TRAVELLING WAVES IN THE COOL FLAME REGIME

22.1 Introduction

Hydrocarbon oxidation develops through a complex network of elementary steps. Depending on the initial thermodynamic conditions, different behaviours are observed ranging from slow combustion to hot ignition [1]. Chain reactions involving radicals, govern all the combustion processes. Most of the time, the operating kinetic mechanism can be approximated by a reduced kinetic scheme which is depending on the initial conditions. In an intermediate range of temperature, cool flames appear as a transition between slow combustion and hot ignition. The existence of cool flames is often associated with knocking in engines.

Cool flames were observed for the first time very early by Davy [2] and many studies have been devoted to determining their chemistry. It appears now clearly that these flames are characterized by a chain branching mechanism [3]. Cool flames associated with the oxidation of organic substrates sometimes take the form of transient oscillatory phenomena [4]: pressure pulses have been detected in closed vessels, and several luminous waves have been observed in an open tube. This periodic character was a strong motivation of the fundamental studies of cool flames [4]. Despite some experimental works considering cool flames as reactive waves [5,6,7], most of the efforts of the theoretical and experimental studies have been devoted to identifying the chemical mechanism of this incomplete combustion regime [8,9] with the objective in mind of describing the dynamical behaviour of this incomplete combustion regime in spatially homogeneous conditions as in well stirred reactors [4].

The purpose of this paper is to clarify the propagation mechanisms of cool flames which can be anticipated to be quite different from the ordinary hot flames which have been well described by the pioneering theoretical work of Zeldovich & Frank Kamenetskii [14] and by more advanced theoretical studies developed recently to take into account the effects of a complex chemistry as for example for hydrogen-oxygen [17,18] or hydrogen-halogens [19] or hydrocarbon-air [20] mixtures. Travelling waves are resulting from the coupling of heat and
species molecular diffusion transfer mechanisms with the particular chemical kinetics associated with cool flames. The present study is carried out in the framework of the Fick and Fourier laws for the diffusion transfer and of the kinetic model proposed by Gray & Yang [8] which has been proved to represent well the main properties of cool flames observed in well stirred reactors [6,10,11].

The paper is structured as follows. The Gray & Yang model [8] is presented in the next section. The theoretical background of reaction diffusion waves is recalled in the following section. Then, the problem of the propagation of cool flame is formulated. The nature of the solutions of the corresponding equations as well as the resulting flame structure are analyzed for a given pressure in terms of the temperature of the initial mixture. Analytical expressions for the flame speed are provided in two limiting cases for relatively small and relatively high temperature. In the first limiting case, the propagation mechanism is of a nature similar to the case studied in a hot flame context by Zeldovich & Frank-Kamenetskii [14] (ZFK). But in the second limiting case, the nature of the travelling waves is similar to the case studied by Kolmogorov, Petrovskii & Piskunov [13] (KPP) in a biological context. As shown by a numerical analysis, these two analytical expressions are in most of the cases sufficient to cover the whole range of the initial temperatures.

22.2 Gray-Yang model

Cool flame phenomena have been characterized in closed vessels and well stirred reactors [6,10,11] by the following properties:

(i) They occur during the oxidation process of most hydrocarbons, in the range of temperature of 500-800°K, with a weak exothermicity (ΔT=50-200°K). The temperature rise is of kinetic significance but does not lead to the thermal runaway,

(ii) They correspond to an incomplete combustion.

(iii) A faint blueish luminescence characterizing the excited formaldehyde radical is observed.

(iv) More than one cool flame may occur in succession [1].

(v) They are characterized by an autocatalytic kinetic mechanism selfdecelerated with the increase in temperature. Selfquenching of an autocatalytic process associated with a negative temperature coefficient of the reaction rate, is rather unique and is considered as the main characteristic of cool flames.

