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FLAME FRONTS WITH COMPLEX CHEMICAL NETWORKS

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ABSTRACT

For laminar flame fronts with general complex chemistry networks, we present a systematic method to reduce the detailed chemistry in the limit of high-activation-energy asymptotics. We detail the method on a global multistep hydrocarbon model. Generic flame profile structures are discussed, and extensions to networks with zero activation energies are outlined.

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1. Introduction

Complex chemistry involves in flames a mix of reactions with both high and small activation energies. Since the pioneering works of Frank-Kamenetskii [11] and Zeldovich [16,17], it has been recognized that large activation energies E_i determine a hierarchy of scales

$$\varepsilon_i = \frac{RT_+}{E_i} \frac{T_+}{T_+ - T_-}, \quad \varepsilon_i \ll 1,$$

where T_- is the cold mixture temperature, and T_+ a typical adiabatic flame final temperature. The ε_i are the inverse of the (large) Zeldovich numbers.

In this paper we develop the asymptotic flame theory with complex chemistry first outlined in [7-8]. We specifically consider the case of finite ratios $E_i/E_j \neq 1$ for the subclass of High Activation Energy (H.A.E.) reactions. Case where $E_i \sim E_j$ lead to merged flames structures and are essentially limiting cases of our theory.

We first develop concepts which are common to all reactions networks: admissible reactant allocations, which yield the final burned state of the flame; and admissible reactant suballocations to the network, which determine feasible chemical network pathways along the front (Sec. 1.2). The latter correspond to partial subgroups of reactions which go to completion at temperatures lower than the final one. The notion of convex set of admissible allocations (Sec. 2.2) turns out to be a convenient tool.

Next, to determine the actual pathways within the network and along the flame profile, we construct normalized power gauge functions (Sec. 1.3) for both H.A.E. and Z.A.E. (Zero Activation Energy) reactions.

Unnormalized power rate functions have already been used implicitly by Frank-Kamenetskii [11] and Liñan [12]. We derive systematic comparison principles based on these gauge functions.

In Section 2, we detail our method on a global hydrocarbon two-step model. We evidence some generic flame structures present in complex networks: merged flames, competition flames and tandem flames.

In Section 3, we outline the methodology for general networks.

1.1 The Flame Front Equations for a Chemical Network.

Let n chemical species $A_1, A_2, \dots, A_n$ be involved in r reactions $R_1, R_2, \dots, R_r$; symbolically

where $v(j,i)$ (resp. $\lambda(j,i)$) is the stoichiometric coefficient of species j on the left side (resp. right side) of reaction i . Both v and λ are non-negative integers; $v(j,i)$ is zero if species j is not a reactant in reaction i , while $\lambda(j,i)$ is zero if it is not a product. Each reaction yields heat releases $Q_1, Q_2, \dots, Q_r$.

The flow field is described by the temperature T and the vector of rescaled mass concentrations (fractions):

$$(1.2) \quad \underline{Y} = (Y_1, Y_2, \dots, Y_n) \quad ,$$

where the rescaled Y_j , $j = 1, \dots, n$, are the actual mass fractions (concentrations) of species j divided by the corresponding molecular mass m_j (this rescaling somewhat simplifies the flame front equations 1.6). The

full state vector $\underline{U}$ is

$$(1.3) \quad \underline{U} = (T, \underline{Y}) = (T, Y_1, \dots, Y_n) \quad .$$

Each reaction can be characterized by an n-dimensional reaction vector $\underline{V}_i$, $i = 1, \dots, r$, which represents the net change in the number of molecule grams (moles) of the various species in reaction R_i :

$$(1.4) \quad \begin{aligned} \underline{V}_i &= (\lambda(1,i) - v(1,i), \lambda(2,i) - v(2,i), \dots, \lambda(n,i) - v(n,i)) \\ &= (v_i^{(1)}, v_i^{(2)}, \dots, v_i^{(n)}) \quad . \end{aligned}$$

The extended (n+1) dimensional reaction vector $\underline{K}_i$, $i = 1, \dots, r$, is defined as:

$$(1.5) \quad \underline{K}_i = (Q_i, \underline{V}_i) \quad ;$$

Example 1.1. Consider the network of sequential reactions.

then $\underline{Y} = (Y_1, Y_2)$, $\underline{U} = (T, Y_1, Y_2)$, $\underline{V}_1 = (-1, +1)$, $\underline{V}_2 = (0, -1)$, $\underline{K}_1 = (Q_1, -1, +1)$, $\underline{K}_2 = (Q_2, 0, -1)$.

Example 1.2. Consider the network of competing reactions

then $\underline{U} = (T, Y)$, $\underline{K}_1 = (Q_1, -1)$, $\underline{K}_2 = (Q_2, -1)$.

With the above vector notations, the equations for a one-dimensional traveling flame front, in a system of coordinates moving with the front, and in the constant pressure approximation, reduce to the system of $(n+1)$ equations in $T, Y_1, \dots, Y_n$:

$$(1.6) \quad -(D(\underline{U}) \underline{U}_x)_x + M \underline{U}_x = \sum_{i=1}^r \omega_i(\underline{U}) \underline{K}_i ;$$

where $D(\underline{U})$ is a $(n+1) \times (n+1)$ diffusion matrix (positive definite); M is the unknown mass flux, which equals wave velocity if the density is unity. The scalar functions ω_i are the rates of the reactions R_i . The system 1.6 is closed by the perfect gas law:

$$(1.7) \quad \bar{P}_c = (\rho T)(\sum_j Y_j) ,$$

where $\rho(x)$ is the mixture global density and $\bar{P}_c$ the constant pressure in the isobaric, small Mach number limit. Finally, the cold state

$$(1.8) \quad \underline{U}^- = \underline{U}(-\infty) = (T_-, Y_1^-, \dots, Y_n^-)$$

is prescribed at $x = -\infty$.

