Activation Energy Asymptotic Analysis of Premixed Flames: Lecture 2

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December 12-24, 2015
Introduction

Asymptotic analyses of flame structures

- activation-energy asymptotic (AEA) analyses describe chemistry by one-step overall reaction
- rate-ratio asymptotic (RRA) analyses employ reduced chemistry deduced from elementary chemical-kinetic mechanisms

Both analyses use singular perturbation techniques to demonstrate the existence of (a) an “outer zone” that is either frozen or inert and (a) a thin reaction zone, comprising several reaction layers, where the chemistry takes place.
Aspects of Asymptotic Analysis Described

- Activation-energy asymptotic analysis (AEA)
  - Premixed flames
  - Nonpremixed flames

- Rate-Ratio asymptotic analysis (RRA)
  - Premixed flames
  - Nonpremixed flames

- relation between AEA analysis and RRA analysis
Phenomenological Analysis

Consider a stationary plane deflagration wave

\[
\begin{align*}
\delta &= \text{thickness of the wave.} \\
\nu_u &= \text{burning velocity.} \\
T_u &= \text{initial temperature of reactant mixture.} \\
\rho_u &= \text{initial density of reactant mixture.} \\
T_b &= \text{adiabatic flame temperature.} \\
q &= \text{heat release per unit mass of reactant mixture.} \\
w_m &= \text{rate of mass consumption of reactant mixture per unit volume.} \\
c_p &= \text{heat capacity of reactant mixture assumed to be constant.} \\
\lambda &= \text{thermal conductivity of reactant mixture.} \\
Le_i &= \text{Lewis number of species } i \text{ assumed to be equal to unity.}
\end{align*}
\]
Phenomenological Analysis: Energy Conservation

The wave is adiabatic

\[ q = c_p(T_b - T_u) \]

Rate of heat release (per unit area per unit time)

\[ qw_m \delta \]

Heat conducted upstream (per unit area per unit time)

\[ \lambda \frac{dT}{dx} \approx \lambda \frac{T_b - T_u}{\delta} \]

Hence

\[ c_p(T_b - T_u) w_m \delta = \lambda \frac{dT}{dx} \approx \lambda \frac{T_b - T_u}{\delta} \]

Thickness of Reaction Zone

\[ \delta = \left( \frac{\lambda}{c_p w_m} \right)^{0.5} \]
Phenomenological Analysis: Mass Conservation

Rate of consumption of reactant mixture (mass per unit area per unit time)

\[ w_m \delta \]

Hence

\[ w_m \delta = w_m \left( \frac{\lambda}{c_p w_m} \right)^{0.5} = \rho_u \nu_u \]

Burning velocity

\[ \nu_u = \frac{1}{\rho_u} \left( \frac{\lambda}{c_p w_m} \right)^{0.5} \]
Phenomenological Analysis

The reaction rate $w$

$$w_m \sim p^n \exp\left[-E/(RT)\right]$$

where $E$ is the activation energy, $T$ the temperature, $p$ the pressure, $n$ the order of reaction, $R$ the gas constant. Note $\rho_u \sim p$

Thus

$$v_u = \frac{1}{\rho_u} \left(\frac{\lambda}{c_p w_m}\right)^{0.5} \sim p^{n/2-1} \exp\left[-E/(2RT_b)\right]$$

and

$$\delta = \left(\frac{\lambda}{c_p w_m}\right)^{0.5} \sim p^{-n/2}$$

Also

$$\delta = \frac{\lambda}{c_p \rho_u v_u}$$

for $v_u = 50$ cm/s, $\delta \approx 10^{-2}$ cm
Premixed Flames Based on One-Step Activation Energy Asymptotics

Theory developed by Frank-Kamenetzkii in 1938. Formally analyzed by Bush and Fendell (CST 1, 421:1970).
Consider the chemistry to take place as one-step process

$$\nu_F \text{Fuel} + \nu_{O_2} \text{Oxygen} \rightarrow \text{Products}$$

The reaction rate is presumed to be of the first order with respect to the fuel and oxygen. Thus

$$w = B \frac{\rho Y_{O_2}}{W_{O_2}} \frac{\rho Y_F}{W_F} \exp \left( -\frac{E}{RT} \right)$$

where $B$ is the frequency factor and $E$ the activation energy. For simplicity the approximation

$$Le_i = \frac{\lambda}{\rho c_p D_i} = 1$$

is introduced. Also the heat capacity $c_p$ is presumed to be constant.
Premixed Flames Based on One-Step Activation Energy Asymptotics

The system is adiabatic, the reactants have excess oxygen. Outer structure is made up of preheat zone and the postflame zone. Inner structure is the thin reaction zone.

