TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2024 SUMMER SCHOOL ON COMBUSTION

Combustion Physics

Chung K. Law
Princeton University

July 07-13, 2024

Combustion Physics
(Day 1 Lecture: Introduction)

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What is Combustion?

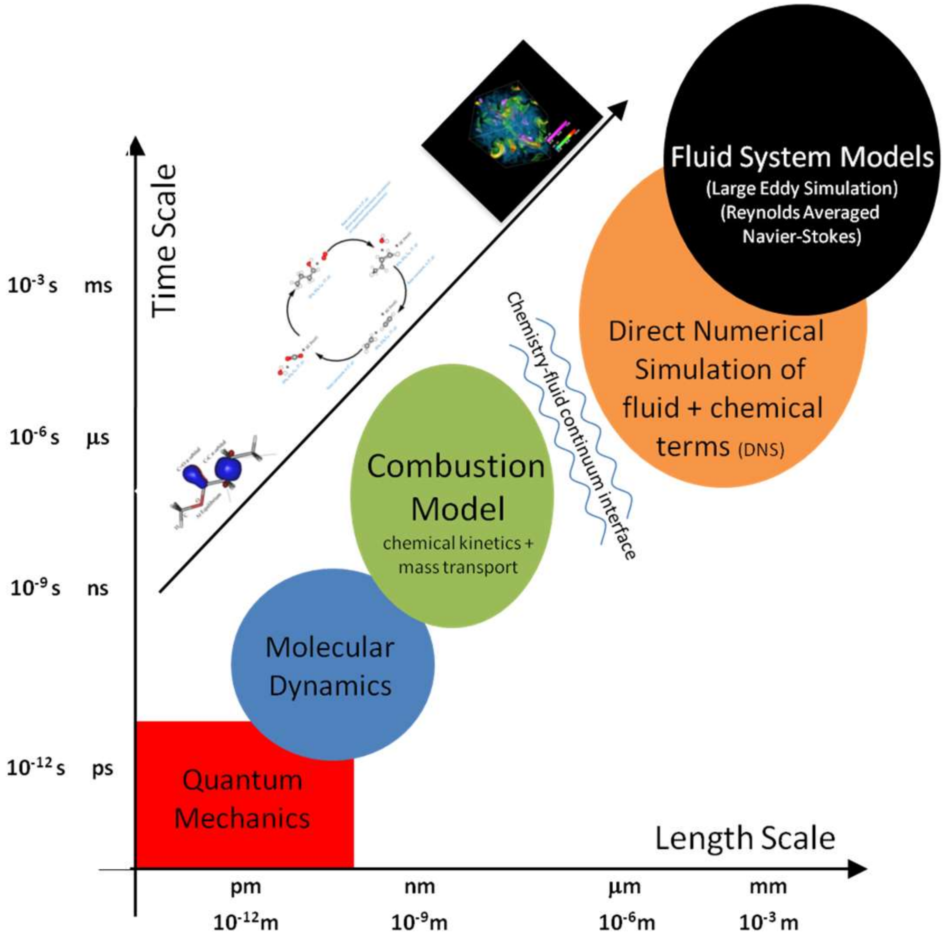
- Study of chemically reacting flows with highly exothermic, temperature-sensitive reactions

A Laminar Bunsen Flame

A Turbulent Jet Flame

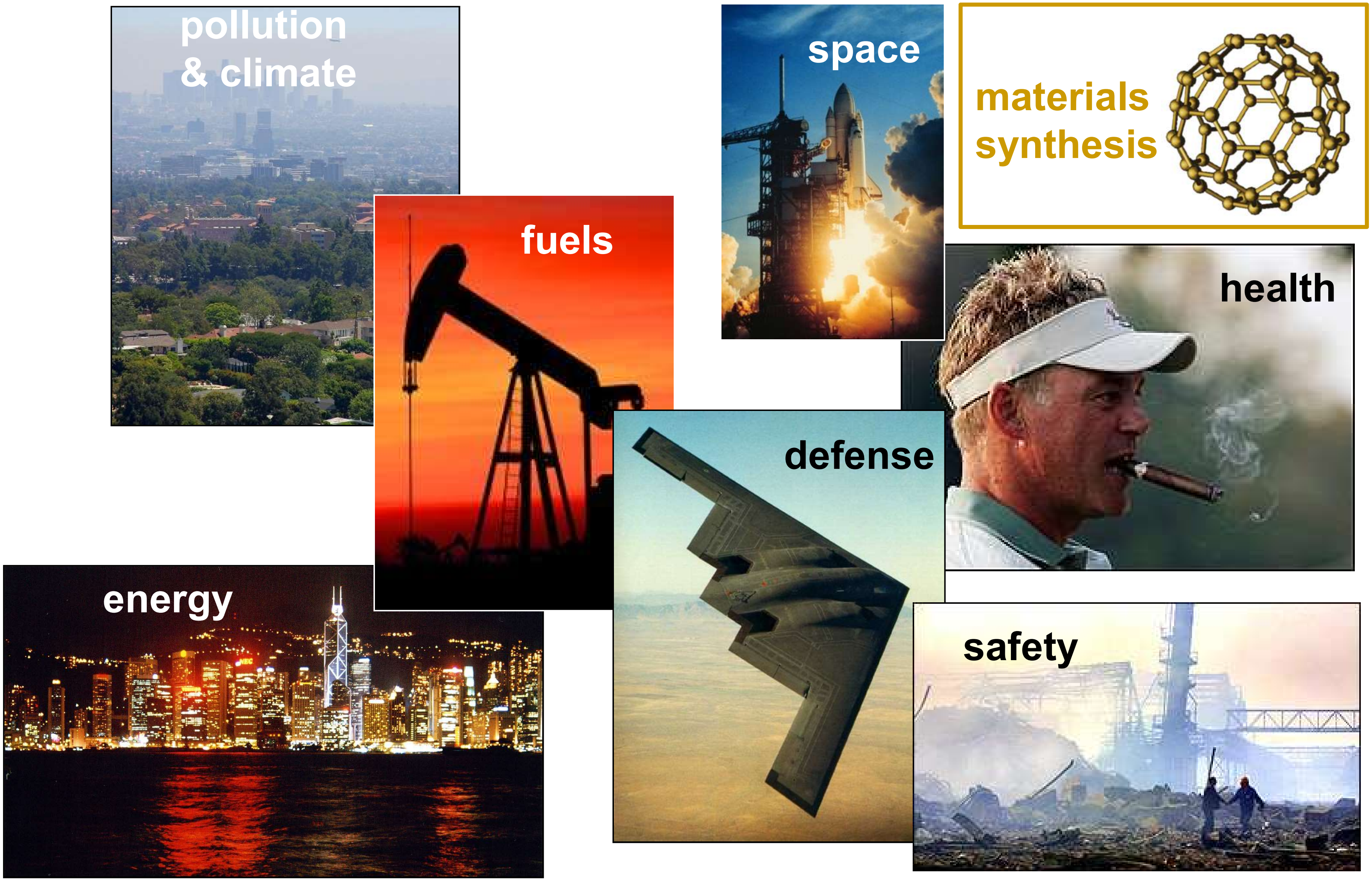
Combustion is A Multi-physics & Multi-scale Science

- Combustion is a multi-physics science, embodying two major branches of nonlinear science:
  - Chemical kinetics
  - Fluid mechanics
- Combustion is a multi-scale science
  - Electronic and inter-/intra-molecular interactions
  - Molecular rearrangement
  - Nano-particulate formation (e.g. soot)
  - Turbulent fuel/air mixing



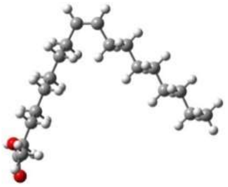
Courtesy: J.H. Chen

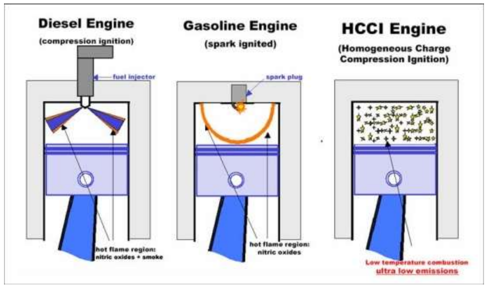
Combustion is
A Major Technology Driver



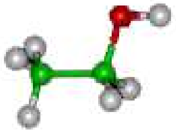
Role of Combustion in An Energy-Constrained World

- Burning of fossil fuels constitutes ~85% of the world's energy needs, negatively impacts
  - Energy sustainability
  - Energy security
  - Climate change

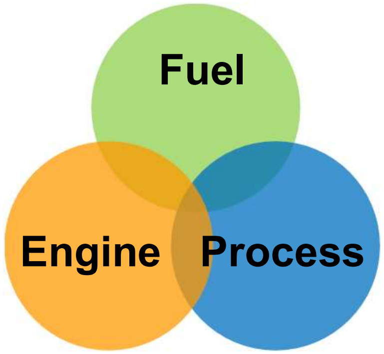




- In response, energy infrastructure is changing
  - Fuels: heavy hydrocarbons (coal, oil shale, tar sand…); Renewable biofuels (alcohols, biodiesel…)
  - Engines: New concepts (direct injection, HCCI, EVs…)



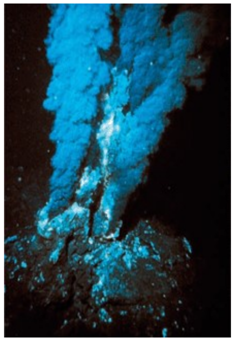
- Combustion-enabled solutions
  - Improve combustion efficiency & emissions
  - Use synfuels & carbon-neutral biofuels
  - (Co-)design/develop new fuels & engines

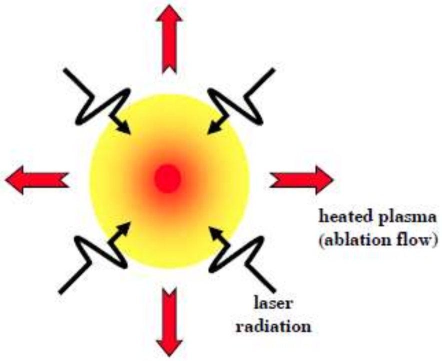


New Frontiers of Combustion

- Study of ~~chemically~~ reacting flows
- Transdisciplinary:

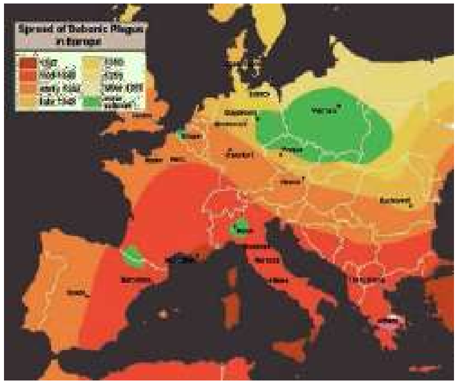
Biological science:
health; cellular transport & reactions; network analysis of biological processes; origin of life from ocean thermal vents





Nuclear science: nuclear reactions; hydrodynamic front instability in inertial confinement fusion (Clavin & Williams)

Astrophysics:
origin of universe; supernova

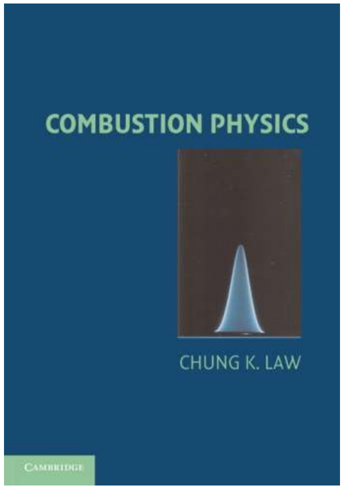


Societal science: social network; traffic network; spreading of disease fronts (bubonic plaque in 14th century)

Course Content

Topics of Daily Lectures

- Day 1: Chemical thermodynamics and kinetics
- Day 2: Generalized formulations
- Day 3: Diffusion flames and heterogeneous combustion
- Day 4: Laminar premixed flames
- Day 5: Combustion in complex flows



Day 1: Chemical Thermodynamics and Kinetics

1. **Chemical Thermodynamics**
   - Chemical equilibrium
   - Energy conservation & adiabatic flame temp., T_{ad}
2. **Chemical Kinetics**
   - Reaction rates and approximations
   - Theories of reaction rates
   - Straight and branched chain reactions
3. **Oxidation Mechanisms of Fuels**
   - Hydrogen, CO, hydrocarbons

Day 2: Generalized Formulations

1. **Conservation Equations**
    1. Derivation and constitutive relations
    2. Simplified diffusion-controlled system
    3. Conserved scalar formulations
2. **Discontinuity Surface Formulations**
    1. Generalized reaction-sheet formulation
    2. Reaction-sheet analysis of diffusion flames
    3. Rankine-Hugoniot waves in premixtures

Day 3: Diffusion Flames and Heterogeneous Combustion

1. **Burke-Schumann and counterflow flames**
2. **Heat & mass transfer with condensed fuels**
3. **Droplet combustion**
   1. The d^2-Law
   2. Multicomponent fuels
4. **Other heterogeneous systems**
   1. Carbon and metal particles
   2. Spray flames

Day 4: Laminar Premixed Flames

1. **The standard premixed flame**
    1. Phenomenological and asymptotic solutions
    2. Parametric dependence
    3. Chemical structure
2. **Limit phenomena**
    1. The S-curve concept
    2. Extinction through volumetric heat loss
3. **Aerodynamics of flames**
    1. Hydrodynamic stretch
    2. Flame stretch
    3. Flamefront instabilities

Day 5: Combustion in Complex Flows

1. **Turbulent flows**
    1. General concepts of turbulent flows
    2. Simulation and modeling
    3. Premixed burning: regime diagram and burning velocities
2. **Boundary-layer flows**
    1. Consideration of similarity
    2. Diffusion flame in the ablating Blasius flow
    3. Ignition in the Blasius flow
    4. Stabilization of the jet flame
3. **Supersonic flows**
    1. Sound waves in reactive flows
    2. Structure of detonation waves
    3. Direct and indirect detonation initiation

! Daily Specials !

Overarching Messages of the Course:
Appreciate the Beauty!

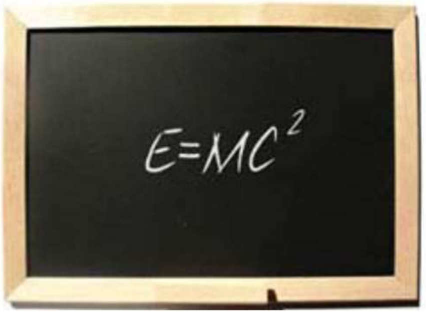
- Beauty is the driving force of the human intellect
- Unification is the ultimate goal of the scientific pursuit

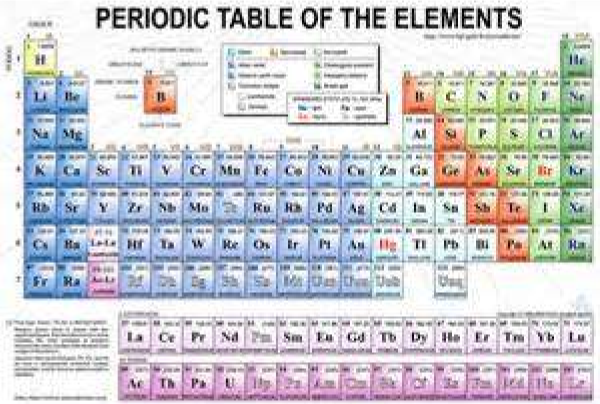
$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

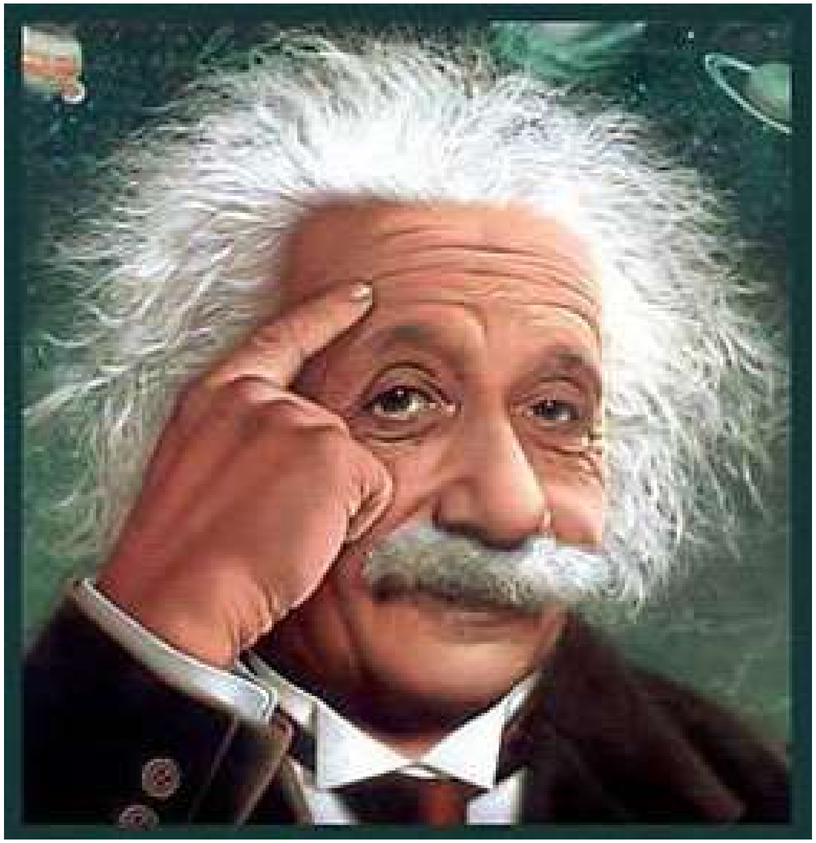
$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$



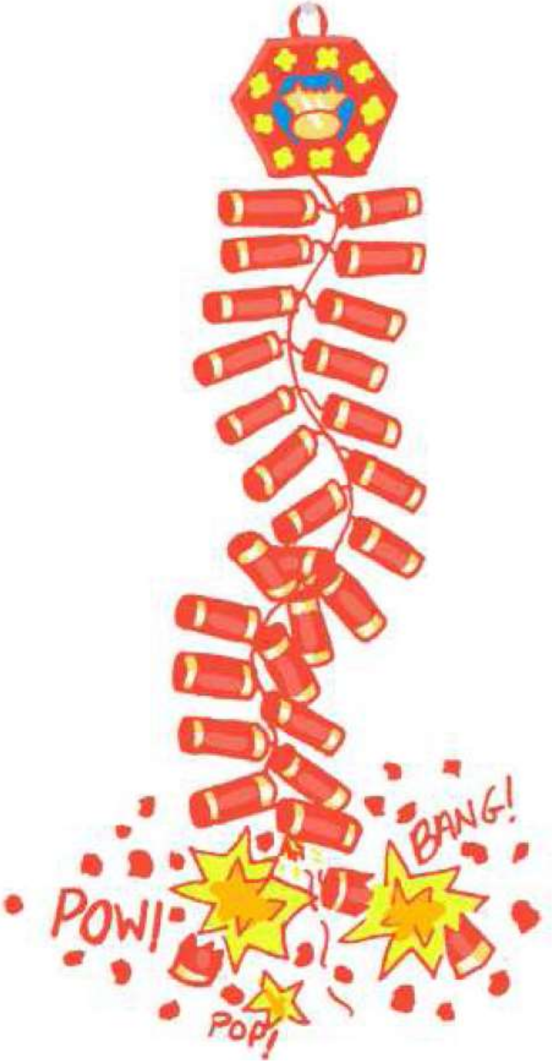


Unified concepts and theories are inevitably beautiful

Overarching Messages of the Course:
Expand the Mind!



Course Commences!!



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3. **Oxidation Mechanisms of Fuels**
   - Hydrogen, CO, hydrocarbons

1. Chemical Thermodynamics

Chemical Equilibrium (1/2)

- First and Second Laws

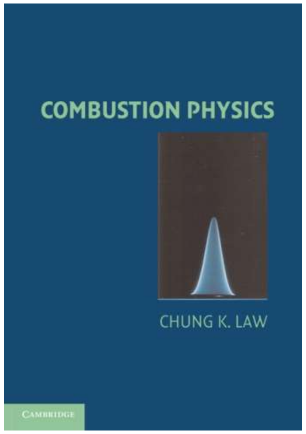
$$dE \leq TdS - pdV \qquad (1.2.4)^{*}$$

- Thermodynamic function: $E = E(S, V, Ni)$

$$dE = TdS - pdV + \sum_{i=1}^{N} \bar{\mu}_i dN_i \qquad (1.2.6)$$

- Criterion for chemical equilibrium

$$\sum_{i=1}^{N} \bar{\mu}_i dN_i = 0 \qquad (1.2.11)$$



*** Equation numbers refer to those in *Combustion Physics***

Chemical Equilibrium **(1/2)**

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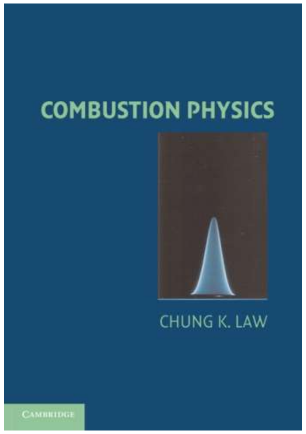

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Chemical Equilibrium (2/2)

- From element conservation for a general chemical reaction

$$\sum_{i=1}^{N} \nu_i' \mathrm{M}_i \rightleftarrows \sum_{i=1}^{N} \nu_i'' \mathrm{M}_i$$ e.g.: $H + O_2 \leftrightarrow OH + O$

we have $$\frac{dN_i}{\nu_i'' - \nu_i'} = \frac{dN_j}{\nu_j'' - \nu_j'} \qquad (1.2.14)$$

- Consequently, chemical equilibrium:

$$\sum_{i=1}^{N} \bar{\mu}_i dN_i = 0 \quad \Rightarrow \quad \sum_{i=1}^{N} \bar{\mu}_i (\nu_i'' - \nu_i') = 0 \qquad (1.2.17)$$

Equilibrium Constant for Reaction

- Chemical potential: $\bar{\mu}_i(T, p_i) = \bar{\mu}_i^o(T) + R^o T \ln(p_i/p^o),$ (1.2.29)
- Apply equilibrium criterion: $\sum_{i=1}^{N} \bar{\mu}_i(\nu_i'' - \nu_i') = 0$

$$\boxed{\prod_{i=1}^{N} p_i^{(\nu_i''-\nu_i')} = K_p(T),} \quad (1.2.30)$$

$$K_p(T) = \exp\left\{-\left[\sum_{i=1}^{N}(\nu_i''-\nu_i')\mu_i^o(T)\right]\bigg/(R^o T)\right\} \quad (1.2.31)$$

  - (LHS; RHS): Function of (concentrations; temperature)
  - $K_p(T)$: Tabulated for a given reaction

Equilibrium composition of a (fuel, oxidizer, inert) mixture at *T* and *p* can be calculated using the $K_p(T)$'s for all reactions

- **Comment:**

Procedure is cumbersome: needs tabulation for each reaction; there could be 100's to 1000's of reactions for oxidation of a fuel

Equilibrium Constant for Formation

- Simplification: Relate $K_p(T)$ to formation reaction of each species

$$\sum_{j=1}^{L} v'_{i,j} \mathrm{M}^{o}_{i,j} \rightleftarrows \mathrm{M}_i \qquad (1.2.32)$$

$\mathrm{M}^{o}_{i,j}$: element in standard state

$$K^{o}_{p,i}(T) = \exp[-\bar{\mu}^{o}_{i}(T)/(R^{o}T)] \qquad (1.2.33)$$

$$\boxed{K_p(T) = \prod_{i=1}^{N} K^{o}_{p,i}(T)^{(v''_i - v'_i)}} \qquad (1.2.34)$$

- **Comment:**

Number of species ~10's to 100's => Much reduced tabulation

Energy Conservation in Adiabatic System

(State 1 ⟶ State 2)

- $$\boxed{\sum_{i=1}^{N} N_{i,1}\bar{h}_i\left(T_1;T^o\right)=\sum_{i=1}^{N} N_{i,2}\bar{h}_i\left(T_2;T^o\right)}$$ (1.4.17)
- $$\underbrace{\bar{h}_i\left(T;T^o\right)}_{\text{total enthalpy}} = \underbrace{\bar{h}_i^o\left(T^o\right)}_{\text{heat of formation}} + \underbrace{\bar{h}_i^s\left(T;T^o\right)}_{\text{sensible heat}}$$ (1.4.16)

Heat of Formation, $\bar{h}_i^0(T^o)$: heat required to form one mole of reactants from its elements in their standard states, at a reference temperature T^o, $\sum_{j=i}^{L} \nu'_{i,j} M^o_{i,j} \rightarrow M_i$.

Sensible Heat: energy required to raise the temperature of substance from T^o to T, $\boxed{\bar{h}_i^s(T;T^o)=\int_{T^o}^{T}\bar{c}_{p,i}(T)dT.}$ (1.4.14)

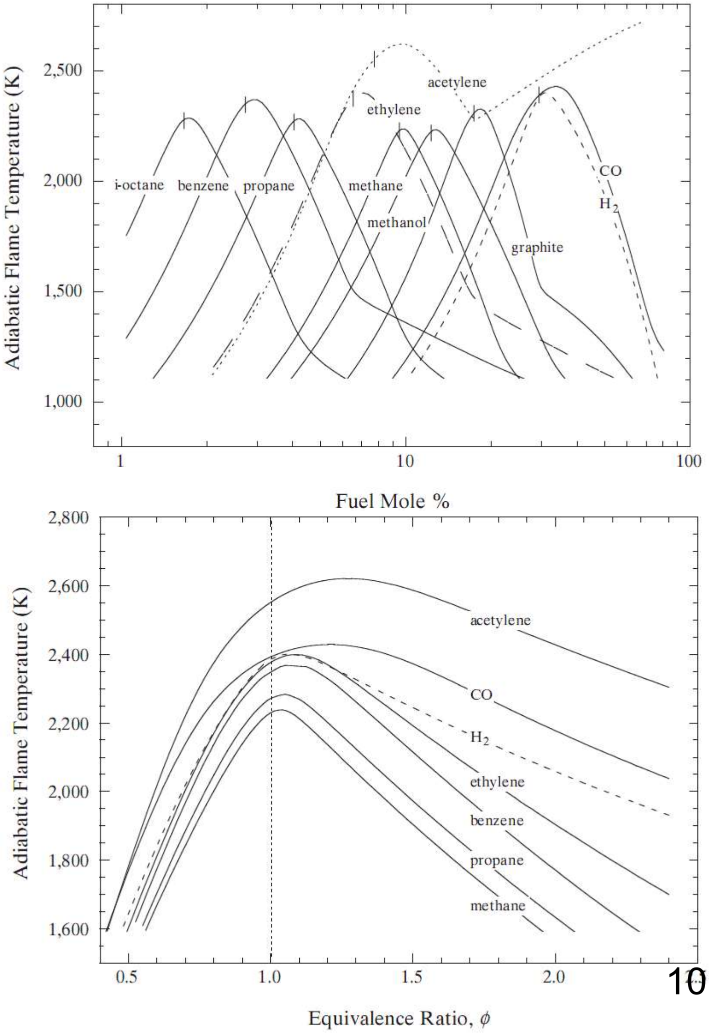
Specific Heat: function of degree of excitation,

$$\bar{c}_{p,i}\left(T\right)=\left(\partial\bar{h}_i^s/\partial T\right)_p.$$ (1.4.13)

- $$\boxed{\sum_{i=1}^{N} N_{i,1}\bar{h}_i^o(T^o)-\sum_{i=1}^{N} N_{i,2}\bar{h}_i^o(T^o)=\sum_{i=1}^{N} N_{i,2}\bar{h}_i^s(T_2;T^o)-\sum_{i=1}^{N} N_{i,1}\bar{h}_i^s(T_1;T^o).}$$ (1.4.18)

Adiabatic Flame Temperature (1/2)

- For a mixture (fuel, oxidizer, inert) of given composition and temperature T_1, determine the final, equilibrium temperature, T_{ad}, and product composition; the process is conducted adiabatically and at given pressure p.
  - T_{ad} calculated using $K_p(T)$, energy conservation, and element conservation
  - This is the single, most important parameter for a reacting mixture
- T_{ad} is most sensitive to mixture composition
  - Fuel/oxidizer equivalence ratio, $\boxed{\phi = \frac{(F/O)}{(F/O)_{st}}.}$
  - T_{ad} peaks slightly on the rich side of $\phi = 1$
  - Excess reactants (CO, H_2 for rich mixtures) serve as inert.
  - Amount and c_p of inert serve as heat sink.



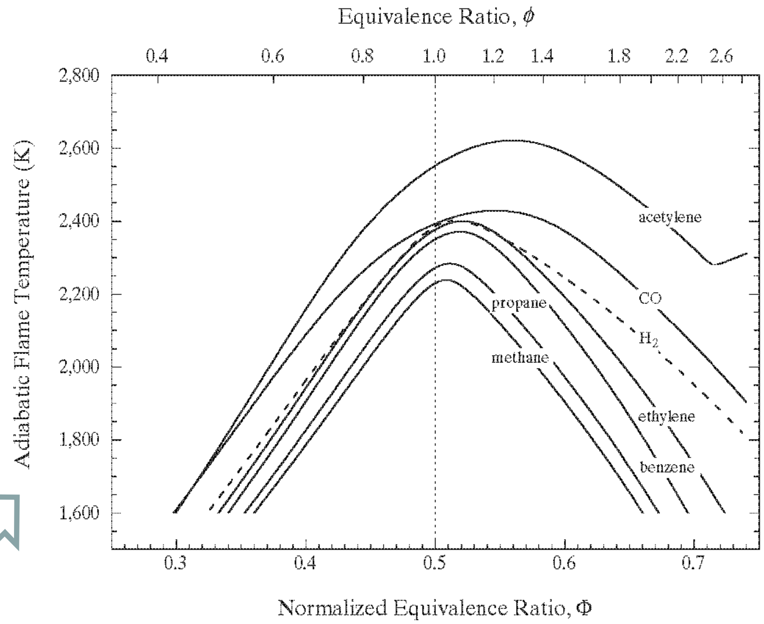
Adiabatic Flame Temperature (2/2)

- Slope asymmetry of $T_{ad}(\phi)$ largely due to asymmetrical definition of ϕ;

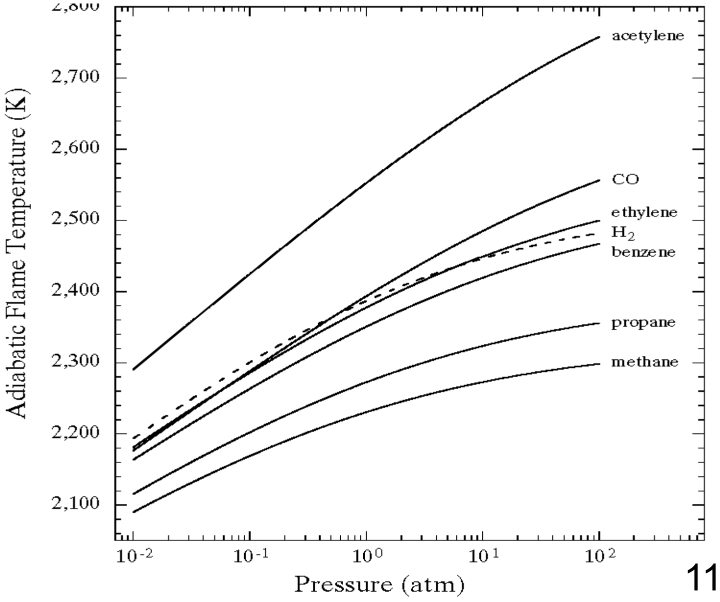
$$(\text{lean; rich}) = (0 < \phi < 1; 1 < \phi < \infty)$$

- Near-symmetry attained by using normalized equivalence ratio, $\boxed{\Phi = \dfrac{\phi}{1+\phi}}$;

$$(\text{lean; rich}) = (0 < \Phi < 0.5; 0.5 < \Phi < 1)$$



- T_{ad} slightly increases with increasing pressure due to reduced product dissociation



2. Chemical Kinetics

Introduction

- Chemical thermodynamics: relates the initial to the final equilibrium states of a reactive mixture; does not distinguish the path and time in the process (e.g.: acceptable cycle analysis for i.c. engines, but not NO_x formation)
- Chemical kinetics describes the path and rates of individual reactions and reactants; can be extremely complex – 10^3 intermediates and 10^4 elementary reactions.

Law of Mass Action

- For a single-step forward reaction: $\sum_{i=1}^{N} v_i' \mathrm{M}_i \xrightarrow{k_f} \sum_{i=1}^{N} v_i'' M_{i,}$
  - Molar rate of change: $\hat{\omega}_i = dc_i / dt$
  - i and j related by: $\frac{\hat{\omega}_i}{v_i'' - v_i'} = \frac{\hat{\omega}_j}{v_j'' - v_j'} = \omega,$ (2.1.3)
- Law of mass action:
  - Reaction rate proportional to product of concentrations (c_i)
  - Scaled reaction rate is given by: $\boxed{\omega = k_f(T) \prod_{i=1}^{N} c_i^{v_i''}}$ (2.1.4)
  - Proportionality constant $k_f(T)$: reaction rate constant; only function of temperature
- Example: $H + HO_2 \rightarrow OH + OH$

$$\omega = -\frac{d[\mathrm{H}]}{dt} = -\frac{d[\mathrm{HO_2}]}{dt} = \frac{1}{2}\frac{d[\mathrm{OH}]}{dt}, \qquad \omega = k_f\ [\mathrm{H}][\mathrm{HO_2}].$$

Reverse Reaction

- Every forward reaction has a backward reaction:

$$\sum_{i=1}^{N} v_i'' \mathrm{M}_i \xrightarrow{k_b} \sum_{i=1}^{N} v_i' \mathrm{M}_i$$

  - Net reaction rate: $\widehat{\omega}_i = \widehat{\omega}_{i,f} + \widehat{\omega}_{i,b} = (v_i'' - v_i')(\omega_f - \omega_b) = (v_i'' - v_i')\omega$

$$\omega = k_f \prod_{i=1}^{N} c_i^{v_i'} - k_b \prod_{i=1}^{N} c_i^{v_i''} \qquad (2.1.6)$$

  - At equilibrium: $\omega \equiv 0 \;\Rightarrow\; \dfrac{k_f}{k_b} = \prod_{i=1}^{N} c_i^{(v_i'' - v_i')} = K_c$ (2.1.7,8)
  - Implying: $\omega = k_f \left(\prod_{i=1}^{N} c_i^{v_i'} - K_c^{-1} \prod_{i=1}^{N} c_i^{v_i''} \right)$ (2.1.9)
- (2.1.6) referred to (2.1.6) because K_c can be determined more accurately than k_b
- Irreversible reaction approximation: $\omega \approx k_f \prod_{i}^{N} c_i^{v_i'}$

Multiple Reactions

- Practical reactions involving

  Reactants → Products

  e.g.: $2H_2+O_2 \rightarrow 2H_2O$

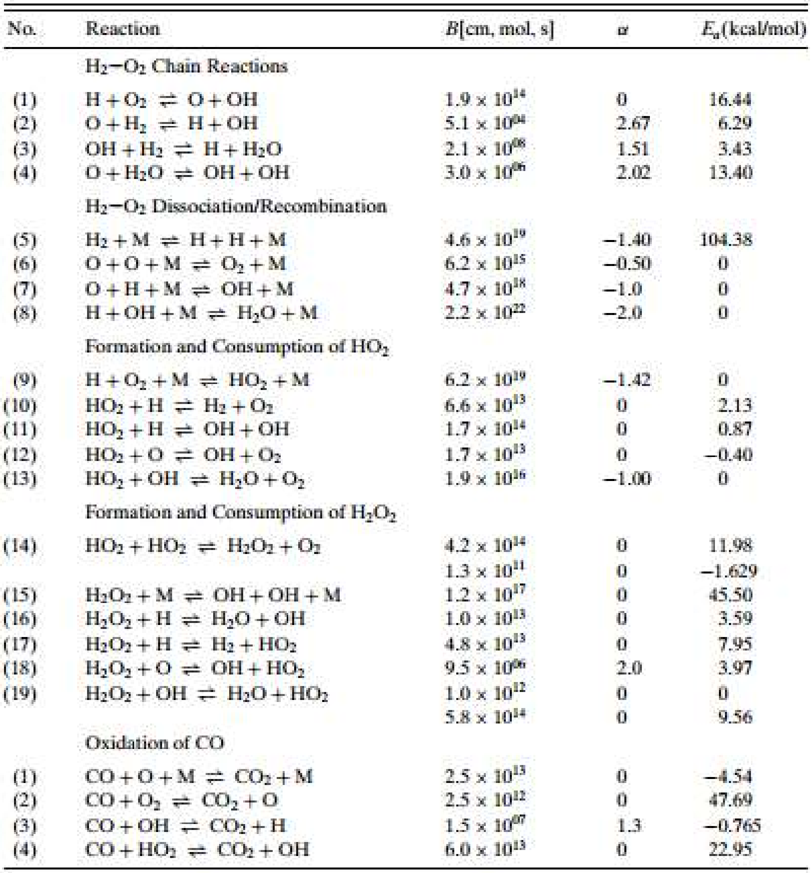
  Rarely (never!) occurs in one step between reactants (e.g.: two H_2 directly reacting with one O_2)

- Reality: For H_2-O_2: (at least) 19 reversible reactions and 8 species (H_2, O_2, H, O, OH, H_2O, HO_2, H_2O_2)
- Rate for K reactions :

$$\sum_{i=1}^{N} \nu'_{i,k} M_i \underset{k_{k,b}}{\overset{k_{k,f}}{\rightleftarrows}} \sum_{i=1}^{N} \nu''_{i,k} M_i, \quad k = 1, 2, \ldots, K,$$

$$\omega_k = k_{k,f} \prod_{i=1}^{N} c_i^{\nu'_{i,k}} - k_{k,b} \prod_{i=1}^{N} c_i^{\nu''_{i,k}},$$

$$\hat{\omega}_i = \sum_{k=1}^{K} (\nu''_{i,k} - \nu'_{i,k}) \omega_k. \qquad (2.1.14)$$



No.	Reaction	B[cm, mol, s]	α	E_a(kcal/mol)
	H_2-O_2 Chain Reactions			
(1)	$H + O_2 \rightleftharpoons O + OH$	1.9×10^{14}	0	16.44
(2)	$O + H_2 \rightleftharpoons H + OH$	5.1×10^{04}	2.67	6.29
(3)	$OH + H_2 \rightleftharpoons H + H_2O$	2.1×10^{08}	1.51	3.43
(4)	$O + H_2O \rightleftharpoons OH + OH$	3.0×10^{06}	2.02	13.40
	H_2-O_2 Dissociation/Recombination			
(5)	$H_2 + M \rightleftharpoons H + H + M$	4.6×10^{19}	−1.40	104.38
(6)	$O + O + M \rightleftharpoons O_2 + M$	6.2×10^{15}	−0.50	0
(7)	$O + H + M \rightleftharpoons OH + M$	4.7×10^{18}	−1.0	0
(8)	$H + OH + M \rightleftharpoons H_2O + M$	2.2×10^{22}	−2.0	0
	Formation and Consumption of HO_2			
(9)	$H + O_2 + M \rightleftharpoons HO_2 + M$	6.2×10^{19}	−1.42	0
(10)	$HO_2 + H \rightleftharpoons H_2 + O_2$	6.6×10^{13}	0	2.13
(11)	$HO_2 + H \rightleftharpoons OH + OH$	1.7×10^{14}	0	0.87
(12)	$HO_2 + O \rightleftharpoons OH + O_2$	1.7×10^{13}	0	−0.40
(13)	$HO_2 + OH \rightleftharpoons H_2O + O_2$	1.9×10^{16}	−1.00	0
	Formation and Consumption of H_2O_2			
(14)	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	4.2×10^{14}	0	11.98
		1.3×10^{11}	0	−1.629
(15)	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.2×10^{17}	0	45.50
(16)	$H_2O_2 + H \rightleftharpoons H_2O + OH$	1.0×10^{13}	0	3.59
(17)	$H_2O_2 + H \rightleftharpoons H_2 + HO_2$	4.8×10^{13}	0	7.95
(18)	$H_2O_2 + O \rightleftharpoons OH + HO_2$	9.5×10^{06}	2.0	3.97
(19)	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.0×10^{12}	0	0
		5.8×10^{14}	0	9.56
	Oxidation of CO			
(1)	$CO + O + M \rightleftharpoons CO_2 + M$	2.5×10^{13}	0	−4.54
(2)	$CO + O_2 \rightleftharpoons CO_2 + O$	2.5×10^{12}	0	47.69
(3)	$CO + OH \rightleftharpoons CO_2 + H$	1.5×10^{07}	1.3	−0.765
(4)	$CO + HO_2 \rightleftharpoons CO_2 + OH$	6.0×10^{13}	0	22.95

Yetter & Dryer

Rational Approximations

- Approximations based on comparison of rates of certain reaction entities
  - Quasi-steady-state (QSS) species approximation
  - Partial equilibrium (PE) reaction approximation

QSS Species Approximation

- Some chain carriers are generated and consumed at rapid rates such that their concentrations remain at low values and their net change rates are very small.
  - For $\widehat{\omega}_{\mathrm{i}} = \dfrac{dc_i}{dt} = \widehat{\omega}_i^{+} - \widehat{\omega}_i^{-}$,
  - If $\left|\dfrac{dc_i}{dt}\right| << (\widehat{\omega}_i^{+}, \widehat{\omega}_i^{-})$,
  - Then $\widehat{\omega}_i^{+} = \widehat{\omega}_i^{-}$.
- Consequence: (implicit) algebraic instead of differential solution
- Note: dc_i/dt may not be negligible compared to other rates

Partial Equilibrium Approximation

- If both the forward and backward rates of a reaction *k* is much larger than its net reaction rate,
  - then set: $\omega_k = k_{k,f}\prod_{i=1}^{N} c_i^{\nu'_{i,k}} - k_{k,b}\prod_{i=1}^{N} c_i^{\nu''_{i,k}} \approx 0$
  - such that $$k_{k,f}\prod_{i=1}^{N} c_i^{\nu'_{i,k}} \approx k_{k,b}\prod_{i=1}^{N} c_i^{\nu''_{i,k}} \qquad (2.1.17)$$
  - which yields an algebraic relation between c_i's.
- Note: ω_k not necessarily small compared to $\widehat{\omega}_i$.
- Example: formulation of the transition state theory of reaction rates, to be shown later.

Approximation by Global and Semi-global Reactions

- Successive application of QSS species and PE reactions will eventually lead to a one-step global reaction (at least theoretically!).
  - o The process is tedious; results still depend on the individual reaction rate parameters most of which are not known.
  - o Solution also requires iterations.
- May as well just start with a one-step reaction

$$\text{Fuel} + \text{Oxidizer} \xrightarrow{k} \text{Products}$$

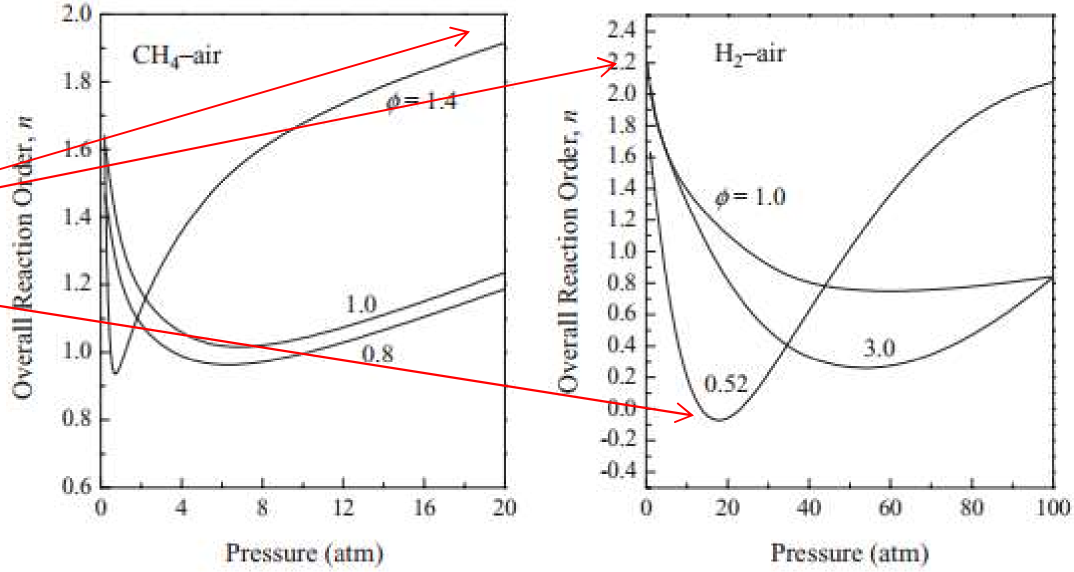
described by $\omega = k\prod_{i=1}^{N} c_i^{n_i}$,

where n_i is the reaction order, and is empirical

Reaction Order and Molecularity

- Molecularity, ν_i : number of colliding molecules in an elementary reaction
  - ν_i is a fundamental parameter; $\nu_i = 1, 2, 3.$
  - $\nu_i = 3$ is important for recombination reactions (negative influence on progression of reaction

    e.g. $\mathrm{H+O_2+M \rightarrow HO_2+M}$.
- Reaction order, n_i : indicates influence of concentration of i on the reaction rate
  - n_i is an empirical parameter
  - n_i mostly < 2
  - n_i can be negative!
  - $n_i = n_i(p)$.



The Arrhenius Law

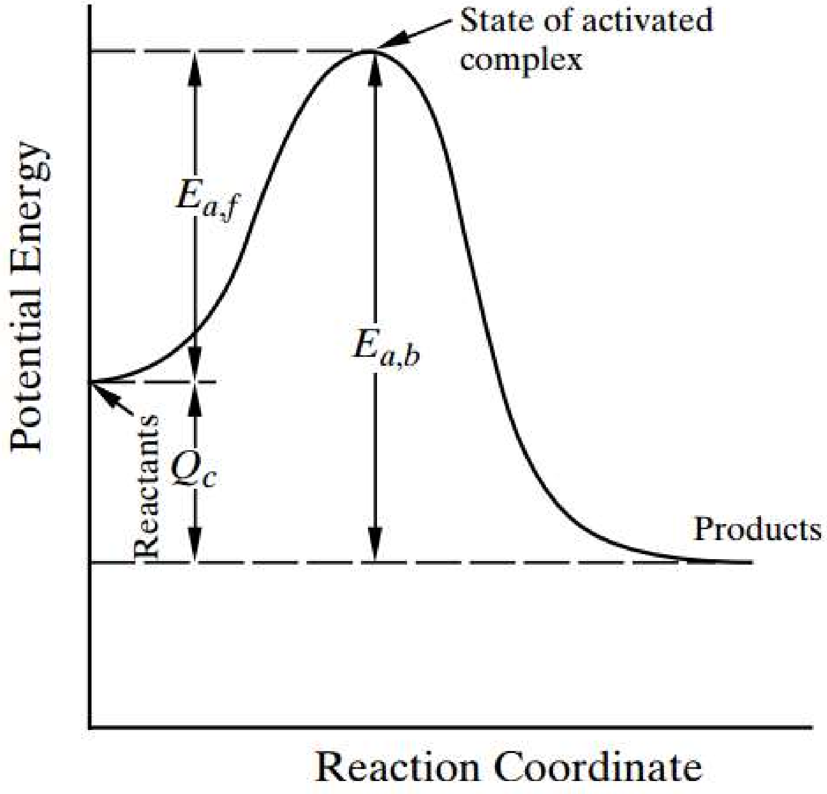
- Prescribes the dependence of the reaction rate constant on temperature:

$$\frac{d\ \ln k(T)}{dT}=\frac{E_a}{R^o T^2},$$

  - For constant E_a: $\boxed{k(T) = Ae^{-E_a/R^o T}}$
  - Modified form: $A = A(T) = BT^{\alpha}$

The Activation Energy, E_a

- $E_{a,f}$: minimum energy needed to initiate a reaction
  - Large E_a leads to temperature sensitivity
  - Some reactions (e.g. 3-body termination) have $E_a \equiv 0$.



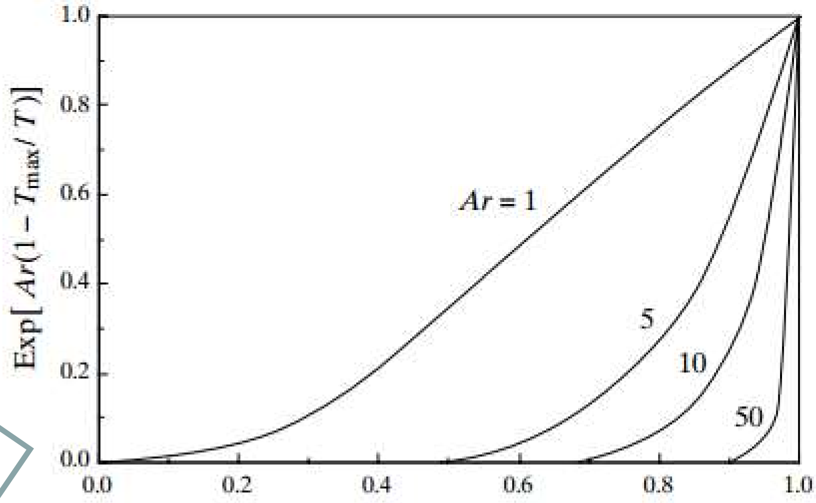
The Arrhenius Number, Ar

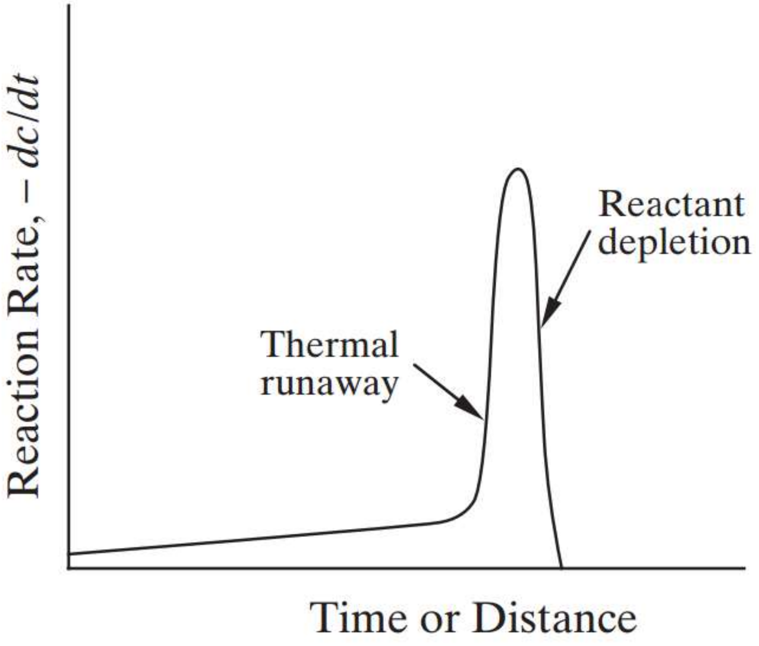
$$Ar = \frac{E_a}{R^o T_{\max}} = \frac{T_a}{T_{\max}}$$

$$\frac{\exp\ (-T_a/T)}{\exp\ (-T_a/T_{\max})} = \exp\left[Ar\left(1-\frac{T_{\max}}{T}\right)\right]$$

- Reaction is temperature sensitive for Ar≫1
- Combustion systems: Ar≫1
- Ar≫1 => localizes reaction regions (spatial or temporal)

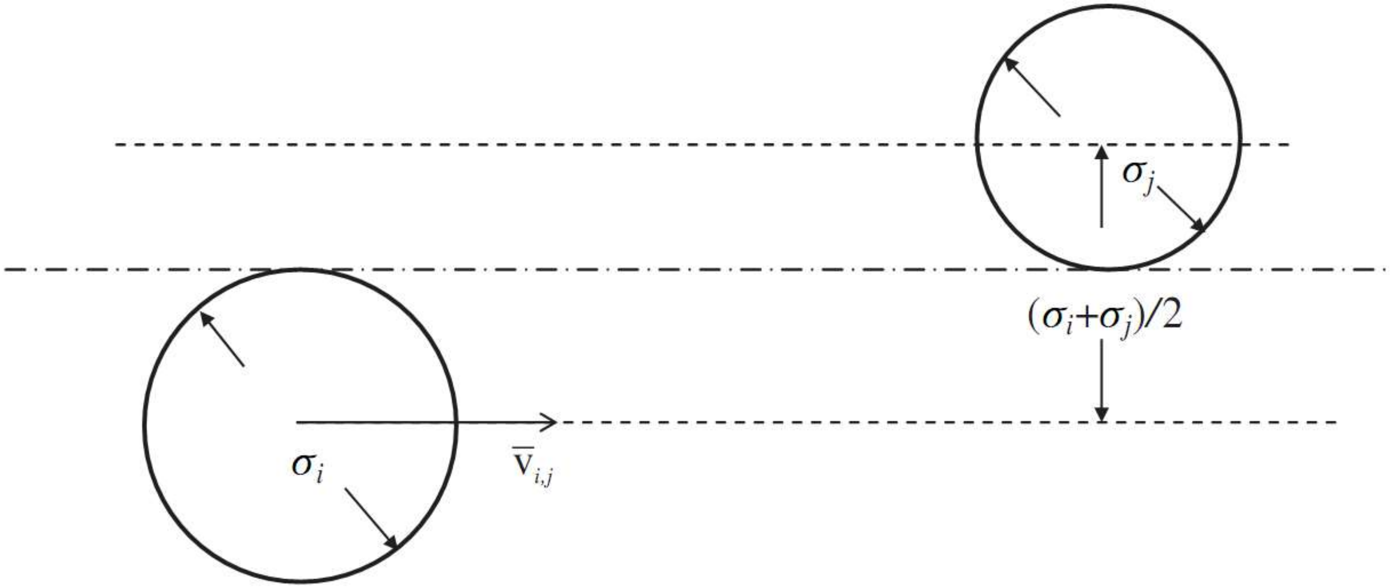
$$\frac{dc}{dt} = -Bce^{-E_a/R^oT}$$





Collision Theory of Reaction Rate (1/3)

- Assumptions:
  - Equilibrium Maxwell velocity distribution
  - Two-body hard-sphere collision
  - Reaction occurs if collision (translational) energy exceeds activation energy



Collision Theory of Reaction Rate (2/3)

- Reduced mass: $m_{i,j} = m_i m_j /(m_i + m_j)$
- Collision diameter: $\sigma_{i,j} = (\sigma_i + \sigma_j)/ 2$
- Collision velocity: $\overline{V}_{i,j} = \left(\dfrac{8k^oT}{\pi m_i}\right)^{1/2}$,
- Collision frequency per volume: $Z_{i,j} = \pi\sigma_{i,j}^2 n_i n_j \left(\dfrac{8k^oT}{\pi m_{i,j}}\right)^{1/2}$.
- Boltzmann velocity distribution: $\dfrac{n^*}{n} = e^{-E^*/R^oT}$.
- Collision frequency with energy in excess of $(E_i + E_j = E_a)$

$$Z^*_{i,j} = \pi\sigma_{i,j}^2 n^*_i n^*_j \left(\frac{8k^oT}{\pi m_{i,j}}\right)^{1/2} = Z_{i,j} e^{-E_a/R^oT} = -\frac{dn_i}{dt} = -\frac{dn_j}{dt}$$

Collision Theory of Reaction Rate (3/3)

- Relating $c_i = n_i / A^0$

$$\omega = -\frac{dc_i}{dt} = A^o \sigma_{i,j}^2 \left(\frac{8\pi k^o T}{m_{i,j}} \right)^{1/2} c_i c_j e^{-E_a / R^o T} = A(T) c_i c_j e^{-E_a / R^o T}.$$

- Comparing:

$$A(T) = A^o \sigma_{i,j}^2 \left(\frac{8\pi k^o T}{m_{i,j}} \right)^{1/2}, \qquad \alpha = 1/2$$

- Deviation from theory accounted by steric factor

$$A \rightarrow Z\psi$$

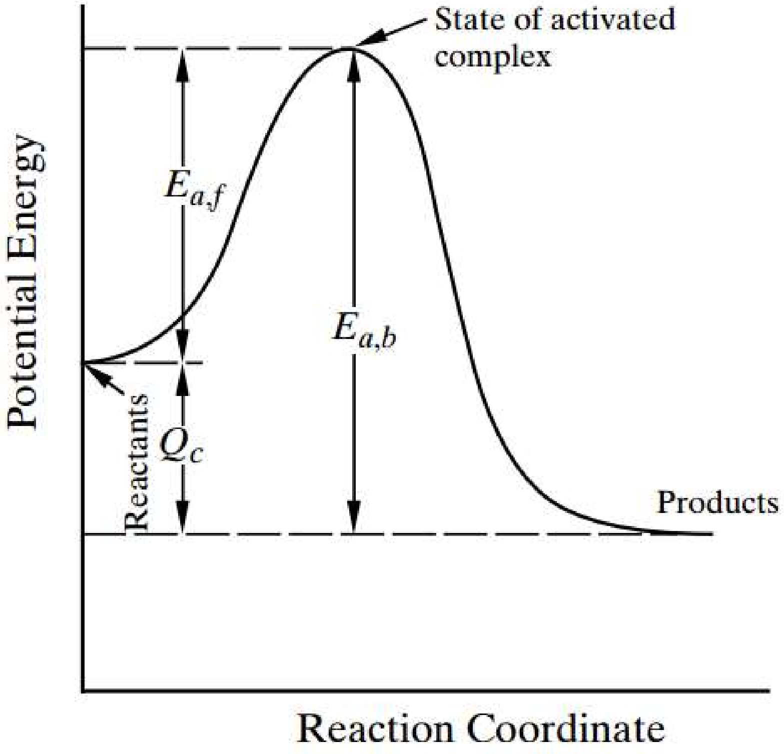
Transition State Theory of Reaction Rate (1/3)

- Overall reaction consists of two steps:
  - Activation: $\sum_{i=1}^{N} \nu_i' R_i \underset{k_{1,b}}{\overset{k_{1,f}}{\rightleftarrows}} \mathrm{R}^{\ddagger}$
  - Product formation: $\mathrm{R}^{\ddagger} \xrightarrow{k_2} \sum_{i=1}^{N} \nu_i'' \mathrm{P}_i,$

- Reaction rates for R_i and $R^{\ddagger}$

$$\frac{dc_{\mathrm{R}_i}}{dt} = -\nu_i' k_{1,f} \prod_{j=1}^{N} c_j^{\nu_j'} + \nu_i' k_{1,b} c_{\mathrm{R}^{\ddagger}}$$

$$\frac{dc_{\mathrm{R}^{\ddagger}}}{dt} = k_{1,f} \prod_{j=1}^{N} c_j^{\nu_j'} - k_{1,b} c_{\mathrm{R}^{\ddagger}} - k_2 c_{\mathrm{R}^{\ddagger}}.$$



Transition State Theory of Reaction Rate (2/3)

- Assumptions:
  - Partial equilibrium for activation step

$$dc_{\mathrm{R}_i}/dt = 0 \qquad c_{\mathrm{R}^\ddagger} = \mathrm{K}_c^\ddagger \prod_{j=1}^{N} c_j^{\nu'_j}$$

  - Steady-state for activated complex, $\mathrm{R}^\ddagger$

$$\frac{dc_{\mathrm{R}_i}}{dt} + \nu' \frac{dc_{\mathrm{R}^\ddagger}}{dt} = -\nu'_i k_2 c_{\mathrm{R}^\ddagger}.$$

$$\frac{dc_{\mathrm{R}^\ddagger}}{dt} << \frac{dc_{\mathrm{R}_i}}{dt}$$ yields

$$\frac{dc_{\mathrm{R}_i}}{dt} \approx -\nu'_i k_2 c_{\mathrm{R}^\ddagger} = -\nu'_i k_2 K_c^\ddagger \prod_{j=1}^{N} c_j^{\nu'_j},$$

- Compared with $\frac{dc_{\mathrm{R}_i}}{dt} = -\nu'_i k \prod_{j=1}^{N} c_j^{\nu'_j}$ yields $\boxed{k = k_2 K_c^\ddagger}$

Transition State Theory of Reaction Rate (3/3)

- To estimate k_2:
  - Kinetic energy = Vibrational energy

$$2 \cdot (\frac{1}{2} k^o T) = h^0 \nu$$

  - Assume products form during one vibration

$$k_2 \approx \nu$$

- Therefore:

$$\boxed{k \;=\; \left(\frac{k^o T}{h^o} \right) K_c^{\ddagger}.}$$

Theory of Unimolecular Reactions

A unimolecular reaction

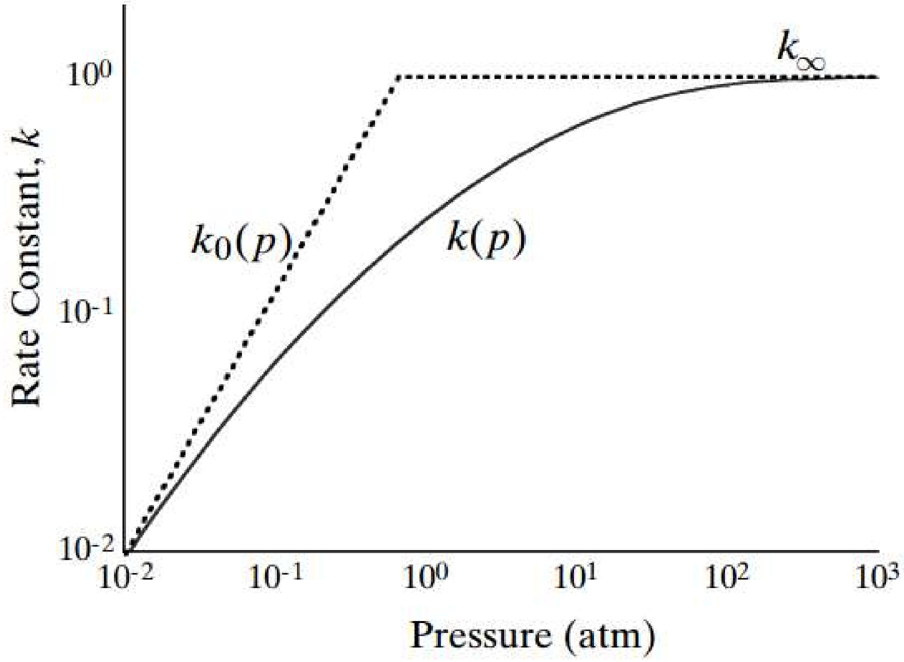
$$R \xrightarrow{k} P,$$

is really the high pressure limit of a second-order reaction

$$R+M \to P + M$$

where M is a collision partner

- $$\frac{dc_R}{dt} = -kc_R$$



- $k \to k_\infty$ = constant as $p \to \infty$

  $\Rightarrow$ First-order reaction

- $k \to k_0 p \sim k_0 c_R$ as $p \to 0$

  $\Rightarrow$ Second-order reaction

Straight Chain Reactions: Halogen-Hydrogen System (1/3)

- Straight chain: The consumption of one radical produces another radical
- Hydrogen-halogen system (X_2: I_2, Br_2, Cl_2, F_2)

$$\mathrm{X_2 + M} \xrightarrow{k_{1,f}} \mathrm{X + X + M} \qquad \text{Chain initiation} \quad (\mathrm{X1}f)$$

$$\mathrm{X + H_2} \xrightarrow{k_{2,f}} \mathrm{HX + H} \qquad \text{Chain carrying} \quad (\mathrm{X2}f)$$

$$\mathrm{H + X_2} \xrightarrow{k_{3,f}} \mathrm{HX + X} \qquad \text{Chain carrying} \quad (\mathrm{X3}f)$$

$$\mathrm{X + X + M} \xrightarrow{k_{1,b}} \mathrm{X2 + M} \qquad \text{Chain termination} \quad (\mathrm{X1}f)$$

$$\mathrm{H + HX} \xrightarrow{k_{2,b}} \mathrm{X+ H2} \qquad \text{Chain carrying} \quad (\mathrm{X2}f)$$

Straight Chain Reactions: Halogen-Hydrogen System (2/3)

- Reaction rates:

$$\frac{d[\mathrm{H_2}]}{dt} = -k_{2,f}[\mathrm{X}][\mathrm{H_2}] + k_{2,b}[\mathrm{H}][\mathrm{HX}]$$

$$\frac{d[\mathrm{X_2}]}{dt} = -k_{1,f}[\mathrm{X_2}][\mathrm{M}] - k_{3,f}[\mathrm{H}][\mathrm{X_2}] + k_{1,b}\ [\mathrm{X}]^2\ [\mathrm{M}]$$

$$\frac{d[\mathrm{H}]}{dt} = k_{2,f}[\mathrm{X}][\mathrm{H_2}] - k_{3,f}[\mathrm{H}][\mathrm{X_2}] - k_{2,b}[\mathrm{H}][\mathrm{HX}]$$

$$\frac{d[\mathrm{X}]}{dt} = 2k_{1,f}[\mathrm{X_2}][\mathrm{M}] - k_{2,f}[\mathrm{X}][\mathrm{H_2}] + k_{3,f}[\mathrm{H}][\mathrm{X_2}]$$

$$+ k_{2,b}[\mathrm{H}][\mathrm{HX}] - 2k_{1,b}[\mathrm{X}]^2\ [\mathrm{M}]$$

$$\frac{d[\mathrm{HX}]}{dt} = k_{2,f}[\mathrm{X}][\mathrm{H_2}] + k_{3,f}[\mathrm{H}][\mathrm{X_2}] - k_{2,b}[\mathrm{H}][\mathrm{HX}]$$

- Apply steady-state assumption for H and X:

$$\frac{d[\mathrm{H}]}{dt} = 0$$

$$\frac{d[\mathrm{X}]}{dt} = 0$$

Straight Chain Reactions: Halogen-Hydrogen System (3/3)

- Detailed analysis yields:

$$\boxed{\frac{d[\mathrm{HX}]}{dt}=\frac{2k_{2,f}(k_{1,f}/k_{1,b})^{1/2}[\mathrm{H}_2][\mathrm{X}_2]^{1/2}}{1+(k_{2,b}/k_{3,f})[\mathrm{HX}]/[\mathrm{X}_2]}.} \qquad (2.4.8)$$

- One-step reaction yields:

$$\mathrm{H}_2+\mathrm{X}_2 \xrightarrow{k_0} 2\mathrm{HX} \qquad (\mathrm{X0})$$

$$\frac{d[\mathrm{HX}]}{dt}=\boxed{2k_0\,[\mathrm{H}_2][\mathrm{X}_2],} \qquad (2.4.1)$$

- Comparing with detailed analysis (2.4.18) shows
  - Complex instead of linear dependence on $[\mathrm{X}_2]$
  - Inhibiting effect of [HX]

Branched Chain Reactions:

H_2-O_2 System

- The consumption of one radical generates more than one radical

$H + O_2 \rightarrow OH + O$ Chain branching (H1)

$O + H_2 \rightarrow OH + H$ Chain branching (H2)

$OH + H_2 \rightarrow H_2O + H$ Chain carrying (H3)

- The net of (H1) to (H3) yields 2H per cycle:

$3H_2 + O_2 \rightarrow 2H_2O + 2H$

- Different radicals have different reactivities => Chain carrying steps can be weakening

$H + O_2 + M \rightarrow HO_2 + M$ (HO_2 less reactive than H)

$CH_4 + H \rightarrow CH_3 + H_2$ (CH_3 less reactive than H)

Branched Chain Reactions:

Pressure Effect (1/2)

$nR \xrightarrow{k_1} C$ Initiation

$R + C \xrightarrow{k_2} aC + P$ Chain branching cycle

$C + R + R \xrightarrow{k_g} P$ Gas termination

$C \xrightarrow{k_w} P$ Wall termination

$$\frac{\mathrm{d[C]}}{dt} = k_1[\mathrm{R}]^n + (a-1)k_2[\mathrm{R}][\mathrm{C}] - k_g[\mathrm{R}]^2[\mathrm{C}] - k_w[\mathrm{C}]$$

$$= k_1\ [\mathrm{R}]^n + k_2[\mathrm{R}](a - a_\mathrm{c})[\mathrm{C}]$$

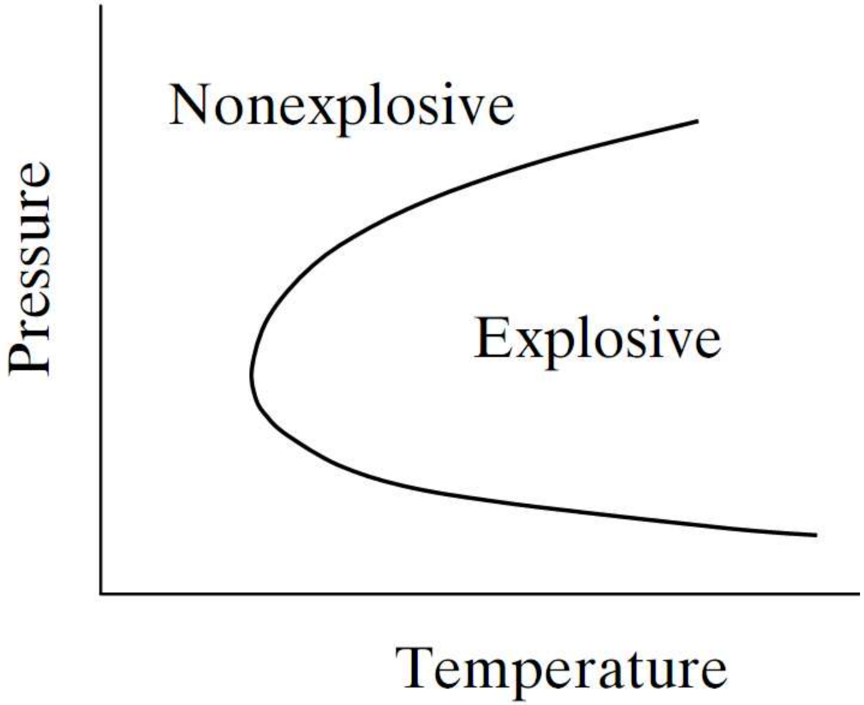
$$a_c = 1 + \frac{k_g[\mathrm{R}]^2 + k_w}{k_2[\mathrm{R}]}.$$

Branched Chain Reactions:

Pressure Effect (2/2)

- $$\frac{d[\mathrm{C}]}{dt} = k_1[\mathrm{R}]^n + k_2[\mathrm{R}](a - a_c)[\mathrm{C}], \qquad (2.4.15)$$

  - ○ blows up for a > a_c
  - ○ delays for a < a_c



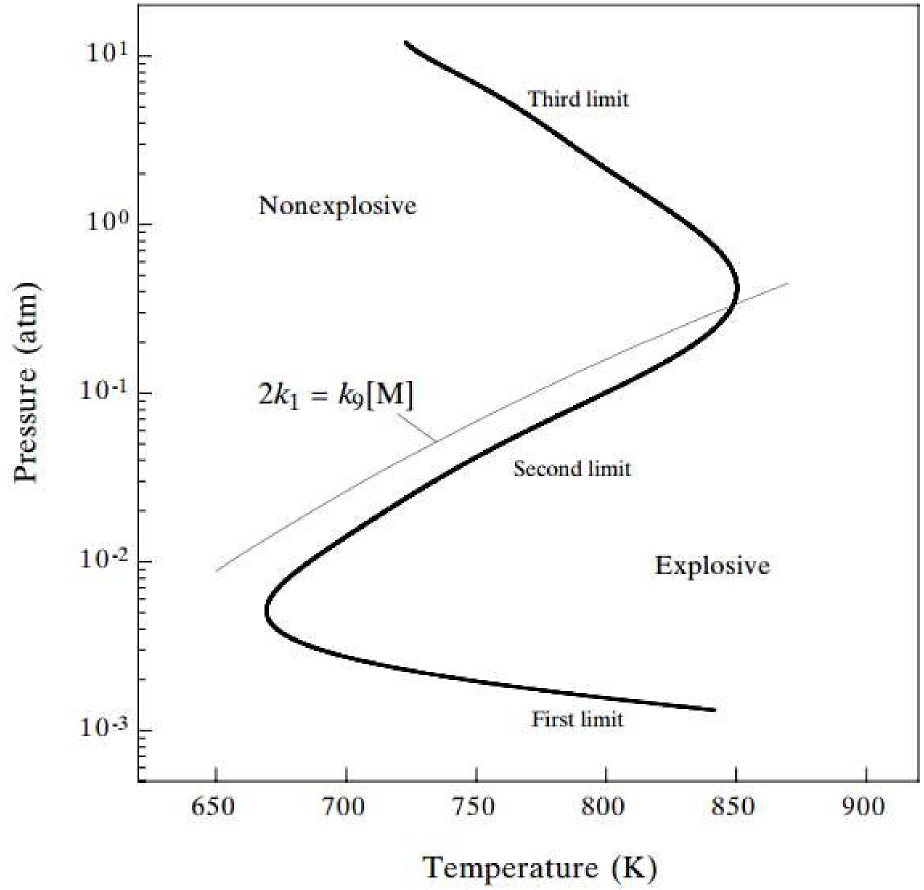
- $$\boxed{a_c = 1 + \frac{k_g[\mathrm{R}]^2 + k_w}{k_2[\mathrm{R}]}}$$

$$\rightarrow 1 + \frac{k_w}{k_2[\mathrm{R}]} \rightarrow \infty \qquad as \quad p \rightarrow 0$$

$$\rightarrow 1 + \frac{k_g[\mathrm{R}]}{k_2} \rightarrow \infty \qquad as \quad p \rightarrow \infty$$

3. Oxidation Mechanisms of Fuels

Oxidation of Hydrogen (1/2)



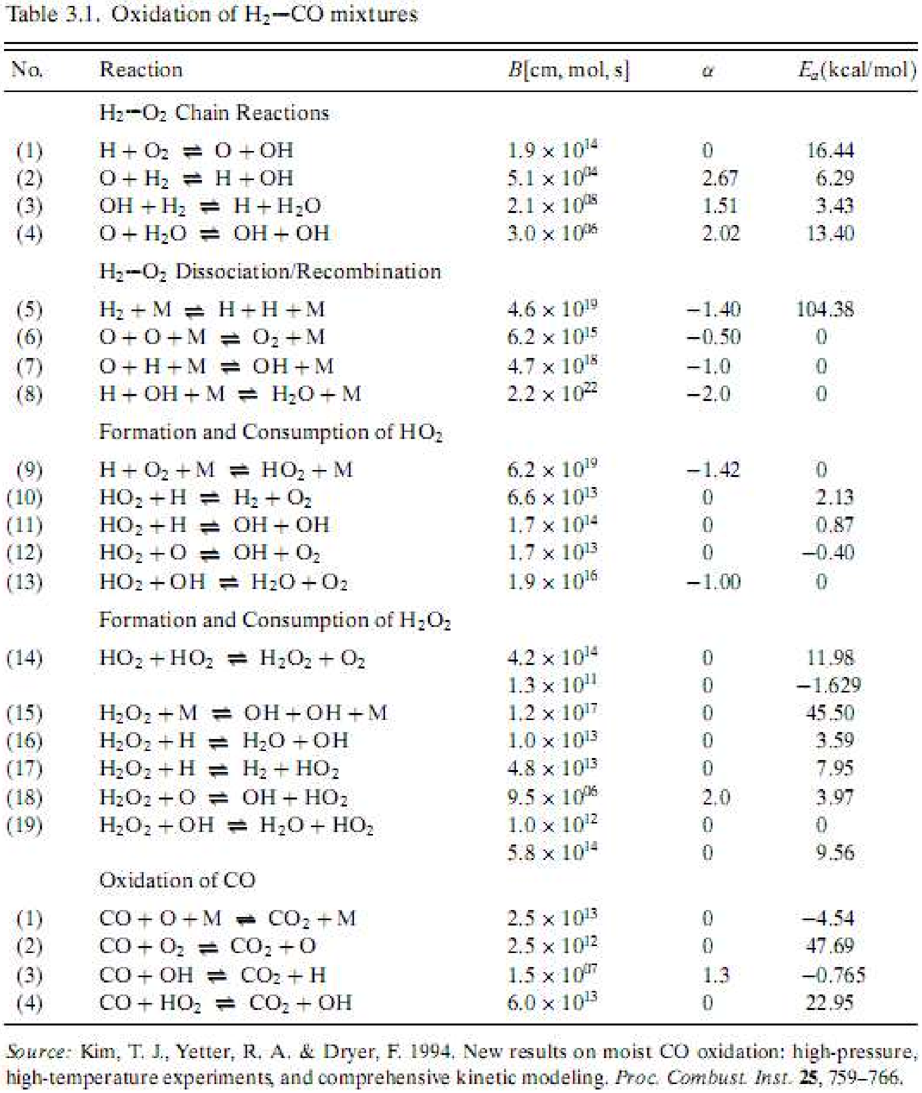


Table 3.1. Oxidation of H_2—CO mixtures

No.	Reaction	B[cm, mol, s]	α	E_a(kcal/mol)
	H_2—O_2 Chain Reactions			
(1)	$H + O_2 \rightleftharpoons O + OH$	1.9×10^{14}	0	16.44
(2)	$O + H_2 \rightleftharpoons H + OH$	5.1×10^{04}	2.67	6.29
(3)	$OH + H_2 \rightleftharpoons H + H_2O$	2.1×10^{08}	1.51	3.43
(4)	$O + H_2O \rightleftharpoons OH + OH$	3.0×10^{06}	2.02	13.40
	H_2—O_2 Dissociation/Recombination			
(5)	$H_2 + M \rightleftharpoons H + H + M$	4.6×10^{19}	−1.40	104.38
(6)	$O + O + M \rightleftharpoons O_2 + M$	6.2×10^{15}	−0.50	0
(7)	$O + H + M \rightleftharpoons OH + M$	4.7×10^{18}	−1.0	0
(8)	$H + OH + M \rightleftharpoons H_2O + M$	2.2×10^{22}	−2.0	0
	Formation and Consumption of HO_2			
(9)	$H + O_2 + M \rightleftharpoons HO_2 + M$	6.2×10^{19}	−1.42	0
(10)	$HO_2 + H \rightleftharpoons H_2 + O_2$	6.6×10^{13}	0	2.13
(11)	$HO_2 + H \rightleftharpoons OH + OH$	1.7×10^{14}	0	0.87
(12)	$HO_2 + O \rightleftharpoons OH + O_2$	1.7×10^{13}	0	−0.40
(13)	$HO_2 + OH \rightleftharpoons H_2O + O_2$	1.9×10^{16}	−1.00	0
	Formation and Consumption of H_2O_2			
(14)	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	4.2×10^{14}	0	11.98
		1.3×10^{11}	0	−1.629
(15)	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.2×10^{17}	0	45.50
(16)	$H_2O_2 + H \rightleftharpoons H_2O + OH$	1.0×10^{13}	0	3.59
(17)	$H_2O_2 + H \rightleftharpoons H_2 + HO_2$	4.8×10^{13}	0	7.95
(18)	$H_2O_2 + O \rightleftharpoons OH + HO_2$	9.5×10^{06}	2.0	3.97
(19)	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.0×10^{12}	0	0
		5.8×10^{14}	0	9.56
	Oxidation of CO			
(1)	$CO + O + M \rightleftharpoons CO_2 + M$	2.5×10^{13}	0	−4.54
(2)	$CO + O_2 \rightleftharpoons CO_2 + O$	2.5×10^{12}	0	47.69
(3)	$CO + OH \rightleftharpoons CO_2 + H$	1.5×10^{07}	1.3	−0.765
(4)	$CO + HO_2 \rightleftharpoons CO_2 + OH$	6.0×10^{13}	0	22.95

Source: Kim, T. J., Yetter, R. A. & Dryer, F. 1994. New results on moist CO oxidation: high-pressure, high-temperature experiments, and comprehensive kinetic modeling. *Proc. Combust. Inst.* **25**, 759–766.

