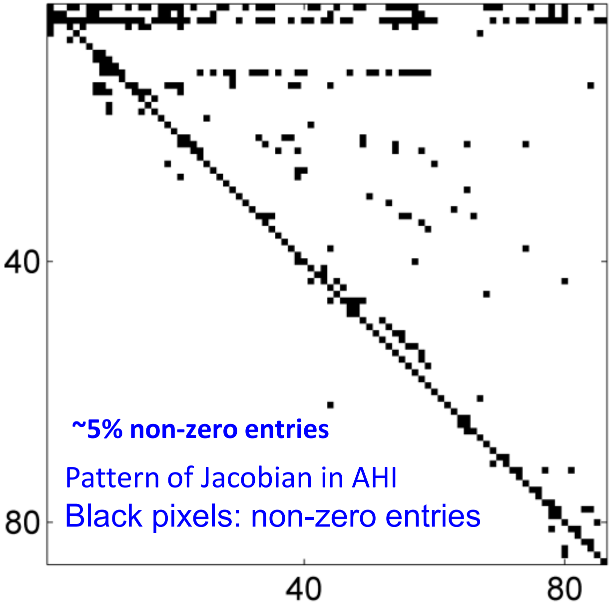
$$\Delta t = 2 \times 10^{-6} s$$

(Gao et al., US Meeting 2015)

Analytic & Sparse Jacobian Techniques

- Chemical Jacobian is sparse, even sparser with AHI
- High computational efficiency can be achieved by combining analytic Jacobian, AHI, Sparse techniques (AHI-S) (Xu et al., CNF submitted)

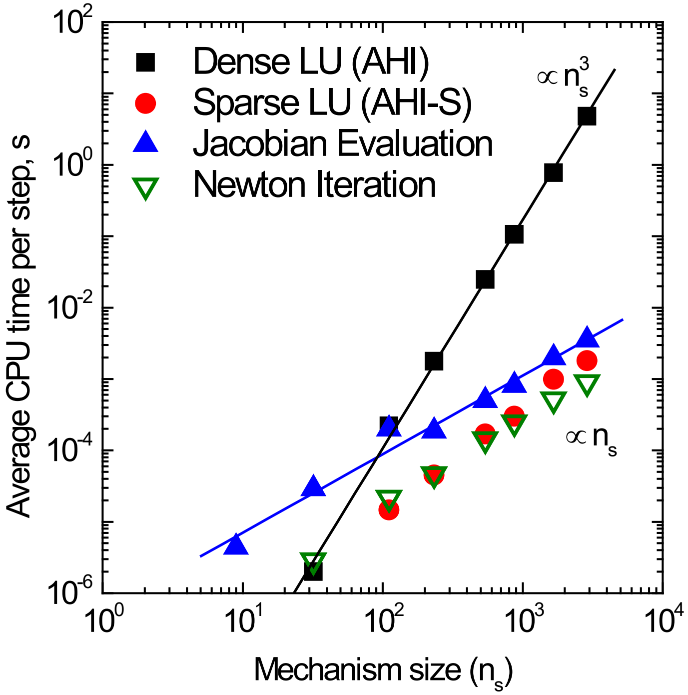
111-speceis USC-Mech II, CH_4/air
$\phi = 0.5\ ,\ p = 50\ atm$
$T_0 = 1200\ K\ ,\ \Delta t = 10^{-7} s$
Time instance : $2\tau_{ign}$



~5% non-zero entries

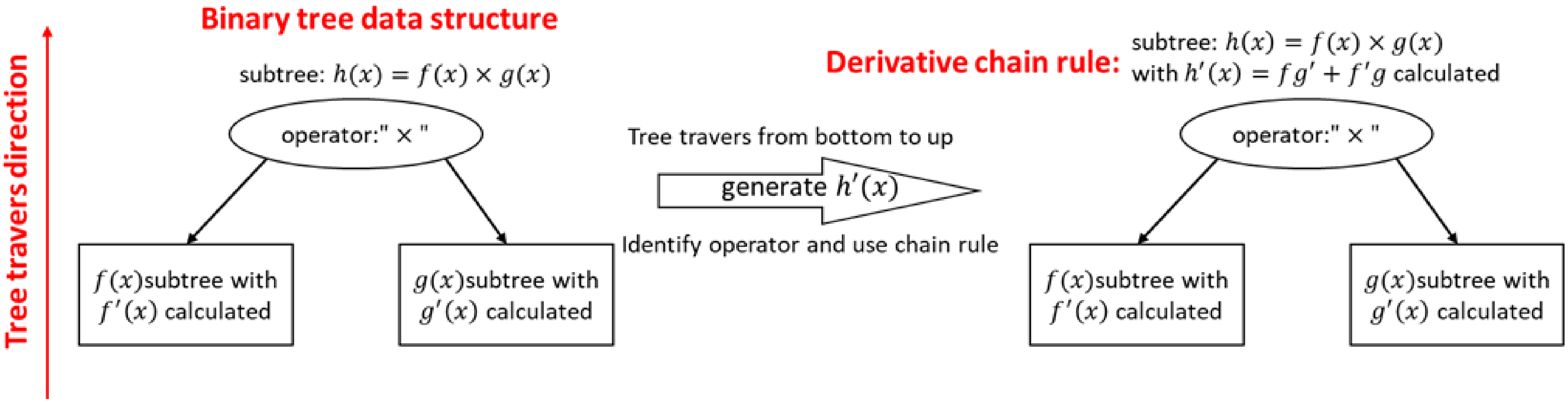
Pattern of Jacobian in AHI
Black pixels: non-zero entries

Cost of major operations in typical stiff chemistry solvers



Auto-differentiation (ADF) for Jacobian Generation (Wang et al, AIAA 2021)

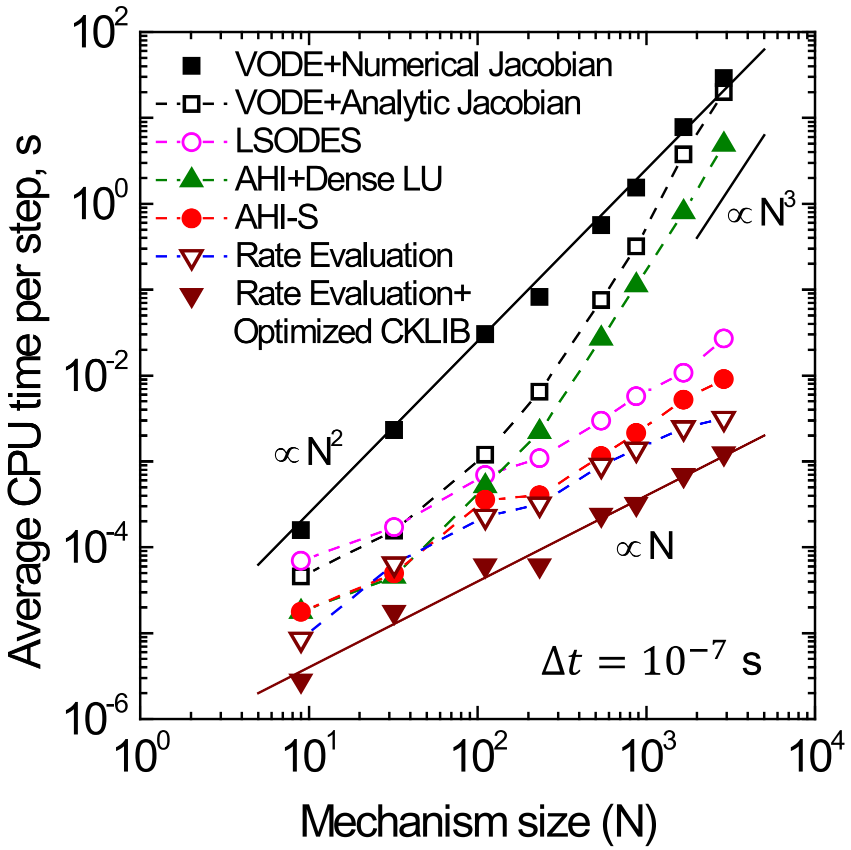
- Jacobian can be hand-derived, but ADF can save effort
- A general formulation can be expressed as a series of unitary/binary operations
  - Can be expressed as a binary tree
  - Use chain rule to differentiate the operator
  - This process can be made recursive to handle arbitrary expressions


Binary tree data structure

Derivative chain rule:

Tree travers direction

Comparison of Chemistry Solvers



VODE+Numerical Jacobian: $O(n_s^3)$

VODE+Analytic Jacobian: $O(n_s)\sim O(n_s^3)$

AHI+Dense LU: $O(n_s)\sim O(n_s^3)$

AHI-S: $O(n_s)$

Rate evaluation (CKLIB): $O(n_s)$

Rate evaluation (Optimized CKLIB): $O(n_s)$

CPU cost of AHI-S

- Linearly correlated to mechanism size
- Much faster than dense solvers
- Up to 3 times as that of one rate evaluation using CKLIB

(Xu et al., CNF 2016)

Concluding Remarks

- There is a lot of room to improve stiff chemistry solvers
- Splitting schemes may not work for stiff problems
- Explicit time integration is possible with stiffness removal
- Linear scaling is possible for implicit solvers with analytic & sparse Jacobian

Reactor Network Model (RNM)

(Wu & Lu ESSCI 2020)

Background

- Reactor Network Model (RNM) is an efficient method to incorporate the detailed chemistry
  - prediction of pollutant emissions (NO, soot, CO …)
  - semi-quantitative analyses of flame responses (blow out) to various inlet conditions
- The RNM has been used decades ago (Bragg 1950s), can involve perfectly stirred reactors (PSR) and/or plug flow reactors (PFR)

A systematic RNM construction method is proposed
An efficient solver for RNM is developed

Challenges in RNM Construction

RNM construction methods

- Empirical construction
  - Manual combustor segmentation and estimated inter-reactor fluxes
  - Parameter "tuned" to fit selected reactor responses
  - (Sturgess et al, 1996; Bhargava et al, 1999; Malte et al, 2007 …)
- CFD based systematic construction
  - Automatically probe CFD flow fields and construct computer-generated RNMs
  - Has been implemented into various commercial CFD codes
  - (Benedetto et al, 2000; Falcitelli et al, 2002 …)

Lack of rigorous flame feature segmentation criteria

Chemical Explosive Mode Analysis

- Chemical Explosive Mode Analysis (CEMA)
  - A universal and robust flame diagnostic (Lu et al., JFM 2010)
  - Can rigorously distinguish different flame zones in various laminar and turbulent flames (Luo et al, CNF 2012; Shan et al, CNF 2012)

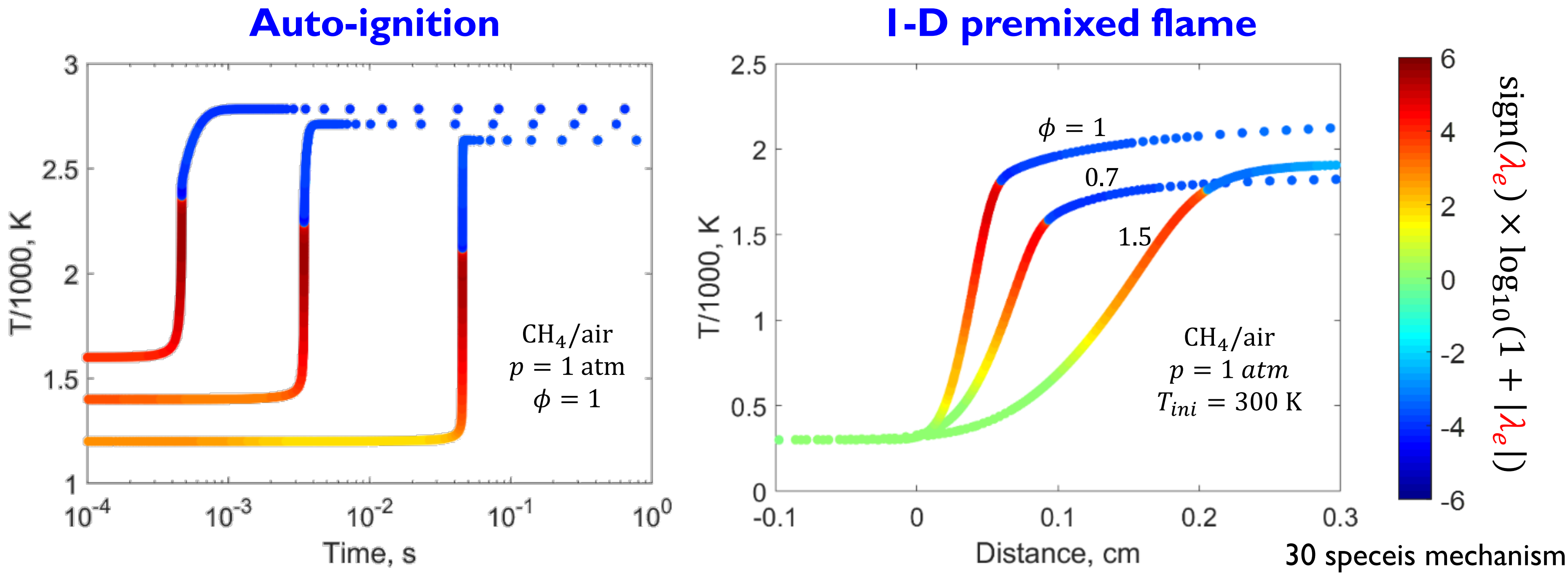
- Chemical Explosive Mode (CEM)
  - Associated with positive eigenvalue, $\lambda_e > 0$, of the chemical Jacobian:

$$\mathbf{J}_{\boldsymbol{\omega}} = \frac{\partial \boldsymbol{\omega}}{\partial \mathbf{y}} \qquad \lambda_e = \boldsymbol{b}_e \cdot \mathbf{J}_{\boldsymbol{\omega}} \cdot \boldsymbol{a}_e$$

$\boldsymbol{\omega}$: Chemical source term
$\boldsymbol{y}$: dependent variables
$\mathbf{J}_{\boldsymbol{\omega}}$: Chemical Jacobian
$\boldsymbol{b}_e/\boldsymbol{a}_e$: left/right eigenvector
λ_e: eigenvalue of chemical Jacobian matrix

  - Indicating the propensity of a mixture to ignite if isolated

CEMA in Flame Segmentation



Auto-ignition

1-D premixed flame

30 speceis mechanism (Lu & Law, CNF 2008)

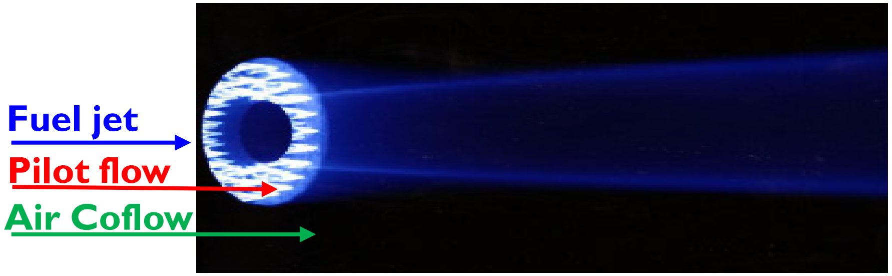
- $\lambda_e > 0$: Explosive → Fresh mixtures (pre-ignition)
- $\lambda_e < 0$: Non-explosive → Products (post-ignition)
- $\lambda_e = 0$: Ignition points & premixed reaction fronts

A CEMA-aided systematic RNM generation based on CFD result is proposed

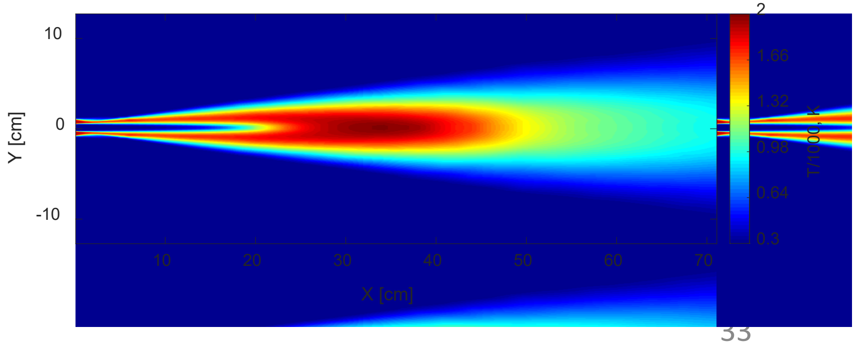
CFD Result for RNM Generations

- Sandia Flame D
  - Fuel jet: a mixture of 75% air and 25% CH_4 by volume
  - Stabilized by a pilot flame generated by the same composition
- Simulation approach
  - RANS/PaSR approach is applied to simulate the statistically stationary flame
  - 16-species chemical mechanism
  - Standard k−ε turbulence model
  - Using the finite-volume open source package OpenFOAM-2.2.x
  - In total around 3300 control volumes in the simulation

Flame geometry

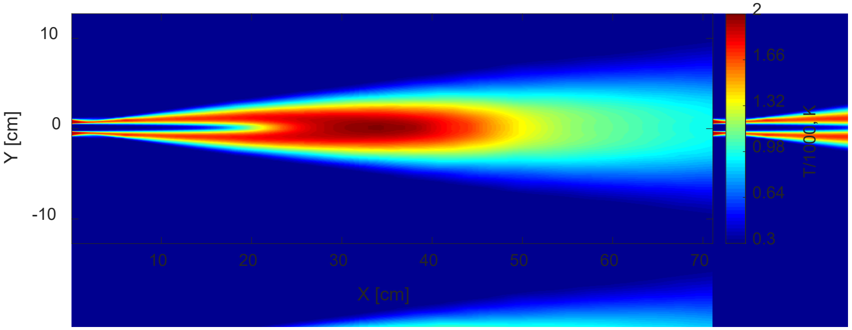


Simulation results



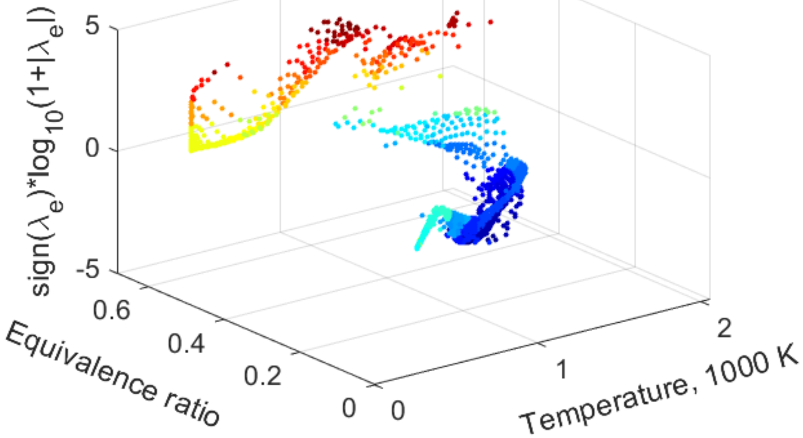
Systematic Aggregation of Control Volumes

Simulation results



T, ϕ, λ_e

Control volume aggregation

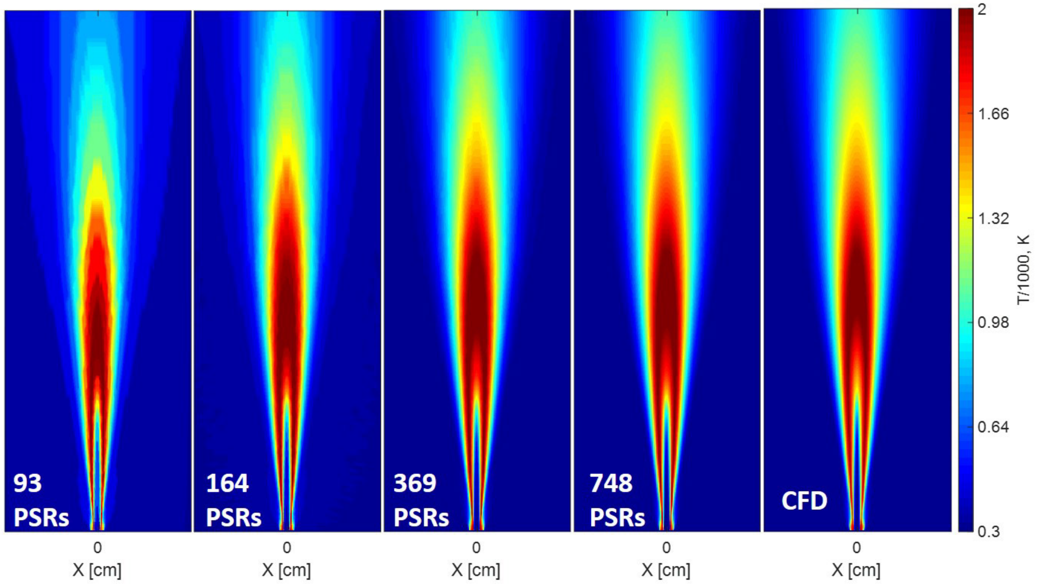


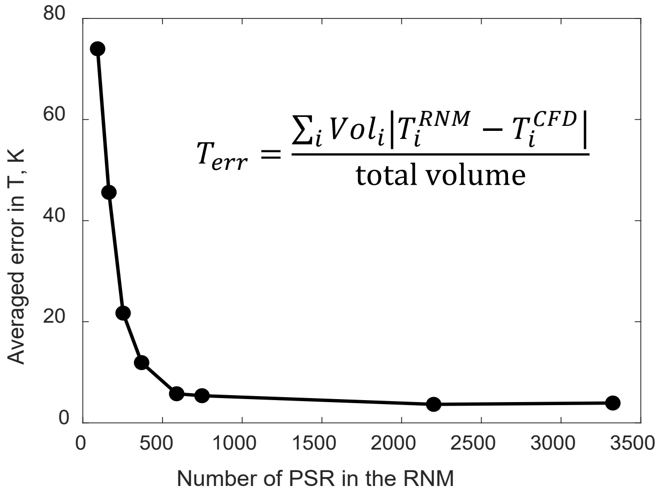
Aggregate control volumes in CFD into PSRs

- Similar thermodynamic states
  - Characterized by temperature (T), equivalence ratio (ϕ), and eigenvalue of CEM (λ_e)
  - User-specified threshold is applied
- Spatially adjacent
  - Identified by graph algorithm

RNMs for Sandia Flame D

93 PSRs —smaller threshold / more reactors→ **748 PSRs** **CFD**

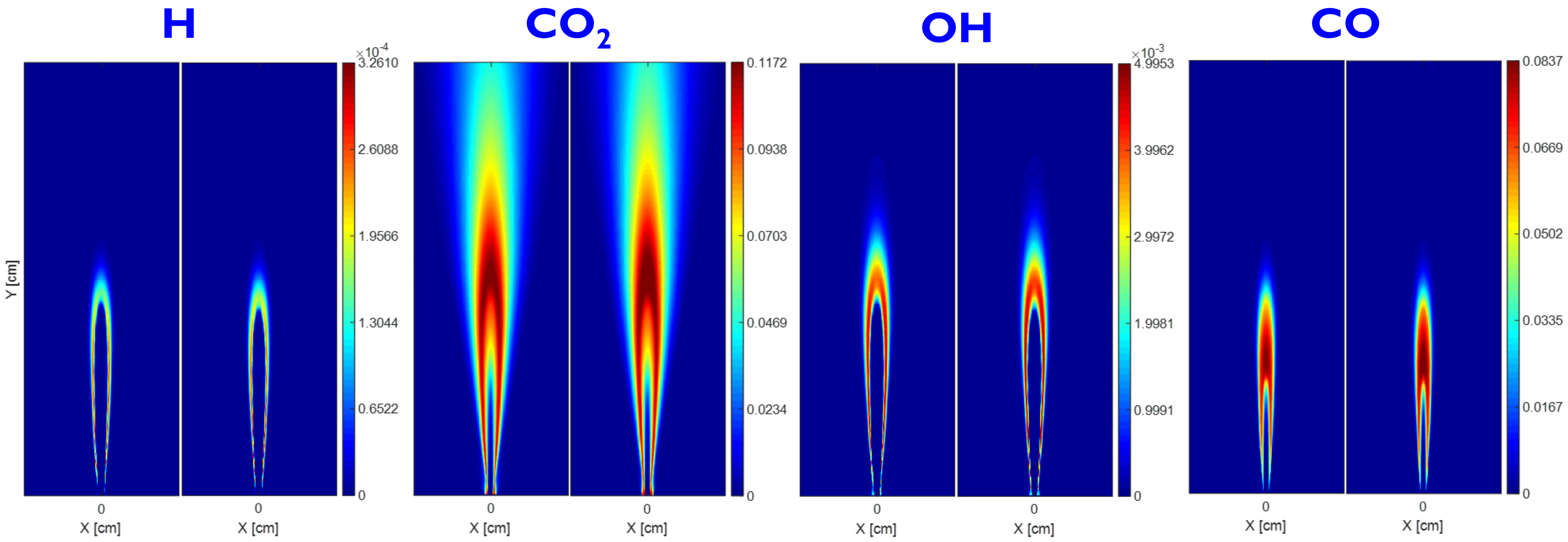




$$T_{err} = \frac{\sum_i Vol_i \left| T_i^{RNM} - T_i^{CFD} \right|}{\text{total volume}}$$

- Accuracy of RNM is controlled by a user-specified threshold value in cell aggregation
- RNM results converge to CFD results as the threshold value decreases (more reactors)

Validations of RNMs

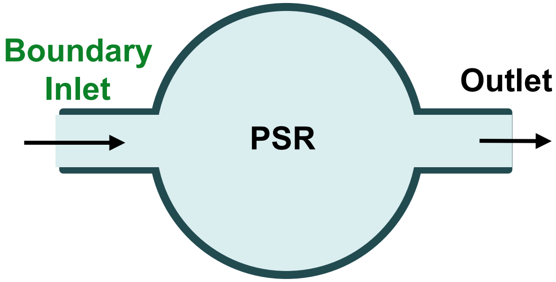


- Major and minor species concentrations are compared
- Very good agreements are observed between 748-PSRs RNM and CFD results

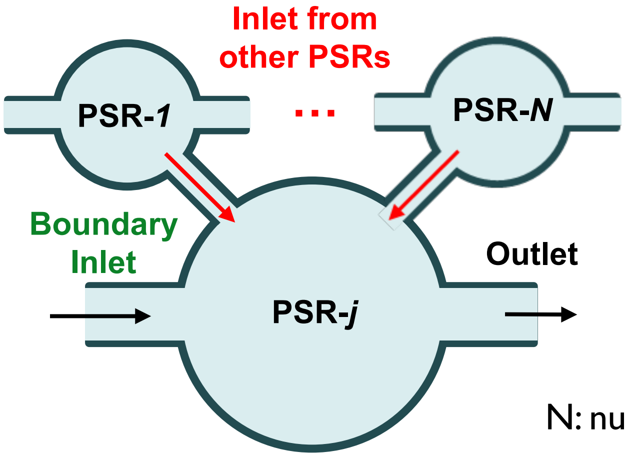
Governing Equations of RNM

Schematic diagrams

Single PSR



RNM



N: number of PSRs

Governing equations

$$0 = \boldsymbol{\omega}(\boldsymbol{\phi}) + \boldsymbol{s}(\boldsymbol{\phi})$$

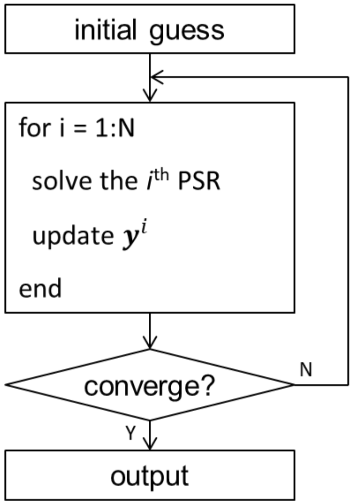
$$0 = \boldsymbol{\omega}^j\left(\boldsymbol{\phi}^j\right) + \boldsymbol{s}\left(\boldsymbol{\phi}^j\right) + \sum_{i=1, i\neq j}^{N} A^{i,j}\boldsymbol{m}\left(\boldsymbol{\phi}^j, \boldsymbol{\phi}^i\right)$$

Flow splitting factor, $A^{i,j}$

- The contribution of reactor *i* to the overall mass flow rate into reactor j
- The splitting factor matrix ***A*** indicates the couplings between the PSRs

Iterative Solver of RNM

Diagram of iterative solver



initial guess

```
for i = 1:N
    solve the $i^{th}$ PSR
    update $\boldsymbol{y}^i$
end
```

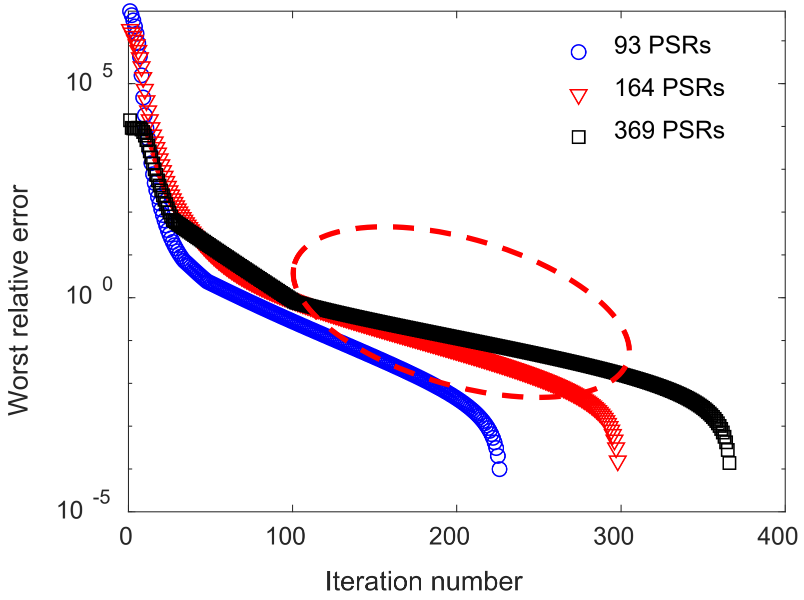
converge?

N

Y

output

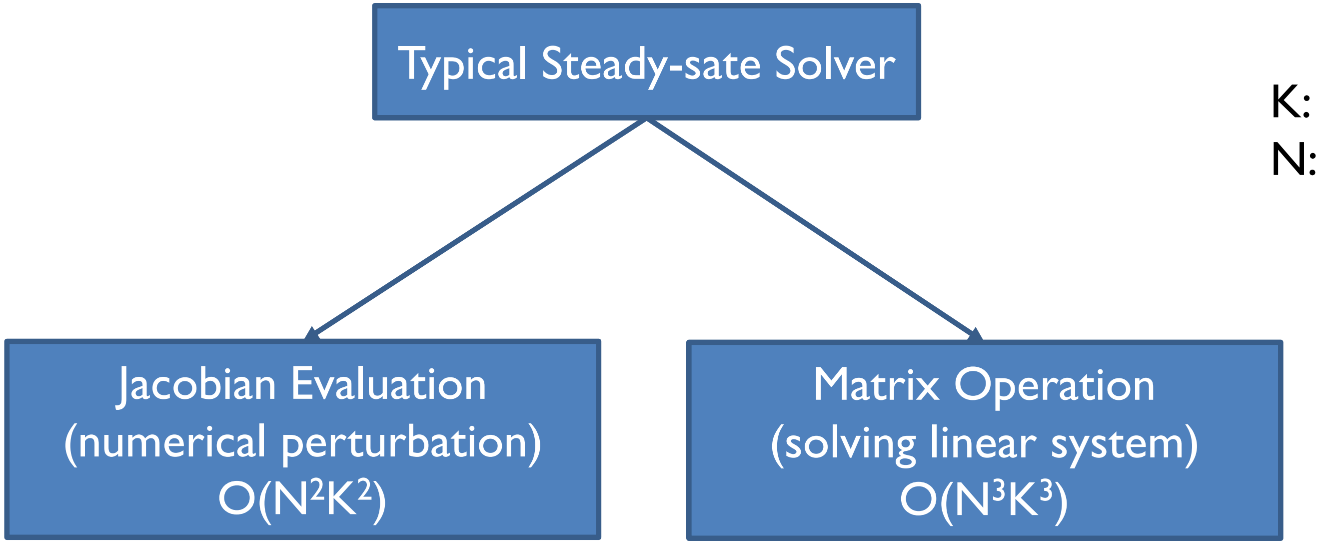
Slow convergence rate



- The commonly used iterative solver solves reactors sequentially
- The convergence rate for the iterative solver is slow, especially for a large number of reactors

A direct solver is needed for faster convergence

Challenges in the Direct Solver



Typical Steady-sate Solver

Jacobian Evaluation
(numerical perturbation)
$O(N^2K^2)$

Matrix Operation
(solving linear system)
$O(N^3K^3)$

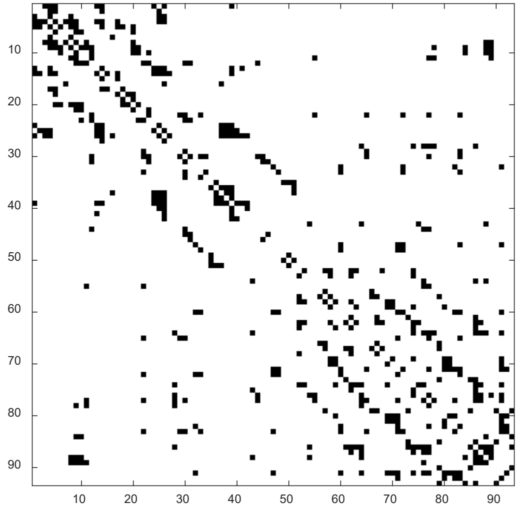
K: number of species
N: number of PSRs

- Time complexity of $O(N^3K^3)$ is *NOT* affordable for large-size RNM and detailed mechanism
- Sparse matrix operations and analytical Jacobian evaluations are used to improve the efficiency

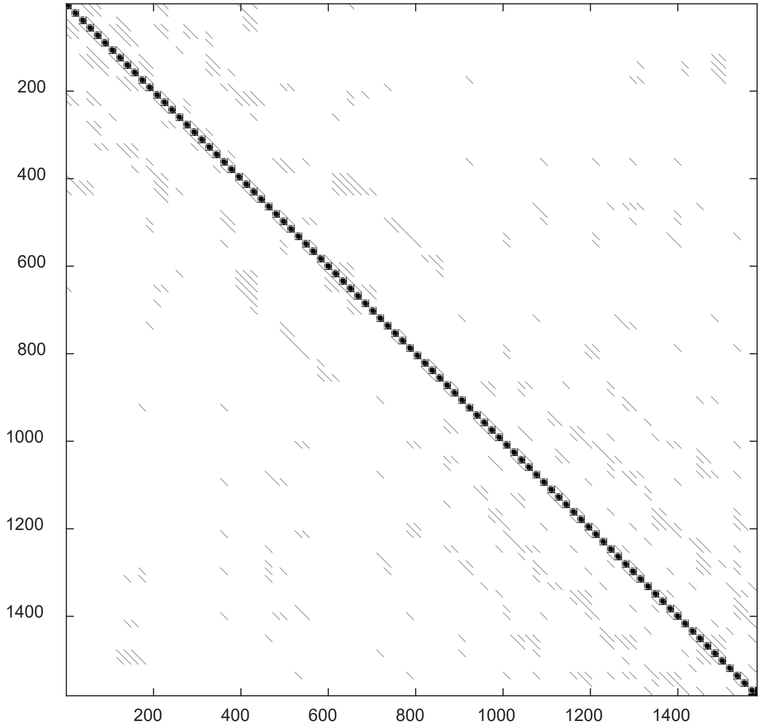
Sparsity of the Jacobian

16 species
93 PSRs

PSR coupling in RNM



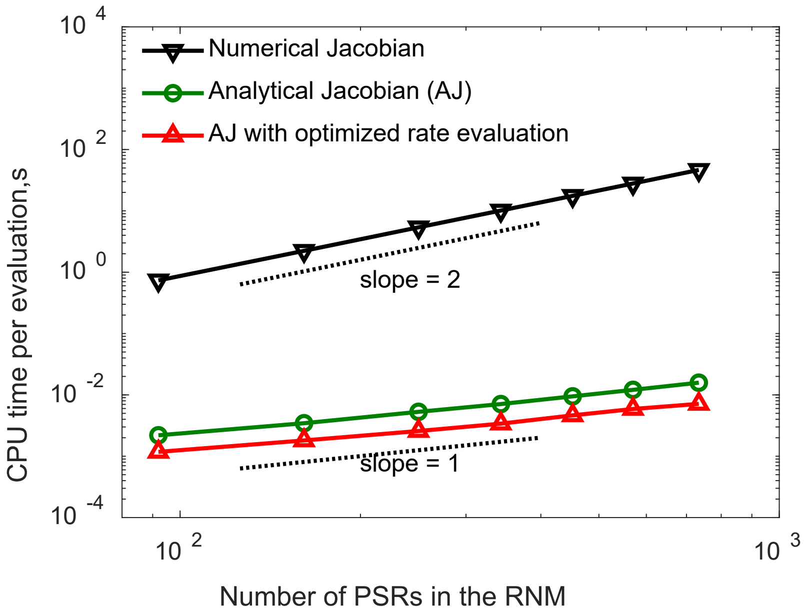
Jacobian pattern



- In the RNM, the PSRs are typically sparsely coupled
- The Jacobian matrix of the entire RNM system is highly sparse
- Sparse matrix operations are applied to improve the solver efficiency

Analytical Jacobian and Optimized Rate Evaluation

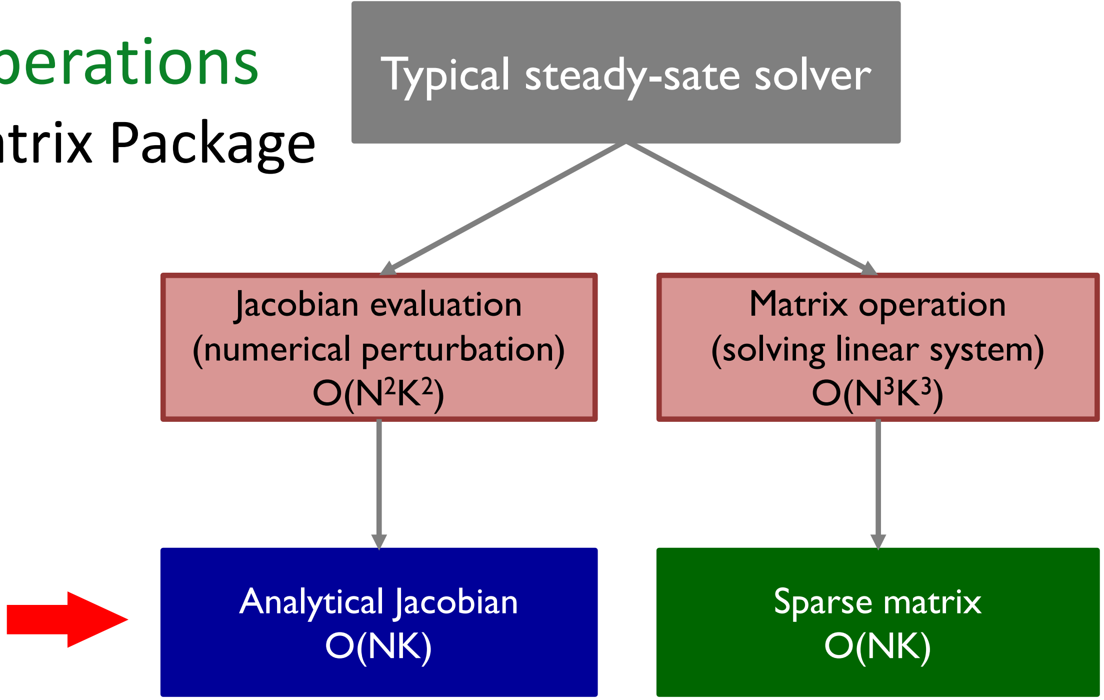
Jacobian evaluation of RNM of different sizes



- Analytical Jacobian (AJ) can dramatically reduce the computational cost, especially for large sized mechanism.
- AJ with optimized rate evaluation can further improve the efficiency
  - The rate expressions are transformed to reduce the evaluation cost
  - The rate parameters are hard coded to save memory retrieving time

Solver Summary

- TWOPNT subroutine with pseudo time stepping
  - Faster convergence and high robustness
- Analytical Jacobian with optimized rate evaluation
  - In house generated
  - Mechanism specific
- Sparse matrix operations
  - Yale Sparse Matrix Package



