“Graph-Related” Methods in Combustion Chemical Kinetics

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MATH 789R
Experiments

Simulations

Shock boundary layer interactions
Isolator shock train
Low-speed turbine
Low-speed nozzle (closed)
Flow
Low-speed inlet (closed)
High-speed inlet (open)
Combustor
Isolator
High-speed nozzle (open)
Definitions

Chemical kinetic model:
Collection of elementary reactions

Law of mass action:
The reaction rate is proportional to the reactant concentrations

Reaction Rate “Constant”:
Parameterizes the law of mass action
Example of a Chemical Kinetic Model

### Table 1  
H$_2$/O$_2$ Reaction Model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$</th>
<th>$n$</th>
<th>$E_a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $H + O_2 = O + OH$</td>
<td>1.04E+14</td>
<td>0.00</td>
<td>1.531E+04</td>
<td>* [42]</td>
</tr>
<tr>
<td>(2) $O + H_2 = H + OH$</td>
<td>Duplicate</td>
<td></td>
<td>7.948E+03</td>
<td>* [20]</td>
</tr>
<tr>
<td>(3) $H_2 + OH = H_2O + H$</td>
<td>2.16E+08</td>
<td>1.51</td>
<td>3.430E+03</td>
<td>[147]</td>
</tr>
<tr>
<td>(4) $OH + OH = O + H_2O$</td>
<td>3.34E+04</td>
<td>2.42</td>
<td>$-1.930E+03$</td>
<td>* [20]</td>
</tr>
<tr>
<td>(5) $H_2 + M = H + H + M$</td>
<td>4.58E+19</td>
<td>$-1.40$</td>
<td>1.040E+05</td>
<td>[81]</td>
</tr>
</tbody>
</table>

$\varepsilon_{H_2} = 2.5$, $\varepsilon_{H_2O} = 12.0$, $\varepsilon_{CO} = 1.9$, $\varepsilon_{CO_2} = 3.8$, $\varepsilon_{Ar} = 0.0$, $\varepsilon_{He} = 0.0$

...  
19 Reactions, 10 species + Thermodynamic Data

$$k_t = AT^n \exp \left( -\frac{E_a}{R_uT} \right)$$
Role of CK model in reacting flow simulations

Conservation of species (Compressible Navier-Stokes equations)

\[ \frac{\partial \rho Y_i}{\partial t} + \nabla \cdot [\rho Y_i (\mathbf{V}_i + \mathbf{u})] = \omega_i \]

Simplified reactor (0-D)

\[ \frac{dY_i}{dt} = \omega_i \]

Note: Molar concentrations \([\mathbf{M}]\) and mass fractions \(Y\) are algebraically related; Can easily interchange them.

\[ \omega_i = \sum_{l=1}^{R} (v_{li}' - v_{li}'')q_l \]

\[ q_l = k_l(T,P) \prod_{n=1}^{N_l} [\mathbf{M}]_n^{v_{ln}'} - \frac{K_l^E(T)}{k_l(T,P)} \prod_{n=1}^{N_l} [\mathbf{M}]_n^{v_{ln}''} \]

\[ k_l = AT^n \exp \left( - \frac{E_a}{R_u T} \right) \]
Example – 0-D Reactor

- Initial temperature $T_0$ and fuel + air
- Temperature vs. time graph showing ignition time
- Plot of $t^+$ vs. time in $10^{-4}$ s and temperature $T$ in $10^3$ K
Size of CK models

Ethylene combustion:
\(~ 100 \) species,
\(~ 1000 \) reactions

Bio-derived fuels:
\(~ 1000 \) species
\(~ 5000 \) reactions
Detailed CK is “Sparse”
Research Questions

• Reduction of Computational Cost
  • What is the minimum set of species and reactions that can reproduce experimental data (or the initial “detailed” model) without loss of accuracy?
  • What approximations can be applied to trace but highly reactive species?
  • What computational strategy can be explored to limit the number of evaluations of the reactive term?

