3-4

CHEMICAL MODEL REDUCTION 2

(Fitted models, in-situ tabulation and species lumping)

Why is it necessary?

- Reactive flow models may involve resolving complex 3D turbulent flows within complex geometries.
- In order to achieve realistic computational times something has to be sacrificed:
  - **Spatial resolution**
  - **Highly averaged turbulence models**
  - **Use of simplified chemistry.**
- Detailed chemistry is often sacrificed but some phenomena require models that couple turbulent mixing and chemical processes in a resolved way.
- **Can we simplify detailed chemistry in such a way that we do not loose the important chemical information?**

Types of chemical model reduction

- **Skeletal model reduction – usually local i.e. specific C, *P, T***
  - Methods for removing species and reactions that are not required to accurately simulate the desired target quantities or phenomena.
  - Sensitivity or graph theory based.
- **Time-scale based methods**
  - Rely on the fact that chemical processes take place on a wide range of time-scales and both SLOW and FAST processes can be simplified.
  - Usually processes faster than the mixing time-scales can be assumed to locally equilibrate, a kind of quasi-steady-state, QSS.
  - Simplified expressions can then be found for these QSS species so that their rate equations need not be solved.
- **Lumping**
  - Can be applied to reactions or species based on different principles.
  - Reaction lumping based on QSS arguments.
  - Species lumping based on reactive or structural similarities of species.
- **Tabulated or functional representations of chemistry**
  - Pre-solve chemical problem in someway and store the results for use in CFD.

LUMPING

What does lumping mean?

- Combining information into “lumps” in such a way that we can still represent detailed kinetics but with fewer species or equations.
- Can take two forms:
  - Reaction Lumping $A \rightarrow B \rightarrow C$
    becomes: $A \rightarrow C$

    Vertical
  - Species Lumping [Y] = [A] + [B] + [C]

    Horizontal
- **WHY?**
  - Skeletal mechanism reduction methods are useful but sometimes not sufficient to make the mechanism small enough for use in e.g. CFD codes.
  - By combining species or reactions we can compress the mechanism further and potentially reduce the number of equations we need to solve.

Advantages and Disadvantages

Advantages

- Reduction in number of variables and therefore equations to solve.
- When combined with time-scale analysis a reduction in system stiffness.
- Computational speed-up.
- Less species to “transport” in CFD code.

Disadvantages

- Lumped model cannot always be expressed as a kinetic scheme.
- Lumped scheme may “loose” information that was contained in full scheme.
- Cannot always recover original species concentrations.
- Need a method to define lumped reaction rates.

Vertical lumping using quasi-steady-state assumption QSSA

- Goes all the way back to Bodenstein (1913)
- Here **time-scales are associated with species directly**.
- Error induced by assuming QSSA for a species relates to its chemical lifetime within the system – 1/diagonal Jacobian element and its net production rate (Turányi et al., 1993).

$$\Delta Y_i = \left(- \frac{\mathrm{d}\, Y_i}{\mathrm{d}\, t} \right) \left(- \frac{1}{J_{ii}} \right)$$

- Or for coupled groups of QSS species: $$\frac{\mathrm{d}\, \mathbf{Y}^{(QSS)}}{\mathrm{d}\, t} = \mathbf{J}^{(QSS)} \Delta \mathbf{Y}^{(QSS)}$$
- Consistent with ***small local error for species consumed in fast reactions*** and in such cases the local production rate of the QSS species can be large - counter intuitive.
- Term quasi-steady state means that concentrations do not change significantly ***with respect to the slow species*** which may exhibit steep concentration gradients in time.

How to apply QSSA

- Set right hand side of rate equation to zero and solve algebraically.
- Some times this can be done using symbolic algebra and a lumped reaction can be formed completely removing QSS species.

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} \mathrm{C}\ .$$

- If QSSA applied to B

$$\frac{d[B]}{dt} = 0, \qquad [B] = \frac{k_1}{k_{-1}+k_2}[A]$$

$$\frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2 [A]}{k_{-1}+k_2}$$ and

B can be removed providing the global reaction step: A → C

with $$k' = \frac{k_1 k_2}{k_{-1}+k_2}$$

- In other cases numerical iteration methods are needed.