- In the preheat zone the reactants are preheated, thickness of the order of unity
- In the reaction zone chemical reactions take place, thickness of the order of $\delta$
- In the postflame zone, the products are in equilibrium and the temperature is equal to its adiabatic value $T_b$. 
Describing Equations

**Mass Conservation**

\[ \dot{m} = \rho_u \nu_u \]

where \( \nu_u \)—burning velocity, subscript \( u \)—conditions in the unburnt mixture.

**Species balance**

\[ \dot{m} \frac{dY_F}{dx} = \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dY_F}{dx} \right) - \nu_F W_F w \]

\[ \dot{m} \frac{dY_{O_2}}{dx} = \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dY_{O_2}}{dx} \right) - \nu_F W_{O_2} w \]

**Energy Conservation**

\[ \dot{m} \frac{dT}{dx} = \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dT}{dx} \right) + \frac{\nu_F W_F Qw}{c_p} \]

where \( Q \) is the heat release per unit mass of fuel consumed. Initial conditions at \( x \to -\infty \)

\[ Y_F = Y_{F,u}, \quad Y_{O_2} = Y_{O_2,u}, \quad T = T_u. \]

In the postflame zone as \( x \to \infty \)

\[ Y_F = 0, \quad Y_{O_2} = Y_{O_2,b}, \quad T = T_b. \]
Nondimensionalization

Introduce the nondimensional variables

- independent

\[ \xi = \dot{m} \int_0^x \frac{c_p}{\lambda} dx \]

- dependent

\[ y_F = \frac{Y_F}{Y_{F,u}}, \quad y_{O_2} = \frac{Y_{O_2} \nu_F W_F}{Y_{F,u} \nu_{O_2} W_{O_2}}, \quad \tau = \frac{T - T_u}{T_b - T_u} \]

The equations describing the flame structure are

Energy Conservation

\[ \frac{d\tau}{d\xi} = \frac{d^2\tau}{d\xi^2} + \Lambda' y_F y_{O_2} \exp \left( -\frac{E}{RT} \right) \]

where use is made of the relation \( Y_{F,u} Q = c_p \left( T_b - T_u \right) \). The quantity \( \Lambda' \) contains the burning velocity. It is defined as

\[ \Lambda' = \frac{B \nu_{O_2} \lambda \rho^2 Y_{F,u}}{W_F c_p \rho_u \nu_u^2} \]
Coupling Functions

- Coupling relations between temperature and mass fractions

\[
\frac{d}{d\xi}(\tau + y_F) = \frac{d^2}{d\xi^2}(\tau + y_F) \\
\frac{d}{d\xi}(\tau + y_{O_2}) = \frac{d^2}{d\xi^2}(\tau + y_{O_2})
\]

- Initial conditions at \(\xi \to -\infty\)

\[y_F = 1, \quad y_{O_2} = y_{O_2,u}, \quad \tau = 0.\]

- In the postflame zone as \(\xi \to \infty\)

\[y_F = 0, \quad y_{O_2} = y_{O_2,b}, \quad \tau = 1.\]

- Integration of the coupling relations gives

\[\tau + y_F = 1 \quad \tau + y_{O_2} = y_{O_2,u} = 1 + y_{O_2,b}\]
Energy Conservation Equation (Nondimensional)

\[
\frac{d\tau}{d\xi} = \frac{d^2\tau}{d\xi^2} + \Lambda y_F y_{O_2} \exp \left[ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_b} \right) \right]
\]

where

- $\xi$—the independent variable.
- $y_F$ and $y_{O_2}$—normalized mass fraction of fuel and oxygen
- $\tau = (T - T_u) / (T_b - T_u)$. Note $\tau \to 0$ as $\xi \to -\infty$

Damköhler number, $\Lambda$ (eigenvalue):

\[
\Lambda = \frac{B \nu_{O_2} \lambda \rho^2 Y_{F,u}}{W_F c_p \rho_u^2 v_u} \exp \left[ -\frac{E}{(RT_b)} \right]
\]

