Iran First International Combustion School (ICS2019)
Tehran, 24-26 August 2019

Combustion Modeling
4. Advanced techniques for reacting flows with detailed kinetics

Alberto Cuoci

References

[Cuoci2019] A. Cuoci, *Numerical modeling of reacting systems with detailed kinetic mechanisms*, Computer Aided Chemical Engineering, 45, p. 675-721 (2019)

[Lu2009] Lu T.F. and Law C.K., *Toward accommodating realistic fuel chemistry in large-scale computations*, Progress in Energy and Combustion Science, 2009. 35(2): p. 192-215

[Lu2017] T. Lu, *Mechanism Reduction and Advanced Chemistry Solv*ers, 2017 Princeton-Combustion Institute Summer School on Combustion

[Kee2017] R.J. Kee, M.E. Coltrin, P. Glarborg, *Chemically Reacting Flow: Theory and Practice*, Wiley, 2 edition, 2017

Outline

1. **Acceleration of simulations by reduction of species**
    a) Skeletal reduction
    b) Quasi Steady-State Approximation (QSSA)
    c) Dynamic Stiffness Removal (DSR)
    d) Dynamic Adaptive Chemistry (DAC)
2. **Acceleration of simulation by reduction of reacting environments**
    a) Reaction Network Analysis (RNA) and Kinetic Post-Processor (KPP)
    b) Dynamic Adaptive Clustering
    c) ISAT (In Situ Adaptive Tabulation)
3. **Species bundling for diffusion coefficient reduction**
4. **Computation Cost Minimization**
5. **Numerical tools for analysis of kinetic mechanisms**

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The time complexity

T. Lu, Mechanism Reduction and Advanced Chemistry Solvers, 2017 Princeton-Combustion Institute Summer School on Combustion

- **Time complexity of major components:**
  - Chemistry: $\sim NR \sim NS$ (NR : # of reactions, NS : # of species)
  - Jacobian (brute force): $\sim NR \times NS \sim NS^2$
  - Diffusion (mixture average): NS^2

- **Reducing NR and NS is an obvious approach to accelerate combustion simulations - mechanism reduction**

- **Implicit solvers (Jacobian, chemistry, diffusion)**
  - Time steps typically limited by the CFL condition
  - $\tau_{imp} \sim NS^2$
  - Most effective acceleration approaches: analytic Jacobian, sparse Jacobian techniques, reduced diffusion models

- **Explicit solvers (chemistry, diffusion)**
  - Time steps limited by the shortest chemical timescale
  - $\tau_{exp} \sim NS^2$
  - Most effective acceleration approaches: chemical stiffness removal, reduced diffusion models

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
  - …

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Reduction of detailed kinetic mechanisms

Objective

to eliminate the unimportant species and reactions from a detailed kinetic mechanism

Problem

identification of unimportant species and unimportant reactions

Quantification of the importance of species:

1. Jacobian analysis

The Jacobian matrix coefficients can be arbitrarily large (i.e. difficult to choose a threshold)

2. Directed Relation Graph (DRG)

Relative error on species *A* induced by elimination of species *B*

Adapted from: **Lu T.,** *Computational Tools for Diagnostics and Reduction of Detailed Chemical Kinetics*, Princeton-CEFRC Summer School on Combustion (2012)

Skeletal reduction

- **Throwing away unimportant species and/or reactions**

- **Example methods for skeletal reduction**
  - Global sensitivity analysis (GSA)
  - Local sensitivity analysis (LSA)
  - 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)
  - Species-Targeted Sensitivity Analysis (Stagni et al.)

- **Error control is critical for computational cost**
  - Method with a priori error control do not require reduced model validation
  - Any method without a priori error control requires reduced model validation, is effectively a GSA

- **No reduction method is "wrong", as long as the reduced model is validated**

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Identification of Important Pathways

- **Reaction rates are determined by temperature, pressure, and species concentrations (T, P, C), i.e. local reaction states**

- **Different reaction pathways are controlling at different reaction states**

- **Any mechanism reduction is specific to a target set of 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 is required for reduction

- **Reactors for reaction state sampling**
  - Auto-ignition
  - Perfectly stirred reactors (PSR)
  - 1-D laminar flames
  - Turbulent flames?

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Reaction State Sampling

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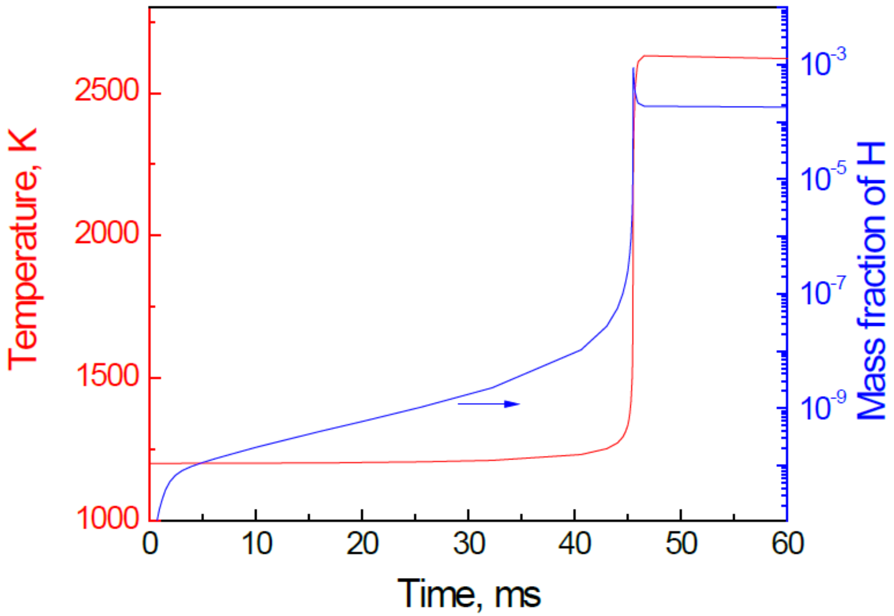
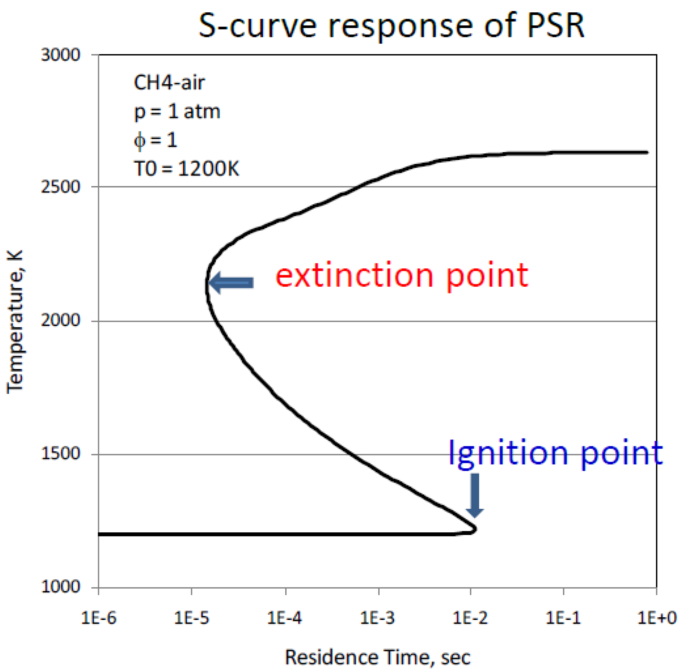
Methane-air, ϕ = 1.0, p = 1 atm, T0 = 1200K





Sample reaction states from **auto-ignition** are representative for ignition chemistry, important for compression ignition engines, detonation waves etc.

The states from the upper and middle branches of a PSR are representative to flame chemistry, important for spark ignition engines, jet engines, etc.

Directed Relation Graph (DRG)

$$r_{AB} = \frac{\sum_i |\upsilon_{A,i} r_i \delta_{Bi}|}{\sum_i |\upsilon_{A,i} r_i|}$$

Extent of coupling between species A and B

$$\delta_{Bi} = \begin{cases} 1 & if\ reaction\ i\ involves\ species\ B \\ 0 & otherwise \end{cases}$$

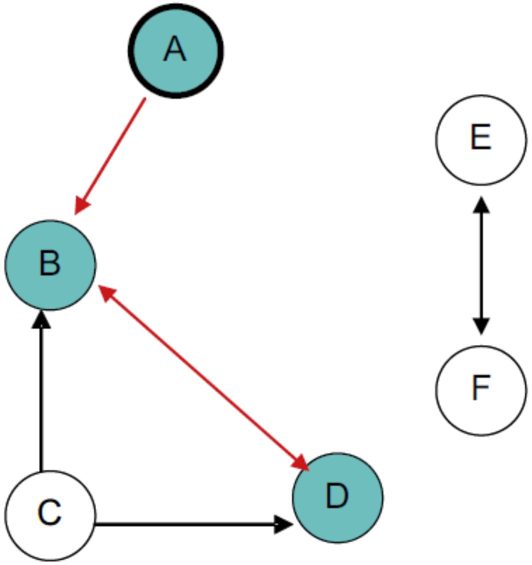
$\upsilon_{A,i}$ = stoichiometric coefficient of A in reaction i
r_i = net reaction rate of reaction i

B is important to A if (and only if) $r_{AB} > \varepsilon$, a user-specified threshold

Construction of DRG

- Vertex species (A,B,C,…)
- Edges: species dependence, $r_{AB} > \varepsilon$
- Starting vertices: species known to be important (e.g. H, fuel, oxidizer, products, a pollutant, …)

- A → B indicates that the elimination of species B will induce a non-negligible error to species A.
- If A is retained in the skeletal mechanism, B should also be retained.



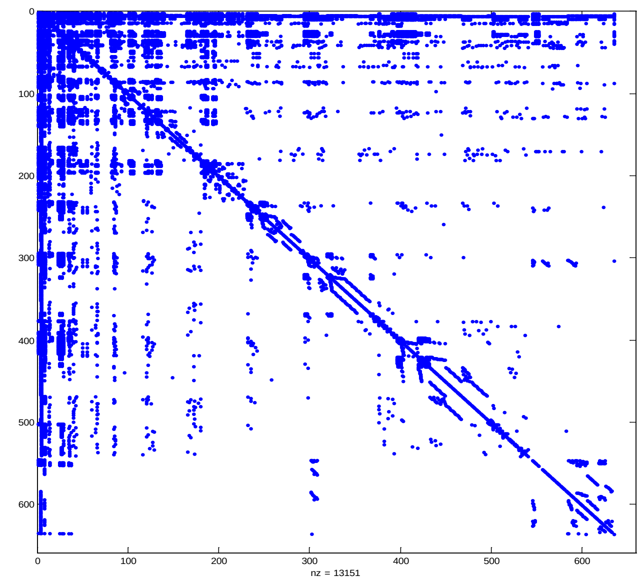
Adapted from: **T.F. Lu, C.K. Law**, *Toward accommodating realistic fuel chemistry in large-scale computations*, Progress in Energy and Combustion Science, 35, p. 192–215 (2009)

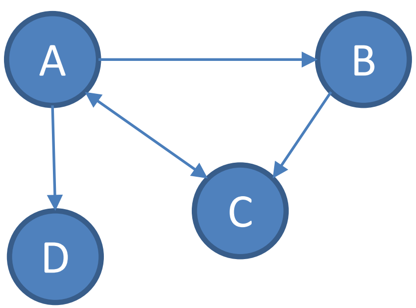
DRG and Sparse Chemical Couplings

An alternative graph representation: adjacency matrix ***E***: $E_{i,j} = 1 \quad if \;\; r_{i,j} > \varepsilon$

- Possible non-zero entries are similar to that in the chemical Jacobian
- DRG is a sparse graph
- Many algorithms in graph theory can take advantage of the sparsity (e.g. depth-first search (DFS), …)

LLNL n-heptane
Species: 658
Jacobian matrix sparsity pattern

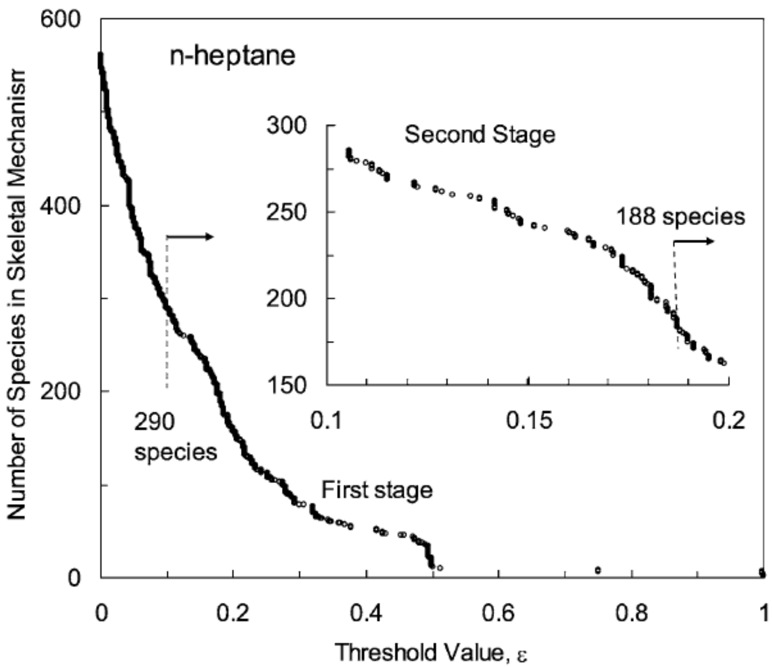




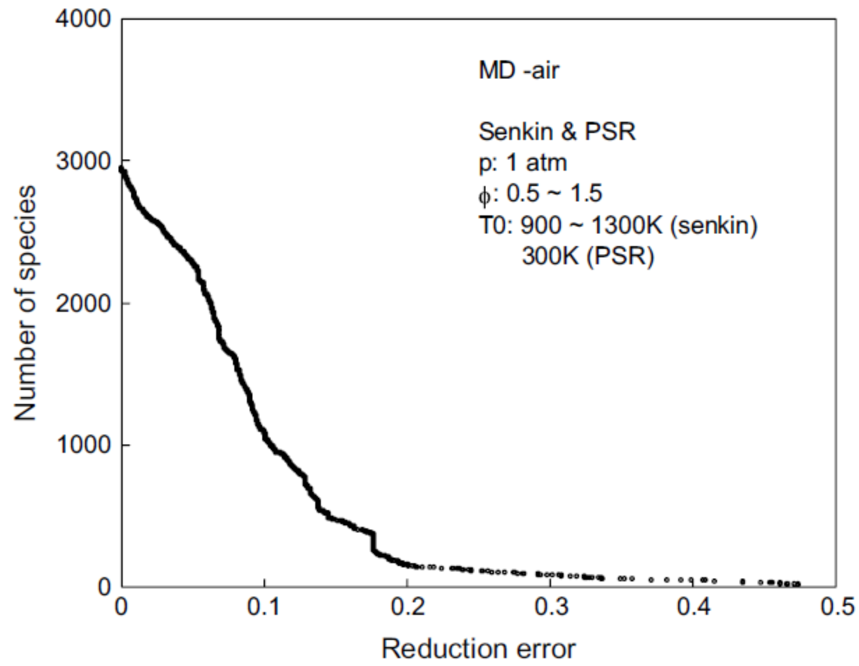
	A	B	C	D
A	1	1	1	1
B	0	1	1	0
C	1	0	1	0
D	0	0	0	1

DRG: reduction curves

A **two-stage DRG** reduction can produce a skeletal mechanism smaller than that from a single-stage DRG reduction.
The 1st stage of DRG reduction is the major reduction (a large number of species is eliminated), and the 2ns stage is a minor stage.

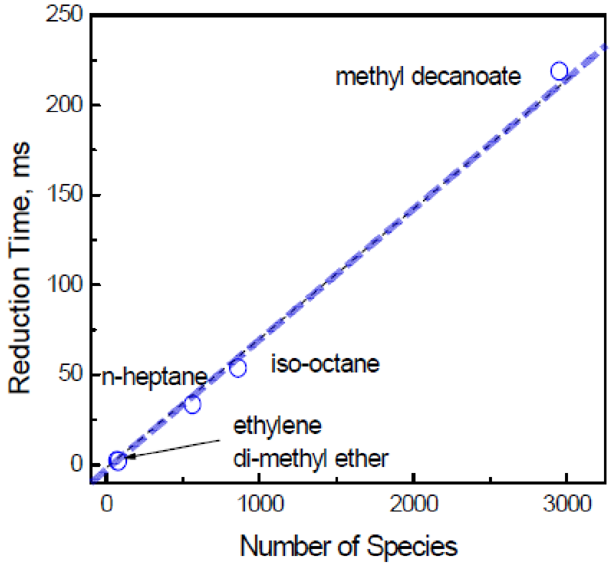


Plot from: **T.F. Lu, C.K. Law**, Linear time reduction of large kinetic mechanisms with directed relation graph: n-Heptane and iso-octane, Combustion and Flame 144, p. 24-36 (2006)



Plot from: **T.F. Lu, C.K. Law**, *Toward accommodating realistic fuel chemistry in large-scale computations,* Progress in Energy and Combustion Science, 35, p. 192–215 (2009)

More about DRG



DRG is very suitable for large detailed mechanisms

- Linear reduction time: cost **linear** with number of species
- Error control at reduction time
- Fully automated

Other graph-based reduction methods

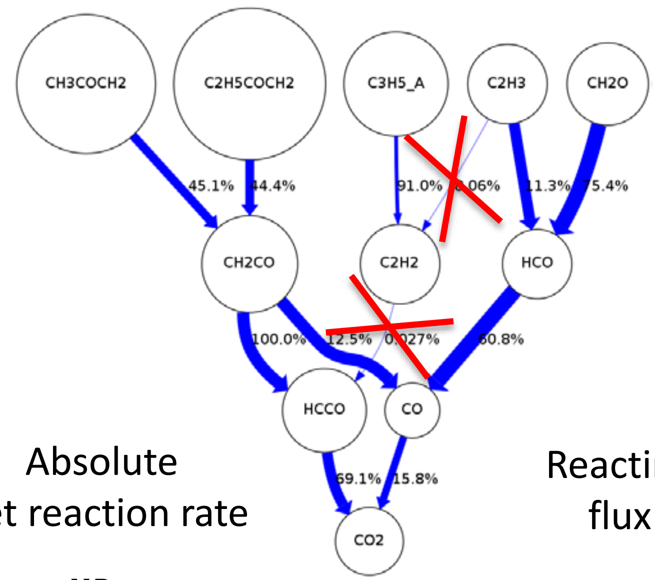
- DRG aided sensitivity analysis (**DRGASA**) [Zheng et al., 2007; Sankaran et al. 2007]
- **DRG with error propagation (DRGEP) [Pepiot-Desjardins and Pitsch 2008; Liang et al. 2009, Shi et al. 2010]**
- Path flux analysis (**PFA**) [Sun et al., 2009]
- DRGEP with sensitivity analysis (**DRGEPSA**) [Niemeyer et al. 2010]
- Transport flux based DRG (on-the-fly reduction) [Tosatto et al. 2011]
- DRG with expert knowledge (**DRGX**) [Lu et al. 2011]

Adapted from: **Lu T.,** *Computational Tools for Diagnostics and Reduction of Detailed Chemical Kinetics*, Princeton-CEFRC Summer School on Combustion (2012)

Species-Targeted Sensitivity Analysis (I)

1. Reacting Flux Analysis

Ranking species according to **production and consumption** rate history in ideal reactors.



