REACTIVE-DIFFUSIVE STABILITY OF PREMIXED FLAMES WITH MODIFIED ZELDOVICH-LIÑÁN KINETICS

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Abstract. A modified version of the Zeldovich-Liñán model for chemical kinetics is found to be relatively easily studied analytically, providing information about the effect of intermediate energetic reactants on adiabatic and non-adiabatic premixed flames and their stability. The model involves an autocatalytic chain-branching reaction step and a recombination step that is first order in the concentration of intermediate species, with a rate that is independent of temperature. An asymptotic description for large activation energy of the chain-branching step takes the form of simple linear interface conditions that must hold at a free boundary, which entirely summarises the effect of the branching reaction to leading order; this contrasts with the analogous conditions that arise for a one-step model, which are highly nonlinear. Solutions in a simple reactive-diffusive formulation give insight into the buffering role that energetic intermediate reactants play through removing energy from the original fuel, as it breaks down, and releasing heat, as they are converted into final products. The mechanism for a flammability limit with this type of kinetic model is made clear as are the roles of the Lewis numbers of both fuel and intermediates in flame structure and stability.

Key words: Zeldovich-Liñán kinetics, chain-branching, intermediate kinetics, crossover temperature, free boundary, nonadiabatic premixed flame, flammability limit, flame stability.

1. INTRODUCTION

The one-step model for exothermic chemistry, in which the activation temperature is taken to be large, has provided a cornerstone for the majority of the progress that has been made so far in developing the theory of combustion (see for example [1]–[13]). The leading-order asymptotic structure that emerges, in which a thin
reaction zone can be entirely summarised through the jump conditions that it imposes on chemically inert ‘outer’ regions, offers a tractable approach that has led to transparent descriptions of many forms of flame structure, stability and behaviour.

Attempts to employ more complex models have not yet been able to explore the same range and depth of phenomena, largely because they do not offer the same degree of simplicity [9, 11, 13]. Reduced-chemistry models, mainly based on rate-ratio asymptotics [13]–[17], have been appealing in that they have helped to uncover the main roles of key species in real hydrocarbon oxidation (see Figure 1) but the models still remain relatively complex when it comes to seeking the degree of generality that analytical solutions can provide—they are of course extremely useful for numerical simulations.

The success of the one-step model can mainly be attributed to its ability to capture the essence of at least some of the main physical processes in a reacting mixture (along with other simplifying assumptions about fluid-flow or diffusive and conductive properties) with sufficient overall simplicity for analytical progress to be made. An important feature of real flames that the one-step model cannot reproduce is the role of intermediate chemical reactants [18]. As well as playing a key role in the initiation of chemical activity (usually as radical chain-branching processes overcome chemical and physical mechanisms for the removal of radicals at high enough temperatures) intermediate reactants act as a buffer between the release of chemical energy, as the original reactants are decomposed, and the generation of heat, as intermediates are converted into final products. In the one-step model fuel and oxidant are converted directly into heat.

A relatively simple generalisation of the one-step model is provided by the Zeldovich-Liñán model [19, 20]

\[
\begin{align*}
F + Z & \rightarrow 2Z : \quad k_B = A_B e^{-T_h/T} \\
Z + Z & \rightarrow 2P : \quad k_C = A_C
\end{align*}
\]

in which a fuel molecule F is catalysed by a ‘radical’ Z to produce another radical, and two radicals recombine to create the product P. The first, autocatalytic chain-branching, reaction step is considered to have a temperature-sensitive rate constant...
\( k_B(T) \) and the second, completion step, has a constant rate-constant \( k_C \). This model was first used by Zeldovich [3, 19] to describe planar premixed flames.

Kapila examined the role of a similar model under spatially homogeneous conditions [6]. Joulin et al [20] used the mechanism to model planar premixed flames in a limiting case where the conversion of radicals to products is fast compared with the time-scale for heat conduction, a case that was developed further by Chao and Law [21]. Mikolaitis [22] examined the model under more general conditions but did not examine the limit of large activation temperature of the intermediate reaction. Tam [23, 24] used an asymptotic approach which reinforced earlier results of Seshadri and Peters [25] concerning stretch resistance of laminar flames driven by kinetics of the form (1). Stability of flames was not examined.

