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Structure and Dynamics of Combustion Waves in Premixed Gases

Paul Clavin

Aix-Marseille Université
ECM & CNRS (IRPHE)

Lecture VI

Thermal quenching of flames and flammability limits

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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

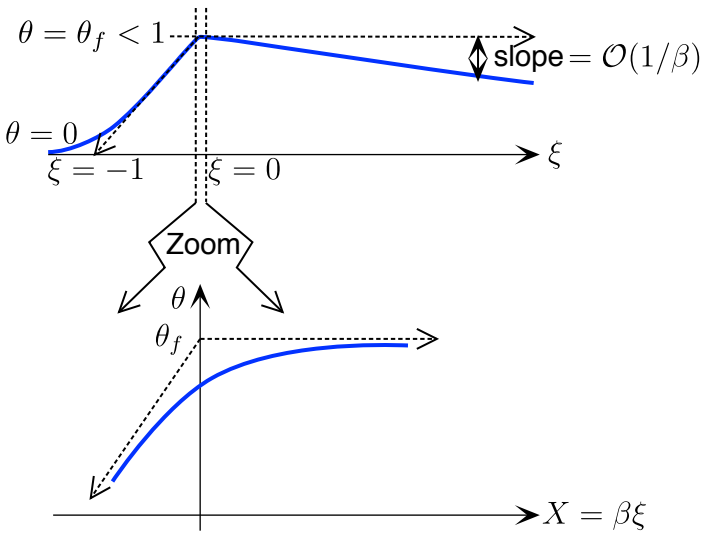
Formulation (volumetric heat loss in a planar flame)



Davy 1830



Zeldovich 1941



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

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

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

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

Asymptotic analysis for small heat release and a one step reaction

(Joulin Clavin 1976)

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

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

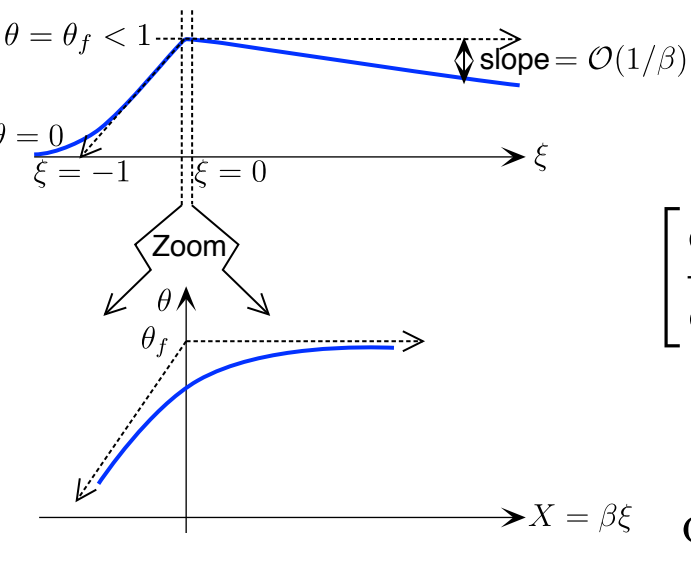
jumps across the thin reaction zone :

