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ASYMPTOTIC FLAME THEORY WITH COMPLEX CHEMISTRY

by

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ABSTRACT

We investigate the structure of laminar flames with general complex chemistry networks in the limit of high activation energy asymptotics. Depending on the specific reaction network and other given thermomechanical data, a wide variety of flame configurations are possible. Here we present a first version of a systematic asymptotic reduction of complex chemistry networks and give practical criteria to determine the dominant reactions when transport and chemistry are coupled.

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1. INTRODUCTION

Mathematically, the subject of this presentation can be considered to be traveling waves for reaction-diffusion systems

$$U_t = DU_{zz} + f(U) \quad , \quad (1.1)$$

where $U \in \mathbb{R}^n$, D is a positive definite transport matrix, and f has the form

$$f(U) = \sum_{j=1}^m \omega_j(U) K_j \quad .$$

Here ω_j are scalar functions, $K_j \in \mathbb{R}^n$, and each ω_j depends in a certain way on a small parameter ε_j . Typically,

$$\omega_j(U) = \kappa_j(\varepsilon_j) \psi_j\left(\frac{U - U_j}{\varepsilon_j}\right)$$

for certain reference vectors U_j , constants κ_j , and nonnegative functions ψ_j with $\psi_j(0) = 0$.

Physically, the traveling wave represents a combustion front in a premixed reactive gas. Then the components of U specify the dimensionless temperature and the concentrations of the reactants. There are m chemical reactions involved in the burning process; ω_j are their rates. The smallness of ε_j expresses the fact that these rates depend strongly on temperature (the reactions have high activation energy). Nearly all actual flames have a large reaction network, most of it unknown. Very often it is modeled by a network consisting of a few reactions with high activation energy, and these are the cases in which the present analysis may be useful. Even more commonly, only some of the model reactions have high

activation energy; better asymptotic procedures need to be developed for that case.

Traveling waves with velocity c are solutions of the form $U(z,t) = U(z+ct)$; but the traveling wave equation

$$DU'' - \bar{M} U' + f(U) = 0 \quad (1.2)$$

will here be written with the symbol $\bar{M}$ replacing c . Here $\bar{M}$ is mass flux, which equals velocity if the density is unity. When the density is not taken to be constant, but the pressure is (often a good approximation), the evolution equation is more complicated than (1.1); nevertheless, the problem of determining traveling wave solutions can be reduced to (1.2).

We are concerned with exploiting the smallness of ε_j to obtain approximate wave front solutions. The procedures are linked to the properties of the underlying reaction network, which supplies the vectors K_j . These procedures are well known in the case when the network is modeled by a single reaction $A \rightarrow P$. (By way of introduction, this case is reviewed in Sec. 2.) An approach similar to the one in this paper was used in treating two-reaction networks of parallel, sequential, and competing-fuel types in [3] and [4], and it was clear that the extension of this approach to more complex schemes could uncover a baffling array of possibilities. A systematic formalism was called for, and hopefully is provided in part by the present paper.

The methods are those of asymptotic analysis. Roughly speaking, to lowest order this means developing rational procedures for replacing the original problem with a limit problem in which the ε_j do not appear explicitly. The limit problem is expected to yield an approximate

solution, and is easy to solve. A rigorous justification of this expectation has been given recently for the case of a single reaction [1].

Many other parameters besides ε_1 enter the problem, for example, the elements of the matrix D and of the unburned state vector of the gas, U_- . Throughout the paper, we assume that these magnitudes do not interfere with the asymptotics. Particularly, we assume that any constants not depending explicitly on ε_1 , B_1 , or θ_1 are $O(1)$ quantities. This especially refers to elements of D and D^{-1} , reference dimensionless T_j , their differences $T_i - T_j$ and the heat releases Q_j . These restrictions are relaxed, and a more meticulous account of the other parameters is taken in [4].

For background and previous work on asymptotic methods in flame theory, the reader is referred to [2]. A number of papers have been written on the multiple reaction case; see the references in [3].

2. THE CASE OF A SINGLE-REACTION MECHANISM

Although this argument has appeared in the literature many times before, it will be convenient to review here the asymptotic analysis of simple flames, that is, those with a single reaction $A \rightarrow P$, hence a single K :

$$DU'' - \bar{M}U' = -\omega(u)K, \quad U(-\infty) = U_-. \quad (2.1)$$

Here $U = (T, Y)$, the temperature and molar concentration of A , $K = (Q, -1)$, and we take

$$\omega(U) = BY e^{-Q/T}, \quad (2.2)$$

for positive constants B, θ . As $z \rightarrow \infty$, the reaction must go to equilibrium, that is,

$$Y(\infty) = 0 \quad . \quad (2.3)$$

Integrating (2.1), we find $w(U(z))$

$$[DU' - MU]_{-\infty}^{\infty} = - \int_{-\infty}^{+\infty} w(U(z)) dz \quad K \equiv -\beta K \quad ,$$

hence $U(\infty) - U(-\infty) = \alpha K$, $\alpha = \beta/M$. Applying (2.3), we find $\alpha = Y_-$, so

$$U(\infty) \equiv U_+ = U_- + Y_- K \equiv (T_+, 0) \quad . \quad (2.4)$$

We define $\varepsilon = T_+^2/\theta$, and assume

$$0 < \varepsilon \ll 1 \quad (2.5)$$

In a neighborhood of $T = T_+$, $Y = 0$, we approximate

$$w(U) = \frac{\eta}{\varepsilon} \left(\frac{Y}{\varepsilon} \exp[(T - T_+)/\varepsilon] \right) \equiv \frac{\eta}{\varepsilon} y e^t \quad ,$$

where $v = (t, y) \equiv (U - U_+)/\varepsilon$, and

$$\eta = B \varepsilon^2 \exp(-\theta/T_+) \quad .$$

This approximation is obtained by taking the first two terms in the Taylor series expansion of the exponent θ/T in (2.2) about $T = T_+$. The remainder is $\theta(\varepsilon)$ and is discarded. A careful analysis of this approximation is given in [4].