In seeking simple analytical descriptions, one problem with the model (1) is that the recombination reaction rate is a nonlinear function of the concentration of \( Z \) even though it is independent of temperature. A seemingly minor further simplification of the Zeldovich-Liñán model, namely the reaction steps

\[
F + Z \rightarrow 2Z : k_B = A_B e^{-T_B/T} \\
Z + M \rightarrow P + M : k_C = A_C
\]

removes this problem. The symbol \( M \) represents any molecule that is needed to trigger the conversion of the intermediate reactant \( Z \) into product \( P \), but that is not changed by the reaction. The effect of these two reactions is that, at a high enough temperature (above some ‘crossover’ temperature) there can be a chain-branching growth in the concentration of intermediate species. At lower temperatures intermediate reactants are removed from the system (converted into products) too quickly for a chain-branching growth to occur. This is a well-known feature of hydrocarbon oxidation where, in homogeneous isothermal systems, a chain-branching process is observed, typically happening at temperatures above about 900 K at atmospheric pressure [18]. The first, branching reaction in (2) can be considered to occur in a thermally sensitive way with activation temperature \( T_B \).

Taking \( T_B/T \) to be large proves to be particularly effective at generating a simple asymptotic structure [19] which appears to reflect all of the main features of the model with finite, realistic values of the activation temperature [11]. Applied to flame balls [26], the asymptotic solutions reveal the role of intermediate reactants in determining both structure and stability. For premixed flames, this mechanism provides a valuable generalisation of the one step model and it is relatively simple to study asymptotically, as this article demonstrates. Although heat can be considered to be released by both reactions in (2) this article will describe only the case in which all exothermicity occurs in the second, recombination, reaction. The analysis extends relatively easily to include moderate degrees of heat generation in the branching process [27].

Another preliminary point worth making is that the species \( Z \) in (1) or (2) does not necessarily represent a single ‘radical’ species. Although we might loosely refer to \( Z \) as representing a radical, it should be thought of as representing a ‘pool’ of energetic active intermediate species (including radicals and, amongst others, hydrogen and carbon monoxide, as illustrated in Figure 1). Related work [26] has already shown that any form of thermally-sensitive production of these intermediate species (not only in chain branching reactions) generates essentially the same flame structures and the same stability properties.
2. PRODUCTION OF INTERMEDIATES

Taking the rates of the reactions in the kinetic scheme (2) to be determined by elementary kinetics, appropriate reactive diffusive conservation equations are

\[ \rho (\partial_t + \mathbf{u} \cdot \nabla) Y_F = \rho D_F \nabla^2 Y_F - W_F \omega_B \]
\[ \rho (\partial_t + \mathbf{u} \cdot \nabla) Y_Z = \rho D_Z \nabla^2 Y_Z + W_Z \omega_B - W_Z \omega_C \]
\[ \rho C_p (\partial_t + \mathbf{u} \cdot \nabla) T = \lambda \nabla^2 T + Q \omega_C - \ell \]
\[ \omega_B = A_B \frac{\rho Y_F}{W_F} \frac{\rho Y_Z}{W_Z} e^{-T_h/T}, \quad \omega_C = A_C \frac{\rho Y_Z}{W_Z} \rho \]

where \( Q \) is the energy released in converting a mole of the intermediate species into products. The molecular weights of the fuel and intermediate species are denoted by \( W_F \) and \( W_Z \), respectively, and \( A_B \) and \( A_C \) are the pre-exponential factors in the Arrhenius rate laws for the branching and completion reactions. The absolute temperature \( T(t,x) \) and the mass fractions of fuel and the intermediate reactant \( Y_F(t,x) \) and \( Y_Z(t,x) \) are functions of time \( t \) and position \( x \). For simplicity, the density \( \rho \), diffusion coefficients \( D_F \) and \( D_Z \), the mean molecular weight \( W \), the specific heat \( C_p \) and the thermal conductivity \( \lambda \) are all taken to be constant. The fluid velocity is \( \mathbf{u} \) and \( \ell \) represents the rate of heat loss to infinity by radiation. For a planar flame travelling along an \( x \)-axis from large positive values of \( x \), suitable ‘unburnt’ boundary conditions are

\[ \lim_{x \to -\infty} (Y_F, Y_Z, T) = (Y_{F0}, 0, T_0). \]