The reaction rates ω_i are given by the usual law of mass action and Arrhenius factors:

$$(1.9) \quad \omega_i = \prod_{j=1}^n Y_j^{v(j,i)} B_i \exp(-\frac{E_i}{T})$$

where E_i is the activation energy of reaction i and B_i the corresponding pre-Arrhenius factor; strictly speaking, B_i is a slowly varying function of

T and ρ , hence of T and Y_j through (1.7); we will in the sequel neglect its dependence w.r.t. Y_j , taking for instance the context of a reacting mixture diluted in some inert species.

In this presentation, we omit reversible reactions. The extension to reversible reactions has been completed and will be presented in [9].

We are concerned with exploiting the high activation energies E_i to obtain approximate wave front solutions. The E_i determine scales

$$(1.10) \quad \varepsilon_i = \frac{T_+}{E_i} \frac{T_+}{T_+ - T_-} \ll 1, \quad$$

where T_+ is a typical final (burned) temperature and the ε_i are inverse Zeldovich numbers (T has been renormalized so that the gas constant is unity). The sharp sensitivity of Arrhenius terms $\exp(-E_i/T)$ w.r.t. variations of T enable a systematic High Activation Energy (H.A.E.) asymptotic analysis. The procedures are linked to properties of the underlying reaction network, which supplies the vectors $\underline{K}_j$. These procedures are well known in the case when the network is modeled by a single reaction $A \rightarrow P$. (See [2] and the review article [3] in these proceedings.) An approach similar to the one in this paper was used in treating two-reaction networks of competing, sequential, and competing-fuel types in [7] and [8], 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 was provided in part by the authors in [8].

The methods are those of asymptotic analysis. Roughly speaking, to the lowest order this means developing rational procedures for replacing

the original problem with a limit problem in which the ε_i do not appear explicitly. The limit problem is expected to yield an approximate solution, and is easy to solve. In the limit, flame sheets appear as free boundaries with $\underline{U}$ continuous across, but with jumps in the gradients. A rigorous justification of this expectation has been given recently for the case of a single reaction [1]. Reactions are concentrated on flame sheets (internal layers) with pure convective-diffusive flow in between, if there are no reactions with $E_i = 0$:

$$(D(\underline{U}) \underline{U}_x)_x - M \underline{U}_x = 0$$

between the flame sheets. The flame sheets correspond to a Dirac-function in temperature limiting behavior of the ω_i as $\varepsilon_i \rightarrow 0$. If there is a mix of reactions with H.A.E. $E_i \gg 1$, $i = 1, \dots, p$ and with zero activation energies (Z.A.E.) $E_i = 0$, $i = p+1, \dots, r$, there are still flame sheets (free boundaries) associated to the R_i , $i = 1, \dots, p$; but the flow in between is convective-diffusive-reactive due to the Z.A.E. reactions. The latter "thicken" the wave front profiles.

Many other parameters besides ε_i enter the problem, for example, the elements of the matrix D and of the unburned state vector of the gas, $\underline{U}^-$. Throughout the paper, we assume that their magnitudes do not interfere with the asymptotics. Particularly, we assume that any constants not depending explicitly on ε_i , B_i , or E_i (as defined in 1.9 and 1.10) 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_i . These restrictions are relaxed, and a more meticulous account of the other parameters is taken in [10].

For background and previous work on asymptotic methods in flame theory, the reader is referred to [2] and [3] in these proceedings. A number of papers have been written on the multiple reaction case; see the references in [2], [4], [12], and [17].

We remark that the consideration of realistic chemical networks avoids the so-called "cold boundary difficulty" [2], where $\underline{U}^-$ is not an equilibrium state of the chemical network. In realistic chemical networks, the initial zero concentration of intermediate radicals species insures equilibrium at the cold side; a good example is the autocatalytic chain network investigated by Liñan [12]:

where P and M are inert; the initial concentration of the intermediate radical A_2 is null. Here, $\underline{K}_1 = (Q_1, -1, +1)$ and $\underline{K}_2 = (Q_2, 0, -2)$.

1.2. The Reactant Allocations and Suballocations to a Chemical Network.

The final state on the burned side

$$(1.12) \quad \underline{U}^+ = \underline{U}(+\infty) = \underline{U}(T_+, Y_1^+, \dots, Y_n^+)$$

is actually coupled with the initial state $\underline{U}^-$ through conservation laws which are the equivalent of the Rankine-Hugoniot conditions for nonreactive flows. To see this, integrate (1.6) from $x = -\infty$ to $x = +\infty$, use $\underline{U}_x = 0$ at $x = \pm\infty$ to obtain:

$$(1.13a) \quad M(\underline{U}^+ - \underline{U}^-) = \sum_{i=1}^r \Omega_i \underline{K}_i$$

where Ω_i is the integrated power rate function for R_i along the flame profile:

$$(1.13b) \quad \Omega_i = \int_{-\infty}^{+\infty} \omega(\underline{U}(x)) dx ;$$

now setting $\alpha_i = \Omega_i/M$,

$$(1.14) \quad \underline{U}^+ - \underline{U}^- = \sum_{i=1}^r \alpha_i \underline{K}_i ,$$

hence the difference between the asymptotic state vectors lies in the linear span of the extended reaction vectors $\underline{K}_i$.

Moreover, the α_i , $i = 1, \dots, r$, must satisfy constraints such that the final concentration vector $\underline{Y}^+$ insures the network equilibrium:

$$(1.15) \quad \underline{Y}_k^+ = 0 = \underline{Y}_k^- + \sum_{i=1}^r \alpha_i \underline{V}_i^{(k)}$$

for some integer subset $\{k\}$ such that $\omega_i(\underline{U}^+) = 0$, $\forall i$. Because of (1.14) and (1.15), M must be considered as an unknown nonlinear eigenvalue for the general system (1.6).

