



WEDNESDAY 3-2 (ALISON TOMLIN)

Reduction of reaction mechanisms 2
(Species lumping and fitted models)



LUMPING



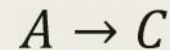
What does lumping mean?

- 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*



becomes:



- *Species Lumping*

$$[Y] = [A] + [B] + [C]$$

Why Lump?

- Skeletal mechanism reduction methods are useful for removing redundant species and reactions from a mechanism.
- Sometimes this is 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 “lose” information that was contained in full scheme.
- Cannot always recover original species concentrations.
- Need a method to define lumped reaction rates.

Where is lumping most commonly applied?

- Can be useful for models involving the combustion of complex hydrocarbons where comprehensive mechanisms may contain many isomers with complex multi-step pathways.
- The reactions for each isomer and its intermediates may be qualitatively similar.
- The rates of reaction may even be similar between isomers.
- We may be able to represent the weighted sum of isomer concentrations as a single species.
- Can also be useful in systems with either timescale separation or with groups of species which react on similar timescales.

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.

Methodologies used.

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



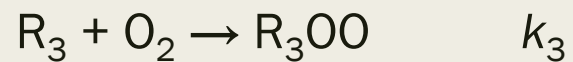
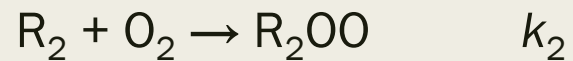
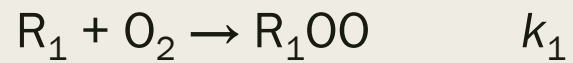
Chemical Lumping

- Has some commonality with topics discussed in the lecture 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 O₂ to form HO₂ and conjugate olefins.
 3. Direct and reverse O₂ 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 HO₂ and conjugate olefins.etc.

How?

- Reference rate parameters can be defined for each reaction class based on literature data or similarity rules.
 - *E.G. values can be defined for the abstraction of a hydrogen radical based on its location at a primary, secondary or tertiary site, or for isomerization reactions for hydrogen transfer from different sites .*
- 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).

For example, within the *n*-heptane scheme described there are 4 alkyl radicals noted by R_1, R_2, R_3, R_4 giving rise to 4 reactions involving the addition of O_2 .



The lumped alkyl radical is then defined by:

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

with the corresponding lumped reaction given by:



How to define the rate constant for the lumped reaction?

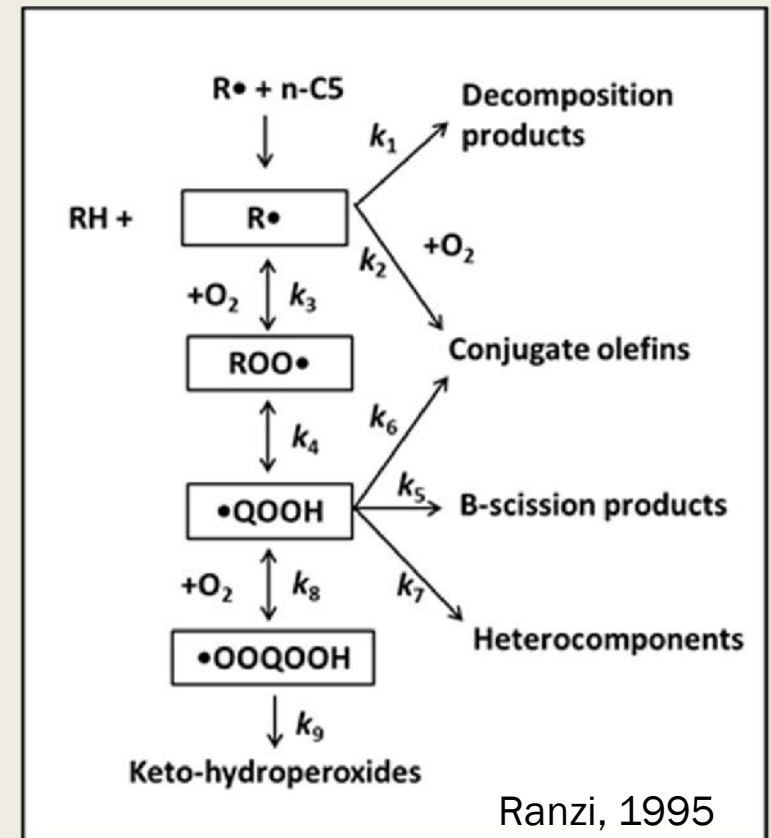
- By fitting with respect to experimental data or with respect to the complex full model (remember MAMOX, Milan).
- By weighted averages for the different component isomers depending on the relative weights within the initial fuel.
- From the weighted mean of the elementary rate coefficient for the individual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

$$k_5 = \frac{k_1[R^\bullet_1] + k_2[R^\bullet_2] + k_3[R^\bullet_3] + k_4[R^\bullet_4]}{[R^\bullet]}$$