These peculiar properties are the result of a very complex real chemistry [3]. A reduced kinetic model proposed by Gray & Yang [8] has been proved to be successful in representing the main characteristics of cool flames. This thermokinetic model has been partially justified for the acetaldehyde oxidation [9,10]. The backbone of skeleton is a weakly exothermic chain branching reaction (Q_b>0) with a moderate activation energy (activation temperature T_{ba}=3500°K). This chain branching reaction competes with two chain breaking reactions. The first one, which is very exothermic (Q_1>Q_b), presents a high activation energy
Figure 22.1. Temperature dependence of the logarithm of the rate constants of scheme (I) used by Gray & Yang [8].

(T_{ia}=8000^\circ K>T_{ba}) and is responsible for the quenching of the overall reaction at high temperature (T>T_*) above a cross-over temperature $T^*=710^\circ K$ corresponding roughly to the equality of the two rate constants $K_b$ and $K_{c1}$ (see Figure 22.1). The second chain breaking reaction, which is athermic ($Q_2=0$) with a zero activation energy ($E_2=0$), quenches the reaction at low temperature under an ignition temperature $T_1=550^\circ K$ which corresponds roughly to $K_b=K_{c2}$ (see Fig. 22.1). The radical can also be generated by an initiation reaction which has a very high activation energy ($T_{ia}=12000^\circ K$). The reduced kinetic scheme is written as:

Initiation (i): $A \rightarrow X + Q_1$, $T_{ia} = 12000^\circ K$ (1a)

Chain branching (b): $A + X \rightarrow 2X + Q_b$, $T_{ba} = 3500^\circ K$ (1b)

Chain breaking (c1): $X \rightarrow P_1 + Q_1$, $T_{1a} = 8000^\circ K$ (1c)

Chain breaking (c2): $X \rightarrow P_2 + Q_2$, $T_{2a} = 0^\circ K$ (1d)
The rate constants (of the reaction $j$) used by Gray & Yang are plotted in Fig. 22.1 and are represented by Arrhenius law

$$K_j = B_j \exp(-T_{ja}/T)$$  \hspace{1cm} (1e)$$

where $B_j$ and $T_{ja}$ are respectively the prefactor and the activation temperature of the reaction $j$. $X$ is a radical and $P_1$, $P_2$ are products considered as inert species. The reactant $A$ is considered to be largely in excess and the variation of its concentration can be neglected during the cool flame. The limiting process of the reaction is not the consumption of the reactant $A$ but the quenching mechanism at high temperature ($T>T^*$) produced by the chain breaking reaction (c1). The activation temperature $T_{ia}$ of the initiation reaction (i) being much higher than the one of reaction (b), the effect of (i) upon the flame propagation can be neglected and the mechanism of propagation is sustained by the molecular diffusion of the autocatalytic carriers $X$ which are produced by the chain branching reaction (b).

Before presenting the results concerning the travelling waves sustained by the kinetic scheme (1) it is worthwhile to recall some general results of travelling waves.

22.3 Reaction diffusion waves

The simplest model for a planar reaction diffusion wave consists of a single nonlinear reaction diffusion equation for a scalar $\theta$ which represents either the reduced temperature or the reduced mass fraction of the reaction products ($1-\theta$ is the reduced mass fraction of the reactant). In the moving frame of the reaction front, this equation takes the form

$$M\theta \xi' - \theta'' \xi = W(\theta) \geq 0$$  \hspace{1cm} (2)$$

with the following boundary conditions

$$\xi \to -\infty: \theta = 0 \text{ and } \xi \to +\infty: \theta = 1$$  \hspace{1cm} (3)$$

where the initial condition ($\theta = 0$) corresponds to an unstable steady state $W(\theta=0) = 0$ but $(dW/d\theta \mid \theta=0) > 0$ and the final state is a stable equilibrium state $W(\theta=1) = 0$ and $(dW/d\theta \mid \theta=1) < 0$.