2.1. Crossover temperature in a homogeneous system

In a spatially uniform system, the mass fraction of the intermediate species \( Z \) satisfies

\[ \frac{dY_Z}{dt} = \rho Y_Z \left( \frac{A_B}{W_F} Y_F e^{-T_h/T} - \frac{A_C}{W} \right) \]

which makes it clear that an equilibrium at \( Y_Z = 0 \) is unstable if the right hand side is positive for small positive values of \( Y_Z \) and is stable if the right side is negative. This identifies a critical ‘crossover temperature’ \( T_c \) at which

\[ e^{T_h/T_c} = \frac{W A_B}{W_F A_C} Y_{F0}. \]

In a homogeneous mixture, small concentrations of \( Y_Z \) will grow with time provided \( T > T_c \). Hydrocarbon reactions typically display a similar form of crossover behaviour [9], with radical production being very slow below a temperature of about 900 K at atmospheric pressure [18]. It is interesting to note that, for unburnt temperatures \( T_0 \) that are below the crossover temperature \( T_c \), the two-step kinetic model (2) does not suffer from the so called ‘cold boundary difficulty’ of the one-step model. This is not true of the Zeldovich-Liñán model (1).

2.2. Crossover temperature with diffusive removal of intermediates

In a spatially varying system, the diffusive removal of intermediate reactants must also be taken into account. Production and consumption of intermediates satisfy

\[ (\partial_t + \mathbf{u} \cdot \nabla) Y_Z = \rho Y_Z \left( \frac{A_B}{W_F} Y_F e^{-T_h/T} - \frac{A_C}{W} \right) + D_Z \nabla^2 Y_Z \]
in which the Laplacian of $Y_Z$ appears. Generally speaking, the maximum concentration of intermediate species arises where they are produced most strongly so that, at this point, the Laplacian of $Y_Z$ should be negative. Hence, in a spatially varying system, the latter term removes intermediates, making it more difficult to sustain the chain-branching process; temperatures around the crossover temperature $T_c$ are no longer enough.

Instead, a higher ‘branching temperature’ $T_b$ should characterise the stage at which significant chain branching activity takes place. In order to estimate the value of $T_b$, it is useful to define $\theta = T_b/T_a$ and to consider $\theta$ to be large for large activation temperatures $T_B$. As a point of reference, it is worth noting that the activation temperature of the rate-limiting chain-branching reaction $H + O_2 \rightarrow OH + O$ [18] is very nearly 8500 K.

To begin with, because $\frac{d}{dt} e^{-T_b/T} = \frac{T_b}{T^2} e^{-T_b/T}$, changes in temperature of the order of $\theta^{-1}$ about $T_b$ must change the Arrhenius factor $e^{-T_b/T}$ by an order one amount. If temperatures increase much above $T_b \times (1 + O(\theta^{-1}))$ the Arrhenius factor $e^{-T_b/T}$ increases considerably so that values of $Y_F$ must decrease to very small values, bringing the branching reaction to a halt. At temperatures much below $T_b \times (1 - O(\theta^{-1}))$ the factor $e^{-T_b/T}$ becomes very small, effectively freezing the reaction. Thus, the branching reaction is only likely to be significant in a relatively narrow range of temperatures around $T_b$, namely where $T - T_b = O(T_b/\theta)$. Outside this range, the conservation equation for intermediate species has the approximate form

$$\left( \frac{\partial}{\partial t} + u \cdot \nabla \right) Y_Z \approx D_Z \nabla^2 Y_Z - \rho \frac{A_C}{W} Y_Z$$

(8)

with the first term on the right hand side representing diffusion of intermediate reactants and the second representing the rate of their chemical conversion into products and heat. A natural length scale $r_s$ for consumption and diffusion of intermediates is therefore arrived at by balancing the terms on the right of this equation, giving

$$r_s^2 \approx \frac{D_Z W}{\rho A_C}.$$ 

(9)

Because the completion reaction also generates heat, which has a diffusivity $\lambda/(\rho C_p)$ that should be of the same order of magnitude as the diffusivity of the intermediate species $D_Z$, temperatures can be expected to change by the order of $T_b$ over a similar length scale.

The length scale of the region in which chain branching chemistry is active, where temperatures change by about $T_F/\theta$, should therefore be approximately $r_s/\theta$. Likewise, anticipating that $Y_F$ changes by the order of $Y_{F0}$ over the length scale $r_s$, we would expect to also find $Y_F \approx Y_{F0}/\theta$ where the branching reaction is active in equation (7). Finally, because the concentration of intermediate species must be highest where they are produced, values of $Y_Z$ will only change by an amount of order $Y_Z/\theta$ in the same region.

