

TSINGHUA-PRINCETON-COMBUSTION INSTITUTE
2022 SUMMER SCHOOL ON COMBUSTION

**MECHANISM REDUCTION AND STIFF
CHEMISTRY SOLVERS**

Tianfeng Lu
University of Connecticut
July 13,15, 2022



TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2022 SUMMER SCHOOL ON COMBUSTION

Schedule					
Beijing Time	July 11 (Mon.)	July 12 (Tue.)	July 13 (Wed.)	July 14 (Thu.)	July 15 (Fri.)
08:00 ~ 11:00			Mechanism Reduction and Stiff Chemistry Solvers Tianfeng Lu VMN: 52667557219		Mechanism Reduction and Stiff Chemistry Solvers Tianfeng Lu VMN: 52667557219
*10:00 ~ 12:00		Virtual Poster Session 10:00~12:00 VMN: 388239275		Virtual Lab Tour 10:00~12:00 VMN: 231842246	
14:00 ~ 17:00 Session I	Fundamental of Flames Suk Ho Chung VMN: 42399313194			Combustion in Microgravity and Microscale Kaoru Maruta VMN: 71656262918	
14:00 ~ 17:00 Session II	Soot Markus Kraft VMN: 39404905340			Current Status of Ammonia Combustion William Roberts VMN: 80506726244	
19:00 ~ 22:00 Session I	Combustion Chemistry and Kinetic Mechanism Development Tiziano Faravelli VMN: 35989357660				
19:00 ~ 22:00 Session II	Combustion Fundamentals of Fire Safety José Torero VMN: 57002781862				

Note:

¹Session I and Session II are simultaneous courses.

²VMN: Voov Meeting Number

Guidelines for Virtual Participation

1. General Guidelines

- Tencent Meeting software(腾讯会议) is recommended for participants whose IP addresses locate within Mainland China; Voov Meeting (International version of Tencent Meeting) is recommended for other IP addresses. The installation package can be found in the following links:
 - a) 腾讯会议
<https://meeting.tencent.com/download/>
 - b) Voov Meeting
<https://voovmeeting.com/download-center.html?from=1001>
- All the activities listed in the schedule are “registrant ONLY” due to content copyright.
- To facilitate virtual communications, each participant shall connect using stable internet and the computer or portable device shall be equipped with video camera, speaker (or earphone) and microphone.

2. Lectures

- The lectures are also “registrant ONLY”. Only the students who registered for the course can be granted access to the virtual lecture room.
- To enter the course, each registered participant shall open the software and join the conference using the corresponding Voov Meeting Number (VMN) provided in the schedule; only participants who show unique identification codes and real names as “xxxxxx-Last Name, First Name” will be granted access to the lecture room; the identification code will be provided through email.
- During the course, each student shall follow the recommendation from the lecturer regarding the timing and protocol to ask questions or to further communicate with the lecturer.
- For technical or communication issues, the students can contact the TA in the virtual lecture or through emails.
- During the course, the students in general will not be allowed to use following functions in the software: 1) share screen; 2) annotation; 3) record.

3. Lab Tour

- The event will be hosted by graduate students from Center for Combustion Energy, Tsinghua University and live streamed using provided Voov Meeting Number.
- During the activity, the participants will not be allowed to use following functions in the software: 1) share screen; 2) annotation; 3) record.
- Questions from the virtual participants can be raised using the chat room.

4. Poster Session

- The event will be hosted by the poster authors (one Voov Meeting room per poster) and live streamed using provided Voov Meeting Number.
- During the activity, the participants will not be allowed to use following functions in the software: 1) share screen; 2) annotation; 3) record.
- Questions from the virtual participants can be raised using the chat room or request access to audio and video communication.

Teaching Assistants

- **Fundamentals of Flame (Prof. Suk Ho Chung)**

TA1: Hengyi Zhou (周恒毅); zhouhy19@mails.tsinghua.edu.cn

TA2: Xinyu Hu (胡馨予); hxy21@mails.tsinghua.edu.cn

- **Combustion Chemistry and Kinetic Mechanism Development (Prof. Tiziano Faravelli)**

TA1: Shuqing Chen (陈舒晴); chen-sq19@mails.tsinghua.edu.cn

TA2: Jingzan Shi (史京瓚); sjz21@mails.tsinghua.edu.cn

- **Current Status of Ammonia Combustion (Prof. William Roberts)**

TA1: Yuzhe Wen (温禹哲); wyz20@mails.tsinghua.edu.cn

TA2: Haodong Chen (陈皓东); chd20@mails.tsinghua.edu.cn

- **Soot (Prof. Markus Kraft)**

TA1: Yuzhe Wen (温禹哲); wyz20@mails.tsinghua.edu.cn

TA2: Haodong Chen (陈皓东); chd20@mails.tsinghua.edu.cn

- **Combustion Fundamentals of Fire Safety (Prof. José Torero)**

TA1: Xuechun Gong (巩雪纯); gxc19@mails.tsinghua.edu.cn

TA2: Weitian Wang (王巍添); wwt20@mails.tsinghua.edu.cn

- **Combustion in Microgravity and Microscale (Prof. Kaoru Maruta)**

TA1: Hengyi Zhou (周恒毅); zhouhy19@mails.tsinghua.edu.cn

TA2: Xinyu Hu (胡馨予); hxy21@mails.tsinghua.edu.cn

- **Mechanism Reduction and Stiff Chemistry Solvers (Prof. Tianfeng Lu)**

TA1: Shuqing Chen (陈舒晴); chen-sq19@mails.tsinghua.edu.cn

TA2: Jingzan Shi (史京瓚); sjz21@mails.tsinghua.edu.cn



Mechanism/Model Reduction and Advanced Chemistry Solvers

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Tsinghua-Princeton-Combustion Institute
Summer School on Combustion
July 11-15, 2022



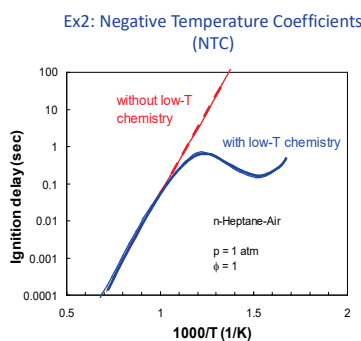
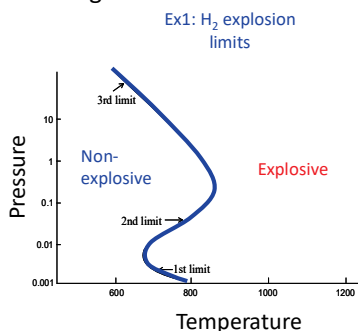
Outline

- Introduction
 - Detailed & reduced chemistry
 - Typical combustion problems and reaction state sampling
- Methods Mechanism reduction
 - Skeletal reduction
 - Timescale-based reduction
 - HyChem models for real fuels
 - Model/mechanism tuning
- Advanced chemistry solvers
 - Stiffness removal for explicit time integration
 - Operator splitting for stiff problems
 - Hybrid solvers
- Concluding remarks



Need of Realistic Chemistry

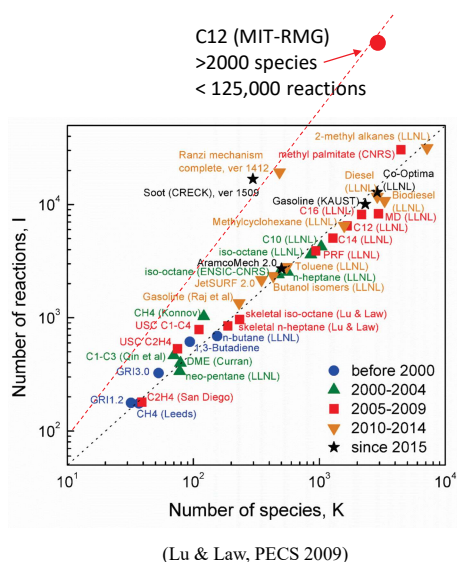
- One-step chemistry fails to capture many critical combustion features, e.g.



- Radical & chain reactions play a critical role in combustion
 - Self-catalytic
 - Various activation energy
 - Multi-steps in nature



Size of Detailed Chemistry



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



Example of Detailed Mechanisms

Hydrogen

9 species, 19 reactions

No.	Reaction	$B[\text{cm, mol, s}]$	α	$E_a(\text{kcal/mol})$
H₂-O₂ Chain Reactions				
(1)	$\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$	1.9×10^{14}	0	16.44
(2)	$\text{O} + \text{H}_2 \rightleftharpoons \text{H} + \text{OH}$	5.1×10^{14}	2.67	6.29
(3)	$\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$	2.1×10^{10}	1.51	3.43
(4)	$\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}$	3.0×10^{10}	2.02	13.40
H₂-O₂ Dissociation/Recombination				
(5)	$\text{H}_2 + \text{M} \rightleftharpoons \text{H} + \text{H} + \text{M}$	4.6×10^{19}	-1.40	104.38
(6)	$\text{O} + \text{O} + \text{M} \rightleftharpoons \text{O}_2 + \text{M}$	6.2×10^{15}	-0.50	0
(7)	$\text{O} + \text{H} + \text{M} \rightleftharpoons \text{OH} + \text{M}$	4.7×10^{18}	-1.0	0
(8)	$\text{H} + \text{OH} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M}$	2.2×10^{22}	-2.0	0
Formation and Consumption of HO₂				
(9)	$\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$	6.2×10^{19}	-1.42	0
(10)	$\text{HO}_2 + \text{H} \rightleftharpoons \text{H}_2 + \text{O}_2$	6.6×10^{13}	0	2.13
(11)	$\text{HO}_2 + \text{H} \rightleftharpoons \text{OH} + \text{OH}$	1.7×10^{14}	0	0.87
(12)	$\text{HO}_2 + \text{O} \rightleftharpoons \text{OH} + \text{O}_2$	1.7×10^{13}	0	-0.40
(13)	$\text{HO}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	1.9×10^{16}	-1.00	0
Formation and Consumption of H₂O₂				
(14)	$\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2$	4.2×10^{14}	0	11.98
		1.3×10^{11}	0	-1.629
(15)	$\text{H}_2\text{O}_2 + \text{M} \rightleftharpoons \text{OH} + \text{OH} + \text{M}$	1.2×10^{17}	0	45.50
(16)	$\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{H}_2\text{O} + \text{OH}$	1.0×10^{13}	0	3.59
(17)	$\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{H}_2 + \text{HO}_2$	4.8×10^{13}	0	7.95
(18)	$\text{H}_2\text{O}_2 + \text{O} \rightleftharpoons \text{OH} + \text{HO}_2$	9.5×10^{16}	2.0	3.97
(19)	$\text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2$	1.0×10^{12}	0	0
		5.8×10^{14}	0	9.56

GRI Mech 2.11

49 species, 279 reactions

No.	Reaction	Forward Rate Coefficient*		
		<i>A</i>	<i>b</i>	<i>E</i>
C-H-O Reactions				
1	O + O + M → O ₂ + M	1.20E+17	-1.0	0.0
2	O + H + M → OH + M	5.00E+17	-1.0	0.0
3	O + H ₂ → H + OH	5.00E+04	2.67	6,290
4	O + HO ₂ → OH + O ₂	2.00E+13	0.0	0.0
5	O + H ₂ O ₂ → OH + HO ₂	9.63E+06	2.0	4,000
6	O + CH → H + CO	5.70E+13	0.0	0.0
7	O + CH ₂ → H + HCO	8.00E+13	0.0	0.0
8 ^b	O + CH ₂ (S) → H ₂ + CO	1.50E+13	0.0	0.0
9 ^b	O + CH ₂ (S) → H + HCO	1.50E+13	0.0	0.0
10	O + CH ₃ → H + CH ₂ O	8.43E+13	0.0	0.0
11	O + CH ₄ → OH + CH ₃	1.02E+09	1.5	8,600
12	O + CO + M → CO ₂ + M	6.02E+14	0.0	3,000
13	O + HCO → OH + CO	3.00E+13	0.0	0.0
14	O + HCO → H + CO ₂	3.00E+13	0.0	0.0
15	O + CH ₂ O → OH + HCO	3.90E+13	0.0	3,540
... ..				
277	NH ₃ + H → NH ₂ + H ₂	5.40E+05	2.4	9,915
278	NH ₃ + OH → NH ₂ + H ₂ O	5.00E+07	1.6	955
279	NH ₃ + O → NH ₂ + OH	9.40E+06	1.94	6,460