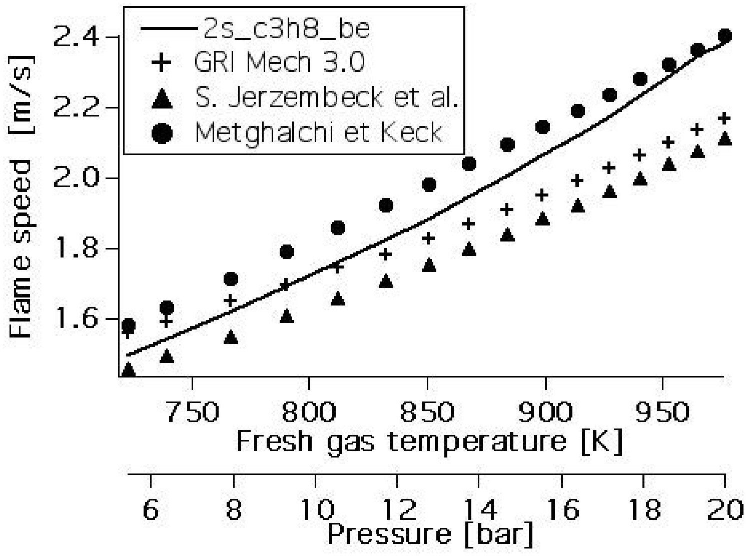
Global reaction schemes

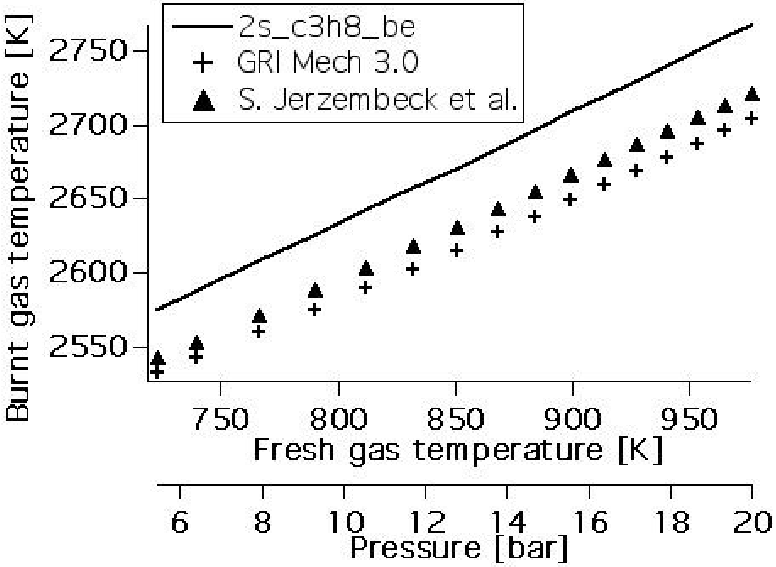
- Global reaction schemes often used in complex reacting flows are usually generated using similar approaches to this e.g. (Peters & Rogg, 1993).
- Few species may be contained in the global schemes but the reaction rates contain complex expressions due to QSSA based lumping of reactions.
- Or they can be fitted as Arrhenius expressions to e.g. full model or experimental data.

Example from CERFACS – **note non-integer stoichiometries**:

Reaction 1 reaction("C3H8 + 3.5 O2 => 3 CO + 4 H2O", [5.82320E+12, 0, 34000], order = " C3H8:0.8 O2:0.86 ")

Reaction 2 reaction("CO + 0.5 O2 <=> CO2", [2.00000E+09, 0, 12000])





Crucial issues for successful species lumping

1. To determine which species are to be lumped;
2. To classify how the selected species should contribute to the lumped species, *i.e.* define the **lumping transformation**;
   - could also require defining the **inverse transformation** i.e. how to get back to the original species from the lump;
3. To estimate kinetic parameters for the reactions of the lumped species.

Two types of methodology are commonly used:

i) ***Chemical Lumping***: based on chemical knowledge of species involved e.g. structural similarities.

ii) ***Mathematical Lumping***: based on looking for similar mathematical quantities or applying mathematical rules.

The two can often be equivalent since species with the same reaction steps and rate constants will lead to mathematical similarities within the equations.

Using mathematical approaches does not usually rely on chemical knowledge or intuition.

Chemical Lumping

- Has some commonality with topics on automatic mechanism generation since often based on ***isomers*** being involved in the same ***reaction classes***.
- For *n*-heptane the classes of propagation routes are defined as:
  1. Decomposition and isomerization of alkyl radicals R.
  2. H-abstraction with O_2 to form HO_2 and conjugate olefins.
  3. Direct and reverse O_2 addition to R to form peroxy radicals ROO.
  4. Internal isomerisation between ROO and hydroperoxyalkyl radicals QOOH.
  5. Decomposition of QOOH radicals to form olefins.
  6. Decomposition of QOOH radicals to form HO_2 and conjugate olefins.

  etc.
- Reference rate parameters defined for each reaction class based on literature data or **similarity rules**.
- The **pathways for each isomer** and the resulting intermediate radicals can then potentially be **lumped** to give a simplified scheme with only a single pathway representing degradation to the average products of all the isomers (Ranzi et al., 1995).
  - Commonly used by Polimi in their mechanism generation.

***n*-heptane** scheme - 4 alkyl radicals noted by R_1, $R_{2,}$ $R_{3,}$ R_4 giving rise to 4 reactions involving the addition of O_2.

$R_1 + O_2 \rightarrow R_1OO \quad k_1$

$R_2 + O_2 \rightarrow R_2OO \quad k_2$

$R_3 + O_2 \rightarrow R_3OO \quad k_3$

$R_4 + O_2 \rightarrow R_4OO \quad k_4$

The lumped alkyl radical is then defined by:

$[R] = [R_1] + [R_2] + [R_3] + [R_4]$,

with the corresponding lumped reaction given by:

$R + O_2 \rightarrow ROO \qquad k_5$

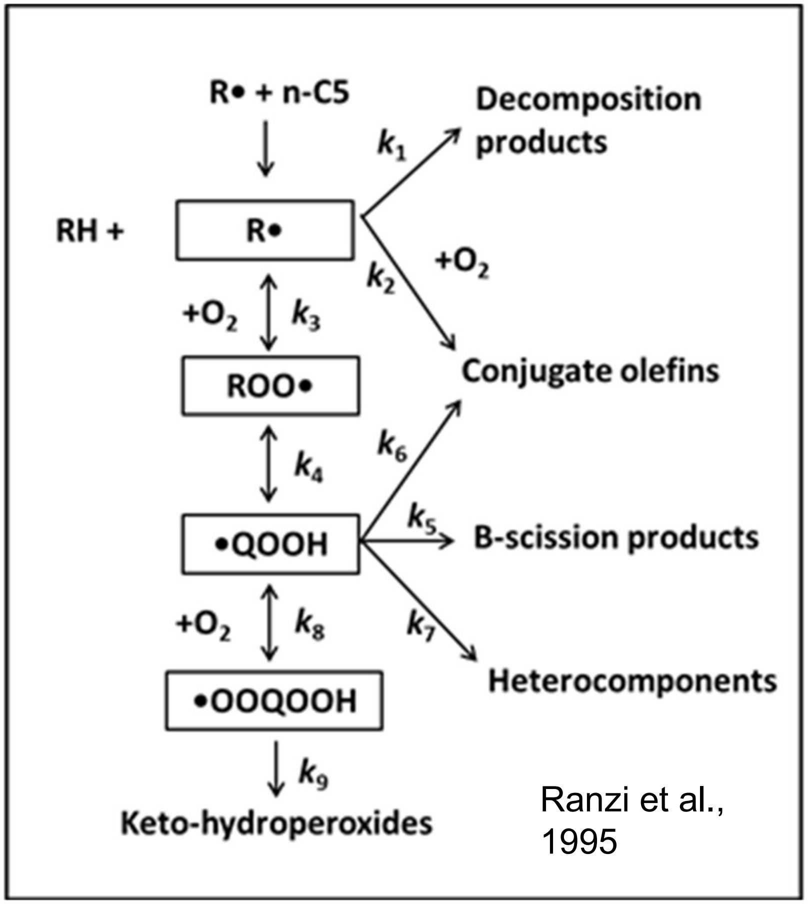
Lumped rates defined by **fitting** with respect to experimental data or with respect to the complex full model (MAMOX, Milan) or **weighted averages** for the different component isomers depending on the relative **weights** within the initial fuel or from the **weighted mean of the elementary rate coefficient** for the individual isomers (Fournet et al., 2000):

