THE EFFECT OF REVERSIBILITY AND HIGH PRESSURE ON SOOT FORMATION

by

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A thesis submitted in conformity with the requirements for the degree of Doctorate of Philosophy
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Abstract

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Reducing soot emissions from combustion processes is important due to the negative health and environmental effects of atmospheric soot. In order to achieve this goal, there has to be a fundamental understanding of the mechanisms of soot formation to allow for the determination of economically viable methods of reducing these emissions. Due to the highly complex nature of soot formation, detailed numerical models are employed to gain fundamental understanding of the factors that affect each mechanism of soot evolution. Since most practical combustion devices operate at elevated pressures, it is important to understand the effect of pressure on soot formation. The overall goal of this thesis is to improve the currently employed models by replacing tunable constants with fundamental physics, with secondary goals of applying the model to high pressure conditions. This thesis is divided into four research studies. The first is a detailed description and validation of the numerical code utilized to simulate soot formation, denoted as the CoFlame code. The second study develops a novel model for two key soot formation processes, which are the polycyclic aromatic hydrocarbon (PAH) nucleation and condensation processes. The novel reversible PAH clustering (RPC) model is shown to be superior to previous models. The third study enhances the RPC model to include nucleation and condensation events from a wide range of PAHs. It is shown that smaller PAHs contribute the most to the nucleation process, while all PAHs contribute to the condensation process. The fourth and final study applies the CoFlame code to high pressure flames and determines that shear between the air and fuel streams is responsible for the formation of recirculation zones at elevated pressures and complete conversion of fuel to soot.
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Chapter 1

Introduction

1.1 Motivation

The use of controlled fires has always had a major role in the day to day activities of human civilization. Combustion processes can be used for cooking food, light generation, home heating, tool manufacturing, power generation, transportation, and material synthesis. Fossil fuel combustion is the main source of today’s energy supplies (more than 90%) and it is likely to remain this way for many years to come [1].

Emissions from combustion processes have been an ever increasing topic of concern for combustion researchers. One such emission, soot, has garnered specific attention in recent years. This attention is due to atmospheric soot, often referred to as black carbon, or particulate, being known to have detrimental effects on both human health and the global environment. Soot particles, which are typically 10-300 nm in diameter, can be absorbed deeply into the lungs, causing respiratory diseases such as asthma and bronchitis. The particles can be small enough to pass into the bloodstream leading to possible heart disease [2]. Polycyclic Aromatic Hydrocarbons (PAHs), which are pre-cursors to soot formation, have been classified as known carcinogens by the International Agency for Research on Cancer (IARC) as well. Additionally, soot is an environmental concern as it is the second most important factor in global warming behind carbon dioxide, due to soot being a strong absorber of solar energy [3]. A portion of the sun’s energy is reflected when it hits the atmosphere or earth’s surface; however, an increase in soot deposits reduces the amount of energy that gets reflected, through thermal absorption and heating of the particles. Due to all these concerns, there is a need to reduce soot emissions from combustion devices. In order to do so, the factors that affect soot emission levels must be understood.

Due to the very complex nature of soot formation, it is still not fully comprehended; however, the
current theories are presented. Soot formation begins in the gaseous phase when aromatic rings are formed in the combustion process. These aromatic rings grow into PAHs through chemical reaction with other gas phase species. These PAHs will start to combine into solid particles, in a process which is referred to as nucleation. Once these incipient solid particles have formed, several concurrent processes take place. The individual particles undergo growth via hydrogen-abstraction-carbon-addition (HACA) and PAH condensation. Additionally, particles may coalesce to form larger particles, or coagulate to form aggregates in a fractal, chain-like structure. Competing against these growth mechanisms is surface oxidation and aggregate fragmentation [4,5]. It should be noted that final soot emissions from a combustion process is determined by the difference of growth processes and oxidation; as long as all the formed soot is oxidized, there will be no emission.

Due to the highly complex nature of soot formation, detailed numerical models, such as the CoFlame code, are employed to gain fundamental understanding of the factors that affect each mechanism of soot evolution. The recent European emission standard for land vehicles, EURO 6, will include regulations on particle number density in addition to total particle mass (and in turn particle size). In order for numerical models to be useful in meeting these regulations, models must be able to predict particle number densities in addition to total mass. To achieve this predictive capability, models must be based on fundamental physics rather than being empirical. Most practical combustion devices operate at elevated pressure; therefore, models must have predictive capability at elevated pressures as well.

1.2 Objectives

The main goal of this research is to improve the models for PAH clustering (nucleation and condensation) used in the detailed numerical CoFlame code by introducing fundamental physics and reducing their semi-empirical nature. The end goal is a model that not only displays good agreement with the experimental measurements for these target flames, but has a reduced reliance on tunable constants and thus has increased predictive capability. The objectives of the research are:

1) Development of novel soot formation models relying on fundamental physics
2) Applying standard and novel models to high pressure conditions

1.3 Outline of the thesis

This thesis is composed of four journal articles (three accepted, and one to be submitted at the time of thesis submission) that address the two objectives outlined above. Each publication contains its own
Chapter 1. Introduction

literature review, methodologies, results and analyses, and conclusions, with additions to enhance the self-contained nature of a thesis. The first publication [i], which is presented in Chapter 2 and accepted, is a detailed description of the models utilized within the CoFlame code and served as a release paper for the CoFlame code. The second publication [ii], which is presented in Chapter 3 and has been accepted, describes the importance of considering the reversibility of the nucleation and condensation processes and develops a novel model that directly includes reversibility effects. The new model is referred to as the reversible PAH clustering (RPC) model. The third publication [iii], which is presented in Chapter 4 and has been accepted, enhances the RPC model by including nucleation and condensation events from a wide range of PAHs and the effects of carbonization. The fourth paper [iv], presented in Chapter 5 and is currently in preparation to be submitted, investigates the effect of high pressure on the flow field of co-flow diffusion flames and the subsequent effect on soot formation. Finally, the overall conclusions and recommendations for the entire body of work are present in Chapter 6.


Chapter 2

CoFlame: A Refined and Validated Numerical Algorithm


2.1 Introduction

Reducing soot emissions from combustion processes is important due to the negative health and environmental effects of atmospheric soot. In order to achieve this goal, there has to be a fundamental understanding of the mechanisms of soot formation, including growth and oxidation, to allow for the determination of economically viable methods of reducing these emissions. Due to the highly complex nature of soot formation, detailed numerical models are employed to gain fundamental understanding of the factors that affect each mechanism of soot evolution. While significant progress has been made in this area, there are still many uncertainties.

2.1.1 Soot Formation Processes

There are a significant number of physical processes that occur during soot formation. These include polycyclic aromatic hydrocarbon (PAH) gas-phase growth, particle nucleation, surface growth via surface reaction and PAH condensation, surface oxidation, particle coalescence, particle coagulation and fragmentation, gas-phase scrubbing, and radiation [6].
The first step is the formation of PAHs in the gas-phase. The formation of the first ring, or benzene, is thought to be the rate limiting step, thus much research has been done on the formation pathways for benzene. The primary routes involve $\text{C}_2\text{H}_2$ (acetylene), $\text{C}_4\text{H}_4$, $\text{C}_3\text{H}_3$ (propargyl), $\text{C}_5\text{H}_5$ (cyclopentadiene), and $\text{CH}_3$ [7–10]. Subsequent growth to larger aromatics has predominantly been accepted to occur via the hydrogen-abstraction-carbon-addition (HACA) mechanism [7], where a hydrogen is abstracted and a small aliphatic is added, primarily $\text{C}_2\text{H}_2$. However, key reactions involving reactions between PAHs and PAH radicals [5,11,12] and $\text{C}_4\text{H}_2$ (diacetylene) [12] have recently been shown to be important as well.

The next step is nucleation, which is the birth of a soot primary particle, and is theorized to occur from gas phase PAHs. The exact mechanism of nucleation is still unclear; however, there are three main theorized routes. The proposed routes are growth into curved fullerene-like structures [13], physical coalescence (dimerization) [14], and chemical reaction into cross-linked structures [14, 15]. The first pathway relies on the HACA mechanism, which is known to be too slow to account for soot nucleation rates on its own [15]. The other two pathways may not necessarily be mutually exclusive, and it is hypothesized that the relative ratio between the two mechanisms is a function of temperature and radical populations [14].

After nucleation occurs, soot primary particles undergo multiple concurrent processes. Primary particles grow via surface reaction in a manner similar to the HACA mechanism for gas-phase PAHs [5,16–18] and PAH condensation (a physical binding of PAHs to the surface of existing soot particles). Nucleation and condensation both rely on physical PAH bonds; however, one acts to create new soot primary particles, while the other one acts to increase the size of existing soot primary particles. Individual soot primary particles can collide and form larger primary particles (coalescence) or form chains of primary particles or soot aggregates (coagulation). Either of these two events are not 100% efficient due to the thermal rebound effect [19,20].

Soot primary particles can reduce in size due to surface oxidation from OH and $\text{O}_2$, with OH oxidation dominating in fuel-rich regions and under $\text{O}_2$ fuel-lean conditions. Finally, soot aggregates may undergo oxidation-driven fragmentation to form smaller aggregates containing fewer primary particles [21,22]. In premixed flames, oxidation is concurrent with growth processes, which is not true in diffusion flames.