Oxidation of Hydrogen (2/2)

- Initiation:
  - $H_2 + M \rightarrow H + H + M$ $\quad \bar{q}_p = 104\,\text{kcal/mole}$
  - $O_2 + M \rightarrow O + O + M$ $\quad 118\,\text{kcal/mole}$
  - $H_2 + O_2 \rightarrow HO_2 + H$ $\quad 55\,\text{kcal/mole; preferred}$
- First-limit chemistry:
  - Wall termination of H as $p \downarrow$
- Second-limit chemistry
  - Branching & carrying:
    - $H + O_2 \rightarrow O + OH$
    - $O + H_2 \rightarrow H + OH$
    - $OH + H_2 \rightarrow H + H_2O$
  - Termination:
    - $H + O_2 + M \rightarrow HO_2 + M$ (3-body reaction promoted as p↑)
    - $HO_2 \rightarrow$ wall termination

Second-limit Chemistry

$$\frac{d[\mathrm{H}]}{dt} = -k_1[\mathrm{H}][\mathrm{O}_2] + k_2[\mathrm{O}][\mathrm{H}_2] + k_3[\mathrm{OH}][\mathrm{H}_2] - k_9[\mathrm{H}][\mathrm{O}_2][\mathrm{M}]$$

$$\frac{d[\mathrm{O}]}{dt} = k_1[\mathrm{H}][\mathrm{O}_2] - k_2[\mathrm{O}][\mathrm{H}_2]$$

$$\frac{d[\mathrm{OH}]}{dt} = k_1[\mathrm{H}][\mathrm{O}_2] + k_2[\mathrm{O}][\mathrm{H}_2] - k_3[\mathrm{OH}][\mathrm{H}_2].$$

- Assume steady state for O and OH:

$$\frac{d[\mathrm{H}]}{dt} = (2k_1 - k_9[\mathrm{M}])[\mathrm{H}][\mathrm{O}_2] = 2\omega_1 - \omega_9 \qquad (3.2.4,5)$$

  - System explodes if $(2k_1 - k_9[\mathrm{M}]) > 0$
  - Second limit: $\boxed{2k_1 = k_9[\mathrm{M}]}$ $\quad p = \frac{2k_1}{k_9} R°T.$

Third-Limit Chemistry

- [HO_2] increases with increasing pressure, leading to:

$$HO_2 + H_2 \rightarrow H_2O_2 + H$$

$$H_2O_2 + M \rightarrow OH + OH + M$$

- At high temperatures and pressures, more radicals are produced, leading to radical-radical reactions

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

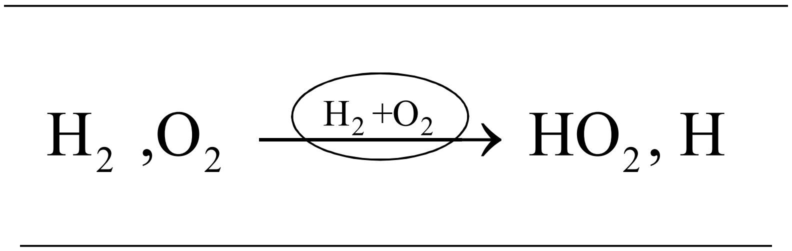
$$HO_2 + H \rightarrow OH + OH$$

$$HO_2 + O \rightarrow OH + O_2$$

Role of Initiation Reaction

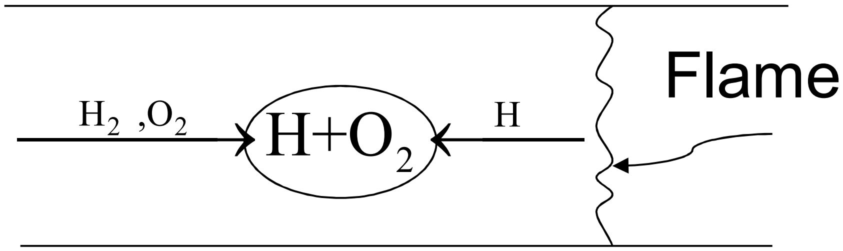
Homogeneous System

- Shock tube, flow reactor,…
- No diffusive transport
- Radicals generated from original reactants
- e.g.: $\boxed{H_2 + O_2 \rightarrow HO_2 + H}$



Diffusive System with Flame

- Radical produced in high-temperature flame
- Radical back diffuses and reacts with incoming reactant
- e.g.: $\boxed{H + O_2 \rightarrow OH + O}$
- Different (lower) global activation energy



Oxidation of Carbon Monoxide

- Direct oxidation rarely relevant:

$$CO + O_2 \rightarrow CO_2 + O$$

  - High activation energy (48 kcal/mole)
  - No branching
  - Hence no dry CO oxidation
- Dominant oxidation route:

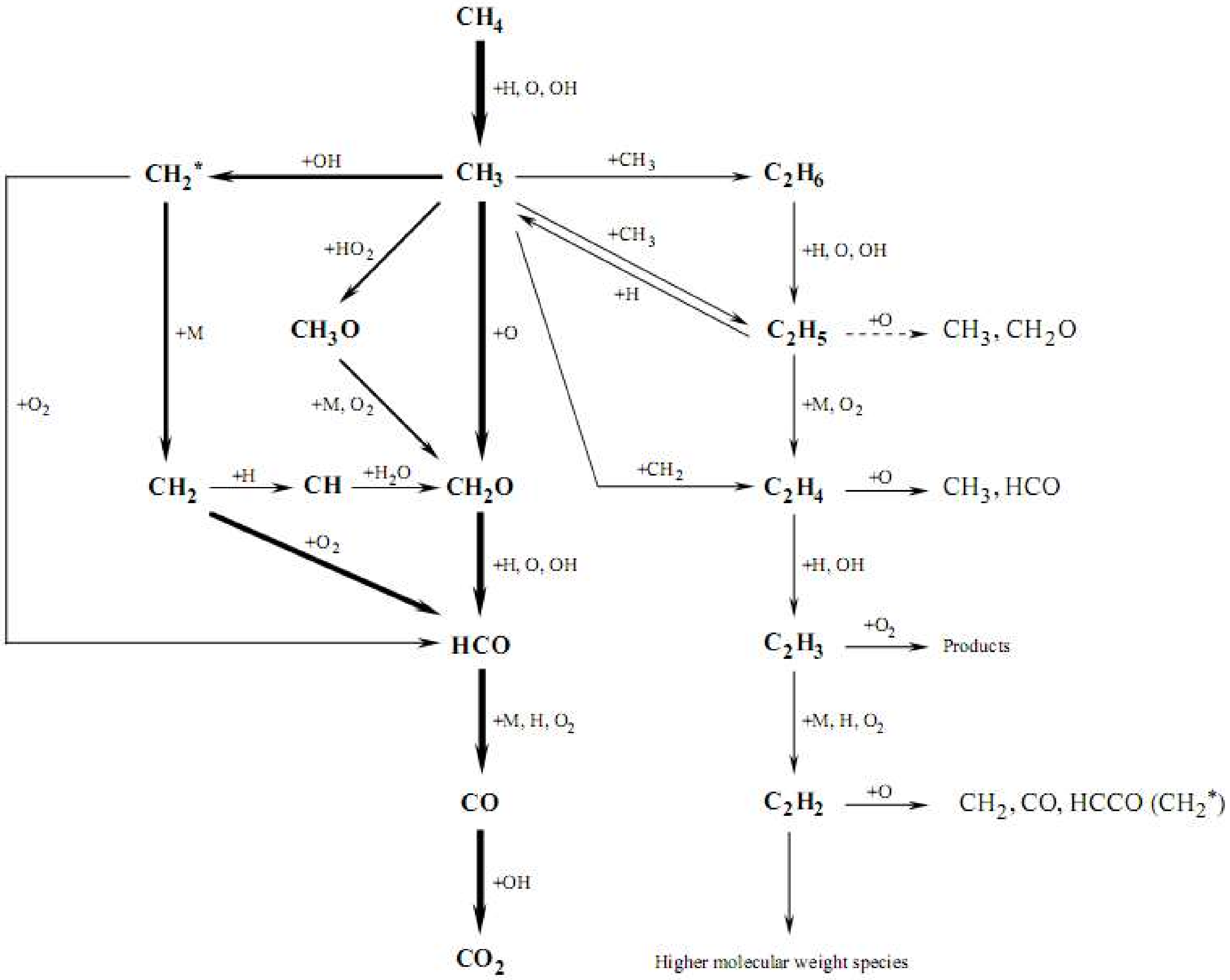
$$\boxed{CO + OH \rightarrow CO_2 + H} \qquad \text{(CO3)}$$

  - Integrated to the H_2-O_2 chain
  - H_2, H_2O are catalysts for CO oxidation
  - Extremely sensitive to moisture content

General Considerations of Hydrocarbon Oxidation

- Most important reactions in HC oxidation:
  - Chain initiation: (H, HO_2)
  - Chain branching: $H+O_2 \rightarrow OH+O$
  - Heat release: $CO+OH \rightarrow CO_2+H$
- HC oxidation is hierarchical:
  - Large HC molecule breaks down into smaller C_1, C_2, C_3 fragments in the low-temperature region/regime, with small heat release, which subsequently undergo massive oxidation with large heat release
- Dominant low-temperature chemistry: HO_2 chemistry
- Dominant high-temperature chemistry: H_2-O_2 chain

Methane Oxidation



Methane Initiation Reactions

- High-temperature route:

  $CH_4 + M \rightarrow CH_3 + H + M$

  $H + O_2 \rightarrow OH + O$

  $CH_4 + (H, O, OH) \rightarrow CH_3 + (H_2, OH, H_2O)$

  ○ $CH_4+H \rightarrow CH_3+H_2$ is retarding (exchange H by CH_3)

  Ignition delay time increases with $[CH_4]$!

- Low-temperature route:

  $CH_4 + O_2 \rightarrow CH_3 + HO_2$

  $CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$

  $H_2O_2 + M \rightarrow OH + OH + M$

Methyl (CH_3) Reactions

- Oxidation path:
  - Continuous stripping of H eventually leads to CO_2
  - Oxidation of H leads to H_2O
- Growth path:
  - $CH_3 + CH_3 + M \rightarrow C_2H_6 + M$

    latched onto the ethane oxidation path
  - $CH_3 + CH_3 \rightarrow C_2H_5 + H$

    latched onto the ethyl oxidation path

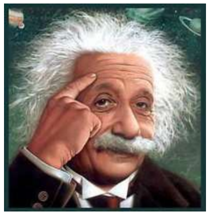
Closing Remarks of Day 1 Lecture (1/2)

- Adiabatic flame temperature, T_{ad} , and equilibrium composition, c_i
  - Consequence of chemical equilibrium and energy conservation
  - Single most important property of a combustible mixture; usually peaks slightly on the rich side of $\phi = 1$,
  - Is there a T_{ad} for nonpremixed systems?

Closing Remarks of Day 1 Lecture (2/2)

- Oxidation mechanisms of fuels are described by a plethora of coupled, nonlinearly interacting elementary reactions
    - Track radicals in branching, carrying & termination reactions
    - (H, HO_2) are key radicals in (high, low) temperature regimes
    - Increasing T favors 2-body,large E_a reactions; increasing pressure favors 3-body, termination reactions, with E_a=0
    - Combustion is characterized by large values of overall E_a; i.e. the Arrhenius number, Ar, when referenced to T_{ad}
    - Large Ar confines reactions to narrow spatial regions or time intervals

Day 1 Specials



1. Significance of normalized parametric representation (e.g.: scatters in laminar flame speed determination)
2. Growth & reduction of complexity in combustion CFD
3. Cubic description of the H_2-O_2 Z-curve: towards “analytical” chemistry

1. Significance of Normalized Parametric Representation: The Equivalence Ratio

- Assessment of premixed systems frequently are based on equivalence ratio:

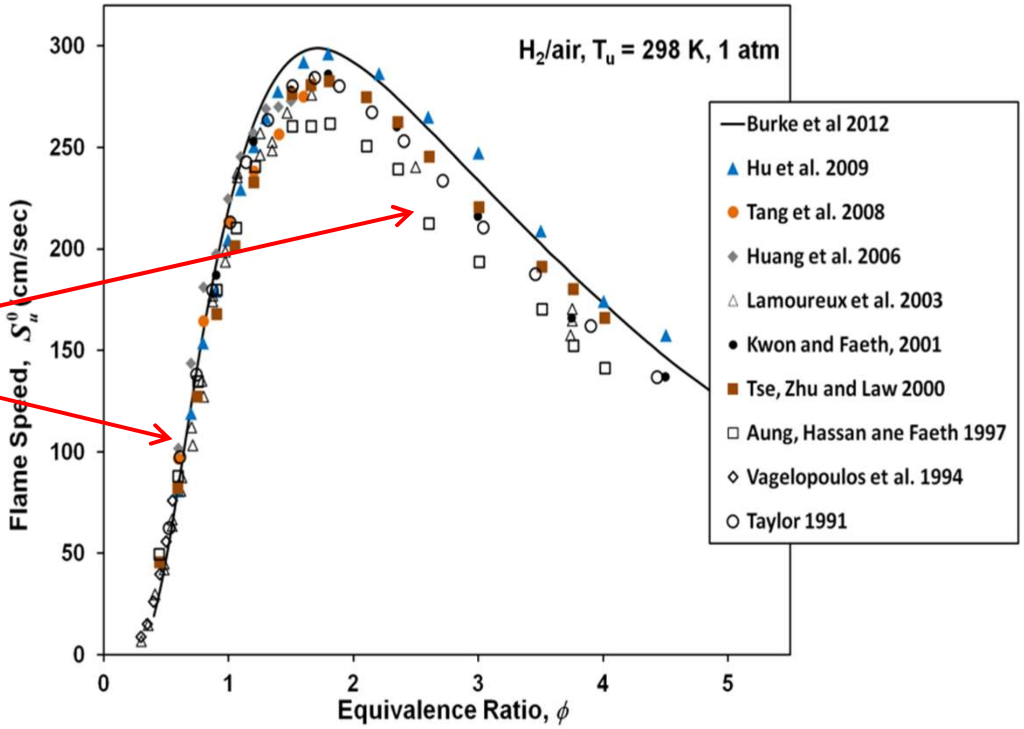
$\phi = \frac{(F/O)}{(F/O)_S}$; Lean $(0 < \phi < 1)$; Rich $(1 < \phi < \infty)$

- A normalized, symmetrical definition:

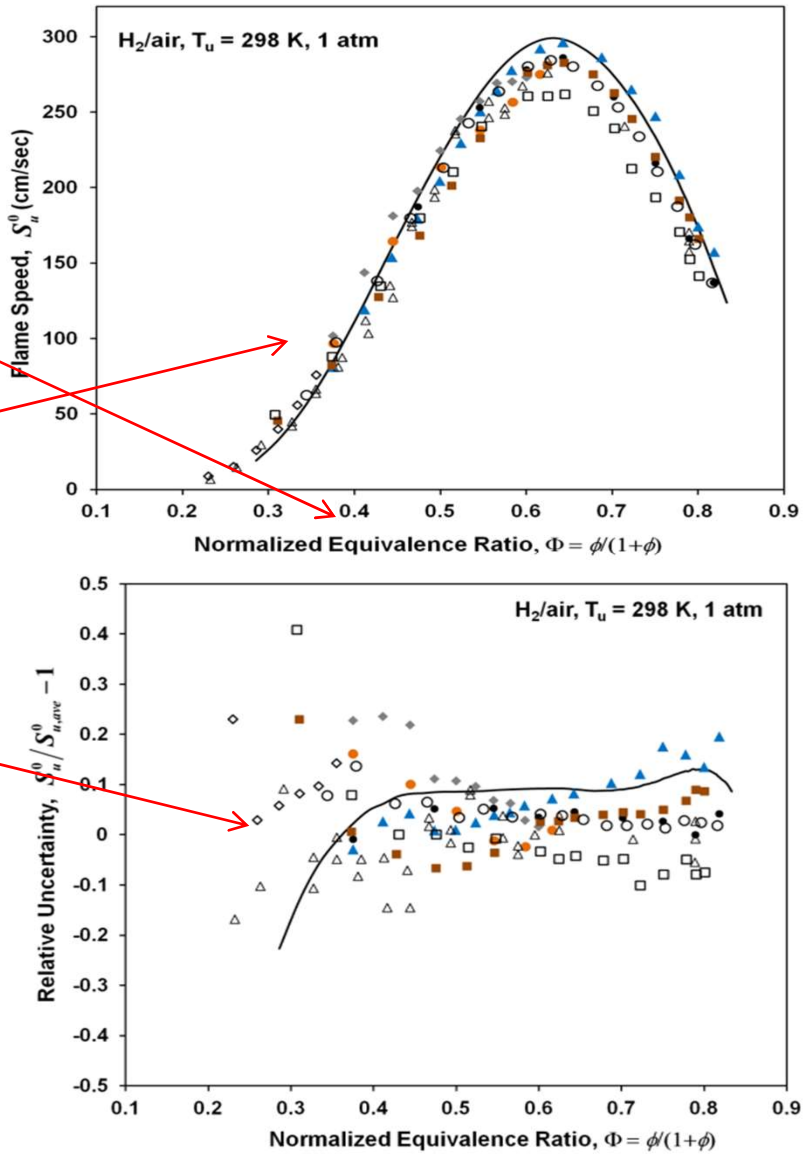
$\Phi = \frac{\phi}{1+\phi}$; Lean $(0 < \Phi < 0.5)$; Rich $(0.5 < \Phi < 1)$

Example: Hydrogen/Air Flame Speeds

- Hydrogen/oxygen kinetics forms the backbone of hydrocarbon chemistry
- Laminar flame speed is a key component in validating the mechanism
- When plotted in ϕ, tight correlation on lean side versus wider scatter on rich side has led to concern on adequacy of rich chemistry



Normalized (x, y) Representations



- Use of Φ moderates difference in scatters
- Furthermore, since regime of lean flames consists of more low flame speeds, normalizing the flame speeds (y-axis) shows even larger scatter on the lean side!
- As such, lean/rich chemistry are equally accurate/inaccurate!

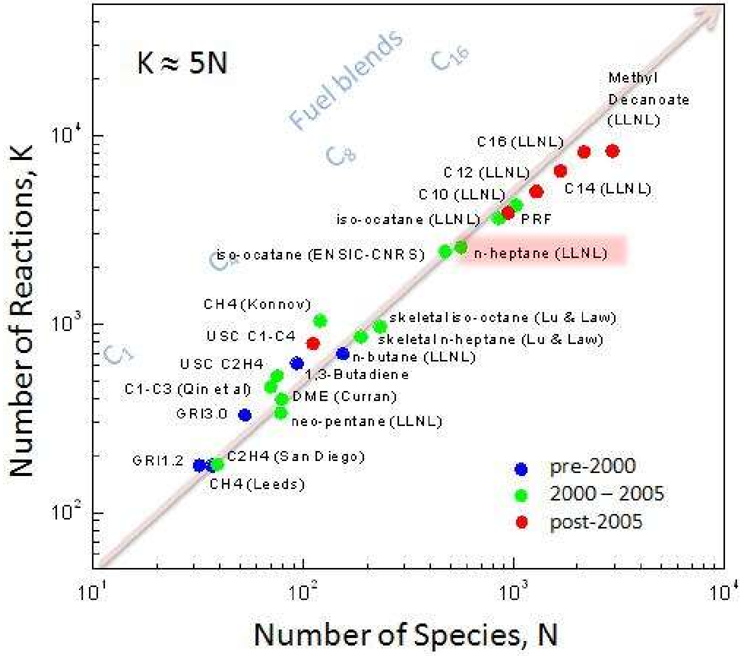
Further Thoughts

- Could the use of ϕ instead of Φ have caused misinterpretation in other combustion phenomena (e.g. sensitivity of NOx formation)?
- In scientific investigations, parameters representing the ratio of two processes/factors are frequently used to simplify/focus analysis & understanding; but it could skew interpretation & hinder unification
- Consider the following parameters: *Re*, *Gr*, *Pe*, *Da*, *Ka*,…
- Try a formulation of the N-S equations based on a normalized *Re*, as $Re_N = Re/(1+Re)$

2. The Unrelenting Growth of Size of Reaction Mechanism!

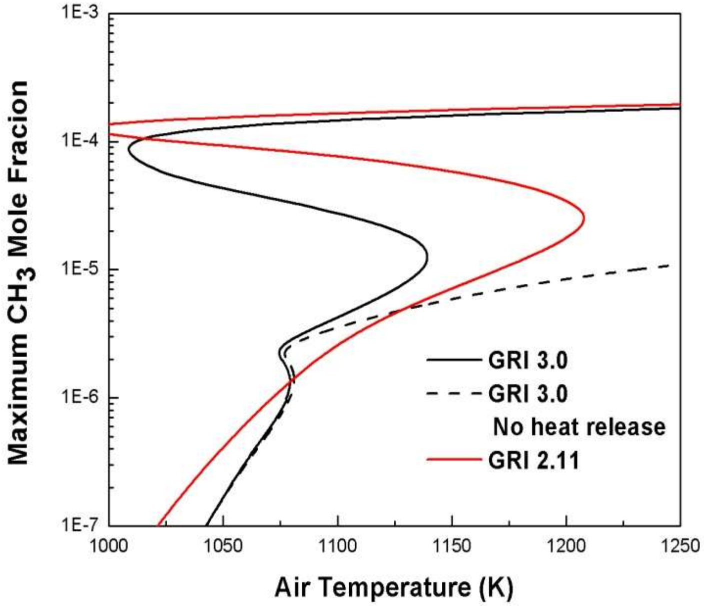
- Exponential growth of mechanism size with increasing fuel size
    - $N \sim 10^3$; $K \sim 10^4$
    - Empirically: $K \approx 5N$
- Size prohibitively large:
    - For insight even with sensitivity analysis
    - For CFD: Not even possible for simple 1D flames; compete with fluid-scale resolution for turbulent flames

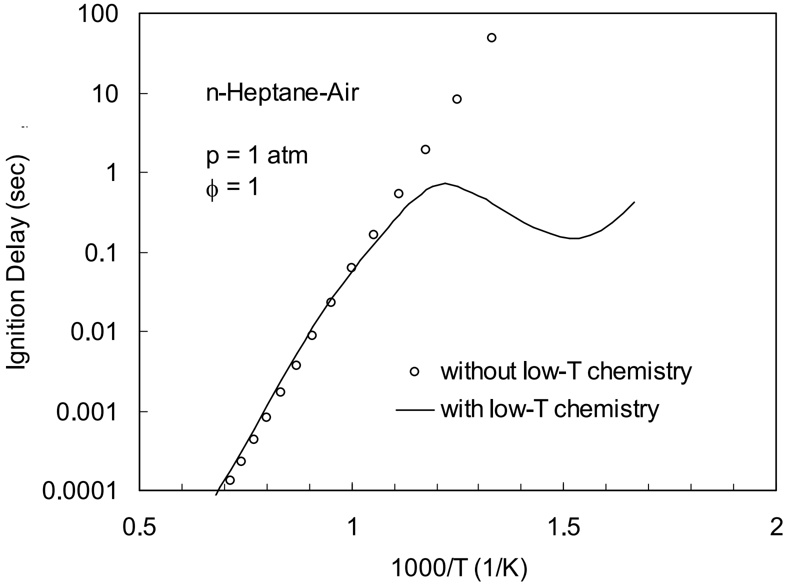
Lu-Law Diagram



- Will this growth forever enslave us to the super-computer?
- Need systematic reduction in all aspects of computation
- Hope & goal: Chemistry-limited asymptotic size

Additional Concerns: Inadequate State of Mechanism Development

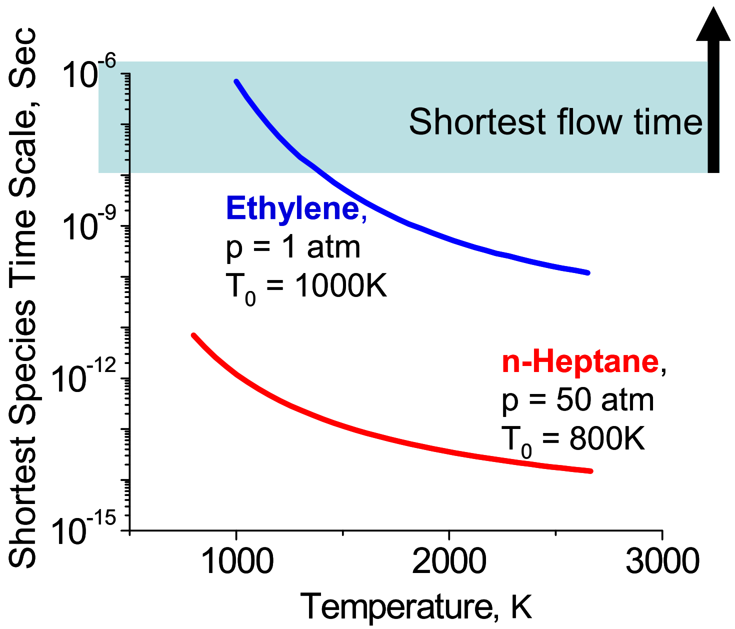




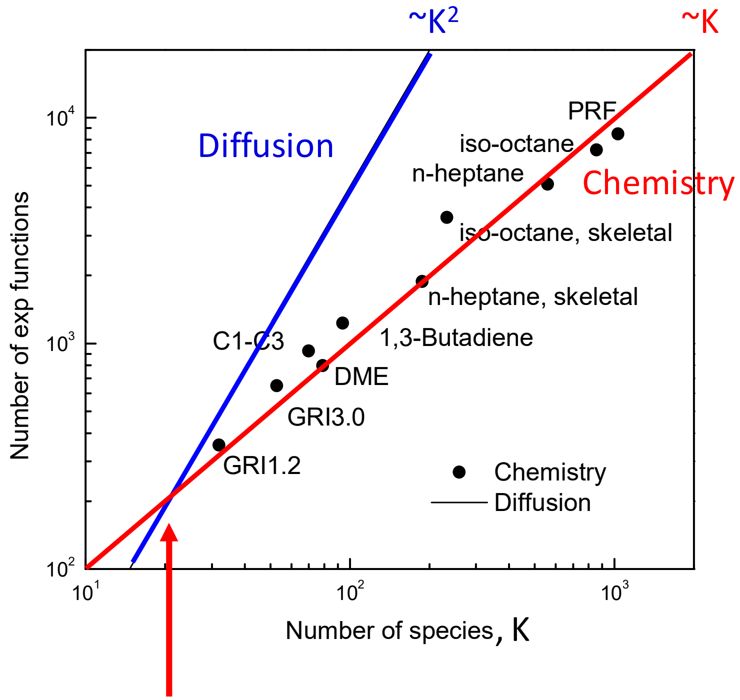
Example: Various versions of GRI-Mech yield qualitatively different results

- **Adoption of mechanisms beyond applicability range**
- **One generally cannot get the right physics with the wrong reactions!**

Further Challenges in Computation



Stiffness in reaction rates



Crossing point:
K~20

Evaluation of diffusion coefficients can overwhelm that of chemistry

Strategy for Facilitated Computation

Detailed mechanisms

CH_4: 30 species

C_2H_4: 70 species

nC_7H_{16}: 500 species

Skeletal mechanisms

CH_4: 13 species

C_2H_4: 30 species

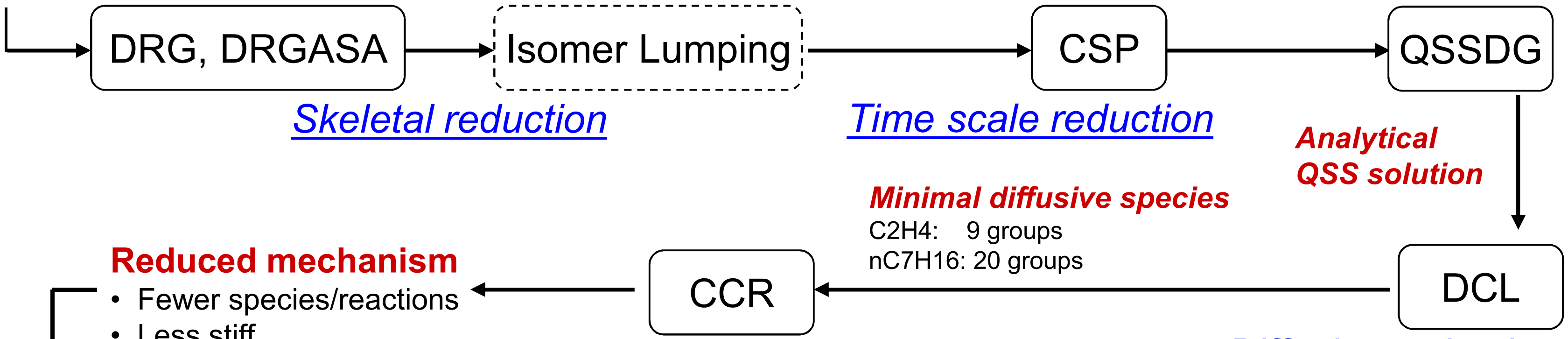
nC_7H_{16}: 80 species

Reduced mechanisms

CH_4: 9 species

C_2H_4: 20 species

nC_7H_{16}: 60 species



Skeletal reduction

Time scale reduction

Analytical QSS solution

Minimal diffusive species

C2H4: 9 groups

nC7H16: 20 groups

Diffusion reduction

Computation cost reduction

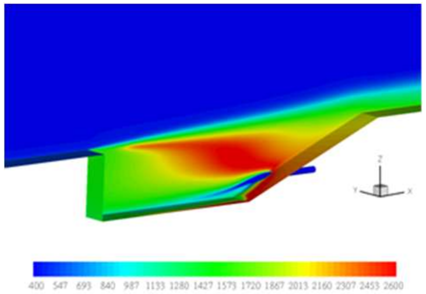
Reduced mechanism

- Fewer species/reactions
- Less stiff
- Faster simulation

CFD simulations

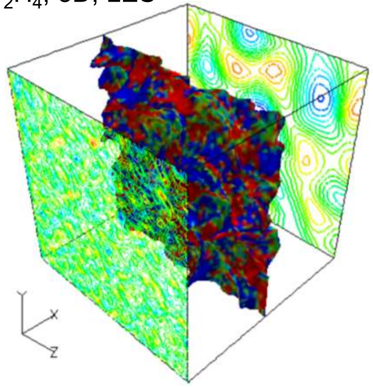
WP Air Force Base

C_2H_4, VULCAN



Georgia Tech

C_2H_4, 3D, LES



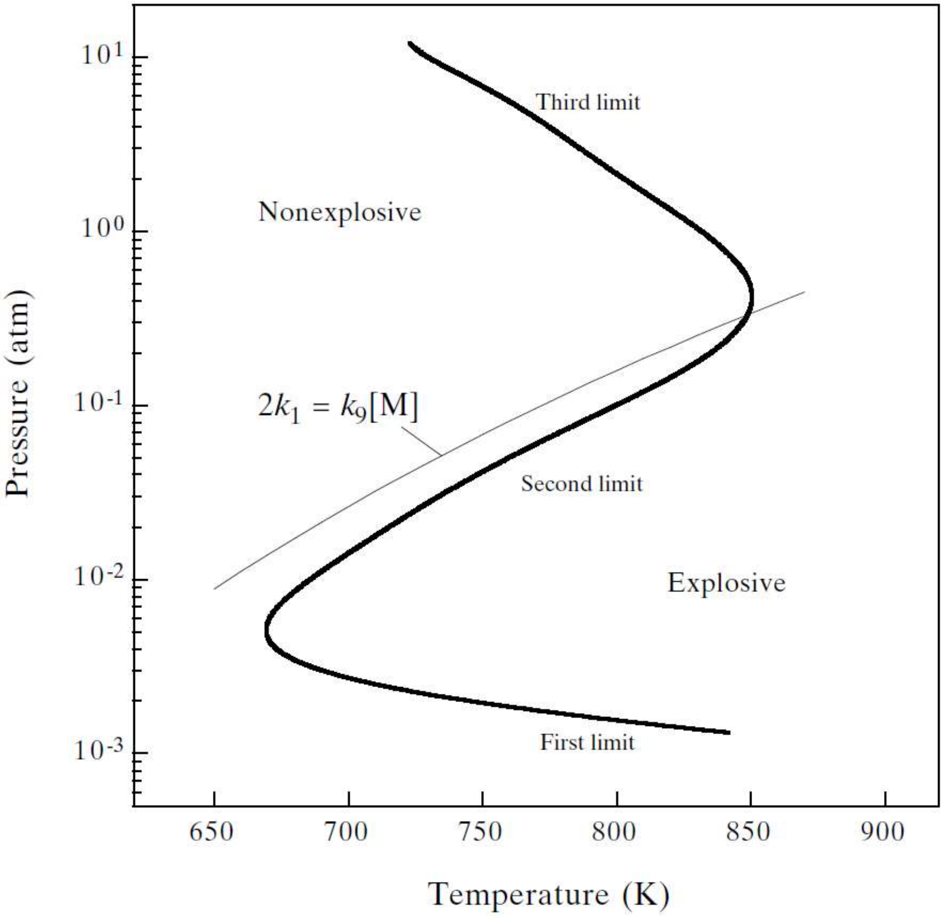
SANDIA

CH_4, 3D, DNS

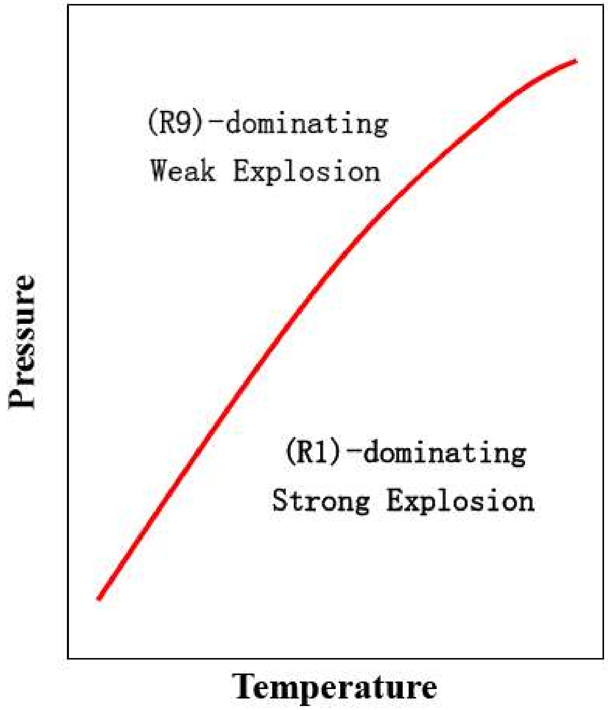
Time savings: factors of 10 ~ 100

3. Structure & Cubic Description of the H_2-O_2 Explosion Z-Curve

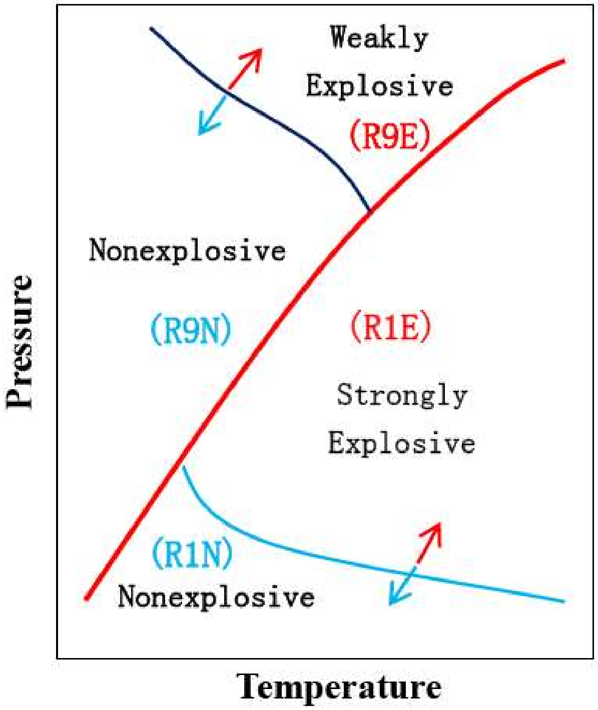
- Explicit expression was derived for the 2nd limit. How about the entire Z-curve?
- Shape of Z-curve suggests 3rd degree polynomial description
- Explicit expression can be used to rule out unphysical situations



Structure of H_2-O_2 Z-Curve



The backbone 2nd limit



1st and 3rd limits due to surface deactivation

Cubic Description of H_2-O_2 Z-Curve

- Assume steady state for O, OH and H_2O_2
- Detailed analysis yields:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}[\mathrm{H}]\\ [\mathrm{HO_2}]\end{pmatrix} = A_{\mathrm{H,HO_2}}\begin{pmatrix}[\mathrm{H}]\\ [\mathrm{HO_2}]\end{pmatrix} + \begin{pmatrix}I\\ I\end{pmatrix}$$

$$A_{\mathrm{H,HO_2}} = \begin{bmatrix} 2k_1[\mathrm{O_2}] - k_9[\mathrm{O_2}][\mathrm{M}] - k_{\mathrm{H}} & 3k_{17b}[\mathrm{H_2}] \\ k_9[\mathrm{O_2}][\mathrm{M}] & -k_{17b}[\mathrm{H_2}] - k_{\mathrm{HO_2}} \end{bmatrix}$$

- Neutral condition yields cubic equation in [M] ~ p:

$$a(T)[\mathrm{M}]^3+b(T)[\mathrm{M}]^2+c(T)[\mathrm{M}]+d(T) = 0$$

- Cubic equation yields explicit expressions for three limits, high & low pressure parabola, & loss of non-monotonicity

Combustion Physics

(Day 2 Lecture)

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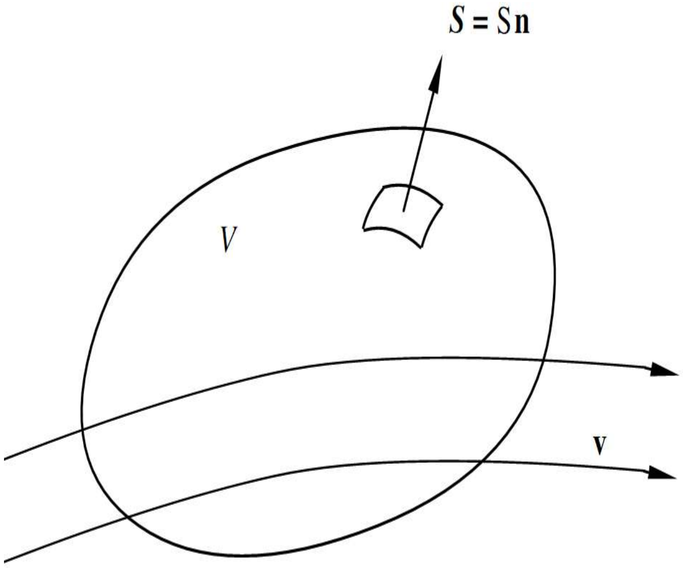
Tsinghua-Princeton-Combustion Institute
Summer School on Combustion
July 7-13, 2024

Day 2: Generalized Formulations

1. **Conservation Equations**
    1. Derivation and constitutive relations
    2. Simplified diffusion-controlled system
    3. Conserved scalar formulations
2. **Discontinuity Surface Formulations**
    1. Generalized reaction-sheet formulation
    2. Reaction-sheet analysis of diffusion flames
    3. Rankine-Hugoniot waves in premixtures

1. Conservation Equations

Control Volume Derivation



- Definitions of velocities
  - ○ ν_i velocity of species i

    ν mass-weighted velocities $\sum \rho_i \nu_i = \rho \nu$

    $\mathbf{V}_i$ molecular diffusion velocity $\mathbf{V}_i = \nu_i - \nu$
  - ○ Consequently: $\sum \rho_i \mathbf{V}_i = \sum \rho_i \nu_i - \rho\nu \equiv 0$

    $\sum \rho_i / \rho \mathbf{V}_i = \sum Y_i \mathbf{V}_i \equiv 0$; Y_i: mass fraction
- General equation of change
  - ○ (extensive, intensive) fluid property: $(\boldsymbol{\Psi}, \boldsymbol{\psi})$

    $$\frac{\delta \Psi}{\delta t} = \frac{\partial}{\partial t}\int_V \psi dV + \int_S \psi(\mathbf{v}\cdot\mathbf{n})dS$$
  - ○ Divergence theorem: $\int_S \psi(\mathbf{v}\cdot\mathbf{n})dS = \int_V (\nabla\cdot\psi\mathbf{v})\,dV,$

    $$\boxed{\frac{\delta \Psi}{\delta t} = \int_V \left(\frac{\partial \psi}{\partial t} + \nabla\cdot\psi\mathbf{v}\right) dV.} \qquad (5.1.5)$$

Conservation of Total Mass

$$\left(\Psi = m, \psi = \rho\right)$$

$$\frac{\delta m}{\delta t} = \int_V \left(\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} \right) dV.$$

- Mass conserved in chemical reaction: $\frac{\delta m}{\partial t} = 0.$
- Therefore: $\boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0.}$ (5.1.7)

(Continuity equation)

Conservation of Individual Species

$$\left(m_i\,,\,\rho_i\right)$$

$$\frac{\delta m_i}{\delta t} = \int_V \left(\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{v} \right) dV.$$

- Sources and sinks of $\delta m_i / \delta t$:
  - ○ Volumetric (from reaction, w_i): $\int_V w_i dV$
  - ○ Surface (from diffusion flux, $\mathbf{V}_i$): $-\int_S (\rho_i \mathbf{V}_i \cdot \mathbf{n})\, dS$

  $\mathbf{V}_i \cdot \mathbf{n} > 0 \Rightarrow$ loss, hence negative sign

- $$\frac{\partial \rho_i}{\partial t} + \nabla \cdot [\rho_i (\mathbf{v} + \mathbf{V}_i)] = w_i, \qquad i = 1, 2, \ldots, N. \qquad (5.1.10)$$
- Since $\rho_i = \rho Y_i$, $$\boxed{\frac{\partial (\rho Y_i)}{\partial t} + \nabla \cdot [\rho (\mathbf{v} + \mathbf{V}_i) Y_i] = w_i} \qquad (5.1.11)$$

  we have $$\boxed{\rho \frac{DY_i}{Dt} = -\nabla \cdot (\rho \mathbf{V}_i Y_i) + w_i,} \qquad (5.1.12)$$

  where $$\frac{D}{Dt}(\cdot) = \frac{\partial}{\partial t}(\cdot) + \mathbf{v} \cdot \nabla (\cdot)$$

Conservation of Momentum $(\mathbf{M}, \rho\mathbf{v})$

$$\frac{\delta \mathbf{M}}{\delta t} = \int_V \left(\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot \rho \mathbf{v}\mathbf{v} \right) dV.$$

- Sources and sinks of $\delta \mathbf{M} / \delta t$:
  - Surface source (by stress, **P**): $-\int_S (\mathbf{P} \cdot \mathbf{n})\, dS$

    $\mathbf{P} \cdot \mathbf{n} > 0 \;\Rightarrow$ system exerting force on surrounding, hence negative sign
  - Volumetric source (by body force, $\mathbf{f}_i$): $\sum_{i=1}^{N} \int_V \rho_i \mathbf{f}_i \, dV$
- $$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot \rho \mathbf{v}\mathbf{v} = -\nabla \cdot \mathbf{P} + \rho \sum_{i=1}^{N} Y_i \mathbf{f}_i ,$$

$$\boxed{\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot \mathbf{P} + \rho \sum_{i=1}^{N} Y_i \mathbf{f}_i} \qquad (5.1.17)$$

Conservation of Energy

$$\left(E,\ \rho e + \rho v^2\right)$$

$$\frac{\delta E}{\delta t} = \int_V \left[\frac{\partial \rho (e + v^2/2)}{\partial t} + \nabla \cdot \rho \mathbf{v} (e + v^2/2) \right] dV.$$

- Sources and sinks of $\frac{\delta E}{\delta t}$:
  - Surface source (by energy flux **q**)

    $$Q = -\int_S (\mathbf{q} \cdot \mathbf{n})\, dS = -\int_V \nabla \cdot \mathbf{q}\, dV.$$

  - Surface source (by surface stress):

    $$W_S = \int_S \mathbf{v} \cdot d\,\mathbf{F}_S = -\int_S \mathbf{v} \cdot (\mathbf{P} \cdot \mathbf{n})\, dS = -\int_V \nabla \cdot (\mathbf{v}.\mathbf{P})\, dV$$

  - Volumetric source (by body force, $\mathbf{f}_i$):

    $$W_V = \sum_{i=1}^{N} \int_V \mathbf{v}_i \cdot d\mathbf{F}_{V,i} = \sum_{i=1}^{N} \int \mathbf{v}_i \cdot (\rho_i \mathbf{f}_i)\, dV = \sum_{i=1}^{N} \int_V (\mathbf{v} + \mathbf{V}_i) \cdot (\rho_i \mathbf{f}_i)\, dV.$$

- $$\boxed{\rho \frac{D\left(e + v^2/2\right)}{Dt} = -\nabla \cdot \mathbf{q} - \nabla \cdot \left(\mathbf{v} \cdot \mathbf{P}\right) + \sum_{i=1}^{N} \left(\mathbf{v} + \mathbf{V}_i\right) \cdot \left(\rho_i \mathbf{f}_i\right).} \quad (5.1.24)$$

Summary of Conservation Equations

Continuity:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

Species:

$$\rho \frac{DY_i}{Dt} = w_i - \nabla \cdot (\rho Y_i \mathbf{V}_i), \qquad i = 1, \ldots, N$$

Momentum:

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla \cdot \mathbf{P} + \rho \sum_{i=1}^{N} Y_i \mathbf{f}_i$$

Energy:

$$\rho \frac{De}{Dt} = -\nabla \cdot \mathbf{q} - \mathbf{P} : (\nabla \mathbf{v}) + \rho \sum_{i=1}^{N} Y_i \mathbf{f}_i \cdot \mathbf{v}_i .$$

- The conservation equations are supplemented (*i.e.* completed) by the specifications of:

  Diffusion velocity, $\mathbf{V}_i$

  Pressure tensor, $\mathbf{P}$

  Heat flux vector, $\mathbf{q}$

  Reaction rate, w_i

Constitutive Relations

Diffusion velocity, $\mathbf{V}_i$

$$\nabla X_i = \sum_{i=1}^{N}\left(\frac{X_i X_j}{D_{i,j}}\right)\left(\mathbf{V}_j - \mathbf{V}_i\right) + \left(Y_i - X_i\right)\left(\frac{\nabla p}{p}\right) + \left(\frac{\rho}{p}\right)\sum_{j=1}^{N} Y_i Y_j \left(\mathbf{f}_i - \mathbf{f}_j\right)$$

$$+\sum_{j=1}^{N}\left[\left(\frac{X_i X_j}{\rho D_{i,j}}\right)\left(\frac{D_{T,j}}{Y_j} - \frac{D_{T,i}}{Y_i}\right)\right]\left(\frac{\nabla T}{T}\right), \qquad i = 1,\ldots,N. \qquad (5.2.5)$$

Pressure tensor, $\mathbf{P}$

$$\mathbf{P} = \left[p + \left(\frac{2}{3}\mu - \kappa\right)(\nabla \cdot \mathbf{v})\right]U - \mu[(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T], \qquad (5.2.6)$$

Heat flux vector, $\mathbf{q}$

$$\mathbf{q} = -\lambda \nabla T + \rho \sum_{i=1}^{N} h_i Y_i \mathbf{V}_i + R^o T \sum_{i=1}^{N}\sum_{j=1}^{N}\left(\frac{X_j D_{T,i}}{W_i D_{i,j}}\right)(\mathbf{V}_i - \mathbf{V}_j) + \mathbf{q}_R, \qquad (5.2.7)$$

Reaction rate, w_i

$$w_i = W_i \sum_{k=1}^{K} (\nu''_{i,k} - \nu'_{i,k}) B_k T^{\alpha_k} \exp(-E_{a,k}/R^o T) \prod_{j=1}^{N} c_j^{\nu'_{j,k}}, \qquad i = 1,\ldots,N, \qquad (5.2.8)$$

Discussion on Diffusion Velocity, $\mathbf{V}_i$

$$\nabla X_i = \sum_{i=1}^{N}\left(\frac{X_i X_j}{D_{i,j}}\right)\left(\mathbf{V}_j - \mathbf{V}_i\right) + \left(Y_i - X_i\right)\left(\frac{\nabla p}{p}\right) + \left(\frac{\rho}{p}\right)\sum_{j=1}^{N} Y_i Y_j \left(\mathbf{f}_i - \mathbf{f}_j\right)$$

$$+\sum_{j=1}^{N}\left[\left(\frac{X_i X_j}{\rho D_{i,j}}\right)\left(\frac{D_{T,j}}{Y_j} - \frac{D_{T,i}}{Y_i}\right)\right]\left(\frac{\nabla T}{T}\right), \qquad i = 1,\ldots,N. \quad (5.2.5)$$

- Diffusion can be induced through:
  - ○ Concentration gradient (Fickian)
  - ○ Pressure gradient, ∇p
  - ○ Body force, $\mathbf{f}_i$
  - ○ Temperature gradient, ∇T (Soret diffusion): Important for light (H, H_2) and heavy (large HC's, polymers, soot) species; respectively up & down the ∇T

Discussion on Diffusion Coefficient

- Allow only concentration diffusion

$$\nabla \ln X_i = \sum_{j=1}^{N} \left(\frac{X_j}{D_{i,j}} \right) \left(\mathbf{V}_j - \mathbf{V}_i \right), \ i = 1, 2, \ldots, N,$$

- Assume equal diffusivity: $\boxed{D_{i,j} = D}$

$$\mathbf{V}_i = -D \nabla \ln Y_i, \qquad (5.2.16)$$

This is Fick's law of mass diffusion

- Assume $\boxed{D_{i,j}=D_{i,\mathrm{N}}}$, N: an abundant species

(e.g. N_2) $$\mathbf{V}_i = -D_{\mathrm{i,N}} \nabla \ln Y_i \qquad (5.2.17)$$

Discussion on Pressure Tensor, $\mathbf{P}$

- $\mathbf{P}$ discussed in fluid mechanics texts
  - Controls the fluid motion, both inertia and viscous
  - Temperature and hence density variations inherently important in flames
  - Constant density is a poor assumption
  - Buoyancy effect inherently important
  - Role of electromagnetic, body force, is unclear

Discussion on Heat Flux Vector, $\mathbf{q}$

- Heat flux consists of:
  - Conduction due to temperature gradient
  - $\rho \sum_{i=1}^{N} h_i Y_i \mathbf{V}_i \equiv 0$ for $h_i = h$; heat diffusion for different $c_{p,i}$
  - Heat transfer due to concentration gradient (Dufour effect): Generally not important
  - Radiation q_R; reduces flame temperature and hence reaction rate; relevant for large-scale phenomena (e.g. furnace flame, building and wildland fires) and sooty flames

Auxiliary Relations

- Ideal Gas Equation of State

$$p = \rho R^o T / \sum_{i=1}^{N} X_i W_i = \rho R^o T \sum_{i=1}^{N} \frac{Y_i}{W_i} = \frac{\rho R^o T}{\overline{W}},$$

- Energy–Enthalpy Relation

$$h = \sum_{i=1}^{N} Y_i h_i = e + p / \rho.$$

- Calorific Equation of State

$$h_i = h_i^0(T^o) + h_i^s(T;T^o) \qquad h_i^s(T;T^o) = \int_{T^o}^{T} c_{p,i} dT.$$

- Mole and Mass Fractions

$$X_i = \frac{Y_i / W_i}{\sum_{j=1}^{N} Y_j / W_j}, \qquad Y_i = \frac{X_i W_i}{\sum_{j=1}^{N} X_j W_j}.$$

Important concept: Combustion is a mixed-unit discipline

- Convection is mass based, described by Newtonian mechanics
- Reaction is mole based, describing frequency of collision
- Concentration diffusion is mole based

A Simplified Diffusion-Controlled System

- Specialize to subsonic flows
- Four (minimum) key processes included:
  - Unsteadiness
  - Diffusion: 2nd order, highest order differential
  - Convection: 1st order, describes fluid mechanics
  - Reaction
- Derivation only involves energy (with separate sensible & chemical terms) and species equations, which explicitly show reaction terms
- Momentum does not explicitly contain reaction term
  - Indirectly chemical heat release ⇒ temperature variation ⇒ density variation ⇒ momentum equation is variable density

Isobaric Assumption

- Relevant for subsonic flows

$$\rho u \frac{du}{dx} = -\frac{dp}{dx}, \qquad \left(\frac{\rho_o u_o^2}{p_o}\right)\left(\hat{\rho}\hat{u}\frac{d\hat{u}}{dx}\right) = -\frac{d\hat{p}}{dx}, \qquad \gamma M_o^2\left(\hat{\rho}\hat{u}\frac{d\hat{u}}{dx}\right) = -\frac{d\hat{p}}{dx}$$

- Let $\hat{p}(x,t) = \hat{p}_0(x,t) + \hat{p}_1(x,t)$

$$\hat{p}_o = O(1) \qquad \hat{p}_1 = O(M_o^2).$$

$$O(1): \quad \frac{d\hat{p}_o}{dx} = 0, \qquad O(M_o^2): \ \gamma M_o^2\left(\hat{\rho}\hat{u}\frac{d\hat{u}}{dx}\right) = -\frac{d\hat{p}_1}{dx}$$

- Therefore: $\nabla \hat{p}_o = 0$ or $p_o = p_o(t).$ (5.2.24)

$p_0(t) = \rho RT$ = thermodynamic pressure

$p_1(x, t)$ = dynamic pressure

Distinct Specific Heat and Diffusivity Formulations

- Distinct specific heat: $\boxed{c_{p,i} \text{ distinct}, \ D_{i,j} = D}$
  - Energy conservation:

$$\frac{\partial}{\partial t}(\rho h^s) + \nabla \cdot \left[\rho \mathbf{v} h^s - \rho D \nabla h^s + \lambda \left(\frac{1}{Le} - 1 \right) \nabla T \right] = \frac{dp}{dt} - \sum_{i=1}^{N} h_i^o w_i .$$

Note role of Le ≠ 1 in energy conservation

  - Species conservation:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \mathbf{v} Y_i - \rho D \nabla Y_i) = w_i, \quad i = 1, 2, \ldots, N.$$

- Distinct diffusivity: $\boxed{c_{p,i} = c_p; \ \ D_{i,j} = D_{i,N}}$

Density Weighting and Pressure Independence of Transport Coefficients

- In the conservation equations just shown, $\boldsymbol{v}$, and D, does not appear by itself, but is each weighted by the density ρ, and appears as

$$\boxed{\rho \boldsymbol{v}} \quad \text{and} \quad \boxed{\rho D}$$

- Physically, $\rho\boldsymbol{v}$ is the momentum of the flow, representing the extent of convective transport, and hence is the fundamental quantity, instead of $\boldsymbol{v}$, to designate convective transport
- Also, since $D \sim 1/\rho$ and $\neq \text{fn}(p)$, then $\rho D \neq \text{fn}(p)$
- Similarly, thermal conductivity λ, viscosity coefficient μ, and c_p are also independent of pressure
- Above observations have profound implications on combustion properties, to be demonstrated later

A Set of Final Conservation Equations (with Appropriate Assumptions)

- $$\left[\frac{\partial\tilde{\rho}}{\partial\tilde{t}}+\tilde{\nabla}\cdot(\tilde{\rho}\tilde{\mathbf{v}})-\tilde{\nabla}^2\right]\tilde{h}^s=-\tilde{w}_F \qquad (5.6.6)$$
- $$\left[\frac{\partial\tilde{\rho}}{\partial\tilde{t}}+\tilde{\nabla}\cdot(\tilde{\rho}\tilde{\mathbf{v}})-\frac{1}{Le}\tilde{\nabla}^2\right]\tilde{Y}_i=\tilde{w}_F \qquad (5.6.7)$$
- $$\tilde{w}_F=-Da_C\tilde{Y}_O^{\nu'_O}\tilde{Y}_F^{\nu'_F}e^{-E_a/R^oT} \qquad (5.6.8)$$
- Governed by 3 parameters: *Le*, *Da*$_c$, *E*$_a$

Nondimensional Numbers (1/2)

- **Lewis number: *Le* ≈ 1**:

  Le = thermal diffusivity/mass diffusivity

  = $(\lambda/c_p)/(\rho D)$

- **Collision Damköhler number: Da_c (>>1):**

$$Da_C = \frac{\ell_o^2/(\lambda/c_p\rho_o)}{(\rho_o/B_C)} = \frac{\text{Characteristic diffusion time}}{\text{Characteristic collision time}}.$$

- **Reaction Damköhler number: $Da = \mathrm{O}(1)$:**

$$Da = Da_{\mathrm{C}}\exp(\text{-}Ar) = \frac{\text{Characteristic flow time or diffusion time}}{\text{Characteristic reaction time}}.$$

Nondimensional Numbers (2/2)

- **Reaction Damköhler number: $Da = O(1)$:**

$$Da = Da_C \exp(-Ar) = \frac{\text{Characteristic flow time or diffusion time}}{\text{Characteristic reaction time}}.$$

$$\tilde{w}_F = -Da_C \tilde{Y}_O^{\nu'_O} \tilde{Y}_F^{\nu'_F} e^{-E_a/R^o T} = -Da \tilde{Y}_O^{\nu'_O} \tilde{Y}_F^{\nu'_F} \exp\left[Ar\left(1 - \frac{\tilde{T}_{\max}}{\tilde{T}}\right)\right]$$

$$Ar(1 - \tilde{T}_{\max} / \tilde{T}) = O(1) \quad \Rightarrow \quad (\tilde{T}_{\max} - \tilde{T}) = O(T / Ar) \approx O(T_{\max} / Ar) = O(Ze^{-1})$$

Zel'dovich number: Ze >> 1

$$Ze = \frac{Ar}{\tilde{T}_{\max}} = \frac{\tilde{T}_a}{\tilde{T}_{\max}^2}.$$

Conserved Scalar Formulations

Conserved Scalar Formulation: Rationale

- Chemical source term $\omega_i \sim Y_i^{n_i} Y_j^{n_j} \exp\left(-E_a / R^o T\right)$
  - o is nonlinear in both Y_i and T
  - o couples the conservation equations for Y_i and T
- Stoichiometry relates the reaction entities $\Rightarrow$ conserved quantities during a reaction

  e.g. Chemical + sensible enthalpies; two reacting species
- Are these quantities still "conserved" (i.e. not affected by reaction) in a convective-diffusive medium?

Coupling Function Formulation (1/5)

- Species conservation (for $\boxed{D_{i,j} = D}$):

$$L(Y_i) = w_i, \qquad L\,(\cdot) = \left[\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v} - \rho D \nabla)\right](\cdot)$$

- For $\sum_{i=1}^{N} \nu_i' \mathrm{M}_i \rightarrow \sum_{i=1}^{N} \nu_i'' \mathrm{M}_i.$

$$\omega = \frac{w_i}{W_i(\nu_i'' - \nu_i')} = BT^{\alpha} \exp(-E_a / R^o T) \prod_{j=1}^{N} c_j^{\nu_j'}$$

  - Thus $L(Y_i) = \omega W_i(\nu_i'' - \nu_i')$ $\qquad L\left[\frac{Y_i}{W_i(\nu_i'' - \nu_i')}\right] = \omega$ (A)
  - Similarly for j: $L\left[\frac{Y_j}{W_j(\nu_j'' - \nu_j')}\right] = \omega$ (B)

- Subtracting (B) from (A) $L\left[\frac{Y_i}{W_i(\nu_i'' - \nu_i')} - \frac{Y_j}{W_j(\nu_j'' - \nu_j')}\right] = 0$ (C)

which does not depend on the reaction rate ω !

Coupling Function Formulation (2/5)

- Thus $\boxed{\frac{Y_i}{W_i(\nu_i'' - \nu_i')} - \frac{Y_j}{W_j(\nu_j'' - \nu_j')} = \beta_{i,j}}$ is a conserved scalar

  for the reacting flow system, with $L(\beta_{i,j}) = 0$

  - Consequently, the fundamental variable is not Y_i, but a stoichiometrically-weighted variable $\frac{Y_i}{W_i(\nu_i'' - \nu_i')}$

- Can also define a nondimensional function

  $$\tilde{Y}_i = \frac{W_n(\nu_n'' - \nu_n')}{W_i(\nu_i'' - \nu_i')} \frac{Y_i}{Y_{n,B}}$$

  n: a reference species;

  B: a boundary

  - Then $\boxed{\beta_{i,j} = \tilde{Y}_i - \tilde{Y}_j}$

Coupling Function Formulation (3/5)

- For energy conservation (with $\boxed{Le = 1}$)

$$L(h^s) = \frac{dp}{dt} - \sum_{i=1}^{N} h_i^o w_i = \frac{dp}{dt} - \left[\sum_{i=1}^{N} h_i^o W_i (\nu_i'' - \nu_i') \right] \omega.$$

- Define $\tilde{h}^s = \dfrac{h^s}{Y_{n,B} q_{c,n}}, \quad \tilde{T} = \dfrac{c_p T}{Y_{n,B} q_{c,n}},$

$$q_{c,n} = \frac{\sum_{k=1}^{N} h_k^o W_k (\nu_k'' - \nu_k')}{W_n (\nu_n'' - \nu_n')}, \qquad \tilde{p} = \rho \tilde{T} \qquad L(\tilde{h}^s) = \left(1 - \frac{1}{\gamma}\right) \frac{d\tilde{p}}{dt} - w_n \qquad \text{(D)}$$

- Adding (A) and (D) results $L(\beta_i) = \left(1 - \dfrac{1}{\gamma}\right) \dfrac{d\tilde{p}}{dt}.$
  - ○ $L(\beta_i)=0$ for $\dfrac{d\tilde{p}}{dt} = 0.$

Coupling Function Formulation (4/5)

- Thus in chemically reacting flows, a diffusive system governed by (N+1) equations

$$L(\tilde{Y}_i) = \omega_n \qquad i = 1, 2, 3, ..., N \qquad \text{(E)}$$

$$L(\tilde{h}^s) = -\omega_n \qquad \text{(F)}$$

can be alternatively described by

$$L(\beta_i = \tilde{Y}_i + \tilde{h}^s) = 0 \qquad i = 1, 2, 3, \ldots, N$$

$$L(\tilde{h}^s) = -\omega_n$$

or any other linear combination of (E) and (F)

Coupling Function Formulation (5/5)

- Consequently, N equations can be solved for the conserved scalars β_i (or $\beta_{i,j}$)
- Chemical information is contained in the (N+1)th equation, say $L(\tilde{h}^s) = -\omega_n$ which is solved last
- Key assumption: Equal diffusivity for all quantities: $D_{i,j} = D$, $Le = \lambda/\rho c_p = 1$

Other Formulations

- ✓ **Coupling function formulation** requires equal diffusivity or unity Lewis number
- Local coupling function formulation: holds only in the reaction region, governed by reaction and diffusion
- Near-equidiffusion formulation: Since *Le* ≈ 1 for most gases, expand around *Le* = 1
- Element conservation formulation: an element is a conserved scalar; still requires *Le* = 1 assumption because elements are associated with molecules; insufficient relations because N >> L
- ✓ **Mixture fraction formulation**: Normalized coupling function; a mixture fraction can be used as a generalized independent variable; useful for nonpremixed flame formulation.
- Progress variable formulation: Normalized product concentration; useful for premixed flame formulation
- ✓ **Reaction-sheet formulation**

Mixture Fraction Formulation (1/3)

Appropriate for nonpremixed (diffusion) flame analysis

- From coupling function formulation (for Le_i=1)

$$L(\beta_{i,j}) \equiv 0$$

- Define mixture fraction for (F,O) as $\boxed{Z = \frac{\beta_{F,O} - \beta_{F,O,B^-}}{\beta_{F,O,B^+} - \beta_{F,O,B^-}}}$, (5.4.39)
  - $Z \equiv 0$ and 1 at boundaries of F and O,
  - Then $L(Z) \equiv 0$ (5.4.40)
- Superficially Z is just a normalized definition of β
  - Utility of Z is actually rather broad, subjected nevertheless to the $Le_i \equiv 1$ assumption

For any *i*, and using *j* = F, we have

$$L(\beta_{i,F}) = 0 \qquad (5.4.41)$$

- Observing (5.4.40) and (5.4.41), a possible solution for $\beta_{i,F}$ is $\beta_{i,F} = c_{1,i} + c_{2,i} Z$ (5.4.42)
  - Solution degenerates to that of (5.4.42) and (5.4.40)

Mixture Fraction Formulation (2/3)

- Unique features of $\beta_{i,F}(Z)$
  - Z is now an independent variable
  - $\beta_{i,F}$ varies linearly with Z
  - $\beta_{i,F}$ is configurationally independent. (e.g., spherical flame, stagnation flame, turbulent flame), hence general.
  - But only for $Le_i \equiv 1$
- Let i=O, then applying b.c. on (5.4.42) at Z = (0,1) yields $\tilde{Y}_O - \tilde{Y}_F = -\tilde{Y}_{F,B^-} + (\tilde{Y}_{F,B^-} + \tilde{Y}_{O,B^+})Z.$ (5.4.44)

  Similar operation for $\beta = \tilde{h}^s + \hat{Y}_i$ yields

$$\tilde{h}^s + \tilde{Y}_F = (\tilde{h}^s_{B^-} + \tilde{Y}_{F,B^-}) + (\tilde{h}^s_{B^+} - \tilde{h}^s_{B^-} - \tilde{Y}_{F,B^-})Z, \quad (5.4.45)$$

$$\tilde{h}^s + \tilde{Y}_O = \tilde{h}^s_{B^-} + (\tilde{h}^s_{B^+} - \tilde{h}^s_{B^-} + \tilde{Y}_{O,B^+})Z. \quad (5.4.46)$$

Mixture Fraction Formulation (3/3)

- To study effects of chemistry in Z-space, transform

$$\rho\frac{\partial\tilde{h}^s}{\partial t}+\rho\mathbf{v}\cdot\nabla\tilde{h}^s-\nabla\cdot(\rho D\nabla\tilde{h}^s)=-w_n. \quad (5.4.49)$$

from (*t, x, y, z*) to (τ, *X, Y, Z*)

- Designate 2D tangential operator in X and Y as

$$\nabla_t=\left(\frac{\partial}{\partial X},\frac{\partial}{\partial Y},0\right)$$

(5.4.49) is transformed to

$$\rho\frac{\partial\tilde{h}^s}{\partial t}+\rho\mathbf{v}_t\cdot\nabla_t\tilde{h}^s=-w_n+\rho D\left|\nabla Z\right|^2\frac{\partial^2\tilde{h}^s}{\partial Z^2}+\nabla_t\cdot(\rho D\nabla_t\tilde{h}^s) \quad (5.4.53)$$

- If we identify *Z*=constant surface as that of a flame, and if the flame is very thin such that , $\nabla_t \ll \frac{\partial}{\partial Z}$, then (5.4.53) simplifies to $\boxed{\rho\frac{\partial\tilde{h}^s}{\partial t}=\rho D\left|\nabla Z\right|^2\frac{\partial^2\tilde{h}^s}{\partial Z^2}-w_n}$
- Note that $D\left|\nabla Z\right|^2$ has the dimension of t^{-1}

⇒ Inverse of characteristic diffusion time of the flame; called scalar dissipation rate

2. Discontinuity Surface Formulations

2.1 Reaction-Sheet Formulation

For reactions of large activation energy, reaction region can be approximated as a reaction sheet

- Gradients of properties (e.g., T, Y_i) change discontinuously across the reaction sheet; values are continuous
- Mathematically this is a weak discontinuity; in contrast a shock is a strong discontinuity across which the property values change
- A reaction sheet is a source and sink for the reaction entities
- Jump relation: change in the slopes across the sheet represents conservation relation.

