
The Role of CSP in Reduced Chemistry Modeling

(October 13-15, 1999, IMA Mini-symposium, University of
Minnesota)

S. H. (Harvey) Lam

Princeton University

<http://www.princeton.edu/~lam>

Physically Meaningful Representations

The master kinetic equations:

$$\frac{d\vec{x}}{dt} = \vec{g}(x, \dots),$$

$$\vec{g}(x, \dots) = \sum_{r=1}^R \vec{s}_r F^r(x, \dots)$$

\vec{s}_r is the *stoichiometric vector* of the r-th reaction

F^r is the r-th reaction's *reaction rate*

The Goals of Reduced Chemistry Modeling

- *Insights* and *understandings*.
- To enable numerical simulations of highly complex problems by reducing the needed computing resources (*memory*, *stiffness* and *computing cycles*).

The Scenarios Prior to the Age of Computers

- Traditional theoreticians applied *quasi-steady* and *partial-equilibrium* approximations, and analytically derived the reduced model which contains just a few unknowns driven by a few reactions,
- *Intuition* and *experience* played a crucial role in such derivations.

Alternative Representation of

$$\vec{g}(x, \dots)$$

- What would be a more *useful* representation of $\vec{g}(x, \dots)$?
- A *dream* exact representation:

$$\vec{g} = \vec{g}_{\text{exhausted}}(\vec{x}, \dots) + \vec{g}_{\text{active}}(\vec{x}, \dots) + \vec{g}_{\text{dormant}}$$

- The first term can be neglected, because ...
- The last term can be neglected, because ...
- ***The middle term is the reduced model.***

Exhausted and Dormant Modes

- Exhausted modes are “decaying fast modes;” the amplitudes of these modes are small because of “cancellations.”
- Dormant modes are modes whose amplitudes are inherently zero or small. Examples of dormant modes are: conservation of atomic species, slow radioactive decays, etc.

The Ultimate Reduced Model: Chemical Equilibrium Flows

- State variables of *strictly* chemical equilibrium flows are:

p *pressure,*

T *temperature,*

A_α *concentration of atomic elements,*

$$\alpha = C, O, H, N, \dots$$

- The ultimate reduced model:

$$x_n = X_n(p, T, A_\alpha)$$

*These are called **equations of state.***

The Manifold for Chemically Equilibrium Flows

- For strictly chemically equilibrium flows, the currently active \vec{g}_{active} subspace is empty. Modes are either exhausted or dormant.
- The *control variables* are then:
 p, T and $A_\alpha, \alpha = O, H, C, \dots$.
- For hydrocarbon combustion problems, the number of control variables is thus at least **5**, and usually more.

Approximations Available for Combustion Problems

- Pressure p usually can be approximated by a constant,
- When species diffusions are neglected and the upstream species conditions are uniform, the A_α 's are constants.
- When both of the above are true, temperature T is the only “control variable” for chemical equilibrium flows.

Chemically Non-equilibrium Flows

- When the \vec{g}_{active} subspace is not empty, the flow is a chemically non-equilibrium flow.
- For problems in which species diffusion is important, the A_α 's are not constants.
- Finding the *active subspace* is doing reduced chemistry modeling.

The ODE for $g(\mathbf{x})$ (no matter how nonlinear)

- Given

$$\frac{d\vec{x}}{dt} = \vec{g}(\vec{x})$$

- Differentiating \vec{g} , we obtain:

$$\frac{d\vec{g}}{dt} = \overline{J} \circ \vec{g}$$

where J is the Jacobian.

Methodologies for Reduced Chemistry Modeling

- *Traditional theoreticians* guessed at the “best” basis vectors to span the currently active subspace,
- *ILD*M uses the eigenvectors of J,
- *CSP* provides formal refinement procedures to *improve* any given basis vectors. Eigenvectors of J are the obvious choice as trial basis vectors.