Typical steady-sate solver

Jacobian evaluation
(numerical perturbation)
$O(N^2K^2)$

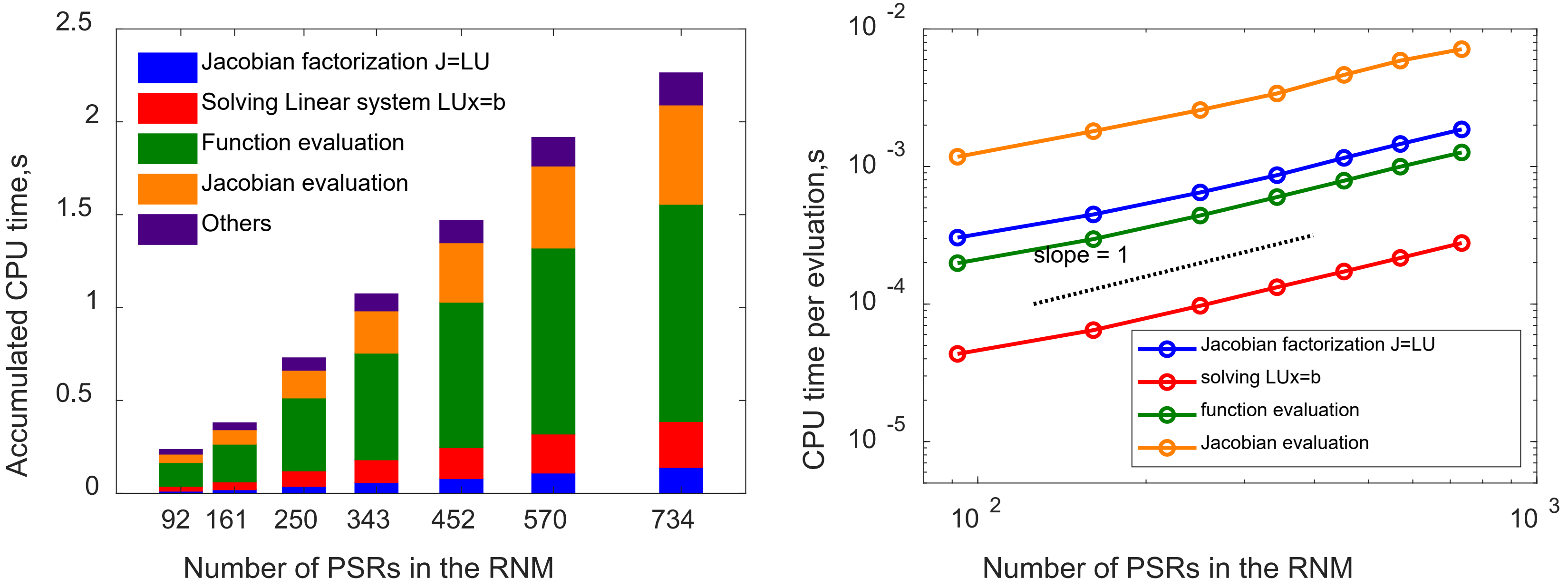
Matrix operation
(solving linear system)
$O(N^3K^3)$

Analytical Jacobian
$O(NK)$

Sparse matrix
$O(NK)$

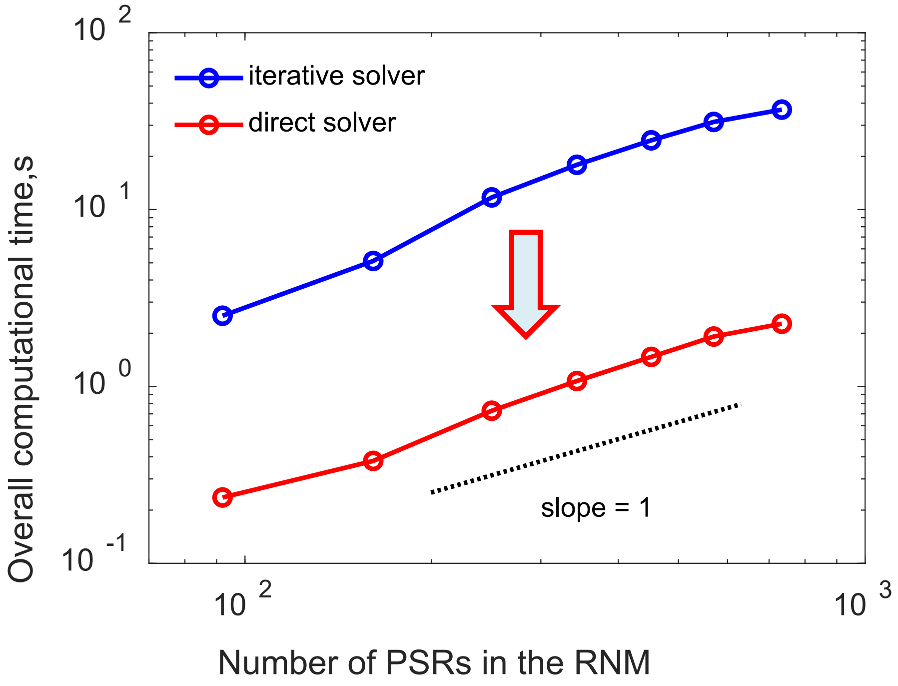
Linear time complexity

Time complexity



- Dominant components in computational cost: Jacobian evaluation, function evaluation, Jacobian factorization J=LU and solving linear system LUx=b
- The computational cost of each component scales *linearly* with the size of the RNM

Iterative Solver Vs. Direct Solver



- Both solvers show a ***linear trend*** in computational time regarding the number of PSRs in RNM
- The direct solver is much faster than the iterative solver

Conclusions

- An automated RNM construction method based on CFD is developed
  - CEMA is employed in flame segmentation and cell aggregation
  - The RNM results converge to the CFD results as the user-specified threshold value of aggregation decreases

- An efficient direct solver is developed by solving all the variables in the RNM simultaneously
  - Significant speedup is achieved compared with the conventional iterative solver
  - A linear scaling in computational cost is achieved as a function of the number of reactors in the RNM

Plasma Assisted Ignition Modeling based on Machine Learning

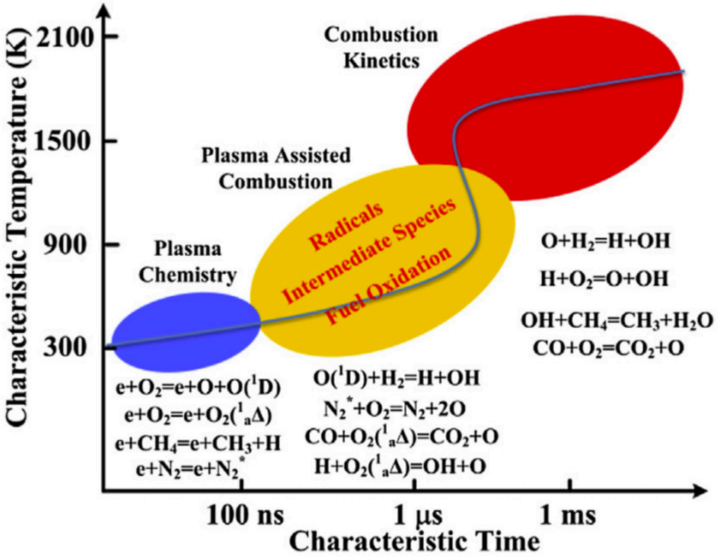
(Kabil & Lu, ESSCI 2022)

Background: Plasma Assisted ignition modeling

- Non-equilibrium plasma can assist combustion:
  - Shorten ignition delay
  - Stabilize flames

- Challenges
  - Non-equilibrium processes
  - Multi-timescales
  - Complex chemical kinetics

- Commons solution approaches
  - Reduce Plasma Chemistry
  - Lump excited species
  - Phenomenological models



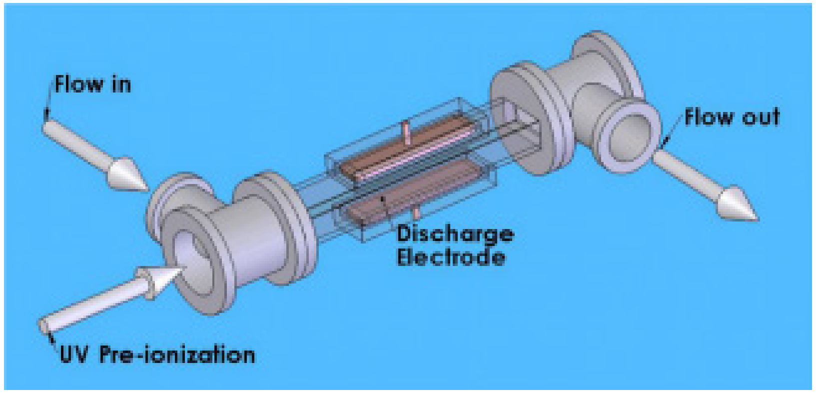
* Y. Ju, W. Sun, Plasma assisted combustion: Dynamics and chemistry, Progress in Energy and Combustion Science 48 (2015)

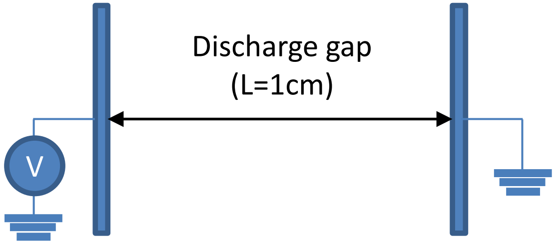
NRP Plasma in Air

Takashima experiment

- Operating Conditions
  - 1D plane-to-plane geometry
  - Pressure = 0.07 [atm] ~ 50 [torr]
  - Temperature = 300 [K]
  - Applied Electric potential (V_{app})
    - $t_{pulse} = 100\ [ns]$
    - V_{app} range [- 22 : 17] KV
  - Plasma kinetics:

    Based on (Uddi 2009, Nagaraja 2013)
    - 18-species, 115-reactions





Keisuke Takashima *et al* 2013 *Plasma Sources Sci. Technol.* **22** 015013

1D Governing Equations

- **Governing equations during the Pulse**

$$\frac{\partial n_k}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{\Gamma_k} = \dot{\Omega}_k$$ → Species equations

$$\boldsymbol{\Gamma}_{\mathbf{k}} = q_k \mu_k n_k \boldsymbol{E} - D_k \boldsymbol{\nabla} n_k$$ → Drift diffusion assumption

$$\boldsymbol{E} = -\boldsymbol{\nabla}\phi$$

$$\boldsymbol{\nabla} \cdot \varepsilon_r \boldsymbol{\nabla} \varphi = -\frac{e}{\varepsilon_0}\left(n_+ - n_- - n_e\right)$$

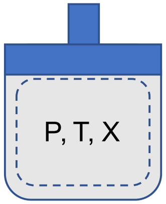
$$\rho \frac{\partial e_g}{\partial t} = -\nabla \cdot \boldsymbol{q} + A_{coll} + \dot{Q}_{JH}$$

$$q = \lambda \boldsymbol{\nabla} T_g + \sum_k \boldsymbol{\Gamma_k} C_{p,k} T_g$$

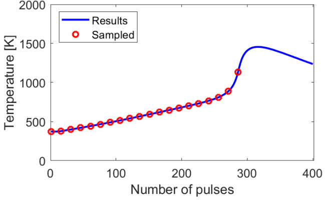
$$A_{coll} = \frac{3}{2} k_b n_e \frac{2m_e}{m_g} \nu_{e,g}\left(T_e - T_g\right) + \sum_j \Delta E_j^g r_j$$

$$\dot{Q}_{JH} = e\boldsymbol{E} \cdot \sum_k q_k \boldsymbol{\Gamma_k}$$

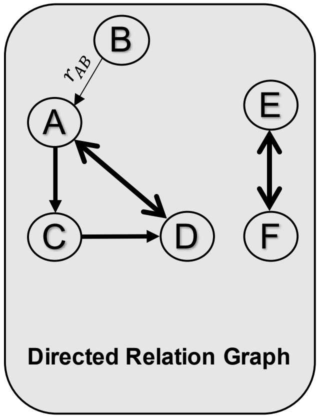
Procedure of Model Training



Features : $\{P, T, X_{1:kk}\}$ at the start of the pulse
Labels : $\{\omega_{1:kk}\}$ over a single pulse

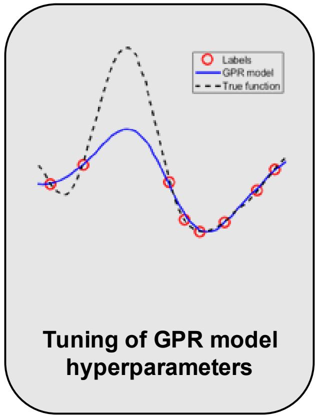


Dataset



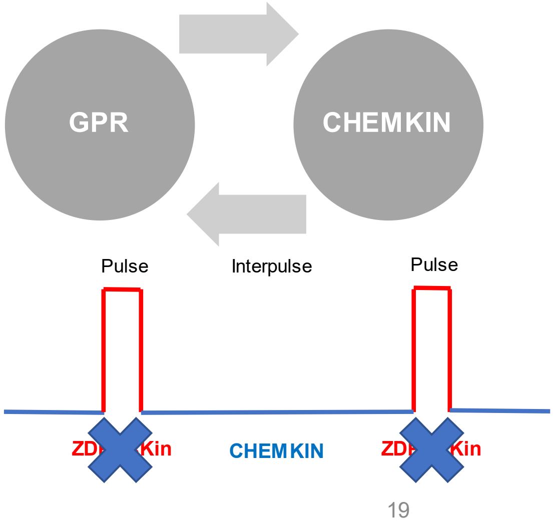
Directed Relation Graph

RRT(P,T,X)



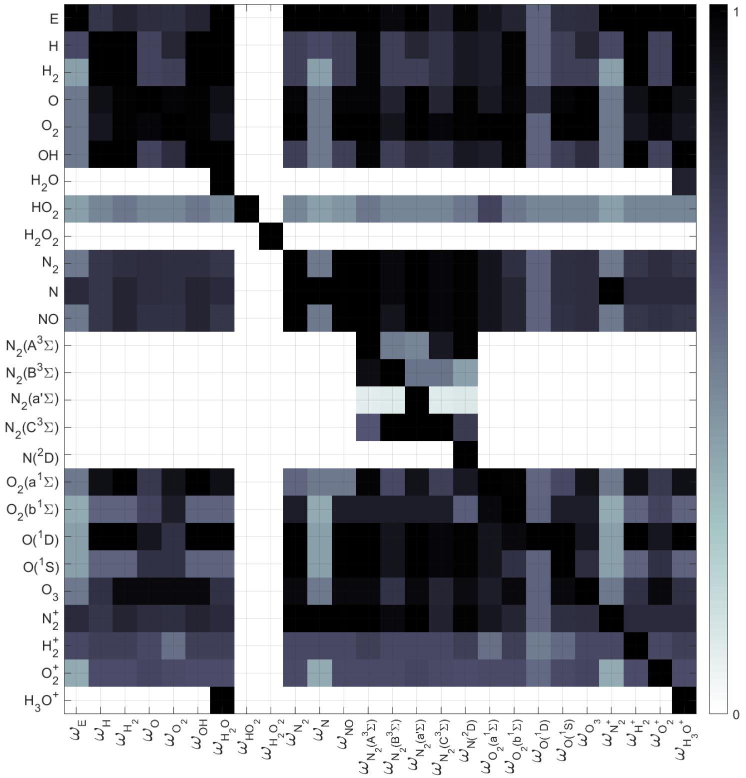
Tuning of GPR model hyperparameters

Dataset



Feature Selection – Directed Relation Graphs (DRG)

- Weigh the coupling of species (B) to the production rate of a specific species (A)
- $\boldsymbol{r_{AB}} = \dfrac{\sum_{\boldsymbol{i=1,I}} \left|\boldsymbol{\nu_{A,i}\omega_i\delta_{Bi}}\right|}{\sum_{\boldsymbol{i=1,I}} \left|\boldsymbol{\nu_{A,i}\omega_i}\right|}$
- Species having couplings stronger than a specified threshold ε are kept as part of feature subset of that source term
- This process is done for each species of interest to select the most important features $(S_{1:kk})$ for its production.



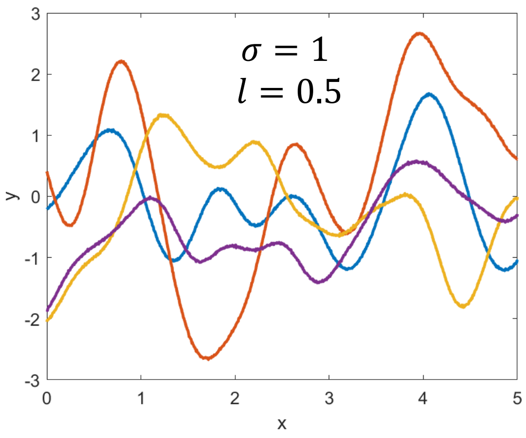
GPR Model Training

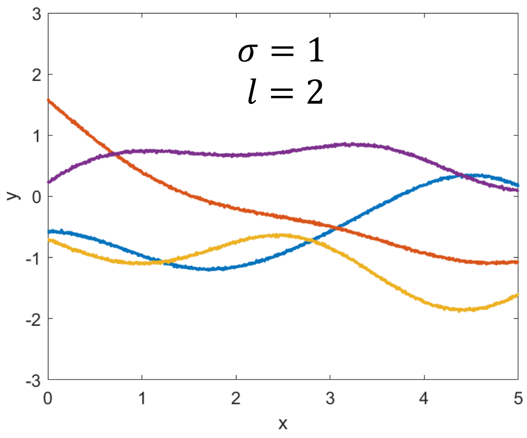
- **Method**
  - Gaussian process regression GPR with an exponential kernel

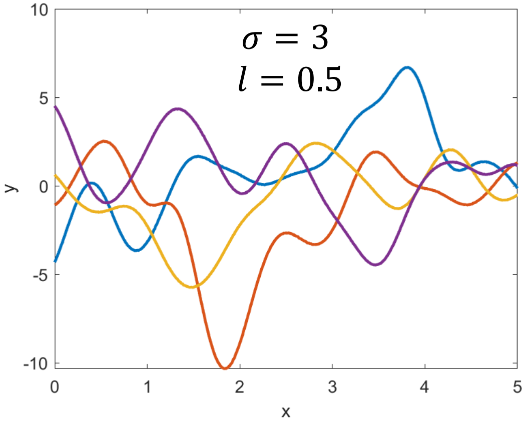
$$Cov(x_i, x_j) = \sigma^2 exp(-\frac{\sqrt{(x_i - x_j)^T (x_i - x_j)}}{l})$$

  - Model hyper-parameters are varied to maximize the likelihood of reproducing the target output

Trained models hold normalized RMSE below 3%







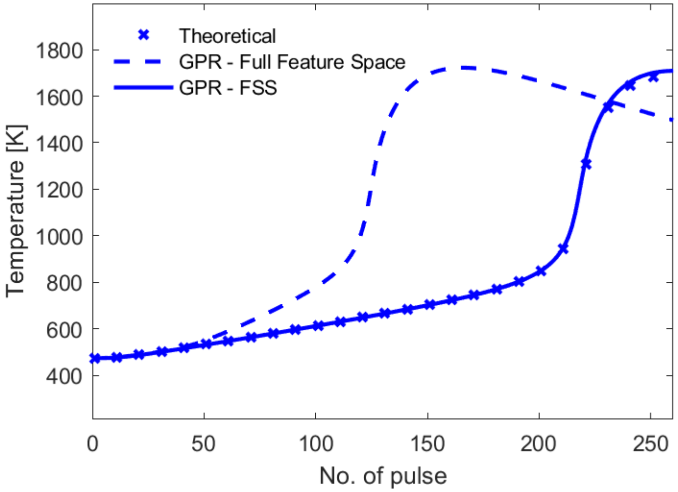
Effect of Feature Selection

- Same dataset

- GPR – Full features:
  - Trained on the whole feature matrix

- GPR – Reduced features:
  - Trained on feature matrix subsets selected via DRG per species source term.

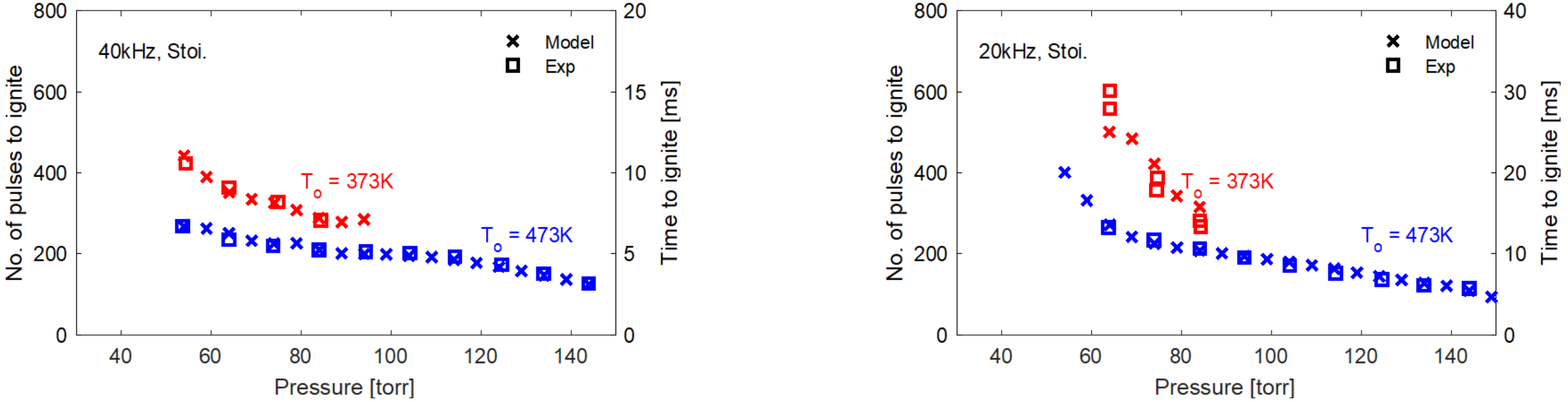
- Test case shown:
  - P = 84Torr
  - 40 kHz
  - Stoichiometric H_2/Air mixture



Development of Data-driven Models

Outcome

- A methodology to identify the important subset of features for each plasma species source terms is developed.
- Trained ML models based on GPR hold 3% normalized RMSE when trained on the reduced feature matrices.
- GPR model gives up to 30-fold speedup in evaluating the plasma source terms compared to ZDPlasKin using detailed chemistry.



Computational Flame Diagnostics

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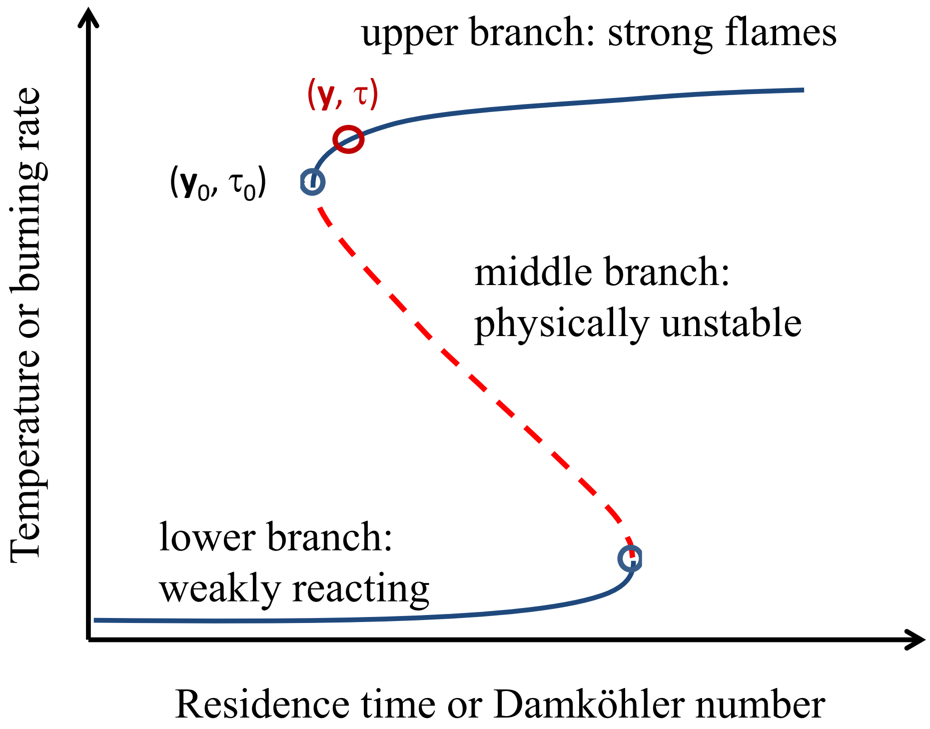
2024 Summer School on Combustion
July 7-13, 2024

Bifurcation Analysis of Ignition/Extinction on S-curves

Limit Phenomena in Steady Flames: Mathematical Interpretation

- The canonical “S”-curve



Governing equations:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}, \tau) = 0$$

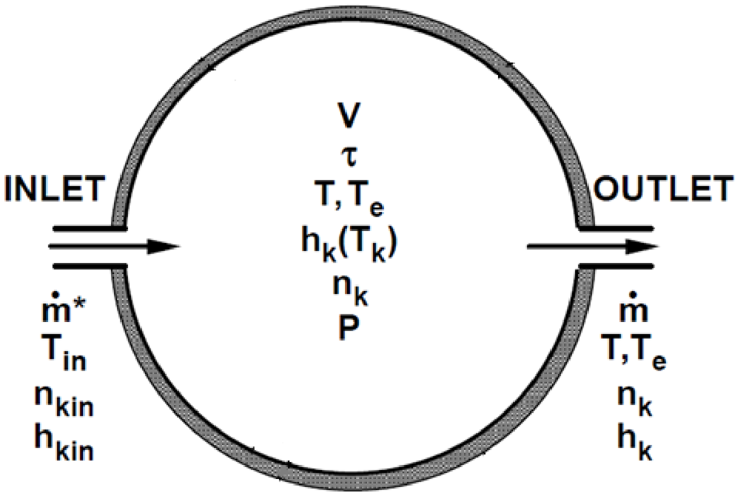
Expansion at a turning point:

$$\mathbf{g}(\cancelto{}{\mathbf{y}}, \tau) \approx \mathbf{g}(\mathbf{y}_0 \cancelto{}{,} \tau_0) + \left(\frac{\partial \mathbf{g}}{\partial \mathbf{y}}\right)_{\mathbf{y}=\mathbf{y}_0} (\mathbf{y} - \mathbf{y}_0) + \left(\frac{\partial \mathbf{g}}{\partial \tau}\right)_{\tau=\tau_0} (\tau - \tau_0)$$

$$\frac{d\mathbf{y}}{d\tau} \approx \frac{(\mathbf{y} - \mathbf{y}_0)}{(\tau - \tau_0)} = -\mathbf{J}^{-1} \underset{\substack{\Uparrow \\ \text{finite}}}{\left(\frac{\partial \mathbf{g}}{\partial \tau}\right)_{\tau=\tau_0}} = \infty$$

- **J** is singular ($\lambda = 0$) at turning points: bifurcation points
  What does this mean chemically?

An Example of Steady State Reactors: Perfectly Stirred Reactor (PSR)



(from CHEMKIN manual)

Governing equations:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y})$$

ω: chemical source

s: mixing term

The Jacobian:

$$\mathbf{J}_{\mathbf{g}} = \frac{\partial \mathbf{g}}{\partial \mathbf{y}} = \frac{\partial \boldsymbol{\omega}}{\partial \mathbf{y}} + \frac{\partial \mathbf{s}}{\partial \mathbf{y}} = \mathbf{J}_{\boldsymbol{\omega}} + \mathbf{J}_{\mathbf{s}}$$

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

Jacobian Matrix J of PSR

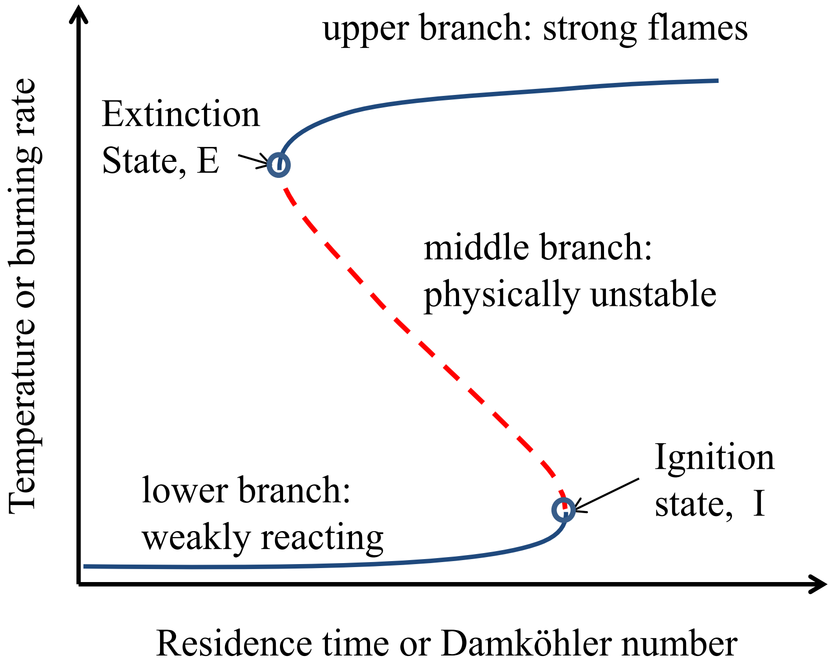
Governing equations: $$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}) \qquad \mathrm{y} = [Y_1,\ \ Y_2,\ \ \ldots\ \ Y_K,\ \ T]^T$$

Jacobian matrix: $$\mathbf{J}_{\mathbf{g}} = \frac{d\mathbf{g}}{d\mathbf{y}} = \frac{d\boldsymbol{\omega}}{d\mathbf{y}} + \frac{d\mathbf{s}}{d\mathbf{y}} = \boxed{\mathbf{J}_{\omega}} + \boxed{\mathbf{J}_{s}}$$

$$\begin{bmatrix}
\frac{\partial \omega_1}{\partial y_1} & \frac{\partial \omega_1}{\partial y_2} & \cdots & \frac{\partial \omega_1}{\partial y_K} & \frac{\partial \omega_1}{\partial T} \\
\frac{\partial \omega_2}{\partial y_1} & \frac{\partial \omega_2}{\partial y_2} & \cdots & \frac{\partial \omega_2}{\partial y_K} & \frac{\partial \omega_2}{\partial T} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
\frac{\partial \omega_K}{\partial y_1} & \frac{\partial \omega_K}{\partial y_2} & \cdots & \frac{\partial \omega_K}{\partial y_K} & \frac{\partial \omega_K}{\partial T} \\
\frac{\partial \omega_{K+1}}{\partial y_1} & \frac{\partial \omega_{K+1}}{\partial y_2} & \cdots & \frac{\partial \omega_{K+1}}{\partial y_K} & \frac{\partial \omega_{K+1}}{\partial T}
\end{bmatrix} = \frac{d\boldsymbol{\omega}}{d\mathbf{y}} = \mathbf{J}_{\boldsymbol{\omega}}$$

$$\mathbf{J}_{\mathbf{s}} = \frac{d\mathbf{s}}{d\mathbf{y}} = \begin{bmatrix}
\frac{\partial s_1}{\partial y_1} & \frac{\partial s_1}{\partial y_2} & \cdots & \frac{\partial s_1}{\partial y_K} & \frac{\partial s_1}{\partial T} \\
\frac{\partial s_2}{\partial y_1} & \frac{\partial s_2}{\partial y_2} & \cdots & \frac{\partial s_2}{\partial y_K} & \frac{\partial s_2}{\partial T} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
\frac{\partial s_K}{\partial y_1} & \frac{\partial s_K}{\partial y_2} & \cdots & \frac{\partial s_K}{\partial y_K} & \frac{\partial s_K}{\partial T} \\
\frac{\partial s_{K+1}}{\partial y_1} & \frac{\partial s_{K+1}}{\partial y_2} & \cdots & \frac{\partial s_{K+1}}{\partial y_K} & \frac{\partial s_{K+1}}{\partial T}
\end{bmatrix}$$

Role of Chemistry at Ignition/Extinction



- The Jacobian

$$\mathbf{J_g} = \frac{\partial \mathbf{g}}{\partial \mathbf{y}} = \frac{\partial \boldsymbol{\omega}}{\partial \mathbf{y}} + \frac{\partial \mathbf{s}}{\partial \mathbf{y}} = \mathbf{J}_{\boldsymbol{\omega}} + \mathbf{J}_{\mathbf{s}}$$

- The eigenvalue

$$\lambda = \mathbf{b} \cdot \mathbf{J_g} \cdot \mathbf{a} = \mathbf{b} \cdot (\mathbf{J}_{\boldsymbol{\omega}} + \mathbf{J}_{\mathbf{s}}) \cdot \mathbf{a}$$

$$= \lambda_{\boldsymbol{\omega}} + \lambda_{\mathbf{s}} = 0$$

- Contribution of mixing: $\lambda_{\mathbf{s}} < 0$
- Contribution of chem.: $\lambda_{\boldsymbol{\omega}} > 0$
- Timescales:

$$\tau_\omega(chemical) = \frac{1}{|\lambda_\omega|},$$

$$\tau_s(mixing) = \frac{1}{|\lambda_s|}$$

At ignition/extinction (turning points):

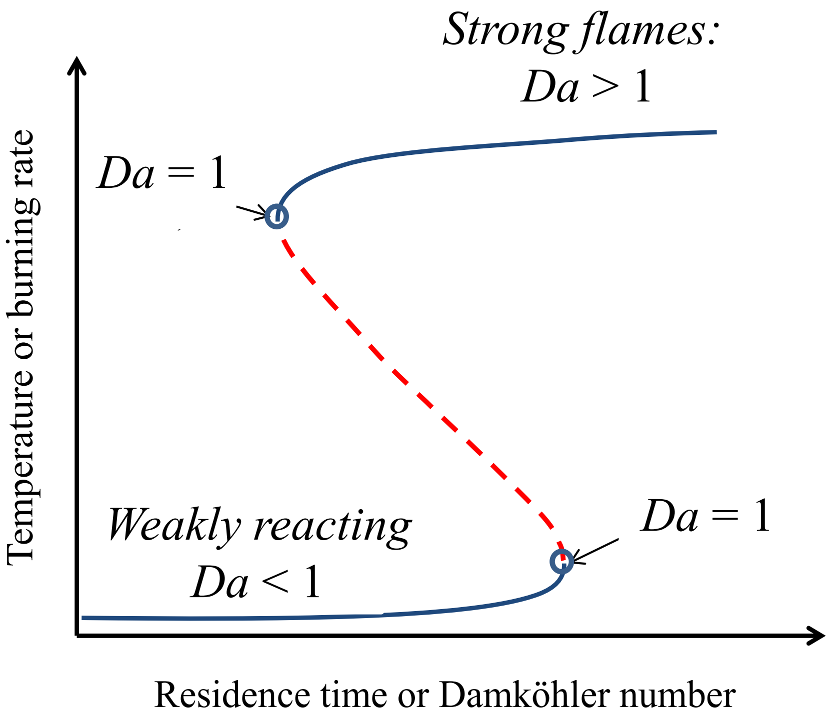
- Chemistry “balances” mixing: $\tau_\omega = \tau_s$
- Explosive chemical process involved

A Damköhler Number (*Da*)

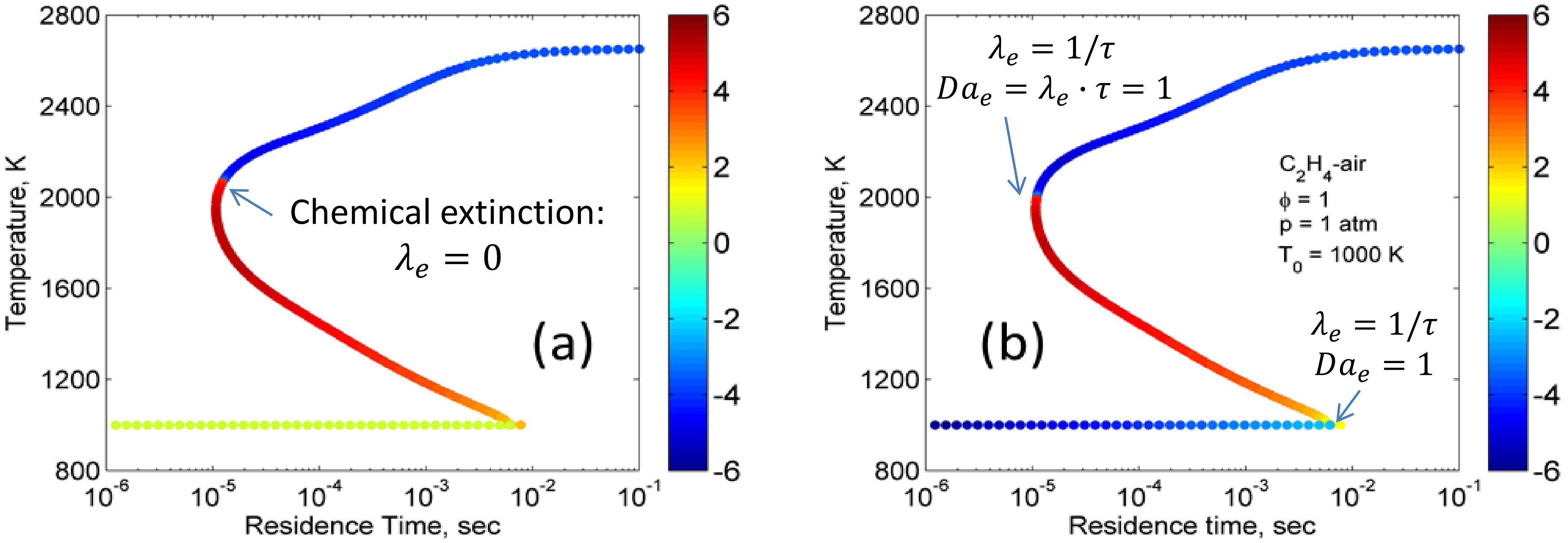
- Relative strength of chemistry and mixing:

$$Da = \frac{\tau_s}{\tau_\omega}$$

- Strongly burning flames:
  - $Da > 1$
  - Typical rate limiting reactions: $CO + OH = CO_2 + H$
- Weakly reacting states:
  - $Da < 1$
  - Rate-limiting reactions slower than mixing
- Ignition/extinction states: $Da = 1$



Ignition & Extinction of Steady State PSR

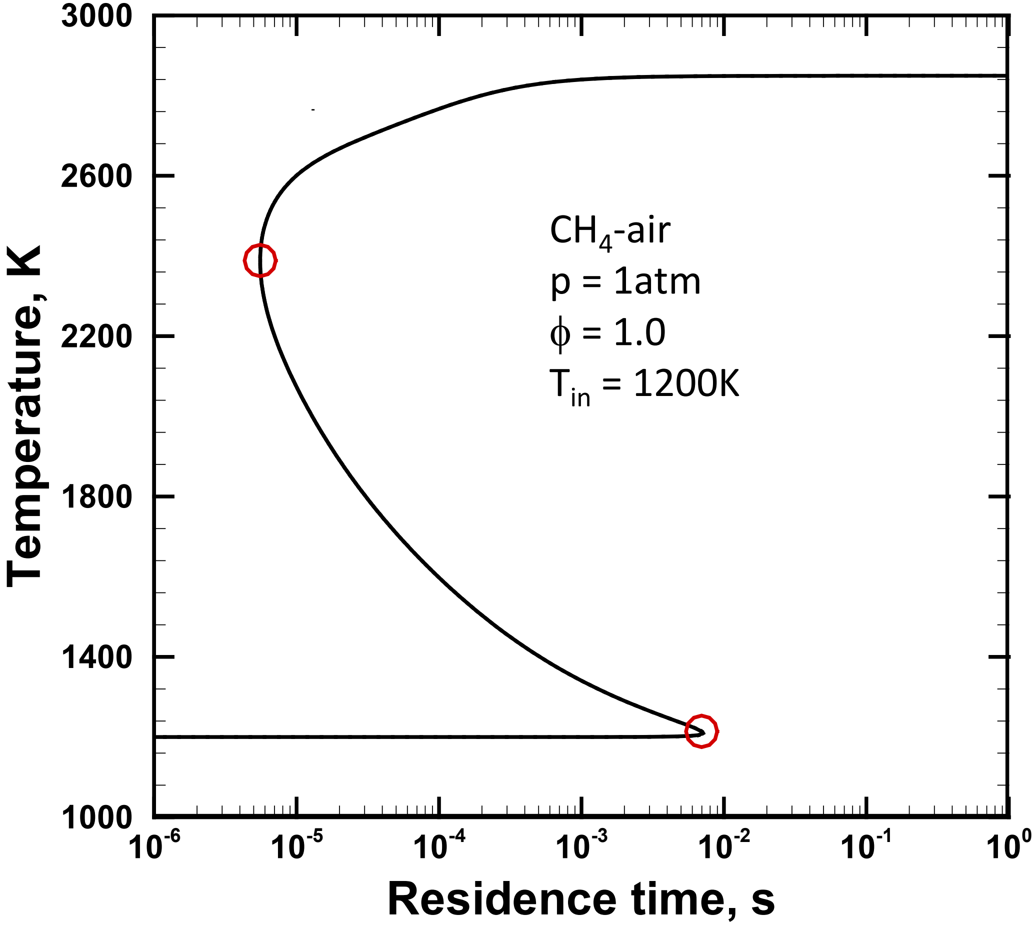


sign(λ_e)×$\log_{10}(1+|\boldsymbol{\lambda_e}|)$ sign(λ_e-1/τ)×$\log_{10}(1+|\boldsymbol{\lambda_e - 1/\tau}|)$

- $\lambda_s = -\frac{1}{\tau} < 0\,, \lambda_e = \lambda_\omega > 0$ at the turning points
- $Re(\lambda_e) > 0$: near- and post-extinction mixtures in PSR
- $Da = 1$: ignition/extinction states in steady PSR