We will call the set of positive or null numbers $\alpha_1, \alpha_2, \dots, \alpha_r$ an allocation of the initial concentration vector $\underline{Y}^-$ to the network. To make this point of view more systematic, we first need a basic assumption about the reaction vectors.

$$(1.16) \quad \underline{\text{Assumption 1.}} \quad \text{If } \sum_{i=1}^m \alpha_i \underline{V}_i = 0 \quad \text{and } \alpha_i \geq 0, \text{ then } \alpha_i \equiv 0.$$

This assumption assures, as we shall see, that equilibrium can only be reached when each reaction rate is zero. It can easily be generalized to cover reversible reactions [9].

Definition 1. $Y \in \mathcal{C}$ is an equilibrium state if, for all T ,

$$(1.17) \quad \sum_{i=1}^m \omega_i(Y, T) V_i = 0.$$

It follows from (1.16) that this can only happen if each $\omega_i = 0$.

For each $i = 1, \dots, r$, 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). 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:

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

$$\mathcal{C} = \sum_{i=1}^m \mathcal{C}_i.$$

(This is, of course, a cone imbedded in a set of coordinate hyperplanes.)

For simplicity only we require

Assumption 2. $V_i \notin \mathcal{C}_i$, for all i .

Definition 2: Given an input state $\underline{Y}^- \in \mathcal{C}$, an allocation of $\underline{Y}^-$ to the network is a set of numbers $\alpha_i \geq 0$, $i = 1, \dots, r$, such that

$$(1.18) \quad \underline{Y}^- + \sum_{i=1}^m \alpha_i V_i \in$$

Example. Consider the network of competing reactions described in Example 1.1. Clearly $\mathcal{C} = \{0\}$. Expliciting Eq. (1.15) for T and Y_1 gives:

$$T_+ = T_- + \alpha_1 Q_1 + \alpha_2 Q_2; \quad 0 = Y_1^+ = Y_1^- - \alpha_1 - \alpha_2 ;$$

but each α_i can a priori take values between zero and Y_1^- . Setting $\alpha_1 = \theta Y_1^-$, $0 \leq \theta \leq 1$, we have $\alpha_2 = (1-\theta)Y_1^-$ and:

$$T_+ = T_- + Y_1^-(\theta Q_1 + (1-\theta)Q_2) .$$

The final temperature can be any temperature between $T_1 = T_- + Y_1^- Q_1$, adiabatic temperature of a pure reaction R_1 , and $T_2 = T_- + Y_1^- Q_2$, adiabatic temperature of a pure reaction R_2 .

Indeed this network of competing reactions is the canonical example of nonuniqueness of allocations. In more complex networks, there is usually a whole array of possible allocation vectors which are restricted to the boundaries of a specific convex set (simplex) defined by:

$$(1.19) \quad \alpha_i \geq 0, \quad i = 1, \dots, r$$

$$\underline{Y}_j^- + \sum_{i=1}^r \alpha_i v_i^{(j)} \geq 0, \quad j = 1, \dots, n .$$

(see Section 2 for examples of such convex sets). In general, we must consider the final states $\underline{U}^+(\alpha_1, \dots, \alpha_r)$ and $T_+(\alpha_1, \dots, \alpha_r)$ as functions of the α_i . Nonunique allocations reflect the possibility of different chemical pathways in the network. Indeed, experimental and numerical simulations show that within a flame profile, there is a sequence of

temperatures where some subgroups of reactions are completed, while some other reactions are still frozen [13]. For instance, in heavy hydrocarbon flames [13] peak concentrations of a typical radical occur at a distinctly different temperature than the temperature band where most of the fuel is consumed [14].

This leads to the notion of suballocations (to be developed in Sections 2 and 3) such that a partial subgroup of reactions go to completion at temperatures lower than T_+ , within a partial subnetwork.

1. Normalized Power Rate Functions.

The actual chemical pathways and chemical subnetworks in a flame are determined by the competing rates w_i ; the latter can vary sharply not only in absolute but also in relative magnitude as temperature increases across the flame front. Hence the need for some normalized gauge functions to systematically exploit these relative variations.

Consider now the integrated power rate functions Ω_i in Eq. (1.13):

$$(1.20) \quad \Omega_i = \int_{-\infty}^{+\infty} w_i(\underline{U}(x)) dx ;$$

writing the first component in 1.13a yields the exact relation:

$$(1.21) \quad M(T_+ - T_-) = \sum_{i=1}^r Q_i \Omega_i ,$$

i.e., the relative contribution of each reaction to the temperature profile is its heat release Q_i weighted by its integrated power rate function. But if the reaction R_i with high activation energy E_i is isolated then

classical H.A.E. analysis for a single step reaction [2] insures that:

$$(1.22) \quad \Omega_i = C_i \varepsilon_i (B_i \exp -E_i/T_+)^{\frac{1}{2}}$$

where C_i is some proportionality constant; i.e., the integrated power rate is concentrated in the flame sheet. For networks with partial H.A.E., the Ω_i for the H.A.E. reactions are still concentrated in a sequence of flame sheets (possibly merged) at various temperatures, the last one at T_+ .

As the Ω_i are large at the respective flame sheet temperatures, we are led to the following choice for normalized power rate gauge functions $H_i(T)$ to compare the relative powers of reactions R_i :

Definition 3. Power Rate Gauge Functions:

$$(1.23a) \quad H_i(T) = \bar{\varepsilon} [\ln B_i - \frac{E_i}{T}]$$

$$(1.23b) \quad \bar{\varepsilon} = \min \varepsilon_i = \min \frac{T_+}{E_i} \frac{T_+}{T_+ - T_-}, \quad i = 1, \dots, r.$$

In (1.23a) we allow T to vary, since the flame sheet temperatures are a priori unknown (non unique allocations). We also allow the same definitions (1.23a-b) whether reaction R_i is H.A.E. or Z.A.E. Indeed:

1) if R_i is H.A.E., then

$$H_i(T) = \bar{\varepsilon} (2 \ln \Omega_i + O(\ln \bar{\varepsilon})) ,$$

which insures that the variation of $H_i(T)$ over the whole flame temperature profile is $O(1)$;

2) if R_i is Z.A.E., then

$$H_i = \bar{\varepsilon} \ln B_i \approx \text{Constant} ,$$

as $B_i(T)$ varies weakly with T ; nevertheless we should keep in mind that physical B_i may be very large indeed, anywhere from 10^{11} to 10^{19} ; so the normalized H_i are still $O(1)$ or smaller.