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

external solutions : $w = 0$

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

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



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

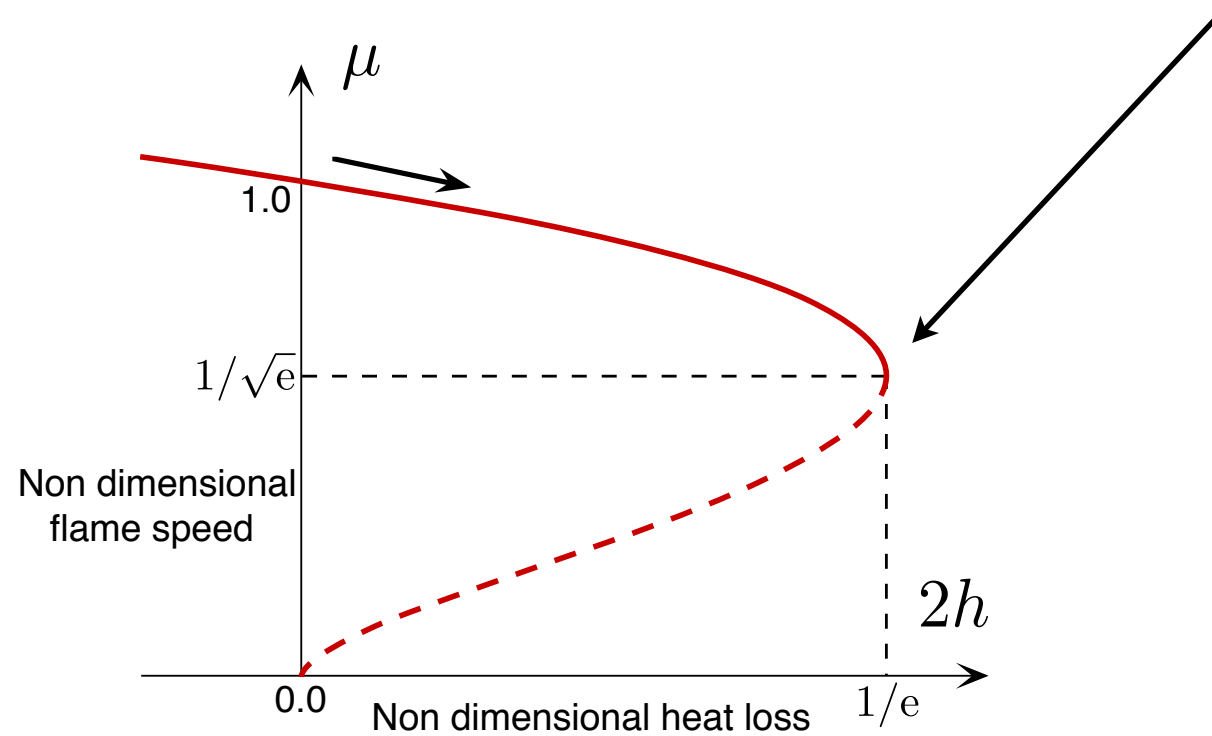
$$\left[\frac{d\theta}{d\xi} + \frac{1}{\text{Le}} \frac{d\psi}{d\xi} \right]_{0-}^{0+} = 0 \quad \Rightarrow \quad -(h/\beta\mu)\theta_f - (\mu + h/\beta\mu)\theta_f + \mu = 0$$

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

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

$$\mu^2 \ln \mu^2 = -2h$$

C-shaped curve: no solution for $2h > 1/e$
 quenching at finite flame velocity $U_L/U_{Ladia} = 1/\sqrt{e}$



VI-2) Basic concepts in chemical kinetics

Combustion of hydrogen Sanchez Williams 2014

units: moles/cm³, s⁻¹ and Kelvin

$$dc_{ij}/dt = -\omega_j$$

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

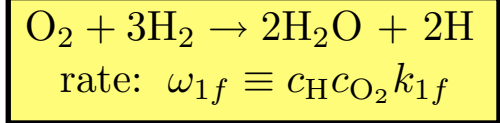
$$\tilde{k}_j = \tilde{B}_j T^{\nu_j} e^{-T_{aj}/T}$$

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

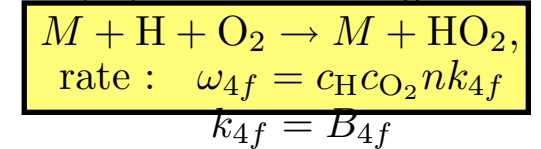
shuffle reactions

(1f), (2f), (3f)

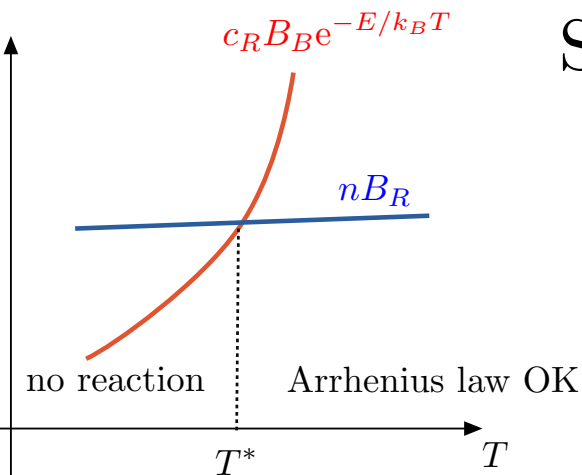
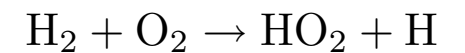
chain branching



(4f) chain breaking

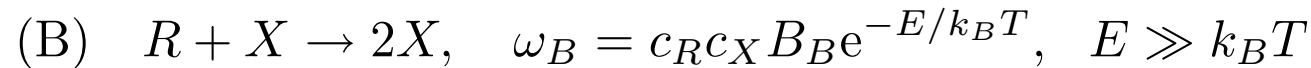


(8b) initiation



Simplified two-step model: crossover temperature

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

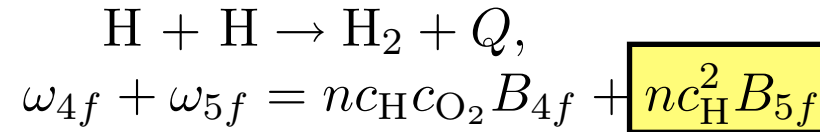
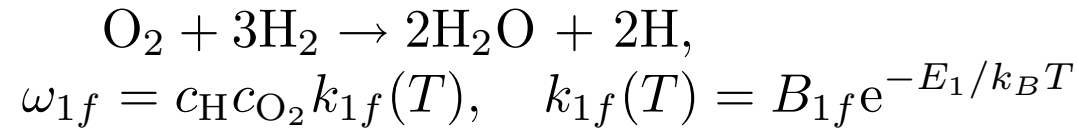


