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Skeletal mechanism generation with CSP and validation for premixed n-heptane flames

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Introduction – Model reduction

skeletal mechanism generation

- elimination of unimportant species and reactions
- subset of detailed mechanism
- sensitivity analysis, reaction flux analysis
- directed relation graphs (DRG)
- optimization techniques
- quasi steady state assumption, partial equilibrium approximation

model reduction

- pseudo species
- global reaction steps
- lumping of isomers

- Computational Singular Perturbation (CSP)
- Intrinsic Low-Dimensional Manifold (ILDM)

Computational Singular Perturbation (CSP)

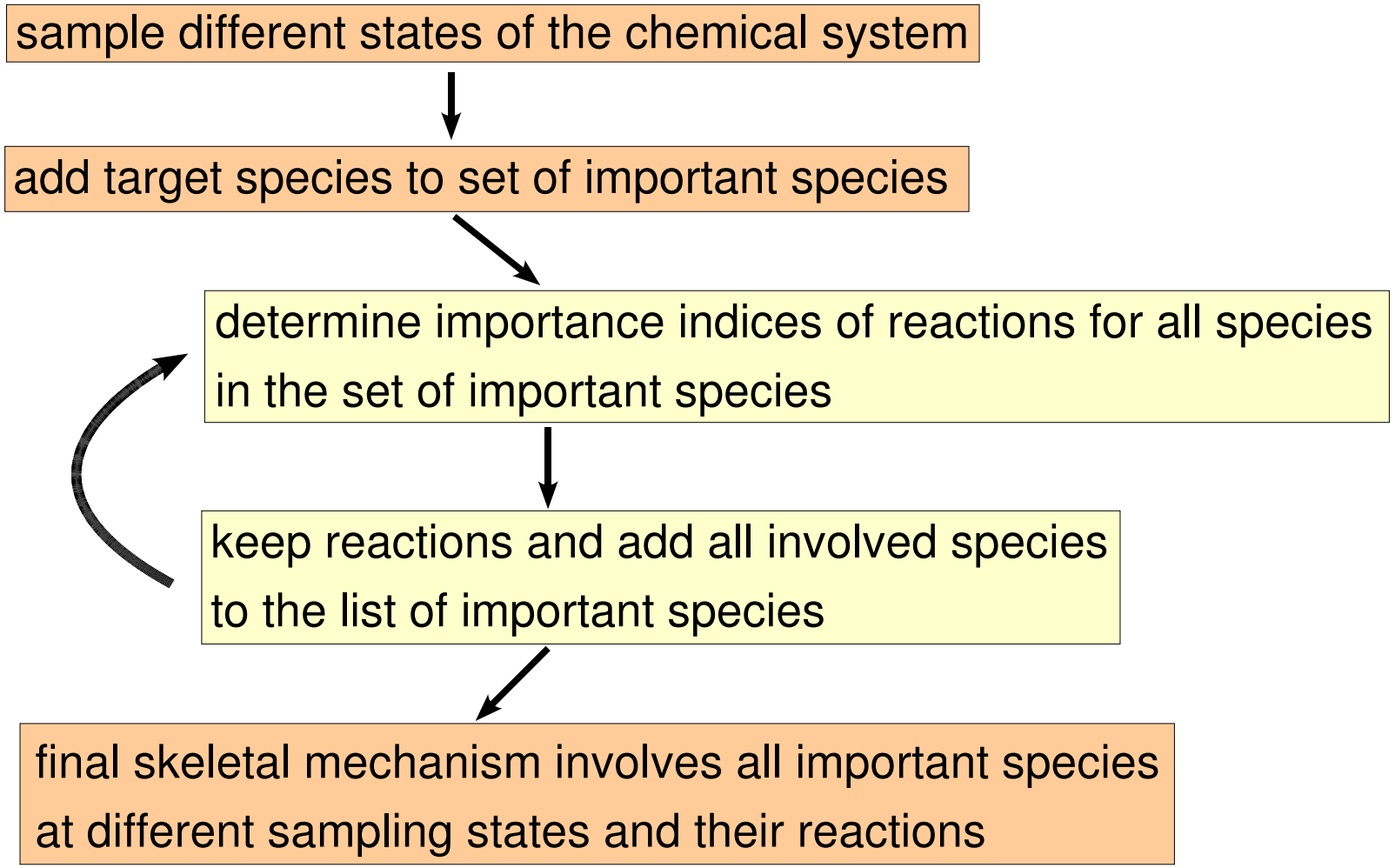
$$\frac{d\vec{u}}{dt} = S\vec{R} = \sum_{\text{modes } m} \vec{a}_m h^m \qquad \vec{u} = (Y_1, \ldots, Y_{N_s-1}, T)^T$$

$$h^m = \sum_{\text{processes } k} h_k^m = \sum_{\text{processes } k} (\vec{b}^m \cdot \vec{S}_k) R^k$$

$$\frac{du^i}{dt} = \sum_{\text{modes } m} a_m^i \sum_{\text{processes } k} h_k^m \qquad (I_k^i)_{slow} = \frac{\sum_{slow} a_m^i h_k^m}{\sum_{all\ k} |\sum_{slow} a_m^i h_k^m|}$$

- dynamical analysis
- decomposition of fast and slow processes
- identify important reactions for fast and slow processes separately
- automatic

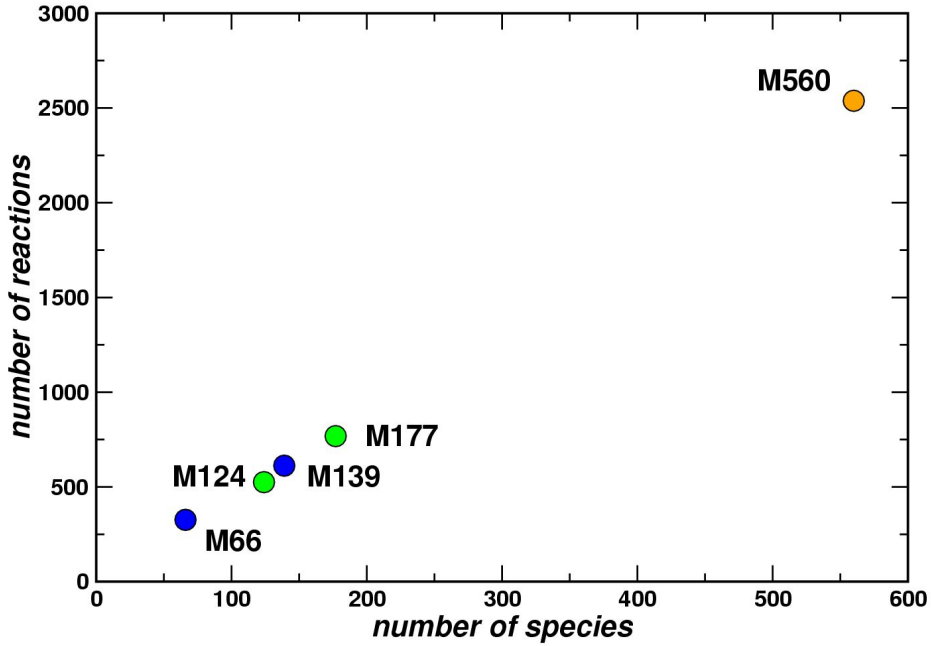
Algorithm of skeletal-mechanism generation with CSP



Accuracy of skeletal mechanism has to be tested a posteriori.