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.
- $\text{Q7OOH} \rightarrow \text{OH} + 0.3\text{HCHO} + 0.32\text{C}_5\text{H}_{10} + 0.3\text{C}_4\text{H}_8 + 0.35\text{CH}_3\text{CHO} + 0.31\text{C}_3\text{H}_6 + 0.35\text{C}_2\text{H}_5\text{CHO} + 0.4\text{C}_2\text{H}_4 + 0.06\text{C}_7\text{H}_{14}$
- Rate coefficients for lumped scheme obtained by fitting against predictions from full scheme



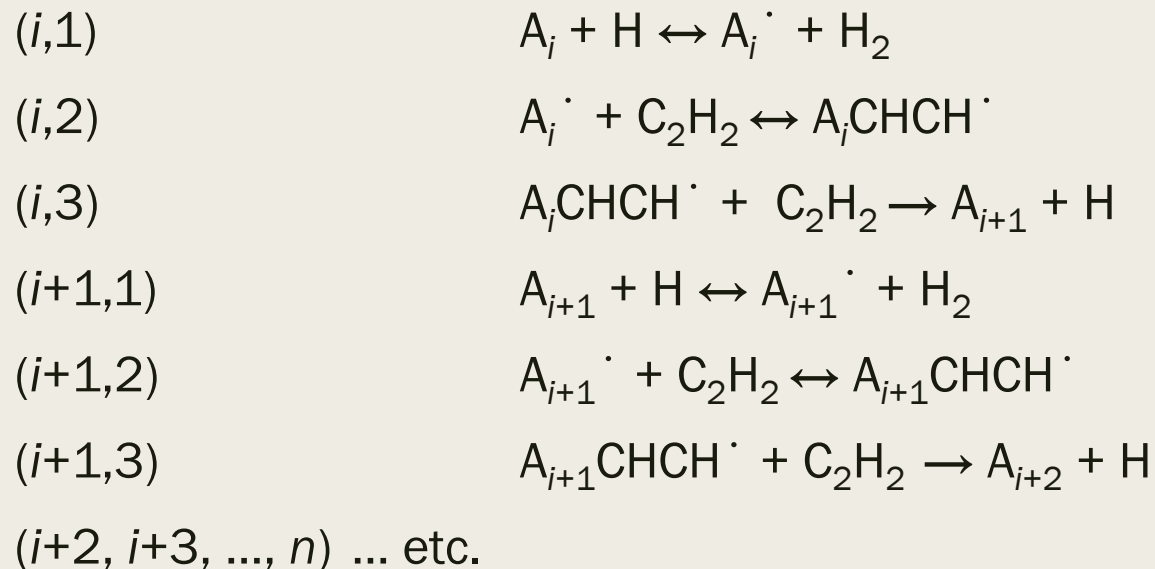
Applications of Chemical Lumping

- 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 the automatic reaction generation software EXGAS in order to allow the user to limit the size and improve the computational efficiency of the generated schemes where required.

Lumping in Soot Formation Mechanisms

- Chemical reactions describing polymer growth are of the same type, while the rate parameters and thermodynamic data vary only slightly between polymer sizes.
- For soot formation the reaction is described by a distribution function for the degree of polymerization, and a repeating reaction cycle for particle growth . The structure and rate coefficients for each repeated cycle are treated as being the same.
- A suggested mechanism of PAH (Polycyclic Aromatic Hydrocarbon) growth proceeds by a replication process involving hydrogen abstraction and the addition of acetylene (HACA mechanism).
- Lumping can be guided by similarities in structure of the hydrocarbon species in the repeating sequence (Frenklach, 1990).

HACA Reaction Sequence



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

In non-lumped form the reaction system is described by the following set of rate equations:

$$\frac{d[A_i]}{dt} = r_o - k_1[A_i][H] + k_{-1}[A_i^\cdot][H_2]$$

$$\frac{d[A_i^\cdot]}{dt} = k_1[A_i][H] - k_{-1}[A_i^\cdot][H_2] - k_2[A_i^\cdot][C_2H_2] + k_{-2}[A_iCHCH^\cdot]$$

$$\frac{d[A_iCHCH^\cdot]}{dt} = k_2[A_i^\cdot][C_2H_2] - k_{-2}[A_iCHCH^\cdot] - k_3[A_iCHCH^\cdot][C_2H_2]$$