Remark 1.1. The power gauge functions $H_i(T)$ are monotone increasing in T . Any linear combination of $H_i(T)$ is a monotone (decreasing or increasing) function of T .

Our basic comparison principle is based on the following inequalities:
if

$$H_p(T) > H_q(T)$$

at a given T , then, if both R_p and R_q are H.A.E.:

$$\Omega_p(T) \gg \Omega_q(T)$$

and R_p quenches R_q at T . An equilibrium configuration might still be obtained for some distinguished temperatures T_p and T_q (possibly equal) such that $H_p(T_p) = H_q(T_q)$ and $\Omega_p(T_p)/\Omega_q(T_q) = O(1)$. We will detail the systematic use of the comparison principle to construct flame fronts in Sections 2 and 3.

As a simple example, we show how the power gauge functions resolve the nonuniqueness of allocations in the competing reactions network (example 1.1). Recall that T_+ can vary anywhere between T_1 and T_2 (single reactions adiabatic temperatures). Let $E_1 \gg 1$, $E_2 \gg 1$ and $E_1/E_2 = O(1)$; three cases are possible:

1) $H_1(T) > H_2(T)$ for $\forall T \in [T_1, T_2]$, then R_1 globally quenches R_2 , and there is a single flame sheet at T_1 ; the allocation is $(Y_1^-, 0)$;

2) $H_2(T) > H_1(T)$ for $\forall T \in [T_1, T_2]$, then there is a single flame sheet at T_2 , with allocation $(0, Y_1^-)$;

3) $H_1(T_*) = H_2(T_*)$ for some T_* , $T_1 < T_* < T_2$; T^* is unique because of Remark 1.1, and the two reactions are at equilibrium at the flame sheet temperature $T_* \equiv T_*$; with $T_* = \theta T_1 + (1-\theta)T_2$, $0 < \theta < 1$, the allocations are $\alpha_1 = \theta Y_1^-$, $\alpha_2 = (1-\theta)Y_2^-$. The full layer analysis of this competition flame has been done by the authors in [7]. In Section 2, we show that competition type flame regimes can in fact be generic for more complex networks, due to competing subnetworks.

Finally extending formula (1.23) to Z.A.E. reactions insures that our comparison principle covers classical pseudo-steady state analysis: if $H_p(T) > H_q(T)$ for R_p and R_q both Z.A.E., then for all temperature ranges $\omega_p \neq \omega_q$ (as H_p and H_q are nearly constant) and the usual pseudo-steady state reduction of R_p can be done.

2. A Global Hydrocarbon Two-Step Model

2.1 The Two-Step Dryer-Westbrook Model.

Hydrocarbon flames are usually modelled by global one-step models:

where n_1, n_2, n_3 are positive integers, and the global reaction rate w is

$$(2.1b) \quad w = B(T) \exp\left(-\frac{E}{RT}\right) [\text{Fuel}]^\alpha [\text{O}_2]^\beta;$$

the pre-Arrhenius factor B and the exponents α and β are usually adjusted to fit calculated flame parameters to some experimental data; α and β turn

out to be positive fractional numbers. As pointed out in [15], the single-step model predicts flame speeds reliably over a considerable range of reactions; but it systematically overpredicts the total heat of reaction and the final adiabatic temperature. Moreover, at temperatures characteristic of hydrocarbon fuels ($\sim 2000^\circ\text{K}$), substantial amount of CO and H_2 exist in equilibrium in the combustion products with CO_2 and H_2O . It is also well recognized that typical hydrocarbons burn in a sequential manner; i.e., the fuel is partially oxidized to CO and H_2 , which are not appreciably consumed until all of the hydrocarbon species have disappeared [6]. From these observations, and following a similar model for methane by Dryer and Glassmann [5], Westbrook and Dryer [15] have proposed the following global two-step reaction mechanism:

with empirically derived reaction rates for both reactions; for R_2 :

$$(2.3a) \quad \omega_2 = 10^{14.6} \exp\left(-\frac{40}{RT}\right) [\text{CO}]^1 [\text{H}_2\text{O}]^{0.5} [\text{O}_2]^{0.25}$$

and for R_1 :

$$(2.3b) \quad \omega_1 = B_1 \exp\left(-\frac{E_1}{RT}\right) [\text{Fuel}]^\alpha [\text{O}_2]^\beta$$

For Octane C_8H_{18} , $B_1 = 5.7 \times 10^{11}$, $E_1 = 30.0$ kcal/mole, $\alpha = 0.25$ and $\beta = 1.5$. In general, for all hydrocarbons except methane CH_4 , $E_1 \sim 30$ kcal, and $B_1 \propto 10^{14.6} = B_2$. So:

Remark 2.1. For the global two-step model (2.2), the power gauge functions $H_1(T)$ and $H_2(T)$ always intersect at some T_* such that:

$$(2.4) \quad \bar{\varepsilon}(\ln \frac{B_2}{B_1}) = \bar{\varepsilon}(\frac{E_2 - E_1}{T_*})$$

since $B_2 \gg B_1$ and $E_2 - E_1 \sim 10$ kcal. Competing flames and subnetworks are possible.