Mechanism selection – Homogeneous ignition calculations

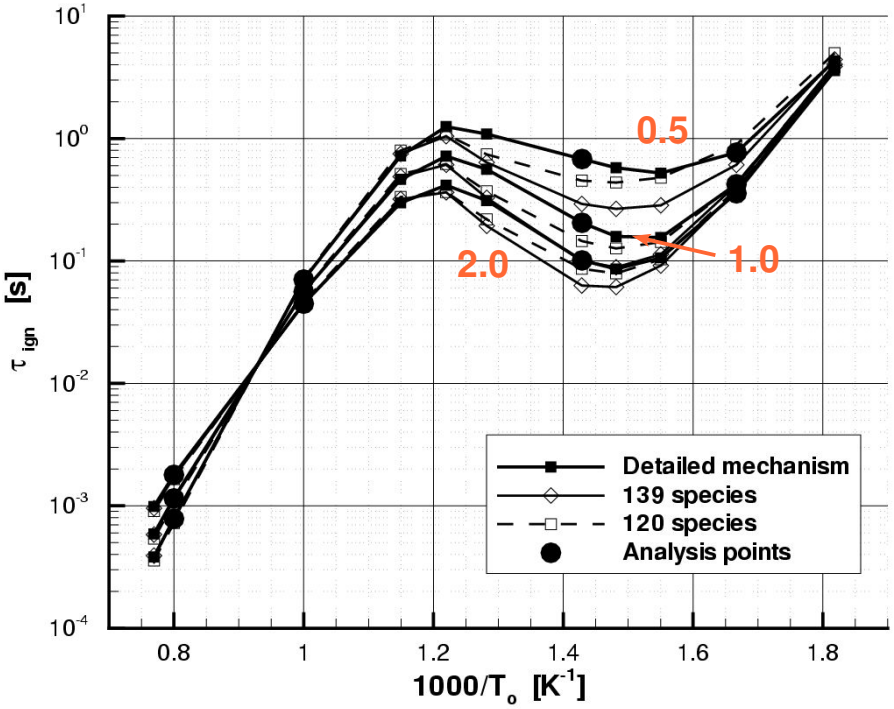
- detailed mechanism:
  Curran et al. (2004)
  M560 2538 reactions

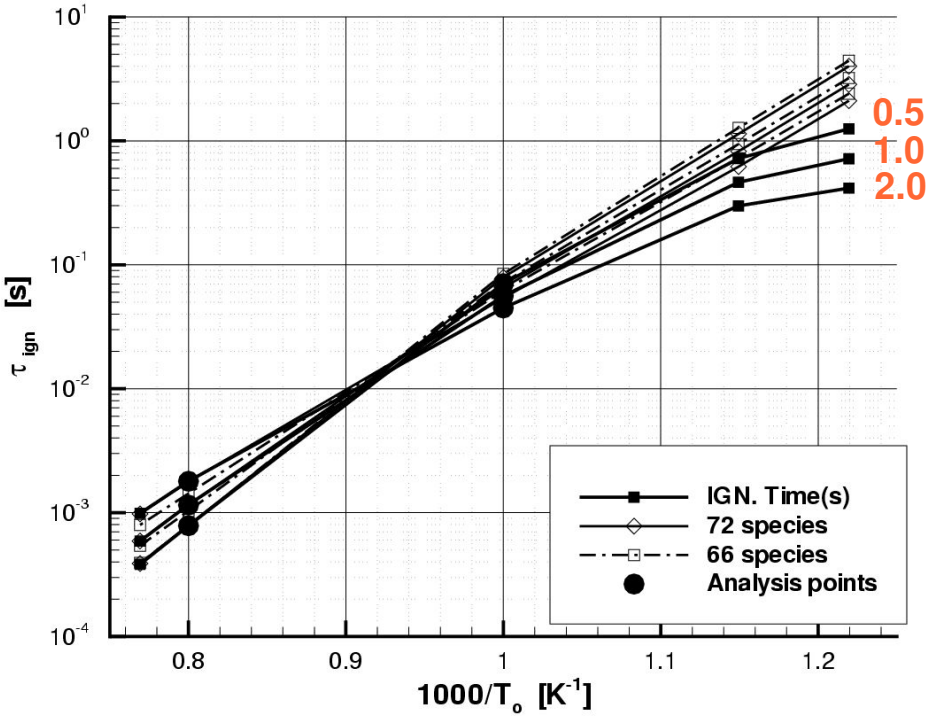


- target set: T, nC_7H_{16}, CO_2
- 1st set of mechanisms: 1atm, φ=0.5/1.0/2.0
  M66 (T_0=1000K-1250K)and **M139** (T_0=600K-1250K)
- 2nd set of mechanisms: φ=1, 6.5/40 bar, T_0=640K-1240K
  M124 and **M177**

Mechanism selection – Homogeneous ignition calculations

Valorani et al, ECCOMAS CFD (2006):





M139:

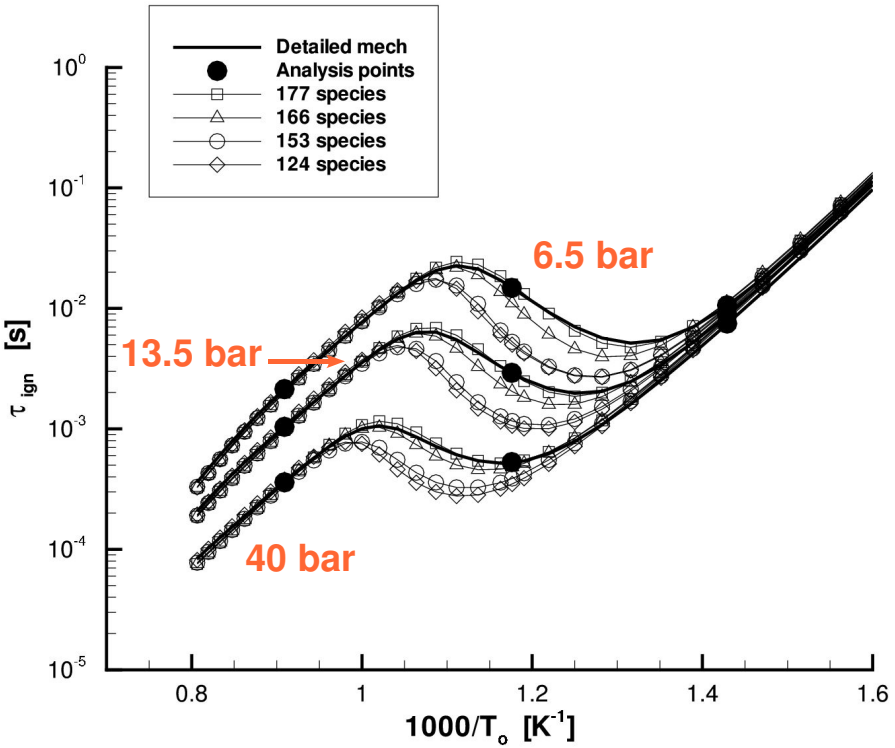
- avg. τ errors ~ 20% for T_0>1000K
- accurate flame speed and temperature profile for φ=1

