

Reduced Chemistry-Diffusion Coupling

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Abstract: In reacting flow problems involving large numbers of chemical species and reactions, *reduced chemistry modeling* is used to approximately describe, with fewer unknowns, the slow chemical evolutions after the rapid but brief initial transients have decayed. Diffusion transport terms, if present, are modified by the reduced chemistry approximations. This article reiterates that the use of *unmodified* diffusion terms along with reduced chemistry terms is unjustified in general, and discusses the potential impacts of diffusion on the use of “slow manifolds” to reduce the number of unknowns. In addition, the proper way to handle sidewall reactive-diffusion boundary layers is presented.

Keywords: Chemical kinetics; Diffusion; Reduced chemistry; Slow manifolds

INTRODUCTION

In problems involving reactive fluid mixtures, diffusions of chemical species are often of interest. For such problems, the original partial differential equations (PDEs) must retain both chemistry and diffusion terms. In the current reacting flows literature, the following strategy is often employed in theories or computations:

- replace the chemistry terms by *reduced chemistry* terms originally derived for homogeneous problems, and

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- continue to use the same diffusion terms (same as when chemistry is absent) *without modifications*.

It was pointed out by Maas and Pope (1992a, 1992b) and Lam (1993; see its §7.6) that this strategy is not justifiable. The present article focuses on the *coupling* of reduced-chemistry modeling and diffusion by working out a toy problem in some details—using conventional analysis (Williams, 1985) and CSP (Lam, 1993; Lam and Goussis, 1994; Lam, 1995). While no overt adverse consequences have been attributed to this strategy in the literature, it is nevertheless incorrect mathematically.

A major goal of reduced chemistry modeling is to reduce the number of unknowns. Reduction of the number of unknowns is possible when the solution is known to stay in a *slow manifold* in the species concentration space. The present paper points out that reduction of unknowns is hampered whenever diffusion is locally competitive with fast chemistry—as would be the case inside thin sidewall reactive-diffusive layers or inside thin diffusion-controlled propagating flame zones. In addition, the correct methodology to accommodate arbitrary sidewall boundary conditions is provided.

A TOY PROBLEM

To simplify the exposition, a three species ($N = 3$) unsteady reactive-diffusive toy problem is considered. The characteristic physical length of the spatial region is L . The solution for $t = O(1)$ (appropriately scaled) inside this physical region is of interest. The three governing PDEs are:

$$\frac{D}{Dt} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} = \begin{bmatrix} \alpha \mathcal{R}^{fast} + \mathcal{R}_1 \\ \beta \mathcal{R}^{fast} + \mathcal{R}_2 \\ -\mathcal{R}^{fast} + \mathcal{R}_3 \end{bmatrix} = \underbrace{\begin{bmatrix} \alpha \\ \beta \\ -1 \end{bmatrix} \mathcal{R}^{fast}}_{\text{fast chemistry}} + \begin{bmatrix} \mathcal{R}_1 \\ \mathcal{R}_2 \\ \mathcal{R}_3 \end{bmatrix} \quad (1)$$

where α, β are positive, finite constants and

$$\mathcal{R}^{fast}(y_1, y_2, y_3; \epsilon) \equiv \frac{y_3 - \mathcal{Y}(y_1, y_2)}{\epsilon} \quad (2a)$$

$$\mathcal{R}_n(y_1, y_2, y_3; D_n) \equiv \underbrace{f_n(y_1, y_2, y_3)}_{\text{slow chemistry}} + \underbrace{\nabla \cdot (D_n \nabla y_n)}_{\text{diffusion}}, \quad n = 1, 2, 3 \quad (2b)$$

Here D/Dt denotes the substantial derivative, ∇ and ∇y_n are gradient and divergence operators in physical space, the y_n 's are $O(1)$ reactant concentrations, ϵ a small positive timescale, and the D_n 's are $O(1)$ diffusion coefficients. The chemical reaction terms are divided into “fast” and “slow” reactions by the small parameter $\epsilon > 0$. The fast chemical reaction

is represented explicitly by both its stoichiometric coefficients $(\alpha, \beta, -1)$ and its net reaction rate \mathcal{R}^{fast} , while the remaining slow chemistry terms are generically represented by the $f_n(y_1, y_2, y_3)$'s.

As defined by Eq. (2a), the fast reaction has been assumed reversible. Without loss of generality, \mathcal{R}^{fast} is assumed to depend on y_3 linearly and to depend on y_1 and y_2 via some positive differentiable $O(1)$ function $\mathcal{Y}(y_1, y_2)$. Both $d\mathcal{Y}/dy_1$ and $d\mathcal{Y}/dy_2$ are assumed non-negative and bounded. These assumptions are not crucial, but are adopted to simplify the expositions. Both α and β are assumed to be $O(1)$. If α or β are $O(1)$ but \mathcal{Y} is small, then the problem can be transformed into a small α or a small β problem.

To further simplify the exposition, the physical region of interest is assumed one-dimensional, $L \geq x \geq 0$. At the initial instant $t = 0$, arbitrary initial conditions are provided: $y_n(x, 0) = y_n^{(I)}(x)$. At the sidewall boundaries (at $x = 0$ and $x = L$), arbitrary (time dependent) boundary conditions for the y_n 's are provided. In general, the initial condition and the boundary conditions are not assumed to be in any "slow manifold."

Since $\alpha, \beta, \epsilon, \mathcal{Y}(y_1, y_2)$, the $f_n(y_1, y_2, y_3)$'s, the D_n 's and the initial/boundary conditions have been left arbitrary (except for their orders of magnitude), this toy problem should be able to emulate any three species reactive-diffusive problem with one fast chemistry mode. For example, it includes the problem treated in Davis and Skodje (1999) as a special case.

In the small ϵ limit, the governing PDEs are asymptotically stiff. The nominal Damkohler numbers for both of these PDEs are $O(1/\epsilon)$, thus the diffusion terms are formally not competitive with the fast chemistry term—except locally in some thin regions of thickness $O(\epsilon^{1/2})$.

CONVENTIONAL ASYMPTOTIC ANALYSIS

The toy problem explicitly identified the fast chemical reaction. After a brief initial transient, the fast chemistry reaction is expected to exhaust itself.

Alternative Exact PDEs

Consider the following linear combinations of the original PDEs:

$$\frac{D}{Dt}(y_1 + \alpha y_3) = f_1 + \alpha f_3 + \nabla \cdot (D_1 \nabla y_1 + \alpha D_3 \nabla y_3) \tag{3a}$$

$$\frac{D}{Dt}(y_1 + \beta y_3) = f_2 + \beta f_3 + \nabla \cdot (D_2 \nabla y_2 + \beta D_3 \nabla y_3) \tag{3b}$$

The notable feature of this pair of alternative exact PDEs is that the fast chemistry term has been removed without the use of any approximation. These two special PDEs may replace any two of the original three PDEs whenever it is advantageous to do so.