2.1.2 Soot Formation Models

Soot models can be divided into three general categories; empirical, semi-empirical, and detailed [23]. Empirical soot models are developed on the basis of experimentally derived phenomenological corre-
lations of soot formation rates with combustion conditions such as pressure, equivalence ratio, and temperature. Such models are easy to understand, easy to implement, and do not require heavy computational loads. This is why most of the empirical modeling of soot formation can be found in literature that is related to gas turbine and diesel engines that are otherwise computationally intensive to simulate. The disadvantages of this type of soot model is the loss of detailed insights into the soot formation processes and lack of broad applicability. The next level of soot modeling with semi-empirical soot models attempts to incorporate some aspects of the physics and chemistry of the phenomenon, as opposed to a correlation of experimental data. The widely used two-equation soot model of Fairweather et al. [24] is an example of the semi-empirical soot models. Although some insights into soot formation mechanisms can be obtained from this type of model, it cannot provide detailed soot properties such as soot aggregate structure and size distribution, due to the neglect of the aggregate structure and polydispersity of soot particles.

As computational resources have improved and the use of parallel computing has increased, modeling of soot formation for academic purposes has shifted towards using detailed models. Problems that were not previously computational tractable are now feasible. Detailed chemical kinetic mechanisms describing the pyrolysis of hydrocarbon fuels and the formation of soot nucleating PAH species have originally been proposed by Frenklach and coworkers [5, 16, 17], with subsequent works by Marinov et al. [25] and Slavinskaya and Frank [11, 26]. In addition, different approaches for modeling soot particle evolution under concurrent nucleation, coagulation, surface growth and oxidation processes have also been developed. Representative approaches are the moment method [17, 27], the stochastic method [28–30] and the sectional method [31–35]. Sectional aerosol dynamics models can provide the mean properties and the size distribution of soot particles. Conventional sectional models solve for only one variable per section such as soot mass fraction [31], which is not adequate for modeling soot aggregate structure. To model the formation and coagulation of the fractal-like soot aggregates, Park et al. [32] developed an advanced sectional model which solves two equations (number densities of aggregates and primary particles) per section. This advanced model has been implemented into a laminar coflow flame code, CoFlame [36–39]. The CoFlame code has undergone multiple improvements since it was originally developed [26, 40–48]. Development has focused on bringing fundamental understanding into the submodels to the greatest extent possible. The CoFlame code, which has been refined in terms of coding structure, can be downloaded from http://combustion.mie.utoronto.ca/?page_id=1005.
2.1.3 Agenda

In the present study, the updated and architecturally refined CoFlame code is described in detail. The code is validated on atmospheric pressure ethylene-air and methane-air coflow diffusion flames and the computational performance is investigated.

2.2 Numerical Model

2.2.1 Governing Equations

For the gaseous phase, the fully coupled elliptical conservation equations for mass, momentum, energy, and species mass fraction are solved. CoFlame utilizes the axi-symmetrical nature of the flame, and equations are solved in the two-dimensional \((z \text{ and } r)\) cylindrical co-ordinate system. The equations are the same as in previous studies [26,36,38,40–49].

Conservation of mass:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \rho u \right) + \frac{\partial}{\partial z} \left( \rho u \right) = 0 \tag{2.1}
\]

Conservation of axial and radial momentum:

\[
\rho v \frac{\partial u}{\partial r} + \rho u \frac{\partial u}{\partial z} = - \frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \mu \frac{\partial u}{\partial r} \right) + 2 \frac{\partial}{\partial z} \left( \mu \frac{\partial u}{\partial z} \right) - \frac{2}{3} \frac{\partial}{\partial z} \left[ \mu \frac{\partial}{\partial r} \left( rv \right) \right] - \frac{2}{3} \left[ \mu \frac{\partial u}{\partial z} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left( r \mu \frac{\partial v}{\partial z} \right) + \rho g_z \tag{2.2}
\]

\[
\rho u \frac{\partial v}{\partial r} + \rho u \frac{\partial v}{\partial z} = - \frac{\partial p}{\partial r} + \frac{2}{r} \frac{\partial}{\partial r} \left( r \mu \frac{\partial v}{\partial r} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial v}{\partial z} \right) - \frac{21}{3} \frac{\partial}{\partial r} \left[ \mu \frac{\partial}{\partial r} \left( rv \right) \right] - \frac{21}{3} \left[ r \mu \frac{\partial u}{\partial z} \right] + \frac{\partial}{\partial z} \left( \mu \frac{\partial u}{\partial r} \right) - \frac{2 \mu v}{r^2} + \frac{2}{3} \frac{\mu}{r^2} \frac{\partial}{\partial r} \left( rv \right) \tag{2.3}
\]

Conservation of species mass fractions:
\[ \rho v \frac{\partial Y_k}{\partial r} + \rho u \frac{\partial Y_k}{\partial z} = -\frac{1}{r} \frac{\partial}{\partial r} \left( r \rho Y_k V_{k,r} \right) - \frac{\partial}{\partial z} \left( \rho Y_k V_{k,z} \right) + W_k \dot{\omega}_k \]  

\[ (k = 1, 2, ..., KK) \]

Conservation of energy:

\[ C_p \left( \rho v \frac{\partial T}{\partial r} + \rho u \frac{\partial T}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right) - \sum_{k=1}^{KK} h_k W_k \dot{\omega}_k \]

\[ - \sum_{k=1}^{KK} \left[ \rho C_{p,k} Y_k \left( V_{k,r} \frac{\partial T}{\partial r} + V_{k,z} \frac{\partial T}{\partial z} \right) \right] \]

\[ - \rho C_{p,s} Y_s \left( V_{s,r} \frac{\partial T}{\partial r} + V_{s,z} \frac{\partial T}{\partial z} \right) \]

\[ - h_s W_s \dot{\omega}_s + Q_r \]

In the preceding equations, \( u \) is the axial velocity, \( v \) is the radial velocity, \( \rho \) is the mixture density, \( \mu \) is the viscosity, \( g_z \) is the acceleration due to gravity, \( Y_k \) is the \( k^{th} \) species mass fraction, \( V_{k,r} \) and \( V_{k,z} \) are the \( k^{th} \) species radial and axial diffusion velocities, \( W_k \) is the molecular weight of the \( k^{th} \) species, \( \dot{\omega}_k \) is the production rate of the \( k^{th} \) species due to gas phase chemical reaction and interactions with the solid soot phase, \( C_p \) is the mixture specific heat capacity at constant pressure, \( T \) is the temperature, \( \lambda \) is the mixture thermal conductivity, \( h_k \) is the specific enthalpy of the \( k^{th} \) species, \( C_{p,k} \) is the specific heat capacity of the \( k^{th} \) species at constant pressure, \( C_{p,s} \) is the specific heat capacity of soot at constant pressure (assumed to be the same as graphite), \( Y_s \) is the soot mass fraction, \( V_{s,r} \) and \( V_{s,z} \) are the soot radial and axial diffusion velocities, \( h_s \) is the specific enthalpy of soot (assumed to be the same as graphite), \( W_s \) is the molecular weight of soot (same as carbon), and \( Q_r \) is the radiative heat transfer by soot, \( \text{H}_2\text{O}, \text{CO}_2, \text{and CO}. \)

Soot particle dynamics are described using a fixed sectional method, in which soot particle mass ranges are divided logarithmically into thirty-five discrete sections. Thirty-five sections are sufficient to ensure the results for average soot morphological parameters no longer change when increasing the number of sections, as variations in the results are no longer seen when the number of sections is increased beyond thirty-five. Soot aggregates are assumed to be composed of spherical primary particles of equal size with a constant fractal dimension of 1.8 [50, 51]. Two transport equations are solved for each section: those being aggregate number density (\( N_i^a \)) and soot primary particle number density (\( N_i^p \)), where \( i = 1, 2, ..., 35. \) The soot sectional model includes several processes, those being nucleation (\( \nu \)), PAH
condensation and HACA surface growth \((s)\), surface oxidation \((ox)\), coagulation \((co)\), fragmentation \((fr)\), particle diffusion \((D_p)\), and thermophoresis \((V_{Ts})\). Below are the governing soot particle dynamics equations:

*Conservation of soot aggregate number density:*

\[
\rho v \frac{\partial N_a^i}{\partial r} + \rho u \frac{\partial N_a^i}{\partial z} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho D_a^i \frac{\partial N_a^i}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho D_a^i \frac{\partial N_a^i}{\partial z} \right) \right) - \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho N_a^i V_{Ts,r} \right) - \frac{\partial}{\partial z} \left( \rho N_a^i V_{Ts,z} \right) + \rho \frac{\partial N_a^i}{\partial t} \bigg|_{nu} 
\]

\((i = 1, 2, ..., 35)\)

*Conservation of soot primary particle number density:*

\[
\rho v \frac{\partial N_p^i}{\partial r} + \rho u \frac{\partial N_p^i}{\partial z} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho D_p^i \frac{\partial N_p^i}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho D_p^i \frac{\partial N_p^i}{\partial z} \right) \right) - \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho N_p^i V_{Ts,r} \right) - \frac{\partial}{\partial z} \left( \rho N_p^i V_{Ts,z} \right) + \rho \frac{\partial N_p^i}{\partial t} \bigg|_{nu} 
\]

\((i = 1, 2, ..., 35)\)

### 2.2.2 Soot Formation Model

In order to close the system of equations, a number of models are required for the terms in Eq. 2.6 and 2.7. The utilized models are discussed below.