M66:

- avg. τ errors ~ 20% for T_0>600K
- larger errors for T_0<1000K
- accurate flame speed and temperature profile for φ=1

Mechanism selection – Homogeneous ignition calculations

Valorani et al, Proc. Comb. Inst. (2007):



M124:

- avg. τ error ~50% for T_0=850K
  ~10% for T_0=700K
  ~3% for T_0=1100K

M177:

- avg. τ error ~10% for T_0=700K
  ~7% for T_0=850K
  ~8% for T_0=1100K

Motivation for current study

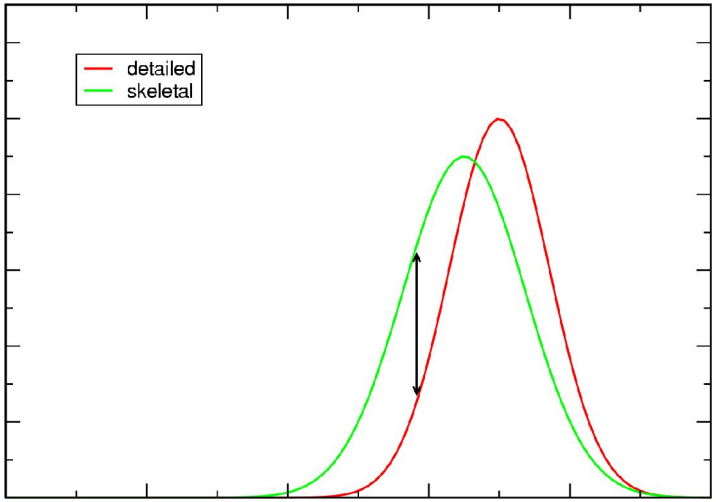
(1) evaluate accuracy of skeletal mechanisms derived from ignition databases for laminar flames

(2) compare error levels of skeletal mechanisms in ignition calculation and premixed flames

(3) evaluate accuracy with/without low-temperature chemistry

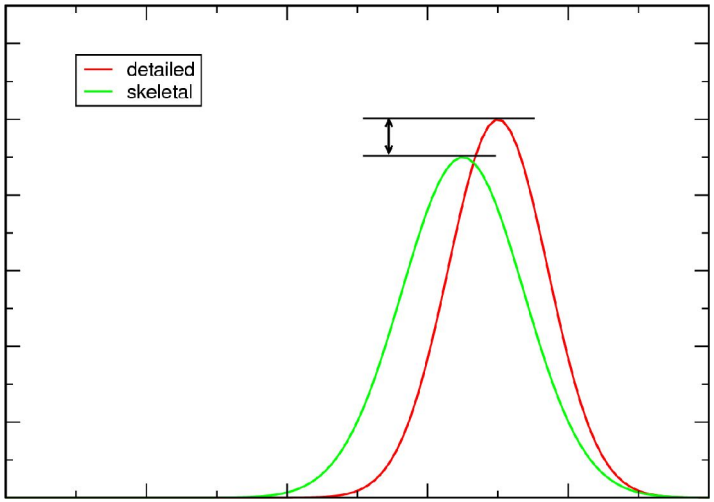
(4) examine range of timescales of skeletal mechanisms

Methods – Error measures



$$E = \frac{\max_x \left| X^{M560} - X^{Skeletal} \right|}{\max_x \left(X^{M560} \right)}$$

- sensitive to shifts
- upper limit for error

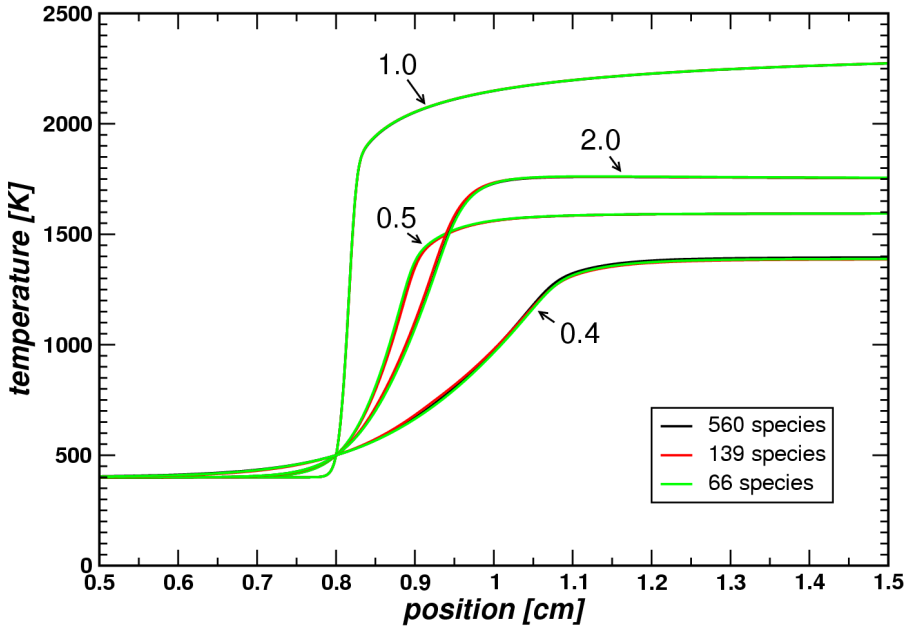


$$E = \frac{\left| \max_x \left(X^{M560} \right) - \max_x \left(X^{Skeletal} \right) \right|}{\max_x \left(X^{M560} \right)}$$

- independent of spatial coordinate
- insensitive to shifts and errors away from the maximum
- not for species without maximum