The Rapid Initial Transient

When initial conditions (in the Lagrangian sense) are general and ϵ is small, brief rapid initial transients for all three species (when $\alpha, \beta \neq O(\epsilon)$) are expected. For $t = O(\epsilon)$, Eq. (3a) and Eq. (3b) says $y_1 + \alpha y_3$ and $y_2 + \beta y_3$ are nearly constants during the brief transient because there is not enough time for its right hand sides to exert significant impacts. Hence $y_1 + \alpha y_3$ and $y_2 + \beta y_3$ have no fast transients:

$$y_1(x, t) + \alpha y_3(x, t) = y_1^{(I)}(x) + \alpha y_3^{(I)}(x) + O(\epsilon), \quad t = O(\epsilon) \quad (4a)$$

$$y_2(x, t) + \beta y_3(x, t) = y_2^{(I)}(x) + \beta y_3^{(I)}(x) + O(\epsilon), \quad t = O(\epsilon) \quad (4b)$$

When there are M fast modes in a N -species problem, there are as many as $N - M$ such (linearly independent) *pseudo-conservation laws*. During the brief initial transients, Eq. (4a) and Eq. (4b) may be exploited in the same way as conventional *conservation of atomic species* is usually exploited in chemical kinetics problems.

On a y_3 versus y_1 plot, the initial condition ($y_3^{(I)}(x)$ and $y_1^{(I)}(x)$) can be displayed as a line on this graph with x as a parameter. During the rapid initial transient, Eq. (4a) says that each x point on this initial condition curve moves along a straight line trajectory with slope $-1/\alpha$. Similar comments apply to the y_3 versus y_2 plot.

After the brief initial transient is spent, the solution reached is the “effective” initial condition for the reduced chemistry model which governs the subsequent slow evolutions.

Partial Equilibrium Approximation

For the toy problem, the identity of the fast reaction is known. In the paper and pencil approach, the exhaustion of an identified fast chemical reaction is exploited by the *partial equilibrium* (PE) approximation:

$$\mathcal{R}^{fast} = O(1), \quad t \gg O(\epsilon) \quad \epsilon \ll 1 \quad (5)$$

This is an algebraic equation relating the three unknowns. Solving for y_3 , one obtains:

$$y_3 = \mathcal{Y}(y_1, y_2) + O(\epsilon) \quad (6)$$

This is an approximate *algebraic relation* between the unknowns. Such relation is commonly called the *slow manifold* of the reactive system. In the present article, a slow manifold is defined as the thin region in the close vicinity of a smooth surface in the N -dimensional y space. The thickness of the thin region is $O(\epsilon)$. Unlike pseudo-conservation laws (e.g., Eq. (4a) and Eq. (4b)), slow manifolds are independent of initial or boundary conditions. In CSP papers, such approximate algebraic relations were called *equations of state*. Finding slow manifolds is one of the major goals of reduced-chemistry modeling (Keck and Gillespie, 1971; Roussel and Fraser, 1993; Gorban and Karlin, 2003; Ren and Pope, 2006). Once slow manifolds such as Eq. (6) have somehow been found, variables such as y_3 —often called a “fast variable”—can in principle be removed from the problem. Reducing the number of unknowns is one of the main payoffs of reduced-chemistry modeling.

On the y_3 versus y_1 and y_2 plots mentioned in the previous section, Eq. (6) also provides a line in each graph. The solution point for each value of x on each graph moves rapidly along straight lines with slope $-1/\alpha$ or $-1/\beta$ during the rapid initial transient, makes an abrupt turn upon reaching it, then moves slowly along Eq. (6) afterwards. In other words, it stays inside the slow manifold after reaching it.

How does one exploit Eq. (6)—however it was found? It is worth pointing out that Eq. (6) cannot be used to evaluate \mathcal{R}^{fast} —it merely confirms Eq. (5) without providing an usable value for \mathcal{R}^{fast} via Eq. (2a). It is clear that if Eq. (6) is used in any of the original governing equations of the toy problem, no useful answers are obtained when $\alpha, \beta = O(1)$. However, Eq. (6) can be freely used in both Eq. (3a) and Eq. (3b) to remove y_3 , yielding two approximate PDEs for y_1 and y_2 . Indeed Eq. (3a) and Eq. (3b) are special (Williams, 1985). When supplemented by Eq. (6), they are the PE approximation-derived reduced-chemistry model for the toy problem when $\alpha, \beta = O(1)$.

An issue which remains to be resolved is the sidewall boundary conditions for the y_n 's. This will be treated later.

Quasi-Steady State Approximation

If both α and β are $O(\epsilon)$, then Eq. (6) can freely be used in the original PDEs for y_1 and y_2 , and Eq. (3a) and Eq. (3b) are correctly recovered. In the chemical kinetics literature, Eq. (6) is known as the *quasi-steady state approximation*, or QSSA. It is conventionally “derived” by neglecting the substantial derivative of the “fast variable” in its governing equation. Traditionally, the identification of the fast variable—often called a “radical” or an “intermediary”—is based on the experiences and insights of the investigators. It is obvious that substitution of Eq. (6) back

into the original PDE for y_3 makes no progress. Similarly, the identification of fast reactions in real problems (to apply the PE approximation to) is also based on experiences and insights of the investigators. In the chemical kinetics literature, QSSA is more ubiquitous than the PE approximation. Mathematically, QSSA is seen to be a special case of the PE approximation. When $\alpha, \beta = O(1)$, the QSSA approximation is not valid for the toy problem, while the PE approximation is always applicable provided equations analogous to Eq. (3a) and Eq. (3b) have been found.