$$k_5 = \frac{k_1[\mathrm{R}^{\bullet}{}_1] + k_2[\mathrm{R}^{\bullet}{}_2] + k_3[\mathrm{R}^{\bullet}{}_3] + k_4[\mathrm{R}^{\bullet}{}_4]}{[\mathrm{R}^{\bullet}]}$$

Much easier if all the rate constants are the same!

Applications of Chemical Lumping

- Mechanisms developed in Milan tend to incorporate lumping and have now addressed a large number of parent fuel compounds.
- Key example is that for *n*-heptane which contains only 4 lumped radicals.
- High degree of lumping leads to reactions with non-integer stoichiometries which represent the relative weights of the different product channels.
- Q7OOH → OH + 0.3HCHO + 0.32C_5H_{10} + 0.3C_4H_8 + 0.35CH_3CHO +0.31C_3H_6 + 0.35C_2H_5CHO + 0.4C_2H_4 + 0.06C_7H_{14}



Ranzi et al., 1995

Applications of Chemical Lumping

- Battin Leclerc et al. (2000) reduced primary mechanism for *n*-heptane combustion from 410 free radicals and 70 molecules in 1654 reactions, to a lumped scheme with only 25 free radicals and 70 molecules in 189 reactions.
- The lumped mechanism was shown to give a good representation of the prediction of *n*-heptane conversion compared to the full scheme in the negative temperature coefficient regime.
- Lumping process included as an integral part of automatic reaction **generation software EXGAS and Mamox** in order to allow the user to limit the size and improve the computational efficiency of the generated schemes where required.

Soot modelling – the HACA Reaction Sequence

- Chemical reactions describing polymer growth are of the same type**, rate parameters and thermodynamic data vary only slightly with polymer size**.
- Reaction described by distribution function for degree of polymerization, and repeating reaction cycle for particle growth with structure and rate coefficients for each cycle treated as the same.
- Lumping guided by similarities in structure of hydrocarbon species (Frenklach, 1990).

(i,1) $A_i + H \leftrightarrow A_i^{\cdot} + H_2$
(i,2) $A_i^{\cdot} + C_2H_2 \leftrightarrow A_iCHCH^{\cdot}$
(i,3) $A_iCHCH^{\cdot} + C_2H_2 \rightarrow A_{i+1} + H$
(i+1,1) $A_{i+1} + H \leftrightarrow A_{i+1}^{\cdot} + H_2$
(i+1,2) $A_{i+1}^{\cdot} + C_2H_2 \leftrightarrow A_{i+1}CHCH^{\cdot}$
(i+1,3) $A_{i+1}CHCH^{\cdot} + C_2H_2 \rightarrow A_{i+2} + H$
(i+2, i+3, …, n) … etc.

where A_i is an aromatic molecule containing i fused aromatic rings, $A_i^{\cdot}$ is an aromatic radical formed by H abstraction and $A_iCHCH^{\cdot}$ is a radical formed by adding C_2H_2 to $A_i^{\cdot}$

- Rate coefficients k_j assumed to have **same value for each cycle** due to **chemical similarities** between the species.
- Allows chemical lumping to be applied in order to reduce the number of variables.
- Most severe lumping comes from summing together all species giving:

$$\frac{dM_o}{dt} = r_o$$

where $M_o = [A_i] + [A_i^{\cdot}] + [A_iCHCH^{\cdot}] + [A_{i+1}] + \dots$.

- This one dimensional system describes the evolution of the total PAH concentration M_o. The **details of the dynamics of the system are lost** however if such a severe lumping is used.
- Another approach is to multiply each of the equations by an integer which roughly corresponds to the molecular mass of the species *i.e.* the number of carbon atoms, before summing the terms.

$$\frac{d\mathrm{M}_1}{dt} = \left(m_o \frac{d[\mathrm{A}_i]}{dt} + m_o \frac{d[\mathrm{A}_i^{\cdot}]}{dt} + (m_o + 2)\frac{d[\mathrm{A}_i\mathrm{CHCH}^{\cdot}]}{dt} + (m_o + 4)\frac{d[\mathrm{A}_{i+1}]}{dt} + \cdots . \right)$$

$$= m_o r_o + 2k_2[\mathrm{C_2H_2}]\sum_i [\mathrm{A}_i^{\cdot}] - 2k_{-2}\sum_i [\mathrm{A}_i\mathrm{CHCH}^{\cdot}] + 2k_3[\mathrm{C_2H_2}]\sum_i [\mathrm{A}_i\mathrm{CHCH}^{\cdot}]$$

where $M_1 = m_o[\mathrm{A}_i] + m_o[\mathrm{A}_i^{\cdot}] + (m_o + 2)[\mathrm{A}_i\mathrm{CHCH}^{\cdot}] + (m_o + 4)[\mathrm{A}_{i+1}] + (m_o + 4)[\mathrm{A}_{i+1}^{\cdot}] + \cdots$,

is the total number of carbon atoms accumulated in the PAHs *i.e.* **the first moment of the PAH distribution.**