$$\frac{d[A_{i+1}]}{dt} = k_3[A_iCHCH^\cdot][C_2H_2] - k_1[A_{i+1}][H] + k_{-1}[A_{i+1}^\cdot][H_2]$$

$$\frac{d[A_{i+1}^\cdot]}{dt} = k_1[A_{i+1}][H] - k_{-1}[A_{i+1}^\cdot][H_2] - k_2[A_{i+1}^\cdot][C_2H_2] + k_{-2}[A_{i+1}CHCH^\cdot]$$

$$\frac{d[A_{i+1}CHCH^\cdot]}{dt} = k_2[A_{i+1}^\cdot][C_2H_2] - k_{-2}[A_{i+1}CHCH^\cdot] - k_3[A_{i+1}CHCH^\cdot][C_2H_2]$$

... etc.

- 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 $M_o = [A_i] + [A_i^*] + [A_iCHCH^*] + [A_{i+1}] + \dots$

- 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.

$$\begin{aligned}\frac{dM_1}{dt} &= \left(m_o \frac{d[A_i]}{dt} + m_o \frac{d[A_i\cdot]}{dt} + (m_o + 2) \frac{d[A_i\text{CHCH}\cdot]}{dt} + (m_o + 4) \frac{d[A_{i+1}]}{dt} + \dots \right) \\ &= m_o r_o + 2k_2[\text{C}_2\text{H}_2] \sum_i [A_i] - 2k_{-2} \sum_i [A_i\text{CHCH}\cdot] + 2k_3[\text{C}_2\text{H}_2] \sum_i [A_i\text{CHCH}\cdot]\end{aligned}$$

where $M_1 = m_o[A_i] + m_o[A_i\cdot] + (m_o + 2)[A_i\text{CHCH}\cdot] + (m_o + 4)[A_{i+1}] + (m_o + 4)[A_{i+1}\cdot] + \dots$, 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:

$$\begin{aligned}\hat{c}_1 &= \sum_i [A_i] \\ \hat{c}_2 &= \sum_i [A_i\cdot] \\ \hat{c}_3 &= \sum_i [A_i\text{CHCH}\cdot]\end{aligned}$$

- The corresponding lumped equation system is then given by:

$$\begin{aligned}\frac{d\hat{c}_1}{dt} &= r_o - k_1[\text{H}]\hat{c}_1 + k_{-1}[\text{H}_2]\hat{c}_2 + k_3[\text{C}_2\text{H}_2]\hat{c}_3 \\ \frac{d\hat{c}_2}{dt} &= k_1[\text{H}]\hat{c}_1 - k_{-1}[\text{H}_2]\hat{c}_2 - k_{-2}\hat{c}_3 \\ \frac{d\hat{c}_3}{dt} &= k_2[\text{C}_2\text{H}_2]\hat{c}_2 - k_{-2}\hat{c}_3 - k_3[\text{C}_2\text{H}_2]\hat{c}_3\end{aligned}$$

- The example shows that 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 LUMPING



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 \mathbf{Y} to a new transformed variable vector $\hat{\mathbf{Y}}$ using the transformation function \mathbf{h} :

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

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

$$\frac{d\hat{\mathbf{Y}}}{dt} = \hat{\mathbf{f}}(\hat{\mathbf{Y}}, \mathbf{k}) \qquad \hat{\mathbf{Y}}(t_0) = \hat{\mathbf{Y}}_0$$

Inverse transformation

- An important feature is the ability to recover the original vector of concentrations from the transformed variables.

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

- Inverse mapping is not unique but its existence is a necessary condition of formally exact lumping.
- Inverse mapping also provides a link between the lumped species (which will be solved for in the lumped system) and the original species.
- In practical applications the inverse transformation may not be necessary since often lumped species (e.g. total PAH) may be sufficient.
- Lumping is often not “exact” in practical systems.

Linear Lumping

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

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

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

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

This lumping matrix transforms an original concentration vector (Y_1, Y_2, Y_3, Y_4) to the concentration vector of lumped species, where (\hat{Y}_1, \hat{Y}_2) and

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

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

Simple example of first-order systems

Can be described by the following initial value problem:

$$\frac{d\mathbf{Y}}{dt} = -\mathbf{K} \mathbf{Y} \quad \mathbf{Y}(t_0) = \mathbf{Y}_0$$

Linear species lumping results in the following different initial value problem:

$$\frac{d\hat{\mathbf{Y}}}{dt} = -\hat{\mathbf{K}} \hat{\mathbf{Y}} \quad \hat{\mathbf{Y}}(t_0) = \hat{\mathbf{Y}}_0$$

Wei and Kuo (1969) have shown that the necessary and sufficient condition of exact linear lumping is the following equation:

$$\mathbf{MK} = \hat{\mathbf{K}}\mathbf{M}$$

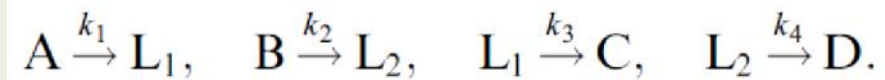
which is always possible to define but is not necessarily unique.