We next introduce new variables

$$x = z\eta^{\frac{1}{2}}, \quad \bar{M} = M\eta^{-\frac{1}{2}} \quad (2.6)$$

in (2.1) to obtain (differentiation is now with respect to x)

$$D\ddot{U} - M\dot{U} = -\frac{1}{\varepsilon} \psi\left(\frac{U-U_+}{\varepsilon}\right) K, \quad (2.7)$$

where (recall $u = (U-U_+)/\varepsilon$)

$$\psi(u) = y e^t. \quad (2.8)$$

We may position the origin in space at will; we choose to place it where $Y = \varepsilon$ ($y = 1$). Rewriting (2.7) with stretched variables $\xi = x/\varepsilon$, $u = (U-U_+)/\varepsilon$, and discarding terms formally of order ε , we obtain the "flame layer" equation

$$D \frac{\partial^2 u}{\partial \xi^2} + \psi(u) K = 0. \quad (2.9)$$

This is to be solved under the boundary conditions $u(\infty) = 0$, $y(0) = 1$. To do so, we observe that (2.9) and the condition $u(\infty) = 0$ imply

$$u = \sigma(\xi) D^{-1} K \quad (2.10)$$

for some scalar function σ . Substituting into (2.9), we have

$$\sigma'' + \psi(\sigma D^{-1} K) = 0, \quad \sigma(\infty) = 0.$$

This has a first integral

$$(\sigma')^2 - \Omega(\sigma) = 0,$$

where $\Omega(\sigma) = 2 \int_{\sigma}^0 \psi(sD^{-1}K) ds$. Assuming that $D^{-1}K$ has first component positive and the second negative, we see from (2.8) that $\Omega(-\infty)$ exists. Thus the layer problem has a unique solution, and

$$D \frac{\partial u}{\partial \xi}(-\infty) = \beta K ,$$

where $\beta = (\Omega(-\infty))^{\frac{1}{2}}$. Matching with the solution outside the flame layer requires, in the limit $\varepsilon \rightarrow 0$, that

$$D\dot{U}(0-) = \beta K, D\dot{U}(0+) = 0 .$$

Finally, for $x < 0$, $T < T_+$ and the strong dependence of ψ on T shows that it can be neglected in (2.7). For $x > 0$, Y is already nearly zero if ε is small, so ψ can again be neglected. What is left is the problem

$$D\ddot{U} - M\dot{U} = 0 , x \neq 0 , \quad (2.11)$$

$$[D\dot{U}]_{0-}^{0+} = -\beta K , \quad (2.12)$$

$$U(\pm\infty) = U_{\pm} . \quad (2.13)$$

This problem has a unique solution. Integration of (2.11) reveals (from (2.4)),

$$[D\dot{U}]_{-\infty}^{0-} = M[U]_{-\infty}^{0-} = M(U_+ - U_-) = MY_-K$$

Adding this to (2.12) above

$$0 = [DU]_{-\infty}^{0+} = MY_-K - \beta K .$$

Hence,

$$M = \beta/Y_- .$$

And with M known, (2.11) can be integrated backward with initial conditions at $x = 0$ to yield the total profile for $x < 0$. For $x > 0$, the only solution is $U \equiv U_+$.

In summary, asymptotics have shown the way to a limit problem (2.11) - (2.13) with nonlinearity replaced by a jump condition (2.12). The coefficient β is known independently from a layer analysis, and $(M, U(x))$ are to be determined. In the original variables, U and $\bar{M}$ are determined by reversing the transformation (2.6).

3. FEASIBLE ALLOCATIONS

We begin by assuming given a reaction network, which is simply a specification of which reactions take place in the combustion process. It is usually symbolized by arrows, such as:

(In this example, there are three reactions involving three reacting species A_i , and one inert product P .) In general, we symbolize the reactions by R_i , the total number of reactions by m , and the number of species by n .

The vector $Y = (Y_1, \dots, Y_n)$ signifies mass concentration of the various species, and will be a function of space and time. We will be

concerned only with nonnegative concentrations, so restrict Y to the nonnegative cone $\mathcal{Y}$ of n -dimensional (species) space.

Associated with each reaction R_j is a reaction vector $V_j \in \mathcal{Y}$. It represents the net change in the number of units of the various species during a reaction event of reaction R_j . For example, in the above network (3.1), the three reaction vectors are $(-1, -1, 1)$, $(0, -2, -1)$, and $(1, 0, 0)$. Our basic assumption about these vectors is as follows:

Assumption 1. If $\sum_{j=1}^m \alpha_j V_j = 0$ and $\alpha_j \geq 0$, then $\alpha_j \equiv 0$. (3.1)

This assumption excludes, for example, reversible reactions, in which $V_2 = -V_1$ (say). More generally, it assures, as we shall see, that equilibrium can only be reached when each reaction rate is zero.