Slow Evolution in the Slow Manifold

After the solution has settled into the slow manifold, the approximate Eq. (6) can be used as an equation of state to eliminate y_3 from both sides of Eq. (3a) and Eq. (3b). One obtains after some amount of algebra:

$$\frac{Dy_1}{dt} = \frac{(1 + \beta \frac{\partial \mathcal{Y}}{\partial y_2})\mathcal{R}_1 - \alpha \frac{\partial \mathcal{Y}}{\partial y_2} \mathcal{R}_2 + \alpha \mathcal{R}_3}{1 + \alpha \frac{\partial \mathcal{Y}}{\partial y_1} + \beta \frac{\partial \mathcal{Y}}{\partial y_2}} + O(\epsilon) \quad (7a)$$

$$\frac{Dy_2}{dt} = \frac{(1 + \alpha \frac{\partial \mathcal{Y}}{\partial y_1})\mathcal{R}_2 - \beta \frac{\partial \mathcal{Y}}{\partial y_1} \mathcal{R}_1 + \beta \mathcal{R}_3}{1 + \alpha \frac{\partial \mathcal{Y}}{\partial y_1} + \beta \frac{\partial \mathcal{Y}}{\partial y_2}} + O(\epsilon) \quad (7b)$$

Since the \mathcal{R}_n 's were defined as the sum of the slow chemistry and the diffusion terms of the n -th species, the right hand sides of Eq. (7a) and Eq. (7b) can be similarly written as the sum of a reduced chemistry term and a *modified* diffusion term:

$$\frac{D}{Dt} \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} (\text{reduced chemistry})_1 \\ (\text{reduced chemistry})_2 \end{bmatrix} + \begin{bmatrix} \nabla \cdot D_1(\nabla y_1) + \Delta_1 \\ \nabla \cdot D_2(\nabla y_2) + \Delta_2 \end{bmatrix} + O(\epsilon) \quad (8)$$

The reduced chemistry terms are identical to those derived using the PE approximation in the absence of diffusion. In other words, the reduced chemistry terms are not affected by diffusion. However, there is no question that the approximations used in the derivation of reduced chemistry modeling modified the diffusion terms by the Δ_n 's:

$$\begin{bmatrix} \Delta_1 \\ \Delta_2 \end{bmatrix} \equiv \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \frac{-\frac{\partial \mathcal{Y}}{\partial y_1}(\nabla \cdot D_1(\nabla y_1)) - \frac{\partial \mathcal{Y}}{\partial y_2}(\nabla \cdot D_2(\nabla y_2)) + \nabla \cdot D_3(\nabla \mathcal{Y})}{1 + \alpha \frac{\partial \mathcal{Y}}{\partial y_1} + \beta \frac{\partial \mathcal{Y}}{\partial y_2}} \quad (9)$$

Note that $\nabla \mathcal{Y} = (\partial \mathcal{Y} / \partial y_1) \nabla y_1 + (\partial \mathcal{Y} / \partial y_2) \nabla y_2$. The Δ_n 's represent the coupling of diffusions as a consequence of the fast chemistry. Note that Eq. (8) and Eq. (6) together is the conventionally derived reduced-chemistry model, which, unlike the original Eq. (1), is no longer stiff in the small ϵ limit. Side-wall boundary conditions are discussed later.

In the main region, the number of PDE unknowns has been reduced from 3 to 2. The solution for y_3 is provided algebraically by Eq. (6).

When Can Unmodified Diffusion Terms be Used? In general, an error is committed if the unmodified diffusion terms were used instead of the correct modified terms. Eq. (8) shows that the diffusion terms for y_1 and y_2 are unmodified to leading order if $\alpha = O(\epsilon)$ and $\beta = O(\epsilon)$, respectively. For $\alpha, \beta = O(1)$, it is possible to justify the use of unmodified diffusion terms (instead of the modified terms) under the following conditions (Ren and Pope, 2006):

$$D_1 \approx D_2 \approx D_3 \quad \text{and} \quad \frac{\partial^2 \mathcal{Y}}{\partial y_1^2} \frac{\partial^2 \mathcal{Y}}{\partial y_1 \partial y_2} \frac{\partial^2 \mathcal{Y}}{\partial y_2^2} \approx 0 \quad (10)$$

Under such circumstances, the physics of the diffusion of the fast-chemistry-coupled species are seen to be approximately indistinguishable. Thus under Eq. (10) the unmodified diffusion terms remain valid does make physical sense. In realistic problems, the adverse consequences of using unmodified diffusion terms had not been noticeable probably because the requirements in Eq. (10) were not severely violated.

Sidewall Boundary Conditions

Since arbitrary sidewall boundary conditions are allowed, the diffusion terms must always be competitive at the sidewalls—regardless of how fast the fast chemistry is. Unless the sidewall boundary conditions already honor Eq. (6), a thin reactive-diffusive boundary layer must be present at the sidewalls. *It is important to note that inside such sidewall layers, Eq. (6) is not honored in general.*

Consider the sidewall located at $x = 0$ with boundary conditions $y_n(0, t) = y_n^{(B)}(t)$. To study the solutions adjacent to this sidewall, a boundary layer coordinate η is introduced:

$$\eta = \frac{x}{\sqrt{\mathcal{D}_m \epsilon}} \quad (11)$$

where \mathcal{D}_m denote the maximum value of either D_1, D_2 or D_3 , whichever is bigger. When derivative with respect to x is replaced by derivative with respect to η , the diffusive terms in the original PDEs are now formally $O(1/\epsilon)$ —diffusion is now fully capable of being competitive with the fast chemistry term. In other words, the thicknesses of the reactive-diffusive layers are determined by the need for the diffusion to be competitive—i.e., the relevant characteristic Dämkohler numbers in these very thin layers are necessarily $O(1)$.

In terms of η , the three *original* PDEs in Eq. (1) can be rewritten as follows:

$$\alpha(y_3 - \mathcal{Y}(y_1, y_2)) + \frac{\partial}{\partial \eta} \left(\frac{D_1}{D_m} \frac{\partial y_1}{\partial \eta} \right) = \epsilon \left(\frac{Dy_1}{Dt} - f_1 \right) \quad (12a)$$

$$\beta(y_3 - \mathcal{Y}(y_1, y_2)) + \frac{\partial}{\partial \eta} \left(\frac{D_2}{D_m} \frac{\partial y_2}{\partial \eta} \right) = \epsilon \left(\frac{Dy_2}{Dt} - f_2 \right) \quad (12b)$$

$$-(y_3 - \mathcal{Y}(y_1, y_2)) + \frac{\partial}{\partial \eta} \left(\frac{D_3}{D_m} \frac{\partial y_3}{\partial \eta} \right) = \epsilon \left(\frac{Dy_3}{Dt} - f_3 \right) \quad (12c)$$

It is emphasized that these PDEs are exact.