- Equivalent problem is finding *invariant subspaces* of the original equations *i.e.* invariant subspaces of the transpose of the Jacobian $J^T(Y)$.
- This is a system of equations where the *eigenvalues* of $J^T(Y)$ and $J^T(M^{-1}MY)$ *are identical*.
- Straightforward for linear examples where the Jacobian is a constant matrix.
- Difficult task for more general nonlinear ODEs where applying the restrictions imposed by exact lumping may limit the level of reduction possible for the reduced scheme.
- Hence approximate lumping is usually applied based either on chemical similarities and therefore similarities in rate constants, or either time-scale similarities or separation (see later lectures on Computational Singular Perturbation theory).

Example of approximate method

- Huang *et al.* (2005) defined a formal lumping procedure for intermediate species where the fraction of each component within the lump α_i (equivalent to the inverse lumping matrix $\overline{\mathbf{M}}$) is defined in terms of the fractional formation rate of the components of the lump.
- The selection of suitable lumping groups is determined via the calculation of the ratio of the normalised formation rates between candidate species i and j denoted by $\gamma_{i,j}$. If the ratio is approximately constant over the course of the simulation, then the two species can be lumped.

Take the example:



$$\begin{pmatrix} d[A]/dt \\ d[B]/dt \\ d[L_1]/dt \\ d[L_2]/dt \\ d[C]/dt \\ d[D]/dt \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -k_2 & 0 & 0 & 0 & 0 \\ k_1 & 0 & -k_3 & 0 & 0 & 0 \\ 0 & k_2 & 0 & -k_4 & 0 & 0 \\ 0 & 0 & k_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & k_4 & 0 & 0 \end{pmatrix} \begin{pmatrix} [A] \\ [B] \\ [L_1] \\ [L_2] \\ [C] \\ [D] \end{pmatrix}.$$

Define the lump $[L] = [L_1] + [L_2]$

Lumped system:

$$\begin{pmatrix} d[A]/dt \\ d[B]/dt \\ d[L]/dt \\ d[C]/dt \\ d[D]/dt \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \times \begin{pmatrix} -k_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -k_2 & 0 & 0 & 0 & 0 \\ k_1 & 0 & -k_3 & 0 & 0 & 0 \\ 0 & k_2 & 0 & -k_4 & 0 & 0 \\ 0 & 0 & k_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & k_4 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & \alpha_1 & 0 & 0 \\ 0 & 0 & \alpha_2 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} [A] \\ [B] \\ [L] \\ [C] \\ [D] \end{pmatrix}.$$

$$\begin{pmatrix} \alpha_i \\ \alpha_j \end{pmatrix} = \begin{pmatrix} \frac{R_i}{R_i + R_j} \\ \frac{R_j}{R_i + R_j} \end{pmatrix}$$

- True if the initial concentrations of the two species is equal.
- Often the case if species are intermediates since their initial concentration will be zero.

- For a lumped group containing three species A, B, and C, then α is calculated as follows:

$$r_A = \frac{R_A}{R_A + m_1 R_B + m_2 R_C}$$

$$r_B = \frac{m_1 R_B}{R_A + m_1 R_B + m_2 R_C}$$

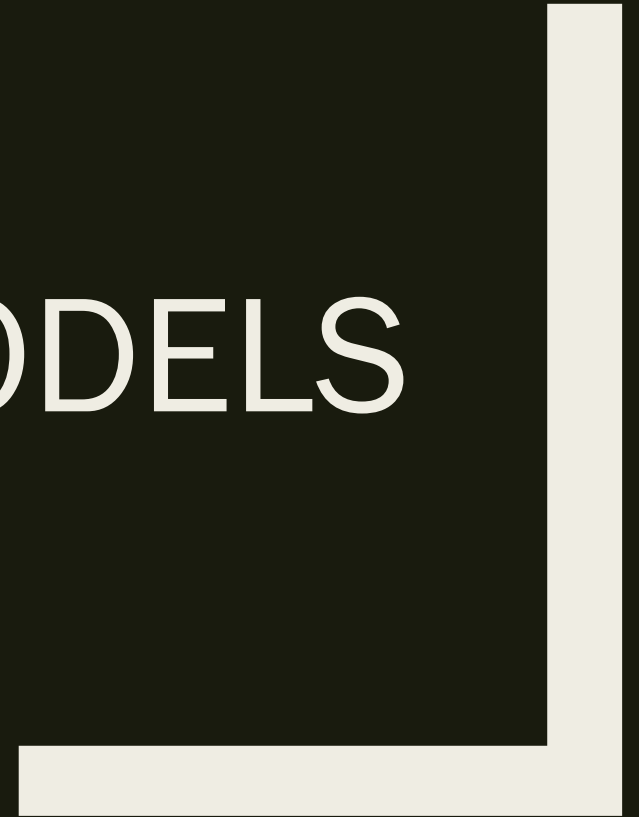
$$r_C = \frac{m_2 R_C}{R_A + m_1 R_B + m_2 R_C}$$