The Law of Mass Action

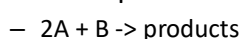
- For a reaction in general form

$$\nu_1' \text{M}_1 + \nu_2' \text{M}_2 + \dots + \nu_K' \text{M}_K = \nu_1'' \text{M}_1 + \nu_2'' \text{M}_2 + \dots + \nu_K'' \text{M}_K$$

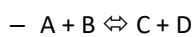
- The reaction rate of the reaction is given by

$$\omega_f = k_f(T) \prod_{i=1}^K c_i^{\nu_i'} \quad \omega_r = k_r(T) \prod_{i=1}^K c_i^{\nu_i''}$$

- For example:



$$\omega_f = k_f(T) c_A^2 c_B$$



$$\omega_f = k_f(T) c_A c_B$$

$$\omega_r = k_r(T) c_C c_D$$

- Calculation of reverse rate $K_c(T) = \frac{k_f(T)}{k_r(T)}$



Reaction Rates of Multi-Reaction Systems

- For a system with the following reactions

$$v_{i,1}''M_1 + v_{i,2}''M_2 + \dots + v_{i,K}''M_K \Leftrightarrow v_{i,1}'M_1 + v_{i,2}'M_2 + \dots + v_{i,K}'M_K \quad i=1,\dots,I$$

- The rate for the i th reaction is:

$$\omega_i = \omega_{if} - \omega_{ir} = k_{if}(T) \prod_{k=1}^K c_i^{v_{i,k}'} - k_{ir}(T) \prod_{k=1}^K c_i^{v_{i,k}''}$$

- In matrix form: $\frac{d\mathbf{c}}{dt} = \mathbf{S} \cdot \boldsymbol{\omega} + \dots = \sum_{i=1,I} \omega_i \mathbf{S}_i + \dots$

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

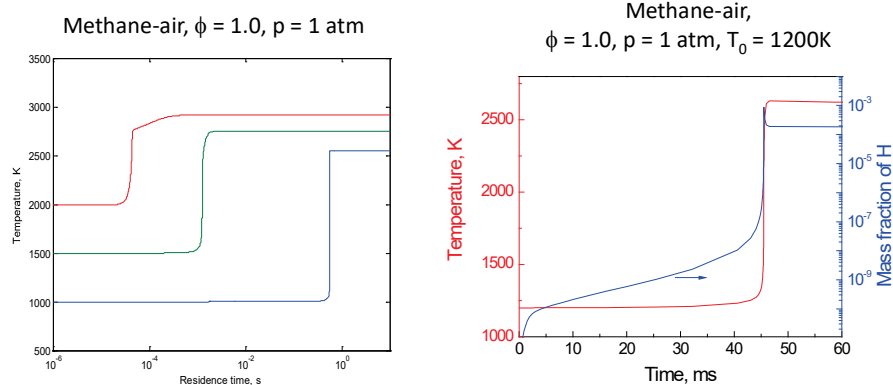


Identification of Important Pathways

- Target(s) of mechanism reduction can be represented by a set of reaction states
 - Reaction rates are determined by temperature and species concentrations (T, C), i.e. local reaction states
 - Different reaction pathways may control different reaction states; important reactions cannot be identified without concentration information, i.e. only using the rate parameters or potential surface information
- Reaction state sampling from representative reactors
 - Auto-ignition
 - Perfectly stirred reactors (PSR)
 - 1-D laminar flames
 - Turbulent flames
 - ...



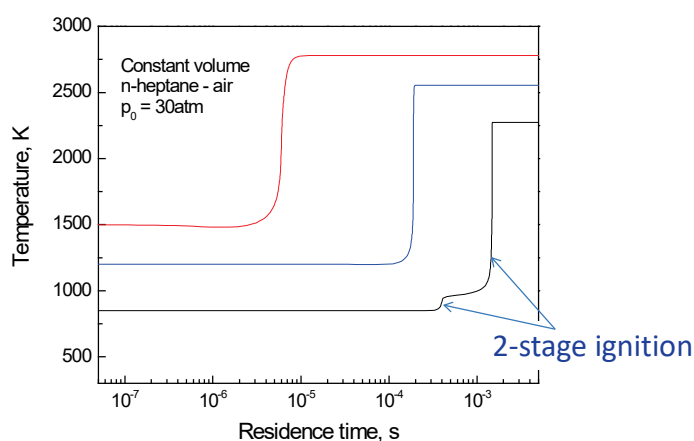
Sampling from Auto-ignition



- Auto-ignition typically involves both radical explosion and thermal runaway
- The radical explosion is slow (in milliseconds), and typically dominates ignition delay time (IDT)
- Thermal runaway is typically much faster (in microseconds)
- Representative for compression ignition engines, detonation waves etc.

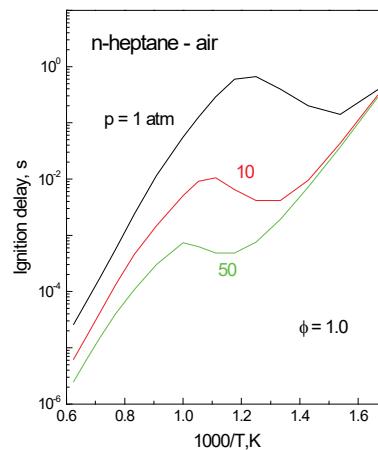
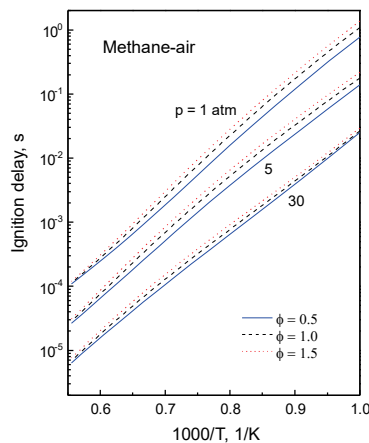


Auto-ignition of Large Hydrocarbons





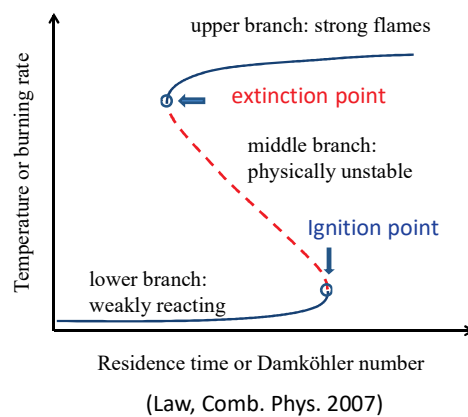
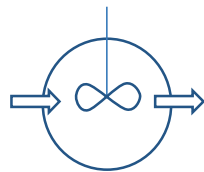
IDT: Low vs. High Hydrocarbons



Slopes indicates effective activation energy



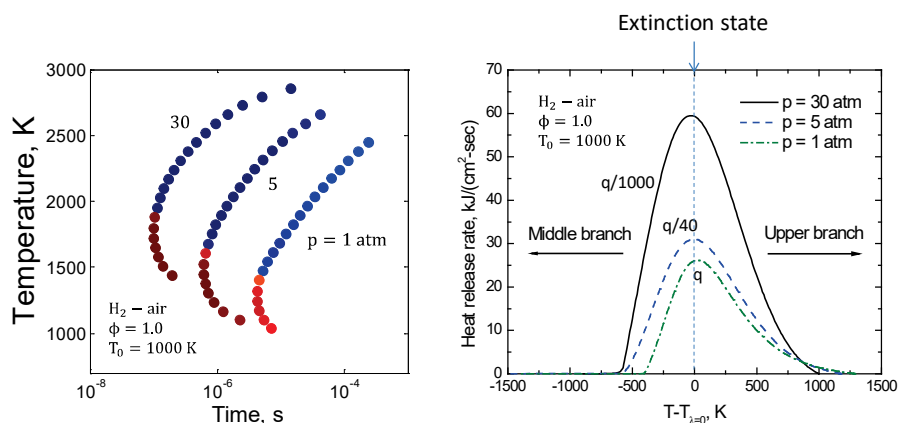
Sampling from Perfectly Stirred Reactors (PSR)



- Continuous-flow reactors feature S-curve responses
- Turning points: extinction/ignition states
- Representative to jet engines, flame holding etc.



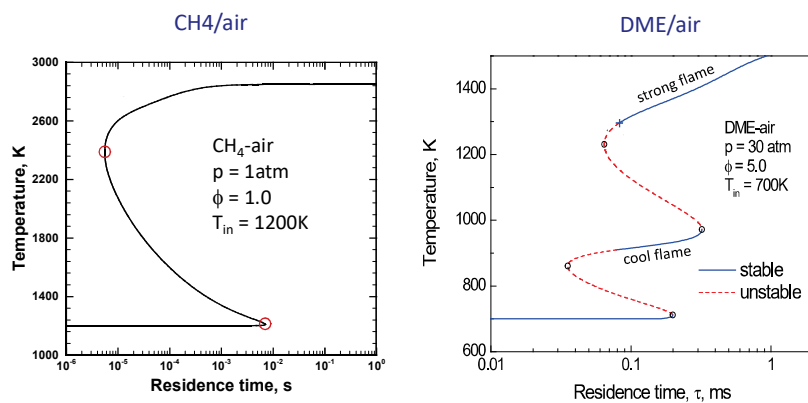
What Happens at Extinction State



- The extinction state indicates the limit of fast reaction

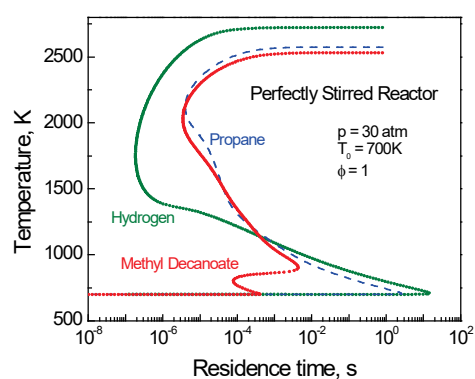


S-Curves for Different Fuels (1/2)





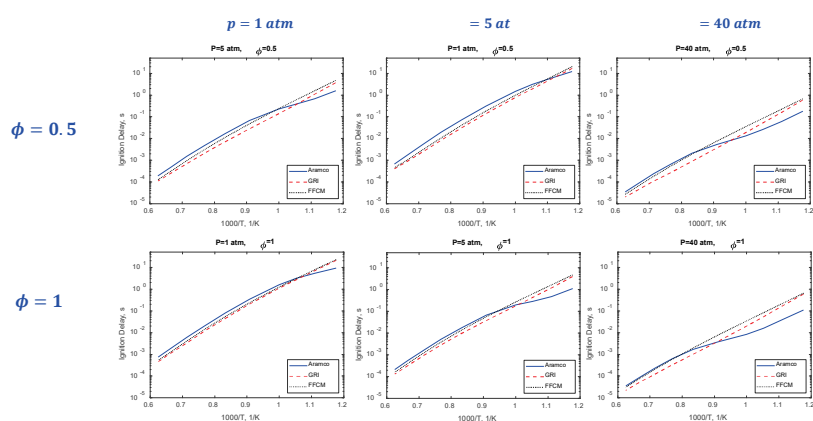
S-Curves for Different Fuels (2/2)



- H₂ is less prone to extinction compared with hydrocarbons:
H₂ can potentially burn much faster than hydrocarbons
- Large hydrocarbons tend to ignition faster due to the NTC behavior



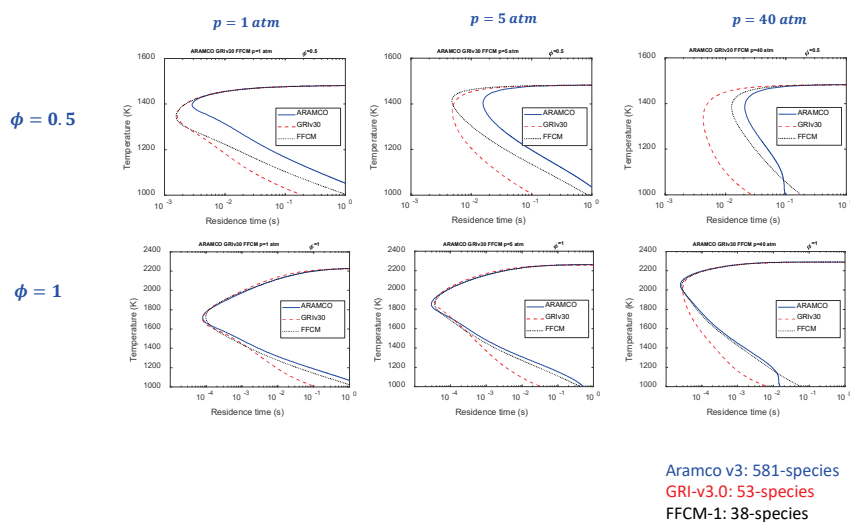
IDT Typically Well Calibrated



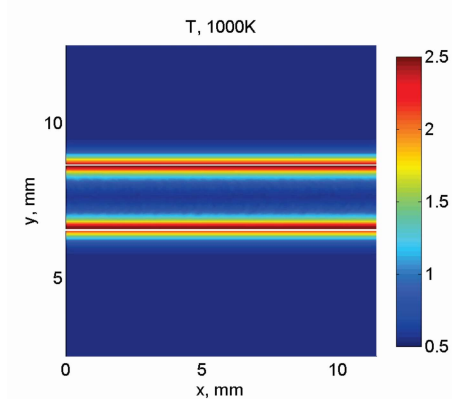
Aramco v3: 581-species
GRI-v3.0: 53-species
FFCM-1: 38-species