Equation (2) describes a wave propagating into the initial state with a constant speed $M$ appearing as an eigenvalue of the problem and depending on the form of the nonlinear reaction rate $W$. The diffusion coefficient and the characteristic reaction time have been incorporated in the definition of the nondimensional space variable $\xi$. Two pioneering analyses of such an equation have been carried out independently by ZFK [14] in a combustion context and by KPP [15] in a biological context. These two studies differ only in the form of the reaction rate $W(\theta)$. The one used by KPP is of a convex type as for the quadratic term associated with an autocatalytic reaction.
and it corresponds to a weak nonlinearity. The one used by ZFK for premixed flames is a stiff nonlinear term characterized by an Arrhenius law with a high value of the reduced activation energy \( \beta \):

\[
W(\theta) = (\beta^2/2)(1-\theta)(e^{-\beta(1-\theta)}-e^{-\beta}).
\] (4b)

The factor \( \beta^2/2 \) is used here for convenience in order to make the reduced flame speed \( M \) of order unity in the asymptotic limit \( \beta \to \infty \).

The term \( e^{-\beta} \) in the r.h.s. is introduced to eliminate the cold boundary difficulty, but does not play any role from a physical point of view as soon as the number \( \beta \) is large enough. The KPP result shows that there is a continuous set of solutions for \( M \), bounded by a minimum value \( M_{\text{KPP}} \), proportional to the square root of \( dW/d\theta |_{\theta=0} \). This minimum speed which can be obtained in this case by linearization of the problem around the initial condition, is the relevant one because it has been proved to be the one selected asymptotically in time for a large class of physical initial conditions [13,16]. The result obtained by ZFK for the reaction rate (4b) with an asymptotic analysis \( \beta \to \infty \), consists in a single solution with a value \( M_{\text{ZFK}} \) proportional to the square root of \( dW/d\theta |_{\theta=0} \). In the limit \( \beta \to \infty \), the major part of the reaction rate is localized around the final equilibrium state \( \theta=1 \) and the flame speed is found to be controlled by the reaction rate of the final state. In fact for finite values of \( \beta \), the spectrum of the possible solutions for \( M \) is also continuous with a minimum flame speed which tends to \( M_{\text{ZFK}} \) in the limit \( \beta \to \infty \). Here also this minimum speed is proved to be the relevant one [16] but the corresponding solution is of a different nature from the KKP case. By noticing that for small \( \beta \), the reaction rate eqn. (4b) reduces to a form similar to eqn. (4a), the transition in the solutions of eqns. (2) and (4b) has been described [15] when \( \beta \) varies from 0 to \( \infty \) connecting the KPP solution to the ZFK one.

In the theoretical study of the propagation of cool flames presented below, a somewhat similar transition will be observed when initial temperature of the fresh mixture varies.

22.4 Travelling waves in the cool flame regime

Steady and planar travelling waves sustained by the Gray-Yang model (1) in which the initiation reaction (i) is neglected, are governed by a system of two coupled reaction-diffusion equations for the reduced temperature \( \phi \) and the reduced mass fraction \( X \) of the chain carrier which can be written in an adimensional form as:

\[
\begin{align*}
  m\phi'_{\chi} - \phi''_{\chi\chi} &= Q(\phi)X, \\
  mX'_{\chi} - (1/Lc)X''_{\chi\chi} &= W(\phi)X
\end{align*}
\] (5a) (5b)
with

\[ W(\phi) = \exp(b\phi) - \exp(\phi) - k \quad (6a) \]

and

\[ Q(\phi) = (a \exp(b\phi) + \exp(\phi)) \quad \text{where } a = (Q_a/Q_1) < 1 \quad \text{and } b = (T_{ba}/T_{1a}) < 1, \quad (6b) \]

and with the boundary conditions:

- initial condition \( x \to -\infty: X = 0 \) and \( \phi = \phi_0 < 0 \) which is given \( (7) \)
- final state \( x \to +\infty: X = 0 \) and \( \phi = \phi_f > 0 \) which is unknown \( (8) \)