Jump Relations (1/4)

- A general curved reaction zone can be treated as locally planar
  - Gradient dominates in normal direction
  - Minimum gradient in tangential direction
- Conservation equations in normal (***n***) direction

$$\frac{\partial}{\partial t}(\rho\tilde{h}^s)+\frac{\partial}{\partial n}\left(\rho u\tilde{h}^s-(\lambda/c_p)\frac{\partial\tilde{h}^s}{\partial n}\right)=\left(1-\frac{1}{\gamma}\right)\frac{d\,\tilde{p}}{dt}-w_n \qquad \text{(A)}$$

$$\frac{\partial}{\partial t}(\rho\tilde{Y}_i)+\frac{\partial}{\partial n}\left(\rho u\tilde{Y}_i-\rho D_i\frac{\partial\tilde{Y}_i}{\partial n}\right)=w_n \qquad \text{(B)}$$

$$\frac{\partial}{\partial t}(\rho\tilde{Y}_j)+\frac{\partial}{\partial n}\left(\rho u\tilde{Y}_j-\rho D_j\frac{\partial\tilde{Y}_j}{\partial n}\right)=w_n \qquad \text{(C)}$$

Jump Relations (2/4)

- Subtracting (C) from (B) eliminates w_n

$$\frac{\partial}{\partial t}[\rho(\tilde{Y}_i-\tilde{Y}_j)]+\frac{\partial}{\partial n}\left[\rho u(\tilde{Y}_i-\tilde{Y}_j)+\left(\rho D_i\frac{\partial \tilde{Y}_i}{\partial n}-\rho D_j\frac{\partial \tilde{Y}_j}{\partial n}\right)\right]=0$$

- Integrate across reaction zone along normal direction, from $n_f^+ < n < n_f^-$

$$\int_{n_f^-}^{n_f^+}\frac{\partial}{\partial t}[\rho(\tilde{Y}_i-\tilde{Y}_j)]\,dn+[\rho u(\tilde{Y}_i-\tilde{Y}_j)]_{n_f^-}^{n_f^+}-\left[\rho D_i\frac{\partial \tilde{Y}_i}{\partial n}-\rho D_j\frac{\partial \tilde{Y}_j}{\partial n}\right]_{n_f^-}^{n_f^+}=0 \qquad \text{(D)}$$

- Shrink reaction zone to a sheet, $n_f^+ \to n_f^-$, assume weak discontinuity such that

$$(\rho u)^+=(\rho u)^-, \qquad Y_i^+=Y_i^-, \qquad T^+=T^-, \qquad \text{etc.}$$

Jump Relations (3/4)

- (D) then yields

$$\left[\rho D_i \frac{\partial \tilde{Y}_i}{\partial n}\right]_{n_f^-}^{n_f^+} = \left[\rho D_j \frac{\partial \tilde{Y}_j}{\partial n}\right]_{n_f^-}^{n_f^+}, \quad \textbf{or} \quad \boxed{\left[\rho D_i \frac{\partial Y_i}{\partial n}\right]_{n_f^-}^{n_f^+} = \sigma_{i,j}\left[\rho D_j \frac{\partial Y_j}{\partial n}\right]_{n_f^-}^{n_f^+}.} \qquad \text{(E)}$$

  - (E) shows the stoichiometric relation between the fluxes of the i^{th} and j^{th} species

- Similar derivation for (A) and (B) yields energy conservation across interface (for $dp/dt = 0$)

$$\boxed{\left(\frac{q_c}{\sigma_i}\right)\left[\rho D_i \frac{\partial Y_i}{\partial n}\right]_{n_f^-}^{n_f^+} = -\left[\lambda \frac{\partial T}{\partial n}\right]_{n_f^-}^{n_f^+},} \qquad \text{(F)}$$

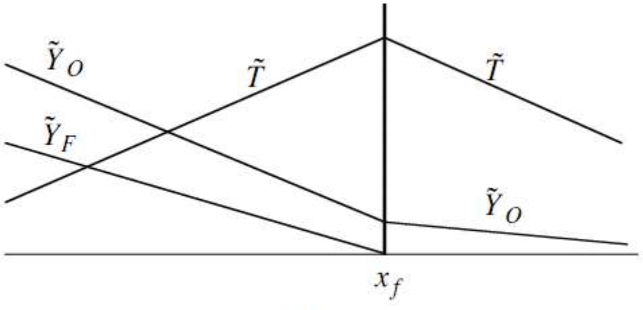
- (E) and (F) are conservation relations for species and energy across the reaction surface

Jump Relations (4/4)

- Premixed flame (e.g., fuel lean, $Y_{F,f}^{+} \equiv 0,$)

$$-[\rho D_F \mathbf{n}\cdot\nabla\tilde{Y}_F]_{n_f^-} = [\rho D_O \mathbf{n}\cdot\nabla\tilde{Y}_O]_{n_f^-}^{n_f^+},$$

$$[\rho D_F \mathbf{n}\cdot\nabla\tilde{Y}_F]_{n_f^-} = [(\lambda/c_p)\mathbf{n}\cdot\nabla\tilde{h}^s]_{n_f^+} - [(\lambda/c_p)\mathbf{n}\cdot\nabla\tilde{h}^s]_{n_f^-}.$$

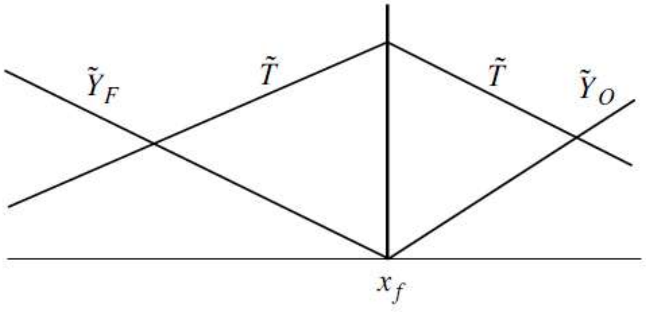


(a)

- Nonpremixed flame ($Y_{F,f}^{+} \equiv 0, Y_{O,f}^{-} \equiv 0$)

$$[\rho D_F \mathbf{n}\cdot\nabla\tilde{Y}_F]_{n_f^-} = -[\rho D_O \mathbf{n}\cdot\nabla\tilde{Y}_O]_{n_f^+},$$

$$[\rho D_F \mathbf{n}\cdot\nabla\tilde{Y}_F]_{n_f^-} = [(\lambda/c_p)\mathbf{n}\cdot\nabla\tilde{h}^s]_{n_f^+} - [(\lambda/c_p)\mathbf{n}\cdot\nabla\tilde{h}^s]_{n_f^-}.$$



(b)

Adiabatic Flame Temperature (1/4)

- General conservation equation

$$\frac{\partial}{\partial t}(\rho h^s)+\nabla\cdot[\rho\mathbf{v}h^s-(\lambda/c_p)\nabla h^s]=-\sum_{i=1}^{N}h_i^o w_i \qquad \text{(A)}$$

$$\frac{\partial}{\partial t}(\rho Y_i)+\nabla\cdot(\rho\mathbf{v}Y_i-\rho D_i\nabla Y_i)=w_i, \quad i=1,2,\ldots,N, \qquad \text{(B)}$$

- For reactions confined to a sheet, regions bounded away from it ($\mathbf{x}<\mathbf{x}_f$ and $\mathbf{x}>\mathbf{x}_f$) are nonreactive

$$\frac{\partial}{\partial t}(\rho\tilde{h}^s)+\nabla\cdot(\rho\mathbf{v}\tilde{h}^s-(\lambda/c_p)\nabla\tilde{h}^s)=0, \qquad \text{(C)}$$

$$\frac{\partial}{\partial t}(\rho\tilde{Y}_i)+\nabla\cdot(\rho\mathbf{v}\tilde{Y}_i-\rho D\nabla\tilde{Y}_i)=0, \quad i=O,F. \qquad \text{(D)}$$

- A general solution (for *Le* = 1) is

$$\boxed{\tilde{h}^s=c_{1,i}+c_{2,i}\tilde{Y}_i,}$$

Adiabatic Flame Temperature (2/4)

- Premixed flame

$$(\tilde{h}^s)^- = c_{1,F} + c_{2,F}\tilde{Y}_F.$$

  - At upstream boundary: $(\tilde{h}^s)^- = \tilde{h}_u^s;\qquad \tilde{Y}_F = \tilde{Y}_{F,u},$
  - At reaction sheet: $(\tilde{h}^s)^- = \tilde{h}_f^s;\qquad \tilde{Y}_F = 0,$
  - Solving for $c_{1,F}$ and $c_{2,F}$ yields

$$(\tilde{h}^s) = \tilde{h}_f^s - \frac{\left(\tilde{h}_f^s - \tilde{h}_u^s\right)}{\tilde{Y}_{F,u}}\tilde{Y}_F. \qquad \text{(E)}$$

  - Substituting (E) into the jump relation just derived, get

$$\tilde{h}_f^s = \tilde{h}_u^s + \tilde{Y}_{F,u}, \quad \textbf{or} \quad \boxed{h_f^s = h_u^s + Y_{F,u}q_c.}$$

which is the relation for adiabatic flame temperature

Adiabatic Flame Temperature (3/4)

- Nonpremixed flame
  - Fuel side: $(\tilde{h}^s)^- = c_{1,F} + c_{2,F}\tilde{Y}_F; \quad (\tilde{h}^s)^- = \tilde{h}_f^s - \dfrac{(\tilde{h}_f^s - \tilde{h}_{B^-}^s)}{\tilde{Y}_{F,B^-}}\tilde{Y}_F$
  - Oxidizer side: $(\tilde{h}^s)^+ = c_{1,O} + c_{2,O}\tilde{Y}_O; \quad (\tilde{h}^s)^+ = \tilde{h}_f^s - \dfrac{(\tilde{h}_f^s - \tilde{h}_{B^+}^s)}{\tilde{Y}_{O,B^+}}\tilde{Y}_O$
  - Substituting into the jump relation yields

$$\frac{\tilde{h}_f^s - \tilde{h}_{B^-}^s}{\tilde{Y}_{F,B^-}} + \frac{\tilde{h}_f^s - \tilde{h}_{B^+}^s}{\tilde{Y}_{O,B^+}} = 1 \qquad \text{(F)}$$

Adiabatic Flame Temperature (4/4)

- Nonpremixed flame:
  - In dimensional form

$$\boxed{(Y_{F,B^-})q_c = (h_f^s - h_{B^-}^s) + \left(\frac{Y_{F,B^-}}{Y_{O,B^+}}\sigma_O\right)(h_f^s - h_{B^+}^s).}$$

  - $\boxed{\phi^* = \frac{Y_{F,B^-}}{Y_{O,B^+}}\sigma_O}$

$$= \frac{\text{Available fuel/Stoichimoetric fuel requirement}}{\text{Available oxidizer/Stoichiometric oxidizer requirement}}$$

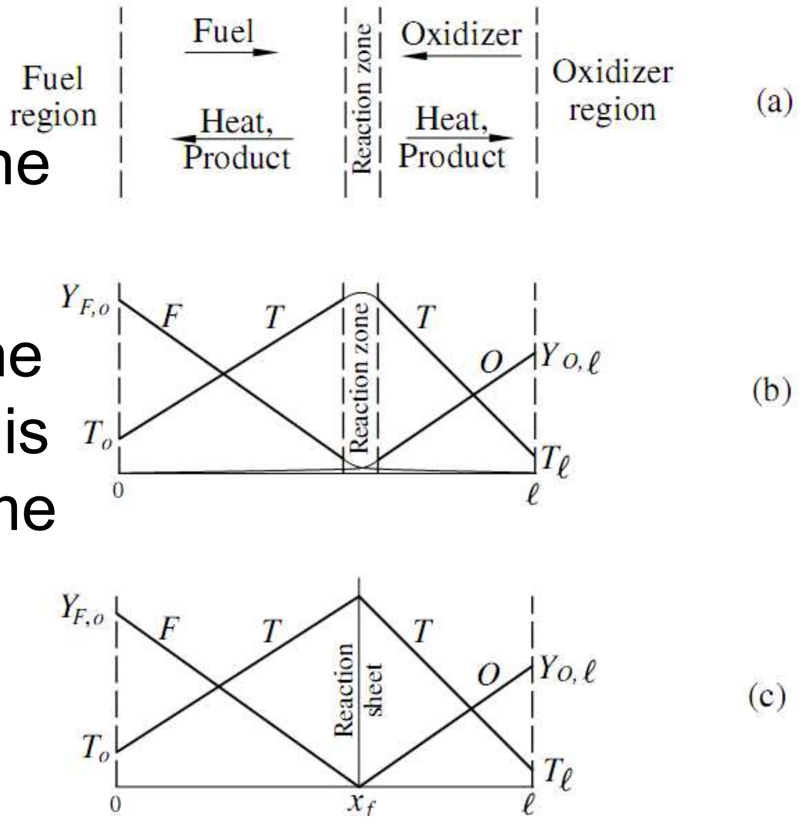
ϕ^* can be interpreted as the equivalence ratio for a nonpremixed flame

2.2. Reaction Sheet Analysis of Diffusion Flames:

1D Chambered Flame as Example

Structure of Diffusion Flames

- **General structure**: thin reaction zone separating a broad fuel-rich zone from a broad oxidizer-rich zone
- **For infinitely fast reaction**, compared to diffusion, reaction zone shrinks to a sheet ⇒ phenomenon is diffusion controlled ⇒ diffusion flame
- **For finite but large reaction rate**
  - Reaction zone broadened
  - Reactants leak through the flame
  - Excessive leakage leads to extinction

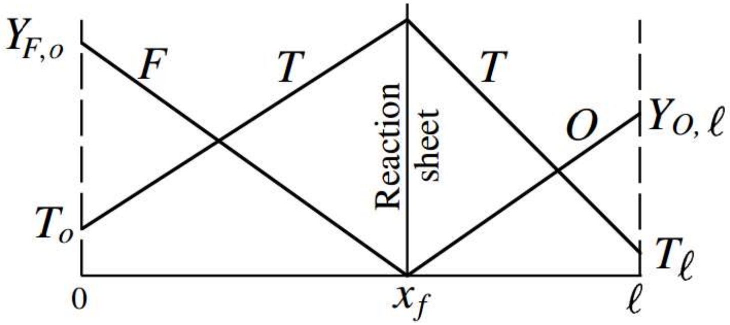


1D Chambered Flame: Coupling Function Formulation

- Problem definition

$$x = 0: \; Y_F = Y_{F,o}, \; Y_O = 0, \; Y_P = 0, \; T = T_0 \qquad (6.1.1)$$
$$x = \ell: \; Y_F = 0, \; Y_O = Y_{O,\ell}, \; Y_P = 0, \; T = T_\ell$$

- Coupling function formulation:



$$\frac{d^2\beta_i}{dx^2} = 0 \Rightarrow \; \beta_i = c_{1,i} + c_{2,i}x$$

- Applying (6.1.1) yields

$$\beta_F = \tilde{T} + \tilde{Y}_F = (\tilde{Y}_{F,O} + \tilde{T}_0) + (\tilde{T}_\ell - \tilde{T}_0 - \tilde{Y}_{F,O})\tilde{x} \qquad (6.1.5)$$

$$\beta_O = \tilde{T} + \tilde{Y}_O = \tilde{T}_0 + (\tilde{T}_\ell - \tilde{T}_0 + \tilde{Y}_{O,\ell})\tilde{x} \qquad (6.1.6)$$

Result is general, not limited to reaction sheet

1D Chambered Flame: Reaction-Sheet Solution

- Now apply reaction-sheet assumption $\Rightarrow$ no reactant leakage:

$$\tilde{Y}_F = 0,\ \tilde{x}_f \le \tilde{x} \le 1;\ \tilde{Y}_O = 0,\ 0 \le \tilde{x} \le \tilde{x}_f \tag{6.1.7}$$

- Apply (6.1.7) to (6.1.5) and (6.1.6) yields

$$\tilde{T}^- = \tilde{T}_0 + (\tilde{T}_\ell - \tilde{T}_0 + \tilde{Y}_{O,\ell})\tilde{x},\quad 0 \le \tilde{x} \le \tilde{x}_f \tag{6.1.8}$$

$$\tilde{T}^+ = (\tilde{T}_0 + \tilde{Y}_{F,0}) + (\tilde{T}_\ell - \tilde{T}_0 - \tilde{Y}_{F,0})\tilde{x},\quad \tilde{x}_f \le \tilde{x} \le 1 \tag{6.1.9}$$

- Apply $\tilde{T}^-$ to β_F and $\tilde{T}^+$ to β_O yields

$$\tilde{Y}_F = \tilde{Y}_{F,0} - (\tilde{Y}_{F,0} + \tilde{Y}_{O,\ell})\tilde{x},\quad 0 \le \tilde{x} \le \tilde{x}_f \tag{6.1.10}$$

$$\tilde{Y}_O = -\tilde{Y}_{F,0} + (\tilde{Y}_{F,0} + \tilde{Y}_{O,\ell})\tilde{x},\quad \tilde{x}_f \le \tilde{x} \le 1 \tag{6.1.11}$$

Problem completely solved – how straightforward!

1D Chambered Flame: Reaction-Sheet Properties

- Flame sheet (i.e. reaction sheet) location:
  - Set $\tilde{Y}_F$=0, or $\tilde{Y}_0$=0 at $\tilde{x} = \tilde{x}_f$ yields

$$\tilde{x}_f = \frac{\tilde{Y}_{F,o}}{\tilde{Y}_{F,o} + \tilde{Y}_{O,\ell}} = \frac{1}{1 + \tilde{Y}_{O,\ell}} = \boxed{\frac{\phi^*}{1+\phi^*} = \Phi^*}$$

Φ^*: Normalized equivalence ratio; flame located closer to deficit reactant

- Flame (-sheet) temperature:
  - Substitute $\tilde{x}_f$ in either (6.1.8) or (6.1.9), $\frac{\tilde{T}_f - \tilde{T}_o}{\tilde{Y}_{F,o}} + \frac{\tilde{T}_f - \tilde{T}_\ell}{\tilde{Y}_{O,\ell}} = 1$
  - Identical to the general expression for flame temperature derived earlier
- Fuel consumption flux:

$$f = -\rho D \left(\frac{dY_F}{dx} \right)_{x_f} = \frac{\rho D}{\ell} \left(Y_{F,0} + \frac{Y_{O,\ell}}{\sigma_O}\right)$$

1D Chambered Flame: Reaction-Sheet Formulation (1/2)

- Assume reaction-sheet right from the beginning
  - o Separately solve for non-reactive regions
  - o Match these solutions by applying jump relations
- Governing equations:

$$0 \le \tilde{x} < \tilde{x}_f : \quad \frac{d^2 Y_F}{d\tilde{x}^2} = 0 \quad \frac{d^2 \tilde{T}^-}{d\tilde{x}^2} = 0; \qquad \tilde{x}_f < \tilde{x} \le 1 : \quad \frac{d^2 \tilde{Y}_o}{d\tilde{x}^2} = 0 \quad \frac{d^2 \tilde{T}^+}{d\tilde{x}^2} = 0.$$

- Solving subject to:

$\tilde{T}^- = \tilde{T}^+ = \tilde{T}_f ; \tilde{Y}_F = \tilde{Y}_O = 0$ *at* $\tilde{x} = \tilde{x}_f$

Note: $\tilde{x}_f$, $\tilde{T}_f$ not known; determined through matching

1D Chambered Flame: Reaction-Sheet Formulation (2/2)

- Solution:

$$0 \le \tilde{x} \le \tilde{x}_f : \quad \tilde{Y}_F = \tilde{Y}_{F,o}\left(1 - \frac{\tilde{x}}{\tilde{x}_f}\right); \quad \tilde{T}^- = \tilde{T}_o + (\tilde{T}_f - \tilde{T}_o)\left(\frac{\tilde{x}}{\tilde{x}_f}\right)$$

$$\tilde{x}_f \le \tilde{x} \le 1 : \quad \tilde{Y}_O = \tilde{Y}_{O,\ell}\frac{\left(\tilde{x} - \tilde{x}_f\right)}{\left(1 - \tilde{x}_f\right)}; \quad \tilde{T}^+ = \tilde{T}_f - (\tilde{T}_f - \tilde{T}_\ell)\frac{\left(\tilde{x} - \tilde{x}_f\right)}{\left(1 - \tilde{x}_f\right)}$$

- Applying matching:

$$\left(\frac{d\tilde{Y}_F}{d\tilde{x}}\right)_{\tilde{x}_f^-} = -\left(\frac{d\tilde{Y}_O}{d\tilde{x}}\right)_{\tilde{x}_f^+}; \qquad \left(\frac{d\tilde{Y}_F}{d\tilde{x}}\right)_{\tilde{x}_f^-} = \left(\frac{d\tilde{T}^+}{d\tilde{x}}\right)_{\tilde{x}_f^+} - \left(\frac{d\tilde{T}^-}{d\tilde{x}}\right)_{\tilde{x}_f^-}$$

yields $\tilde{x}_f$ and $\tilde{T}_f$

2.3. Rankine – Hugoniot Waves in Premixtures

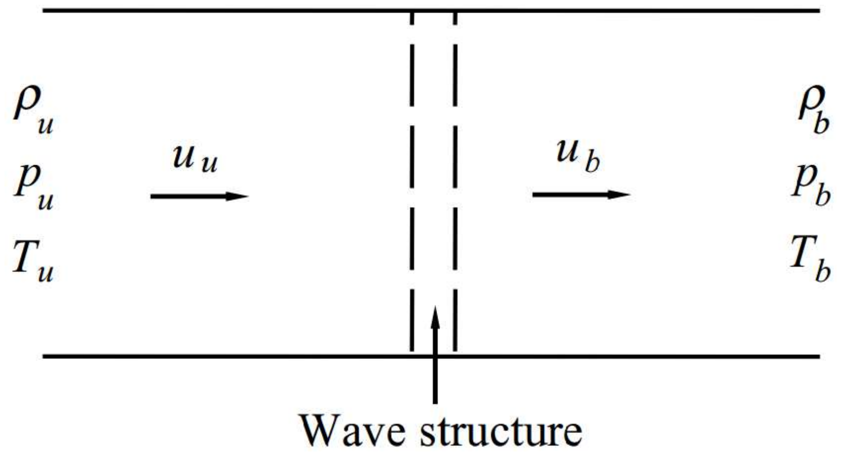
1D Wave Structure in Premixtures

- Nonpremixed (Diffusion) flame is diffusion controlled, through stoichiometry requirement.
  - Diffusion ⇒ subsonic flow
- A premixture is ready to react, not controlled by fuel-oxidizer stoichiometry
  - Once ignited, a chemical wave will propagate through the mixture, converting it to product
  - Propagation rate affected by reaction rate

    (vs. infinite reaction rate for nonpremixed combustion)
  - Propagation is a wave phenomena: can be either subsonic or supersonic

Rankine-Hugoniot Relations (1/4)

- Relates the equilibrium states far upstream and downstream of the wave
- Does not consider the nonequilibrium processes of diffusion and reaction within the wave ⇒problem not completely specified ⇒ wave speed, the most important flame response, is given instead of determined
- Solution shows two branches
  - Subsonic, deflagration wave
  - Supersonic, detonation wave
- Wave speed determined by analyzing the wave structure



Rankine-Hugoniot Relations (2/4)

- Mass: $\rho_u u_u = \rho_b u_b = f$

  Momentum: $\rho_u u_u^2 + p_u = \rho_b u_b^2 + p_b$

  Energy: $h_u + \frac{1}{2}u_u^2 = h_b + \frac{1}{2}u_b^2$

- **Rayleigh Lines**: mass and momentum conservation:

$$p_b - p_u = -(\rho_u u_u)^2 \left(\frac{1}{\rho_b} - \frac{1}{\rho_u} \right) = -f^2(\upsilon_b - \upsilon_u)$$

$$M_u^2 = -\frac{\hat{p}-1}{\gamma(\hat{\upsilon}-1)}, \quad M_b^2 = -\frac{(\hat{p}-1)\hat{\upsilon}}{\gamma(\hat{\upsilon}-1)\hat{p}} \qquad (7.1.5)$$

  - Straight lines passing through $(\hat{p}, \hat{v}) = (1,1)$
  - Negative slope of $-\gamma M_u^2$
  - Solution only for: $(\hat{p} > 1, \hat{\upsilon} < 1)$ i.e. $(\hat{p} > 1, \hat{\rho} > 1)$

    $(\hat{p} < 1, \hat{\upsilon} > 1)$ i.e. $(\hat{p} < 1, \hat{\rho} < 1)$

Rankine-Hugoniot Relations (3/4)

- **Hugoniot Lines**
  - o Using mass, momentum and energy conservation:

$$h_b - h_u = \frac{1}{2}(\upsilon_b + \upsilon_u)(p_b - p_u) \qquad (7.1.8)$$

  - o From chemical heat release: $h_b - h_u = -q_c + c_p(T_b - T_u)$

    and $c_p/\mathrm{R} = c_p/(c_p - c_v) = \gamma/(\gamma - 1)$

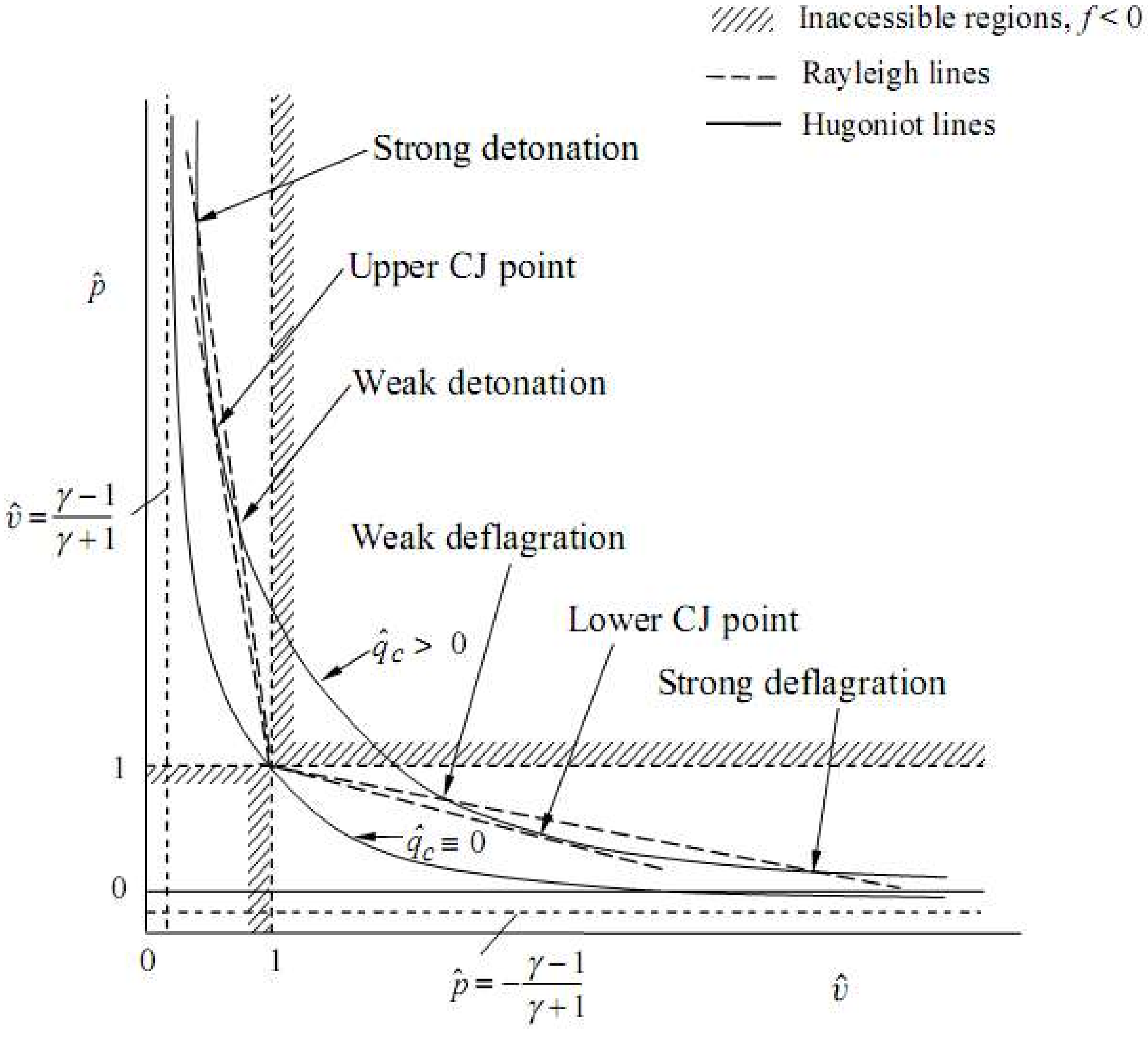
$$h_b - h_u = -q_c + \frac{\gamma}{\gamma - 1}\left(\frac{p_b}{\rho_b} - \frac{p_u}{\rho_u}\right) \qquad (7.1.10)$$

  - o Equating (7.1.8) and (7.1.10)

$$\left(\hat{p} + \frac{\gamma - 1}{\gamma + 1}\right)\left(\hat{v} - \frac{\gamma - 1}{\gamma + 1}\right) = \frac{4\gamma}{(\gamma + 1)^2} + 2\hat{q}_c\left(\frac{\gamma - 1}{\gamma + 1}\right), \qquad (7.1.11)$$

  - o Hyperbolas with asymptotes
    - o $\hat{p} \to -(\gamma - 1)/(\gamma + 1)$
    - o $\hat{\upsilon} \to (\gamma - 1)/(\gamma + 1)$
  - o $\hat{q}_c = 0$ line passes through (1,1)

Rankine-Hugoniot Relations (4/4)



Detonation and Deflagration Waves (1/2)

- Intersection of Rayleigh (7.15) and Hugoniot (7.1.11) lines yields solution

$$\boxed{\hat{p}_{\pm}-1=-\frac{(1-M_u^2)\gamma}{(\gamma+1)}\left\{1\pm\left[1-\frac{2(\gamma^2-1)}{\gamma}\frac{M_u^2}{(1-M_u^2)^2}\hat{q}_c\right]^{1/2}\right\}.} \qquad (7.1.13)$$

- Solution characterized by three parameters:
  - γ : compressibility; $\hat{q}_c$: exothermicity
  - M_u : wave speed that needs to be given
- (7.1.13) shows two solution branches
  - Since $0 < [\cdot]^{1/2} < 1$, $\{\cdot\} > 0$, character of solution depends on $M_u \gtrless 1$
  - Detonation: $M_u > 1, \hat{p} > 1, \hat{\upsilon} < 1, \hat{\rho} > 1$
  - Deflagration: $M_u < 1, \hat{p} < 1, \hat{\upsilon} > 1, \hat{\rho} < 1$

Detonation and Deflagration Waves (2/2)

- Detonation waves
  - Pressure and density increase across wave
  - Two solutions: strong and weak detonations
  - Tangency point: Chapman-Jouguet (CJ) wave
  - Consideration of wave structure
    - Rules out weak detonation
    - CJ wave prevalent
- Deflagration waves
  - Pressure and density decrease across wave
  - Two solutions: strong and weak deflagrations
  - Strong deflagration ruled out: entropy decreasing
  - Weak deflagration prevalent: near isobaric

Chapman-Jouguet Waves

- Tangency point for the Rayleigh and Hugoniot lines
- Additional tangency condition closes problem ⇒ complete solution for given $(\gamma, \hat{q}_c)$

$$(M_{u,\mathrm{CJ}})_{\pm}^{2} = 1 + \frac{(\gamma^{2}-1)\hat{q}_c}{\gamma}\left\{1 \pm \left[1 + \frac{2\gamma}{(\gamma^{2}-1)\hat{q}_c}\right]^{1/2}\right\},$$

$$M_b = 1$$

  - (Strong, weak) detonation: $M_b(<1, >1)$
  - (Strong, weak) deflagration: $M_b(>1, <1)$

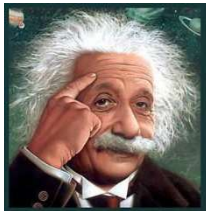
Closing Remarks of Day 2 Lecture (1/2)

- A simplified set of conservation equations were derived for subsonic flows allowing for: unsteadiness, diffusion, convection & reaction
- Controlling nondimensional parameters:
  - Diffusive-reactive: *Le*, *Da*, *Ze* (*Ar*)
  - Fluid mechanics and transport parameters of interest (e.g. *Re*, *Gr*, *Pe*…)
- Two major classes of rational analysis:
  - Conserved scalar (i.e. coupling function)
  - Reaction/flame sheet
  - Caution: *Le* = 1 assumption frequently embedded

Closing Remarks of Day 2 Lecture (2/2)

- Premixed "flames" are wave phenomena
  - Subsonic, deflagration waves
  - Supersonic, detonation waves
    - Chapman-Jouguet wave dominates (sonic downstream)
- "Equivalence ratio" defined for diffusion flames
- Discussion focused on heat and mass transport; inclusion of fluid flow through the momentum equation will greatly enrich potential phenomena of interest

Day 2 Special



Liñán's Unified Formulation of Diffusion and Premixed Flames

A General Analysis of Diffusion Flame Structure

- Use chambered flame as example, with *Le*=1
- Equation system:

$$\frac{d^2\tilde{T}}{d\tilde{x}^2} = -Da_C\tilde{Y}_O\tilde{Y}_F e^{-\tilde{T}_a/\tilde{T}}, \qquad (9.2.2)$$

$$\tilde{T} + \tilde{Y}_O = \tilde{T}_\ell + (\beta + \tilde{Y}_{O,o})(1-\tilde{x}), \qquad (9.2.4)$$

$$\tilde{T} + \tilde{Y}_F = \tilde{T}_o + (1-\beta)\tilde{x}, \qquad (9.2.5)$$

- ➢ $\beta = \tilde{T}_o - \tilde{T}_\ell$ (9.2.6)
- ➢ $\tilde{T}(0) = \tilde{T}_o,\ \tilde{T}(1) = \tilde{T}_\ell,$ (9.2.7) , (9.2.8)

Classification of (Nonreactive) Flows Bounded from Reaction Sheets

Consider vanishing of the reaction term in:

$$\frac{d^2\tilde{T}}{d\tilde{x}^2} = -Da_C\tilde{Y}_O\tilde{Y}_F e^{-\tilde{T}_a/\tilde{T}},$$

- Frozen flow ($Da_c \equiv 0$)

$$\tilde{T} = c_1 + c_2\tilde{x}, \qquad (9.2.9)$$

- Equilibrium flow ($\tilde{Y}_o \equiv 0$)

$$\tilde{T} = (\tilde{T}_o + \tilde{Y}_{O,o}) - (\beta + \tilde{Y}_{O,o})\tilde{x}. \qquad (9.2.10)$$

- Equilibrium flow ($\tilde{Y}_F \equiv 0$)

$$\tilde{T} = \tilde{T}_o + (1-\beta)\tilde{x}. \qquad (9.2.11)$$

Classification of Flames

- A general analysis of diffusion flame structure based on various combinations of frozen and equilibrium flows separated by reaction sheets (*Acta Astro*., 1974):
  - Identified four types of flames
    - Near equilibrium, diffusion flame
    - Premixed flame
    - Partial burning
    - Weakly burning, ignition
  - Reduced structure equations to canonical forms
  - Obtained general semi-empirical solutions for structure equations and ignition-extinction criteria and expressions
- Subsequent studies show analysis applicable to wide range of situations
  - Quasi-1D flows; $Le \neq 1$; loss

Near Equilibrium, Diffusion Flame Regime

- Flame sheet separates two near-equilibrium flow regions.
- To leading order, fuel and oxidizer respectively vanishes in each region

$$\tilde{x} < \tilde{x}_f : \quad \tilde{Y}_{F,0}^{-} = 0, \quad \tilde{T}_0^{-} = \tilde{T}_o + (1-\beta)\tilde{x} \qquad (9.2.12)$$

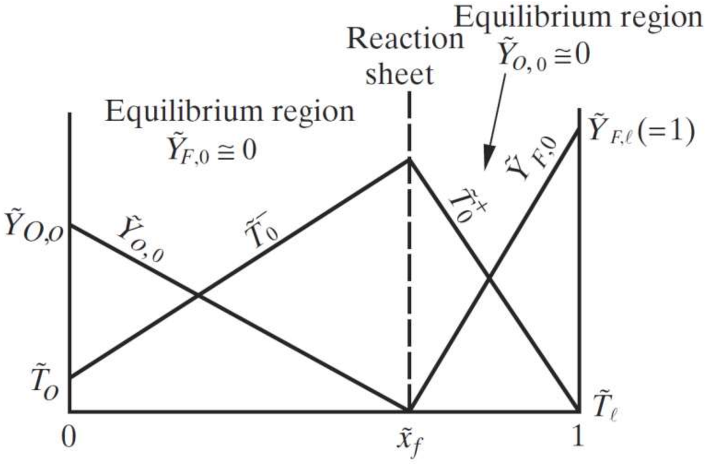
$$\tilde{x} > \tilde{x}_f : \quad \tilde{Y}_{O,0}^{+} = 0, \quad \tilde{T}_0^{+} = \tilde{T}_\ell + (\beta + \tilde{Y}_{O,o})(1-\tilde{x}), \qquad (9.2.13)$$

- Flame temperature and location can be readily evaluated as

$$\tilde{T}_f = \tilde{T}_o + (1-\beta)\frac{\tilde{Y}_{O,o}}{1+\tilde{Y}_{O,o}} = \tilde{T}_\ell + \left(\frac{\beta + \tilde{Y}_{O,o}}{1+\tilde{Y}_{O,o}}\right), \qquad (9.2.14)$$

$$\tilde{x}_f = \tilde{Y}_{O,o} / (1 + \tilde{Y}_{O,o}). \qquad (9.2.15)$$

- This is just the diffusion flame solution. All flame properties are determined at this level
- With decreasing Da$_c$, reactant leakage occurs and will eventually lead to extinction



(a) Near-Equilibrium Regime

Premixed Flame Regime

- Substantial leakage of one reactant is possible, even to the leading order. Leaked reactant freezes after crossing the flame.
- Thus flame separates a frozen flow region from an equilibrium flow region
- For fuel being the leaked reactant, $\tilde{Y}_{O,o} + 2\beta < 1$

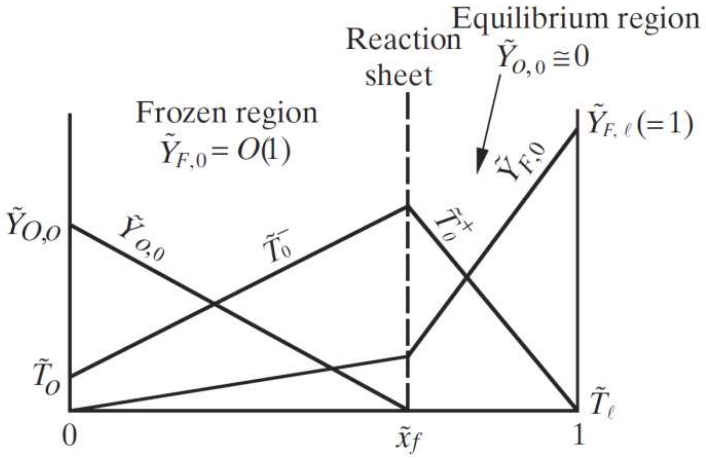
$$\tilde{x} < \tilde{x}_f: \quad \tilde{T}_0^- = \tilde{T}_o + (\tilde{T}_f - \tilde{T}_o)\frac{\tilde{x}}{\tilde{x}_f}, \qquad (9.2.16)$$

$$\tilde{x} > \tilde{x}_f: \quad \tilde{Y}_{O,0}^+ = 0, \quad \tilde{T}_0^+ = \tilde{T}_\ell + (\beta + \tilde{Y}_{O,o})(1 - \tilde{x}), \qquad (9.2.17)$$

- Evaluating at reaction sheet yields

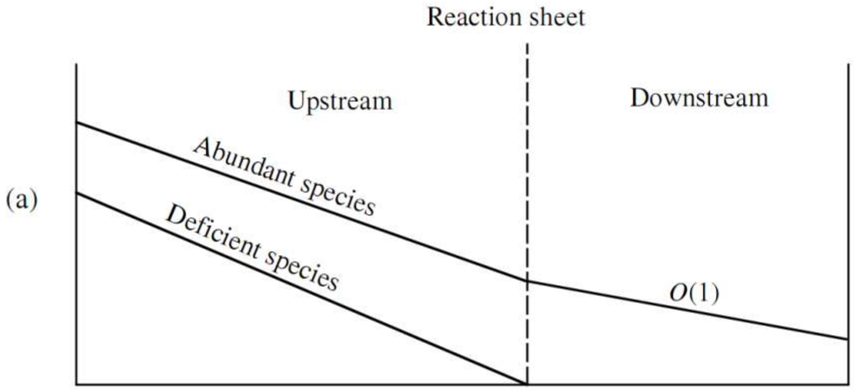
$$\tilde{T}_f = \tilde{T}_\ell + (\beta + \tilde{Y}_{O,o})(1 - \tilde{x}_f). \qquad (9.2.18)$$

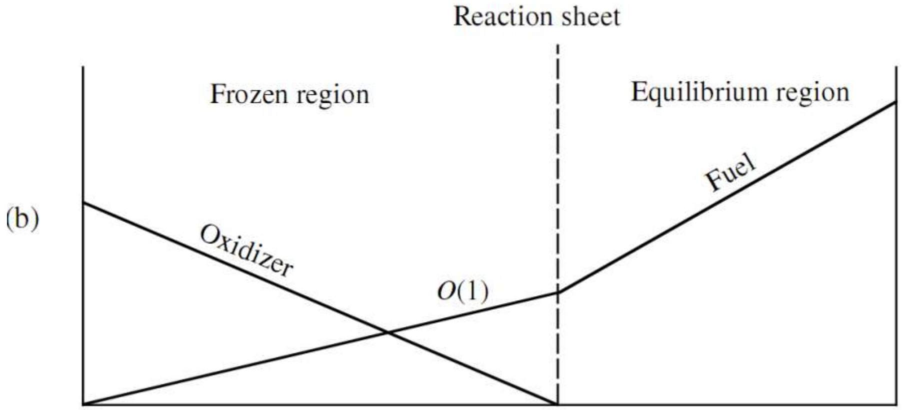
  - ➢ Flame-sheet solution determined to one unknown;
  - ➢ Needs analysis at next order to determine the extra unknown



(b) Premixed Flame Regime

Unified Interpretation of Premixed and Diffusion Flames: Leading-Order Structure





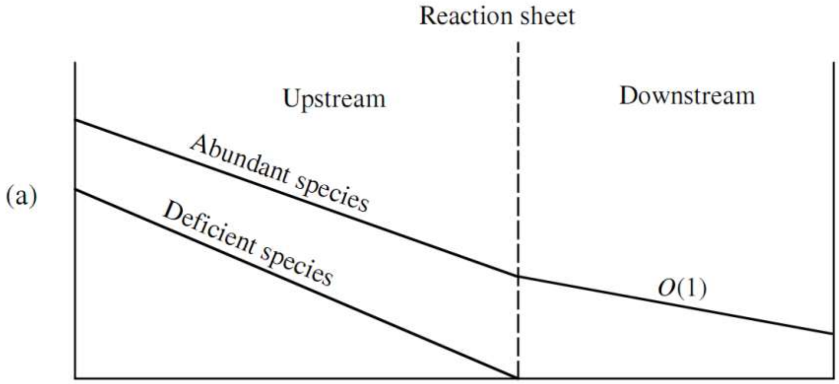
Leading-order Structure of Premixed Flame

Leading-order Structure of Premixed Flame Regime in Diffusion Flame Analysis

Limiting species: Deficient species completely consumed at reaction sheet
Abundant species: Concentration remains O(1) throughout, hence unaffected

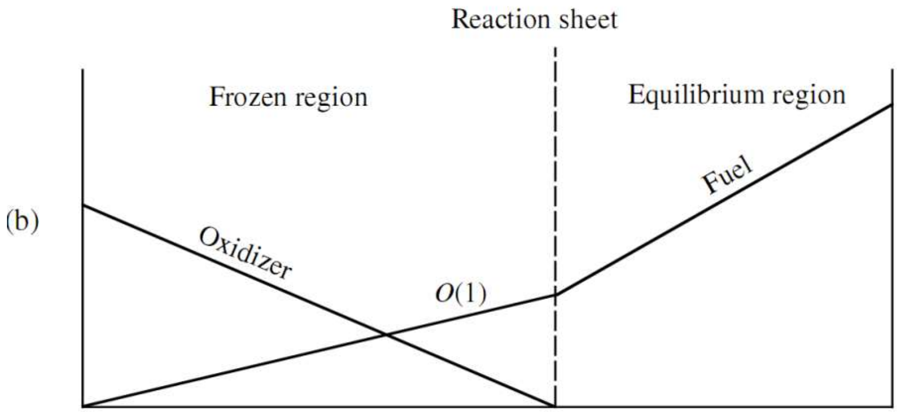
Limiting species: oxidizer (or fuel); completely consumed at reaction sheet
Abundant species: Fuel (or oxidizer) concentration remains O(1) throughout, hence unaffected

Unified Interpretation of Premixed and Diffusion Flames: Reaction Zone Structure



Premixed Flame

$$w \sim [k(T)Y_{\text{abundant}}]Y_{\text{deficient}}$$
$$\sim k'(T)Y_{\text{deficient}}$$



Premixed Flame Regime in Diffusion Flame Analysis

$$w \sim [k(T)Y_{\text{fuel}}]Y_{\text{oxidizer}}$$
$$\sim k'(T)Y_{\text{oxidizer}}$$

Hence complete physical & mathematical correspondence

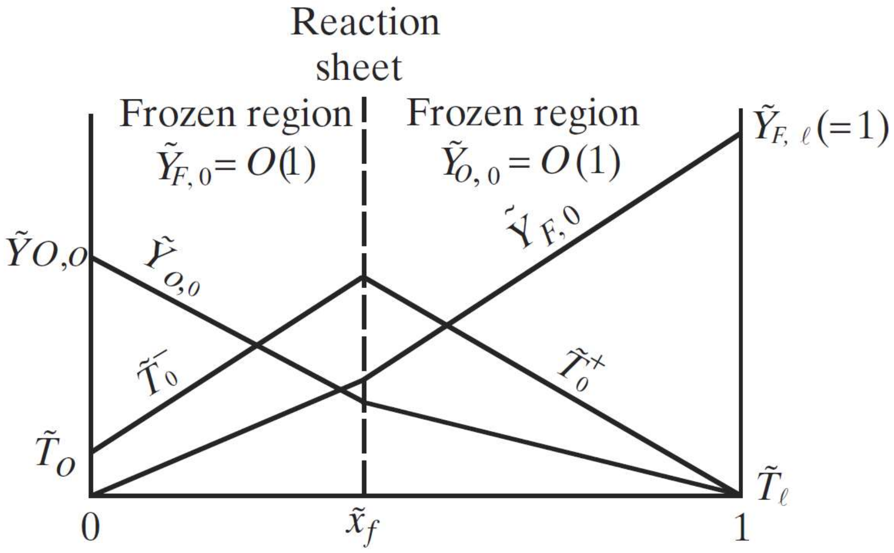
Partial Burning Regime

- Excessive leakage occurs for both reactants
- To leading order, flame sheet separates two frozen regions

$$\tilde{x} < \tilde{x}_f : \quad \tilde{T}_0^- = \tilde{T}_o + (\tilde{T}_f - \tilde{T}_o)\frac{\tilde{x}}{\tilde{x}_f}, \qquad (9.2.19)$$

$$\tilde{x} > \tilde{x}_f : \quad \tilde{T}_0^+ = \tilde{T}_\ell + (\tilde{T}_f - \tilde{T}_\ell)\frac{1-\tilde{x}}{1-\tilde{x}_f}, \qquad (9.2.20)$$

- Flame-sheet solution determined to two unknowns



(c) Partial Burning Regime

Nearly-Frozen Regime

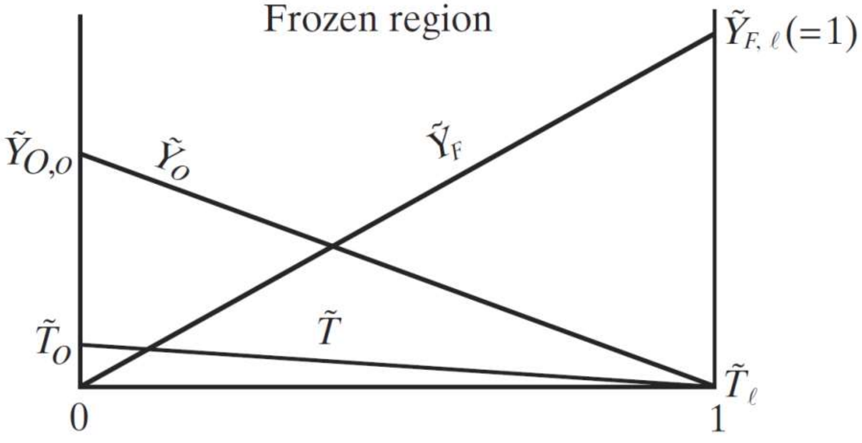
- Reaction is frozen throughout flow field
- Leading order solutions completely determined

$$\tilde{T}_0 = \tilde{T}_o - \beta\tilde{x}. \qquad (9.2.22)$$

$$\tilde{Y}_{F,0} = \tilde{x}, \qquad (9.2.23)$$

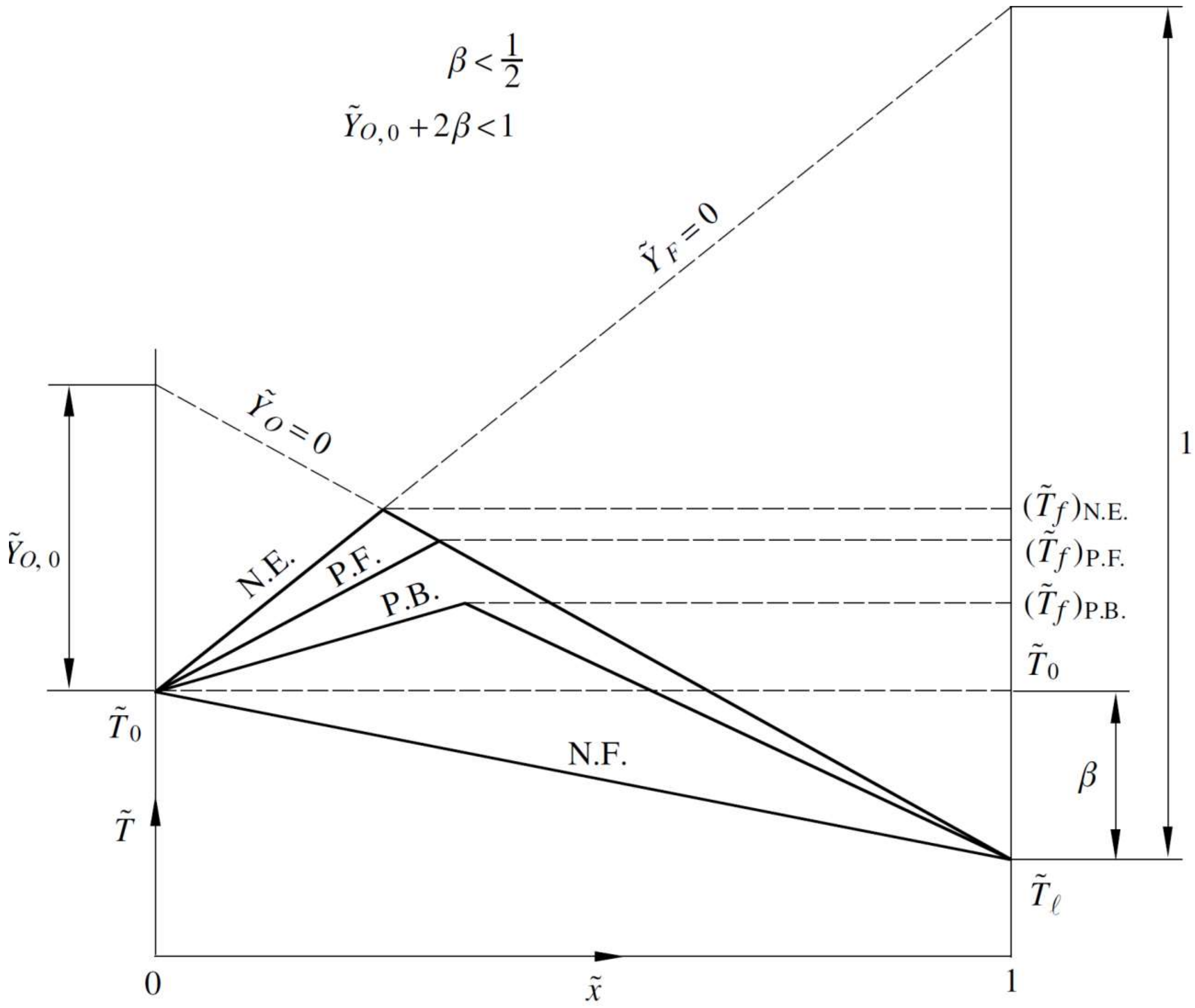
$$\tilde{Y}_{O,0} = (1-\tilde{x})\tilde{Y}_{O,o}. \qquad (9.2.24)$$

- Ignition occurs with finite reaction rates

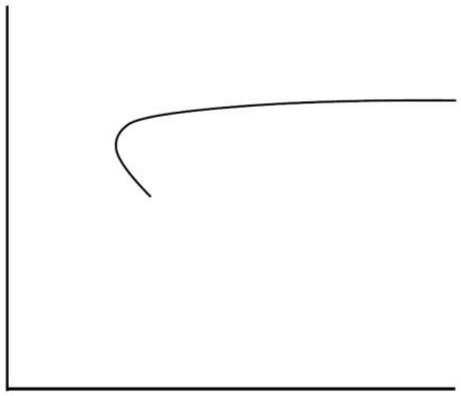


(d) Nearly Frozen Regime

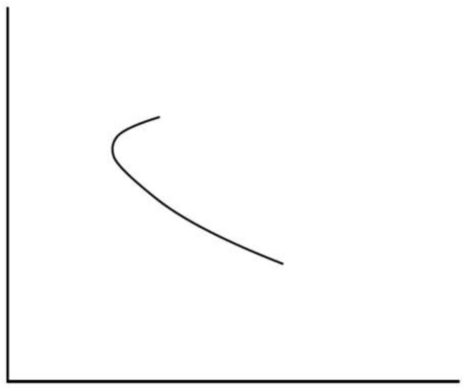
Regime Classifications Based on Energy Levels



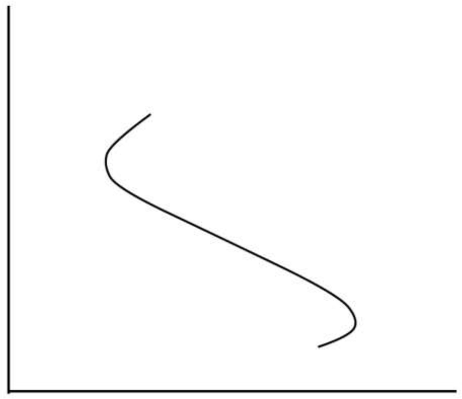
Flame Response with Finite Da_C for Different Regimes



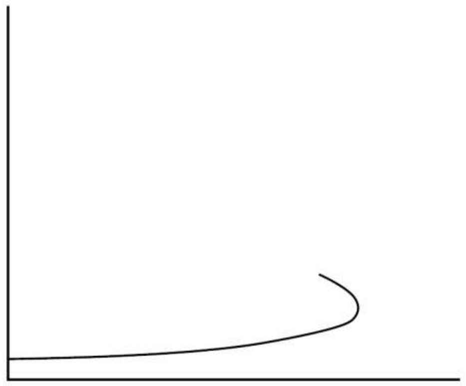
Near-Equilibrium Regime



Premixed Flame Regime



Partial Burning Regime



Nearly Frozen Regime

Analysis of Nearly-Frozen Regime

- Ignition occurs next to hot boundary, x=0
- Similar to hot surface ignition, except Y_F=O(ε) in reaction zone
- Structure equation

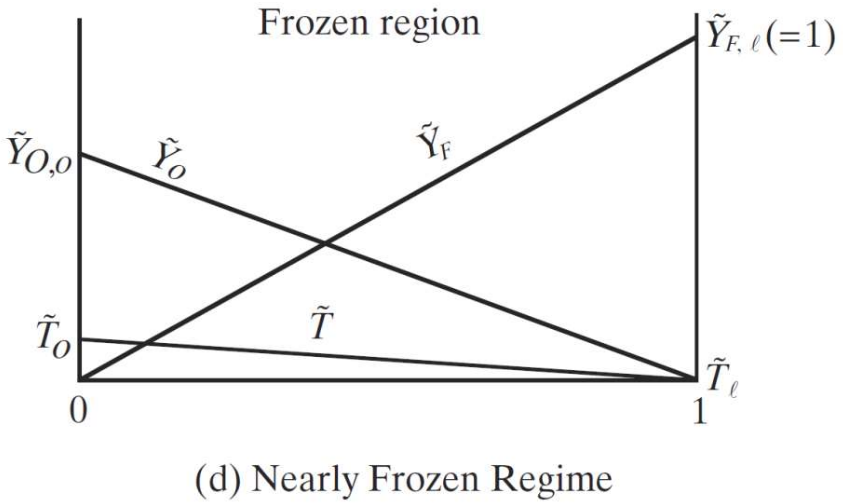
$$\frac{d^2\theta}{d\chi^2} = -\Delta(\chi - \theta)e^{(\theta - \beta\chi)} \qquad (9.3.2)$$

$$\theta(0) = 0 \qquad (9.3.3)$$

$$\left(\frac{d\theta}{d\chi}\right)_{x\to\infty} = 0. \qquad (9.3.6)$$

$$\Delta = \varepsilon^2 \mathrm{Da}_\mathrm{C} \tilde{Y}_{O,o} \exp(-\tilde{T}_a/\tilde{T}_o)$$

$$\beta = \tilde{T}_o - \tilde{T}_l$$



(d) Nearly Frozen Regime

- Ignition occurs if

$$\Delta > \Delta_I(\beta) = \frac{\beta^2/2}{1 + 2.17(1-\beta)/\beta}, \qquad (9.3.7)$$

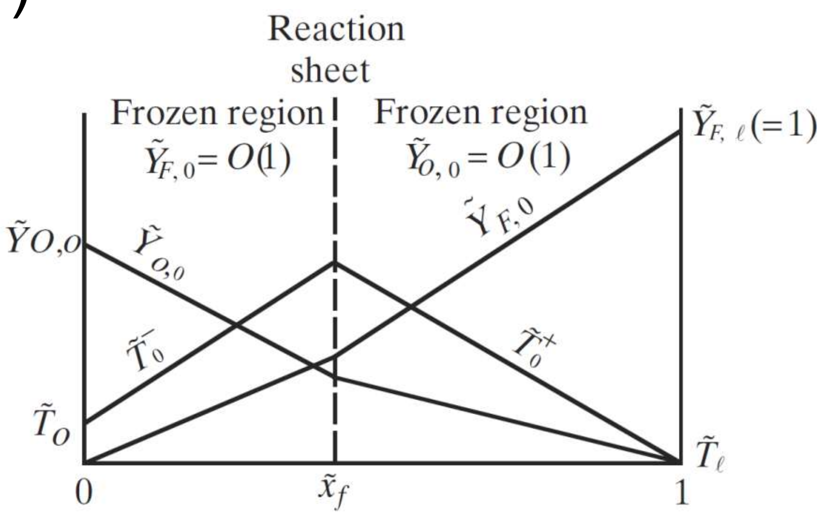
Analysis of Partial Burning Regime

- Reactant concentrations are O(1) in reaction zone
- Structure equation:

$$\frac{d^2\theta}{d\chi^2} = -\Delta e^{\theta}, \quad \Delta = \varepsilon Da_C \tilde{Y}_{o,f} \tilde{Y}_{F,f} \exp(-\tilde{T}_a / \tilde{T}_f)$$

- Solution

$$\theta(\chi) = \theta_m - \ln\left\{\cosh^2\left[\left(\frac{\Delta}{2} e^{\theta_m}\right)^{1/2} (\chi - \chi_m)\right]\right\}, \quad (9.3.8)$$



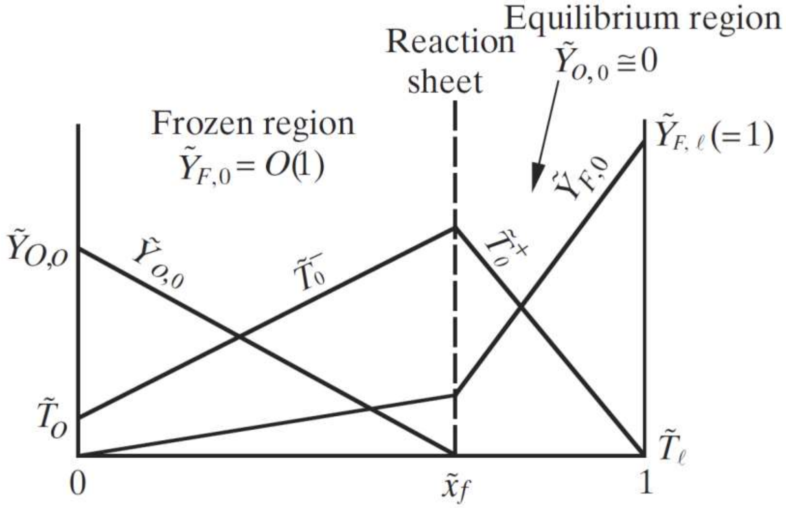
(c) Partial Burning Regime

determined to two unknowns, θ_m and χ_m

- Need to go to second-order analysis to solve the problem, using delta function closure
- Existence of such a flame has yet to be confirmed!

Analysis of Premixed Flame Regime

- Same analysis as that conducted previously
- Concentration of one reactant is O (ε) in reaction zone
- With appropriate definitions, obtained identical structure equation, as previously
- $\Delta = 2\varepsilon^2 Da_C \exp(-\tilde{T}_a / \tilde{T}_f)$



(b) Premixed Flame Regime

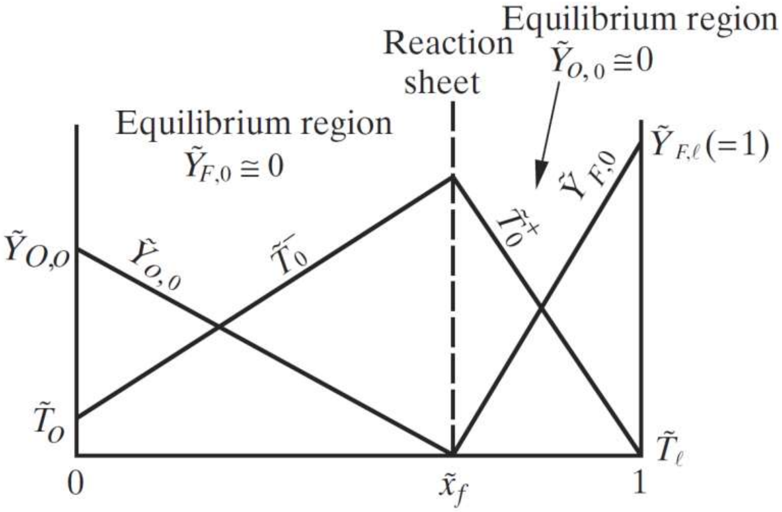
Analysis of Near-Equilibrium Regime

- Concentration of both reactants O (ε) in reaction zone
- Structure equation

$$\frac{d^2\tilde{\theta}}{d\eta^2}=\delta(\tilde{\theta}-\eta)(\tilde{\theta}+\eta)e^{-(\tilde{\theta}+\gamma\eta)},\quad (9.3.23)$$

$$\left(\frac{d\tilde{\theta}}{d\eta}\right)_{-\infty}=-1,\ \left(\frac{d\tilde{\theta}}{d\eta}\right)_{\infty}=1\qquad (9.3.24),\ (9.3.25)$$

$$\delta=\frac{4\Delta}{1+\tilde{Y}_{O,o}^2},\ \Delta=\varepsilon^3 Da_C\exp(-\tilde{T}_a/\tilde{T}_f)$$



(a) Near-Equilibrium Regime

- Extinction occurs for:

$$\delta<\delta_E$$
$$=\{(1-|\gamma|)-(1-|\gamma|)^2+0.26(1-|\gamma|)^3+0.055(1-|\gamma|)^4\}e.\qquad (9.3.23)$$

$$\gamma=1-\frac{2(1-\beta)}{1+\tilde{Y}_{O,o}}=\frac{2(\tilde{Y}_{O,o}+\beta)}{1+\tilde{Y}_{O,o}}-1$$

Combustion Physics
(Day 3 Lecture)

Chung K. Law
Robert H. Goddard Professor
Princeton University
Honorary and Founding Director
Center for Combustion Energy
Tsinghua University

Tsinghua-Princeton-Combustion Institute
Summer School on Combustion
July 7-13, 2024

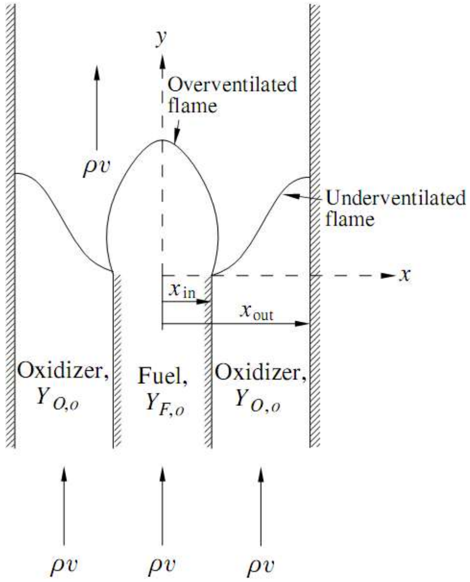
Day 3: Diffusion Flames and Heterogeneous Combustion

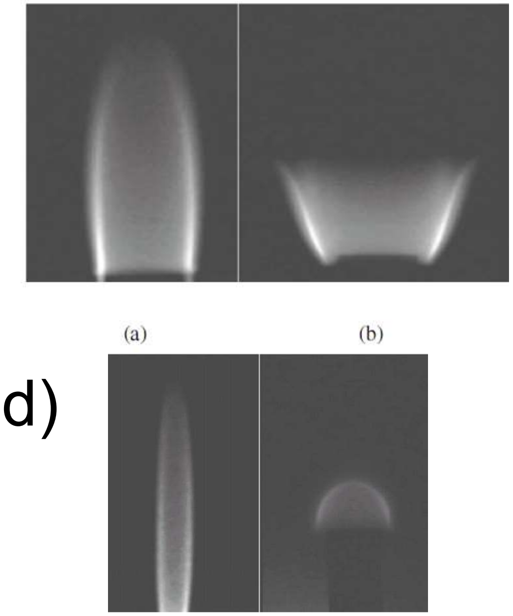
1. **Burke-Schumann and counterflow flames**
2. **Heat & mass transfer with condensed fuels**
3. **Droplet combustion**
   1. The d^2-Law
   2. Multicomponent fuels
4. **Other heterogeneous systems**
   1. Carbon and metal particles
   2. Spray flames

1. Burke-Schumann and Counterflow Flames

The Burke-Schumann Flame

- The first diffusion flame theory formulated based on reaction-sheet concept, in 1928 (1^{st} Comb. Sym.)
- Embodies rich concepts of underlying phenomena
- Problem: Fuel jet entering into a parallel oxidizer jet
  a) Over-ventilated
  b) Under-ventilated
  c) Large jet velocity (convection dominated)
  d) Small jet velocity (diffusion dominated)




(a) (b)
(c) (d)

Precise Problem Definition

- Mass flux in *x*-direction: $\rho u \equiv 0$; no thermal expansion

$$\frac{\partial}{\partial y}(\rho \upsilon) = 0\,; \quad \rho \upsilon = f(x)$$

$\rho \upsilon$ = constant

$\Rightarrow$ same momentum flux for fuel and oxidizer

- Original B-S formulation
  - o neglects y-diffusion
  - o assumes constant ρ
  - o both assumptions unnecessary
- Assume *Le* =1

Governing Equations and Boundary Conditions

- Dimensional governing equation

$$\frac{\partial(\rho\upsilon\beta_i)}{\partial y}-\frac{\partial}{\partial x}\left[(\lambda/c_p)\frac{\partial\beta_i}{\partial x}\right]-\frac{\partial}{\partial y}\left[(\lambda/c_p)\frac{\partial\beta_i}{\partial y}\right]=0$$

- Nondimensional governing equation

$$\boxed{Pe\frac{\partial\beta_i}{\partial\tilde{y}}-\left(\frac{\partial^2\beta_i}{\partial\tilde{x}^2}+\frac{\partial^2\beta_i}{\partial\tilde{y}^2}\right)=0}$$

Peclet Number: $Pe=\dfrac{\rho\upsilon x_{\text{out}}}{\lambda/c_p}$

- Boundary conditions:

$0<\tilde{x}<\tilde{x}_{\text{in}},\ \tilde{y}=0:\ \tilde{Y}_F=\tilde{Y}_{F,0},\tilde{T}=\tilde{T}_0$ $\qquad$ $\tilde{x}_{\text{in}}<\tilde{x}<1,\ \tilde{y}=0:\ \tilde{Y}_O=\tilde{Y}_{O,0},\tilde{T}=\tilde{T}_0$

$\tilde{x}=0,\ \tilde{y}>0:\ \dfrac{\partial(\cdot)}{\partial\tilde{x}}=0$ (adiabatic wall) $\qquad$ $\tilde{x}=0,\ \tilde{y}>0:\ \dfrac{\partial(\cdot)}{\partial\tilde{x}}=0$ (symmetry)

$\tilde{y}\to\infty:$ boundedness.

Solution (1/2)

- Use separation of variables method:

$$\beta_i(\tilde{x},\tilde{y}) = \Theta(\tilde{x})\Phi(\tilde{y}) \qquad \frac{Pe\Phi' - \Phi''}{\Phi} = \frac{\ddot{\Theta}}{\Theta},$$

- Solution yields (e.g. for β_F):

$$\beta_F = \tilde{Y}_F + \tilde{T} = \tilde{T}_o + \tilde{x}_{\text{in}}\tilde{Y}_{F,o} + 2\tilde{Y}_{F,o}\sum_{n=1}^{\infty} G_n\left(\tilde{x},\tilde{y};Pe\right),$$

$$G_n\left(\tilde{x},\tilde{y};Pe\right) = \left(\frac{\sin n\pi\,\tilde{x}_{\text{in}}}{n\pi}\right)\left(\cos n\pi\tilde{x}\right)\exp\left\{\left[Pe - \sqrt{Pe^2 + 4\pi^2 n^2}\right]\tilde{y}/2\right\}.$$

- Apply reaction-sheet approximation in β_F and β_O to solve for (x_f, y_f, T_f)

$$\tilde{Y}_F = 0, \tilde{Y}_O = 0, \tilde{T} = \tilde{T}_f \ at\ x = x_f, y = y_f$$

Solution (2/2)

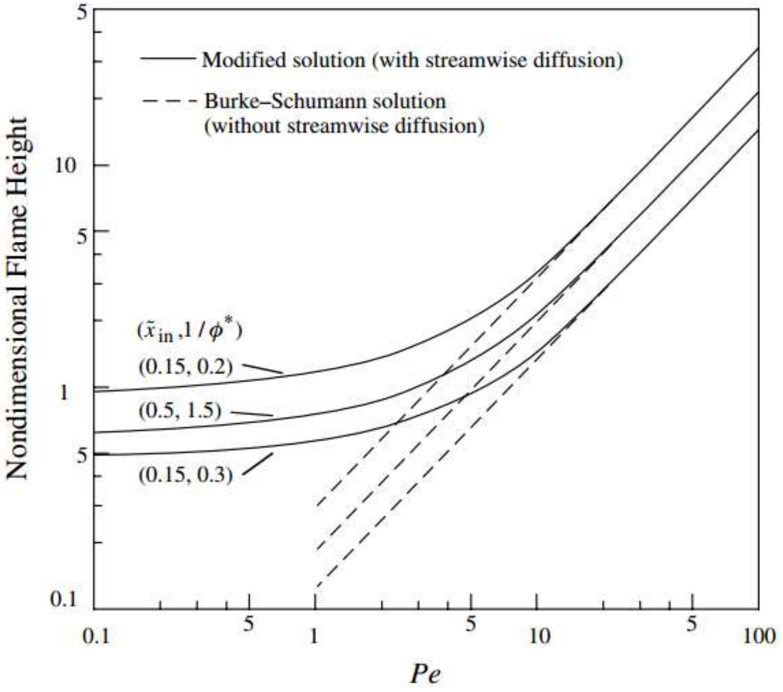
- Solution for reaction sheet $(\tilde{x}_f, \tilde{y}_f, \tilde{T}_f)$

$$(1-\tilde{x}_{\text{in}}) - 2\sum_{n=1}^{\infty} G_n(\tilde{x}_f, \tilde{y}_f; Pe) = \Phi^*, \quad (\tilde{T}_f - \tilde{T}_o) = \tilde{Y}_{O,o}\Phi^*$$

- Transition between under- and over-ventilated flame, $\tilde{y} \to \infty$

$$1-\tilde{x}_{\text{in}} = \phi^*/(1+\phi^*) = \Phi^*$$

  $\Rightarrow$ Diluting fuel (reducing ϕ^*) would require larger inner tube to achieve tip opening



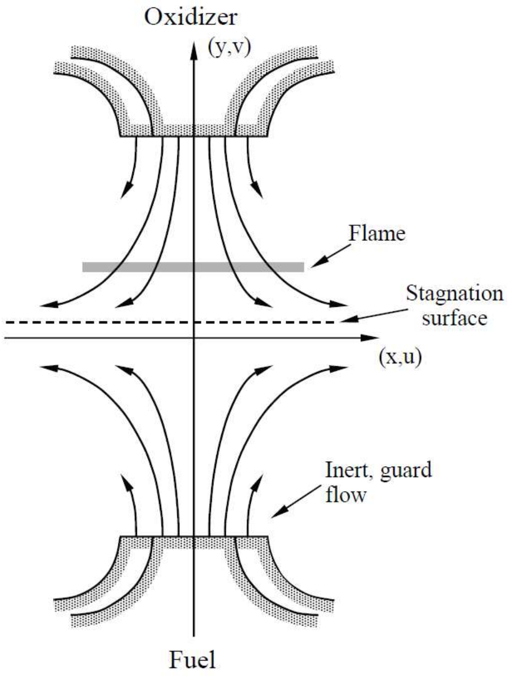
- Flame temperature
  - Same as the general derivation ⇒ does not depend on geometry

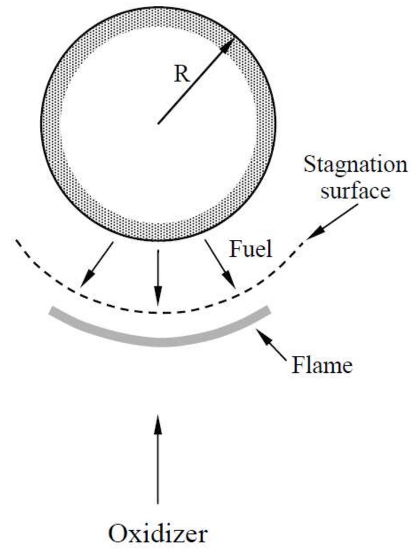
    Solution captures low *Pe* behavior, missed by the original B-S solution

Stagnation/Counterflow Flame

Why counterflow?