The dominant terms in this region must be the branching reaction rate and the diffusion term in equation (7), which therefore lead to the balance

$$\theta^2 e^{T_b/T_b} \approx \frac{W A_B}{W_F A_C} Y_{F0}.$$ 

(10)
Figure 2. The branching temperature $T_b$ and the dimensionless activation energy $\theta$ as functions of the activation temperature $T_B$ for a fixed crossover temperature of $T_c = 900\,\text{K}$.

Using equation (6) and the definition $\theta = T_B/T_b$ this can be expressed as

$$\theta^2 e^\theta \approx e^{T_B/T_c} \quad \text{or} \quad \frac{T_B}{T_c} - \frac{T_B}{T_b} \approx 2 \ln \frac{T_B}{T_b}, \quad (11)$$

For values of $T_B$ that are much larger than the temperature $T_b$, about which chain branching is able to compete with the diffusive removal of intermediates, this relation shows that $T_b$ must exceed the crossover temperature $T_c$ by about $T_c \theta^{-1} \ln \theta^2$.

Solving equation (11) for $T_b$ at different values of $T_B$, with $T_c$ fixed at 900 K, leads to the variations plotted in figure 2 for both $T_b$ and $\theta$. It is interesting to note that the value of the branching temperature $T_b$ is about 1400 K (and $\theta \approx 6$) when the activation temperature for branching $T_B$ has the realistic value of 8500 K. This temperature also typifies the adiabatic flame temperature of hydrocarbon flames near their flammability limit [18].

2.3. Branching reaction region

The governing equations (3) can be made dimensionless by using the rescaling

$$t = t_s t', \quad x = r_s x', \quad T = T_b T', \quad Y_F = Y_{F0} F, \quad Y_Z = Y_{Z0} Z \quad (12)$$

along with the definitions

$$r_s^2 = \frac{D_Z W}{\rho A_C}, \quad t_s = \frac{\rho C_p}{\lambda} r_s^2, \quad u = \frac{r_s}{t_s} u', \quad \ell = \frac{\rho C_p T_b}{t_s} (1 - T'_0) \ell'$$

$$Q = \frac{C_p T_b W_F}{Y_{F0}} (1 - T'_0) Q', \quad \theta^2 e^\theta = \frac{W A_B}{W_F A_C} Y_{F0}, \quad T_b = T_B / \theta \quad (13)$$

$$L_E = \frac{\lambda}{\rho C_p D_F}, \quad L_Z = \frac{\lambda}{\rho C_p D_Z}, \quad Y_{Z0} = \frac{L_E W_Z Y_{F0}}{L_E W_F Y_{F0}}, \quad T_b = T_b T'_0$$
which (after dropping the primes) lead to
\[
\text{Le}_F \left( \partial_t + u \cdot \nabla \right) F = \nabla^2 F - \theta^2 FZk(T) \\
\text{Le}_Z \left( \partial_t + u \cdot \nabla \right) Z = \nabla^2 Z + \theta^2 FZk(T) - Z \\
\left( \partial_t + u \cdot \nabla \right) T = \nabla^2 T + (1 - T_0) \left( \frac{Q}{\text{Le}_F} Z - \ell \right)
\]
\[k(T) = \exp \left( \theta \left( 1 - 1/T \right) \right) \tag{14}\]

The branching reaction is dominant, having \( \theta^2 FZk(T) = O(\theta) \), in a narrow region where the dimensionless temperature is \( T = 1 \pm O(\theta^{-1}) \) and \( F = O(\theta^{-1}) \). In this region, the diffusion terms balance the branching reaction.

For large values of \( \theta \), it is fairly straightforward [26] to arrive at the leading order conditions which this inner branching region must impose, through matching, on an outer region in which the branching reaction remains inert. These take the form of conditions that must hold at and across an interface or free boundary, effectively a ‘reaction sheet’. They can be summarised as requiring that: the quantities \( T, F, Z, \nabla T \) and \( \nabla (F + Z) \) all remain continuous\(^1\); to leading order, temperature takes the value \( T = 1 \) at the free boundary; and the fuel is used up so that \( F = 0 \). However, if temperature has a maximum value of unity at the reaction sheet (so that \( \nabla T = 0 \)) fuel can leak through the sheet allowing non-zero values of \( F \). All of these conditions are expressed in more mathematical form in the next subsection.