The reduced temperature is defined by \( \phi = \beta (T-T^*)(C_p/Q_1) \) and the reduced activation energy by:

\[ \beta = (Q_1/C_p)(T_{1a}/T^*)^2. \quad (9a) \]

The specific heat of the gaseous mixture \( C_p \) is assumed to be constant. The reduced mass fraction of the radical is \( X = Y/\beta \) where \( Y \) represents the mass fraction. The reduced flame speed \( m \) is defined from the flame speed \( U \) by

\[ \beta m = U/(D_t/\tau_r)^{1/2} \quad (9b) \]

where \( D_t = \lambda/\rho C_p \) is the heat diffusion coefficient and \( \tau_r \) the characteristic reaction time defined at the cross-over temperature \( T^* \):

\[ \tau_r = B_b^{-1} \exp(T_{ba}/T^*) = B_1^{-1} \exp(T_{1a}/T^*) \quad (9c) \]

The Lewis number \( Le \) is defined as \( Le = D_t/D_x \) where \( D_x \) is the molecular diffusion coefficient of the radical \( X \). The adimensional rate of the second chain breaking reaction \( \text{(c2)} \) at low temperature is defined by \( k = K_{c2} \tau_r \). The unit of length used in eqns. (5) for the adimensionalization is the thickness of the reaction layer \((D_t\tau_r)^{1/2}/\beta\). The terms \( Q(\phi) \) and \( W(\phi) \) are obtained from Arrhenius terms \((1c)\), in the limit of large values of \( \beta (\beta > 1) \). \( W(\phi) \) which is plotted in Fig. 22.2 for the values of the parameters used by Gray & Yang [8], represents the rate of the overall production of the radical resulting from the competition between the chain branching and chain breaking reactions. The two zeros denoted by \( \phi_i \) and \( \phi_f^* \) correspond to the ignition temperature \( T_i \) and to the inhibition temperature \( T^* \) respectively. In eqns. (5), the reduced flame velocity \( m \) and the reduced flame temperature \( \phi_f \) of the final state.
are two unknowns of the problem. The final state which is an equilibrium stable state \((\phi = \phi_f > \phi^*, X=0)\) propagates at a speed \(m\) into an initial state which is unstable if \(\phi_i < \phi_0 < \phi^*\) or metastable if \(\phi_0 < \phi_i\), depending on the initial temperature \(\phi_0\). Typical profiles of reduced temperature and species concentrations are shown in Fig. 22.6.

The final stable state is a saddle point in the phase space \((X=0\) and \(\phi = \phi_f > \phi^* \Rightarrow W(\phi_f) < 0\)). By taking advantage of the translational invariance, the form of the temperature and concentration profiles for \(x \to +\infty\) can be obtained as solutions of the linearized version of eqn. (5) around the final state to give:

\[
X = \exp(\mu x) \tag{10a}
\]

and
\[
\phi = \phi_f - \exp(\mu \cdot x)Q(\phi_f)/(\mu^2 + \mu \cdot m) \tag{10b}
\]

with
\[
\mu_\perp = \{(Le^2 m^2/4 - Le W(\phi_f))^{1/2} - Le m/2\} < 0, \tag{10c}
\]

the positive root being eliminated because it leads to divergences at \(x \to +\infty\). The upstream profiles can be obtained for \(x \to -\infty\) in a similar manner. When \(\lambda_+ \neq \lambda_-\) one has:
\[
X = A_+ \exp(\lambda_+ x) + A_- \exp(\lambda_- x) \tag{11a}
\]
\[
\phi = \phi_0 + B \exp(mx) + A \exp(\lambda_- x)Q(\phi_0)/(\lambda_-^2 + \lambda_- m) + A_+ \exp(\lambda_+ x)Q(\phi_0)/(\lambda_+^2 + \lambda_+ m) \tag{11b}
\]

