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Lectures on Dynamics of Combustion Waves in Premixed Gases

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Lecture VI
Thermal quenching of flames and flammability limits

Lecture 6: Thermal quenching and flammability limits

6-1. Extinction through thermal loss

6-2. Basic concepts in chemical kinetics

Combustion of hydrogen

Two-step model. Crossover temperature

One-step model with temperature cutoff

6-3. Flame speed near flammability limits

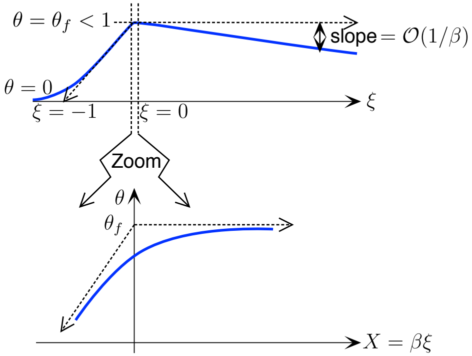
VI-1) Extinction through thermal loss

a small heat loss can quench the flame

Davy 1830

Zeldovich 1941

Formulation (volumetric heat loss in a planar flame)



$$\mu\frac{\mathrm{d}\theta}{\mathrm{d}\xi} - \frac{\mathrm{d}^2\theta}{\mathrm{d}\xi^2} = w - \frac{\tau_L}{\tau_{\mathrm{cool}}}\theta, \qquad \mu\frac{\mathrm{d}\psi}{\mathrm{d}\xi} - \frac{1}{\mathrm{Le}}\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = -w$$

$$\xi \equiv x/d_L \qquad \mu = U_L/U_{Ladia} \qquad 1/\tau_{cool} \approx D_T/R^2$$

$$\tau_L \approx D_T/U_L^2 \;\Rightarrow\; \frac{\tau_L}{\tau_{cool}} \approx \left(\frac{D_T}{R\,U_L}\right)^2 \qquad R = \text{tube radius}$$

$$\xi = -\infty \;:\; \theta = 0,\; \psi = 1, \qquad \xi = +\infty \;:\; \theta = 0,\; \psi = 0$$

Asymptotic analysis for small heat release and a one step reaction

(Joulin Clavin 1976)

$$\beta \to \infty \qquad \tau_L/\tau_{cool} = h/\beta \quad h = O(1) \qquad \beta(1-\theta_f) = O(1) \qquad w(\theta,\psi) = (\beta^2/2)\psi\exp[-\beta(1-\theta)]$$

unknown flame temperature < adiabatic flame temperature : $\theta_f < 1$

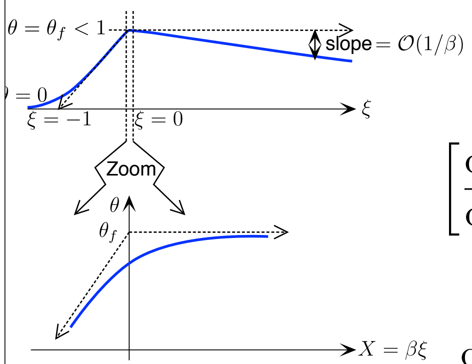
jumps across the thin reaction zone :

$$\mathrm{d}\theta/\mathrm{d}\xi|_{\xi=0-} = e^{-\beta(1-\theta_f)/2} \qquad \left[\frac{\mathrm{d}\theta}{\mathrm{d}\xi} + \frac{1}{\mathrm{Le}}\frac{\mathrm{d}\psi}{\mathrm{d}\xi}\right]_{0-}^{0+} = 0$$

external solutions : $w = 0$

$$\xi < 0 : \begin{cases} \theta_-(\xi) &= \theta_f \mathrm{e}^{[\mu + h/(\beta\mu)]\xi}, \\ \psi_-(\xi) &= 1 - \mathrm{e}^{\mathrm{Le}\,\mu\xi}, \end{cases} \qquad \xi > 0 : \begin{cases} \theta_+(\xi) &= \theta_f \mathrm{e}^{-[h/(\beta\mu)]\xi}, \\ \psi_+(\xi) &= 0, \end{cases}$$

up to first order $O(1/\beta)$



$$\xi < 0: \begin{cases} \theta_-(\xi) & = \theta_f \mathrm{e}^{[\mu + h/(\beta\mu)]\xi}, \\ \psi_-(\xi) & = 1 - \mathrm{e}^{\mathrm{Le}\,\mu\xi}, \end{cases} \qquad \xi > 0: \begin{cases} \theta_+(\xi) & = \theta_f \mathrm{e}^{-[h/(\beta\mu)]\xi}, \\ \psi_+(\xi) & = 0, \end{cases}$$

$$\left[\frac{\mathrm{d}\theta}{\mathrm{d}\xi} + \frac{1}{\mathrm{Le}}\frac{\mathrm{d}\psi}{\mathrm{d}\xi}\right]_{0-}^{0+} = 0 \qquad \Rightarrow \quad -(h/\beta\mu)\theta_f - (\mu + h/\beta\mu)\theta_f + \mu = 0$$