Note that with decreasing temperature, the quantity

\[
\exp \left[ -\frac{E_{eff}}{\hat{R}} \left( \frac{1}{T} - \frac{1}{T_b} \right) \right]
\]

- decreases exponentially if activation energy is **large**
- is of $O(1)$ if activation energy is **not large**
Cold Boundary Difficulty

\[
\frac{d\tau}{d\xi} = \frac{d^2\tau}{d\xi^2} + \Lambda y_F y_{O_2} \exp \left[ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_b} \right) \right]
\]

Energy Equation is not balanced at \( \xi \rightarrow -\infty \)

- No restrictions on the values of Damköhler number and activation energy.
- Damköhler number large and activation energy large (Activation energy asymptotic analysis).
- Damköhler number large and no restrictions on activation energy (Rate-ratio asymptotic analysis).
Cold Boundary Difficulty

\[ \frac{d\tau}{d\xi} = \frac{d^2\tau}{d\xi^2} + \Lambda y_F y_{O_2} \exp \left[ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_b} \right) \right] \]

No Restrictions on Damköhler Number and Activation Energy.

- Ignition Temperature—\( T_{ig} \).
  - Mallard and Le Chatelier (1891) and Von Karman.
  - No chemical reactions for \( T < T_{ig} \).
  - Procedure not available for obtaining \( T_{ig} \).

- Flame-holder—Initial \( T \) and \( dT/dx \) given.
  - Hirschfelder.
  - Initial \( T \) and \( dT/dx \) depends on flameholder.
Cold Boundary Difficulty

\[ \frac{d\tau}{d\xi} = \frac{d^2\tau}{d\xi^2} + \Lambda_{y_F} y_{O_2} \exp \left[ -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_b} \right) \right] \]

Damköhler Number Large and Activation Energy Large.

- Zel’ dovich and Frank-Kamenetskii (1938).
- Chemical reactions are exponentially small in the preheat zone.
- Preheat zone is **frozen**.
- Burning velocity is fundamentally an asymptotic concept.

Fundamental basis of activation energy asymptotic analysis
Cold Boundary Difficulty

Damköhler Number Large and No Restrictions on Activation Energy.

- Use elementary reactions.
- Cross-over temperature—$T^0$.
- Chemical reactions do not take place for $T < T^0$.
- Value of $T^0$ can be calculated from balance between chain branching and chain breaking reactions.
- Preheat zone is inert.

Fundamental basis of rate ratio asymptotic analysis
Analysis of the Outer Structure

- Preheat zone. Chemical reactions are neglected. The energy equation is
  \[ \frac{d\tau}{d\xi} = \frac{d^2\tau}{d\xi^2}. \]

In this convective-diffusive zone

\[ \tau = \exp \xi \]
\[ y_F = 1 - \exp \xi \]
\[ y_{O_2} = y_{O_2,u} - \exp \xi = 1 - \exp \xi + y_{O_2,b} \]

- Postflame zone. Chemical reactions are in equilibrium with \( \tau = 1 \), \( y_F = 0 \), and \( y_{O_2} = y_{O_2,b} \)
Analysis of the Reaction Zone

Near the reaction zone $\xi$ and $1 - \tau$ are small. Hence introduce the expansions

$$\eta = \xi/\epsilon, \quad \tau = 1 - \epsilon y + O(\epsilon^2)$$

where $\eta$ and $y$ are of the order of unity and $\epsilon$ is a small quantity. The coupling relations give

$$y_F = \epsilon y, \quad y_{O_2} = \epsilon (y + b)$$

where $b = y_{O_2,b}/\epsilon$ is presumed to be of the order of unity (moderately lean mixture). Also

$$T = T_b - \epsilon y (T_b - T_u).$$

The exponential term is written as

$$\exp \left( -\frac{E}{RT} \right) = \exp \left\{ -\frac{E}{RT_b} \left[ 1 - \frac{\epsilon y (T_b - T_u)}{T_b} \right]^{-1} \right\}$$

$$= \exp \left( -\frac{E}{RT_b} \right) \exp \left( -Z_e \epsilon y \right).$$

where $Z_e$ is the Zel’dovich number. It is defined as

$$Z_e = \frac{E(T_b - T_u)}{RT_b^2}$$
Analysis of the Reaction Zone

Using the expansions the energy conservation equation is written as:

\[-\epsilon \frac{dy}{d\eta} + \frac{d^2 y}{d\eta^2} = \Lambda' \epsilon^3 y(y + b) \exp \left( -\frac{E}{RT_b} \right) \exp \left( -Z_e \epsilon y \right).\]