with
\[
\lambda_\perp = mL/e/2 \pm (m^2Le^2/4 - Le W(\phi_0))^{1/2} \tag{11c}
\]

and where \(B, A_+ \text{ and } A_-\) are constants of integration which have to be determined with \(m\) and \(\phi_f\) by matching the values and the derivatives of \(X\) and \(\phi\). This matching principle is equivalent to four conditions. If \(\phi_0 < \phi_i\), the initial state is stable \(W(\phi_0) < 0\) and the negative root must be eliminated \(= A_- = 0\). In this case one is left with only four unknowns which are in principle fully determined by the four matching conditions. This yields at most a single solution for the flame speed. For upstream conditions corresponding to \(\phi_0 = \phi_i\), the upstream state is unstable and corresponds to a node in the phase space. One has five unknowns with only four matching conditions and the problem is expected to have a continuous set of solutions. Anticipating that the scenarios described by the results of the one scalar case [13,16] may be extended to the problem (5), this continuous spectrum is expected to be bounded from below by a minimal speed which corresponds to the selected physical flame speed. Depending on the initial temperature \(\phi_0\), this solution is either of a KPP or a ZFK type [15]. For sufficiently large values of \(\phi_0\), the KPP scenario holds and the minimum speed is determined by
\[
\lambda_+ = \lambda_- = mL/e/2 \text{ and } \lim_{x \to -\infty} \{X\} = (Cx + B)\exp(\lambda x) \text{ with } C(\phi_0) < 0 \tag{11d}
\]

and the flame speed is given by
\[
m = m_{\text{KPP}} = 2(W(\phi_0)/Le)^{1/2} \tag{11e}
\]

But a critical value \(\phi_c\) of \(\phi_0\) exists in the range \([\phi_i, \phi^*_i]\) for which \(C(\phi_c) = 0\). When \(\phi_i < \phi_0 < \phi_c\), the constant \(C(\phi_0)\) is positive and the KPP solution (11e) is not acceptable any more because it corresponds to a concentration profile which, according to (11b),
would present upstream negative values. As in the case of an
initial stable state, the minimal speed is determined for \( \phi_i < \phi_0 < \phi_c \) by \( A = 0 \). The critical value \( \phi_c \) corresponds to a transition
from a KPP to a ZFK solution similar to the one observed and
described in simpler cases [15]. Before presenting the numerical
results which confirm these different behaviours, we present an
asymptotic analysis which provides us with an analytical
expression of the flame speed in the ZFK case, complementary to
the result of eqn. (11e).

22.5 Asymptotic analysis

Suppose to simplify that the chain breaking reaction rate at low
temperature is negligible (\( k = 0 \rightarrow \phi_i = -\infty \) and \( \phi^* = 0 \)), all the
possible initial states are unstable. An asymptotic analysis can
be carried out for large negative values of the initial
temperature: \( \phi_0 \rightarrow \infty \). In this limit, the reaction zone where the
chain branching and the chain breaking reactions proceed, is a
very thin layer compared to the preheated zone located just
upstream of the reaction zone. According to eqn. (6), \( W(\phi) \) and
\( Q(\phi) \) become negligible as soon as \( \phi \) takes sufficiently large
negative values. The ratio of the two corresponding thicknesses is
\( \frac{1}{|\phi_0|} \). In the non-reactive preheated zone, the profiles are:

\[
\phi(x) = (\phi^* \phi_0) \exp(mx), m = 0 (|\phi_0|^{-1}), x = 0 (|\phi_0|), \phi_0 = 0(1), (12a)
\]

\[
X(x) = X_f \exp(mx), X_f = 0(1)
\]  