Each reaction R_j is assumed to have a reaction rate $\omega_j \geq 0$ which is a function of Y and of the temperature T .

Def: $Y \in \mathcal{Y}$ is an equilibrium state if

$$\sum_{j=1}^m \omega_j(Y, T) V_j = 0 \quad . \quad (3.2)$$

It follows from (3.2) that this can only happen if each $\omega_j = 0$.

For each $i = 1, \dots, m$, we denote by $J(i)$ the set of all indices j of species A_j entering reaction R_i (appearing on the left side of the arrow). Eventually, a specific form will be assumed for the ω_i ; but at this point we assume $\omega_i = 0$ if and only if $Y_j = 0$ for some $j \in J(i)$. We symbolize the equilibrium cone for each reaction, and the total equilibrium cone, as

follows:

$$\xi_i = \{Y \in \mathcal{Y} : Y_j = 0 \text{ for some } j \in J(i)\} ,$$

$$\xi = \bigcap_{i=1}^m \xi_i .$$

Def: Given an input state $Y_- \in \mathcal{Y}$, an allocation of Y_- to the network is a set of numbers $\alpha_i \geq 0$, $i = 1, \dots, m$, such that

$$Y_- + \sum_{i=1}^m \alpha_i v_i \in \xi \quad (3.4)$$

Ex. 1. In the network (3.1), we have $\xi = \{Y = (Y_1, Y_2, Y_3) \geq 0 : Y_1 = 0, \text{ and } Y_2 \text{ or } Y_3 = 0\}$. Let $Y_- = (1, 1, 1)$. Then the only allocation is $\alpha_1 = 1$, $\alpha_2 = \frac{1}{2}$, $\alpha_3 = 0$.

Ex. 2: $A_1 \xrightarrow{R_1} 2A_2 + P_1$, $A_2 \xrightarrow{R_2} 2A_2 + P_2$, $Y_- = (1, 1)$. Here $\xi = \{0\}$, $V_1 = (-1, 2)$, $V_2 = (2, -1)$. The reader may check that (3.2) is satisfied, but that no allocation exists. Thus, the existence of an allocation is not always guaranteed.

Ex. 3: (3.5)

Here $\xi = \{0\}$, Y_- is a scalar, and (α_1, α_2) is an allocation iff $\alpha_1 + \alpha_2 = Y_-$, $\alpha_i \geq 0$. So, of course, allocations are not necessarily unique.

Besides concentrations, we are also concerned with temperature, so use $n + 1$ -component state vectors $U = (T, Y_1, \dots, Y_n) = (T, Y)$. Associated with each reaction is a heat release $Q_i > 0$. We define the $(n + 1)$ component vectors

$$K_i = (Q_i, V_i) \quad ,$$

and shall refer to Q_i as the 0th component of K_i .

Our basic goal, now, is to find approximations to bounded solutions $(U(x), M)$ of the problem

$$\ddot{DU} - M\dot{U} = \sum_{j=1}^m \omega_j(U, \epsilon_j) K_j \quad , \quad U(-\infty) = U_- = (T_-, Y_-) \quad . \quad (3.6)$$

Here we have indicated the dependence of the rates ω_j on large positive parameters ϵ_j (activation temperatures). Specifically, we take

$$\omega_i = B_i \prod_{j \in J(i)} Y_j^{v(j,i)} e^{-\theta_i/T} \quad (3.7)$$

where $B_i > 0$ also might be large or small, and $v(j,i)$ is the stoichiometric coefficient of species j on the left side of reaction i .

The procedure will be to construct a suitable reduced problem in which each nonlinear term $\omega_j K_j$ is replaced by a jump condition in $\dot{DU}$ at some point x_j , not known in advance. The reduced problem will be fashioned in terms of "feasible allocations," which we proceed to define.

Suppose an allocation $\alpha = (\alpha_1, \dots, \alpha_m)$ is given. Let

$$U_+ = U_- + \sum_{j=1}^m \alpha_j K_j \quad . \quad (3.8)$$

In particular,

$$T_+ = T_+(\alpha) = T_- + \sum_{j=1}^m \alpha_j Q_j \quad (3.9)$$

Using the constants in (3.7), we define m functions

$$H_j(T) = \varepsilon(\ln B_j - \theta_j/T) \quad , \quad (3.10)$$

where

$$\varepsilon \equiv \min_j (T_+^2/\theta_j) \quad . \quad (3.11)$$

We define temperatures T_j , $j = 1, \dots, m$, such that

$$H_j(T_j) \text{ is independent of } j, \text{ and} \quad (3.12)$$

$$\max_j T_j = T_+ \quad .$$

Prop. 3.1. *There exists a unique temperature sequence $\{T_j\}$ satisfying (3.12).*

Proof. Choose the index k so that $H_k(T_+) = \min_j H_j(T_+)$. We set $T_k = T_+$, and define the T_j by $H_j(T_j) = H_k(T_+)$. Since all H_j are increasing functions

of T , it follows that all $T_j \leq T_+$, so there exists such a sequence. This argument also shows there is only one such sequence.

We now reorder the reactions in order of increasing T_j , so that $T_1 \leq T_2 \leq \dots \leq T_m = T_+$. It can happen that some of the T_j coincide. In fact, Example 2 at the end of this section indicates that to be "feasible,"

an allocation may well have to be adjusted so that two of them do coincide. (However, it seems unlikely that the case when three are the same is important.) Let $\{T_i^*\}$, $i = 1, \dots, m^* \leq m$ be the (possibly shorter) sequence of distinct temperatures among the T_j ; we denote the number of them by m^* .