### 2.4. Branching reaction-sheet model

In a final rescaling, it is convenient to scale the unburnt temperature \( T_0 \) out of the problem. For this we define
\[
T = T_0 + (1 - T_0)T.
\]
\[\tag{15}\]

We can take the branching reaction to occur at a sheet of reaction \( \Gamma(t) \subset \mathbb{R}^3 \), with a normal coordinate \( n \) defined at any point on the sheet (chosen, for convenience, to increase into the colder unburnt mixture). At any point that is not in the sheet \( x \notin \Gamma \) the branching reaction rate can be taken to be negligible so that the fuel, intermediate reactant and temperature satisfy
\[
\text{Le}_F \left( \partial_t + u \cdot \nabla \right) F = \nabla^2 F \\
\text{Le}_Z \left( \partial_t + u \cdot \nabla \right) Z = \nabla^2 Z - Z \\
\left( \partial_t + u \cdot \nabla \right) T = \nabla^2 T + \frac{Q}{\text{Le}_F} Z - \ell.
\]
\[\tag{16}\]

At and across the reaction-sheet, the conditions described earlier can be represented by
\[
[T] = [F] = [Z] = [T_n] = [F_n] + [Z_n] = T - 1 = FT_n = 0
\]
\[\tag{17}\]

in which \([ \cdot ]\) represents the difference in value of a quantity evaluated at \( n = 0^+ \) and at \( n = 0^- \). When carried to higher asymptotic orders [26] for large values of \( \theta \) only

\(^1\)If the branching reaction is either exothermic or endothermic, then \( \nabla(T + qF) \) rather than \( \nabla T \) remains continuous, where \( q \) is a dimensionless parameter measuring the heat released in the branching reaction [27].
the condition \( T - 1 = 0 \) is altered.\(^2\)

The last condition \( FT_n = 0 \) in (17) would normally be replaced by \( F = 0 \) because, in most practical cases, the temperature should increase above unity through the sheet (requiring \( T_n < 0 \)). Alternatively, if \( F \neq 0 \) at the sheet, the condition amounts to requiring that \( T_n = 0 \). Thus the condition \( FT_n = 0 \) represents two alternative linear conditions at the sheet. In fact, remarkably, if \( \ell \) and \( u \) are assumed to be suitably specified, all of these equations and boundary conditions can be seen to be linear in the dependent variables \( F, Z \) and \( T \). This makes them eminently suitable for analytical study.

3. PLANAR NONADIABATIC FLAMES AND THEIR STABILITY

To illustrate the utility of this model we can propose a linear model for heat loss by defining \( \ell = aT \), parameterised by \( a \geq 0 \). A planar flame travelling in the negative \( x \) direction at speed \( S \) would then be a steady solution of the equations

\[
\begin{align*}
\text{Le}_F(F_t + SF_x) &= \nabla^2 F \\
\text{Le}_Z(Z_t + SZ_x) &= \nabla^2 Z - Z \\
T_t + ST_x &= \nabla^2 T - aT + QZ/\text{Le}_F
\end{align*}
\]

along with the conditions to be applied at a branching reaction-sheet (at say \( x = 0 \))

\[
[T] = [F] = [Z] = [T_x] = [F_x] + [Z_x] = T - 1 = FT_x = 0.
\]

Boundary conditions far ahead and far behind the flame can be specified as

\[
\lim_{x \to -\infty} (F, Z, T) = (1, 0, 0), \quad \lim_{x \to \infty} (F_x, Z, T_x) = (0, 0, 0).
\]

In fact the steady solutions are precisely

\[
F = F_0(x) = \begin{cases} 1 - e^{\text{Le}_p S x} & \text{for } x < 0 \\ 0 & \text{for } x > 0 \end{cases}
\]

\[
Z = Z_0(x) = \frac{\text{Le}_p S}{\gamma_1 + \gamma_2} \begin{cases} e^{\gamma_1 x} & \text{for } x < 0 \\ e^{-\gamma_2 x} & \text{for } x > 0 \end{cases}
\]