In the sequel, we systematically investigate the simplified network:

where P_1 and P_2 are inert products (e.g., H_2O and CO_2) and R is an intermediate "radical" species (e.g., CO). We take Y_f , Y_{ox} and Y_r to be the respective (rescaled) concentrations of Fuel, Oxygen, and Radical. We take the simplified extended reaction vector (stoichiometric coefficients set equal to one):

$$(2.6) \quad \begin{aligned} \underline{K}_1 &= (Q_1, -1, -1, +1) \\ \underline{K}_2 &= (Q_2, 0, -1, -1) \end{aligned};$$

notice the alternance ± 1 for the last component, as the Radical is produced by R_1 , but consumed by R_2 . The flame front equations for the state vector $\underline{U} = (T, Y_f, Y_{ox}, Y_r)$ are:

$$(2.7) \quad -(D(\underline{U})\underline{U}_x)_x + M \underline{U}_x = \omega_1(\underline{U}) \underline{K}_1 + \omega_2(\underline{U}) \underline{K}_2,$$

with the reaction rates:

$$(2.8) \quad \begin{aligned} \omega_1 &= B_1 Y_f Y_{ox} \exp(-E_1/T) \ , \\ \omega_2 &= B_2 Y_{ox} Y_r \exp(-E_2/T) \ , \end{aligned}$$

and

$$E_1 \gg 1, E_2 \gg 1, \frac{E_2}{E_1} = O(1) \quad .$$

The initial state is:

$$(2.9) \quad \underline{U}^- = (T_-, a, b, 0)$$

with $Y_f^- = a$, $Y_{ox}^- = b$ and $Y_r^- = 0$ (which is the physical situation). Notice that we do not assume reversibility of R_2 ; the reversible case is fully treated in [9].

2.2 The Convex Set of Admissible Allocations.

Let α_1 and α_2 be the allocations to R_1 and R_2 with $\underline{\alpha} = (\alpha_1, \alpha_2)$; possible final states are:

$$\underline{U}^+(\underline{\alpha}) = \underline{U}^- + \alpha_1 \underline{K}_1 + \alpha_2 \underline{K}_2 \quad , \text{ i.e., }:$$

$$(2.10) \quad T_+(\underline{\alpha}) = T_- + \alpha_1 Q_1 + \alpha_2 Q_2$$

$$(2.11) \quad \begin{aligned} Y_f^+ &= a - \alpha_1 \geq 0 \quad , \\ Y_{ox}^+ &= b - \alpha_1 - \alpha_2 \geq 0 \quad , \\ Y_r^+ &= \alpha_1 - \alpha_2 \geq 0 \quad ; \end{aligned}$$

inequalities 2.11 together with the conditions $\alpha_1 \geq 0$, $\alpha_2 \geq 0$ define the convex set of possible allocations in the positive quadrant α_1, α_2 . Since the reactions are not reversible, chemical equilibrium corresponds to some points (α_1, α_2) on the boundary of this simplex. However, equilibrium for the chemical network can be reached in two different ways: first both

$Y_f^+ = 0$ and $Y_r^+ = 0$, which corresponds to an oxygen rich initial mixture. Or $Y_{ox}^+ = 0$, which corresponds to a fuel rich mixture. More precisely:

1) In the oxygen rich case (Fig. 1), $a < b/2$ and $Y_f^+ = a - \alpha_1 = 0$, $Y_r^+ = \alpha_1 - \alpha_2 = 0$, so

$$(2.12) \quad \alpha_1 = \alpha_2 = a = Y_f^- ;$$

the final state is:

$$(2.13) \quad \begin{aligned} Y_f^+ &= 0 && \text{(fuel depletion)} \\ Y_{ox}^+ &= b - 2a > 0 && \text{(excess oxygen)} \\ Y_r^+ &= 0 \end{aligned}$$

(the radical concentration pulses to a maximum and then decreases to zero);

$$(2.14) \quad T^+ = T^- + a(Q_1 + Q_2) .$$

For the oxygen rich case, notice that the admissible allocation (a, a) is unique (edge of the convex set). The case $a = b/2$ corresponds to an initially stoichiometric concentration $\underline{Y}^-$.

Figure 1. The oxygen rich case, $a < b/2$.

2) In the fuel rich case, $a > b/2$, $Y_{ox}^+ = b - \alpha_1 - \alpha_2 = 0$; since $\alpha_2 \geq 0$, we have $b/2 \leq \alpha_1 \leq b$, in fact:

$$(2.15) \quad b/2 \leq \alpha_1 \leq \min(a, b) ;$$

the final allocations are:

$$(2.16) \quad \begin{aligned} Y_f^+ &= a - \alpha_1 && \text{(excess fuel)} \\ Y_{ox}^+ &= 0 && \text{(oxygen depletion)} \\ Y_r^+ &= 2\alpha_1 - b \end{aligned}$$

There usually is some residual radical concentration on the burned side of the flame. The key feature of the fuel rich case is that allocations are not unique: (α_1, α_2) covers a whole closed interval on the line $\alpha_1 + \alpha_2 = b$, with (2.15) and

$$b - \min(a, b) \leq \alpha_2 \leq b/2 .$$

The final temperature is now parameterized by α_1 :

$$(2.17) \quad T_+(\alpha_1) = T_- + \alpha_1 Q_1 + (b - \alpha_1) Q_2 ;$$

to fix ideas, take $Q_2 > Q_1$ and $a \leq b$, so $\min(a, b) = a$; then $T_+(\alpha_1)$ is a decreasing function of α_1 , which reaches its minimum $T_{\min}$ at $\alpha_1 = a$ and its maximum $T_{\max}$ at $\alpha_1 = b/2$:

$$(2.18) \quad \begin{aligned} T_{\min} &= T_- + a Q_1 + (b - a) Q_2 , \\ T_{\max} &= T_- + b/2 (Q_1 + Q_2) . \end{aligned}$$

Figure 2. The fuel rich case, $a > b/2$.