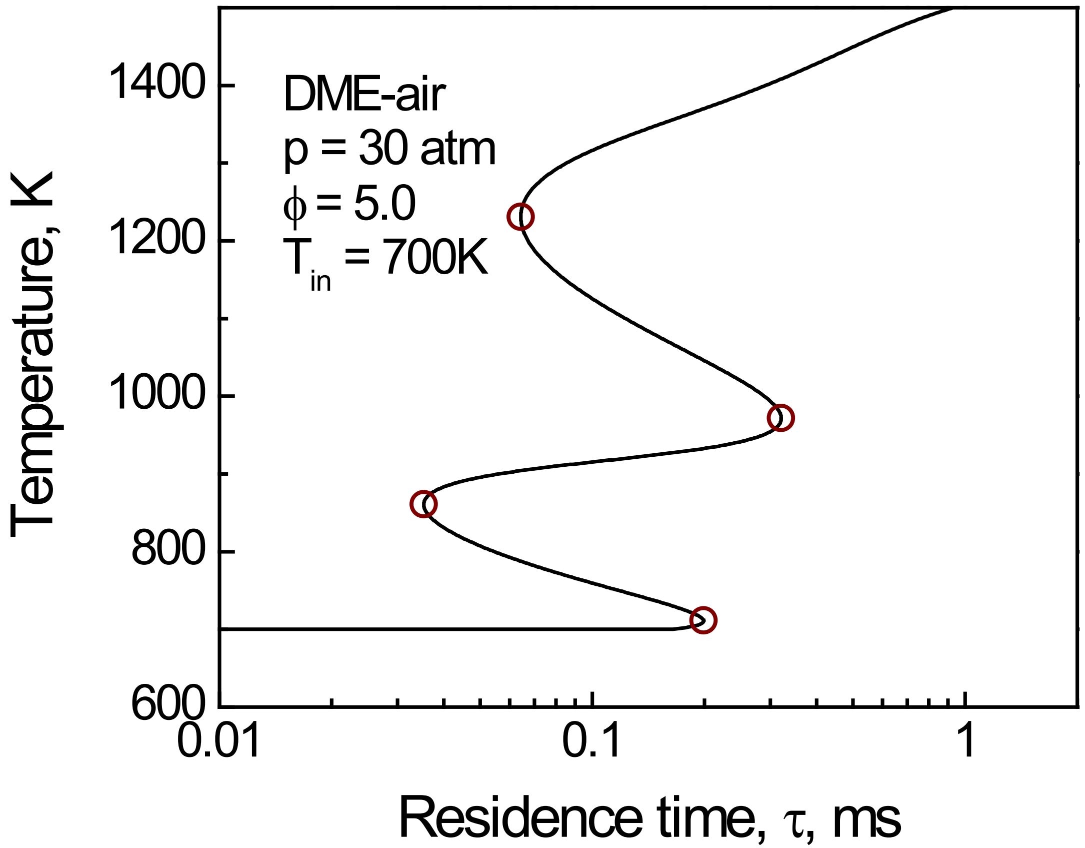
"S"-Curves for Practical Fuels in PSR: Bifurcation Points (1/2)

CH_4-air, GRI3.0



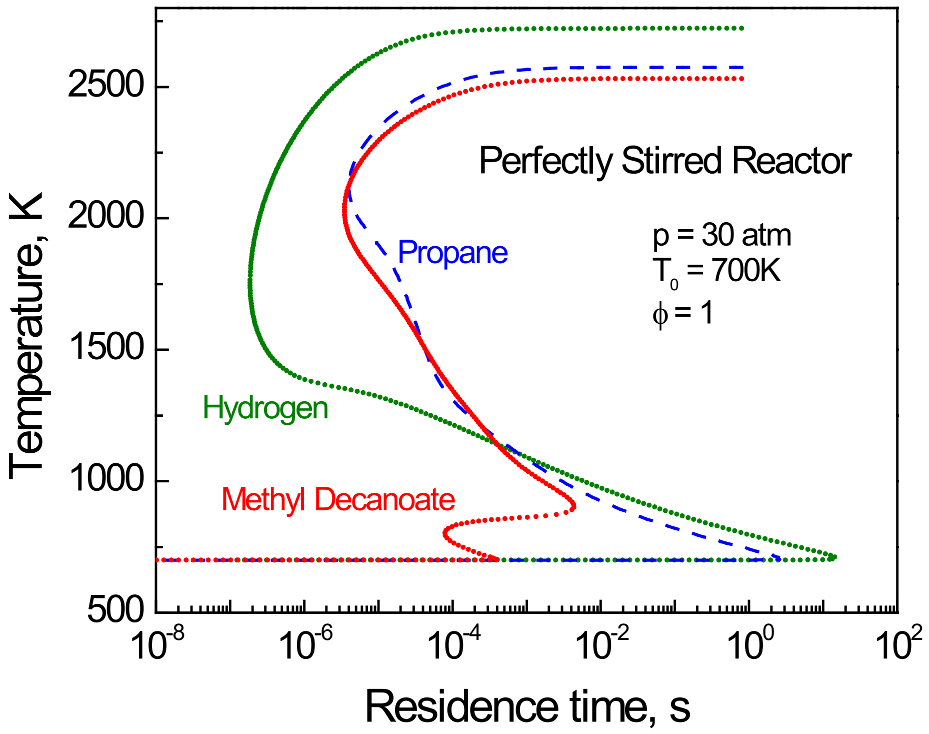
"S"-Curves for Practical Fuels in PSR: Bifurcation Points (2/2)

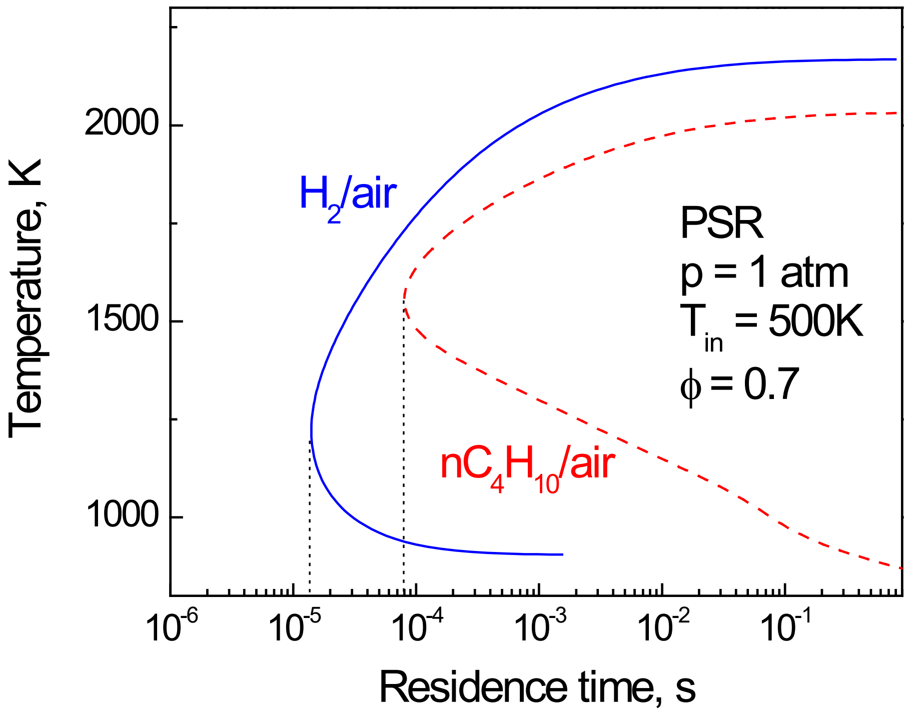
DME-air, with NTC



- Fuels with NTC feature multiple criticalities
- Are the turning points physical ignition/extinction states?

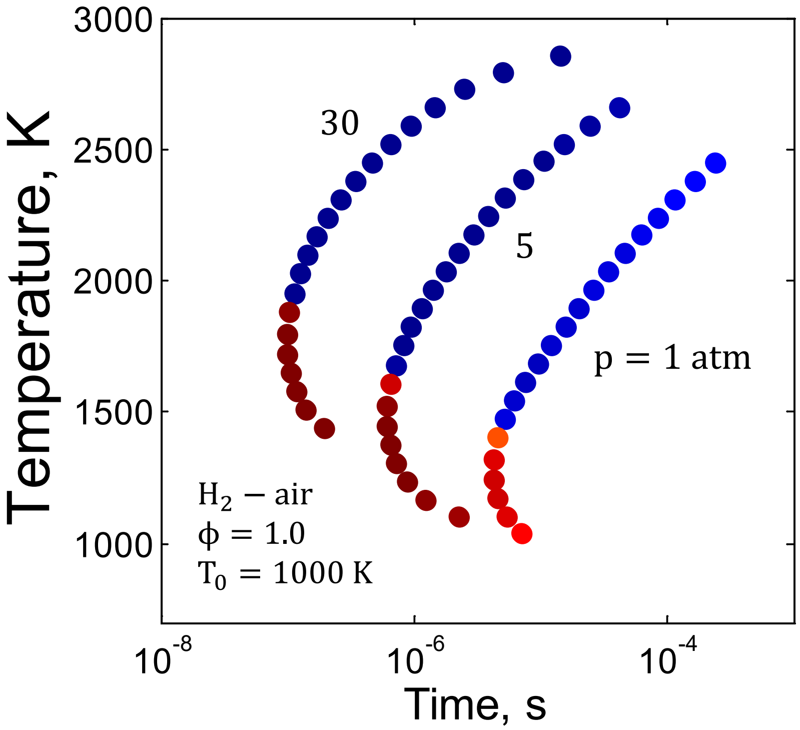
S-Curves for Different Fuels



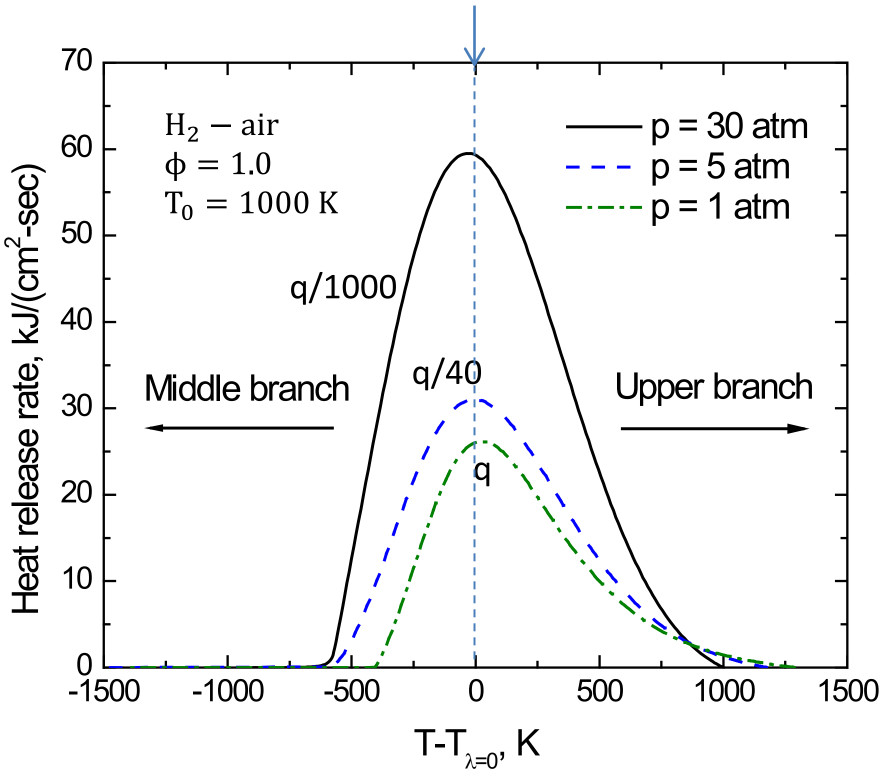


- H2 is less prone to extinction compared with hydrocarbons
- Large hydrocarbons tend to ignition faster due to the NTC behavior

What Happens at Extinction



Extinction state



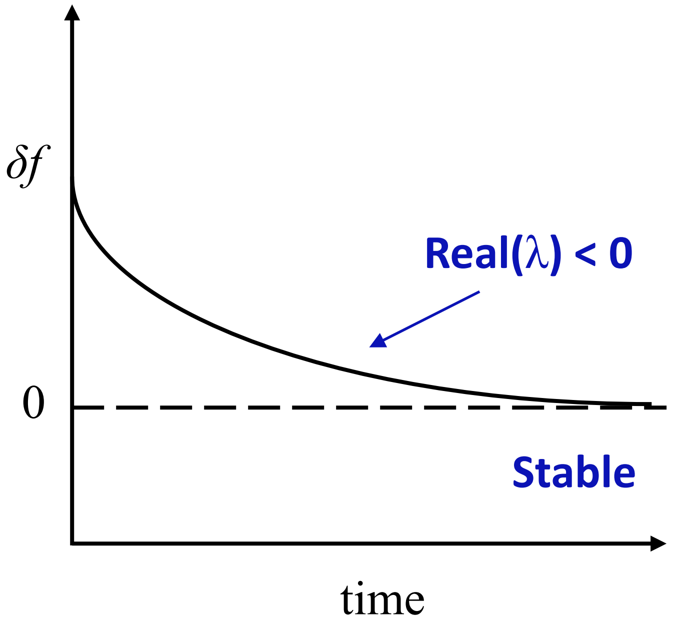
- Burning rate peaks near extinction

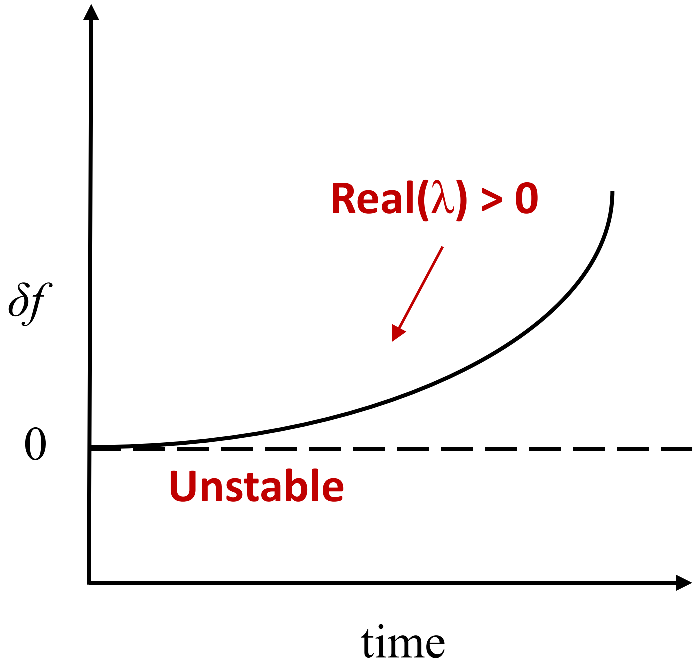
Effect of Eigenvalue λ on Stability: Real λ

$\delta\mathbf{y}$ is a small perturbation on the steady state solution, $\mathbf{y}_s$:

$$\mathbf{y} = \mathbf{y}_s + \delta\mathbf{y} \qquad \frac{d(\delta\mathbf{y})}{dt} = \frac{d(\mathbf{y}_s + \delta\mathbf{y})}{dt} = \mathbf{g}(\mathbf{y}_s + \delta\mathbf{y}) \approx \mathbf{g}(\mathbf{y}_s) + \frac{d\mathbf{g}}{d\mathbf{y}} \cdot \delta\mathbf{y} = \mathbf{J} \cdot \delta\mathbf{y}$$

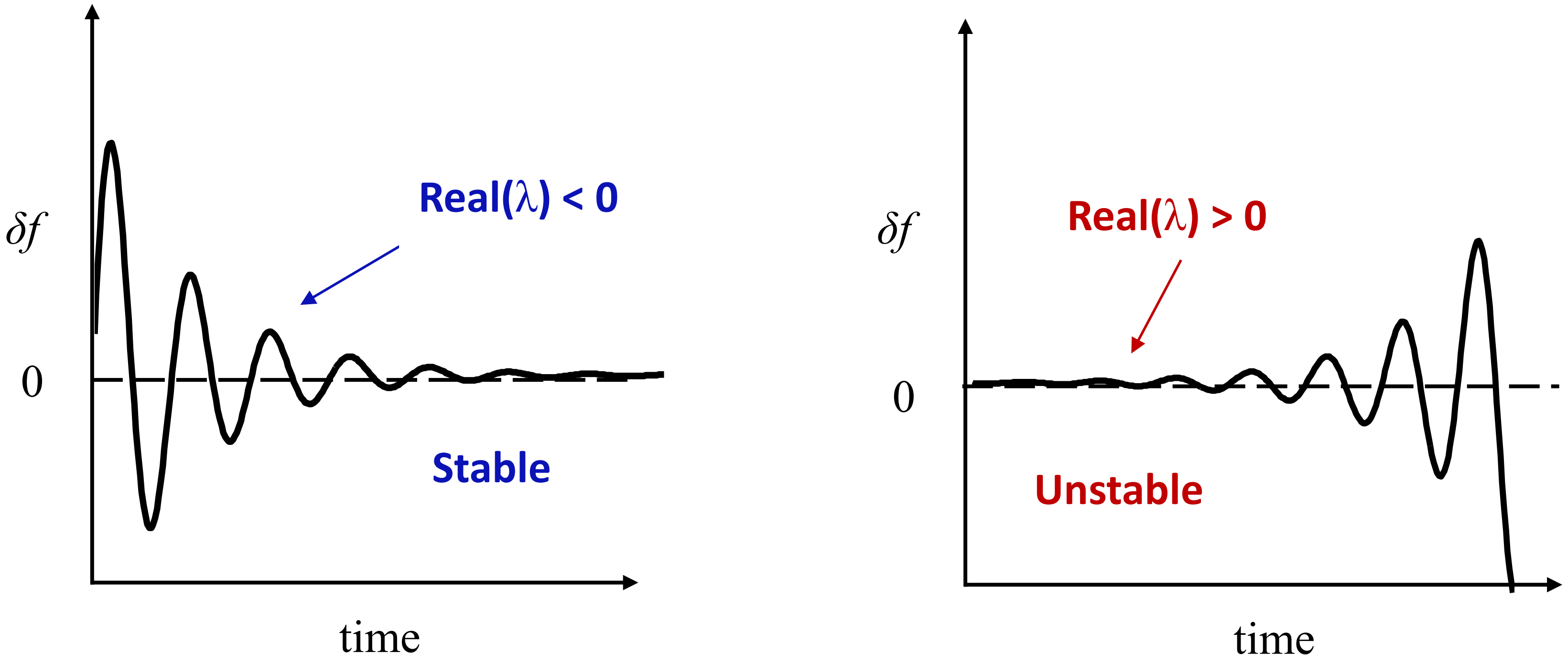
$\delta f = \delta f_{\mathbf{0}} \cdot e^{\lambda t}$ where $\delta f = \mathbf{b} \cdot \delta\mathbf{y}$, **b** is a left eigenvector if **J**





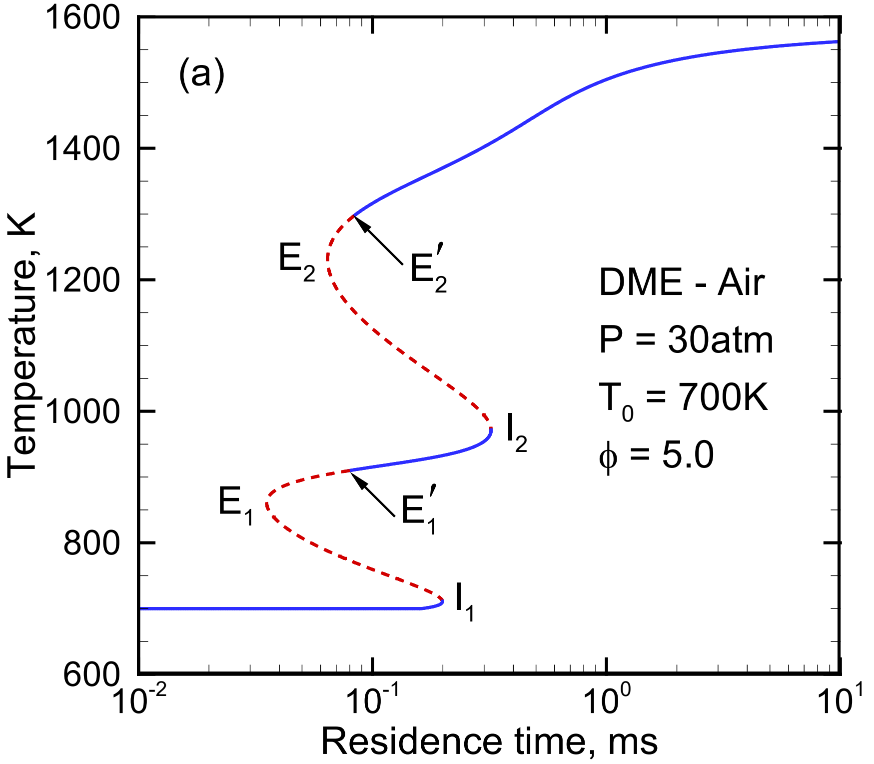
Effect of Eigenvalue λ on Stability: Complex λ

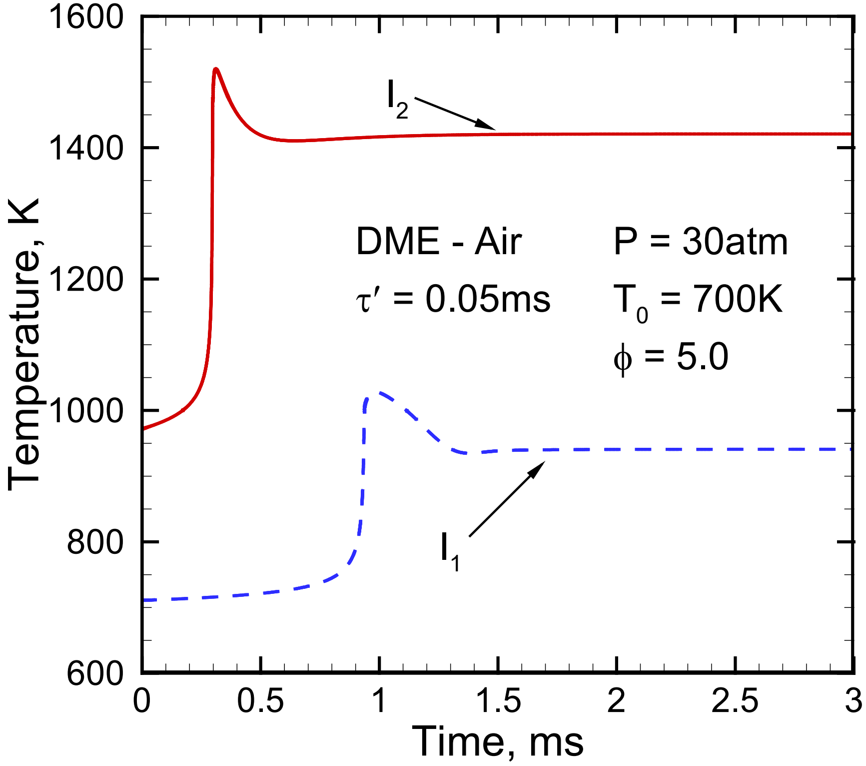
λ : Eigenvalue of Jacobian matrix J_g, Complex number



Real(λ) : Stability
Imag(λ) : Oscillation frequency

Ignition Point I_1 & I_2

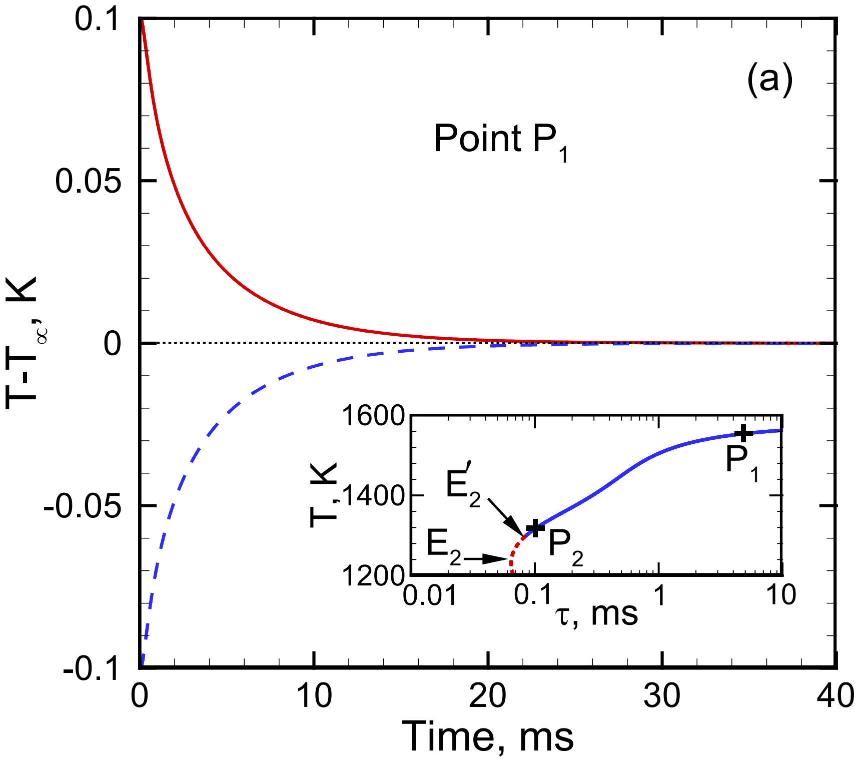




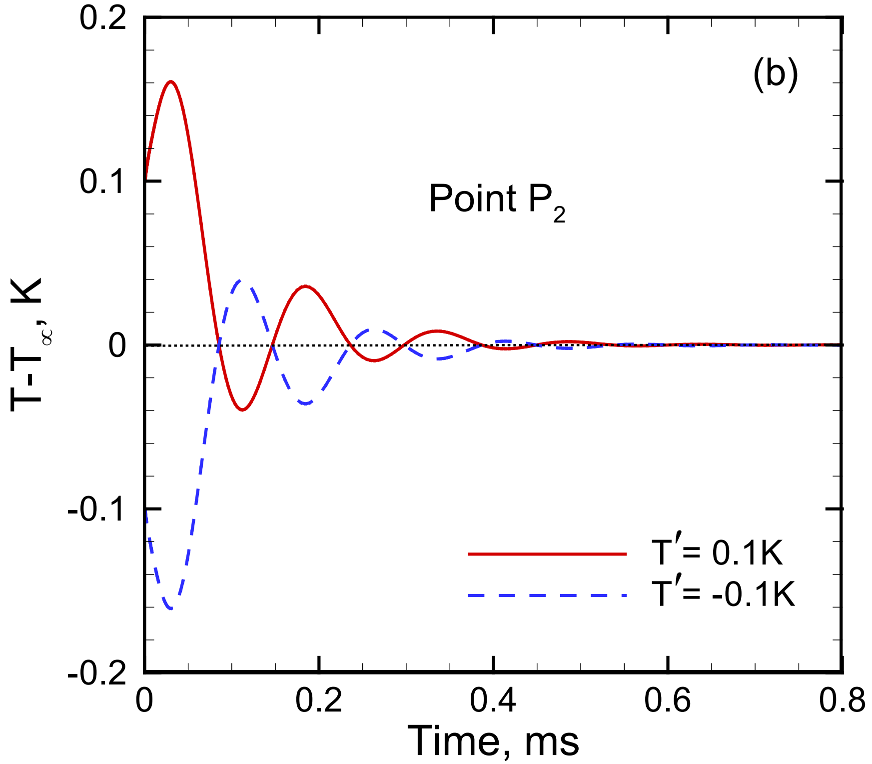
- I_1: Cool flame ignition
- I_2: Strong burning ignition

Point P_1 & P_2 on upper branch: $Re(\lambda_1)<0$, Stable

τ = 4.9ms, λ_1 = -2.1E2 s^{-1}



τ = 0.1ms, λ_1 = -9.5E3+4.2E4*i* s^{-1}



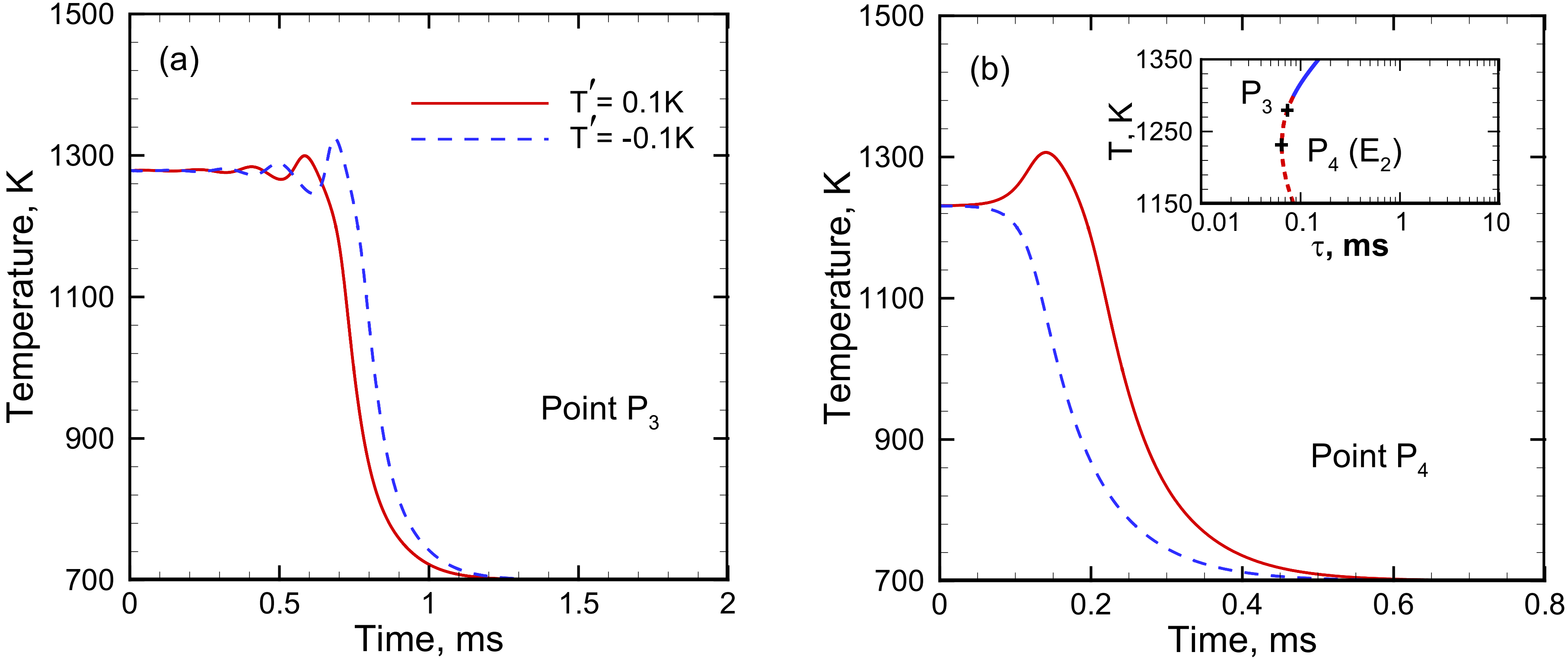
λ_1: the largest eigenvalue

λ_2: the 2^{nd} largest eigenvalue

- Perturbation in T decays to 0
- Oscillation with complex λ_1

Point P_3 & P_4 on upper branch: $Re(\lambda_1)>0$, Unstable

τ = 0.07ms, λ_1=7.8E3 + 3.5E4*i* s^{-1} **τ = 0.06ms, λ_1=5.0E4 s^{-1}, λ_2=0**

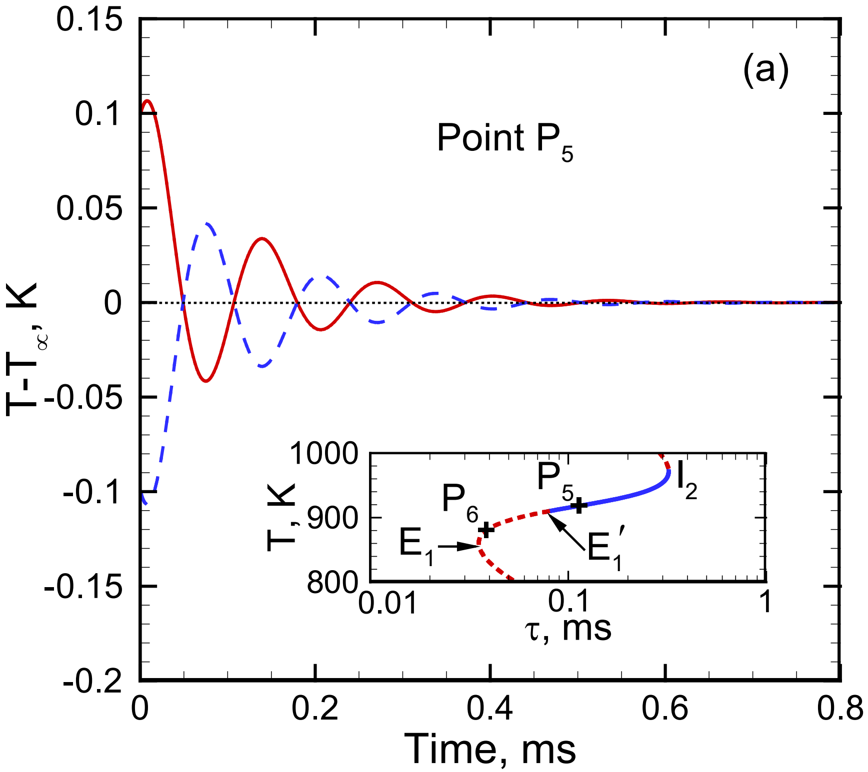


λ_1: the largest eigenvalue
λ_2: the 2nd largest eigenvalue

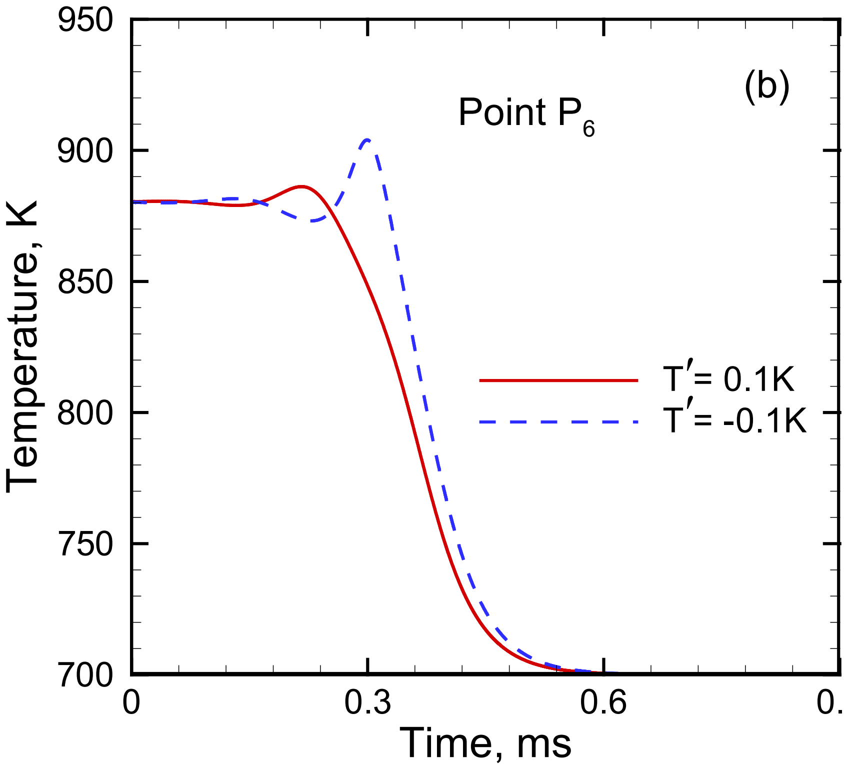
- T decays to inlet temperature
- Oscillation with complex λ_1

Point P_5 & P_6 on cool flame branch

$\tau = 0.1\text{ms}, \lambda_1 = -8.5\text{E}3 + 3.5\text{E}4i\ s^{-1}$



$\tau = 0.04\text{ms}, \lambda_1 = 1.8\text{E}3 + 3.5\text{E}4i\ s^{-1}$

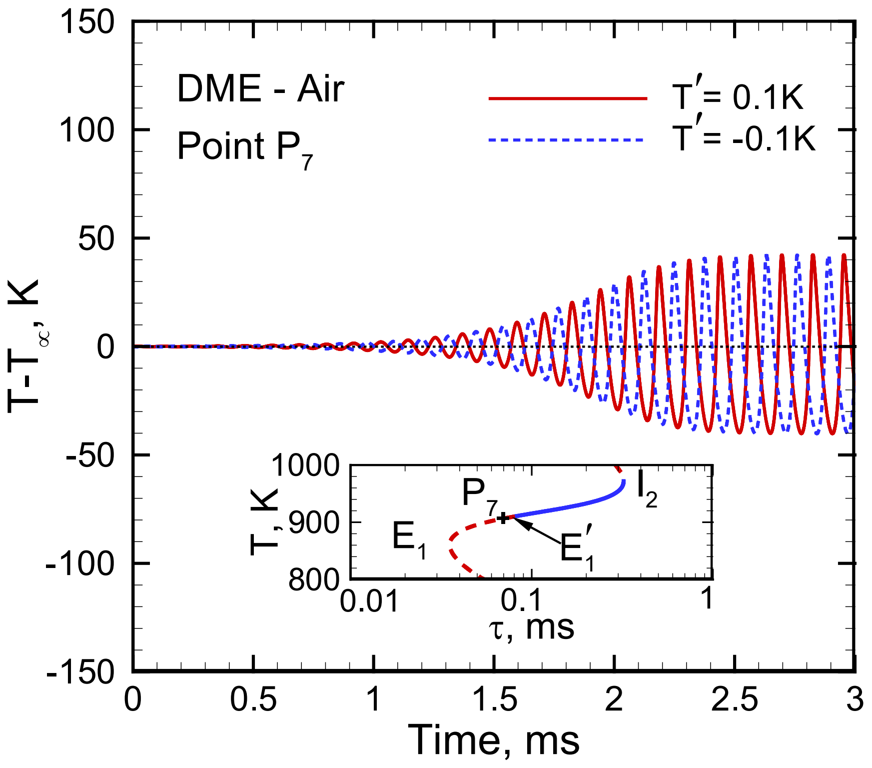


λ_1,: the largest eigenvalue
λ_2: the 2nd largest eigenvalue

- (a) Perturbation in T decays to 0
- (b) T decays to inlet temperature
- Oscillation with complex λ_1

Point P_7 on cool flame branch

τ = 0.07ms, λ_1=3.0E3 + 5.6E4*i* s^{-1}

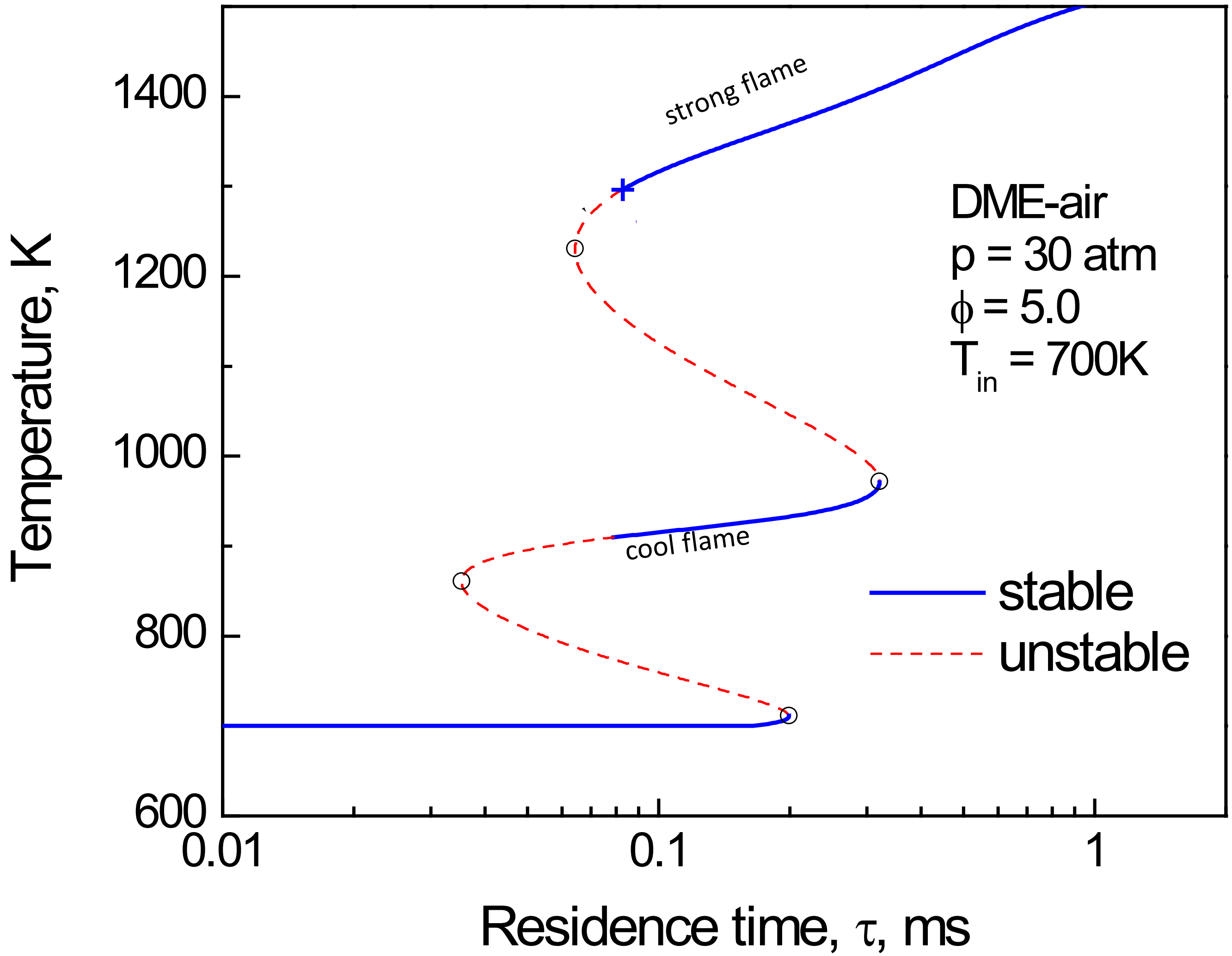


λ_1,: the largest eigenvalue

λ_2: the 2nd largest eigenvalue

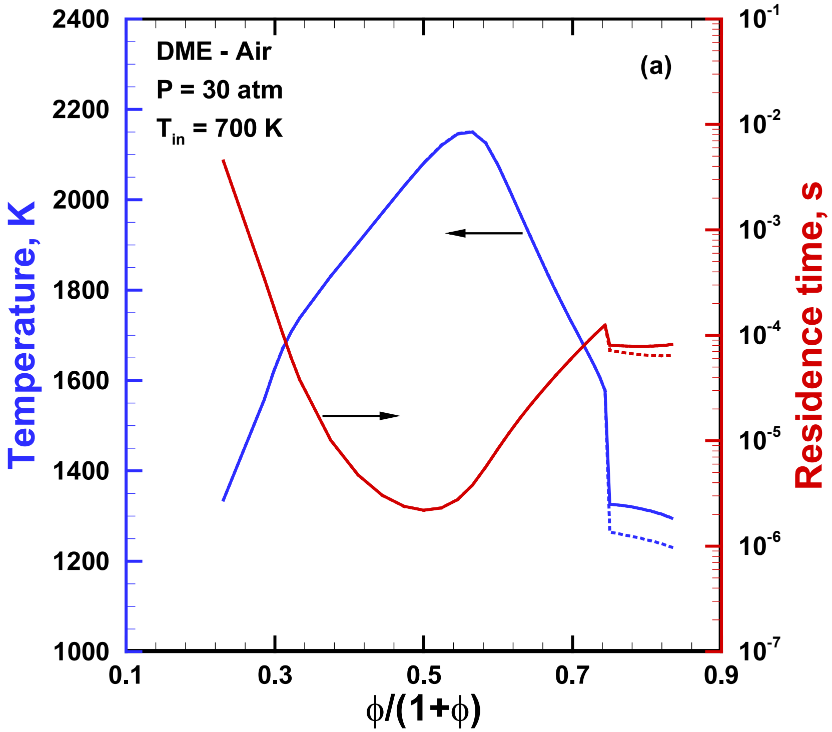
- Perturbation in T keeps oscillating

Flame Stability for PSR: DME (1/2)