- In terms of species lumping we can now see that it is possible to define a new set of variables which define the lumped species:

$$\hat{c}_1 = \sum_i [\mathrm{A}_i]$$

$$\hat{c}_2 = \sum_i [\mathrm{A}_i^{\cdot}]$$

$$\hat{c}_3 = \sum_i [\mathrm{A}_i\mathrm{CHCH}^{\cdot}]$$

- The corresponding lumped equation system is then given by:

$$\frac{d\hat{c}_1}{dt} = r_o - k_1[\mathrm{H}]\hat{c}_1 + k_{-1}[\mathrm{H_2}]\hat{c}_2 + k_3[\mathrm{C_2H_2}]\hat{c}_3$$

$$\frac{d\hat{c}_2}{dt} = k_1[\mathrm{H}]\hat{c}_1 - k_{-1}[\mathrm{H_2}]\hat{c}_2 - k_{-2}\hat{c}_3$$

$$\frac{d\hat{c}_3}{dt} = k_2[\mathrm{C_2H_2}]\hat{c}_2 - k_{-2}\hat{c}_3 - k_3[\mathrm{C_2H_2}]\hat{c}_3$$

- In this case lumping based on **chemical similarities** results in new variables which are simply linear sums of the original species concentrations.
- The lumped system has only 3 variables and in this case since it was assumed that the **rate constants were the same for each species of the same structure** the definition of the lumped rate constants is simple.

Mathematical Approaches: linear lumping

- The previous example showed that a simple linear transformation could be applied to define new lumped variables that were weighted sums of the original species.
- This type of lumping can be written in a more formal way.
- The formal definition of lumping is the transformation of the original vector of variables **Y** to a new transformed variable vector $\widehat{\mathbf{Y}}$ using the transformation function **h**:

$$\hat{\mathbf{Y}} = \mathbf{h}(\mathbf{Y})$$

- The dimension $\hat{n}$ of the new variable vector $\widehat{\mathbf{Y}}$ is smaller than that of the original concentration vector. A new kinetic system of ODEs is formed:

$$\frac{\mathrm{d}\hat{\mathbf{Y}}}{\mathrm{d}t} = \hat{\mathbf{f}}\left(\hat{\mathbf{Y}}, \hat{\mathbf{k}}\right) \qquad \hat{\mathbf{Y}}(t_0) = \hat{\mathbf{Y}}_0$$

Linear Lumping

In the linear case the transformation is simply a matrix multiplication operation:

$$\hat{\mathbf{Y}} = \mathbf{M}\mathbf{Y}$$

where **M** is a matrix of size $\hat{n} \times N_S$. Consider for example:

$$\mathbf{M} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 1 \end{pmatrix}$$

Lumping matrix transforms original concentration vector $\left(Y_1, Y_2, Y_3, Y_4\right)$ to the concentration vector *of lumped species,* $\left(\hat{Y}_1, \hat{Y}_2\right)$

where $\hat{Y}_1 = Y_1$.

$$\hat{Y}_2 = Y_2 + Y_3 + Y_4$$

Linear Lumping in Systems with Time-scale Separation

- Some lumping methods have exploited a time-scale analysis in order to define lumped groups.
- Whitehouse *et al.* (2004) grouped species according to their chemical lifetimes and reactivity structures
  - Applied the methods to the comprehensive tropospheric Master Chemical Mechanism (MCM).
  - Several large lumped groups were achievable composed of peroxy acyl nitrates, nitrates, carbonates, oxepins, substituted phenols, oxeacids and peracids with similar lifetimes and reaction rates with OH.
- This approach could be considered as a formalisation of chemical lumping where chemical similarities are not judged by expert opinion but are calculated on the basis of their reaction rates.

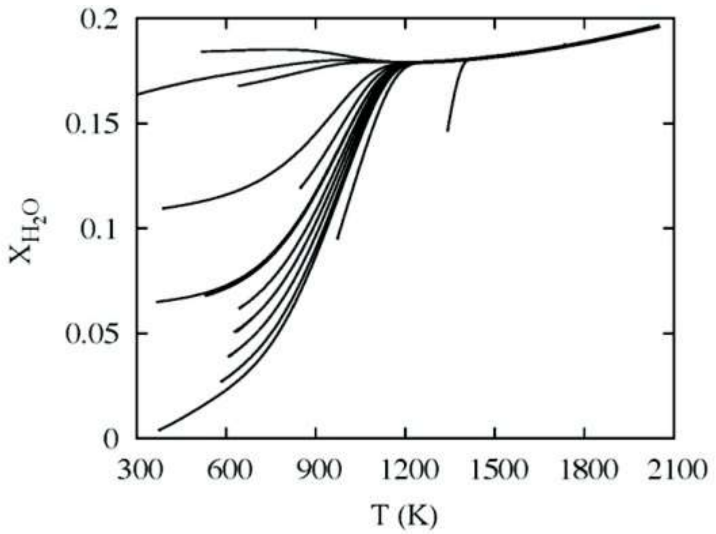
Operator splitting

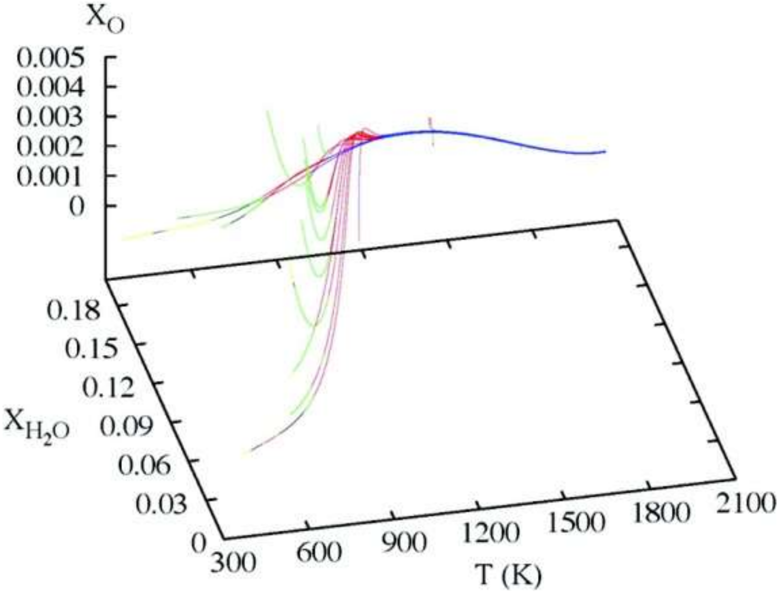
- For many models of reacting flows, the **chemistry equations can dominate the CPU usage**.
- Stiffness adds further issues.
- Using operator splitting the chemical part can be separated from the solution of the flow terms, allowing reduction or special numerical strategies to be applied to chemical source term rather than having to apply them everywhere.
- Sportisse, 2000, suggests that the **stiff terms** should be **solved last** within each time-step.
  - Advection due to mean flow → diffusion, turbulent mixing → chemistry
  - Allows system to relax back onto slow manifold.
- Representation of chemical changes on the slow manifold e.g. using **tabulation** or **fitting** can overcome some of these problems (Pope, 1997). *See later for these methods.*