Insights from CSP Data

- The CSP-reduced K-step mechanism:

$$\begin{aligned} \frac{d\vec{x}}{dt} &= \sum_{k=1}^K \vec{a}_{M+k} f^{M+k} \\ &= \sum_{k=1}^K \vec{a}_{M+k} \vec{b}^{M+k} \circ \vec{g} \\ &= \left(\sum_{k=1}^K \vec{a}_{M+k} \vec{b}^{M+k} \circ \sum_{r=1}^R \vec{s}_r \right) F^r \end{aligned}$$

- The CSP data in the parentheses tells you *who is doing what to whom*.

Strengths and Weaknesses

- *Traditional asymptotic analysis* can be done only for “tractable” problems, and accuracy is sacrificed for simplicity.
- *ILDM* is useful when the number of control variables is small, and advocates table lookup for reduced $g(x)$.
- *CSP* allows user-specified accuracy, and assumes that computational resource is not a problem.

Buckmaster: the manifold is different at different points.

- Of course.
- For flame problems, species diffusions are almost always “important.” Thus the atomic element concentrations A ‘s are not expected to be constants.
- There are chemically non-equilibrium boundary layers (catalytic surfaces?).
- Many Damkohler numbers.

The Trade-off's

- Remember: the theoreticians often used a single model everywhere for their PDE problems (did they do it well?)
- *The trick*: sacrifice accuracy to reduce computational burdens.
- Take advantage of all available approximations: p nearly constant, ϵ 's nearly constant, only moderately large eigenvalue gap, 10% error is OK,

A Role for CSP

- CSP provides a rational mathematical framework for reduced chemistry modeling (*did they do it right?*).
- A *database of CSP basis vectors* can be created which can be interrogated to provide the desired reduced chemistry modeling. (remember, all chemical kineticists have their *private* favorite radicals).

A Brief Description of CSP

- Remember: the whole CSP idea is to find basis vectors so that the fast modes are decoupled from the active modes as much as possible.
- Eigenvectors of J are very good basis vectors.
- CSP provides a refinement procedure to improve your basis vectors.

Effects of Diffusion

- “Reduced chemistry” models derived either classically or via CSP automatically modify the diffusion terms for the control variables.
- In other words: it is *incorrect* to use reduced chemistry models along with unmodified diffusion terms in the equations for the control variables!!!!

Example

- Given a three species system



- Assume the first elementary reaction is much faster than the second one.

The Reaction-Diffusion Eqns

$$\frac{fx_1}{ft} = -\frac{x_1 - x_2^2}{\varepsilon} + (\mu x_1)$$

$$\frac{fx_2}{ft} = +\frac{x_1 - x_2^2}{\varepsilon} + k(x_3 - x_2)$$

$$\frac{fx_3}{ft} = -k(x_3 - x_2)$$

Note: Diffusion is present *only* in the first equation of this example.

Traditional Asymptotic Derivation of Reduced Model

- Adding the first two equations, we have:

$$\frac{d}{dt}(x_1 + x_2) = k(x_3 - x_2) + \mu \quad (\mu$$

- In the asymptotic limit of $\varepsilon \rightarrow 0^+$:

$$x_1 = x_2 + O(\varepsilon)$$

This is the partial equilibrium approximation. The QSSA approximation does NOT work for this problem! (You can try it and see)

The Reduced Model

- Eliminating x_1 in terms of x_2 , we have:

$$\frac{dx_2}{dt} = \frac{k(x_3 - x_2)}{1 + 2x_2} + \frac{2}{1 + 2x_2} \quad (\mu x$$

$$\frac{dx_3}{dt} = -k(x_3 - x_2)$$

Note: The reduced model is valid only after the initial transient ($t \gg \epsilon$). Look! ϵ no longer appears! Look! *a diffusion term shows up where there was none!*

Derivation Using CSP

- Just pick any (random) set of basis vectors. In the small epsilon limit, you need only to refine it once. *Voila!*
- Use the eigenvectors of J . *Voila!* To improve it, refine it once more...
- If your problem is huge and messy, CSP does it the same, programmable way.
- Diffusion is always correctly and automatically treated without fuss.

Bibliography

- You can download most of the CSP papers from
<http://www.princeton.edu/~lam>
- More recent works by Dimitris Goussis can be found in
<http://euklides.iceht.forth.gr:8000/cgi-bin/index-CG.cgi>