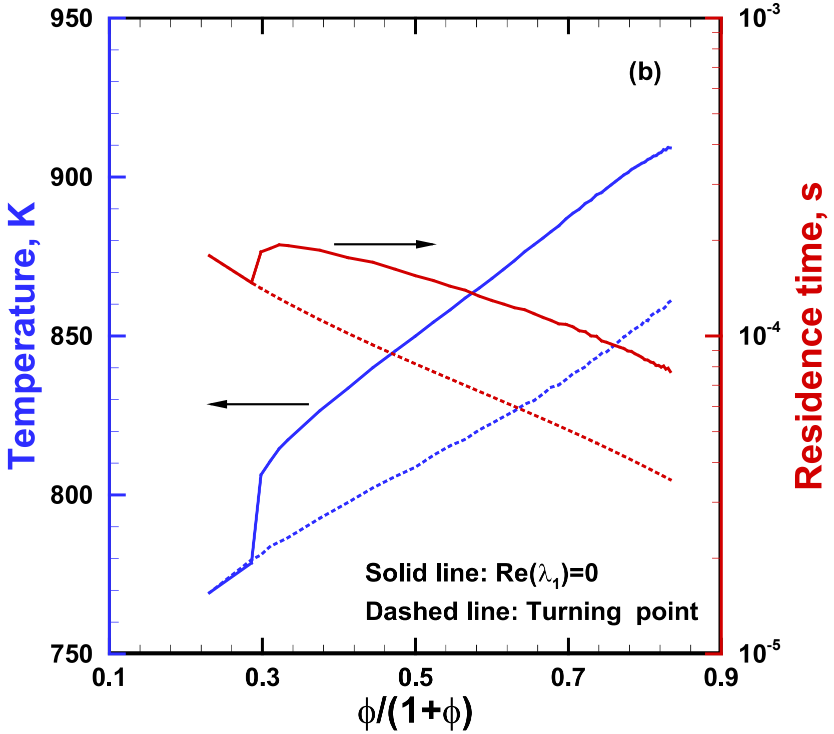


Flame Stability for PSR: DME (2/2)

strong flame extinction



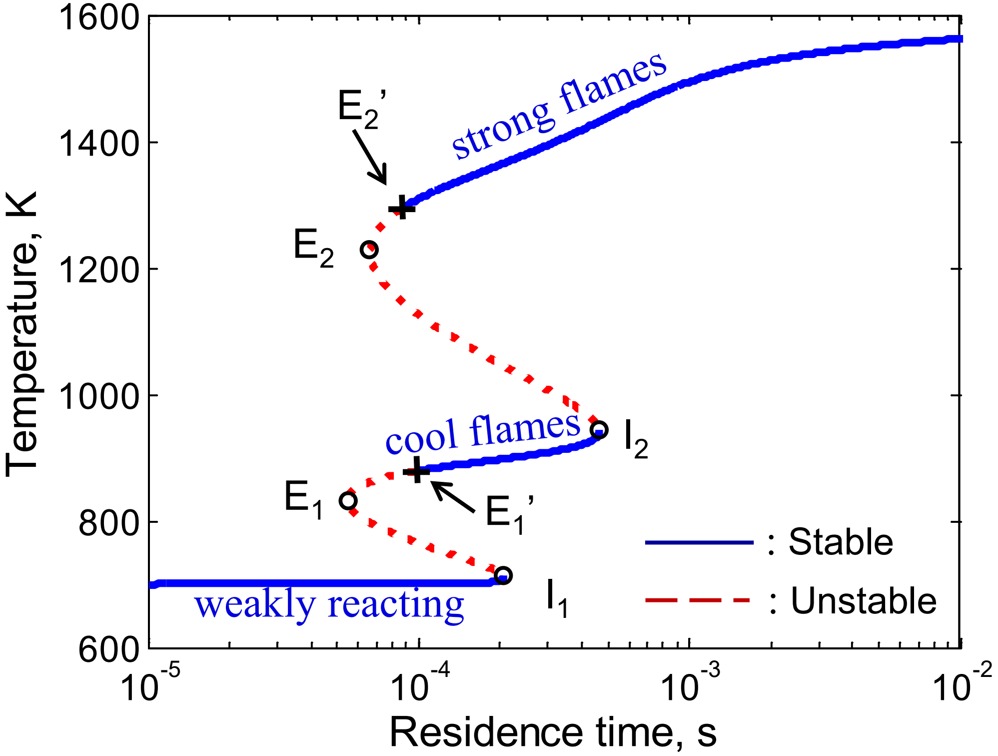
cool flame extinction



- Differences observed for extinction for
  - Rich strong flames; Lean and rich cool flames
- No difference observed for ignition

Summary of Limit Phenomena of DME/Air in PSR

DME-Air
(p = 30atm, T_{in} = 700K, ϕ = 5.0)



- Multiple branches and turnings
- Negative temperature coefficient (NTC) chemistry leads to cool flame branches
- Stable and unstable branches separated by bifurcation points: $Re(\lambda) = 0$
- The turning points: $\lambda = 0$

- I_2/E_2': ignition/extinction of strong flames
- I_1/E_1': ignition/extinction of cool flames

Bifurcation Index (BI)

- The governing equation and Jacobian matrix:

$$\frac{d\mathbf{y}}{dt} = \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}) = \sum_{r=1}^{I} \underset{\substack{\downarrow \\ \text{rth reaction}}}{\boldsymbol{\omega}_r} + \underset{\substack{\searrow \\ \text{mixing}}}{\mathbf{s}(\mathbf{y})} \qquad \mathbf{J_g} = \mathbf{J_\omega} + \mathbf{J_s} = \sum_{r=1}^{I} \underset{\substack{\downarrow \\ \partial\boldsymbol{\omega}_r/\partial\boldsymbol{y}}}{\mathbf{J}_r} + \underset{\substack{\searrow \\ \partial\boldsymbol{s}/\partial\boldsymbol{y}}}{\mathbf{J_s}}$$

$$\lambda = \mathbf{b}\cdot\mathbf{J_g}\cdot\mathbf{a} = \sum_{r=1}^{I} \mathbf{b}\cdot\mathbf{J}_r\cdot\mathbf{a} + \mathbf{b}\cdot\mathbf{J_s}\cdot\mathbf{a} = \sum_{r=1}^{I} \lambda_r + \lambda_{I+1} = 0$$

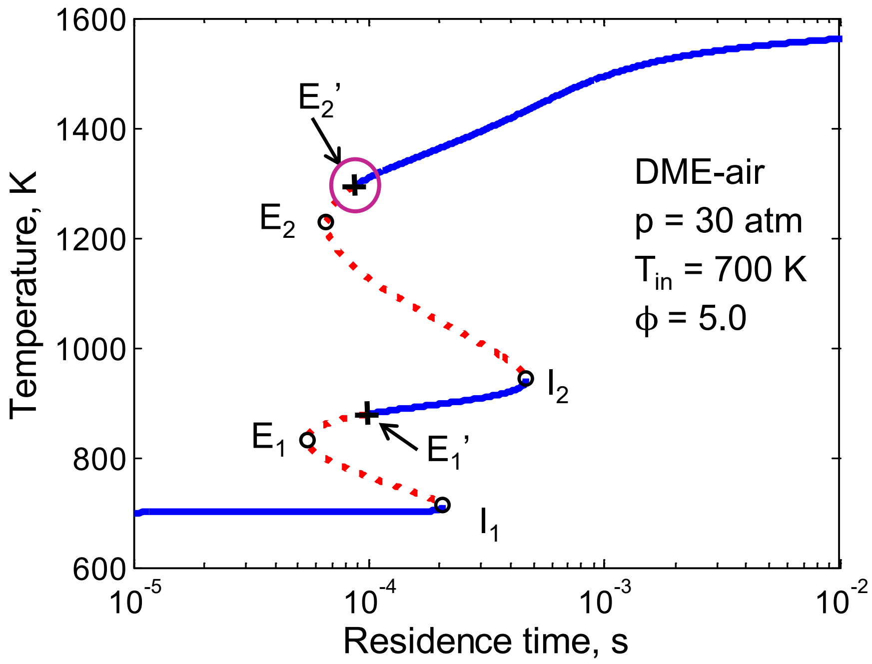
(**b, a**: eigenvectors associated with λ)

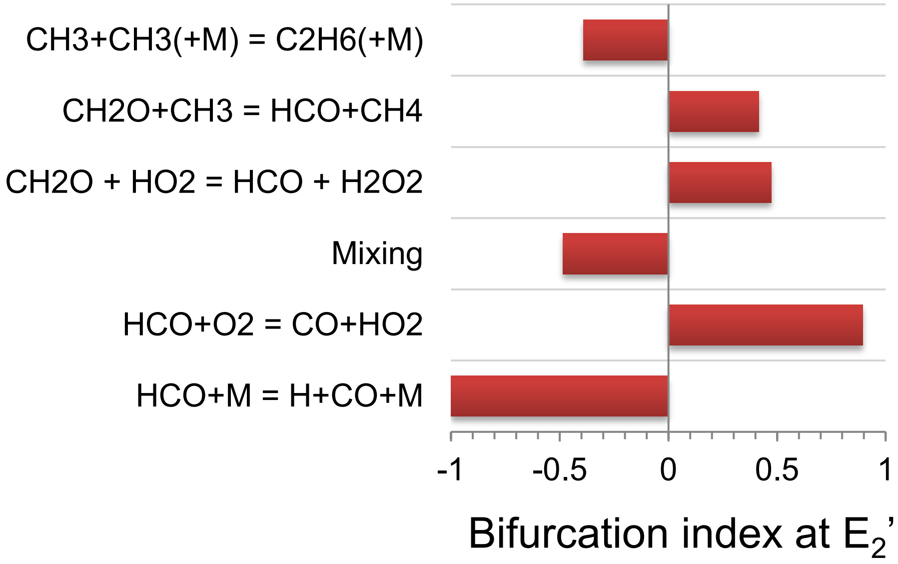
- **Bifurcation Index (BI):**

$$\boxed{\mathrm{BI}^r = \frac{\lambda_r}{\max\left|\lambda_r\right|_{r=1,I+1}}}$$

Contribution of the r$^{\text{th}}$ reaction (or mixing) to the bifurcation (ignition/extinction)

Bifurcation Index for Strong Flame Extinction of DME/Air in PSR





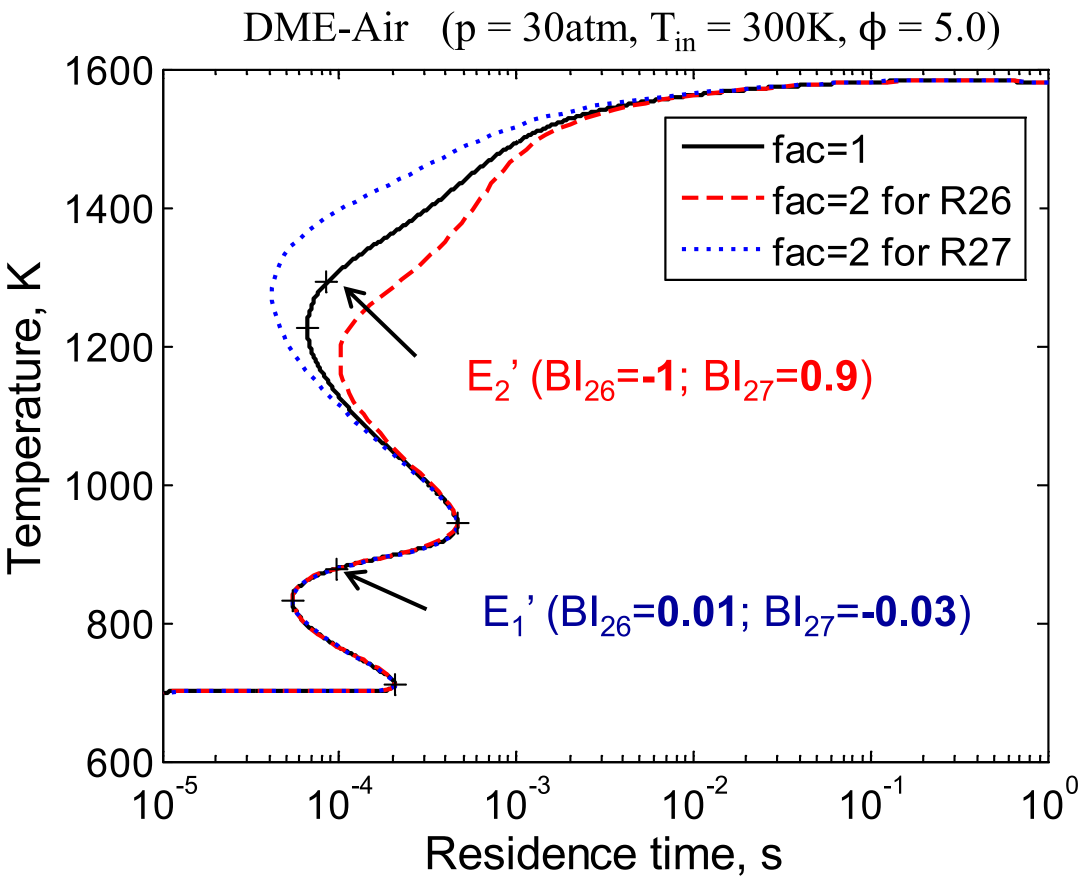
- Strong flame extinction point (E_2') involves small molecules, e.g. those related to CO formation

Effects of Reactions with Large BIs on Strong Flame Extinction

Perturbed A-factors in k = A T^n exp(-E/RT) for

R26: HCO+M = H+CO+M

R27: $HCO+O_2=CO+HO_2$



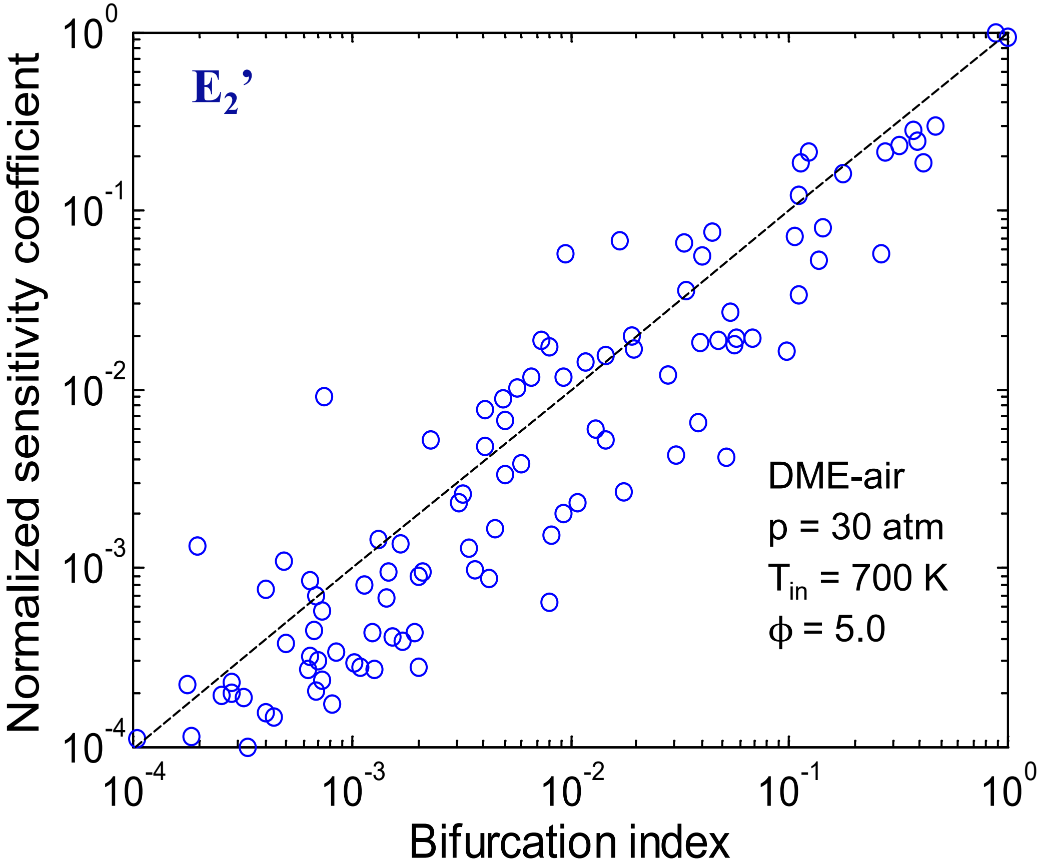
Perturbed A-factors by a factor of 2

Large BI at E_2': significant effects

Small BI at E_1': minor effects

BI vs. Global Sensitivity Analysis for Strong Flame Extinction

Sensitivity of residence time τ with respect to each reaction rate at E_2'

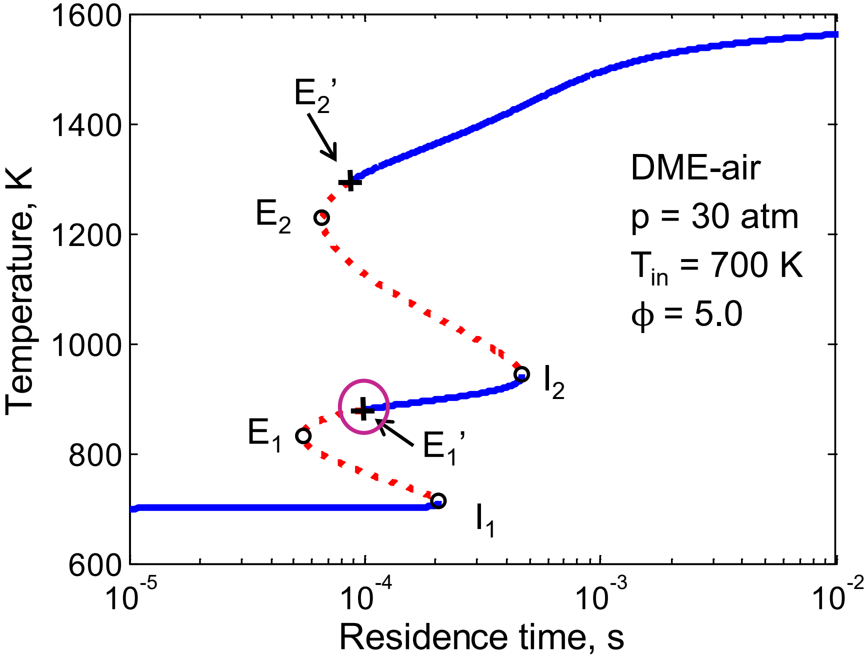


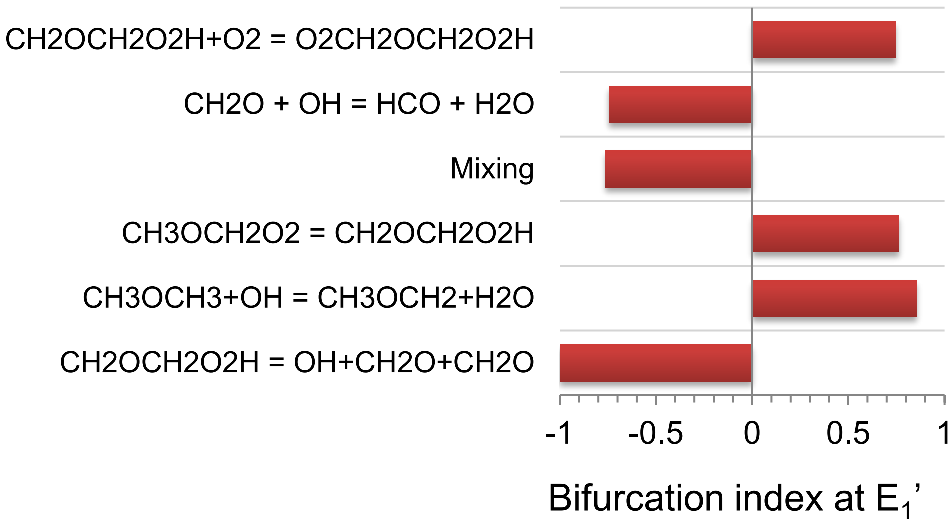
- Sensitivity coefficient:

$$\frac{\left|d \ln \tau / d \ln A\right|}{\max\left|d \ln \tau / d \ln A\right|}$$

- Sensitivity is overall linearly correlated with BI
- Pros of BI:
  - Simple to implement
  - Computationally efficient
  - Directly indicates physical extinction & ignition

Bifurcation Index for Cool Flame Extinction of DME/Air in PSR





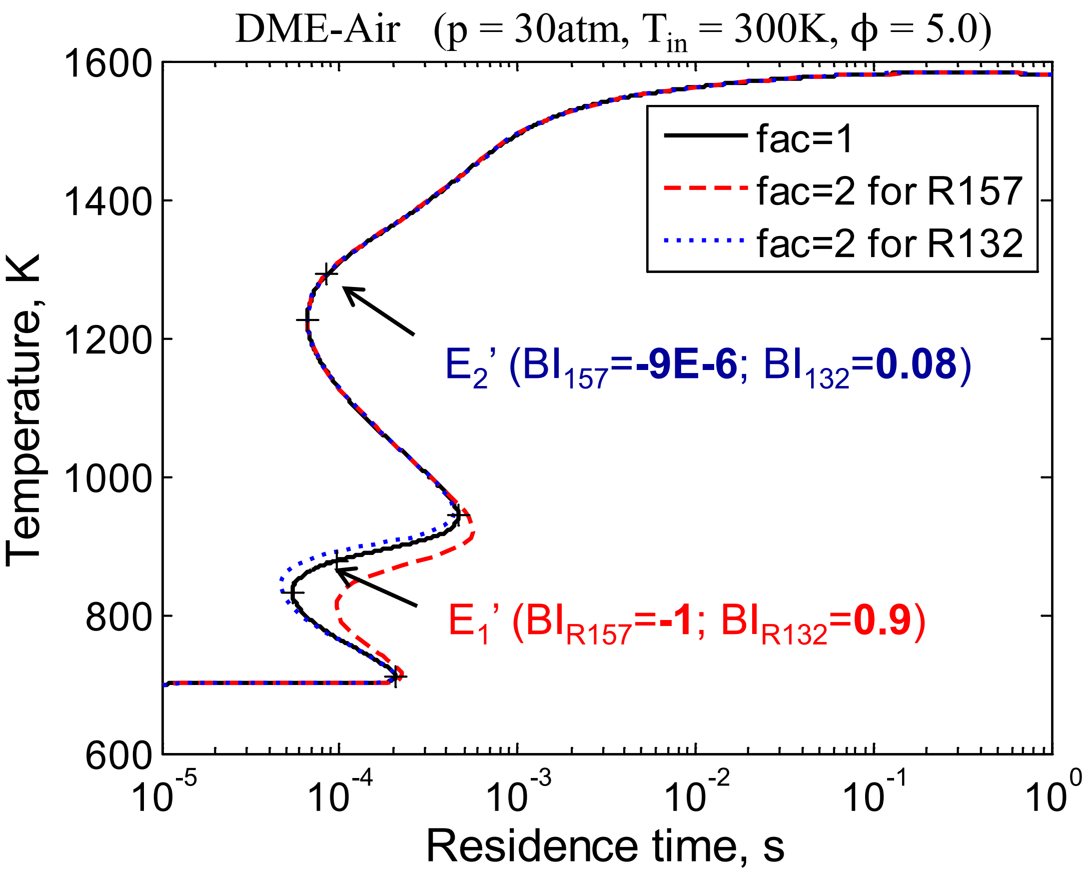
- Cool flame extinction point (E_1') involves larger molecules, e.g. peroxides, related to the NTC chemistry

Effects of Reactions with Large BIs on Cool Flame Extinction

Perturbed A-factors in $k = A\,T^n \exp(-E/RT)$ for

R157: $CH_2OCH_2O_2H = OH + CH_2O + CH_2O$

R132: $CH_3OCH_3 + OH = CH_3OCH_2 + H_2O$



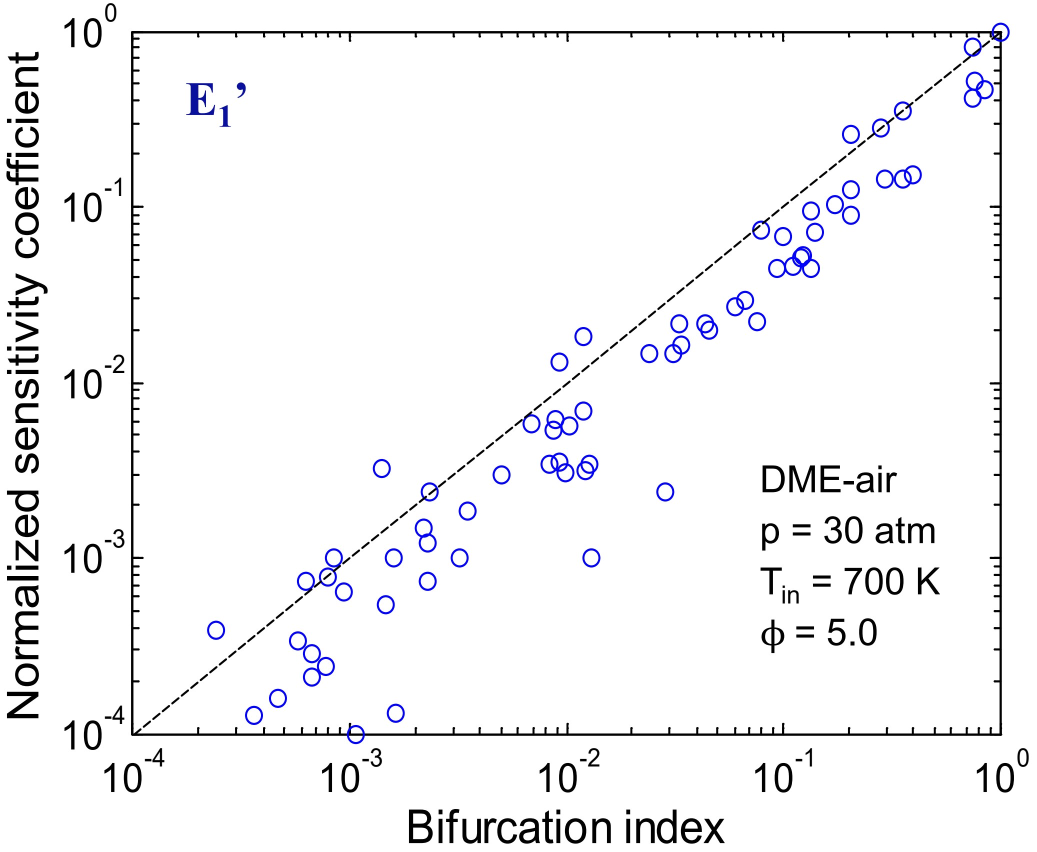
Perturbed A-factors by a factor of 2

Small BI at E_2': minor effects

Large BI at E_1': significant effects

BI vs. Global Sensitivity Analysis at Cool Flame Extinction

Sensitivity of residence time τ with respect to each reaction rate at E_1'



- Sensitivity coefficient :

$$\frac{\left| d \ln \tau / d \ln A \right|}{\max \left| d \ln \tau / d \ln A \right|}$$

- Sensitivity is overall linearly correlated with BI
- BIs can quantify the importance of each reaction

A Semi-Analytic Criterion for Ignition/Extinction Detection

- The zero-crossing eigenvalue can be further decomposed to

$$\lambda_e - \lambda_s = \boldsymbol{b}_e \cdot \sum_{r=1}^{I} \left(\frac{\partial \omega_r}{\partial \boldsymbol{y}} \right) \cdot \boldsymbol{a}_e = \sum_{r=1}^{I} \sum_{i=1}^{K} \alpha_{r,i} \cdot \frac{\partial \omega_r}{\partial y_i}$$

  - *I*: number of processes (reaction & mixing)
  - *K*: number of variables (species concentration and temperature)
  - ***y***: vector of variables
  - $\boldsymbol{S}_r$: stoichiometric coefficient vector of the r^{th} process
  - ω_r: rate of the *r*-th process (reaction & mixing)
- Importance of the i^{th} variable in the r^{th} process

$$\beta_{r,i} = \frac{\left| \alpha_{r,i} \cdot \frac{\partial \omega_r}{\partial y_i} \right|}{max\left(\left| \alpha_{r,i} \cdot \frac{\partial \omega_r}{\partial y_i} \right| \right)}$$

Reduced Criteria for PSR Extinction: Methane and Ethylene

- Methane/Air

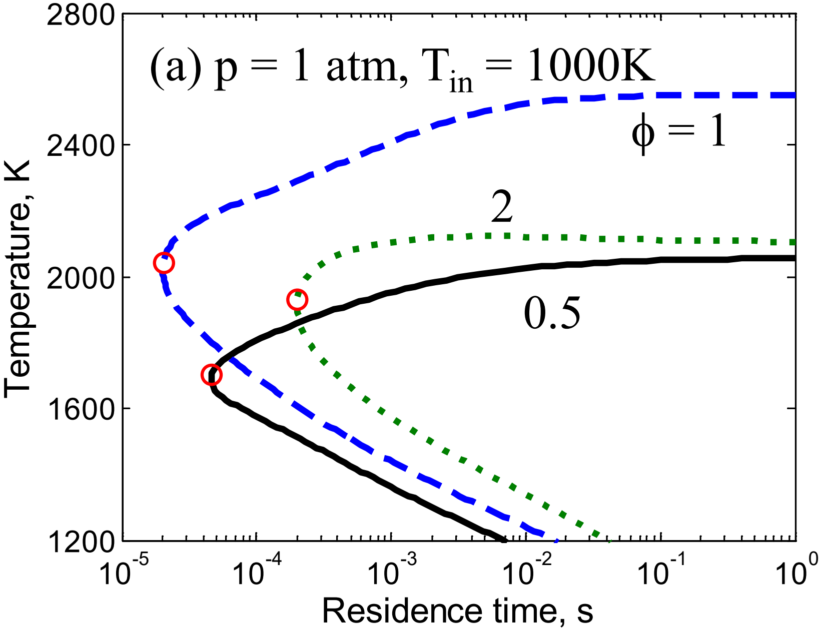
$$\lambda_e = k_r\left(\alpha_{r,H}C_{O2} + \alpha_{r,O2}C_H\right) - 1/\tau$$

- Ethylene/Air

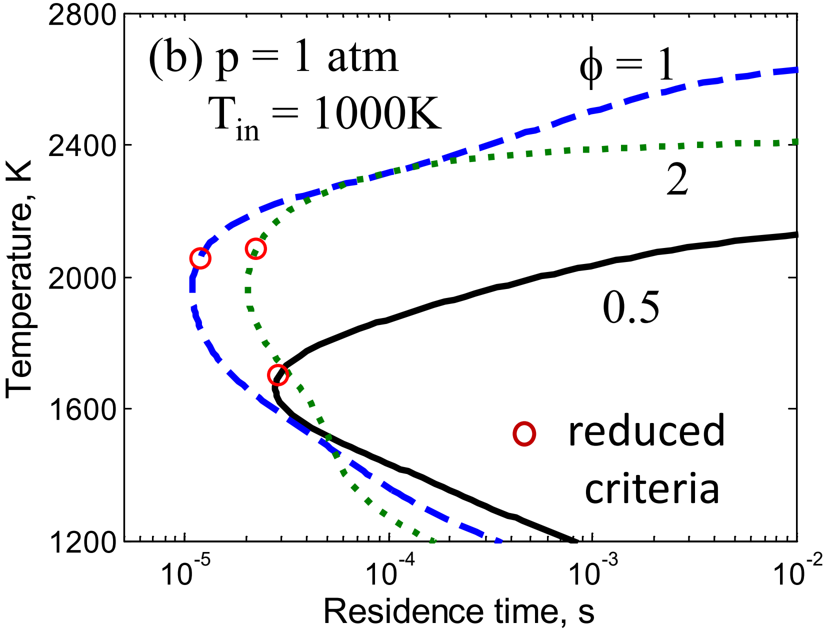
$$\lambda_e = k_r\left(\alpha_{r,H}C_{O2} + \alpha_{r,O2}C_H + \alpha_{r,T}\left(\frac{n}{T} + \frac{E_a}{RT^2}\right)C_H C_{O2}\right) - 1/\tau$$

k_r: reaction rate coefficient for $H + O_2 \rightarrow O + OH$

Methane/air

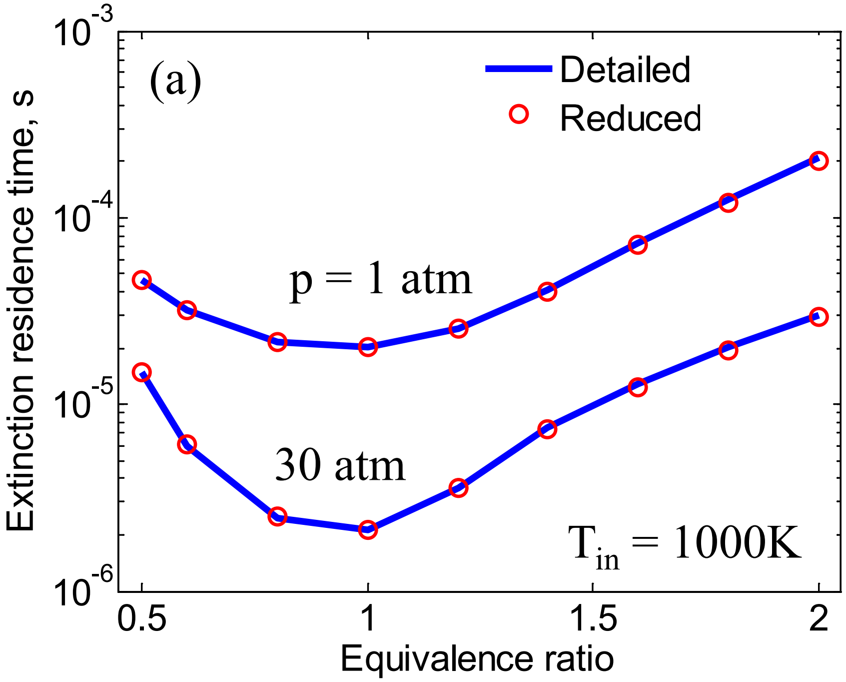


Ethylene/air

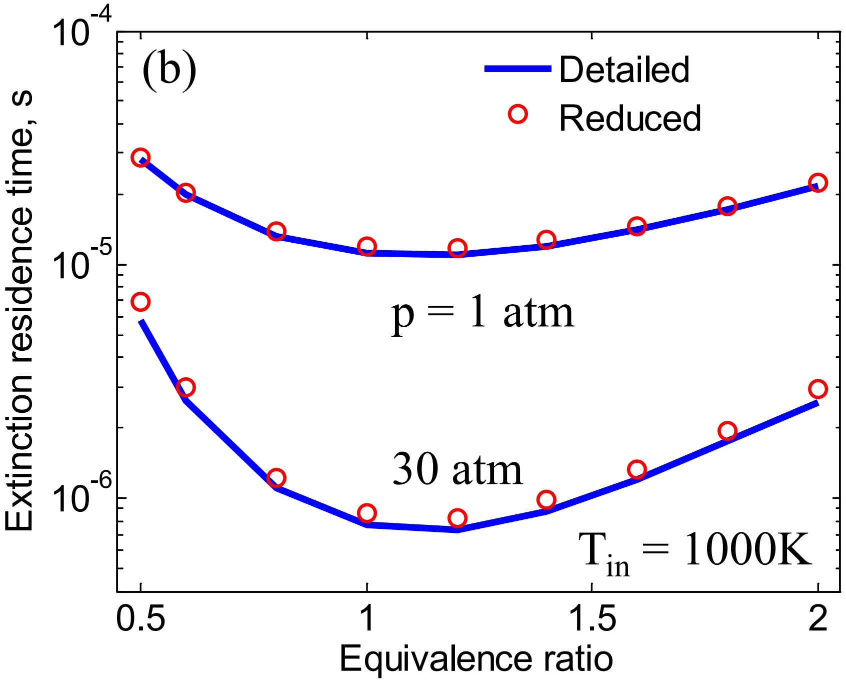


Global Performance for Different Pressures and Equivalence ratios

Methane/air



Ethylene/air



- The semi-analytic criteria accurately capture the extinction behaviors
- Criteria for ignition can be obtained similarly
- Applicable for on-the-fly ignition/extinction detection in large-scale simulations

Chemical Explosive Mode Analysis (CEMA) as a Computational Flame Diagnostic

Chemical Explosive Mode Analysis (CEMA) (Lu et al., JFM 2010)

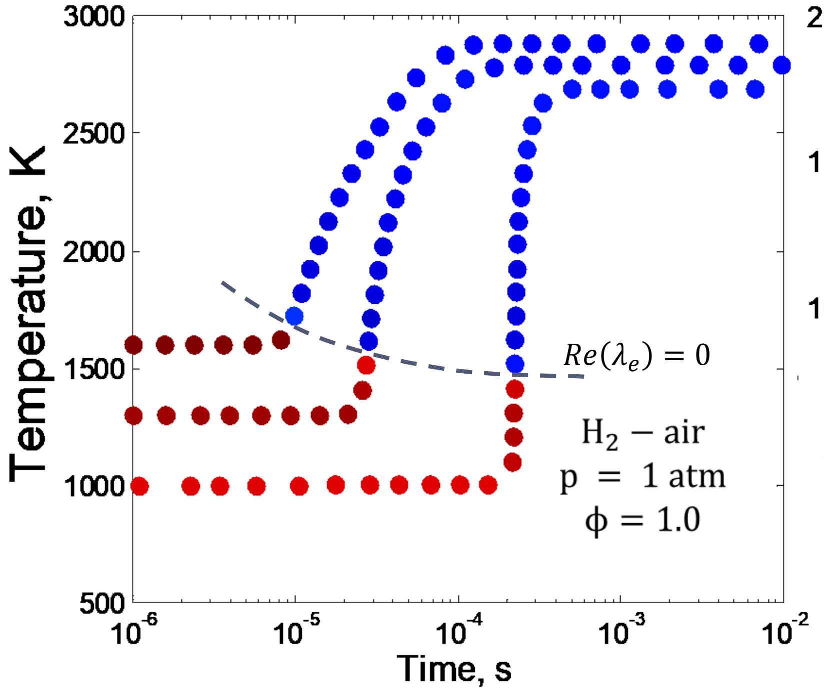
- Governing equations for a chemically reacting flow

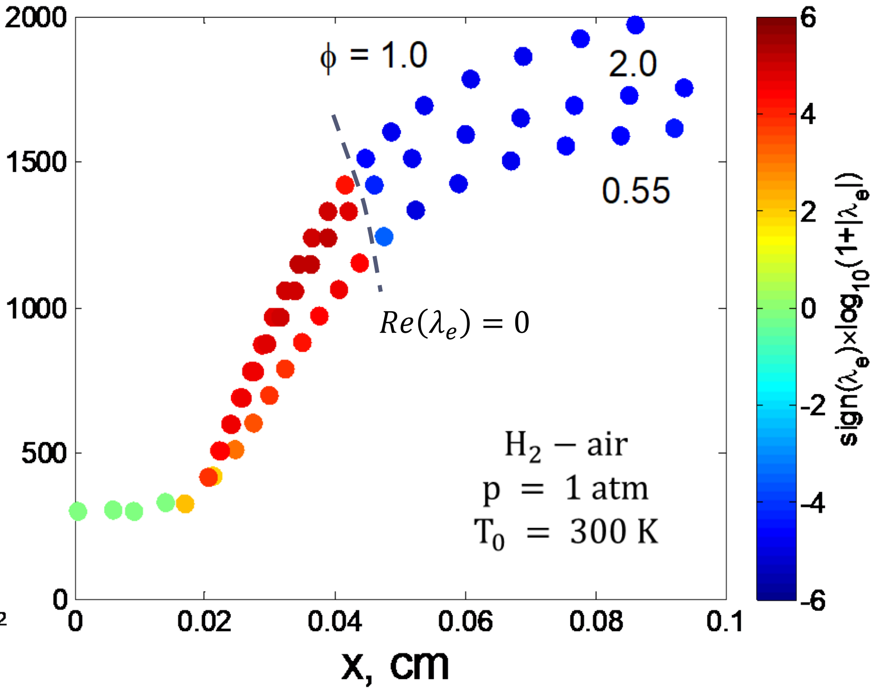
$$\frac{D\mathbf{y}}{Dt} = \mathbf{g}(\mathbf{y}) = \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y})$$

y: the vector of variables (e.g. species concentrations and temperature)
ω: chemical source term
s: other source terms (e.g. diffusion)