In the small ϵ limit, the right hand sides are $O(\epsilon)$ and can be neglected after the brief initial transient. Thus these PDEs can be approximated by ordinary differential equations (ODEs). The given arbitrary sidewall boundary conditions at $\eta = 0$ for the y_n 's, the $y_n^{(B)}(t)$'s, can now be accommodated. The boundary conditions at the "outer edge" of this boundary layer ($\eta \rightarrow \infty$) are $\partial y_n / \partial \eta \rightarrow O(\epsilon^{1/2})$ —which together imply $y_3 \rightarrow \mathcal{Y}(y_1, y_2)$ there. Solution of this system of three coupled ODEs provides the "edge values," the $y_n^{(\infty)}(t)$'s, as functions of the given $y_n^{(B)}(t)$'s: $y_1^{(\infty)}(t) = y_1(\eta \rightarrow \infty)$, $y_2^{(\infty)}(t) = y_2(\eta \rightarrow \infty)$ and $y_3^{(\infty)}(t) = \mathcal{Y}(y_1^{(\infty)}(t), y_2^{(\infty)}(t))$. Exactly the same thing can be said on the sidewall boundary layer on the other sidewall. Together the edge values so determined serve as the boundary conditions for Eq. (8).

The edge values can be analytically related to the given boundary values when α, β, D_1 and D_2 are constants. The diffusion terms dominate when Eq. (3a) and Eq. (3b) are rewritten in terms of η . The diffusion terms now balance *each other* in Eq. (3a) and Eq. (3b), rather than balance against chemistry. Neglecting terms of $O(\epsilon)$, the resulting trivial second order ODEs can be integrated twice with respect to η to yield:

$$D_1 y_1 + \alpha D_3 y_3 = D_1 y_1^{(B)}(t) + \alpha D_3 y_3^{(B)}(t) + O(\epsilon^{1/2}) \quad (13a)$$

$$D_2 y_2 + \beta D_3 y_3 = D_2 y_2^{(B)}(t) + \beta D_3 y_3^{(B)}(t) + O(\epsilon^{1/2}) \quad (13b)$$

where boundary conditions at $\eta = 0$ and $\eta \rightarrow \infty$ have both been applied. Note that these two equations are not the same as Eq. (4a) and Eq. (4b) unless $D_1 = D_2$ and $D_1 = D_3$. The edge values are found by substituting $y_1 \rightarrow y_1^{(\infty)}(t)$, $y_2 \rightarrow y_2^{(\infty)}(t)$ and $y_3 \rightarrow \mathcal{Y}(y_1^{(\infty)}(t), y_2^{(\infty)}(t))$ in Eq. (13a) and Eq. (13b) and solving the resulting equations algebraically. They serve as boundary conditions for y_1 and y_2 in Eq. (8) at $x \approx 0^+$. Note that if

$\alpha = O(\epsilon)$, then $y_1^{(\infty)}(t) \approx y_1^{(B)}(t)$ —there is then no reactive diffusive boundary layer for y_1 , and similarly for the $\beta = O(\epsilon)$ case. When α , β and the D_n 's are not constants, then some computations may be needed.

EVALUATION OF \mathcal{R}^{fast}

Numerical evaluation of \mathcal{R}^{fast} using Eq. (2a) is problematical on any finite precision computer when ϵ is “asymptotically” small and \mathcal{R}^{fast} is $O(1)$. Severe loss of significant figures is expected from Eq. (2a) as the fast chemical reaction approaches partial equilibrium. Can \mathcal{R}^{fast} be computed in some other way? Let \mathcal{R}^{fast} itself be considered an entity of interest. The governing equation for \mathcal{R}^{fast} can readily be derived by differentiating it with respect to time. One obtains, straightforwardly:

$$\frac{D\mathcal{R}^{fast}}{Dt} = -\frac{1 + \alpha \frac{\partial Y}{\partial y_1} + \beta \frac{\partial Y}{\partial y_2}}{\epsilon} (\mathcal{R}^{fast} - \mathcal{R}_\infty^{fast}) \tag{14}$$

$$\mathcal{R}_\infty^{fast} \equiv \frac{-\frac{\partial Y}{\partial y_1} \mathcal{R}_1 - \frac{\partial Y}{\partial y_2} \mathcal{R}_2 + \mathcal{R}_3}{1 + \alpha \frac{\partial Y}{\partial y_1} + \beta \frac{\partial Y}{\partial y_2}} \tag{15}$$

Note that Eq. (14) has no \mathcal{R}^{fast} diffusion term, and \mathcal{R}^{fast} has no independent boundary condition. Thus Eq. (14) is a Lagrangian ODE in time, and not an PDE, as far as \mathcal{R}^{fast} is concerned. It is exact and it plainly says that the value of \mathcal{R}^{fast} following an element of the reacting fluid will rapidly “relax” along the trajectory of the fluid element toward $\mathcal{R}_\infty^{fast}$ —which, as defined by Eq. (15), depends only on the slow chemistry and the diffusion terms. In other words, when the inequality

$$\epsilon \left| \frac{D\mathcal{R}^{fast}}{Dt} \right| \ll |\mathcal{R}^{fast}| \tag{16}$$

can be justified, the QSSA can be applied to Eq. (14), yielding:

$$\mathcal{R}^{fast} = \mathcal{R}_\infty^{fast} + O(\epsilon) \tag{17}$$

Whenever \mathcal{R}^{fast} is $O(1)$, its numerical value is best evaluated with Eq. (17) and Eq. (15) rather than Eq. (2a) because $\mathcal{R}_\infty^{fast}$ as defined by Eq. (15) has no numerical difficulties with significant figures in the small ϵ limit.

If QSSA were applied to y_3 , one would obtain $\mathcal{R}^{fast} = \mathcal{R}_3 + O(\epsilon)$ instead of Eq. (17). It is easy to verify that this QSSA result is mathematically incorrect unless α , $\beta = O(\epsilon)$.

Diffusion and the Magnitude of $\mathcal{R}_\infty^{fast}$

Using Eq. (2a) for \mathcal{R}^{fast} from Eq. (17) and solving for y_3 , one obtains:

$$y_3 = \mathcal{Y}(y_1, y_2) + \epsilon(\mathcal{R}_\infty^{fast} + O(\epsilon)). \quad (18)$$

When $\mathcal{R}_\infty^{fast} = O(1)$ Eq. (18) recovers Eq. (6). It therefore is a slow manifold and can be used as an equation of state [in Eq. (3a) and Eq. (3b)] to remove y_3 in terms of y_1 and y_2 . Thus the number of unknowns is reduced.

However, the magnitude of $\mathcal{R}_\infty^{fast}$ depends on diffusion. When diffusion is competitive with fast chemistry, $\mathcal{R}_\infty^{fast}$ is $O(1/\epsilon)$ —according to Eq. (15) with η as its independent variable. Eq. (18) is then no longer in the form of Eq. (6). When $\epsilon\mathcal{R}_\infty^{fast}$ is kept in Eq. (18), a single non-trivial approximate second-order ODE involving all three y_n 's is obtained. Inside this reactive-diffusive layer, this ODE supplements Eq. (3a) and Eq. (3b) [or Eq. (13a) and Eq. (13b)] to serve as the three leading order governing equations. The number of unknowns is not reduced in the reactive-diffusive layer because this ODE cannot be used as an equation of state.