Large Differences in Fast Burning



Role of Extinction in Non-premixed flames



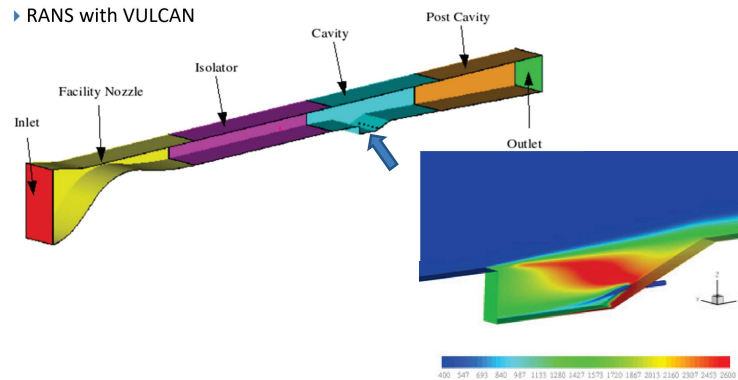
(Lignell et al., CNF 2011)

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



Role of Extinction – Flame Stabilization

- ▶ 3-D cavity stabilized ethylene flame at scramjet conditions
- ▶ C_2H_4 , 19 species
(from Qin et al 2000, 70 species)
- ▶ RANS with VULCAN

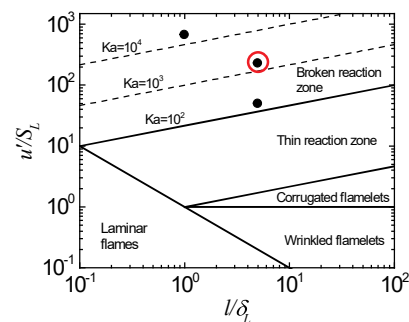


Liu et al, AIAA/ASM 2006



Role of Extinction in A Strongly Turbulent Premixed Flame

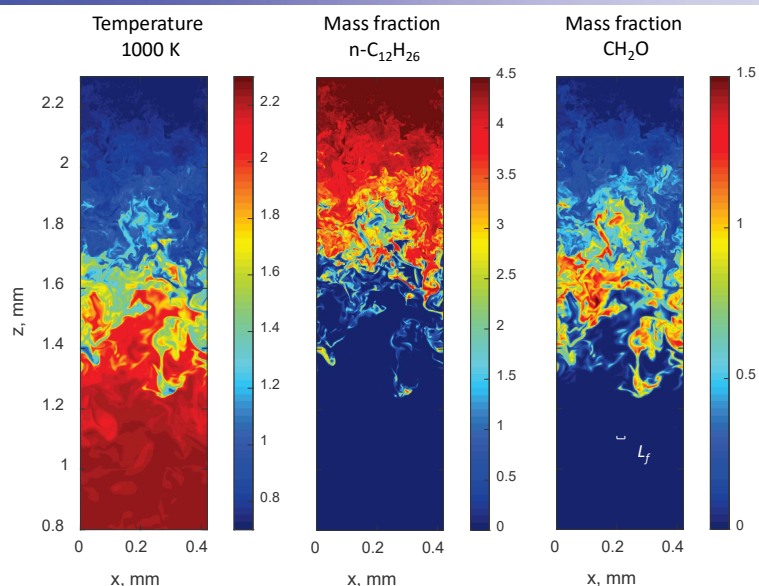
- ▶ DNS by A. Poludnenko
- ▶ Mechanisms:
 - ▶ C12: 24-species reduced model
- ▶ Engine-relevant conditions:
 - ▶ $P = 30 \text{ bar}$, $\phi = 0.7$, $T_0 = 700 \text{ K}$,
 - ▶ $Ka = 10^2, 10^3, 10^4$
- ▶ Domain size: $L \times L \times 8L$, $L = 0.042 \text{ cm}$ ($Ka = 10^3$)
- ▶ Number of grids: $512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



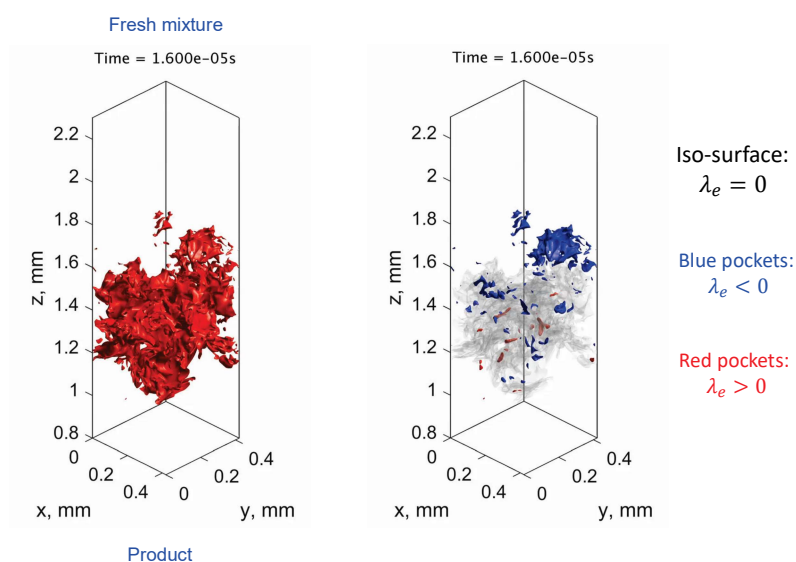
(Xu et al., CNF 2019)



Structure of the n-Dodecane Flame



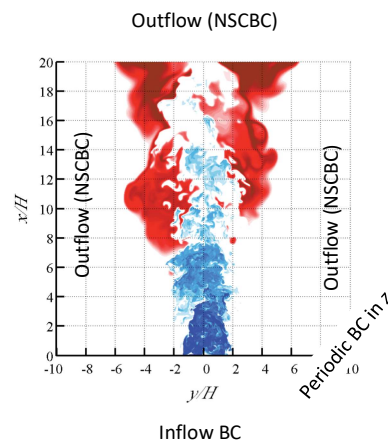
A 3-D nC12 Flame Structure





Role of Extinction - Partially Premixed Flames (1/2)

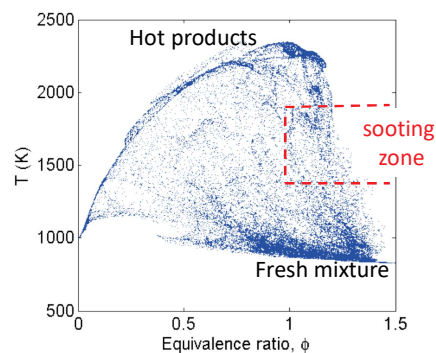
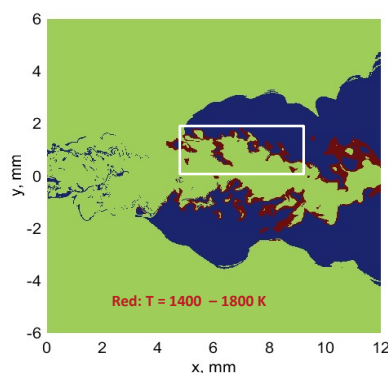
- DME (dimethyl ether) is a oxygenated diesel fuel
- 39 species reduced mechanism
- DNS configuration
 - Pressure: 5 at
 - Reynolds number:
 $Re_j = 11,500, Re_t = 1430$
 - Fuel (0.1DME+0.9N₂ by mole):
 $T_{fuel} = 500\text{ K}; u_j = 138\text{ m/s}$
 - Oxidizer (Air):
 $T_{air} = 1000\text{ K}; u_{air} = 3\text{ m/s}$
 - Jet width: $H = 0.6\text{ mm}$
 - 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:
 $u'/u_j = 0.2, u'/S_L = 31.4$



DNS by Yuki Minamoto



Role of Extinction - Partially Premixed Flames (2/2)



- Soot forms in a narrow temperature window, say 1400K-1800K (Glassman, 1997)
- Sooting window is largely within the rich premixed front
- Extinction/(re)ignition is frequent: low temperature & strong turbulence



Remarks on Reduction Targets & Reaction State Sampling

- IDT: for timescale of radical explosion
- Extinction residence time: for timescale of fastest reaction
- Other options: flame speed, counterflow extinction strain rates, species of interest ...
Note: flame speed, non-premixed flames are overall insensitive to ignition chemistry
- Reaction states should cover
 - Radical explosion in auto-ignition (1st & 2nd stage)
 - Thermal runaway/near-extinction

Skeletal Reduction



Skeletal Reduction

- Throwing away **unimportant** species and/or reactions
- What are **unimportant** species/reactions?
 - Some quantitative measurement is needed
 - Most measurements are for “importance” rather than “unimportance”
- Measures to identify important species/reactions
 - Reaction/production rates
 - Local sensitivity coefficients
 - Mass/element flux
 - Connectivity/popularity
 - ...
- Constructing a skeletal model with the identified important species/reactions?



Skeletal Reduction

- Throwing away **unimportant** species/reactions
- Example methods for skeletal reduction
 - Global sensitivity analysis (GSA): arbitrary reduction methods combined with reduced model validation
 - Local sensitivity analysis
 - Detailed reduction (Wang & Frenklach)
 - Principal component analysis (Turanyi et. al.)
 - Computational singular perturbation (CSP): (Lam)
 - Connectivity based methods, e.g. directed relation graph (DRG) (Lu & Law), DRG with error propagation (Pepiot & Pitsch), Path Flux Analysis (PFA) (Sun et al.), Element flux analysis (He et al), Betweenness centrality (Zhao et al)
 - ...
- Error control primarily affects computational cost
 - Validation of reduced models is typically most time consuming in reduction
 - Better error control requires fewer iterations in validation
- No reduction method is “wrong”, a reduced model is valid as long as it is tested working



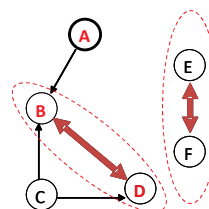
Skeletal Reduction with Directed Relation Graph (DRG) (Lu & Law 2005)

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

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

$v_{A,i}$: 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, \dots)
 - ▶ Edges: species dependence, $r_{AB} > \epsilon$
 - ▶ Starting vertices: target species
e.g. H, fuel, oxidizer, product, a pollutant, ...



- ▶ Graph search: [revised depth-first search \(RDFS\)](#) (Lu & Law, CNF 2006)

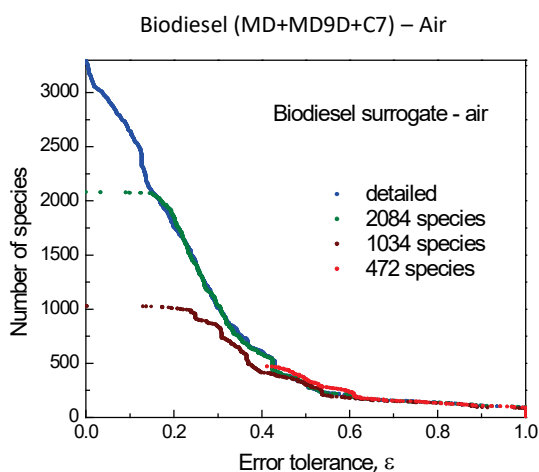


Remarks on Definitions of r_{AB}

- Relative error
- Sensitivity
- Flux
- Degree of connectivity
- ...