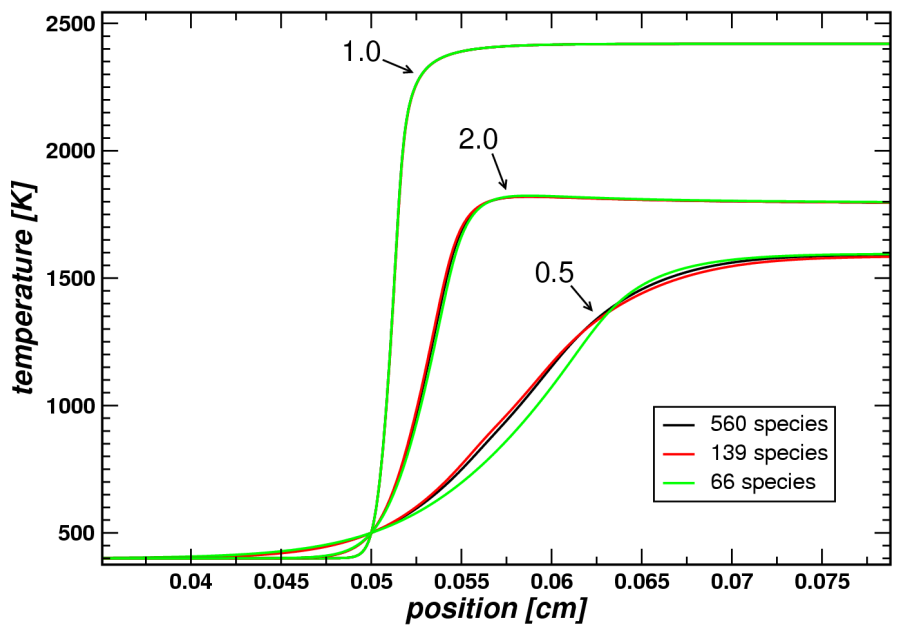
Results – Temperature profiles M66/M139

1atm



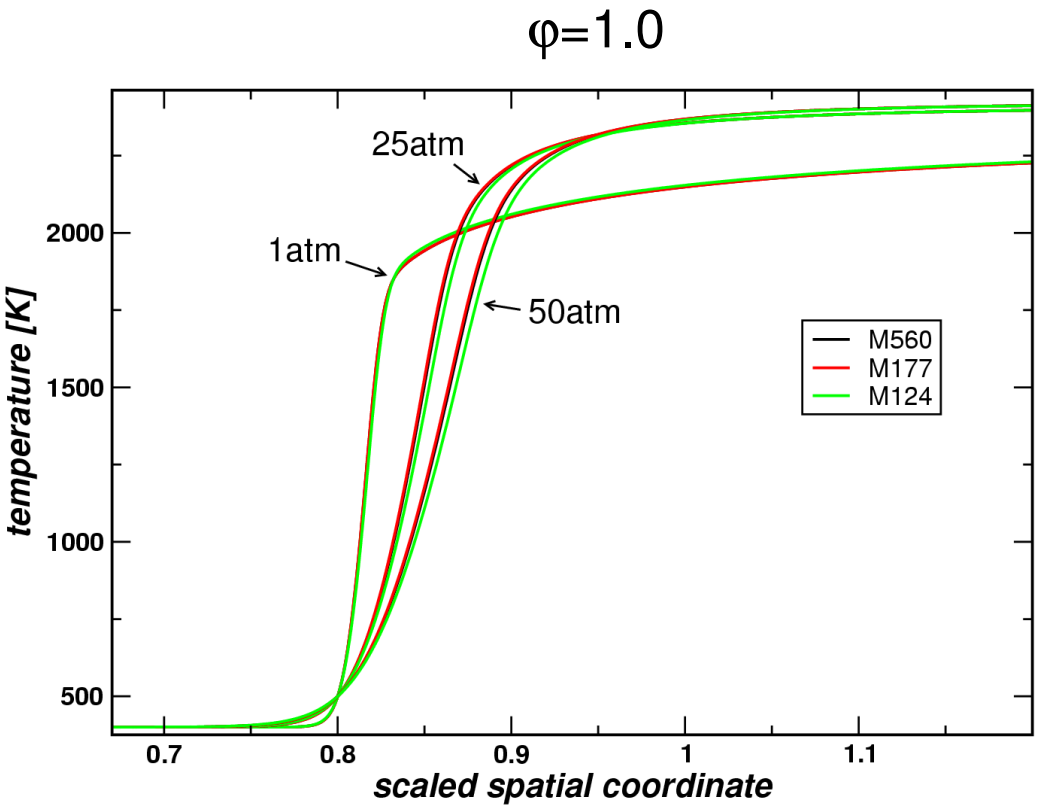
- very good agreement
- some deviations at very lean and rich mixtures

50atm



- outside the validity range of skeletal mechanisms (1atm)
- very good agreement
- some deviations of M66 at very lean mixture

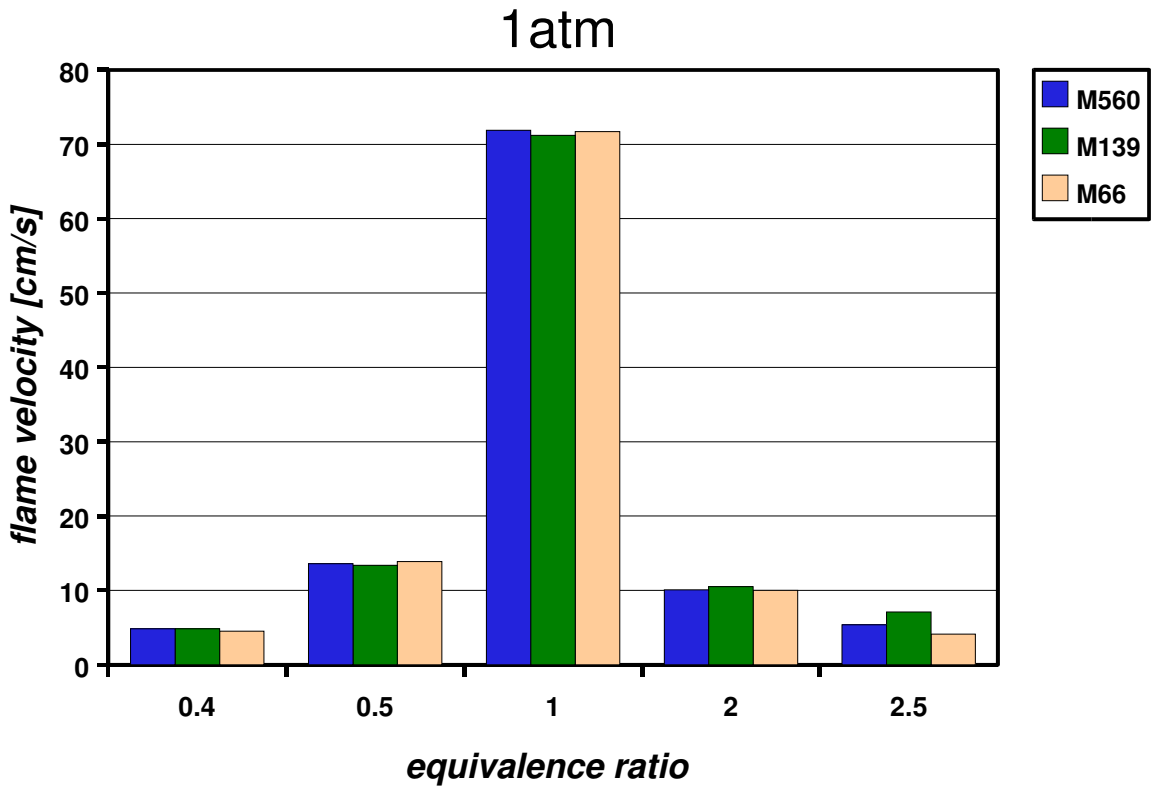
Results – Temperature profiles M124/M177