where R_i is the formation rate of species i , $m_1 = \alpha_{A,B}$, $m_2 = \alpha_{A,C}$ and

$$r_1 + r_2 + r_3 = 1$$

Method was illustrated for isothermal oxidation of fuel-rich methane-oxygen mixtures, where 31 species were lumped into 9 groups giving a reduction in the number of species of 22.

FITTED MODELS



Use of difference equations for time dependent models

- For chemical kinetic systems we are used to solving 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 throughout a simulation.
- In such cases it 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.

Suggested algorithm

1. Time step Δt is selected to achieve good resolution of the characteristic time-scale of the system.
2. Several thousand, spatially homogeneous simulations are carried out with a series of initial concentrations and/or temperatures, which are typical for the circumstances of applications of the final intended model.
3. The $Y(t)$, $Y(t+\Delta t)$ concentration vector pairs are stored in a database.
4. A function G is fitted to the data and can then be used to predict the change in concentration after time step Δt : $Y(t+\Delta t) = G(Y(t))$.

In the context of a CFD code – operator splitting can be used and such a difference equation applied to the chemical time-step.

Different approaches

- Differences in approach boil down to the form of the fitted function G .
- Polynomial functions are often used.
- Piecewise fits are often used in different regions of composition space to improve accuracy.
- Artificial Neural Networks have also been used.
- Critical feature is that ALL conditions to be encountered in final CFD code must be represented in homogenous calculations since polynomials can often behave badly outside of the region in which they were fitted.

Orthonormal Polynomials

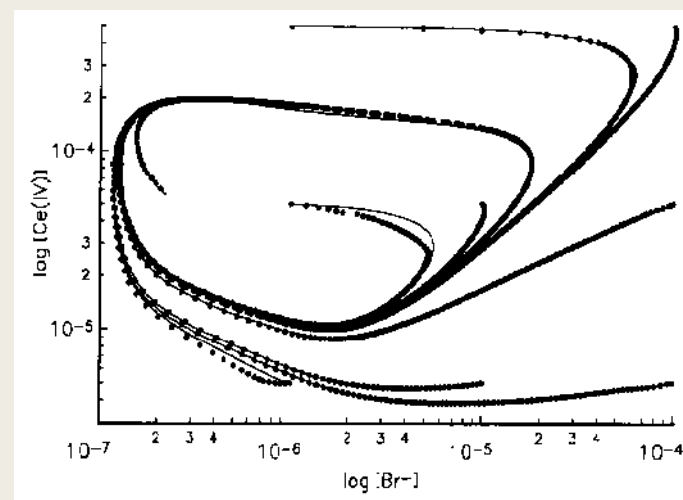
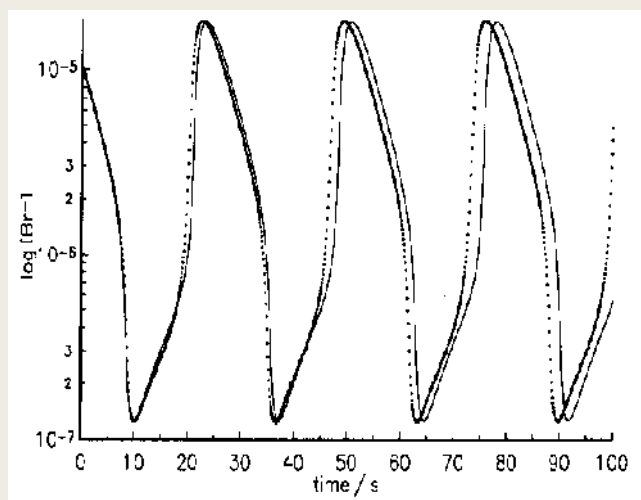
- Methods for the determination of the coefficients of high-order polynomials have to be suitable for fitting a polynomial function to tens of thousands of data points and determining coefficients for the effective variables only, usually using a least squares based method.
- The application of *orthonormal 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.
 - *Each polynomial generated by fitting its constant to the data and calculating the r.m.s. error.*
 - *A new term is then added, an orthonormal polynomial is generated and the new r.m.s. error calculated.*
 - *If the change in r.m.s. error is greater than a pre-set tolerance, then this term is accepted and a new term is tested.*
 - *Polynomial is built up with terms of progressively increasing order in combinations of variables.*
 - *The fitting is stopped when the error becomes lower than a given threshold.*