(12b)

where \( X_f \) and \( \phi_f \) are the maximum values of the radical
concentration and the temperature respectively. The origin of the
\( x \) axis in eqn. (12) is chosen inside the reaction layer. The
diffusive fluxes going into the preheated zone and coming from the
reaction layer are given by:

\[
\frac{d\phi}{dx}_{0-} = A = (\phi_0) m = 0(1)
\]  

(12c)

\[
\frac{dX}{dx}_{0-} = mX_f = 0(|\phi_0|^{-1})
\]  

(12d)

These fluxes may also be obtained from a study of the reaction
layer. The leading order of the constitutive equations is obtained
from written eqns. (5) and can be written in the following form,
free from any unknown:

\[
-\phi''_{xx} = (\alpha \exp(b\phi) + \exp(\phi))X, x = 0(1), X = 0(1), \phi = 0(1)
\]  

(13a)

\[
-(1/Le)X''_{xx} = (\exp(b\phi) - \exp(\phi))X.
\]  

(13b)

Equations (13) have been solved numerically by using a shooting
method starting from the final unknown state $\phi = \phi_f, X=0$ with the same asymptotic behaviour as in eqn. (10) but with $m=0$. The only unknown $\phi_f$ left is determined by matching the $X$ profile with the outer solution (12b). At the dominant order of the asymptotic expansion $|\phi_0| \to \infty$, matching conditions require the following asymptotic upstream behaviour of the solution of eqn. (13): $(dX/dx)_{X \to \infty} = 0$. The corresponding value of the asymptote $(d\phi/dx)_{X \to \infty}$ provides the eigenvalue $A$ which, according to eqn. (12c), yields a single flame speed $m$ which is found to vary as the inverse of the reduced initial temperature

$$m = A |\phi_0|^{-1}$$

(14)

The scalar $A$ is plotted in Fig. 22.3 in terms of the parameter $b$ for different values of $Le$ and for $\alpha = 0.2$ which correspond to the value used in reference [8].

Another instructive asymptotic analysis for $\beta \to \infty$ can be carried out in a KKP case when $T_{ba}=0$ and $k=0$. The corresponding results can be summarized as follows. Let us now define the cross-over temperature $T^*$ as:

$$B_b^{-1} = \beta/(2Le)B_1^{-1}\exp(T_l/T^*)$$

(15)

where $\beta$ is defined by eqn. (9a). The radical concentration is produced in the preheated zone by the branching reaction (1b) and is consumed by the chain breaking reaction (1c) in a thin layer located around the final state $\phi_f$. The continuous set of wave speeds is bounded from below by $m_{\text{KPP}}$ where the leading order of the asymptotic expansion for $\beta \to \infty$ is found to be

$$m_{\text{KPP}} = 2/Le^{1/2}$$

(16a)

which corresponds to the selected flame speed. And the flame temperature is given at the leading order by:

$$m(-\phi_0) = \exp(\phi_f/2)$$

(16b)

22.6 Numerical results

The flame speed $m$ obtained from numerical solutions of eqn. (5) is plotted in Fig. 22.4 in terms of the initial value $\phi_0$ for typical values of the parameters: $\alpha = 0.2$, $b=0.7$ and $k=0.01$. Two numerical methods have been used:

(i) for $\phi_1 < \phi_0 < \phi^*$, a shooting method is used in the phase space starting downstream from the saddle point of the final state described by eqn. (10). A continuous set of solutions (represented by small stars in Fig. 22.4 for $\phi_f = 0.5$) is
Figure 22.3. Leading order of the asymptotic expansion ($\beta_\infty$) for the eigenvalue $\Lambda$ as a function of $b$ for different values of Lewis number $Le$.

obtained. Working with a fixed value of $\phi_F$, one decreases the value of $m$ until the $X$ profile shows negative values in the upstream side. The last value of $m$ (represented by big stars in Fig. 22.4) for which $X$ remains positive for all $x$, determines the minimum speed corresponding to the actual flame speed. As predicted by the theoretical analysis described in the preceding sections, a transition is observed for a critical value $\phi_c$ of the initial temperature which is found to be close to -4. For
Figure 22.4. Numerical results for the minimum flame speed for $k = 0.01$, $b = 0.7$ and $Le = 1$.