Absolute
Net reaction rate

$$R_i(t) = \sum_{j=1}^{NR} \left| v_i^{(j)} r_j \right|$$

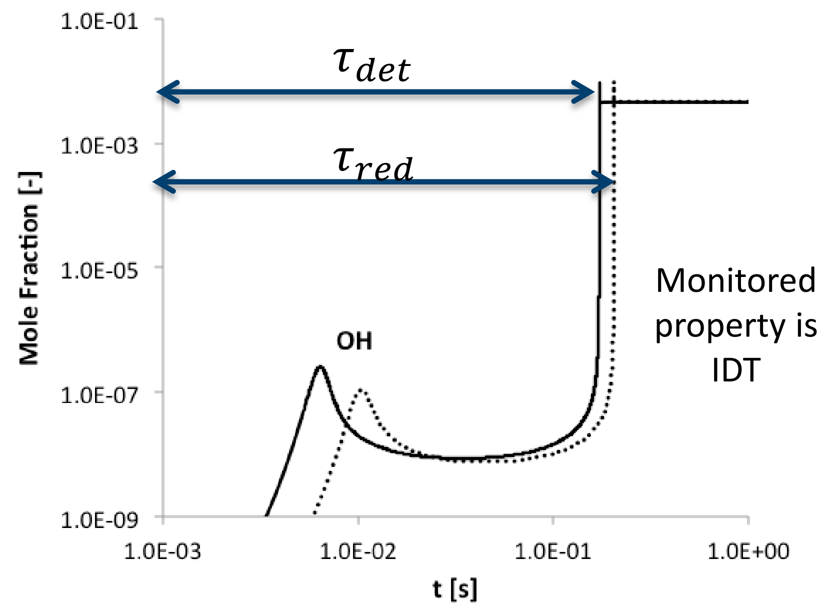
Reacting
flux

$$F_i = \int_0^{\tau_{ign}} \dot{\Omega}_i dt$$

2. Species Sensitivity Analysis

Ranking critical species according to **induced error** in the reduced mechanism

Induced error $\varepsilon = \dfrac{|\tau_{det} - \tau_{red}|}{\tau_{det}}$



Stagni A., Cuoci A., Frassoldati A., Faravelli T., Ranzi E., *Lumping and reduction of detailed kinetic schemes: an effective coupling*, Industrial & Engineering Chemistry Research, 53(22), p. 9004-9016 (2014)

Species-Targeted Sensitivity Analysis (II)

3. Reactions Sensitivity Analysis

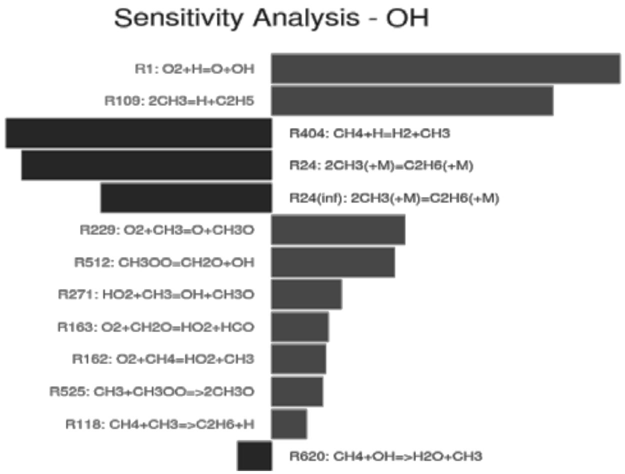
Understanding the **governing** parameters (reaction rates) of **dynamic** systems

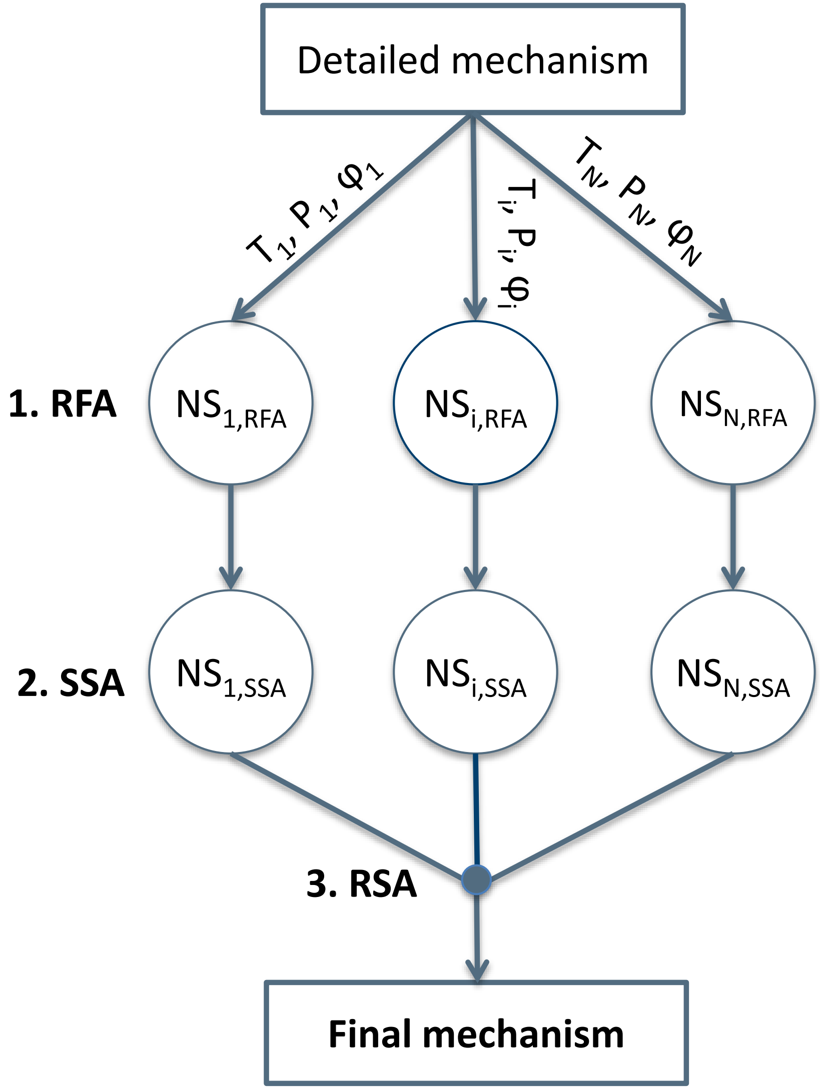
Reactor model

$$\begin{cases} \frac{d\boldsymbol{Y}}{dt} = f(\boldsymbol{Y}, t, \boldsymbol{\alpha}) \\ \boldsymbol{Y}(t_0) = \boldsymbol{Y}_0 \end{cases}$$

Sensitivity coefficients

$$\tilde{s}_{ij} = \frac{\partial ln(Y_i)}{\partial ln(\alpha_i)} = \frac{\partial Y_i}{\partial \alpha_i}\frac{\alpha_i}{Y_i}$$





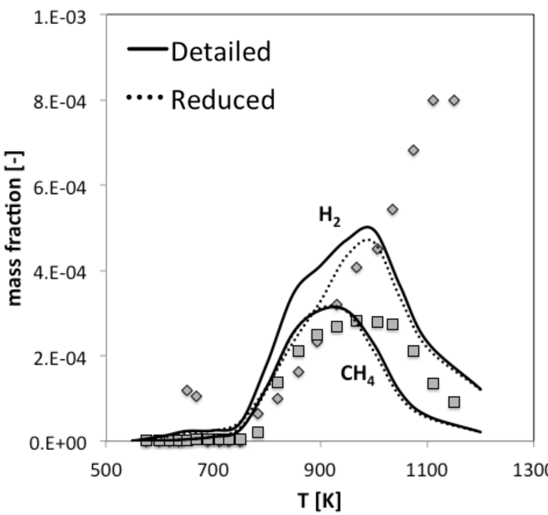
Species-Targeted Sensitivity Analysis (III)

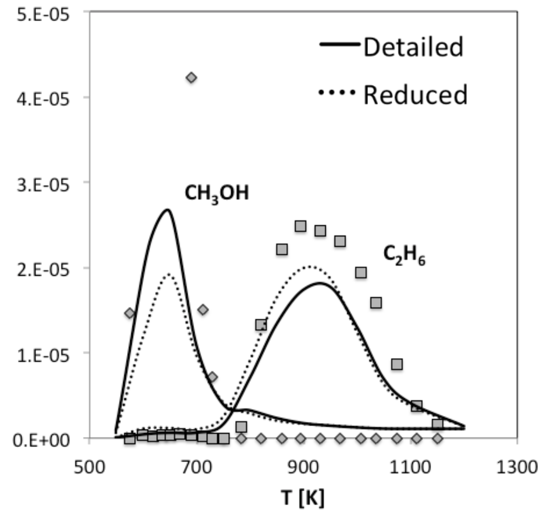
Target: LLNL (1998) n-heptane model: **561** species – **2539** reactions

	Species	Reactions	Max error (%)
Detailed	561	2539	-
DoctorSMOKE	126	560	19.6
* DRGEP	149	714	19.5

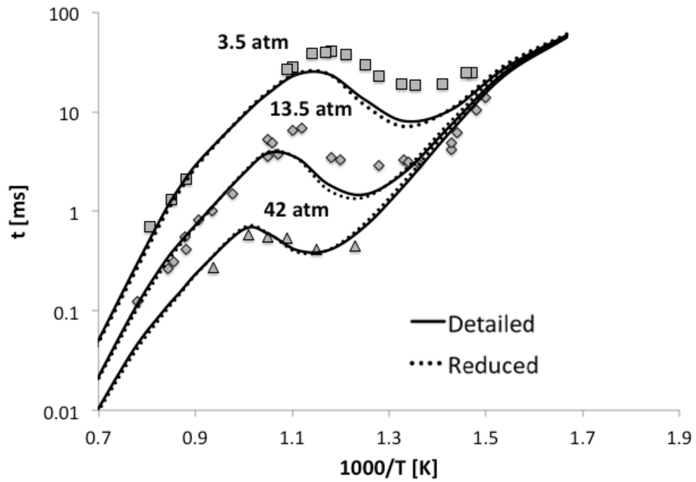
* Comparison with **state-of-the-art** approaches to mechanism reduction (Niemeyer, 2010)

Speciation in isothermal Jet Stirred Reactors





Ignition delay times (ϕ=1)



Niemeyer et al, *Skeletal mechanism generation for surrogate fuels using directed relation graph with error propagation and sensitivity analysis*, Combustion and Flame 157, p. 1760-1770 (2010)

Observations

Strengths

- The performance of the reduced mechanism is similar to that of the detailed one at a reduced computational cost
- No need to dynamically change the mechanism's dimensions allows for a tailored approach to the ODE solution

Weakness

- The operating and initial conditions chosen as reference are defined by the user and are problem dependent
- The possibility of considering transport-driven cases (e.g. 1D laminar flames) is limited by their computational demand (unviable for genetic optimization)

Adapted from: **Perini F.,** *SpeedCHEM, A Sparse Analytical Jacobian Chemistry code for Engine Simulations with Detailed Chemistry*, http://www.federicoperini.info/publications

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Quasi Steady State Approximations (QSSA)

B is a QSS species: consumption much faster than formation $A \xrightarrow{1} B \xrightarrow{1/\varepsilon} C$

The net production rate of the QSS species is therefore negligible compared with both the creation and the destruction rates

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

Its concentration is described by a non-linear, algebraic equation

$$B \approx A\varepsilon = \mathcal{O}(\varepsilon)$$

<u>Hypotheses</u>

1. QSS species stay in low concentrations
2. Reactions involving two QSS reactors are likely unimportant

$\Downarrow$

QSSA are intrinsically a linear problem

$$Q_A + Q_B \rightarrow products$$

$$r = k_f[Q_A][Q_B] = \mathcal{O}(\varepsilon^2)$$

Lu T. and Law C.K. , *A criterion based on computational singular perturbation for the identification of quasi steady state species: A reduced mechanism for methane oxidation with NO chemistry*, Combustion and Flame, 154 p. 761–774 (2008)

Lu T. and Law C.K. , *Systematic Approach To Obtain Analytic Solutions of Quasi Steady State Species in Reduced Mechanisms*, Journal of Physical Chemistry A, 110, p. 13202-13208 (2006)

Solving linear-QSSA Equations

QSS species: algebraic equations

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

Traditional approach
Algebraic iterations

- Slow convergence (inefficiency)
- Possible divergence (crashes, …)

New approach
Linear QSSA (analytic solution)

- Higher accuracy
- Higher efficiency
- Higher robustness

System of linear equations

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

Destruction rate

Formation rate involving other QSS species

Formation rate involving major species

1. the L-QSSA equations can be analytically solved with a directed graph, (QSSG), which is abstracted from the inter-dependence of QSS species.

2. To obtain analytic solutions, the groups of strongly connected QSS species are first identified in the QSSG.

3. The inter group couplings are then resolved by a topological sort, and the inner group couplings are solved with variable elimination by substitution.

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Dynamic Chemical Stiffness Removal (DCSR) (I)

Problem: Mechanisms are still stiff, even after skeletal reduction and QSSA

Consequences: Implicit solvers needed for stiff chemistry

- Evaluation of Jacobian: $\sim\mathcal{O}(N_S)$ or $\sim\mathcal{O}(N_S^2)$
- Factorization of Jacobian: $\sim\mathcal{O}\left(N_S^3\right)$

Idea of Dynamic Chemical Stiffness Removal

- Chemical stiffness is induced by fast reactions
- Fast reactions results in either QSSA or PEA
- Classified a priori
- Analytically solved on the fly

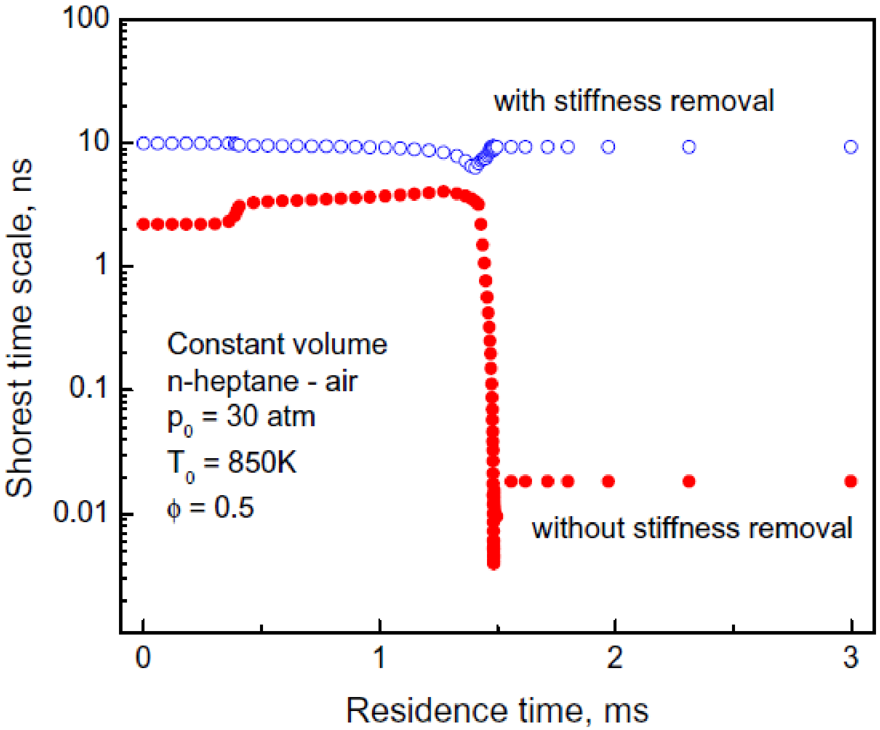
The classification of QSS species and PE reactions is usually time-consuming. Thus, it must be performed *a priori* through tabulation or regression networks.

Explicit solver can be used after DCSR

- Time-step limited by CFL condition
- Cost of DNS: $\sim\mathcal{O}(N_S)$

Adapted from: **Lu T.,** *Computational Tools for Diagnostics and Reduction of Detailed Chemical Kinetics*, Princeton-CEFRC Summer School on Combustion (2012)

Dynamic Chemical Stiffness Removal (DCSR) (II)



Plot from: **Lu et al.**, *Dynamic stiffness removal for direct numerical simulations*, Combustion and Flame 156, p. 1542-1551 (2009)

Shortest time-scale associated with the eigen-modes of the Jacobian, evaluated with and without the stiffness removal procedure, respectively, for constant-volume homogeneous auto-ignition for an initial pressure of 30 atm, equivalence ratio of 0.5, and initial temperature of 850 K.

Notes

The DCSR is particularly suitable for DNS, because of the small integration time-steps imposed by the CFL condition.

The relative reduction error is consequently small due to the small time-step. The stiffness removal procedure should be carefully validated if larger integration steps are assumed, as for example, in large-eddy simulations.

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CFD

$\boldsymbol{\psi} = (\boldsymbol{Y}, T, p)$ $\qquad$ $\bar{\mathbf{S}}(\boldsymbol{\psi})$

Chemistry

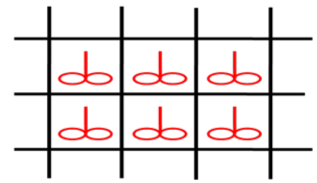
Implicit solver

$$\frac{\partial \boldsymbol{\psi}}{\partial t} = \underbrace{\bar{\mathbf{S}}(\boldsymbol{\psi})}_{\text{Chemical source term}} + \underbrace{\mathbf{M}(\boldsymbol{\psi})}_{\text{Transport and diffusion}}$$

$$\frac{\partial \boldsymbol{\psi}}{\partial t} = \boldsymbol{S}(\boldsymbol{\psi})$$

Stiff and non linear

Chemical step



$$\frac{\partial \boldsymbol{\psi}}{\partial t} = \mathbf{S}(\boldsymbol{\psi})$$

Most of CPU time (>90%) is usually spent for the chemical step, because integration of stiff ODE systems is required

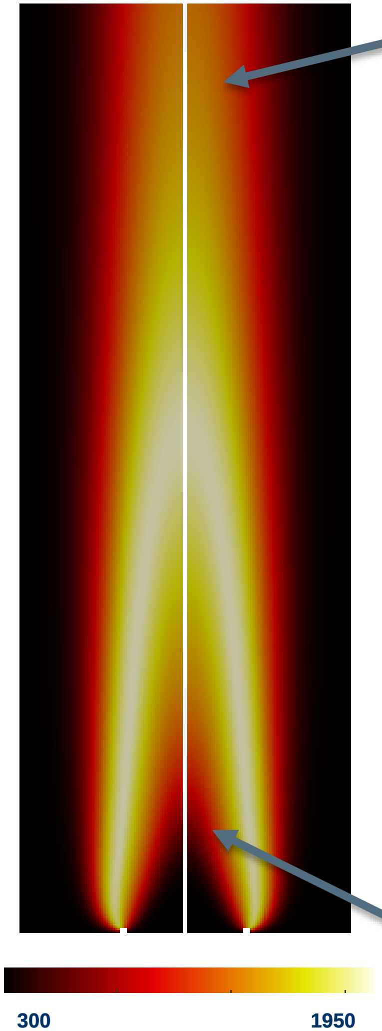
During the chemical time step each cell is an adiabatic batch reactor, i.e. a system closed to exchange of mass of heat

We can locally reduce the complexity of chemical kinetics according to the operating conditions

Dynamic Adaptive Chemistry

Adapted from: **Contino F. et al.**, *Tabulation of Dynamic Adaptive Chemistry: A global approach to include detailed mechanisms in engine simulations*, Fifth OpenFOAM Workshop (2011)

Dynamic Adaptive Chemistry (DAC) (II)



Smaller kinetic scheme

for most practical combustion simulation problems, a relatively smaller number of species and reactions participate in the processes of pivotal importance such as heat release and emissions formation

Larger kinetic scheme

Dynamic Adaptive Chemistry

The detailed mechanism is reduced **locally and instantaneously** into accurate sub-mechanisms at each hydrodynamic time step of the calculation ("on the fly")

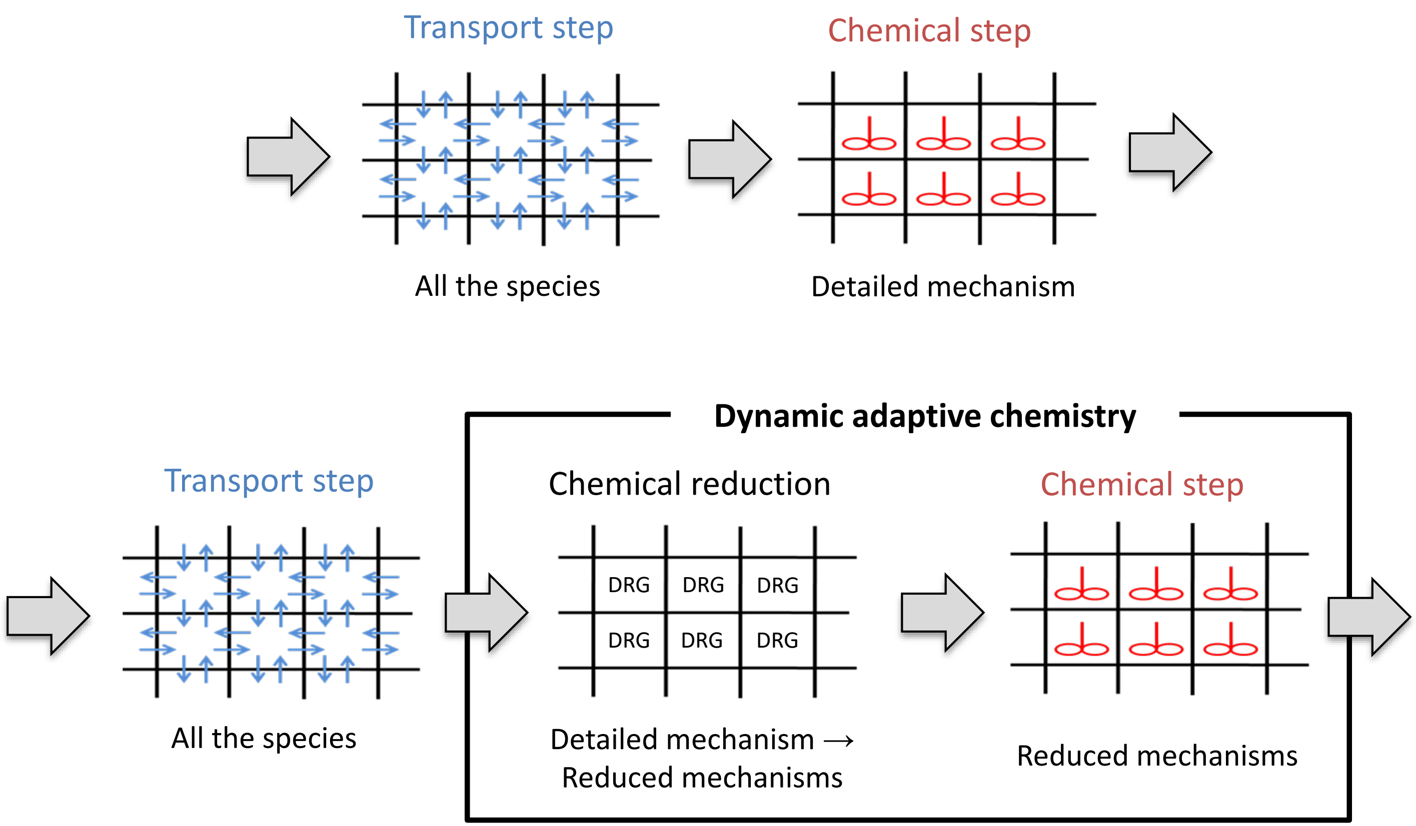
no a priori information regarding simulation conditions is needed.