\[
T = T_0(x) = \frac{QS}{\gamma_1 + \gamma_2} \begin{cases} \frac{\gamma_1 + \gamma_2}{\mu_1 + \mu_2} \frac{e^{\mu_1 x}}{(\gamma_1 - \mu_1)(\gamma_2 + \mu_1)} - \frac{e^{\gamma_1 x}}{(\gamma_1 - \mu_1)(\gamma_1 + \mu_2)} & \text{for } x < 0 \\ \frac{\gamma_1 + \gamma_2}{\mu_1 + \mu_2} \frac{e^{-\mu_2 x}}{(\gamma_2 - \mu_2)(\gamma_1 + \mu_2)} - \frac{e^{-\gamma_2 x}}{(\gamma_2 - \mu_2)(\gamma_2 + \mu_1)} & \text{for } x > 0 \end{cases}
\]

in which \( S \) is, as yet, an unknown parameter. The remaining constants are

\[
\gamma_{1,2} = \frac{1}{2} \left( \sqrt{4 + \text{Le}_Z^2 S^2} \pm \text{Le}_Z S \right), \quad \mu_{1,2} = \frac{1}{2} \left( \sqrt{4a + S^2} \pm S \right)
\]

all being positive (apart from \( \mu_2 \) which is zero only if \( a = 0 \)).

\(^2\)When \( T_n \) and \( Z \) are of order one at the reaction sheet, the temperature at the sheet may vary by an amount of order \( \theta^{-1} \) about \( T = 1 \). If the maximum temperature occurs at the sheet, so that an order one concentration of fuel \( F \) survives the branching reaction (other quantities also having order one values) then the temperature varies by the order of \( \theta^{-1} \) about \( T = 1 - \theta^{-1} \ln \theta^{3/2} \). The dimensional temperature at the reaction sheet is then fairly close to the homogeneous ‘crossover’ temperature \( T_c \).
These solutions already satisfy all of the conditions (19) and (20) apart from setting \( T - 1 = 0 \) at the branching reaction-sheet. Imposing the condition \( T_0(0) = 1 \) yields the formula

\[
Q S \left( \frac{\gamma_1 + \gamma_2}{\gamma_2 + \mu_1} - \frac{\mu_1 + \mu_2}{\gamma_1 + \mu_2} \right) = (\gamma_1 + \gamma_2)(\mu_1 + \mu_2)(\gamma_1 - \mu_1)
\]

Figure 3. The dependence of the planar flame speed \( S \) on the heat-loss parameter \( a \) for selected values of the Lewis number of the intermediate \( \text{Le}_Z \) and the heat of reaction \( Q \).

from which the flame speed \( S \) can be calculated, as plotted in Figure 3. Interestingly, the flame speed does not depend on the Lewis number of the fuel \( \text{Le}_F \), even dimensionally, as can be seen from the scalings (12)–(13). The fact that temperatures must reach \( T = 1 \) at the branching-sheet effectively requires that solutions can only exist for \( Q > 1 \) (representing a flammability limit). In this range, upper and lower branches of solution exist provided the heat-loss parameter \( a \) is below a maximum value at which the upper and lower branches meet in a turning-point bifurcation.

Figure 3 presents flame speeds over a wide range of values of \( \text{Le}_Z \) and \( Q \). Realistic values of the intermediate Lewis number \( \text{Le}_Z \) are likely to be similar to or below the Lewis number of the fuel \( \text{Le}_F \), which in turn can be expected to be of order unity. Also, since maximum flame temperatures rarely exceed about 2500 K, taking the unburnt temperature to be \( T_0 \approx 300 \) K and the branching-reaction temperature to be \( T_b \approx 1400 \) K suggests that realistic values of \( Q \) are likely to be below about two. However, values of \( Q \) would increase for higher unburnt temperatures \( T_0 \). It is worth observing that the maximum value of the heat-loss parameter \( a \) grows approximately like \((Q - 1)^2\) while the maximum flame-speed \( S \) (found for \( a = 0 \)) increases approximately linearly with \( Q - 1 \). Also, the maximum flame-speed and the maximum heat-loss parameter both increase when \( \text{Le}_Z \) is decreased. Lighter intermediate reactants (having increased diffusivity) therefore aid the propagation of planar flames.