- The chemical Jacobian: $\mathbf{J}_{\omega} = \frac{\partial \boldsymbol{\omega}}{\partial \mathbf{y}}$
- Chemical explosive mode (CEM) is associated with positive eigenvalue of $\mathbf{J}_{\omega}$, i.e. $\mathrm{Re}(\lambda_e)>0$
- CEM indicates the propensity of a mixture to ignite if isolated, a chemical property of the mixture

Role of CEM in Auto-Ignition & Premixed Flames: Hydrogen-Air

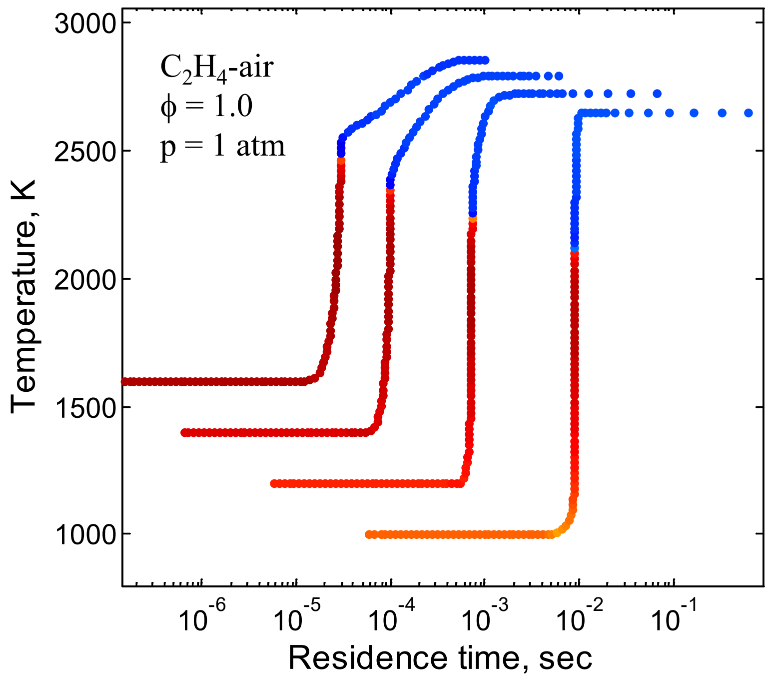

Auto-ignition


1-D premixed flames

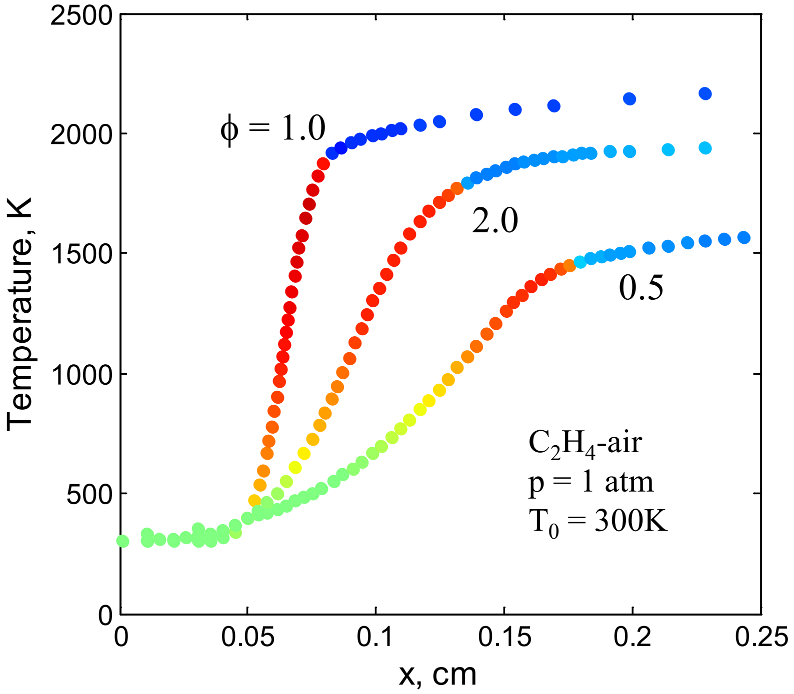
- $Re(\lambda_e) > 0$ for pre-ignition mixtures, λ_e: eigenvalue of the chemical Jacobian
- $Re(\lambda_e) < 0$ for post-ignition mixtures
- $Re(\lambda_e) = 0$ indicates the ignition point or premixed reaction front

Role of CEM in Auto-Ignition & Premixed Flames: Ethylene-Air

Auto-ignition



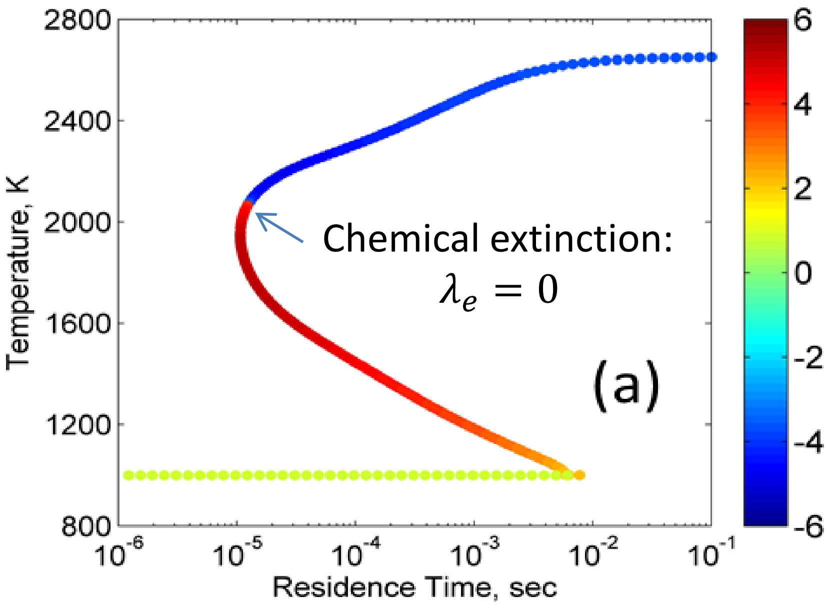
1-D premixed flames



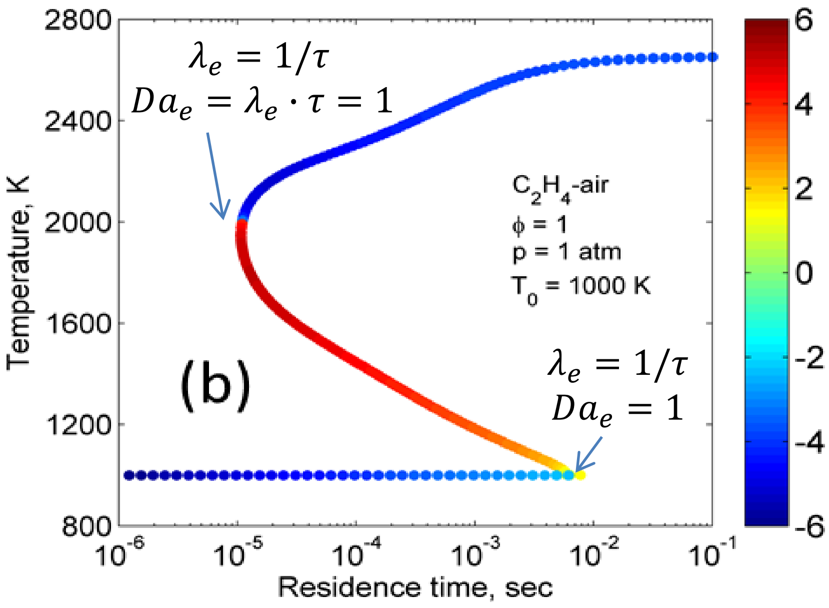
- $Re(\lambda_e) > 0$ for pre-ignition mixtures, λ_e: eigenvalue of the chemical Jacobian
- $Re(\lambda_e) < 0$ for post-ignition mixtures
- $Re(\lambda_e) = 0$ indicates the ignition point or premixed reaction front

Role of CEM in Extinction of PSR

(Luo & Lu, CNF 2012, Shan & Lu CNF 2012)



$\mathrm{sign}(\lambda_e)\times\log_{10}(1+|\boldsymbol{\lambda_e}|)$

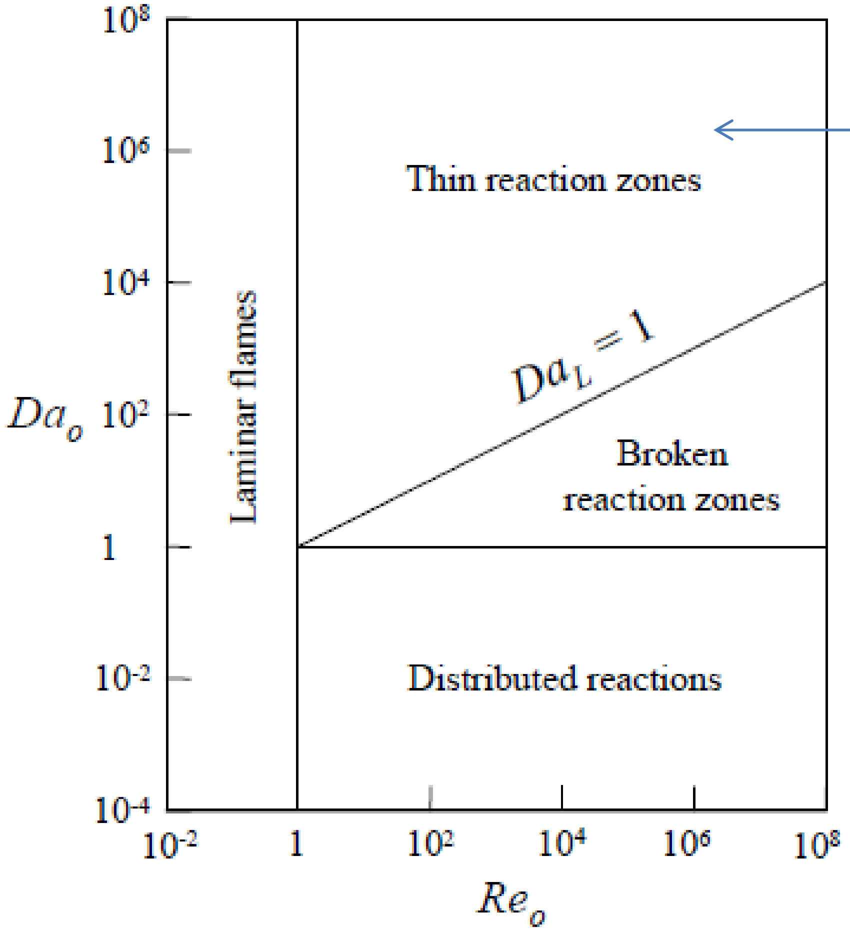


$\mathrm{sign}(\lambda_e-1/\tau)\times\log_{10}(1+|\boldsymbol{\lambda_e-1/\tau}|)$

- PSR extinction ($\lambda_e = 1/\tau$) is induced by competition between CEM and homogeneous mixing
- Chemical extinction ($\lambda_e = 0$) emerges slightly before extinction, due to incomplete reactions and increased reactants, is a precursor of extinction

Turbulent Non-premixed Flames

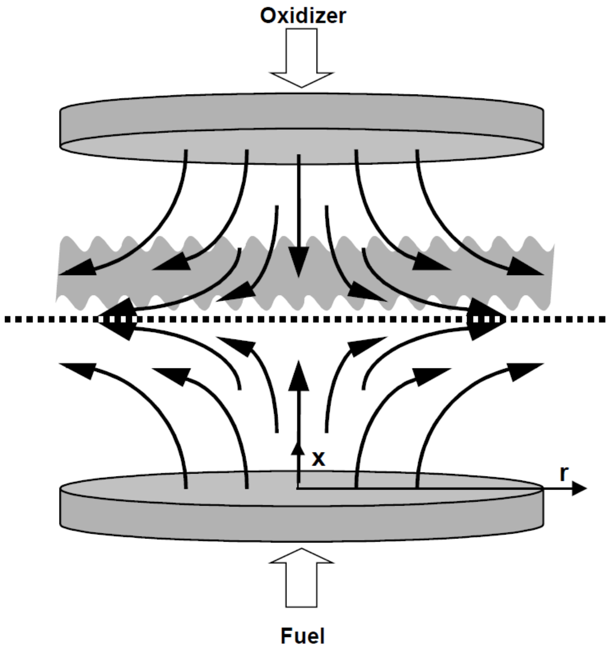
Regime Diagram for Turbulent Non-premixed Flames



Flamelet concept applies

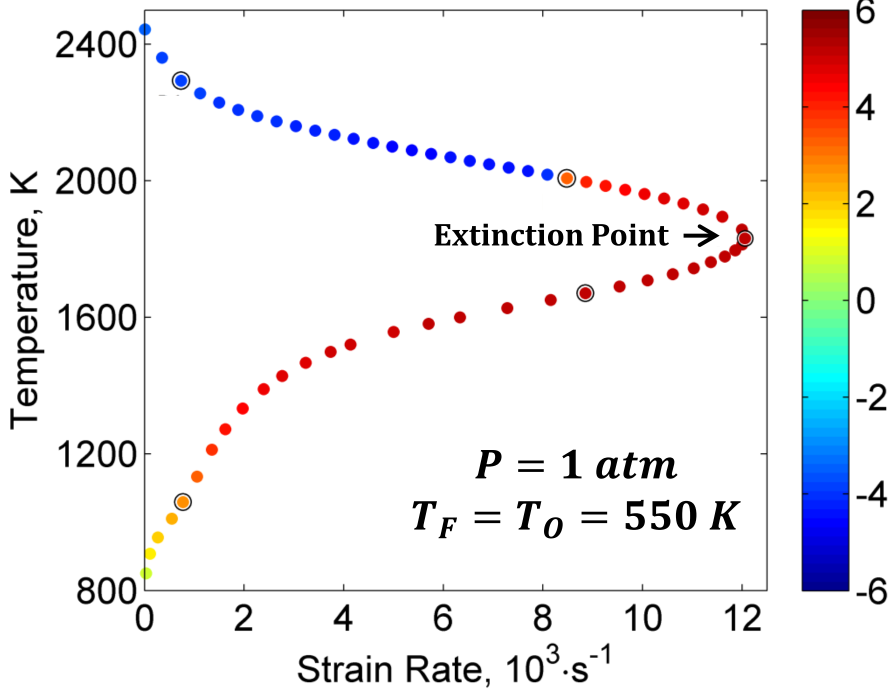
(Combustion Physics, Law 2006)

Role of CEM in Flame Extinction: 1-D Non-premixed Counterflow Flames



(*Kee et al 2000*)

Temperature on the stoichiometric surface

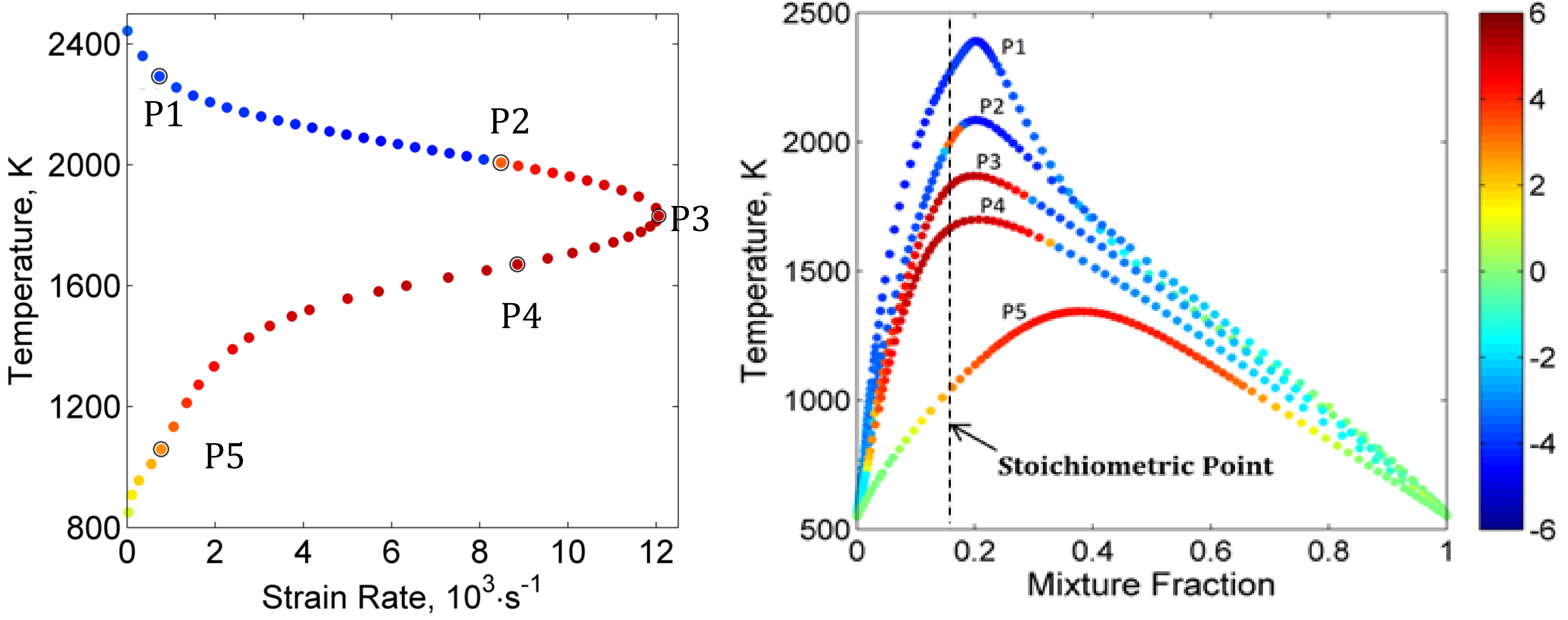


Color: $sign(\lambda_e) \times \log_{10}(|\lambda_e| + 1)$

- Ethylene (47.64%, mole) + N_2 opposed to 30.53% O_2 + N_2
- Solutions characterized by S-curve
- CEM behavior on stoichiometric surface similar to that in PSR

Structures of Different Flames along the S-curve

Temperature & CEM on the stoichiometric surface

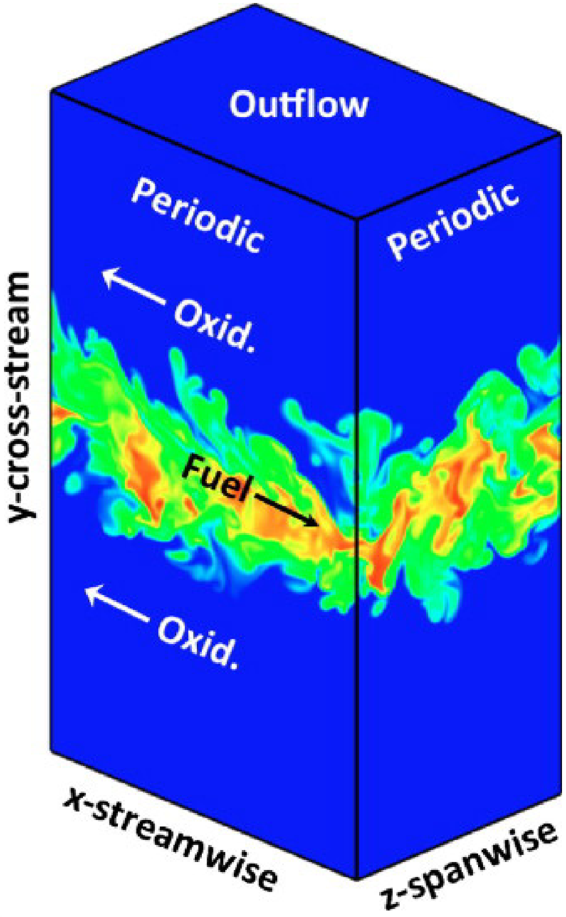


Color: $sign(\lambda_e) \times \log_{10}(|\lambda_e| + 1)$

- Mixtures are non-explosive ($\lambda_e < 0$) in strongly burning flames (e.g. P1)
- Explosive mixture ($\lambda_e > 0$) emerges near the stoichiometric surface near chemical extinction (at P2)
- Extinction front ($\lambda_e = 0$) propagates to both sides marching down the S-curve

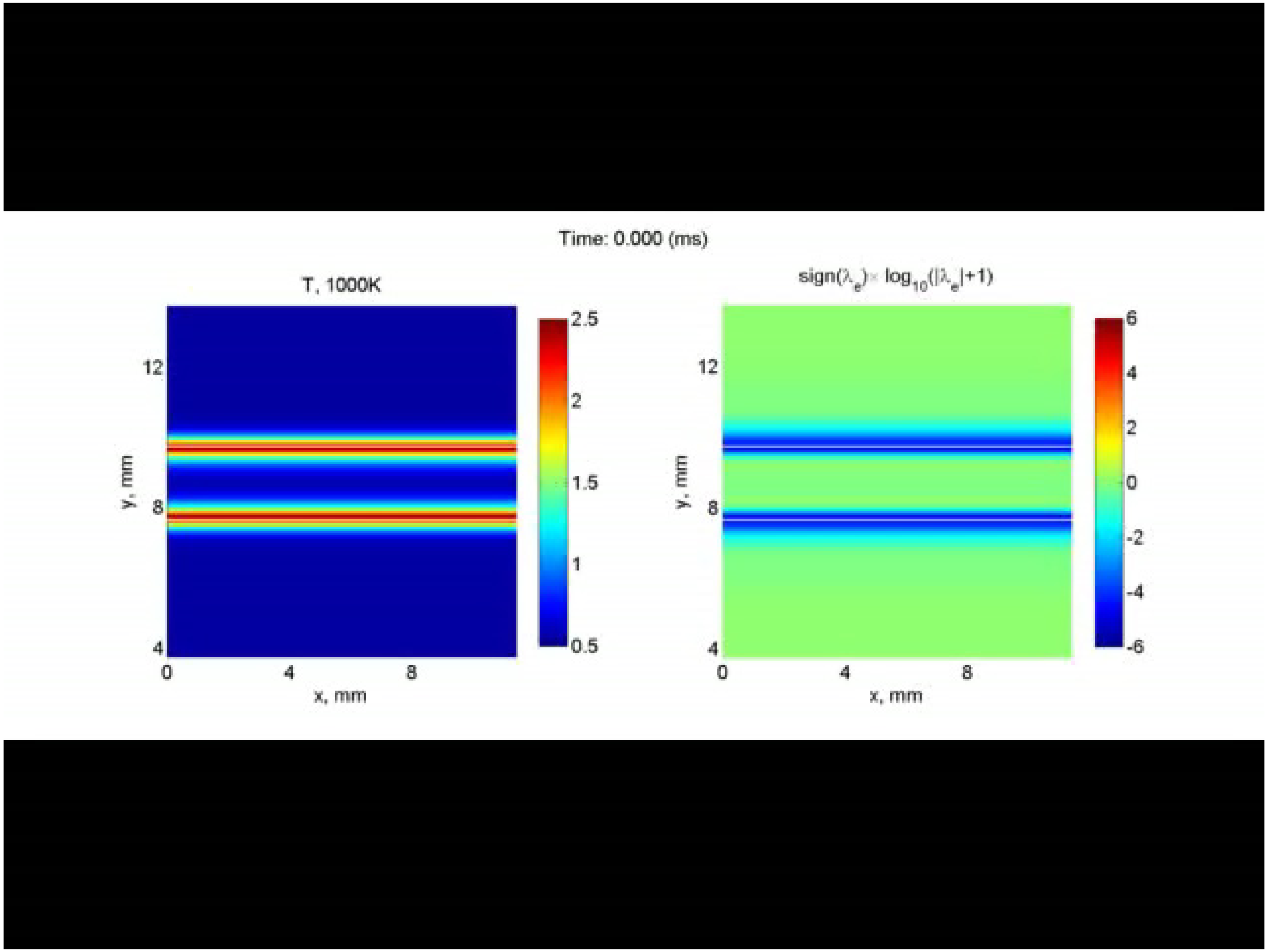
Non-premixed Temporal Jet for Ethylene in Air

DNS of a Non-premixed Turbulent Flame

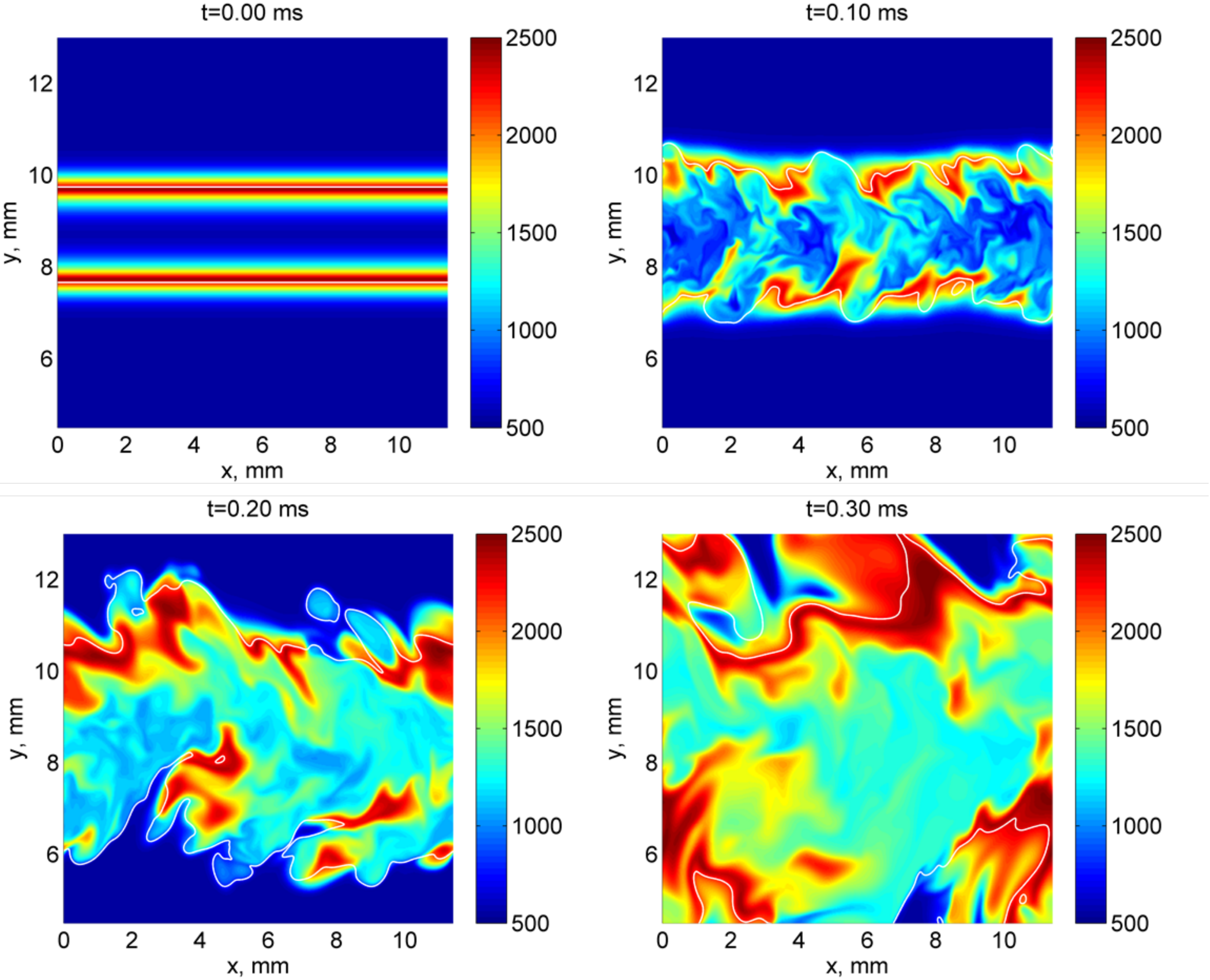


(Lignell et al., CNF 2011)

- Domain size:
  $11.5\ mm \times 16.3\ mm \times 7.7\ mm$
- A slab of nitrogen-diluted ethylene surrounded by nitrogen-diluted oxygen, $P = 1\ atm, T_F = T_O = 550\ K$
- Periodic boundary conditions in x- and z-directions
- Outflow boundary condition in y-direction
- Initial velocity $U_F = -U_O = 98\ m/s$, plus isotropic turbulence in the fuel layer
- $Re_j = 5120$
- $Da = 0.017$
- Initial 1-D flame solution mapped to the fuel-air boundary


Time: 0.000 (ms)
T, 1000K
y, mm
x, mm
12
8
4
0
4
8
2.5
2
1.5
1
0.5
sign(λ_e)× log_10(|λ_e|+1)
y, mm
x, mm
12
8
4
0
4
8
6
4
2
0
-2
-4
-6

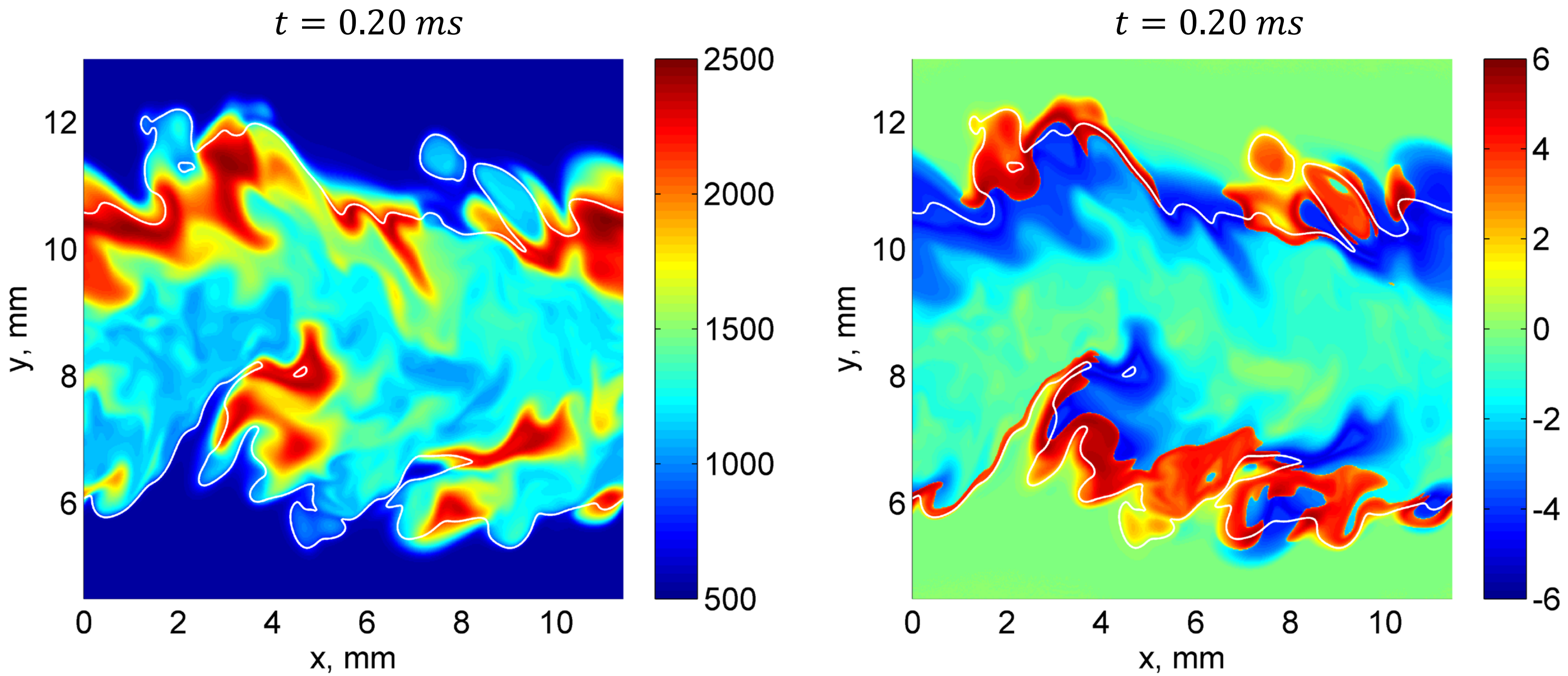
Evolvement of Temperature Field



Temperature at center plane ($z = 0$)

CEMA for the DNS Data

On the center ($z = 0$) plane, **white line is the stoichiometric line**



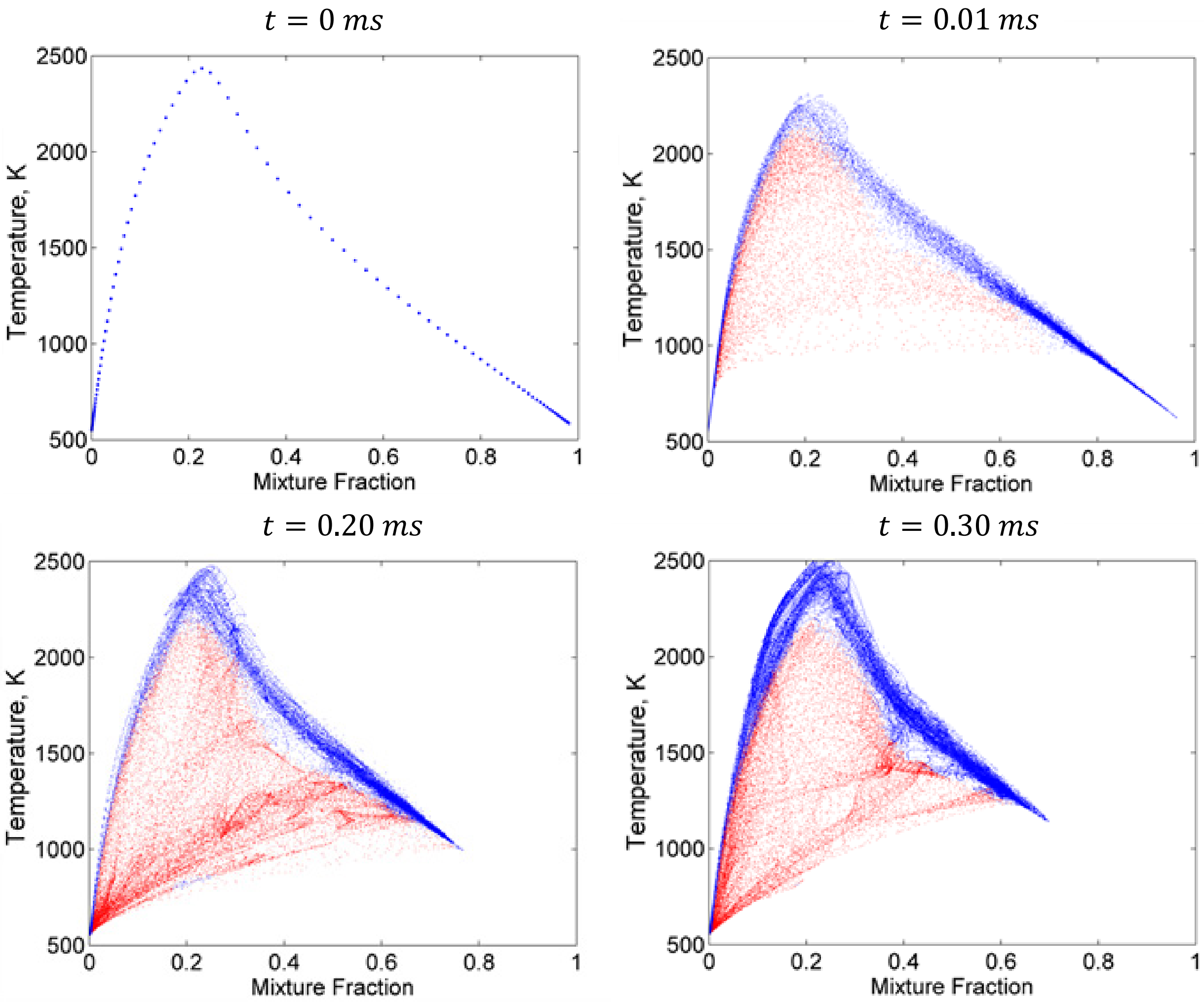
$t = 0.20\,ms$ $t = 0.20\,ms$

Temperature, K

$sign(\lambda_e) \times \log_{10}(|\lambda_e| + 1)$

- $\boldsymbol{\lambda_e > 0}$ is used to detect near- and post-extinction flame segments
- Consistent with the temperature information

Scatter of Temperature



$t = 0\ ms$

$t = 0.01\ ms$

$t = 0.20\ ms$

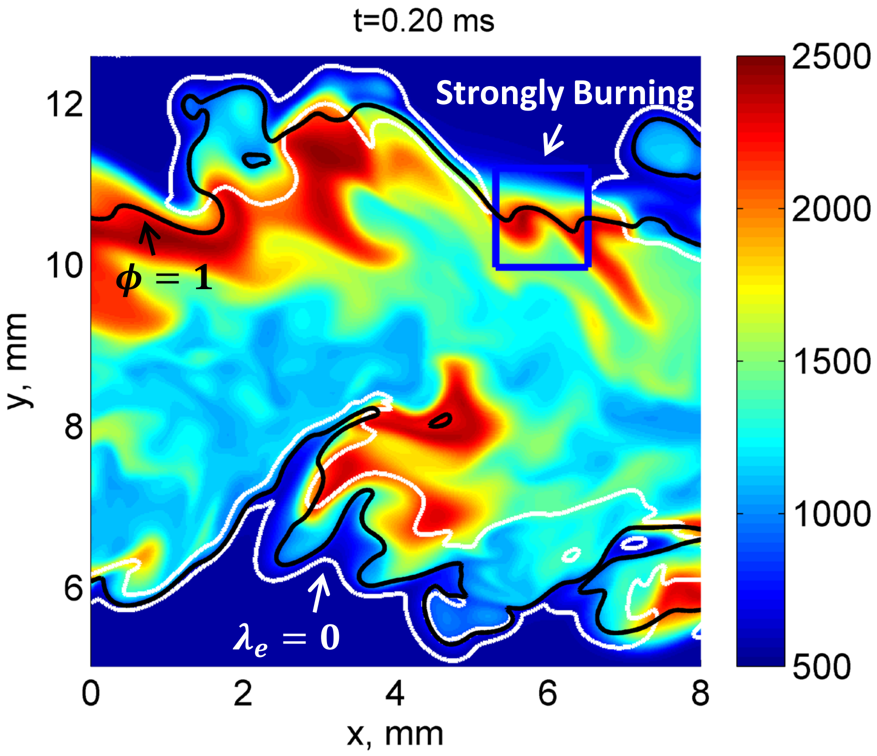
$t = 0.30\ ms$

- Near- and post-extinction mixtures (red) scatter below the equilibrium manifold (blue)

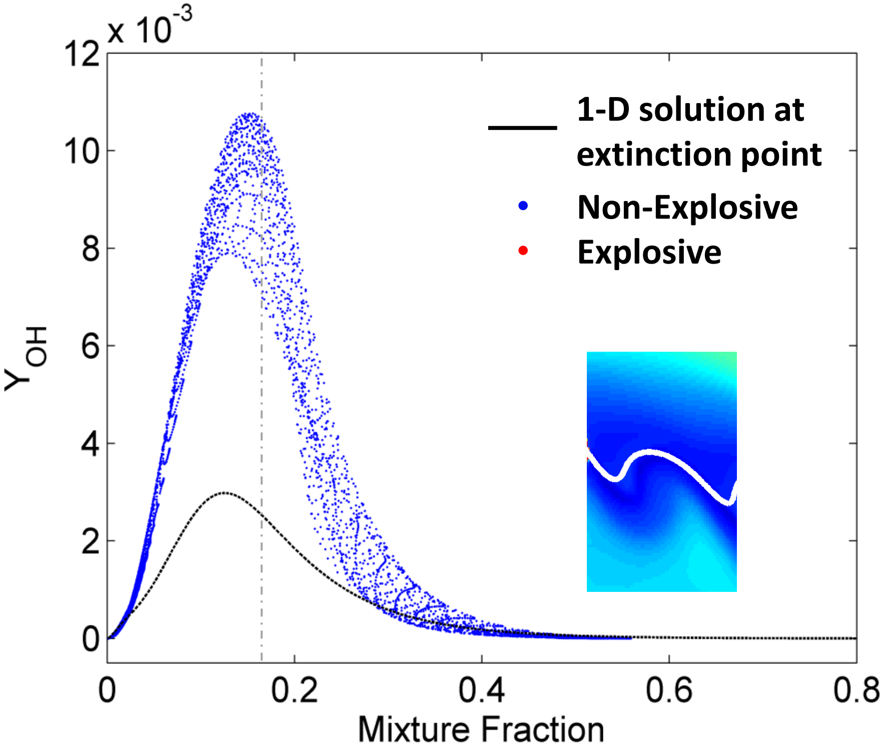
- $\boldsymbol{\lambda_e < 0}$
- $\boldsymbol{\lambda_e > 0}$