For comprehensiveness, more species is better
For computational cost, less species is better

Liang L., Stevens J.G., Farrell J.T., *A dynamic adaptive chemistry scheme for reactive flow computations*, Proceedings of The Combustion Institute, 32, p. 527–534 (2009)

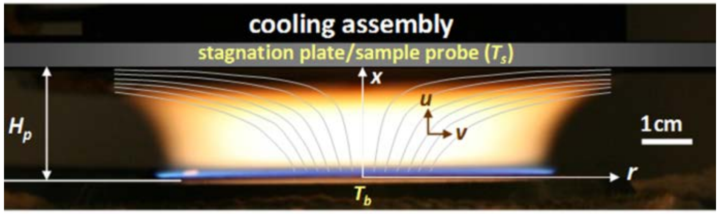
Liang L., Stevens J.G., Raman S., Farrell J.T., *The use of dynamic adaptive chemistry in combustion simulation of gasoline surrogate fuels*, Combustion and Flame, 156, p. 1493–1502 (2009)

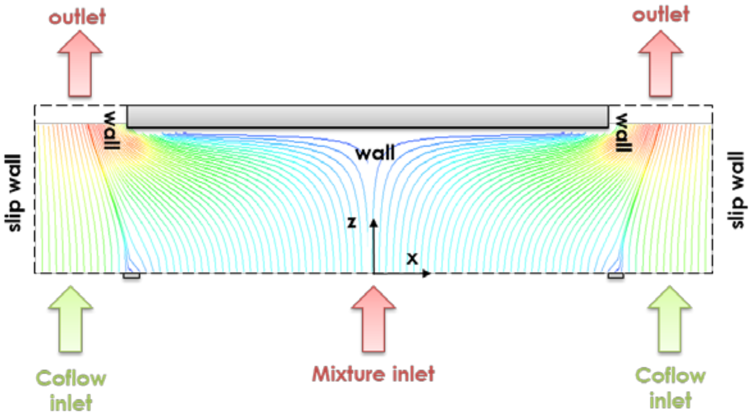
Dynamic Adaptive Chemistry (DAC) (III)



An example: a premixed, laminar flame

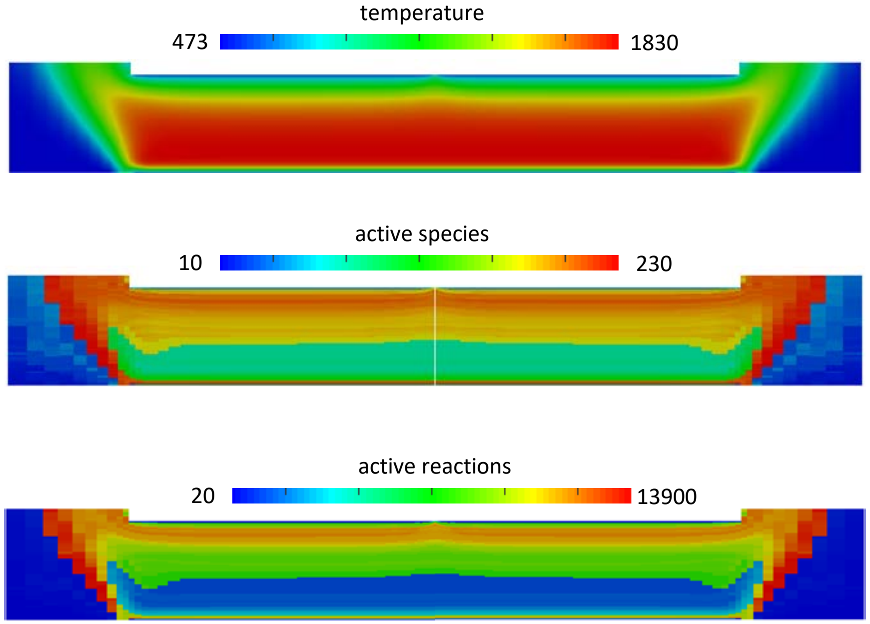
Burner-Stabilized Stagnation Flame





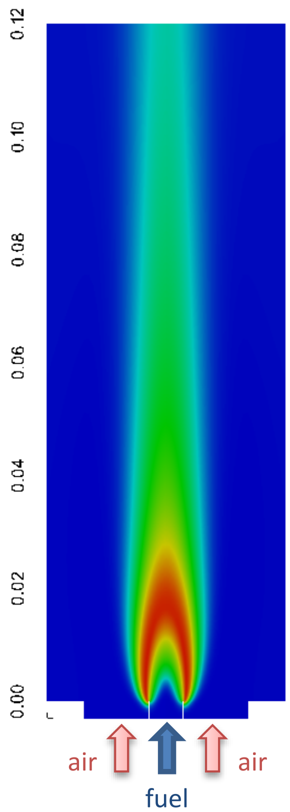
Saggese C. et al., *Modeling Study of Probe-Induced Effects on Soot Sampling in Laminar Premixed Flames in a Benchmark Burner-Stabilized Stagnation Flame*, Manuscript in preparation

Detailed kinetic mechanism: 292 species and ~15,800 reactions



Saggese et al., *Kinetic Modeling of Particle Size Distribution of Soot in a Premixed Burner-Stabilized Stagnation Ethylene Flame*, Combustion and Flame, Accepted

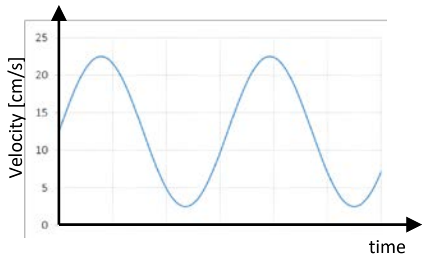
An example: a pulsating, non-premixed flame

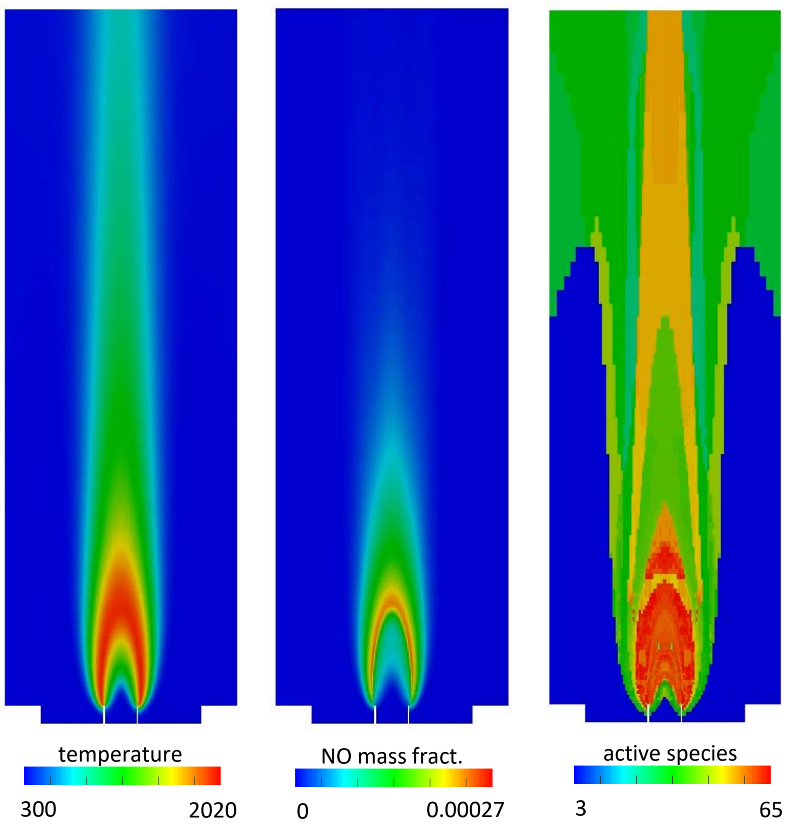


POLIMI kinetic mechanism
Species: 115
Reactions: 2141

Fuel mixture: 34% C_2H_4, 66% N_2
Coflow stream: 21% O_2, 79% N_2

The **transient behavior** is induced by a **10 Hz perturbation** in the fuel velocity profile:





In cooperation with **D. Di Fiore and A. Parente** (Université Libre de Bruxelles)

Outline

1. **Acceleration of simulations by reduction of species**
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   c) Dynamic Stiffness Removal (DSR)
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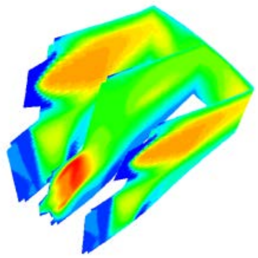
4. **Computation Cost Minimization**

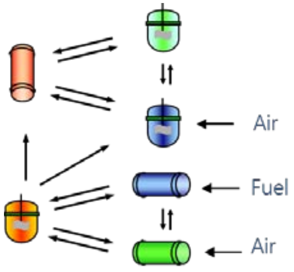
5. **Numerical tools for analysis of kinetic mechanisms**

Reducing the number of reacting environments

CFD simulation



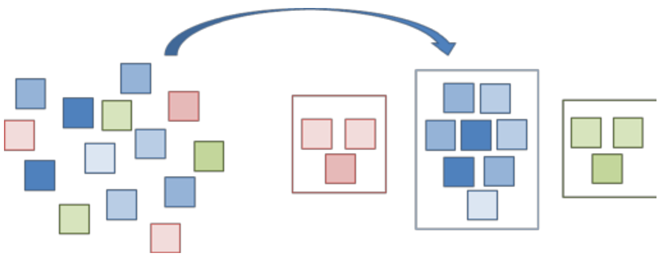
(Static) Reactor Network Analysis



- A network of ideal reactors (PSR and PFR) is built on the basis of CFD velocity and temperature field
- A detailed kinetic mechanism is adopted to solve the network
- Particularly useful as a post-processing tool

Dynamic Cell Clustering

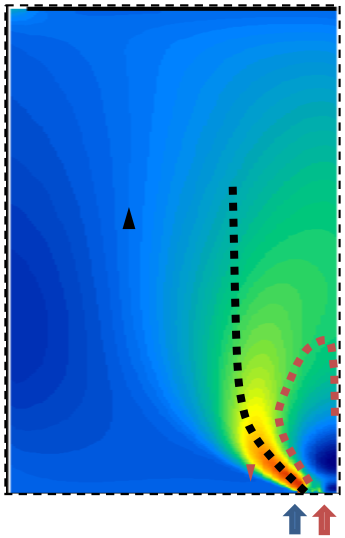
Cells having similar thermochemical conditions (not necessarily closed in physical space) are grouped together. This reduces the number of detailed chemistry calculations executed at every time step, as calculations are now executed for a group of cells (i.e. the cluster), and not for each and every cell.



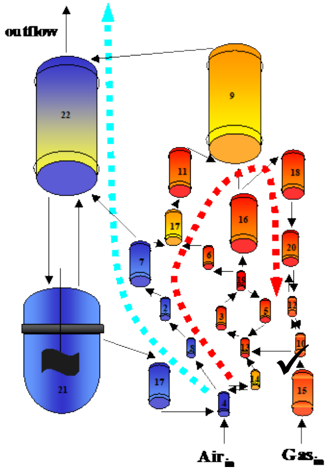
Particularly useful to model internal combustion engines

Reaction Network Analysis (RNA) (I)

1. CFD Simulation



2. Clustering and network construction



- The clustering reduces the overall dimensions of the problem
- According to the clustering, a complex reactor network is constructed

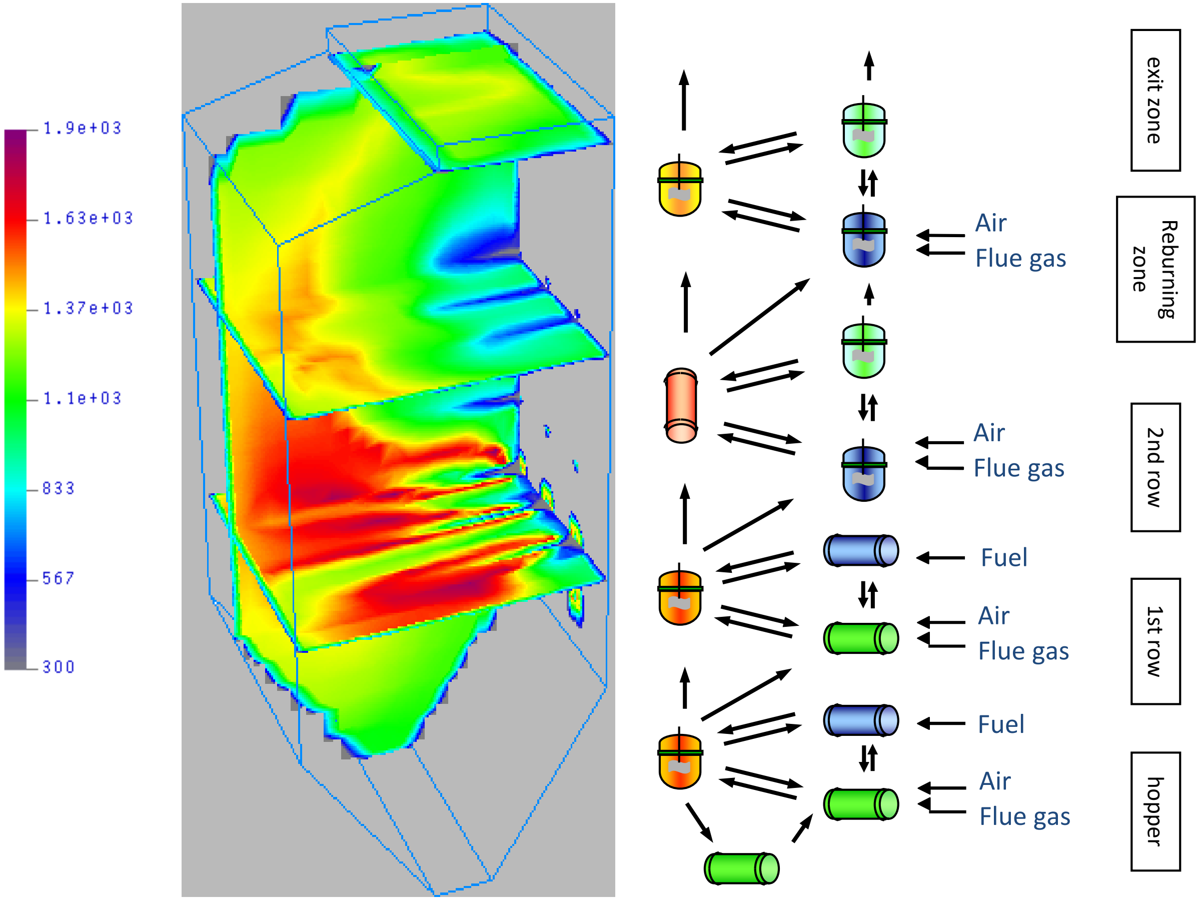
3. Network solution

- A very detailed kinetic scheme is used
- Specifically conceived numerical method
- High number of non linear equations: *example: 500 species x 5,000 reactors = 2,5000,000 eqs*

Ehrhardt K. et al., *Modeling of NOx reburning in a pilot scale furnace using detailed reaction kinetics*. Combust. Sci. Technol. 1998, 131 (1–6), 131–146

Falcitelli M. et al., *CFD + reactor network analysis: An integrated methodology for the modeling andoptimization of industrial systems for energy saving and pollution reduction*, Appl. Therm. Eng. 2002, 22 (8), 971–979

Industrial furnace (Cassano d'Adda, 75 MW)



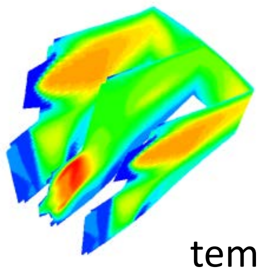
On the basis of the computed three-dimensional (3D) results for flow, temperature, and stoichiometric fields, the volume of the combustion device is reduced to a simplified network of ideal PSRs or plug flow reactors.

Then, within each reactor, a detailed kinetic model is used to predict the concentrations of additional species (especially pollutants like NOx).

WARNING!
it is possible to obtain fairly network-independent results only for proper construction of reactor network

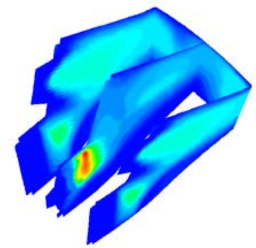
Kinetic post-processing (I)

CFD simulation



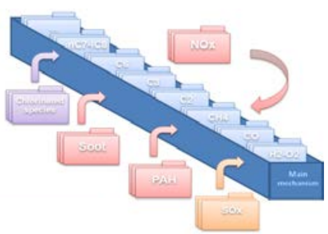
temperature

Post-Processing



nitrogen oxides
"slow" pollutant species

Detailed chemistry



a steady state CFD simulation of the combustion device is performed using a global kinetic mechanism, which allows for the correct prediction of thermal and flow fields, but which cannot give us information on pollutant species

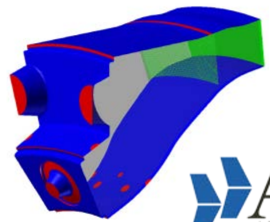
pollutant species usually affect only marginally the main combustion process and consequently do not influence the overall temperature and flow field

Faravelli T. et al., *A new procedure for predicting NOx emissions from furnaces*, Comput. Chem. Eng. 2001, 25 (4–6), 613–618

Skjoth-Rasmussen M. et al., *Post-processing of detailed chemical kinetic mechanisms onto CFD simulations*, Comput. Chem. Eng. 2004, 28 (11), 2351–2361

Fichet, V. et al., *A reactor network model for predicting NOx emissions in gas turbines*, Fuel 2010, 89 (9), 2202–2210.