It also may happen that two of the T_j almost coincide, that is, $0 < |T_i - T_j| = O(\varepsilon_i)$. This case is considered non generic, and is hereby excluded from consideration. Thus, we assume that two temperatures T_i, T_j either coincide (this may be required by the feasibility criterion given later) or differ by a quantity of larger order than $\varepsilon_i + \varepsilon_j$.

Our attempt will be to construct a combustion front in which, roughly speaking, m^* sets of reactions go to completion at the temperature T_j^* in that same order as one proceeds across the front's profile in the (upstream) direction of increasing temperatures. For that purpose, we use the notion of suballocation.

Def: For each $\ell \leq m^*$, suballocations $\alpha^{(\ell)}$ are defined to be allocations for the subnetwork consisting only of the R_j for $T_j \leq T_\ell^*$. Let k_ℓ be the number of such reactions.

Thus, $\alpha^{(\ell)} = (\alpha_1^{(\ell)}, \dots, \alpha_{k_\ell}^{(\ell)})$, but for comparison purposes, we extend them to be sequences of length m by defining $\alpha_j^{(\ell)} = 0$ for $j > k_\ell$. We say $\alpha^{(\ell)} \leq \alpha^{(\ell')}$ if $\alpha_j^{(\ell)} \leq \alpha_j^{(\ell')}$ for all j .

The situation we envisage is when there exist suballocations $\alpha^{(\ell)}$ for all $\ell \leq m^*$ satisfying

$$\alpha^{(\ell)} \leq \alpha^{(\ell+1)}, \quad \ell = 1, \dots, m^*-1; \quad \alpha^{(m^*)} = \alpha. \quad (3.13)$$

If such suballocations exist, we define a new set of reaction vectors v'_j as follows:

For each $k \leq m^*$,

$$\alpha'_k \equiv \sum_j (\alpha_j^{(k)} - \alpha_j^{(k-1)})$$

(of course taking $\alpha_j^{(0)} = 0$). If $\alpha'_k \neq 0$, then

$$v'_k \equiv \frac{\sum_j (\alpha_j^{(k)} - \alpha_j^{(k-1)}) v_j}{\alpha'_k} \quad (3.14)$$

If $\alpha'_k = 0$ for any values of k , we delete those temperatures T_k^* from the sequence and accordingly renumber the temperatures, as well as the v'_j , so there will be a fewer number of each. For convenience we also call the new number m^* .

In summary, we have constructed an alternative set of vectors v'_j , and number α'_j , with the properties that for all $\ell \leq m^*$,

$$Y_- + \sum_{j=1}^{\ell} \alpha'_j v'_j = Y_- + \sum_{j=1}^{\ell} \alpha_j^{(\ell)} v_j \in \sum_{j=1}^{\ell} \xi_j,$$

and

$$\sum_{j=1}^m \alpha_j^* V_j' = \sum_{j=1}^m \alpha_j V_j \quad ,$$

so that

$$Y_- + \sum_{j=1}^m \alpha_j^* V_j' = Y_+(\alpha) \in \xi \quad .$$

In some cases it may be enlightening to think of the V_j' as representing the reaction vector of an alternate reaction R_j' which is the same linear combination of the R_i , $i \leq j$, as is V_j' of the V_i . For instance, in Case 2 of Example 3 below, R_2' and R_3' would be $\frac{1}{2} A_2 \rightarrow P$ and $1/3 A_1 \rightarrow P$, respectively.

Extended vectors K_k' are defined to be the same linear combinations of the K_j as the V_k' are of the V_j (3.14). In particular, the first component Q_k' will be a linear combination of the Q_j 's. We can now determine the temperature at which the suballocation $\alpha^{(\ell)}$ would bring the corresponding subnetwork to equilibrium, if no reaction outside that subnetwork were present. We call it

$$\hat{T}_\ell = \sum_{j=1}^{\ell} \alpha_j^* Q_j' + T_- \quad .$$

Def: The allocation α is feasible if

- (1) there exist, for each $\ell \leq m^*$, suballocations $\alpha^{(\ell)}$ which satisfy (3.13), and
- (2) $T_j^* > \hat{T}_j$ for $j < m^*$.

Example 1. $R_1: A_1 \rightarrow A_2, \quad V_1 = (-1, 1)$
 $R_2: A_1 + A_2 \rightarrow P_1, \quad V_2 = (-1, -1)$
 $R_3: A_2 \rightarrow P_2, \quad V_3 = (0, -1)$
 $R_4: A_1 \rightarrow P_3, \quad V_4 = (-1, 0).$

These V_j satisfy (3.2). $\xi = \{0\}$. We take $Y = (1, 1)$; then all possible allocations are of the form $\alpha = (\theta, \phi, 1 + \theta - \phi, 1 - \theta - \phi)$, where $\theta, \phi \geq 0$ and $\theta + \phi \leq 1$. Suppose that for each α , the new ordering is the same as the old: $T_1 \leq T_2 \leq T_3 \leq T_4$. Then the only allocation with suballocations satisfying (3.13) is the one with $\theta = 1, \phi = 0$; $\alpha = (1, 0, 2, 0)$. The suballocations are $\alpha^{(1)} = (1)$, $\alpha^{(2)} = (1, 0)$, $\alpha^{(3)} = (1, 0, 2)$, $\alpha^{(4)} = \alpha$. We then delete R_2 and R_4 , so $m^* = 2$ and the new $\alpha = (1, 2)$. Criterion (2) for feasibility still needs to be checked. If it is verified, we can expect a combustion front to exist in which only R_1 and R_3 occur, at two different temperatures. Since there is at most one feasible allocation, we expect there is no other such combustion front.