At the center ($z = 0$) plane

A Strongly Burning Non-Premixed Flamelet

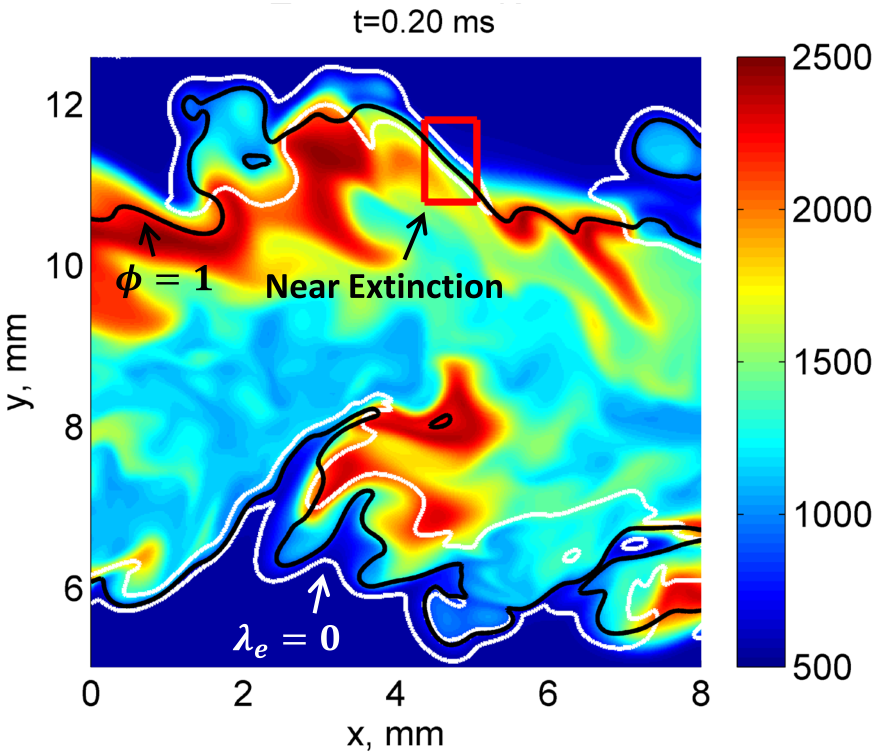


Temperature, K

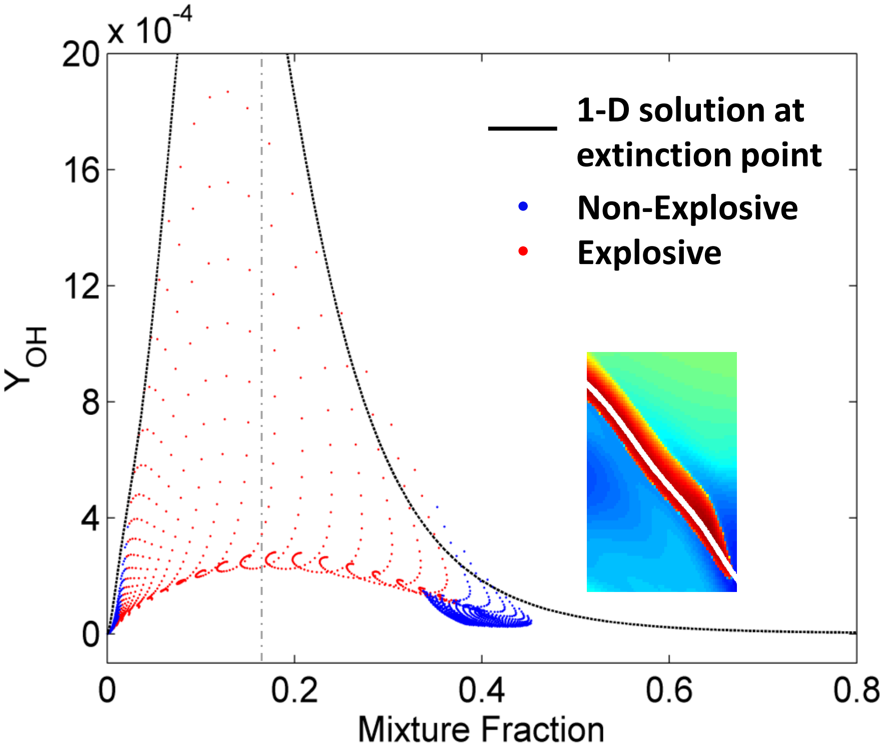


- Strongly burning non-premixed flamelets features non-explosive mixtures ($\lambda_e < 0$) on the stoichiometric surface
- OH mass fraction much higher than that at 1-D extinction state

A Near-Extinction Non-Premixed Flamelet

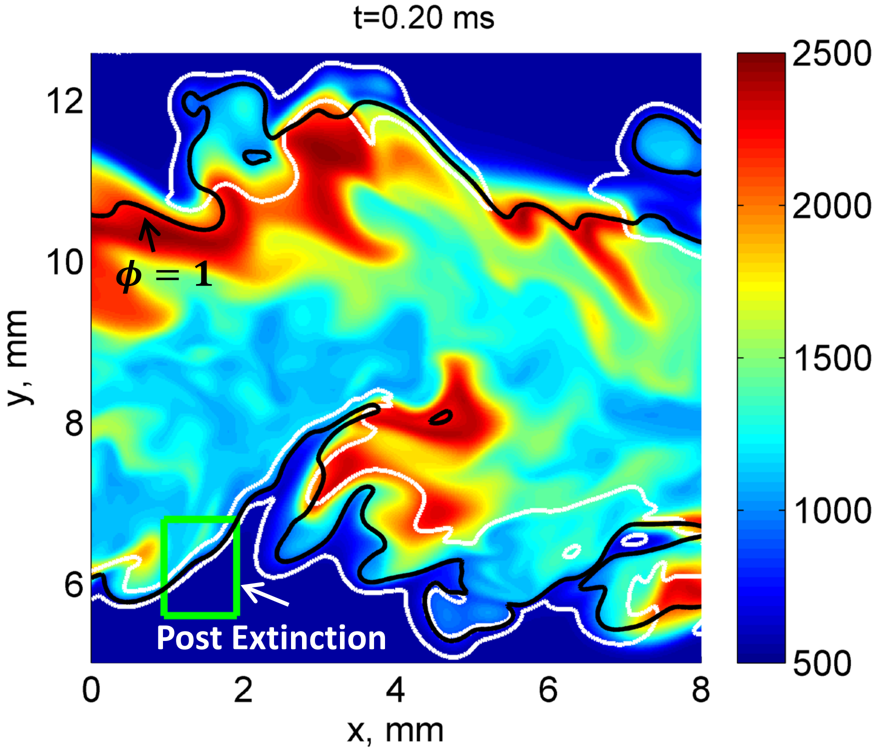


Temperature, K

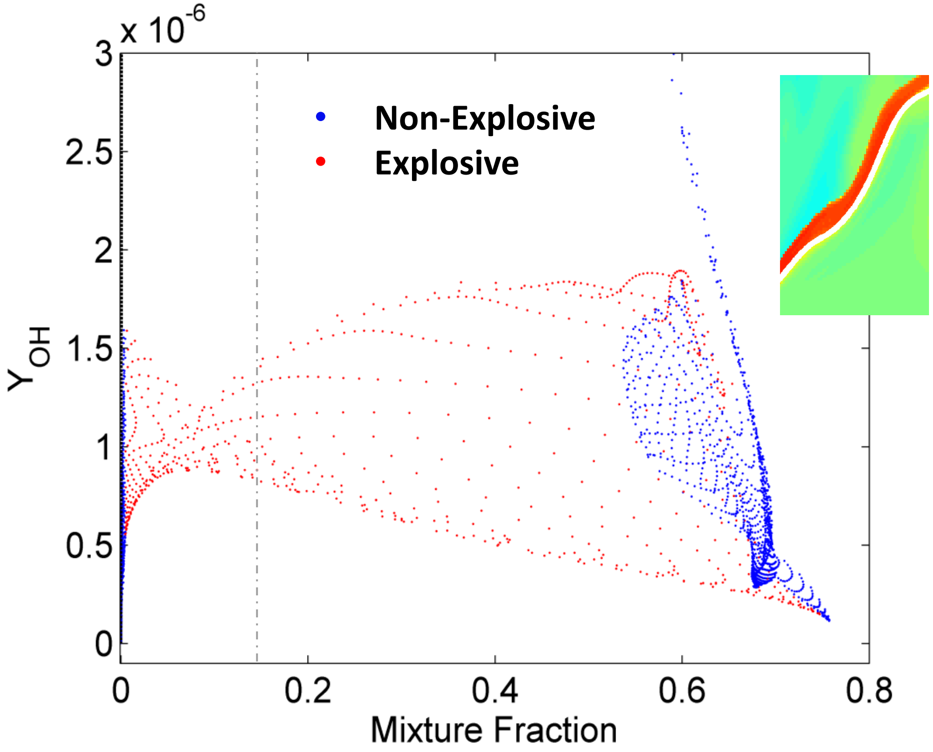


- Features explosive mixtures ($\lambda_e > 0$) at the stoichiometric surface
- OH moderately high, scatter below the 1-D extinction solution

A Post-Extinction Section

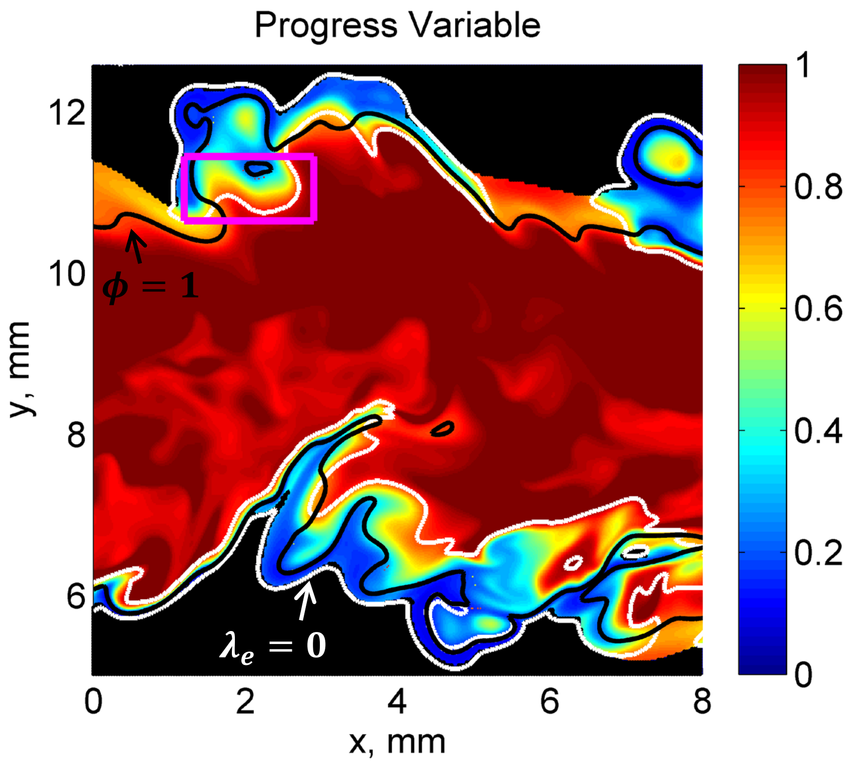


Temperature, K

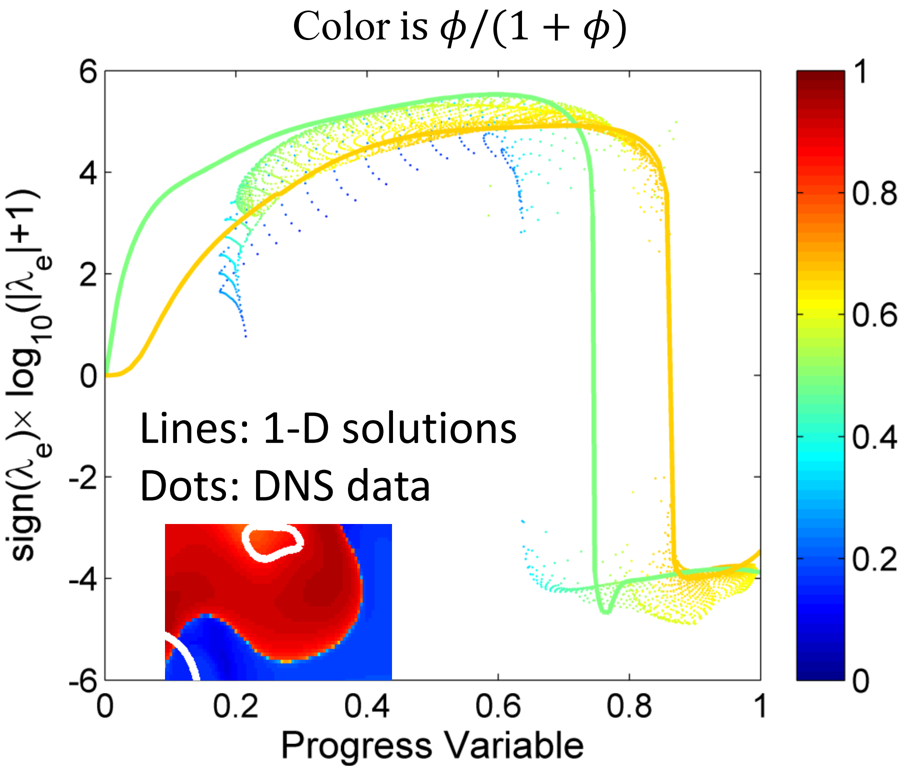


- Post-extinction zones feature positive λ_e near the stoichiometric surface
- OH is low, T is low

A Premixed Flamelet during Re-ignition



Progress Variable



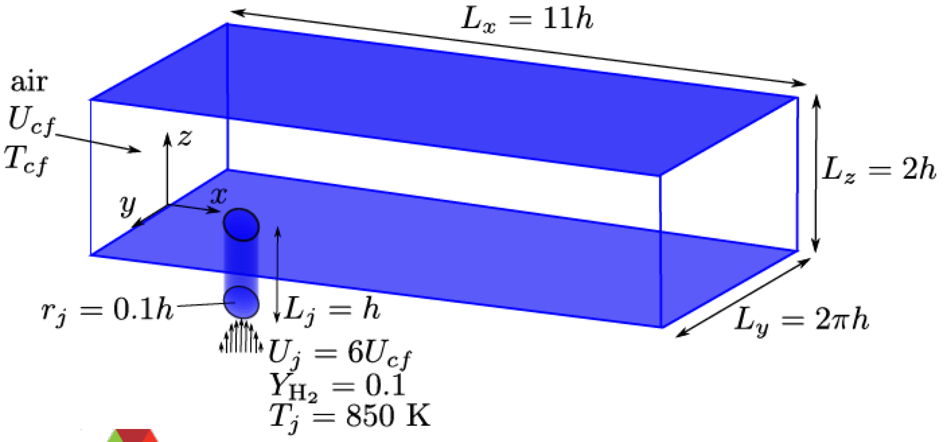
Color is $\phi/(1+\phi)$

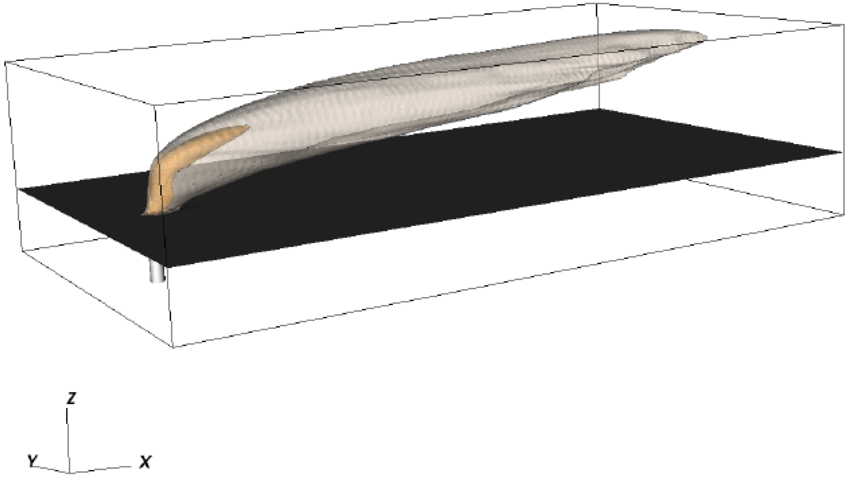
- Progress variable defined as $(T - T_0)/(T_{eq} - T_0)$, $T_0 = 550\ K$ (T of fresh mixtures)
- Scatter plot show signature of 1-D premixed flames

Ignition of a Non-Premixed Flame:
A Jet in Cross Flow (JICF)

Flame Decelerating into Auto-igniting Mixtures: Jet in Cross Flow

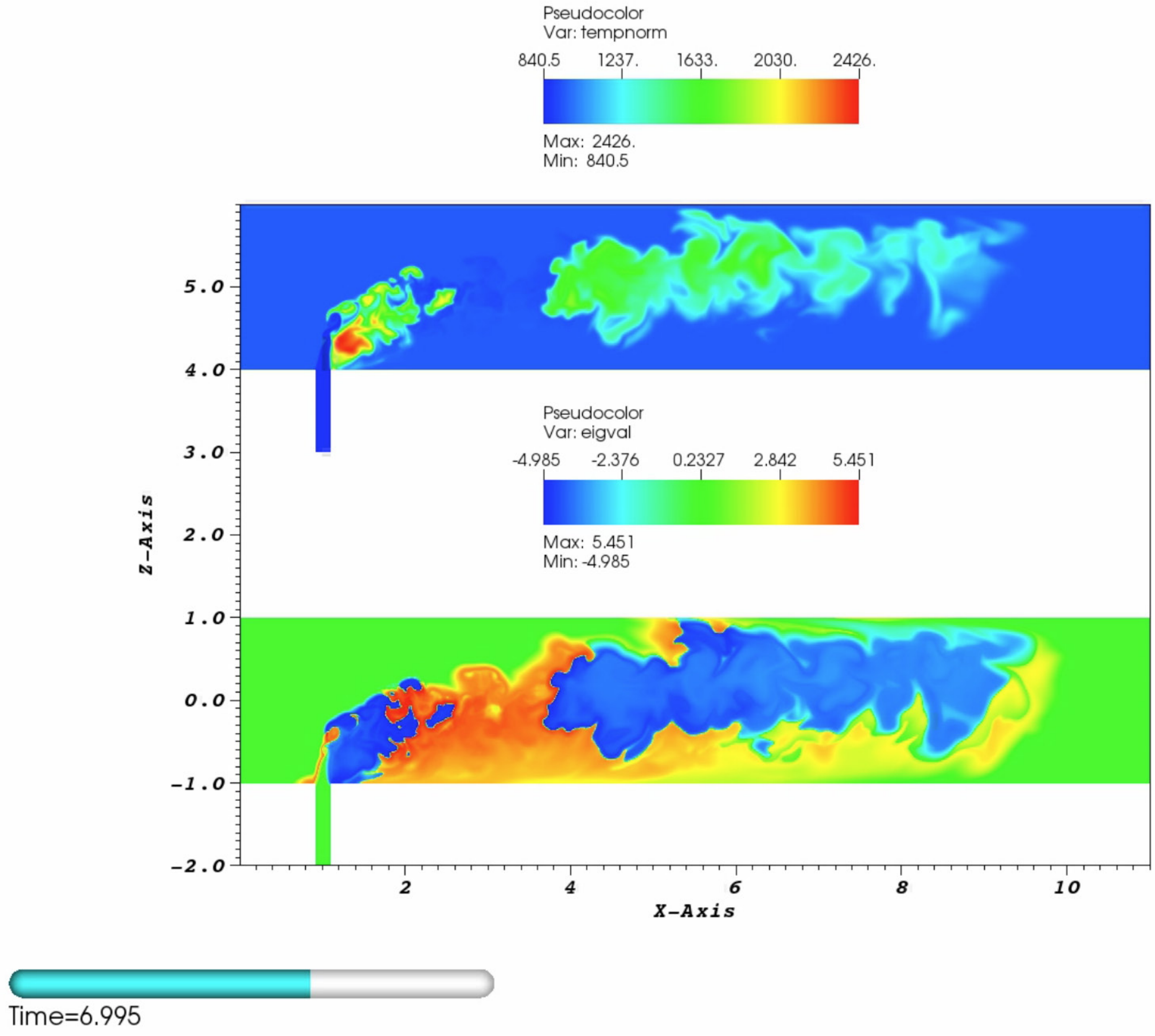
- DNS of incompressible flow
- Detailed H_2 mechanism (Li et al, IJCK 2004)
- Spectral element method, 1.5M elements
- $T_{cf} = 950K, T_j = 850K$
- $Re_t = 180, h = 1cm, U_{cf} = 30.28\ \mathrm{m/s}, t_{ref} = h/U_{cf} = 0.33\ \mathrm{ms}$





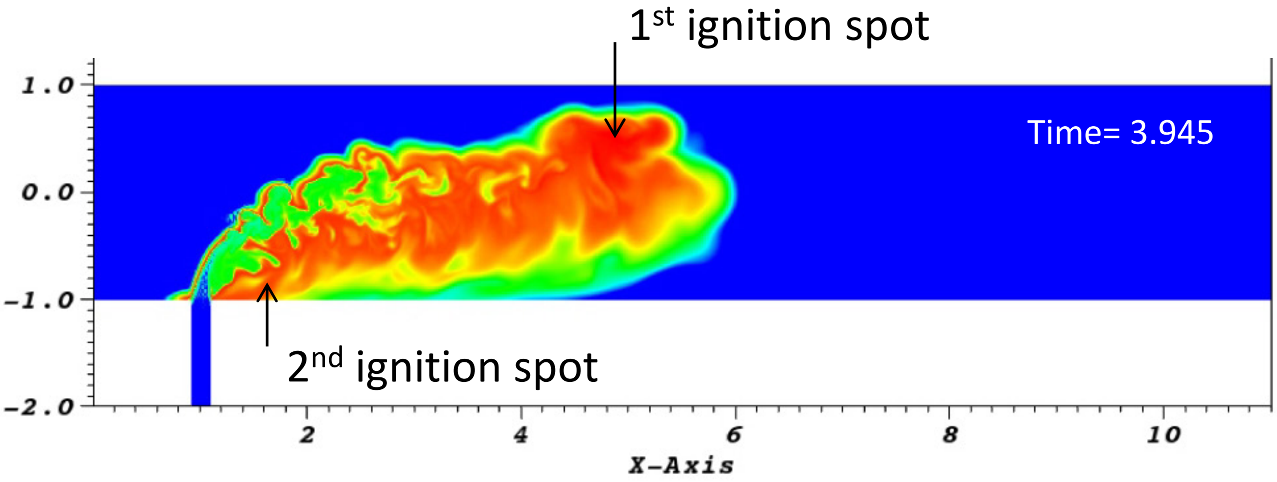
(Abdilghanie et al, US Meeting 2013, Paper# 2D06-070LT-0251)

CEMA for the Jet in Cross Flow DNS



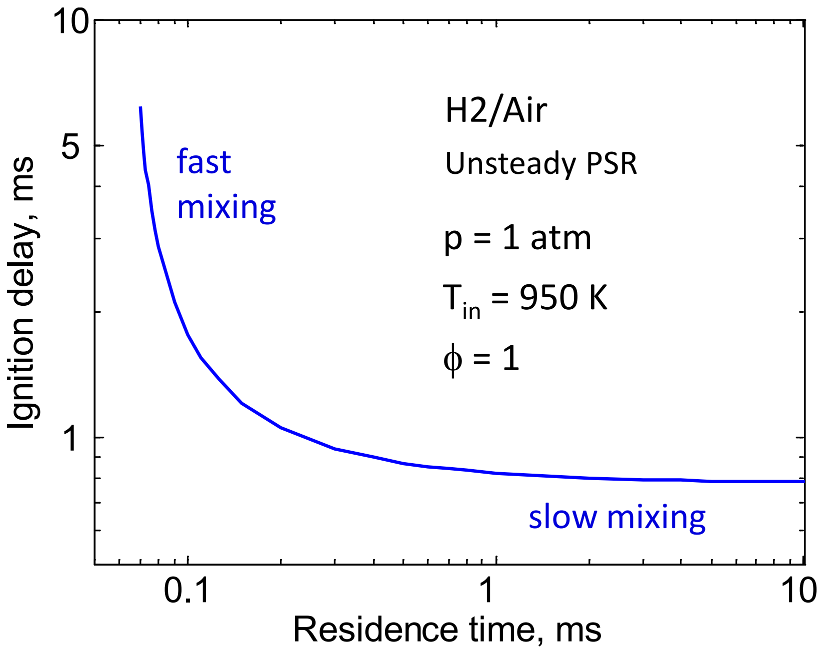
Visualization by
A. Abdilghanie

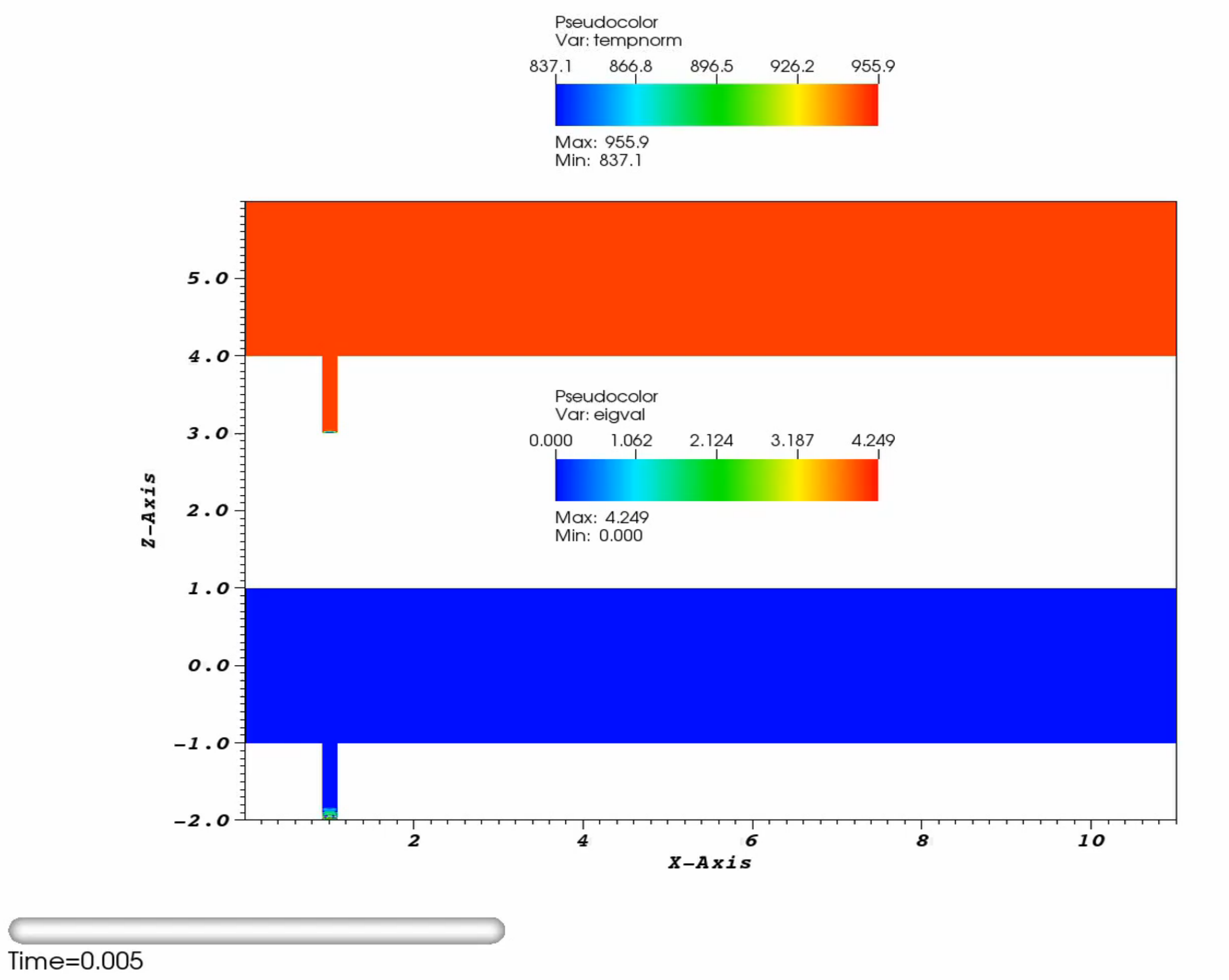
Where does Ignition Occur First?


1st ignition spot

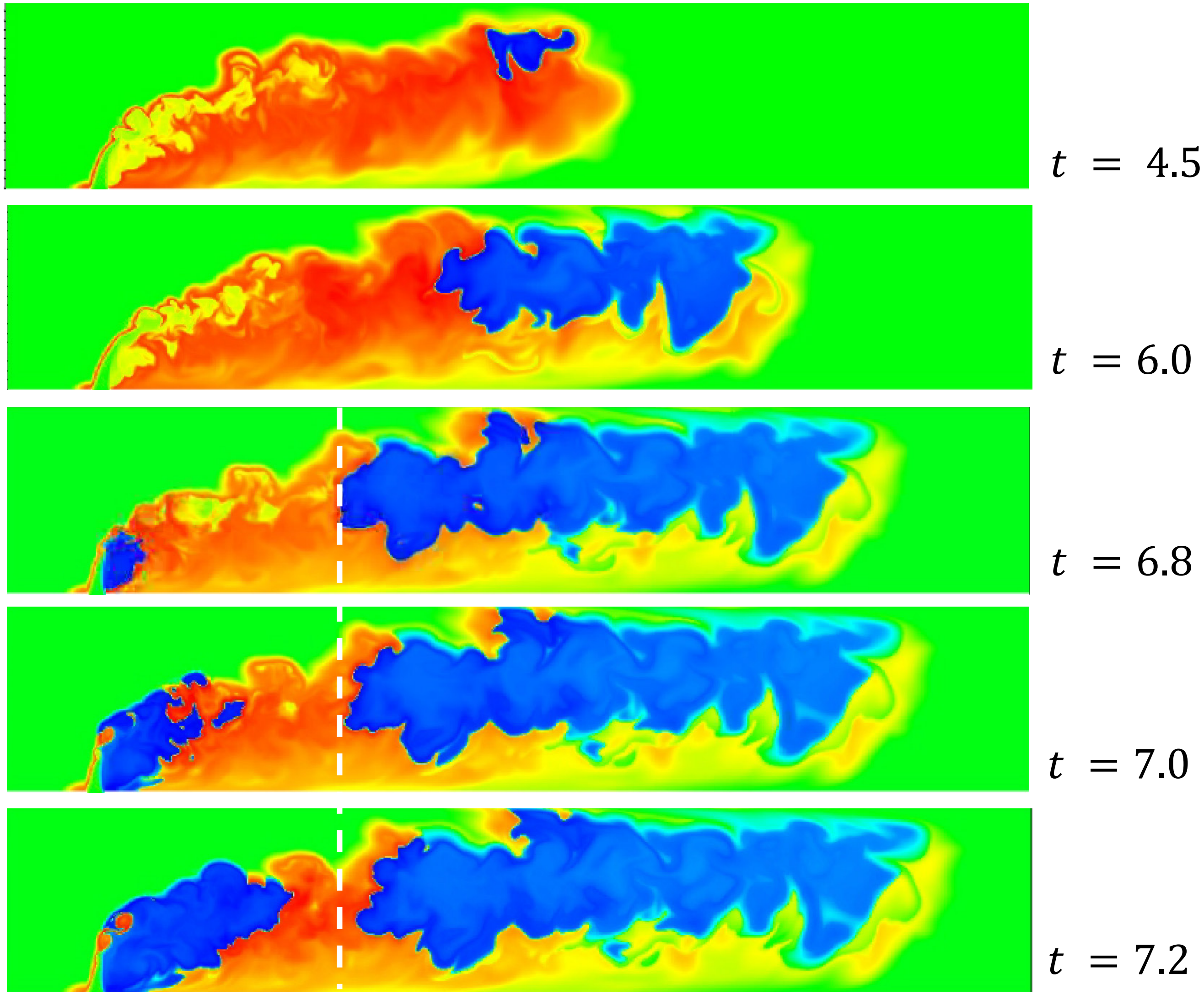
2nd ignition spot

- First ignition occurred downstream (slow mixing)
- Second ignition in the leeward recirculation zone (fast mixing)
- Ignition occurs downstream first due to the slow mixing



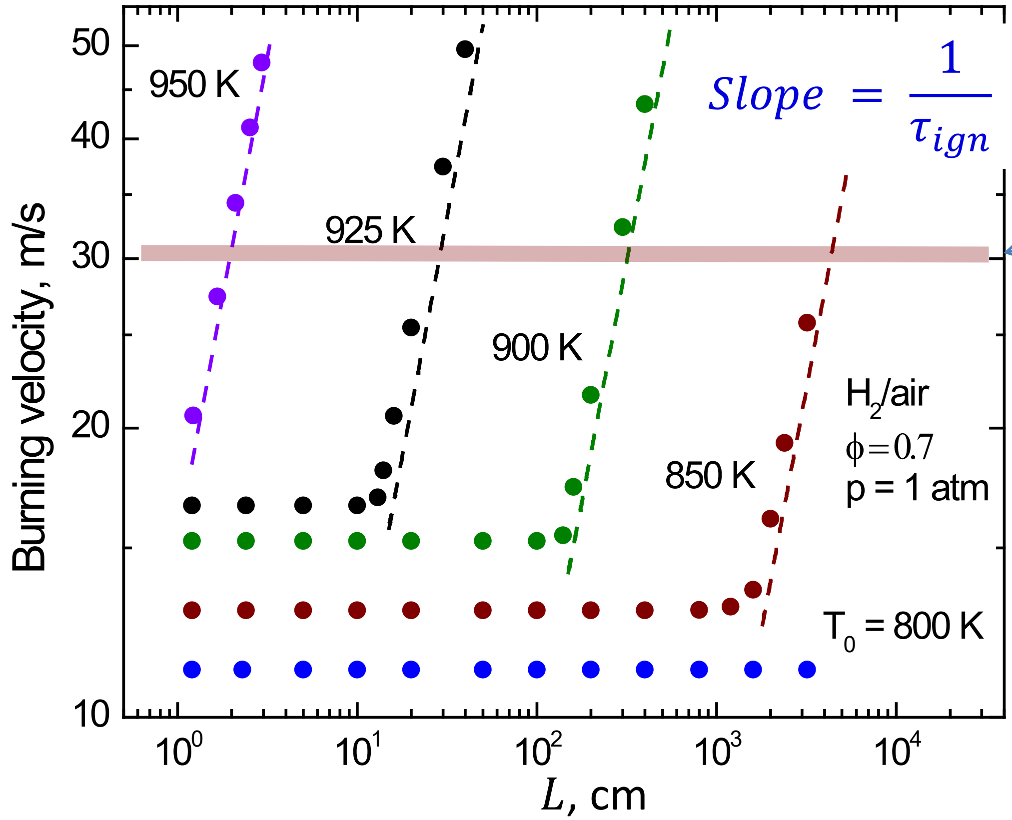

Pseudocolor
Var: tempnorm
837.1
866.8
896.5
926.2
955.9
Max: 955.9
Min: 837.1
Pseudocolor
Var: eigval
0.000
1.062
2.124
3.187
4.249
Max: 4.249
Min: 0.000
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
Z-Axis
2
4
6
8
10
X-Axis
Time=0.005

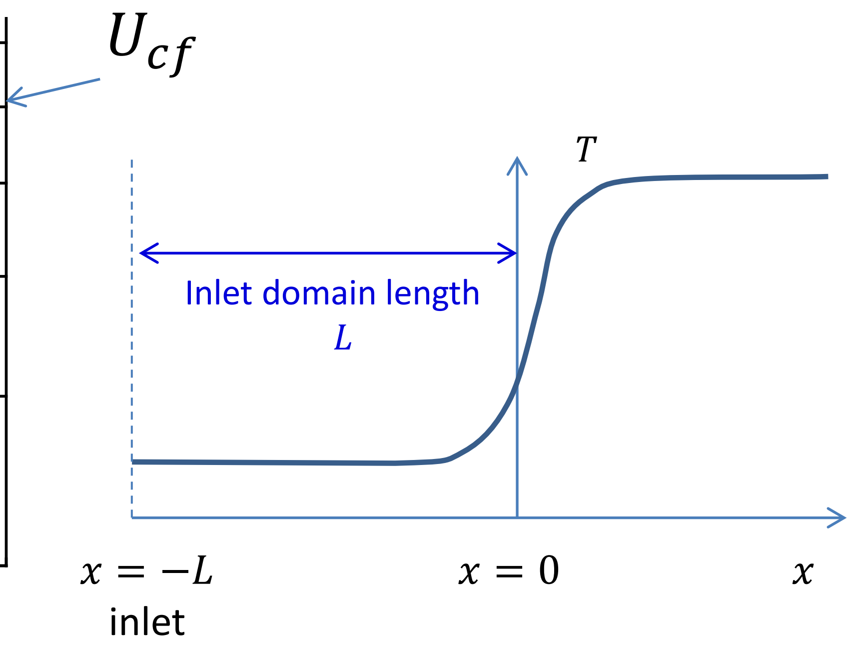
Deceleration Flame Back-Propagation & Ignition in the Leeward Recirculation Zone



Mechanism for the Flame Propagation

- The burning velocity (S_L) is L-dependent
- For low-mid T_0, S_L is approximately a constant ($S_{L,0}$) when $L < S_{L,0} \cdot \tau_{ign}$
- For high T_0 (e.g. > 950K), $S_{L,0}$ is not present



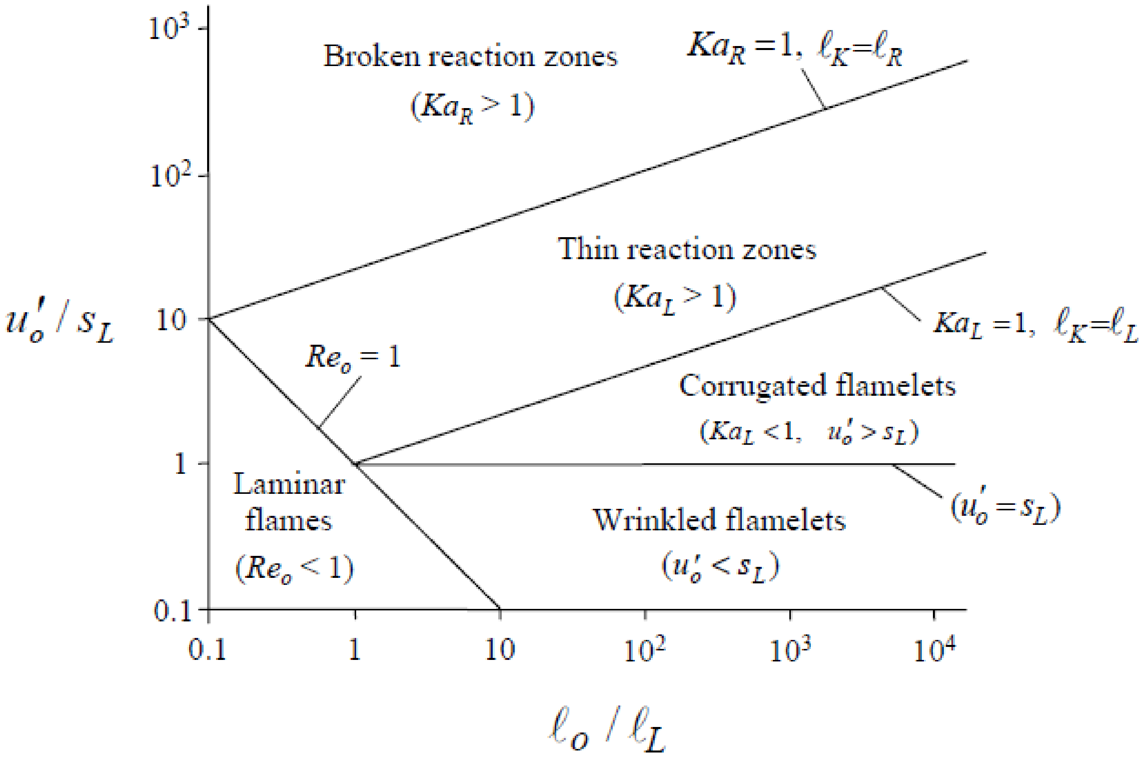


A Strongly Turbulent Premixed Flame

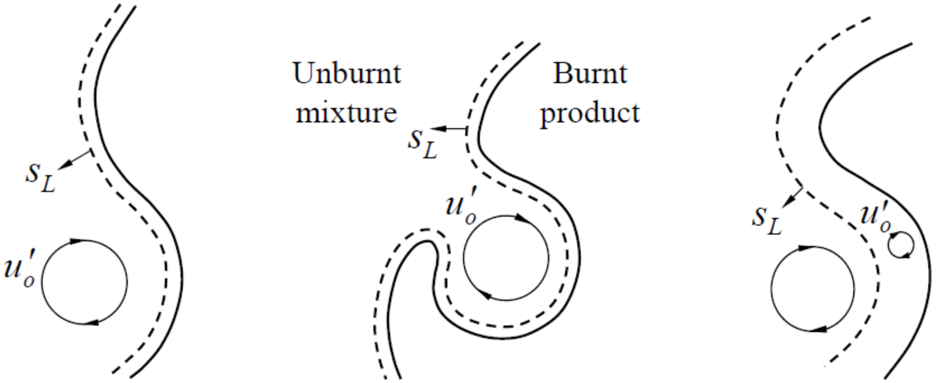
(Xu et al. CNF 2019)

Regime Diagram

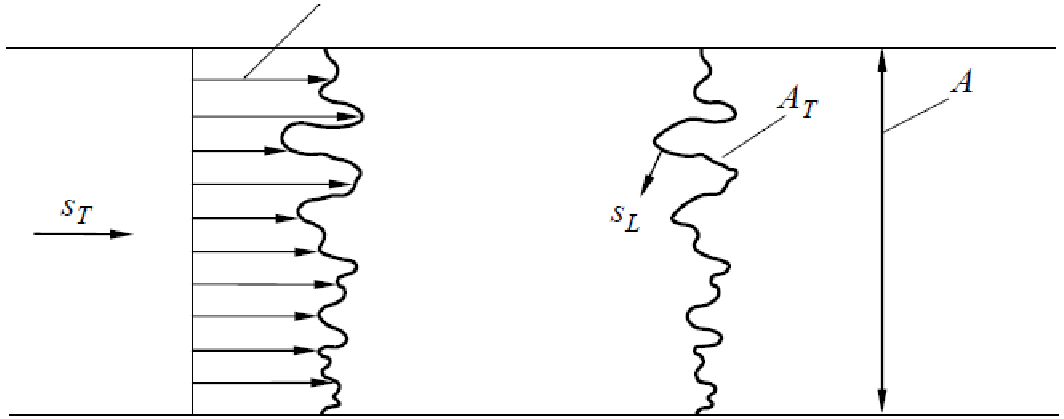
The Borghi Diagram



Premixed Flamelet, Turbulent Flame Speed



(a) (b) (c)