**Gas Phase Chemistry**

The mechanism in Chemkin format that is used with the CoFlame code is the one originally presented in [11], with modifications described in [40] and [26]. This mechanism [26] is chosen due to its ability to accurately predict soot volume fraction levels in all regions of an atmospheric \(\text{C}_2\) fuel (ethylene) flame [40] and enhance performance for methane flames [26]. This mechanism aims to accurately describe \(\text{C}_2/\text{methane oxidation}, \text{with PAH growth up to five aromatic rings, and has been validated for high pressures [11, 41]. It should be noted that this mechanism is a reduced mechanism which employs
lumping of some PAH growth routes, such as diacetylene addition. The CoFlame code is compatible with other chemical mechanisms and has been tested on the mechanisms of Appel et al. [5], Marinov et al. [25], Raj et al. [52], and Wang et al. [53].

**Nucleation**

Soot particle nucleation is modeled by assuming soot nucleates through the collision and sticking of PAH species. The rate of nucleation is calculated according to kinetic theory as:

\[
\frac{\partial N^a_i}{\partial t} \bigg|_{nu} = \beta \frac{8\pi k_B T}{\mu_{AB}} (r_A + r_B)^2 A_v^2 [A][B] 
\]

\[
\frac{\partial N^p_i}{\partial t} \bigg|_{nu} = 0, \quad i = 2, 3, ..., 35
\]

where \( \beta \) is the nucleation efficiency, \( k_B \) is the Boltzmann constant, \( A_v \) is Avogadro’s number, \( \mu_{AB} \) is the collisional reduced mass for the two colliding PAHs, \( r_A \) and \( r_B \) are the radii of the two colliding PAHs, and \([A]\) and \([B]\) are the concentrations of the two colliding PAHs. In this current work, nucleation is modeled to result from collisions of benzo[a]pyrene (BAPYR), secondary benzo[a]pyrenyl (BAPYR*S), and benzo(ghi)fluoranthene (BGHIF) [47]. The parameter \( \beta \) is set to 0.0001 [47].

**Coagulation**

The coagulation terms are calculated based on the collision kernel of soot aggregates in the entire Knudsen number regime [32, 54–56]. The source terms for aggregates and primary particles in the \( i^{th} \) section are calculated as:

\[
\frac{\partial N^a_i}{\partial t} \bigg|_{co} = \sum_{m_{i-1} \leq m_j + m_k \leq m_{i+1}} \sum_{k \leq j \leq i} \left( 1 - \frac{\delta_{j,k}}{2} \right) \eta \beta_{j,k} \xi_{j,k} N^a_j N^a_k - \eta \sum_{k=1}^{35} \beta_{i,k} \xi_{i,k} N^a_k \]

\[
\frac{\partial N^p_i}{\partial t} \bigg|_{co} = \sum_{m_{i-1} \leq m_j + m_k \leq m_{i+1}} \sum_{k \leq j \leq i} \left( 1 - \frac{\delta_{j,k}}{2} \right) \eta p \beta_{j,k} \xi_{j,k} N^a_j N^a_k - \eta p \sum_{k=1}^{35} \beta_{i,k} \xi_{i,k} N^a_k
\]

where \( m_i \) is the representative mass of the \( i^{th} \) section aggregate, \( \delta \) is the Kronecker delta function, \( \beta_{j,k} \) is the collision kernel of two aggregates in the \( j^{th} \) and \( k^{th} \) sections, \( \eta_{p,i} \) is the number of primary particles per aggregate in the \( i^{th} \) section, and \( \xi_{j,k} \) is the coagulation efficiency of two aggregates in the \( j^{th} \) and \( k^{th} \) sections and is set to 0.20 in this work [39]. The parameter \( \eta \) weights the newly formed
mass into two adjacent sections such that the number and the mass of aggregates are conserved and is calculated as:

$$\eta = \begin{cases} \frac{m_{i+1}-(m_j+m_k)}{m_{i+1}-m_i} & \text{if } m_i \leq m_j + m_k \leq m_{i+1} \\ \frac{m_{i-1}-(m_j+m_k)}{m_{i-1}-m_i} & \text{if } m_{i-1} \leq m_j + m_k \leq m_i \end{cases} \quad (2.11)$$

The factor $\eta_p$ assigns primary particles to two adjacent sections so that primary particle size and number are conserved and is calculated as:

$$\eta_p = \frac{m_i}{m_j + m_k} (n_{p,j} + n_{p,i}) \quad (2.12)$$

The collision kernel, $\beta_{j,k}$, is given by [57].

$$\beta_{j,k} = 4\pi R_{abs} (D_j + D_k) f_D \quad (2.13)$$

where $R_{abs}$ is the absorbing sphere cluster radius, $D_j$ and $D_k$ are the diffusion coefficients for soot particles in the $j^{th}$ and $k^{th}$ sections, and $f_D$ is the transition regime correction factor. The expression for the absorbing cluster radius is the same as that suggested by [58].

The diffusion coefficient, $D$, is calculated for both the free molecular and continuum regimes. The total diffusion coefficient utilized in equation 2.13 is the summation of these two values. The diffusion coefficient, $D$, is given by

$$D = \frac{k_B T C_c(Kn)}{3\pi \mu d_m} \quad (2.14)$$

where $k_B$ is the Boltzmann constant, $T$ is the gas temperature, $\mu$ is the gas viscosity, $d_m$ is the mobility diameter, $C_c(Kn)$ is the Cunningham slip correction factor as a function of the Knudsen number $Kn$ and is calculated as [59]

$$C_c(Kn) = 1 + 1.612Kn \quad (2.15)$$

The Knudsen number is defined as

$$Kn = \frac{2\lambda_{mfp}}{d_m} \quad (2.16)$$

where $\lambda_{mfp}$ is the mean free path of the gas, which is taken as the mean free path of air.

The transition regime correction factor $f_D$ is obtained from a simple approximation of flux-matching theory and is calculated as

$$f_D = \frac{1 + Kn_D}{1 + 2Kn_D(1 + Kn_D)} \quad (2.17)$$
where $Kn_D$ is the diffusion Knudsen number which characterizes the transition between continuum and free molecular diffusion and is defined as

$$Kn_D = \frac{\lambda_{mfp,12}}{R_{abs}}$$

(2.18)

where $\lambda_{mfp,12}$ is the diffusion mean free path which is calculated as

$$\lambda_{mfp,12} = \frac{D_j + D_k}{\sqrt{\frac{2k_B T}{\pi}} \left( \frac{1}{m_j} + \frac{1}{m_k} \right)}$$

(2.19)

where $m_j$ and $m_k$ is the mass of soot aggregates in the $j^{th}$ and $k^{th}$ sections.

The mobility diameter of the soot aggregate is calculated by

$$d_m = \begin{cases} 2r_p n_p^{0.43} & \text{free molecular regime} \\ 2R_f \left( \frac{D_f - 1}{2} \right)^{0.7} & \text{continuum regime} \end{cases}$$

(2.20)

where $r_p$ is the primary particle radius, $n_p$ is the number of primary particles in the aggregate, $D_f$ is the fractal dimension, and the outer radius of an aggregate $R_f$ is defined by

$$R_f = r_p (f n_p)^{1/D_f}$$

(2.21)

where $f$ is the volume filling factor and is set to 1.43 [60].

**PAH Condensation, HACA Surface Growth, Oxidation**

The PAH condensation model utilized is based on transition and continuum regime collision theory between soot aggregates and PAHs, with a prescribed collision efficiency, $\gamma$, of 1.0 [39]. The mobility diameter of the PAH is taken to be the Lennard-Jones diameter.

The HACA surface growth and oxidation model utilized is based on the HACA and oxidation soot surface reaction scheme developed by Frenklach and coworkers [5,18]. Table 2.1 displays the six surface reactions that are considered. Except for the reaction of soot with OH radicals (S6) which is modeled based on free molecular regime collision theory between OH and soot with a OH collision efficiency, $\gamma_{OH}$, of 0.13 [61], the kinetics of the other surface reactions are described using the concept of soot surface sites, which can either be saturated ($C_{soot} - H$) or dehydrogenated ($C_{soot}^\cdot$). In order to calculate the reaction rates, the concentrations of these two sites are required for each soot section. The concentration
Table 2.1: HACA-based soot surface growth and oxidation reactions [5]

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$A$</th>
<th>$b$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(cm$^3$ mol$^{-1}$ s$^{-1}$)</td>
<td></td>
<td>(kcal/mol)</td>
</tr>
<tr>
<td>S1</td>
<td>$C_{\text{soot}} - H + H \rightarrow C_{\text{soot}} \cdot + H_2$</td>
<td>$4.2 \times 10^{13}$</td>
<td>0.0</td>
<td>13.0</td>
</tr>
<tr>
<td>S2</td>
<td>$C_{\text{soot}} - H + OH \rightarrow C_{\text{soot}} \cdot + H_2O$</td>
<td>$1.0 \times 10^{10}$</td>
<td>0.73</td>
<td>1.43</td>
</tr>
<tr>
<td>S3</td>
<td>$C_{\text{soot}} \cdot + H \rightarrow C_{\text{soot}} - H$</td>
<td>$2.0 \times 10^{13}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>S4</td>
<td>$C_{\text{soot}} \cdot + C_2H_2 \rightarrow C_{\text{soot}} - H + H$</td>
<td>$8.0 \times 10^{7}$</td>
<td>1.56</td>
<td>3.8</td>
</tr>
<tr>
<td>S5</td>
<td>$C_{\text{soot}} \cdot + O_2 \rightarrow 2CO + \text{product}$</td>
<td>$2.2 \times 10^{12}$</td>
<td>0.0</td>
<td>7.5</td>
</tr>
<tr>
<td>S6</td>
<td>$C_{\text{soot}} - H + OH \rightarrow CO + \text{product}$</td>
<td>$\gamma_{OH} = 0.13$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of total surface sites for soot section $i$, $[C_{\text{soot}} - T]_i$, is calculated by