- A steady, 1D flame that can be readily established
- Centerline flow velocity varies linearly with distance, $v = -ay \Rightarrow$ flow characterized by a single parameter, *a*, the velocity gradient (*i.e.* the strain rate)
- 1/*a* is the characteristic flow time
- Any (locally) nonuniform flow field can be Taylor expanded, so that the first non-constant term varies linearly with distance ⇒ has general utility including turbulent flames





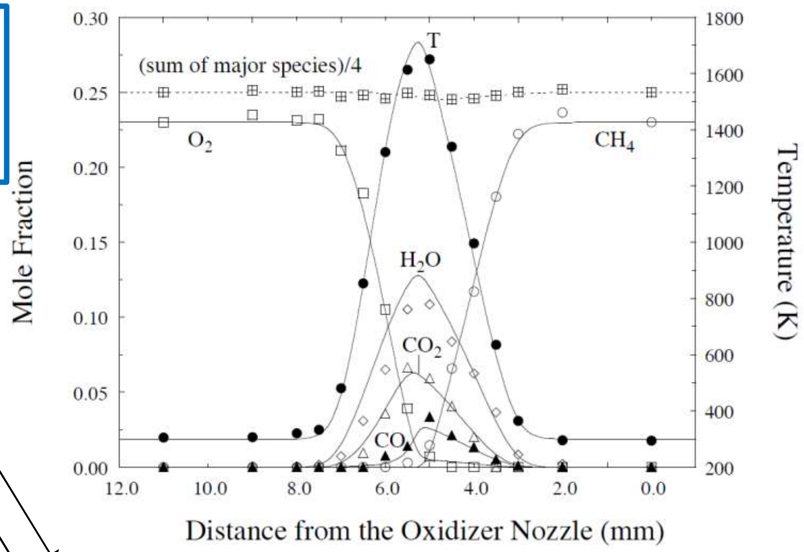
The Counterflow Flame

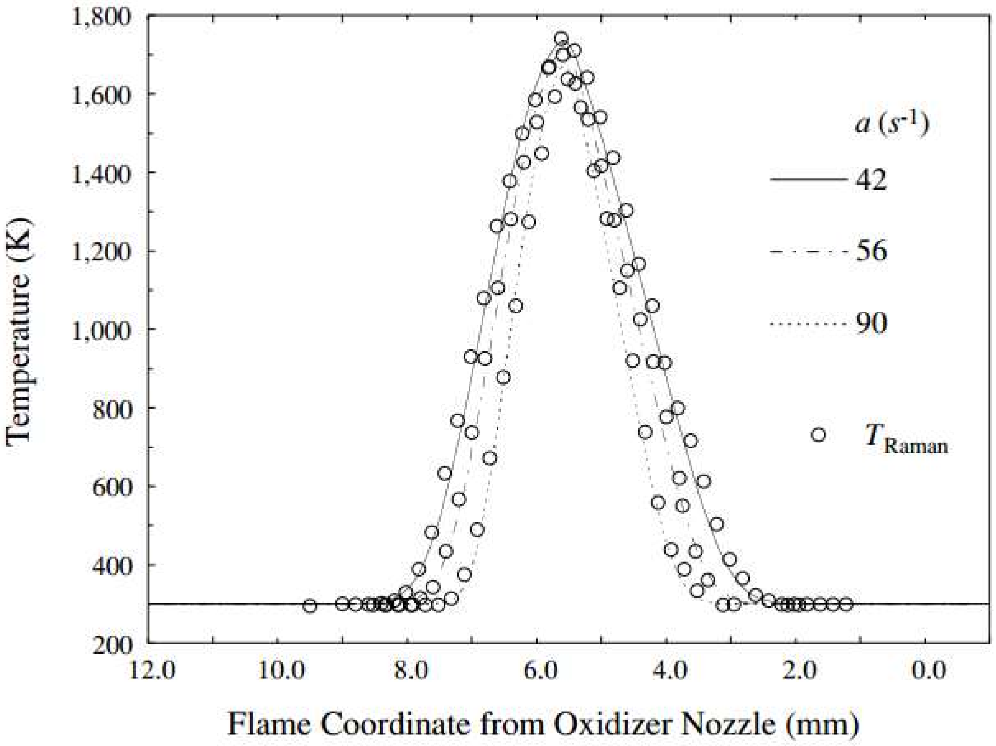
- Governing equation (for potential flow)

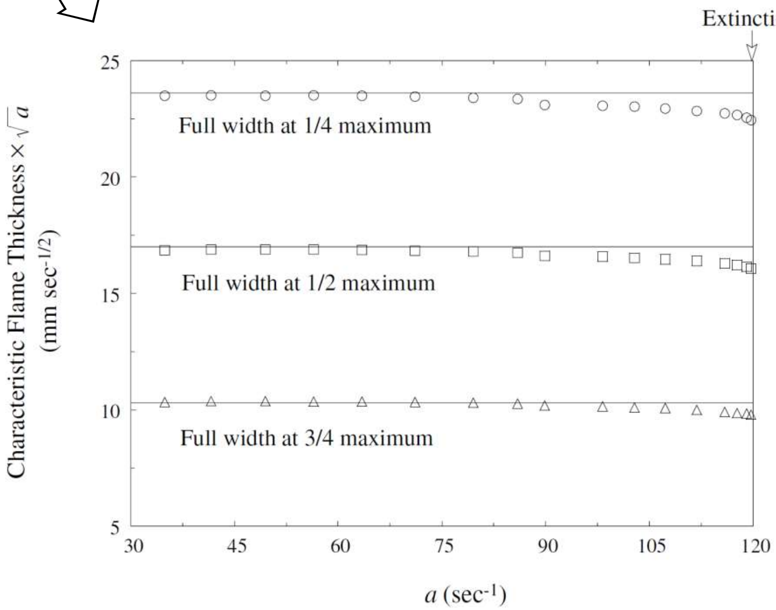
$$\rho a y \frac{d\beta_i}{dy} + (\lambda/c_p)\frac{d^2\beta_i}{dy^2} = 0, \quad \boxed{\tilde{y}\frac{d\beta_i}{d\tilde{y}} + \frac{d^2\beta_i}{d\tilde{y}^2} = 0}$$

- Scaling:

$$\tilde{y} = y/(\lambda/c_p\rho a)^{1/2} \sim y a^{1/2}$$



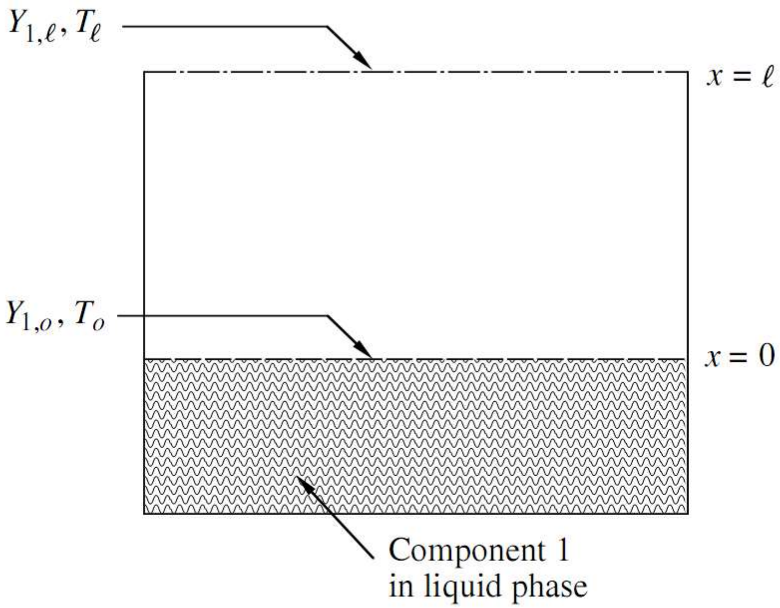




Heat and Mass Transfer with Condensed Fuels

Condensed Fuel Vaporization

- Problem: thermally insolated beaker of water undergoes vaporization (due to concentration gradient), which is sustained by heat transfer from ambience; heat & mass transfer intrinsically coupled
- Net loss of water signifies presence of (Stefan) convection



- Goal: Determine (a) vaporization or condensation rate; (b) temperature of water in beaker

Problem Formulation (1/5)

- One-dimensional, steady
  - $d(\rho u)/dx = 0 \Rightarrow \rho u = f =$ constant
- Species conservation:

$$f\frac{dY_i}{dx} - \frac{d}{dx}\left(\rho D\frac{dY_i}{dx}\right) = 0.$$

- Integrating once:

$$fY_i - \rho D\frac{dY_i}{dx} = \text{constant} = f_i$$

  - f_{i} : sum of diffusive and Stefan convection fluxes
  - Species 2: air which is not condensable $\Rightarrow f_2 = 0$
  - Species 1: water, $f_1 = f - f_2 = f$

Problem Formulation (2/5)

- Species conservation: $fY_1 - \rho D \dfrac{dY_1}{dx} = f = f_1$
- Integrating yields: $\boxed{f = \dfrac{\rho D}{\ell} \ln(1 + B_{m,\upsilon})}$
  - Mass transfer number:

$$\boxed{B_{m,v} = \frac{Y_{1,o} - Y_{1,\ell}}{1 - Y_{1,o}},}$$

- Vaporization (condensation): $B_{m,v} > 0$ (< 0)
  - Slow vaporization limit:

$$f \approx \frac{\rho D}{\ell} B_{m,v} \quad \text{for } B_{m,v} << 1$$

Problem Formulation (3/5)

- Problem incomplete using only species conservation; vapor concentration at surface, $Y_{1,\ell}$, not known
- Need energy conservation: $fc_p \frac{dT}{dx} - \frac{d}{dx}\left(\lambda \frac{dT}{dx}\right) = 0.$
  - Integrating: $fc_p T - \lambda \frac{dT}{dx} = \text{constant}.$
- Apply energy conservation at interface: $\lambda\left(\frac{dT}{dx}\right)_0 = fq_v,$
  - Energy conservation: $fc_p(T - T_o) - \lambda \frac{dT}{dx} = -fq_v$
  - Integrating: $\boxed{f = \frac{\lambda / c_p}{\ell} \ln(1 + B_{h,v}),}$

  Heat transfer number: $\boxed{B_{h,v} = \frac{c_p(T_\ell - T_o)}{q_v}.}$

Problem Formulation (4/5)

- Vaporization (condensation): $B_{h,v} > 0$ (< 0)
- For Le=1:

$$B_{m,v} = B_{h,v} \Rightarrow \frac{Y_{1,o} - Y_{1,\ell}}{1 - Y_{1,o}} = \frac{c_p(T_\ell - T_o)}{q_v} = B_{h,v}.$$

  - $Y_{1,0}$ can then be solved

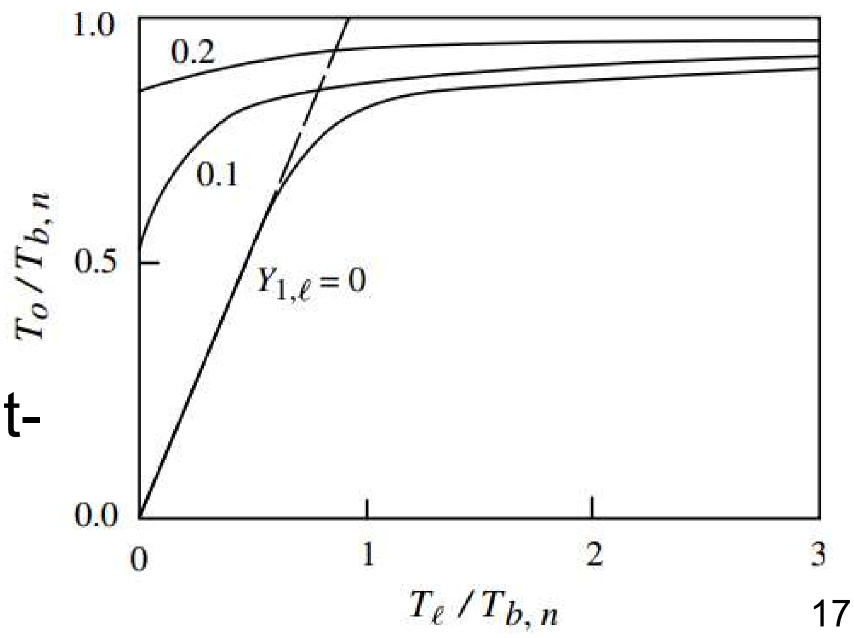
$$Y_{1,o}(T_o) = \frac{Y_{1,\ell} + B_{h,v}}{1 + B_{h,v}},$$

Problem Formulation (5/5)

- Problem still incomplete because T_ℓ is not known
- Need phase change kinetics:
  - Assume equilibrium state ⇒ $\text{M(liquid)} \rightleftarrows \text{M(gas)}$
  - phase change rate >> gas-phase diffusion rate
- Apply Clausius-Clapeyron relation:

$$p_i\left(T\right) = p_n \exp\left[\frac{Q_v}{R^o}\left(\frac{1}{T_{b,n}} - \frac{1}{T}\right)\right]$$

  - Problem is now closed, can solve for f and T_0
  - Liquid temperature is the wet-bulb temperature



d^2-Law of Droplet Vaporization and Combustion

d^2-Law of Droplet Vaporization

- Droplet dynamics, vaporization, and combustion is the unit process in many natural and technological processes
- Spray increases total liquid surface area for gasification; e.g. : spray painting, insecticide spraying, spray combustion
- Droplet processes: ink-jet printing, rain drop formation, nano-particle formation

Formulation (1/2)

- Similar to the beaker problem, except change x-variation to r-variation

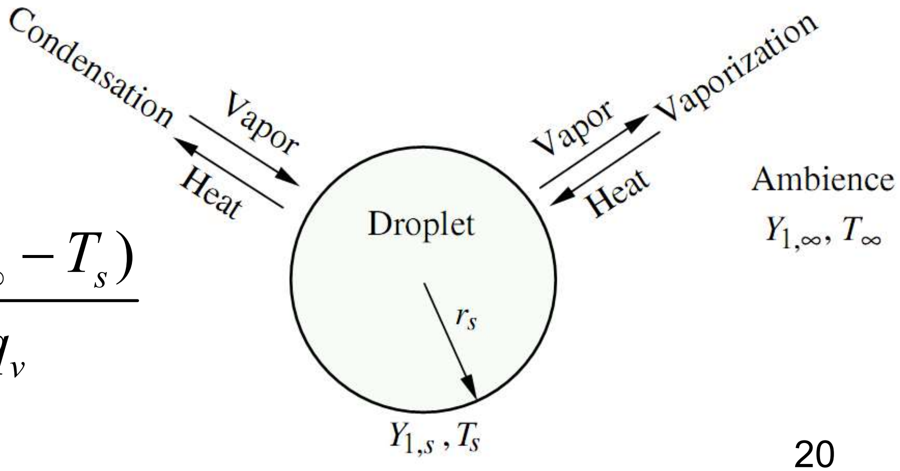
$$\frac{d(r^2\rho u)}{dr}=0 \Rightarrow m_v = 4\pi r^2 \rho u = \text{constant}$$

- Solving $\frac{d}{dr}\left(r^2\rho u Y_1-\rho D r^2\frac{dY_1}{dr}\right)=0$, $\frac{d}{dr}\left(r^2\rho u T-(\lambda/c_p)r^2\frac{dT}{dr}\right)=0$

  yields same expressions as the beaker problem

$$\boxed{\begin{aligned}\tilde{m}_v &= \frac{m_v}{4\pi(\lambda/c_P)r_s}\\ &=1\text{n}(1+B_{m,v})=\ln(1+B_{h,v})\end{aligned}}$$

$$B_{m,v}=\frac{Y_{1,s}-Y_{1,\infty}}{1-Y_{1,s}} \qquad B_{h,v}=\frac{c_p(T_\infty-T_s)}{q_v}$$



Formulation (2/2)

- From overall conservation of droplet mass:

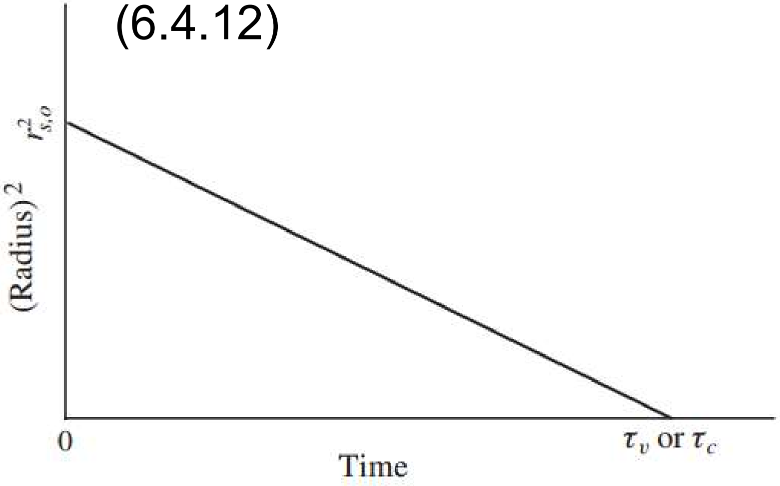
$$m_v = -\frac{d}{dt}\left(\frac{4}{3}\pi r_s^3 \rho_\ell\right) = -2\pi\, \rho_\ell r_s \frac{dr_s^2}{dt} \qquad (6.4.12)$$

- Equating (6.4.12) with (6.4.9):

$$\boxed{\frac{dr_s^2}{dt} = -\frac{2(\lambda/c_p)}{\rho_\ell}\ln(1+B_{h,v}) = -K_v}$$

which upon integration yields

$$r_s^2 = r_{s,o}^2 - K_v t$$

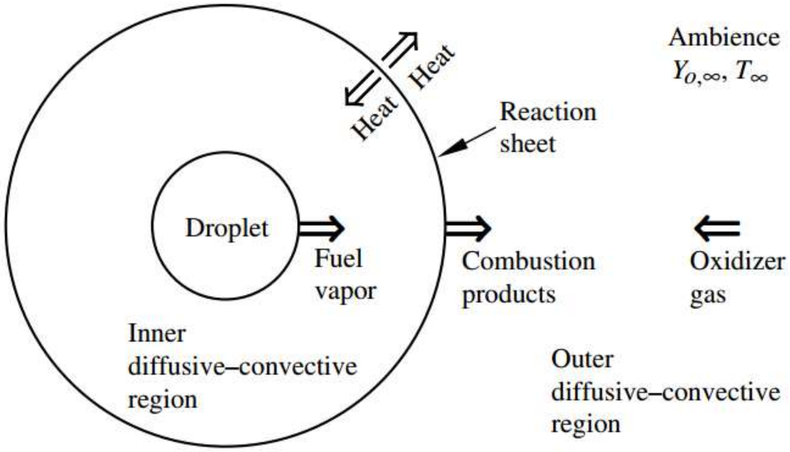


- Complete vaporization time ($r_s \equiv 0$):

$$\tau_v = \frac{r_{s,o}^2}{K_v}$$

This is the d^2-law, indicating vaporization time decreases quadratically with droplet size; hence principle of atomization

d^2-Law of Droplet Combustion: Formulation (1/4)



- By working with coupling function, solution procedure similar to that of pure vaporization

$$\frac{d}{dr}\left[r^2\rho u\beta_i-(\lambda/c_p)r^2\frac{d\beta_i}{dr}\right]=0,\quad i=O,\ F.$$

$$\frac{d}{d\tilde{r}}\left(\tilde{m}_c\ \beta_i-\tilde{r}^2\frac{d\beta_i}{d\tilde{r}}\right)=0,\quad i=O,F$$

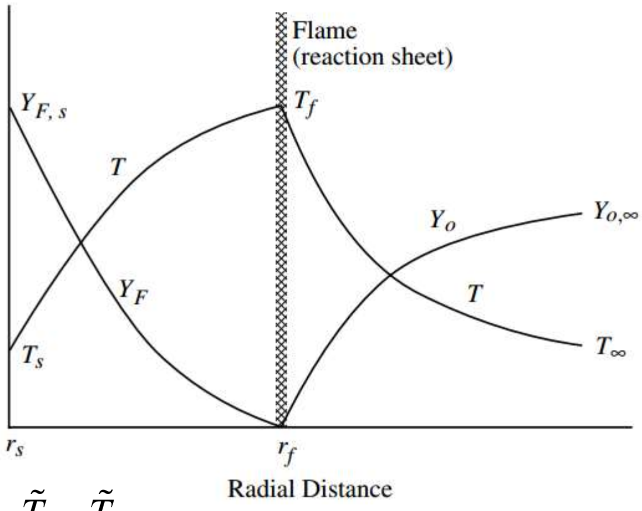
- First and second integration yields

$$\tilde{r}^2\frac{d\beta_i}{d\tilde{r}}=-c_{1,i}+\tilde{m}_c\beta_i \qquad \beta_i(\tilde{r})=\frac{c_{1,i}}{\tilde{m}_c}+c_{2,i}\exp\left(-\frac{\tilde{m}_c}{\tilde{r}}\right),$$

- Boundary conditions:

$$\tilde{r}\to\infty:\quad \tilde{Y}_O=\tilde{Y}_{O,\infty}\quad \tilde{Y}_F=0,\quad \tilde{T}=\tilde{T}_\infty,$$

$$\tilde{r}=1:\quad \tilde{m}_c\tilde{Y}_{O,s}-\left(\frac{d\tilde{Y}_O}{d\tilde{r}}\right)_1=0,\quad \tilde{m}_c\tilde{Y}_{F,s}-\left(\frac{d\tilde{Y}_F}{d\tilde{r}}\right)_1=\tilde{m}_c\,,\quad \left(\frac{d\tilde{T}}{d\tilde{r}}\right)_1=\tilde{m}_c\tilde{q}_\upsilon,\quad \tilde{T}=\tilde{T}_s$$



Formulation (2/4)

- Solution for coupling functions

$$\beta_O = \tilde{T} + \tilde{Y}_O = (\tilde{T}_s - \tilde{q}_\upsilon) + \left\{ \left[\tilde{T}_\infty - (\tilde{T}_s - \tilde{q}_\upsilon) \right] + \tilde{Y}_{O,\infty} \right\} e^{-\tilde{m}_c / \tilde{r}}$$

$$\beta_F = \tilde{T} + \tilde{Y}_F = \left[1 + (\tilde{T}_s - \tilde{q}_\upsilon) \right] + \left\{ \tilde{T}_\infty - \left[1 + (\tilde{T}_s - \tilde{q}_\upsilon) \right] \right\} e^{-\tilde{m}_c / \tilde{r}}.$$

- Apply reaction-sheet assumption

$$\tilde{Y}_O(\tilde{r}_f) = 0, \quad \tilde{Y}_F(\tilde{r}_f) = 0 \qquad \tilde{Y}_O(1) = 0.$$

- Final solution

$$\tilde{m}_c = \ln(1 + B_{h,c}) \qquad q_c = q_\upsilon + c_p(T_f - T_s) + c_p(T_f - T_\infty)\left(\sigma_O + \frac{1 - Y_{O,\infty}}{Y_{O,\infty}} \sigma_O \right)$$

$$\tilde{r}_f = \frac{\tilde{m}_c}{\ln(1 + \tilde{Y}_{O,\infty})} = 1 + \frac{\ln\left[1 + (\tilde{T}_f - \tilde{T}_s)/\tilde{q}_\upsilon \right]}{\ln(1 + \tilde{Y}_{O,\infty})} \qquad B_{h,c} = \frac{(\tilde{T}_\infty - \tilde{T}_s) + \tilde{Y}_{O,\infty}}{\tilde{q}_\upsilon} = \frac{c_p(T_\infty - T_s) + (Y_{O,\infty}/\sigma_O) q_c}{q_\upsilon}$$

Formulation (3/4)

- Driving potential in $B_{h,c}$ consists of an enthalpy term and a chemical term; the latter is much larger
  - $B_{h,c}$ = O(1-10); $B_{h,v} < 1$
- T_f is the adiabatic flame temperature, allowing for latent heat of vaporization
- Droplet temperature is close to the liquid boiling point, and can be approximated by it. However, it can never be reached due to the presence of products and inerts
- Problem specializes to pure vaporization by setting

  $Y_{o,\infty} \equiv 0$ leading to $\tilde{r}_f \to \infty$

Formulation (4/4)

- Relating burning rate $m_c=4\pi(\lambda/c_P)r_s\ln(1+B_{h,c})$ at flame to vaporization rate at surface:

$$m_v=-\frac{d}{dt}\left(\frac{4}{3}\pi r_s^3\rho_\ell\right)$$

  - ○ Assume $m_v=m_c$: $\frac{dr_s^2}{dt}=-\frac{2(\lambda/c_p)}{\rho_\ell}\ln(1+B_{h,c})=-K_c$ (A)
  - ○ Integrating yields: $r_s^2=r_{s,o}^2-K_c t$
  - ○ Total burning time: $\tau_c=\frac{r_{s,o}^2}{K_c}$

This is the d^2-law of droplet burning

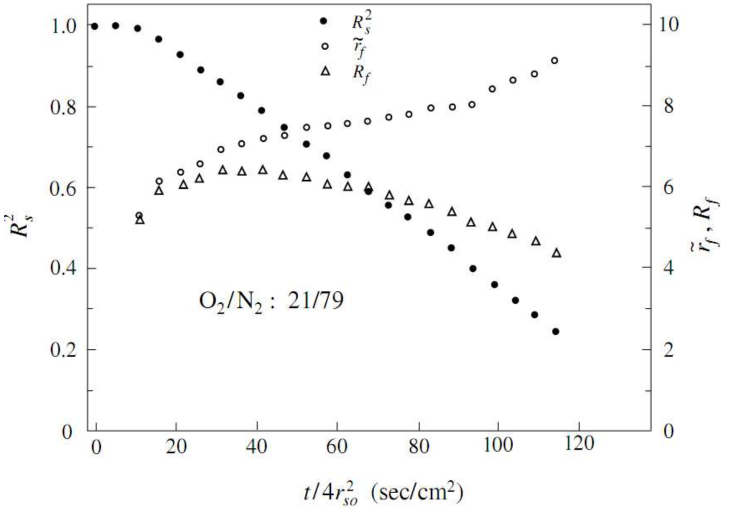
  - ○ (A): $\frac{\lambda/c_p}{\rho_l}\sim K_c;\ \lambda/c_p\sim\rho_g D_g\Rightarrow\frac{K_c}{D_g}\sim\frac{\rho_g}{\rho_\ell}$

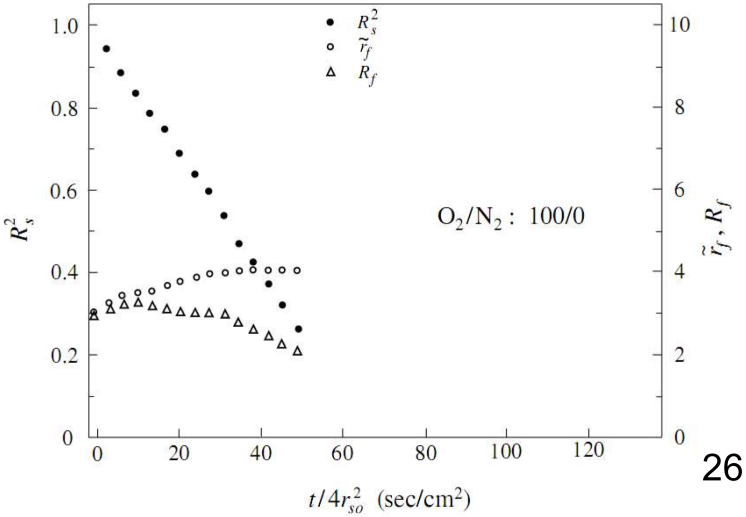
Experimental Observations

- d^2-law predication

$$dR_S^2 / dt = \text{Constant}; \quad \tilde{r}_f = r_f / r_s = \text{Constant} = O(40) \text{ for HC in air}$$

- Experimental observations:
  - Initially, $dR_S^2 / dt << 1$: droplet heating
  - $\tilde{r}_f$ monotonically increases for high $\tilde{Y}_{O,\infty}$, but plateaus for low $\tilde{Y}_{O,\infty}$: fuel vapor accumulation
  - $\tilde{r}_f = O(5-10)$: constant property assumption





Droplet Heating (1/2)

- Because of the large liquid density and hence thermal inertia, droplet heating occurs at the same characteristic rate as that of droplet surface regression ⇒ quasi-steady gas-phase processes grafted onto transient droplet heating

- Heating required is equivalent to an increase in the latent heat of vaporization

$$m_v q_{v,\mathrm{eff}} = m_v q_v + \left(4\pi r^2 \lambda_\ell \frac{\partial T}{\partial r} \right)_{r_s^-} \qquad (13.2.1)$$

Droplet Heating (2/2)

- Diffusion limit: slowest rate

$$\frac{\partial T}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(\alpha_{h,\ell}r^2\frac{\partial T}{\partial r}\right),\quad T(r;t=0)=T_0\left(r\right),\left(\frac{\partial T}{\partial r}\right)_{r=0}=0 \qquad \text{(13.2.2), (13.2.3)}$$

  Three sources of unsteadiness

  - Accumulation term in governing equation
  - Regressing surface, $r_s(t)$
  - Varying surface temperature, $T_s(t)$

- (Artificial) infinite-conductivity, batch-distillation limit: fastest rate
  - Droplet temperature perpetually uniformized:

$$m_v q_{v,\mathrm{eff}}=m_v q_v+\left(\frac{4}{3}\pi r_s^3\rho_\ell c_{p,\ell}\right)\frac{dT_s}{dt} \qquad \text{(13.2.4)}$$

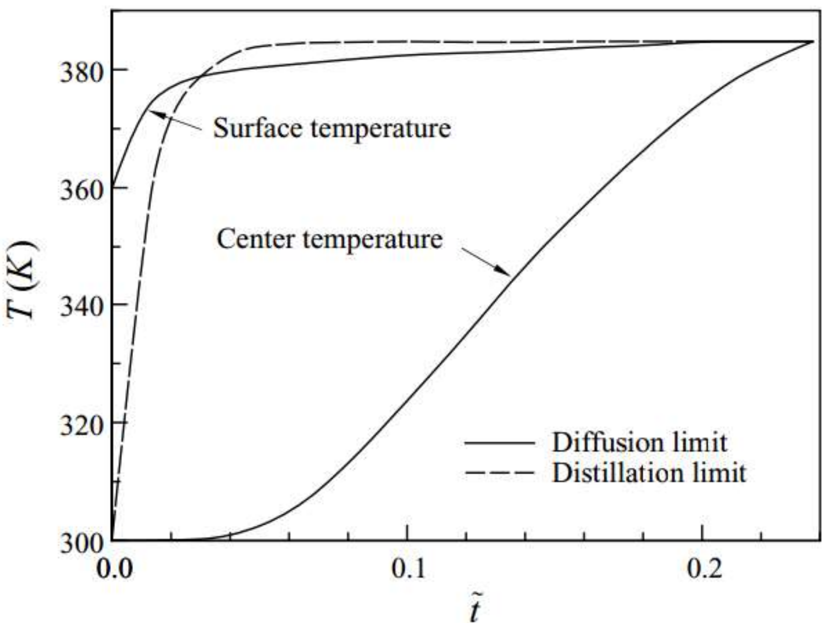
- Discriminating parameter

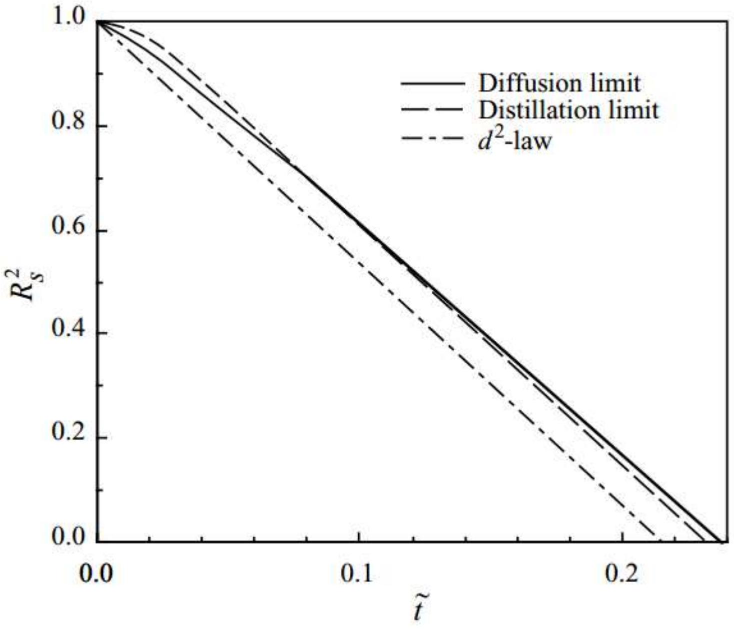
$$Pe_h=\frac{K}{\alpha_{h,l}}$$

<< 1 : Batch distillation limit
>> 1 : Diffusion limit

Characteristics of Droplet Heating

- Active droplet heating and active vaporization occur sequentially, not concurrently
- Active droplet heating occurs in initial 5-10% of droplet lifetime
- Heating of the surface layer constitutes the bulk of the heating budget, and is independent of the heating mode.
- Droplet heating only slightly prolongs droplet lifetime





Fuel Vapor Accumulation (1/5)

- d^2-law formulation assumes gas-phase steadiness
  - Initial state ignored
  - Flame has its steady-state value at $t = 0$
  - Extra fuel in the form of fuel vapor between flame and droplet allowed
  - Amount is substantial
    - r_f^3 : volume effect
    - Large values of $\tilde{r}_f$ (~40)

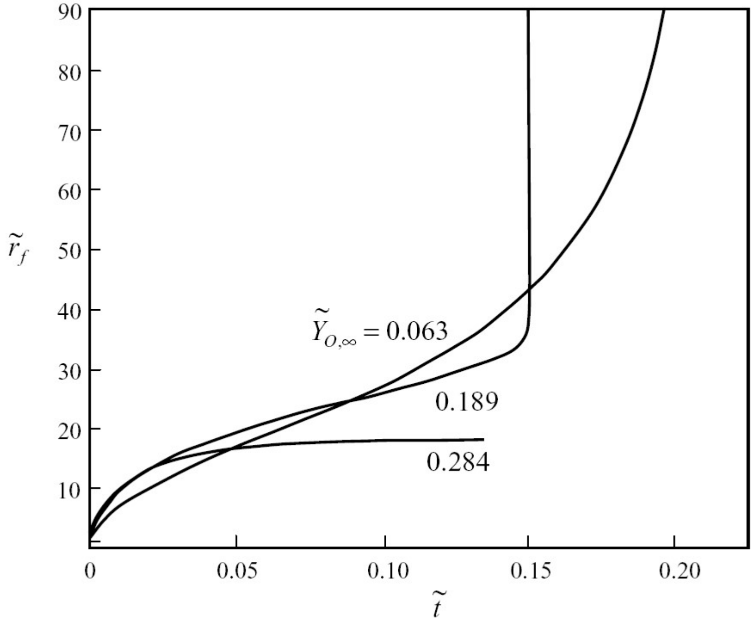
Fuel Vapor Accumulation (2/5)

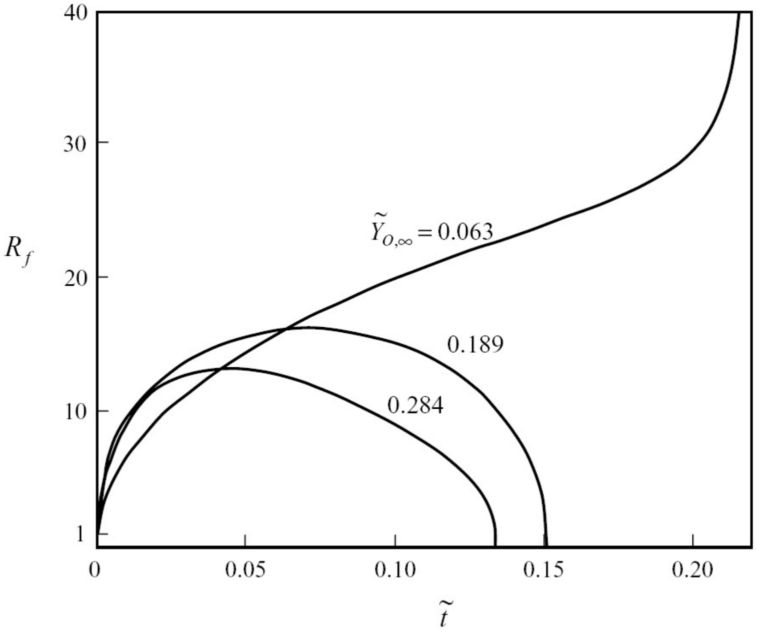
- Physically-realistic situation
  - Initial droplet temperature low ⇒ initial amount of fuel vapor low ⇒ initial flame size small
  - Subsequent vaporization
    - Supports burning
    - Adds fuel vapor to the inner region
    - Leads to growth of flame size
  - Eventually, flame may shrink as droplet size shrinks, consuming the accumulated fuel vapor

Fuel Vapor Accumulation (3/5)

- Allowing for fuel vapor accumulation, overall mass conservation:
  - Gasification rate at droplet surface (m_v)
    = Consumption rate at flame (m_c)
    \+ Accumulation/depletion rate in the inner region,
  - $$m_v = m_c + \frac{d}{dt}\int_{r_s(t)}^{r_f(t)} \left(\rho Y_F\right) 4\pi r^2 dr. \qquad (13.2.5)$$
- d^2–law neglects last term in (13.2.5), with $m_v \equiv m_c$, hence violates mass conservation
- Gas-phase quasi-steadiness still holds
- Process is expected to be significant for all non-planar quasi-steady treatment of combustion with condensed-phase gasification

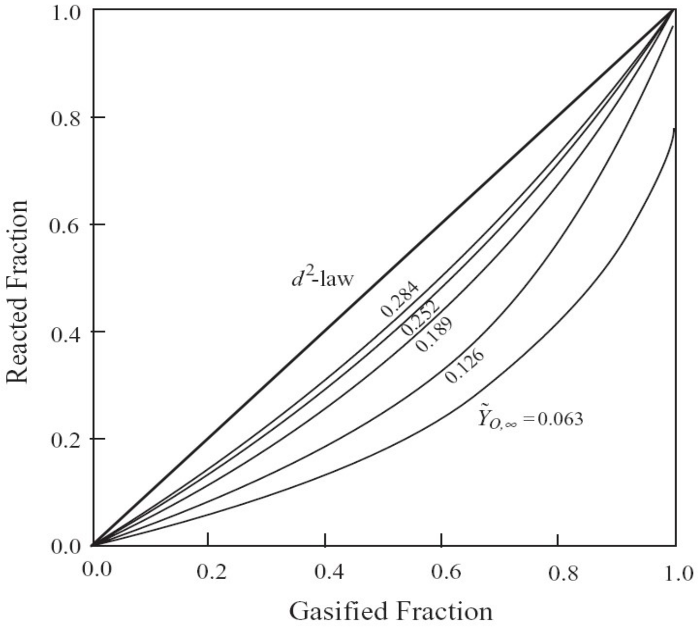
Fuel Vapor Accumulation (4/5)

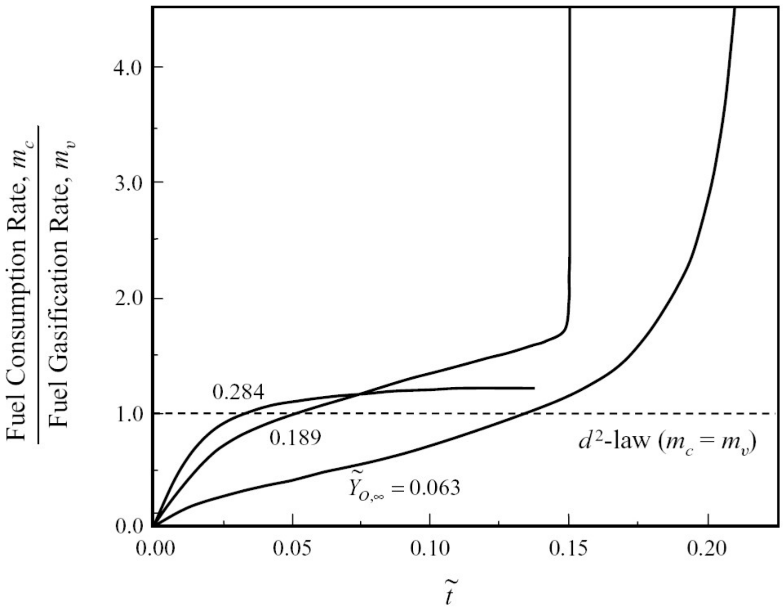




- Two types of responses
  - Low $\tilde{Y}_{O,\infty}$ (including air): flame size grows without bound
  - High $\tilde{Y}_{O,\infty}$ regime: steady $\tilde{r}_f$ attained, r_f increases and then decreases to zero

Fuel Vapor Accumulation (5/5)





- Low $\tilde{Y}_{O,\infty}$ regime
  - Complete fuel consumption not attainable
  - Finite amount of fuel vapor remains at droplet burnout
- High $\tilde{Y}_{O,\infty}$ regime
  - Complete fuel consumption attainable
  - Steady-state burning rate > d^2-law value

Variable Property Effects (1/2)

- Dominant transport processes are different in inner and outer regions of flame:
  - Inner region: heat transfer to effect vaporization
  - Outer region: oxidizer mass transfer to sustain flame
- In formulation, need to differentiate:
  - Transport in inner and outer regions
  - Heat and mass transport ($Le \neq 1$)

Variable Property Effects (2/2)

- $$\tilde{r}_f = 1 + \frac{(\lambda_1 / c_{p,1})}{(\rho D)_2} \frac{\mathrm{In}[c_{p,1}(T_f - T_s)/q_v]}{\mathrm{In}(1+\tilde{Y}_{O,\infty})} \qquad (13.2.7)$$

$$q_c = (c_{p,2}T_f - c_{p,1}T_s + q_v) + \frac{c_{p,2}(T_f - T_\infty)}{[(1+\tilde{Y}_{O,\infty})^{1/Le_2} - 1]}. \qquad (13.2.8)$$

- Controlling process for m_c and $\tilde{r}_f$,
  - ○ $(\lambda_1/c_{p,1})$; $(\rho D)_2$
  - ○ $Le_{eff} = (\lambda_1/c_{p,1}) / (\rho D)_2 \neq 1 \approx$ ⅓ to ½ for liquid HCs
- (13.2.7) then shows $\tilde{r}_f$ also reduced by ⅓ to ½ as compared to *Le* = 1 values ⇒ closer to experimental values
- Since $\tilde{Y}_{O,\infty} << 1$, (13.2.8) shows $[(1+\tilde{Y}_{O,\infty})^{1/Le_2} - 1] \approx \tilde{Y}_{O,\infty} / Le_2 \Rightarrow$

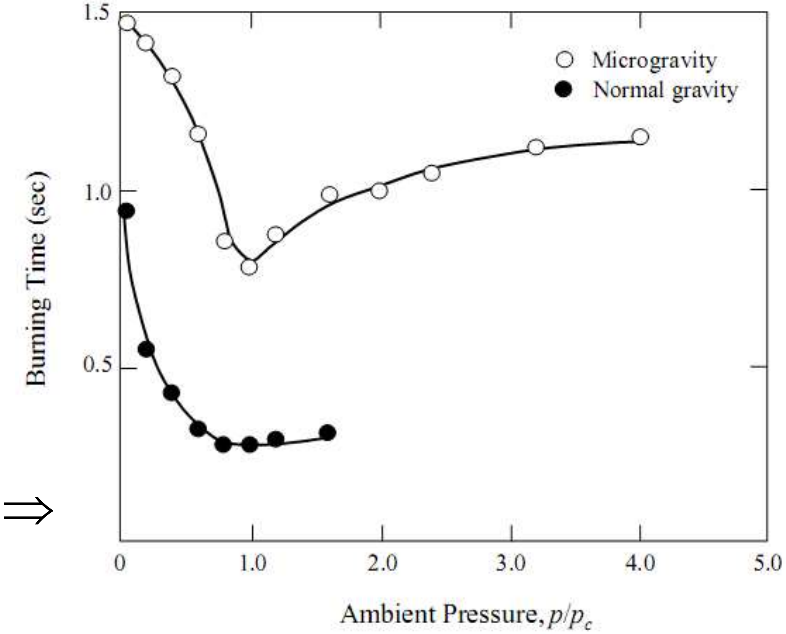
  Diffusional modification of $\tilde{Y}_{O,\infty}$

Gas Phase Transient Diffusion

- Gas-phase quasi-steadiness assumes characteristic gas-phase diffusion time<<surface regression time
- Assumption must breakdown as $r \to \infty$
  - Location of breakdown, r_∞:

    $$r_\infty^2 / D_g \sim r_s^2 / K \qquad (13.2.11)$$
  - From burning rate results:

    $$K / D_g \sim \rho_g / \rho_\ell, \; r_\infty / r_s \sim \left(\rho_\ell / \rho_g\right)^{1/2} \qquad (13.2.12)$$



- Regime of breakdown:
  - Atmospheric pressure, $\rho_g / \rho_\ell = O(10^3) \Rightarrow$ $r_\infty / r = O(30)$; d²-Law range
  - Supercritical pressure, $\rho_g / \rho_\ell = O(1) \quad \Rightarrow$ Complete breakdown!
- In general, processes are unsteady at supercritical pressures

Multicomponent and Unconventional Fuels

Motivation

- Practical liquid fuels are blends of many components (100s!)
    - Consequence of fuel manufacturing
    - Designed for engine operation: ignition, steady burning, pollutant formation, power, safety, etc.
    - Designed to utilize alternative fuels: alcohol/oil (E15, E85), biodiesel, etc.
- State of Mixture
    - Miscible
    - Emulsion: *e.g*. water-oil emulsion
    - Slurries: *e.g*. coal-water slurries, aluminum-oil slurries
- Key question: sequence of gasification
    - Conventional: batch distillation
    - Solid suspension has no volatility

Miscible Mixtures

- **Gasification mechanism**: a component is gasified only if it is exposed at the droplet surface, regardless of its volatility $\Rightarrow$ volatility, and hence batch distillation, cannot be the only factor controlling gasification
- **Exposure mechanism**
  - o Passive: regressing droplet surface
  - o Active: diffusion and internal motion
- **Controlling factor**: liquid-phase mass diffusion; $O(10^{-2})$ of liquid-phase thermal diffusion and surface regression rate
- **Controlling parameter**:

$$Pe_m = \frac{K}{D_\ell}, \qquad \frac{Pe_m}{Pe_h} = \frac{\alpha_{h,\ell}}{D_\ell} = Le_\ell >> 1.$$

Limiting Gasification Behavior ($Pe_m >> 1$)

- **Initial stage**: volatile component in surface layer preferentially gasified; minimum diffusional resistance
- **Second-stage, droplet heating**: volatile component in surface layer largely depleted, supply from inner core limited by diffusion ⇒surface layer concentrated with less volatile component ⇒ droplet temperature increases
- **Diffusion-controlled steady-state stage**: concentration boundary layer established at surface; droplet temperature controlled by boiling point of less volatile component
- **Final, distillation stage**: diminishing droplet size facilitates diffusion; volatility re-asserts importance

Formulation

- Quasi-steady gas-phase solution for single component can still be used, with weighted properties, e.g. $q_v = \Sigma \varepsilon_i q_{v,i} \quad \varepsilon_i = Y_{i,s} / \sum Y_{j,s}$
- Liquid-phase solution (diffusion limit)

$$\frac{\partial Y_{\ell,i}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\partial_\ell r^2 \frac{\partial Y_{\ell,i}}{\partial r}\right), \quad Y_{\ell,i}(r, t = 0) = Y_{\ell,i,o}(r), \quad \text{(13.3. 2), (13.3.3)}$$

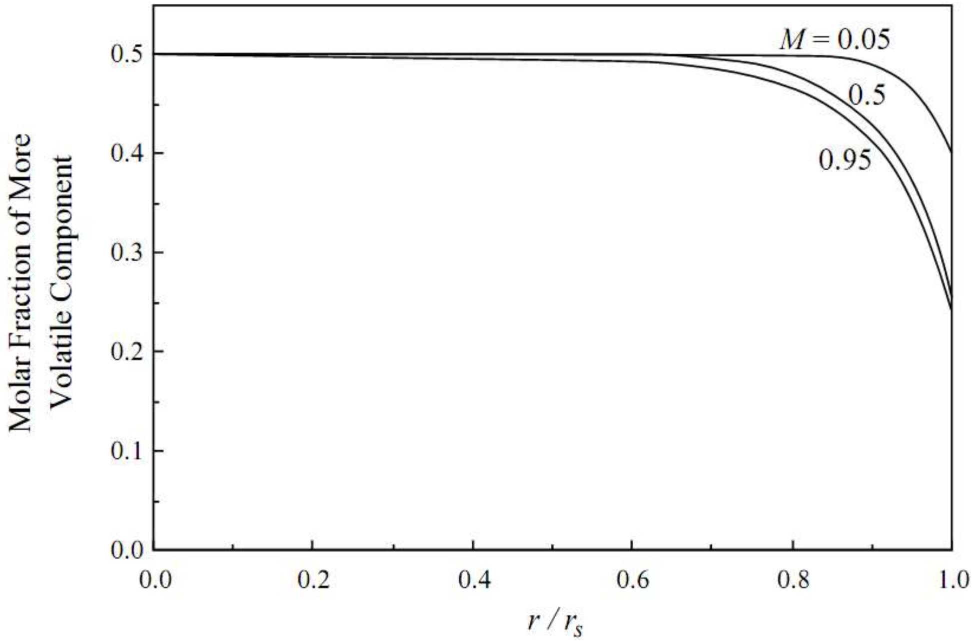
$$\left(\frac{\partial Y_{\ell,i}}{\partial r}\right)_{r=0} = 0, \quad m_v Y_{\ell,i,s} - \left(4\pi r^2 \rho_\ell D_\ell \frac{\partial Y_{\ell,i}}{\partial r}\right)_{r=r_s} = m_{v,i} \quad \text{(13.3.4), (13.3.5)}$$

- Surface equilibrium concentration (Raoult's law)

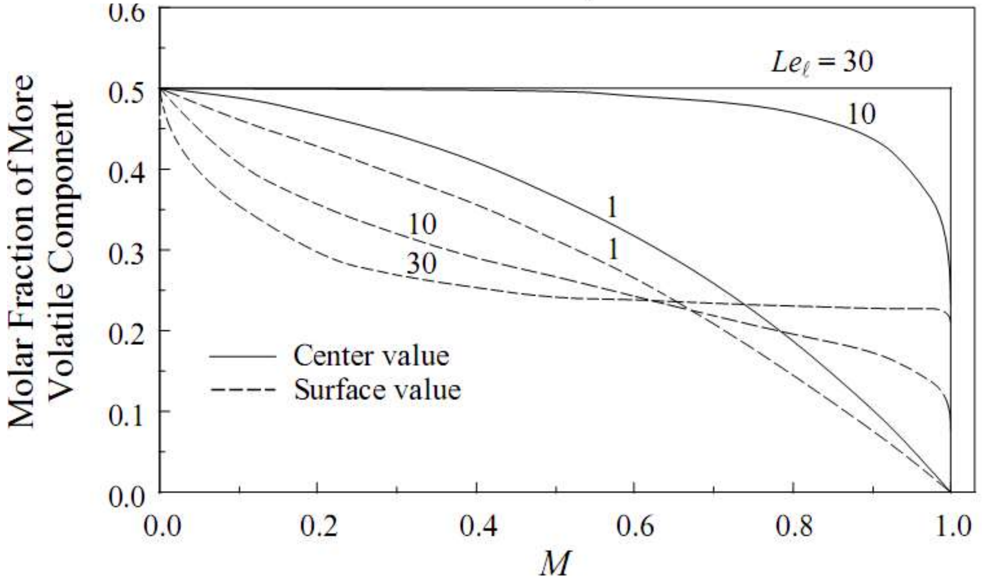
$$p_{i,s} = X_{\ell,i,s}\, p_{i,s,\text{pure}}, \qquad \text{(13.3.6)}$$

- $p_{i,s,\text{pure}}$ given by Clausius-Clapeyron relation

Concentration Boundary Layer

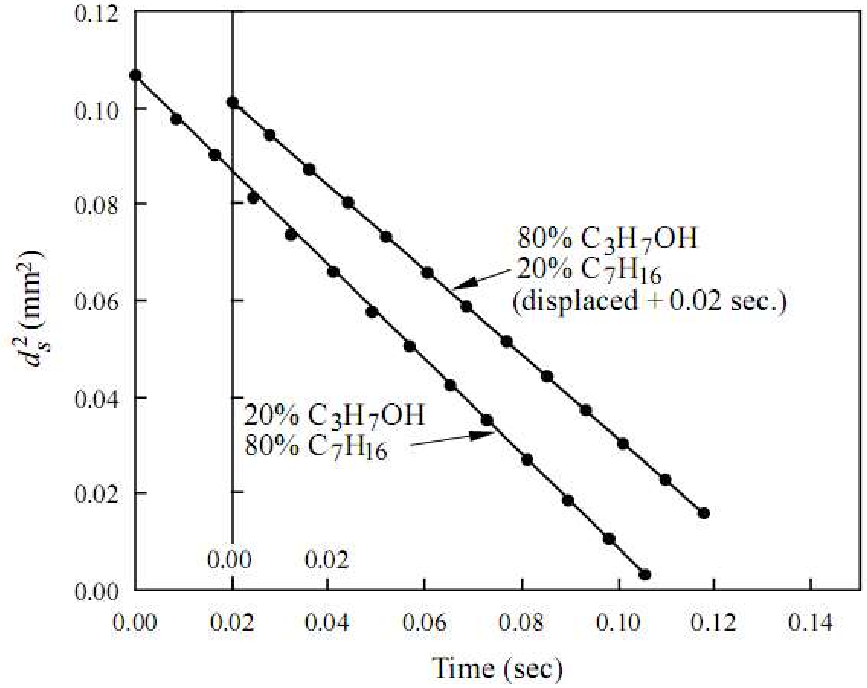


Development of the concentration boundary layer, *Le* = 30

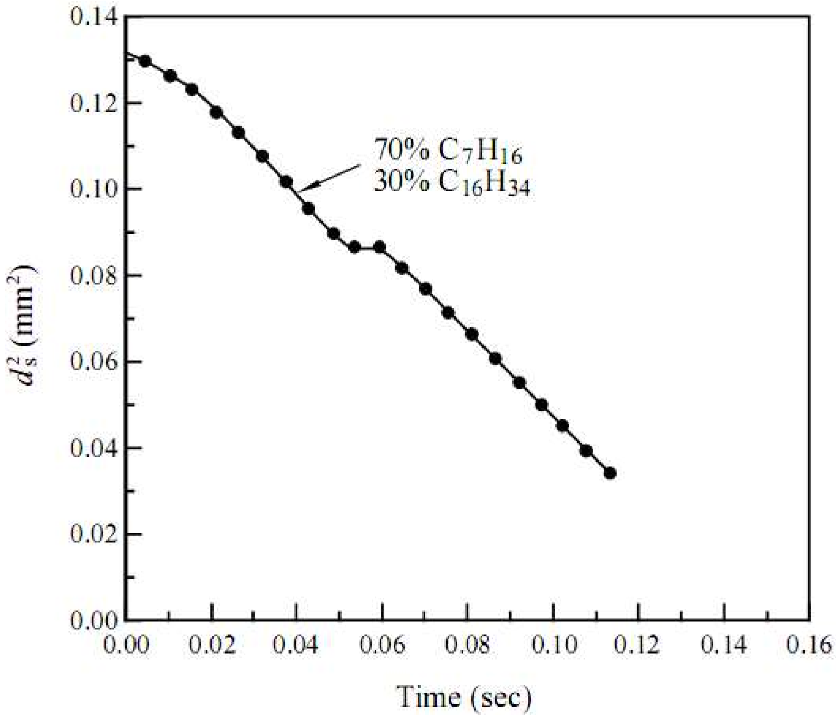


Diffusion-limited concentration values at surface and center

Experimental Observations (1/2)

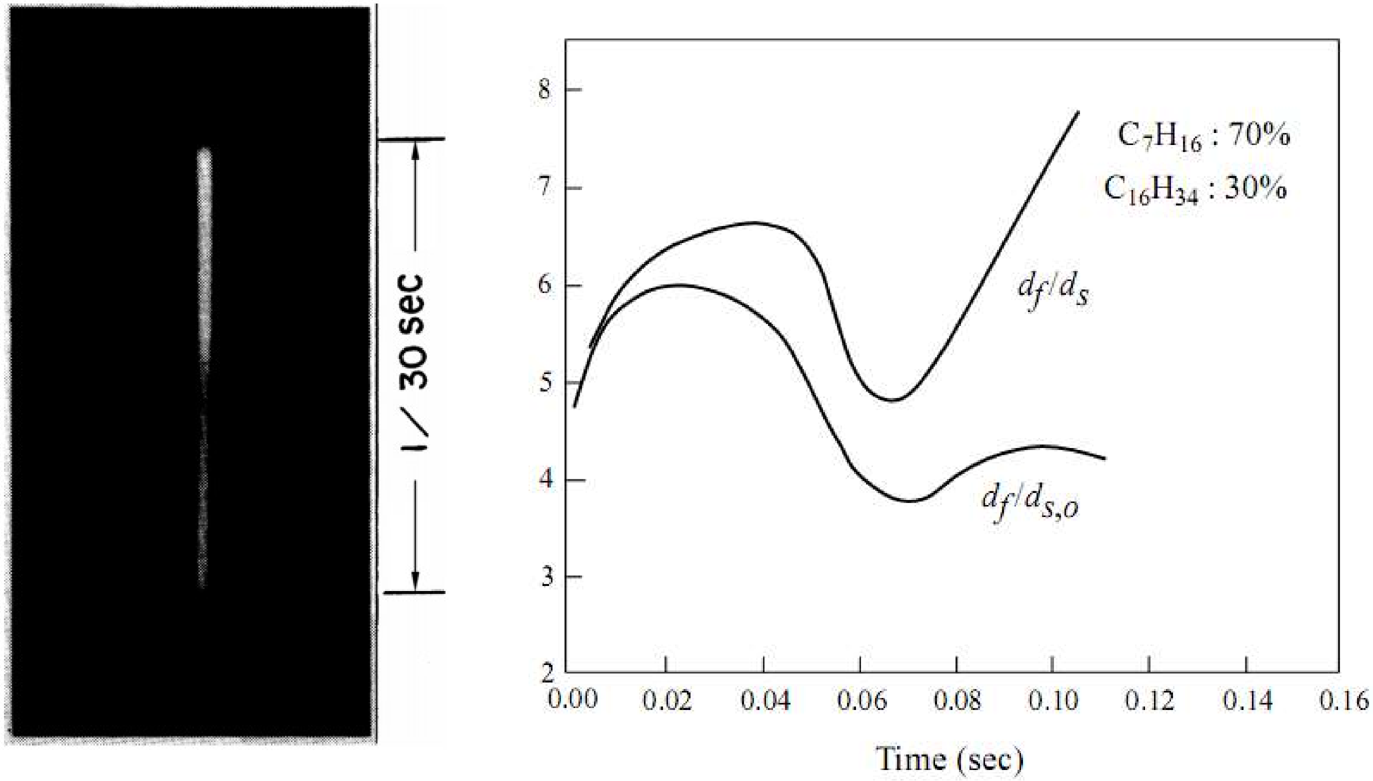


Matched volatility



Large volatility differential,
3-stage behavior

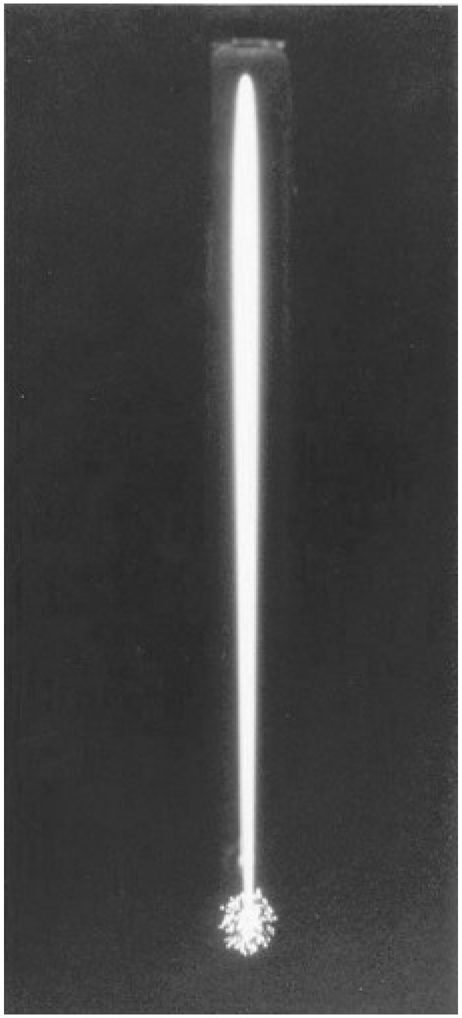
Experimental Observations (2/2)



Flame shrinkage phenomenon

Microexplosion Phenomenon

- Mechanism:
  - Diffusional resistance traps volatile component in droplet interior
  - Droplet temperature close to boiling point of less volatile component
  - Trapped volatile component can homogeneously nucleate when it is heated to the limit of superheat
  - Nucleation and internal gasification violently ruptures droplet
- Microexplosion promoted with:
  - Increasing pressure ⇒ higher boiling point ⇒ higher droplet temperature
  - Equal-volume composition

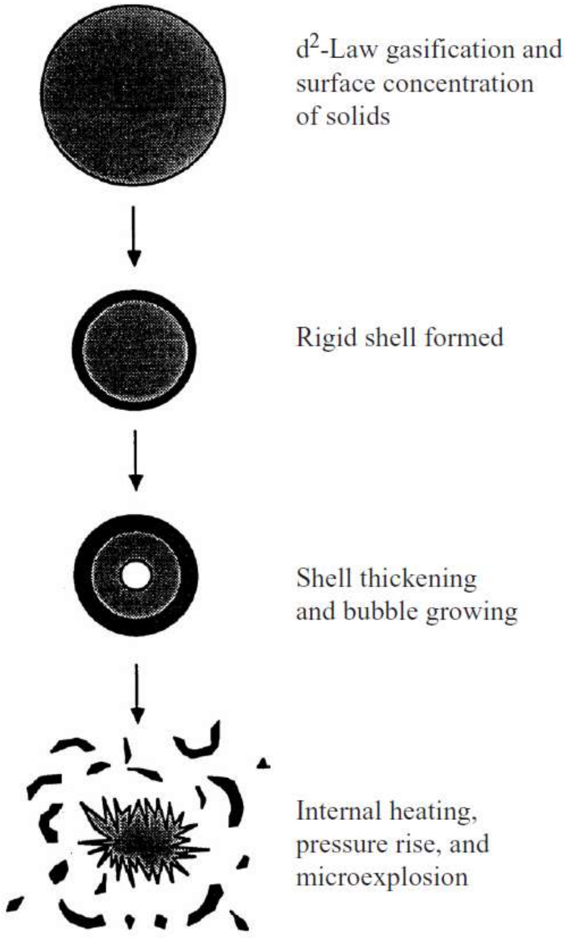


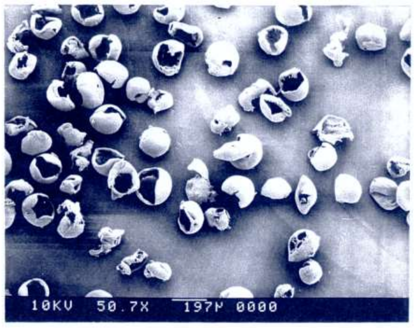
Emulsions

- Practical interests in water-oil emulsions:
  - Microexplosion promotes atomization of heavy oils
  - Intense explosion compared to miscible mixtures
  - Water lowers flame temperature, reduces NO_X formation
  - Fire safe upon spillage
- Unique physical properties
  - Dispersed water micro-droplets do not diffuse $\Rightarrow$ droplet composition profile frozen
  - Water and oil constitute two liquid phases because they do not mix $\Rightarrow$ consequence of attainable droplet temperature

Slurries

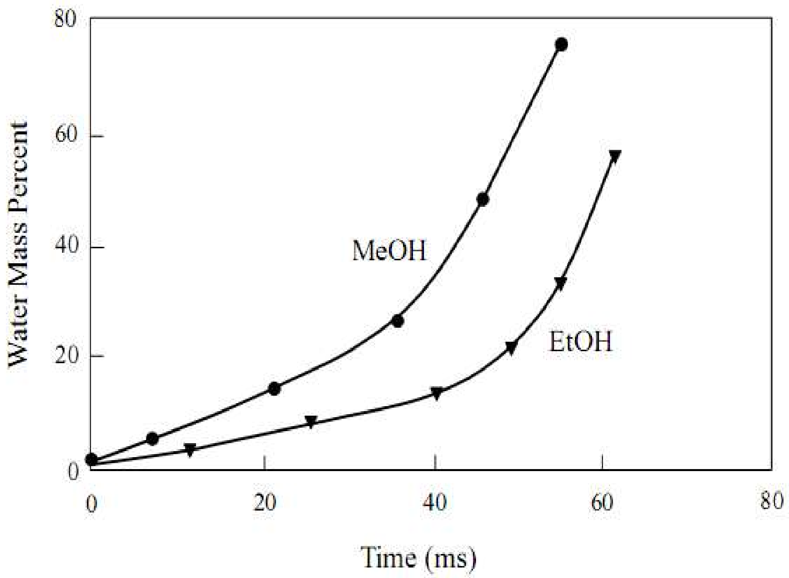
- Practical interests:
    - Coal-oil mixture for pumpability and direct coal burning in liquid-fueled burners
    - Metal particle suspension: energy booster in tactical propellants
- Major difficulty: formation of particle agglomerates
- Gasification mechanism
    - Formation of rigid shell
    - Gasification through thickening of shell (d^3-law)
    - Combustion of shell





Alcohols

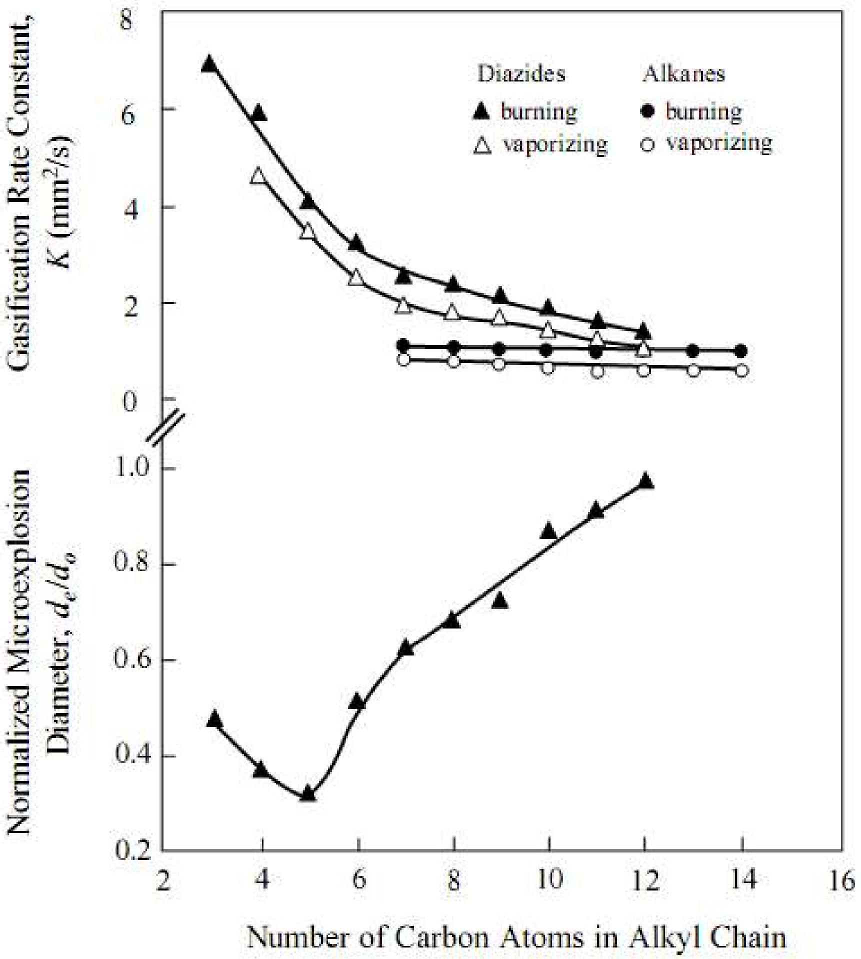
- Practical interests:
    - Methanol: formed through fossil fuel sources
    - Ethanol: food and cellulosic
    - Butanol: biomass



- Considerations as fuel and fuel additive
    - Reduced energy content (presence of O)
    - Could be corrosive
    - MeOH and EtOH are water soluble: absorbs moisture and water produced at flame

Reactive Liquid Propellants: Organic Azides

- **Fuel properties of organic diazides** : N_3-R-N_3
  - Decomposes at 170° C < boiling point
  - Releases 50 kcal/ mole of heat ⇒ high energy density
- **Combustion characteristics**: liquid-phase decomposition generates heat ⇒
  - Extremely fast droplet gasification rate
  - Violent microexplosion



Phenomenology of Coal Particle Burning

- Initial period of pyrolysis (~10% of particle lifetime)
  - Generation and emission of volatile fuel vapor, leading to possible gas-phase flame
  - Particle temperature <1000 K
  - Porous residual particle consisting of 55~97% of carbon, depending on coal type
- Active burning period (remaining 90% of lifetime)
  - Gasification of carbon over both external and internal surfaces
  - Both surface and gas-phase reactions
  - Ash residue: mostly mineral oxides

Kinetics of Carbon Oxidation

- Major surface reactions

$$C + O_2 \rightarrow CO_2 \qquad (C1) \qquad\qquad 2C + O_2 \rightarrow 2CO \qquad (C2)$$

$$C + CO_2 \rightarrow 2CO \qquad (C3) \qquad\qquad C + H_2O \rightarrow CO + H_2. \qquad (C4)$$

  - (C1): Negligible compared to (C2) for $T_s > 1{,}000$ K,
  - (C2): Low-temperature route, $600 < T_s < 1{,}200$ K (saturation)
  - (C3): High-temperature route, $1{,}600 < T_s < 2{,}500$ K (saturation)
  - Product from (C2) and (C3) is CO
- Gas-phase reaction (lumped)

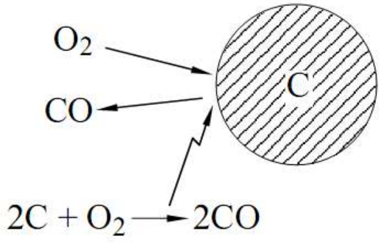
$$2CO + O_2 \rightarrow 2CO_2 \qquad (C5)$$

- Note:
  - Product of gas-phase reaction (C5) is reactant for surface reaction (C3)
  - Conventional fire extinguishing agents, CO_2 and H_2O, are reactants with C, producing CO and H_2 which are themselves combustible.

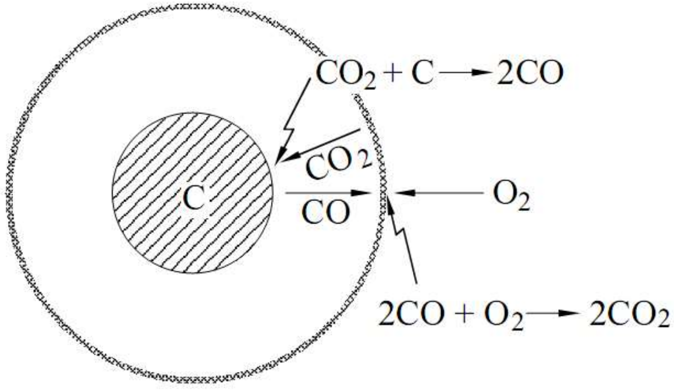
Characteristics of Carbon Particle Burning

- Carbon does not melt; sublimation temperature > 4,000 K (vs. 400~800 K for HC boiling points); Thus carbon is very nonvolatile
    - Carbon particle can therefore be heated to very high temperatures, possibly exceeding burner temperature
- Radiation loss limits carbon temperature to 2,500 - 3,000 K
    - Low particle temperature implies slow gasification rate compared to HC
- Low volatility and high surface temperature ⇒
    - Surface reaction important
    - Possible presence and coupling of both surface and gas-phase reactions

Phenomenology of Carbon Particle Combustion



Frozen Gas-Phase



Detached Flame-Sheet Burning

- Dominant reactions (no H_2O)

  $2C + O_2 \rightarrow 2CO$ (C2)

  $C + CO_2 \rightarrow 2CO$ (C3)

  $2CO + O_2 \rightarrow 2CO_2$ (C5)

  - Presence of (C5) deactivates (C2) and activates (C3)
  - Absence of (C5) deactivates (C3) and activates (C2)

Metal Particle Combustion

- Practical interests
  - Accidental fires and explosions in mine galleries
  - Explosion of fuel tanks
  - Additive in solid and liquid propellants
  - Synthesis of materials
- Fundamental peculiarities and interests
  - Products frequently in condensed phase (vs. H_2O and CO_2 in hydrocarbon combustion)
  - Condensed products do not diffuse
  - High sublimation temperature of oxide limits flame temperature to its boiling point (Glassman hypothesis)
  - Products can condense at particle surface
    - Forms solid surface coating ⇒ inhibits gasification
    - Dissolution into particle interior
  - N_2 could be a reactant

Spray Combustion: Phenomenology (1/3)

- 1D planar configuration
  - Minimum droplet size for complete pre-vaporization:

$$\tau_v = \frac{d_{s,o}^2}{4K_v} = \frac{d_{s,o}^2\rho_\ell}{8(\lambda/c_p)\ln(1+B_v)}, \quad \tau_D = \frac{\ell_D^o}{s_u^o} = \frac{\lambda/c_p\rho_g}{(s_u^o)^2}$$

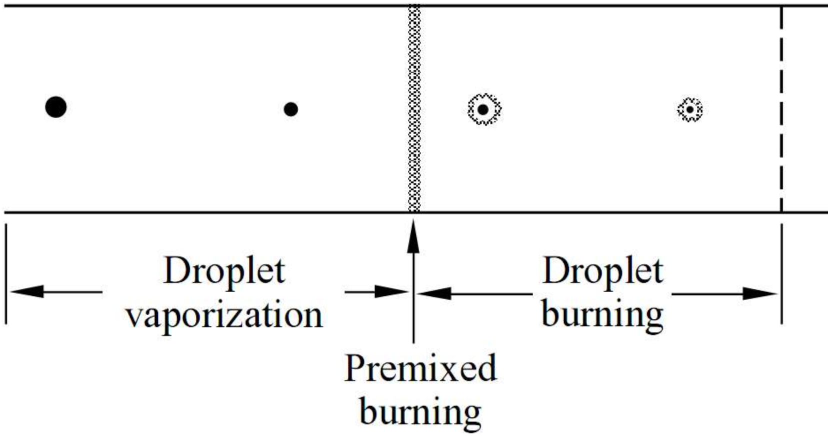
$$d_{s,o,\min}^2 = 8\frac{\rho_g}{\rho_\ell}\left(\frac{\lambda/c_p}{f^o}\right)^2\ln\left(1+B_v\right)$$

Minimum size ≈ 10 μm

  - Minimum size to avoid flame overlap

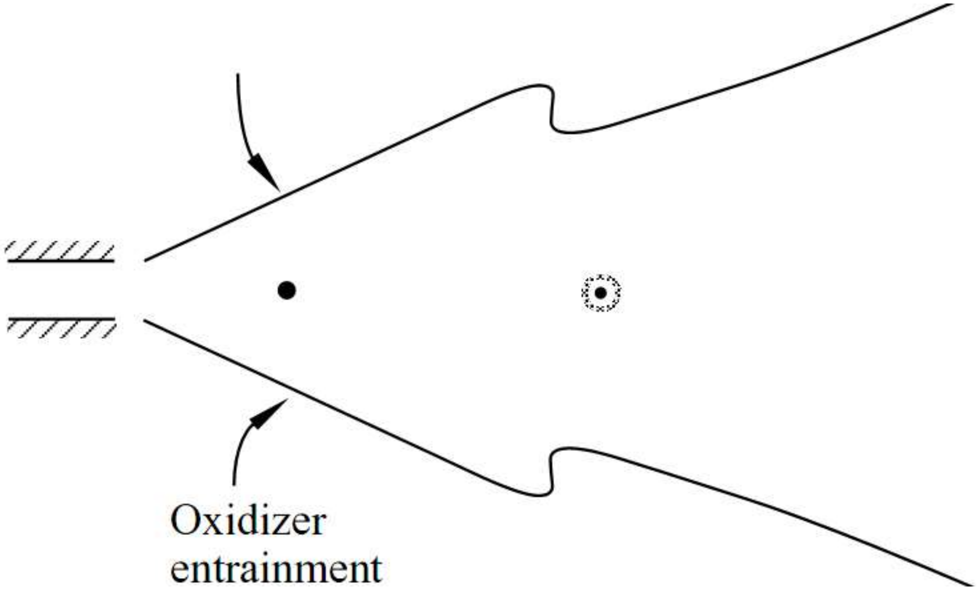
$$F/A \approx \frac{\frac{1}{6}\pi d_s^3\rho_\ell}{\frac{1}{6}\pi d_g^3\rho_g} = \frac{\rho_\ell}{\rho_g}\left(\frac{d_s}{d_g}\right)^3$$

$F/A \approx 0.05 \Rightarrow d_g/d_s \approx 25$



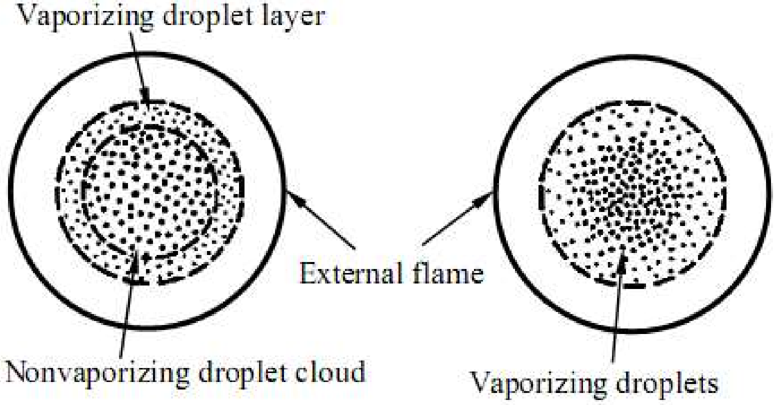
Spray Combustion: Phenomenology (2/3)

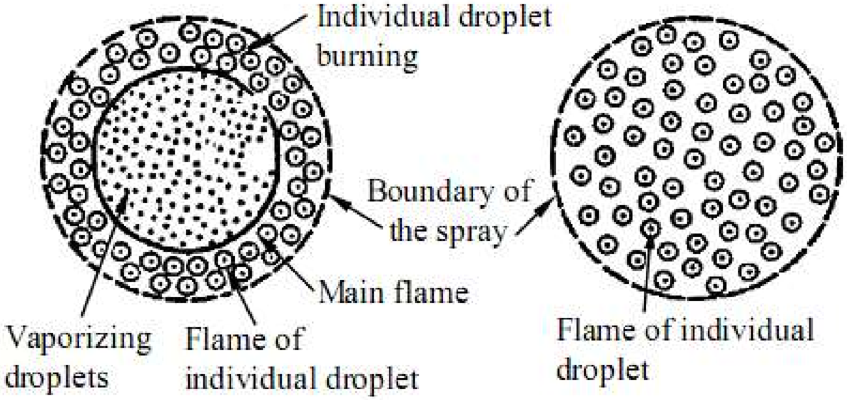
- Spray jet flames
  - o Entrainment rate of hot air >> droplet vaporization rate $\Rightarrow$ individual droplet burning
  - o Entrainment rate of hot air << droplet vaporization rate $\Rightarrow$ jet flame supported by droplet vaporization

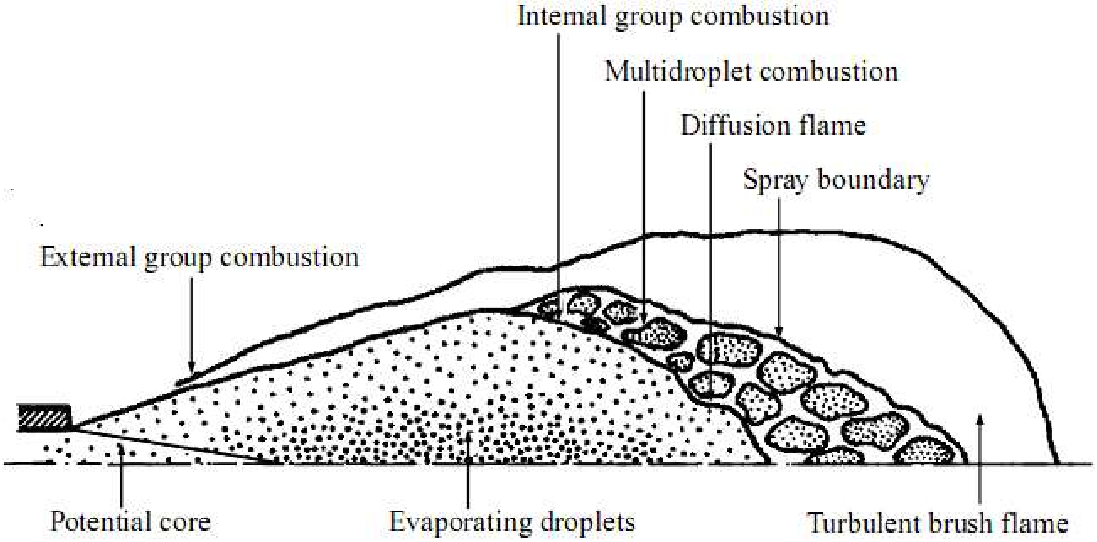


Spray Combustion: Phenomenology (3/3)

- Cloud and dense spray combustion







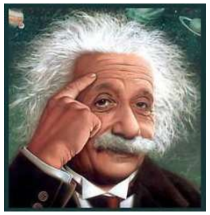
Closing Remarks of Day 3 Lecture (1/2)

- Finite-rate chemistry is irrelevant in the reaction-sheet limit of diffusion flames
  - Degenerates to heat and mass transfer, with discontinuity surfaces of sources/sinks for conservation
  - Transport exerts dominant influence
  - Finite-rate chemistry needed to describe extinction
  - Canonical analysis of diffusion flames by Liñán in 1974 (*Acta Astro*. **1**, 1007; also Chap. 9 of *Combust. Physics*)
- Identified general heat and mass transfer numbers to describe vaporization/condensation and combustion of condensed-phase material

Closing Remarks of Day 3 Lecture (2/2)

- Phenomenology of droplet combustion reasonably well understood
  - Potential for practical gain with judicious blending and inducement of microexplosion
- Outstanding problems
  - Liquid-phase reactions, especially pyrolysis of high-boiling-point liquids leading to cenospheres
  - Coal particle pyrolysis
  - Metal particle combustion
  - Nano-particle and soot formation
  - Spray combustion (e.g. individual vs. group burning)
  - Supercritical vaporization and combustion

Day 3 Specials



1. Synergistic burning of petroleum and biofuel blends
2. Dynamics of droplet impact

1. Synergistic Burning of Petroleum and Biofuel Blends

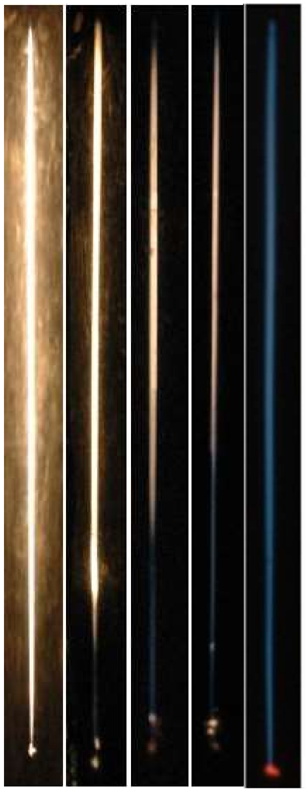
Motivation

- Objective: Explore synergistic blending of ethanol, diesel, and biodiesel
- Merits/de-merits of individual fuels
  - Ethanol: Established supply, biofuel, non-sooting, volatile; low energy content, displaces food supply
  - Diesel: Established supply, aromatics facilitates sealing; a petroleum fuel, sooting
  - Biodiesel: Diverse bio-source, non-sooting; non-volatile