Kinetic post-processing (II)

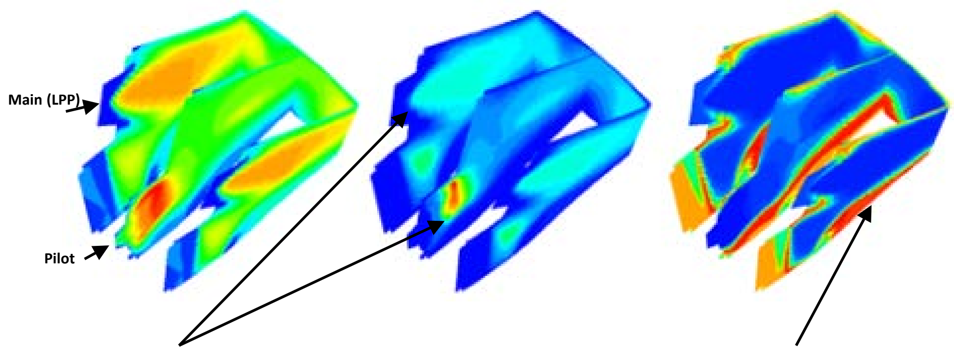


Stagni et al., *A fully coupled, parallel approach for the post processing of CFD data through reactor network analysis* Computers and Chemical Engineering, 60, p. 197-212 (2014).

Frassoldati et al., *Experimental and modeling study of a low NOx combustor for aero-engine turbofan*, Combustion Science and Technology 181, p. 483-495 (2009

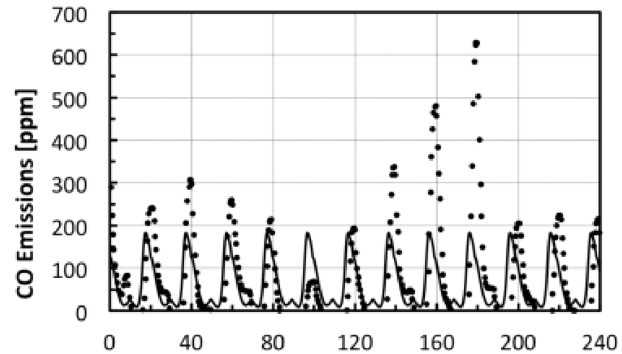
500k cells x 100 species = 50 M equations

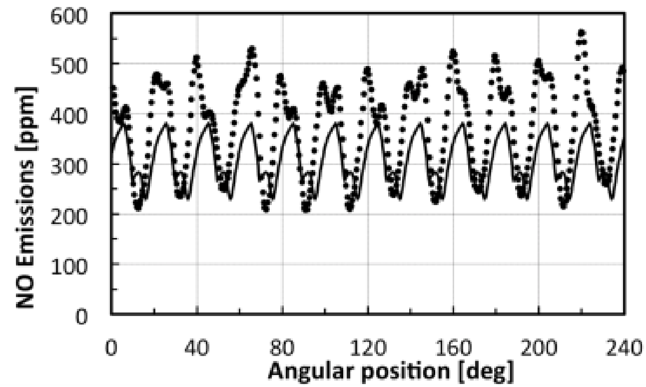
Fully-coupled solution!



Different amounts of NOx formed in the conventional (pilot) and LPP injectors

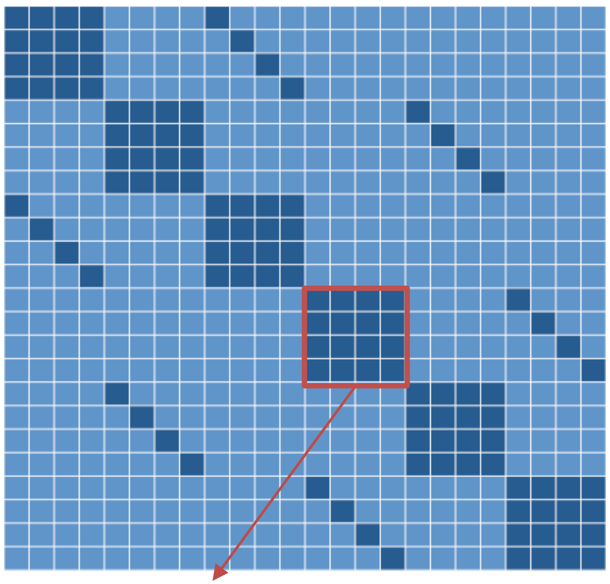
Formation of NO_2 in the low temperature region (film cooling)





Non Linear System (NLS) of equations

Jacobian sparsity pattern



Single reactor

- Jacobian is sparse and block-unstructured
- High degree of accuracy is sought

Convection | Diffusion | Reaction | Evaporation

$$\left(\sum_{k=1}^{N_{AD}} \dot{m}_{k,j}\omega_{k,j,i} - \dot{m}_j\omega_{j,i}\right) + \sum_{k=1}^{N_{AD}}\left(J_{j,k,i}\cdot S_{j,k}\right) + V_j^*\tilde{\Omega}_{j,i} + \Pi_{j,i} = 0$$

Linear

$$J_i = -\frac{\mu_t}{Sc_t}\cdot\nabla\omega_i$$

Linear

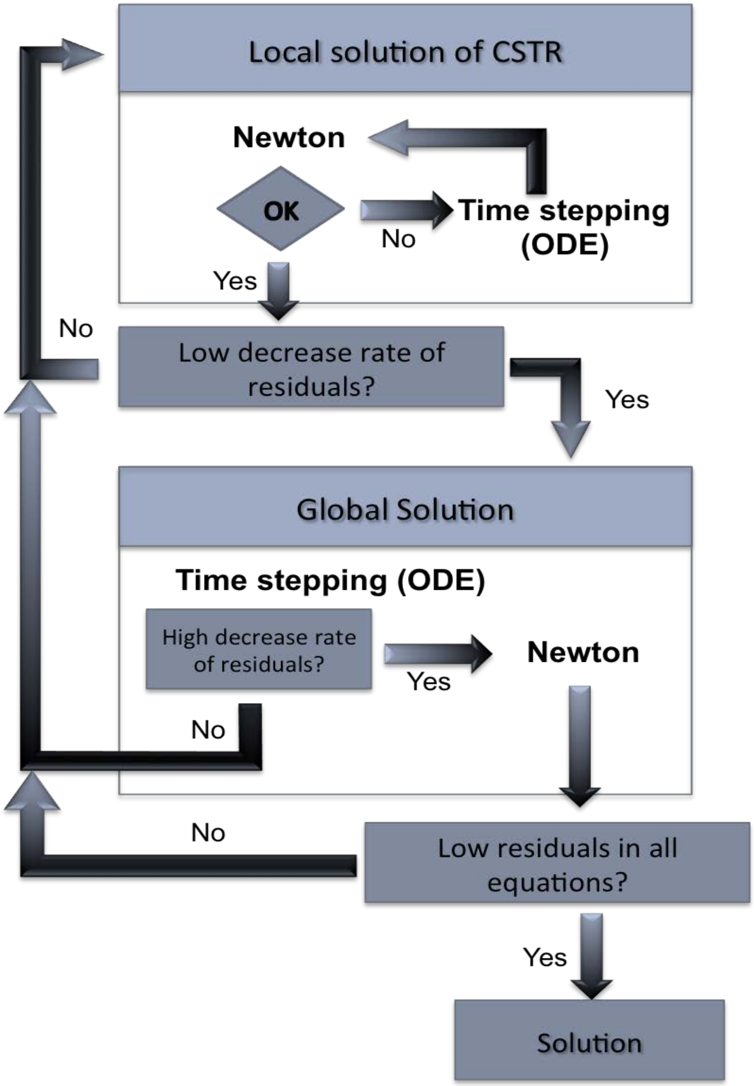
Non Linear (Power Law)

A fully coupled resolution is implemented

$$\mathbf{C}(\boldsymbol{\omega}) + \mathbf{R}(\boldsymbol{\omega}) + \mathbf{f} = \mathbf{0}$$

Linear | Non-Linear | External feeds

Numerical methodology



the numerical procedure combines different techniques to obtain the final solution, because the global Newton's method can be successfully applied only if the first-guess solution is close to the real solution.

1. Global Newton's Method
2. Global ODE (Backward Euler)
3. Direct Substitutions (Local solution)
   a. Local Newton's Method
   b. Local ODE system (stiff solver)

Cuoci, A., Frassoldati, A., Stagni, A., Faravelli, T., Ranzi, E., Buzzi-Ferraris, G., *Numerical modeling of NOx formation in turbulent flames using a kinetic post-processing technique* (2013) Energy and Fuels, 27 (2), pp. 1104-1122, DOI: 10.1021/ef3016987

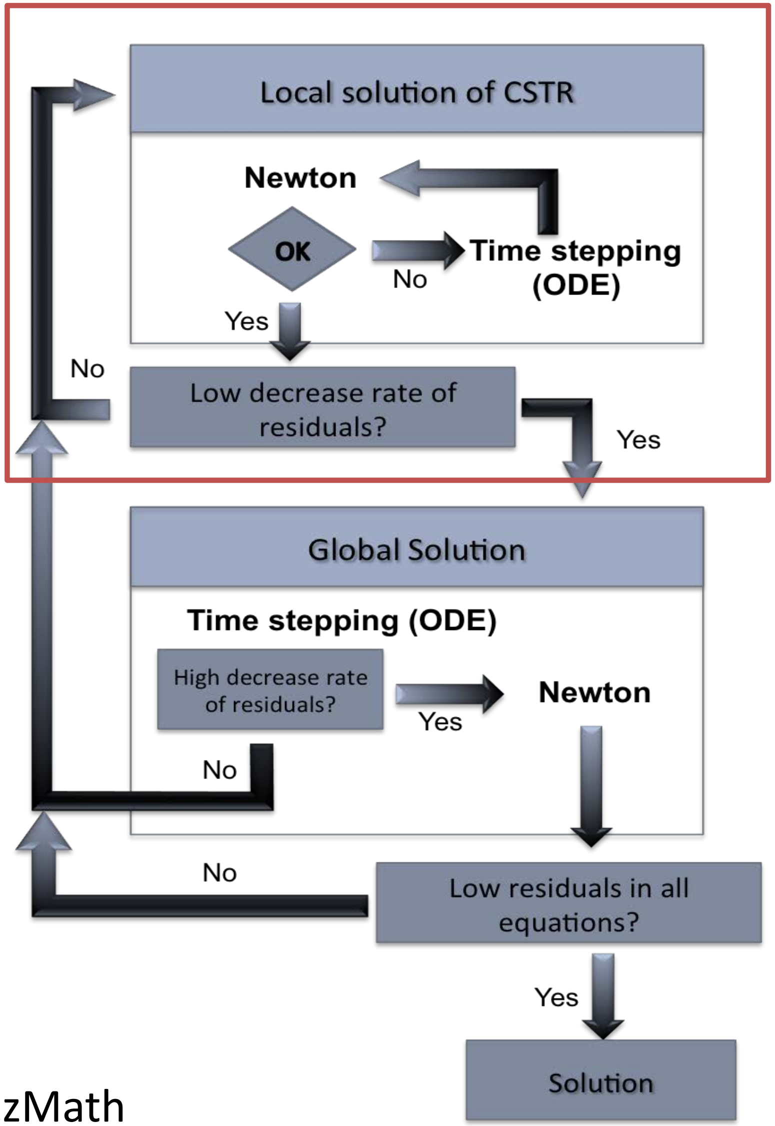
Local solution

The individual reactors are solved sequentially to take the whole system closer to the solution. This means that each reactor is solved using a local Newton's method.

$$\left[\mathbf{C}_{in}(\boldsymbol{\omega})+\mathbf{f}\right]_{old}+\mathbf{C}_{out}(\boldsymbol{\omega})+\mathbf{R}(\boldsymbol{\omega})=\mathbf{0}$$

To improve the robustness, especially in the first iteration, a false transient method is used to solve the single reactors. The NLS is transformed into a ODE system by adding the unsteady term

$$\mathbf{m}\frac{d\boldsymbol{\omega}}{dt}=\left[\mathbf{C}_{in}(\boldsymbol{\omega})+\mathbf{f}\right]_{old}+\mathbf{C}_{out}(\boldsymbol{\omega})+\mathbf{R}(\boldsymbol{\omega})$$



<u>Stiff ODE solvers</u>

OpenSMOKE++, CVODE, DVODE, LSODE, RADAU5, BzzMath

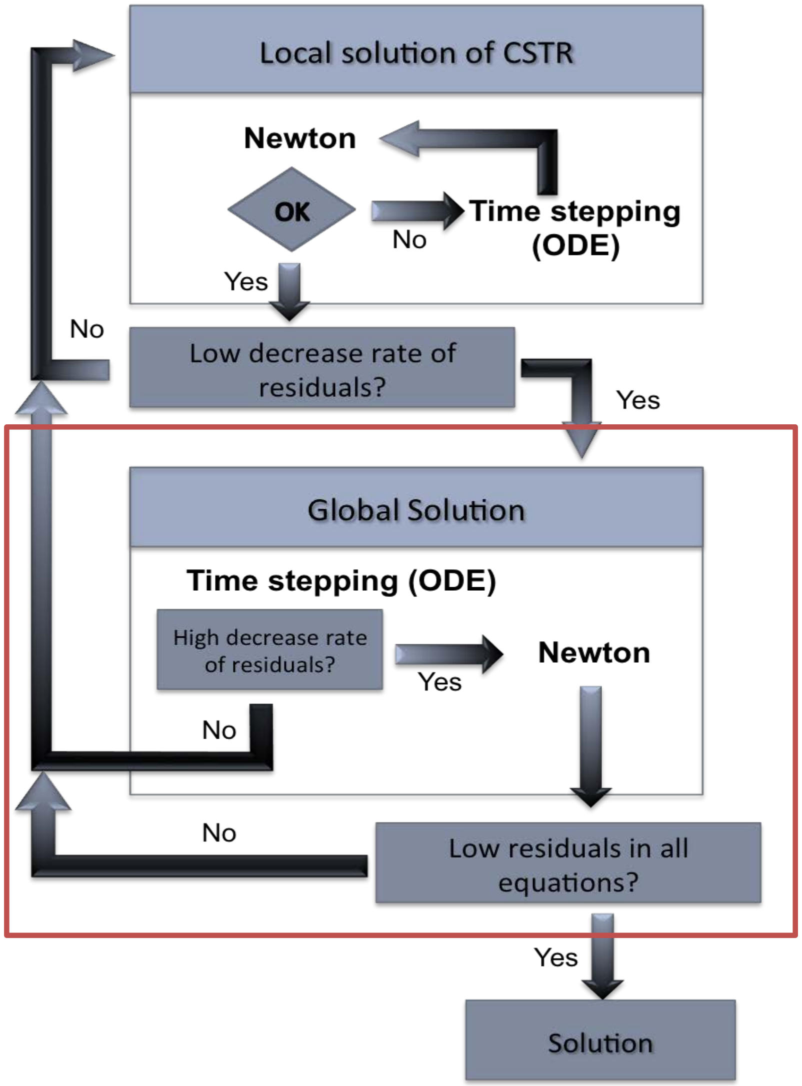
Global solution

the global Newton's method, to ensure the accuracy needed to correctly predict chemical species present in very small amounts (ppm or smaller)

$$\mathbf{C}(\boldsymbol{\omega})+\mathbf{R}(\boldsymbol{\omega})+\mathbf{f}=\mathbf{0}$$

When complex flows are investigated, the sequential approach (i.e., direct substitutions) could not be enough to reduce the residuals of equations to sufficiently small values to successfully apply the global Newton's method. In such a case, a global time-stepping procedure must be taken into account.

$$\mathbf{m}_{tot}\frac{\boldsymbol{\omega}^{n+1}-\boldsymbol{\omega}^{n}}{\Delta t}=\mathbf{C}\left(\boldsymbol{\omega}^{n+1}\right)+\mathbf{R}\left(\boldsymbol{\omega}^{n+1}\right)+\mathbf{f}$$

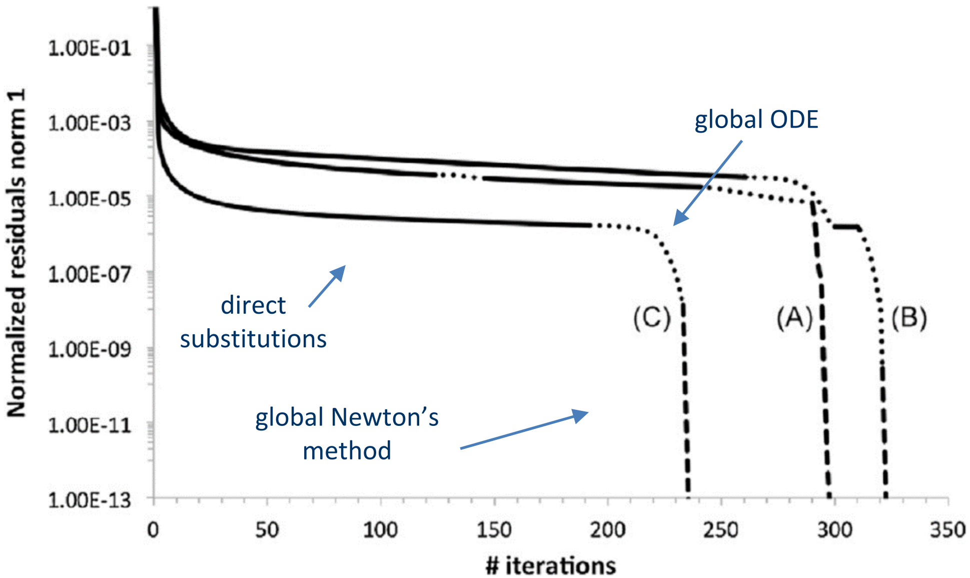


<u>Linear System solvers</u>

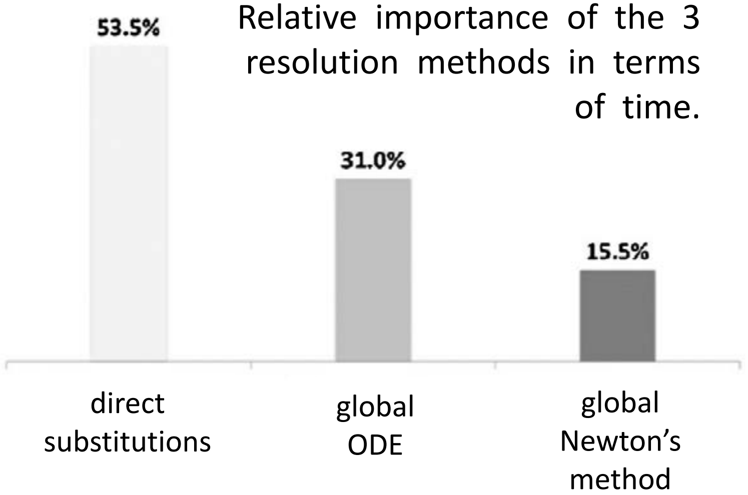
MUMPS 4.10 (Direct Solver), LIS 1.24 (Iterative Solver)

Numerical performances

- A: a tubular combustor (56,150 reactors, 4.8M eqs)
- B: an aircraft combustor (252,885 reactors, 22M eqs)
- C: an aircraft combustor (290,764 reactors, 25M eqs)



Residuals norm 1 trends, normalized with respect to their initial value (set equal to 1)



Relative importance of the 3 resolution methods in terms of time.

POLIMI NC7 kinetic mechanism
86 species and 1427 reactions

Plots from: **Stagni et al.,** *A fully coupled, parallel approach for the post processing of CFD data through reactor network analysis* Computers and Chemical Engineering, 60, p. 197-212 (2014).

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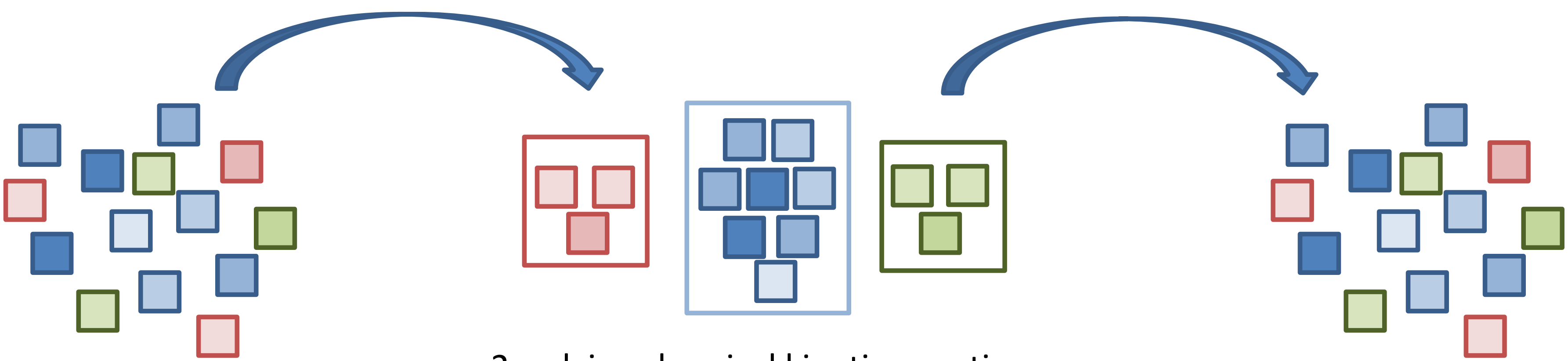
Dynamic Cell Clustering (DCC) (I)

Dynamic Cell Clustering (DCC) dynamically groups/clusters regions of the domain that have similar thermochemical conditions. This reduces the number of detailed chemistry calculations executed at every time step, as calculations are now executed for a group of cells (i.e. the cluster), and not for each and every cell.