Example 2. $R_1: A \rightarrow P_1 \quad V_1 = -1$
 $R_2: A \rightarrow P_2 \quad V_2 = -1$
 $R_3: A \rightarrow P_3 \quad V_3 = -1.$

Again, $\xi = \{0\}$. For $Y_- = 1$, all possible allocations are $\alpha = (\alpha_1, \alpha_2, \alpha_3)$, $\alpha_i \geq 0$, $\sum \alpha_i = 1$, and $T_+(\alpha) = \sum \alpha_j Q_j$. To discuss the feasible ones, we use the symbols $\alpha_*^{(i)}$ to denote the simple allocations: $\alpha_*^{(1)} = (1, 0, 0)$, etc., and let $T^{(i)}$ be the corresponding burning temperatures: $T^{(i)} = T_- + Q_i$. Suppose $T^{(1)} < T^{(2)} < T^{(3)}$. Define $\bar{H}(T^{(j)}) = H_j(T^{(j)})$, then $\alpha_*^{(j)}$

is a feasible allocation. If this is not true for any j , then it is a matter of checking that one of the following two possibilities must occur:

- (a) there exists $T_{12} \in (T^{(1)}, T^{(2)})$ such that $H_1(T_{12}) = H_2(T_{12})$, or
- (b) there exists $T_{23} \in (T^{(2)}, T^{(3)})$ for which H_2 and H_3 have a common value.

In case (a), there is a feasible allocation $(\alpha_1, \alpha_2, 0)$ where α_i are chosen so that $T_{12} = \alpha_1 T^{(1)} + \alpha_2 T^{(2)}$. Similarly, for case (b). Hence there is always at least one feasible allocation. The same conclusion holds for any number of competing reactions of this type.

Example 3. $A_1 \xrightarrow{R_1} A_2 \xrightarrow{R_2} A_3 \xrightarrow{R_3} P,$

$V_1 = (-1, 1, 0)$, $V_2 = (0, -1, 1)$, $V_3 = (0, 0, -1)$. Let $Y_- = (1, 1, 1)$. There is only one possible allocation: $\alpha = (1, 2, 3)$, and so the temperatures T_i are independent of α . We examine two of the possible cases for their ordering.

Case 1: $T_1 < T_2 < T_3$. There exist suballocation $\alpha^{(1)} = (1)$, $\alpha^{(2)} = (1, 2)$, and $\alpha^{(3)} = \alpha$. The question of feasibility rests only on criterion (2).

Case 2: $T_3 < T_2 < T_1$. We reorder the reactions so that R_3 becomes R_1 and vice versa. With the new ordering, $\alpha = (3, 2, 1)$, and there are suballocations $\alpha^{(1)} = (1)$, $\alpha^{(2)} = (2, 1)$, $\alpha^{(3)} = (3, 2, 1)$, satisfying (3.13).

The following table holds:

j	V_j	V'_j	Q'_j	$\hat{T}_j$
1	$(0, 0, -1)$	$(0, 0, -1)$	Q_1	$T_- + Q_1$
2	$(0, -1, 1)$	$(0, -1/2, 0)$	$2Q_1 + Q_2$	$T_- + 2Q_1 + Q_2$
3	$(-1, 1, 0)$	$(-1/3, 0, 0)$	$3Q_1 + 2Q_2 + Q_3$	$T_- + 3Q_1 + 2Q_2 + Q_3$

Moreover, $\alpha' = (1,2,3)$, so that indeed $\sum \alpha_j V_j = \sum \alpha'_j V'_j$. If condition (2) holds, we expect a front with reactions taking place as indicated by the V'_j : First, $A_3 \rightarrow P$ goes to completion at $T_1 (= T_1^*)$; then $A_2 \rightarrow P$ goes at T_2 , with A_3 an intermediate which appears only momentarily (the reaction $R_1: A_2 \rightarrow P$ is much faster than R_2 at this temperature); and finally $A_1 \rightarrow P$, passing through two quick intermediates.

Example 4. $A_1 \xrightarrow{R_1} A_2 \xrightarrow{R_3} P_1, A_1 \xrightarrow{R_2} P_2$:

$\xi = \{0\}$, $V_1 = (-1,1)$, $V_2 = (0,-1)$, $V_3 = (-1,0)$, and all allocations are of the form $\alpha = (\theta, 1+\theta, 1-\theta)$, $\theta \in [0,1]$. The details are tedious, but it can be shown that allocations always exist which satisfy the feasibility criterion (1). If a feasible allocation exists with $\theta \neq 0,1$, then necessarily two of the three T_i 's coincide. This may be the only feasible allocation in some cases, and so is important. On the other hand, it would only accidentally happen that all three coincide.