$$c_R B_B e^{-E_1/k_B T^*} = n B_R \quad T^* \in [900K - 1400K]$$

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

Flammability limit

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



$$\frac{dc_{\text{H}}}{dt} = \left[B_{1f}e^{-E_1/k_B T} - nB_{4f} \right] c_{\text{O}_2}c_{\text{H}} - nB_{5f}c_{\text{H}}^2$$

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

$$T > T^* : \quad c_{\text{H}} \approx c_{\text{O}_2} \frac{[B_{1f}e^{-E_1/k_B T} - nB_{4f}]}{nB_{5f}} \quad T < T^* : \quad c_{\text{H}} = 0$$

One-step model (near the flammability limit) $c_{\text{H}}B_{5f} \ll c_{\text{O}_2}B_{4f} \Rightarrow \omega_{5f} \ll \omega_{4f}$

$$nB_{4f} = B_{1f}e^{-E_1/k_B T^*} \quad 1/\tau^* \equiv (nB_{4f}^2 c_{\text{O}_2}^*)/B_{5f}$$

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

$$m \frac{d\psi}{dx} - \rho D_{\text{O}_2} \frac{d^2\psi}{dx^2} \approx -\frac{\rho}{\tau^*} \psi^2 e^{-\frac{E}{k_B}(\frac{1}{T} - \frac{1}{T^*})} J(T)$$

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

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

reaction of order 2 with a temperature cutoff

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

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

$$m \frac{d\psi}{dx} - \rho D_{\text{O}_2} \frac{d^2\psi}{dx^2} \approx -\frac{\rho}{\tau^*} \psi^2 J(T)$$

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

VI-3) Flame speed near flammability limits

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

$$m \frac{d\theta}{dx} - \rho_b D_T \frac{d^2\theta}{dx^2} \approx \frac{\rho_b}{\tau^*} \psi^2 j(\theta) \quad \begin{cases} \theta > \theta^* : j(\theta) \approx b^*(\theta - \theta^*) \\ \theta < \theta^* : j(\theta) = 0 \end{cases} \quad b^* \equiv \frac{T_u}{T^*} \frac{E}{k_B T^*} \frac{T_b - T_u}{T^*}$$

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

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

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

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

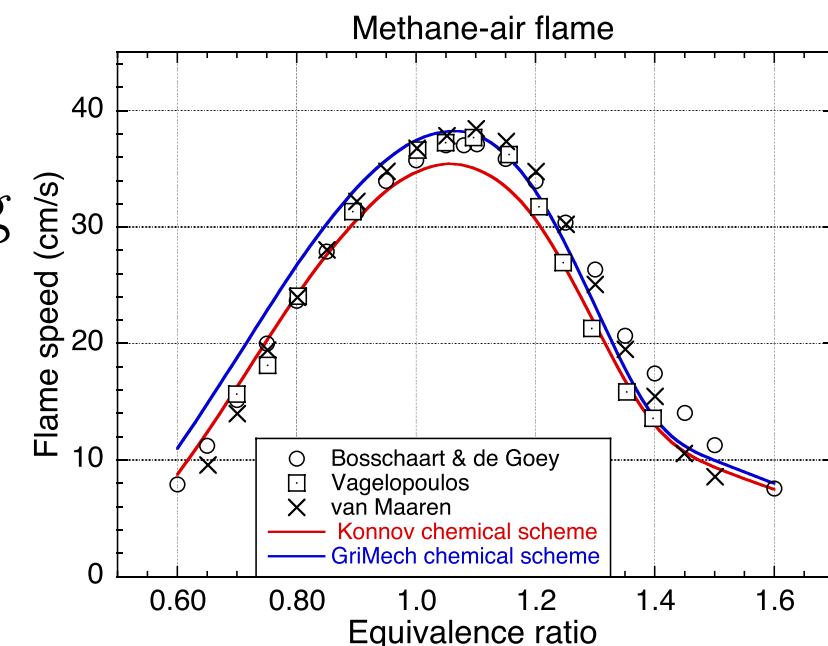
the flame velocity decreases smoothly to zero when approaching the flammability limit $T_b \rightarrow T^*$

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

Divergence of the thermal sensitivity: Thermal quenching

$$\frac{T_b}{U_L} \frac{dU_L}{dT_b} = \frac{2T_b}{T_b - T^*} \nearrow \infty$$

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



Methane flames

Peters Williams 1987

Peters 1997

H₂ – O₂ flames

Sanchez Williams 2014