2.3 Flame Configurations in the Oxygen Rich Case ($a \leq b/2$).

This is characterized by a unique final temperature (2.14):

$$T_+ = T_- + a(Q_1 + Q_2)$$

and a unique final allocation $\underline{\alpha} = (a, a)$. Flame configurations are determined by the relative ordering of the power gauge functions (1.23) $H_1(T)$ and $H_2(T)$ at $T = T_+$. We consider the case $H_1(T_+) = H_2(T_+) + O(\bar{\varepsilon})$ as nongeneric.

Case 1. $H_1(T_+) > H_2(T_+)$: Sequential Flames.

R_1 would tend to quench R_2 at T_+ . A stable flame configuration exists only if R_1 is completed at some flame sheet of temperature $T_1 < T_+$, such that the power H_1 is lowered to a power equilibrium configuration:

$$H_1(T_1) = H_2(T_+) \quad ;$$

such a temperature T_1 exists and is unique because of Remark 1.1

Figure 3.

The flame configuration is sequential with R_1 completed in a flame sheet (1) at T_1 , where all the fuel is burned out; this is followed by a flame sheet at T_+ , where R_2 consumes all the radical created by the sheet (1). The temperature sequence (T_1, T_+) equilibrates the power rates and induces a stable chemical pathway along the flame profile: first R_1 with R_2 frozen, then R_2 with R_1 completed. We remark that there is a suballocation $\underline{\alpha}^{(1)} = (a, 0)$ to the flame sheet (1), and a final allocation $\underline{\alpha}^{(2)} = \underline{\alpha} = (a, a)$ to the sheet (2).

Remark 2.1. In practice the flame profile will be thickened because of Z.A.E. involving other radicals.

Remark 2.2. The principle of determining a sequence of temperatures (possibly equal) to equilibrate all the power gauge functions H_i , systematically induces stable chemical pathways and subnetworks in general complex networks.

Case 2. $H_2(T_+) > H_1(T_+)$: Pseudoreaction $\tilde{R}_1$.

R_2 is now much faster than R_1 at T_+ . We might think of R_2 first taking place at some $T_2 < T_+$, such that $H_2(T_2) = H_1(T_+)$, followed by R_1 at T_+ . However, the corresponding suballocation would be (0,0); that is, such a separated flame sheet cannot exist, as there is no initial radical concentration ($Y_r^- = 0$) to trigger it. The only possible structure is a single flame layer at T_+ , with a pseudo-reaction $\tilde{R}_1$ characterized by the same rate function w_1 , but with an instant heat release $Q_1 + Q_2$. The radical produced by $\tilde{R}_1$ is instantly burned by R_2 within the same flame layer. Strictly speaking, this is a situation with merged layers, but to lowest order, R_2 does not affect the layer analysis at T_+ .

2.4 Flame Configurations in the Fuel Rich Case ($a > b/2$).

Since allocations are not unique (Figure 2), we must compare $H_1(T)$ and $H_2(T)$ over the whole range $[T_{\min}, T_{\max}]$ as defined in 2.17-2.18. Hence, a larger variety of possible configurations than in the oxygen rich situation.

Case 3. $H_1(T) > H_2(T)$ over $[T_{\min}, T_{\max}]$: sequential flames.

R_1 is much faster than R_2 over the whole permissible range of final temperatures. To determine allocations uniquely, we introduce the following physical principle:

Maximum Allocation Principle: if $H_j(T) > H_i(T)$ over some permissible range of final temperatures, then from all possible allocations, a stable chemical pathway maximizes α_j for reaction R_j at the expense of α_i .

In this case, maximizing α_1 for R_1 uniquely yields:

$$\alpha_1 = a, \quad \alpha_2 = b - a,$$

i.e., the rightmost point on the interval of possible allocations (Figure 2). Moreover, $T_+ \equiv T_{\min} = T_- + aQ_1 + (b-a)Q_2$, and $Y^+ = (0, 0, 2a-b)$. Since at $T_{\min}$, R_1 is still much faster than R_2 , the situation is similar to case 1. R_1 is completed in a flame sheet (1) at T_1 such that

$$H_1(T_1) = H_2(T_{\min}),$$

while R_2 is completed in a flame sheet (2) at $T_{\min}$.

Case 4. $H_2(T) > H_1(T)$ over $[T_{\min}, T_{\max}]$: pseudo-reaction $\tilde{R}_1$.

R_2 is much faster than R_1 over the whole permissible range of final temperatures. Applying the Maximum Allocation Principle to R_2 maximizes α_2 :

$$\alpha_2 = b/2, \quad \text{hence } \alpha_1 = b/2,$$

Figure 4.

i.e., the leftmost point on the interval of possible allocations (Figure 2) and $T_+ \equiv T_{\max} = T_- + b/2(Q_1 + Q_2)$, $Y^+ = (a-b/2, 0, 0)$. Since at $T_+ \equiv T_{\max}$, R_2 is still much faster than R_1 , the flame configuration is similar to case 2: pseudo-reaction $\tilde{R}_1$ at $T_{\max}$, with instant heat release $Q_1 + Q_2$.

Case 5. Genuine (stable) Competition Flame.

Here, there exists a unique T_* , $T_{\min} < T_* < T_{\max}$, where both power gauge functions are equal:

$$H_1(T_*) = H_2(T_*) ;$$

α_1 is uniquely determined by 2.17:

$$T_* \equiv T_+ = T_- + \alpha_1 Q_1 + (b - \alpha_1) Q_2 .$$

In this fuel rich context, there is genuine competition between the subnetworks R_1 and R_2 for the initial oxygen concentration.

Figure 5.

The layer analysis at T_* is entirely similar to the canonical example 1.2 of competing reactions [7], hence the genericity of the latter. To insure stability of this competition flame, we need:

$$H_2(T_{\min}) > H_1(T_{\min}) \text{ and } H_1(T_{\max}) > H_2(T_{\max}) .$$

The reasons will be made clear by the next case.

Case 6. A Non-uniqueness Case.