The convective term can be neglected in comparison to the diffusive terms. To make the reactive terms of the same order as the diffusive terms, the distinguished limit

\[Z_e \epsilon = 1\]

\[\Lambda = \Lambda' \epsilon^3 \exp \left( -\frac{E}{RT_b} \right) = O(1)\]

is introduced. The equation describing the reactive-diffusive balance in the reaction zone can be written as

\[\frac{d^2 y}{d\eta^2} = \Lambda y(y + b) \exp(-y).\]

Notice that as \(\eta \to -\infty\), \(y \to \infty\). The solution in this limit is \(y = c_0 - c_1 \eta\). The problem is translationally invariant. This can be illustrated by introducing the variable \(\hat{\eta} = -(c_0 - c_1 \eta)/c_1\). Thus choose \(c_0 = 0\). Boundary conditions for this equation are obtained by matching.
Matching Conditions

- Postflame zone: Matching the reaction zone to the postflame zone in the limit $\eta \to \infty$, obtain $dy/d\eta = y = 0$.

- Preheat zone: To match the reaction zone structure to the preheat zone as $\eta \to -\infty$, introduce the intermediate variable

$$\theta = \xi/\sigma(\epsilon) = \eta[\epsilon/\sigma(\epsilon)]$$

where $1 \gg \sigma(\epsilon) \gg \epsilon$. With $\theta$ fixed and $\epsilon \to 0$, $\xi = \theta\sigma(\epsilon) \to 0$, and $\eta = \theta\sigma(\epsilon)/\epsilon \to -\infty$. Hence in this limit the matching condition is

$$\exp(\xi) - (1 - \epsilon y) = 1 + \theta\sigma(\epsilon) - 1 - c_1\theta\sigma(\epsilon) = 0$$

Hence $c_1 = 1$. The matching conditions as $\eta \to -\infty$ are $y = -\eta$ and $dy/d\eta = -1$. 
Burning Velocity

A first integral of the energy equation is

$$\int_{-1}^{0} d \left( \frac{dy}{d\eta} \right)^2 = 2\Lambda \int_{0}^{\infty} y(y + b) \exp(-y)dy$$

This gives

$$\Lambda = \left[ 2(2 + b) \right]^{-1}$$

The burning velocity is given by

$$v_u^2 = \frac{B\nu_{O_2} \lambda \rho_b^2 Y_{F,u} R^3 T_b^6 2(2 + b)}{W_F c_p \rho_u^2 E^3 (T_b - T_u)^3} \exp \left( -\frac{E}{RT_b} \right)$$

Note the similarity with the phenomenological analysis

$$v_u^2 = \frac{\lambda}{\rho_u^2 c_p} w_m$$
Extinction of Premixed Flame With Volumetric Heat loss

- Volumetric heat loss can influence the burning velocity.
- Let the volumetric heat loss be
  \[ Q_V = -\alpha (T - T_u) \]
- Mass Conservation
  \[ \dot{m} = \rho_u \nu_u \]
  where \( \nu_u \)—burning velocity with heat losses, subscript \( u \)—conditions in the unburnt mixture.
- Species balance
  \[ \dot{\dot{m}} \frac{d Y_F}{d x} = \frac{d}{d x} \left( \frac{\lambda}{c_p} \frac{d Y_F}{d x} \right) - \nu_F W_F w \]
  Energy Conservation
  \[ \dot{\dot{m}} \frac{dT}{d x} = \frac{d}{d x} \left( \frac{\lambda}{c_p} \frac{dT}{d x} \right) + \frac{\nu_F W_F Qw}{c_p} - \frac{\alpha (T - T_u)}{c_p} \]
- Initial conditions at \( x \to -\infty \)
  \[ Y_F = Y_{F,u}, \ Y_{O_2} = Y_{O_2,u}, \ T = T_u. \]
Nondimensionalization

