Soot modeling in unsteady, one-dimensional flames

BYU Chemical Engineering

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Motivation

- Soot formation is a key process in flames and fires
  - Radiative heat transfer
  - Incomplete combustion
  - Environmental and health impacts
- Soot affects radiation, which affects temperature, which affects soot…
- Modeling soot formation is challenging
  - Complex chemistry among many species
  - Representation of the particle size distribution
  - Potentially several PSD coordinates
  - Large range of scales
- Combustion simulations
  - complex chemistry, turbulent flow, multicomponent mass transfer, radiative heat transfer, soot formation
  - Burden on users/developers for submodel expertise
  - Availability of libraries that offload submodels facilitates code development and progress
    - Chemkin, Cantera, RadLib, etc.

https://energy.sandia.gov/programs/nuclear-energy/nuclear-energy-safety-security/

SootLib

- SootLib: library of soot models for simulation
- Open source, C++, no external libraries besides LAPACK
- Documented
- Allows consistent model comparison

Soot Processes

- Nucleation
- Growth
- Oxidation
- Coagulation
- PAH condensation

Particle Distributions

- Monodispersed
- Lognormal
- Quadrature MOM
- MOM-Interpolative Closure
- Sectional

RadLib

- RadLib: library of radiation property models
- Open source, C++
- C++, Python, and Fortran interfaces
- Three models:
  - Planck Mean absorption coefficients
  - Weighted Sum of Gray Gases
  - Rank-Correlation Spectral Line Weighted Sum of Gray Gases

Nucleation

Semi-empirical

Leung et al.

- *K. M. Leung, R. P. Lindstedt, W. P. Jones, A simplified reaction mechanism for soot formation in nonpremixed flames, Combustion and Flame 87 (1991) 289–305*
- $C_2H_2 \rightarrow 2C_{soot} + H_2$

Lindstedt

- *R. P. Lindstedt, Simplified soot nucleation and surface growth steps for non-premixed flames, in: H. Bockhorn (Ed.), Soot Formation in Combustion, no. 59 in Springer Series in Chemical Physics, Springer-Verlag Berlin Heidelberg, 1994, pp. 417–441*
- $C_2H_2 \rightarrow 2C_{soot} + H_2$
- ($C_6H_6 \rightarrow 6C_{soot} + 3H_2$)

Detailed

PAH Nucleation, Blanquart & Pitsch

- *G. Blanquart, H. Pitsch, A joint volume-surface-hydrogen multi-variate model for soot formation, in: H. Bockhorn, A. D'Anna, A. F. Sarofim, H. Wang (Eds.), Combustion Generated Fine Carbonaceous Particles, KIT Scientific Publishing, 2009, pp. 437–463.*
- 8 PAH species
- Free molecular PAH collisions to form PAH Dimers
  - $PAH_i + PAH_i \rightarrow$ Dimer
  - Only self-collision assumed
  - Dimers not distinguished
- Dimer coagulation to form soot
  - Dimer + Dimer $\rightarrow C_{soot}$
  - Dimers assumed in steady state, quadratic eqn:

$$\underbrace{\sum_i^{n_P}\gamma_i\frac{1}{2}\beta_{P_i,P_i}n_{P_i}^2}_{\text{formation}} = \underbrace{\beta_{D,D}\mathbf{n_D}^2}_{\text{soot nuc.}} + \underbrace{\sum_k^{n_s}\beta_{D,C_k}n_{C_k}\mathbf{n_D}}_{\text{condensation}}$$

Growth

Semi-empirical

Leung et al.

- $C_2H_2 + C_{n,soot} \rightarrow C_{n+2,soot} + H_2$
- $R_g \propto \sqrt{A}$

Lindstedt

- $C_2H_2 + C_{n,soot} \rightarrow C_{n+2,soot} + H_2$
- $R_g \propto A$

PAH Condensation

- Consistent with PAH nucleation
- $D_{CxHy} + C_{n,soot} \rightarrow C_{n+x,soot} + (y/2)H_2$
  - Dimer size computed as weighted average over PAH contributions to PAH nucleation

$$R_{cnd,k} = \beta_{D,C_k}n_{C,k}n_D m_D \ \ (=) \ \ \mathrm{kg/m^3s}$$

Detailed

HACA

- *ABF mechanism: Appel, Bockhorn, Frenklach, Combustion and Flame 121:122-136 (2000).*

$$\text{C-H} + \text{H} \rightleftharpoons \text{C*} + \text{H}_2$$
$$\text{C-H} + \text{OH} \rightleftharpoons \text{C*} + \text{H}_2\text{O}$$
$$\text{C*} + \text{H} \rightarrow \text{C-H}$$
$$\text{C*} + \text{C}_2\text{H}_2 \rightarrow \text{(3C)-H} + \text{H}$$
$$\text{C*} + \text{O}_2 \rightarrow 2CO$$