$$[C_{\text{soot}} - T]_i = \frac{\chi_{C_{\text{soot}} - H} A_{s,i} N_i}{A_v}$$ (2.22)

where $\chi_{C_{\text{soot}} - H}$ is the number of sites per unit soot surface area and is set to a constant value of $2.3 \times 10^{15}$ sites/cm$^2$ [18], $A_{s,i}$ is the surface area of soot particles in section $i$, and $N_i$ is the number of soot particles in section $i$. The concentration of dehydrogenated sites for soot section $i$, $[C_{\text{soot}} \cdot]_i$, is calculated from a steady state approximation by

$$[C_{\text{soot}} \cdot]_i = [C_{\text{soot}} - H]_i \frac{(k_1 \chi_H + k_2 \chi_{OH})}{k_{-1} \chi_{H_2} + k_{-2} \chi_{H_2O} + k_4 \chi_{C_2H_2} + k_5 \chi_{O_2} + k_1 \chi_H + k_2 \chi_{OH}}$$ (2.23)

where $\chi_H$, $\chi_{OH}$, $\chi_{H_2}$, $\chi_{H_2O}$, $\chi_{C_2H_2}$, and $\chi_{O_2}$ are mole fractions. The fractional term represents the portion of saturated sites that have been dehydrogenated and arises from a steady state approximation for $[C_{\text{soot}} \cdot]_i$. The equation for $[C_{\text{soot}} \cdot]_i$ is modified from the original form presented in [5, 18] to ensure that the fractional term cannot exceed unity. The concentration of saturated sites is then simply the number of total sites minus the number of dehydrogenated sites.

The source terms due to growth for aggregates and primary particles in the $i^{th}$ section are calculated using the 2-point method [62] as:
\[
\frac{\partial N_{i}^{a}}{\partial t} \bigg|_{sg} = \begin{cases} 
\frac{I_{g,i}}{m_{i+1} - m_{i}} & \text{if } i = 1 \\
\frac{I_{g,i-1}}{m_{i} - m_{i-1}} - \frac{I_{g,i}}{m_{i+1} - m_{i}} & \text{if } i = 2, \ldots, SN-1 \\
\frac{I_{g,i}}{m_{i} - m_{i-1}} & \text{if } i = SN 
\end{cases}
\]

(2.24)

\[
\frac{\partial N_{i}^{p}}{\partial t} \bigg|_{sg} = \begin{cases} 
\frac{I_{o,x,i}}{m_{i+1} - m_{i}} n_{p,i} & \text{if } i = 1 \\
\frac{I_{o,x,i}}{m_{i} - m_{i-1}} n_{p,i+1} - \frac{I_{o,x,i}}{m_{i+1} - m_{i}} n_{p,i} & \text{if } i = 2, \ldots, SN-1 \\
\frac{I_{o,x,i}}{m_{i} - m_{i-1}} n_{p,i} & \text{if } i = SN 
\end{cases}
\]

(2.25)

where \(I_{g,i}\) is the total of PAH condensation and HACA surface growth rates for the \(i^{th}\) section in units of g/cc/sec and is always positive.

The source terms due to oxidation for aggregates and primary particles in the \(i^{th}\) section are calculated using the 2-point method [62] as:

\[
\frac{\partial N_{i}^{a}}{\partial t} \bigg|_{ox} = \begin{cases} 
\frac{I_{o,x,i+1}}{m_{i+1} - m_{i}} + \frac{I_{o,x,i}}{m_{i}} n_{p,i+1} & \text{if } i = 1 \\
\frac{I_{o,x,i}}{m_{i} - m_{i-1}} n_{p,i+1} - \frac{I_{o,x,i+1}}{m_{i+1} - m_{i}} n_{p,i} & \text{if } i = 2, \ldots, SN-1 \\
\frac{I_{o,x,i}}{m_{i} - m_{i-1}} n_{p,i} & \text{if } i = SN 
\end{cases}
\]

(2.26)

\[
\frac{\partial N_{i}^{p}}{\partial t} \bigg|_{ox} = \begin{cases} 
\frac{I_{o,x,i}}{m_{i} - m_{i-1}} n_{p,i+1} + \frac{I_{o,x,i}}{m_{i}} n_{p,i} & \text{if } i = 1 \\
\frac{I_{o,x,i}}{m_{i} - m_{i-1}} n_{p,i} - \frac{I_{o,x,i+1}}{m_{i+1} - m_{i}} n_{p,i+1} & \text{if } i = 2, \ldots, SN-1 \\
\frac{I_{o,x,i}}{m_{i} - m_{i-1}} n_{p,i} & \text{if } i = SN 
\end{cases}
\]

(2.27)

where \(I_{o,x,i}\) is the oxidation rate for the \(i^{th}\) section in units of g/cc/sec and is always negative.

**Fragmentation**

The oxidation-driven fragmentation model utilized assumes a 1:1 fragmentation pattern [39, 49]. The source terms due to fragmentation for aggregates and primary particles in the \(i^{th}\) section are calculated as:

\[
\frac{\partial N_{i}^{a}}{\partial t} \bigg|_{fr} = \begin{cases} 
\Gamma_{i,i+1} S_{i+1}^{a} N_{i+1}^{a} & \text{if } i = 1 \\
(\Gamma_{i,i} - 1) S_{i}^{a} N_{i}^{a} + \Gamma_{i,i+1} S_{i+1}^{a} N_{i+1}^{a} & \text{if } i = 2, \ldots, SN-1 \\
(\Gamma_{i,i} - 1) S_{i}^{a} N_{i}^{a} & \text{if } i = SN 
\end{cases}
\]

(2.28)
\[
\frac{\partial N_{p}^{i}}{\partial t} \bigg|_{fr} = \begin{cases} 
\frac{\Gamma_{i,i+1}S_{i+1}N_{p,ah,i+1}}{f_{s}} & \text{if } i = 1 \\
(\Gamma_{i,i} - 1)S_{i}N_{p,ah,i} + \frac{\Gamma_{i,i+1}S_{i+1}N_{p,ah,i+1}}{f_{s}} & \text{if } i = 2, \ldots, SN - 1 \\
(\Gamma_{i,i} - 1)S_{i}N_{a}n_{p,ah,i} & \text{if } i = SN 
\end{cases}
\] (2.29)

where \( \Gamma_{i,i} \) and \( \Gamma_{i,i+1} \) are breakage distribution functions and are calculated as:

\[
\Gamma_{i,i} = \frac{f_{s} - 2}{f_{s} - 1} \Gamma_{i,i+1} = \frac{f_{s}}{f_{s} - 1} 
\] (2.30)

The distribution functions weight the newly formed mass into two adjacent sections such that the number and mass of aggregates are conserved, and that the number and size of primary particles are also conserved.

The fragmentation rate for aggregates in the \( i^{th} \) section is taken from [63]:

\[
S_{i} = A(n_{p,i})^{1/D_{f}}
\] (2.31)

where \( A \) is a coefficient that governs the overall fragmentation rate. As a first approximation, \( A \) is taken to be a first order function of the specific soot oxidation rate (the rate of removal of soot mass per unit soot surface area) \( r_{ox,s} \),

\[
A = Cr_{ox,s}
\] (2.32)

where \( C \) is a constant and set to \( 1.0 \times 10^{5} \) [39, 49]

**Thermophoresis and Diffusion**

The thermophoretic velocities \( V_{Ts,z} \) and \( V_{Ts,r} \) are calculated according to Gomez and Rosner [64].

\[
V_{Ts,x_{i}} = -0.55 \frac{\mu}{\rho T} \frac{\partial T}{\partial x_{i}} (x_{i} = r, z)
\] (2.33)

The aggregate diffusion coefficients are calculated in the same manner as for coagulation in the transition and continuum regimes.

**2.2.3 Radiation Model**

The radiation is modeled utilizing the discrete-ordinates method (DOM) and a statistical narrow-band correlated-\( k \)-based model developed in [65] and benchmarked in [66]. The DOM integrates the radiative
transfer equation (RTE) along a prescribed number of discrete ordinates defined by a polar and azimuthal angle, which eases obtaining numerical solutions to the RTE. Below is the discrete ordinates form of the RTE in cylindrical co-ordinates:

\[-\kappa I_{m,l} + I_b = \frac{\mu_{m,l}}{r} \frac{\partial r I_{m,l}}{\partial r} + \xi_{m,l} \frac{\partial I_{m,l}}{\partial z} - \frac{1}{r} \left( \frac{\alpha_{m,l+1/2} I_{m,l+1/2} - \alpha_{m,l-1/2} I_{m,l-1/2}}{\omega_{m,l}} \right)\]

where \( m \) is the polar angle index from 1 to \( M \), \( l \) is the azimuthal angle index from 1 to \( L(m) \), \( \mu \) and \( \xi \) are directional cosines, \( \kappa \) is the spectral absorption coefficient, \( I \) is the spectral intensity, \( I_b \) is the spectral black-body intensity, \( \alpha \) is a geometric constant [67], \( \omega \) is a weighting function associated with the direction defined by \((m, l)\), \( r \) is the radial direction, and \( z \) is the axial direction. The set of discrete ordinates is defined using the \( T_3 \) quadrature [68]. The validation of the original implementation of the DOM is available in [69,70]

### 2.2.4 Discretization techniques

As in previous works [26, 36, 38, 40–49, 71], the finite volume method is used to discretize the governing equations. A staggered mesh is used with a semi-implicit scheme to handle the pressure and velocity coupling and to solve the discretized equations at each discrete pseudo-time interval. The diffusive terms are discretized using a second-order central difference scheme while the convective terms are discretized using a power law scheme [72]. Due to using the power law scheme, care must be taken to ensure false diffusion is negligible by using sufficiently small grid spacings [72]. In this present work, numerical diffusion is estimated to be at least one order of magnitude lower than the real diffusion for the grids employed. The thermal properties of the gaseous species and chemical reaction rates are obtained by using CHEMKIN subroutines [73,74]. Based on sensitivity studies performed in [75], transport properties which include mixture-averaged quantities for viscosities, conductivities, and diffusion coefficients, as well as thermal diffusion coefficients for H and H\(_2\), are evaluated using TPLIB [76,77].