Fitted models

- Sometimes e.g. in repeated design calculations, it is possible to solve the chemical source terms and **store** the **information** for use in more complex reactive flow simulations.
- Methods based on e.g.:
  1. Fitting a functional equation e.g. polynomial
  2. Look-up tables
  3. Flamelets
- If not specifically probing kinetics can be useful.
- **Caution:** if chemical scheme updated, stored data can easily go out of date unless in situ methods are used.

Fitting exploits the collapse of system dimension due to time-scale separation





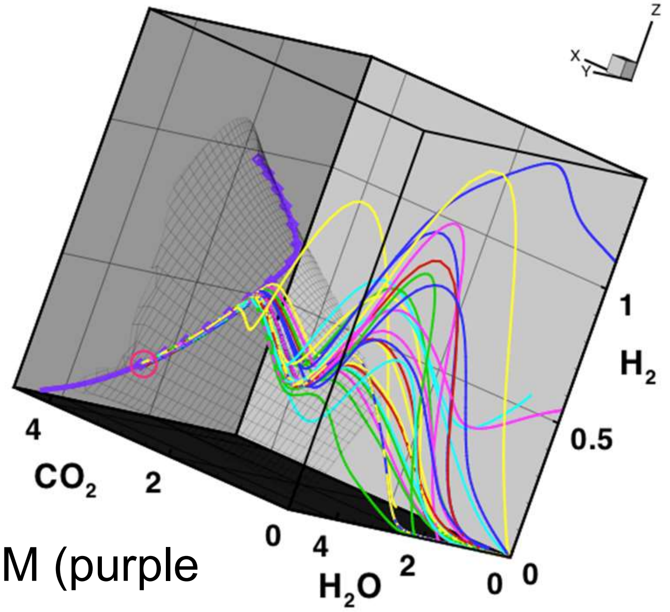
- Example of premixed laminar hydrogen oxygen flame.
- In phase space trajectories converge from all boundary conditions to final equilibrium point.
- Colours show underlying system dimension as the time-scales collapse.
- *n* = 1 (blue), *n* = 2 (red), *n* = 3 (green), *n* = 4 (black), and *n* = 5 (yellow).
- Depending on temperature space the model is trying to predict, different reduced models could be developed.

Davis & Tomlin, 2008

Intrinsic low dimensional manifolds (ILDM)

- The **QSSA** is restrictive in the sense that it **associates time-scales with specific species concentrations**.
- More general formulations look for intrinsic low dimensional hyper-surfaces with the phase space that exist when the fast time scales have collapsed – low dimensional or **slow manifolds**.

- By restricting the chemical changes to such ILDMs the dimensionality of the problem can be vastly reduced.
- **Hard part:** defining the dynamic chemical changes within the manifold.



ILDM (black mesh) for iso-octane-air system 1D ILDM (purple symbols), 0D ILDM (equilibrium, red circle). Lines - homogeneous reactor calculations for different fuels using different reaction mechanisms. (Blasenbrey & Maas, 2000)

Formulation of ILDM

General reaction diffusion system:

$$\frac{\partial\psi}{\partial t} = F(\psi) - \vec{v}\cdot \mathrm{grad}\psi + \frac{1}{\rho}\mathrm{div}D\ \mathrm{grad}\psi$$

where $\psi = (\psi_1, \psi_2, \ldots, \psi_{S+2})^T$ is the thermokinetic state, $\psi = (h, p, w_1, \ldots, w_S)^T$, F the chemical source term, $\vec{v}$ the velocity, ρ the density and D the matrix of transport coefficients.

Using operator splitting the chemical source term can be separated: $\frac{\partial\psi}{\partial t} = F(\psi)$

System is then separated into three parts representing conserved, slow and fast subspaces:

$$(Z_c\ Z_s\ Z_f)\cdot\begin{pmatrix}\tilde{Z}_c\\ \tilde{Z}_s\\ \tilde{Z}_f\end{pmatrix} = I$$

$$\tilde{Z}_c\frac{\partial\psi}{\partial t} = \tilde{Z}_c F(\psi)$$

$$\tilde{Z}_s\frac{\partial\psi}{\partial t} = \tilde{Z}_s F(\psi)$$

$$\tilde{Z}_f\frac{\partial\psi}{\partial t} = \tilde{Z}_f F(\psi)$$

Equilibrate fast time-scales

$$\tilde{Z}_f F(\psi) = 0$$

Project onto slow subspace

$$\frac{\partial\psi}{\partial t} = \left(I - \tilde{Z}_f Z_f\right)F(\psi)$$

(Maas & Pope, 1992; Lam & Goussis, 1994)

Rate-controlled constrained-equilibrium method (RCCE)

- Based on assumption that fast chemical processes lead to an equilibrium state, subject to the conditions that some major species have concentrations which evolve according to kinetics.
- Major species evolve according to differential equations involving detailed chemical kinetics, whilst equilibrated species are determined by **minimising the free energy of the mixture**, subject to ***additional constraints*** (i.e. in addition to the conservation of mass, energy and elements).
- **Constrained species often equivalent to non-QSS species**.