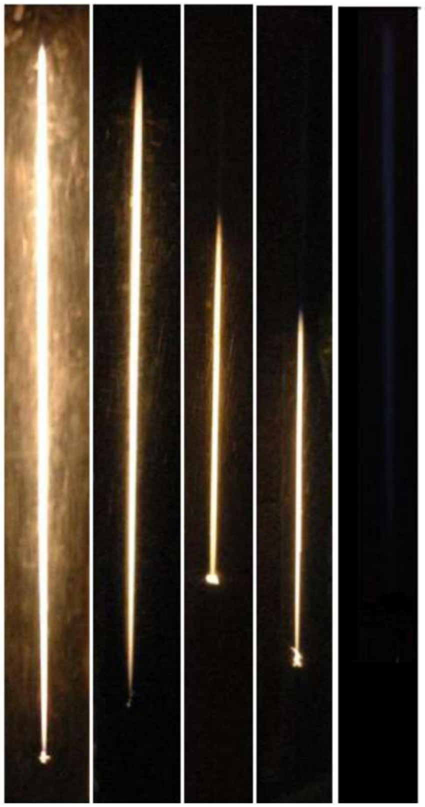
Strategy of Blending

- Capitalize on the volatility differentials of (ethanol > diesel > biodiesel) to reduce soot and facilitate gasification
  - Ethanol and biodiesel will reduce soot in the early and latter periods of droplet gasification
  - High-boiling-point biodiesel facilitates internal nucleation of low-boiling-point ethanol, causing droplet fragmentation

Soot Reduction with Biofuel Blending

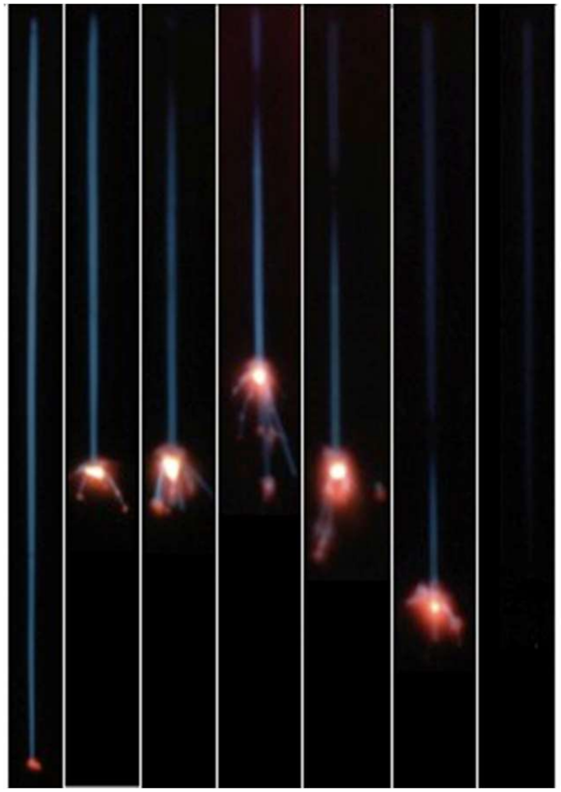


Diesel →Biodiesel

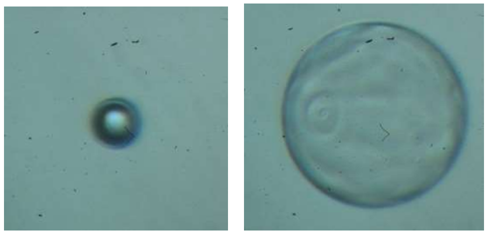


Diesel →Ethanol

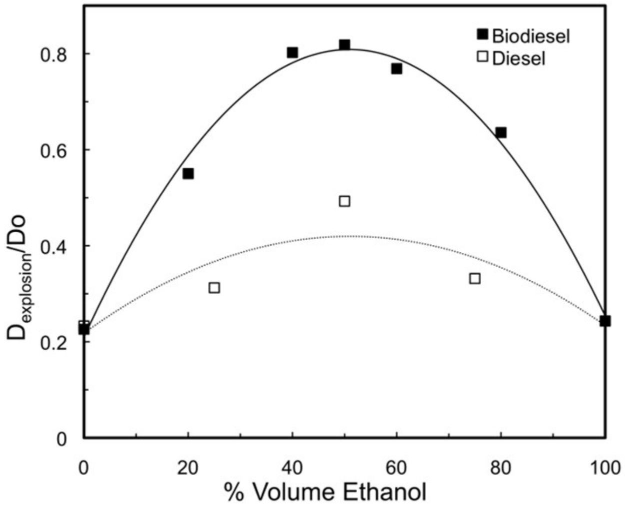
Facilitated Gasification through Microexplosion with Ethanol Blending



Biodiesel →Ethanol



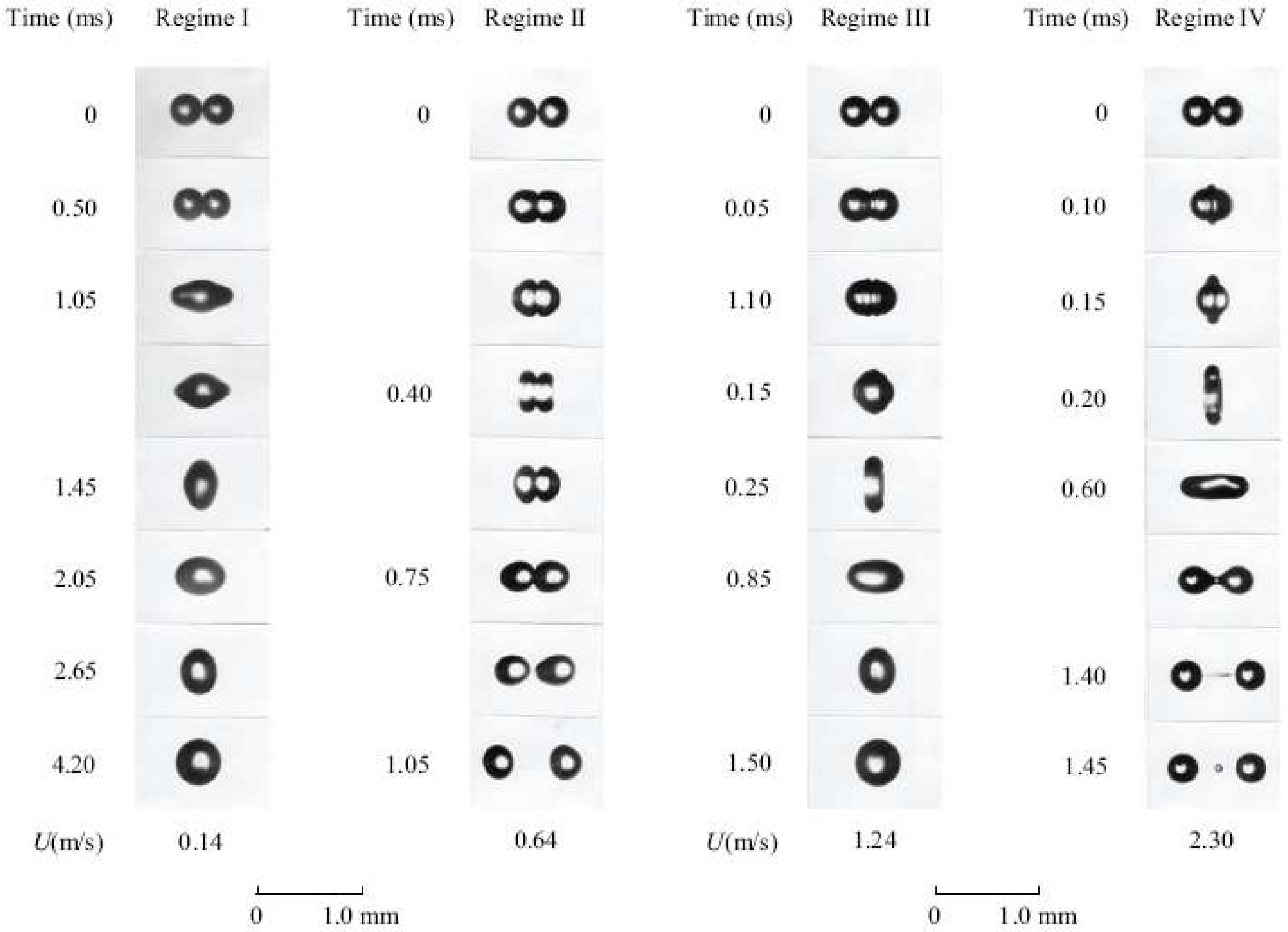
An exploding droplet



Explosion tendency optimized at equal-volume blending

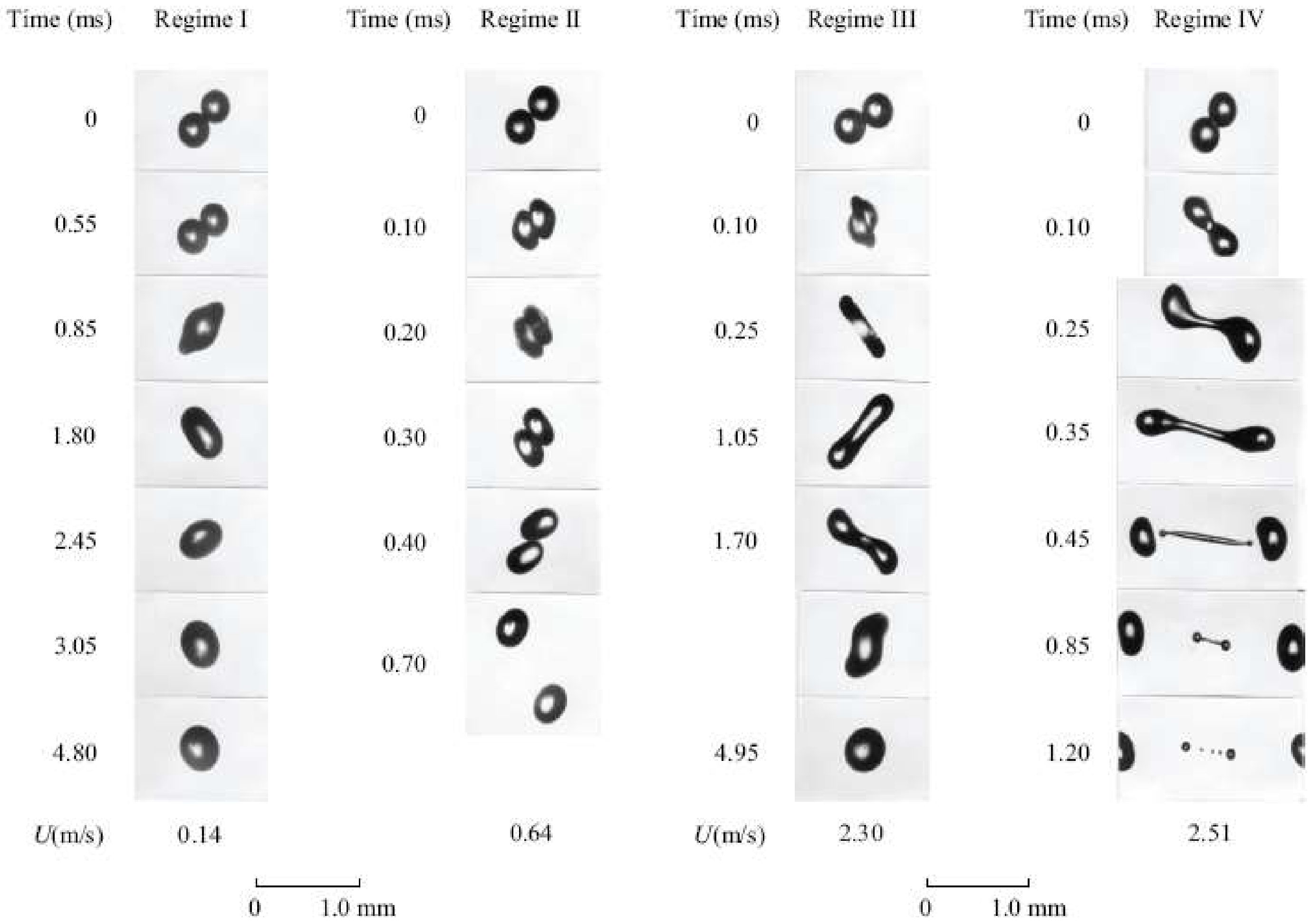
2. Dynamics of Droplet Impact

Merging and Bouncing in Head-on Droplet Collision

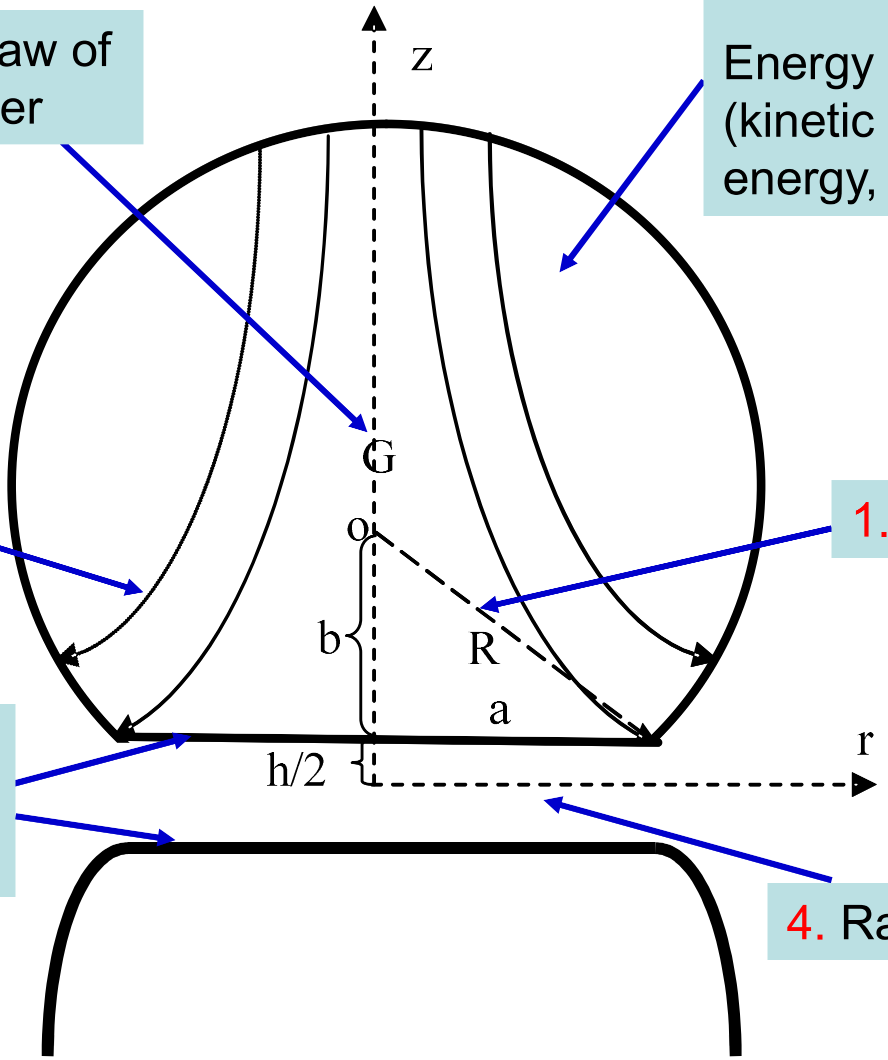


Increasing impact inertia →

Merging and Bouncing in Off-Centered Droplet Collision



Underlying Multi-scale Physics: A Challenging CFD Problem



1\. Newton's second law of motion for mass center

2\. Mass conservation

Energy conservation (kinetic energy, surface energy, viscous loss)

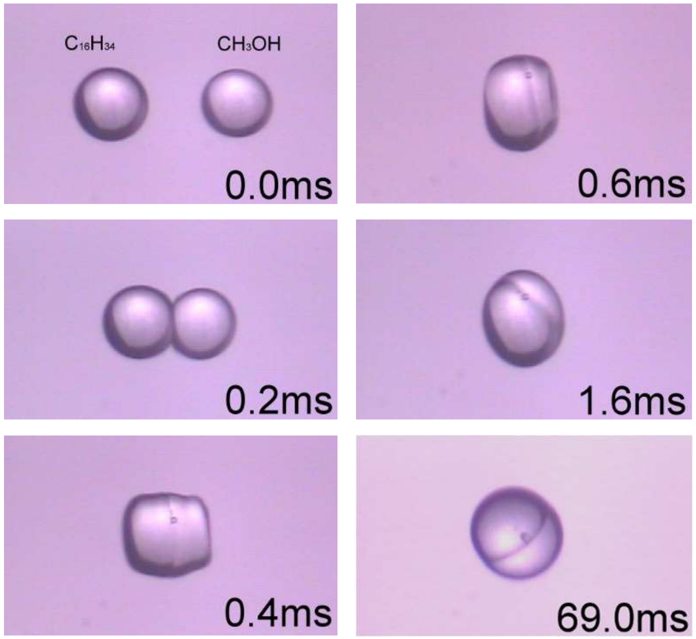
3\. Internal motion ⇒ viscous dissipation

1\. Geometric relation

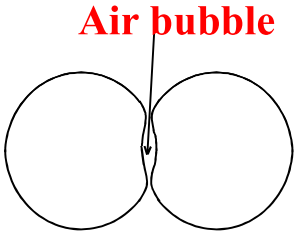
5\. Surface molecular attraction (van der Waals force)

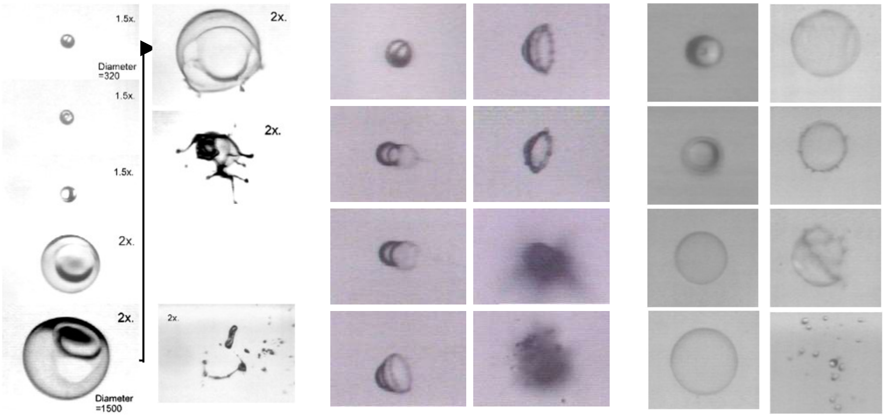
4\. Rarefied gas flow

Bubble Entrapment and Microexplosion



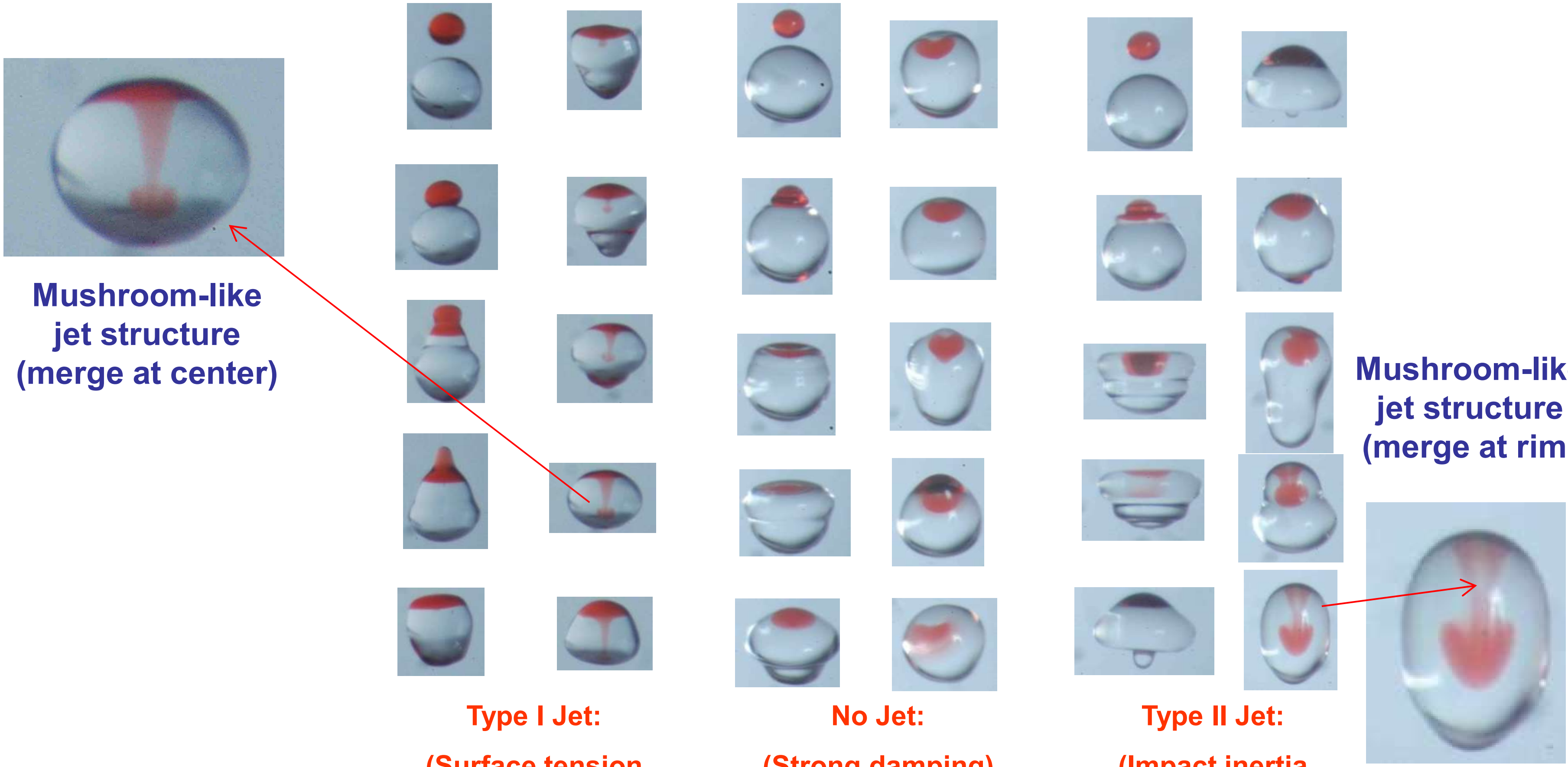
Merged droplet with trapped bubble





Droplet explosion induced by gasification of trapped bubble for droplets with large boiling point differentials (Hexadecane vs Methanol)

Internal Jet Formation & Mixing upon Droplet Merging



Mushroom-like jet structure (merge at center)

Mushroom-like jet structure (merge at rim)

Type I Jet:

(Surface tension driven)

No Jet:

(Strong damping)

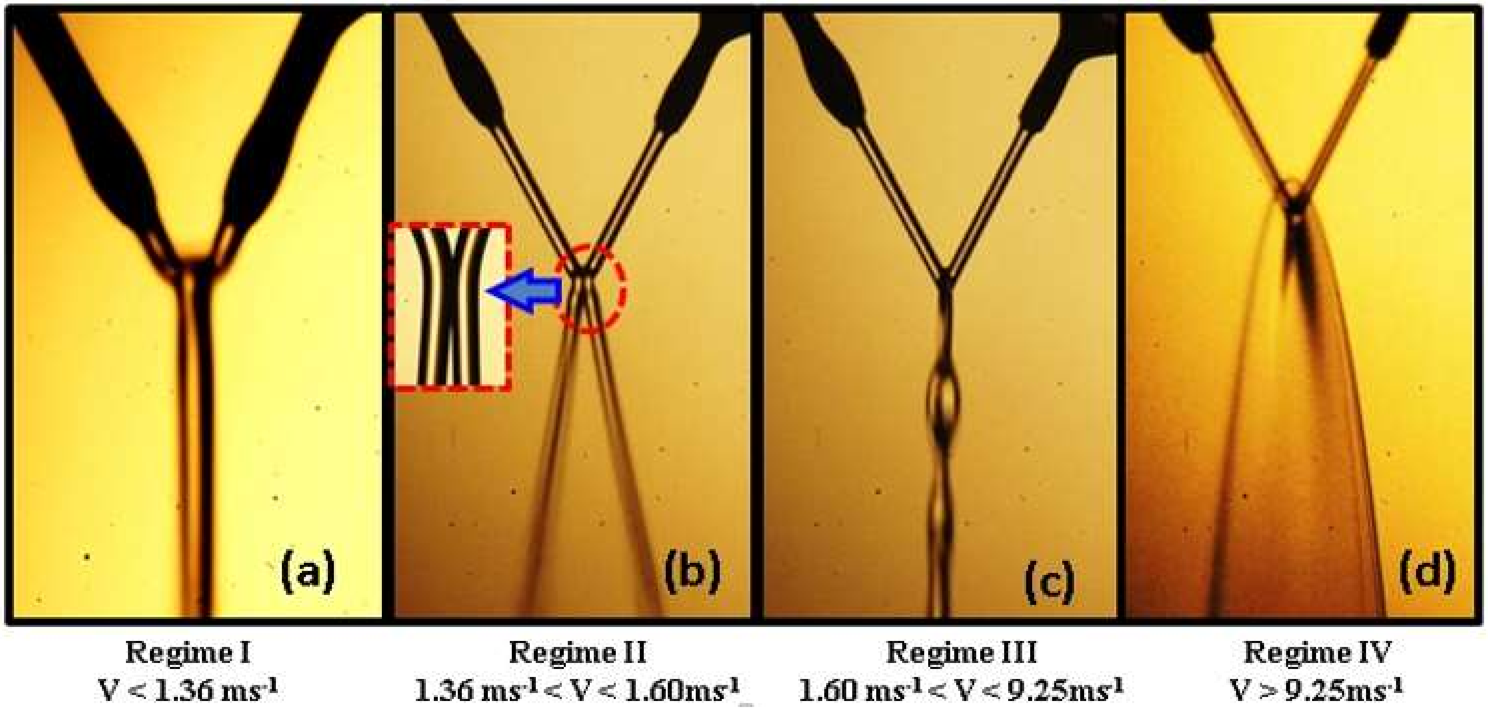
Type II Jet:

(Impact inertia driven)

Increasing Impact Inertia:
Non-monotonic response

Analogous Phenomenon: Jet-Jet Collision

Impact Velocity



Regime I
$V < 1.36\ \mathrm{ms^{-1}}$

Regime II
$1.36\ \mathrm{ms^{-1}} < V < 1.60\ \mathrm{ms^{-1}}$

Regime III
$1.60\ \mathrm{ms^{-1}} < V < 9.25\ \mathrm{ms^{-1}}$

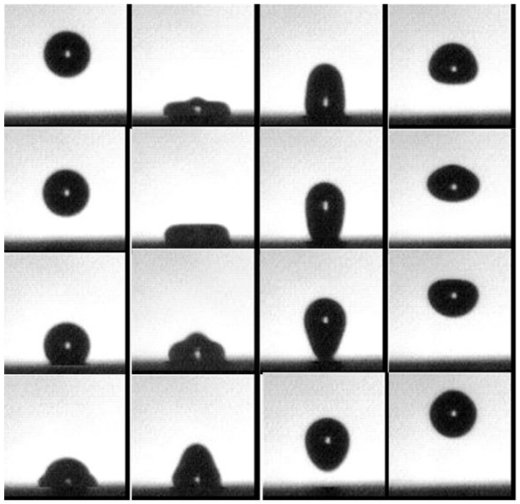
Regime IV
$V > 9.25\ \mathrm{ms^{-1}}$

Soft Merge **Bounce** **Hard Merge** **Break Up**

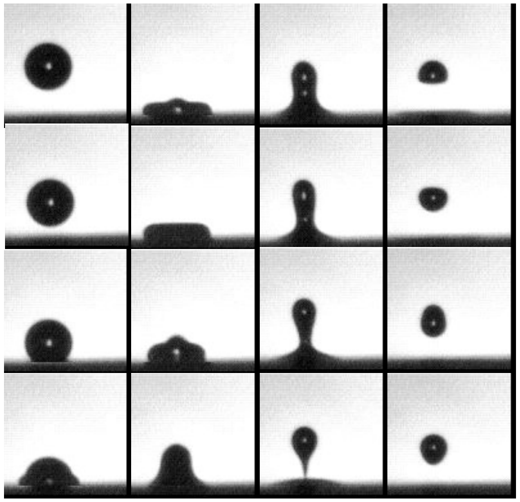
- **Joint bridge structure**
- **Small deformation**

- **Chain structure**
- **Large deformation**

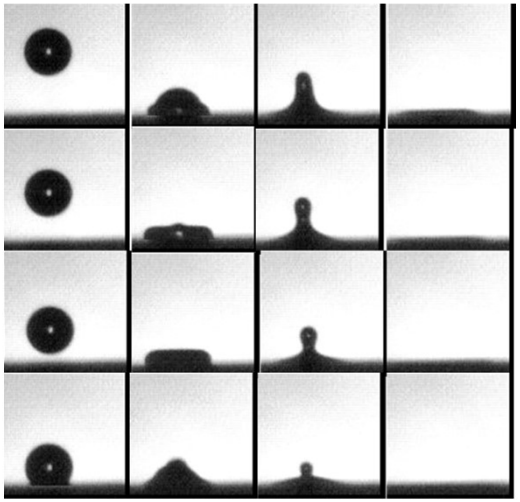
Dynamics of Droplet-film Impact



Bouncing



Partial absorption

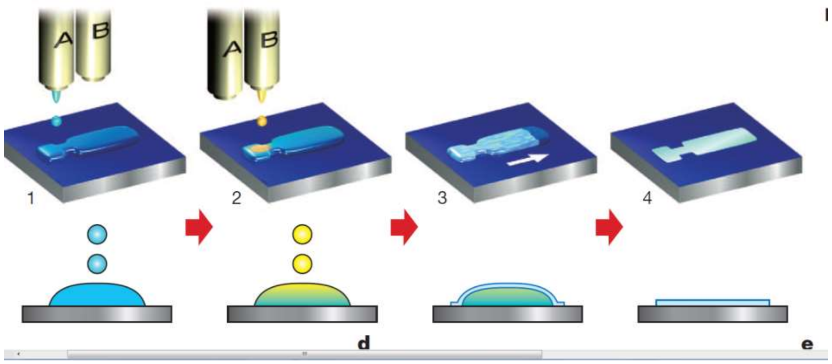


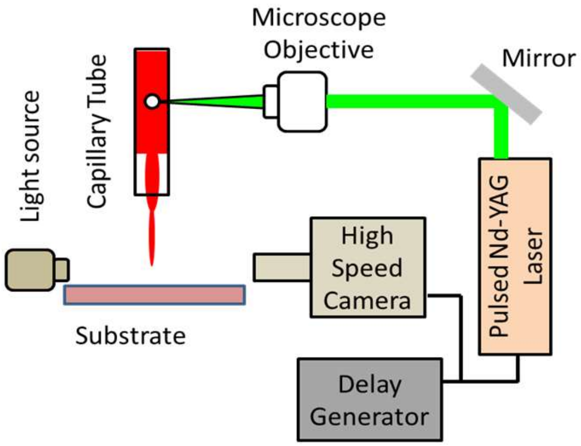
Total absorption

Increasing Impact Inertia →

Transdisciplinary Examples of Applications

- **Materials Synthesis:** merging and mixing of two liquid bodies (droplets or jets) towards forming new materials
- **Hypergolic Propellants:** use of low-volatility green propellants relies on liquid-phase reactions, hence the need for merging and efficient internal merging
- **Ink-Jet Printing:** multi-color/ multi material droplets land and mix → color printing, electronic printing
- **Laser Induced Ultrafast Jet for Drug Injection:** Precise penetration depth and no back splashing





Combustion Physics
(Day 4 Lecture)

Chung K. Law

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Summer School on Combustion
July 7-13, 2024

Day 4: Laminar Premixed Flames

1. **The standard premixed flame**
   1. Phenomenological and asymptotic analyses
   2. Parametric dependence
   3. Chemical structure
2. **Limit phenomena**
   1. The S-curve concept
   2. Extinction through volumetric heat loss
3. **Aerodynamics of flames**
   1. Hydrodynamic stretch
   2. Flame stretch
   3. Flamefront instabilities

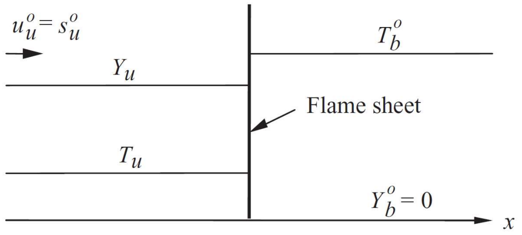
1. The Standard Premixed Flame

Structure of (Standard) Premixed Flame

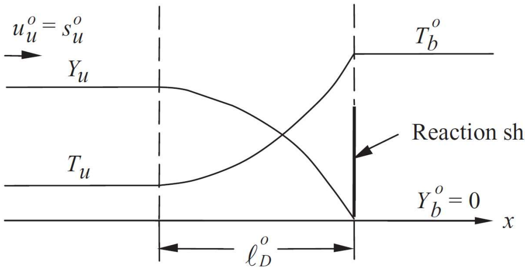
1. Hydrodynamic, Rankine-Hugoniot level (strong discontinuity):
   - Flame sheet
   - Uniform upstream and downstream states
2. Reaction-sheet level (weak discontinuity):
   - Additional preheat, diffusion zone of thickness ℓ_D^o : reaction frozen due to large T_a, diffusion-convection controlling
3. Complete structure
   - Additional reaction zone: $\ell_R^o << \ell_D^o$ for large activation energy
   - Convection negligible relative to diffusion due to small ℓ_R^0 , diffusion-reaction controlling

- System is conservative

$$f = \rho u = \rho_u u_u^o = \rho_b^o u_b^o \ , \qquad c_p(T_b^o - T_u) = q_c Y_u$$



(a)



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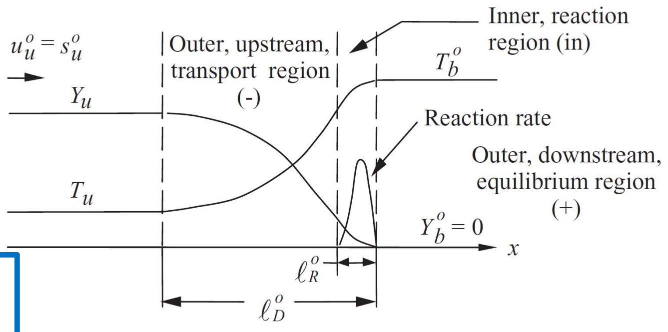


(c)

Flame Characteristics (1/5)

- Characteristic temperature change across reaction zone

$$(\Delta T)_R = [T_b^o - T(x_f^-)] \sim [w/(dw/dT)]_{T_b^o} = (T_b^o)^2 / T_a$$

$$w \sim \exp(-T_a / T)$$

- Continuity of heat flux through preheat and reaction zones

$$\boxed{\frac{\ell_R^o}{\ell_D^o}} \sim \frac{(\Delta T)_R}{T_b^o - T_u} = \frac{(T_b^o)^2}{(T_b^o - T_u)T_a} = \boxed{Ze^{-1} << 1.} \qquad (7.2.5)$$

Flame Characteristics (2/5)

- Convection and diffusion balance in preheat zone:

$$f^o \frac{d}{dx} \sim \frac{d}{dx}[(\lambda / c_p)\frac{d}{dx}], \quad f^o \sim (\lambda / c_p)\frac{d}{dx}$$

$$\boxed{f^o \sim \frac{\lambda / c_p}{\ell_D^o}.} \qquad (7.2.6)$$

- Overall mass flux conservation:

Reactant mass flux entering flame ($Y_u f^o$) =

Reaction flux through reaction zone $(Y_u w_b^o \ell_R^o)$

$$\Rightarrow \qquad \boxed{f^o \sim w_b^o \ell_R^o} \qquad (7.2.7)$$

Flame Characteristics (3/5)

- Solving for f^o and ℓ_D^o from (7.2.6) and (7.2.7), using (7.2.5)

$$\boxed{(f^o)^2 \sim \frac{(\lambda/c_p)w_b^o}{Ze},} \quad \boxed{(\ell_D^o)^2 \sim \frac{(\lambda/c_p)}{w_b^o} Ze} \qquad (7.2.8, 9)$$

- Results show three fundamental quantities governing flame response
  - ○ λ/c_p : diffusion
  - ○ w_b^o : reaction
  - ○ Ze : activation (T_a) and exothermicity (T_b^o)

Flame Characteristics (4/5)

- $\boxed{f^o \sim \sqrt{(\lambda / c_p) w_b^o}}$: propagation rate, which is a response of the flame, is the geometric average of the diffusion and reaction rates, which are the driving forces in forming the flame.

- Dependence on transport:
  - Nonpremixed flame: $f^o \sim \lambda / c_p$; diffusion dominating
  - Premixed flame: $f^o \sim \sqrt{\lambda / c_p}$; “diluted” by reaction
- (7.2.8) and (7.2.9) can be alternately expressed as
  - $\boxed{f^o \ell_D^o \sim \lambda / c_p}$: depends only on transport
  - $\boxed{\dfrac{f^o}{\ell_D^o} \sim \dfrac{w_b^o}{Ze}}$: depends only on reaction

Flame Characteristics: Summary (5/5)

- Since there are only two controlling processes (diffusion and reaction: $\lambda / c_p, w_b^o$), flame characteristics are described by two independent relations, which can be expressed in three different ways to convey different messages
  - Balance of processes:

$$f^o \sim \frac{\lambda / c_p}{\ell_D^o}, \ f^o \sim w_b^o \ell_R^o$$

  - Explicit expressions for the responses:

$$(f^o)^2 \sim \frac{(\lambda / c_p) w_b^o}{Ze}, \ (\ell_D^o)^2 \sim \frac{(\lambda / c_p)}{w_b^o} Ze$$

  - Explicit dependence on individual processes:

$$f^o \ell_D^o \sim \lambda / c_p, \ \frac{f^o}{\ell_D^o} \sim \frac{w_b^o}{Ze}$$

Specific Dependence on Pressure

- $w_b^o \sim p^n;\ \lambda / c_p$ pressure insensitive
  - $f^o \sim [(\lambda / c_p) w_b^o]^{1/2} \sim (w_b^o)^{1/2} \sim p^{n/2},\ \ s_u^o \sim f^o / \rho_u \sim f^o / p \sim p^{(\frac{n}{2}-1)}$

    $\ell_D^o \sim (\lambda / c_p / w_b^o)^{1/2} \sim p^{-n/2}$
- Implications:
  - For $n = 2$: $s_u^o \neq f(p)$; cancellation between density and reaction; this is not a fundamental result
  - For 0 < *n* < 2: f^o increases and s_u^o decreases with increasing *p*
  - Dependence of ℓ_D^o on *p* is through reaction, not diffusion

Asymptotic Analysis

Governing Equations (*Le* =1) (1/2)

- Dimensional:

$$f^o c_p \frac{dT}{dx} - \lambda \frac{d^2T}{dx^2} = q_c w,$$

$$f^o \frac{dY}{dx} - \rho D \frac{d^2Y}{dx^2} = -w$$

- Nondimensional:

$$\begin{array}{ll} \boxed{\begin{array}{l} \dfrac{d^2\tilde{T}}{d\tilde{x}^2} - \dfrac{d\tilde{T}}{d\tilde{x}} = -Da_C^o \tilde{Y} e^{-\tilde{T}_a/\tilde{T}}, \\[2ex] \dfrac{d^2(\tilde{T}+\tilde{Y})}{d\tilde{x}^2} - \dfrac{d(\tilde{T}+\tilde{Y})}{d\tilde{x}} = 0;\ Le = 1 \\[2ex] Da_C^o = \dfrac{\lambda / c_p}{\left(f^o\right)^2} B_C, \quad \tilde{x} = \dfrac{f^o}{\lambda / c_p} x \end{array}} & \begin{array}{l} (7.3.4) \\[4ex] (7.3.5') \\[4ex] \end{array} \end{array}$$

- B.C. :

$$\tilde{x} = -\infty:\ \tilde{T} = \tilde{T}_u, \qquad \tilde{Y} = 1,$$

$$\tilde{x} = \infty:\ \tilde{T} = \tilde{T}_b^o, \qquad \tilde{Y} = 0,$$

$$\tilde{x} = \pm\infty:\ \frac{d\tilde{T}}{d\tilde{x}} = \frac{d\tilde{Y}}{d\tilde{x}} = 0.$$

Governing Equations (2/2)

- Integrating (7.3.5’) once; with b. c. at $\tilde{x}=-\infty$,

$$(\tilde{T}+\tilde{Y})-\frac{d(\tilde{T}+\tilde{Y})}{d\tilde{x}}=(\tilde{T}_u+1). \qquad (7.3.10’)$$

  - Evaluating (7.3.10’) at $\tilde{x}=+\infty$ yields T_{ad}: $\tilde{T}_b^o=1+\tilde{T}_u=\hat{T}_{ad}$

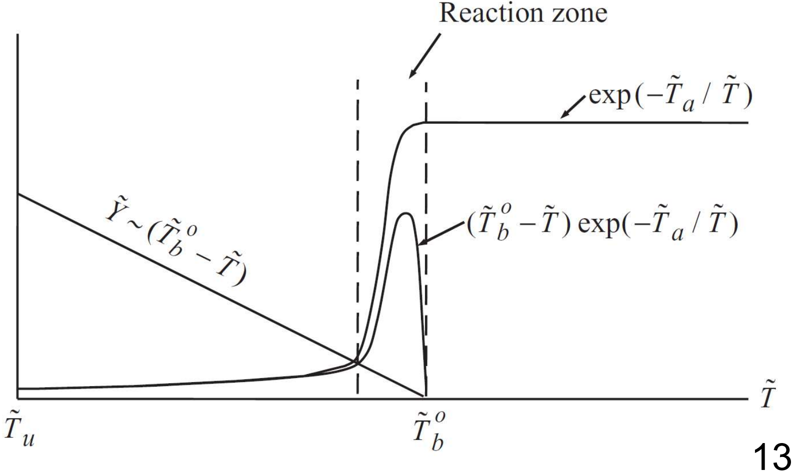
- Integrating (7.3.10’) again:

$(\tilde{T}+\tilde{Y})=\tilde{T}_b^o+c_1e^{\hat{x}}=\tilde{T}_b^o$ for boundedness at $\hat{x}=\infty$

- Substituting $\hat{Y}=\tilde{T}_b^o-\tilde{T}$ into (7.3.4) yields the single equation that needs to be solved:

$$\boxed{\frac{d^2\tilde{T}}{d\tilde{x}^2}-\frac{d\tilde{T}}{d\tilde{x}}=-Da_C^o\left(\tilde{T}_b^o-\tilde{T}\right)e^{-\tilde{T}_a/\tilde{T}}} \qquad (7.3.13)$$

  - This is why $\beta=\hat{T}+\hat{Y}$ is called a (de-)coupling function



The Cold Boundary Difficulty

- Evaluating $\frac{d^2\tilde{T}}{d\tilde{x}^2} - \frac{d\tilde{T}}{d\tilde{x}} = -Da_C^o \tilde{Y} e^{-\tilde{T}_a/\tilde{T}}$, (7.3.4)

  at the $\tilde{x} = -\infty$ freestream, where
  - $\frac{d^2\tilde{T}}{d\tilde{x}^2} = 0, \frac{d\tilde{T}}{d\tilde{x}} = 0 \Rightarrow LHS = 0$
  - $\tilde{Y} = 1,\ \tilde{T} = \tilde{T}_{-\infty} \Rightarrow RHS \neq 0$

  Thus the governing equation is unbalanced ⇒ ill posed

- Difficulty exists for many steady-state problems with premixture at ambience: reactive ambience has infinite time to react ⇒ all reactants would be reacted before arrival of flame ⇒ unphysical posing of problem
- **Recourse**
  - Artificial suppression of reaction term at $\tilde{x} = -\infty$
  - **Asymptotic analysis**: Rational freezing of reaction at $\tilde{x} = -\infty$ due to large activation energy.

Distinguished Limit (1/2)

- Asymptotic analysis capitalizes on the largeness of activation energy which localizes reaction to a thin zone.
- Consider reaction rate: $\tilde{w} \sim Da_C \tilde{Y} e^{-\tilde{T}_a / \tilde{T}}$
- For $\tilde{T}_a >> 1 \to \infty$ and $Da_c \tilde{Y}$ fixed, $\Rightarrow \tilde{w} \to 0 \quad \Rightarrow$

  No reaction in the reaction zone, obviously wrong!
- Thus the limit $\tilde{T}_a \to \infty$ must be taken rationally

Distinguished Limit (2/2)

- Distinguished limit:

$\tilde{T}_a \to \infty$ requires $Da_c \to \infty$ such that $\tilde{w}$ is fixed.

- Express $Da_C \sim Da e^{\tilde{T}_a / \tilde{T}_b^o}$

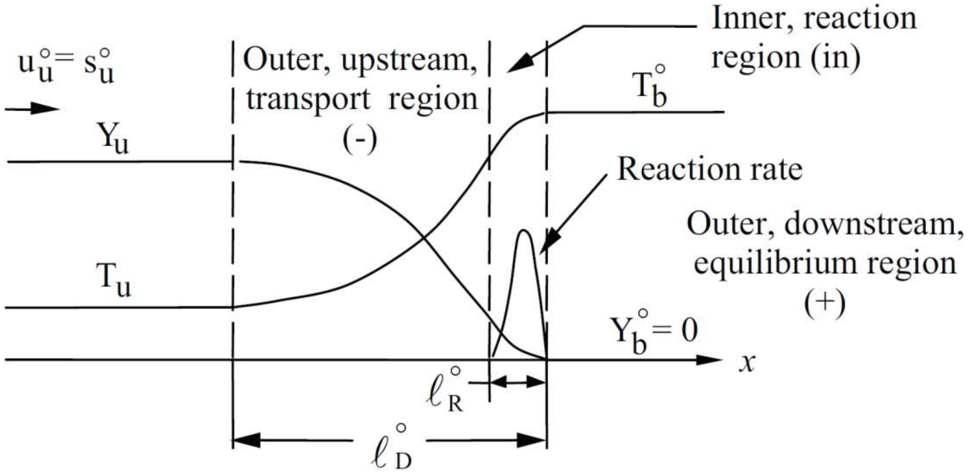
Then $$\tilde{w} \sim Da \exp\left[\tilde{T}_a\left(\frac{1}{\tilde{T}_b^o} - \frac{1}{\tilde{T}}\right)\right] \approx \boxed{Da \exp\left[-Ze\left(\tilde{T}_b^o - \tilde{T}\right)\right]}$$

- Thus for $\tilde{w}$ to remain fixed, $Ze \to \infty$ requires

$\tilde{T} \to \tilde{T}_b^o \Rightarrow$ thin reaction zone

Procedure for Asymptotic Analysis

- Separately obtain (partial) solutions for the three zones:
  - **Broad upstream, convective-diffusive, preheat zone**, subject to b. c. at $\tilde{x} = -\infty$ only. No downstream b. c.
  - **Thin reactive-diffusive zone**, without any b. c.
  - **Broad downstream, equilibrium zone**.
- Partial solutions determined to leading order of reaction sheet $(Ze \rightarrow \infty)$ and next order of broaden reaction zone $(Ze >> 1$, but finite)
- Asymptotically match these partial solutions to determine the various boundary conditions, hence completing the solutions



Structure Equation for Inner, Reaction Zone (1/2)

- Define inner "stretched" variable and inner solution for reaction zone as

$$\chi = \tilde{x}/\varepsilon = O(1) \qquad \tilde{T}_{in}(\chi) = \theta_o - \varepsilon\theta_1(\chi) + O(\varepsilon^2)$$

- Then G.E. becomes

$$\boxed{-\frac{d^2\theta_1}{d\chi^2} + \varepsilon\frac{d\theta_1}{d\chi} = -\left(\varepsilon^2 LeDa^o\right)\theta_1 e^{-\varepsilon Ze\theta_1}.}$$

- Observations:
  - Diffusion term: $O(1)$; Convection term: $O(\varepsilon)$
  - To retain exponential nonlinearity essential to chemical reaction: $\varepsilon Ze \sim O(1) \Rightarrow \varepsilon \sim Ze^{-1}$ identified
  - For reaction term to be $O(1)$ in order to balance diffusion term:

$$\varepsilon^2 Da^o \sim O(1) \Rightarrow Da^0 \sim \varepsilon^{-2}$$

  - ε^2: one ε from thin zone, one ε from reduced concentration

Structure Equation for Inner, Reaction Zone (2/2)

- Final structure equation: $\boxed{\dfrac{d^2\theta_1}{d\chi^2} = \dfrac{\Delta^o}{2}\theta_1 e^{-\theta_1}, \quad \Delta^o = \dfrac{2LeDa^o}{Ze^2}.}$ (7.5.44,45)
- Solution: $\dfrac{d}{d\theta_1}\left(\dfrac{d\theta_1}{d\chi}\right)^2 = \Delta^o\theta_1 e^{-\theta_1}$ (7.5.16)

  Integrating with b. c.: $\theta_1 = d\theta_1/d\chi = 0$ at $\chi \to \infty$

$$\left(\frac{d\theta_1}{d\chi}\right)^2 = \Delta^o \int \theta_1 e^{-\theta_1} d\theta_1 + c_{\text{in}} = -\Delta^o\left(1+\theta_1\right)e^{-\theta_1} + c_{\text{in}}. \qquad (7.5.47)$$

$$= \Delta^o\left[1-\left(1+\theta_1\right)e^{-\theta_1}\right]. \qquad (7.5.48)$$

  Evaluating at $\chi \to \infty$

$$\lim_{\chi\to-\infty}\left(1+\theta_1\right)e^{-\theta_1} = \lim_{\chi\to-\infty}\left[1-\left(c_1^- + \chi\right)\right]e^{\left(c_1^- + x\right)} = 0 \qquad (7.5.49)$$

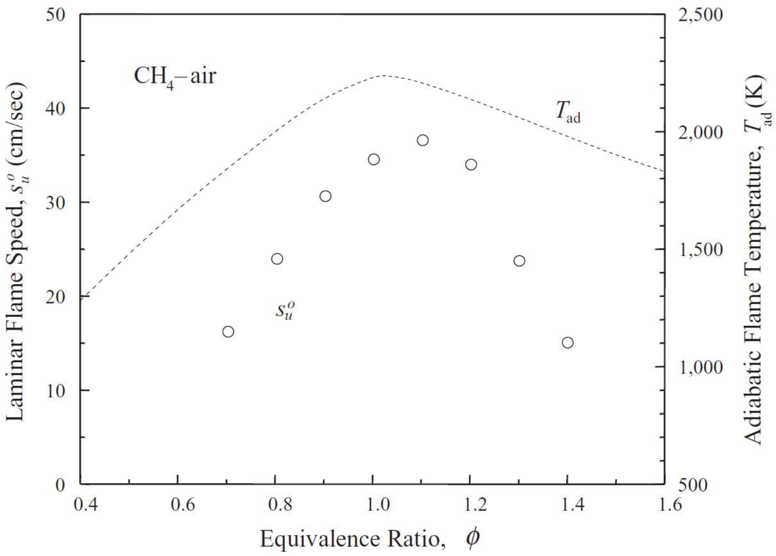
- Final result: $\boxed{\Delta^o = 1}$ as eigenvalue
- In physical terms:

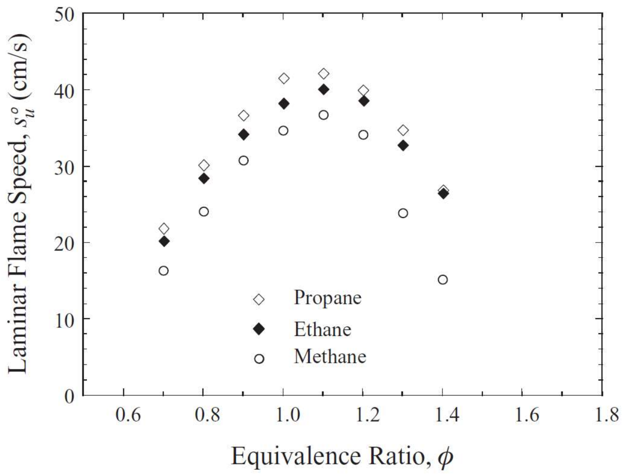
$$\boxed{(f^o)^2 = \frac{2(\lambda/c_p)B_c}{Ze^2} e^{-T_a/T_b^o}}$$

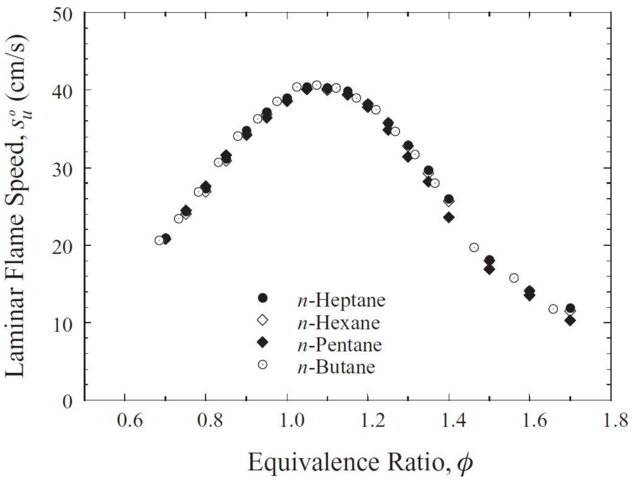
- Phenomenological derivation only missed the term $2Le/Ze$

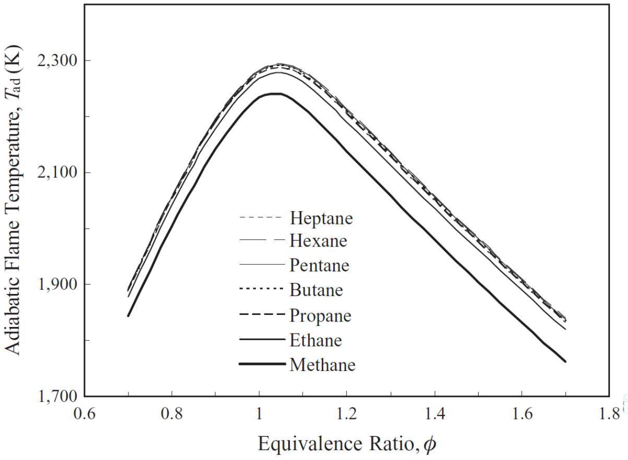
Dependence on T_{ad}

- Correlates well with T_{ad} through heat of combustion
  - Equivalence ratio
  - C/H ratio



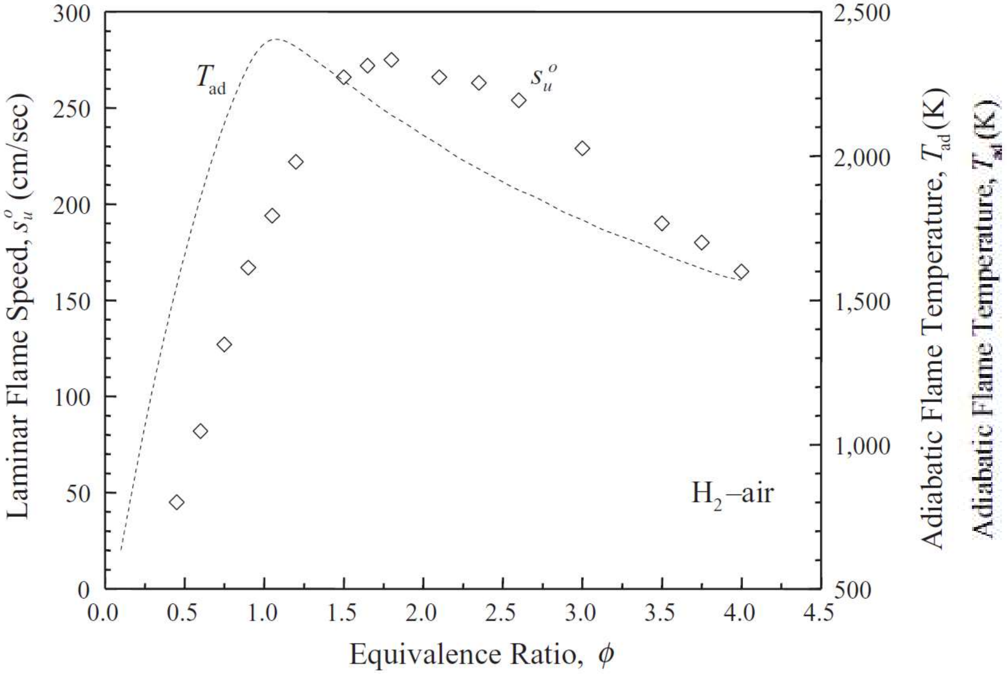






Dependence on *Le*

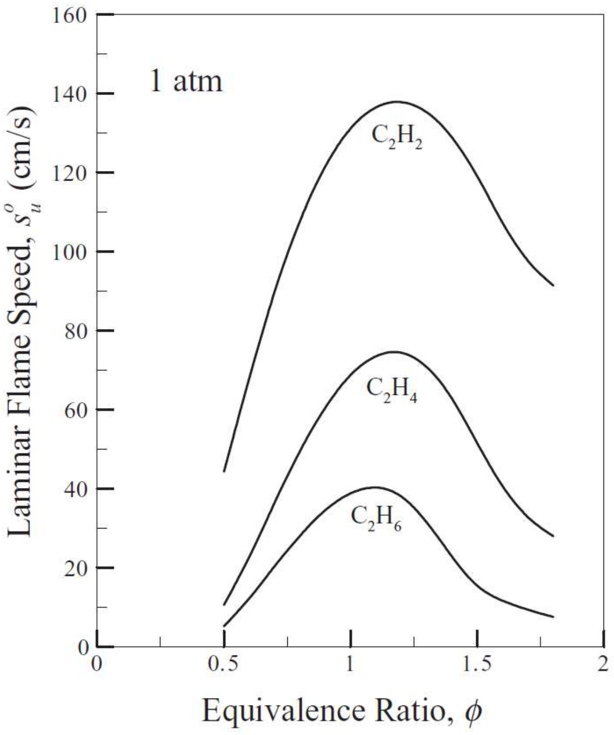
- More rigorous derivation shows $(f^o)^2 \sim Le$
  - **Concentration effect**
  - $T_f \equiv T_{\text{ad}}$ is not affected for the standard flame, hence weak effect; exaggerated for hydrogen ($Le_{\text{lean}} \approx 0.3$, $Le_{\text{rich}} \approx 2.3$)
  - Effects are more significant for stretched flames for which T_f is affected



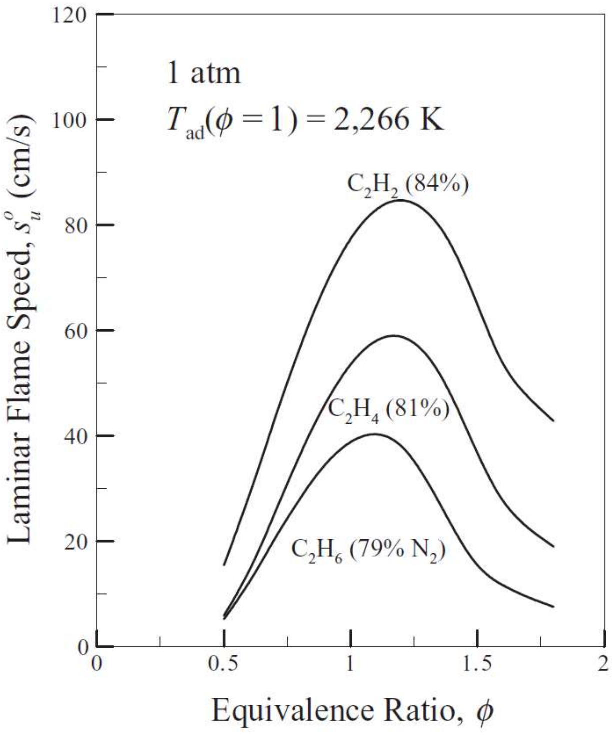
Dependence on Molecular Structure

- Flame speed increases with ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2)

Air as oxidizer

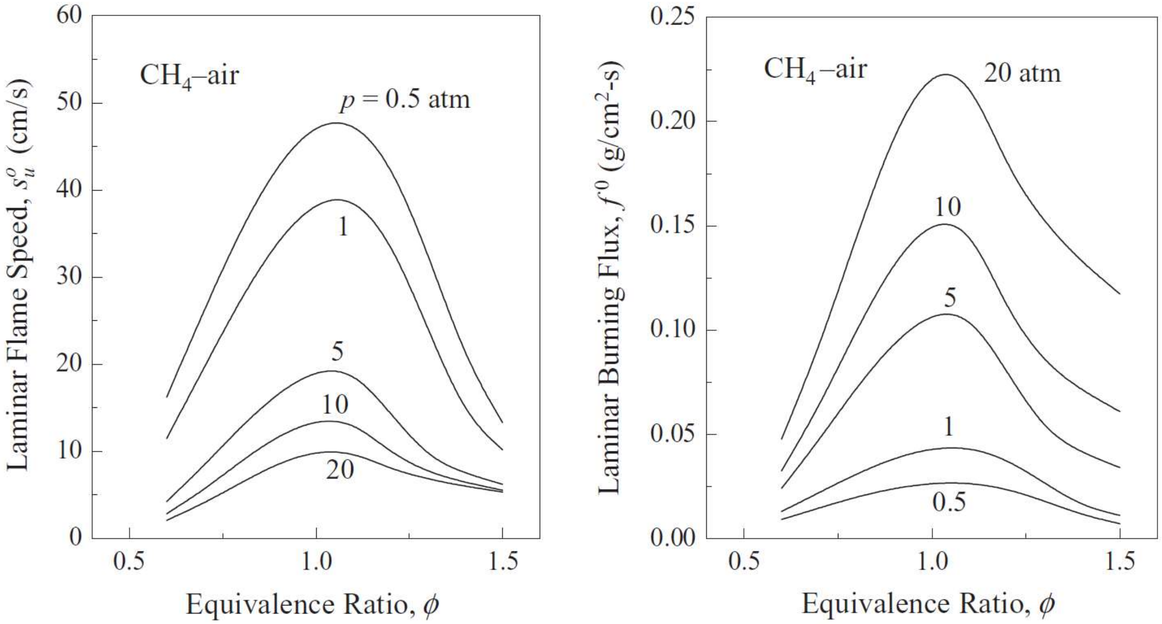


Modified air to match T_{ad}



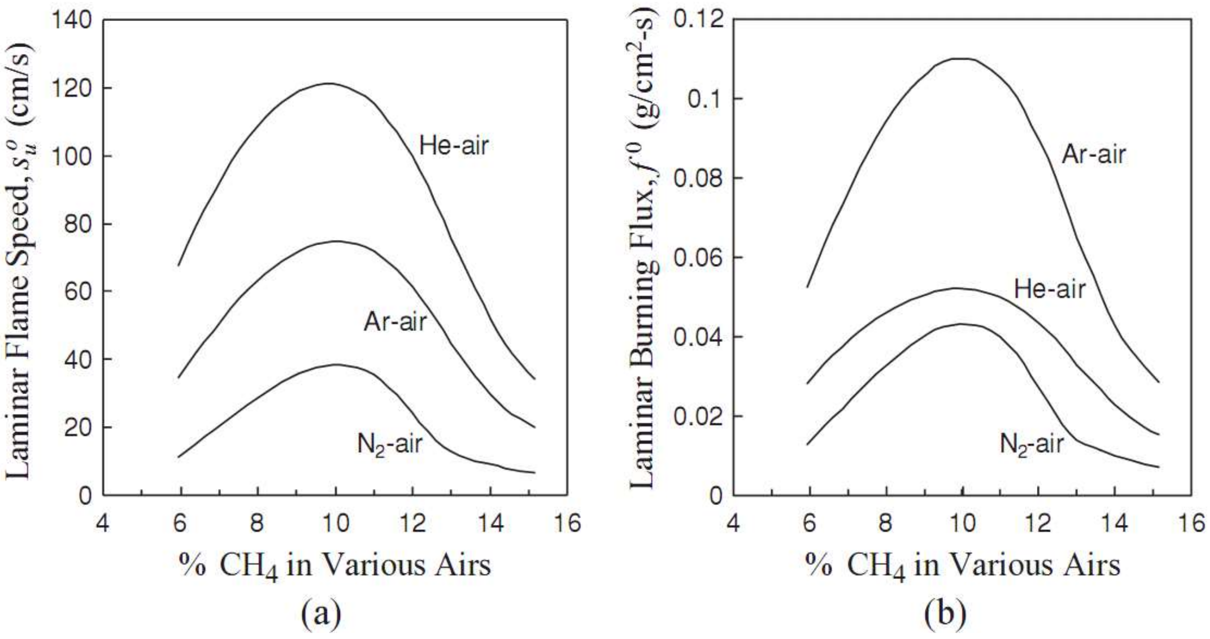
Dependence on Pressure

- Dependence of flame speed on pressure is through
  - **Chemistry**
  - **Density**
- Observed decreasing trend of flame speed with pressure is density effect, not chemistry effect
- f^o is the proper parameter because it is only affected by chemistry
- f^o usually increases with increasing pressure



Dependence on Transport Properties

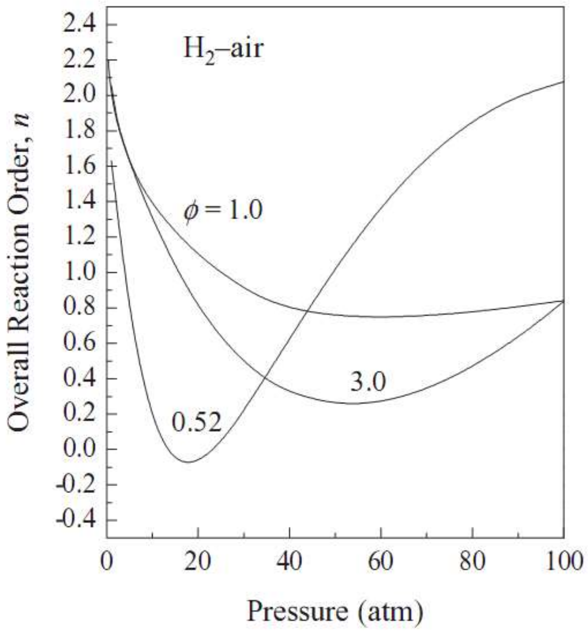
- Flame speed can be manipulated through inert substitution, while keeping oxygen mole fraction fixed
  - N_2 and Ar have similar molecular weights and hence diffusivities, but different c_p, which affects the flame temperature.
  - Ar and He have the same c_p but different diffusivities and densities

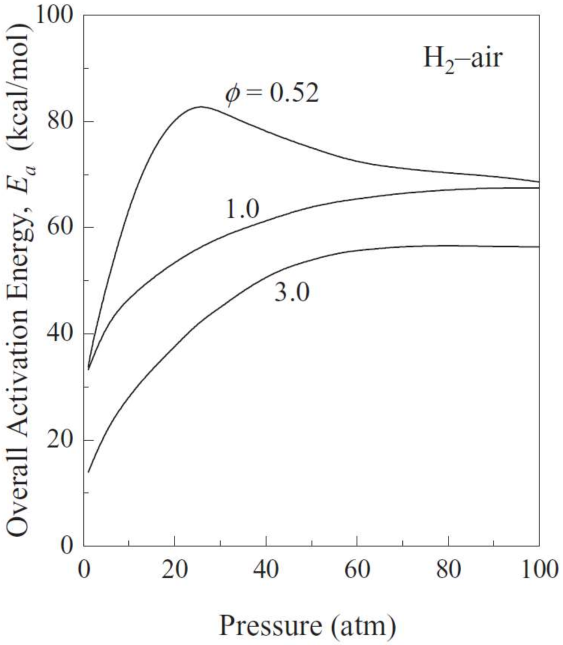


Extraction of Global *n* and E_a

$$n = 2\left(\frac{\partial \ln f^o}{\partial \ln p}\right)_{T_{\mathrm{ad}}}.$$

$$E_a = -2R^o\left[\frac{\partial \ln f^o}{\partial (1/T_{\mathrm{ad}})}\right]_p.$$





- Results demonstrate the role of pressure on two-body branching (promoting with pressure) and three-body termination (retarding with pressure) reaction
- Note: possible *n* < 0

Chemical Structure of Flames

Asymptotic versus Chemical Structure

Asymptotic Structure

- Broad, convective-diffusive, nonreactive zone followed by:
- Narrow, diffusive-reactive zone at downstream end of flame
- One-step overall reaction accounts for both activation and heat release
- Chemical activation is thermal in nature

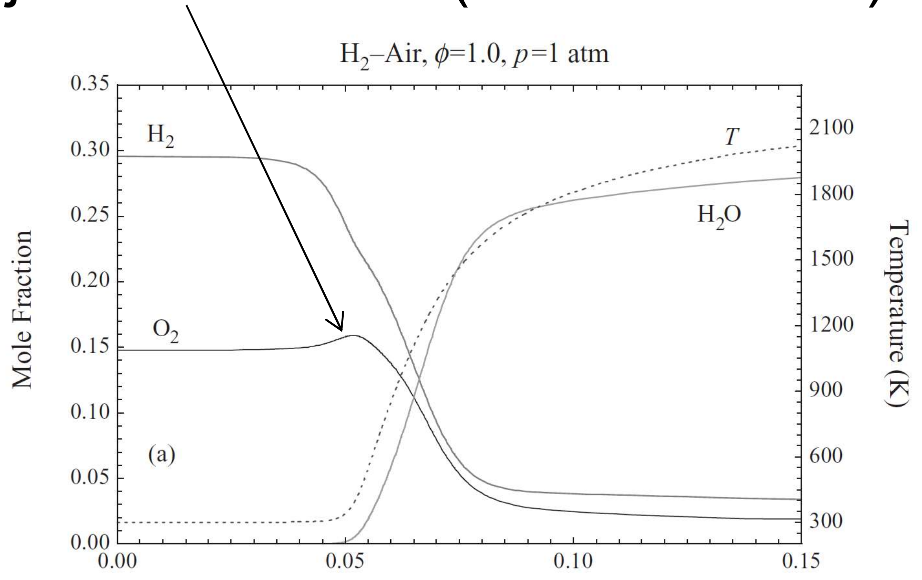
Asymptotic versus Chemical Structure

Chemical Structure (with chain mechanism)

- Termination reaction is temperature insensitive ⇒ can occur in upstream diffusive zone ⇒ reactions take place throughout entire flame structure
- Termination reactions can be highly exothermic ⇒ substantial heat release in preheat zone
- Chemical activation through radicals produced at downstream, high-temperature end that back diffuse to the preheat zone
- In homogeneous system initiating radicals are produced by original fuel-oxidizer species.

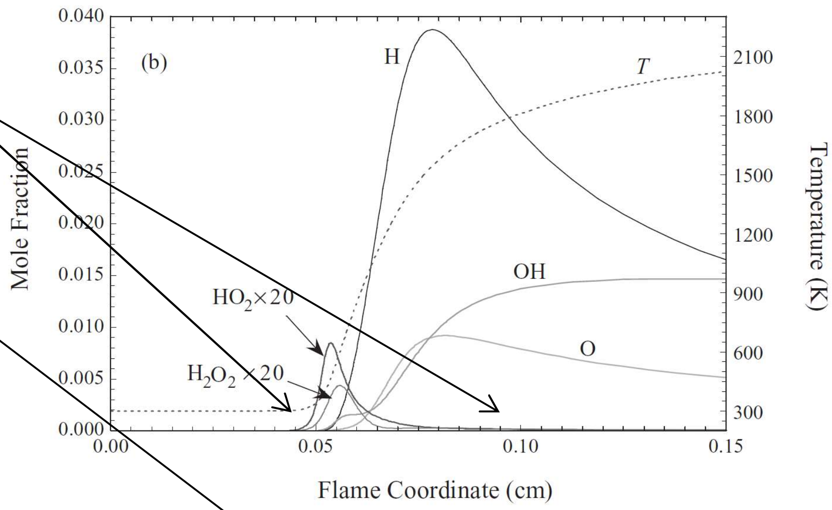
Premixed H_2-Air Flame: Diffusive Structure

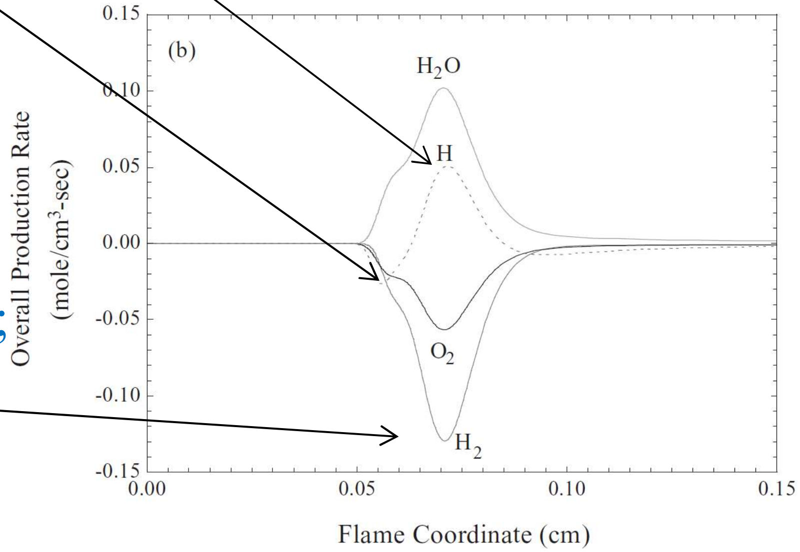
- H_2 diffusion layer is thicker than those of O_2 and heat (T) because of its high diffusivity.
- Rapid reduction in H_2 concentration (due to diffusion, not reaction) causes a bump in mole fraction of O_2. This is not physical, just definitional (on mole basis)



Chain Structure

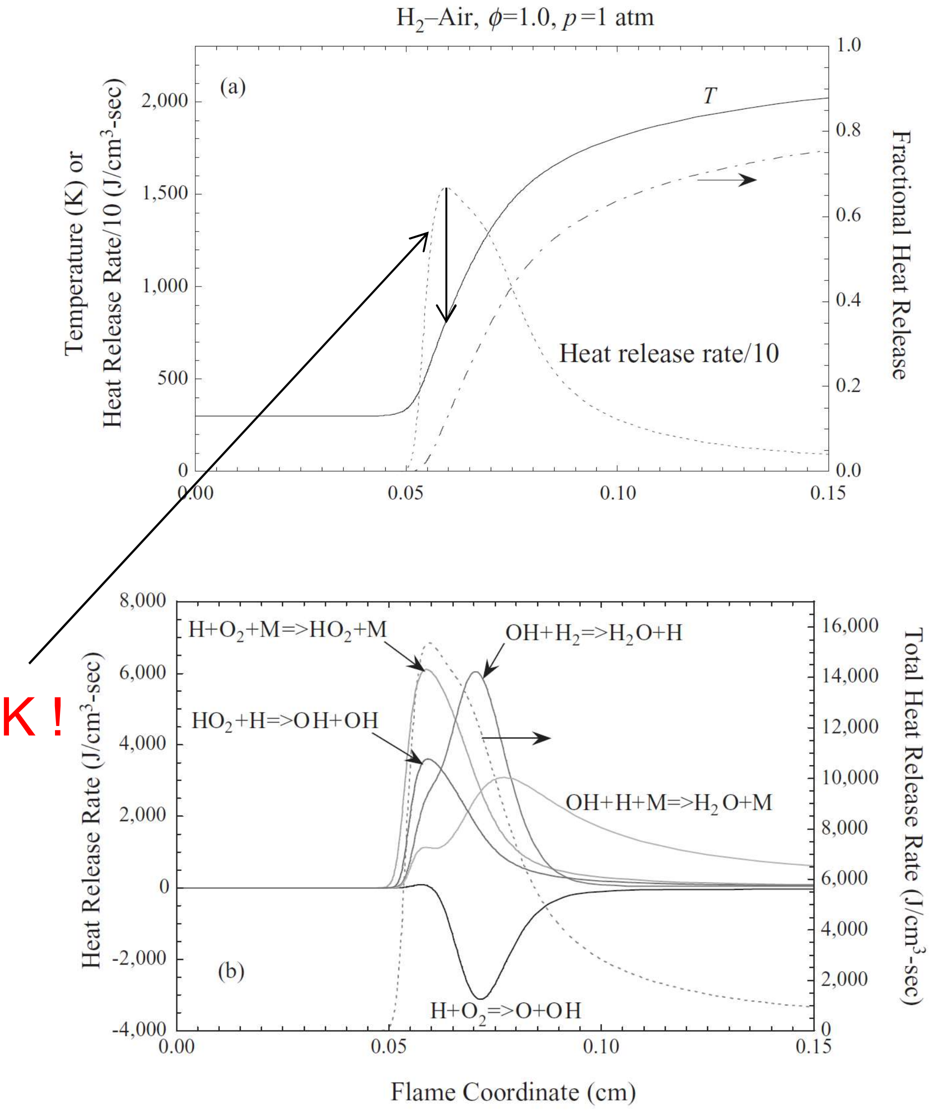
- **Active reaction zone:**
  0.04 cm to 0.1 cm; two zone structure
- **Trailing, H production zone**
  - $O+H_2 \rightarrow OH+H$; $OH+H_2 \rightarrow H_2O+H$
  - H back diffuses
- **Leading, H consumption zone**
  - Back-diffused H reacts with O_2 at low temperature through $H+O_2+M \rightarrow HO_2+M$.
  - HO_2 subsequently forms H_2O_2,
  - Contrasts with $H_2+O_2 \rightarrow HO_2+H$ in homogeneous system.
- Maximum consumption rates of $H_2:O_2 = 2:1$; occurring at same location
- H_2O generated through entire reaction zone.