- good agreement
- larger deviations for M124 at p ≥ 25atm

temperature profiles are well reproduced

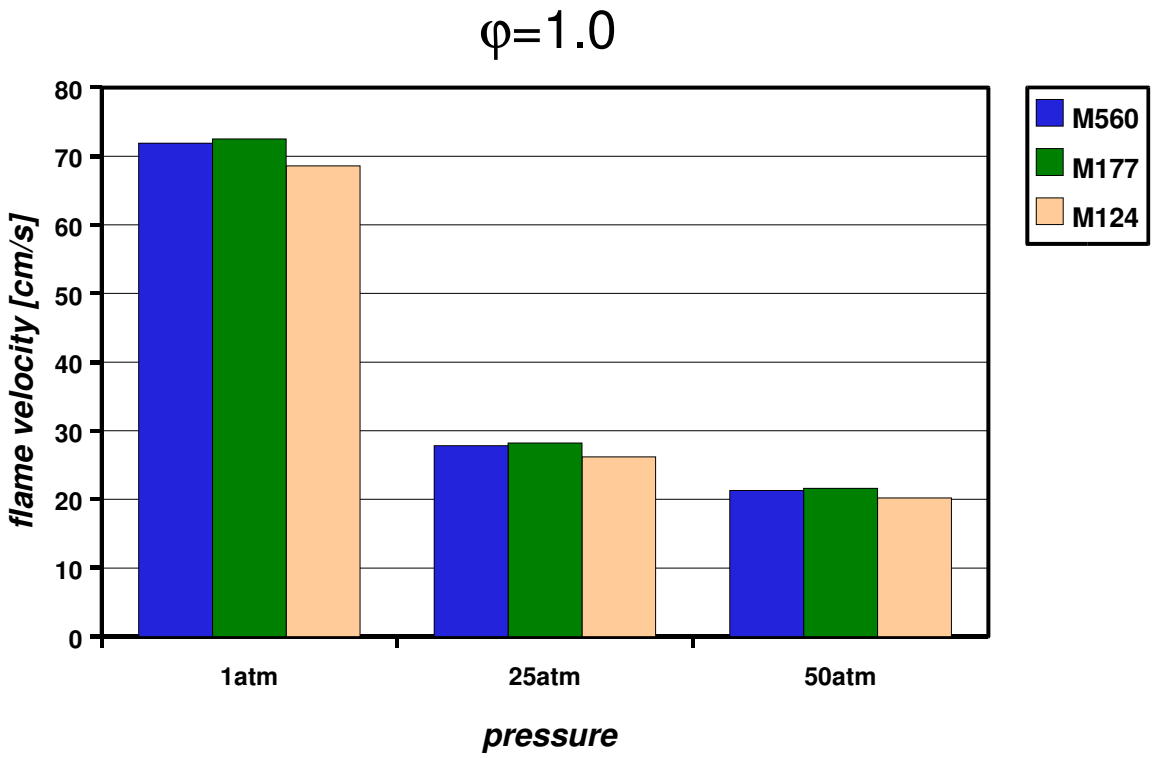
Results – Flame velocity M66/M139



- good agreement for target range φ=[0.5,2.0], max error +3.9% in rich case
- deviations at very rich side, ~20-30%

even M66 shows very good agreement in target range

Results – Flame velocity M124/M177



- no pressure dependence
- good agreement in all cases, max error +1.4% (M177) / -5.8% (M124)
- M124 generally too small velocity

all mechanisms show good agreement in target range

Results – Species profiles M66/M139

1atm	Equivalence ratio					
	0.5		1		2	
	M139	M66	M139	M66	M139	M66
$n\text{-}C_7H_{16}$	1.8%	4.0%	0.4%	1.5%	10.0%	3.3%
O_2	0.7%	1.2%	0.5%	0.1%	2.3%	0.9%
H_2O	1.1%	2.3%	0.2%	0.6%	2.7%	0.7%
CO	2.9%	4.3%	1.2%	0.4%	2.9%	1.9%
CO_2	1.5%	2.2%	0.4%	0.1%	0.9%	1.8%
H_2	2.2%	6.3%	2.2%	2.5%	1.3%	1.9%

- maximum deviation as error measure
- most cases: error well <10%
- most cases: M139 more accurate than M66
- stoichiometric mixture shows best results

Results – Species profiles M124/M177

φ=1.0	Pressure					
	1 atm		25 atm		50 atm	
	M177	M124	M177	M124	M177	M124
$n\text{-}C_7H_{16}$	2.9%	6.0%	5.0%	9.7%	4.5%	9.1%
O_2	0.5%	2.6%	1.2%	4.7%	1.1%	4.7%
H_2O	0.6%	1.5%	1.2%	3.5%	1.2%	3.5%
CO	0.9%	7.3%	2.2%	10.8%	2.0%	10.5%
CO_2	0.2%	1.2%	0.8%	4.1%	0.8%	4.3%
H_2	0.7%	8.0%	1.7%	12.0%	1.9%	13.1%

- M177 up to 5% error
- M124 up to 13% error
- M177 always more accurate then M124
- best restults for p=1atm

Results – Species profiles minor species M66/M139

φ=0.5	φ=1.0	φ=2.0
M139		
• half of species: error < ~60%	• half of species: error < ~20% • 10 species with error > 100%	• half of species: error < ~60%
M66		
←	• half of species: error < ~30%	→
• largest errors <400%	• species with largest errors: C_3H_5O, C_2H_5O, C_2H_5CHO, C_4H_7	• largest errors ~30%-100%

- largest errors for species involved in low-temperature chemistry (up to factor 20): pentyl and heptyl hydroperoxy radicals and ketohydroperoxides
- maximum errors are smaller in M66 because these low-temperature species are missing
- M66 overall less accurate than M139