- C* from QSSA over given reactions
- *Reverse reactions from Ken Revzan and Frenklach 02/15/02 code soot.f: combustion.berkeley.edu/soot/codes/routines.html*
- *Rate is proportional to frac. available surf. sites α*

$$\alpha = \tanh\left(\frac{a}{\log_{10}(M_1/M_0)} + b\right)$$

- a(T), b(T) from *Balthasar and Frenklach, Combust. Flame 140:130-145 (2005)*

Oxidation

O_2 Global: Leung, Lindstedt, Jones 1991

- $C_{soot} + (1/2)O_2 \rightarrow CO$

O_2 Global: Lee, Thring, Beer 1962

- $C_{soot} + (1/2)O_2 \rightarrow CO$

O_2 Elementary: Nagle, Strickland-Constable 1962

- $C_{soot} + (1/2)O_2 \rightarrow CO$
- Graphite rods

OH Elementary Neoh, Howard, Sarofim 1981

- $C_{soot} + OH \rightarrow CO + H$

$$R = 1290 \times 0.13 P_{OH} T^{-0.5}$$

- R (=) kg/m^2s, P_{OH} (=) atm, T (=) K

HACA O_2, OH: Appel, Bockhorn, Frenklach 2000

- $C_{soot} + OH \rightarrow CO + H$; from Neoh
- $C^* + (1/2)O_2 \rightarrow CO$
- Same rate as used in HACA for C* from QSSA

Optimized O_2, OH: Guo, Anderson, Sunderland 2016

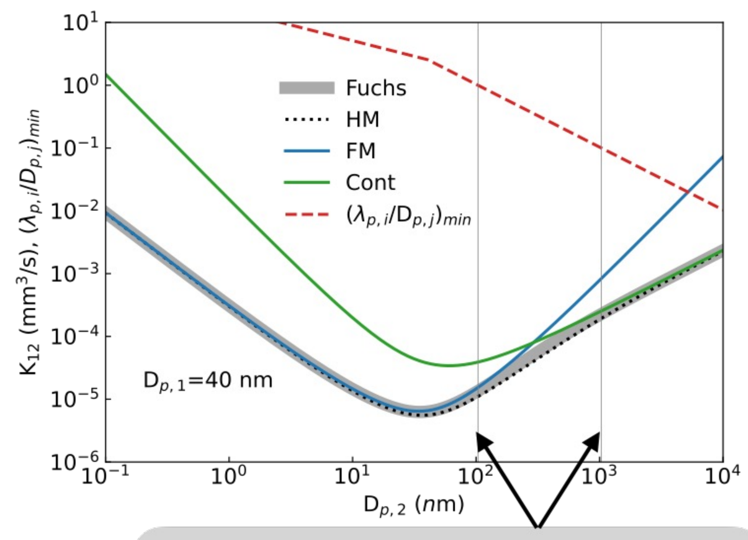
- $C_{soot} + (1/2)O_2 \rightarrow CO$
- $C_{soot} + OH \rightarrow CO + H$
- Optimized among 12 experiments.
  - OH efficiency = 0.1

Optimized O_2, OH: Josephson et al. 2017

- $C_{soot} + (1/2)O_2 \rightarrow CO$
- $C_{soot} + OH \rightarrow CO + H$
- Optimized among 13 experiments using Bayesian statistics.
  - OH efficiency = 0.15

Coagulation

- Assume spherical particles
- Two regimes
  - Free molecular: small particles
    - $D << \lambda_{mfp}$
  - Continuum: large particles
    - $D >> \lambda_{mfp}$
  - Note, λ_{mfp} is the mean free path of the particle, *not* the gas.



$$Kn = \left(\frac{\lambda_{p,i}}{D_{p,j}}\right)_{min} \qquad 0.1 \leq Kn \leq 1$$