RCCE

- System dynamics takes place on the **constrained equilibrium manifold**.
  - Analogous to other invariant manifolds.
- In the limit that the number of constraints equals the number of species in the problem, the RCCE model becomes equivalent to a detailed mechanism.
- Also suggested that the relationship between an RCCE model and a detailed mechanism is analogous to that between statistical mechanics and molecular dynamics in applications to thermodynamics and reaction rate theory (Miller, 2021).
  - Need to have ways to **define constraint species optimally**.

Intrinsic dimensionality

- Two key aspects to using ILDMs/slow manifolds:
  - What is the **required dimension** of manifold to get desired accuracy?
  - How are the **chemical changes** along the **manifold defined**.

Z_s and Z_f *are* defined via invariant subspaces associated with the local Jacobian of the chemical source term according to:

$$F_\psi = \left(Z_c\ Z_s\ Z_f\right) \cdot \begin{pmatrix} N_c & & \\ & N_s & \\ & & N_f \end{pmatrix} \cdot \begin{pmatrix} \tilde{Z}_c \\ \tilde{Z}_s \\ \tilde{Z}_f \end{pmatrix},$$

$$|\lambda_i(N_c)| < \tau_c, \qquad \lambda_i^{\text{real}}\left(N_f\right) < \tau_s < \lambda_i^{\text{real}}(N_s)$$

τ_c is upper limit for the eigenvalues λ associated with very slow processes ("almost conserved scalars"), and τ_s is upper limit for eigenvalues associated with fast relaxing (negative) time-scales.

Hence, by an eigenvalue analysis gaps in the time-scale spectrum can be found and a dimension defined.

Computational Singular Perturbation (CSP) Theory uses a similar approach with slightly different formulation (Lam & Goussis, 1994):

.

Use of difference equations for time dependent models – repro-modelling

- For chemical kinetic systems we **usually solve differential equations** to determine the change in species concentrations over time.
- For large, complex, nonlinear systems requires sophisticated numerical integration techniques.
- For repeated calculations (e.g. in CFD codes) the **same conditions of composition, temperature, pressure may be revisited many times**.
- May be quicker to **store** the model results to **reuse** later.
- This can be achieved via the **tabulation of model quantities** (see later) or by the **use of fitted difference equations**.

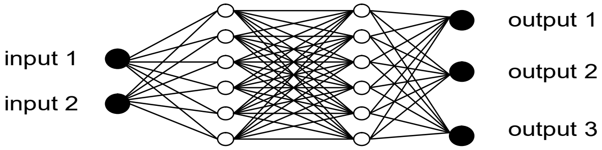
1. Δt is selected to achieve good resolution of the characteristic system time-scale.
2. Several thousand, spatially homogeneous simulations carried out with series of initial concentrations and/or T, representative of circumstances of final applications.
3. $\mathbf{Y}(t)$, $\mathbf{Y}(t+\Delta t)$ concentration vector pairs are stored in a database.
4. Function $\mathbf{G}$ is fitted to data and to predict change in concentration after time step

$$\Delta t : \mathbf{Y}(t+\Delta t) = \mathbf{G}(\mathbf{Y}(t)).$$

Operator splitting allows difference equation to be applied to only chemical time-step.

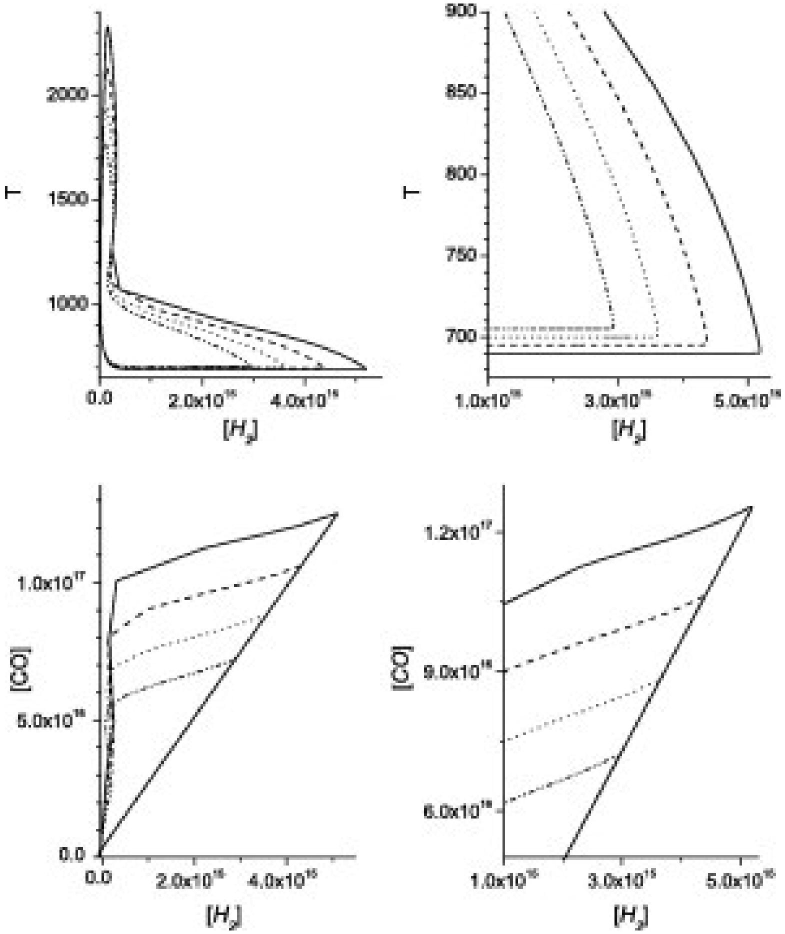
Different approaches

- The application of ***orthonormal polynomials*** (Turányi, 1994) can be advantageous for this task, since their ***coefficients can be determined independently*** from each other.
- Overall aim is to get a good fit using as few monomials as possible.
- For large complex systems, rapidly convergent hierarchical correlated function expansions in the input variables, or HDMR, can be used (as in global sensitivity analysis section).
  - Applied in Li et al. (2008) to the simulation of ignition within homogeneous H_2/air mixtures over wide ranges of temperatures and pressures ($1000 < T0 < 1500$ K, $0.1 < P < 100$ atm)
- Artificial Neural Networks, ANNS, have also been used for this purpose (Christo et al., 1996; Blasco et al., 2000).
- Fitted models can be used to represent dynamics within the slow low dimensional manifold.
- Reduces dimension and stiffness and uses less memory than look-up tables.