### 3.1. Stability

For small-amplitude disturbances with a wavenumber of \( k \) and growth rate \( \lambda \), linear stability can be examined by assuming that the interface is at \( x = e^{\lambda t + iky} \).
(taken to be very small in magnitude) and by assuming that

$$T = T_0 + e^{\lambda t + iky} T_1(x), \quad F = F_0 + e^{\lambda t + iky} F_1(x), \quad Z = Z_0 + e^{\lambda t + iky} Z_1(x).$$

(24)

The equations to be satisfied by $T_1(x)$, $F_1(x)$ and $Z_1(x)$ are then

$$F''_1 - \text{Le}_F SF'_1 - (\text{Le}_F \lambda + k^2) F_1 = 0$$
$$Z''_1 - \text{Le}_Z SZ'_1 - (\text{Le}_Z \lambda + k^2 + 1) Z_1 = 0$$
$$T''_1 - ST'_1 - (\lambda + k^2 + a) T_1 = -QZ_1/\text{Le}_F$$

(25)

in which it can be assumed that $F_1 \equiv 0$ for $x > e^{\lambda t + iky}$. Suitable boundary conditions at infinity are

$$\lim_{x \to \infty} (T_1, F_1, Z_1) = (0, 0, 0), \quad \lim_{x \to \infty} (T_1, Z_1) = (0, 0)$$

(26)

and the jump conditions at $x = 0^\pm$ become

$$[T_0' + T_1] = [F_0' + F_1] = [Z_0' + Z_1] = 0$$
$$[T_0'' + T_1'] = [F_0'' + F_1'] + [Z_0'' + Z_1'] = T_0' + T_1 = 0.$$  

(27)

Solutions are

$$F_1(x) = \begin{cases} \text{Le}_F S e^{\nu x} & \text{for } x < 0 \\ 0 & \text{for } x > 0 \end{cases}$$

$$Z_1(x) = \frac{\text{Le}_F S}{\gamma_3 + \gamma_4} \begin{cases} (\Gamma - \gamma_4) e^{\gamma_4 x} & \text{for } x < 0 \\ (\Gamma + \gamma_3) e^{-\gamma_4 x} & \text{for } x > 0 \end{cases}$$

$$T_1(x) = \frac{QS}{\gamma_3 + \gamma_4} \begin{cases} \frac{\Gamma - \gamma_4}{\gamma_3 - \mu_3} \left( \frac{e^{\mu_3 x}}{\mu_3 + \mu_4} - \frac{e^{\gamma_3 x}}{\gamma_3 + \mu_4} \right) + \frac{\Gamma + \gamma_3}{\gamma_4 + \mu_4} \left( \frac{e^{-\mu_4 x}}{\mu_3 + \mu_4} - \frac{e^{-\gamma_4 x}}{\gamma_4 + \mu_4} \right) & \text{for } x < 0 \\ \frac{\Gamma - \gamma_4}{\gamma_3 + \mu_4} \left( \frac{e^{-\mu_4 x}}{\mu_3 + \mu_4} - \frac{e^{-\gamma_4 x}}{\gamma_4 + \mu_4} \right) & \text{for } x > 0 \end{cases}$$

(28)

in which

$$\nu = \frac{1}{2} \left( \sqrt{4(\text{Le}_F \lambda + k^2) + \text{Le}_F^2 S^2 + \text{Le}_F S} \right)$$
$$\Gamma = (\text{Le}_F - \text{Le}_Z) S - \nu$$
$$\gamma_{3,4} = \frac{1}{2} \left( \sqrt{4(\text{Le}_Z \lambda + k^2 + 1) + \text{Le}_Z^2 S^2 + \text{Le}_Z S} \right)$$
$$\mu_{3,4} = \frac{1}{2} \left( \sqrt{4(\lambda + k^2 + a) + S^2 + S} \right)$$

subject to the dispersion relation

$$\Gamma - \gamma_4 \left( \frac{\mu_3 + \mu_4}{\gamma_3 + \mu_4} - 1 \right) - \frac{\Gamma + \gamma_3}{\gamma_4 + \mu_3}$$
$$= \frac{1}{2} \frac{(\gamma_3 + \gamma_4)(\mu_3 + \mu_4)}{(\gamma_1 + \gamma_2)(\gamma_1 - \mu_1)} \left( \frac{1}{\mu_1 + \mu_2 \gamma_2 + \mu_1} - \frac{1}{\gamma_1 + \mu_2} \right).$$

(30)

For some parameter values, positive real growth rates $\lambda > 0$ are found to exist within a limited range of wavenumbers around $k = 0$. At marginal stability this range shrinks towards $k = 0$ where there is always a neutral eigenvalue $\lambda = 0$.