Dynamic Cell Clustering (DCC) (II)

The grouping of computational cells, in the calculation domain, into clusters is achieved by using **clustering algorithms** which identify cells that have similar thermochemical states. Cell temperature and equivalence ratio are typically used as the thermochemical clustering variables.

On which basis can reacting cells be regarded as similar or different?

The chemical kinetic equations are now solved at the cluster and not at the cell level, using averaged values for the state variables. The cluster averaged chemistry solution is them **mapped back** to the individual cells in each cluster.

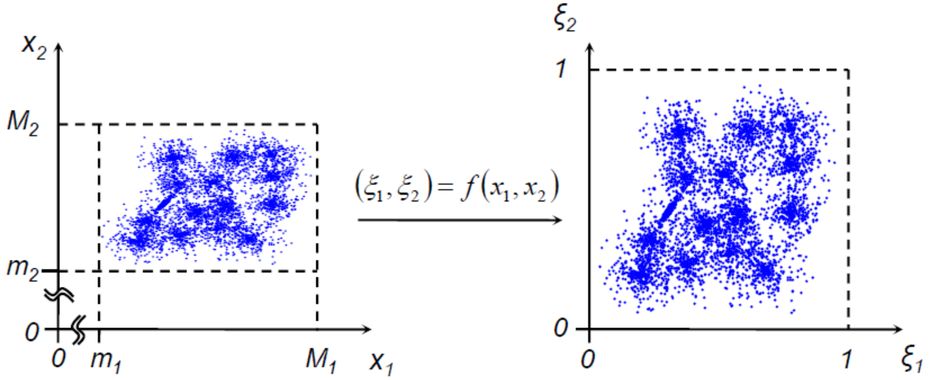
How to conservatively redistribute the species among the different cells, after integration?

Liang L., Stevens J. G., Farrell J.T., *A Dynamic Multi-Zone Partitioning Scheme for Solving Detailed Chemical Kinetics in Reactive Flow Computations*, Combustion Science and Technology 181(11), p.1345-1371 (2009)

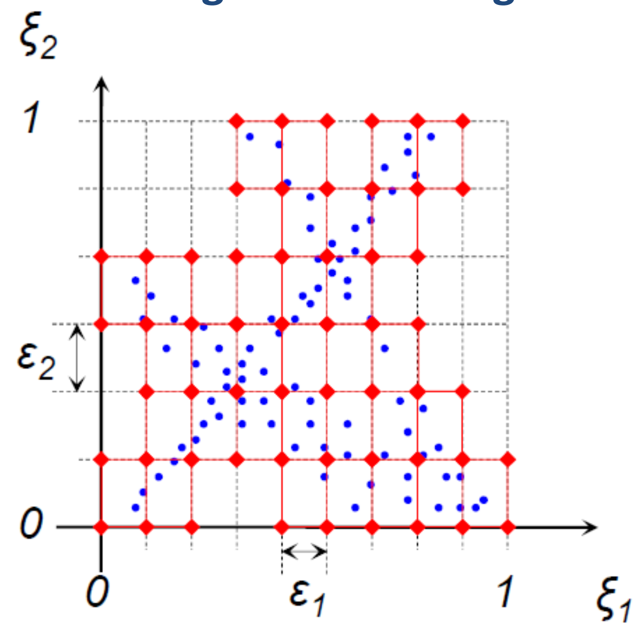
G.M. Goldin, Z. Ren, S. Zahirovic, *A cell agglomeration algorithm for accelerating detailed chemistry in CDF*, Combust. Theory Model., 13, pp. 721–739 (2009)

High dimensional cell clustering

- The clustering space is defined as the d-dimensional cell positions in the state space [T; (d-1) mass fractions]
- Normalized to a unity hyper-box



Bounding-box clustering



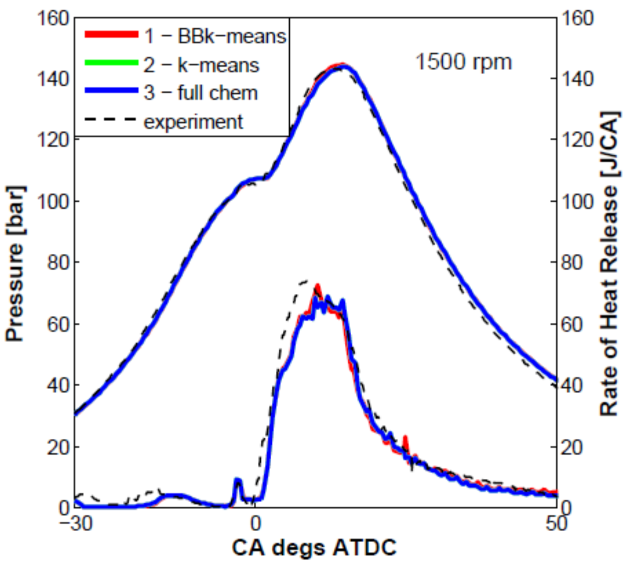
- Cluster initialization as a structured grid
- Each point is contained in a bounding box of 2^d cluster centers
- Clusters have to stay local (bounding-box-constrained k-means algorithm)
- Reduced computational effort (evaluate 2^d distances per point)

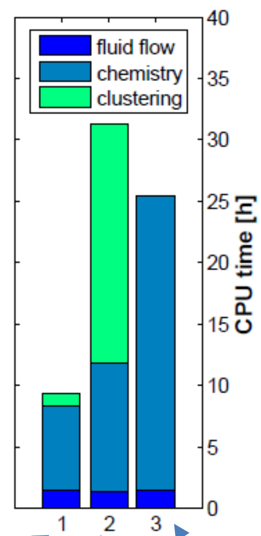
Perini F., *High-dimensional, unsupervised cell clustering for computationally efficient engine simulations with detailed combustion chemistry*, Fuel 106, p. 344–356 (2013)

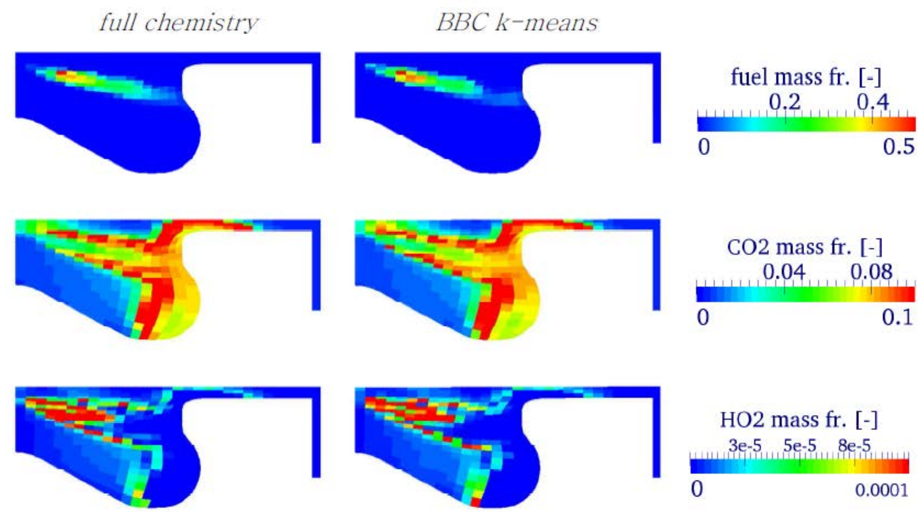
Some results

Fiat 1.3l DI diesel engine (operated with multiple injections)

Cells: ~25,000 (at BDC)
Dimensionality: d=5 (T, nC7H16, O2, CO2, HO2, H2O)







Bounding-box clustering

Traditional clustering

No clustering

Simulations and results from: **Perini F.,** *High-dimensional, unsupervised cell clustering for computationally efficient engine simulations with detailed combustion chemistry*, Fuel 106, p. 344–356 (2013)

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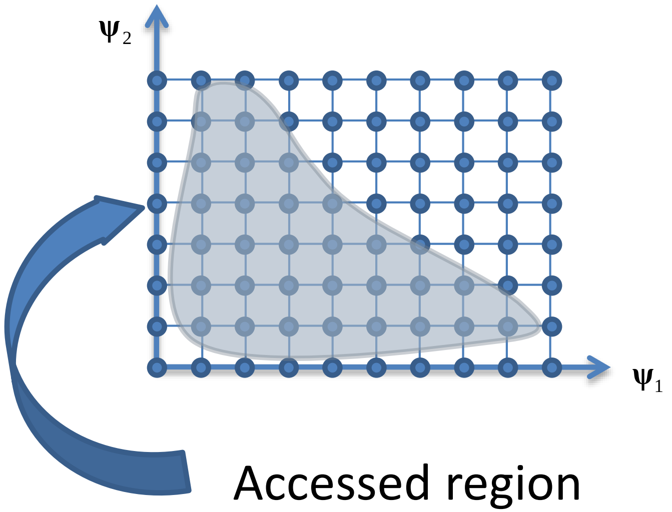
Reaction maps

Operator-splitting algorithms: integration of chemical step

$$\begin{cases} \dfrac{d\boldsymbol{\Psi}}{dt} = \mathbf{S}(\boldsymbol{\Psi}) \\ \boldsymbol{\Psi}(t=0) = \boldsymbol{\Psi}_0 \end{cases}$$

$$\boldsymbol{\Psi}_0 \xrightarrow{reaction} \boldsymbol{\Psi}_{\Delta t} = \mathbf{R}(\boldsymbol{\Psi}_0; t)$$

$\boxed{\mathbf{R}(\boldsymbol{\Psi}_0; t) \quad \text{Reaction map}}$



Example
Number of variables: 5
Number of tabulation points per variable: 100
Total number of points in the tabulation: $100^5=10^{10}$
Required memory: $5 \cdot 8 \cdot 10^{10} = 4 \cdot 10^{11}$ bytes = 400 Gb

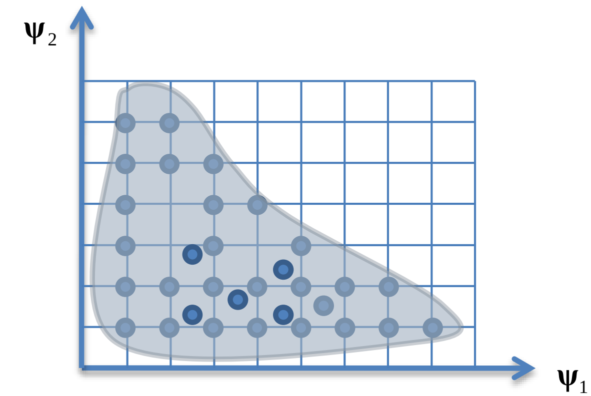
Smart tabulation

ISAT: In Situ Adaptive Tabulation

1. **In Situ:** In situ: Tabulation is carried out only with respect to those points to which the reactive system actually has access (accessed region)

2. **Adaptive:** A specific algorithm is applied in order to minimize the points to be tabulated within the access region, while maintaining good accuracy

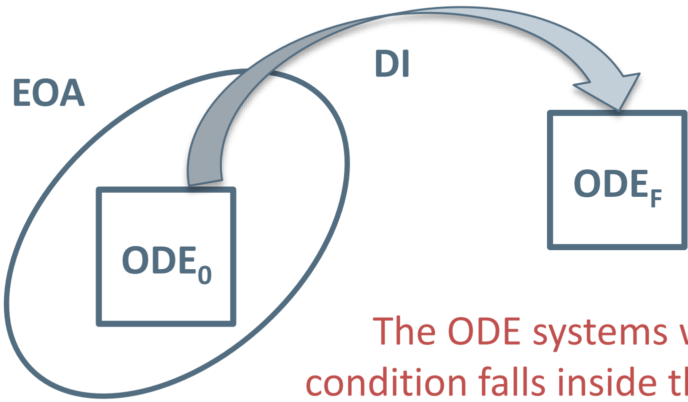
3. **Tabulation:** The tabulation is carried out according to a tree structure, in order to ensure good efficiency in updating the map



Pope S.B., *"Computationally efficient implementation of combustion chemistry using in-situ adaptive tabulation"*, Combustion Theory and Modeling, 1 (1997) 41-63

Singer M.A., Pope S.B., Najm H.M., *"Operator-splitting with ISAT to modelreacting flow with detailed chemistry"*, Combustion Theory and Modeling, 10 (2006) 199-217

ISAT: In Situ Adaptive Tabulation



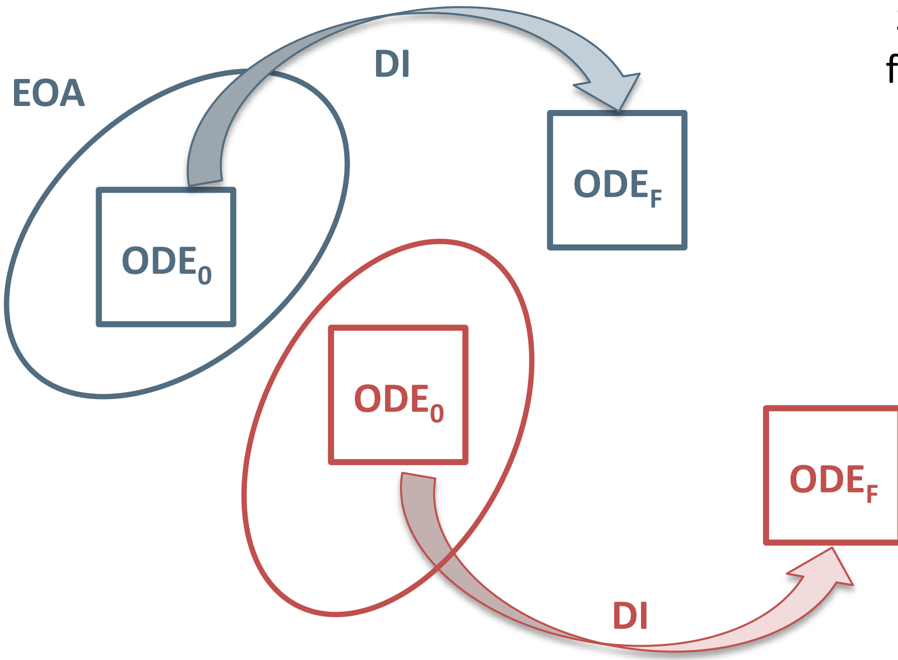
The ODE systems whose initial condition falls inside the EOA could be solved by extrapolating the results of this one with an error at most of $\boldsymbol{\varepsilon_{tol}}$

ISAT Tree

addition

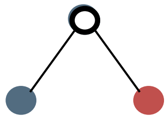
Courtesy of Mauro Bracconi
Politecnico di Milano

ISAT: In Situ Adaptive Tabulation



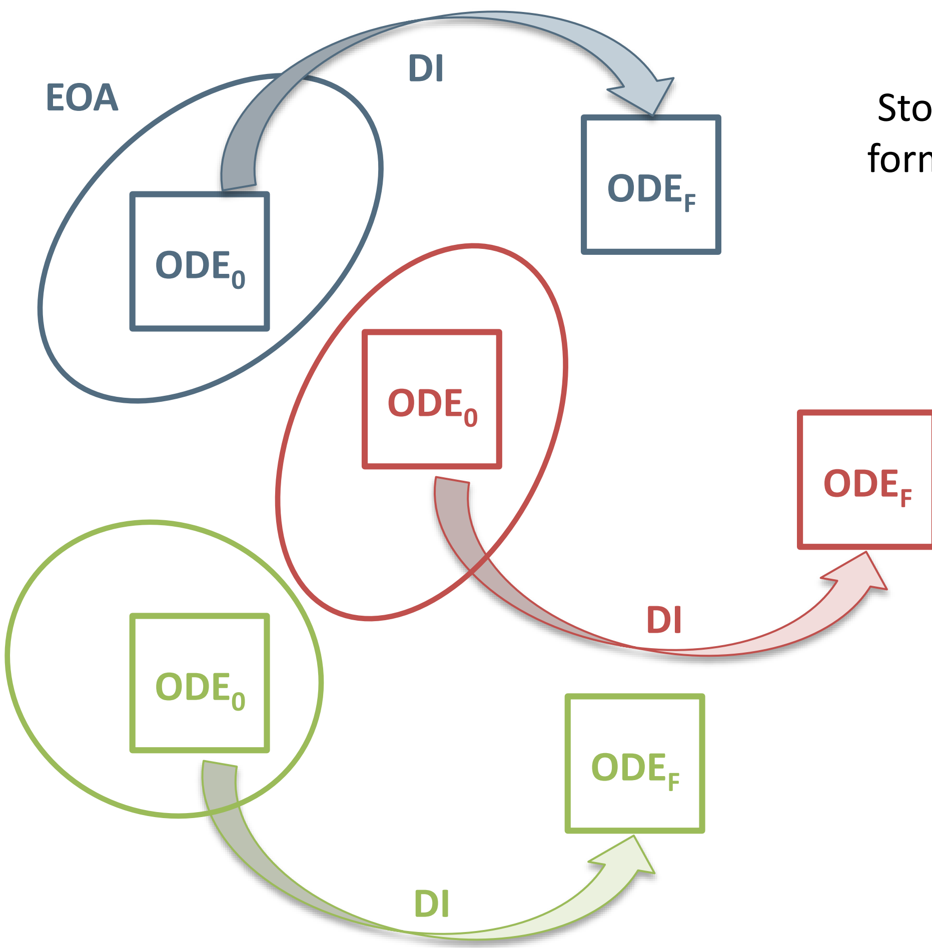
ISAT Tree

Storage table in the form of a binary tree



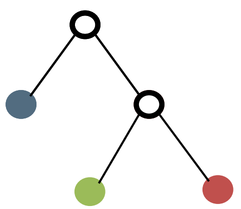
Courtesy of Mauro Bracconi
Politecnico di Milano

ISAT: In Situ Adaptive Tabulation



Storage table in the form of a binary tree

ISAT Tree



Courtesy of Mauro Bracconi
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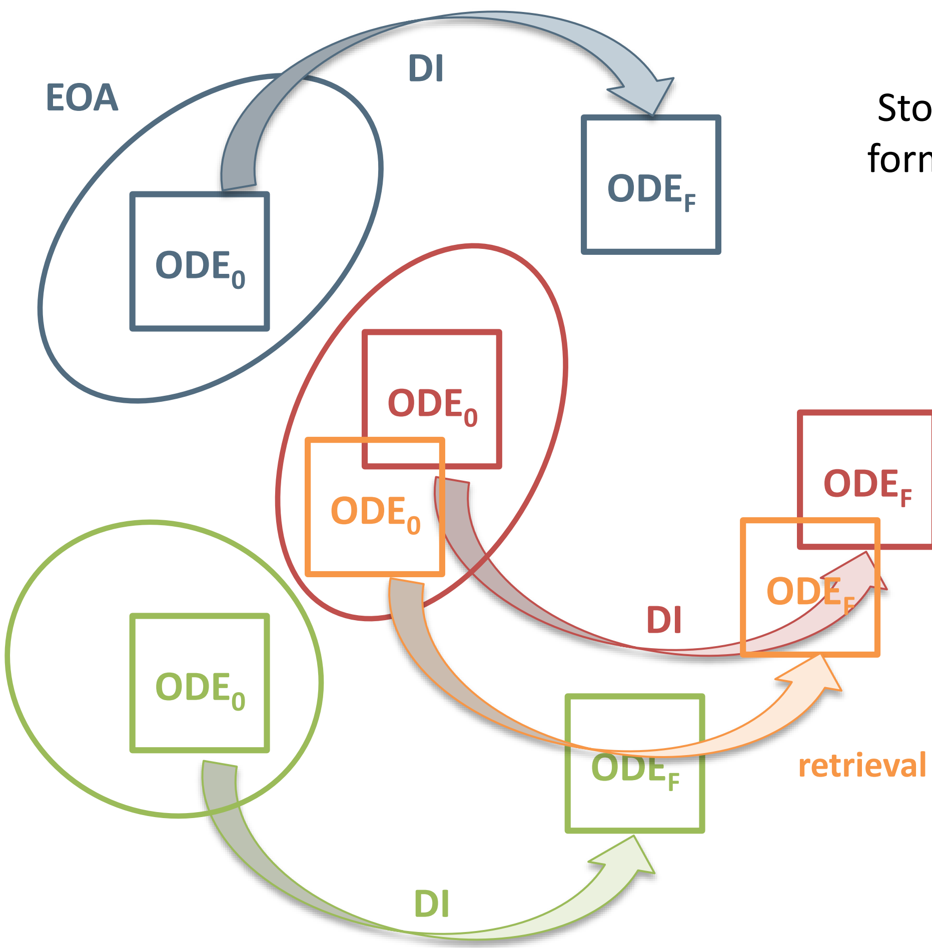
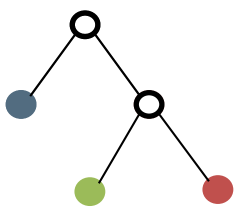