Thermal Structure

- Major exothermic reactions
    - H consumption layer,
      $H+O_2+M \rightarrow HO_2+M$
    - H production layer
      $OH+H_2 \rightarrow H_2O+H$
- Major endothermic reaction
    - $H+O_2 \rightarrow OH+O$
      which is the major branching step



- Maximum heat release occurs at 800 K !
- 30% heat released in H consumption layer, at 1000 K
- Chemical activation, indicated by maximum H production rate, occurs around 1400 K.

Summary of Contrasts with Asymptotic Structure

- Important reactions occur throughout flame structure
- H radical needed for initiation at leading edge is produced in the downstream and back diffuses
- Maximum heat release occurs at front of the active reaction zone
- Substantial heat evolved in the moderately low temperature region of the flame

2. Limit Phenomena

Concepts of Ignition & Extinction

- **Thermal runaway**: Feedback loop involving nonlinear Arrhenius heat generation and linear heat loss
- **Radical runaway**: Radical proliferation through chain branching
- **Unsteady (ignition) analysis**: Tracking the temporal evolution of a reacting mixture upon application of ignition stimulus
- **Steady, S-curve analysis**: Identify states at which steady solution does not exist for a non-reacting situation, signaling ignition, or a strongly burning situation, signaling extinction
- **Ultimate (extinction) consideration**: system adiabaticity

Principle of Well-Stirred Reactor

- In steady-state operation:

$$\dot{V}\rho_o c_p (T_f - T_o) = V Q_c B c_F e^{-T_a/T_f}$$

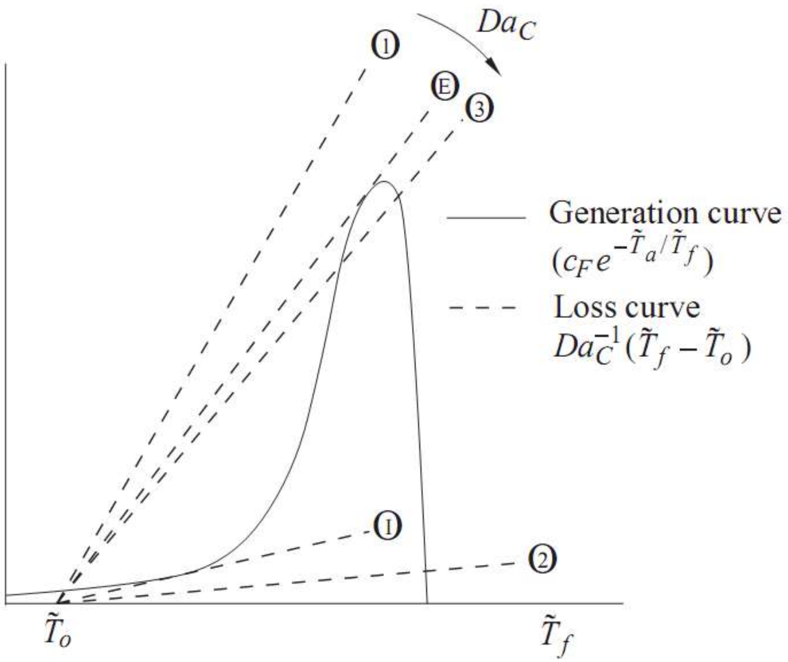
- Using: $\tilde{T} = \hat{T}_{ad} - \tilde{c}_F$

$$\tilde{T}_f - \tilde{T}_o = Da_C(\tilde{T}_{\text{ad}} - \tilde{T}_f)e^{-\tilde{T}_a/\tilde{T}_f},$$

$$Da_C = \frac{B}{\dot{V}/V} = \frac{\text{Characteristic flow time}}{\text{Characteristic collision time}} \quad (8.1.23)$$

- Solutions:
  - 1: Weakly-reactive state
  - 2: Strong-burning state
  - I: Ignition state
  - E: Extinction state
  - 3: Triple solution⇒

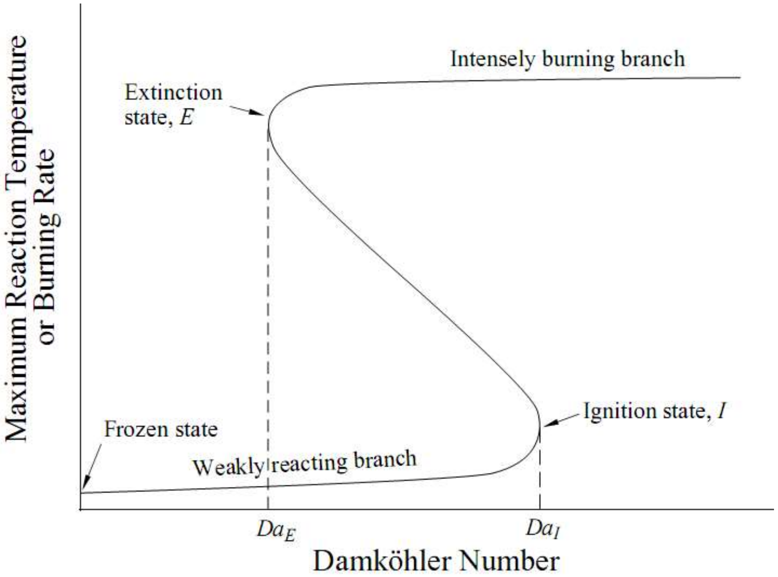
    nonmonotonicity and hysteresis



Concept of S-Curve

- Ignition/extinction turning points defined by

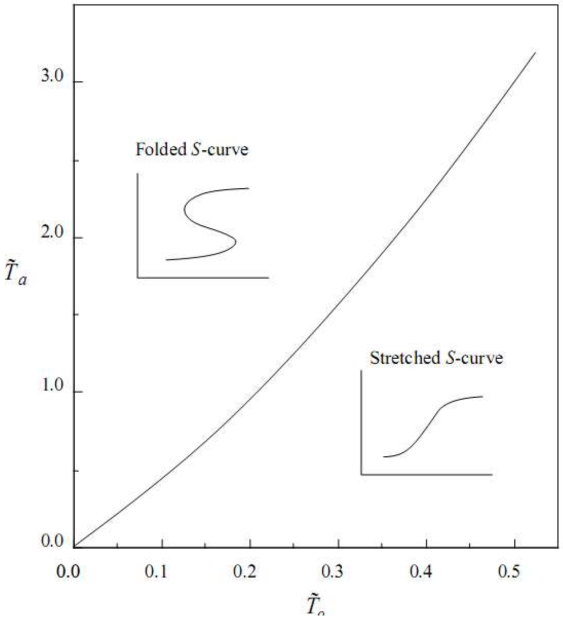
$$\left(\frac{d\ln Da_C}{d\tilde{T}_f}\right)_{\text{cr}} = 0$$



- (8.1.23) yields the two roots

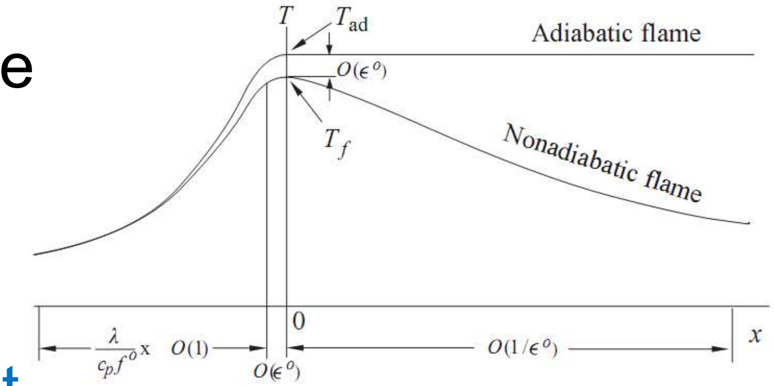
$$\tilde{T}_{f,\,\text{cr}} = \frac{(\tilde{T}_{\text{ad}} + \tilde{T}_o) \pm \{1 - 4(\tilde{T}_o\tilde{T}_{\text{ad}}/\tilde{T}_a)\}^{1/2}}{2(1+1/\tilde{T}_a)}. \qquad (8.1.29)$$

- Folding possible when {·} > 0 in (8.1.29). Otherwise S-curve is stretched for:
    - Low activation energy reactions
    - High initial temperatures



Premixed Flame Extinction (through Heat Loss) (1/3)

- The standard flame, being adiabatic, does not exhibit any extinction behavior, i.e. finite f^o for finite Y_u.
- Heat loss lowers flame temperature from T_{ad}, leading to **abrupt** extinction, at **finite** Y_u. System becomes non-conservative
- Radiation from flame is an inherent heat loss mechanism



- Assume loss occurs only in the preheat zone, and with L being a loss coefficient, then amount of loss is

$$q^- = \int_0^{\ell_D} L\,dx \approx \ell_D L \approx \frac{\lambda / c_p}{f} L$$

Premixed Flame Extinction (2/3)

- Overall energy conservation
  - ○ $fc_p(T_{\mathrm{ad}} - T_u) = fc_p(T_f - T_u) + \frac{\lambda / c_p}{f} L \,.$ (8.4.4)

    $T_f = T_{\mathrm{ad}}(1 - \frac{\lambda / c_p^2}{f^2 T_{ad}} L) = T_{ad}(1 - L' / \tilde{f}^2)$ (8.4.4')
  - ○ $L' = \frac{\lambda / c_p^2}{(f^o)^2 T_{ad}} L; \ \tilde{f} = f / f^o$ (A)
- In analogy to standard flame result

  $(f^o)^2 = \frac{(\lambda / c_p) w^o}{Ze}; \ \ w^o = \exp(-E_a / R^0 T_{ad})$ (B)

  we can write

  $(f)^2 = \frac{(\lambda / c_p) w}{Ze}; \ \ w = \exp(-E_a / R^0 T_f)$ (C)
- Using (8.4.4') in w

  $w \sim \exp[-(E_a / R^0)/(1 - L' / \tilde{f}^2)] = \exp(-E_a / R^0) \exp(-\tilde{L} / \tilde{f}^2)$

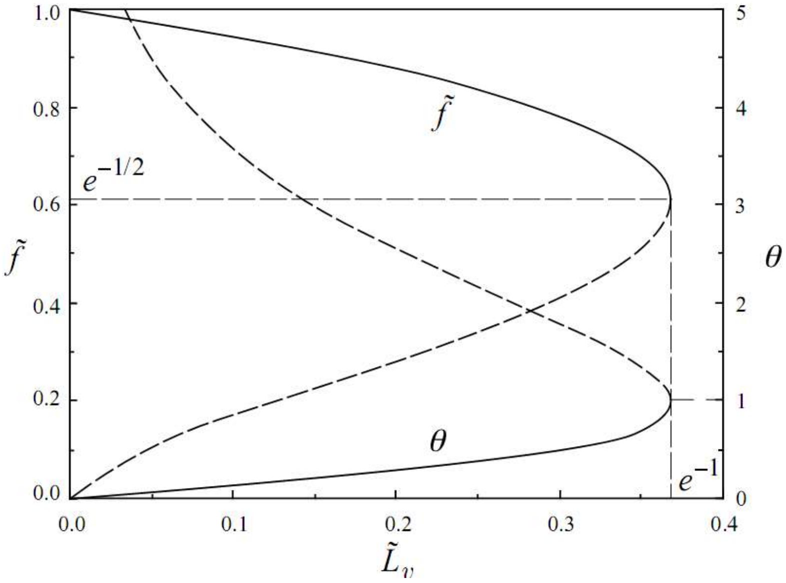
  $\tilde{L} = (E_a / R^0) L'$ (D)

Premixed Flame Extinction (3/3)

- C/B using D:
  - $\tilde{f}^2 = (f/f^o)^2 = w/w^o = \exp(-\tilde{L}/\tilde{f}^2)$,

    from which $\boxed{\tilde{f}^2 \ln \tilde{f}^2 = -\tilde{L}\ .}$ (8.4.9)
- (8.4.9) is the generalized equation governing flame propagation with loss.
  - For $\tilde{L} \equiv 0, \tilde{f} = 1, f = f^0$
  - Extinction, turning point:

    $$\left(\frac{d\tilde{L}}{df^2}\right)_{ex} = 0$$
  - Solving: $\boxed{\tilde{L}_E = e^{-1}, \tilde{f}_E = e^{-1/2}}$



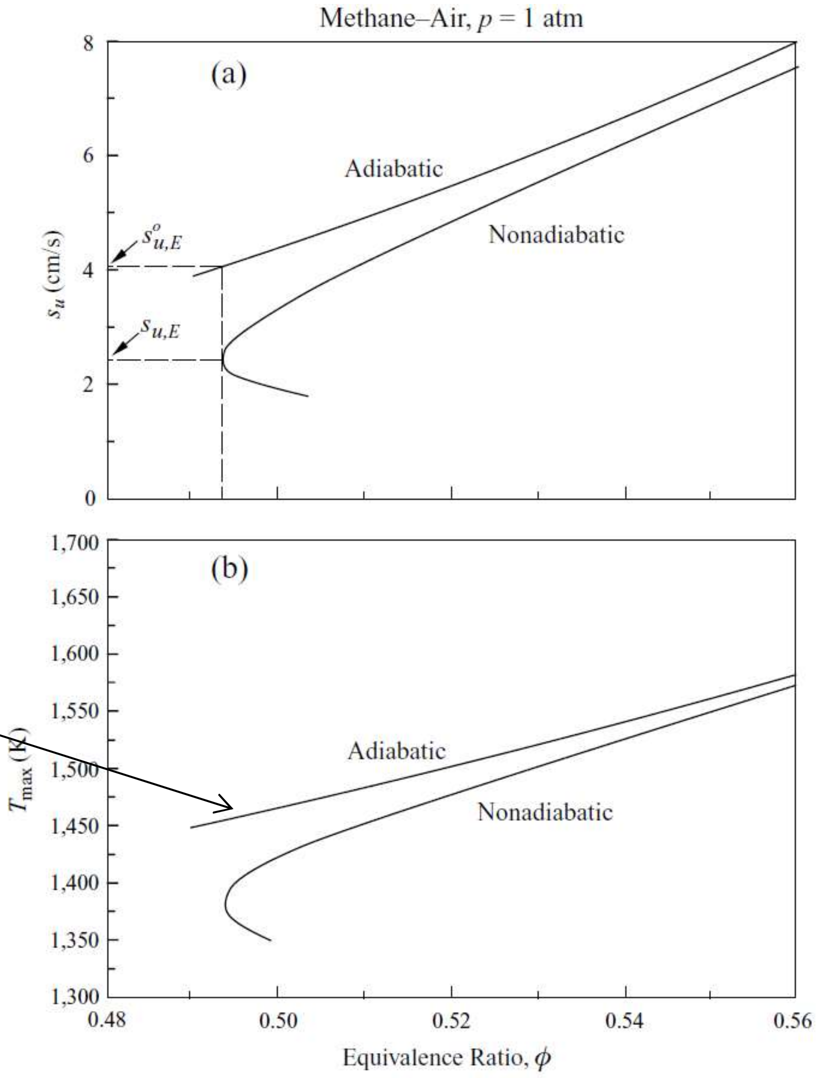
Other Limit Phenomena

- Flammability Limits:
  - For given mixture temperature and pressure, the leanest and richest concentrations beyond which flame propagation is absolutely not possible
  - Set the ultimate boundaries for extinction

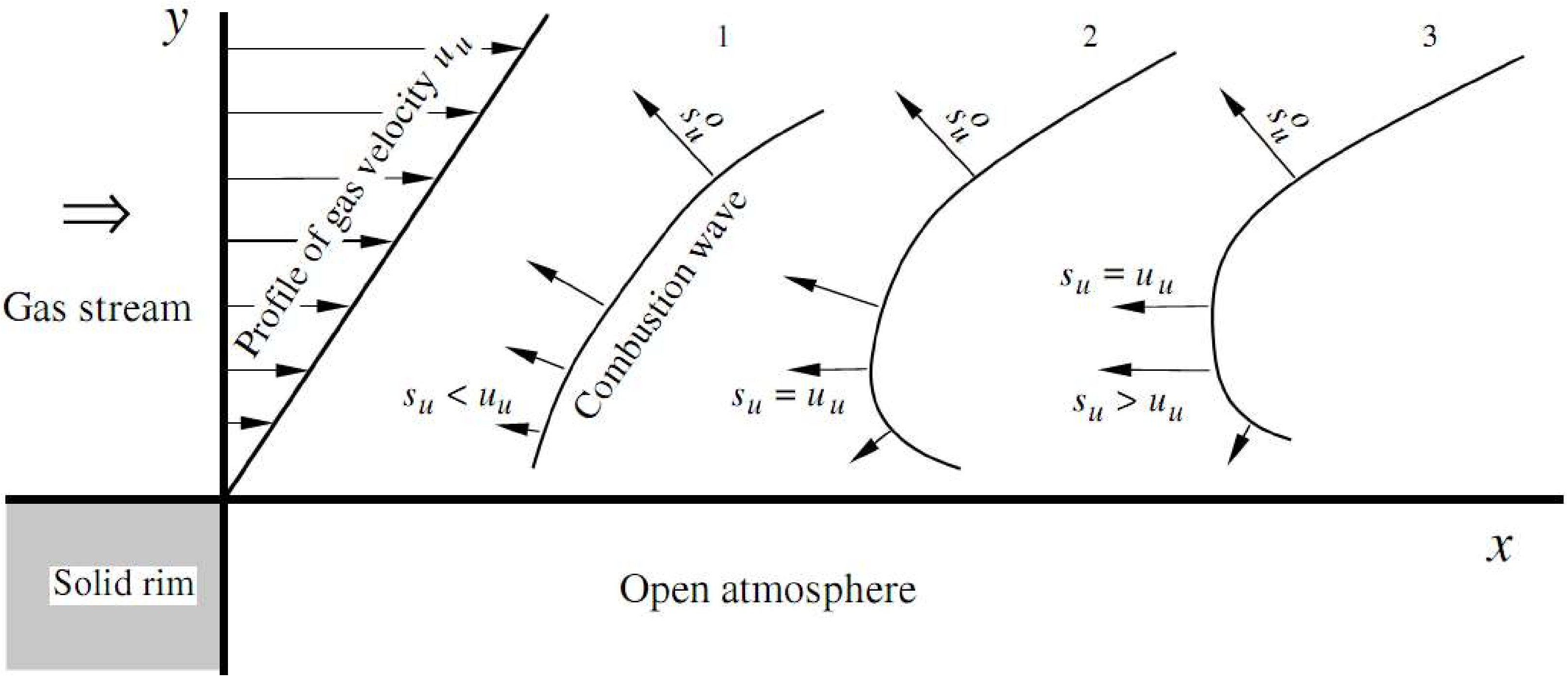
- Blowoff and Flashback
  - Consequence of lack of dynamic balance between flame speed and flow speed
  - Has nothing to do with extinction and ignition

Flammability Limit

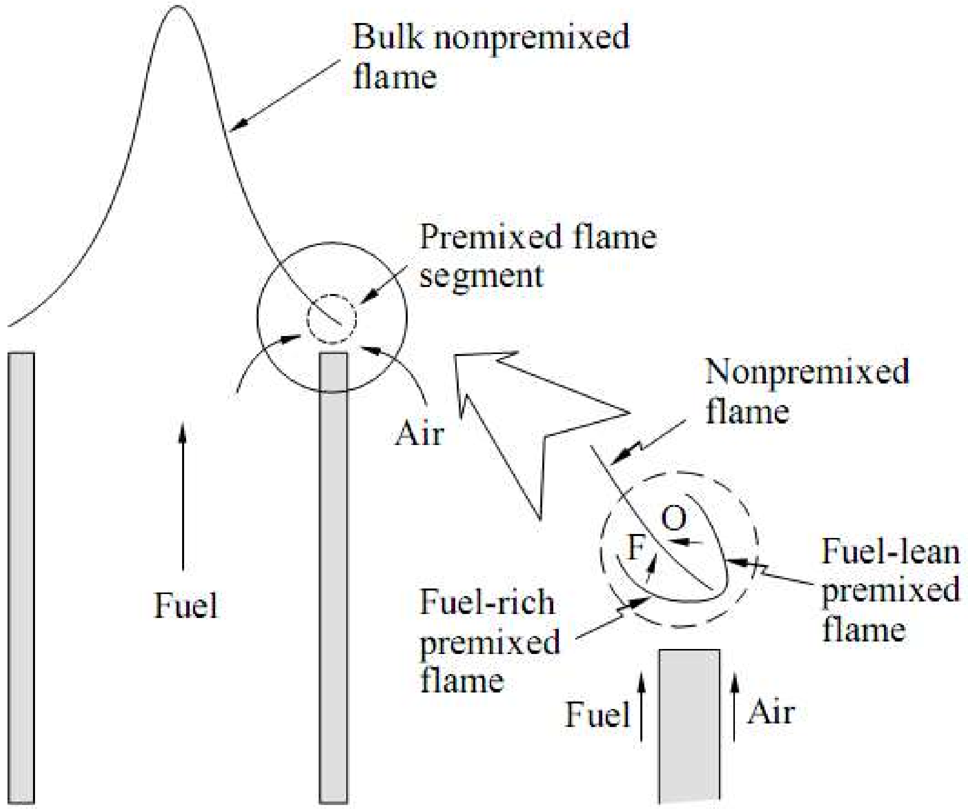
- Simulation for methane/air mixtures shows
  - Extinction $\phi = 0.493$
    Empirical: $\phi = 0.48$
  - $f/f^o = e^{-1/2} \approx 0.6$
  - $(T_f)_{ext} \approx 1{,}450$ K
- Extinction temperature result corroborates with the concept of limit temperature for hydrocarbon fuels



Stabilization Mechanism of Premixed Flame at Burner Rim

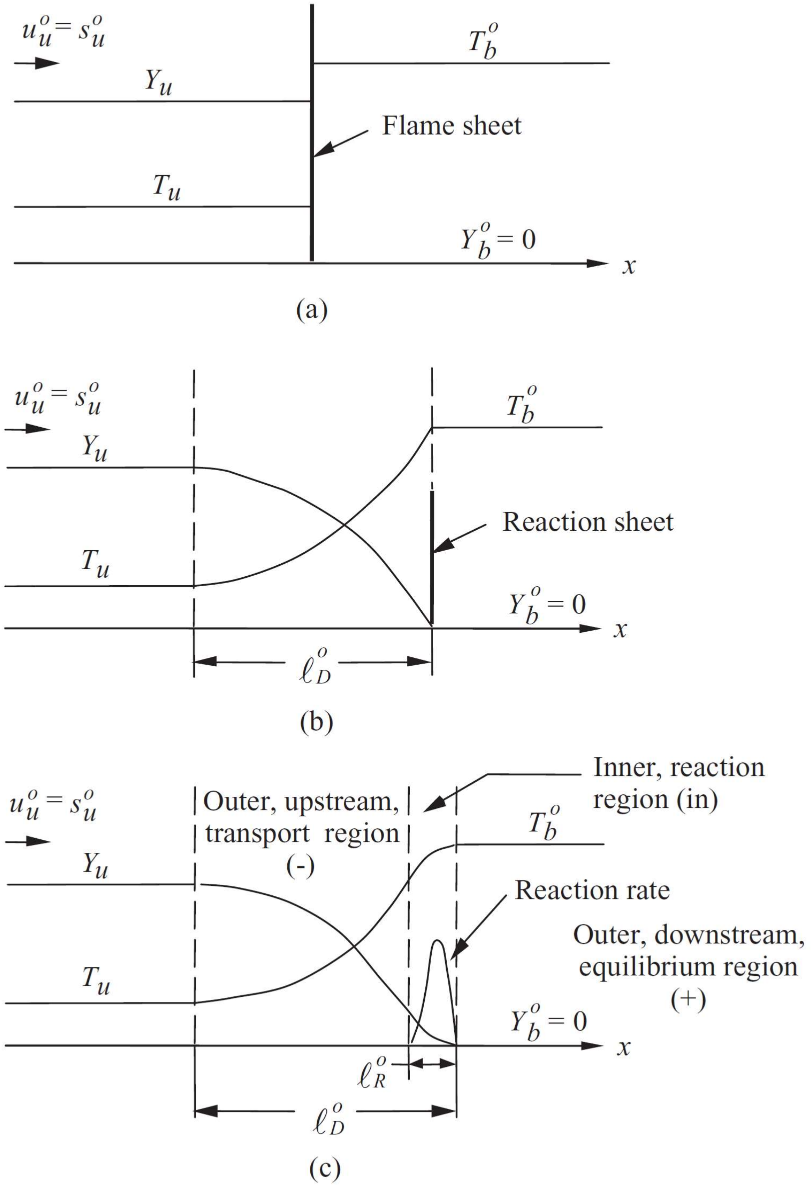


Triple-Flame Stabilization Mechanism of Nonpremixed Flame at Burner Rim



3. Aerodynamics of Laminar Flames

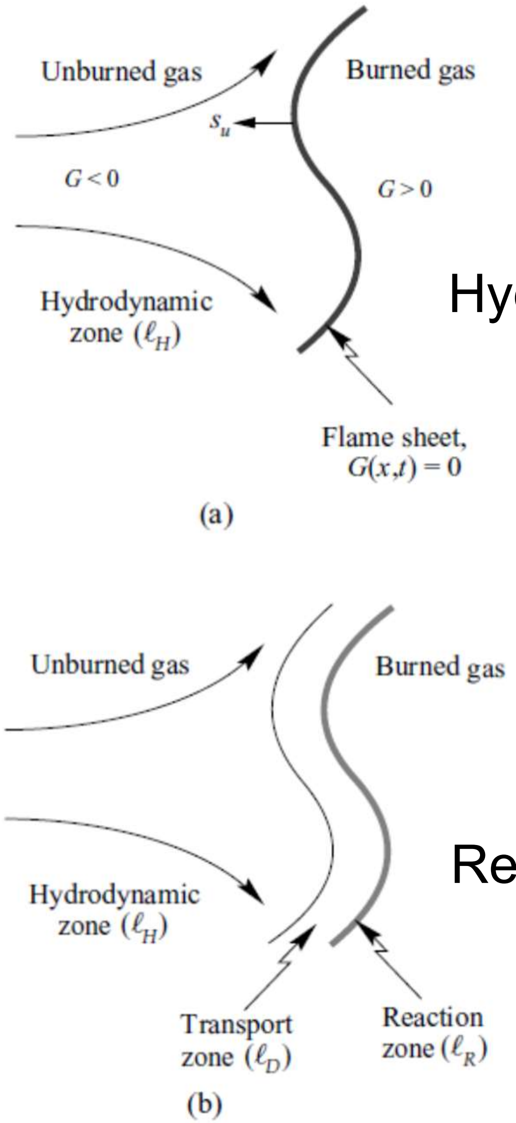
Standard Flame vs. Real Flame (1/2)



(a)

(b)

(c)



(a)

(b)

Hydrodynamic Limit

Reaction-Sheet Limit

Standard Flame vs. Real Flame (2/2)

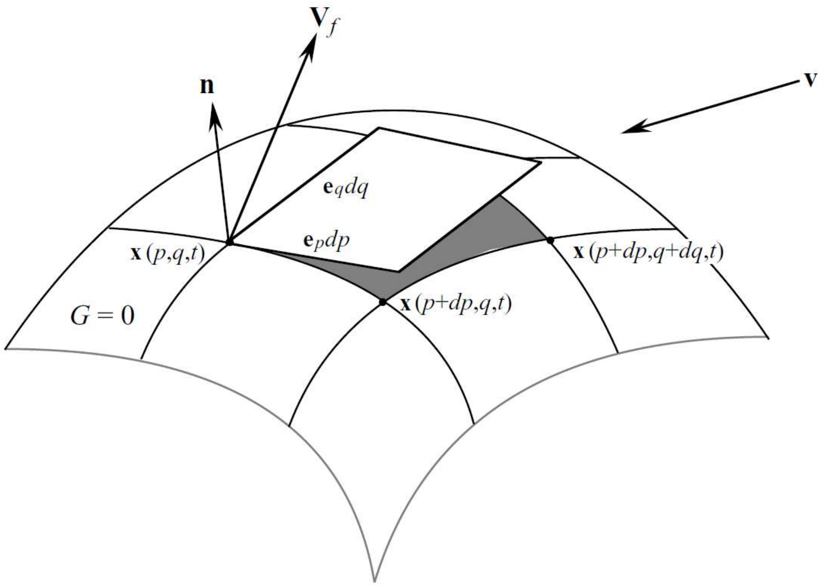
- Standard 1D Planar Flame
  - $\boxed{f^o = f^o(q_c, Le_{i,j}, w_k)}$
  - System is conservative, $\boxed{T_b^o = T_b^o(q_c)}$
  - $f^o \sim \sqrt{Le_{i,j}}$
- General Stretched Flame
  - $\boxed{f = f(q_c, Le_{i,j}, w_k; Ka, L)}$
    - Ka: Karlovitz number, representing aerodynamic effects of flow nonuniformity, flame curvature, flame/ flow unsteadiness
    - L: Generalized loss parameter
  - System could become locally or globally nonconservative

    $\boxed{T_b = T_b(q_c, Le_{i,j}, w_k; Ka, L)}$
  - O(ε) modification of flame temperature leads to O(1) change in flame speed ⇒ locally intensified burning or extinction

The Stretch Rate

- Definition: Lagrangian time derivative of the logarithm of area A of a surface $\kappa = \frac{1}{A}\frac{dA}{dt}$

$\mathbf{A}(p,q,t) = (\mathbf{e}_p dp) \times (\mathbf{e}_q dq) = (dpdq)\mathbf{n}$



- Letting $\mathbf{V}_{f,t} = \mathbf{v}_{s,t}$

$$\boxed{\kappa = \nabla_t \cdot \mathbf{v}_{s,t} + (\mathbf{V}_f \cdot \mathbf{n})(\nabla \cdot \mathbf{n})}$$

$$\mathbf{v}_{s,t} = \mathbf{n} \times (\mathbf{v}_s \times \mathbf{n})$$

- Sources of stretch:

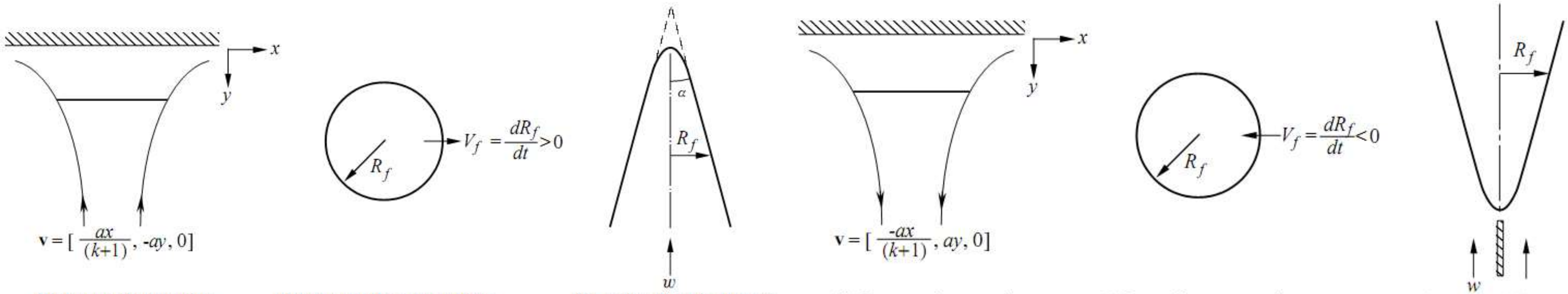
Flow nonuniformity: $\mathbf{v}_s$

Flame curvature: $\mathbf{n}$

Flame oblique to flow $\mathbf{v}_s \times \mathbf{n} \neq 0.$

Flame unsteadiness ($\mathbf{V}_f \neq 0$), with curvature $\nabla \cdot \mathbf{n} \neq 0$

Examples of Stretched Flames



(a) Forward stagnation flame

(b) Outwardly propagating spherical flame

(c) Axisymmetric Bunsen flame

(d) Rearward stagnation flame

(e) Inwardly propagating spherical flame

(f) Inverted flame

- Stagnation Flame: $\mathbf{v} = \left\{ \frac{a}{(k+1)} x, -ay, 0 \right\}, \kappa = a > 0$
- Expanding Spherical Flame: $\kappa = \frac{2}{R_f} \frac{dR_f}{dt} > 0$
- Bunsen Flame: $\kappa = \frac{w \sin 2a}{2R_f} < 0$
- Each of above has its opposite analog

Effects of Stretch (1/2)

- Hydrodynamic stretch: Flame-sheet limit
  - **Tangential velocity gradient**: changes flame surface area and hence total burning rate, $\int f\,\mathrm{dA}$
  - **Normal velocity**: Balances flame speed
  - **Net effect**:

    Distortion of flame geometry

    Modifies total burning rate (e.g. higher burning rate in turbulent flame through surface wrinkling)

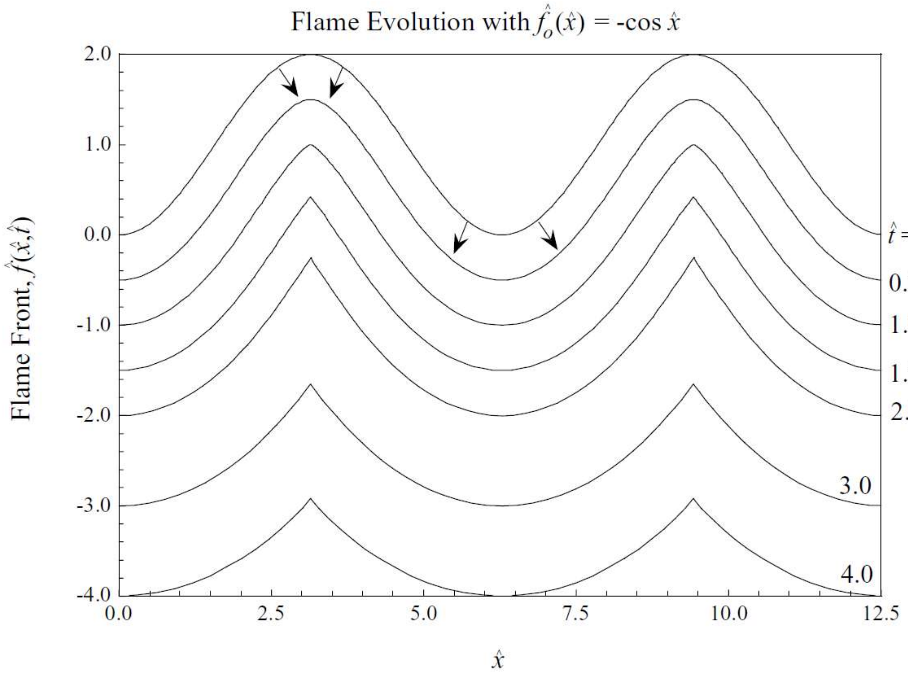
Effects of Stretch (2/2)

- Flame stretch: reaction-sheet limit
  - Tangential velocity affects normal mass flux f_b entering reaction zone
  - For $Le \neq 1$, modifies temperature and concentration profiles differently ⇒ modifies total enthalpy and flame temperature

    ⇒ locally non-conservative
- Hydrodynamic stretch and flame stretch strongly coupled
- Stretch (i.e. convection) in thin reaction zone is unimportant

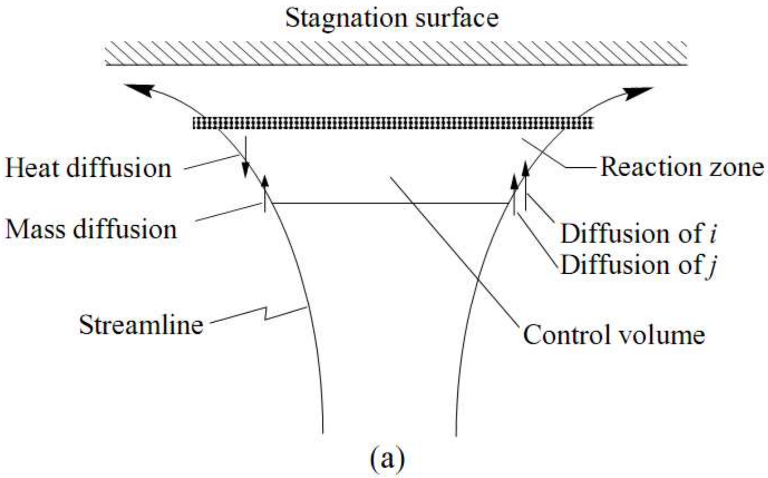
Example of Hydrodynamic Stretch:
Corner Formation in Landau Propagation

- Landau propagation: $s_u = s_u^o$
- Concave segment develops into a corner; convex segment flattens
- Positive curvature and hence stretch dominate
- Mathematically described by Burgers equation, similar to that for shock formation



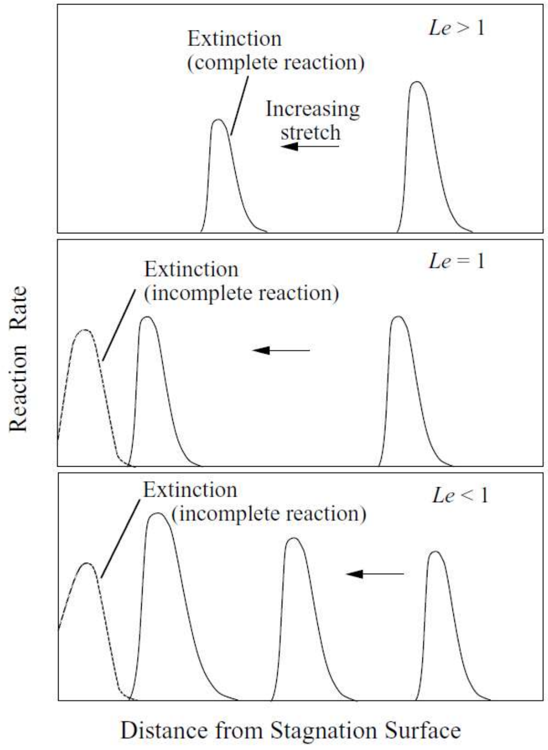
Flame Stretch due to Flow Straining: The Stagnation Flame (1/2)

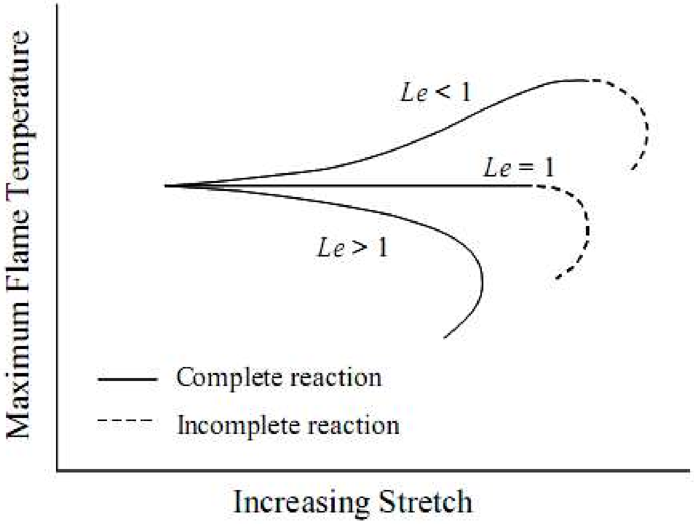
- Stretch is positive, $\kappa>0$; situation reversed for $\kappa<0$
- Consider total energy conservation in control volume
  - Diffusion: normal to reaction sheet
  - Convection: along (divergent, $\kappa>0$) streamline
- $Le>1$: More heat loss than reactant mass gain $\Rightarrow$ system sub-adiabatic
- With increasing κ:
  - Flame temperature decreases, until extinction
  - Flame at finite distance from stagnation surface at extinction
  - Complete reactant consumption at extinction



The Stagnation Flame (2/2)

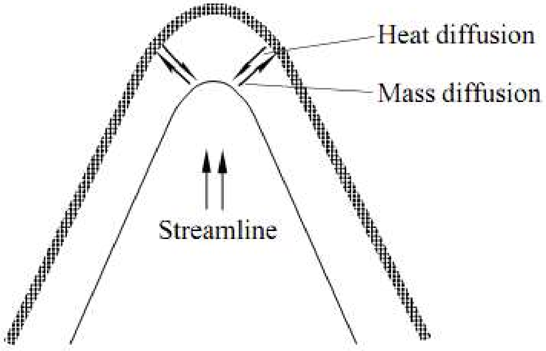
- $Le<1$: More reactant mass gain than heat loss $\Rightarrow$ system super-adiabatic
- With increasing κ:
  - Flame temperature increases, extinction not possible as long as the flame is away from surface
  - Eventually flame is pushed to the stagnation surface, leading to incomplete reaction and eventually extinction





Flame Stretch due to Flame Curvature: The Bunsen Flame

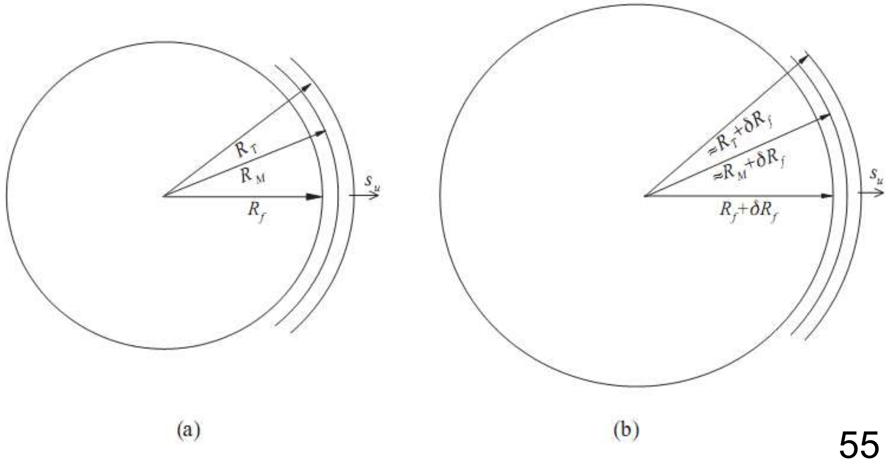
- For the concave flame curvature, $\kappa<0$; expect opposite response from the $\kappa>0$ stagnation flame
- (Negative) flame curvature focuses heat and defocuses mass in the diffusion zone
  - o $Le>1$: Super-adiabatic, burning at flame tip intensified relative to shoulder
  - o $Le<1$: Sub-adiabatic, burning at tip weakens, lead to extinction (i.e. tip opening)



(b)

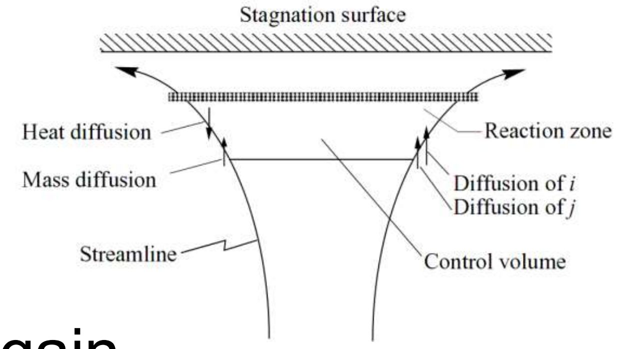
Flame Stretch due to Flame Motion: the Unsteady Spherical Flame

- For the expanding flame, κ >0 ; expect similar behavior as the stagnation flame.
- An increase in flame radius R_f by δR_f leads to an increased amount ($4\pi R_T^2 \delta R_f$) of heat transferred to the preheat zone, and ($4\pi R_M^2 \delta R_f$) of mass transferred.
  - o $Le>1$: Sub-adiabatic, more heat transferred away
  - o $Le<1$: Super-adiabatic, less heat transferred away
- Stretch rate, κ = $(2/\mathrm{R}_f)(dR_f/dt)$ continuously decreases with increasing R_f , approaching the planar limit



Analysis (1/2)

(Based on Stagnation Flame Analogy)



- Energy loss/ gain in control volume

$$\boxed{f_u c_p (T_{ad} - T_f) = (\lambda \frac{T_f - T_u}{\ell_T})(\frac{\kappa}{s_u / \ell_T}) - (q_c \rho D \frac{Y_u}{\ell_M})(\frac{\kappa}{s_u / \ell_M})}$$

  - $\lambda (T_f - T_u)/\ell_T$ Normal heat flux; loss
  - $(q_c \rho D Y_u)/\ell_M$ Normal chemical energy flux; gain
  - $\kappa / (s_u / \ell)$ Fraction of flux diverted out of control volume due to stretch

- In nondimensional form

$$\tilde{T}_{ad} - \tilde{T}_f = -Ka^0 (Le^{-1} - 1) / \tilde{f}^2 = -S^0 / \tilde{f}^2 \qquad \text{(A)}$$

  - $S^0 = Ka^0 (Le^{-1} - 1)$
  - Karlovitz number, $Ka^0 = \kappa / (s_u^0 / \ell_T^0)$; nondimensional stretch rate

Analysis (2/2)

- Following same analysis as that for premixed flame with heat loss, yields

$$\boxed{\tilde{f}_u^2 \ln \tilde{f}_u^2 = \sigma^o,} \qquad \boxed{\sigma^o = Ze^o S^o = Ze(Le^{-1} - 1)Ka^o}$$

- $-\sigma^o$ has the same role as *L* in (8.4.9), showing extinction for $\sigma<0$ (i.e. loss due to stretch)
- Further define **Markstein number** as

$$\boxed{Ma^o = Ze^o\left(Le^{-1} - 1\right)}$$

- Then: $\sigma^o = Ma^o Ka^o$

Response of Stretched Flame

- From (A): $T_f (>,<) T_{\mathrm{ad}}$ for $S^o (<, >) 0$

  Since $S^o = (Le^{-1} - 1)Ka^o$, influence is lumped for nonequidiffusion and stretch.

  $T_f > T_{\mathrm{ad}}$ for $(Ka^o > 0, Le < 1)$ or $(Ka < 0, Le > 1)$

  $T_f < T_{\mathrm{ad}}$ for $(Ka^o > 0, Le > 1)$ or $(Ka < 0, Le < 1)$

  $T_f \equiv T_{\mathrm{ad}}$ for either $Ka^o = 0$ $(Le \neq 1)$ or $Le = 1$ $(Ka \neq 0)$
- Super-lumped parameter for flame speed:

  $\sigma^o = Ze^o(Le^{-1} - 1)Ka^o$

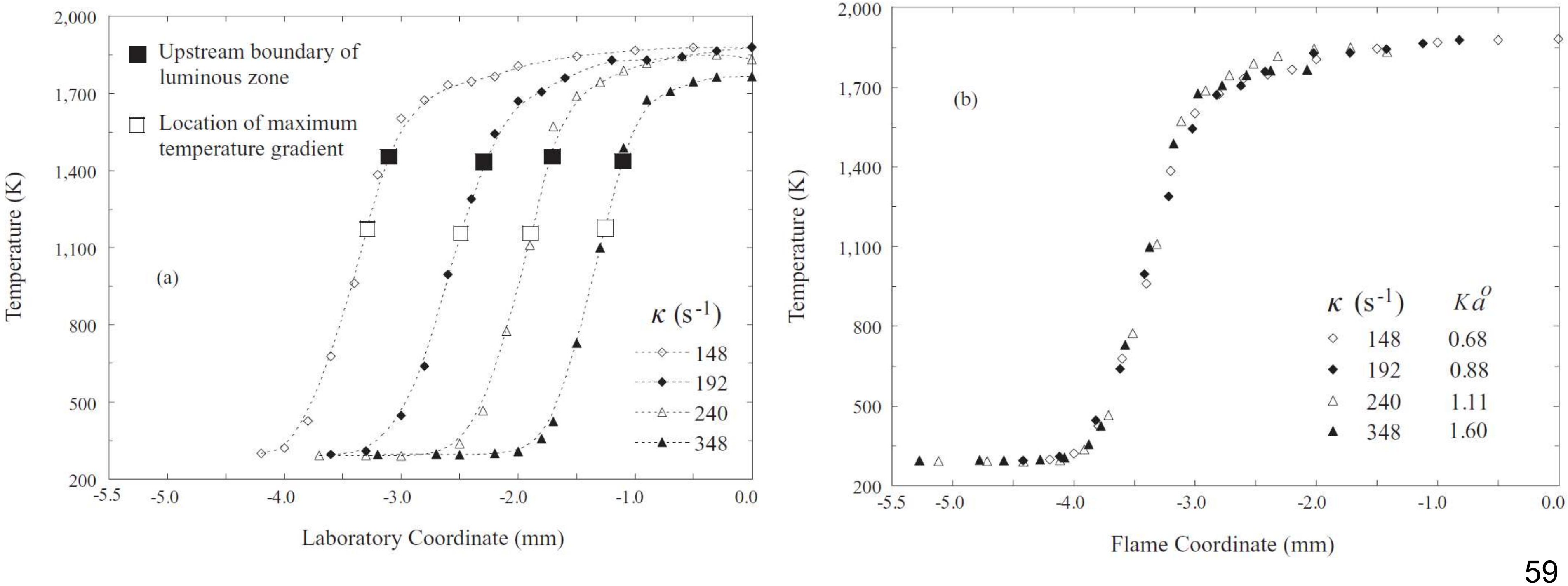
  Reactivity χ nonequidiffusivity χ stretch
- Markstein number, $Ma^o = Ze^o(Le^{-1} - 1)$:

  Reactivity χ nonequidiffusivity; a property of the mixture.

Results on Stretched Equidiffusive Flame

- Stretched flame ($\kappa \neq 0$) for equidiffusive mixture (Le = 1) is not affected by stretch:

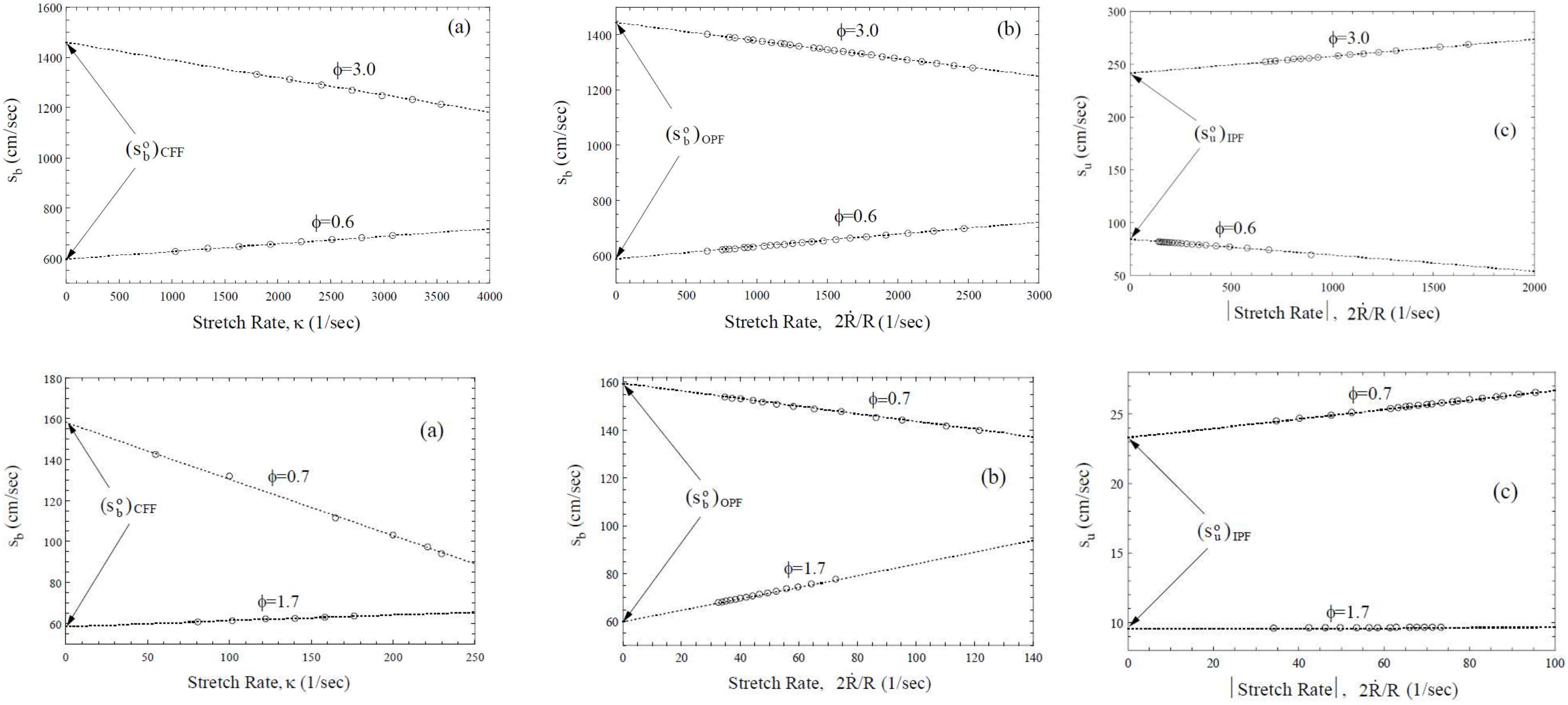
$$S^o=(Le^{-1}-1)\kappa \equiv 0$$



Nonequidiffusive Mixtures

Mixture for Simulation	$Le \neq 1$ Interpretation	$D_i \neq D_j$ Interpretation
Lean hydrogen–air	$Le_{H_2} < 1$	$D_{H_2} > D_{CH_4} > D_{O_2} > D_{C_3H_8}$
Lean methane–air	$Le_{CH_4} < 1$	
Rich propane–air	$Le_{O_2} < 1$	
Rich hydrogen–air	$Le_{O_2} > 1$	
Rich methane–air	$Le_{O_2} > 1$	
Lean propane–air	$Le_{C_3H_8} > 1$	

Results on Stretched Nonequidiffusive Flame



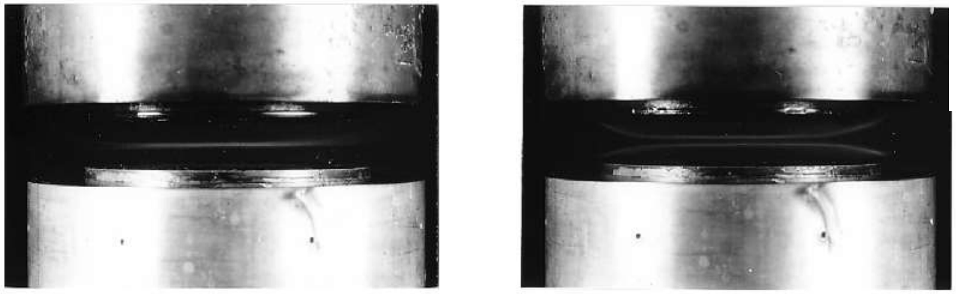
(a) Counterflow flame

(b) Outwardly propagating flame

(c) Inwardly propagating flame

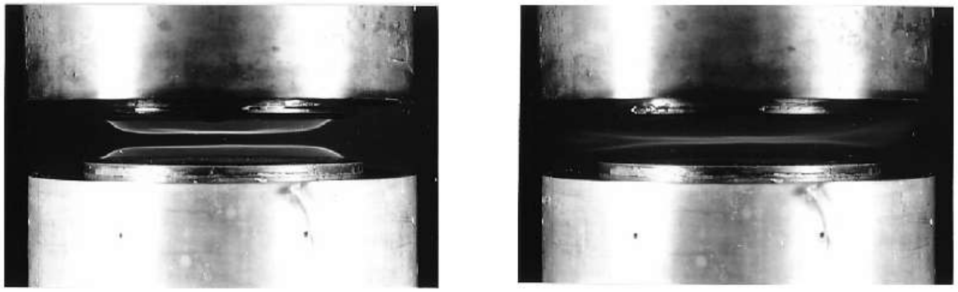
Flame Images

$\kappa > 0$



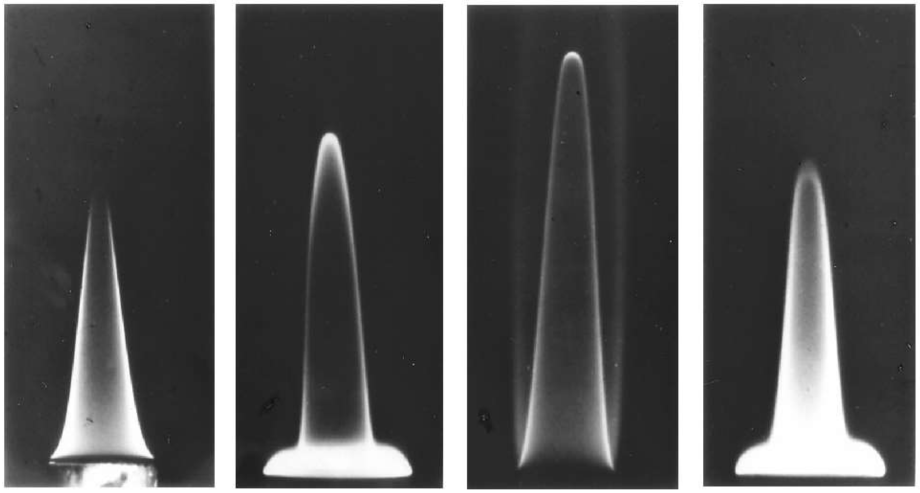
(a) Lean methane–air: $Le < 1, S^o > 0$

(b) Rich methane–air: $Le > 1, S^o < 0$



(c) Lean propane–air: $Le > 1, S^o < 0$

(d) Rich propane–air: $Le < 1, S^o > 0$



(a)

Rich propane–air
($Le < 1, S^o < 0$)

(b)

Lean propane–air
($Le > 1, S^o > 0$)

(c)

Rich methane–air
($Le > 1, S^o > 0$)

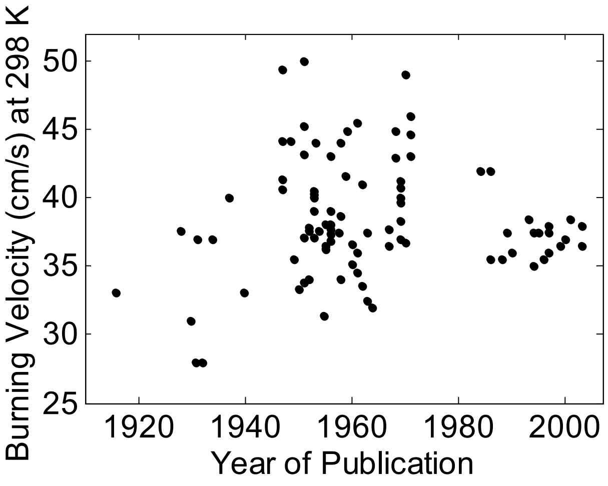
(d)

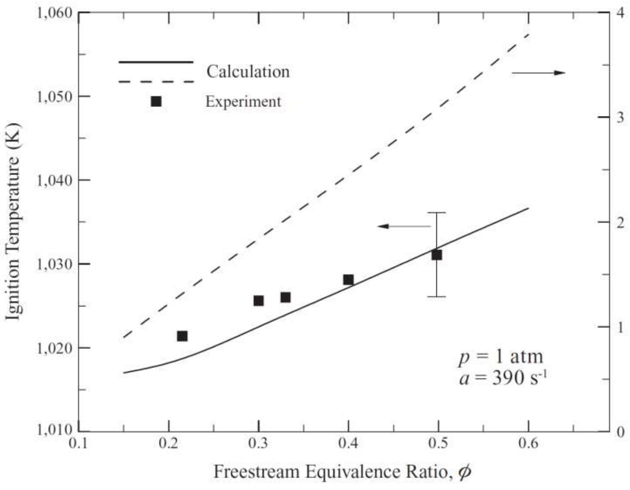
Lean methane–air
($Le < 1, S^o < 0$)

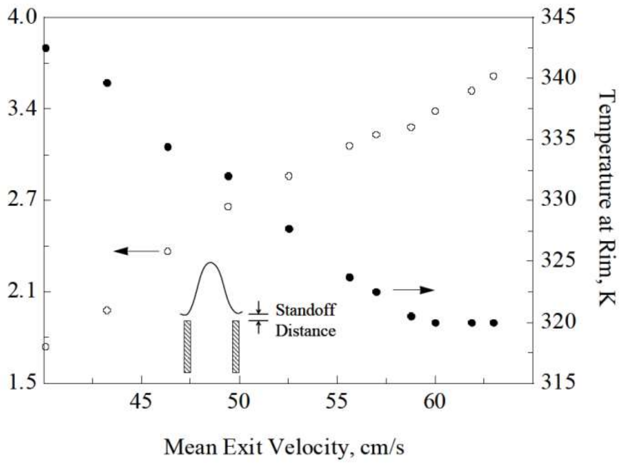
$\kappa < 0$

Further Implications of Stretched Flame Phenomena

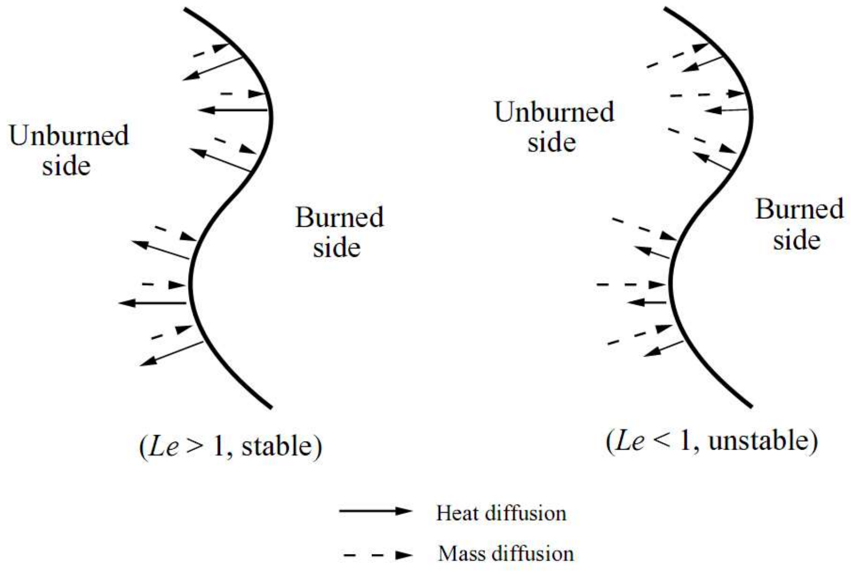
- Determination of laminar flame speeds
- Concentration and temperature modifications in flame chemistry
- Flame stabilization and blowoff



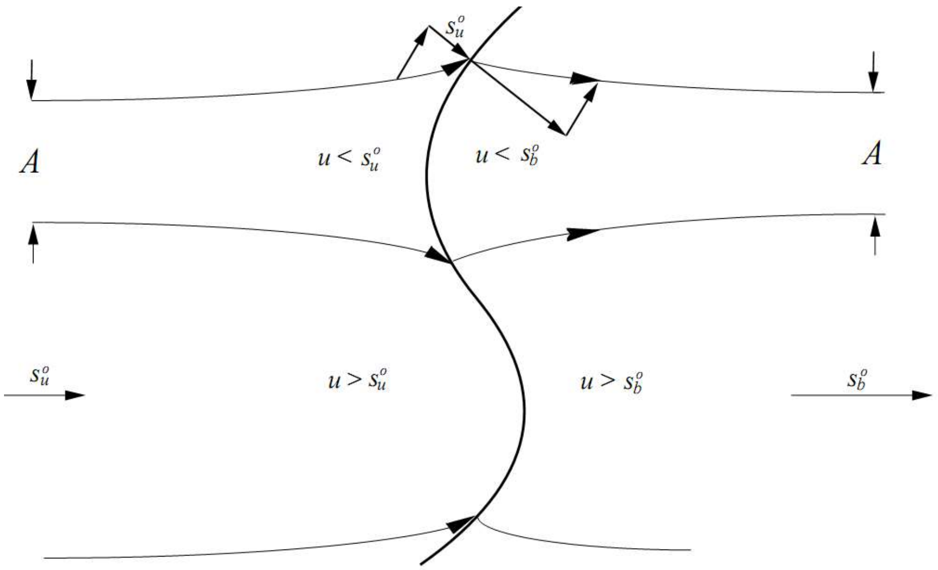




Flame Front Instabilities (1/2)

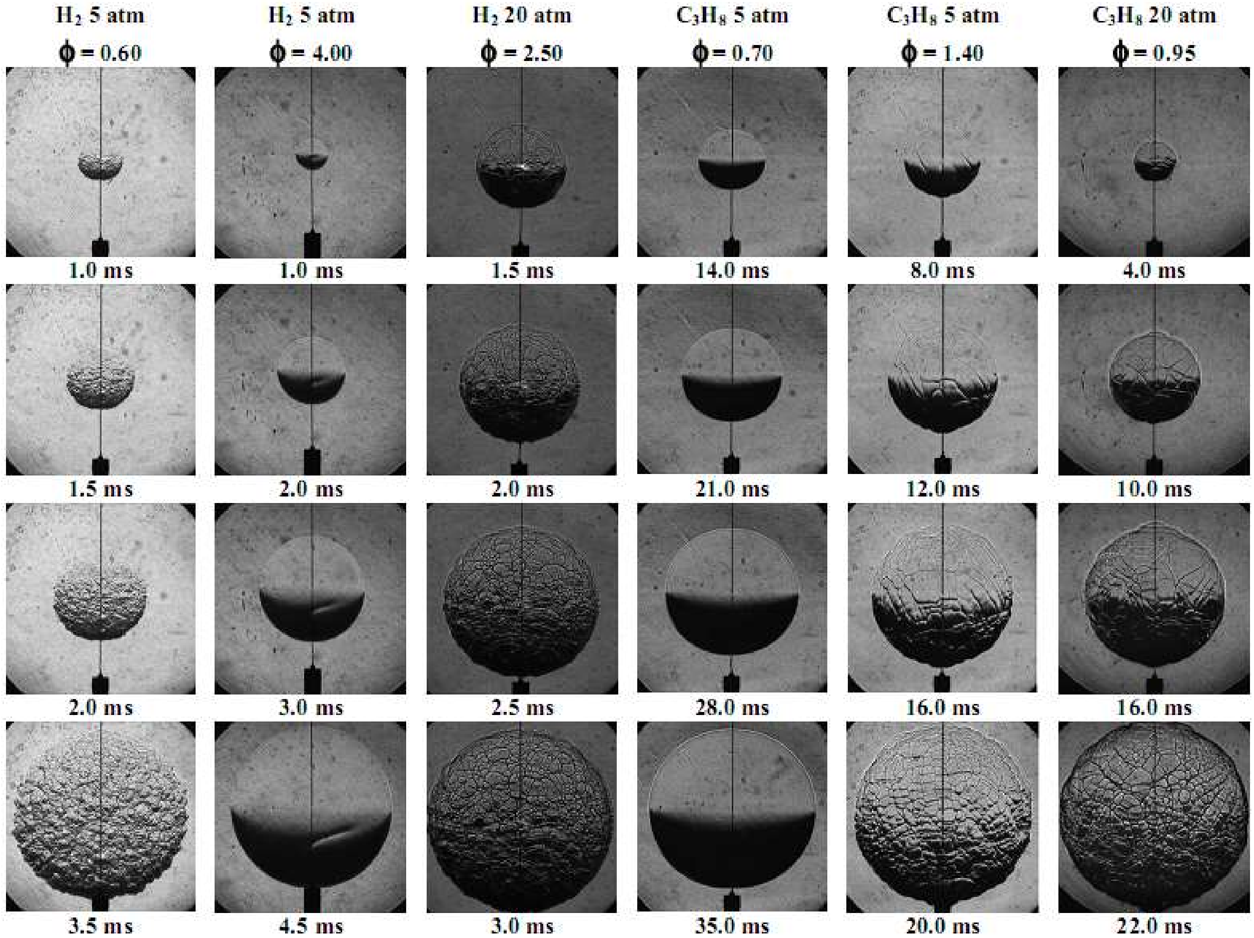


Diffusional Thermal Instability



Hydrodynamic Instability (Flame sheet, constant flame speed; density jump)

Flame Front Instabilities (2/2)



Diffusional-Thermal **DL** **Diffusional-Thermal** **DL**

Le<1 **Le>1** **Le>1** **Le>1** **Le<1** **Le>1**

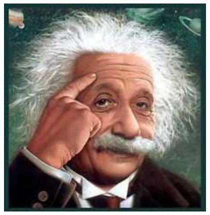
Closing Remarks of Day 4 Lecture (1/2)

- The standard premixed flame
  - **Concepts introduced**: asymptotic analysis; cold boundary difficulty; distinguished limit; flame structure based on one-step and detailed chemistry; extraction of global kinetic parameters
- Further studies:
  - Need chemical structure of hydrocarbon flames
  - Explain the lack of influence on laminar flame speed by: (a) low-temperature chemistry, and (b) molecular size for large n-alkanes
  - Is it possible to derive a semi-empirical expression for the laminar flame speed based on T_{ad} and extracted global kinetic parameters?

Closing Remarks of Day 4 Lecture (2/2)

- **Limit phenomena**: Extinction is due to insufficient reaction time while flame blowoff/out is due to imbalance between flame and flow speeds
- Extinction is in general caused by enthalpy loss in the preheat zone, leading to O(ε) reduction in flame temperature and O(1) reduction in flame speed
- Need to distinguish flame stabilization by auto-ignition or flame holding
- What is the fate of a freely-propagating flame to increasing strength of imposed strain rate?
- Need detailed study of the chemical structure of stretched flames

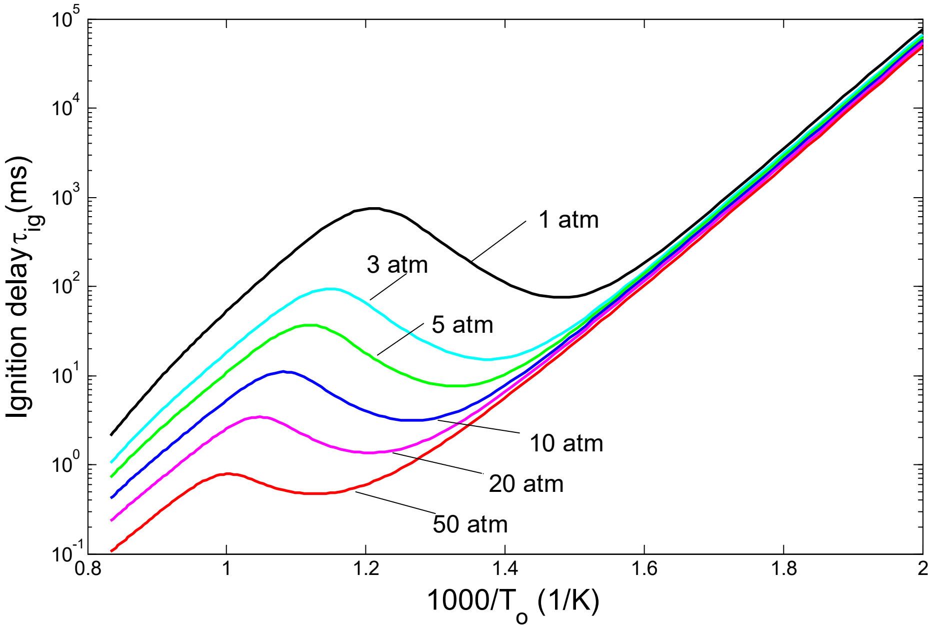
Day 4 Specials



1. Low-temperature, NTC flames
2. Pulsations in premixed and diffusion flames:
    a. Extinction
    b. Spiral patterns
3. Pulsation in self-propagating high-temperature synthesis

1. Low-temperature, NTC Flames

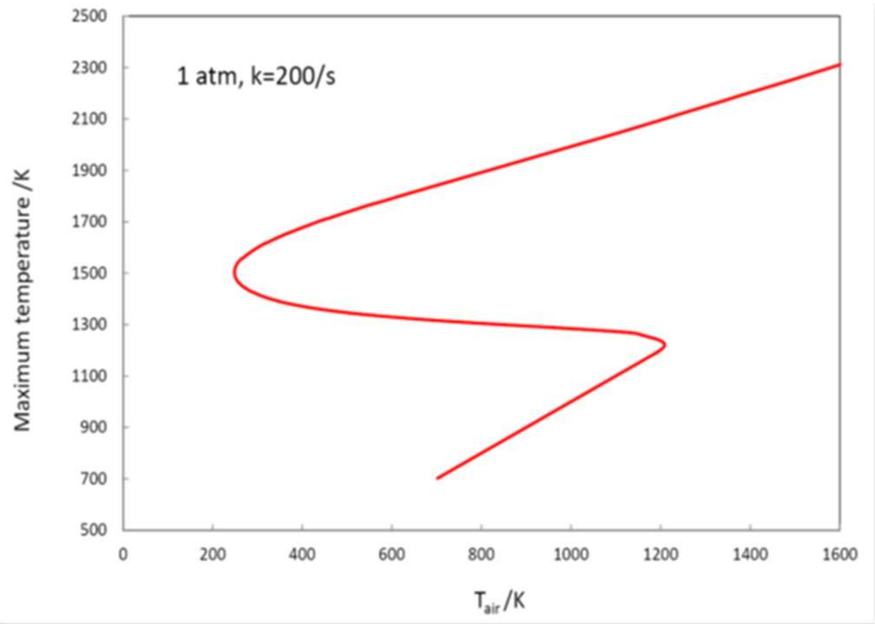
The Issue



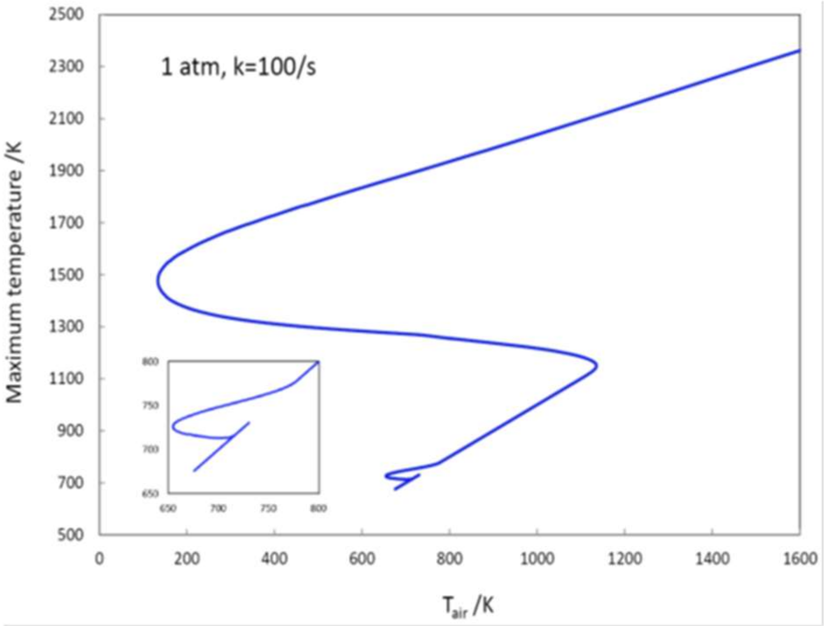
- NTC behavior observed for homogeneous mixtures in low- to intermediate-temperature range

- NTC behavior not observed in extensive counterflow experiments & simulations
  - ○ Finite residence time shifts ignition temperature to >1000K, hence moves ignition chemistry out of the NTC regime
  - ○ Can NTC behavior be manifested for:
    - ▪ Low strain rate flows?
    - ▪ High pressures?

NTC Behavior Predicted at Low Strain Rates !