Under adiabatic conditions, when $a = 0$, Figure 4 presents the range of conditions where stability and instability arise. Each curve represents conditions for marginal (or neutral) stability at a fixed Lewis number of the intermediate species. The curves
Figure 4. Stability boundaries under adiabatic conditions \((a = 0)\) in the plane of fuel Lewis number \(\text{Le}_F\) and heat of reaction \(Q\) for varying Lewis numbers of the intermediate species \(\text{Le}_Z\).

Figure 5. Stability boundaries on the upper-branch of solutions in Figure 3 under nonadiabatic conditions \((0 \leq a \leq a_c)\) in the plane of fuel and intermediate Lewis numbers, \(\text{Le}_F\) and \(\text{Le}_Z\), for selected heats of reaction \(Q > 1\) and fixed values of \(\sqrt{a/a_c}\).
for \( \frac{1}{2} \leq \text{Le}_Z \leq 1 \) are likely to be the most relevant for real hydrocarbon flames and it is interesting to note that there is not a great deal of variation within this range, especially at smaller heats of reaction where \( Q \leq 2 \). Increasing \( Q \) has a stabilising effect, as does increasing \( \text{Le}_F \) or decreasing \( \text{Le}_Z \). As is the case for flames described using a one-step model for the chemistry, this ‘cellular’ form of instability only arises for \( \text{Le}_F < 1 \) under adiabatic conditions.

Under nonadiabatic conditions, Figure 5 shows how the neutral stability boundaries change in the space of the two Lewis numbers at selected heats of reaction \( Q > 1 \). In order to highlight the effect of heat losses when \( a \) is near zero, these are plotted for various values of \( \sqrt{a/a_c} \) (ranging between zero and one) where \( a_c \) is the maximum value of \( a \), at which the upper and lower branches of flame-speed merge. At \( a = a_c \) (and throughout the lower branch of flame-speeds) the flame is also unstable to planar (zero-wavenumber) disturbances. It can be noted that, especially at moderate values of \( Q \leq 2 \), changes in stability are more sensitive to changes in \( \text{Le}_F \) than in \( \text{Le}_Z \). It can also be noted that, for \( Q \geq 2 \), flames can be stable even for very small values of \( \text{Le}_F \), provided \( \text{Le}_Z \) is also suitably small. However, when \( \text{Le}_Z > 1 \), large enough heat losses can also induce cellular instability for fuel Lewis numbers greater than unity. This does not happen under adiabatic conditions.

4. CONCLUSIONS

The modified Zeldovich-Liñán kinetic scheme (2) offers a relatively simple means for the asymptotic description of premixed flames in which the effect of energetic intermediate reactants is taken into account. Unlike the one-step model, which gives rise to intrinsically nonlinear interface conditions at a reaction sheet, the scheme (2) gives rise to linear interface conditions (to leading order for a large activation temperature of the branching reaction). There is still a form of nonlinearity inherent in the mere presence of a free boundary, as evidenced by the existence of multiple solutions and fold bifurcations even when all equations, boundary and interface conditions are formulated to be completely linear. Nonlinear interface conditions do arise at higher order in the asymptotics [26, 27] but it appears that the major features of adiabatic and nonadiabatic premixed flames can all be captured by a straightforward leading-order description that also includes at least some of the effects of intermediate kinetics.

The asymptotic arguments highlight the fact that there must be a distinction between the ‘crossover temperature’ above which radical production exceeds its rate of chemical consumption (leading to acceleration of a reaction in homogeneous systems [17, 18]) and the temperature that characterises radical chain-branching in premixed flames. In the latter case, diffusive removal of radicals is actually much stronger than their rate of chemical removal and requires a higher temperature for chain branching to be sustained.

This article has summarised the main features of the modified Zeldovich-Liñán scheme (2) when used to describe nonadiabatic planar premixed flames, in a reactive-diffusive formulation with linear heat-loss. The results provide a more general picture than is possible using one-step kinetics; qualitatively similar forms of multiple flame-speed arise at fixed values of a heat-loss parameter, but the origin of these is distinctly different. A firm flammability limit arises if the heat of reaction \( Q \) is decreased towards unity; the details of this limit would be modified (allowing \( Q \) to drop slightly below unity) if higher order effects were taken into account [27].
results also reveal the interplay between the two Lewis numbers, heat loss and heat of reaction in determining the conditions for the emergence of cellular instability.

REFERENCES