ISAT Tree

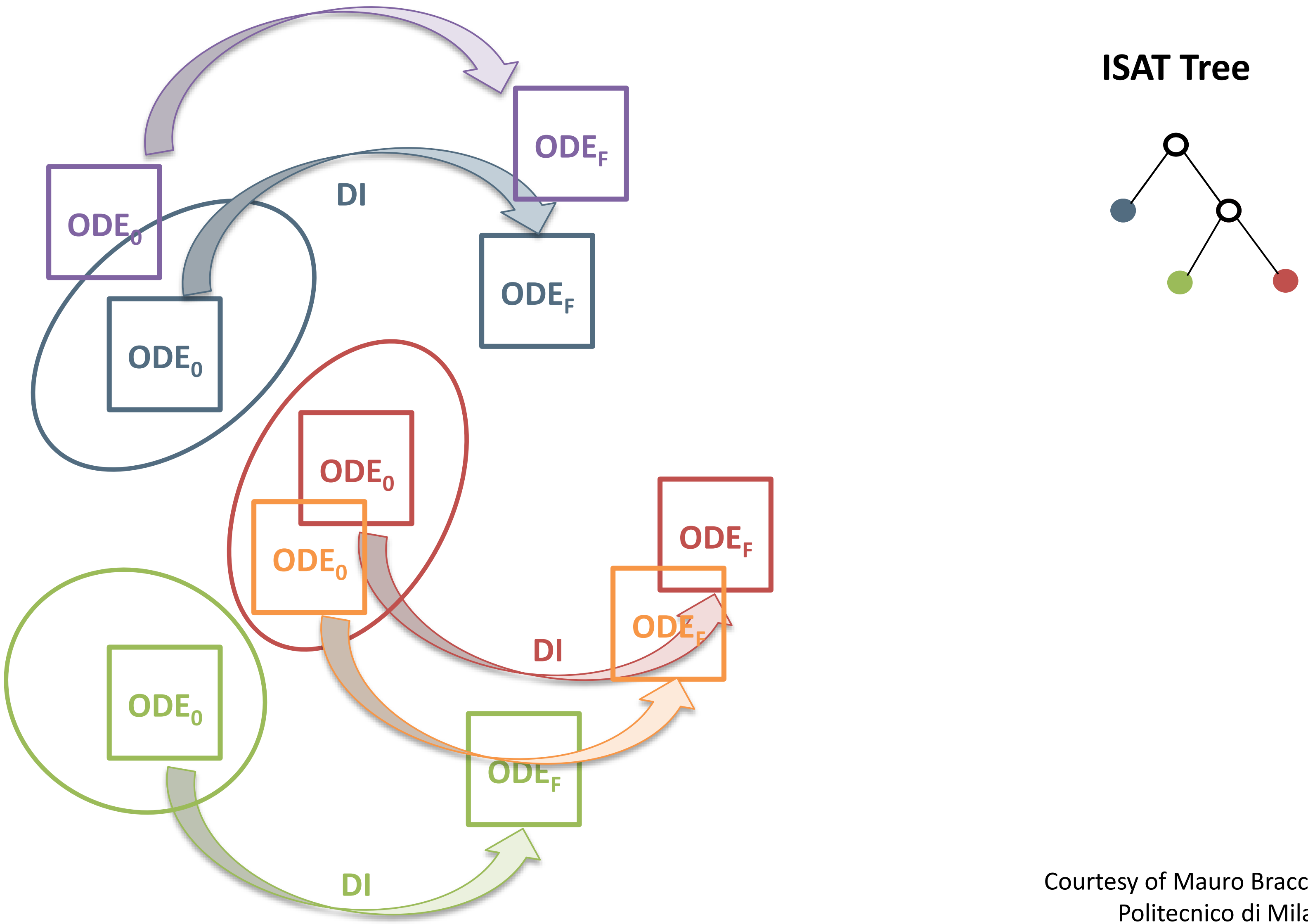


Storage table in the form of a binary tree

The information recovered during previous integration are exploited to approximate the ODE solution

Courtesy of Mauro Bracconi
Politecnico di Milano

ISAT: In Situ Adaptive Tabulation



Courtesy of Mauro Bracconi
Politecnico di Milano

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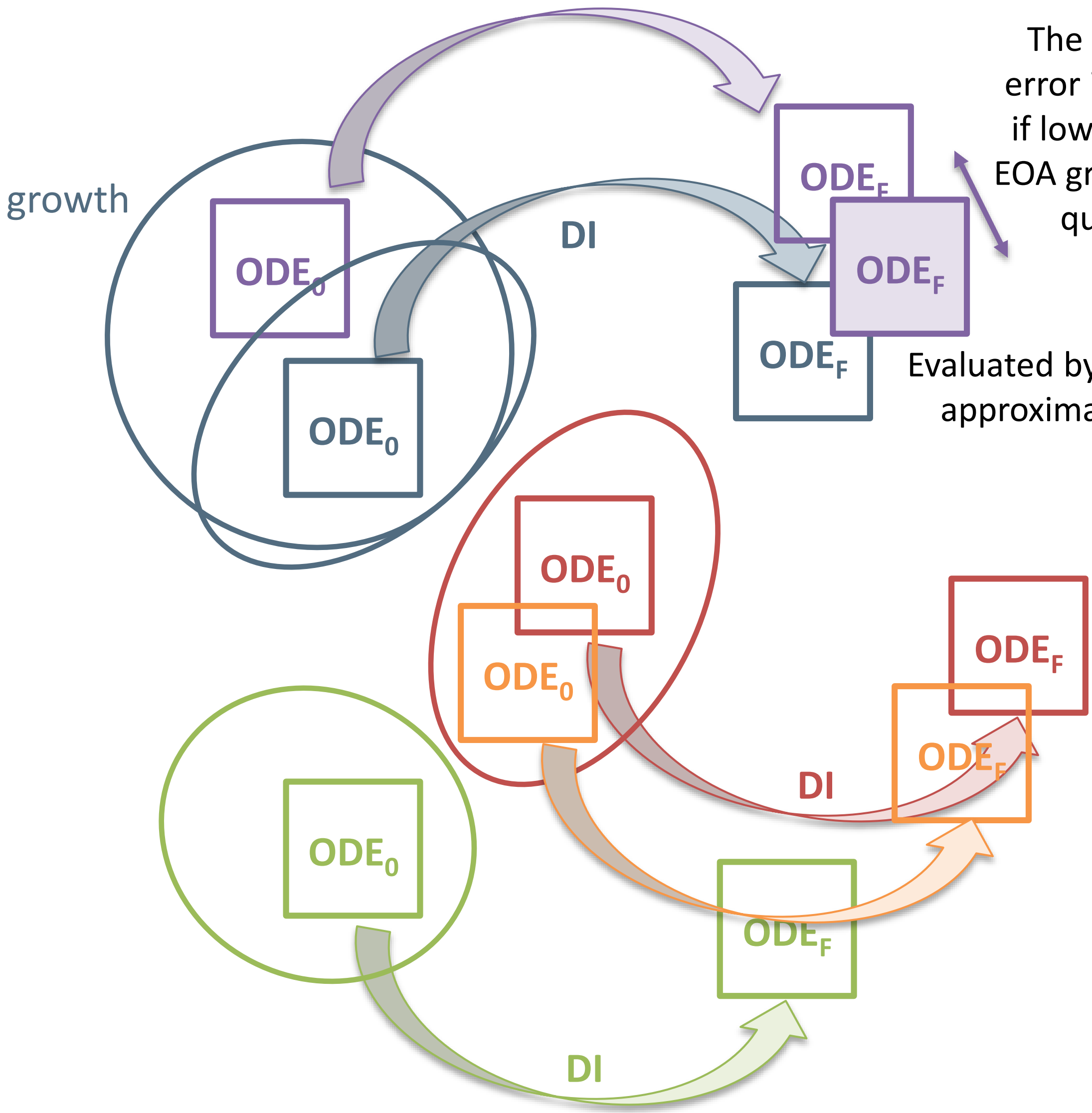
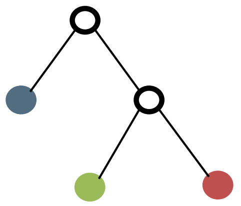


The approximation error is evaluated and if lower than $\boldsymbol{\varepsilon_{tol}}$ the EOA grows to cover the query $\varepsilon < \varepsilon_{tol}$

Evaluated by linear approximation



Courtesy of Mauro Bracconi
Politecnico di Milano

ISAT: Reaction mapping

$$\mathbf{R}(\boldsymbol{\Psi}_0;t) \stackrel{\text{def}}{=} \boldsymbol{\Psi}(t)$$

Evolution of reacting map

$$\begin{cases} \dfrac{d\boldsymbol{R}}{dt}(\boldsymbol{\Psi}_0;t) = \mathbf{S}\big(\mathbf{R}(\boldsymbol{\Psi}_0;t)\big) \\ \mathbf{R}(\boldsymbol{\Psi}_0;t) = \boldsymbol{\Psi}_0 \end{cases}$$

Reaction-mapping Jacobian matrix

$$\boldsymbol{A}(\boldsymbol{\Psi}_0;t) \stackrel{\text{def}}{=} \frac{d\boldsymbol{R}}{\partial\boldsymbol{\Psi}_0}(\boldsymbol{\Psi}_0;t)$$

Sensitivity of **R** with respect to the initial conditions

$$\begin{cases} \dfrac{\partial\boldsymbol{A}}{\partial t}(\boldsymbol{\Psi}_0;t) = \boldsymbol{J}\big(\mathbf{R}(\boldsymbol{\Psi}_0;t)\big)\boldsymbol{A}(\boldsymbol{\Psi}_0;t) \\ \boldsymbol{A}(\boldsymbol{\Psi}_0;t) = \boldsymbol{I} \end{cases}$$

System of ordinary differential equations (ODEs) with initial conditions

ISAT: Direct Integration (DI)

The **direct integration** consists in going to solve directly, through an appropriate algorithm for stiff problems, the differential system starting from an assigned initial condition. At the same time, however, the calculation of matrix A is also carried out

$$\begin{cases} \dfrac{d\boldsymbol{R}}{dt}(\boldsymbol{\Psi}_0;t) = \mathbf{S}\big(\mathbf{R}(\boldsymbol{\Psi}_0;t)\big) & N \text{ equations} \\[2ex] \dfrac{\partial \boldsymbol{A}}{\partial t}(\boldsymbol{\Psi}_0;t) = \boldsymbol{J}\big(\mathbf{R}(\boldsymbol{\Psi}_0;t)\big)\boldsymbol{A}(\boldsymbol{\Psi}_0;t) & N^2 \text{ equations} \end{cases}$$

The ODE system resolution above allows you to have all the information you need to create a node in the reaction map:

$$\boldsymbol{\Psi}_0 \xrightarrow{DI} \begin{cases} \boldsymbol{\Psi}_{\Delta t} = \mathbf{R}(\boldsymbol{\Psi}_0;\Delta t) \\[2ex] \boldsymbol{A}(\boldsymbol{\Psi}_0;t) \end{cases} \qquad \text{High computational cost}$$

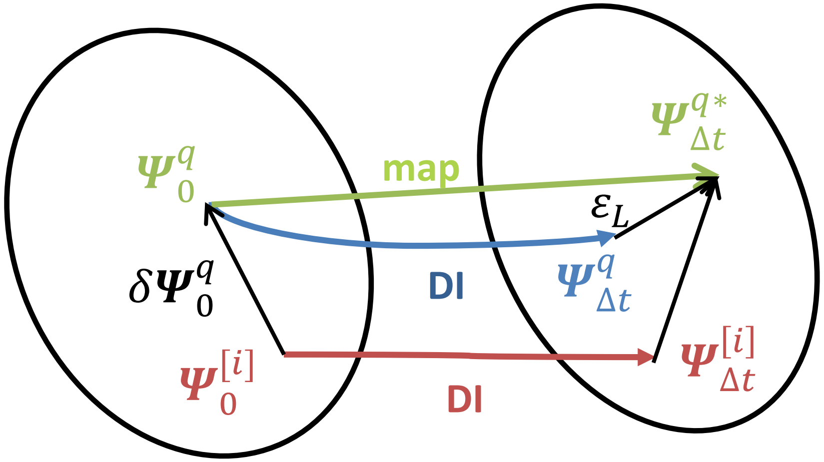
ISAT: linear interpolation

We have a reaction map with a certain number of nodes, calculated through a DI (index i). Let's imagine now to have to integrate the stiff system for new initial conditions (query point):

$\boldsymbol{\Psi}_0^{[i]}$ neighboring point

$\boldsymbol{\Psi}_0^{q}$ query point

$$\delta\boldsymbol{\Psi}_0^q \stackrel{\text{def}}{=} \boldsymbol{\Psi}_0^q - \boldsymbol{\Psi}_0^{[i]}$$



Direct integration

$$\boldsymbol{\Psi}_{\Delta t}^q = \mathbf{R}\left(\boldsymbol{\Psi}_0^q;\Delta t\right) = \mathbf{R}\left(\boldsymbol{\Psi}_0^{[i]} + \delta\boldsymbol{\Psi}_0^q;\Delta t\right)$$

Difference between linear interpolation and DI

$$\varepsilon_L \stackrel{\text{def}}{=} \boldsymbol{\Psi}_{\Delta t}^{q*} - \boldsymbol{\Psi}_{\Delta t}^{q}$$

Taylor's expansion

$$\delta\boldsymbol{\Psi}_{\Delta t}^q \stackrel{\text{def}}{=} \boldsymbol{\Psi}_{\Delta t}^{q*} - \boldsymbol{\Psi}_{\Delta t}^{[i]} = \boldsymbol{A}\left(\boldsymbol{\Psi}_0^{[i]};\Delta t\right)\delta\boldsymbol{\Psi}_0^q$$

$$\boxed{\boldsymbol{\Psi}_{\Delta t}^{q*} \approx \boldsymbol{\Psi}_{\Delta t}^{[i]} + \boldsymbol{A}\left(\boldsymbol{\Psi}_0^{[i]};\Delta t\right)\left(\boldsymbol{\Psi}_0^q - \boldsymbol{\Psi}_0^{[i]}\right)}$$

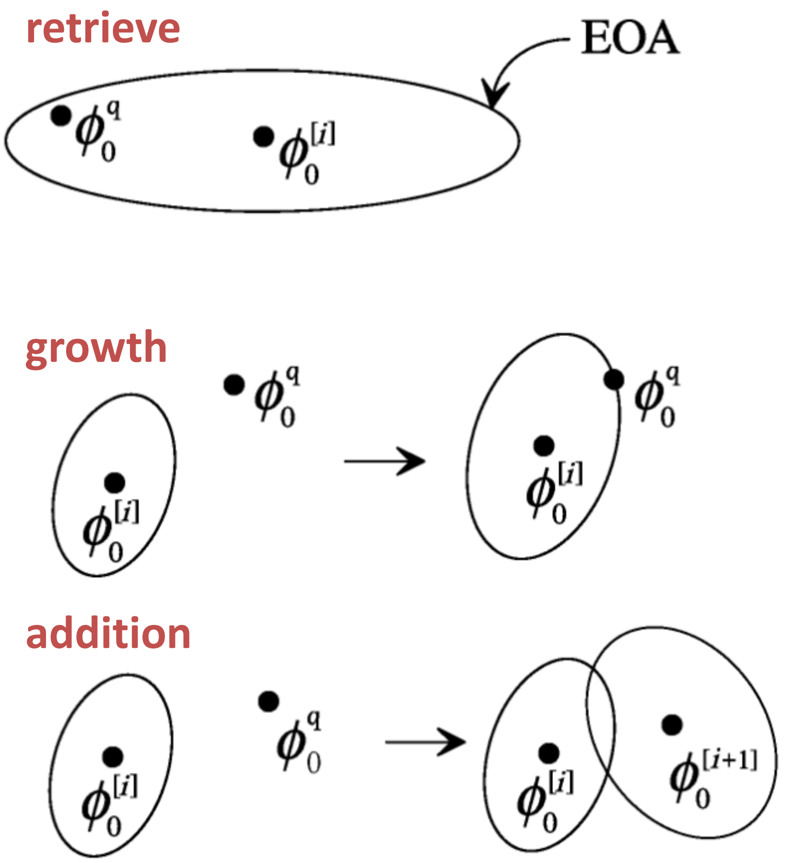
ISAT: Ellipsoid of Accuracy (EOA)

The EOA can be estimated from the sensitivity matrix A once a tolerance ε is defined

Retrieve
The query point falls within the EOA and therefore the linear interpolation is adequate
$\boldsymbol{\Psi}_{\Delta t}^{q*} \approx \boldsymbol{\Psi}_{\Delta t}^{q}$

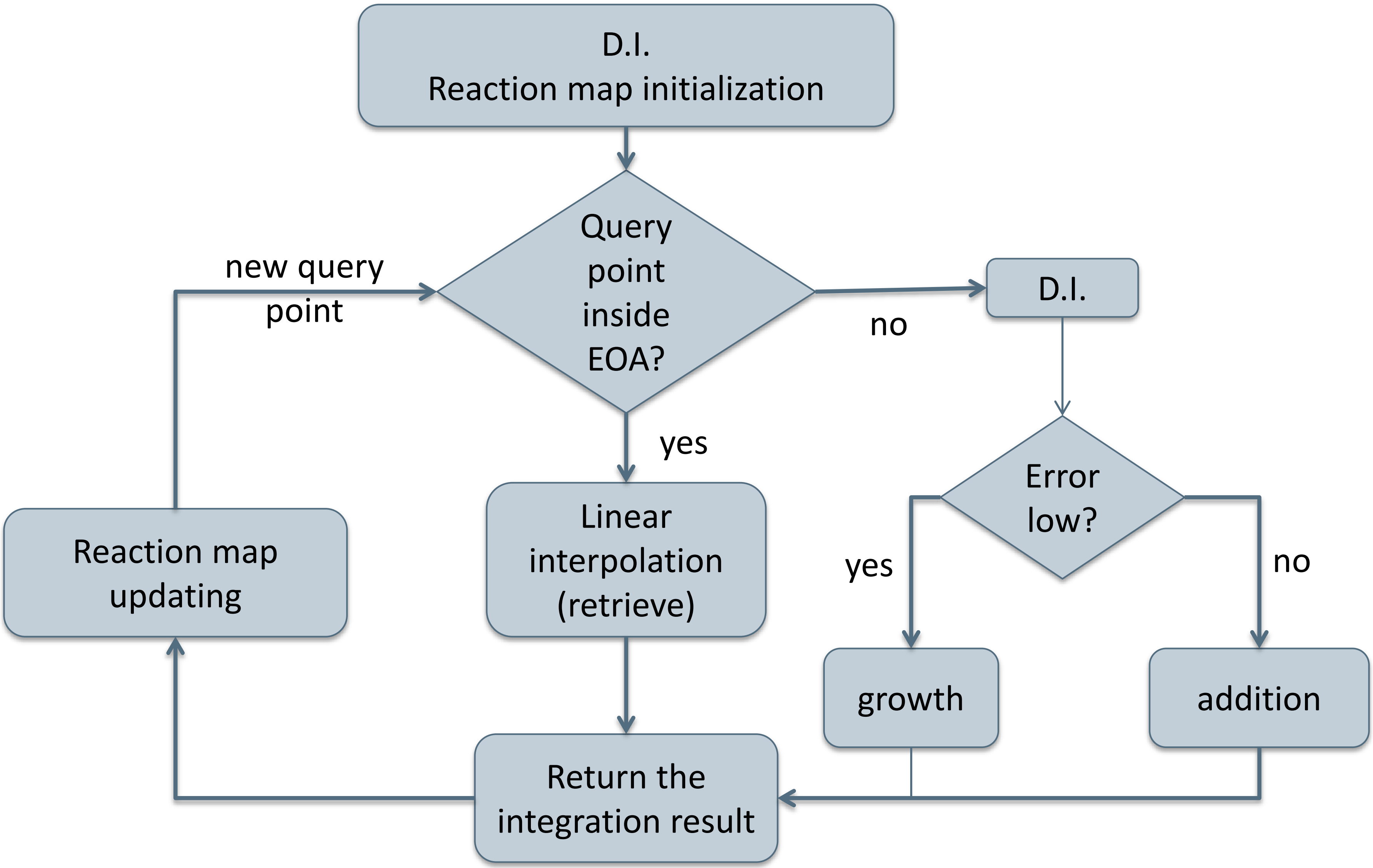
Growth
The point is outside of the EOA, but through the DI we have $\varepsilon_L < \varepsilon_{tol}$
The EOA is then expanded to include the new