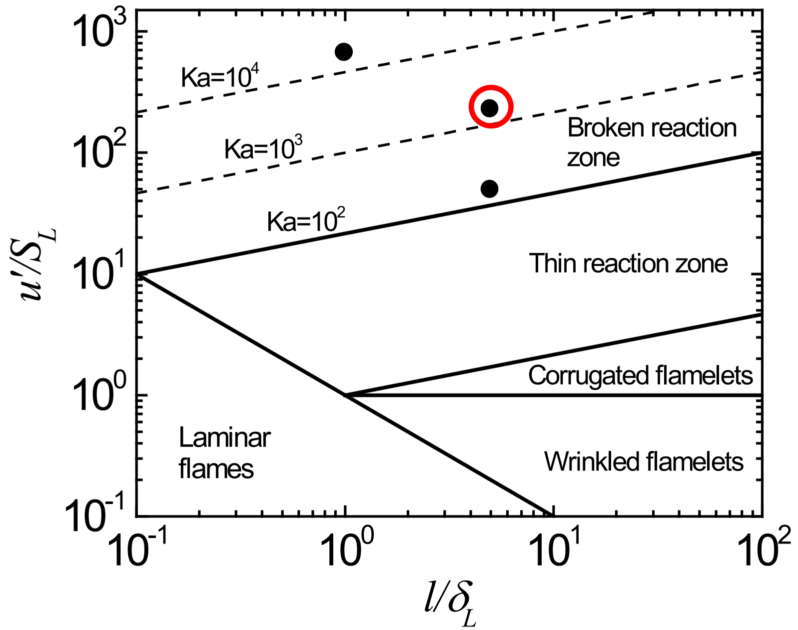


$$S_T A = S_L A_T$$

- Turbulent flame speed is higher than S_L due to the flame wrinkling
- Laminar flame speed plays an important role, but the real world is complicated

DNS of a Strongly Turbulent Premixed Flame

- DNS by A. Poludnenko
- Mechanisms:
  - CH4: 19-species reduced model
  - C12: 24-species reduced model
- Engine-relevant conditions:
  - $P = 30\ bar$, $\phi = 0.7$, $T_0 = 700\ K$,
- $Ka = 10^2, 10^3, 10^4$
- Domain size: $L \times L \times 8L$, $L = 0.042\ cm$ $(Ka = 10^3)$
- Number of grids: $512 \times 512 \times 4096$ $(Ka = 10^3)$
- Following analysis is focused on $Ka = 10^3$ unless otherwise mentioned

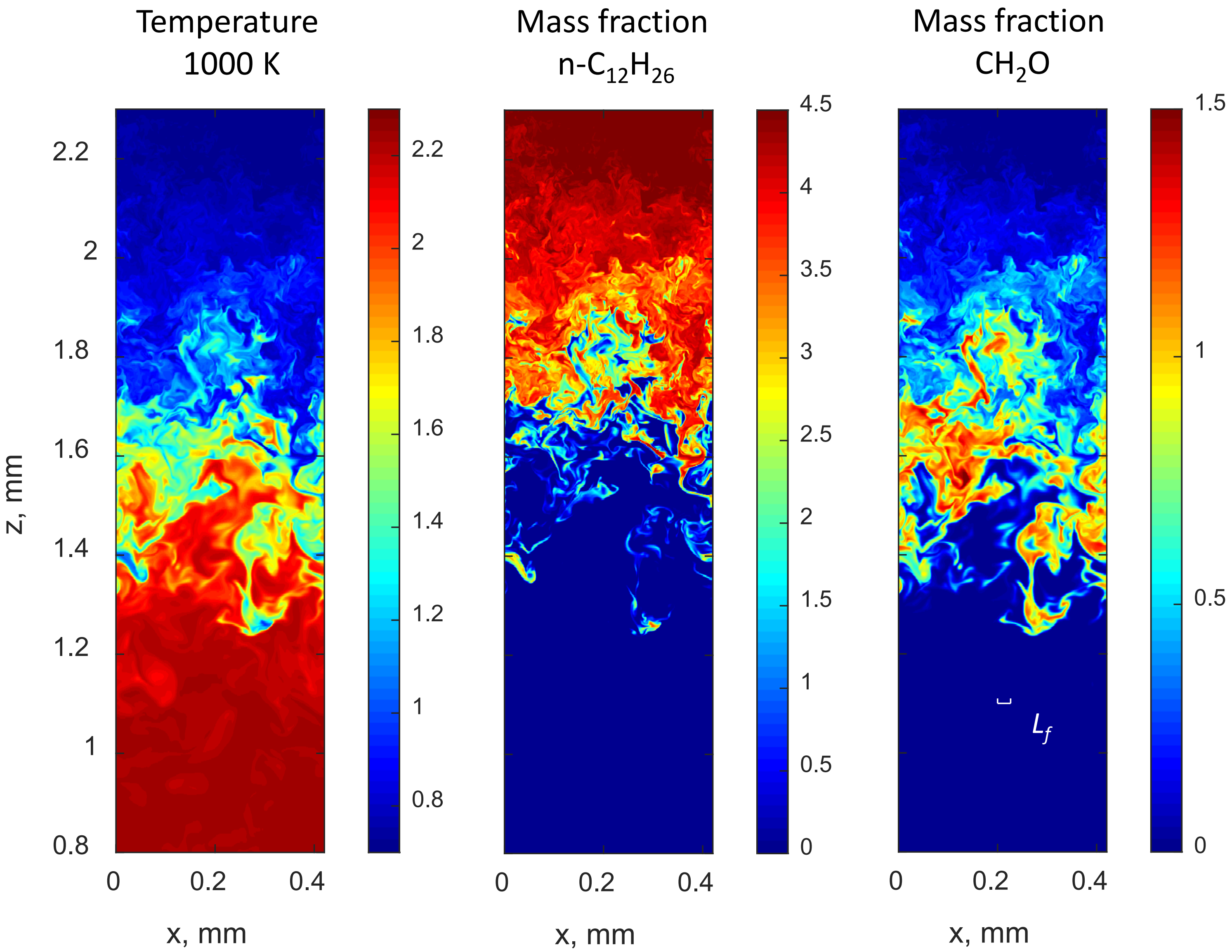


Laminar flame properties

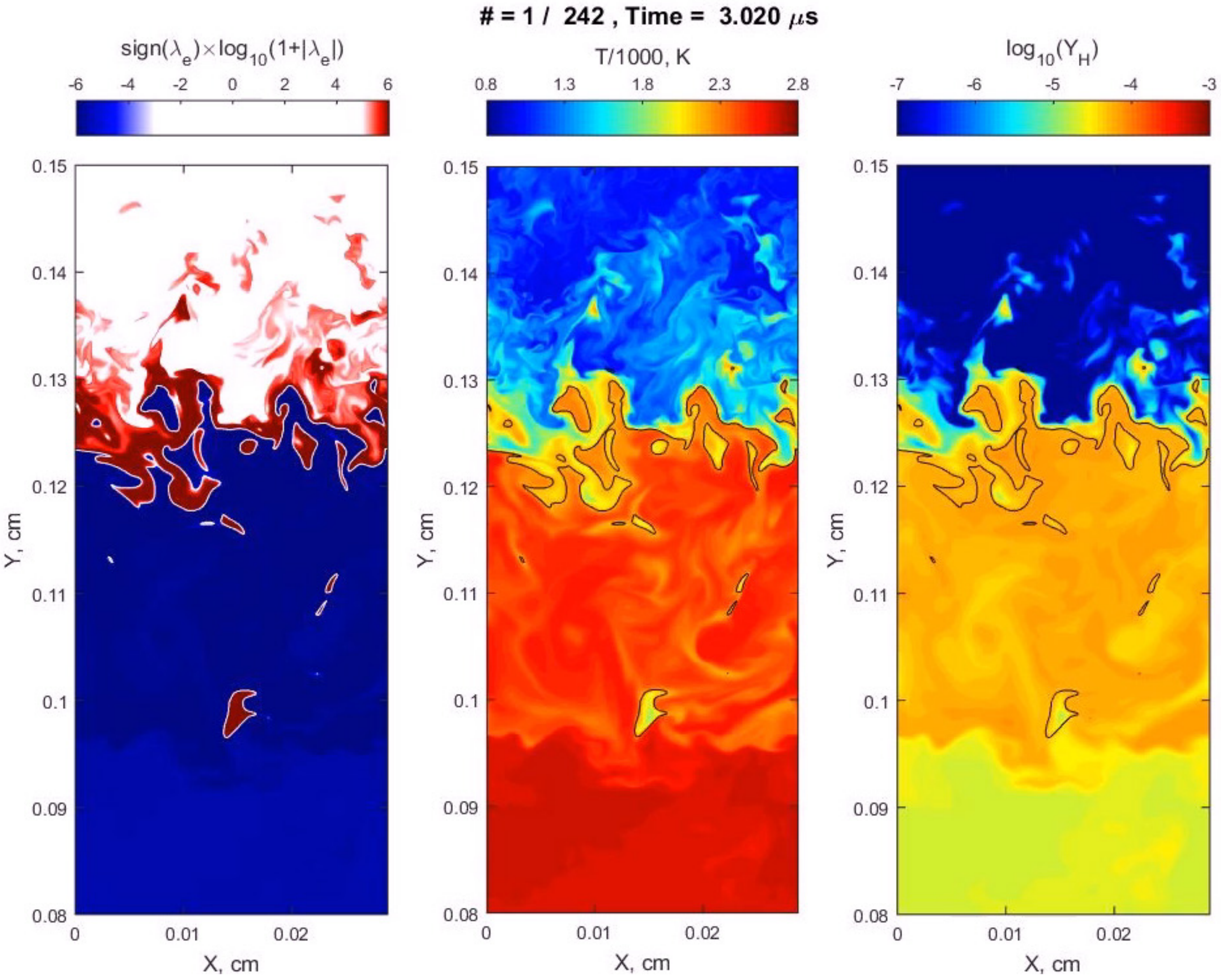
	Flame speed	Flame thickness	Flame time-scale
CH4	24.42	4.11×10^{-3}	1.68×10^{-4}
C12	39.03	2.63×10^{-3}	6.75×10^{-5}

All in cm-g-s unit

Structure of the n-Dodecane Flame

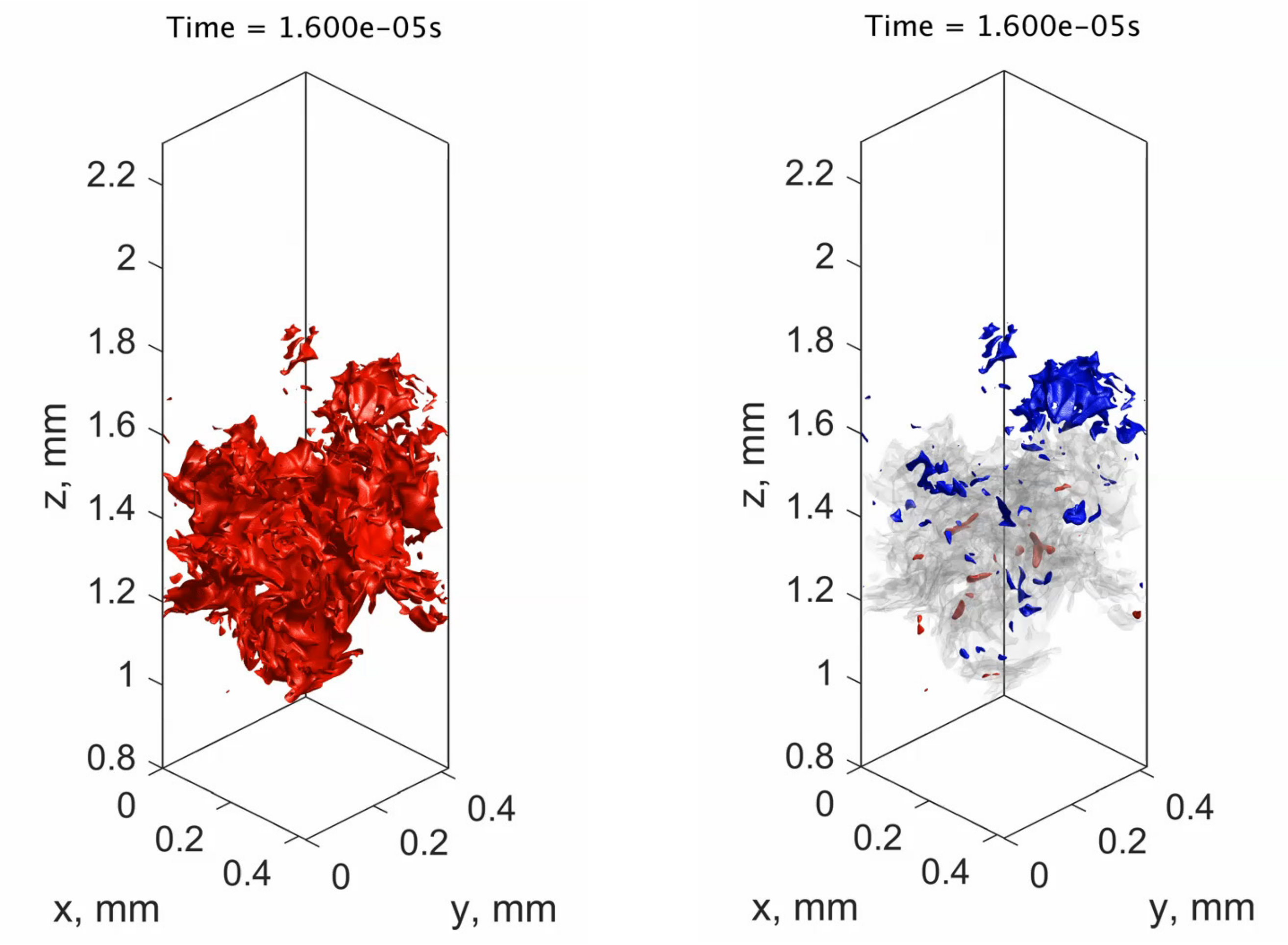


Structure of the C12 Flame: 2-D Cuts



3-D Flame Structures (n-Dodecane)

Fresh mixture



Product

Iso-surface:
$\lambda_e = 0$

Blue pockets:
$\lambda_e < 0$

Red pockets:
$\lambda_e > 0$

Summary

- Non-premixed flames tends to become partially premixed in strong turbulence

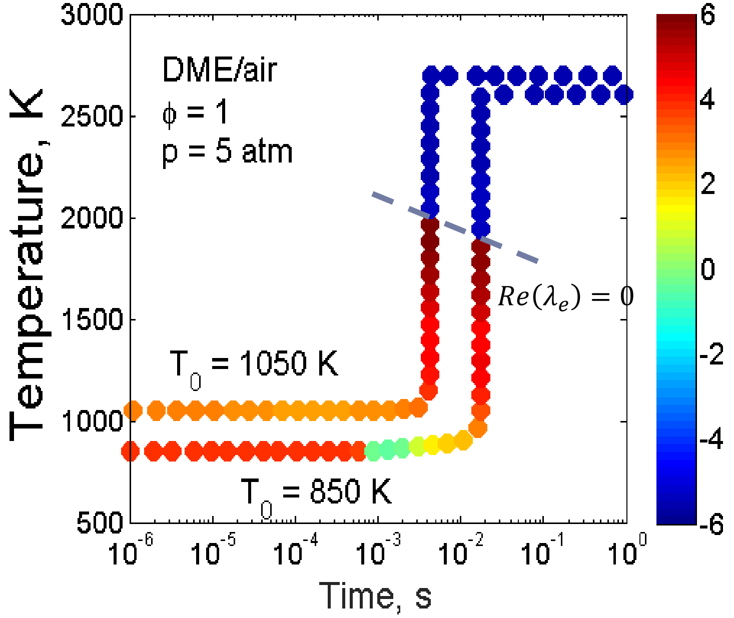
- Premixed reaction fronts may propagate in different modes
  - Deflagration mode (with predictable flame speed, S_L)
  - Auto-igniting fronts (with arbitrary flame speed / burning rate)

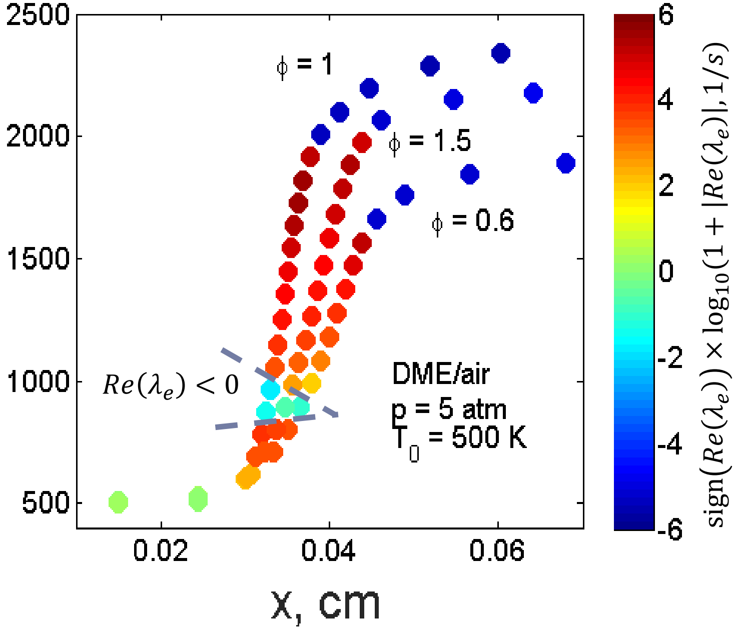
- Premixed flames involve local extinction/re-ignition in strong turbulence
  - Overall reaction zone is thickened (volumetric rather than interfacial)
  - Cannot be described by flamelets

- Modeling remains a challenge (premixed & non-premixed)

Thank you

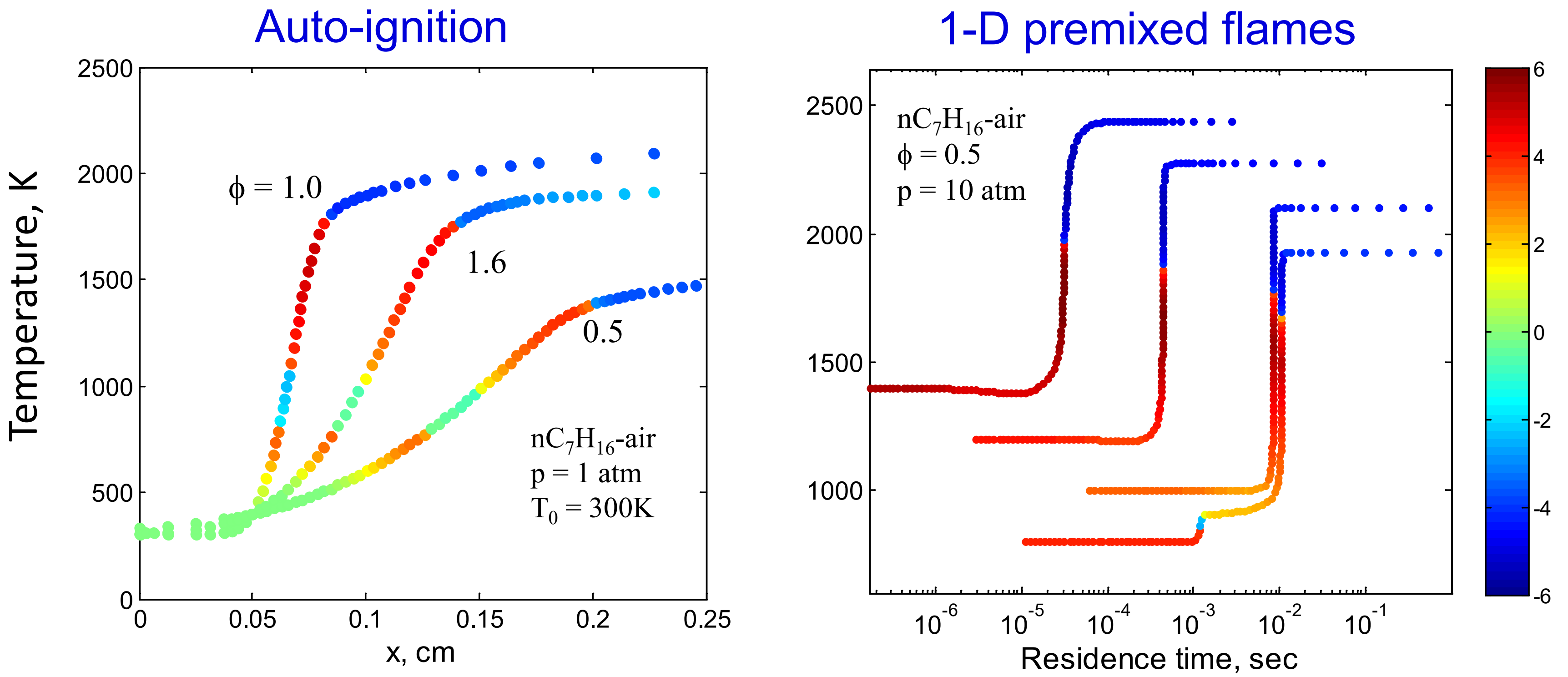
Role of CEM in Auto-Ignition & Premixed Flames: DME-Air


Auto-ignition


1-D premixed flames

- $Re(\lambda_e) > 0$ for pre-ignition mixtures, λ_e: eigenvalue of the chemical Jacobian
- $Re(\lambda_e) < 0$ for post-ignition mixtures
- $Re(\lambda_e) = 0$ indicates the ignition point or premixed reaction front
- Cool flames are present

Role of CEM in Auto-Ignition & Premixed Flames: *n*-Heptane - Air



Color indicates $\mathrm{sign}(\mathrm{Re}(\lambda_e))\times\log_{10}(1+|\mathbf{Re}(\lambda_e)|)$.

- $Re(\lambda_e) > 0$ for pre-ignition mixtures, λ_e: eigenvalue of the chemical Jacobian
- $Re(\lambda_e) < 0$ for post-ignition mixtures
- $Re(\lambda_e) = 0$ indicates the ignition point or premixed reaction front
- Cool flames are present

CEMA for Ignition:
Homogeneous Charge Compression Ignition (HCCI)

(Ignition & Premixed flame propagation)

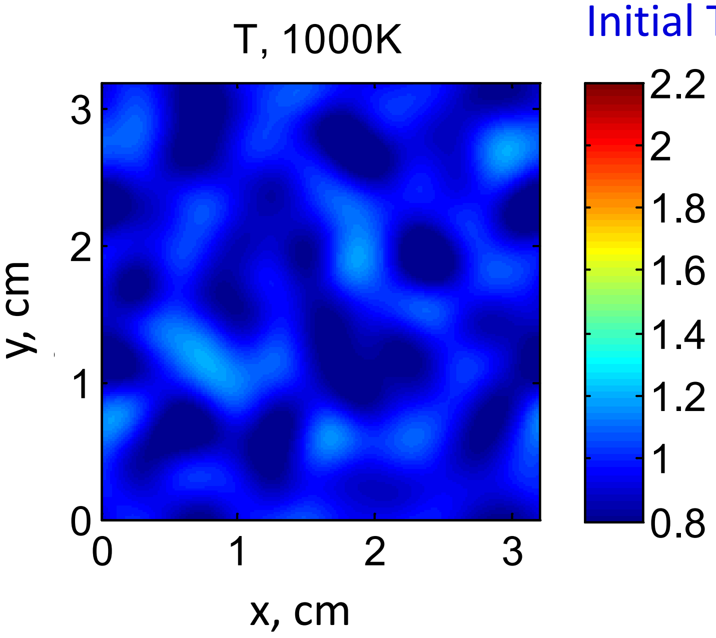
Homogeneous Charge Compression Ignition (HCCI) Combustion with CEMA

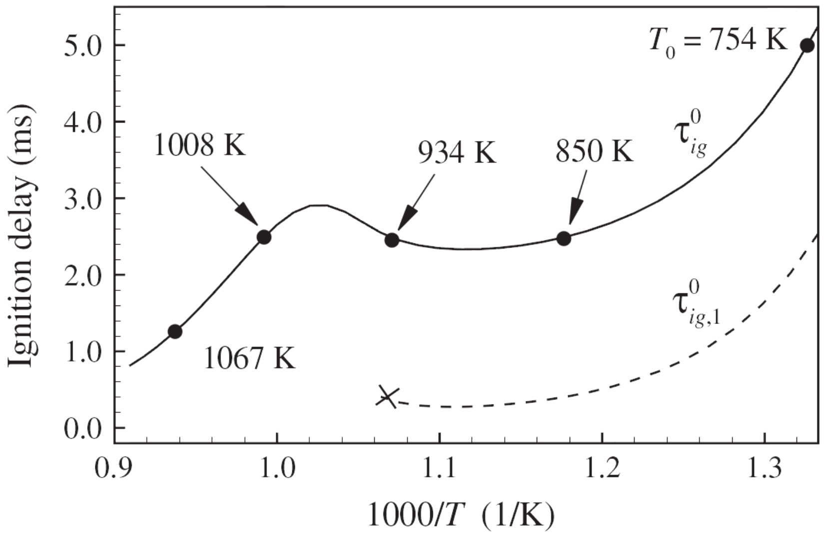
- 2-D HCCI
- nC_7H_{16}, 58-species non-stiff
- Domain size: 3.2mm x 3.2mm
- Grid size: 2.5μm, uniform

Initial conditions:

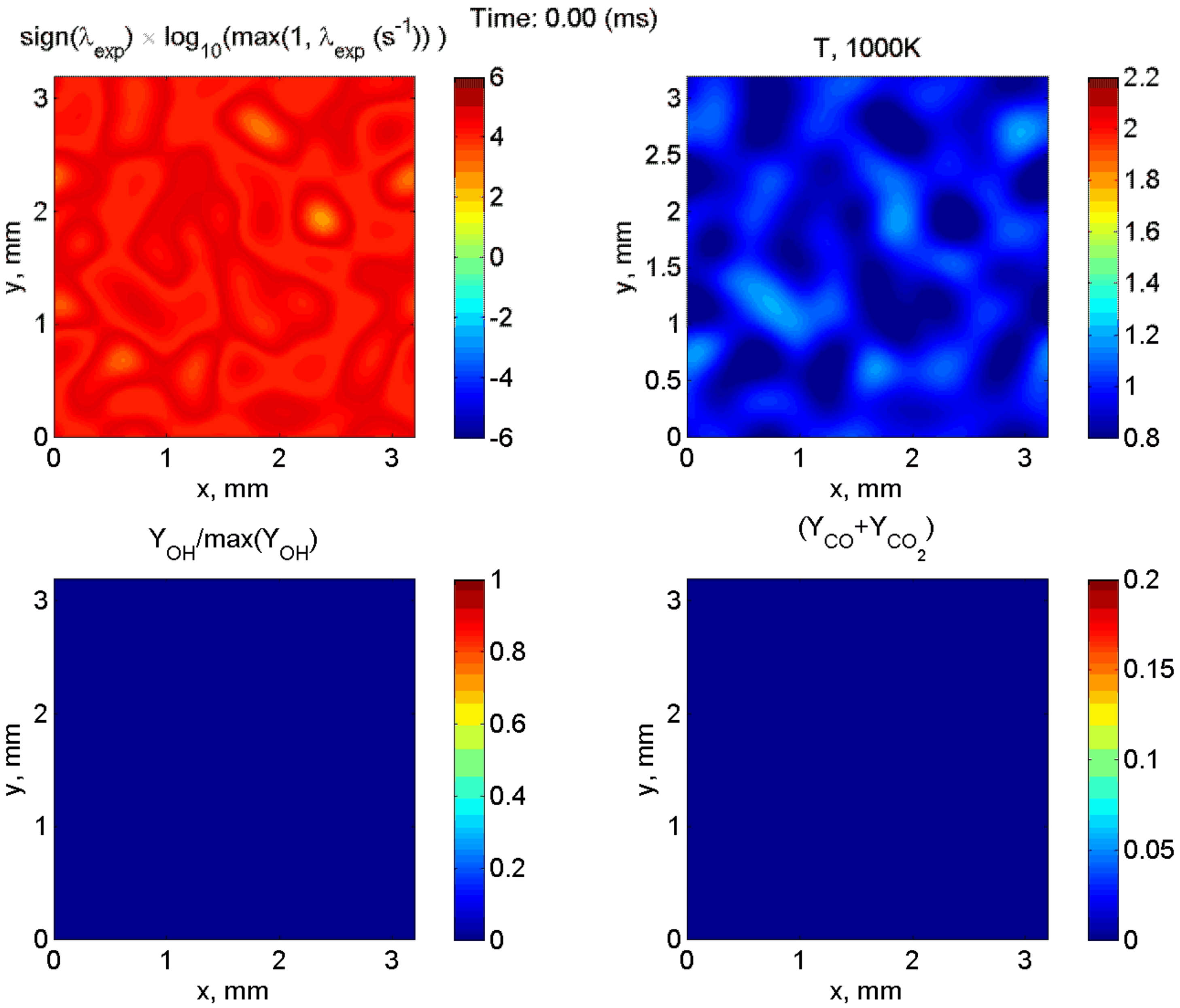
- $\phi = 0.3$
- p = 40 atm
- T_{mean} = 934K, T' = 100K (RMS)
- Isotropic turbulence, u' = 5m/s

Initial Temperature Distribution

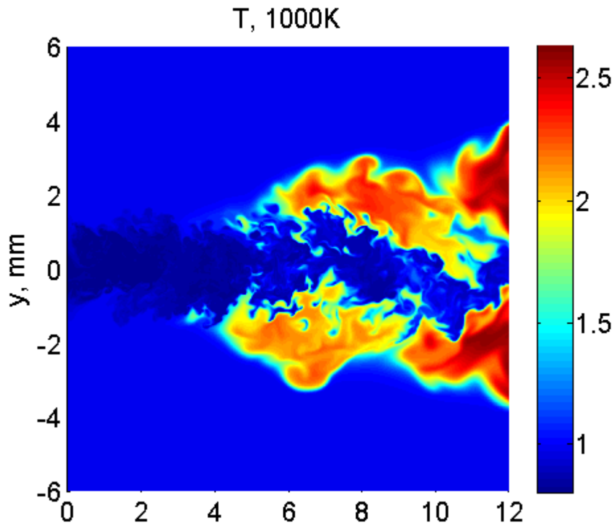




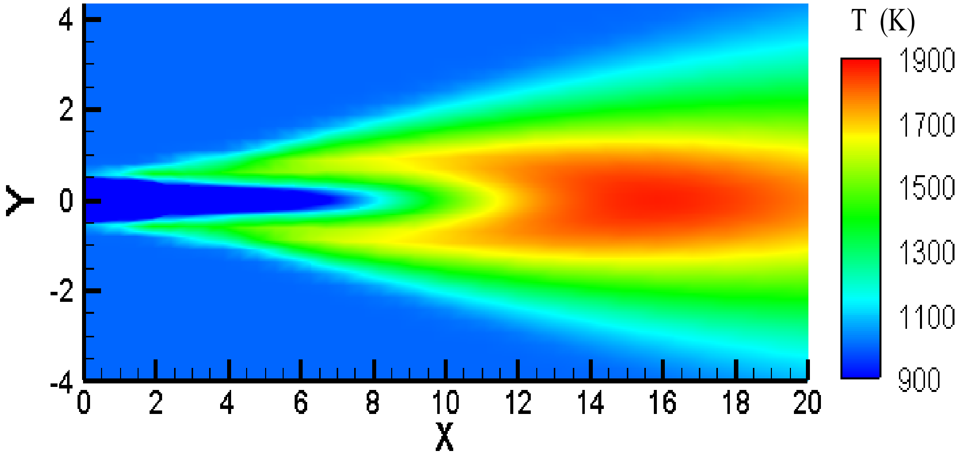
(Yoo et al, CNF, 2011)


Time: 0.00 (ms)
$\mathrm{sign}(\lambda_{exp}) \times \log_{10}(\max(1, \lambda_{exp}\ (s^{-1})))$
T, 1000K
$Y_{OH}/\max(Y_{OH})$
$(Y_{CO}+Y_{CO_2})$
y, mm
x, mm
0
1
2
3
0.5
1.5
2.5
6
4
2
0
-2
-4
-6
2.2
1.8
1.6
1.4
1.2
0.8
0.6
0.4
0.2
0.15
0.1
0.05

EDC for the lifted DME jet flame



DNS



RANS with EDC (by Pengfei Li)

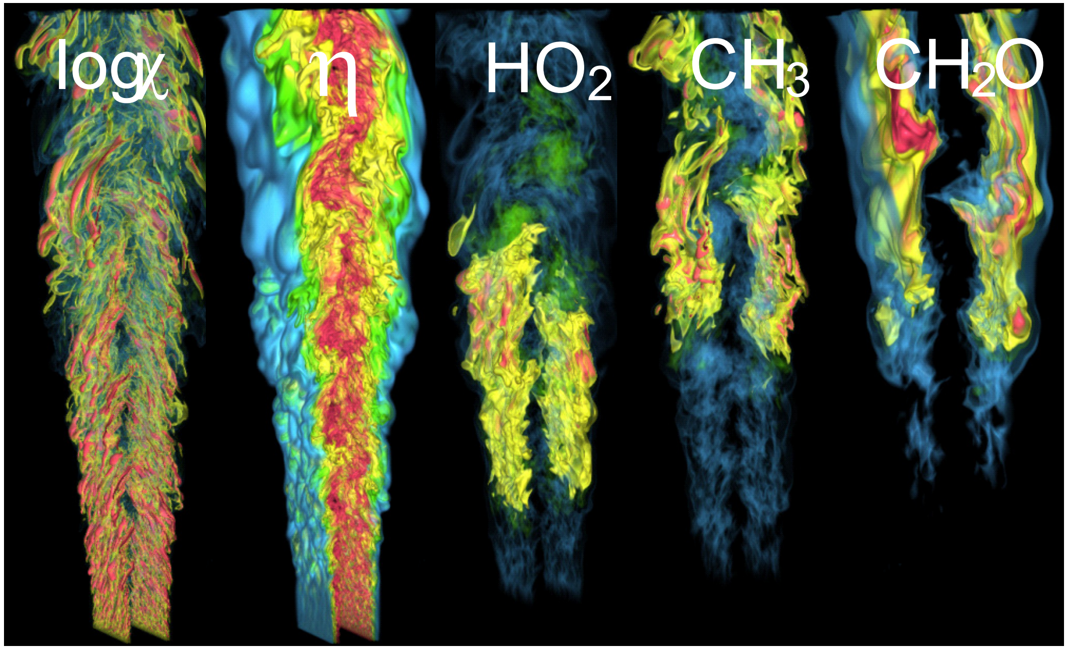
CEMA for Lifted Flames:
Ethylene Jet into Heated Coflowing Air

(Ignition, Extinction, Premixed flame fronts, Non-premixed flamelets)

Challenges for Diagnostics of DNS Data: Lifted Ethylene Jet Flame

- 3-D lifted ethylene jet flame (Yoo et al, POCI, 2011)
- 22-species reduced mechanism
- 1.3 billion grid points
- 14 million CPU hours

- Fuel: 18% C2H4+82%N2, 550K, 204m/s
- Air: 1550K, 20m/s
- Re: 10000
- Domain size: 30mm x 40mm x 6mm



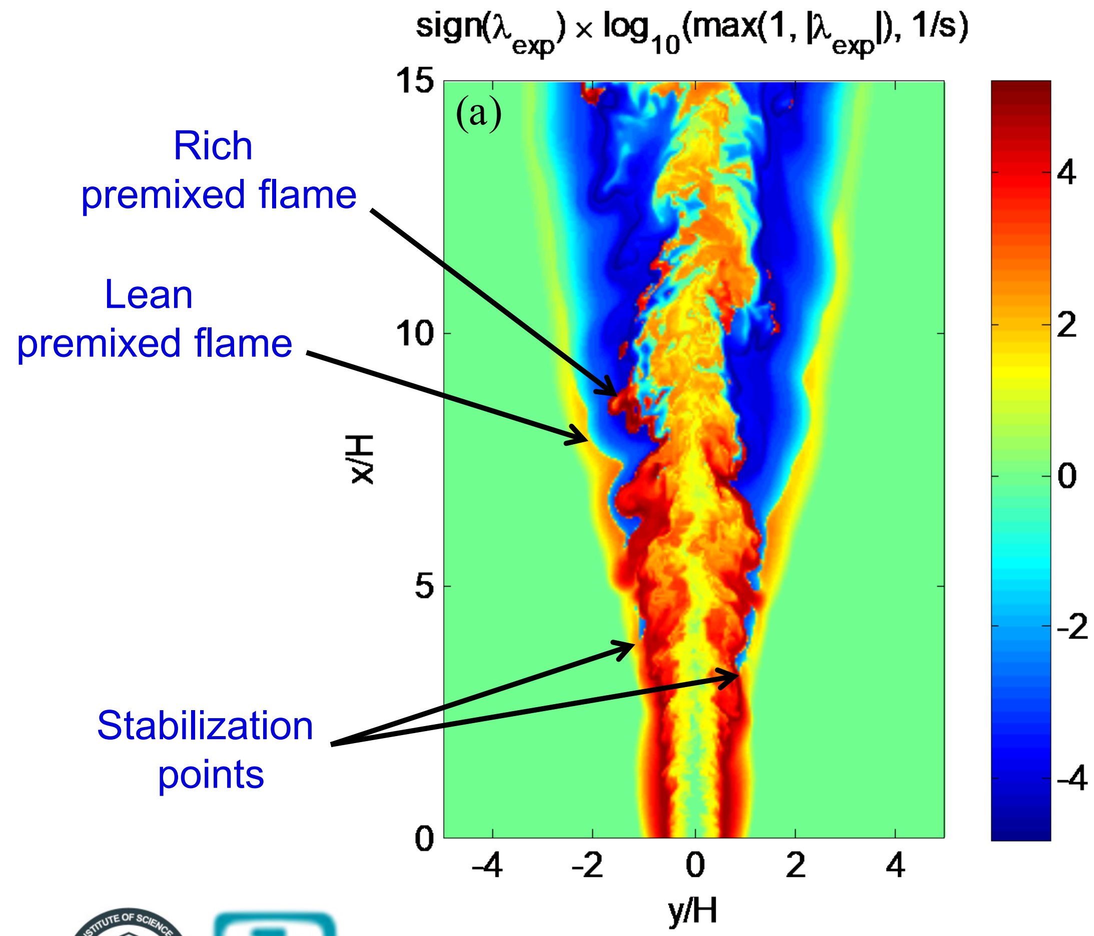
DNS by C.S. Yoo

Volume rendering by H. Yu

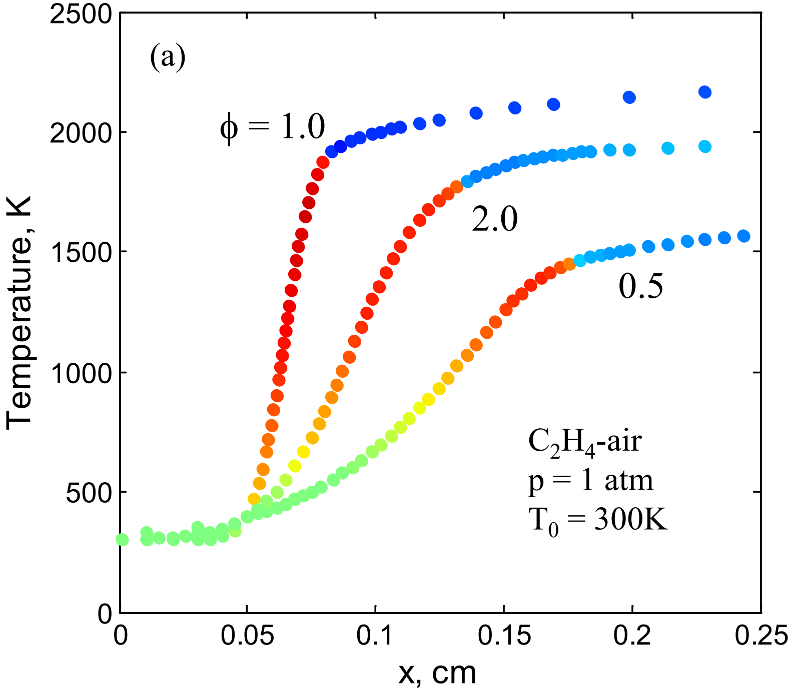
Systematic algorithms needed to extract salient information from massive datasets