- KPP solution eqn. (11e); - ZFK solution eqn. (14); big '*': numerical results for the flame speed; small '*': continuous set of solutions $m$ obtained by shooting method for $\phi_f = 0.5$.

initial state such that $\phi_c < \phi_0 < \phi^*$, the flame speed is found to be exactly equal to the KPP value (11e). For $\phi_1 < \phi_0 < \phi_c$, the numerical flame speed is surprisingly found to be very close to the asymptotic result, eqn. (14). This shooting method is not well adapted to the case $\phi_0 < \phi_1$ corresponding to a single speed which is not easily kept with two unknowns $m$ and $\phi_f$.

(ii) A direct numerical simulation, using the adaptive gridding method developed by Larrouturou [21] has been carried out to solve the unsteady version of eqn. (5) describing the unsteady propagation of one-dimensional waves into a given initial state. The steady solutions are obtained asymptotically in time. A single flame speed is obtained by this procedure which is found to be very close to the asymptotic result (14) for $\phi_0 < \phi_c$ which confirms the results obtained by the shooting method for $\phi_1 < \phi_0 < \phi_c$. Moreover this numerical analysis shows that the minimum speed is effectively selected in the range $\phi_1 < \phi_0 < \phi^*$ and that the corresponding solution is stable against one-dimensional small perturbations. The above-mentioned numerical result concerns a case where the
Figure 22.5. Numerical results for the minimum flame speed at the bifurcation point $k = k_c = 0.13$, for $Le = 1$. --- KPP solution with $m_{KPP} = 2(1 - \phi_0^2)^{1/2}$; '*' numerical values of the flame speed.

The relative effect of the second chain breaking reaction is small. According to eqn. (6a), the maximum admissible value of $k$ is $k_c \approx 0.13$ for $b = 0.7$. When $k > k_c$, $W(\phi)$ is negative for all $\phi$ and there is no cool flame any more. In order to check the generic character of the results presented above, we have also carried out a numerical analysis for values of $k$ near the critical condition $k = k_c$. At the corresponding bifurcation point, the problem may be written in the following generic form free from any parameter:

$$m \phi' - \phi'' \frac{w}{r} = X \quad (17a)$$

$$mX' - \frac{1}{Le} \phi'' \frac{w}{r} = (1 - \phi^2) X \quad (17b)$$

Here, the dimensional flame speed $U$ is related to the non-dimensional eigenvalue $m$ of eqns. (17a-b) by eqn. (17c) which replaces eqn. (9b),

$$U = \beta \left( \frac{D_t W_m}{r_f} \right)^{1/2} \quad (17c)$$
Figure 22.6 (see facing page). Typical profiles of the reduced concentration of $X$ and of the reduced temperature $\phi$ of a propagating cool wave travelling from right to left.

where, close the bifurcation, $W_m = (k_c - k) > 0$ is a small parameter corresponding to the maximum value of the reduced production term $W(\theta)$ given by eqn. (6a). The maximum value of the mass fraction of the chain carrier behaves as $\beta (k_c - k)^{3/2}$ and the dimensional flame thickness is $d = (D_t \tau_f)^{1/2}/\beta (k_c - k)^{1/2}$. The inflammation and cross over temperature correspond to $\phi = -1$ and $\phi^* = 1$ respectively. As shown by the numerical results for $m$ plotted in Fig. 22.5, the scenario is qualitatively the same as in the preceding case with a transition at the reduced temperature $\phi_c \sim -0.25$. Typical temperature and concentration profiles are plotted in Fig. 22.6 for $\phi_0 = -3$, in the reduced units of eqns. (17a-b).