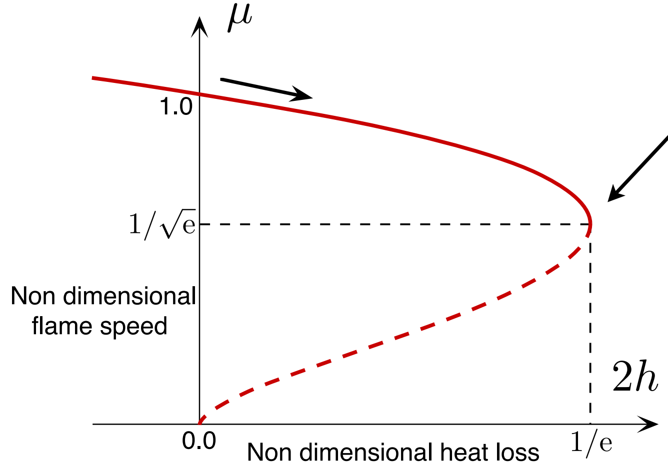
$$\theta_f - 1 = O(1/\beta) \;\Rightarrow\; \boxed{\beta(1-\theta_f) = 2h/\mu^2}$$

$$\mathrm{d}\theta/\mathrm{d}\xi|_{\xi=0-} = e^{-\beta(1-\theta_f)/2} \quad \Rightarrow \quad \mu = \exp(-h/\mu^2)$$

$$\boxed{\mu^2 \ln \mu^2 = -2h}$$

C-shaped curve: no solution for $2\,h > 1/\mathrm{e}$

quenching at finite flame velocity $U_L/U_{Ladia} = 1/\sqrt{\mathrm{e}}$



VI-2) Basic concepts in chemical kinetics

Law 2006

Combustion of hydrogen

Sanchez Williams 2014

units: moles/cm^3, s^{-1} and Kelvin

$$\mathrm{d}c_{ij}/\mathrm{d}t = -\omega_j$$

$$\omega_j = \tilde{k}_j c_{1j} c_{2j} \quad \text{or} \quad \omega_j = \tilde{k}_j c_{1j} c_{2j} c_{3j}$$

$$\tilde{k}_j = \tilde{B}_j T^{\nu} \mathrm{e}^{-T_{aj}/T}$$

Label	Reaction	$\tilde{k}_j$	$\tilde{B}_j$	ν_j	T_{aj}
1	$O_2 + H \rightleftharpoons OH + O$	$\tilde{k}_{1f}$	3.52×10^{16}	-0.7	8590
		$\tilde{k}_{1b}$	7.04×10^{13}	-0.264	72
2	$H_2 + OH \rightleftharpoons H_2O + H$	$\tilde{k}_{2f}$	1.17×10^{9}	1.3	1825
		$\tilde{k}_{2b}$	1.29×10^{10}	1.196	9412
3	$H_2 + O \rightleftharpoons OH + H$	$\tilde{k}_{3f}$	5.06×10^{4}	2.67	3165
		$\tilde{k}_{3b}$	3.03×10^{4}	2.63	2433
4f	$O_2 + H + M \rightarrow HO_2 + M$	$\tilde{k}_{4f}$	5.79×10^{19}	-1.4	0
5f	$H + H + M \rightarrow H_2 + M$	$\tilde{k}_{5f}$	1.30×10^{18}	-1	0
6f	$H + OH + M \rightarrow H_2O + M$	$\tilde{k}_{6f}$	4.00×10^{22}	-2	0
7f	$HO_2 + H \rightarrow OH + OH$	$\tilde{k}_{7f}$	7.08×10^{13}	0	148
8f	$HO_2 + H \rightarrow H_2 + O_2$	$\tilde{k}_{8f}$	1.66×10^{13}	0	414
9f	$HO_2 + OH \rightarrow H_2O + O_2$	$\tilde{k}_{9f}$	2.89×10^{13}	0	-250

shuffle reactions
(1f), (2f), (3f)
chain branching

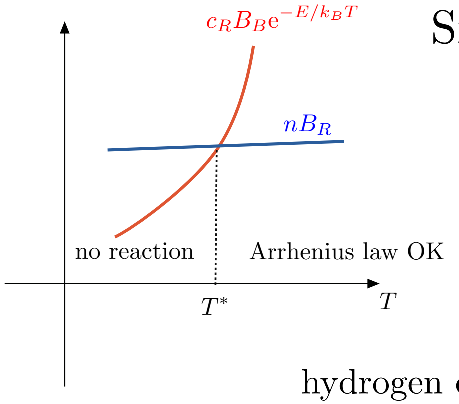
$$O_2 + 3H_2 \rightarrow 2H_2O + 2H$$
$$\text{rate:} \;\; \omega_{1f} \equiv c_{\mathrm{H}} c_{\mathrm{O_2}} k_{1f}$$