Results – Species profiles minor species M124/M177

1.0 atm 25 atm 50 atm

M177

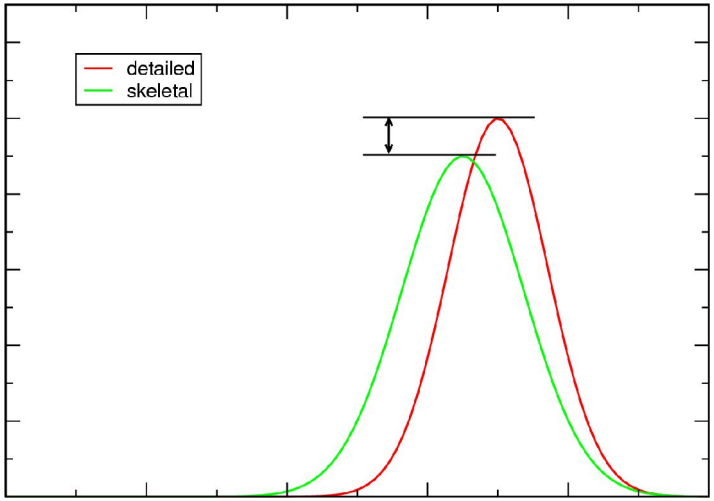
- half of species: error < ~30%
- species with largest errors:
  C_3H_5, C_4H_7, C_4H_7O, lowT species
  up to 140%

M124

- half of species: error < ~30%
- half of species: error < ~60%
- species with largest errors:
  C_3H_4, C_4H_7 up to 400%
  and some lowT species

Results – Species profiles: dependence on error measure

Using 2nd error measure:



- some major species ½ error
- maximum errors and average errors approximately the same
- M124 largest reduction in error in accordance with shift in temperature profile

difference is caused by different temperature profiles

Results – Comparison to ignition calculation M66/M139

Errors in species profiles for constant pressure homogenous ignition for T_0=600K/1000K/1250K:

M139

- largest errors in the same low-temperature species
- errors decrease with increasing T_0
- main species have approx. same errors for T_0>1000K
- larger errors for ignition at T_0=600K

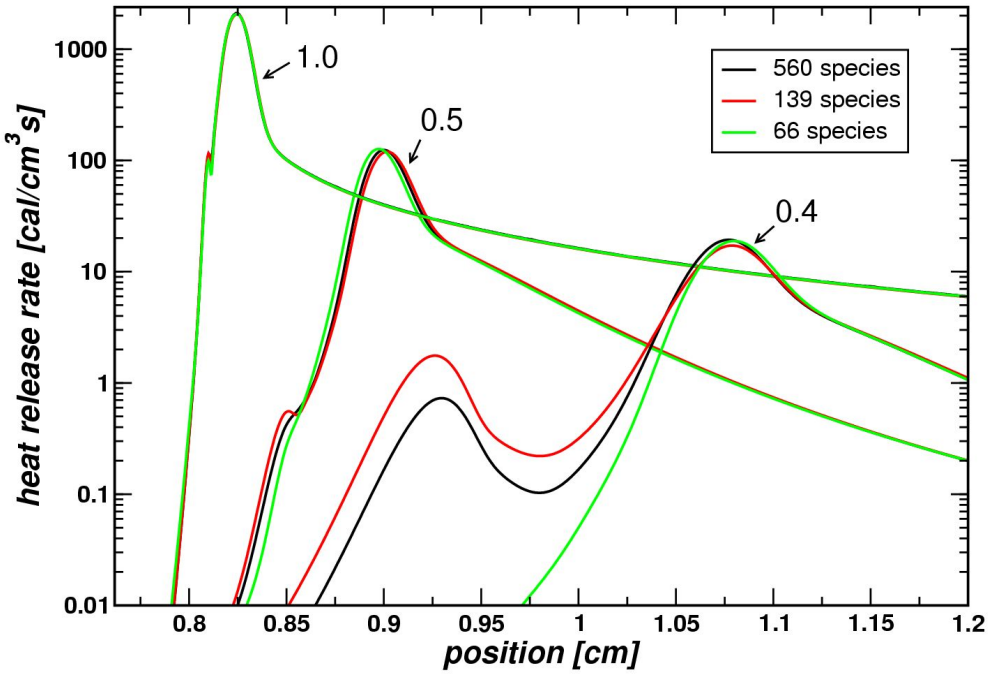
M66

- largest errors in the same species as premixed flames

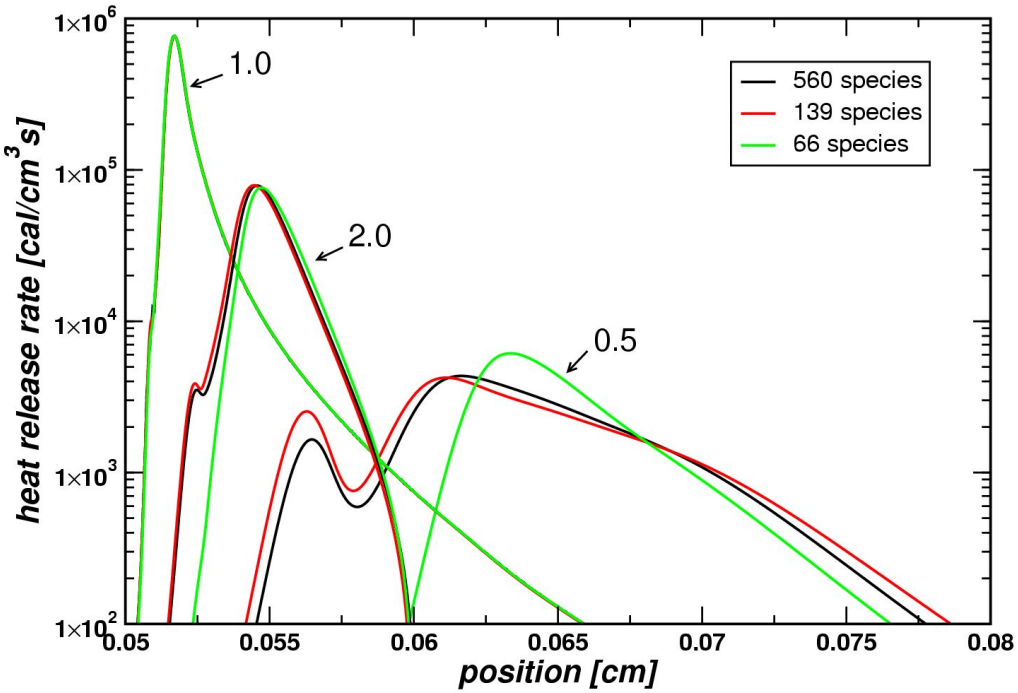
similar errors in ignition and premixed flames – similar phase space