### 2.2.5 Computational Domain

A generic schematic of a co-flow burner, flame, and computation domain along with boundary conditions utilized by the CoFlame code is depicted in Fig. 2.1. The boundary conditions are as described in [26, 36, 38, 40–49], using free-slip conditions on the outer radial boundary, zero-gradient conditions on
the outflow, and a symmetry boundary on the central axis. The inlet velocity is set as a top-hat profile as results are insensitive to the utilized profile type (top-hat or parabolic) as in previous studies [40]. There are two regions of interest for soot formation in the flame, those being the wing region (depicted on the schematic) and the centerline region, which runs along the central axis of the flame. Conjugate heat transfer between the fuel and air streams and the solid fuel tube is modeled by the harmonic mean method [42,72,78]. The harmonic mean method works by setting a very high value for viscosity for the control volumes in the solid fuel tube region when solving the momentum equations. The high viscosity allows a zero velocity inlet boundary condition to propagate and prevail in this region, consistent with it being a solid. To model the heat transfer in the fuel tube, values of specific heat capacity and conductivity for steel are assigned for the fuel tube region when solving the energy equation. This harmonic mean method alleviates the need to have separate solid and fluid domains with different discretizations and a heat transfer interface condition. Finally, to account for radiative heat transfer to and from the burner, the adsorption coefficient of control volumes within the solid fuel tube is set to a large number such that the fuel tube is optically nontransparent.

2.2.6 Parallelization Strategy

Due to the computational intensity of the problem, solutions would be intractable with serial processing. Therefore, distributed-memory parallelization with strip-domain decomposition is employed as described in [79]. The computational domain is divided uniformly into \(N_{PROC}\) subdomains with the boundaries of each subdomain perpendicular to the z-axis, where \(N_{PROC}\) is normally equal to the number of grid lines in the axial direction. The algorithm uses the Message Passing Interface [80] library to distribute the workload. The computations are performed on the General Purpose Cluster (GPC) and Sandy Bridge Cluster of the SciNet Computing Consortium, on 100 4-core Intel Xeon E5540s with 2.53 GHz chip speeds (GPC) or 50 8-core Intel Xeon E5-2650 2.0 GHz chip speeds (Sandy Bridge) and InfiniBand network interconnect. The algorithm requires a MPI Intel FORTRAN compiler for compatibility with other clusters.

2.2.7 Solution Algorithm

Pseudo-transient continuation is used to aid convergence from an arbitrary starting estimate [39]. At each pseudo-time step, after the momentum and pressure correction equations are solved globally [72] by the tri-diagonal matrix algorithm (TDMA) for penta-diagonal matrices, the gaseous species equations are solved in a coupled manner at each control volume to effectively deal with the stiffness of the system
and speed up the convergence process. After iteration of the species equations, the sectional transport equations are also solved simultaneously in a similar fashion. The energy equation is then solved using TDMA to generate an updated global temperature field and a convergence check is performed. The algorithm is determined to be converged when the global rate of change of each variable (or residual) is less than 0.001.
2.3 CoFlame Code Performance

In this section, the performance of the CoFlame code is investigated by performing validation against experimental data for an ethylene and a methane co-flow flame, parallel scaling tests, and discussing computational costs.

2.3.1 Validation

2.3.2 Fluid Dynamics Solver

To validate the fluid dynamics solver utilized by the CoFlame code, simulations for an axi-symmetric pipe with a sudden expansion are performed for a range of Reynolds Numbers and compared with experimental data available from Macagno and Hung [81]. Fig. 2.2 displays a diagram of the flow problem. The value of \( D_O \) is 2.1 cm, \( D \) is 4.2 cm, and \( h \) is 1.05 cm. \( x_r \) represents the re-attachment length and varies with the flow Reynolds number, for which experimental data is available for Reynolds numbers from 10-140. The computational domain begins 2.0 cm below the expansion and extends a total of 35.2 cm in the axial direction, and is divided into 704 \((z) \times 84 \,(r)\) uniform control volumes. The results are verified to not be sensitive to increased length of the domain below the expansion, extent in the axial direction, and number of control volumes. For the inlet, a parabolic velocity profile for fully-developed laminar pipe flow is utilized as sensitivity to the inlet profile is observed for these flow cases.

Fig. 2.2 displays a comparison between the numerical results from the CoFlame code with the experimental values obtained by Macagno and Hung [81] for re-attachment length for a range of Reynolds numbers. Overall, the trend with reattachment length is very well captured by the CoFlame code. It can be seen that the CoFlame results are in excellent agreement with the experimental values at lower Reynolds numbers, and at high Reynolds numbers the reattachment length is slightly over-predicted. As can be seen in the following section, the CoFlame code accurately predicts the axial velocity profiles in an ethylene-air diffusion flame, thus the employed fluid dynamics solver is suitable for the intended purpose of the CoFlame code.

To verify the implementation of the discretization scheme, a calculation with the Reynolds number equal to 160 is performed on 4 additional meshes, one finer (1408x168) and three coarser (352x42, 176x21, 88x10). The re-attachment length predicted by the finer grid is taken to be the correct solution and an error scaling analysis is performed with the solutions for the four coarser grids. The power law scheme employed by the CoFlame code is expected to be between first and second order accurate, dependent
upon the local grid Peclet numbers, thus a scaling between -1 and -2 is expected. It is found that the error scales with grid spacing to the -1.85, thus it can be concluded that the power law scheme has been implemented correctly.

**Ethylene Flame**

The flame chosen is the co-flow laminar diffusion ethylene-air flame originally investigated in [82], and has been exhaustively studied by multiple groups [40, 45, 50, 82–87]. This flame is the only co-flow C2-fuel diffusion flame with published experimental data for soot aggregate and primary particle size and number densities. These characteristics make it an excellent choice for preliminary soot model validation. The inner diameter of the fuel tube is 1.11 cm and of the co-flowing air tube is 10.20 cm. The fuel and air velocities are 3.98 cm/s and 8.90 cm/s respectively. The computational domain extends to 19.46 cm in the axial direction and 4.16 cm in the radial direction, and is divided into 400 ($z$) x 238 ($r$) non-uniform control volumes. The spacing in the $z$ starts at 0.03 cm, and stretches beyond $z = 9.8$ with a stretching factor of 1.0335. The spacing in the $r$ starts at 0.0125 cm, and stretches beyond control volume 189 ($r = 1.175$ cm) with a stretching factor of 1.05. It should be noted that the grid is refined in the radial direction from $r = 0.1$ to 0.5 to have a spacing of 0.003125 cm. This refinement is required to achieve a mesh independent solution. When performing a further halving of the spacing in both co-ordinate directions, all soot parameters change by less than 10%. The first 1.0 cm in the $z$ direction are below
the fuel tube exit plane. This distance is sufficient to ensure the temperature gradients at \( z = 0.0 \) (the bottom of the computational domain) are negligible, thus ensuring accurate boundary conditions. The outer radial boundary is within the radius of the oxidizer tube, thus the oxidizer tube is not included in the computational domain. The sensitivity of the results to the location of the outer radial boundary is tested by extending the outer radial boundary to 5.0 cm and negligible changes to the solution is observed.

Fig. 2.3 displays a comparison between the experimental values and those computed with the CoFlame code for soot volume fraction along a) the pathline of maximum soot along the wings, and b) the centerline. Experimental data are those measured by Santoro et al. [83] using laser extinction, McEnally et al. [87] using thermocouple particle deposition (TPD), and Köylü et al. [86] by thermophoretic sampling particle diagnostic (TSPD) and transmission electron microscope (TEM) images. Experimental uncertainties for the Santoro et al. data are derived by accounting for the variation in plausible values of \( E(m) \), the refractive index of soot [88], which has been done in previous studies [41, 48], while uncertainties for the other two data sets are taken directly from the source publications. Along the wings, the CoFlame code predicted soot profile is broader than the experimental profile; however, the computed data are qualitatively correct and within the experimental uncertainty in the growth region and slightly shifted in the oxidation region. A similar trend is observed along the centerline, with the numerically predicted profile being broader. The peak predicted soot volume fraction along the centerline is within experimental uncertainty; however, it is on the lower end of the range. The underprediction of centerline soot volume fraction at atmospheric pressure is prevalent in the literature [31, 36, 39–41, 47] and has been observed for many different soot formation models. The cause of the observed underprediction may be due to missing physics or formation pathways leading to increased soot growth rates along the centerline of diffusion flames.