(4f) chain breaking

$$M + H + O_2 \rightarrow M + HO_2,$$
$$\text{rate :} \quad \omega_{4f} = c_{\mathrm{H}} c_{\mathrm{O_2}} n k_{4f}$$
$$k_{4f} = B_{4f}$$

(8b) initiation

$$H_2 + O_2 \rightarrow HO_2 + H$$



Simplified two-step model: crossover temperature

Zeldovich 1961, Liñan 1971, Peters Williams 1987, Peters 1997

$$\text{(B)} \quad R + X \rightarrow 2X, \quad \omega_B = c_R c_X B_B \mathrm{e}^{-E/k_B T}, \quad E \gg k_B T$$

$$\text{(R)} \quad M + X \rightarrow P + Q, \quad \omega_R = c_X n B_R, \quad E_R = 0$$

$$c_R B_B \mathrm{e}^{-E_1/k_B T^*} = n B_R \qquad T^* \in [900K - 1400K]$$

hydrogen combustion: $k_{1f}(T^*) \equiv B_{1f} \mathrm{e}^{-E_1/k_B T^*} = n B_{4f}$

Flammability limit

$$T_b = T^* \Rightarrow q_R Y_u^* \equiv c_p (T^* - T_u)$$

Two-step model for rich hydrogen flames near the flammability limit

(consumption of hydroperoxide included)

$$\mathrm{O_2} + 3\mathrm{H_2} \rightarrow 2\mathrm{H_2O} + 2\mathrm{H},$$
$$\omega_{1f} = c_{\mathrm{H}} c_{\mathrm{O_2}} k_{1f}(T), \quad k_{1f}(T) = B_{1f} \mathrm{e}^{-E_1/k_B T}$$

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H_2} + Q,$$
$$\omega_{4f} + \omega_{5f} = n c_{\mathrm{H}} c_{\mathrm{O_2}} B_{4f} + n c_{\mathrm{H}}^2 B_{5f}$$

$$\frac{\mathrm{d}c_H}{\mathrm{d}t} = \left[B_{1f}\mathrm{e}^{-E_1/k_B T} - nB_{4f}\right] c_{O_2} c_H - nB_{5f} c_H^2$$

$(B_{1f}\mathrm{e}^{-E_1/k_B T} - nB_{4f})/nB_{4f} \ll 1$ tri molecular recombination reaction (5f) $\Rightarrow$ H in quasi-steady state

$$T > T^* : \quad c_{\mathrm{H}} \approx c_{\mathrm{O_2}}^2 \frac{[B_{1f}\mathrm{e}^{-E_1/k_B T} - nB_{4f}]}{nB_{5f}} \qquad T < T^* : \quad c_{\mathrm{H}} = 0$$

One-step model

$$nB_{4f} = B_{1f}\mathrm{e}^{-E_1/k_B T^*} \qquad 1/\tau^* \equiv (nB_{4f}^2 c^*_{\mathrm{O_2}u})/B_{5f}$$

$$m\frac{\mathrm{d}\theta}{\mathrm{d}x} - \rho D_T \frac{\mathrm{d}^2\theta}{\mathrm{d}x^2} \approx \frac{\rho}{\tau^*}\psi^2 J(T)$$
$$m\frac{\mathrm{d}\psi}{\mathrm{d}x} - \rho D_{\mathrm{O_2}} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} \approx -\frac{\rho}{\tau^*}\psi^2 \mathrm{e}^{-\frac{E}{k_B}(\frac{1}{T}-\frac{1}{T^*})} J(T)$$

$$\begin{cases} T > T^* : & J(T) \equiv \dfrac{T_u}{T}[\mathrm{e}^{-\frac{E}{k_B}(\frac{1}{T}-\frac{1}{T^*})} - 1] \\ T < T^* : & J(T) = 0 \end{cases}$$

$$x = -\infty : \ \theta = 0, \qquad x = +\infty : \ \theta = 1$$

reaction of order 2 with a temperature cutoff

very close to the flammability limit $\quad \dfrac{T_b - T^*}{T^*} \ll \dfrac{k_B T^*}{E} \quad \Rightarrow \quad [\mathrm{e}^{-\frac{E}{k_B}(\frac{1}{T}-\frac{1}{T^*})} - 1] \approx \dfrac{E}{k_B}(\dfrac{1}{T^*} - \dfrac{1}{T}) \ll 1$

$$m\frac{\mathrm{d}\theta}{\mathrm{d}x} - \rho D_T \frac{\mathrm{d}^2\theta}{\mathrm{d}x^2} \approx \frac{\rho}{\tau^*}\psi^2 J(T)$$
$$m\frac{\mathrm{d}\psi}{\mathrm{d}x} - \rho D_{\mathrm{O_2}} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} \approx -\frac{\rho}{\tau^*}\psi^2 \mathrm{J}(T)$$

$$\begin{cases} T > T^* : & J(T) \approx \dfrac{T_u}{T^*}\dfrac{E}{k_B T^*}\dfrac{T - T^*}{T^*} \\ T < T^* : & J(T) = 0 \end{cases}$$