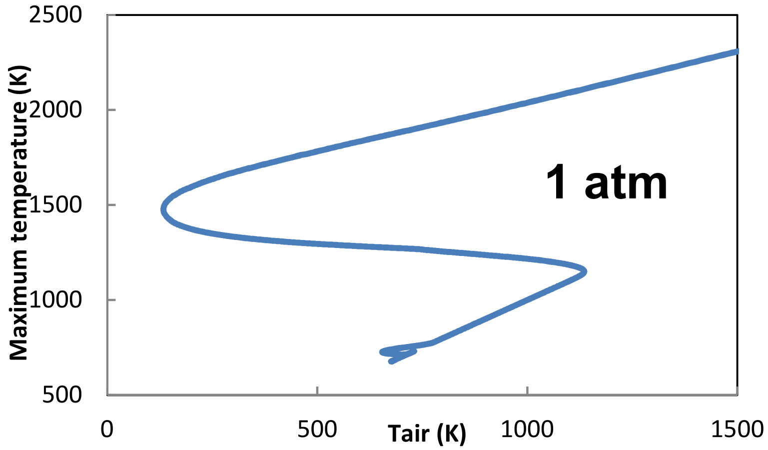
k = 200/s

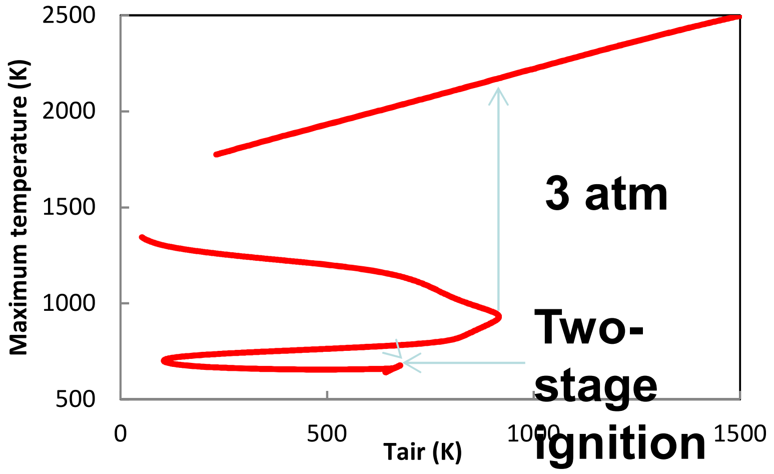


k = 100/s

Pressure:1 Atm.

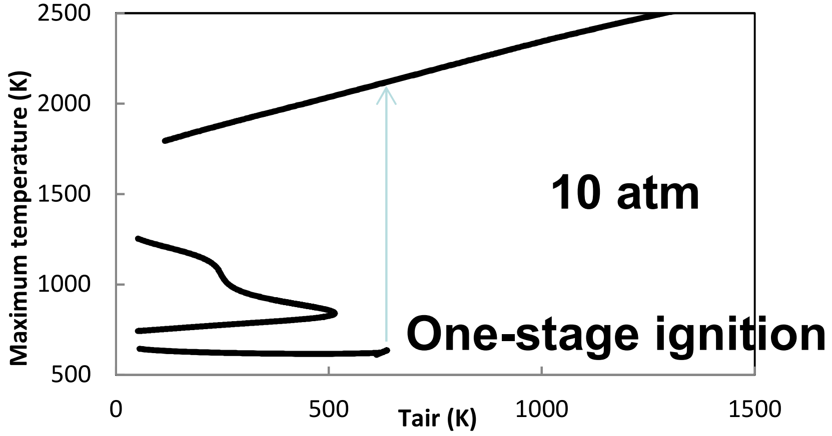
NTC Behavior Exaggerated with Increasing Pressure





Two-stage ignition

k = 100/s

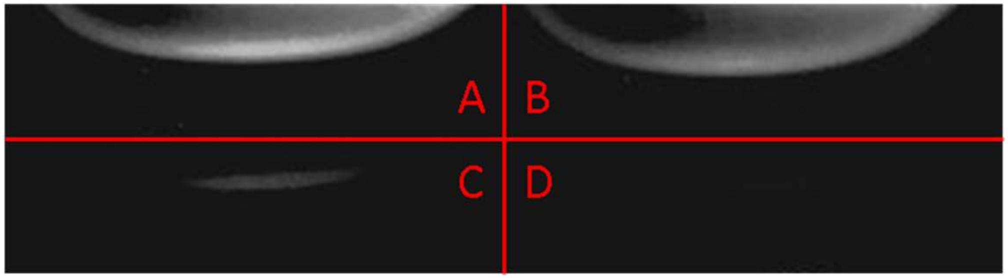


One-stage ignition

- At lower pressures, ignition occurs in two stages, final ignition controlled by high-temperature chemistry
- At higher pressures, ignition occurs in one stage, controlled by low-temperature chemistry

Experimental Observation of Nonpremixed LTC Flame

Infrared Images at Ignition (1 atm, strain rate: 60 /s)



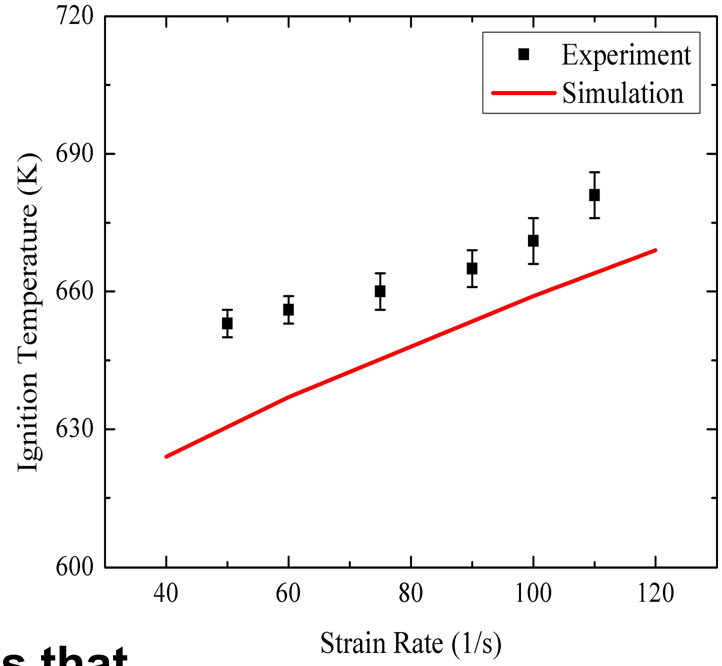
A: Air vs DME

B: N_2 vs DME

C: Ignition (Air vs DME)

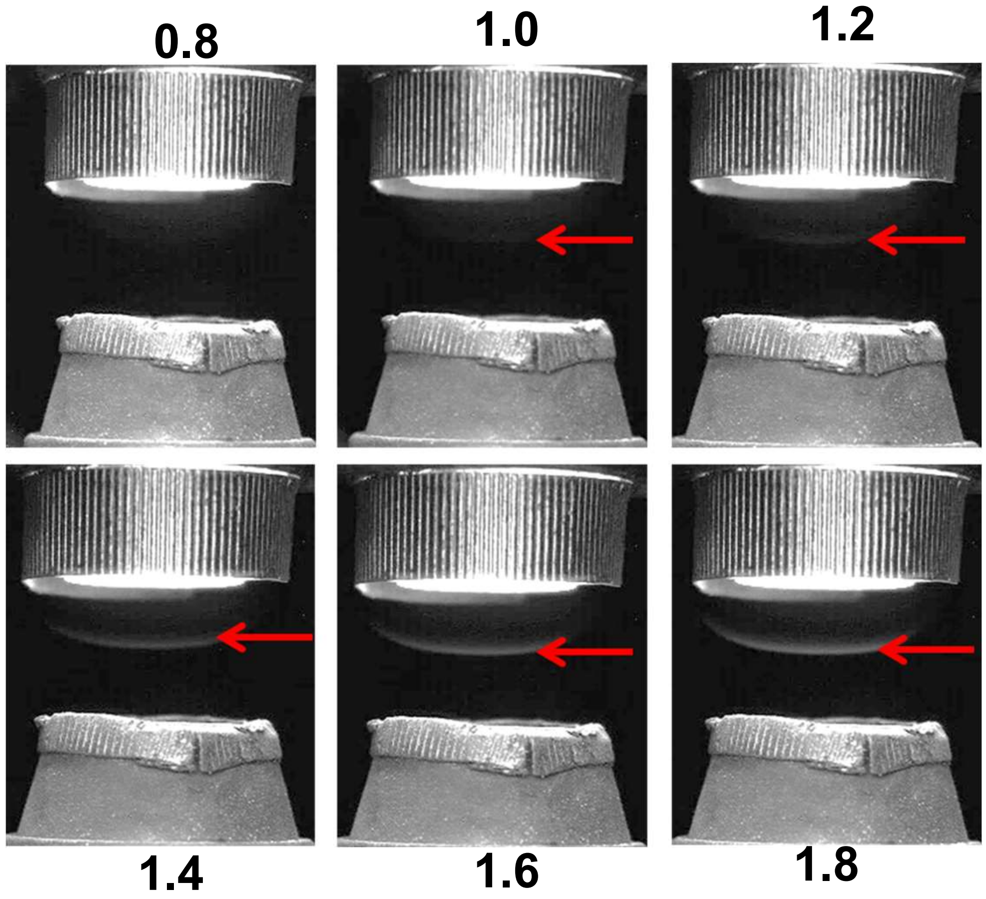
D: Ignition (N_2 vs DME)

Ignition Temperature



- **Detailed chemical structure study shows that such flames are governed by LTC**

Experimental Observation of Premixed LTC Flame

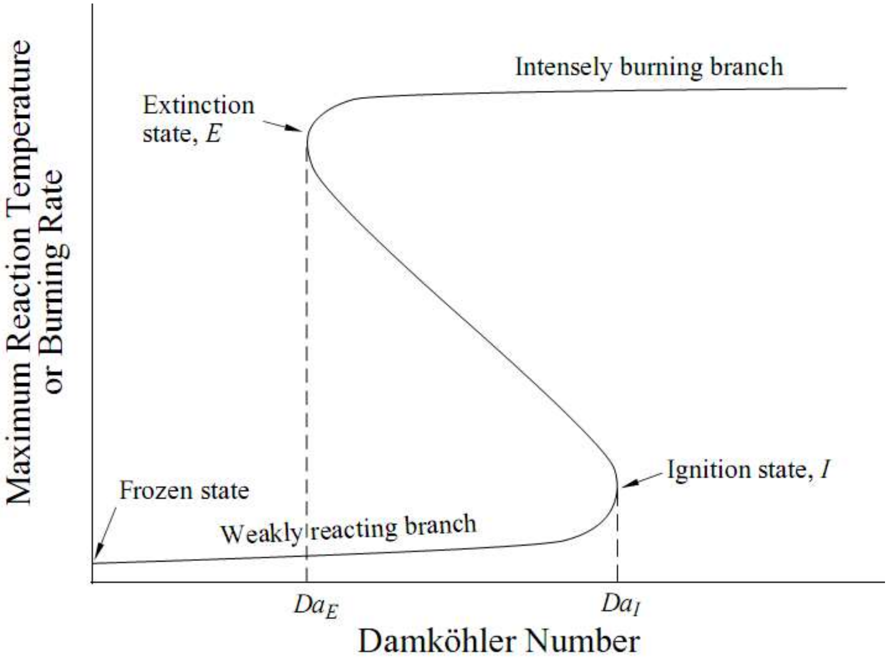


- Different behavior from hot flames
- Insensitive of flame location, implying small variation in flame speed with Φ variation
- Stronger chemiluminescence for richer cases

2a. Pulsating Extinction of Premixed and Diffusion Flames

The Issue:
Heightened Sensitivity Near Extinction

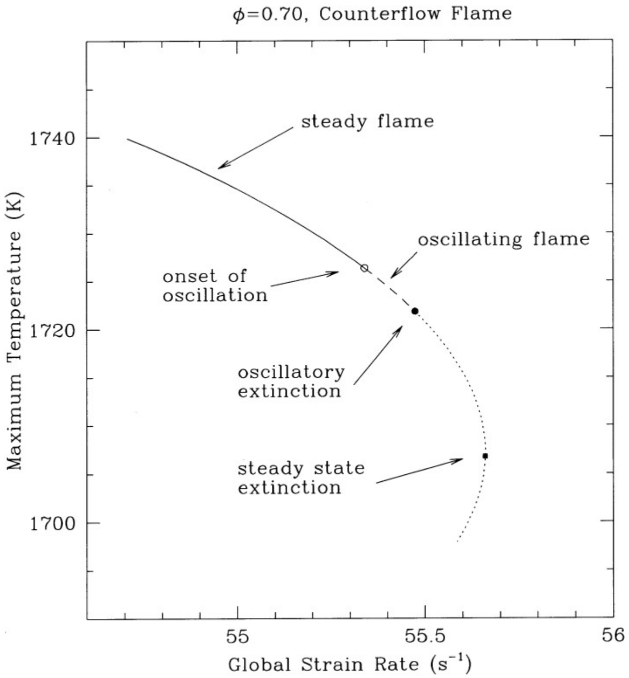
- S-curve analysis is based on steady-state considerations, showing on-off states
- Near state of extinction, the burning intensity of flame is reduced, implying larger effective activation energies
- Flamefront pulsating instabilities are also promoted with increasing activation energy
- Could extinction occurs in a pulsating manner, especially for *Le* > 1 flames?



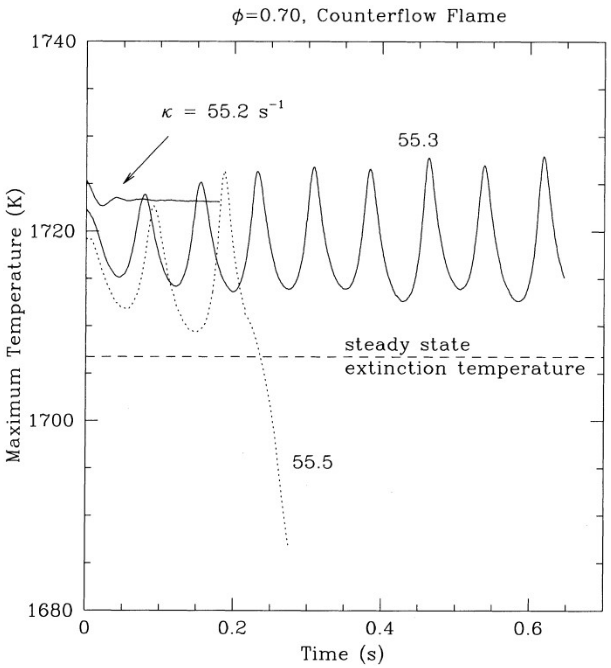
The Issue: Intrinsic Chemical Influence Near Diffusion Flame Extinction

- Finite-rate chemistry plays no role in the reaction-sheet limit of diffusion flames
- Flamefront (pulsating) instability intrinsically requires consideration of finite-rate chemistry
- Since finite-rate chemistry is responsible for extinction, then could extinction occur in a pulsating manner even for diffusion flames, if $Le > 1$ for one of the reactants?

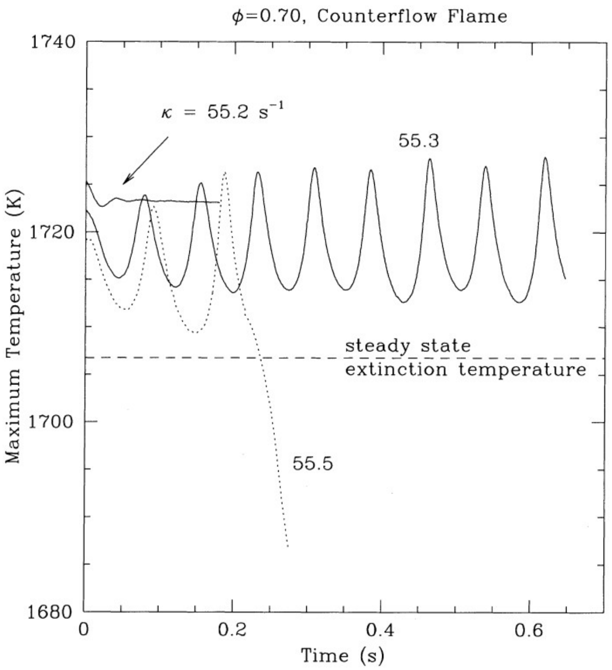
Oscillatory Extinction of Le > 1 Premixed Flame



Calculated S-curve, showing earlier extinction due to pulsation

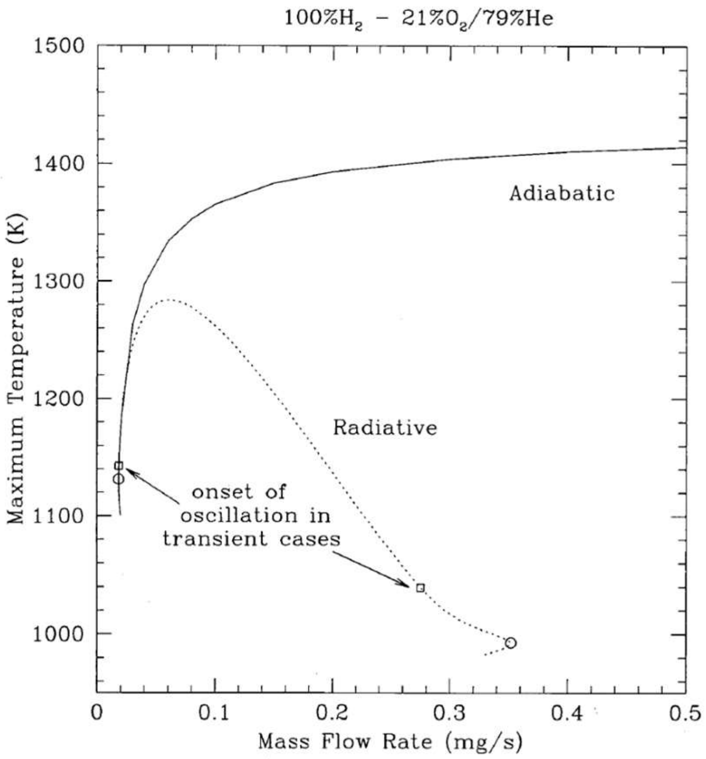


Calculated extinction dynamics; extinction controlled by steady-state extinction temperature

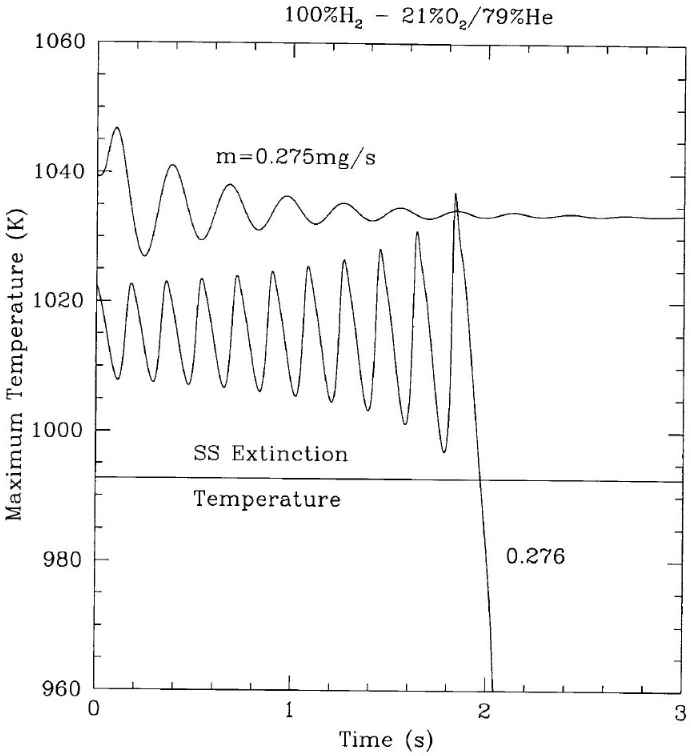


Experimental observation of oscillatory luminosity

Oscillatory Extinction of Diffusion Flames: Computation

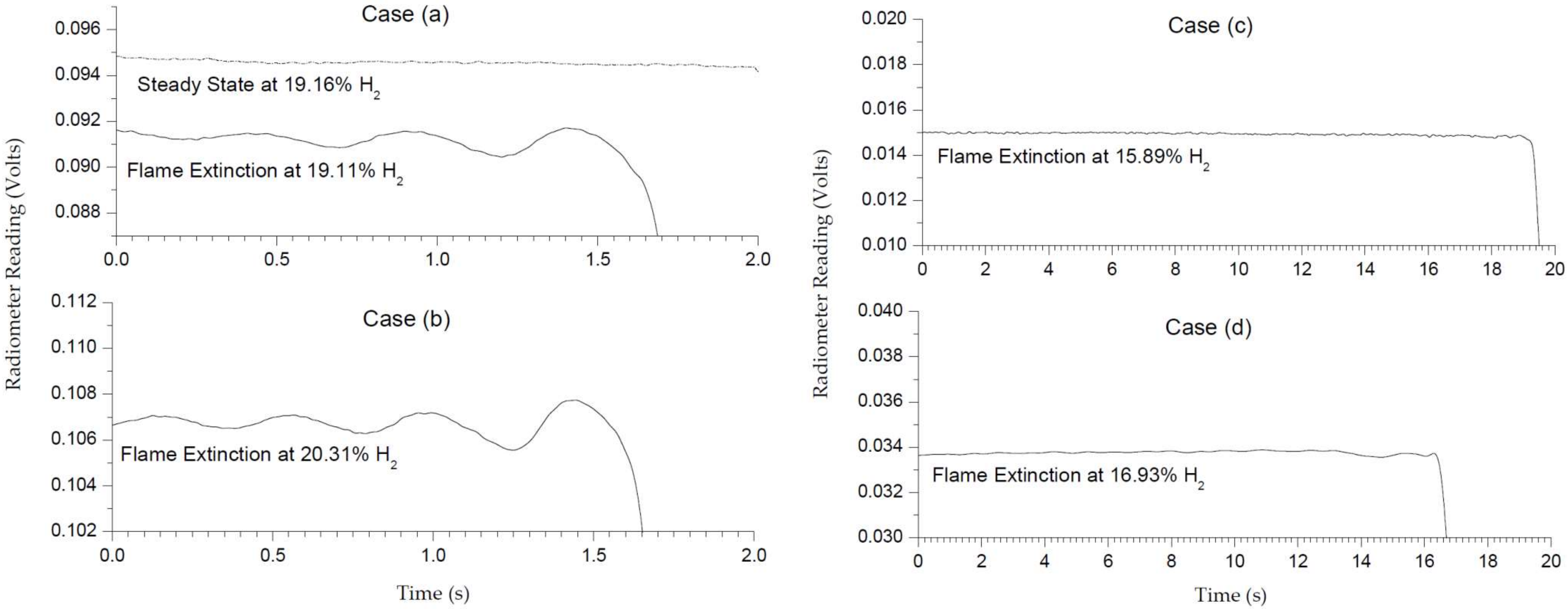


Calculated S-curve, showing earlier extinction due to pulsation



Calculated extinction dynamics; extinction controlled by steady-state extinction temperature

Oscillatory Extinction of Diffusion Flames: Experiment



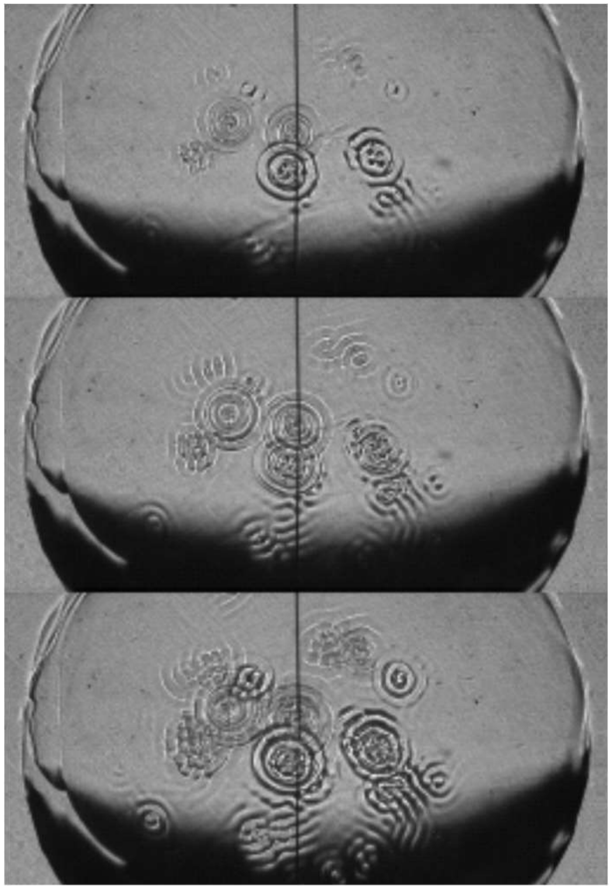
Experimentally observed steady and oscillatory extinction of diffusion flames

2b. Observations of Spirals over Flame Surfaces

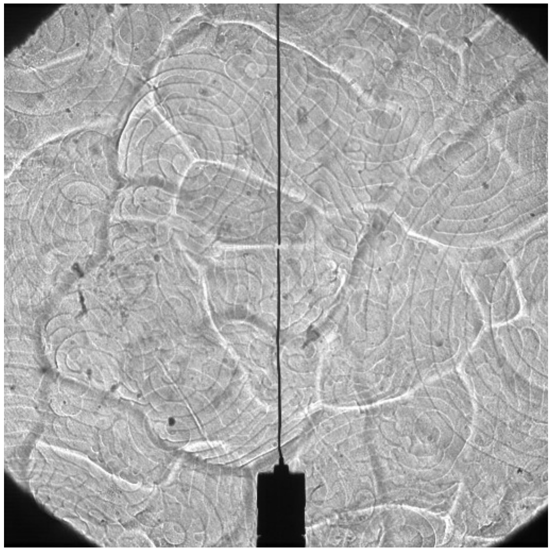
Target Patterns ($Le > 1$)

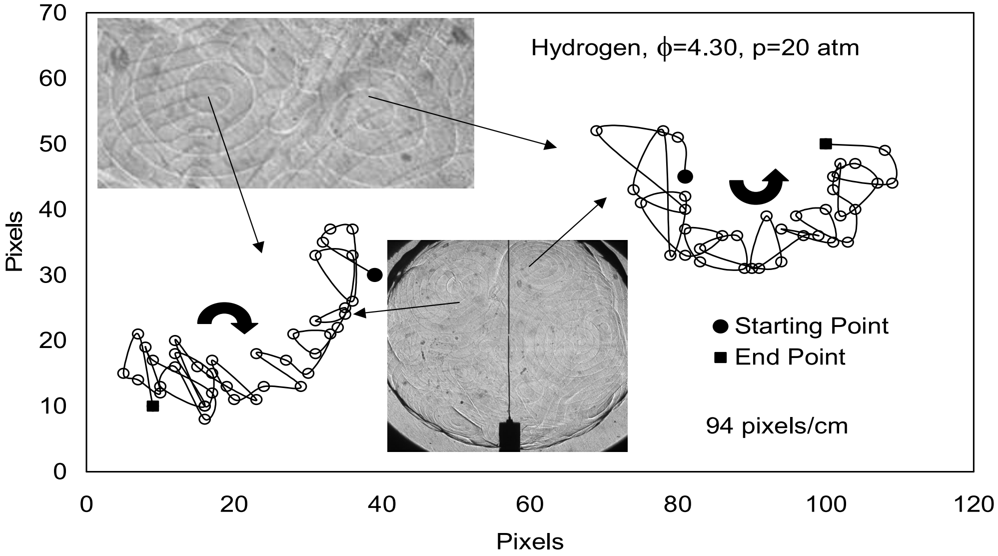
Experimental conditions:

- Lean butane-air, $\phi = 0.59$
- 30 atm. pressure
- Consecutive frames at framing rate of 15000 fps
- Frame dimension: 2.73cm × 5.46cm



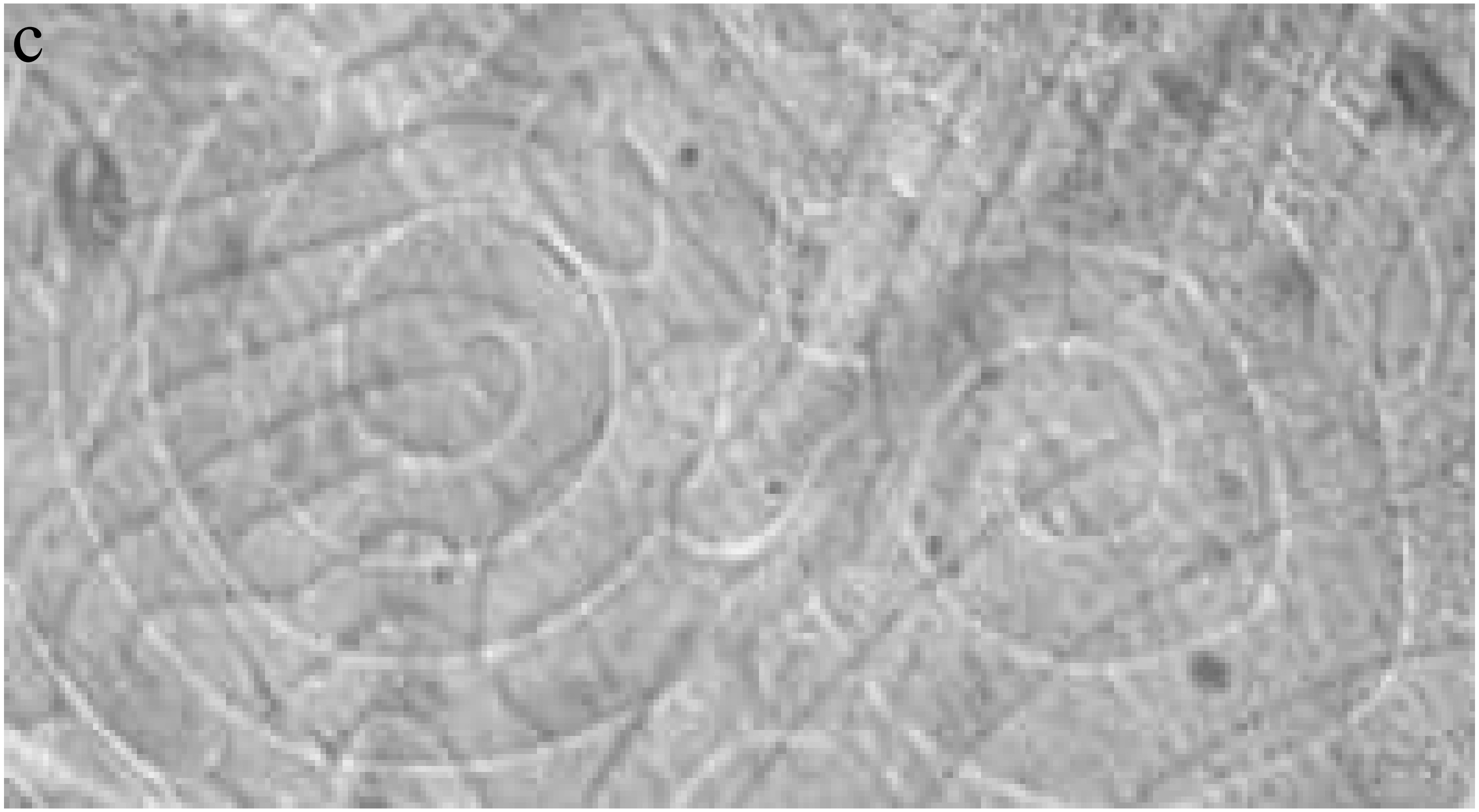
Regular Spirals





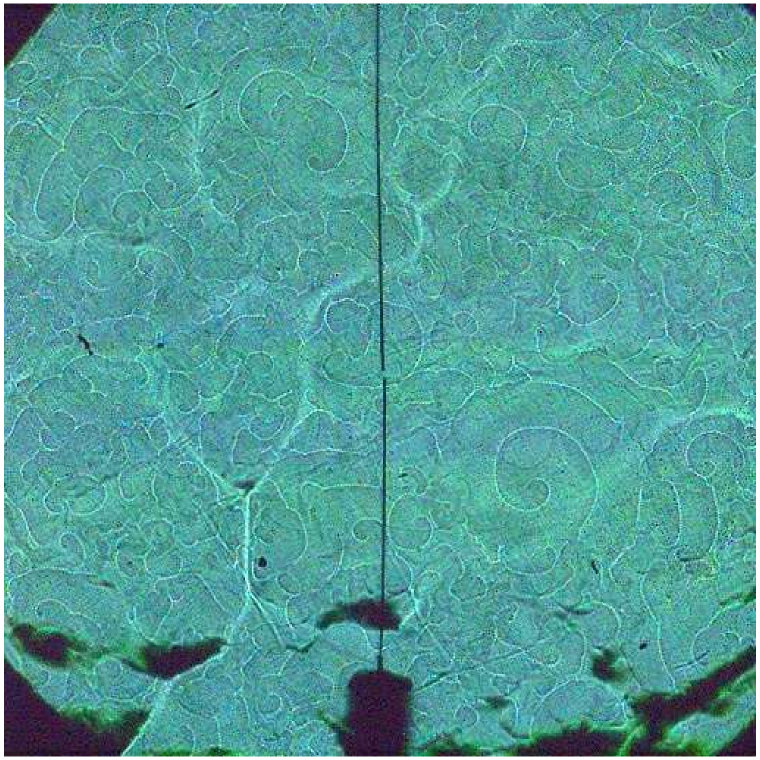
- Rich hydrogen-air flame ($\phi = 4.30$) at 20 atm.
- Spirals confined within hydrodynamic cells
- Spiral can be either clockwise or counter-clockwise

Magnified View of the Spirals



Disordered Spirals

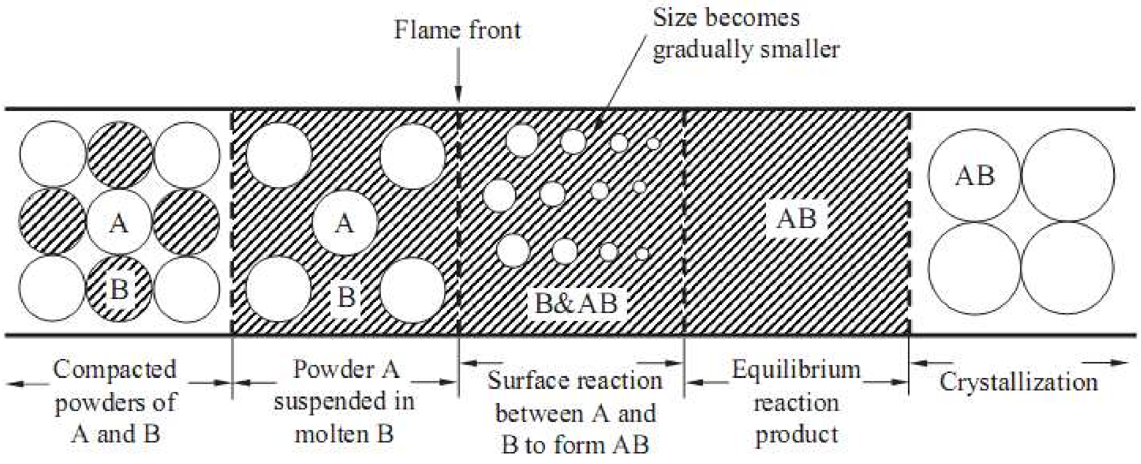
- Hydrogen-oxygen flame at 30 atm. and $\phi = 6.00$
- Disordered spirals

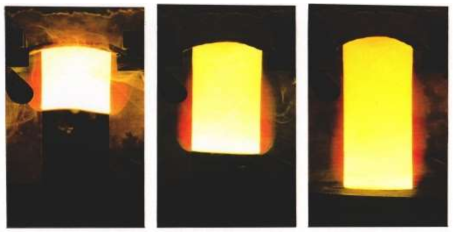


3. Pulsation in Self-propagating High-temperature Synthesis

Pulsation in Condensed-Phase Flames

- A curious result:
  - Propagation of solid flames exhibit temperature-sensitive Arrhenius behavior, e.g. pulsation
  - But reaction for individual particles is in diffusion flame-sheet limit ⇒ no finite rate chemistry





Laminated product structure due to pulsation

Pulsation in Condensed-Phase Flame

- Explanation: Arrhenius behavior from temperature-sensitive solid-phase diffusivity
- Gas-phase flame speed: $f_{\text{gas}}^2 \sim (\rho D)_g \omega \sim (\rho D)_g e^{-T_a/T_{\text{ad}}} \sim e^{-T_a/T_{\text{ad}}}$
- Condensed-phase flame speed:

$$f_{\text{SHS}}^2 \sim (\rho D)_s \omega_{SHS} \sim (\rho D)_s K_c$$

$$\text{Since } K_c = (2\rho_B D / \rho_A)_s \ln(1 + Y_B / \sigma_O) \sim D_s \quad \Rightarrow \quad f_{\text{SHS}}^2 \sim D_s^2$$

$$\text{But } D_s \sim e^{-T_d/T}, \quad \text{therefore:} \quad f_{\text{SHS}} \sim e^{-T_d/T_{\text{ad}}}$$

Combustion Physics
(Day 5 Lecture)

Chung K. Law
Robert H. Goddard Professor
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Honorary and Founding Director
Center for Combustion Energy
Tsinghua University

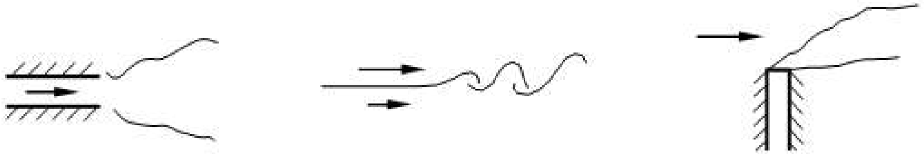
Tsinghua-Princeton-Combustion Institute
Summer School on Combustion
July 7-13, 2024

Day 5: Combustion in Complex Flows

1. **Turbulent flows**
    1. General concepts of turbulent flows
    2. Simulation and modeling
    3. Premixed burning: regime diagram and burning velocities
2. **Boundary-layer flows**
    1. Consideration of similarity
    2. Diffusion flame in the ablating Blasius flow
    3. Ignition in the Blasius flow
    4. Stabilization of the jet flame
3. **Supersonic flows**
    1. Sound waves in reactive flows
    2. Structure of detonation waves
    3. Direct and indirect detonation initiation

1. Combustion in Turbulent Flows

Examples of Turbulent Flows



Jet

Mixing Layer

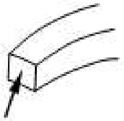
Jet in Cross Flow

Unconfined Flows

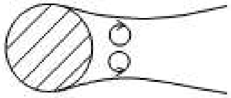
Forced Convection Boundary Layer

Natural Convection Boundary Layer

Semiconfined Flows



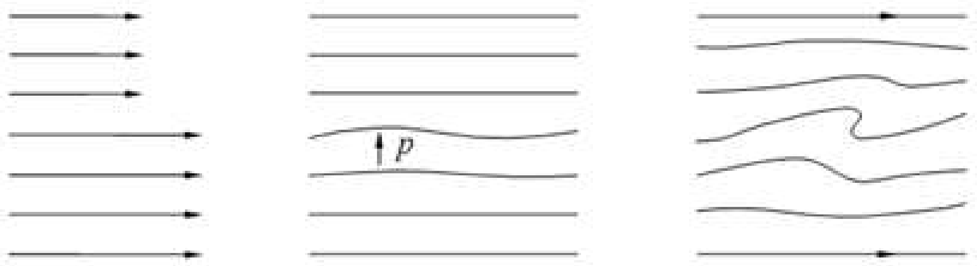
Confined Flow



Wake Flow

Mechanism of Flow Instability

- Distortion of streamline ⇒ change in velocity ⇒ imbalance in pressure ⇒ further distortion



- Growth of instability can be moderated by viscosity
- Relevant parameter governing turbulent flows:

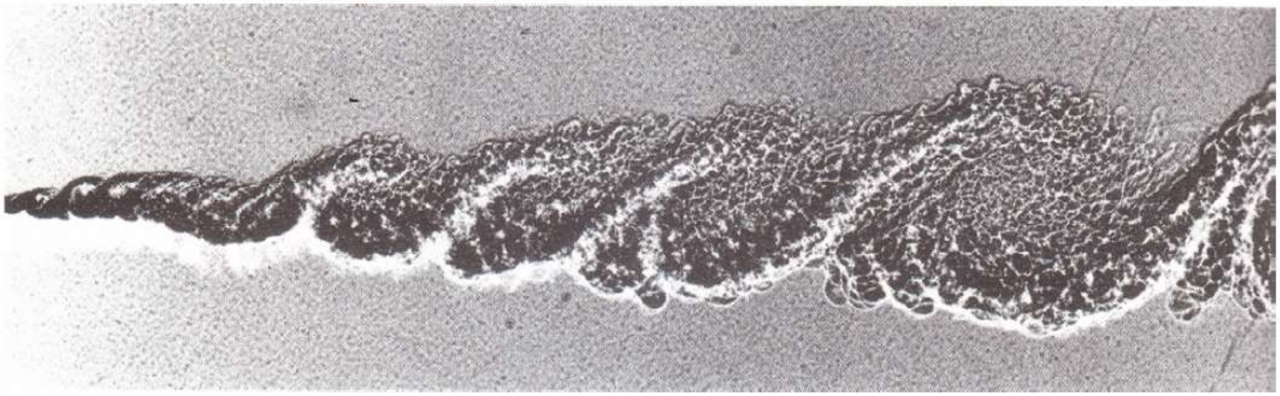
$\mathrm{Re} = \rho UL/\mu$; $\mathrm{Re} >> 1$ for turbulent flows

$\mathrm{Re} << 1$ for laminar flows

- *Re* >>1:
  - Indicates mechanism for turbulence generation
  - Need for large kinetic energy to sustain turbulence in presence of viscous dissipation

Structure of Turbulent Flows

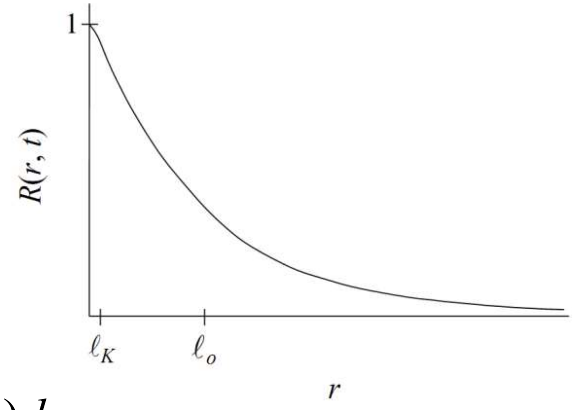
- Instability can lead to:
  - **Chaotic motion**: random fluctuation in space and time
  - Laminar, organized, multi-dimensional motion (e.g. Benard cells)
- Structure of turbulent flows
  - Cascading of large, (kinetic)-energy-containing eddies to smaller ones that eventually dissipate through viscosity
  - Coherent structure: large parcels of turbulent flows
  - May grow in size through pairing



Structure of Reacting Turbulent Flows

- Turbulence in general increases burning intensity through enhanced mixing and increased flame surface area
- Excessive intensity can cause local extinction
- Effects of chemical reactions
  - Heat release
    - laminarizing $\mathrm{Re} \sim \rho / \mu \sim T^{-(\alpha+1)} \quad (\alpha > 0)$
    - supplies energy to sustain turbulence
  - Turbulence generated through baroclinic torque: $\nabla(1/\rho)\times\nabla(p)$
  - Turbulence generated through flamefront instabilities

Turbulence Scales and Energy Cascade (1/3)



- Determine correlation function to indicate extent of interaction between eddies;

  e.g. $R_{11}(\mathbf{x}, \mathbf{r}, t) = \overline{u'(\mathbf{x}, t)u'(\mathbf{x}+\mathbf{r}, t)} / \overline{u'^2(\mathbf{x}, t)},$
- Define integral scale $\ell_o(\mathbf{x}, t) = \int_0^\infty R_{11}(\mathbf{x}, r, t)dr.$
- Identify characteristic velocity fluctuation $u'_o = (\overline{u'^2})^{1/2}$
- Define turbulent Reynolds number $Re_o = \frac{u'_o \ell_o}{\nu}$
- Identify turbulent kinetic energy $k \approx \frac{3u'^2_o}{2}$

Turbulence Scales and Energy Cascade (2/3)

- For large Re_o, transfer of energy from large to small eddies is independent of viscosity, for a range of turbulence scales (inertial subrange)
- From dimensional analysis
  - Rate of energy transfer: $\varepsilon \approx \frac{u_o'^3}{\ell_o} \approx \frac{k^{3/2}}{\ell_o}$
  - Period of cascade (turbulent time or turnover time of integral scale eddies): $\tau_o \approx \frac{\ell_o}{u_o'} \approx \frac{k}{\varepsilon}$.
- Dissipation eventually dominates at a sufficiently small scale – the Kolmogorov scale
- For given ε and ν, dimensional analysis yields Kolmogorov time, length, and velocity as $\tau_K \approx \left(\frac{\nu}{\varepsilon}\right)^{1/2}, \quad \ell_K \approx \left(\frac{\nu^3}{\varepsilon}\right)^{1/4}, \quad u_K' \approx (\nu\varepsilon)^{1/4}$.

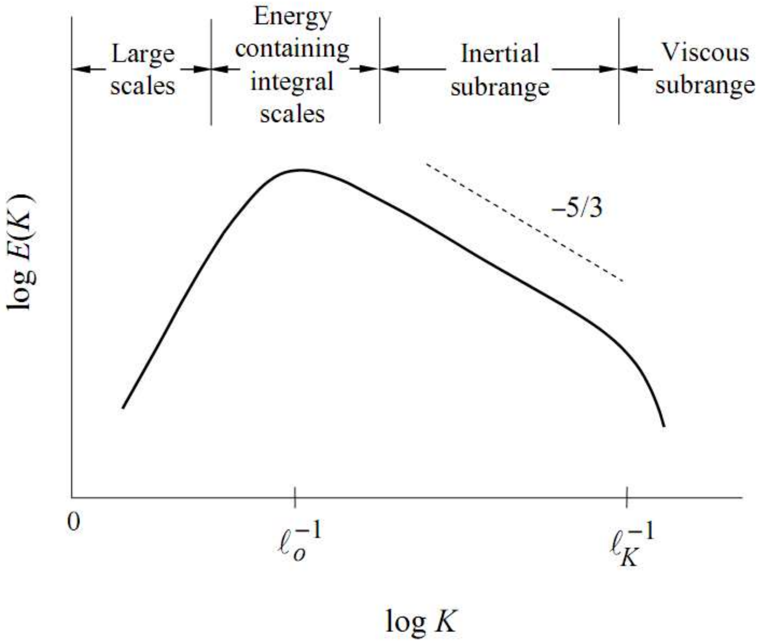
Turbulence Scales and Energy Cascade (3/3)

- Relation between integral and Kolmogorov scales

$$\frac{\ell_o}{\ell_K} \approx Re_o^{3/4}, \quad \frac{\tau_o}{\tau_K} \approx Re_o^{1/2},$$

- Energy transfer rate: $\varepsilon \approx \frac{u_o'^3}{\ell_o} \approx \frac{u_o'^2}{\tau_o} \approx \frac{u_K'^3}{\ell_K} \approx \frac{u_K'^2}{\tau_K}.$
- Turbulent kinetic energy spectrum $(K \sim 1/\ell_o)$; the " -5/3 law "

$$E(K) = \frac{dk}{dK} \sim \frac{k}{K} \approx \frac{(\varepsilon \ell_o)^{2/3}}{K} \approx \frac{\varepsilon^{2/3}}{K^{5/3}},$$



Challenge in Direct Numerical Simulation (DNS)

- Computational demand to spatially and temporally resolve a turbulent flow of D dimension;

$$(\ell_o/\ell_K)^D(\tau_o/\tau_K) = (Re_o^{3D/4})(Re_o^{1/2}) = Re_o^{(3D/4)+(1/2)}$$

$$= Re_o^{11/4} \approx Re_o^3 \quad \text{for } D = 3$$

- For Re_o= 10^4, need 10^{11} grids, which is huge
- Problem further compounded by chemistry, described by reactions with rates spanning many orders of magnitude
- Highly sensitive to boundary and initial conditions for Re>>1 flows
- Resort to probabilistic description

Probabilistic Description

- Reynolds averaging
  - $u(\mathbf{x}, t) = \overline{u}(\mathbf{x}, t) + u'(\mathbf{x}, t)$
  - $\overline{u'} \equiv 0$
  - $\overline{u'^2} = \overline{(u-\overline{u})^2} = \overline{u^2} - 2\overline{u}^2 + \overline{u}^2 = \overline{u^2} - \overline{u}^2 \neq 0$

- Favre averaging (for variable density)
  - $u(\mathbf{x}, t) = \tilde{u}(\mathbf{x}, t) + u''(\mathbf{x}, t)$
  - Define $\tilde{u} = \overline{\rho u} / \overline{\rho} \Rightarrow \overline{\rho u''} = 0$

- Favre versus Reynolds averaging
  - Reynolds: $\overline{\rho u v} = \tilde{\rho}\tilde{u}\tilde{v} + \overline{\rho}\,\overline{u'v'} + \overline{u}\,\overline{\rho' v'} + \overline{v}\,\overline{\rho' u'} + \overline{\rho' u' v'}$,
  - Favre: $\overline{\rho u v} = \bar{\rho}\tilde{u}\tilde{v} + \overline{\rho u'' v''} = \bar{\rho}\tilde{u}\tilde{v} + \bar{\rho}\widetilde{u'' v''}$
    - Similar to constant ρ expression $\overline{uv} = \overline{u}\,\overline{v} + \overline{u'v'}$.
    - Diffusion term messed up

Closure Problem in Turbulence Studies

- Consider momentum transport
  - $$\frac{Du_i}{dt} \equiv \frac{\partial \rho}{\partial t} + \frac{\partial\left(\rho u_\alpha\right)}{\partial x_\alpha} = -\frac{\partial p}{\partial x_i} + \frac{\partial \sigma_{i\alpha}}{\partial x_\alpha} + \rho g_i \qquad (11.2.2)$$

    summation convention: $u_\alpha \frac{\partial u_i}{\partial x_\alpha} = u\frac{\partial u_i}{\partial x} + v\frac{\partial u_i}{\partial y} + w\frac{\partial u_i}{\partial z}$
- Apply Favre averaging

$$\frac{\tilde{D}\tilde{u}_i}{\tilde{D}t} = -\frac{\partial \bar{p}}{\partial x_i} + \frac{\partial}{\partial x_\alpha}\left(\bar{\sigma}_{i\alpha} - \bar{\rho}\widetilde{u''_\alpha u''_i}\right) + \bar{\rho} g_i$$

- Insufficient relations to determine terms $\boxed{\bar{\rho}\widetilde{u''_\alpha u''_i}\ ,\bar{\rho}\widetilde{u_\alpha{}''\phi''}}$
  - Represents exchanges between fluctuating quantities
  - Need to be modeled

Turbulence Modeling I:

Reynolds-Averaged Navier-Stokes Models

- **Gradient Transport (*First Moment*) Models**: Relate the Reynolds stress and flux terms, $\bar{\rho}u_i''u_j''$ and $\bar{\rho}u_i''\phi''$, through turbulent diffusivity, $-u_i''\phi'' = \frac{\nu_T}{\sigma_\phi}\frac{\partial\tilde{\phi}}{\partial x_i}$
  - **Prandtl's mixing length model**

    In analogy with molecular diffusive mixing, $\nu_T \sim u^*\ell^*$,

    Mixing rate, $u^* \approx \ell_m \left|\frac{\partial\tilde{u}}{\partial y}\right| \quad \Rightarrow \quad \nu_T \sim u^*\ell_m \sim \ell_m^2\left|\frac{\partial\tilde{u}}{\partial y}\right|$
  - $k-\varepsilon$ **model**
    - Relate $u^* \approx \tilde{k}^{1/2}, \quad \ell^* \approx \tilde{k}^{3/2}/\tilde{\varepsilon}, \quad \nu_T \sim \tilde{k}^2/\tilde{\varepsilon}$
    - Develop transport equations for $\tilde{k}$ and $\tilde{\varepsilon}$
    - Correlation terms still need to be modeled
- **Reynolds Stress (*Second Moment*) Models**: Develop differential equations directly for the Reynolds stress and flux terms. Modeling and closure are delayed to the next level

Turbulence Modeling II

- Large Eddy Simulation (LES)
  - Resolve the energy-containing, large-scale structure
  - Model the dissipative, small-scale processes

- Probability Density Functions (PDF)
  - $\tilde{u}_i$ and $\widetilde{u_i u_j}$ are simply the first and second moments of the probability density function of the velocity, $P(\mathbf{u};\mathbf{x},t)$
  - It is therefore more fundamental to develop a transport equation for P, from which the moments can be evaluated
  - Equation analogous to the Boltzmann equation for the velocity distribution function in the kinetic theory of gases

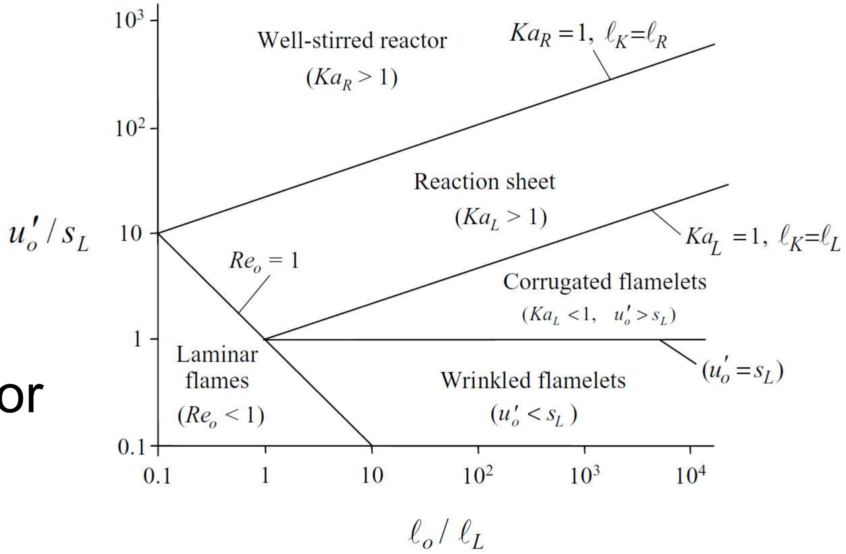
Regime Diagram of Premixed Combustion (1/2)

- Classify mode of turbulent combustion based on turbulent velocity (u'_0/s_L) and length (ℓ_o/ℓ_L) scales
- Characterization of turbulence intensity

$$Re_o = u'_o\ell_o/\nu = (u'_o/s_L)(\ell_o/\ell_L) \quad ;(\nu \approx \lambda/(c_p\rho) \sim s_L\ell_L)$$

- Laminar diffusive structure is destroyed for $Ka_L = O(1)$,$u'_o/s_L = Ka_L^{2/3}(\ell_o/\ell_L)^{1/3}$; based on the Kolmogorov scale
- Entire flame structure destroyed when reaction zone is extinguished, at $Ka_R = O(1)$

$$Ka_R = \tau_R/\tau_K = (\ell_R/\ell_K)^2 = (\ell_R/\ell_L)^2(\ell_L/\ell_K)^2 = Ze^{-2}Ka_L$$



Regime Diagram of Premixed Combustion (2/2)

- Diagram constructed for

  $\mathrm{Re}_0 = Ka_L = Ka_R = 1 \;\; (\text{for } \; Ze = 10)$
- **Five regimes identified**
  - Laminar flame regime

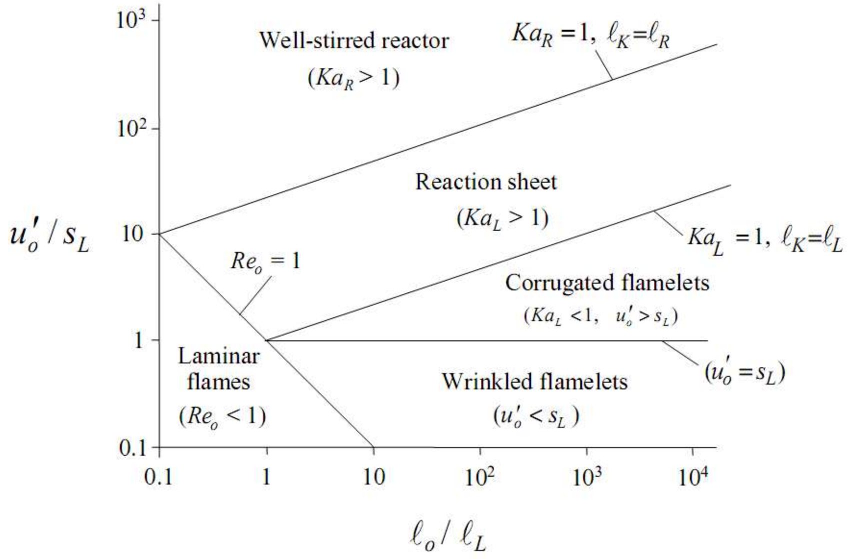
    $(\mathrm{Re}_o < 1)$
  - Wrinkled flamelet regime

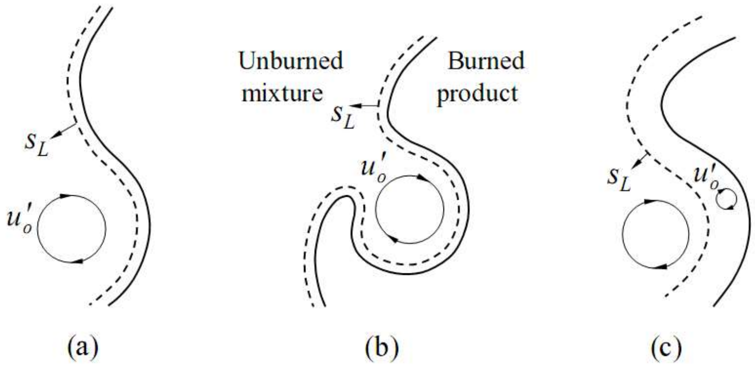
    $(\mathrm{Re}_o < 1, \; u_0' / s_L < 1)$
  - Corrugated flamelet regime

    $(\mathrm{Re}_o < 1, \; Ka_L < 1, \; u_o' / s_L > 1)$
  - Reaction-sheet regime

    $(\mathrm{Re}_o > 1, \; Ka_L > 1, \; Ka_R < 1)$
  - Well-stirred reactor regime

    $(\mathrm{Re}_o > 1, \; Ka_R > 1)$
- Classification does not account for flame movement and flamefront instabilities

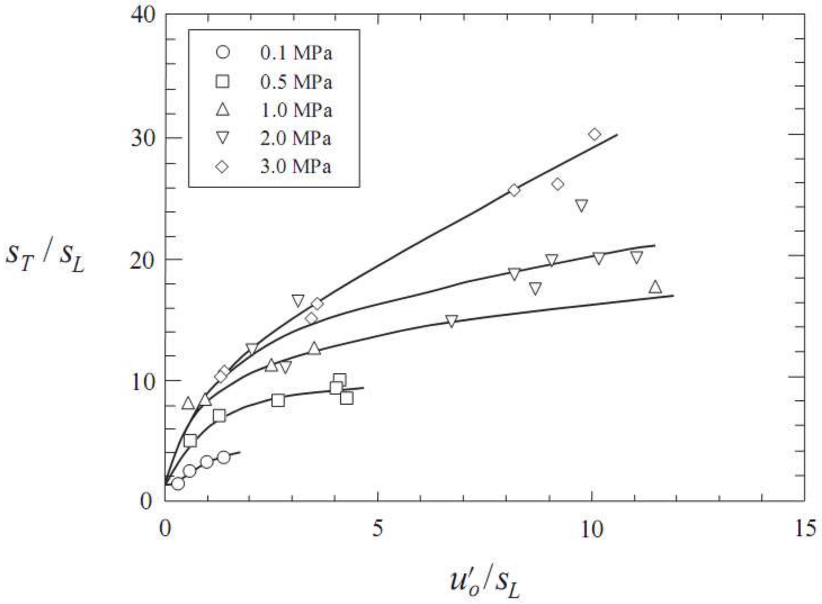




Turbulent Burning Velocity

- Unlike laminar burning velocity, turbulent burning velocity is not just a property of the mixture. It also depends on the flow properties
- Experimental techniques
  - Bunsen flame
  - Rod-stabilized flame
  - Stagnation/counterflow flame
  - Expanding spherical flame
- Key observation:

Bending effect of s_T / s_L vs. u'_o / s_L



Phenomenological Descriptions of Turbulent Burning Velocities

- Reaction-sheet description
  - Turbulent eddy size < laminar flame thickness

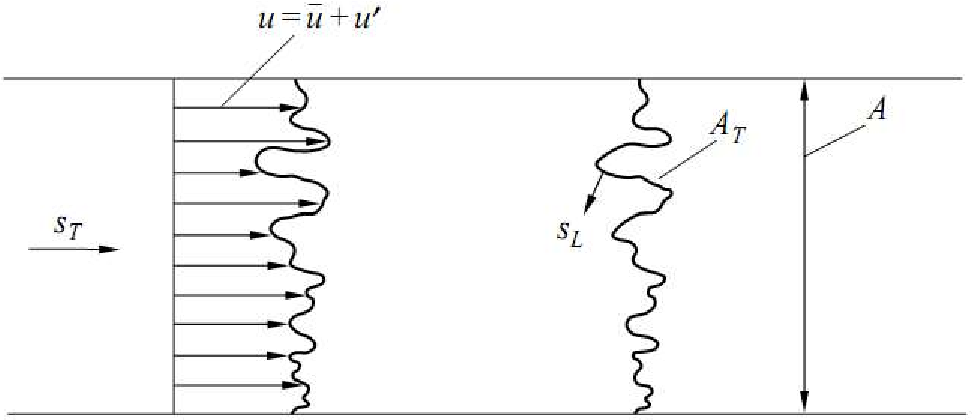
    $s_L \sim D^{1/2} \sim \nu^{1/2};\ s_T \sim D_T^{1/2} \sim \nu_T^{1/2} \sim (u_o{}'\ell_o)^{1/2}$

    $s_T / s_L = \sqrt{u_o'\ell_o / \nu} = \sqrt{Re_o}$

- Flame-sheet description
  - Wrinkling increases flame surface area

    $s_T A = s_L A_T;\ \ s_T / s_L = A_T / A$

  - Problem degenerates to determination of A_T / A

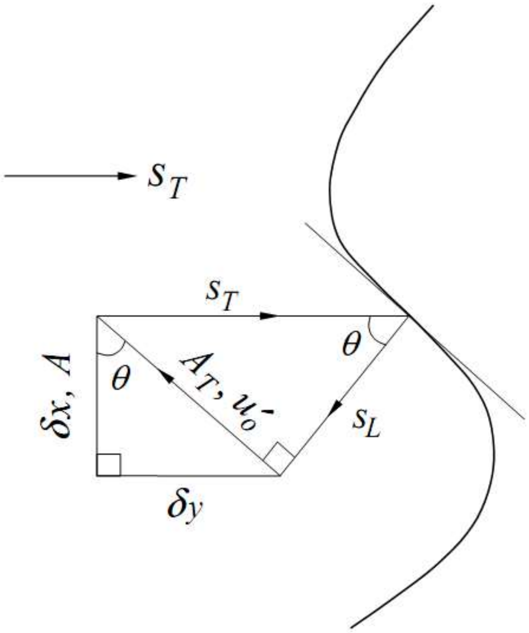


Flame-Sheet Descriptions: Vector Description

$$\frac{s_T}{s_L} = \frac{A_T}{A} = \frac{\sqrt{\delta x^2 + \delta y^2}}{\delta x} = \sqrt{1 + \left(\frac{\delta y}{\delta x}\right)^2} =$$

$$= \sqrt{1 + \tan^2 \theta} = \sqrt{1 + \left(\frac{u_o'}{s_L}\right)^2} \approx$$

$$\approx \begin{cases} 1 + \frac{1}{2}\left(u_o' / s_L\right)^2, & \text{for } u_o' / s_L << 1 \\ u_o' / s_L, & \text{for } u_o' / s_L >> 1 \end{cases}$$

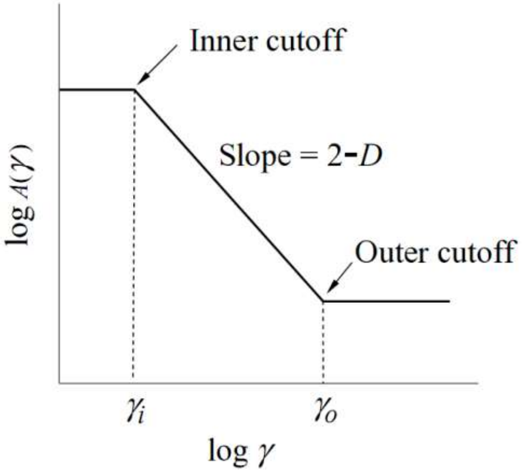


- For the strong turbulence limit, $s_T \approx u_o'$ => flame speed completely dominated by turbulence

Flame-Sheet Descriptions: Fractal Description

- Fractal representation

$$N\gamma^{\mathrm{D}} = 1,\ D = -\log N / \log \gamma$$



- Examples: $\gamma = 1/N$
  - Line: $N = n,\ D = 1$
  - Square: $N = n^2,\ D = 2$
  - Cube: $N = n^3,\ D = 3$
- For a general surface of non-integral dimension:

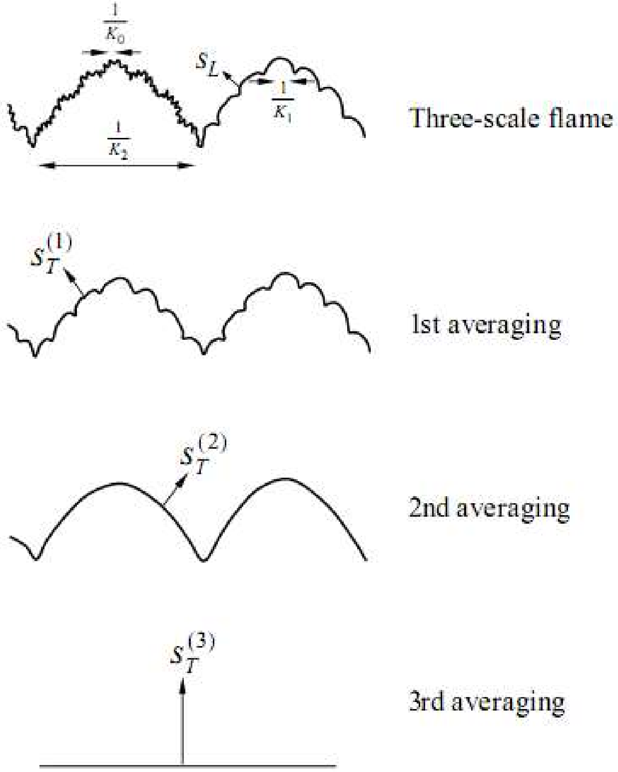
$$A \sim N\gamma^2 \sim \gamma^{2-D}$$

$$s_T / s_L = A_T / A = \left(\gamma_{inner} / \gamma_{outer}\right)^{2-D} = \left(\ell_K / \ell_o\right)^{2-D} = \mathrm{Re}_o^{3(D-2)/4}$$

Flame-Sheet Descriptions: Renormalization Theory

- Successive averaging over gradually increasing scales
- The result exhibits bending

$$\left(\frac{s_T}{s_L}\right)^2 \ln\left(\frac{s_T}{s_L}\right)^2 = 2\left(\frac{u'_o}{s_L}\right)^2$$

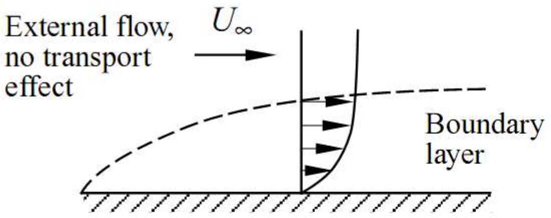


2. Combustion in Boundary Layer Flows

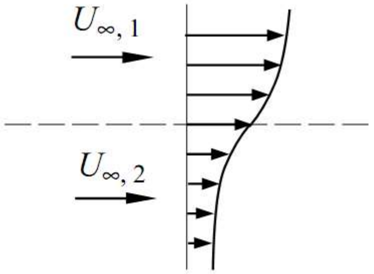
Characteristics of Boundary Layer Flows

- High-speed flow adjacent to a solid surface or slower stream slows down or stops to meet boundary condition
- For small viscosity, adjustment occurs in a thin layer such that $\mu\left(\frac{\partial u}{\partial y}\right) = O(1)$; ordering will be defined later
- Similar values of μ, λ/c_p, and ρD implies boundary layers for momentum, heat and mass are of close magnitude.
- Boundary layer flows are intrinsically 2D
  - Diffusive transport predominant in y-direction ⇒ $\frac{\partial^2}{\partial y^2} >> \frac{\partial^2}{\partial x^2}$
  - Problem is parabolic
- Seek similarity solution: $\eta = \eta(x, y)$
- Abundant similarity solutions exist for nonreactive flows
- Such a similarity is mostly violated in reactive flows

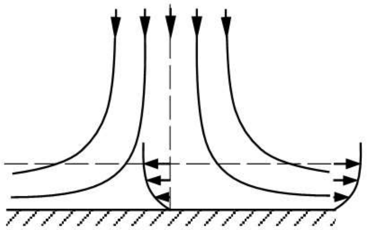
Examples of Boundary Layer Flows



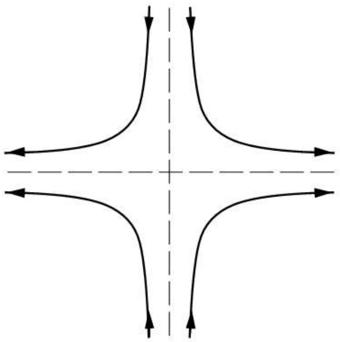
Flat Plate



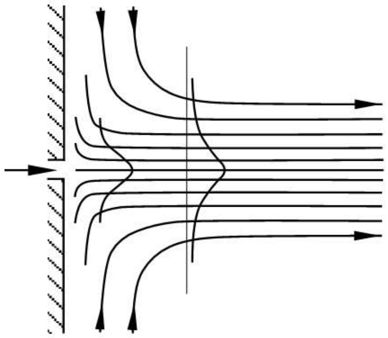
Mixing Layer



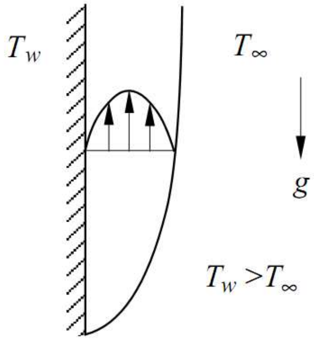
Stagnation Point



Counterflow



Jet



Free Convection

Similarity Considerations: Governing Equations of 2D Flows

- Continuity:

$$\frac{\partial(\rho u)}{\partial x}+\frac{\partial(\rho v)}{\partial y}=0 \qquad (12.1.1)$$

- x-Momentum:

$$\underbrace{u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}}_{(U_\infty^2/\ell)}=\underbrace{\frac{1}{\rho}\left\{-\frac{\partial}{\partial x}\left[\frac{2}{3}\mu\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}\right)\right]+\frac{\partial}{\partial x}\left(2\mu\frac{\partial u}{\partial x}\right)+\frac{\partial}{\partial y}\left(\mu\frac{\partial v}{\partial x}\right)\right\}}_{Re_\ell^{-1}(U_\infty^2/\ell)}$$

$$\underbrace{+\frac{1}{\rho}\frac{\partial}{\partial y}\left(\mu\frac{\partial u}{\partial y}\right)}_{Re_\ell^{-1}(\ell/\delta)^2(U_\infty^2/\ell)}-\frac{1}{\rho}\frac{\partial p}{\partial x} \qquad (12.1.2)$$

- y-Momentum:

$$\underbrace{u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y}}_{(\delta/\ell)(U_\infty^2/\ell)}=\underbrace{\frac{1}{\rho}\left\{-\frac{\partial}{\partial y}\left[\frac{2}{3}\mu\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}\right)\right]+\frac{\partial}{\partial y}\left(2\mu\frac{\partial v}{\partial y}\right)+\frac{\partial}{\partial x}\left(\mu\frac{\partial u}{\partial y}\right)\right\}}_{Re_\ell^{-1}(\ell/\delta)(U_\infty^2/\ell)}$$

$$\underbrace{+\frac{1}{\rho}\frac{\partial}{\partial x}\left(\mu\frac{\partial v}{\partial x}\right)}_{Re_\ell^{-1}(\delta/\ell)^2(U_\infty^2/\ell)}-\frac{1}{\rho}\frac{\partial p}{\partial y} \qquad (12.1.3)$$

Similarity Consideration: Ordering

$$\frac{\partial}{\partial x} \sim \frac{1}{\ell} \text{ and } \frac{\partial}{\partial y} \sim \frac{1}{\delta}, \tag{12.1.5}$$

- From continuity: $v \sim u \frac{\delta}{\ell}.$ (12.1.6)

  Examine x-momentum equation

  - Invoke *b. l.* assumption: $\delta / \ell << 1$ (12.1.7)
  - Neglect all terms: $\mathrm{Re}_\ell^{-1}\left(U_\infty^2 / \ell\right) << \mathrm{Re}_\ell^{-1}\left(\ell / \delta\right)\left(U_\infty^2 / \ell\right)$
  - Balance inertia term, $\left(U_\infty^2 / \ell\right)$, with viscous term, $\mathrm{Re}_\ell^{-1}\left(\ell / \delta\right)\left(U_\infty^2 / \ell\right)$, $\Rightarrow$

$$Re_\ell \sim \left(\frac{\ell}{\delta}\right)^2 >> 1. \tag{12.1.8}$$

  y-momentum equation drops out

- Similar consideration for energy and species equations

Simplified Governing Equations

- Continuity: $$\frac{\partial(\rho u)}{\partial x}+\frac{\partial(\rho v)}{\partial y}=0 \qquad (12.1.1)$$
- x-Momentum: $$L_b(u)=\left[\rho u\frac{\partial}{\partial x}+\rho v\frac{\partial}{\partial y}-\frac{\partial}{\partial y}\left(\mu\frac{\partial}{\partial y}\right)\right]u$$ $$=-\frac{\partial p}{\partial x}=\rho_\infty U\frac{dU}{dx} \qquad (12.1.12)$$
- Energy: $$L_b(\tilde{T})=-w_F \qquad (12.1.13)$$
- Species: $$L_b(\tilde{Y}_i)=w_F \qquad (12.1.14)$$

Transformation to B.L. Variables

- Define stream function satisfying continuity equation

$$\rho u = \partial\psi / \partial y \quad \text{and} \quad \rho v = -\partial\psi / \partial x \tag{12.1.16}$$

- Define *b.l.* variables
  - Streamwise independent variable for constant U_∞

$$s = \rho_\infty \mu_\infty \int_0^x U(x')dx' = \rho_\infty \mu_\infty U_\infty x \sim x \tag{12.1.17}$$

  - Transverse independent variable

$$\eta = \frac{U(x)}{\sqrt{2s}} \int_0^y \rho(x,y)dy \xrightarrow{\rho=\text{const}} \frac{\rho_\infty U(x)}{\sqrt{2s}} y \xrightarrow{U_\infty=\text{const}} \frac{y}{\sqrt{x}} \tag{12.1.18}$$

  - Stream function $f(s,\eta) = \dfrac{\psi(x,y)}{\sqrt{2s}}$ (12.1.19)

- Chapman-Rubesin assumption:
  - $\rho\mu = \text{const} \quad \Rightarrow \quad \rho^2 D = \text{const}$
  - Contrast with the usual $\rho D = \text{const.}$ assumption

Final Boundary Layer Equations

$$\frac{\partial^2 u}{\partial \eta^2} + f\frac{\partial u}{\partial \eta} + 2s\frac{\partial f}{\partial s}\frac{\partial u}{\partial \eta} - 2s\frac{\partial f}{\partial \eta}\frac{\partial u}{\partial s} = -\left(\frac{2s}{\mu_\infty U}\right)\frac{1}{\rho}\frac{dU}{dx} \qquad (12.1.24)$$

$$\frac{\partial^2 \tilde{T}}{\partial \eta^2} + f\frac{\partial \tilde{T}}{\partial \eta} + 2s\frac{\partial f}{\partial s}\frac{\partial \tilde{T}}{\partial \eta} - 2s\frac{\partial f}{\partial \eta}\frac{\partial \tilde{T}}{\partial s} = \left(\frac{2s}{\rho_\infty \mu_\infty U^2}\right)\frac{w_F}{\rho} \qquad (12.1.25)$$

- System is self-similar if all properties depend on *η* only
- The RHS, source term for the boundary layer equations all depend explicitly on *s* ⇒ all flow properties shall depend on (*s*, *η*) instead of *η* only
- Minimum requirement for similarity is to suppress the dependence of the RHS on *s*

Discussion on Similarity

- Chemically frozen flow $w_F \equiv 0 \Rightarrow$ only need to suppress s-dependence of momentum equation. Require

$$\boxed{\frac{2s}{\rho_\infty \mu_\infty U^2(x)} \frac{dU(x)}{dx} = \text{const}} \qquad (12.1.29)$$

$\Rightarrow \quad U(x) \sim x^m, \quad m = \text{const};$ this is the class of **Falkner-Skan flows**

- Chemically-reacting flows $(w_F \neq 0)$ also require

$$\boxed{\frac{2s}{\rho_\infty \mu_\infty U^2(x)} = \text{const}} \qquad (12.1.31)$$

$\Rightarrow \quad U(x) \sim x = ax$; this is the stagnation flow and counterflow

$\Rightarrow \quad \eta \sim y \quad \Rightarrow$ all properties vary only with y

$\Rightarrow$ Iso-surfaces are parallel to stagnation surface

  - Reason for similarity: both x-velocity and reaction vary linearly with distance, hence only two characteristic time scales.