Results – Heat release rate M66/M139

1atm



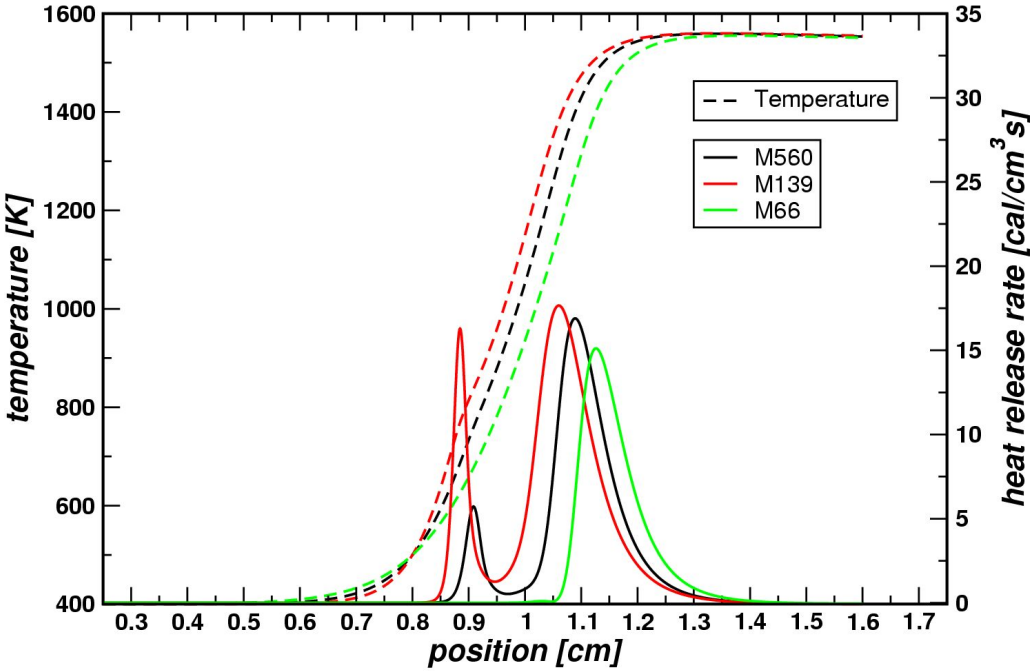
50atm



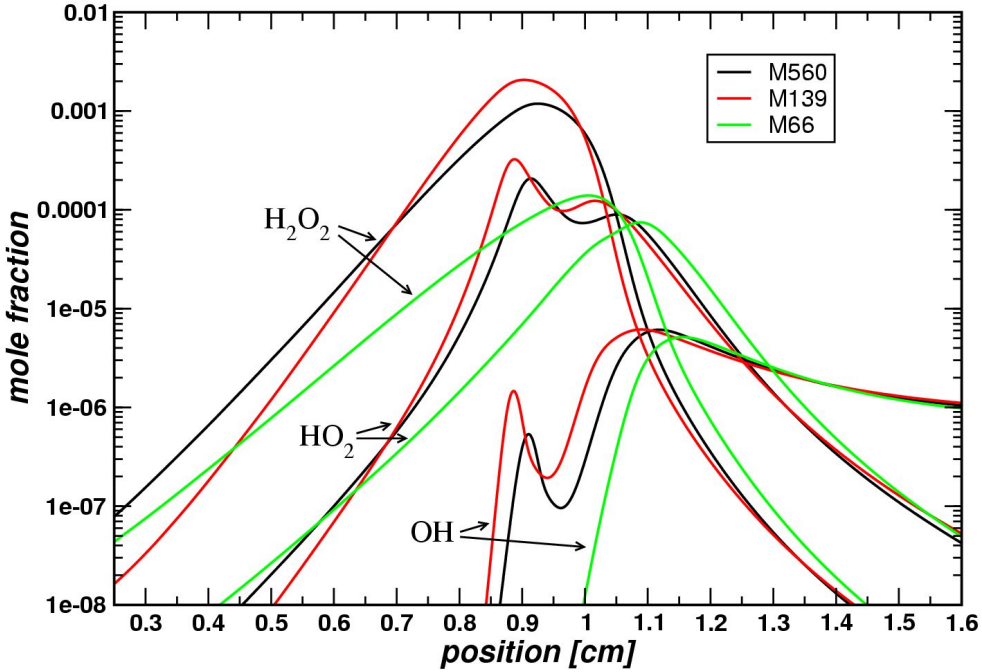
- maximum reproduced within 4% for target equivalence ratios at 1atm
- low-temperature heat-release peak is significant for very lean/rich mixtures
- low-temperature region is more pronounced at higher pressure
- M66 can be used to determine importance of lowT-chemistry

Results – Heat release rate and radicals M66/M139

heat release rate, 1atm, φ=2.5



radicals, 1atm, φ=2.5

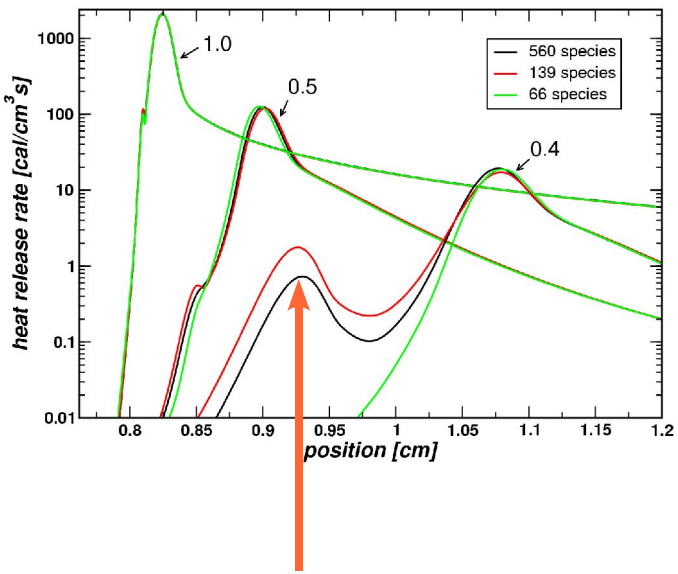


- largest influence of low-temperature chemistry for φ=2.5
- M139 overshoots heat-release peak, M66 misses it completely
- influence on important radicals that are involved in lowT-chemistry

Results – CSP analysis of temperature in lowT-zone M560

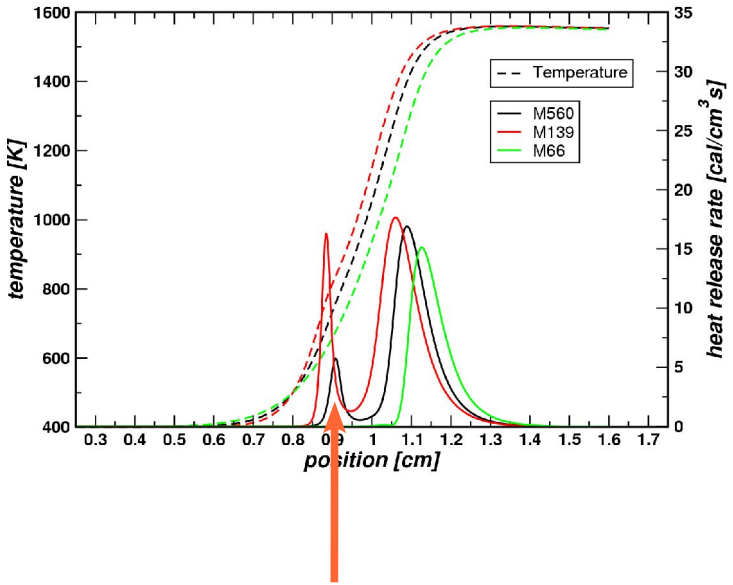
analysis at position of maximum low-temperature heat-release