Reduction Curves of DRG

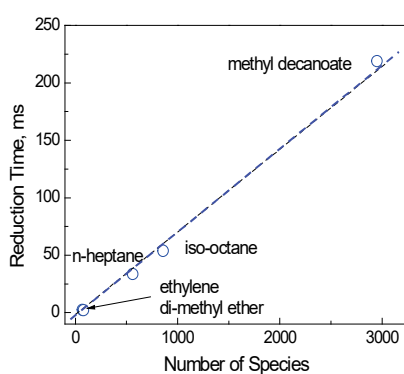


- ▶ Detailed mechanism (LLNL 2010):
 - ▶ 3329 species
 - ▶ 10,806 reactions
- ▶ Skeletal Mechanism
 - ▶ 472 species
 - ▶ 2337 reactions
- ▶ Error $\epsilon/(1 + \epsilon)$: ~30% (worst case)
- ▶ Parameter range:
 - ▶ p : 1-100 atm
 - ▶ ϕ : 0.5 - 2.0
 - ▶ Ignition & extinction
 - ▶ $T_0 > 1000\text{K}$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

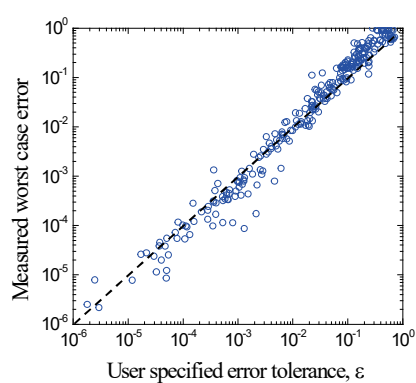


Efficiency and Error Control of DRG

- Linear reduction time
i.e. reduction time \sim # of species



- ▶ A priori error control
Worse-case measured error $\sim \epsilon$



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

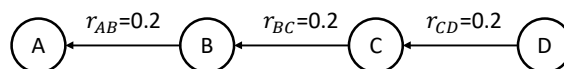


Other Methods Related to DRG

- DRG with expert knowledge (DRGX): (Lu et al, 2011)
- 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)
- ...
- Major differences are in the modeling of error propagation



Error Propagation in DRG and DRGEP



$$r_{AD}^{\text{DRG}} = \min(r_{AB}, r_{BC}, r_{CD}) = 0.2 \quad r_{AD}^{\text{DRGEP}} = r_{AB} \times r_{BC} \times r_{CD} = 0.008$$

- DRG: errors may not decay along the graph-search paths
 - Tends to **overestimate** the errors in species downstream
 - Tends to result in under-reduction
- DRGEP: errors geometrically decay along a graph-search path
 - Tends to **underestimate** the error in species downstream
 - Tends to result in over-reduction, and subsequent refinements



Linearized Error Propagation (LEP)

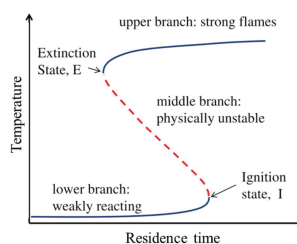
(Wu et al., CNF 2020)

- To estimate the propagation of small errors
- Based on PSR solutions (ignition & extinction)
 - Governing equations

$$(\mathbf{y} - \mathbf{y}_{in})/\tau = \mathbf{s}(\mathbf{y})$$

\mathbf{y} : mass fractions \mathbf{s} : chemical source term

\mathbf{y}_{in} : inlet mass fractions τ : residence time



(Law, *Combustion Physics*, 2006)

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Reduction Error Estimation in LEP

When a species r is eliminated in skeletal reduction, all the reactions involving r are eliminated from the detailed mechanism

$$(\mathbf{y}_k - \mathbf{y}_{k,in})/\tau = \mathbf{s}_k(\mathbf{y}_k) + \mathbf{s}_r(\mathbf{y}_k, \mathbf{y}_r)$$

\mathbf{y}_k : exact solution for the retained species
 \mathbf{y}_r : exact solution for a removed species
 \mathbf{s}_k : rates from kept reactions
 \mathbf{s}_r : rates from removed reactions
 \mathbf{y}'_k : solution after species elimination

The error in the kept species: $\delta \mathbf{y}_k \equiv \mathbf{y}_k - \mathbf{y}'_k$ can be linearized as:

$$\delta \mathbf{s}_k \approx \left(\frac{\mathbf{I}}{\tau} - \mathbf{J} \right)^{-1} \mathbf{s}_r, \quad \mathbf{J} = \partial \mathbf{s}_k / \partial \mathbf{y}_k$$

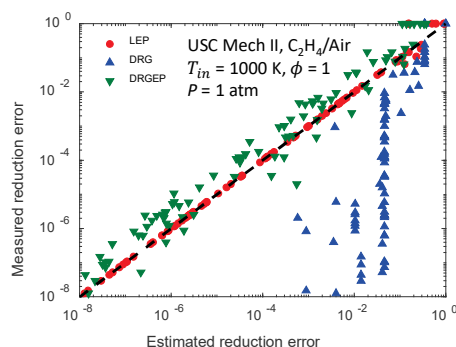
Estimated error in B induced by eliminating A

$$R_{AB}^{LEP} = \frac{|\delta y_A|}{|\delta y_A| + |y_A|} \Big|_{r=B}$$

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Comparison in Error Estimation



- LEP can estimate small reduction errors rather accurately
- DRG overestimates the reduction error, resulting in under reduction
- DRGEP underestimate the error, resulting in unsafe species elimination
- Better error modeling will always be helpful!

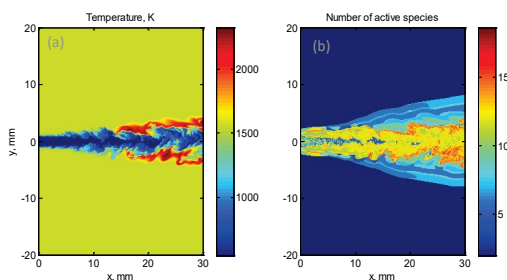
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On-the-fly Reduction with Dynamic Adaptive Chemistry (DAC)

- Number of active species varies dramatically spatially and temporally
- DRG-based methods feature low overhead for DAC (Long et al, 2009)

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



- Open issue for DAC: a species to become important in the future may not be identifiable at the current time



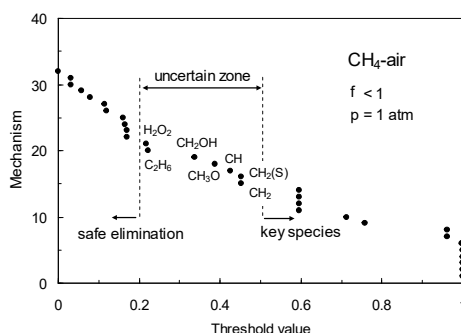
Global Sensitivity Analysis

- Trial & error: simple but working
- Time consuming
 - High computational cost for each perturbation
 - Large numbers of perturbation sequences
- Typically used as the last step in mechanism reduction



DRG Aided Sensitivity Analysis (DRGASA)

- Species cannot be eliminated by DRG may be eliminated through GSA
- Species elimination sequence exploits DRG information for reduced computational cost
- Resulting skeletal mechanism is minimal
- Substantially more computationally demanding than DRG



(Zheng et al, 2007;
Sankaran et al 2007)

Timescale Based Reduction



Timescale based Reduction

- Detailed chemistry involves vastly different timescales
- Fast chemical processes (species or reactions) quickly become exhausted and result in algebraic equations
- Example methods based on timescale analysis
 - Linear problems: eigenmode analysis
 - Intrinsic low dimensional manifold (ILDm) (Maas & Pope)
 - Computational singular perturbation (CSP) (Lam & Goussis)
 - Quasi steady state (QSS) & Partial equilibrium (PE) assumption
 - ...



Eigenmodes & Timescales in Linear Systems (1/2)

- A typical linear system of finite dimensions

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

– \mathbf{g} : vector of dependent variables

– $\mathbf{J} = \frac{\partial \mathbf{f}}{\partial \mathbf{g}}$: a constant matrix

- Eigenvalue (λ) & eigenvectors (\mathbf{a} , \mathbf{b}) of \mathbf{J}

– $\mathbf{b} \cdot \mathbf{J} = \lambda \mathbf{b}$ \mathbf{b} : left eigenvector (row)

– $\mathbf{J} \cdot \mathbf{a} = \lambda \mathbf{a}$ \mathbf{a} : right eigenvector (column)



Eigenmodes & Timescales in Linear Systems (2/2)

- Eigenmode ($f \equiv \mathbf{b} \cdot \mathbf{g}$)

$$LHS = \mathbf{b} \cdot \frac{d\mathbf{g}}{dt} = \frac{d(\mathbf{b} \cdot \mathbf{g})}{dt} = \frac{df}{dt}$$

$$RHS = \mathbf{b} \cdot \mathbf{J} \cdot \mathbf{g} = \lambda \mathbf{b} \cdot \mathbf{g} = \lambda f$$

$$\frac{df}{dt} = \lambda f$$

- Solution of the eigenmode

$$f = f_0 e^{\lambda t}$$

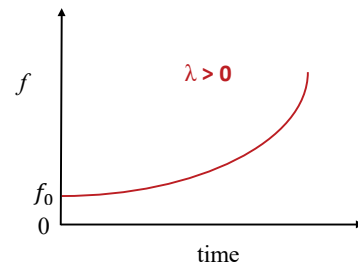
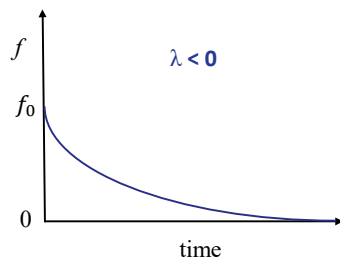
f_0 : initial condition

λ : reciprocal timescale of f



Dynamics of Real Eigenmodes

$$f = f_0 e^{\lambda t}$$

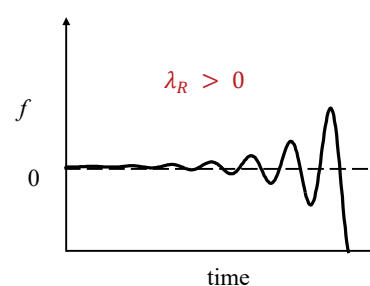
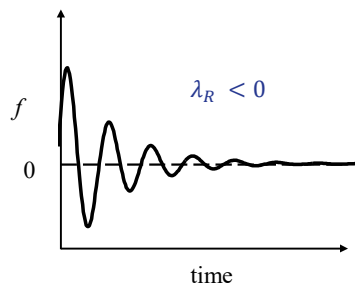


- $\lambda < 0$: decaying mode, $\frac{df}{dt} \ll \lambda f$, or $f = \mathbf{b} \cdot \mathbf{g} \approx 0$ when $\lambda t \ll -1$ (quasi steady state approximation of the eigenmode)
- $\lambda > 0$: explosive mode



Dynamics of Complex Eigenmodes

$$f = f_0 e^{\lambda t} \rightarrow \begin{aligned} f_R &= f_{R0} e^{\lambda_R t} \cos(\lambda_I t) - f_{I0} e^{\lambda_R t} \sin(\lambda_I t) \\ f_I &= f_{R0} e^{\lambda_R t} \sin(\lambda_I t) + f_{I0} e^{\lambda_R t} \cos(\lambda_I t) \end{aligned}$$



- $\lambda_R < 0$: decaying mode, $\frac{df}{dt} \ll \lambda f$, or $f = \mathbf{b} \cdot \mathbf{g} \approx 0$ when $\lambda_R t \ll -1$ (quasi steady state approximations of the eigenmodes, note: two algebraic equations)
- $\lambda_R > 0$: explosive mode
- λ_I : oscillatory frequency



Intrinsic Low Dimensional Manifold (ILDM) for Nonlinear Chemistry (1/2) (Maas & Pope 1992)

- The governing ODEs:

$$\frac{dy}{dt} = g(y)$$

y : vector of dependent variables (temperature, species concentrations etc.)