CSP WITH DIFFUSION

The toy problem is sufficiently simple to be handled by conventional asymptotic analysis using paper and pencil. CSP (computational singular perturbation) translates the analytical paper and pencil procedure into a programmable computational procedure. With CSP, it is not necessary to make order of magnitude estimates, to non-dimensionalize the variables, to have insights on which are the fast chemistry terms or to identify the small parameter ϵ . Thus, it can be used on problems too complicated for paper and pencil analysis, so long as there is actually a “gap” in time scales, and all the fast modes are decaying modes.

The generic PDEs of interest can be represented in the following vector form:

$$\frac{D\mathbf{y}}{Dt} = \mathbf{g}(\mathbf{y}; \dots) \quad (19)$$

where \mathbf{y} and \mathbf{g} are N -dimensional column vectors, and $\mathbf{g}(\mathbf{y}; \dots)$ contains *both* chemistry and diffusion terms (non-diagonal mass diffusion matrix and thermal diffusion [8] can be routinely handled without difficulty). Energy equation can be included by including temperature as an element of the \mathbf{y} vector. Dimensional variables can be used. The number of exhausted fast chemistry modes in the time interval of interest is denoted

by M —which can be computationally determined on the fly. The M -dimensional *fast manifold*—defined as the complement of the slow manifold—can always be spanned by a set of M CSP-refined $\mathbf{a}_m^o(t)$ (column) and $\mathbf{b}_o^m(t)$ (row) N -dimensional basis vector pairs. These basis vectors are orthonormal to each other:

$$\mathbf{b}_o^m \odot \mathbf{a}_{m'}^o = \delta_{m'}^m \quad m, m' = 1, \dots, M \quad (20)$$

where $\delta_{m'}^m$ is the Kronecker Delta and \odot is the N -dimensional inner product operator. The ideal set of \mathbf{a}_m^o and \mathbf{b}_o^m would totally decouple the fast and slow modes of the solution. CSP improves the decoupling quality of any “trial set” by a *two-step iterative procedure* which generates a new *refined* set, \mathbf{a}_m^o and \mathbf{b}_o^m . In the absence of diffusion, each full refinement cycle improves the decoupling quality of the set by $O(\epsilon)$ where ϵ is identified with the eigenvalue gap of \mathbf{J} , the Jacobian of all the chemistry terms in $\mathbf{g}(\mathbf{y}; \dots)$.

Once the \mathbf{a}_m^o 's and \mathbf{b}_o^m 's have somehow been found, the *fast manifold projector* is defined by:

$$\mathbf{Q}_o^{o(fast)}(M) \equiv \sum_{m=1}^M \mathbf{a}_m^o \mathbf{b}_o^m \quad (21)$$

and the *slow manifold projector* is defined by:

$$\mathbf{Q}_o^{o(slow)}(M) \equiv \mathbf{I} - \mathbf{Q}_o^{o(fast)}(M) \quad (22)$$

where \mathbf{I} is the $N \times N$ identity matrix. Note that both the fast and the slow manifold projectors are completely determined by \mathbf{a}_m^o and \mathbf{b}_o^m . The reduced-chemistry model—valid after the initial transients have decayed—is obtained by neglecting the fast manifold projection of the right hand side of Eq. (19). The order of magnitude of the time scale of the currently active chemistry terms of the reduced-chemistry model can be estimated by the magnitude of the reciprocal of the $(M+1)$ -th largest eigenvalue of \mathbf{J} .

From the mathematical point of view, the methodologies of CSP and ILDM are similar. In ILDM (Maas and Pope, 1992a, 1992b), the fast (left and right) eigenvectors of the full chemistry Jacobian are used as the fast basis vectors—which agree to leading order with any once-refined CSP set in the small ϵ limit. The difference is that in the absence of diffusion CSP refinements can be applied recursively to improve (if needed) the quality of any set (see Appendix on the impacts of diffusion), while ILDM devoted no effort on this score, but introduced the interesting and useful idea of using tabulations to facilitate numerical computations.

The Toy Problem with CSP

The toy problem has $N = 3$ and $M = 1$, and $\epsilon \ll 1$. The CSP procedure shall be analytically applied to the toy problem so that the results can be analytically compared to results obtained by conventional asymptotic analysis.

A trial set $\mathbf{a}_1, \mathbf{b}^1$ of random numbers which are mutually orthonormal can be used as the initial iterant to obtain the leading order refined set using the CSP two-step refinement procedure (step #1 refines \mathbf{b}^1 , step #2 refines \mathbf{a}_1 . See Appendix). For asymptotically small ϵ , the leading order once-refined CSP fast basis vectors for the toy problem are:

$$\mathbf{a}_1^0 = \begin{bmatrix} \alpha \\ \beta \\ -1 \end{bmatrix} \quad \mathbf{b}_0^1 = \frac{\left[\frac{\partial Y}{\partial y_1}, \frac{\partial Y}{\partial y_2}, -1 \right]}{1 + \alpha \frac{\partial Y}{\partial y_1} + \beta \frac{\partial Y}{\partial y_2}} \quad (23)$$

Note that the above leading order CSP refined basis vectors are independent of the $f_n(y_1, y_2, y_3)$'s or the choice of the trial set $\mathbf{a}_1, \mathbf{b}^1$. They depend only on the fast chemistry term(s). Geometrically, \mathbf{b}_0^1 is seen to be parallel to the normal vector of the surface defined by $\mathcal{R}^{fast}(\mathbf{y}, \epsilon) = O(1)$ (i.e., \mathbf{b}_0^1 is the gradient of \mathcal{R}^{fast} in the N -dimensional \mathbf{y} space), and \mathbf{a}_1^0 is recognized to be the stoichiometric vector of the fast reaction.