Brackets the transition region

$$\dot{S}_{\mathrm{coag}}(m) = \frac{1}{2}\int_0^m \beta_{\mu,m-\mu}n(\mu)n(m)d\mu - \int_0^\infty \beta_{\mu,m}n(\mu)n(m)d\mu$$

$$\beta_{m,\mu}^{FM} = c\epsilon_c\left(\frac{\pi k_b T}{2}\right)\left(\frac{6}{\pi\rho_s}\right)^{2/3}\left(\frac{1}{m}+\frac{1}{\mu}\right)^{1/2}(m^{1/3}+\mu^{1/3})^2$$

$$\beta_{m,\mu}^{C} = \frac{2k_bT}{3\mu_v}\left(\frac{C_m}{m^{1/3}}+\frac{C_\mu}{\mu^{1/3}}\right)(m^{1/3}+\mu^{1/3})$$

Transition Region

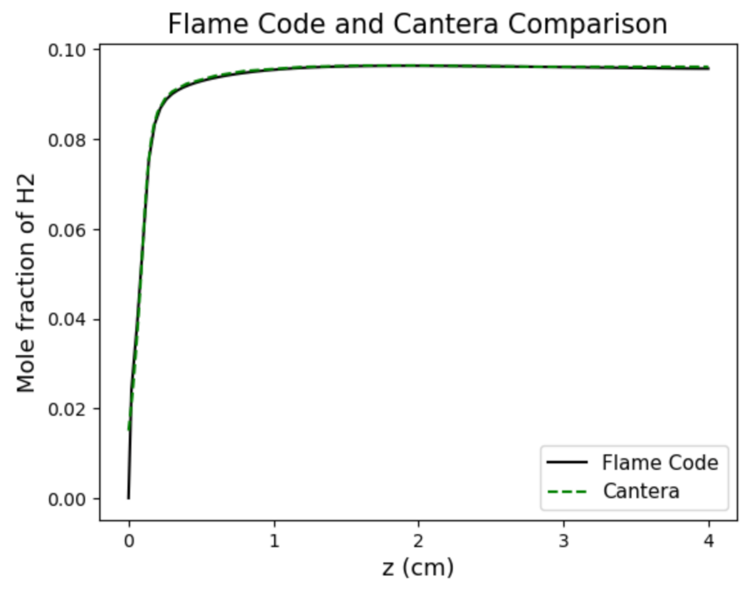
- Harmonic mean $\quad HM = \dfrac{C \cdot FM}{C + FM}$
- A more theoretically-based transition by Fuchs is also implemented

1-D Unsteady Flame Code

- Has unsteady and steady solvers.
- Open source, C++
- Can bring in Cantera, SootLib, RadLib, and other libraries.
- Solves burner-stabilized premixed and non-premixed flames.
- Two methods for calculating fluxes: mixture averaged and unity Lewis number.

Cantera vs. Flame Code

- Cantera has a burner-stabilized flame code that solves the steady problem.
- However, integrating soot formation into Cantera is difficult.
- Only works for the simplest soot models.
- Cantera is used to calculate the gas state.
- Using unity Le, Cantera and this flame code are in agreement.



Sectional Models

- Can't afford to consider all soot sizes
  - 50 nm particle ~ 6 million C's
- Divide the PSD into sections
- Assume uniform size within a section
- Geometrically spaced