This is again the case of intersecting power curves at T_* , but now

$$H_2(T_{\max}) > H_1(T_{\max}) , \text{ and}$$

$$H_2(T_{\min}) < H_1(T_{\min}) .$$

We have three flame configurations possible: a competition flame at T_* (as in Case 5); sequential flames with R_2 completed at $T_{\min}$ (as in Case 3); or a pseudo-reaction $\tilde{R}_1$ with a merged single flame layer at $T_{\max}$ (as in Case 4).

Figure 6.

We conjecture that the competition flame at T_* is unstable; and that both flames at $T_{\min}$ and $T_{\max}$ are possible, depending on initial transient regimes.

The previous analysis has been done with the assumption $b/2 < a < b$, to simplify the algebra. The same cases occur for $a > b$.

3. Extending the Method to General Networks.

The detailed study of the hydrocarbon model evidences several features generic to complex networks:

- depending on whether the initial mixture is fuel rich or fuel lean, the same network can exhibit tandem (sequential) flame sheets, or genuine competition flame sheets; or merged flame sheets dominated by a single reaction (the other ones being quasi-instantaneous);
- for competition flames to occur, we need not only power gauge functions to intersect at some common temperature, but also a whole range of possible allocations; this is possible only if some deficient reactant is common to the two competing subnetworks;
- for some power gauge curves configurations, the three flame regimes are a priori possible; such as non-uniqueness can only be resolved by a dynamical stability analysis, and is reminiscent of non-uniqueness in isothermal chemical : is (hysteresis?).

With these points in mind, we will survey the extension of the method to general networks (without reversible reactions).

Remark 3.1. We consider the case of three power gauge functions intersecting at the same T_* as non-generic.

Remark 3.2. For networks with reversible reactions, another type of flame sheet can appear, where the sheet temperature locks onto the equilibrium temperature of some reversible reaction [9].

3.1 The Hierarchy of Power Rate Functions.

Let an allocation be given:

$$(3.1) \quad \underline{\alpha} = (\alpha_1, \alpha_2, \dots, \alpha_r) \quad \text{and}$$

$$(3.2) \quad T_+(\underline{\alpha}) = T_- + \sum_{i=1}^r \alpha_i Q_i \quad .$$

Our basic principle is to construct a temperature sequence

$$T_1, T_2, \dots, T_r$$

such that power gauge functions are equal along this temperature sequence. Specifically:

$$(3.3) \quad \begin{aligned} &1) \quad \text{set } T_r \equiv T_+(\underline{\alpha}) \quad ; \\ &2) \quad \text{pick the reaction } R_m \text{ which has the } \underline{\text{minimal}} \text{ power at } T_+ : \\ &\quad H_m(T_+) = \min H_i(T_+), \quad i = 1, \dots, r \quad ; \\ &3) \quad \text{define the } T_i \text{ by} \\ &\quad H_i(T_i) = H_m(T_+), \quad 1 \leq i < r, \quad i \neq m \quad . \end{aligned}$$

There exists a unique temperature sequence $\{T_i\}$ satisfying (3.3) for a given $\underline{\alpha}$; this is insured by Remark 1.1. We now reorder the reactions in order of increasing T_i , so that

$$(3.4) \quad T_1 \leq T_2 \leq \dots \leq T_r = T_+ \quad ,$$

where the new T_r corresponds to the former reaction R_r . The new sequence $\{T_i\}$ defined in (3.4) equilibrates the power rates of the reactions. It induces a hierarchy within the reactions and generates a stable chemical pathway in the flame profile. It is entirely possible that some of the T_i coincide, corresponding to competition flame sheets (cf., cases 5 and 6, section 2.4). Figure 8 shows such a configuration. Here the possible allocations are a priori nonunique, with an allowable range for α on the boundary of the convex set of allocations. T_+ and α are actually determined by setting $T_+ = T_*$, intersection of the power gauge curves of R_r and R_{r-1} , the two reactions with the smallest power gauge functions over the interval $[T_{\min}, T_{\max}]$ of possible final temperatures.

Figure 7.

To cover such a situation, let $\{\tilde{T}_i\}$, $i = 1, \dots, p \leq r$ be the possibly shorter sequence of distinct temperatures among the T_i in (3.4):

$$(3.5) \quad \tilde{T}_1 < \tilde{T}_2, \dots, < \tilde{T}_{p-1} < \tilde{T}_p = T_+;$$

we denote their number by p .

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 $\varepsilon_i + \varepsilon_j$. We also

Figure 8.

assume that at each $\tilde{T}_i$, all but perhaps two of the quantities $H_k(\tilde{T}_i)$ are distinct.

Our attempt will be to construct a combustion front in which, roughly speaking, p sets of reactions go to completion at the temperatures $\tilde{T}_i$ 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.

3.2 Suballocations to Subnetworks.

Definition 4. For each $\ell \leq p$, suballocations $\underline{\alpha}^{(\ell)}$ are defined to be allocations for the subnetwork consisting only of the R_i for $\tilde{T}_i \leq \tilde{T}_\ell$. Let k_ℓ be the number of such reactions.

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

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

$$(3.6) \quad \underline{\alpha}^{(\ell)} \leq \underline{\alpha}^{(\ell+1)}, \quad \ell = 1, \dots, p-1; \quad \underline{\alpha}^{(p)} = \underline{\alpha}.$$