4. THE LIMIT PROBLEM, LEVEL 1.

The fact is that the existence of a feasible allocation is by no means ensured; Example 3 above demonstrates this. If one does exist, the formulation of the appropriate limit problem will under certain conditions, be described below. It is, in some sense a formal approximation to the front problem and has a unique solution. We conjecture that there always exists an allocation satisfying criterion (1). If this allocation does not satisfy (2), then it may be possible to find two (or more) fronts traveling at different speeds such that the combined effect of the faster followed by the slower is to attain the burned state $U_+(\alpha)$, the various reactions

implied by the suballocation going to completion is the prescribed order. This is certainly true in Example 3 at the end of Sec. 3. In general, suppose that criterion (1) holds, and also (2) for all j except one, say $j = \ell$. Then it is expected that there will exist a fast front, with burning governed by the "reactions" corresponding to $\alpha^{(\ell)}$ and final state $\hat{U}_\ell = U_- + \sum_{j=1}^{k_\ell} \alpha_j' K_j'$. There will also be a slower front with input $\hat{U}_\ell$, reactions described by the V_j' for $j > \ell$, and final state U_+ .

Given a feasible allocation, we have the problem of determining the front's approximate speed and profile. The description of the procedure will be given below for the case when all the T_j are distinct, and D is diagonal; i.e.,

$$T_j = T_j^* ; \quad D \text{ is diagonal} . \quad (4.1)$$

The point of departure is the following boundary value problem, the natural extension of (2.1) to the case of several reactions:

$$DU'' - \bar{M}U' = - \sum_{j=1}^m \omega_j(U) K_j , \quad U(-\infty) = U_- , \quad U(\infty) = U_+(\alpha) . \quad (4.2)$$

Here the vectors K_j are extended reaction vectors defined in Sec. 3.

The limit procedure proceeds under the approximation that all reaction rates vanish except where T is near one of the T_j^* 's; and that in the neighborhood of T_j^* , the requisite reactions which ensure that all R_k , for $k \leq k_j$, reach equilibrium, all go to completion. The principle is that the effect of those reactions at T_j^* can be accounted for by prescribing a jump discontinuity in $\dot{U}$ at that point.

First, we need to rescale the problem as in Sec. 2. For each $j = 1, \dots, m$, we define

$$\varepsilon_j = T_+^2 / \theta_j, \quad (4.3)$$

$$\eta_j = B_j \varepsilon_j^2 \exp(-\theta_j / T_j), \quad (4.4)$$

and approximate

$$\omega_j(U) \approx \frac{\eta_j}{\varepsilon_j} \psi_j(u^{(j)}),$$

where $u^{(j)} = \frac{U - U_j}{\varepsilon_j}$, and U_j is the value of U (not completely known beforehand, except when $j = m$) at the temperature T_j . Here ψ_j will be functions analogous to (2.8). Let $\eta = \eta_m$, and rescale as (2.6). The result is the equation

$$D\ddot{U} - M\dot{U} = - \sum_{j=1}^m \frac{r_j}{\varepsilon_j} \psi_j\left(\frac{U - U_j}{\varepsilon_j}\right) K_j, \quad (4.5)$$

where

$$r_j = \eta_j / \eta. \quad (4.6)$$

If x_j are the positions where $T = T_j^*$, the equations then become

$$D\ddot{U} - M\dot{U} = 0, \quad x \neq x_j, \quad j = 1, \dots, m^*. \quad (4.7)$$

$$[D\dot{U}]_{x_j} = -\beta_j K'_j, \quad T(x_j) = T_j^*, \quad (4.8)$$

$$U(-\infty) = U_-, \quad U(\infty) = U_+(\alpha), \quad (4.9)$$

where $[D\dot{U}]_{x_j} = \lim_{x \downarrow x_j} D\dot{U}(x) - \lim_{x \uparrow x_j} D\dot{U}(x)$, and the K'_j are the vectors defined

in Sec. 3.

There are two conditions which we need to impose on the β_j in order to ensure a well posed problem. According to our definition of the suballocations $\alpha^{(\ell)}$, for each of the concentration vector

$$\hat{Y}_\ell \equiv Y_- + \sum_{j=1}^{k_\ell} \alpha_j^{(\ell)} V_j = Y_- + \sum_{j=1}^{\ell} \alpha'_j V'_j$$

is in equilibrium with respect to the set of reactions R_j , $j \leq k_\ell$. The vector $\hat{Y}_{\ell-1}$, however, is not in this same equilibrium cone; otherwise $\alpha'_\ell = 0$ and we would have discarded the temperature T_ℓ^* and renumbered the others. This means there is some index $\kappa(\ell)$ such that the κ -th component of $\hat{Y}_\ell$ vanishes, but not the κ -th component of $\hat{Y}_{\ell-1}$. Since $\hat{Y}_\ell - \hat{Y}_{\ell-1} = \alpha'_\ell V'_\ell$, this implies that the κ -th component of V'_ℓ is negative, and that the coefficient α'_ℓ is uniquely determined by the knowledge of $\kappa(\ell)$. For notational convenience, we set $\mathcal{E}_\kappa^0 = \{Y \in \mathcal{Y} : Y_\kappa = 0\}$. Thus, necessarily there is a function $\kappa(\ell)$ such that $\hat{Y}_\ell \in \mathcal{E}_{\kappa(\ell)}^0$, but $\hat{Y}_{\ell-1} \notin \mathcal{E}_{\kappa(\ell)}^0$. We shall require that the solution $U(x)$ of the reduced problem has the same

property:

$$Y(x) \in \mathcal{E}_{\kappa(\ell)}^0 \text{ for } x > x_\ell.$$

Since D is diagonal, this implies $D \dot{Y} \in \mathcal{E}_{\kappa(\ell)}^0$, $x > x_\ell$. In particular,

$$Y(x_\ell) \in \mathcal{E}_{\kappa(\ell)}^0, \quad D \dot{Y}(x_\ell+) \in \mathcal{E}_{\kappa(\ell)}^0. \quad (4.10)$$