VI-3) Flame speed near flammability limits

$$\theta \equiv \frac{(T-T_u)}{(T_b-T_u)} \in \boxed{[\theta^*,1]} \qquad \theta^* \equiv \frac{(T^*-T_u)}{(T_b-T_u)} \qquad T_b > T^* \;\Rightarrow\; \boxed{\theta^* < 1 \text{ but close to } 1}$$

$$m\frac{\mathrm{d}\theta}{\mathrm{d}x} - \rho_b D_T \frac{\mathrm{d}^2\theta}{\mathrm{d}x^2} \approx \frac{\rho_b}{\tau^*}\psi^2 j(\theta)$$

$$m\frac{\mathrm{d}\psi}{\mathrm{d}x} - \rho_b D_{O_2} \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} \approx -\frac{\rho_b}{\tau^*}\psi^2 j(\theta)$$

$$\begin{cases} \theta > \theta^* : & j(\theta) \approx b^*(\theta-\theta^*) \\ \theta < \theta^* : & j(\theta) = 0 \end{cases} \qquad b^* \equiv \frac{T_u}{T^*}\frac{E}{k_B T^*}\frac{T_b-T_u}{T^*}$$

$$\text{reaction zone: } \psi = \mathrm{Le}(1-\theta), \qquad D_T\frac{\mathrm{d}^2\theta}{\mathrm{d}x^2} = \frac{\mathrm{Le}^2 b^*}{\tau^*}(1-\theta)^2[(\theta-1)-(\theta^*-1)] \qquad \mathrm{Le} \equiv D_T/D_{O_2}$$

$$\times\frac{\mathrm{d}\theta}{\mathrm{d}x} + \int_{\theta^*}^{1}\mathrm{d}\theta + \text{matching} \;\Rightarrow\; D_T\left.\frac{\mathrm{d}\theta}{\mathrm{d}x}\right|_- \approx \mathrm{Le}\sqrt{\frac{b^*}{6}(1-\theta^*)^2}\sqrt{\frac{D_T}{\tau^*}} \qquad \frac{\rho_u}{\rho_b}\frac{U_L}{\sqrt{D_T/\tau^*}} \approx \mathrm{Le}\sqrt{\frac{b^*}{6}(1-\theta^*)^2}$$

$$0 < \frac{T_b-T^*}{T_b-T_u} \ll 1 \;\Rightarrow\; \boxed{\frac{\rho_u}{\rho^*}\frac{U_L}{\sqrt{D_T/\tau^*}} \approx \mathrm{Le}\sqrt{\frac{b^*}{6}\left(\frac{T_b-T^*}{T^*-T_u}\right)^2}} \qquad \text{Peters 1997}$$

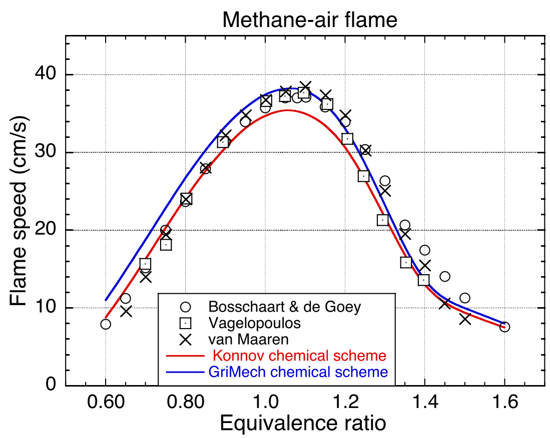
the flame velocity decreases smoothly to zero when approaching the flammability limit $T_b \to T^*$

the flame thickness d_L^* diverges, $T_b \to T^*$: $\dfrac{d_L^*}{d_L} \propto \dfrac{1}{\beta^2}\left(\dfrac{T^*-T_u}{T_b-T^*}\right)^2$

Divergence of the thermal sensitivity: Thermal quenching

$$\frac{T_b}{U_L}\frac{\mathrm{d}U_L}{\mathrm{d}T_b} = \frac{2T_b}{T_b-T^*} \nearrow \infty$$

the least heat loss quenches the flame at a non zero velocity



Methane flames

Peters Williams 1987 Peters 1997

$H_2 - O_2$ flames

Sanchez Williams 2014