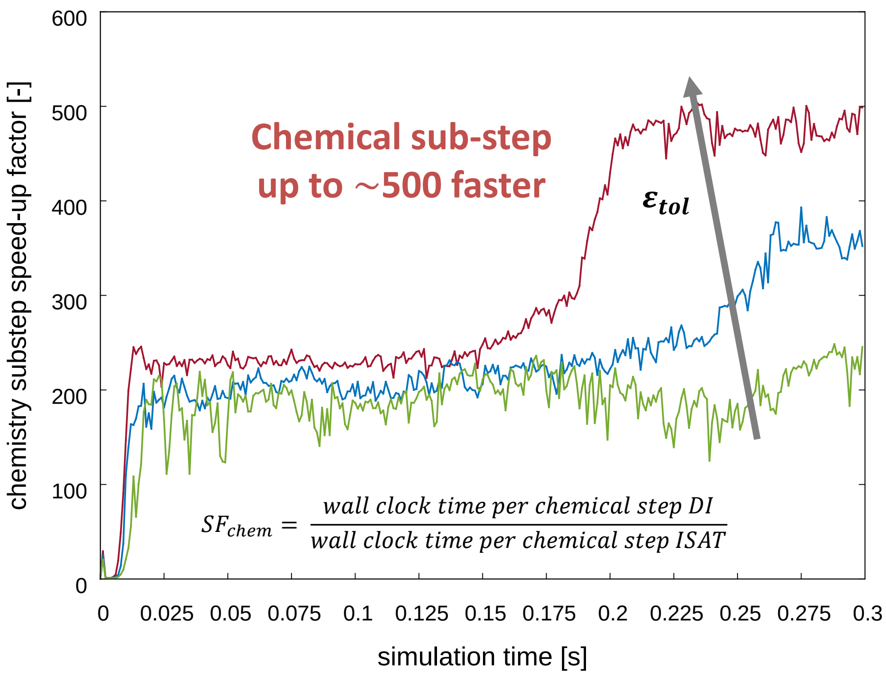
Addition
If neither the retrieved nor the growth conditions are met, a new node must be tabulated through the DI

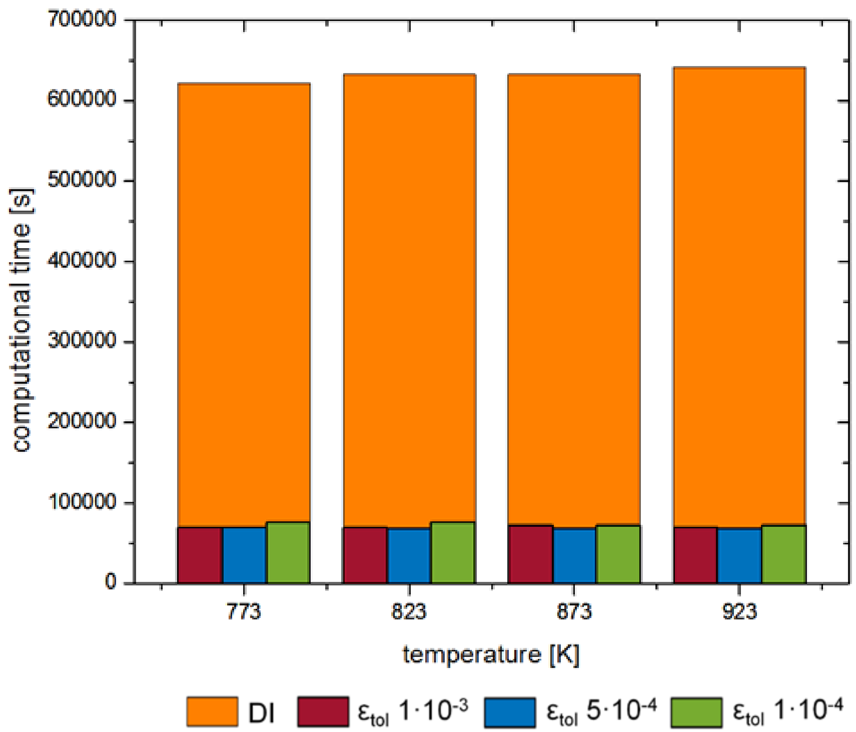


Pope S.B., *"Computationally efficient implementation of combustion chemistry using in-situ adaptive tabulation"*, Combustion Theory and Modeling, 1 (1997) 41-63

Costruzione della reaction map







Bracconi, M., Maestri, M., Cuoci, A., *In situ adaptive tabulation for the CFD simulation of heterogeneous reactors based on operator-splitting algorithm* (2017) AIChE Journal, 63 (1), pp. 95-104, DOI: 10.1002/aic.15441

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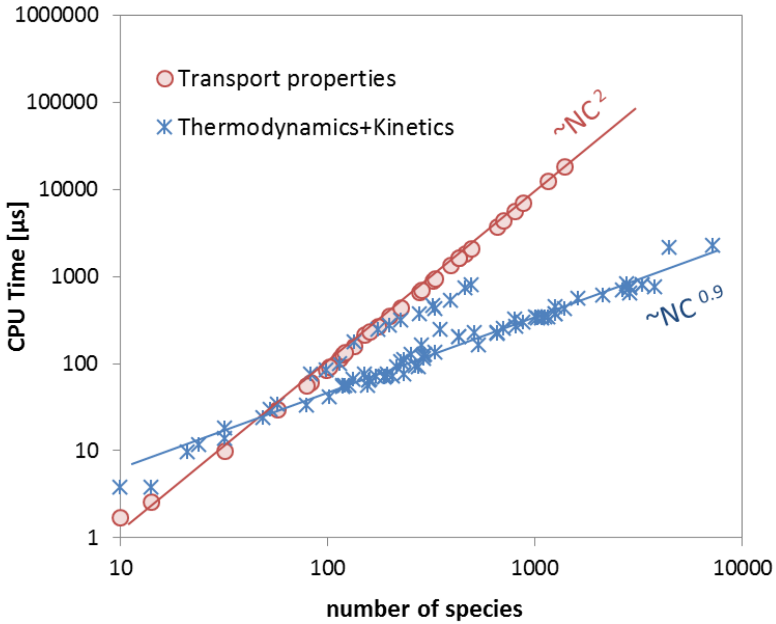
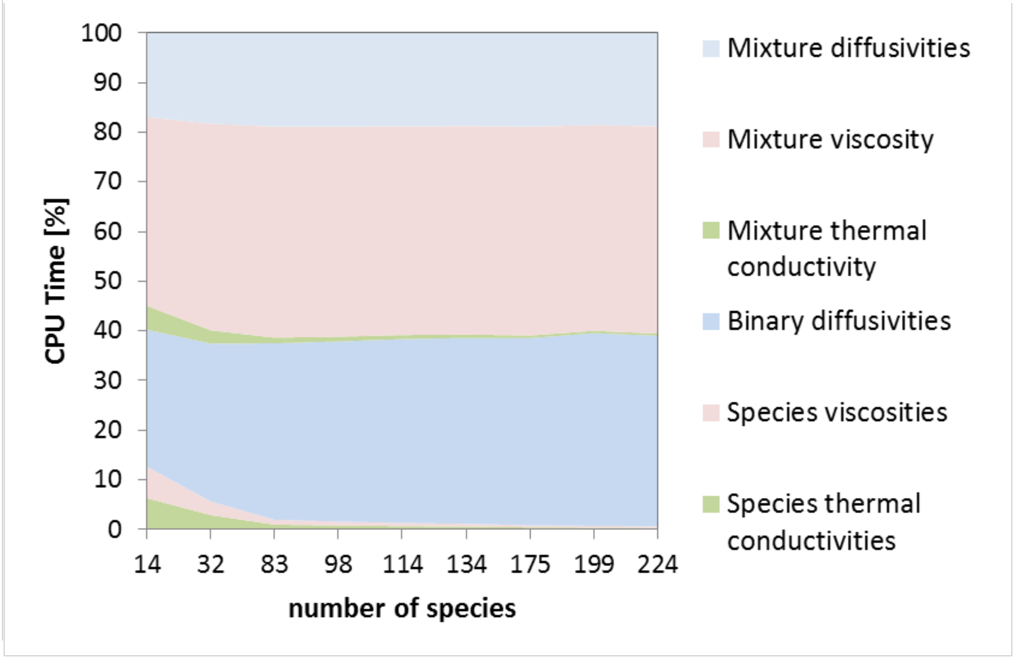
5. **Numerical tools for analysis of kinetic mechanisms**

What about transport properties?





- **Mixture-averaged** models are usually adopted
- The cost of evaluation of transport properties (in particular diffusion) increases **quadratically** with the number of species
- For large mechanisms (>100 species) the computational cost of transport properties is not negligible
- In fully-coupled methods proper techniques must be applied to **reduce the computational cost of transport properties** (they can be the **bottleneck** in evaluation of Jacobian matrix)

Species bundling for diffusion coefficient reduction (I)

Global computational cost

Jacobian evaluation

Jacobian factorization (with implicit solvers)

$$C = C_0 + \alpha N_S + \boldsymbol{\beta N_S^2} + \gamma \boldsymbol{N_S^3}$$

Computation over-head

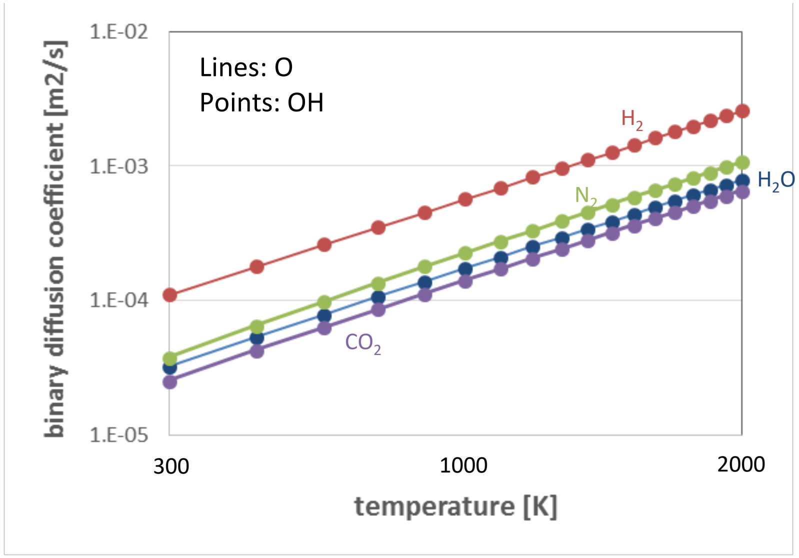
Diffusion

Many species possess similar diffusivities because of similar molecular properties (molecular weight, structure, collision cross section, etc.)

Such species are expected to behave similarly in terms of diffusive transport

Species with similar diffusivities can be bundled in a same group with a representative species

The diffusivities of O and OH with other species are almost identical



Lu, Law, *Diffusion coefficient reduction through species bundling*, Combustion and Flame, 148, p. 117-126 (2007)

Species bundling for diffusion coefficient reduction (II)

Similarity of a pair of species

$$\epsilon_{i,j} = \max_{\substack{k=1,\dots,NC \\ T_{min}<T<T_{max}}} \left| \ln\left(\frac{\Gamma_{i,k}}{\Gamma_{j,k}}\right) \right|$$

1. How to measure the similarity between species i and j?

Relative error induced by representing the species i by the species j (i.e. a measure of how much species i and j are similar in terms of diffusion coefficients)

Given a user-specified threshold value ϵ, species I and j are considered similar if and only if $\epsilon_{i,j} < \epsilon$

Usually the binary diffusion coefficients are fitted with an N-th order polynomial

$$p\Gamma_{i,j} \approx e^{\sum_{n=0}^{N} a_{n,i,j}(\ln T)^n}$$

$$\epsilon_{i,j} = \max_{\substack{k=1,\dots,K \\ T_{min}<T<T_{max}}} \left| \sum_{n=0}^{N} \left(a_{n,i,k} - a_{n,j,k}\right)(\ln T)^n \right|$$

The pressure can be removed from the definition, since it is the same for all the species

Species bundling for diffusion coefficient reduction (III)

NC x NC adjacency matrix

$$A_{i,j} = \begin{cases} 1 & if\, \epsilon_{i,j} < \epsilon \\ 0 & otherwise \end{cases}$$

2. How to find the minimum number of groups?

Integer programming

Minimize: $\sum_{j=1}^{NC} x_i$

Each $x_i = 1$ indicates a group represented by the i-th species

The objective is to minimize the number of groups

Constraints:

$$\begin{cases} \sum_{j=1}^{NC} A_{i,j} x_j \geq 1 & i = 1, 2, \dots, K \\ x_i \in \{0, 1\} & i = 1, 2, \dots, K \end{cases}$$

Each species j must be represented at least by one group (i.e. by at least by one i species)

If a j species is represented by more than one i species, the i species ensuring the minimum error is chosen as the representative species

Species bundling for diffusion coefficient reduction (IV)

$\hat{\boldsymbol{\Gamma}}$ Reduced binary diffusion matrix NG x NG

$$\hat{\Gamma}_{n,m} = \Gamma_{r(n),r(m)}$$

$r(n)$ is the representative species for group n

Mixture averaged formulation

$$D^*_{k,mix} = \frac{1 - X_k}{\sum_{j \neq k}^{NC} X_j / \Gamma_{kj}}$$

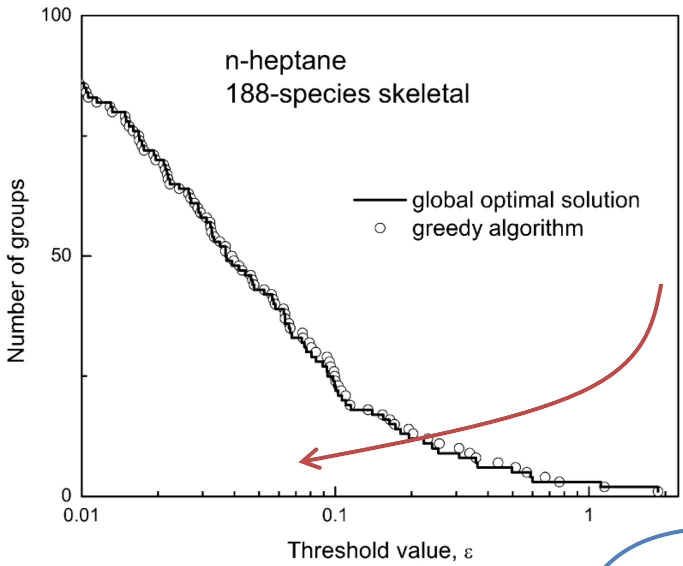
Original formulation with the complete NC x NC matrix of binary diffusion coefficients

$$D^*_{k,mix} = \frac{1 - X_k}{Q_{g(k)} - \frac{X_i}{\hat{\Gamma}_{g(k),g(k)}}}$$

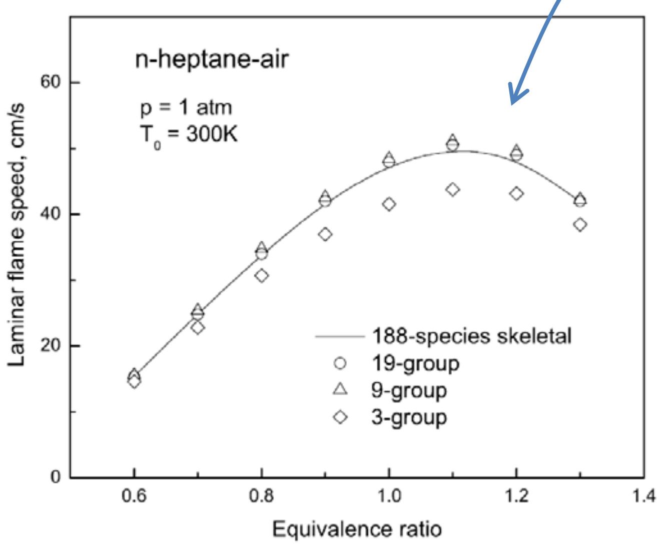
$$\begin{cases} Q_n = \sum_{j=1}^{NG} \frac{\hat{X}_j}{\hat{\Gamma}_{n,j}} \\ \hat{X}_j = \sum_{g(l)=m} X_m \end{cases}$$

$g(k)$ is the group number for species k

Species bundling for diffusion coefficient reduction (V)

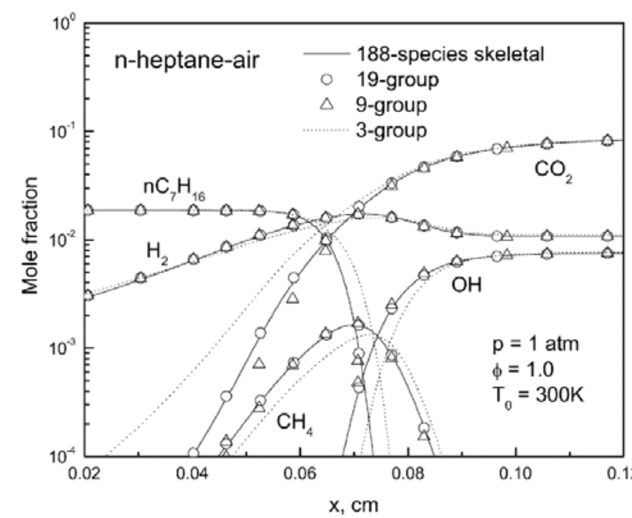


The number of species groups decreases dramatically as the ε value increases. A roughly linear trend is observed in the reduction curve for ε<0.1in the log plot, showing the rapid decrease in the number of groups for even a slight increase in the reduction error.