The leading order fast and slow manifold projectors for the toy problem are straightforwardly obtained:

$$\mathbf{Q}_o^{o(fast)}(1) = \frac{1}{1 + \alpha \frac{\partial Y}{\partial y_1} + \beta \frac{\partial Y}{\partial y_2}} \begin{bmatrix} \alpha \frac{\partial Y}{\partial y_1} & \alpha \frac{\partial Y}{\partial y_2} & -\alpha \\ \beta \frac{\partial Y}{\partial y_1} & \beta \frac{\partial Y}{\partial y_2} & -\beta \\ -\frac{\partial Y}{\partial y_1} & -\frac{\partial Y}{\partial y_2} & 1 \end{bmatrix} \quad (24a)$$

$$\mathbf{Q}_o^{o(slow)}(1) = \frac{1}{1 + \alpha \frac{\partial Y}{\partial y_1} + \beta \frac{\partial Y}{\partial y_2}} \begin{bmatrix} 1 + \beta \frac{\partial Y}{\partial y_2} & -\alpha \frac{\partial Y}{\partial y_2} & \alpha \\ -\beta \frac{\partial Y}{\partial y_1} & 1 + \alpha \frac{\partial Y}{\partial y_1} & \beta \\ \frac{\partial Y}{\partial y_1} & \frac{\partial Y}{\partial y_2} & \alpha \frac{\partial Y}{\partial y_1} + \beta \frac{\partial Y}{\partial y_2} \end{bmatrix} \quad (24b)$$

These projectors can be used for problems with different slow chemistry terms and different diffusion (laminar or turbulent) terms in the main region—provided the fast chemistry terms are the same (except that the value of $\epsilon > 0$ is irrelevant so long as it is small). The three diagonal elements of $\mathbf{Q}_o^{o(fast)}(1)$ are the *radical pointers* (Lam, 1993; see its §6.4).

For this simple toy problem, the leading order CSP projectors depend only on $\alpha, \beta, d\mathcal{Y}/dy_1$ and $d\mathcal{Y}/dy_2$. The original set of PDEs can

be rewritten using these two complementary manifold projectors as follows:

$$\begin{aligned} \frac{D}{Dt} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} &= (\mathbf{Q}_o^{o(fast)}(1) + \mathbf{Q}_o^{o(slow)}(1)) \odot \begin{bmatrix} \alpha \mathcal{R}^{fast} + \mathcal{R}_1 \\ \beta \mathcal{R}^{fast} + \mathcal{R}_2 \\ -\mathcal{R}^{fast} + \mathcal{R}_3 \end{bmatrix} \\ &= \begin{bmatrix} \alpha \\ \beta \\ -1 \end{bmatrix} \mathcal{G}_1^{(fast)} + \mathbf{Q}_o^{o(slow)}(1) \odot \begin{bmatrix} \mathcal{R}_1 \\ \mathcal{R}_2 \\ \mathcal{R}_3 \end{bmatrix} \end{aligned} \quad (25)$$

where

$$\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots) \equiv \mathbf{b}_o^1 \odot \mathbf{g} = \mathcal{R}^{fast} - \mathcal{R}_\infty^{fast} \quad (26)$$

and $\mathcal{R}_\infty^{fast}$ was given previously by Eq. (15). Eq. (25) is exact—*no approximation or assumption had been introduced*. Diffusion contributes terms to both $\mathcal{G}_1^{(fast)}$ and the \mathcal{R}_n 's.

Note that Eq. (14), which is exact, says $\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots) = O(\epsilon D R^{fast} / Dt)$ always. Thus it is expected to first decay rapidly and then evolve slowly for $t \gg O(\epsilon)$ —*even when diffusion is present and is competitive*. Thus CSP recommends $\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots)$ as a candidate term to be neglected, especially when the direct numerical evaluation of $\mathbf{b}_o^1 \cdot \mathbf{g}$ encounters major cancellation difficulties. Note that $\mathcal{G}_1^{(fast)}$ itself need not be small in comparison to the other slow terms in Eq. (25) to be neglected. In fact, whenever Eq. (26) encounters major cancellations in the evaluation of $\mathcal{G}_1^{(fast)}$, its neglect from Eq. (25) can be justified even though it is not yet “small enough.” The CSP “radical correction” (Lam, 1993; Lam and Goussis, 1994) can improve the approximation. It is interesting to note that the neglect of $\mathcal{G}_1^{(fast)}$ is equivalent to approximating \mathcal{R}^{fast} by $\mathcal{R}_\infty^{fast}$ without the need to compute $\mathcal{R}_\infty^{fast}$. The CSP-refined \mathbf{a}_1^o guarantees that the second term in Eq. (25) is free of the fast chemistry terms. All the fast chemistry terms are collected inside $\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots)$. But $\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots)$ —unlike $\mathcal{R}^{fast}(\mathbf{y}, \epsilon)$ —contains more than just the fast chemistry terms. It also contains diffusion terms.

When there are M fast modes in a general problem, the original PDEs can be rewritten using the fast and slow manifold projectors:

$$\frac{Dy}{Dt} = \sum_{m=1}^M \mathbf{a}_m^o \mathcal{G}_m^{(fast)} + \mathbf{Q}_o^{o(slow)}(M) \odot \mathbf{g}(\mathbf{y}; \dots) \quad (27)$$

$$\mathcal{G}_m^{(fast)} \equiv \mathbf{b}_o^m \odot \mathbf{g}(\mathbf{y}; \dots), \quad m = 1, \dots, M \quad (28)$$

CSP-based codes are programmed to monitor the numerical values of all the $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots)$'s on the fly. Theoretically, the magnitude of the $\mathcal{G}_m^{(fast)}$'s are $O(\epsilon^K)$ where K is the number of CSP (step #1) refinements performed. The m -th fast mode is declared "exhausted" whenever the value of $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots)$ is found negligible as judged by some *user-specified* accuracy requirement (different requirements for different components of the \mathbf{y} vector are allowed). When the contributions of all the exhausted CSP-refined fast modes [e.g., the first term in Eq. (25)] are judged negligible and are omitted from the calculations, one obtains the CSP-derived reduced chemistry model for the original problem:

$$\frac{D\mathbf{y}}{Dt} = \mathbf{Q}_o^{(slow)}(M) \odot \mathbf{g}(\mathbf{y}; \dots) + O(\delta), \quad (29)$$

where the $O(\delta)$ term is a vector and it symbolically represents the user-specified accuracy requirement. Arbitrary sidewall boundary conditions are allowed. The fast chemistry terms in \mathbf{g} have been removed in Eq. (29) by the slow projector (provided at least one full CSP refinement had been performed), and the solution of Eq. (29) is automatically consistent with the neglect of $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots)$ *even when the diffusion terms inside the $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots)$'s are competitive*—provided that the (effective) initial conditions are also consistent with it. Since each $\mathcal{G}_m^{(fast)}$ is always the sum of a chemistry term and a diffusion term, then whenever $\mathcal{G}_m^{(fast)} = O(\delta; m)$ the *net* values of these two terms must be competitive—since they must nearly cancel each other. With CSP, the competitiveness of the diffusion term in $\mathcal{G}_m^{(fast)}$ can be judged by the value of the largest *participation index* (Lam, 1993) among the diffusion contributions. It is worthy of note that the capacity of $\mathcal{G}_m^{(fast)}$ to influence \mathbf{y} is of the order of $\mathcal{G}_m^{(fast)}$ times the time scale of the m -th mode. Thus, for given δ the effective threshold for the neglect of $\mathcal{G}_m^{(fast)}$ depends on m . It is interesting to note that whenever direct numerical evaluation of $\mathcal{G}_m^{(fast)} = \mathbf{b}_o^m \odot \mathbf{g}$ encounters significant figures difficulty (because of near cancellations of big terms), the $\mathcal{G}_m^{(fast)}$ term is most probably ripe for neglect.