Location of Premixed Flame Fronts

A 2-D Center Cut



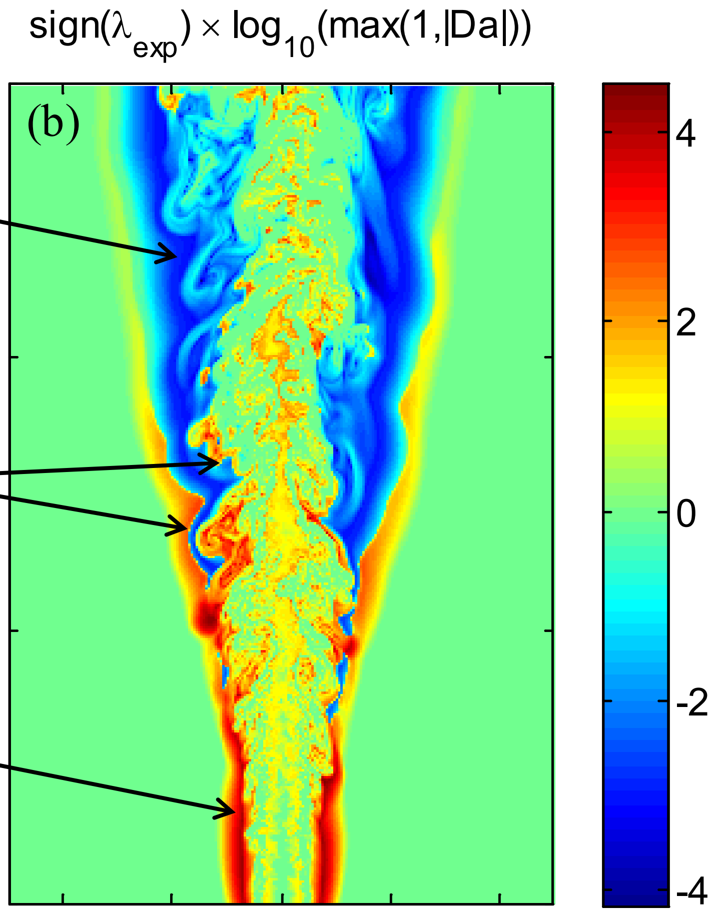
1-D Premixed Flames



CEM vs. Mixing: The Damköhler Number

$$Da = \mathrm{Re}(\lambda_e)\cdot\chi^{-1}$$

χ: scalar dissipation rate



$Da << -1$
Reaction zone in diffusion flames

$Da \sim 1$
Reaction zone in premixed flames

$Da >> 1$
auto-igniting zone

- The flame is stabilized by auto-ignition

Identification of Controlling Species & Reactions

- Explosion Index for Species

$$\mathbf{EI} = \frac{diag\,|\,\mathbf{a}_{\exp}\mathbf{b}_{\exp}\,|}{sum(diag\,|\,\mathbf{a}_{\exp}\mathbf{b}_{\exp}\,|)}$$

a: the right eigenvector

The correlation of the species with the chemical explosive mode

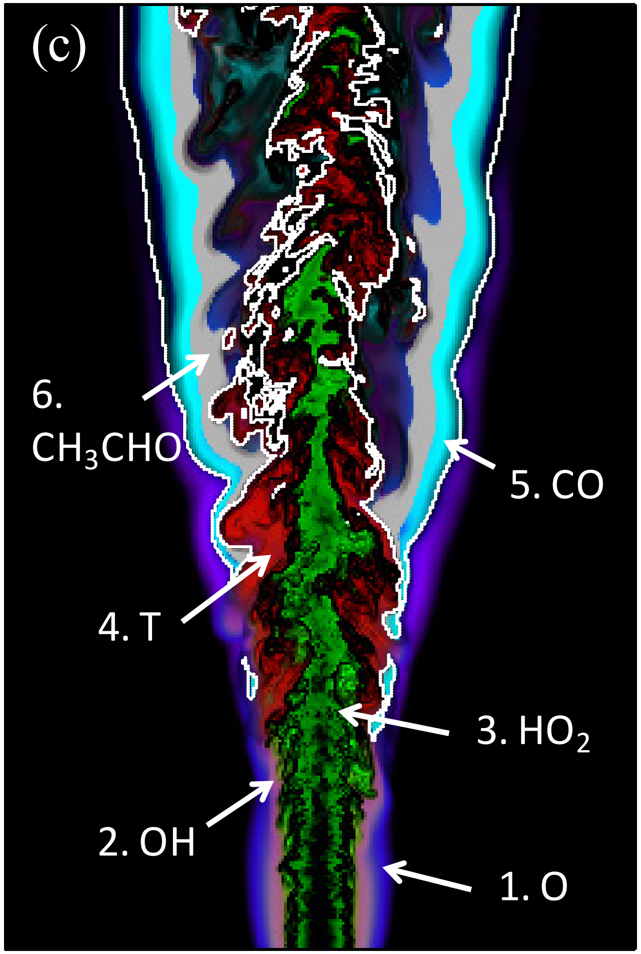
- Participation Index for Reactions

$$\mathbf{PI} = \frac{\left|\left(\mathbf{b}_{\exp}\cdot\mathbf{S}\right)\otimes\mathbf{R}\right|}{sum(|\left(\mathbf{b}_{\exp}\cdot\mathbf{S}\right)\otimes\mathbf{R}\,|)}$$

S: the stoichiometric coefficient matrix
R: the vector of net rates for the reactions
$\otimes$: element-wise multiplication

The contribution of the reactions to the chemical explosive mode

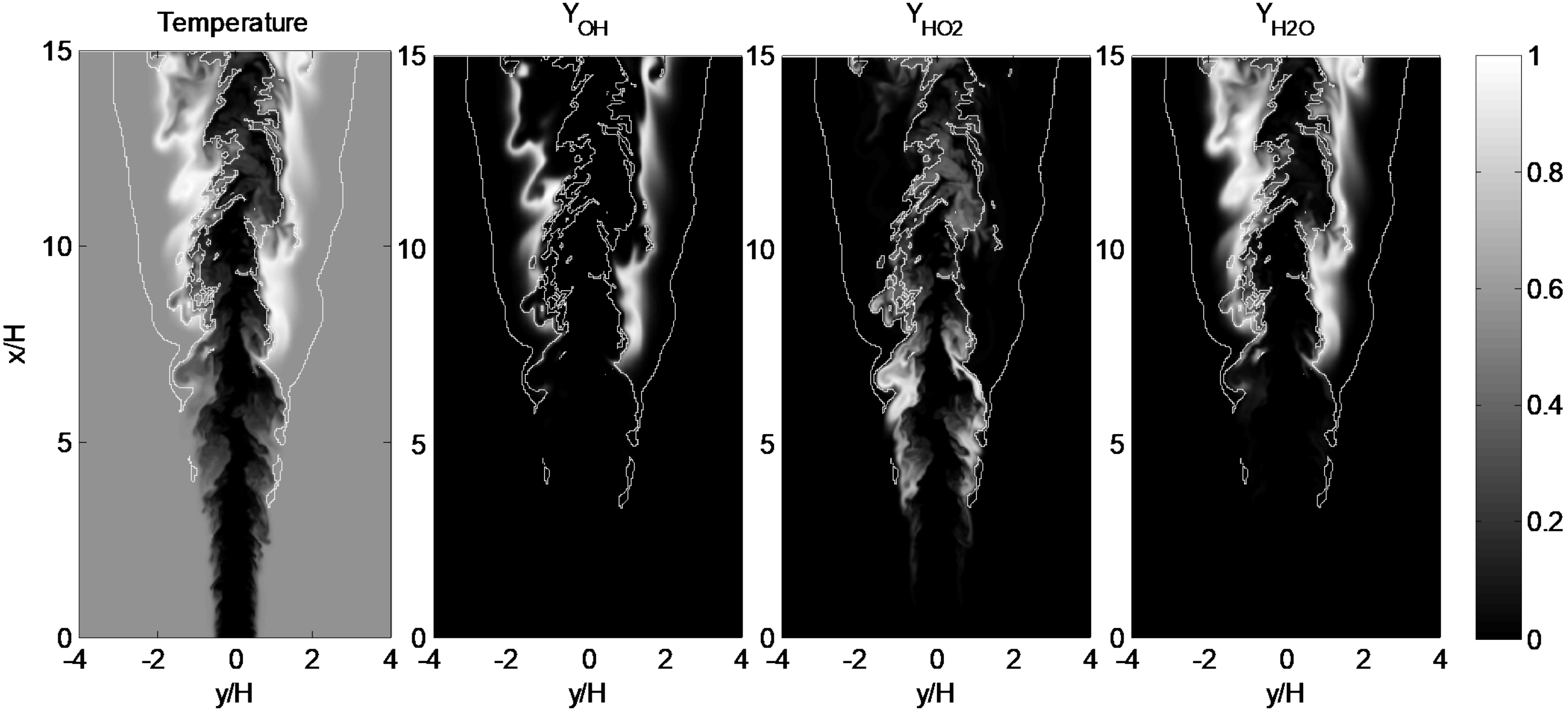
Rate-Limiting Species & Reactions in the Lifted Ethylene Flame



Da-weighted **EI**

Points	PI	Reactions
1	0.24 0.20	H + CH2O + M = CH3O + M O2 + CH3 = O + CH3O
2	0.15 0.14 0.13	O2 + C2H3 = O + CH2CHO O + C2H4 = CH3 + HCO HCO + M = H + CO + M
3	0.21 0.12 0.12	OH + C2H4 = H2O + C2H3 O2 + C2H3 = O + CH2CHO HCO + O2 = HO2 + CO
4	0.12 0.08 0.08	O2 + C2H3 = O + CH2CHO OH + C2H4 = H2O + C2H3 HCO + M = H + CO + M
5	0.65	OH + CO = H + CO2
6	0.57 0.20	CH3 + HCO + M = CH3CHO + M OH + CO = H + CO2

CEMA vs. Conventional Scalars



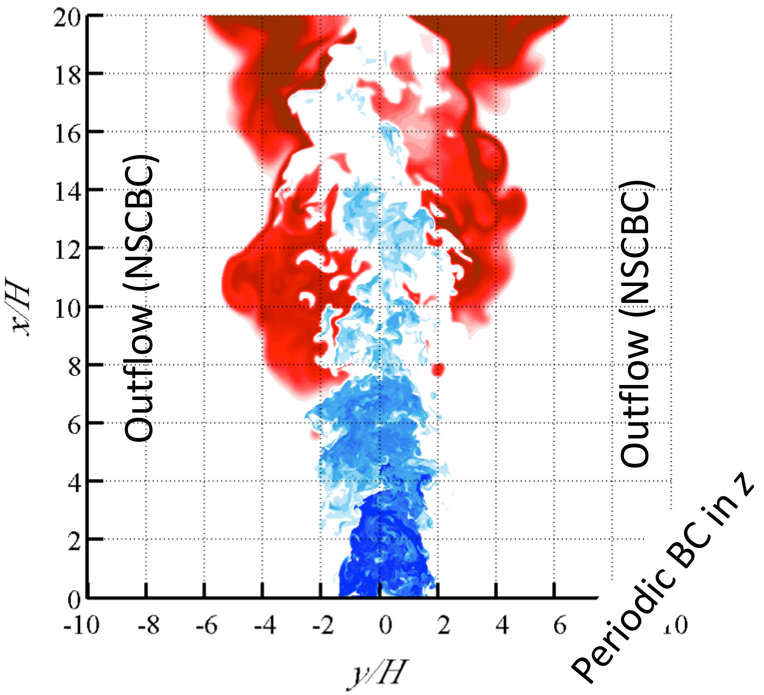
CEMA for Lifted Flames:
DME Jet into Heated Coflowing Air

(Ignition, Extinction, Cool flames, Premixed flame fronts, Non-premixed flamelets)

DNS of a Lifted DME Jet Flame

- DME (dimethyl ether) is a oxygenated diesel fuel
- 39 species reduced mechanism
- DNS configuration
  - Pressure: 5 atm
  - Reynolds number: $Re_j = 11{,}500, Ret = 1430$
  - Fuel ($0.1DME+0.9N_2$ by mole): $T_{fuel} = 500\,K;\ u_j = 138\,m/s$
  - Oxidizer (Air): $T_{air} = 1000\,K;\ u_{air} = 3\,m/s$
  - Jet width: $H = 0.6\,mm$
  - Domain size (L_x, L_y, L_z): $20H \times 20H \times 5H$
  - Number of grid points: $1512 \times 896 \times 384$
  - Large eddy scale: $l_E/H = 1.41$
  - Turbulence intensity: $u'/u_j = 0.2, u'/S_L = 31.4$

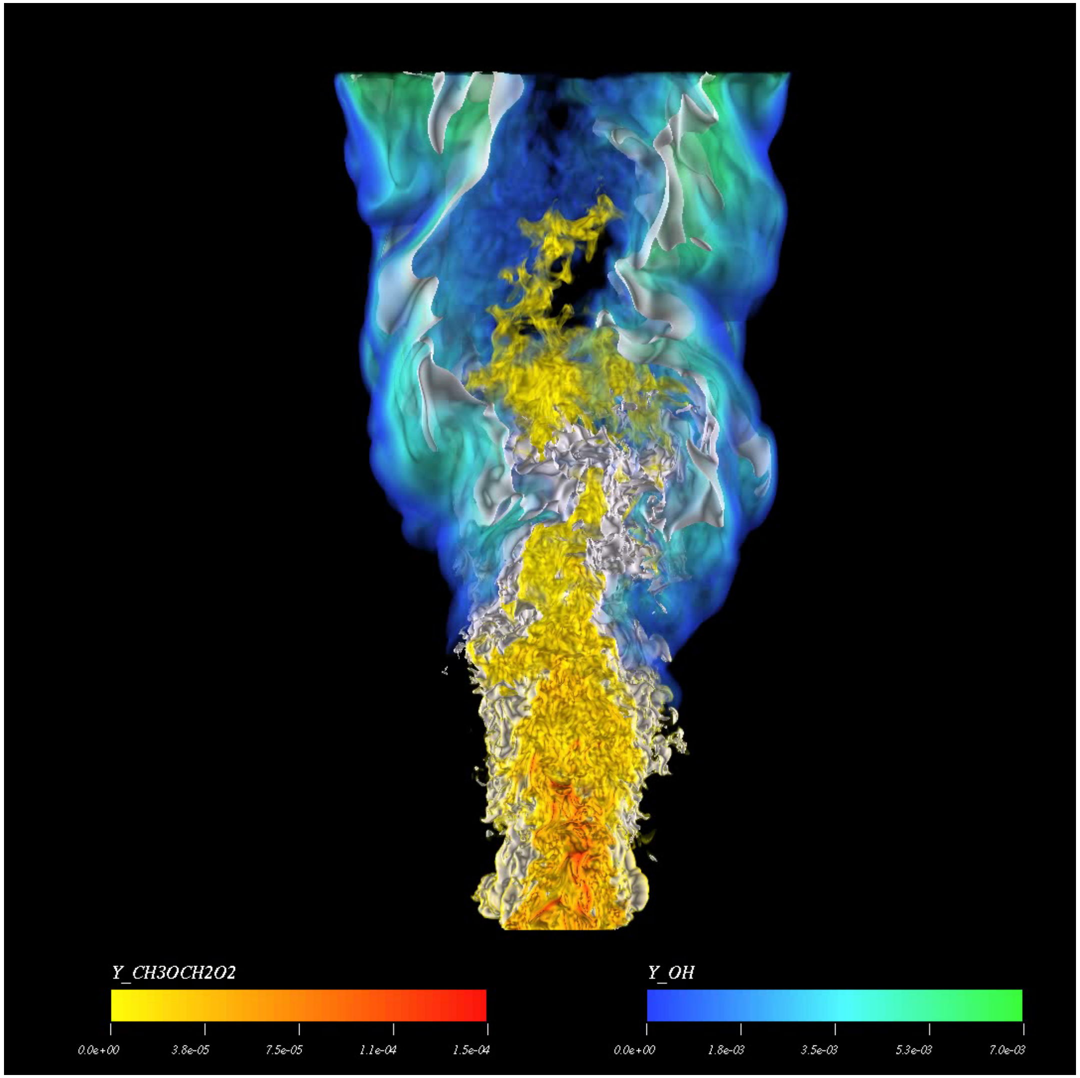
Outflow (NSCBC)



Inflow BC

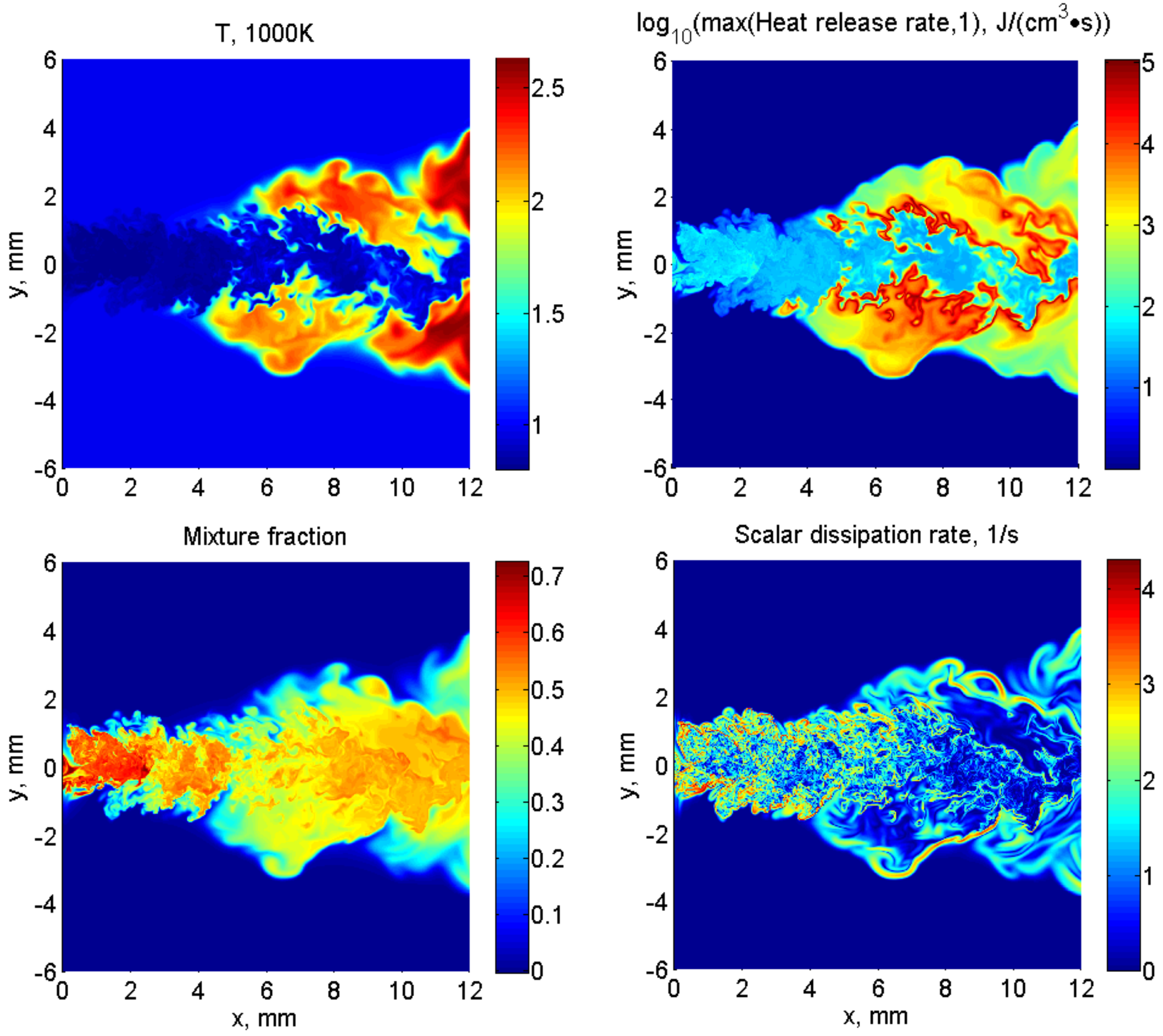
DNS by Yuki Minamoto

3-D Structure of the Lifted Flame



Volume rendering
by
Hongfeng Yu

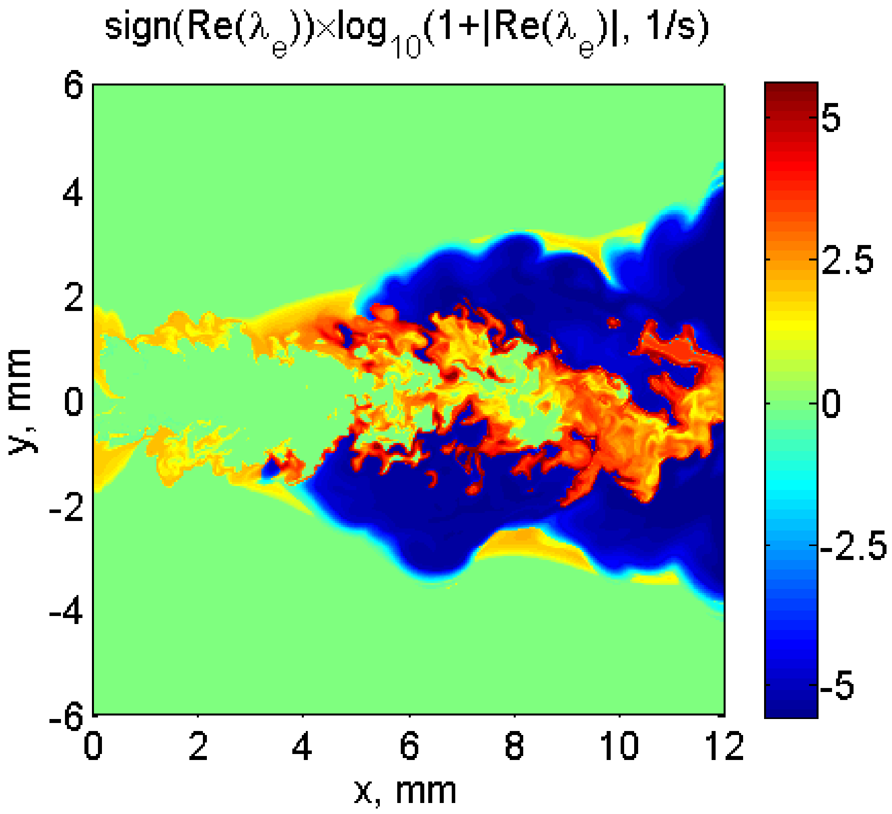
Selected Scalars Fields



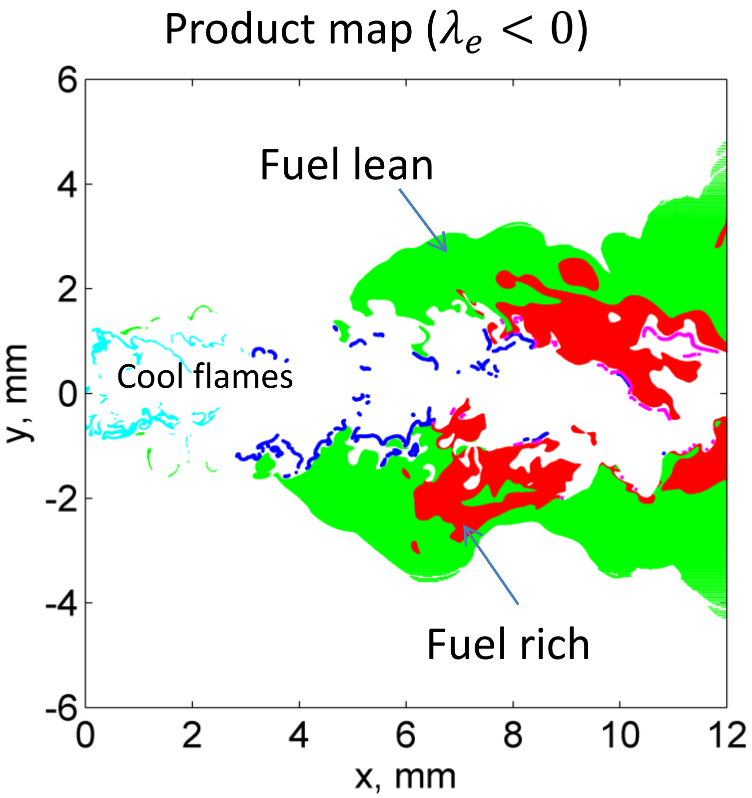
$z = 0$

$t = 0.22\ ms$

Flame Structure Visualized by CEMA



$\mathrm{sign}(\mathrm{Re}(\lambda_e))\times\log_{10}(1+|\mathrm{Re}(\lambda_e)|,\ 1/s)$

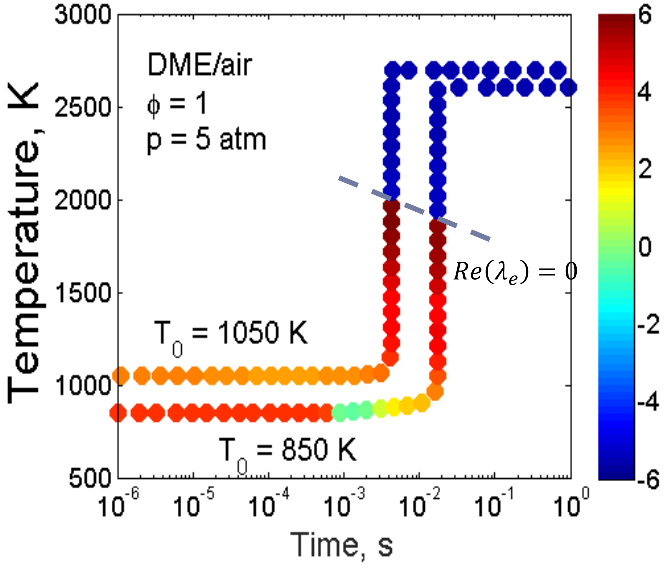


Product map ($\lambda_e < 0$)

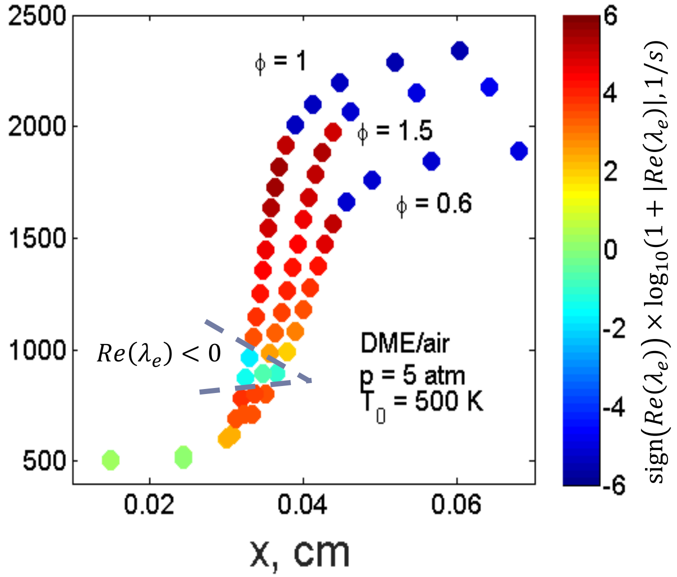
- Non-premixed flame core: $\lambda_e \ll 0$
- Igniting mixing layer $\lambda_e > 0$
- Premixed fronts are present $\lambda_e = 0$

Cool Flames: Active & Passive (1/2)

Auto-ignition

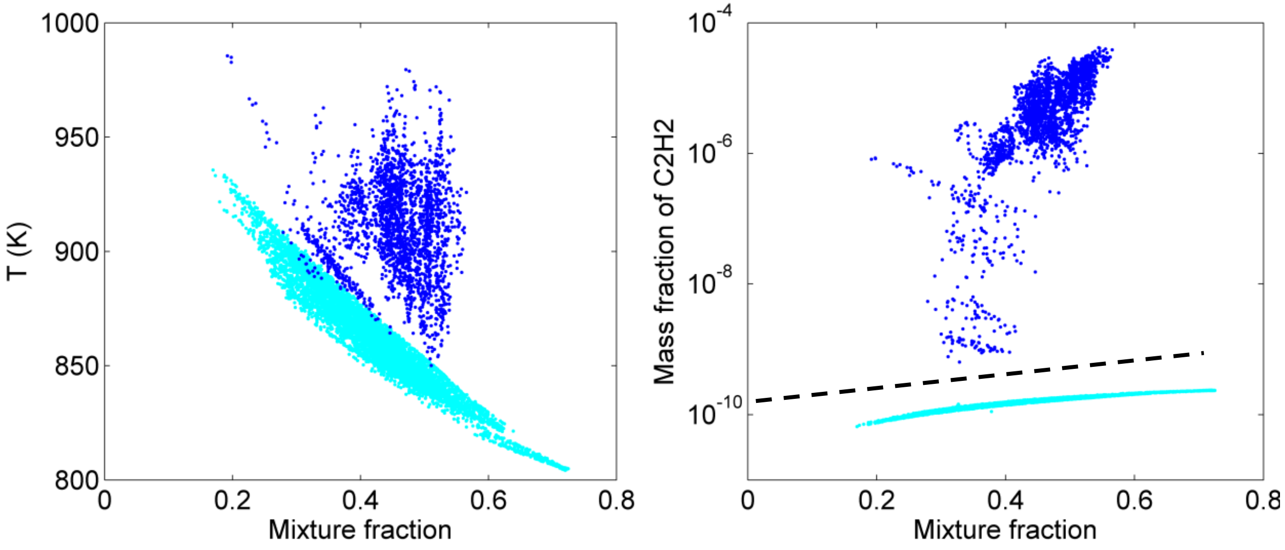


1-D premixed flames

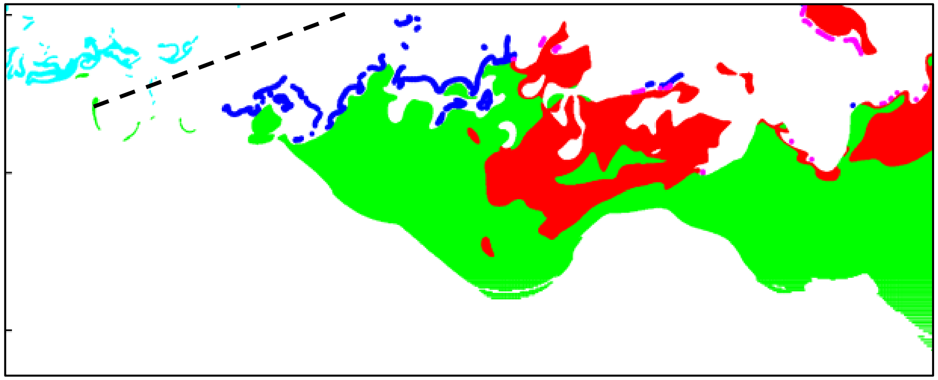


- Cool flames result from low-temperature chemistry (T < 1000K)
- Can be important for compression ignition engines
- Different cool flames: active versus passive
  - Active cool flames: a necessary stage in auto-ignition processes
  - Passive cool flames: a sub structure in premixed front propagation

Cool Flames: Active & Passive (2/2)

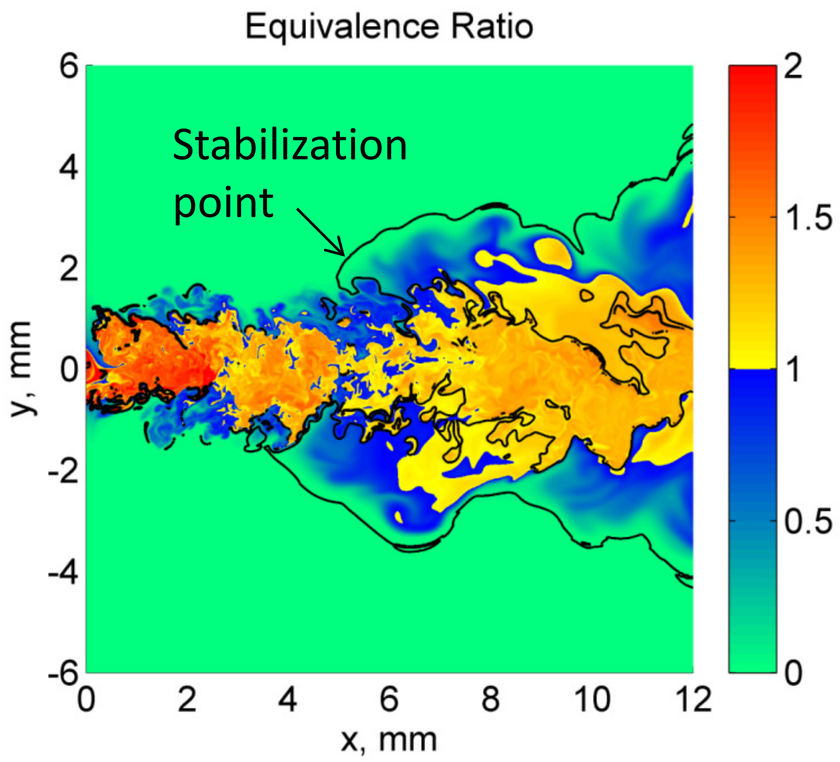

Temperature

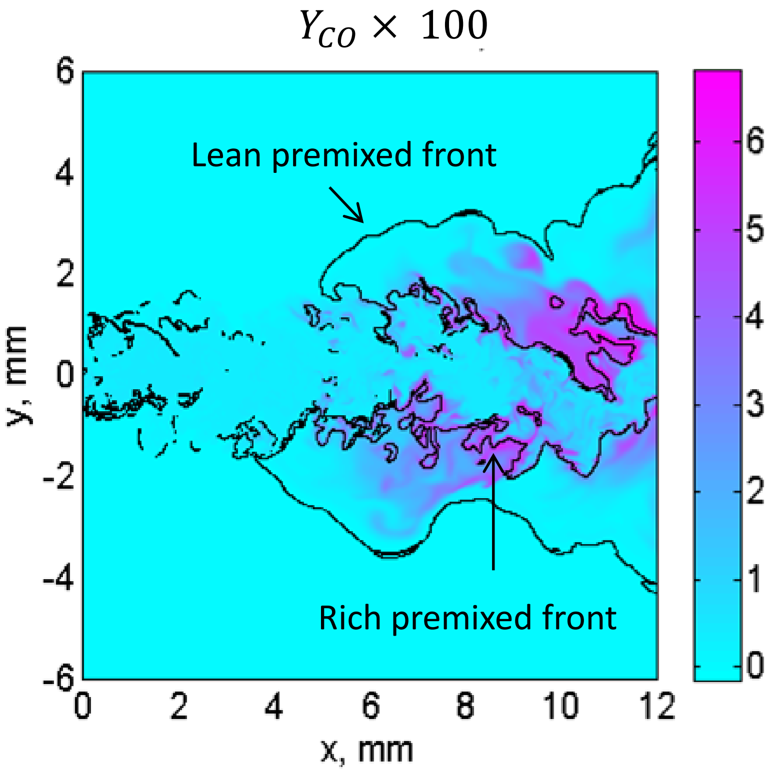
C_2H_2



- Passive & active cool flames overlap in temperature range (800-1000K)
- Signature of passive cool flames: trace amount of flame species from the reaction zone, e.g. C_2H_2

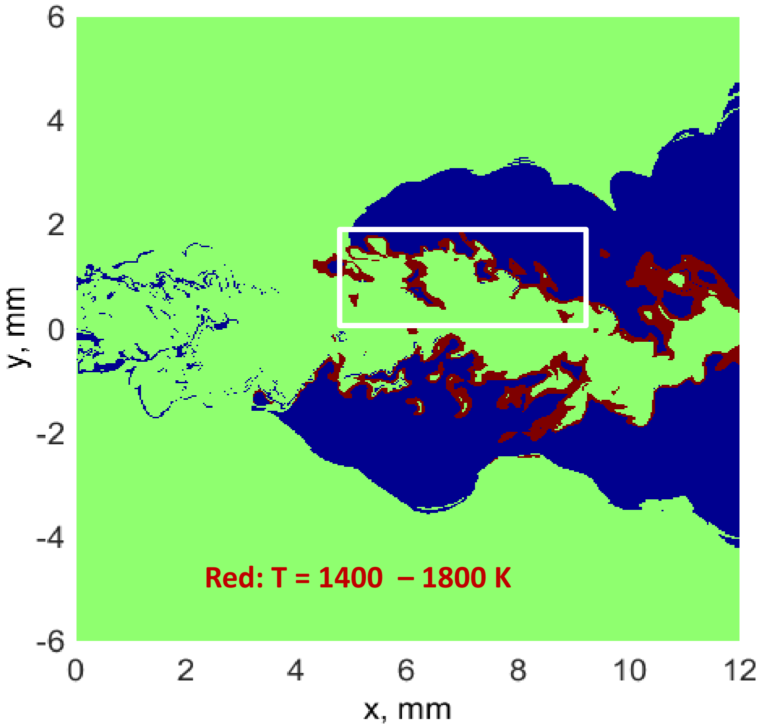
Premixed Flame Fronts

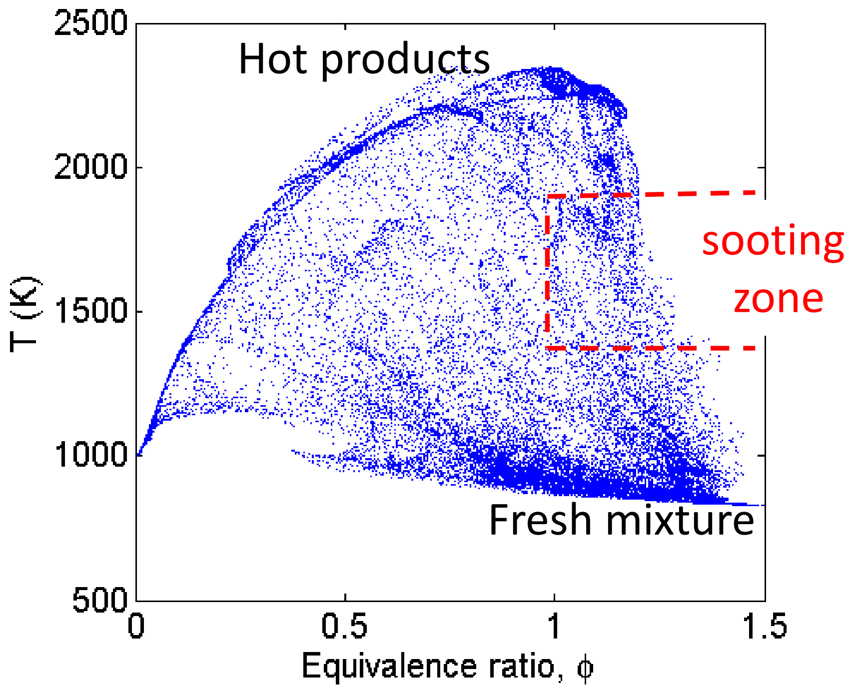




- Premixed fronts: $\lambda_e = 0$ (Black isoline)
- The stabilization point is the leading edge of the premixed fronts
- The rich premixed front is severely disturbed by intense turbulence

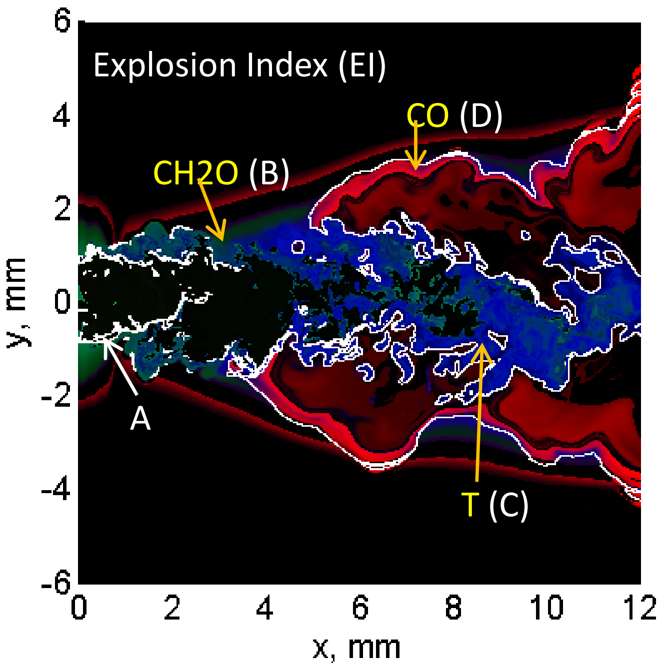
The Rich Premixed Front & Emissions





- Soot forms in a narrow temperature window, say 1400K-1800K (Glassman, 1997)
- Sooting window is largely within the rich premixed front
- NO concentrations jump across premixed flames
- The premixed front modeling is critical to predict emissions

Chemical Structure of the Lifted DME Flame



- Controlling species and reactions are zone dependent
- Participating species and reactions can be identified based on their contribution to the explosive mode

Explosion Index (EI) for Species
(Importance of a species to the CEM):

$$EI = \frac{diag|\boldsymbol{a}_e\boldsymbol{b}_e|}{sum(diag|\boldsymbol{a}_e\boldsymbol{b}_e|)}$$

$\mathbf{a}_{e,}$ $\mathbf{b}_{e}$: the right and left eigenvectors

Important species & reactions in different flame zones

Points	Location	EI, Species	PI, Reactions
A	x = 0.68mm y = -0.73mm	0.53, H_2 0.22, H_2O 0.07, CH_3OCH_3	0.10, R157: $CH_2OCH_2O_2H = OH + CH_2O + CH_2O$ 0.08, R136: $CH_3OCH_3 + HO_2 = CH_3OCH_2 + H_2O_2$ 0.08, R158: $CH_2OCH_2O_2H + O_2 = O_2CH_2OCH_2O_2H$
B	x = 3.2mm y = 1.4mm	0.44, CH2O 0.18, H2O2 0.12, HO2 0.11, T	0.15, R47: $CH_3 + HO_2 = CH_3O + OH$ 0.12, R48: $CH_3 + CH_3$ (+M) = C_2H_6 (+M) 0.10, R46: $CH_3 + O_2 = CH_2O + OH$ 0.09, R53: CH_3 + HO= = CH_4 + O2
C	x = 9.7mm y = -1.4mm	0.64, T 0.20, CH_2O 0.05, H_2O_2	0.12, R47: $CH_3 + HO_2 = CH_3O + OH$ 0.10, R48: $CH_3 + CH_3$ (+M) = C_2H_6 (+M) 0.09, R16: H_2O_2 (+M) = OH + OH (+M)
D	x = 7.8mm y = 3.0mm	0.81, CO 0.15, T	0.16, R9: H + O_2 (+M) = HO_2 (+M) 0.13, R25: CO + OH = CO_2 + OH 0.10, R1: H + O_2 = O + OH