• How do you “optimize” the model, via the reaction parameters, taking in account the uncertainties on the data and the model?
A Reaction Network Perspective

\[
\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2 \\
\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O} \\
\ldots
\]

Weighted, Directed Graph
- Species <-> Nodes
- Reactions <-> Edges
- Weights <-> Reaction rates
Graph-related Reduction Approaches


Consider species A and B. Normalized contribution of species B to the production rate of species A (time and possibly space dependent):

\[ r_{AB} = \frac{\sum_{i=1}^{NR} |v_{A,i} \omega_i \delta_{Bi}|}{\sum_{i=1}^{NR} |v_{A,i} \omega_i|} \]

(\( \delta_{Bi} \) is 1 when species A and B are in the same elementary reaction)
Graph-related Reduction Approaches (DRG)

- There exist an edge between A and B if $r_{AB} \geq \epsilon$
- If there is an edge, $r_{AB}$ is its weight

Operative Considerations

- The user chooses an initial set of “important species”
- Choose an “error” threshold $E$
- Traverse the graph from the starting species and identify a subgraph by neglecting all edges that have a weight below $E$
- Find the simulation associated with the subgraphs at different levels of $E$

$$r_{AB} = \frac{\sum_{i=1}^{NR} |v_{A,i} \omega_i \delta_{Bi}|}{\sum_{i=1}^{NR} |v_{A,i} \omega_i|}$$
Typical Results
Better defined weight $r_{AB}$
- $P_a$: Production of species A from reactions including species B
- $C_a$: Consumption of species A from reactions including species B

“Error propagation”: there may be several paths connecting species A and B
- Define an index associated with a path $p$ via nodes $S_i$’s
- Iteratively search for subgraphs (nodes) based on an error threshold on $R_{AB}$
Typical Results
Path Flux Analysis

Sun et al. 2010

- Separately analyze consumption and production rates (different graphs?)
- Introduce “first” and “second” generation coefficients
- Lump all interactions coefficients (not necessary) and use same algorithm as DRG

\[
P_A = \sum_{i=1,n_R} \max(0, v_{i,A} \omega_i), \quad P_{AB} = \sum_{i=1,J} \max(v_{A,i} \omega_i \delta_B, 0).
\]

\[
C_A = \sum_{i=1,n_R} \max(0, -v_{i,A} \omega_i), \quad C_{AB} = \sum_{i=1,J} \max(-v_{A,i} \omega_i \delta_B, 0).
\]

\[
r_{AB}^{\text{pro-1st}} = \frac{P_{AB}}{\max(P_A, C_A)}
\]

\[
r_{AB}^{\text{con-1st}} = \frac{C_{AB}}{\max(P_A, C_A)}
\]

\[
r_{AB}^{\text{pro-2nd}} = \sum_{M_i \neq A,B} \left( r_{AB}^{\text{pro-1st}} r_{AM_i}^{\text{pro-1st}} \right)
\]

\[
r_{AB}^{\text{con-2nd}} = \sum_{M_i \neq A,B} \left( r_{AB}^{\text{con-1st}} r_{M_iB}^{\text{con-1st}} \right)
\]

\[
r_{AB} = r_{AB}^{\text{pro-1st}} + r_{AB}^{\text{con-1st}} + r_{AB}^{\text{pro-2nd}} + r_{AB}^{\text{con-2nd}}
\]
Example

- **DRG: E = 0.205 (6 SPECIES)**
  - M5 – M8, C and D are 6 selected species due to direct value of threshold
  - Total target flux = 29.4 %

- **DRGEP: E = 0.146 (6 SPECIES)**
  - M5-M6 direct relation to A
  - M7,M8 indirect relation via M5, M6
  - C selected via M5 and M7
  - D selected via M6 and M8
  - Total target flux = 29.4 %

- **PFA: E – 0.215**
  - First select B
  - Then select M1-M4 via oath from A to B
  - Total target flux 66.4 %
Typical Results
Accuracy Requirements

S.B. Pope, PROCI 2012: “Small scales, many species and the manifold challenges of turbulent combustion”

Important conclusions from research in the last two [...] are that, for simple hydrocarbon fuels, accurate descriptions over a range of conditions are possible with of order 20–40 species, but certainly not with of order five species.

Note: Not only DRG-based but sensitivity based!
Questions: MATH 789R

• Can you use a rigorous graph theory to frame “DRG”-based reduction methods?
• Can any of the centrality/communicability measures introduced in class improve or justify the algorithmic choices in “DRG”-based reduction methods?
• Can hub and authority rankings provide more insight in the CK models?
• Beyond reduction, should large CK models be regarded as “complex networks” (scale free, small-world, etc.)? If yes, how can this guide the development?