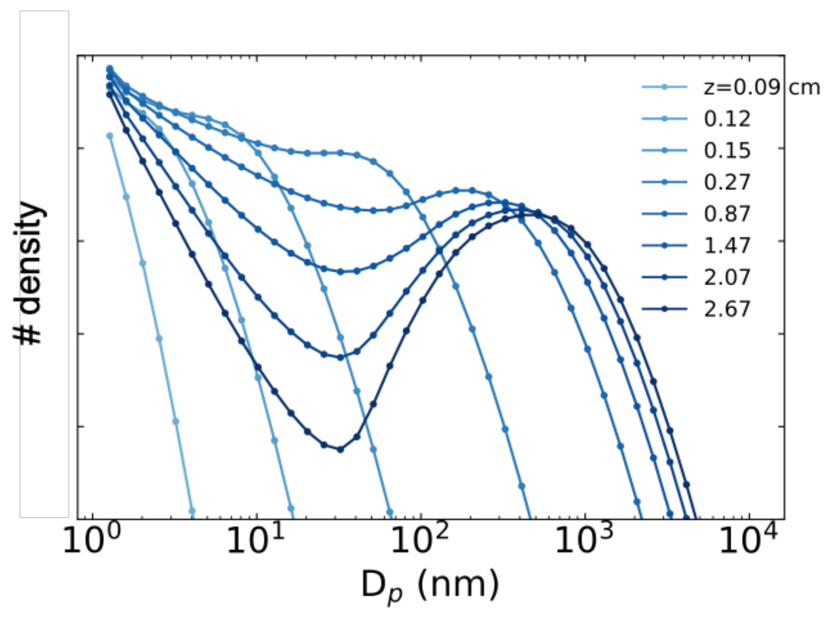
$$m_{min}\left(F^0,\ F^1,\ F^2,\ldots,\ F^{N-1}\right)$$

- Nucleation is into the first bin
- Growth and oxidation are transport in the size coordinate, written in n_i.

$$\frac{dn_{i,g}}{dt} = \frac{k_g A_{i-1}n_{i-1}}{m_i - m_{i-1}} - \frac{k_g A_i n_i}{m_{i+1} - m_i}$$

- Coagulation "lands" between bins
  - Assign to neighbors: conserve # and m

Example: premixed flame evolution



Method of Moments (MOM)

- Sectional models still require many bins
- Instead, solve for moments of the PSD

$$\frac{dn(m)}{dt} = \dot{S}(n(m))$$

$$M_k = \int m^k n(m)dm$$

$$\frac{dM_k}{dt} = \int m^k \dot{S}dm = \dot{S}_k$$

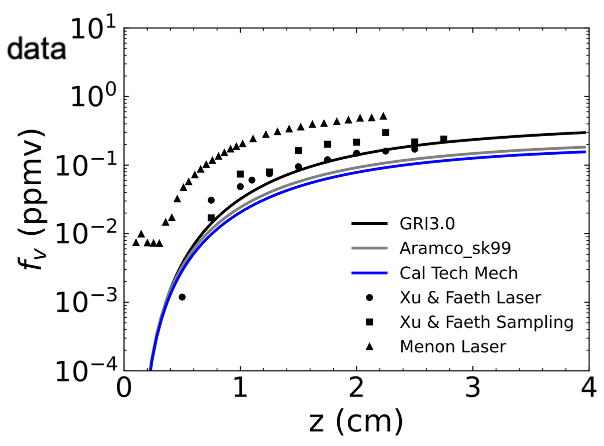
- The moment source term involves integration over the unknown size distribution n(m).
- This requires a method for closure
- For soot growth, the closure of the fractional moments $M_{k-1/3}$ are needed.