- Using the chain rule:

$$\frac{dg}{dt} = \frac{dg}{dy} \frac{dy}{dt} = J \cdot g$$

The Jacobian J is a function of y and time dependent

- Projected to an eigenvector ($b \cdot J = \lambda b$)

$$b \cdot \frac{dg}{dt} = b \cdot J \cdot g = \lambda b \cdot g$$

Note: $b \cdot \frac{dg}{dt} \neq \frac{d(b \cdot g)}{dt}$



Intrinsic Low Dimensional Manifold (ILDM) for Nonlinear Chemistry (2/2) (Maas & Pope 1992)

- “... the components of the velocity in direction of the eigenvectors corresponding to the n_f -most negative eigenvalues vanish.” (Maas & Pope CNF 1992)

$$b \cdot \frac{dg}{dt} = \lambda b \cdot g \approx 0$$

- Equivalent to assuming $b \cdot \frac{dg}{dt} = 0$



Computational Singular Perturbation (CSP)

(Lam & Goussis 1980s)

- When projecting the governing equations to an (eigen)vector \mathbf{b} :

$$\begin{aligned} \mathbf{b} \cdot \left\{ \frac{d\mathbf{g}}{dt} = \mathbf{J} \cdot \mathbf{g} \right\} \\ \downarrow \\ \frac{d\mathbf{b} \cdot \mathbf{g}}{dt} - \frac{d\mathbf{b}}{dt} \cdot \mathbf{g} = \mathbf{b} \cdot \mathbf{J} \cdot \mathbf{g} \\ \downarrow \\ \frac{df}{dt} - \frac{d\mathbf{b}}{dt} \cdot \mathbf{g} \\ \downarrow \\ \frac{df}{dt} = \lambda \left[\lambda^{-1} \left(\frac{d\mathbf{b}}{dt} + \mathbf{b} \cdot \mathbf{J} \right) \right] \cdot \mathbf{g} = \lambda \mathbf{b}_0 \cdot \mathbf{g} \end{aligned}$$

- \mathbf{b}_0 : refined CSP vector



CSP Refinement

- Reduced models:

$$\text{CSP:} \quad \lambda \mathbf{b}_0 \cdot \mathbf{g} = \frac{d(\mathbf{b}_0 \cdot \mathbf{g})}{dt} \approx 0$$

$$\text{ILDm/EigenD.:} \quad \lambda \mathbf{b} \cdot \mathbf{g} = \mathbf{b} \cdot \frac{d\mathbf{g}}{dt} \approx 0$$

- Putting multiple CSP vectors together

$$\mathbf{B}_{f0} = \mathbf{\Lambda}_f^{-1} \cdot \left(\frac{d\mathbf{B}_f}{dt} + \mathbf{B}_f \cdot \mathbf{J} \right), \quad \mathbf{\Lambda}_f = \left(\frac{d\mathbf{B}_f}{dt} + \mathbf{B}_f \cdot \mathbf{J} \right) \cdot \mathbf{A}_f$$

- \mathbf{B} : matrix of row vectors
- \mathbf{A} : matrix of column vectors, $\mathbf{A} = \mathbf{B}^{-1}$
- The scaling/blending (choice of $\mathbf{\Lambda}_f^{-1}$) is insignificant

- Reduced CSP models: $\mathbf{B}_{f0} \cdot \mathbf{g} \approx 0$, or $\left(\frac{d\mathbf{B}_f}{dt} + \mathbf{B}_f \cdot \mathbf{J} \right) \cdot \mathbf{g} \approx 0$



Remarks on $\frac{d\mathbf{b}}{dt}$

- Key to CSP, and if ignored the method degenerates to the standard linear algebra

$$\mathbf{b}_0 \equiv \lambda^{-1} \left(\frac{d\mathbf{b}}{dt} + \mathbf{b} \cdot \mathbf{J} \right) = \lambda^{-1} \mathbf{b} \cdot \mathbf{J} = \lambda^{-1} \lambda \mathbf{b} = \mathbf{b}$$

- Not well defined in general cases: \mathbf{b} is a subspace rather than a particular vector

$$\mathbf{b} \cdot \mathbf{J} = \lambda \mathbf{b}$$

- Difficult to compute even if direction and length of \mathbf{b} are both unique
- Ignored in the literature except for a few toy problems



Remarks on the Order of Accuracy

- Errors CSP vs. ILDM/Eigen-decomposition

$$\text{CSP:} \quad \lambda \mathbf{b}_0 \cdot \mathbf{g} = \frac{d(\mathbf{b} \cdot \mathbf{g})}{dt} \approx 0$$

$$\text{ILDM/E.D.:} \quad \lambda \mathbf{b} \cdot \mathbf{g} = \mathbf{b} \cdot \frac{d\mathbf{g}}{dt} \approx 0$$

- CSP can achieve higher order accuracy if

$$\left| \frac{d(\mathbf{b} \cdot \mathbf{g})}{dt} \right| = \left| \mathbf{b} \cdot \frac{d\mathbf{g}}{dt} + \frac{d\mathbf{b}}{dt} \cdot \mathbf{g} \right| \ll \left| \mathbf{b} \cdot \frac{d\mathbf{g}}{dt} \right|, \quad \text{or } \mathbf{b} \cdot \frac{d\mathbf{g}}{dt} \approx -\frac{d\mathbf{b}}{dt} \cdot \mathbf{g}$$

- For an eigenvector $\mathbf{b} = \alpha(t) \hat{\mathbf{b}}$, where α is the length of \mathbf{b} and $\|\hat{\mathbf{b}}\| = 1$

– $\hat{\mathbf{b}}$ is determined, in ideal cases, by the definition of eigenvector, $\mathbf{b} \cdot \mathbf{J} = \lambda \mathbf{b}$

– $\alpha(t)$ is arbitrary

$$- \mathbf{b} \cdot \frac{d\mathbf{g}}{dt} + \frac{d\mathbf{b}}{dt} \cdot \mathbf{g} = 0 \quad \rightarrow \quad \alpha \hat{\mathbf{b}} \cdot \frac{d\mathbf{g}}{dt} + \left(\alpha \frac{d\hat{\mathbf{b}}}{dt} + \frac{d\alpha}{dt} \hat{\mathbf{b}} \right) \cdot \mathbf{g} = 0 \quad \rightarrow \quad \alpha \frac{d(\hat{\mathbf{b}} \cdot \mathbf{g})}{dt} + \frac{d\alpha}{dt} (\hat{\mathbf{b}} \cdot \mathbf{g}) = 0$$

– Not all selections of α and $\frac{d\alpha}{dt}$ give higher order of accuracy



Eigenmode Analysis involving Non-chemical Processes

- Chemical rates $\mathbf{g} = \mathbf{g}(\mathbf{y})$ depend only on local thermodynamic states \mathbf{y} (p, T, concentrations)

$$\frac{D\mathbf{g}}{Dt} = \frac{d\mathbf{g}}{d\mathbf{y}} \frac{D\mathbf{y}}{Dt} = \mathbf{J} \cdot \frac{D\mathbf{y}}{Dt} = \mathbf{J} \cdot (\mathbf{g} + \mathbf{d} + \dots)$$

$$\mathbf{b} \cdot \left\{ \frac{D\mathbf{g}}{Dt} = \mathbf{J} \cdot (\mathbf{g} + \mathbf{d} + \dots) \right\}$$

$$\mathbf{b} \cdot \frac{D\mathbf{g}}{Dt} = \mathbf{b} \cdot \mathbf{J} \cdot (\mathbf{g} + \mathbf{d} + \dots) = \lambda \mathbf{b} \cdot (\mathbf{g} + \mathbf{d} + \dots)$$

$$\mathbf{b} \cdot (\mathbf{g} + \mathbf{d} + \dots) = \frac{1}{\lambda} \left(\mathbf{b} \cdot \frac{D\mathbf{g}}{Dt} \right) = O\left(\frac{1}{\lambda}\right) \approx 0$$

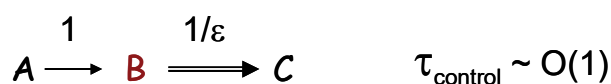
– \mathbf{d} : diffusion term

- Fast chemistry maintains a balance with slow chemistry and diffusion (and ...)
- Typically either a quasi steady state approximation (QSSA) or a partial equilibrium approximation (PEA)



Canonical Quasi Steady State Assumptions

- Example



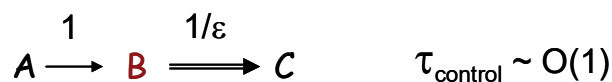
- Destruction much faster than creation
- B is a QSS species:

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

- Good news: QSSA for real chemistry is an approximately linear (or weakly nonlinear) problem



Canonical QSSA, $\varepsilon = 1/1000$



$$\frac{d}{dt} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = J \begin{pmatrix} A \\ B \\ C \end{pmatrix} \quad J = \begin{pmatrix} -1 & 0 & 0 \\ 1 & -1000 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

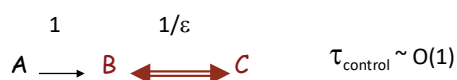
B =

$$\begin{pmatrix} 0.0010 & 0.0010 & 1.0000 \\ -0.0010 & \mathbf{1.0000} & 0 \\ 1.0000 & 0 & 0 \end{pmatrix} \quad \begin{matrix} \lambda_1 = 0 \\ \lambda_2 = \mathbf{-1000} \\ \lambda_3 = -1 \end{matrix}$$



Canonical Partial Equilibrium Assumptions

- An example:



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

$$\frac{B}{\varepsilon} \approx \frac{C}{\varepsilon} \quad \longrightarrow \quad B \approx C$$

- Not directly usable: $\frac{dC}{dt} = \frac{B}{\varepsilon} - \frac{C}{\varepsilon} = 0?$



Canonical PEAs, $\varepsilon = 1/1000$



$$\frac{d}{dt} \begin{pmatrix} A \\ B \\ C \end{pmatrix} = J \begin{pmatrix} A \\ B \\ C \end{pmatrix}$$

$J =$

$$\begin{pmatrix} -1 & 0 & 0 \\ 1 & -1000 & 1000 \\ 0 & 1000 & -1000 \end{pmatrix}$$

$B =$

$$\begin{pmatrix} 1 & 1 & 1 \\ -0.0005 & 1 & -1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\lambda_1 = 0$$

$$\lambda_2 = -2000$$

$$\lambda_3 = -1$$

$$\frac{dB}{dt} + \frac{dC}{dt} = -\frac{dA}{dt}$$

$$\frac{dB}{dt} - \frac{dC}{dt} = 0.0005 \frac{dA}{dt}$$



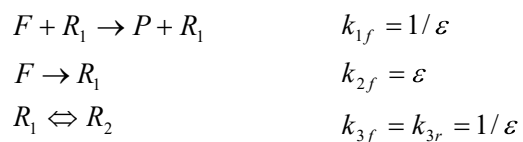
Properties of QSS & PE

QSS Species	PE involved species
Concentration $\sim O(\varepsilon)$	Concentration can be arbitrary
Can be removed from transport equations	Must be retained in transport equations (unless “modelled”)
# of equation = # of fast species: can directly solve for fast species concentrations – straightforward to apply	# of equation > # of fast species: can only related fast species, but not directly solving for their concentrations – more complicated to apply
Easy to apply, widely used	Difficult to apply for real life problems

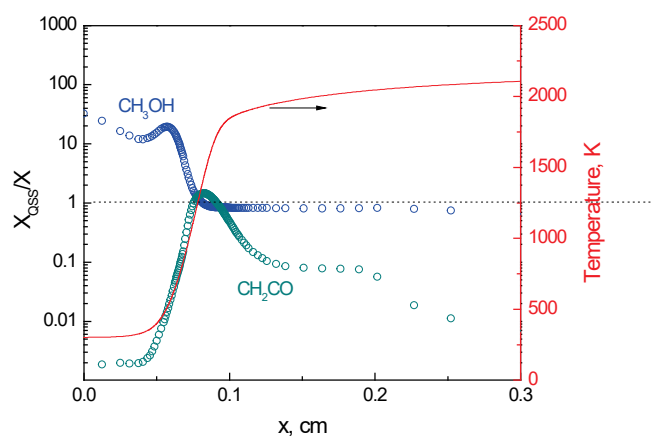


Identification of QSS Species

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



Error Induced by Bad QSSA





Selection of QSS Species

- A criterion based on fast-slow separation

$$\frac{d\mathbf{f}}{dt} = \mathbf{A} \cdot \mathbf{f}$$

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_{fast} & \\ & \mathbf{A}_{slow} \end{pmatrix} \quad \mathbf{A} = (\mathbf{A}_{fast} \quad \mathbf{A}_{slow}) \quad \mathbf{B} = \begin{pmatrix} \mathbf{B}_{fast} \\ \mathbf{B}_{slow} \end{pmatrix}$$

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

Necessary & sufficient condition:

$$Q_{i,i} < \varepsilon \iff \text{Species } i \text{ is in QSS}$$

ε : relative induced error



Selection of QSS Species (CH4)

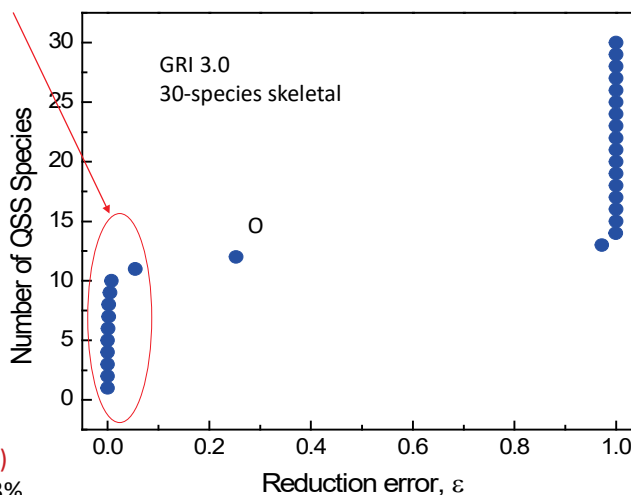
11 QSS species:

HCCO
CH₂
C₂H₅
C₂H₃
CH₃O
HCO
CH
CH₂(S)
CH₂OH
C
CH₂CHO

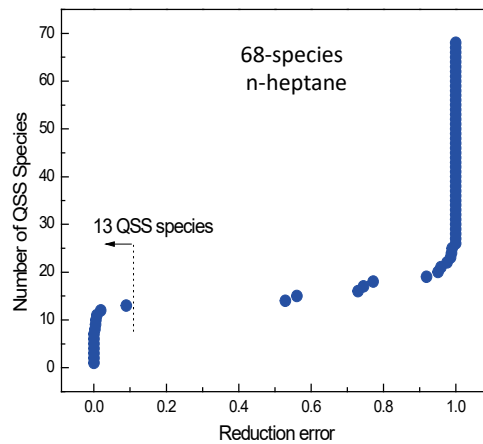
Reduced:

15-step (19 species)

Reduction error: 13%



Selection of QSS Species (heptane)



Next Step: Solving QSS Equations



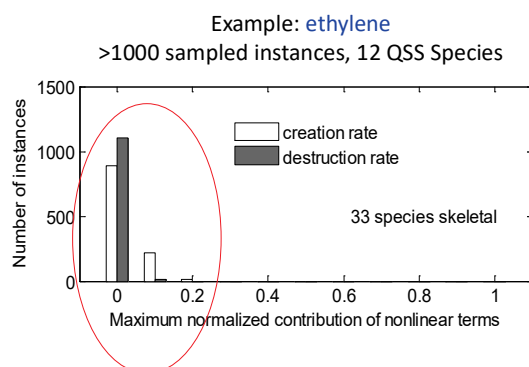
$$\frac{dy_{QSS}}{dt} = \mathbf{g}_{QSS}(\mathbf{y}_{QSS}; \mathbf{y}_{major}, p, T) = \mathbf{0}$$

- 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: $O(\varepsilon^2)$



Analytic Solution of LQSSA

Equation LQSSA:

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

↖
↑
↖

Destruction rate
Creation Rate involving other QSS species
Creation Rate involving major species

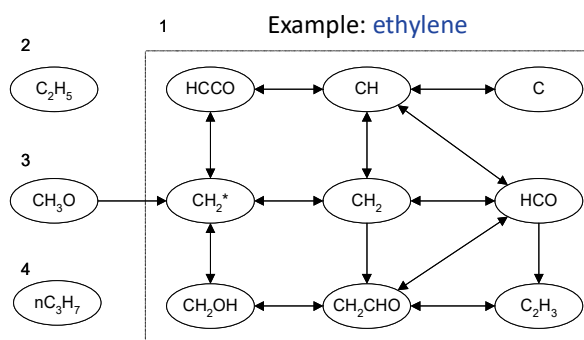
Standard form: $x_i = \sum_{j \neq i} A_{ij} x_j + A_{i0}$ $A_{ij} \geq 0, A_{i0} \geq 0$

- Gaussian elimination $\sim N^3$
- The coefficient matrix **A** is **sparse**

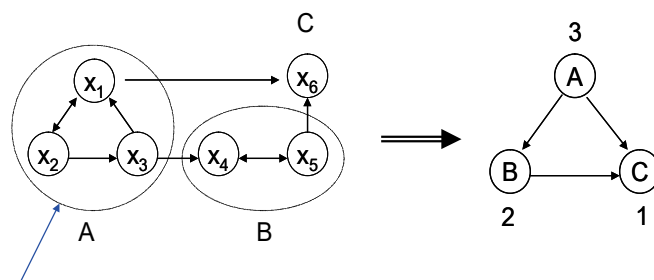


QSS Graph (QSSG)

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



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

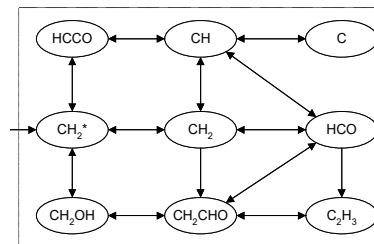
- Treat SCC as composite vertex
- Acyclic graph obtained by topological sort
- Species groups can be solved **explicitly** in topological order



Solving Implicit Kernels

- Paper & pencil:
eliminate the most isolated variables first

- Systematic: **a spectral method**



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

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

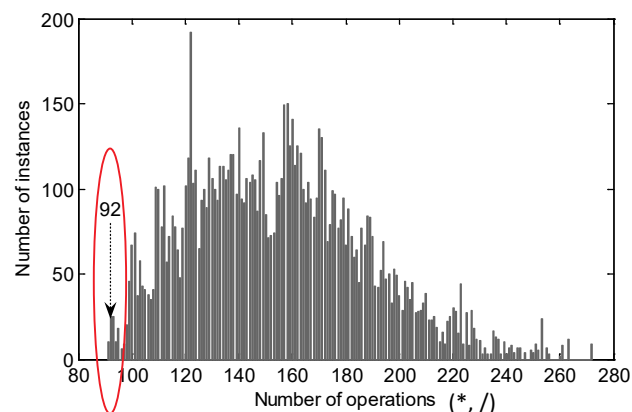
$$L_{ij} = E_{ij} / \sum_{k=1}^M E_{kj}$$

\mathbf{c} : Expansion cost vector,
 \mathbf{L} : Averaging operator
 \mathbf{E} : the adjacency matrix



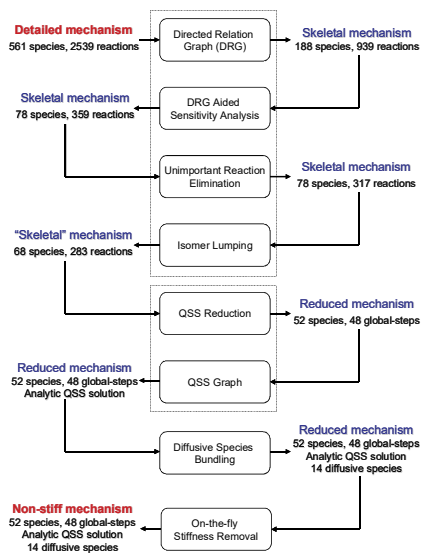
Efficiency of the Analytic Solution

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





A Systematic Reduction Approach



Sample reduced mechanisms:

- ▶ CH_4 (GRI3.0): 53 → 19 species
- ▶ C_2H_4 (USC Mech II): 75 → 22 species
- ▶ DME (Zhao et al): 55 → 30 species
- ▶ Ethanol (Mittal et al): 145 → 28 species
- ▶ n-Heptane (LLNL): 561 → 52 species
- ▶ iso-Octane (LLNL): 874 → 99 species
- ▶ PRF (LLNL): 1271 → 116 species
- ▶ n-Dodecane (LLNL): 2115 → 106 species
- ▶ Biodiesel (LLNL): 3299 → 115 species

▶ Download at <http://www.engr.uconn.edu/~tlu/mechs>

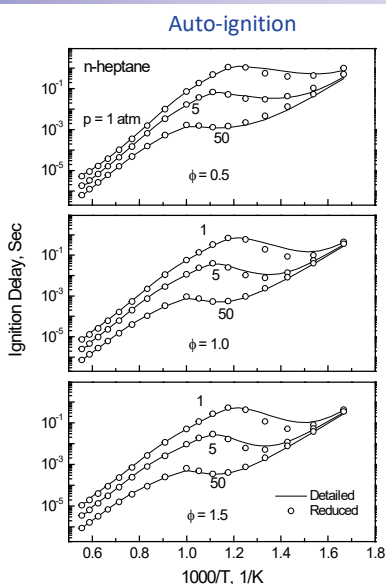
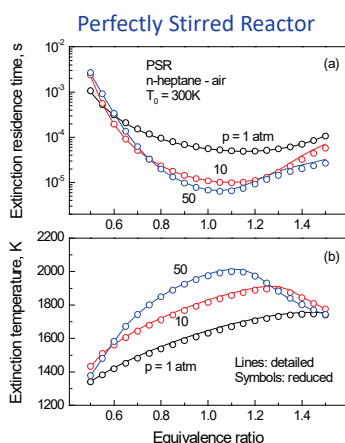
(Lu & Law PECS 2009)



Accuracy of Reduced Mechanisms:

n- C_7H_{16} (1/2)

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

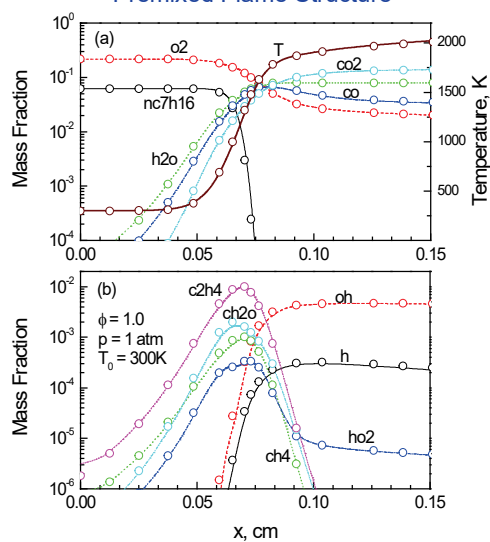




Accuracy of Reduced Mechanisms:

n-C₇H₁₆ (2/2)

Premixed Flame Structure



Other reduced mechanisms (All suitable for DNS)

- ▶ CH₄ (GRI3.0): 19 species
- ▶ C₂H₄ (USC Mech II): 22 species
- ▶ DME (Zhao et al): 30 species
- ▶ nC₇H₁₆ (LLNL): 58 species
- ▶ Biodiesel (LLNL): 73 species
- ▶ ...

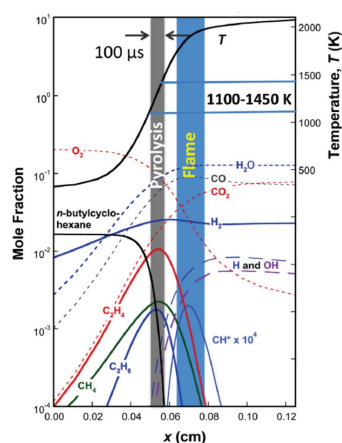
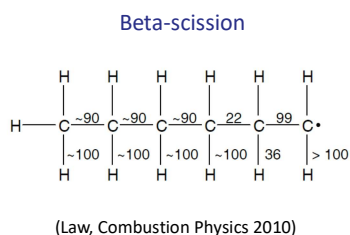
More reduced mechanisms:

<http://www.engr.uconn.edu/~tlu>

Reduced HyChem Models for Real Fuels



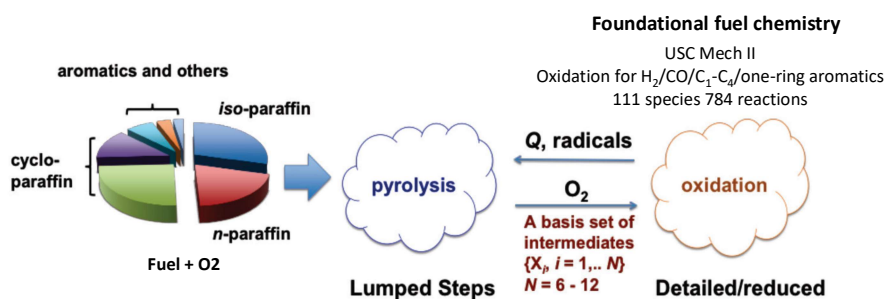
Background: Beta Scission & Decoupled Fuel Cracking and Flame Zones



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



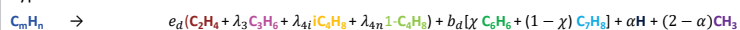
(Xu et al., CNF 2018)