The worst error in the flame speed is about 1 cm/s for 19 and 9 groups, a value which is smaller than typical uncertainties in experimental measurements

For a premixed, flat laminar flame, the 19-group model agrees very well with the original model and there is no almost visible error



Plots from: **Lu, Law**, *Diffusion coefficient reduction through species bundling*, Combustion and Flame, 148, p. 117-126 (2007)

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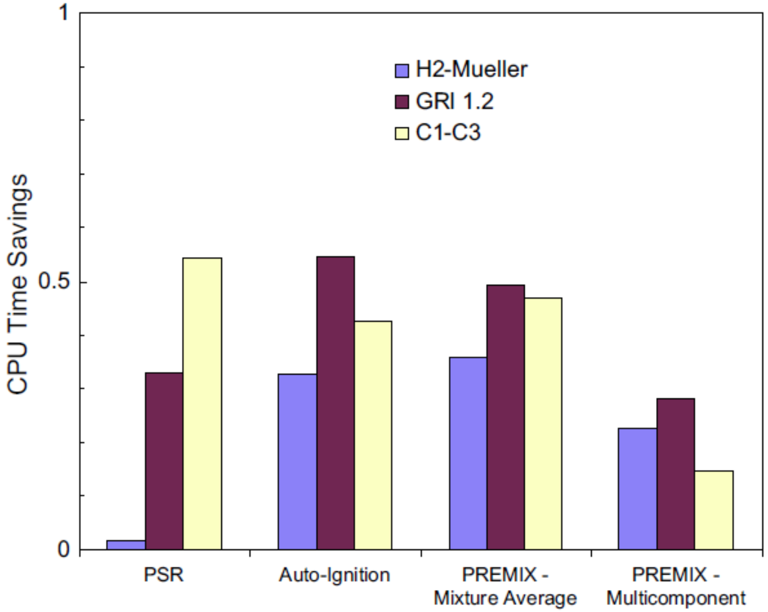
Computation Cost Minimization

A set of strategies that expedite simulations with little or no accuracy loss through optimization of the computation sequences (Lu & Law, 2009)

- **code reformulation:** many parts of the numerical algorithms are reformulated in a less intuitive way in order to minimize the number of flops needed to perform some calculations
- **caching:** the code is written in order to cache as much as possible, which means storing items for future use in order to avoid retrieving or recalculating them
- **object pools:** they are a technique for avoiding the creation and deletion of a large number of objects during the code execution
- **optimized functions:** the numerical algorithms are often reformulated in order to exploit the Intel® MKL Vector Mathematical Functions Library (VML)

An example: code reformulation

Calculated savings in CPU time with CCM normalized by that of detailed mechanisms for H2, CH4, and C2H4



Plot from: **T.F. Lu, C.K. Law**, Prog. Energy Comb. Sci., 35 (2009)

Natural implementation

$$k = AT^n exp\left(-\frac{E}{RT}\right)$$

1 power: ~50 flops
1 exponentiation : ~50 flops
5 multiplications: ~5 flops
Total: ~105 flops

Smart implementation

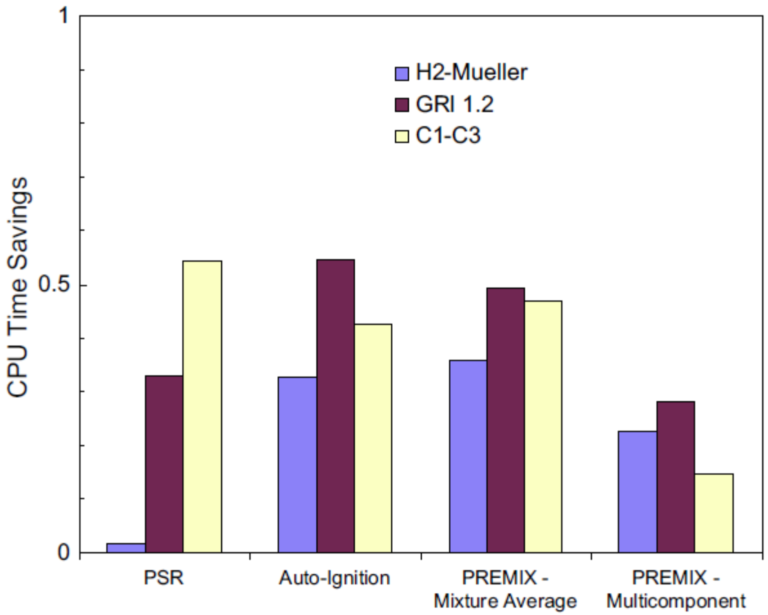
$$k = exp(ln(A) + \alpha ln(T) - E/RT)$$

1 exponentiation: ~50 flops
3 multiplications: ~3 flops
2 additions: ~2 flops
Total: ~55 flops

The *ln(T)* term in the above expression only has to be evaluated once for each call of the rate evaluation subroutine, and the *ln(A)* and *E/R* terms can be pre-evaluated.

An example: code specialization

Calculated savings in CPU time with CCM normalized by that of detailed mechanisms for H2, CH4, and C2H4



Plot from: **T.F. Lu, C.K. Law**, Prog. Energy Comb. Sci., 35 (2009)

Reaction rate evaluation is expensive due to the exponential form of the Arrhenius term and the large number of reactions involved

$$k = AT^n exp\left(-\frac{E}{RT}\right)$$

because of the large number of radicals in detailed mechanisms, there are frequently many elementary reactions with zero activation energy, especially the three-body termination reactions. Furthermore, the value of a is frequently an integer or even zero:

$$k = \begin{cases} A & \alpha = 0, E = 0 \\ exp\big(ln(A) + \alpha ln(T)\big) & \alpha \neq 0, E = 0 \\ exp(ln(A) + \alpha ln(T) - E/RT) & \alpha \neq 0, E \neq 0 \\ exp(ln(A) - E/RT) & \alpha = 0, E \neq 0 \\ A\underbrace{T \dots T}_{\alpha} & \alpha\ integer, E = 0 \end{cases}$$

The *ln(T)* term in the above expression only has to be evaluated once for each call of the rate evaluation subroutine, and the *ln(A)* and *E/R* terms can be pre-evaluated.

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Sensitivity Analysis

Sensitivity analysis is very important for kinetic studies, since it allows the quantitative understanding of **how the numerical solution of the governing equations depends on the various parameters** contained in the model itself.

In most cases, only the first-order sensitivity coefficients with respect to the reaction rate coefficients (pre-exponential factors, activation energy or kinetic constant) are calculated.

The calculation of sensitivity coefficients exploits the linearity of the differential equations governing the sensitivity coefficients, regardless of any non-linearities in the problem itself. The equations for the sensitivity coefficients can be easily obtained starting from the ODE system describing the system under investigation:

ODE equations
$$\frac{d\boldsymbol{y}}{dt} = \boldsymbol{S}(\boldsymbol{y}, t; \boldsymbol{\alpha})$$

First-order sensitivity coefficients
$$\sigma_{ij} = \frac{\partial y_i}{\partial \alpha_j}$$

$\boldsymbol{y}$ = unknowns (NE)

$\boldsymbol{\alpha}$ = parameters (M)

$\boldsymbol{\sigma}$ = sensitivity coefficients $(M \times N)$

Sensitivity Analysis (I)

If we differentiate the ODE system with respect to the parameters, we get the following M additional ODE systems:

$$\begin{cases} \dfrac{d\boldsymbol{\sigma}_j}{dt} = \boldsymbol{J}\boldsymbol{\sigma}_j + \dfrac{\partial S}{\partial \boldsymbol{\sigma}_j} \qquad j = 1, \dots, M \\ \\ \boldsymbol{\sigma}_j(t_0) = \mathbf{0} \end{cases}$$

$$\boldsymbol{\sigma}_j \stackrel{\text{def}}{=} \left[\frac{\partial y_1}{\partial \alpha_j}, \frac{\partial y_2}{\partial \alpha_j}, \dots, \frac{\partial y_N}{\partial \alpha_j} \right]$$

$\boldsymbol{J}$ is the Jacobian matrix of the original ODE model: $J_{ij} \stackrel{\text{def}}{=} \dfrac{\partial S_i}{\partial y_j}$

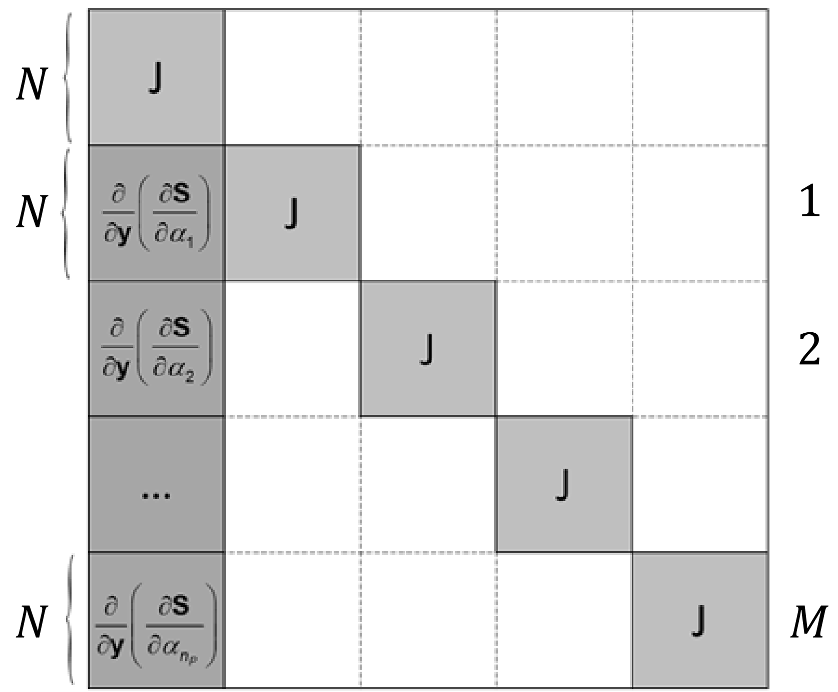
- the original ODE system is not coupled to the sensitivity equations above, and can be solved independently of the sensitivity equations, although the sensitivity equations are dependent on the original system
- the sensitivity equations above are linear in the sensitivity coefficients with the same Jacobian matrix employed for the state equations.

Sensitivity Analysis (II)

The overall system (original ODE and sensitivity ODEs) can be solved directly only if the number of parameters of interest is relatively small. This is impossible for very large kinetics, with thousands of reactions. In such cases, it is possible to calculate the sensitivity coefficients using a modified version of the staggered direct method.

Since the second term in the r.h.s. of sensitivity equations does not depend on the sensitivity coefficients, the structure of the Jacobian matrix associated with the overall ODE system is very sparse and block-structured.

Instead of solving the whole ODE system, we can solve M independent ODE systems (beside the main ODE).



Example of the overall Jacobian sparsity pattern for a 1D problem

Sensitivity Analysis (III)

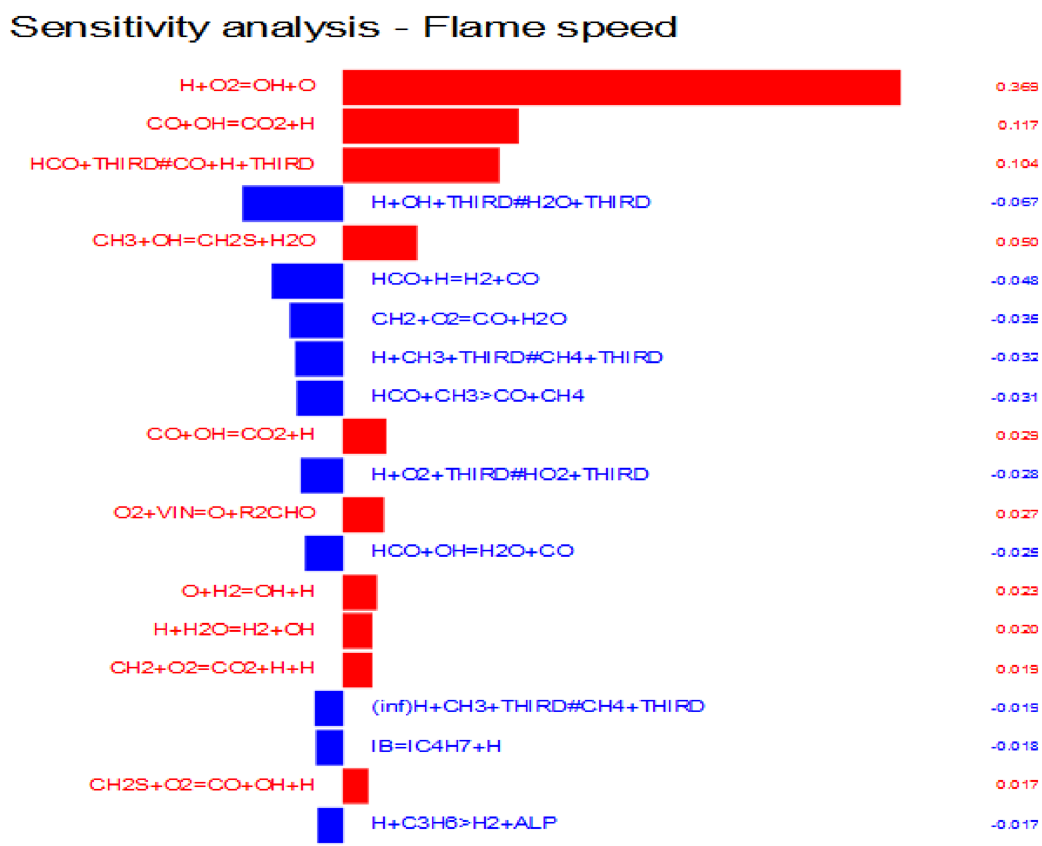
Example

Laminar freely propagating flame

N = 220 points x 180 species = 40,000

M = 5,000 reactions

N x M = 200 millions of sensitivity coeff



Rate of Production Analysis (RoPA) (I)

The **rate of production analysis (RoPA)** is another useful tool to better understand chemical paths in the simulation of reacting systems.

The rate of production analysis determines the contribution of each reaction to the production or destruction rates of a species.

For each species i and each reaction j it is possible to define a normalized production coefficient C_{ij}^{+} and a normalized consumption coefficient C_{ij}^{-}:

$$C_{ij}^{+} \stackrel{\text{def}}{=} \frac{max\left(v_{ij}^{f} - v_{ij}^{b}, 0\right) r_j}{\sum_{k=1}^{NR} max\left(v_{ij}^{f} - v_{ij}^{b}, 0\right) r_k} \qquad C_{ij}^{-} \stackrel{\text{def}}{=} \frac{min\left(v_{ij}^{f} - v_{ij}^{b}, 0\right) r_j}{\sum_{k=1}^{NR} min\left(v_{ij}^{f} - v_{ij}^{b}, 0\right) r_k}$$

The normalized coefficients sum to 1 (i.e. and). They compare the **relative importance of each reaction to the production or destruction rates of a species**.

Rate of Production Analysis (RoPA) (II)

Example

Adiabatic, constant volume batch reactor

T0 = 1000 K

P0 = 1 atm

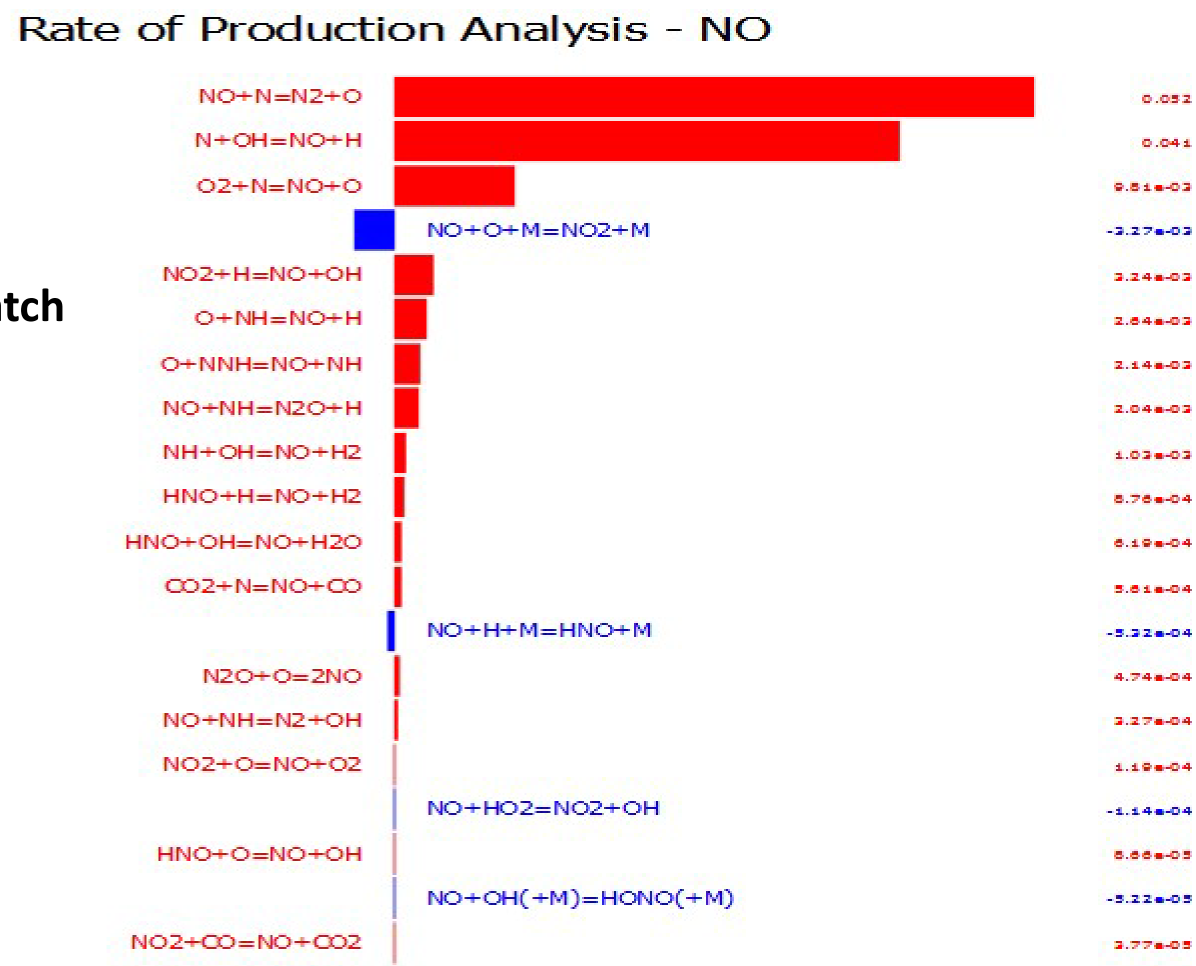
Fuel: H2/CO (4/60% mol.)

Oxidizer: O2/N2 (21/79% mol)

Equivalence ratio: 1

Kinetic mechanism:

POLIMI_H2CO_NOX_1412



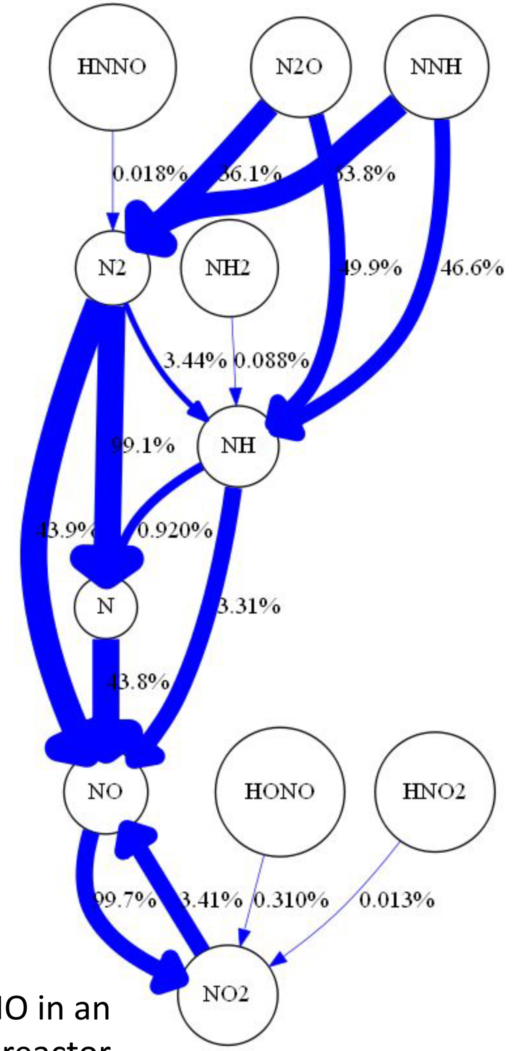
Reaction Path Analysis (I)

Reaction path analysis is an accounting of the exchange of material among species in a chemically reacting system, which can be conveniently visualized by a reaction path diagram.

In mathematical terms a reaction path diagram is a directed graph whose nodes are the chemical species.

An edge connects two species if a reaction moves material from one to the other. The edge is drawn as an arrow from the reactant to the product.

The thickness of an arrow may indicate the rate of material exchange among species.



Reaction Path Analysis for production of NO in an adiabatic, constant volume batch reactor

Reaction Path Analysis (II)

Over the region of interest, atoms of element e move from species A to species B at the rate $T(e, A, B)$:

$$T(e, A, B) = \sum_{j=1}^{N} \int_V n_j(e, A, B) r_j dV$$

V is the whole region of space, while $n_j(e, A, B)$ is the number of atoms of elements e that a single forward instance of reaction j moves from A to B. The sign determines the direction of the arrow: if positive then $A \rightarrow B$, if negative $B \rightarrow A$.

The conserved scalar approach gives reaction path diagrams the following properties:

- the amount of material removed from the species at the base of any path equals the amount contributed to the species at the head;
- the sum of the thicknesses of all paths into a species equals the sum of the thicknesses of all paths going out.

Grcar J.F., Day M.S., and Bell J.B., *A taxonomy of integral reaction path analysis*. Combustion Theory and Modelling, 2006. 10(4): p. 559-579.