HDMR

- Previous method has several advantages;
 - *the fitted function is the best approximation,*
 - *most of the coefficients within the high-order polynomial are likely to be zero.*
- However, in high-dimensional nonlinear cases with many variables and the requirement of a high order approximation, the number of non-zero coefficients can be very large, making the creation and evaluation of multi-variate high-order polynomials very expensive.
- In such cases, rapidly convergent hierarchical correlated function expansions in the input variables, or HDMR, can be used (as in global sensitivity analysis section).
- Applications have shown that the order of the correlations between the independent variables dies off rapidly and therefore only a few terms are usually required to represent even highly nonlinear input–output relationships.
- Applied in Li et al. (2008) to the simulation of ignition within homogeneous H₂/air mixtures over wide ranges of temperatures and pressures ($1000 < T_0 < 1500$ K, $0.1 < P < 100$ atm)

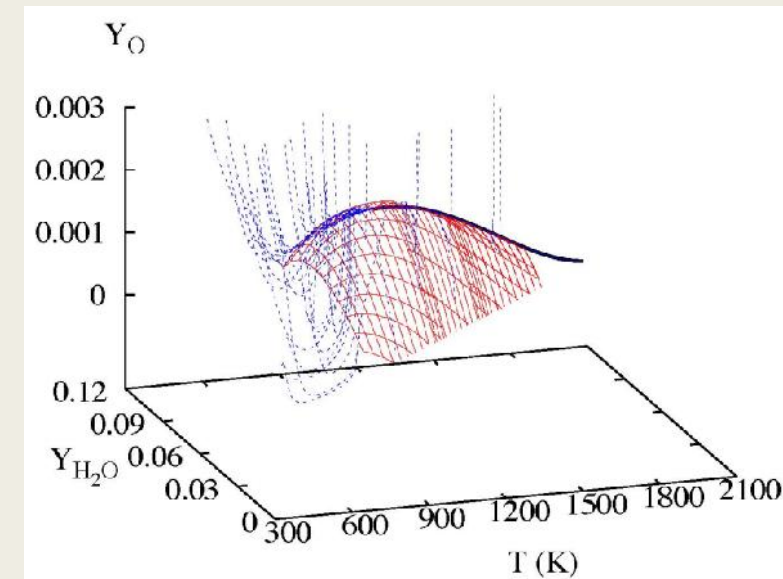
Example - Belousov–Zhabotinsky oscillating reaction.

- Original model first simulated 200 times using different initial concentrations and $\Delta t = 0.1$. 20,000 data sets collected.
- 8th order polynomials used for fit.
- Speed up x 50.



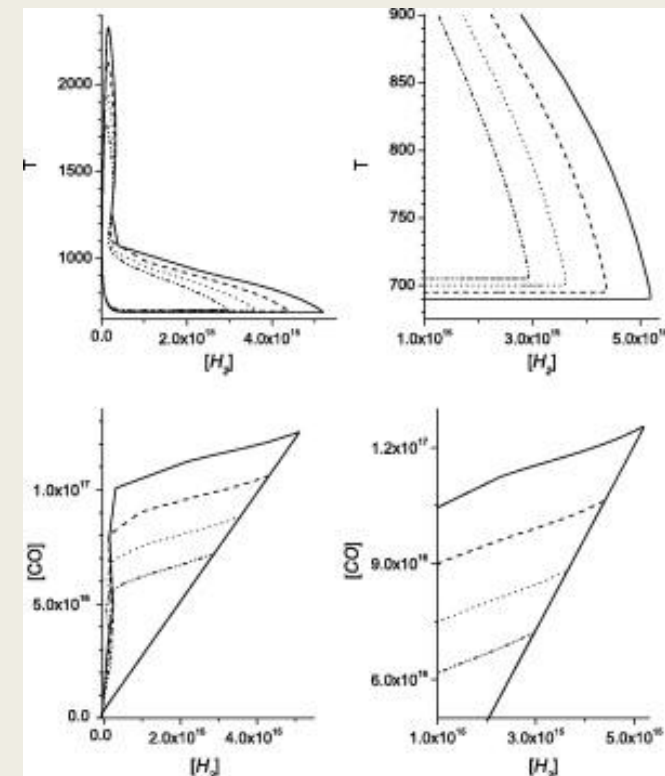
Use of slow manifolds

- Timescale analysis can reveal low dimensional slow manifolds within combustion systems.
- Behaviour collapses onto these lower dimensional manifolds after initial transient period.
- Therefore fitted models can be restricted to such low dimensional spaces.
 - *can lead to big reduction in numbers of variables.*
 - *can circumvent the need to define differential equations on these manifolds.*
 - *can potentially be computationally faster than using look-up tables (see Goussis lectures).*