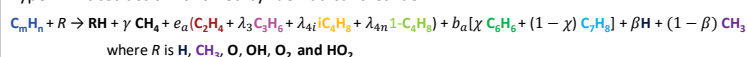
Formulation of the Fuel Cracking Steps

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

Type I: C-C fission like reaction

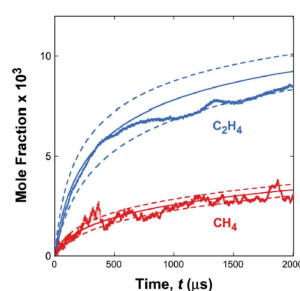


Type II: H-abstraction followed by fuel radical breakdown



- Determination of the stoichiometric coefficients

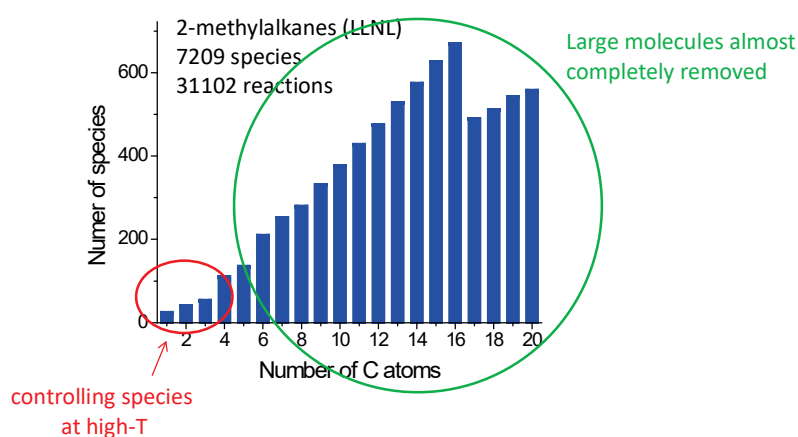
- Element conservation
- Branching ratios determined from experimental measurements



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





Reduced A2/C1 Mixture Model

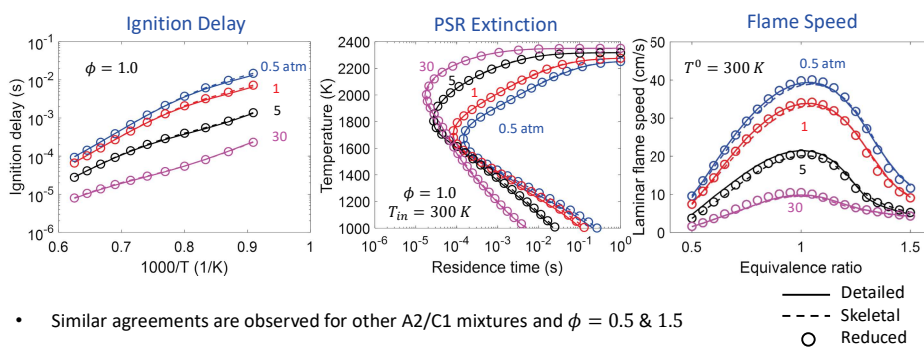
Parameter ranges

$\phi = 0.5 - 1.5$
 $p^0 = 0.5 - 30 \text{ atm}$
 $T_0 = 1000 - 1600 \text{ K}$ for ignition delay
 $T_{in} = 300 \text{ K}$ 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

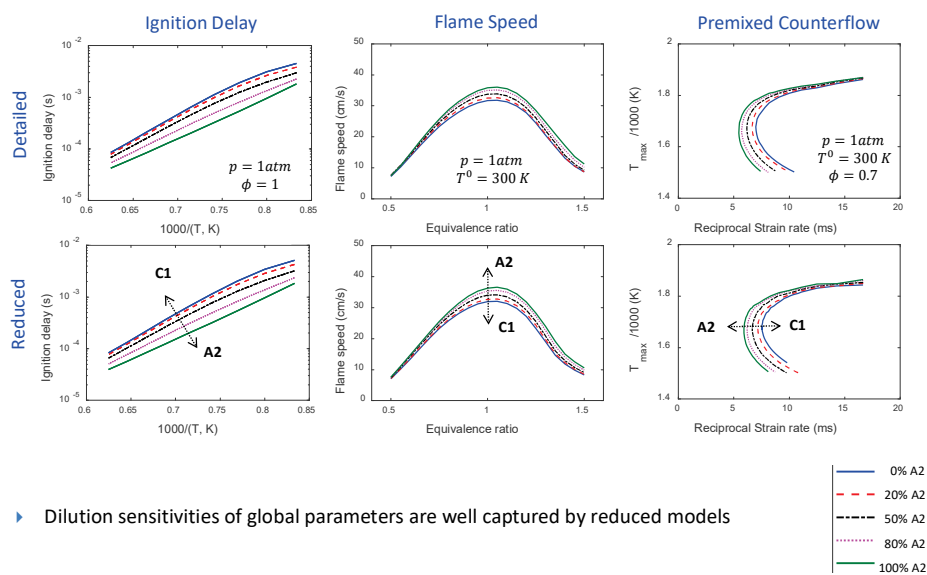
Selected validations (50% of A2 in A2/C1 mixture)



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



Dilution Sensitivities in Reduced Models





Reduced Models with NTC

Parameter ranges

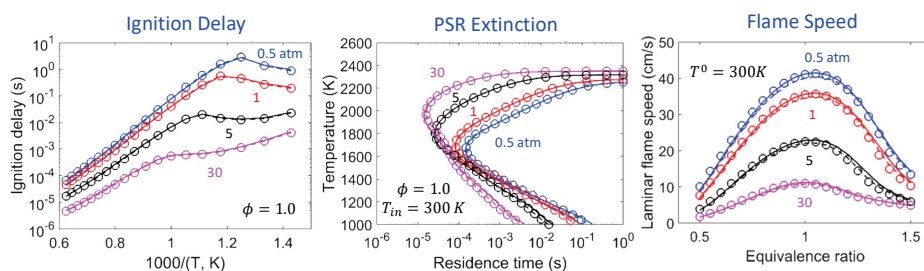
$\phi = 0.5 - 1.5$
 $p^0 = 0.5 - 30 \text{ atm}$
 $T_0 = 700 - 1600 \text{ K}$ for ignition delay
 $T_{in} = 300 \text{ K}$ for PSR extinction

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)



- 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)

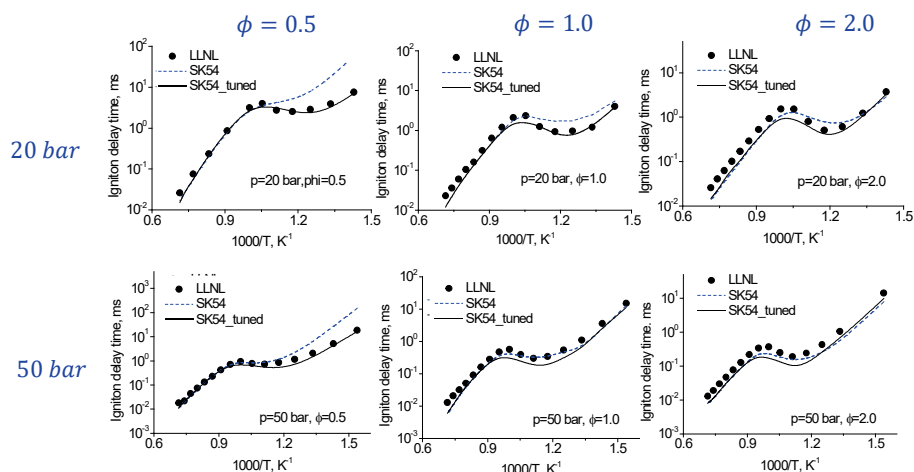


- C₀-C₄ core chemistry
 - A high-T skeletal model based on JetSurf
 - 32 species, 191 reactions
- C₅-C₁₂ sub-mechanism
 - Starting model: (You et al, PCI 2009)
 - Skeletal sub-model: 18 species, 60 reactions
- Low-T sub-mechanism
 - Semi-global scheme (4 species, 18 lumped reactions) (Bikas & Peters, CNF 2001)
 $\text{C}_{12}\text{H}_{25}\text{O}_2$, C_{12}OOH , $\text{O}_2\text{C}_{12}\text{H}_{24}\text{OOH}$, $\text{OC}_{12}\text{H}_{23}\text{OOH}$
 - Rate parameters need tuning
- Final models (Yao et al., US Meeting 2015):
 - Skeletal: 54-species, 269 reactions
 - Reduced: 37 species



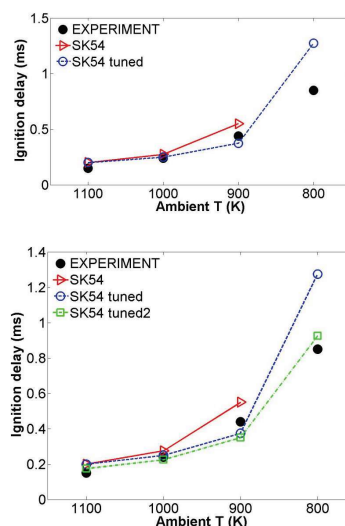
Tuning Against the LLNL Mechanism

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



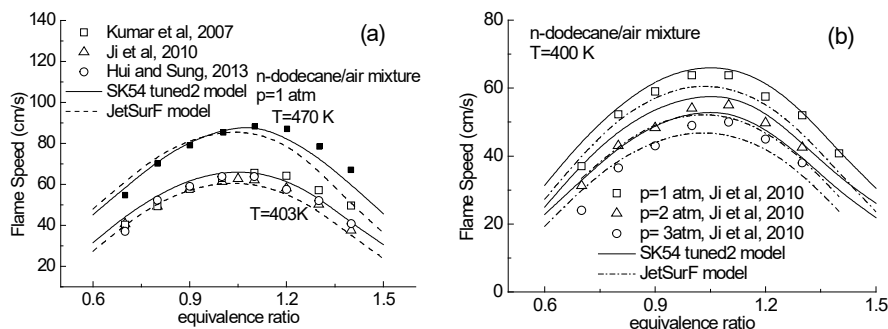
Tuning Based on ECN Data

- 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



Tuning Over-Reduced Models (1/2)

- Tuning rate parameters is a common practice for
 - Detailed mechanism compilation
 - Over-reduced models
- Needs to avoid over-fitting
- Consider a model with a set of parameters, $\mathbf{x} = \begin{pmatrix} \mathbf{y} \\ \mathbf{z} \end{pmatrix}$
 - \mathbf{z} : imperfect parameters with uncertainties (induced by calculation/calibration errors or over-reduction etc)
 - \mathbf{y} : parameters to be tuned to match a set of targets $\mathbf{g}(\mathbf{y}, \mathbf{z}; \dots) = \mathbf{0}$
- $\mathbf{h}(\mathbf{y}, \mathbf{z}; \dots) = \mathbf{0}$ are targets not covered in the tuning
- The tuning objective function (subscript 0: true parameters):
$$\mathbf{g}(\mathbf{y}_0 + \mathbf{y}', \mathbf{z}_0 + \mathbf{z}') = \mathbf{g}(\mathbf{y}_0, \mathbf{z}_0) = \mathbf{0}$$



Tuning Over-Reduced Models (2/2)

- Assume small uncertainties & perturbations

$$g(y_0 + y', z_0 + z') \approx g(y_0, z_0) + \frac{\partial g}{\partial y} y' + \frac{\partial g}{\partial z} z' = J_{11} y' + J_{12} z' = 0$$

- The solution of the optimization is

$$y' = -(J_{11}^T J_{11})^{-1} J_{11}^T J_{12} z', \quad J = \frac{\partial \begin{pmatrix} g \\ h \end{pmatrix}}{\partial (y, z)} = \begin{bmatrix} \frac{\partial g}{\partial y} & \frac{\partial g}{\partial z} \\ \frac{\partial h}{\partial y} & \frac{\partial h}{\partial z} \end{bmatrix} = \begin{bmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{bmatrix}$$

Local sensitivity

- When predicting new targets h :

$$\begin{aligned} h(y_0 + y', z_0 + z') &\approx h(y_0, z_0) + J_{21} y' + J_{22} z' \\ &= \left[-J_{21} (J_{11}^T J_{11})^{-1} J_{11}^T J_{12} + J_{22} \right] z' = A z' \end{aligned}$$

- A is arbitrary, depending on the sensitivities of the new targets h on the parameters – **in general tuned models are not predictive**



Strategies to Mitigate Overfitting

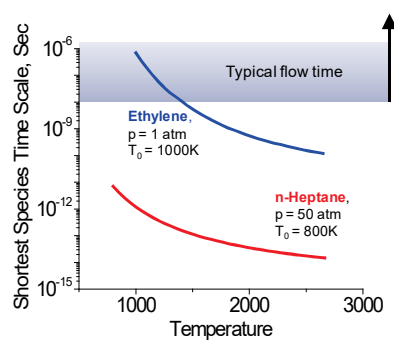
- Avoid over-reduction/tuning if possible
- Try not to tune models with too many knobs
- Use more validation targets (experimental & numerical)
- Use training/test/validation sets
- ...