Introduce the nondimensional variables

- independent and dependent variables

\[ \zeta = \rho_u \int_0^x \frac{c_p}{\lambda} \, dx; \quad y_F = \frac{Y_F}{Y_{F,u}}; \quad \tau = \frac{T - T_u}{T_b - T_u} \]

- reaction rate \( \omega \); and heat loss \( \pi \)

\[ \omega = \frac{\nu_F W_F w \lambda}{c_p Y_{F,u} \rho_u s_L^2}; \quad \pi = \frac{\alpha \lambda}{(c_p \rho_u s_L)^2} \]

- The burning velocity

\[ M = \frac{v_u}{s_L} \]

The equations describing the flame structure are

- Species Balance

\[ M \frac{d y_F}{d \zeta} = \frac{d^2 y_F}{d \zeta^2} - \omega \]

- Energy Conservation

\[ M \frac{d \tau}{d \zeta} = \frac{d^2 \tau}{d \zeta^2} + \omega - \pi \tau \]
Flame Structure

- Introduce the variable $h = \tau + y_F - 1$
  
  $$M \frac{dh}{d\zeta} = \frac{d^2 h}{d\zeta^2} - \pi \tau$$

- Energy Conservation
  
  $$M \frac{d\tau}{d\zeta} = \frac{d^2 \tau}{d\zeta^2} + \omega - \pi \tau$$
The approximation that $\pi \ll 1$ is introduced.

The temperature in the post-flame zone is written as

$$\tau = 1 + \pi z$$

Integration of the equation for $h$ from $-\infty$ to $O^+$ is

$$M \frac{dh}{d\zeta} = \frac{d^2 h}{d\zeta^2} - \pi \tau$$

$$Mh(0^+) = \left( \frac{dh}{d\zeta} \right)_{0^+} - \pi \int_{-\infty}^{0^+} \tau d\zeta$$

$$h(0^+) = (\tau + y_F - 1)_{0^+} = \pi z^0$$

where $z^0 = z(0^+)$, and $y_F(0^+) = 0$
Integration of Energy Conservation equation in the preheat-zone

\[ M \frac{d\tau}{d\zeta} = \frac{d^2\tau}{d\zeta^2} \]

\[ \tau = \exp(M\zeta) \]

Introduce the contracted co-ordinate \( \bar{\zeta} = \pi\zeta \)

Equation for \( h \) in the post-flame zone

\[ M \frac{dh}{d\bar{\zeta}} = \pi \frac{d^2h}{d\bar{\zeta}^2} - \tau \approx -\tau \]

It follows that

\[ \left( \frac{dh}{d\zeta} \right)_{0^+} = \left( \frac{d\tau}{d\zeta} \right)_{0^+} = -\frac{\pi}{M} \]
Substituting in the equation

\[ M h(0^+) = \left( \frac{dh}{d\zeta} \right)_{0^+} - \pi \int_{-\infty}^{0^+} \tau d\zeta \]

\[ M \pi z^0 = -\frac{\pi}{M} - \pi \int_{-\infty}^{0^+} \exp(M\zeta) d\zeta \]

Hence the temperature perturbation is

\[ z^0 = -2/M^2 \]
The Burning Velocity

- The burning velocity for a premixed flame
  \[ s_L = \exp \left( -\frac{E}{2RT_b} \right) \]

- At the 0
  \[ T^0 = T_b + \pi z^0 (T_b - T_u) \]

- Thus
  \[ M = \exp \left[ -\frac{E}{2R} \left( \frac{1}{T^0} - \frac{1}{T_b} \right) \right] \]
  \[ \frac{1}{T^0} = \frac{1}{T_b} - \frac{\pi z^0 (T_b - T_u)}{T_b^2} \]

- The is the Zel’dovich number, \( Z_e \)
  \[ Z_e = \frac{E(T_b - T_u)}{RT_b^2} \]

- Obtain the result
  \[ M^2 = \exp (Z_e \pi z^0); \quad z^0 = -2/M^2; \quad M^2 \ln M^2 = -2\pi Z_e \]
Premixed Flame Extinction

◮ Upper branch is stable solution. The burning velocity decreases as the heat loss parameter $\pi$ increases.

◮ There is a maximum value for $\pi Ze$ beyond which no solution exists.

◮ $M_{ex} = 0.61$ for AEA and $M_{ex} = 0.64$ for RRA.

◮ AEA is a good approximation for the temperature sensitivity of hydrocarbon flames.