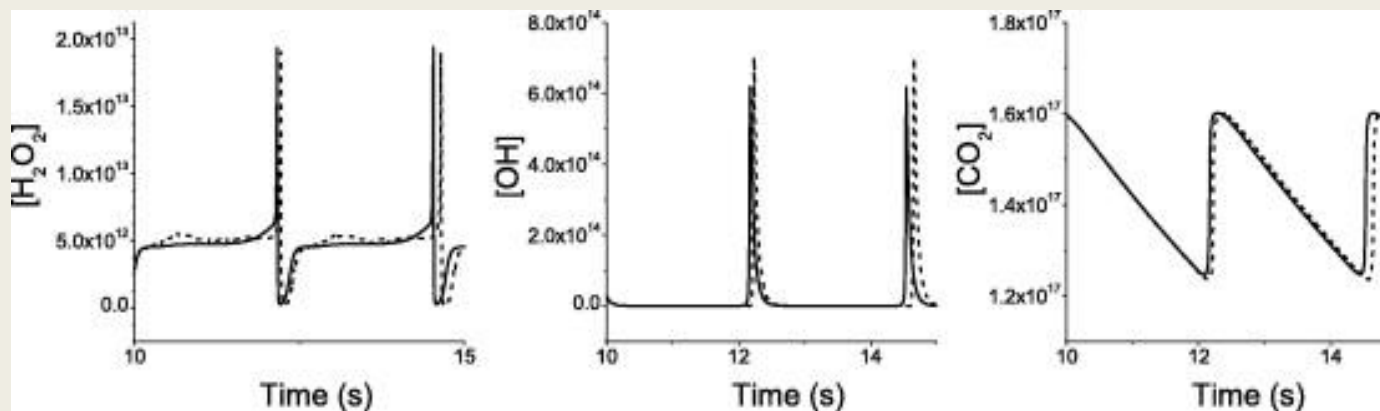
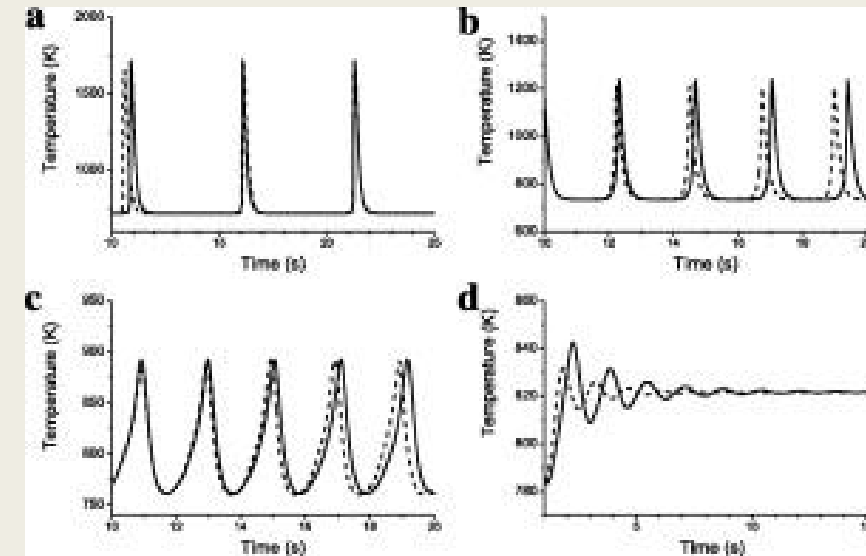
Oscillatory ignition example

- Orthonormal polynomials used for the generation of a repro-model describing the oscillatory ignition of CO-H₂ 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.
- [H₂], [O₂], [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.