Fig. 2.4 displays a comparison between the experimental values and those computed with the CoFlame code for primary particle diameter (\( d_p \)) along a) the pathline of maximum soot along the wings, and b) the centerline. Experimental data along the wings is taken from Megaridis and Dobbins [84], and those along the centerline by Köylü et al. [86]. Experimental uncertainties are taken directly from the source publications. Once again, the CoFlame code predicts a broader profile than the experiment along the wings and centerline; however, peak values are within experimental uncertainty. Along the centerline the numerical predictions capturing the overall flat nature of the experimental profiles but failing to predict the right magnitudes. Given that centerline soot volume fraction is on the low end of the experimental uncertainty along the centerline, the underprediction of primary particle diameters can be attributed to an insufficient amount of surface growth, either by the HACA mechanism or PAH condensation. For a
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Figure 2.3: Comparison of experimental values and those computed with the CoFlame code for soot volume fraction along a) the pathline of maximum soot on the wings and b) the centerline for the ethylene-air Santoro Flame [83, 86, 87].

given number density, soot volume fraction will scale with $d_p^3$. Due to low radical pools, the centerline of a diffusion flame is PAH condensation dominated [40–42]; therefore, the underpredictions are attributed to insufficient PAH condensation.

Fig. 2.5 displays a comparison of $N_p$ (primary particle number density) along the wings, with experimental data taken from Megaridis and Dobbins [85], and Puri et al. [50]. The experimental uncertainties for the Puri et al data are taken from the source publication, while for the Megaridis and Dobbins data the variation of $E(m)$ and uncertainty in the $d_p$ measurements used to derive the data are considered. Measurement data for $N_p$ along the centerline are not available. With the exception of very low axial heights, the CoFlame code predictions are within experimental uncertainty.

Fig. 2.6 displays a comparison of $N_a$ (aggregate number density) along the a) wings and b) cen-
Figure 2.4: Comparison of experimental values and those computed with the CoFlame code for primary particle diameter ($d_p$) along a) the pathline of maximum soot on the wings and b) the centerline for the ethylene-air Santoro Flame [84,86].

The experimental uncertainty for Puri et al. is taken from the source publication, while the variation of $E(m)$ is considered [88] to derive the uncertainty for the Santoro et al. data. The CoFlame code predictions are within experimental uncertainty along the wings; however, along the centerline the predicted profile is shifted axially, although the shape is well captured. Fig. 2.7 displays a comparison of $n_p$ (average number of primaries per aggregate) along the a) wings and b) centerline, with experimental data taken from Iyer et al. [89], Puri et al. [50], and Köylü et al. [86]. The experimental uncertainties are taken directly from the source publications; however, no uncertainty is available for the Iyer et al. data. The CoFlame code predicted profile shapes are similar to the experimental data; however, the magnitudes are underpredicted, particularly on the centerline.

Fig. 2.8, 2.9, 2.10, and 2.11 display a comparison of radial cuts of OH mole fraction, C$_2$H$_2$ mole fraction, temperature, and axial velocity, at various axial heights, with experimental data taken from
Figure 2.5: Comparison of experimental values and those computed with the CoFlame code for primary particle number density \(N_p\) along the pathline of maximum soot on the wings for the ethylene-air Santoro Flame [50,85].

Santoro et al. [83], and Kennedy et al. [90]. Experimental uncertainties are taken from the source publications. The qualitative and quantitative agreement between the experimental data and CoFlame results is excellent for all four parameters.

**Methane Flame**

The flame chosen is a co-flow laminar diffusion methane-air flame [91]. The burner geometry is the same as in [82]; however, the fuel and air velocities are 7.75 cm/s and 7.96 cm/s respectively. The computational domain and all model parameters are unchanged from the ethylene flame calculations. However, it should be noted that the refinement between \(r = 0.1\) to 0.5 cm required for mesh independence for the ethylene-flame is not required for the methane-air flame although it is still used for these presented results. This flame was chosen as there are measurements for primary particle diameters in addition to soot volume fraction available.

Fig. 2.12 displays a comparison between the experimental values and those computed with the CoFlame code for soot volume fraction a) at the location of maximum soot volume fraction at each axial height, and b) along the centerline. Experimental data are those measured by Lee et al. [91] using laser extinction, with uncertainties determined by considering the range of plausible values of \(E(m)\) [88]. On both the wings and centerline, the CoFlame code underpredicts soot volume fraction, particularly at lower axial heights. Peak predicted values along the wing and centerline are within a factor of 3 of the experimental data.

Fig. 2.13 displays a comparison between the experimental values and those computed with the
Figure 2.6: Comparison of experimental values and those computed with the CoFlame code for aggregate number density ($N_a$) along a) the pathline of maximum soot on the wings and b) the centerline for the ethylene-air Santoro Flame [50, 83].

CoFlame code for the maximum $d_p$ observed at various axial heights. Experimental data along the wings is taken from Lee et al. [91], with uncertainties taken from the publication as well. The numerically predicted profile is shifted axially and of lower magnitude than the experimental values; however, the shape is well captured. Similar to the centerline of the ethylene-air flame, the underprediction of soot volume fraction can be attributed to insufficient surface growth, particularly PAH condensation. Given the scaling of soot volume fraction with $d_p$, an increase in predicted soot volume fractions by approximately a factor of 2.2 would occur if diameters were predicted accurately.
Figure 2.7: Comparison of experimental values and those computed with the CoFlame code for number of primaries per aggregate \( n_p \) along a) the pathline of maximum soot on the wings and b) the centerline for the ethylene-air Santoro Flame [50, 83].

Figure 2.8: Comparison of experimental values and those computed with the CoFlame code for radial cuts of OH mole fraction at two axial heights above the burner [83].
2.3.3 Code Performance

Computational Cost

From an arbitrary initial solution field (air at 1900K), the CoFlame code takes a wall-time of approximately 152 hours on 400 CPUs to reach a fully converged solution for the ethylene-air coflow diffusion flame and 134 hours on 400 CPUs for the methane-air diffusion flame. The total computational cost varies significantly depending on the disparity from the initial solution field and the final solution. Once an initial converged solution is obtained for a given flame, re-converging the solution for different model parameters is significantly faster, by a factor of 2 to 4.
Figure 2.11: Comparison of experimental values and those computed with the CoFlame code for radial cuts of axial velocity at various axial heights above the burner [83].

Fig. 2.14 displays the total CPU-time taken for each of the sub-models in the CoFlame code during one iteration for the ethylene-air diffusion flame using the same computational domain as for the validation testing using 1 CPU processor. It can be seen that the solution of the species and soot equations dominates the computation cost. Solving for the temperature also takes significant CPU resources. It should be noted that both the discrete ordinates method (DOM) and solving of the pressure correction equation are entirely serial processes in the CoFlame code, thus parallel scaling is limited by these two subroutines.

**Strong Scaling**

Strong scaling tests are performed on the CoFlame code with the same domain size and chemical mechanism as utilized for the ethylene-air diffusion flame validation case. Fig. 2.15 displays the parallel efficiency of the CoFlame code for 2 to 400 CPUs with the base model, and with one with double the number of sections for the soot sectional model. For the base model, the parallel efficiency remains above 75% up to 80 CPUs; however, there is a significant drop in efficiency when adding additional CPUs. The efficiency at 400 CPUs, which is the maximum parallelization for the strip-domain scheme utilized by the CoFlame code, is 39%. The reduction in parallel efficiency is primarily due to the serial nature of the DOM radiation model and pressure correction equation solution procedure employed by the CoFlame code (such reductions have been noted in other codes [92]) and the increase in required inter-node communication. Due to the solution algorithm utilized for solving the gas-phase species and soot particle dynamics equations, the parallel scaling of the CoFlame code will improve as chemical
mechanisms increase in size or the number of soot sections or equations per section are increased [40]. The increased scaling is due to the time required for the DOM algorithm and inter-process communication becomes smaller compared to the time required for solution of the species conservation of mass equations. Fig. 2.15 displays that when doubling the number of sections utilized to 70, the parallel efficiency at 80 CPUs increases from 77% to 91%, and at 400 CPUs from 39% to 70%. Very similar results for improved parallel efficiency are obtained when a chemical mechanism is utilized with 202 species as opposed to 94 in the base model.

Weak Scaling

Weak scaling tests are performed on the CoFlame code with a domain equal to $NUMP \times 238$, where $NUMP$ is the number of CPUs used. Fig. 2.16 displays the time per iteration for 4 to 512 CPUs.
Figure 2.13: Comparison of experimental values and those computed with the CoFlame code for the maximum primary particle diameter ($d_p$) at a given axial height for the methane-air \[91\].

Figure 2.14: Distribution of time taken for the various sub-models of the CoFlame code for the ethylene-air diffusion flame (readers are referred to the online version to view the image in color).

with the base model and the model with 70 sections for the soot dynamics solver. The time per iteration is relatively constant up to 64 CPUs; however, it increases significantly after that point. As displayed in the previous section, the scaling of the CoFlame code improves with increases in the number of sections in the sectional model or the size of the chemical kinetics mechanism.

### 2.4 Conclusions

The details of the CoFlame code have been described in length, inclusive of modeling techniques, mathematical equations, and solution algorithm and procedure. The CoFlame code can model co-flow, laminar, axi-symmetric, sooting diffusion flames. The code solves axial and radial velocity, temperature, species
conservation, and soot aggregate and primary particle number density equations. The sectional particle dynamics model includes nucleation, PAH condensation and HACA surface growth, surface oxidation, coagulation, fragmentation, particle diffusion, and thermophoresis. The public release of the CoFlame code, which has been refined in terms of coding structure, to the research community accompanies this paper.