Finally, there is a condition on β_m . First, suppose that $K_m = K'_m$; i.e., only reaction R_m goes forward at $T_m = T_+$. Then the flame layer analysis given in Sec. 2 for the determination of β then can also be done at T_m ; the reason essentially is that $U \equiv U_+ = \text{const}$ for $x > 0$. As a result, we have

$$\beta_m = \left(2 \int_{-\infty}^0 \psi_m(s) D^{-1} K_m ds \right)^{1/2}. \quad (4.11)$$

On the other hand if $K_m \neq K'_m$, then we have to account for other reactions occurring. Their rate functions will be of larger order of magnitude than that of R_m , and it turns out that a certain pseudo-steady-state approximation is valid near T_m , and reduces the analysis to the previous case. This results in a condition (4.11) with a slightly altered ψ_m , and K_m replaced by K'_m .

We need to state precisely what the problem consists of.

Limit Problem, Level 1: Let U_+ , K'_j , and T_j be determined from a feasible allocation α , and assume (4.1). Solve (4.7) - (4.9) under the conditions (4.10), (4.11) (possibly modifying (4.11) as indicated). Then the

(approximate) actual mass flux and profile are given by

$$\bar{M} = M \eta^{\frac{1}{2}}, \quad \bar{U}(z) = U(\eta^{\frac{1}{2}} z) \quad .$$

The limit problem is easily solved. In fact, (4.7) shows that $D\dot{U} - MU$ is constant between the points X_j . In other words,

$$[D\dot{U} - MU]_{x_{j-1}^+}^{x_j^-} = 0, \quad \text{and (4.8) can be written } [D\dot{U} - MU]_{x_j^-}^{x_j^+} = -\beta_j K'_j.$$

Summing both over j , from 1 to ℓ , we find

$$[DU - MU]_{-\infty}^{x_\ell^+} = - \sum_{j=1}^{\ell} \beta_j K'_j \quad .$$

But the left side is $D\dot{U}(x_\ell^+) - MU(x_\ell) + MU_-$. We divide by M and disregard the 0-th component of this equation, to obtain

$$Y_- + \sum_{j=1}^{\ell} \frac{\beta_j}{M} V'_j = Y(x_\ell) - \frac{1}{M} DY(x_\ell^+) \quad ,$$

which by requirement (4.10) must lie in $\mathcal{E}_{\kappa(\ell)}^0$. But we also know that

$$\hat{Y}_\ell = Y_- + \sum_{j=1}^{\ell} \alpha'_j V'_j \in \mathcal{E}_{\kappa(\ell)} \quad \text{and } \hat{Y}_{\ell-1} \text{ is not. By the previous argument, the}$$

coefficients α'_j are uniquely determined by the $\kappa(\ell)$, so necessarily

$$\frac{\beta_j}{M} = \alpha'_j \quad . \tag{4.12}$$

We determine M by setting $j = m$ and using (4.11). Knowing M , we can find the β_j for $j < m$ from (4.12) again.

We arbitrarily set $x_m = 0$. For $x > 0$, $D\ddot{U} - M\dot{U} = 0$, so $D\dot{U} - MU = \text{const} = -MU_+$. Thus $U = U_+ + e^{MD^{-1}x}C$ for some C . But since D^{-1} is positive definite the only bounded solution is with $C = 0$. Therefore $U(x) \equiv U_+$ for $x > 0$. From (4.8), we have $D\dot{U}(0-) = \beta_m K'_m$. Solving (4.7) now, with initial data $U = U_+$, $D\dot{U}$ prescribed at $x = 0$, gives

$$U(x) = \hat{U}_{m-1} + \alpha'_m K'_m e^{MD^{-1}x}, \quad x_{m-1} < x < x_m, \quad (4.13)$$

where

$$\hat{U}_{m-1} = U_+ - \alpha'_m K'_m = U_- + \sum_{j=1}^{m-1} \alpha'_j K'_j$$

is the end state given by the suballocation $\alpha^{(m-1)}$. Its first component is $\hat{T}_{m-1}$, defined earlier. The function on the right of (4.13) approaches $\hat{U}_{m-1}$ as $x \rightarrow -\infty$, so the condition $T_{m-1} > \hat{T}_{m-1}$ in the definition feasibility ensures the existence of an $x_{m-1} < 0$ such that the first component of the right side of (4.13) equals T_{m-1} at $x = x_{m-1}$. This determines x_{m-1} , as well as $U(x_{m-1})$ and $D\dot{U}(x_{m-1}^+)$. Hence $D\dot{U}(x_{m-1}) = D\dot{U}(x_{m-1}^+) + \beta_{m-1}K'_{m-1}$ is found. Integrating backwards again, we may determine successively all the x_j and the complete profile.

A comment is in order regarding assumption (4.1). As shown in Example 3 of Sec. 3, for networks with competing reactions, it may happen that α must be chosen so that two of the T_j coincide; but it seems unlikely that there would be more than just one coincident pair. If $T_2 = T_{2+1}$, say, then the limit problem (4.7-9) looks the same except that for $j = 2$, the right side of (4.8) is replaced by a linear combination of vectors K_k for

$k \leq k_\ell$, whose coefficients are not known a priori. They must be found from a flame layer analysis. The simplest example is that of the network of two competing reactions $A \rightarrow P_1$, $A \rightarrow P_2$. In this case, the details are given in [3].