Ablative Blasius Flow $\left(dU/dx \equiv 0\right)$

- Flow is similar: $\frac{d^2u}{d\eta^2} + f\frac{du}{d\eta} \equiv 0 \quad ; \quad u \sim \frac{df}{d\eta}$

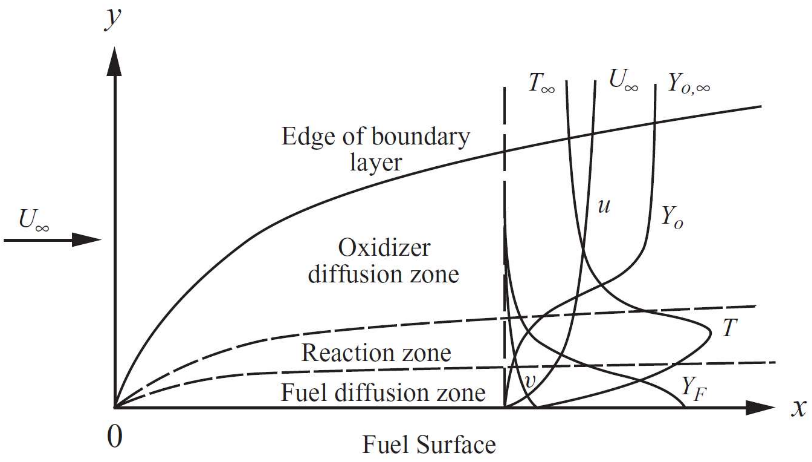
$$\text{or} \quad f''' + ff'' = 0 \quad \text{(Blasius equation)}$$

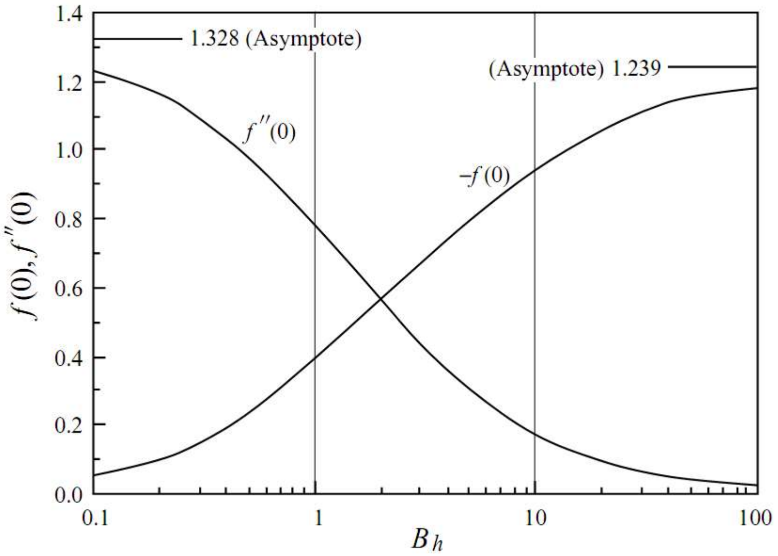
- Coupling function, $\beta_i = \tilde{Y}_i + \tilde{T}$, does not depend on w, and hence u is also similar: $\frac{d^2\beta_i}{d\eta^2} + f\frac{d\beta_i}{d\eta} = 0$
- Solution: $\beta_i = a_i + b_i u = a_i + c_i f'(\eta)$
- Applying boundary conditions:

$$\eta = 0: \quad T = T_s, \ Y_F = Y_{F,s}, \ Y_O = Y_{O,s}, \ \left(\lambda\frac{\partial T}{\partial y}\right)_0 = (\rho v)_0 q_v,$$

$$\eta = \infty: \quad T = T_\infty, \ Y_F = 0, \ Y_O = Y_{O,\infty}$$

- Note: same heat transfer number as for droplets
- Increasing $B_{h,c}$ leads to:
  - Increasing gasification rate: $-f(0)$
  - Decreasing drag: $f''(0)$





Flame-Sheet Properties

- Apply flame-sheet assumption yields flame-sheet location and temperature

$$f'(\eta_f) = \frac{\tilde{Y}_{F,s}}{\tilde{Y}_{F,s} + \tilde{Y}_{O,\infty}} = \Phi^* \qquad (12.2.5)$$

$$(\tilde{T}_f - \tilde{T}_s) = (\tilde{Y}_{O,\infty} + \tilde{T}_\infty - \tilde{T}_s)\Phi^* \qquad (12.2.6)$$

- (12.2.5) and (12.2.6) are analogous with solution for chambered flame, with

$$\tilde{x}_f = \Phi^* \qquad (6.1.14)$$

$$(\tilde{T}_f - \tilde{T}_o) = (\tilde{Y}_{O,l} + \tilde{T}_l - \tilde{T}_0)\Phi^* \qquad (6.1.15)$$

Ignition Along A Flat Plate (1/3)

- Governing equations:

$$\frac{\partial^2 \tilde{T}}{\partial \eta^2} + f\frac{\partial \tilde{T}}{\partial \eta} - 2xf'\frac{\partial \tilde{T}}{\partial x} = \left(\frac{2x}{U_\infty}\right)\frac{w_F}{\rho} \quad (12.3.8)$$

$$\frac{\partial^2 \tilde{Y}_i}{\partial \eta^2} + f\frac{\partial \tilde{Y}_i}{\partial \eta} - 2xf'\frac{\partial \tilde{Y}_i}{\partial x} = -\left(\frac{2x}{U_\infty}\right)\frac{w_F}{\rho}. \quad (12.3.9)$$

- Even flow is Blasius, coupling function may not be similar because boundary condition for $\tilde{T}$ and $\tilde{Y}_i$ are of different nature:

$$\tilde{T}(0) = \tilde{T}_O \neq \text{function}(s);$$

$$\partial \tilde{Y}_i / \partial y = 0 \Rightarrow \tilde{Y}_i(s, \eta) = \text{function}(s)$$

Ignition Along A Flat Plate (2/3)

- The following derivation is different from text
- Consider behavior of (12.3.8) around η =0, where ignition occurs:

$$f(\eta) \sim f(0) + f'(0)\eta + \frac{1}{2} f''(0)\eta^2 + \ldots \qquad \text{(A)}$$

$$f'(\eta) \sim f'(0) + f''(0)\eta \sim f''(0)\eta \qquad \text{(B)}$$

- Substituting (A), (B) into (12.3.8) where $\tilde{T} \rightarrow \tilde{T}_{in}$, and let χ=η/ε , we get

$$\frac{\partial^2 \tilde{T}_{in}}{\partial \chi^2} + \frac{1}{2} f''(0)\varepsilon^3 \frac{\partial \tilde{T}_{in}}{\partial \chi} - 2xf''(0)\varepsilon^3 \chi \frac{\partial T_{in}}{\partial x} = \frac{2x}{U_\infty} \varepsilon^2 \frac{w_F}{\rho} \qquad \text{(C)}$$

Ignition Along A Flat Plate (3/3)

- 2^{nd} and 3^{rd} terms in (C) are O (ε^3) of the first term, hence dropped
  - Dropping of 3^{rd} term changes (C) from PDE to ODE; **a local similarity approximation**
  - O(ε^3): ε^2 from $\partial^2/\partial\eta^2$; ε from f' as $\eta \to 0$
- (C) becomes an ODE

$$\frac{\partial^2 \tilde{T}_{in}}{\partial \chi^2} \approx \varepsilon^2 \left(\frac{2x}{U_\infty}\right) \frac{w_F}{\rho} \qquad \text{(D)}$$

which can be solved more easily.

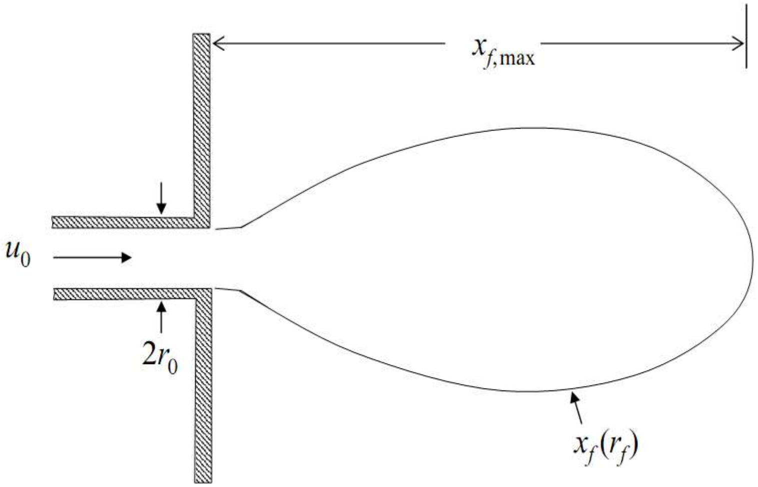
- **Local similarity approximation**: Reaction rate increases with x => non-similarity exhibited parametrically instead of differentially => no history effect

Jet Flows

- Continuity and momentum conservation

$$\frac{\partial(\rho u r)}{\partial x}+\frac{\partial(\rho v r)}{\partial r}=0 \qquad (12.4.1)$$

$$\rho u r\frac{\partial u}{\partial x}+\rho v r\frac{\partial u}{\partial r}=\frac{\partial}{\partial r}\left(\mu r\frac{\partial u}{\partial r}\right) \qquad (12.4.2)$$



- Boundary conditions

$$r=0:\ \frac{\partial u}{\partial r}=0,\ \ v=0 \qquad (12.4.3)$$

$$r\to\infty:\ \frac{\partial u}{\partial r}=0,\ u=0 \qquad (12.4.4)$$

- Similarity variables

$$\eta=\frac{\tilde{r}}{x}, \qquad \psi(x,y)=\frac{\mu_o x}{\rho_o}f(\eta) \qquad (12.4.9),\ (12.4.10)$$

$$\tilde{r}^2=2\int_0^r\frac{\rho}{\rho_o}r\,dr. \qquad (12.4.11)$$

- Boundary conditions

$$f(0)=0,\quad f''(0)=0,\quad f'(\infty)=0 \qquad (12.4.16)$$

Jet Flows: Solution

$$u(x,\eta) = \frac{3}{8\pi}\left(\frac{J}{\mu_o C x}\right)\frac{1}{\left(1+\frac{k\eta^2}{4}\right)^2}, \qquad (12.4.19)$$

- Conserved momentum

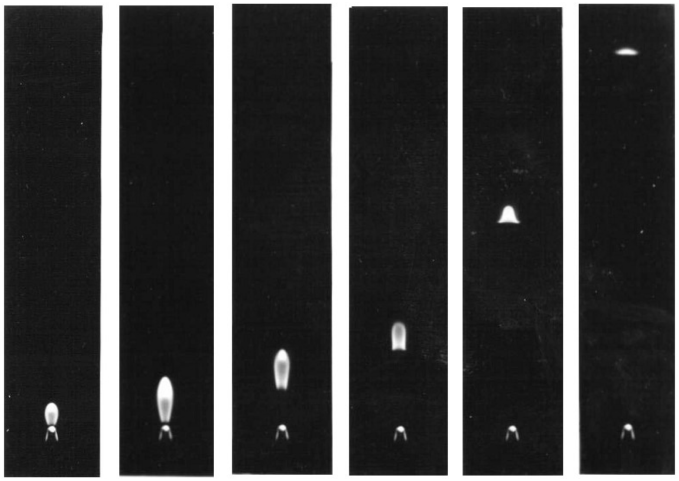
$$J = \int_0^\infty \rho u^2 (2\pi r) dr = \int_0^{r_o} \rho u^2 (2\pi r)\, dr = \pi r_o^2 \rho_o u_O^2. \qquad (12.4.6)$$

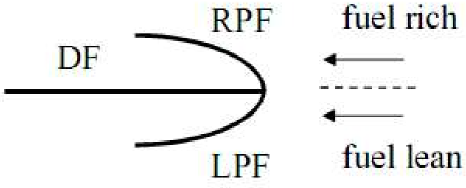
- $$k = \frac{3}{16\pi}\left(\frac{\rho_o J}{\mu_o^2 C^2}\right). \qquad (12.4.18)$$

Chapman-Rubesin parameter

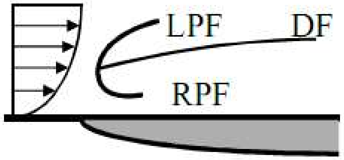
$$C = \frac{\mu \rho r^2}{\mu_o \rho_o \overline{r}^2} \qquad (12.4.15)$$

Stabilization and Blowout of Lifted Flames

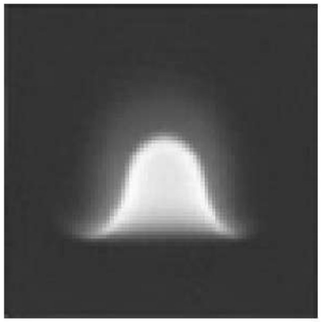


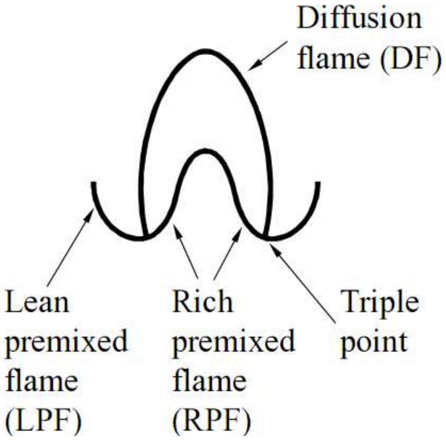


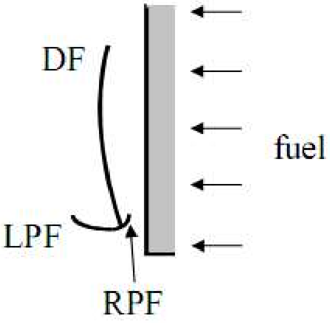
2D Mixing Layer



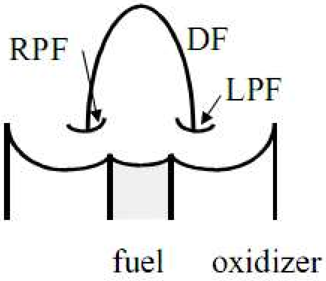
Flame Spread







Boundary Layer



Composite Propellant

Phenomenology of Flame Stabilization

- This is strictly a problem of flame dynamics, involving balance between the flame speed and flow speed at a single point
- Large liftoff distance $\Rightarrow$ flame has minimal influence on the flow
- Stabilizing flame segment varies from lean to rich, hence strongest point is at stoichiometric $\Rightarrow$ this is the stabilization point
- Flow slows down due to entrainment; momentum mixing accompanied by species mixing which changes stoichiometry $\Rightarrow$ Sc is an important parameter
- Solution given by the u-velocity and species distribution

Solution (1/2)

- u-velocity

$$u(x,\eta)=\frac{3}{8\pi}\left(\frac{J}{\mu_o Cx}\right)\frac{1}{\left(1+\frac{k\eta^2}{4}\right)^2} \qquad (12.4.19)$$

- Y_F distribution

$$\rho ur\frac{\partial Y_F}{\partial x}+\rho vr\frac{\partial Y_F}{\partial r}=\frac{\partial}{\partial r}\left(\frac{\mu r}{Sc}\frac{\partial Y_F}{\partial r}\right), \qquad Y_F(x,\eta)=\frac{y_F(\eta)}{x} \qquad (12.4.28.\ 32)$$

- At stabilization point $(x_L,\eta_L):\quad u\equiv S_{u,st};\ Y_F\equiv Y_{F.st}$

$$s_{u,\,\mathrm{st}}(x_L,\eta_L)=\frac{3}{8\pi}\left(\frac{J}{\mu_o Cx_L}\right)\frac{1}{(1+\frac{k\eta_L^2}{4})^2}, \qquad (12.4.33)$$

$$Y_{F,\mathrm{st}}(x_L,\eta_L)=\frac{(1+2Sc)}{8\pi}\left(\frac{I}{\mu_o Cx_L}\right)\frac{1}{\left(1+\frac{k\eta_L^2}{4}\right)^{2Sc}} \qquad (12.4.34)$$

Solution (2/2)

- Solving for (x_L, η_L)

$$\frac{\mu_o/\rho_o}{s_{u,\text{st}}}\left(\frac{x_L}{r_o^2}\right)=\frac{1}{8C}\left[\frac{3^{Sc}}{(1+2Sc)}\frac{Y_{F,\text{st}}}{Y_{F,o}}\right]^{\frac{1}{(Sc-1)}}\left(\frac{u_o}{s_{u,\text{st}}}\right)^{\frac{(2Sc-1)}{(Sc-1)}} \qquad (12.4.35)$$

$$\frac{k\eta_L^2}{4}=\left[\frac{3}{(2Sc+1)}\frac{Y_{F,\text{st}}}{Y_{F,o}}\frac{u_o}{s_{u,\text{st}}}\right]^{-\frac{1}{2(Sc-1)}}-1. \qquad (12.4.36)$$

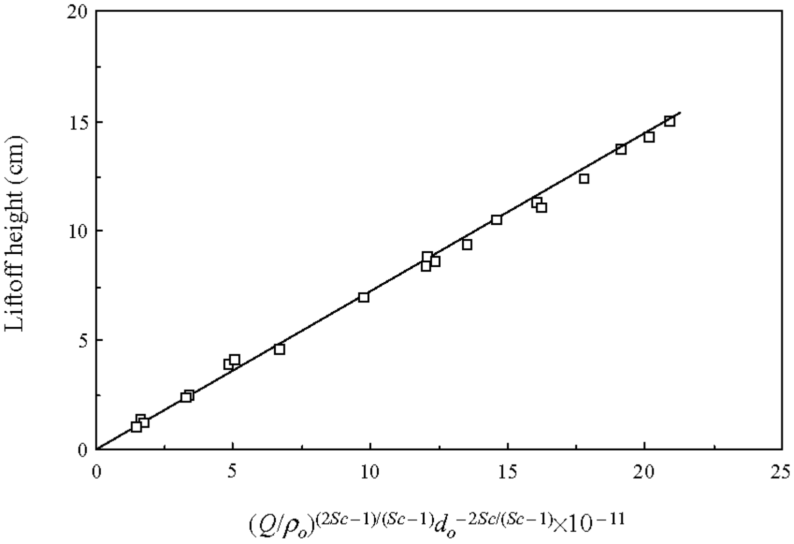
- Only $Sc > 1$ mixtures (propane, butane) can be stabilized
- $0.5 < Sc < 1$: methane, ethane, unstable

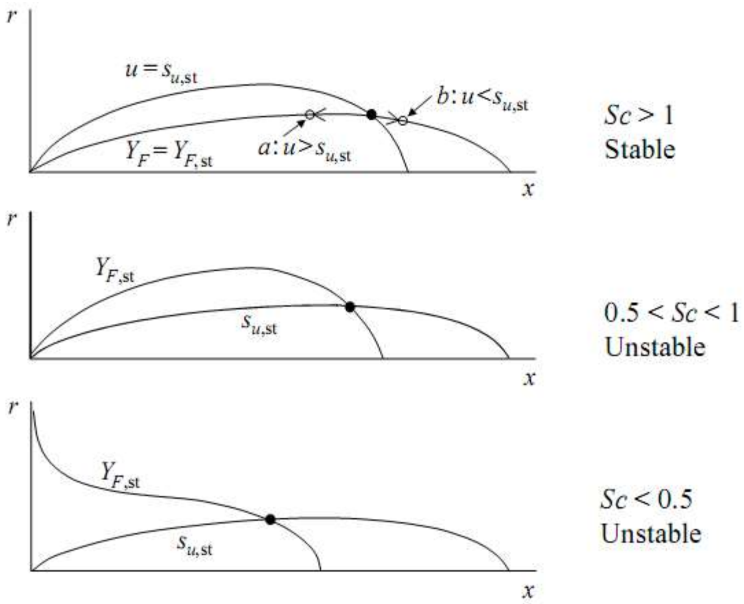
  $Sc < 0.5$: hydrogen; can't be blown off
- $\eta_L^2 > 0$ in (12.4.36) and $Sc > 1 \Rightarrow$

$$\frac{3}{(2Sc+1)}\left(\frac{Y_{F,\text{st}}}{Y_{F,o}}\right)\frac{u_o}{s_{u,\text{st}}}\le 1 \qquad (12.4.38)$$

  - Blowout velocity

$$u_{o,BO}=\frac{(2Sc+1)_{s_{u,\text{st}}}}{3}\left(\frac{Y_{F,o}}{Y_{F,\text{st}}}\right), \qquad (12.4.39)$$





3. Combustion in Supersonic Flows

- Weakly perturbed flows
- Detonation waves

General Considerations

- Terminology: compressible vs. low-speed flows
  - **(Aerodynamically) compressible (M≥0.3) flows**: density variation due to high flow velocity
  - **Low-speed flows**: density variation due to heat release, even aerodynamically incompressible
- Fundamental differences for high-speed flows
  - No isobaric assumption
  - Kinetic energy can be comparable to chemical energy
  - Diffusion can be negligible compared to convection
  - PDEs are hyperbolic (instead of elliptic or parabolic)
  - Flow variation effected by surfaces of discontinuities (Mach lines and shocks)

Governing Equations for Nondiffusive Flows

Governing equations

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \qquad (14.1.1)$$

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p \qquad (14.1.2)$$

$$\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} \qquad (14.1.3)$$

$$\rho \frac{DY_i}{Dt} = w_i, \quad i = 1, 2, ..., N, \qquad (14.1.4)$$

Equations of state

$$h = h(p, \rho, Y_i) \qquad (14.1.5)$$

$$T = T(p, \rho, Y_i) \qquad (14.1.6)$$

Entropy Production

- From Chap. 1, Eq. (1.2.7), in terms of material derivative

$$T\frac{Ds}{Dt}=\frac{Dh}{Dt}-\frac{1}{\rho}\frac{Dp}{Dt}+\sum_{i=1}^{N}(\bar{\mu}_i/W_i)\frac{DY_i}{Dt}. \qquad (14.1.8)$$

- Substituting (14.1.3) and (14.1.4):

$$\boxed{\frac{Ds}{Dt}=\frac{1}{\rho T}\sum_{i=1}^{N}(\bar{\mu}_i/W_i)w_i.} \qquad (14.1.9)$$

- Conditions for constant entropy: $\frac{Ds}{Dt}=0$
  - Frozen flow:

$$w_i=0 \qquad (14.1.11)$$

  - Equilibrium flow:

$$\sum_{i=1}^{N}(\bar{\mu}_i/W_i)w_i \sim \sum_{i=1}^{N}(\bar{\mu}_i/W_i)dY_i \sim \sum_{i=1}^{N}\bar{\mu}_i\ dN_i=0. \qquad (14.1.12)$$

Speed of Sound

- From $h = h(p, \rho, Y_i)$:

$$dh = \left(\frac{\partial h}{\partial p}\right)_{\rho, Y_i} dp + \left(\frac{\partial h}{\partial \rho}\right)_{p, Y_i} d\rho + \sum_{i=1}^{N} \left(\frac{\partial h}{\partial Y_i}\right)_{p, \rho, Y_j\,(j \neq i)} dY_i. \qquad (14.1.13)$$

- Substitute into (14.1.7)

$$Tds = \left[\left(\frac{\partial h}{\partial p}\right)_{\rho, Y_i} - \frac{1}{\rho}\right] dp + \left(\frac{\partial h}{\partial \rho}\right)_{p, Y_i} d\rho + \sum_{i=1}^{N} \left[\left(\frac{\partial h}{\partial Y_i}\right)_{p, \rho, Y_j, (j \neq i)} + \left(\frac{\overline{\mu}_i}{W_i}\right)\right] dY_i. \qquad (14.1.14)$$

- For sound propagation in frozen flow:

$$ds \equiv 0,\ dY_i \equiv 0 \ \Rightarrow \quad a_f^2 = \left(\frac{\partial p}{\partial \rho}\right)_{s, Y_i} = -\frac{(\partial h / \partial \rho)_{p, Y_i}}{(\partial h / \partial p)_{\rho, Y_i} - (1/\rho)}. \qquad (14.1.15)$$

- For sound propagation in equilibrium flow, have additional relation

$$Y_{i,e} = Y_{i,e}(p, \rho) \quad \text{or} \quad p = p(\rho, Y_i = Y_{i,e}) \qquad (14.1.16)$$

then

$$\left(\frac{\partial p}{\partial \rho}\right)_{s, Y_i = Y_{i,e}} = \left(\frac{\partial p}{\partial \rho}\right)_{s, Y_i} + \sum_{i=1}^{N} \left(\frac{\partial p}{\partial Y_i}\right)_{s, \rho, Y_j\,(j \neq i)} \left(\frac{\partial Y_i}{\partial \rho}\right)_{s, Y_i = Y_{i,e}}, \qquad (14.1.19)$$

$$a_e^2 = a_f^2 + d < a_f^2 \quad (d < 0)$$

Acoustic Equations (1/2)

- Define a streamfunction ϕ as

$$p' = -\rho_o \frac{\partial \phi}{\partial t}, \quad \mathbf{v}' = \nabla \phi, \qquad (14.1.31)$$

satisfying perturbed momentum equation

$$\rho_o \frac{\partial \mathbf{v}'}{\partial t} = -\nabla \cdot p' \qquad (14.1.24)$$

- Perturb all properties of flow by small amounts, governing equations degenerate to

$$\boxed{\tilde{\tau}_o \frac{\partial}{\partial t}\left(\frac{1}{a_{f,o}^2}\frac{\partial^2 \phi}{\partial t^2} - \nabla^2 \phi\right) + \left(\frac{1}{a_{e,o}^2}\frac{\partial^2 \phi}{\partial t^2} - \nabla^2 \phi\right) = 0,} \qquad (14.1.32)$$

- Relaxation time $\tau_o = \dfrac{\rho_o}{[(\partial w / \partial Y)_{p,T}]_o}$ (14.1.22)

defined through $\dfrac{DY}{Dt} \approx -\dfrac{Y - Y_e}{\tau_o}$ (14.1.21)

$\tau_0 \rightarrow 0$ **equilibrium flow**

$\tau_0 \rightarrow \infty$ **frozen flow**

Acoustic Equations (2/2)

- Frozen flow, $\tau_0 \rightarrow \infty$

$$\frac{\partial}{\partial t}\left(\frac{1}{a_{f,o}^2}\frac{\partial^2 \phi}{\partial t^2} - \nabla^2 \phi\right) = 0,$$

$$\Rightarrow \frac{1}{a_{f,o}^2}\frac{\partial^2 \phi}{\partial t^2} - \nabla^2 \phi = \mathrm{fn}(\mathbf{x}). \qquad (14.1.34)$$

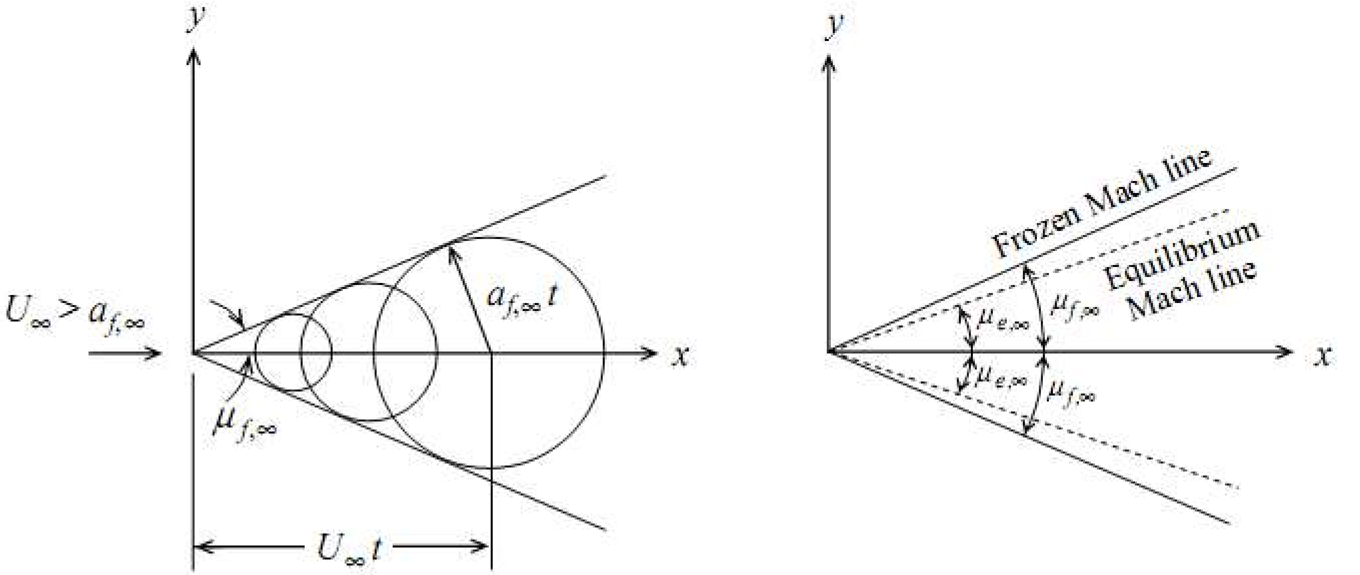
for fn(**x**) ≡ 0, $$\frac{1}{a_{f,o}^2}\frac{\partial^2 \phi}{\partial t^2} - \nabla^2 \phi = 0 \qquad (14.1.35)$$

- For equilibrium flow, $\tau_0 \rightarrow 0$

$$\frac{1}{a_{e,o}^2}\frac{\partial^2 \phi}{\partial t^2} - \nabla^2 \phi = 0 \qquad (14.1.36)$$

Uniform Flow over Slender Body

- The front of the disturbance wave propagates with the frozen speed of sound, carving out the leading Mach cone



(a) (b)

Quasi-1D Nozzle Flows (1/2)

- Governing equations
  - ○ $\rho u A = \text{const} \Rightarrow \frac{d\rho}{\rho} + \frac{du}{u} + \frac{dA}{A} = 0$ (14.3.1, 2)
  - ○ $\rho u du + dp = 0$ (14.3.3)
  - ○ $u du + dh = 0$ (14.3.4)
  - ○ $\rho u \frac{dY_i}{dx} = w_i, \quad i = 1, 2, \ldots, N.$ (14.3.5)
- Combing Eqs. (14.3.2) and (14.3.3) yields

$$\boxed{\frac{du}{u} = \frac{dA/A}{\frac{u^2}{(dp/d\rho)} - 1}.} \qquad (14.3.6)$$

- For an isentropic flow, $dp/d\rho = a^2$

$$\frac{du}{u} = \frac{dA/A}{M^2 - 1}, \qquad (14.3.7)$$

  - ○ Classical result: *M* = 1 at the throat $(dA = 0)$
  - ○ Flow transitions from *M* < 1 to *M* > 1 at throat of converging-diverging nozzle

Quasi-1D Nozzle Flows (2/2)

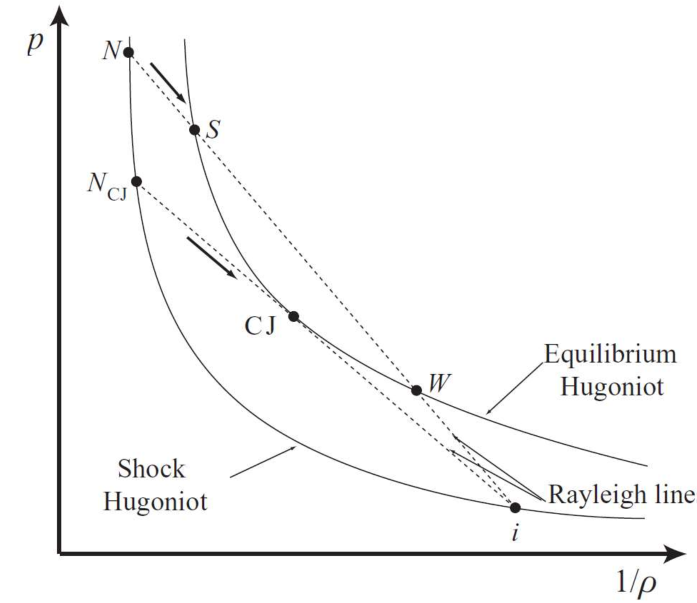
- For finite reaction rates

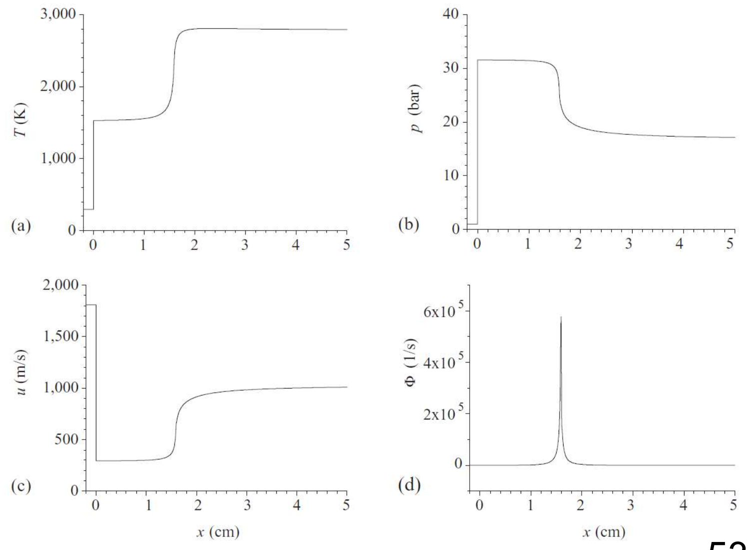
$$\frac{du}{u}=\frac{\frac{dA}{A}-\left[\rho\left(\frac{\partial h}{\partial \rho}\right)_{p,Y_i}\right]^{-1}\sum_{i=1}^{N}\left(\frac{\partial h}{\partial Y_i}\right)_{p,\rho,Y_{i(j\neq i)}}dY_i}{M_f^2-1}. \qquad (14.3.8)$$

- Vanishing of numerator implying attainment of sonic states is displaced from throat; displacement is usually downstream of the throat

ZND Structure of Detonation Wave

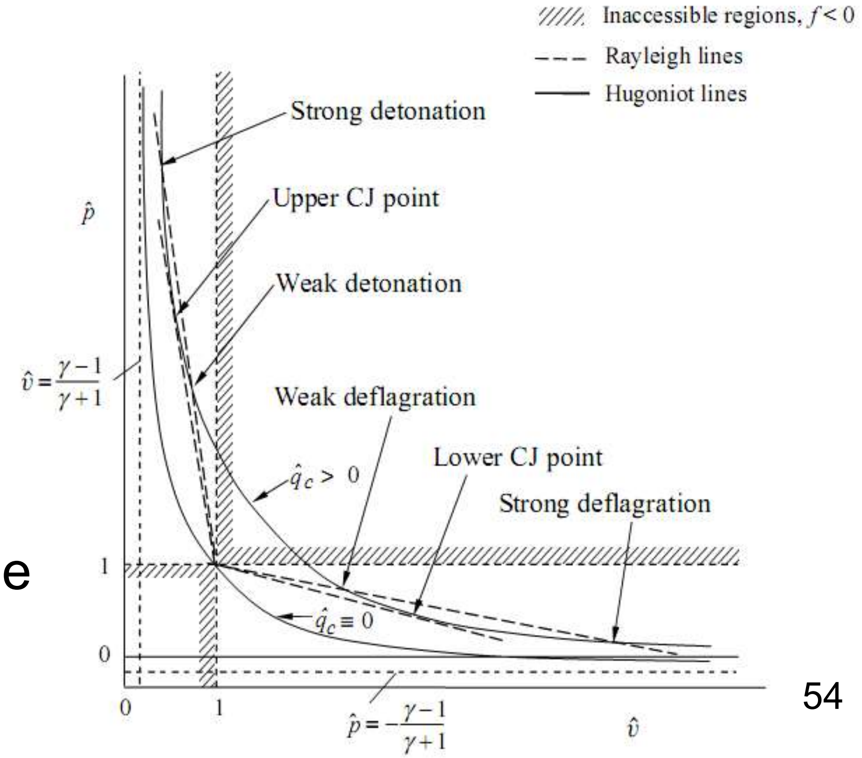
- ZND (Zel’dovich, von Neumann, Döring) Structure:
  - Leading shock of zero thickness; immediately downstream of shock: Neumann state
  - Shock compression initiates reaction
  - “Explosion” after an induction period
- Structure rules out weak detonation: i →N → S $\not\twoheadrightarrow$ W because S → W requires expansion shock, which violates entropy consideration
- C-J (Chapman-Jouguet) Structure:
  - Strong detonation: i →N → S
  - C-J wave: i →N_{CJ} → CJ





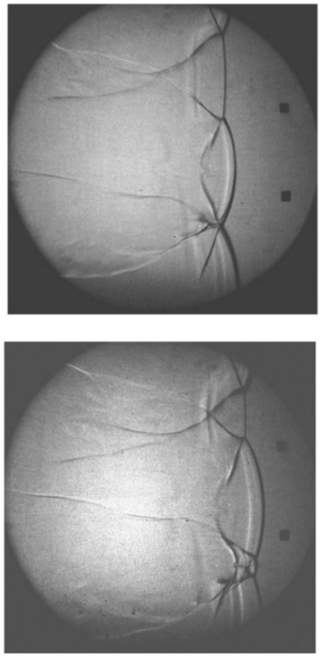
Chapman-Jouguet Detonation

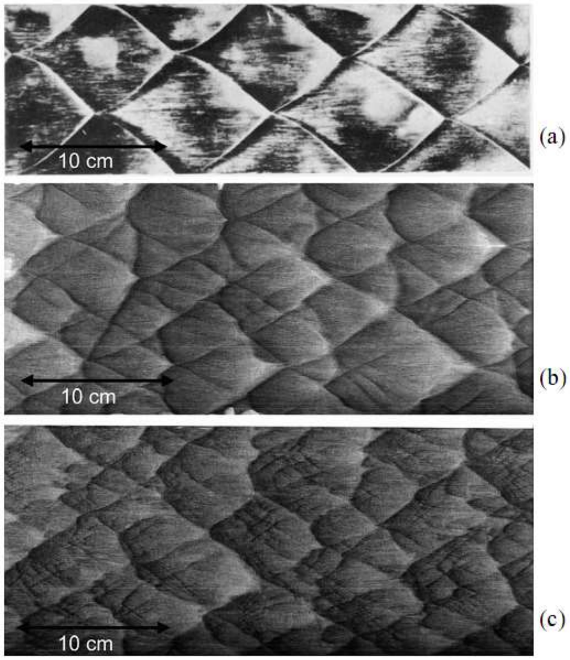
- Solution and structure: (1) equilibrium conservation of mass, momentum and energy; (2) downstream sonic condition
  - Solution uniquely defined, does not require knowledge of internal wave structure including chemistry
  - Solution agrees well with experiment except for near-limit propagations
- **Physical interpretations**: for overall mass conservation, compression by leading wave must be balanced by rarefaction downstream
  - 1D propagation from closed end of tube
  - 1D propagation from open end of tube
  - Propagation of spherical wave



Intrinsic 3D Detonation Structure

- Mach shock reflection results in regular and irregular diamond structure consisting of triple-shock units



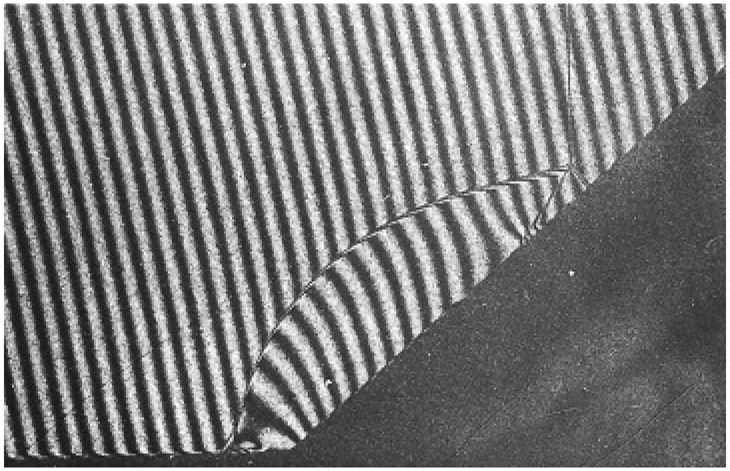


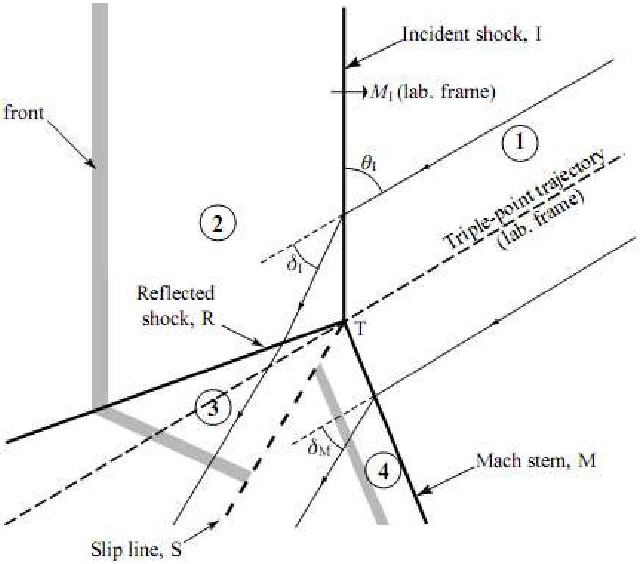
Analysis of Triple Shock

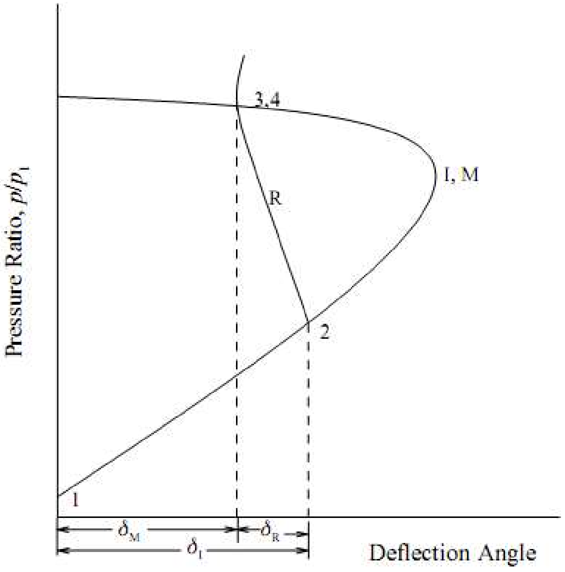
$$M_2^2 = \frac{2+(\gamma-1)M_1^2}{2\gamma M_1^2 \sin^2\theta_I - (\gamma-1)} + \frac{2M_1^2\cos^2\theta_I}{2+(\gamma-1)M_1^2\sin^2\theta_I} \qquad (14.6.3)$$

$$\cot\delta_I = \tan\theta\left[\frac{(\gamma+1)M_I^2}{2(M_I^2\sin^2\theta_I - 1)} - 1\right] \qquad (14.6.4)$$

$$\frac{p_2}{p_1} = \frac{2\gamma M_I^2\sin^2\theta_I - (\gamma-1)}{(\gamma+1)}. \qquad (14.6.5)$$

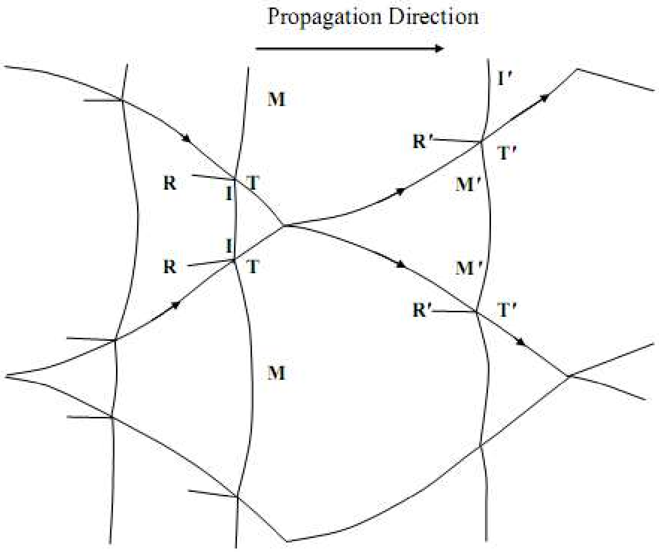


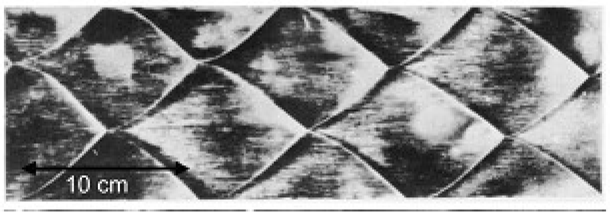




Triple Shock Interactions

- Incident shock (TI) of first triple-shock unit becomes Mach shock (T’I’) of second triple-shock unit upon collision, hence strengthened. Process repeats upon successive collision





Direct Detonation Initiation

- Zel'dovich criterion: Detonation successful if
  - Radius of blast wave = induction length of CJ wave, l_{ig}
  - When velocity of blast wave ≈ CJ wave
- Predicted critical energy for initiation

$$E_{j,\mathrm{cr}} = k_j \rho_1 D_{\mathrm{CJ}}^2 \ell_{\mathrm{ig}}^{j+1} \tag{14.8.1}$$

j = 0, 1, 2: planar, cylindrical, spherical geometries

- Result underpredicts observation by 6 to 8 orders of magnitude!
- Rigorous solution involves analyses of:
  - Propagation of strong blast wave
  - Structure and extinction of expanding, curved wave

Theory of Strong Blast Waves

- Deposition of energy E leads to formation of expanding blast wave
- Interested to determine subsequent history, in nonreacting environment
- Strong shock relations $\frac{\rho_2}{\rho_1} = \frac{\gamma+1}{\gamma-1}; \quad \frac{p_2}{p_1} \sim \frac{\rho_1 u_1^2}{p_1} \sim M_1^2 >> 1 \Rightarrow p_2 >> p_1$
- Problem characterized by two parameters: *E* and ρ_1
- There are three fundamental units: *M*, *L*, and *T* $\Rightarrow$

  Problem is self-similar
- From *E*, ρ_1, *r* and *t*, form nondimensional similarity parameter

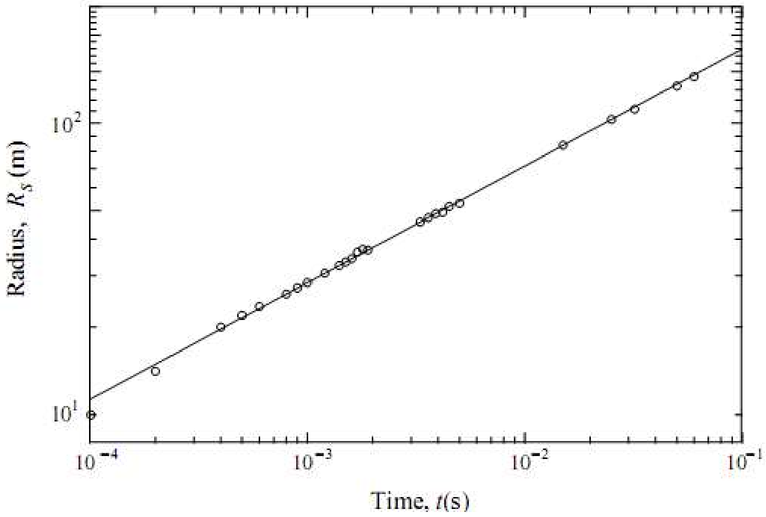
$$\xi = \frac{r}{(E/\rho_1)^{1/5} t^{2/5}}. \qquad (14.7.1)$$

Therefore: $R_s(t) \sim t^{2/5}$ (14.7.2)

$$D(t) = \frac{dR_s(t)}{dt} = \frac{2}{5}\frac{R_s}{t} \sim t^{-3/5} \qquad (14.7.3)$$

- Detailed analysis yields

$$E = \left[\frac{4\pi}{3}\frac{(3\gamma-1)}{(\gamma-1)(\gamma+1)^2}\right]\rho_1 D^2 R_s^3 \qquad (14.7.13)$$



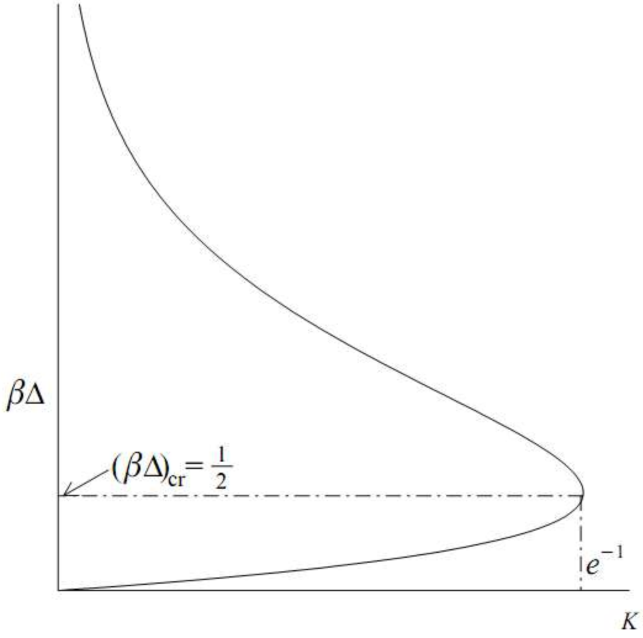
First Atomic Bomb Test

Curvature-Induced Quenching Limit

- Rigorous analysis shows effect of stretch through flow divergence, e.g. for continuity,
  - Lab co-ordinate: $\frac{\partial\rho}{\partial t}+\frac{\partial(\rho v)}{\partial r}+\frac{2\rho v}{r}=0$ (14.8.2)
  - Wave co-ordinate: $\frac{\partial\rho}{\partial\tau}+\frac{\partial(\rho u)}{\partial\chi}+\frac{2\rho(D-u)}{(R_s-\chi)}=0$ (14.8.6)
  - Assume quasi-steady and quasi-planar: $\frac{d(\rho u)}{d\chi}=-\frac{2\rho(D-u)}{R_s}$ (14.8.9)

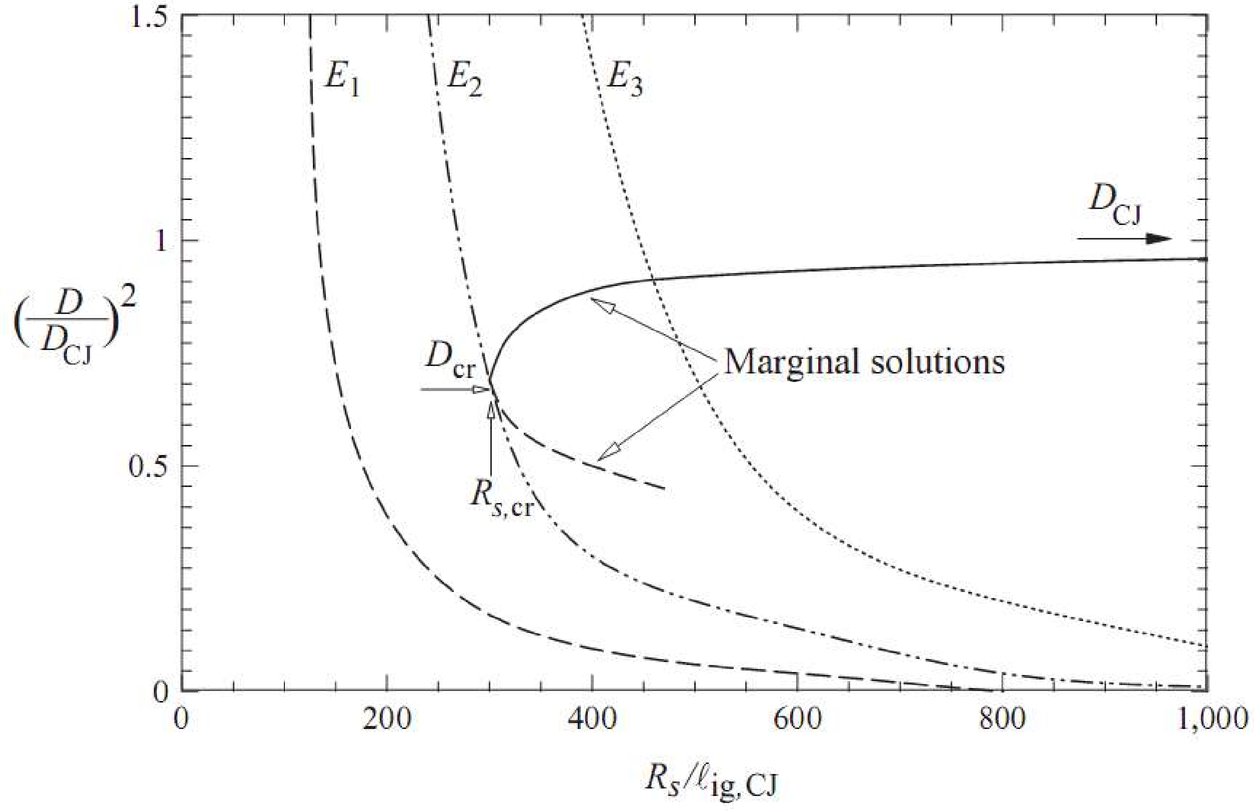
$$\frac{2(D-u)}{R_s}\equiv \text{stretch rate}$$

- **Physical interpretation**: Flow divergence after shock slows down the flow ⇒ facilitates weakening of shock by downstream rarefaction wave ⇒ failure to form detonation
- Analysis yields dual solution, turning point behavior with quenching limit



Curvature–Affected Initiation Limit

- Combine blast wave theory with quenching limit analysis yields initiation limit
- Result agrees with experimental observations



Indirect Detonation Initiation:
Synchronized Initiation

- Zel'dovich hypothesis:
  - Reactivity (e.g. temperature, radical concentration) gradient, g, in nonuniform mixture leads to sequential explosion of fluid elements
  - If compression wave generated propagates at same speed as the sequential explosion, then resonance occurs, leading to formation of detonation
- Four possible outcomes depending on $U_{spon}=1/g$:

(a) $U_{spon} > D$: Constant volume explosion

(b) $a < U_{spon} < D$: Transition to detonation

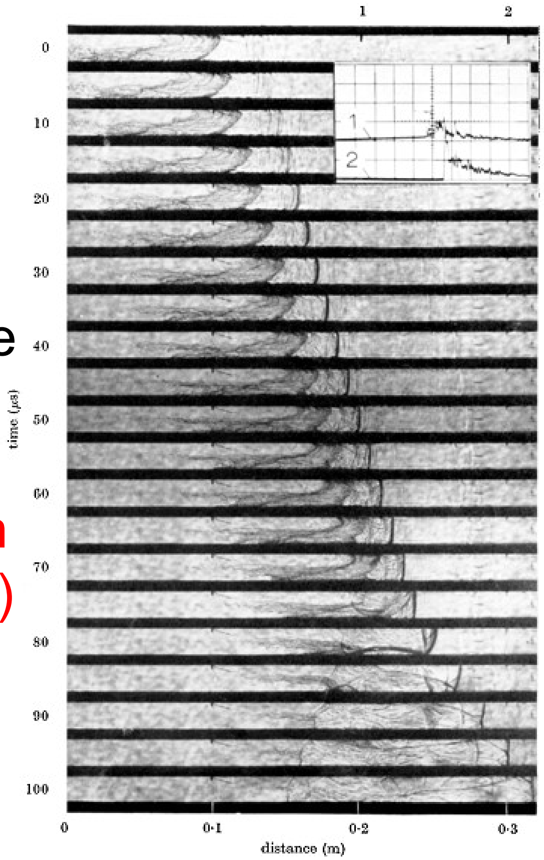
(c) $s_L < a < U_{spon}$: Failure of transition

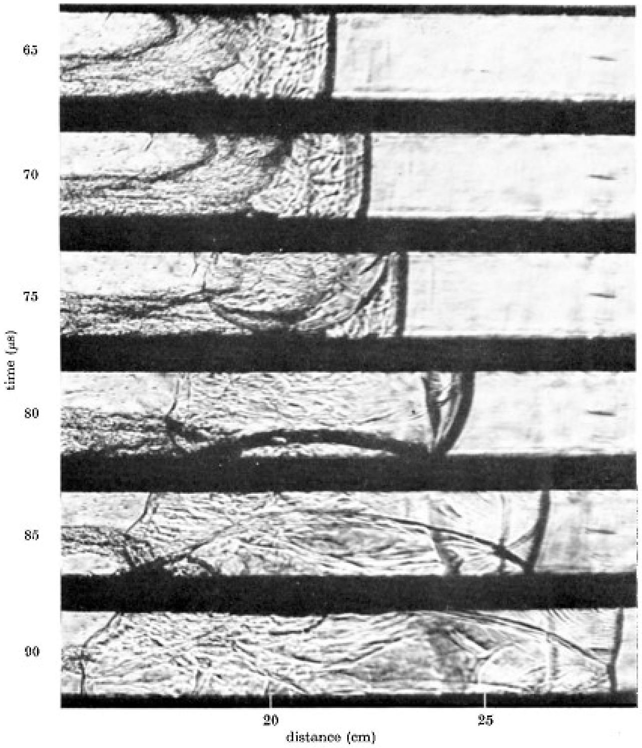
(d) $U_{spon} < s_L$: Diffusion dominates; laminar flame formation

Indirect Detonation Initiation:

Deflagration to Detonation Transition (DDT)

- **Analogy with shock formation**: successive generation and coalescence of compression wave by propagating laminar flame lead to shock and detonation formation; predicted induction length excessively long (e.g. km)
- Acceleration through obstacles and upstream turbulence generation





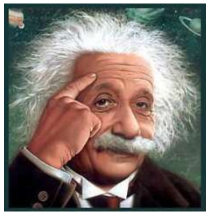
Closing Remarks of Day 5 Lecture (1/2)

- Theoretical combustion can benefit much from the many elegant and useful results of fluid mechanics (with heat and mass transfer)
- Needs in study of turbulent flows:
  - Role of heat release and flamefront instabilities in transition to and structure of turbulent flames
  - Revision of regime diagram: effects of *Le*, transiency of stretch, flamefront instabilities,…
  - Description of local extinction and re-ignition
  - Turbulence-chemistry coupling
  - Sub-grid modeling in LES

Closing Remarks of Day 5 Lecture (2/2)

- Boundary layer flows
  - Finite-rate reaction destroys similarity in most boundary layer flows; although localized reaction can lead to local similarity
  - Few theoretical studies of chemically reacting turbulent boundary layer flows
  - Need analysis of flame stabilization in the leading edge of a boundary layer
- Supersonic flows
  - Asymptotic analysis of weakly perturbed flows
  - Does an expanding cellular detonation self accelerate?
  - Mechanism of deflagration-to-detonation transition in free space

Day 5 Specials

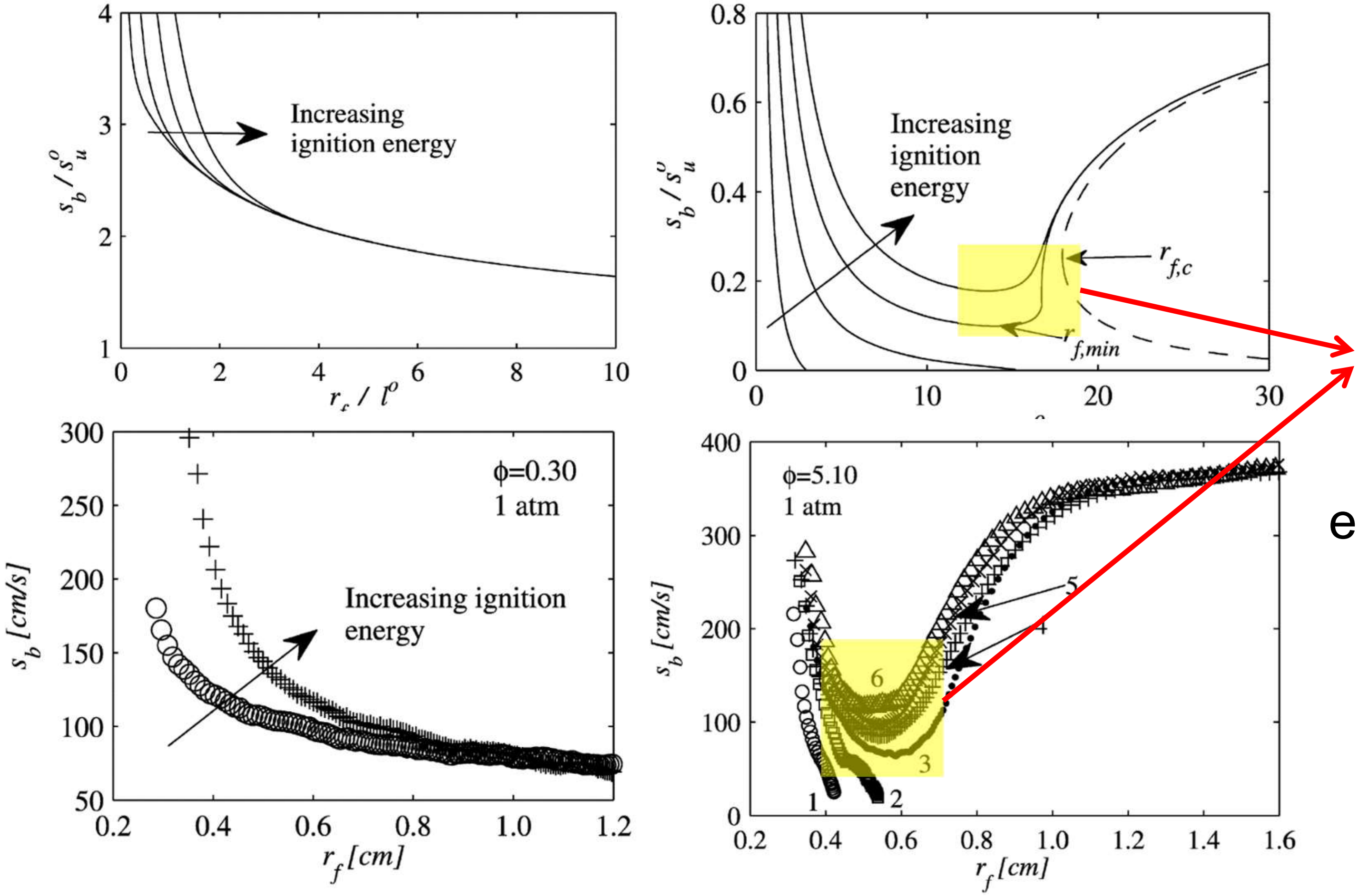


1. Facilitated ignition through turbulence
2. Astro-combustion: detonative propagation of the Crab Nebula front

1. Facilitated Ignition through Turbulence

Spark Ignition in Quiescence

***Le* < 1** ***Le* > 1**

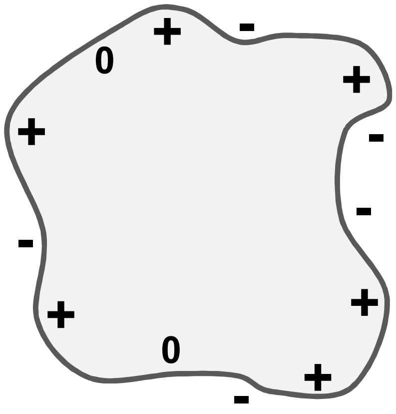


Critical state!

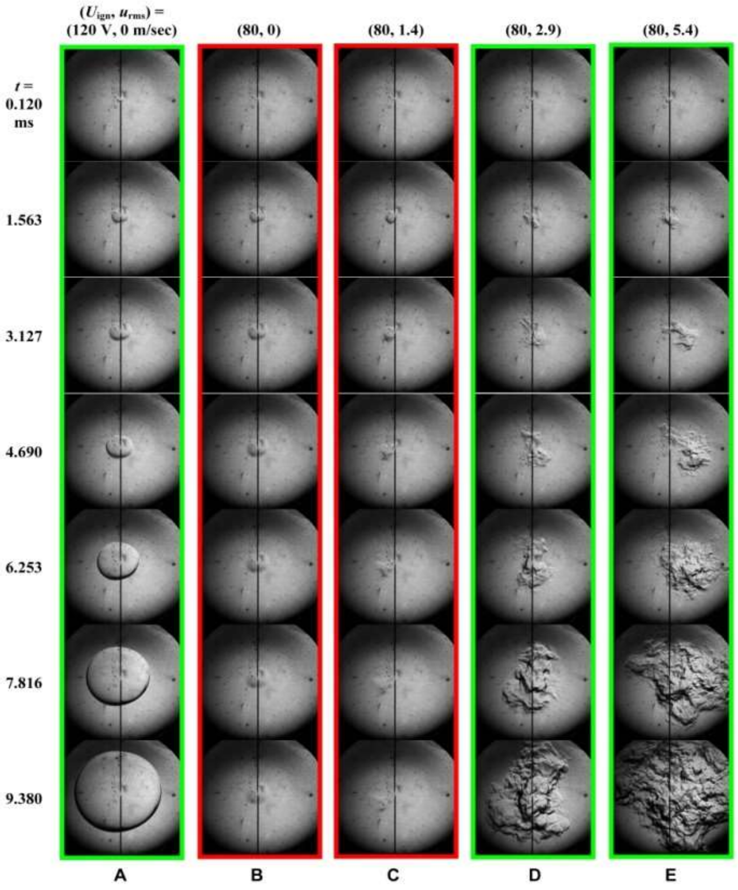
Competition between initial energy deposit and stretch effect

Spark Ignition in Turbulence

- What is the effect of turbulence on ignition?
- Conventional **understanding**:
  - **Turbulence increases the dissipation rate of deposited energy**
  - **Therefore m**ore difficult to ignite in turbulence
- However, turbulence can create locally zero-stretch or negatively-stretched flamelet, which is favorable for Le > 1



Ignition Can Indeed Be Facilitated by Turbulence!



H_2/Air

- Fine-structure stretch effect could facilitate local & hence global ignition (*Le* >1 mixtures)
- A: Ignition in quiescence
- B: Failure in quiescence (reduced spark energy)
- C-E: at same reduced spark energy, ignition achieved with increasing turbulence
- Facilitating result supported by extensive mixture variations

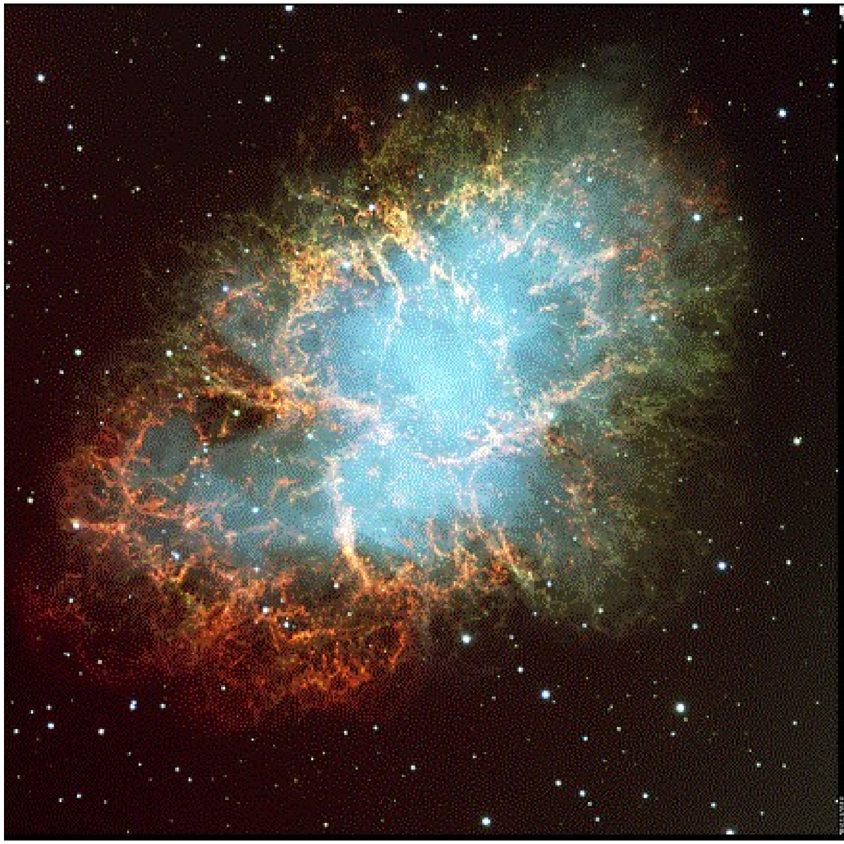
2. Astro-combustion:

Detonative Propagation of the Crab Nebula Front

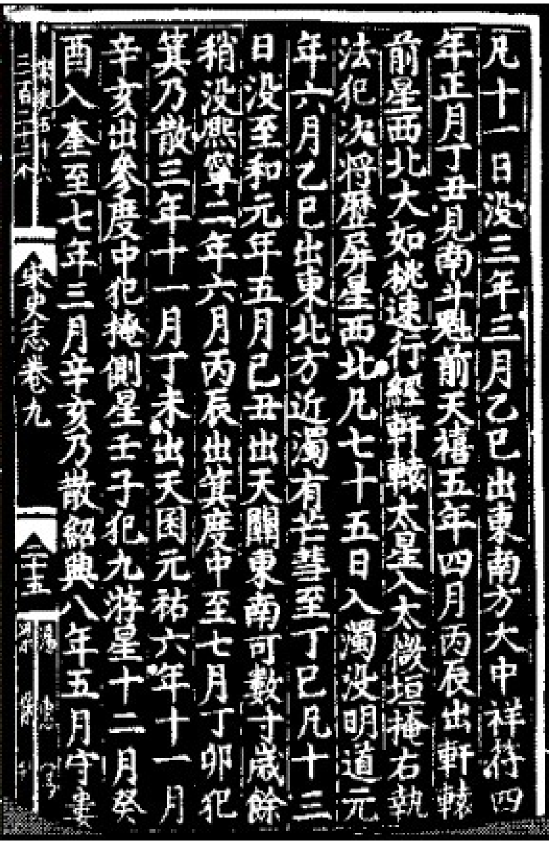
The Crab Nebula: Remnant of Supernova A.D. 1054

《宋史•天文志 第九》：至和元年五月己丑，出天关东南可数寸，岁余稍没。

Hubble view of the remnant



《宋会要》



凡十一日没三年三月乙巳出東南方大中祥符四年正月丁丑見南斗魁前天禧五年四月丙辰出軒轅前星西北大如桃速行經軒轅大星入太微垣掩右執法犯次將歷屛星西北凡七十五日入濁没明道元年六月乙巳出東北方近濁有芒彗至丁巳凡十三日没至和元年五月己丑出天關東南可數寸歲餘稍没熙寧二年六月丙辰出箕度中至七月丁卯犯箕乃散三年十一月丁未出天囷元祐六年十一月辛亥出參度中犯掩側星壬子犯九游星十二月癸酉入奎至七年三月辛亥乃散紹興八年五月守婁

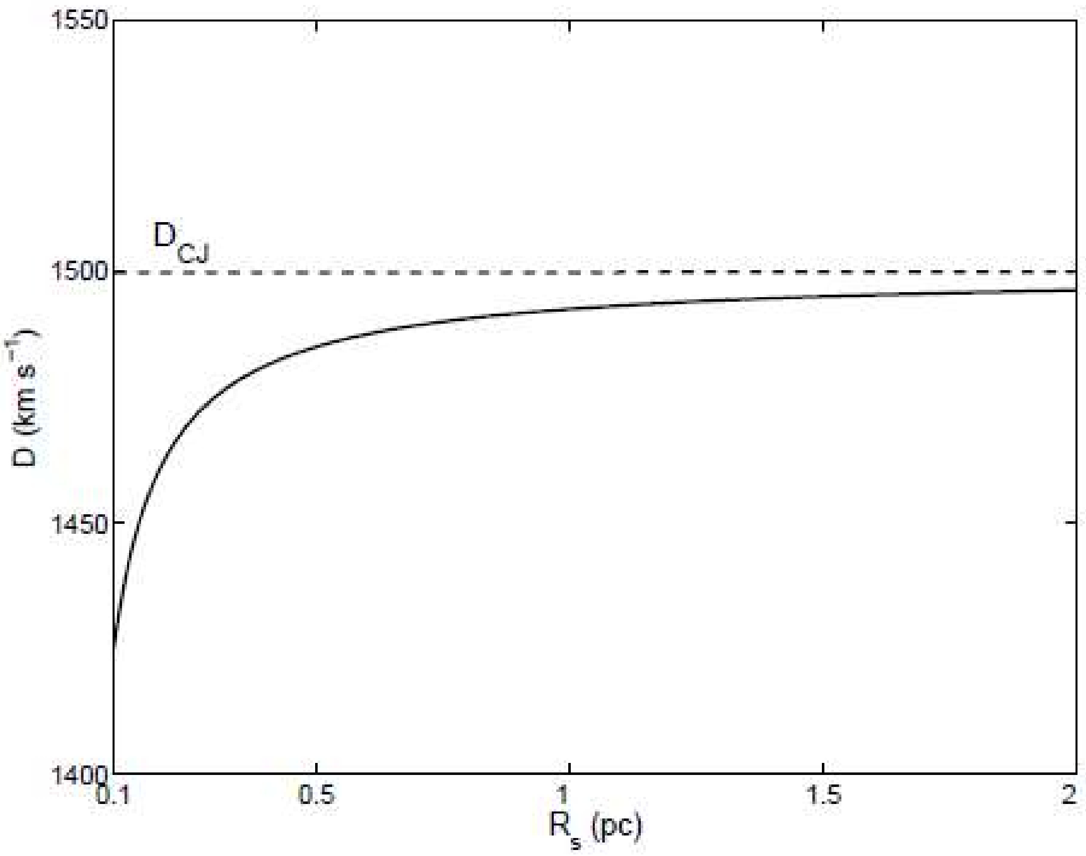
宋史志卷九

二五

The Puzzle

- Crab nebula was first observed in 1054
- Data from 1939 to 1992 yield birth in 1130±16 years, assuming constant front propagation velocity
- Discrepancy suggests front acceleration (8.2×10^{-4} cm/s^2)
- Furthermore, un-sustained shock front should actually decelerate
- Consequently, shock is actually a detonation wave, with energy release behind it to at least arrest the deceleration
- But what is causing the acceleration?

Accelerative Expansion of the Nebula Outer Envelope



Evolution of radius of the nebula outer envelope vs. its expansion velocity

Sustenance of the expanding envelope: Detonation instead of non-reactive shock wave

Nature of the acceleration: Relaxation of the curvature effect

Overarching Messages of the Course:
Appreciate the Beauty!

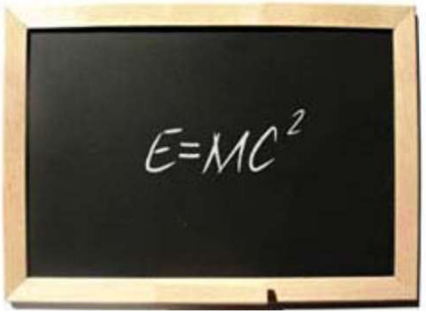
- Beauty is the driving force of the human intellect
- Unification is the ultimate goal of the scientific pursuit

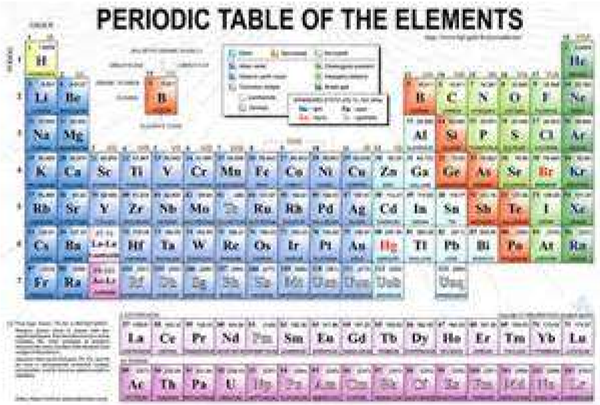
$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$





Unified concepts and theories are inevitably beautiful

Overarching Messages of the Course:
Expand the Mind!