There are many ways to proceed from here. The straightforward way is to continue to work with the N PDEs in Eq. (29)—which are no longer stiff. In this approach, the number of unknowns is not reduced. A more attractive way would be to remove certain selected M PDEs from Eq. (29), and supplement the remaining $N-M$ PDEs with $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots) = \mathbf{b}_o^m \odot \mathbf{g} = O(\delta; m)$ —which are formally M ODEs because of the diffusion terms. While in principle any M species can be selected for removal, in practice the best choices are those which are qualified to be "CSP radicals"—as judged by the CSP radical pointers (Lam, 1993). When the diffusion terms in some of these $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots) = O(\delta; m)$

equations are not competitive with the fast chemistry terms, then these equations are effectively algebraic relations, and they can be treated as approximate equations of state. When $\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots) = O(\delta; 1)$ is used to remove y_3 from Eq. (29), the top two equations become identical to Eq. (7a) and Eq. (7b), and the third equation, being the equation for a qualified CSP radical, is consistent with $\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots) = O(\delta; 1)$ and can be ignored. In other words, the number of unknowns is reduced when the diffusion terms in $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots) = O(\delta; m)$ are not competitive. However, when diffusion terms in some of the $\mathcal{G}_m^{(fast)}(\mathbf{y}; \dots) = O(\delta; m)$ equations are competitive with the fast chemistry terms—as is the case inside the sidewall boundary layers—then those equations are *bona fide* ODEs. In fact, they are stiff ODEs. As such, they cannot play the role of equations of state, and the number of unknowns in Eq. (29) cannot be algebraically reduced. Furthermore, the CSP radical correction procedure (Lam, 1993; Lam and Goussis, 1994)—if employed for non-linear problems—need to properly account for the diffusion terms.

In CSP-based codes, the values of the exhausted $\mathcal{G}_m^{(fast)}$'s should continued to be monitored to ensure that they remain exhausted. In real problems where the eigenvalue gap, ϵ , is not a constant, revivals of exhausted fast modes are entirely possible. It is worth emphasizing that δ , the accuracy requirement of the reduced-chemistry model, is at the beck and call of the user. With CSP, the user does need to know what ϵ is.

The recent “close-parallel assumption” results obtained by Ren and Pope (2006) can easily be shown to be identical to this CSP result. The use of $\mathcal{G}_1^{(fast)}(\mathbf{y}; \dots) = 0$ was used by Singh et. al. (2002) to replace one of their PDEs (the analog of the three PDEs in Eq. (29) here) for their $N = 2$ test problem. Numerical simulations (using equally spaced Lagrangian grid points and same numerical algorithm everywhere) were presented, showing excellent results in comparison to direct simulations using the original PDEs.

Propagating Flame Zones

Of course, diffusion can play a major role inside the flame zone of a propagating flame (Goussis, 2005; Valorani et al., 2003, 2006). In a propagating flame problem, convection can be coupled with diffusion (which includes heat conduction in a realistic flame model) and the currently active chemistry terms inside the flame zone. The “rapid initial transient” for the flame occurs at the upstream end of the propagating flame front. If the flame velocity is $O(\sqrt{D_m/\epsilon})$ and its thickness is $O(\sqrt{D_m/\epsilon})$, then D/Dt is $O(1/\epsilon)$ and convection inside this flame zone is competitive with both fast chemistry and diffusion. For such problems, the relevant $\mathcal{G}_m^{(fast)}$

terms in Eq. (27) are not negligible inside the propagating thin flame zones.

Further Fast/Slow Uncoupling

For the $N = 3$ toy problem, the reduced chemistry model still has two slower modes after the fast chemistry reaction is exhausted. It is entirely possible that a fast/slow gap exists between the two remaining time scales. If so, a further simplified model is possible. This can be routinely handled—without explicit knowledge of the $f_n(y_1, y_2, y_3)$'s—by setting $M = 2$ and monitoring the amplitude of $G_2^{(fast)}$.

NUMERICAL ISSUES

In conventional paper and pencil analysis, thin boundary layer coordinates (such as η) are introduced wherever the diffusive terms are expected—via perceptive insights—to be competitive with the local dominant terms. Thus, thin boundary layer coordinates are needed at the side-walls, and inside propagating flames. When diffusion is competitive with fast chemistry in some thin layers, the governing equations are essentially ODEs. In the main region where the fast chemistry terms are spent, the governing equations are PDEs. Mathematical insights from conventional asymptotic analysis can be most helpful to deal with numerical issues.

CSP assumes that the numerical method used in the computations of the solution is capable of properly handling the governing equations. Its main contribution is to identify the stiff terms as candidates which can be safely neglected—and the user is explicitly asked to specify the quantitative accuracy requirement for *each* component of the y vector. The numerical issues include both the choice of the spatial grids and the integration algorithms. Since CSP can provide the time scale of the currently active chemistry terms at any point in the reacting flow field, this quantitative information can be computationally exploited to make intelligent choices on grid size (and the size of the Lagrangian time step). The “use the same grid size everywhere” brute-force strategy can obviously be improved. Since the number of unknown to be computed is greatly reduced by a coarser grid, algorithms for adaptive gridding are most useful for such problems. To be safe, numerical solutions should always pass the traditional “halving the grid size” test to make sure that the non-uniform spatial grid used is fine enough in all the spatial regions of interest.

When PDEs are discretized and solved numerically, the diffusion terms can be treated either explicitly, implicitly, or some mixture of the two. When they are treated explicitly, the diffusion terms are treated as

some benign correction terms in the (Lagrangian) time-marching algorithm. Coarser grids are acceptable. When they are treated implicitly, the diffusion terms can dominate, and they can insist on a sufficiently fine grid to respect the (spatial) ODE character of diffusion. During a CSP run, it is straightforward to computationally determine whether the major participant in the diffusion term in $\mathcal{G}_m^{(fast)}$ is competitive with the major participant in the chemistry term. This information—together with the quantitative knowledge of the time scale of the currently active chemistry terms—can be exploited to make intelligent choices of the integration algorithm. Thus the “use the same algorithm everywhere” strategy can also be improved.