There is a further condition which we shall require the $\underline{\alpha}^{(\ell)}$ to satisfy which is a generalized maximum allocation principle: Let us fix $\ell \leq p$ and $\underline{\alpha}^{(\ell-1)}$. There may be many suballocations $\underline{\alpha}^{(\ell)} \geq \underline{\alpha}^{(\ell-1)}$. We say that $\underline{\alpha}^{(\ell)}$ is "maximal" if it allocates a maximal amount of reactants to those reactions with the largest values of H at the temperature $\tilde{T}_\ell$. This, simply put, is the principle that among competing reactions, the one with the largest rate (as defined by the functions $H_i(T)$) wins out. The precise

definition is as follows. First, suppose all the quantities $H_k(\tilde{T}_\ell)$ ($\tilde{T}_\ell$ fixed) are distinct. Let k_1 be the index that yields the largest of them; then k_2 the next largest, etc. Out of all possible suballocations $\underline{\alpha}^{(\ell)} \geq \underline{\alpha}^{(\ell-1)}$, $\alpha_{k_1}^{(\ell)}$ is required to be maximal. With it known, $\alpha_{k_2}^{(\ell)}$ is then maximal, etc. In this case, $\underline{\alpha}^{(\ell)}$ is uniquely determined. Next, suppose two of the $H_k(\tilde{T}_\ell)$ coincide, say $H_{k_1}(\tilde{T}_\ell) = H_{k_2}(\tilde{T}_\ell)$. Then instead of maximizing $\alpha_{k_1}^{(\ell)}$, we maximize $\alpha_{k_1}^{(\ell)} + \alpha_{k_2}^{(\ell)}$. In this respect, we generalize the principle introduced in Sec. 2, cases 3 and 4.

For such suballocations, k_ℓ sets of reactions go to completion at $\tilde{T}_\ell$. We can now determine the temperature at which the suballocation $\underline{\alpha}^{(\ell)}$ would bring the corresponding subnetwork to equilibrium, if no reaction outside that subnetwork were present. We call it

$$(3.7) \quad \hat{T}_\ell = T_- + \sum_{i=1}^{k_\ell} \alpha_i^{(\ell)} Q_i.$$

We are now ready to give the exact mathematical criterion to select from all possible final allocations those which are feasible:

Definition 5: The allocation $\underline{\alpha}$ is feasible if

- 1) there exists for each $\ell \leq p$, suballocations $\underline{\alpha}^{(\ell)}$ which are maximal and satisfy $\underline{\alpha}^{(p)} = \underline{\alpha}$, and
- 2) $\tilde{T}_i > \hat{T}_i$ for $\forall i < p$.

The last condition insures that there is a flame front with tandem sheets traveling at the same speed. If condition (2) is not satisfied,

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 $\underline{U}^+(\underline{\alpha})$, the suballocations going to completion in the prescribed order.

Example. Consider again case 3 in the fuel rich situation of Sec. 2. There, $\underline{\alpha} = (a, b-a)$ is determined so that $\alpha_1 = a$ maximizes allocations for the reaction R_1 with maximal power over $[T_{\min}, T_{\max}]$. This fixes $T_+ \equiv T_{\min}$. The suballocation $\underline{\alpha}^{(1)} = (a, 0)$ is such that $H_1(T_1) = H_2(T_{\min})$, and

$$\underline{\alpha}^{(1)} = (a, 0) < \underline{\alpha} = (a, b-a) ;$$

the allocation is feasible if:

$$\hat{T}_1 = T_- + a Q_1 < T_1 ,$$

in which case a steady tandem profile exists.

Once feasible suballocations have been determined it remains to analyze the mathematical asymptotic limit problems, that is:

- 1) solve the various internal layer equations for each flame sheet;
- 2) determine in a self-consistent manner the transmission conditions between different sheets (in particular their geometric separation);
- 3) determine the mass flux eigenvalue M .

For details, we refer to our papers [9] and [10]. We simply remark that if only H.A.E. reactions are involved, then the last layer equation on the burned side (T_+) uniquely determines M . If this layer involves a single

pseudoreaction, 1 is given by the usual explicit formulas [17,2]. If it involves a competition flame layer, the analysis is more complex and only intrinsic formulas exist [7]. Nevertheless, successive flame sheets separations are calculated working backwards from the burned side.

3.3 Some Remarks on the Methodology for Z.A.E. Reactions.

We briefly review how our methodology extends to a mix of H.A.E. and Z.A.E. reactions on the simple chain reaction model (1.11) investigated at length by Liñan [1%]:

with $\underline{K}_1 = (Q_1, -1, +1)$, $\underline{K}_2 = (Q_2, 0, -2)$, $Q_1 > 0$, $Q_2 > 0$. The branching reaction R_1 has H.A.E. $E_1 \gg 1$; whereas the recombination reaction R_2 has Z.A.E. The initial concentration of the radical A_2 is $Y_2^- = 0$. The unique final allocation is

$$\alpha_1 = Y_1^-, \quad \alpha_2 = Y_1^-/2,$$

with final temperature $T_+ = T_- + Y_1^-(Q_1 + Q_2/2)$. Notice that the adiabatic temperature of a pure flame (1) involving only R_1 is $T_1 = T_- + Y_1^- Q_1$.

By considering the normalized power gauge functions:

$$H_1(T) = \bar{\epsilon} \left(\ln B_1 - \frac{E_1}{T} \right),$$

$$H(T) = \bar{\epsilon} \ln B,$$

$$\bar{\varepsilon} = \varepsilon_1 = \frac{T_+}{E_1} \frac{T_+}{T_+ - T_-} ,$$

and comparing them over the temperature interval $[T_1, T_+]$, we immediately exhibit the three flame structures studied by Liñan:

- 1) if $H_2 > H_1$ over $[T_1, T_+]$, there is a merged flame structure at T_+ ; the radicals do not diffuse out of the flame sheet;
- 2) if $H_1 > H_2$ over the interval, we have a pure flame (1) at T_1 , followed by very slow radical recombination; this is reflected by a suballocation:

$$\underline{\alpha}^{(1)} = (Y_1^-, 0) ,$$

- 3) if $H_1(T_*) = H_2(T_*)$ at some unique T_* in the interval, we have a competition flame situation: a thin layer at T_* for R_1 , imbedded in a thick radical flame.

The general methodology for H.A.E. plus Z.A.E. reactions will be presented elsewhere. We simply remark that the generic flame cases evidenced in Section 2 are still present, provided that one allows for thick radical flames.

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