Advanced Stiff Chemistry Solvers



Chemical Stiffness

- Detailed/reduced chemistry is typically stiff due to the short timescales induced by
 - Fast depleting species - typically the radicals
 - Partial equilibrium reactions





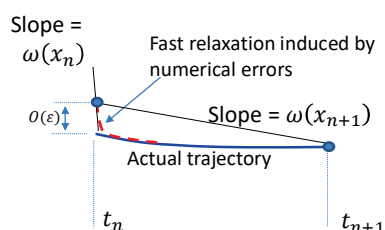
An example stiff problem

- Governing equation for a species x :

$$\frac{dx}{dt} = \omega(x, \dots)$$

- Discretized form:

$$\frac{x_{n+1} - x_n}{t_{n+1} - t_n} \approx \omega(x, \dots)$$



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

- A QSS type stiff problem: $C \rightarrow x \xrightleftharpoons[k=1/\varepsilon]{} P$
 - x : a radical
 - C : diffusion + chemical formation
 - Consumption rate of x : $D = kx = x/\varepsilon$

- Governing equation:

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

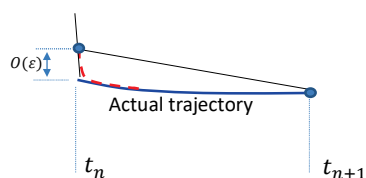
- Obtaining a correct slope:

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

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

- c_k^1 : a shadow concentration to obtain a correct slope

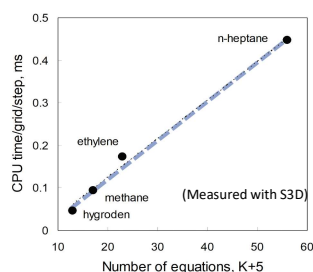
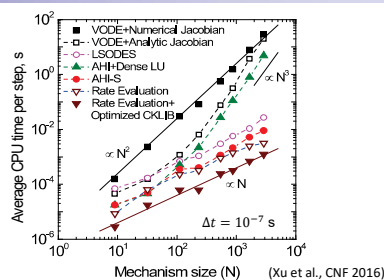
$$\omega(x^1) = -\frac{x^1}{\varepsilon} + C = \frac{x^0 - x_n}{h} \approx \frac{x_{n+1} - x_n}{h}$$





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

- Computational cost of explicit solvers
 - Cost in evaluation of Jacobian $\sim O(K^2)$
 - Cost in factorization of Jacobian $\sim O(K^3)$
 - Overall: $O(K^2)$ for small-moderately large mechanisms, $O(K^3)$ for extremely large mechanisms
- Cost of explicit solve with DCSR: $O(K)$
 - Readily applicable to compressible flows with time steps $< \sim 20$ ns
 - May be extended to larger time steps $\sim O(10^{-6} \text{ s})$, (Xu & Lu, USNCM 2017)



Splitting Schemes

- Spatially discretized governing equations

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

- Chemistry and transport substeps (Strang splitting):

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

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

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

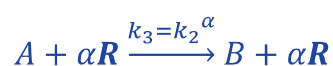
- Could the splitting incur major errors?



A Toy Problem

Transport:

$$T_R = 1$$

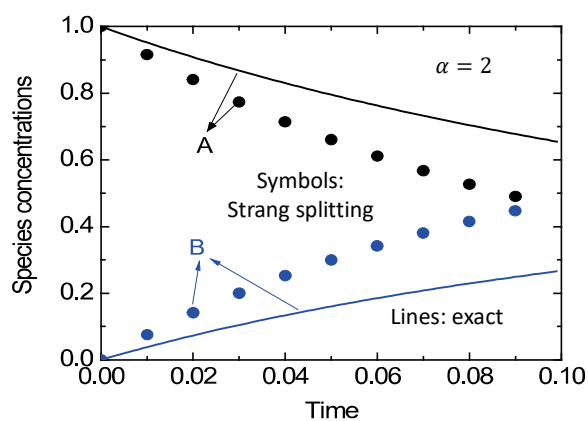


Radical **R**:

- ▶ 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) \sim 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

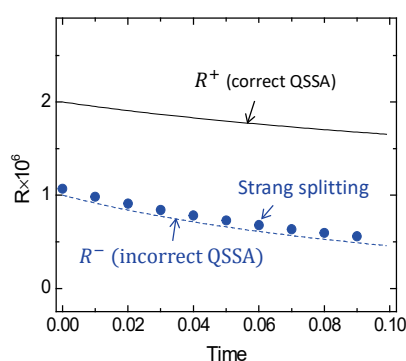
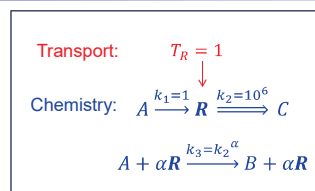
- R is in QSS:

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

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



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

- Governing equations

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

- 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 1st order scheme constructed (Gao et al, CNF 2015)

$$\frac{d}{dt} \begin{bmatrix} \Phi_f \\ \Phi_s \end{bmatrix} = S_f + g_s$$

$$S_f = \sum_{i=1}^m \nu_i \Omega_i, \quad g_s = \sum_{i=m+1}^{n_r} \nu_i \Omega_i + T$$

Fast chemistry

Slow chemistry & transport



Separation of Fast & Slow Chemistry

- Timescale of a reaction (Lam, CNF 2013)

$$\tau_i \equiv |\mathbf{J}_i \cdot \mathbf{v}_i|^{-1}, \mathbf{J}_i = \frac{\partial \Omega_i}{\partial \mathbf{c}} = \begin{bmatrix} \frac{\partial \Omega_i}{\partial c_1} & \frac{\partial \Omega_i}{\partial c_2} & \dots & \frac{\partial \Omega_i}{\partial c_k} & \dots & \frac{\partial \Omega_i}{\partial c_{n_s}} \end{bmatrix}$$

\mathbf{J}_i : Jacobian of reaction rate Ω_i , \mathbf{v}_i : stoichiometric coefficients

- Criterion for a fast reaction (i)

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

- Criterion for a fast species (k)

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

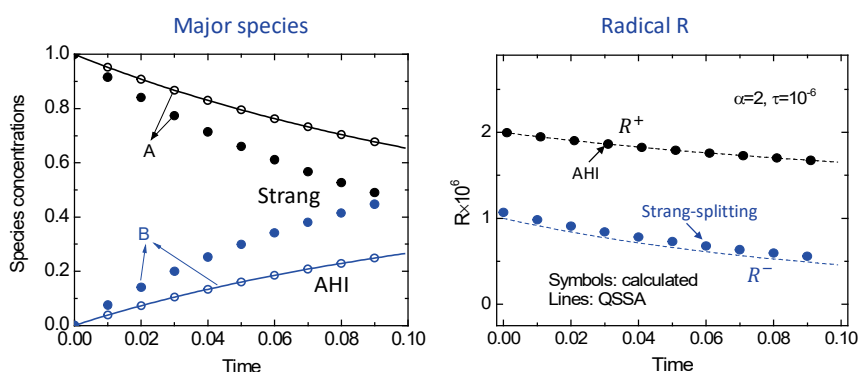
- A first-order AHI scheme

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

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



Comparison with Strang-Splitting



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

- Strang-Splitting: $O(1)$ errors in every species
- AHI: errors suppressed



A Second-order AHI (AHI2) Scheme

(Wu et al. CNF 2021)

$$\phi_f^{mid} - \phi_f^n = \frac{h}{2} (F_f(\phi_f^{mi}, \phi_s^n) + S_f(\phi_f^n, \phi_s^n))$$

$$\phi_s^{mid} - \phi_s^n = \frac{h}{2} (F_s(\phi_f^{mi}, \phi_s^n) + S_s(\phi_f^n, \phi_s^n))$$

$$\phi_s^{n+\frac{1}{2}} - \phi_s^n = \frac{h}{2} (F_s(\phi_f^n, \phi_s^n) + S_s(\phi_f^{mid}, \phi_s^{mid}))$$

$$\phi_f^{n+1} - \phi_f^n = \frac{h}{2} [F_f(\phi_f^{n+1}, \phi_s^{n+\frac{1}{2}}) + F_f(\phi_f^n, \phi_s^{n+\frac{1}{2}})] + h S_f(\phi_f^{mi}, \phi_s^{mid})$$

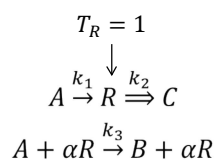
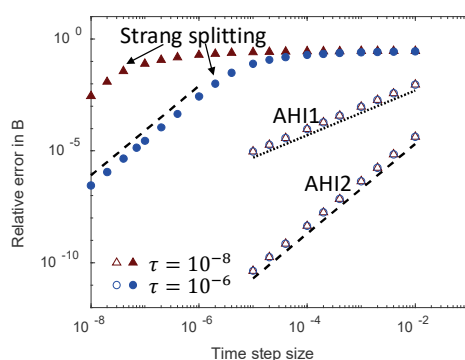
$$\phi_s^{n+1} - \phi_s^n = \frac{h}{2} [F_s(\phi_f^{n+1}, \phi_s^{n+\frac{1}{2}}) + F_s(\phi_f^n, \phi_s^{n+\frac{1}{2}})] + h S_s(\phi_f^{mid}, \phi_s^{mid})$$

- Hybrid mid-point and trapezoidal rule

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Comparison with Strang Splitting: Accuracy for a Toy Problem

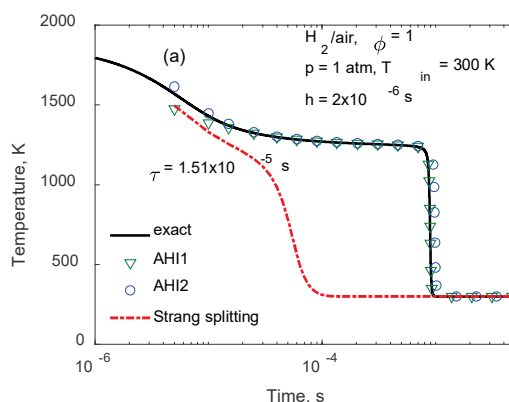


Timescale of R:
 $\tau = k_2^{-1} = 10^{-6}$

- Strang splitting: time step $\sim O(\tau)$ to show 2^{nd} order behavior
- AHI (1st order): error significantly smaller and independent of τ



PSR Extinction of H₂/Air



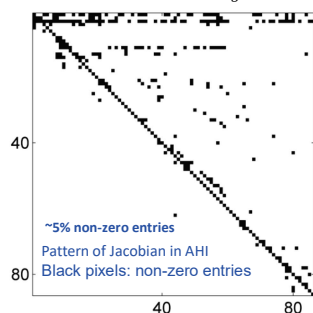
Initial condition perturbed from the
extinction turning point
 $p = 1 \text{ atm}, T_{in} = 300 \text{ K}, \phi = 1$
 $\Delta t = 2 \times 10^{-6} \text{ s}$



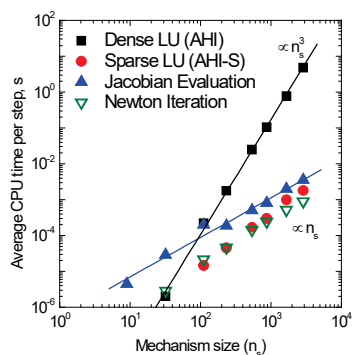
Analytic & Sparse Jacobian Techniques

- 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-species USC-Mech II, CH₄/air
 $\phi = 0.5, p = 50 \text{ atm}$
 $T_0 = 1200 \text{ K}, \Delta t = 10^{-7} \text{ s}$
Time instance: $2\tau_{ign}$

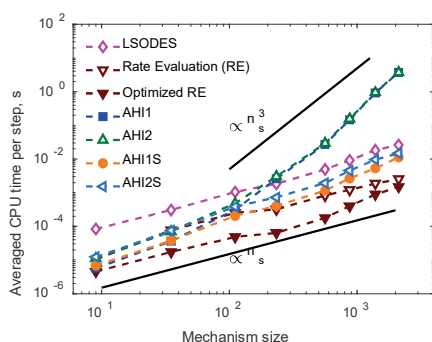


Cost of major operations in
typical stiff chemistry solvers





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**



Concluding Remarks

- Important aspects for model reduction
 - Reaction state sampling for model reduction: ignition & extinction
 - Error control strategies
 - QSSA for timescale-based reduction
 - HyChem models for high-T real fuels
 - Avoid rate parameter tuning if possible
- Important aspects for advanced chemistry solvers
 - Substantial efficiency improvement without loss of accuracy
 - Do not split stiff problems if possible
 - Rate correction is key, explicit time integration is possible after correction
 - Take advantage of the sparse chemical Jacobian
 - Linear scaling is possible for both implicit and explicit solvers