When diffusion is competitive with the currently active CSP modes but is merely a perturbation to the fast CSP modes, a slow manifold such as Eq. (6) exists. All solution trajectories automatically stay in the slow manifold provided the correctly modified diffusion terms are used. When unmodified diffusion terms are used, inconsistencies are present. For example, in “time-splitting” algorithms, the chemistry segment may need to retain the fast chemistry terms in order to repair the damages done by the diffusion segment.

CONCLUDING REMARKS

Major conclusions found include:

1. In general, whenever the chemistry term is replaced by reduced chemistry terms, the diffusion terms must be modified.
2. The use of unmodified diffusion terms with reduced chemistry terms can only be justified when certain conditions [i.e., Eq. (10)] are met.
3. The CSP manifold projectors derived from the chemistry terms is dominated by the fast chemistry terms. Once obtained (and tabulated), it can be used on problems with different initial and sidewall boundary conditions, different diffusion terms, and different slow chemistry terms. The modified vector of diffusion terms is obtained by applying the CSP-refined slow manifold projector on the original vector of diffusion terms.
4. The order of magnitude of the diffusion term is determined by the need of the local diffusion process to compete with the fast chemistry term. At any sidewall boundary, diffusion is always competitive to accommodate for arbitrary boundary conditions.
5. The order of magnitude of the change of \mathbf{y} contributed by the m -th fast CSP mode is $O(\mathcal{G}_m^{(fast)} \tau_m)$ where τ_m is the time scale of the m -th fast mode. Since τ_m is a function of m , the thresholds for the neglect of $(\mathcal{G}_m^{(fast)})$ —for a fixed accuracy requirement δ —is thus m -dependent (i.e., $O(\delta; m)$).

6. After the CSP fast modes have decayed, M approximate relations are provided: $\mathcal{G}_m^{(fast)} = O(\delta; m)$. Only those relations in which diffusion is not competitive with the fast chemistry terms provide a slow manifold—which can be used to algebraically reduce the number of unknowns. If diffusion is indeed competitive in some of these relations, they are ODEs and do not describe a slow manifold. The number of unknowns cannot be reduced by these ODEs.
7. If the detailed structures inside the thin sidewall boundary layer are not of interest, one could find and use the edge values as described in §3.6 as effective sidewall boundary conditions for Eq. (29), and omit the thin boundary layers altogether.
8. A slow manifold is an approximate algebraic relation between the unknowns. In general, regardless of how it is found and whether it is given analytically or as a tabulated numerical database, it cannot be indiscriminately used in the original PDEs.

For example, Eq. (6) cannot be used in the original PDE for y_1 if $\alpha = O(1)$, cannot be used in the original PDE for y_2 if $\beta = O(1)$, and can never be used in the original PDE for y_3 . It can freely be used only in equations where the net reaction rates of the fast reactions (such as $\mathcal{R}^{(fast)}$) are not needed, such as any of the three PDEs in Eq. (29) (i.e., CSP-derived reduced chemistry models) or Eq. (3a) and Eq. (3b).

9. Mathematical insights from conventional asymptotic analysis are helpful in the design and selection of grids and algorithms in the computations of numerical solutions.

APPENDIX: DIFFUSION AND CSP REFINEMENT

Let $\mathbf{a}_m(t)$, $\mathbf{b}^m(t)$ be a set of M basis vector pairs which are mutually orthonormal to each other. The value of M —the number of exhausted fast modes—is determined computationally on the fly. The initial trial set can be chosen randomly. The CSP-refined set $\mathbf{a}_m^{(o)}(t)$, $\mathbf{b}_o^m(t)$ is computed from $\mathbf{a}_m(t)$, $\mathbf{b}^m(t)$ by the following two-step refinement procedure (Lam, 1993; Lam and Goussis, 1994; Lam, 2006):

$$\mathbf{b}_o^m = \sum_{m'=1}^M \left[\left(\frac{D\mathbf{b}^m}{Dt} + \mathbf{b}^m \odot \mathbf{J} \right) \odot \mathbf{a}_{m'} \right]^{-1} \left(\frac{D\mathbf{b}^{m'}}{Dt} + \mathbf{b}^{m'} \odot \mathbf{J} \right) \text{ step\#1} \quad (30a)$$

$$\mathbf{a}_m^o = \sum_{m'=1}^M \left(-\frac{D\mathbf{a}_{m'}}{Dt} + \mathbf{J} \odot \mathbf{a}_{m'} \right) \left[\left(\frac{D\mathbf{b}_o^{m'}}{Dt} + \mathbf{b}_o^{m'} \odot \mathbf{J} \right) \odot \mathbf{a}_m \right]^{-1} \text{ step\#2} \quad (30b)$$

where \mathbf{J} is the $N \times N$ Jacobian matrix of *all the chemistry terms* in \mathbf{g} (i.e., all the algebraic terms) with respect to all the dependent variables y_n 's. At

least one full cycle of the two-step refinement procedure is required to achieve leading order accuracy. Each additional step #1 refinement improves the quality of the \mathbf{b}_o^m 's, while each additional step #2 refinement improves the quality of the \mathbf{a}_m^o 's.

The validity of the CSP refinement procedure for homogeneous systems has been verified analytically to all orders (Zagaris et al., 2004). To leading order, the substantial derivative terms such as $D\mathbf{b}^m/Dt$, $D\mathbf{a}_m/Dt$, etc. and the slow chemistry terms are not competitive with fast chemistry (except potentially inside propagating flame zones), thus the leading order refined set is independent of them. However, they are crucial to the higher order refined sets.

Diffusion impacts the refinement procedure only through the substantial derivative terms. Thus it plays no role on the leading order CSP-refined set. Hence the leading-order refined set is usable for any diffusion terms of interest provided $\mathcal{D}_m \ll L^2/\varepsilon$.

A significant amount of algebra is usually involved to obtain analytical formulas for the substantial derivatives—with or without the diffusion terms. When numerical methods are involved, however, substantial derivatives can be represented by finite difference formulas, and as such they can be handled straightforwardly—as a correction term—by the use of some iterative procedures.

Pragmatically, the usefulness of going beyond leading-order reduced chemistry models is limited since higher order models provide only minor incremental advantage over the leading order model.

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