The CoFlame code is validated against experimental data for an axi-symmetric pipe experiencing a sudden expansion and all data available for ethylene-air and methane-air diffusion flames without altering any model parameters. The code shows good parallel scaling up to 80 CPUs and continual significant reduction in wall-clock time up to 400 CPUs. Future work should be aimed at removing
empirically fitted constants with fundamental physics or well-validated functional forms.
Chapter 3

The Importance of Reversibility in Soot Formation Modeling


3.1 Introduction

Reducing soot emissions from combustion processes is important due to the negative health and environmental effects of atmospheric soot. In order to achieve this goal, there has to be a fundamental understanding of the mechanisms of soot formation to allow for the determination of economically viable methods of reducing these emissions. Due to the highly complex nature of soot formation, detailed numerical models are employed to gain fundamental understanding of the factors that affect each mechanism of soot evolution. The current theories of how soot forms involve three main mechanisms; those being nucleation, hydrogen-abstraction-carbon-addition (HACA) surface growth, and polycyclic aromatic hydrocarbon (PAH) condensation. Extensive studies have been performed to characterize the nature of HACA surface growth; however, the processes involved in nucleation and PAH condensation are still unclear. Nucleation, which is the birth of a soot particle, is theorized to occur from the dimerization of gas phase PAHs. PAH condensation is the process by which gas phase PAHs can condense onto the surface of a soot particle. Both of these processes rely on physical PAH bonds; however, one acts to create new soot particles, while the other one acts to increase the size of existing soot particles.

The upcoming European emission standard for land vehicles, EURO 6, will include regulations on
particle number density in addition to total particle mass (and hence particle size), thus accurate modelling of particle number density and size is important. In a recent study [47], it was shown that the relative efficiency of nucleation versus condensation heavily influences soot primary particle diameter predictions. Lower nucleation efficiencies resulted in larger predicted primary particle diameters, while lower condensation efficiencies produced smaller primary particle predictions. While this study [47] did display the importance in the relative strengths of nucleation to condensation for primary particle diameter predictions, the model relied on introducing tunable constants for nucleation and condensation efficiencies to increase agreement with the experimental results. It should be noted that all other soot formation models in the literature rely on efficiencies. These efficiencies can be tunable constants, or functional forms based on theoretical assumptions [33], pre-dominantly with both processes modeled to occur via pyrene. In order to accurately predict soot particle size for a wide range of conditions, numerical models must be able to accurately model nucleation and condensation, and their relative contributions to total soot mass, without reliance on efficiencies for nucleation and condensation.

3.1.1 Physical PAH Bonding Processes

There has been a significant amount of recent investigations into the nature of physical PAH nucleation and condensation. In work by Sabbah et al. [93], it was shown that at flame temperatures, the dimerization of two pyrene molecules was not thermodynamically favored. A temperature-dependent equilibrium constant for the dimerization of pyrene was proposed and based on its very small magnitude at flame temperatures, it was determined that dimerization must be highly reversible. It is asserted in the work of Sabbah et al. that any proposed efficiency for the nucleation process should be a function of equilibrium ratios or constants. There has been some work into attempting to define an equilibrium constant for the dimeration of other PAHs as well. In a review article by Wang [15], statistical mechanics was utilized to define an equilibrium constant for the dimerization of pyrene, ovalene, and circumcoronene using binding energies taken from [94]. Some assumptions had to be made, with the most significant being the average frequency of the vibration modes created during the dimerization process. Investigations have been performed into the magnitude of these vibration modes in the work of Totton et al. [95] for pyrene, coronene, ovalene, hexabenzocoronene, and circumcoronene dimers. In Totton et al. [95], a more advanced model for determining the binding energies between PAHs was developed. Molecular dynamics simulations were utilized to propose a coagulation efficiency for PAH-PAH (nucleation) and PAH-PAH cluster (condensation) collisions that had dependencies on temperature and collisional reduced mass. Rapacioli et al. [96, 97] looked at the frequencies of the vibration modes for coronene stacks containing
up to 8 coronenes and vibration modes for various PAH dimers. Their conclusion was that in general, as PAH stack sizes increase, as would occur during the condensation process, vibration frequencies reduce. Finally, in Elvati and Violi [98], and Chung and Violi [99], it was determined that the addition of aliphatic chains, and not only a PAH’s size, influence whether or not a dimerization was favored. All of these works reached the conclusion that PAHs much larger than pyrene (ovalene and larger) would need to be present for physical PAH attraction to play a role in nucleation and condensation.

The experimental work performed by Teini et al. [100], where High Resolution Transmission Electron Microscopy (HRTEM) was used to investigate the types of particles found within nascent soot, seemed to conflict with the results of these recent thermodynamic investigations. The HRTEM showed that the sizes of particles within nascent soot were fairly constant at the core and edges, and consistent with PAHs containing approximately 20 carbon atoms, or 5-rings. Even though these smaller PAHs are not thermodynamically favored to physically bond, they have been found within the cores and edges of nascent soot particles, leading to the assertion that species of this size are important to nucleation and condensation processes. This finding is consistent with the much earlier work of [101], where laser microprobe mass spectrometry was used to determine the mass of PAHs found within nascent soot particles. The masses were found to be consistent with PAHs consisting of approximately 20 to 21 carbons. It should be noted that in [101], PAHs containing as many as 38 carbons were detected in more mature soot particles. This [101] study demonstrates that PAH-based nucleation and condensation may not be controlled by equilibrium, but rather kinetics, for which accounting for reversibility is highly important. The work of Schuetz and Frenklach [102] supports this notion, as molecular dynamics simulations displayed that the lifetime of a pyrene dimer may be sufficiently long to support subsequent growth.

3.1.2 Agenda

In the present study, a novel, fundamental, nucleation and condensation model is developed that explicitly accounts for reversibility while reducing the need for arbitrary tunable constants. The model is implemented into the detailed code utilized in [40], enhanced in [42, 47], and described in detail in the previous chapter, and the computational results are compared with experimental measurements and other alternative models.
3.2 Problem formulation

3.2.1 Flame and Model Description

The flame chosen for this investigation is the steady, non-smoking, co-flow laminar diffusion ethylene-air flame originally investigated in [82], and since exhaustively studied by multiple groups [40, 50, 82–87]. This flame is the only co-flow C2-fuel diffusion flame to have published experimental data for soot aggregate and primary particle size and number densities. These characteristics make it an excellent choice for comparisons of various soot models. This flame has been extensively studied both experimentally and numerically, thus the details of the burner and flame may be viewed in [50, 83, 84]. It should be noted that while this present work focuses on PAH based soot formation processes, multiple other studies have demonstrated the important role of acetylene in this flame.

For the gaseous phase, the fully coupled elliptical conservation equations for mass, momentum, energy, species mass fraction, soot aggregate number densities, and primary particle number densities are solved. The model utilizes the axi-symmetrical nature of the flame, and equations are solved in the two-dimensional (z and r) cylindrical co-ordinate system. Conjugate heat transfer between the solid fuel tube and the fuel and air streams is modeled using the harmonic mean method [42, 72]. In a recent work [47], nucleation and condensation were modified to result from 5-ring aromatic (A5) collisions, specifically benzo[a]pyrene (BAPYR), secondary benzo[a]pyrenyl (BAPYR*S), and benzo(ghi)fluoranthene (BGHIF), as opposed to from pyrene, which resulted in better centerline soot predictions. The mechanism that is used for this investigation is the one originally presented in [11], with modifications described in [12, 40]. The computational domain used in this investigation extends 19.57 cm in the axial direction and 4.16 cm in the radial direction, and is divided into 384 (z) x 140 (r) non-uniform control volumes. The first 1.0 cm in the z direction is below the fuel tube exit plane. This distance is sufficient to ensure the temperature gradients at z = 0.0 (the bottom of the computational domain) are negligible.

3.2.2 Nucleation and Condensation Model Development

Following the assumptions of others [15, 95], statistical mechanics will be utilized to determine the enthalpy and entropy of the nucleation and condensation processes for any arbitrary PAH-PAH or PAH-Soot collision event. These values can in turn be used to determine an equilibrium constant and subsequently reverse rate co-efficients.
The enthalpy and entropy change are given by [103]:

\[
\Delta H = -E_0 - 4k_BT + \sum_{i=1}^{6} \left( 1 + \frac{1}{e^{hcv_i/(k_BT)} - 1} \right)hcv_i
\]  

(3.1)

\[
\frac{\Delta S}{R_u} = \ln \left[ \left( \frac{m_3hcB_1B_2}{2m_1m_2B_3} \right) \frac{h^3P}{\pi^2(k_BT)^4} \frac{\sigma_2\sigma_1}{\sigma_3} \right] - 4 + \sum_{i=1}^{6} \left[ \frac{hcv_i/k_BT}{e^{hcv_i/(k_BT)} - 1} \right] - \ln \left[ 1 - e^{-hcv_i/(k_BT)} \right]
\]  

(3.2)

where \( \Delta H \) is the enthalpy change, \( \Delta S \) is the entropy change, \( R_u \) is the universal gas constant, \( k_B \) is the boltzmann constant, \( T \) is the gas temperature, \( h \) is Plank’s constant, \( c \) is the speed of light, \( m_1 \) and \( m_2 \) are the masses of the two colliding entities, \( m_3 \) is the combined mass of the two entities, \( \sigma_i \) are the symmetry numbers, with dimers and soot primary particles assumed to have no symmetry (\( \sigma_i = 1 \)), and \( B_i \) are the rotational constants, utilizing the correlation presented in [104] and assuming the rotational constants of a dimer are half of a monomer PAH [15] and that the rotation constants of the soot primary particle are unaffected by the condensation process (\( B_2 = B_3 \)).