22.7 Non-adiabatic case

Periodicity of cool flames is produced by heat losses [4,11,12]. The first cool flame brings the mixture in a stable state ($W(\phi') < 0$) at a temperature slightly higher than $T_*$. Cooling by heat losses brings back the mixture in an unstable case at $T < T_*$ from where a second cool flame starts. In a closed vessel this process is limited by depletion of the reactant $A$, but in well stirred reactors true limit cycles can be observed [4,11,12]. Such a mechanism may take the form of wave trains when the propagation is observed in tubes with non-adiabatic walls. The purpose of this section is limited to pointing out a limiting case for which the oscillatory behaviour may be described analytically. The corresponding results must be considered as a first step toward a theoretical study of travelling wave trains. Considering an homogeneous case and neglecting the consumption of species $A$, the evolution equations of the kinetic scheme (1) in non-adiabatic conditions are:

$$X_t = W(\phi)X + \epsilon'$$  \hspace{1cm} (18a)

$$\phi_t = Q(\phi)X + \epsilon(\phi - \phi_e)$$  \hspace{1cm} (18b)

where $\epsilon' = K_i \tau[A]$ represents the effect of the initiation reaction.

The second term of the r.h.s. of eqn. (18b) is a reduced Newtonian heat loss rate and $\phi_e$ is the reduced surrounding temperature.

Equations (18) have been extensively studied [8,22]. An asymptotic study of the relaxation oscillation regimes occurring in the limit $\epsilon \rightarrow 0$ with $\epsilon' = 0(\epsilon)$ can be carried out as follows. Let $\phi_n$ be a reduced temperature in the unstable domain ($\phi_i < \phi_n < \phi^*$, $W(\phi_n) > 0$) and $\phi'_n$ the maximum temperature reached according to eqn. (18)
Figure 22.7. Return mapping associated with the relaxation oscillations for a weak heat loss intensity. The limit cycle corresponds to the intersection point $N$.

with $\varepsilon = \varepsilon' = 0$ for an initial temperature $\phi_n (\phi^* < \phi_n^- W(\phi_n^-) < 0)$. The cooling mechanism which is negligible in this fast heating process proceeds on a relatively long consecutive step to bring back the mixture in the unstable domain at a temperature $\phi_{n+1} (\phi_i < \phi_{n+1} < \phi^*, W(\phi_{n+1}) > 0)$. A direct integration of eqn. (18) yields

$$
\int_{\phi_n^-}^{\phi_n^+} [W(\phi)/Q(\phi)] \, d\phi = (X_n^- - X_n^+)(1 + O(\varepsilon)) \quad (19a)
$$
\[
\frac{\phi_{n+1}}{\phi_n} = \varepsilon \log(\frac{X_{n+1}}{X_n}) + 0(\varepsilon^2) \quad (19b)
\]

Anticipating the following scaling \( X_n = 0(\varepsilon), X'_n = 0(\varepsilon), X_{n+1} = 0(\varepsilon) \), the leading order of eqns. (19) takes a similar form but with zero in the r.h.s. This yields a return mapping \( \phi_n \rightarrow \phi_{n+1} \) plotted in Fig. 22.7 and describing the relaxation oscillations.

22.8 Conclusions

Transitions from KPP to ZFK scenarios have been described in the propagation mechanism of cool flames when the initial temperature varies. For ordinary values of the parameters, the flame speed is well approximated by eqns. (9b) and (11e) for an initial temperature \( \phi_0 \) corresponding to \( \phi_c < \phi_0 < \phi^* \) and by eqns. (9b) and (14) when \( \phi_0 < \phi_c \). It is worthwhile noticing that for adiabatic conditions, the analysis predicts that cool flames can propagate into mixtures at ordinary temperature conveniently ignited. Moreover, travelling wave trains are predicted to be observed in non-adiabatic conditions. In two dimensional geometry, such wave trains may take the form of spirals as usual for chemical systems presenting bulk oscillations described by a limit cycle.

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References