φ=0.4, 1atm



- heat conduction
- n-C_7H_{16} + OH ↔ C_7H_{15} + H_2O
- oxygen addition to CH_3

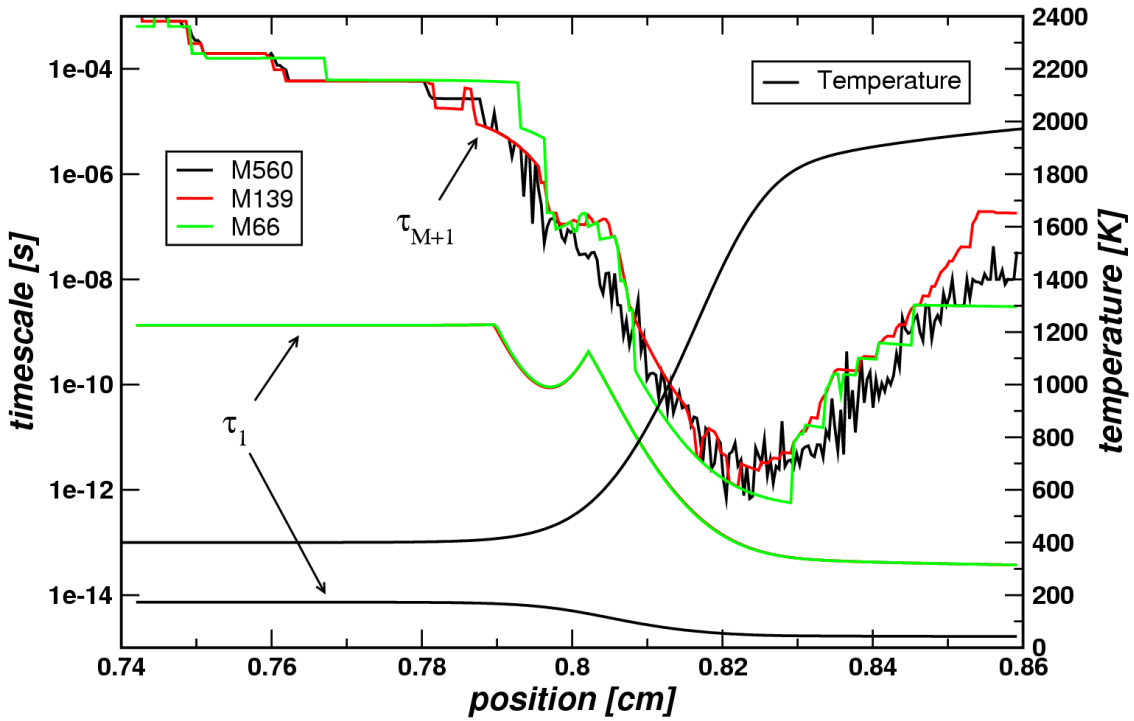
φ=2.5, 1atm



- oxygen addition to C_2H_5 and CH_3
- isomerization of heptyl-peroxy radical
  $C_7H_{15}O_2$ ↔ $C_7H_{14}OOH$
- formation of ketohydroperoxides
  $O_2C_7H_{14}OOH$ ↔ n-C_7ket + OH

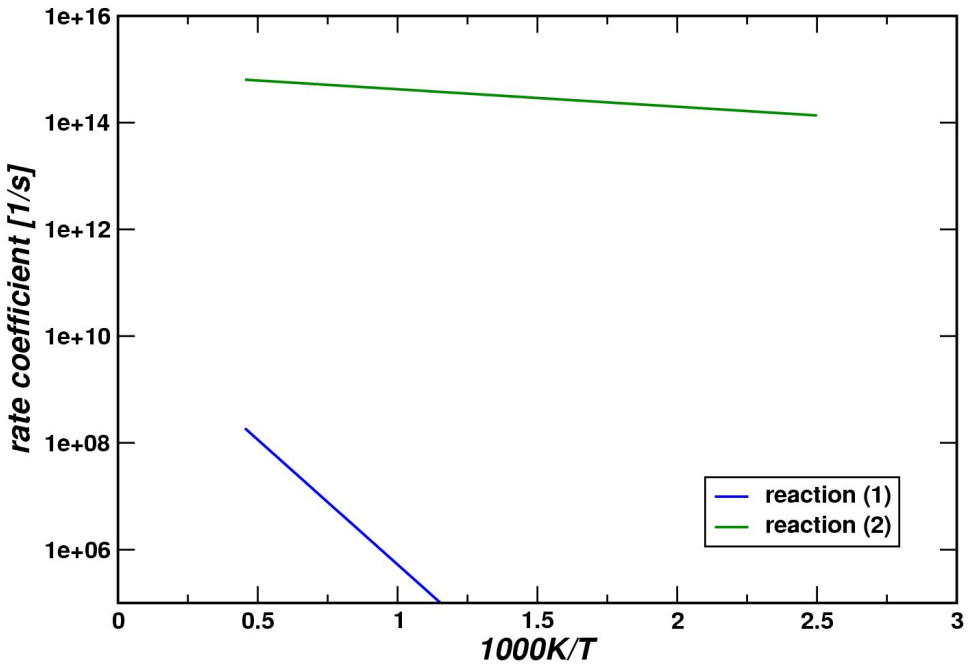
Results – Timescales

φ=1.0, 1atm



- M560 smallest timescale ~10^{-15} s, missing in M139/M66
- difference in fastest timescale: cold zone: 5 orders of magnitude, hot zone: factor 20
- driving timescales approximately the same in all mechanisms

Results – Fastest timescale M560



reactions with highest CSP participation indices of fastest mode:

internal hydrogen abstraction of the peroxy-hydroperoxy-neopentyl radical:

(1) neo-$C_5H_{10}OOH$-O_2 ↔ neo-$C_5H_9(OOH)_2$-n

decomposition of the dihydroperoxy-neopentyl radical:

(2) neo-$C_5H_9(OOH)_2$-n ↔ neo-C_5ket + OH

Conclusions

- skeletal mechanisms developed for homogeneous ignition can be used for premixed flames
- largest errors in low-temperature species
- well reproduced flame velocities, temperature profiles, main species, heat release rates
- higher importance of low-temperature chemistry for lean and rich flames because of lower total heat release
- large differences in smallest timescales of the mechanisms
- computational effort scales quadratically with number of species