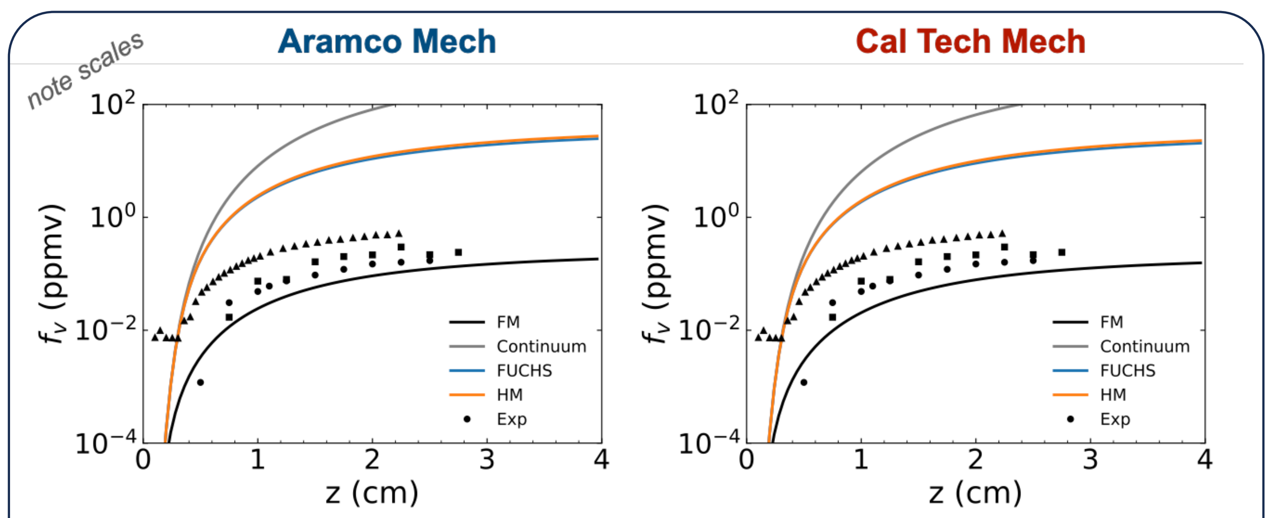
Closure Approaches

- **Assumed shape n(m)**
  - Monodispersed
  - Lognormal
  - (Power-law + lognormal)
- **Interpolative closure**
  - Interpolate whole order moments to fractional moments
- **Quadrature**
  - QMOM
  - (DQMOM)
  - (CQMOM)

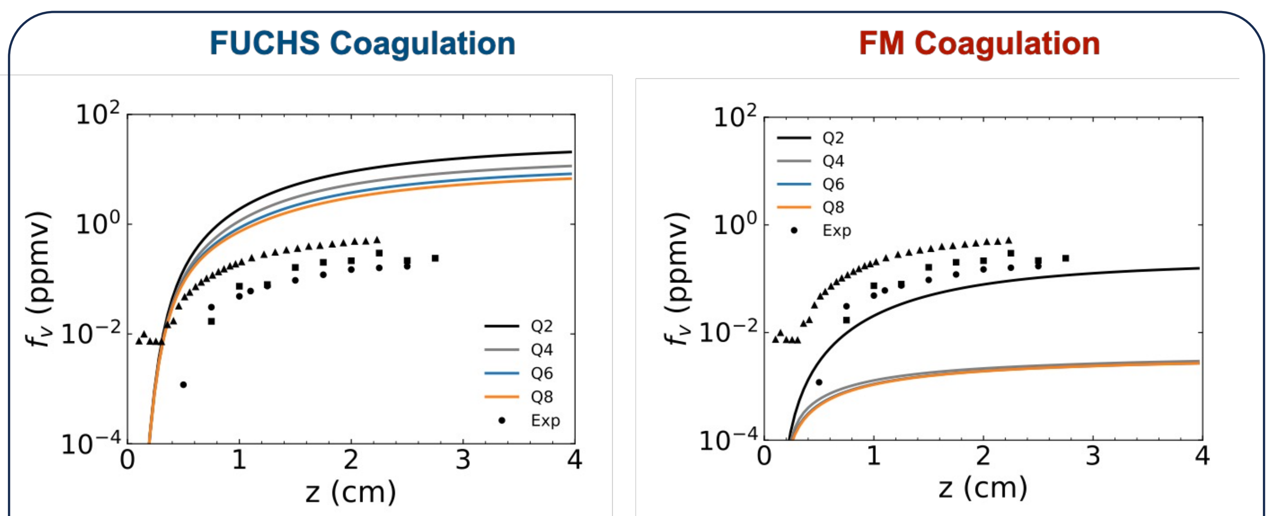
Results

- Burner stabilized premixed flame
- Significant scatter in experimental data
- ISF laminar premixed flame 2
  - C_2H_4-air
  - $\Phi = 2.34$
  - $v_0 = 6.73$ cm/s
- Post-process data with SootLib
  - Fixed T(z) profile, experimental
- Models
  - Gas chemistry: Multiple
  - Nucleation: Lindstedt
  - Growth: Lindstedt
  - Oxidation: Leung
  - Coagulation: FM
  - PSD: QMOM (nsoot = 2)





- Large variation with coagulation models used → 3 orders of magnitude difference
- HM and Fuchs give nearly identical results
- Lower FM f_v from fewer particles → lower surface area for growth
- Soot models should consider effects of all model components



- QMOM shows convergence with increasing environments
  - Q2 has 2 moments, 1 quadrature node (equivalent to monodispersed)
  - Q4 has 4 moments, 2 quadrature nodes
  - Q6 has 6 moments, 3 quadrature nodes
  - Q8 has 8 moments, 4 quadrature nodes
- Q2 → Q8 at z=4 cm