Oscillatory ignition example

- Orthonormal polynomials used for the generation of a repro-model describing the **oscillatory ignition of CO-H_2 mixtures** in a continuously stirred tank reactor (CSTR) at very low pressures (Brad et al., 2007).
- **4-variable repro-model based on 6th order polynomials**, successful representation of the regions of steady state, cool flames and large temperature oscillations achieved based on fits to a 14-variable full model.
- [H_2], [O_2], [CO] and T used for fitted model.
- Dynamically complex system.
- Regions of high accuracy were required during oscillatory ignition.
- Whole composition space was partitioned to achieve accurate fits.



PRISM (Piecewise Reusable Maps)

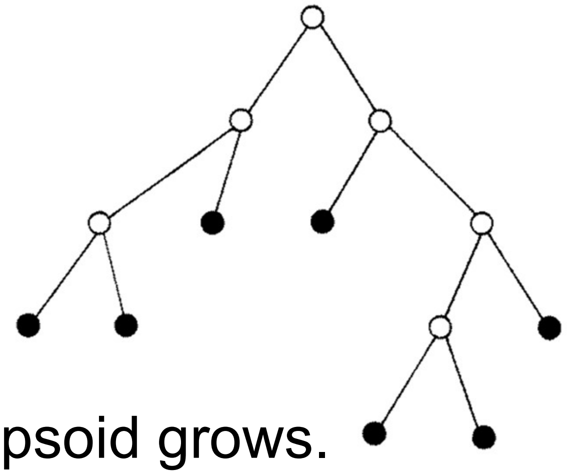
- Polynomial approach (Tonse et al., 1999) whereby fitted polynomial functions are ***developed during the calculation***, and then ***reused*** when the region of composition space is revisited in subsequent time steps or different spatial regions (c.f. ISAT later).
- Uses **second-order polynomials** so that in order to cover the realisable region, multiple expressions are used, each valid over a different portion of composition space.
- Integration of full kinetic equations provides the solution at selected points throughout a hypercube, in order to determine the polynomial coefficients.
    - Increase in accuracy with reduced hypercube size.
- Trade-off between accuracy and the efficiency of polynomial generation as well as storage and retrieval.
    - **Polynomial construction only allowed for those hypercubes that are revisited enough times to make the construction worthwhile.**
- Successful application to hydrogen ignition, a 1D laminar hydrogen flame, a 2D axisymmetric turbulent jet (Tonse et al., 1999; Tonse et al., 2003) and a turbulent premixed hydrogen flame (Bell et al., 2000).

The use of look-up tables

- Key quantities of chemical changes e.g. species concentrations and rates of change calculated using simple models:
  - Perfectly stirred reactors, laminar flames
- Stored as a function of key quantities:
  - *T*, concentrations, reaction progress variable.
- Key aspect is coverage of **appropriate phase space** that will be encountered in CFD model.
- When CFD code receives input vector, it locates points within table close to input point. Output vector is composed using linear interpolation between output vector elements at the storage points.
- Critical aspects are **accuracy**, **storage** and **efficiency** of retrieval.
- Latter two can be vastly improved by tabulating on ILDMs which are much lower dimensional than the full composition space.
  - **Use of full mechanism and tabulation gives improvement compared to creating table from global mechanism**.

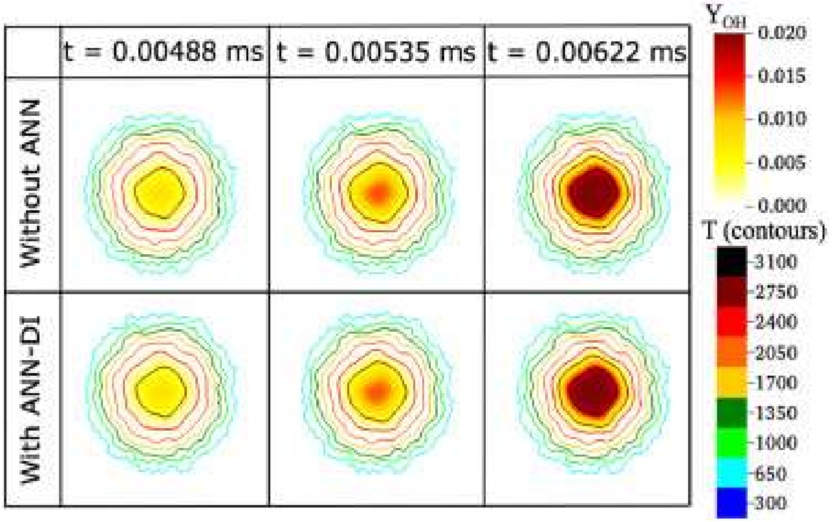
In situ adaptive tabulation (ISAT), (Pope, 1997)

- Exploits the fact that during reactive flow calculations, regions of composition space may be **revisited many times**.
- Calculate the first time and then **store and retrieve** in subsequent requests.
- Since systems naturally **relax to low dimensional manifolds** over time, creating tables on the fly automatically requires fewer variables and hence much smaller tables.
- Storage within a **binary tree structure**.
- Interpolation error controlled by adaptive refinement of mesh.
- Error controlled using ellipsoid of accuracy for stored points – as new points are tabulated ellipsoid grows.
- Many examples of use in turbulent reacting flows by incorporating operator splitting.