The reason for assuming D to be diagonal is to be able to conclude (4.10) from the fact that $Y(x) \in \mathcal{E}_{(\ell)}^0$ for $x > x_\ell$. But this is only a mathematical requirement resulting from the assumption that D is constant. Physically, the $\kappa(\ell)$ -th component of $D\dot{Y}$ represents the flux of $Y_{\kappa(\ell)}$, and that flux will certainly be zero, since $Y_{\kappa(\ell)} = 0$ for $x > x_\ell$. Also physically, D will generally not be diagonal, but there is no contradiction because it is also nonconstant, and depends on Y in such a manner that $(D\dot{Y})_\kappa = 0$ when $Y_\kappa = \dot{Y}_\kappa = 0$.

5. THE LIMIT PROBLEM, LEVEL 2

On level 1, the limit problem contains the following apparent inconsistency: the jump conditions (4.8) replace the action of the rate functions $\omega_j(U)$ in (4.2). Therefore the β_j should be related to the ω_j . However, the only such relation used is that for $j = m$; indeed the other β 's are determined uniquely as part of the solution process, with no reference to the ω 's or ψ 's. This, of course, is a great advantage in solving actual problems, because only one flame layer analysis (namely, that with $j = m$) need be performed.

It is not a true inconsistency at that level of approximation, however. To explain it, we proceed to level 2, where the relation between the ψ 's and β 's is brought in.

We assume (4.1) as before, and begin by defining the "flame locations" x_j more precisely as the positions where $Y_{K(j)} = \varepsilon_j$, the function (j) being that in Sec. 4. We then define $U_j \equiv U(x_j)$; and in particular, $T_j = T(x_j)$. This differs from the definition of T_j used in level 1, where these were obtained from (3.12). The difference turns out to be small, and this justifies using the former prescription for the T_j at the lowest level of approximation. Anticipating the small difference, we use the symbol T_j^0 for the sequence defined by (3.12), so

$$H_j(r_j^0) = H_m(T_+) \text{ for all } j, \quad (5.1)$$

and express

$$T_j = T_j^0 + \varepsilon_j T_j'.$$

Limit Problem, Level 2. Let the U_+ , K_j' , and T_j^0 be determined from a feasible allocation α , and assume (4.1). Solve (4.7) - (4.9) for M , $U(x)$, x_j , and β_j under conditions (4.10), (4.11). Also determine the T_j' for $j < m$ in accordance with the flame layer analyses to be described below. Then $\bar{M}$ and $\bar{U}(z)$ are found as before.

In the case $K_j = K_j'$, the flame layer analysis proceeds by using stretched variables

$$\xi = \frac{x - x_j}{\varepsilon_j}, \quad u(j) = \frac{U - U_j}{\varepsilon_j}.$$

the flame equation analogous to (2.9) is then

$$D \frac{\partial^2 u^{(j)}}{\partial \xi^2} + r_j \psi_j(u^{(j)}) K_j = 0 \quad . \quad (5.2)$$

It turns out that for any given vectors p_+ with 0-th component ≥ 0 and $p_- = p_+ + \beta_j K_j$, there exists a positive number r_j such that (5.2) has a solution satisfying

$$D \frac{\partial u^{(j)}}{\partial \xi} (\pm\infty) = p_{\pm} \quad .$$

This problem of determining r_j can be reduced to a standard problem of Liñan [5], [4]. The $p_{\pm}$ have already been determined from (4.7) - (4.9) as before; this now gives us r_j . Finally, taking the log of (4.6), using (4.4) and (3.10), we find

$$\varepsilon \ln r_j = (H_j(T_j^0 + \varepsilon_j T_j') + 2\varepsilon \ln \varepsilon_j) - (H_m(T_+) + 2\varepsilon \ln \varepsilon_m) \quad .$$

We write

$$H_j(T_j^0 + \varepsilon_j T_j') \approx H_j(T_j^0) + \varepsilon_j H_j'(T_j^0) T_j' = H_j(T_j^0) + \left(\frac{T_+}{T_j^0}\right)^2 \varepsilon_j T_j' \quad .$$

Hence from (5.1),

$$\ln r_j = \left(\frac{T_+}{T_j^0}\right)^2 T_j' + 2 \ln \left(\frac{\varepsilon_j}{\varepsilon_m}\right) \quad .$$

This determines T_j' . If $\frac{\varepsilon_j}{\varepsilon_m} \neq 0(1)$, then $|T_j'| > 0(1)$, but at least the temperature corrections $\varepsilon T_j' \ll 1$, since $\varepsilon = \min_i \varepsilon_i$.

In the case $K_i' \neq K_j$, the comments in Sec. 4 regarding pseudo-steady-state analysis apply here as well.

6. FUTURE DIRECTIONS

Many aspects of the present treatment remain to be fully explored, for example, procedures for finding all possible feasible allocations, a systematic flame layer analysis in cases when $K_j \neq K_j'$, more than formal justification, etc. More importantly, the theory needs to be extended to cases ([6] being an example) where some reactions have zero or small activation energy. This is all in the context of plane laminar flames. But other crucial problems in flame theory abound; the significance of multiple reactions is then needs to be explored. Some of these directions are under current active investigation.

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