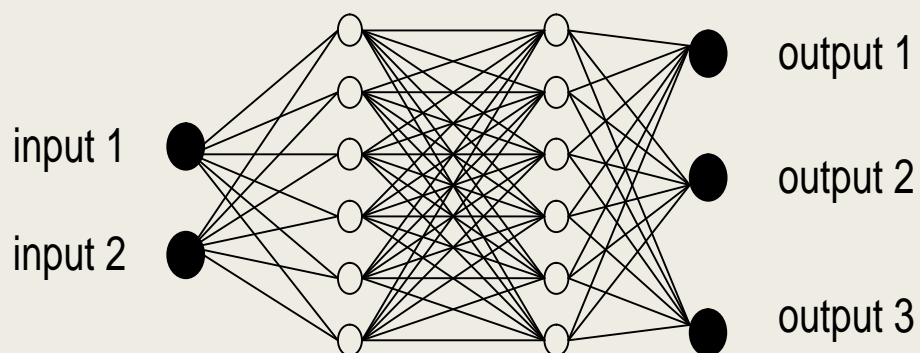
Avoiding the build-up of errors

- Higher accuracy was demanded in regions where trajectories were divergent in composition space.
- More tricky than a model where everything tends towards equilibrium!
- Mass was conserved by fitting the non-dynamic variables as functions of the dynamic ones.
 - *Analogous to the QSSA assumption.*



Artificial Neural Networks

- In principle capable of representing highly nonlinear functions such as those which arise in chemical kinetic systems.
- Therefore fall into the class of fitted model approaches.
- Designed to attempt to recreate the way a human brain works by constructing a network of neurons or nodes linked to each other by a series of 'synapses'.
- This artificial model of a brain can then be 'trained' by presenting it with examples and adjusting the effect the neurons have on each other until the system 'recognises' the examples.
- Not really that different in concept from other non-linear fitting approaches...



Strengths of connections between the different neurons are stored as weights which are determined by an appropriate learning algorithm.

ANN'S

- Mathematically represented as:

$$y_i^l = f \left(\sum_{j=1}^{K_{l-1}} w_{ij}^l y_j^{l-1} + w_i^l \right) \quad i=1, \dots, K_l, l=1, \dots, L$$

- where y_i^l is the output of the i -th neuron of the l '-th layer, w_{ij}^l is the weight value of connection between the j -th neuron of the $(l-1)$ layer and the i -th neuron of the l '-th layer and w_i^l is the bias value of the i -th neuron of the l '-th layer.
- The nonlinear transfer function $f(.)$ is commonly a sigmoidal or hyperbolic-tangent function.
- Through presenting input-output examples to the system and adjusting the synaptic weights in an appropriate manner, the system can be trained to recognise patterns or replicate complicated functions. The learning algorithm provides the means of adjusting the weights in order to reduce the fitting error of the ANN when compared to the training data.

Applications and issues

- (Christo et al. (1996) successfully applied ANNs in the modelling of a velocity-scalar joint pdf transport equation for H_2/CO_2 turbulent jet diffusion flames based on a global 3-step scheme.
- Several authors have combined ANNs with other reduction approaches such as ISAT (Chen et al., 2000; Ihme et al., 2009), and Rate Controlled Equilibrium (Chatzopoulos and Rigopoulos 2013) e.g. for non-premixed and non-piloted, $\text{CH}_4/\text{H}_2/\text{N}_2$ turbulent flames).
- Possible disadvantages
 - *lack of definitive guidelines for optimising important features such as appropriate number of layers and neurons in each layer (Christo et al. 1996a).*
 - *optimising the network becomes effectively an iterative trial and error procedure.*
 - *large numbers of weights are capable of providing a highly accurate fit to training data, but can lead to poor results for unseen data (over-fitting),*
 - *analogous way to using polynomials of too high order.*
 - *since the ANNs typically use exponential functions, their evaluation requires more computer time than using polynomials.*

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).

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 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-site (e.g. PRISM) needs to be re-fitted each time model updated.
- Can provide significant speed-ups over implicit integration methods.
- Extrapolation dangerous.

Summary of lecture 3-2

- We briefly reviewed simple lumping methods for reducing the number of species in a chemical kinetic model.
 - *Approximate lumping methods are seen to be more appropriate for combustion models due to their inherently non-linear nature.*
- The rate constants for lumped reactions can be developed either by fitting to simulations of the full scheme, or through algebraic relations to the original rate constants if functions can be developed.
 - *Easier if structural similarities have been used to estimate rate constants!*
 - *Applies to large hydrocarbon systems with many parallel pathways of similar isomers.*
- Even through lumping, integer stoichiometric coefficients in a kinetic scheme can be lost - or we lose the kinetic formulation altogether i.e. we are left with a mathematical model and not chemical reactions.
- In fitted models this is very much the case – the models have a highly empirical basis and are only applicable in the region of fitting.
 - *Extrapolate at your peril!*