Offline training vs. On-the-fly

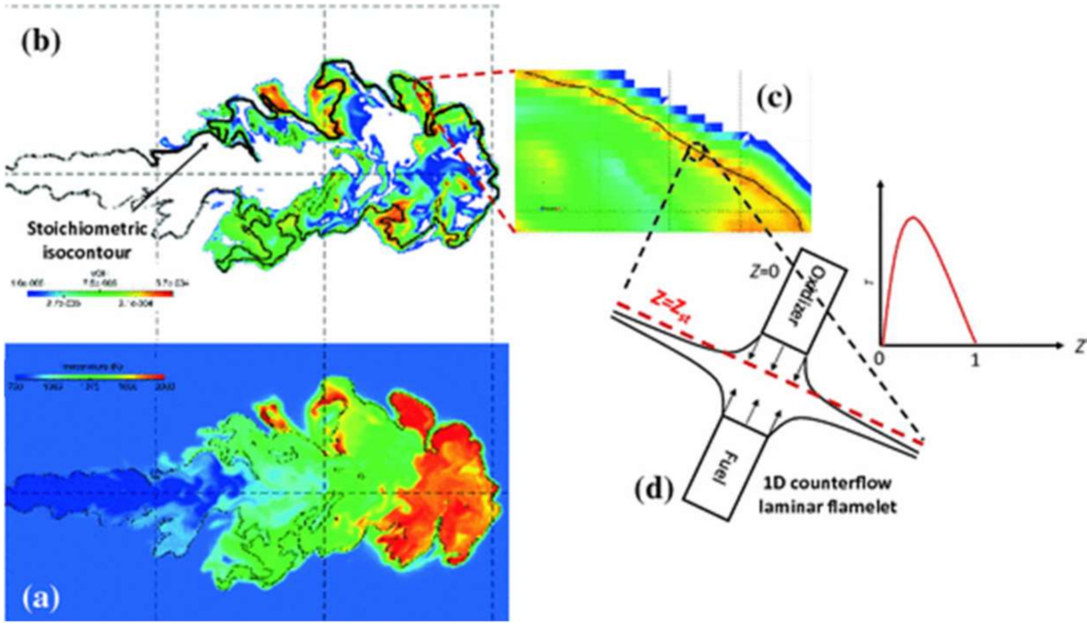
- There have been a number of applications of fitted/trained kinetic models within combustion models including for simulations of turbulent flames.
- Earlier examples used offline training.
- Disadvantages
  - If a regime is encountered which is outside the training data.
  - Many chemical mechanisms are regularly updated, which would mean re-training an ANN for example.
- More recent methods include on-the-fly training, in common with PRISM, ISAT and other in-situ methods.
  - Disadvantage here may be that the ANN would be less general overall.



- **On-the-fly ANN method**
  developed in Chi et al. (2021) for Direct Numerical Simulation (DNS) predictions of hot spot ignition in turbulent flames.
- ANN regression is achieved through a multilayer (4 layers) perceptron (MLP), involving a sum of non-linear basis functions and coefficients (biases and weights) to fit the input-output training dataset.
- Biases and weights adjusted for each layer of the MLP to obtain a minimal error at the output layer compared to full integration.
- Data clustering used for 1) burned-gas zone, 2) reaction zone, 3) preheated zone, and 4) unburned zone (fresh gas region).
- Stored ANN models are created during simulation and used to replace the expensive ODE integrations in later simulation steps.
  - Retrained and updated throughout simulation.
- Speed up factor of 3.5 but memory requirements very low compared to say ISAT.

Flamelets (Bray, 2016)

- Used to approximate the edge of a turbulent flame by an **ensemble of discrete, steady laminar flames**, called flamelets.
- Individual flamelets assumed to have a similar structure to laminar flames for the same concentration, *T* conditions.
  - Detailed calculations of flamelet chemistry obtained from lower dimensional numerical calculations and potentially stored as **look-up tables** of species compositions and reaction rates in terms of suitably chosen reaction progress variable.
  - Coupling with assumed probability density function (PDF) for this variable then provides an estimate for mean properties.
  - Alternative is to provide a laminar flamelet expression for the PDF, $P(c;\mathbf{x})$.



Kundu et al, 2018

Flamelets (Bray, 2016)

Advantages:

- Rapid and usually low dimensional in terms of numbers of state variables.
- Commonly used in CFD packages using RANs and LES approaches.
- Detailed chemistry can be used in developing flamelet tables and hence problems with using global reactions can be avoided.

Disadvantages:

- Can fail in situations of significant flame stretch, intense small-scale turbulence, and flame-flame interactions.
- Difficult to estimate errors induced by assumption except by comparison with DNS.
- DNS data suggests that preheat zone structure differs from that of an unstretched laminar flame much more strongly than the high temperature side.

YOU NEED TO KNOW FROM WHAT CHEMISTRY THE FLAMELET WAS GENERATED…

Tabulation vs. Fitted Models?

Tabulation

- Highly accurate at tabulation points.
- Requires interpolation methods in between so accuracy depends on resolution.
- Trade off between resolution and storage and retrieval requirements.
- Can provide significant speed-ups over implicit integration methods.
- If in situ-then unlikely to lead to poor extrapolation but this leads to higher cost penalty.

Fitted Models

- Need to store far less information since not storing all input-output mapping – just fitted coefficients.
- Not necessarily 100% accurate anywhere. Depends on quality of fit and therefore sample size OR hypercube fitting region resolution.
- Unless calculated in-situ (e.g. PRISM, On-the-fly ANN) needs to be re-fitted each time model updated.
- Can provide significant speed-ups over implicit integration methods.
- Extrapolation dangerous.

Final Considerations on reduction methods

- The level of detail you decide to use to represent chemistry depends on your research goals.
- If you are probing kinetics, then a skeletal model may be ideal, so that elementary reactions can be retained and explored.
- To simulate turbulent combustion, tabulation/fitting may be only way to gain enough speed to incorporate detailed chemistry.
- Should always be aware of underlying chemistry:
  - If using a table/flamelet when was it created and using which detailed scheme? ***Is it up to date?***
  - If using global reaction scheme, ***are sufficient intermediates retained***, are underlying rate constants up to date?
- **Always be wary of over-extrapolation.**
- **Tracking uncertainties always useful** if affordable.
  - Tells us whether our model is likely to be robust or if process may be missing.
  - With SA tells us areas of model to focus on to improve the models predictive capabilities.