Both the enthalpy and entropy change, and subsequently the reverse rates, are very sensitive to \( E_0 \), the binding energy, and \( v_i \), the \( i \)th (of 6 in total) vibration mode frequencies created when a nucleation or condensation process occurs. A larger binding energy, and lower vibrational frequencies will reduce reversibility. It should be noted that in this model, it is assumed that the frequency of vibration modes already present are not altered by the nucleation or condensation processes, thus only the 6 newly created modes are considered. While this assumption is a significant one, it is adequate due to the non-bonding interaction and has been used in previous studies of the nucleation process [15,95]. For the condensation process, this assumption is similar to that used to develop the Langmuir adsorption model for gases adsorbing on a solid surface [105]. In the Langmuir model, only the vibrations between the gas particles and the solid surface are considered, and the gas adsorption process can be considered analogous to the PAH condensation process being modeled in this work.

In [94], it is shown that binding energy is linearly proportional to the reduced mass of the colliding entities (whether they be individual PAHs, or a PAH colliding with an existing PAH stack), and in [95] the binding energy for two colliding pyrene molecules is shown to be 41.8 kJ/mol, which matches well with the values determined in the study in [93] and suggested to be more accurate than the values given in [94]. Given the more accurate binding energies proposed in [95] and the linear proportionality displayed in [94], the binding energy for any two colliding PAHs (nucleation), or a PAH colliding with a pre-existing...
PAH stack (condensation) can be determined by calculating the reduced mass of the colliding entities and comparing it to the reduced mass of two colliding pyrene molecules provided in [95]. The study in [95] also provides the 6 needed vibration frequencies for the collision of various pairs of PAHs; however, not for A5-sized PAHs such as benzo[a]pyrene. It is clear though that the frequencies do not vary significantly between differing PAH pairs, with an average frequency of approximately 25 cm$^{-1}$. The work done in [93] suggests an effective average vibration frequency of 18 cm$^{-1}$ based on the proposed equilibrium constant for pyrene dimerization. Furthermore, given the more accurate anharmonic treatment of the phase space in that study, a value of 18 cm$^{-1}$ is used for the nucleation process in this work.

While limited, work has been performed to determine the frequency of the six vibration modes created when a PAH is added to a pre-existing PAH stack (condensation). The study by Rapacioli et al. [96] looks at vibration mode frequencies present in coronene dimers, tetramers, and octomers. It is demonstrated that the frequencies of the added vibration modes generally reduce as the stack size increases, with previous vibration modes decreasing in frequency as well. When considering a tetramer versus an octomer, the additional vibration modes in the octomer have frequencies ranging from 50 - 1.8 cm$^{-1}$. Finally, the method employed in [96] is known to over-predict vibration frequencies [95]. Based on the trend of both added and previously present vibration mode frequencies decreasing as stack size increases, it is determined that a reasonable estimate for the average added vibration frequency for all condensation processes is 0.5 cm$^{-1}$. It should be noted that the vibration frequencies in the model represent true physical parameters, which could be further verified with investigations similar to those in [95,96]. It is likely the frequencies created will vary depending on the size of the PAH stacks, and that the assumption of previously present vibration modes not altering in frequency should be relaxed at least for small cluster sizes.

Once $\Delta H$ and $\Delta S$ have been determined, $\Delta G$ can be determined, followed by the equilibrium constants $k_p$ and $k_c$. Given $k_c$ and the forward rate constant, the reverse rate constant can be determined. The forward rates are given by $R = \beta Z$, where $Z$ is the collision rate between PAHs or PAHs and existing PAH stacks (soot particles) [39], and $\beta$ is the collision efficiency and is equal to $1 - (1 + E_0/R_uT) \exp(-E_0/R_uT)$ [106]. It should be noted that for the temperature range of 300 K to 2200 K, $\beta$ only varies from 1 to 0.75 for nucleation and condensation processes. The reverse rates for nucleation and reverse rates of condensation for the $ith$ section are given by:

$$R_{\text{nuc,rev}} = k_{\text{rev,nuc}}[\text{Dimers}]$$

$$R_{\text{cond,rev},i} = k_{\text{rev,cond}}[\text{PAH}_{\text{Soot},i+1}]$$
where $[\text{Dimers}]$ is the concentration of dimers, and $[\text{PAH}_{\text{Soot},i+1}]$ is the concentration of PAH molecules on the surface of the soot particles in the $(i+1)th$ section. In order to determine $[\text{PAH}_{\text{Soot},i}]$, an additional transport equation per section is solved that tracks the number density of PAHs on the surface of the soot particles in that section ($\text{PAH}_{\text{Soot},i}$), in a similar manner in which a second equation was added per section to track primary particles [32, 62]. The model for $[\text{PAH}_{\text{Soot},i}]$ assumes that carbonization rates are fast since all PAHs within soot particles (other than those on the surface) are considered chemically bonded. It should be noted that when calculating the reverse condensation rate, a cut-off is used to disallow negative condensation rates, consistent with the assumption of fast carbonization. Satisfactory numerical results could not be obtained without the fast carbonization assumption, as predicted soot volume fractions were very low. This finding is consistent with the works in [95] and [99], where molecular dynamics simulations displayed that in the absence of any chemical bonds, PAH clusters would not grow to significant sizes.

The source terms for the $[\text{PAH}_{\text{Soot},i}]$ transport equation are as follows. The source term for nucleation is twice that as for aggregates, as two surface PAHs are created for each nucleation event. The source terms from HACA surface growth, condensation, and oxidation in the $\text{PAH}_{\text{Soot},i}$ transport equation are the same form as in [39], except the $n_{p,i-1}$ (the number of primary particles per aggregate entering section $i$ due to surface growth of particles in the $i-1$ section) and $n_{p,i+1}$ (the number of primary particles per aggregate entering section $i$ due to oxidation of particles in the $i+1$ section) terms are replaced with $\text{PAH}_{i-1}$ and $\text{PAH}_{i+1}$ and are given by:

$$\text{PAH}_{i-1} = \frac{m_i - m_{i-1}}{N_C m_C} A_{\text{SGS}} + \text{PAH}_{\text{Soot},i-1} \left(1 - A_{\text{SGS}} \frac{m_i - m_{i-1}}{m_C} \frac{1}{A_{\text{soot}}} \right)$$ (3.5)

$$\text{PAH}_{i+1} = \text{PAH}_{\text{Soot},i+1} \left(1 - \frac{m_{i+1} - m_i}{m_C} \frac{1}{C_{\text{soot}}} \right)$$ (3.6)

where $m_i$ is the representative mass of particles in the $i$th section, $N_C$ is the number of carbons in the species causing surface growth, $m_C$ is the mass of a carbon atom, $A_{\text{SGS}}$ is the projected area of the surface growth species determined from the Lennard-Jones diameter, $A_{\text{soot}}$ is the surface area of a soot aggregate in section $i-1$, and $C_{\text{soot}}$ is the number of carbons on the surface of a soot aggregate in the $i+1$ section, determined by assuming the surface carbon density is the same as for benzo[a]pyrene. The equation for $\text{PAH}_{i-1}$ allows this model to capture the effect of surface growth covering existing PAHs on the surface of a soot particle, while adding more surface PAHs if the growth is occurring via PAH condensation.

There are additional variations to the equations for $\text{PAH}_{i-1}$ and $\text{PAH}_{i+1}$ as follows. The first term
in $PAH_{i-1}$ is set to zero if the growth process is not PAH condensation, and if the second term is negative (the surface growth process completely covers the soot particle in the $(i+1)$th section), the second term is set to zero. Additionally, if the second term is negative and the process is PAH condensation, then the entirety of $PAH_{i-1}$ is determined assuming the process produces a soot particle that is now completely covered in PAHs on its surface. If $PAH_{i+1}$ is negative (the oxidation process would remove all carbons on the surface of a soot aggregate in the $(i+1)$th section), $PAH_{i+1}$ is set equal to zero as well, consistent with the fast carbonization assumption.

With $PAH_{Soot,1}$ known, [Dimers] can be determined by calculating $[PAH_{Soot,1}]/2$. If all soot particles in section 1 are dimers, the ratio $PAH_{Soot,1}/2$ will be equal to $N_1^a$, the number of aggregates in the first section. If not all soot particles in section 1 are dimers, $PAH_{Soot,1}/2$ will be less than $N_1^a$, indicating that some particles in section 1 are not incipient soot particles, but rather small soot particles that resulted from oxidation of larger mature soot particles.

### 3.3 Results and discussion

#### 3.3.1 Model Performance

Computational results for three different model configurations are compared to various soot particle measurements taken for the Santoro ethylene-air diffusion flame [82]. The first model uses both the reversible nucleation and condensation models as described in the previous section, and the two other models utilize a reversible nucleation model; however, they use efficiencies to calculate condensation rates and do not directly consider condensation reversibility. Two different efficiencies are chosen, those being 100%, and 1%. Nucleation is modeled based on the dimerization of benzo[a]pyrene, and condensation based on all PAHs containing 18 or more carbons (including PAHs below 18 did not alter results). Thus, two equations per section are added, one to track surface PAHs with 20 carbons, and one to track surface PAHs with 18 carbons, which increased computational costs by an order of magnitude. It should be noted that the surface PAH model does qualitatively reproduce the experimentally observed trend in the study by Dobbins et al. [101], in which the PAHs on the surface of soot particles increase in size with increasing height above the burner. For each of the three models, $\alpha$, on which HACA surface growth rates are linearly dependent, is kept constant at a value of 0.60 [40]. Finally, attempts were made to utilize a functional form for condensation efficiency, proposed by Totton et. al. [95], that has dependencies on temperature and collisional reduced mass; however, satisfactory results could not be obtained.
Fig. 3.1 displays a comparison between the experimental values and those computed with the three models for soot volume fraction along a) the pathline of maximum soot along the wings, and b) the centerline. Experimental data are those measured by Santoro et al. [83] using laser extinction, McNally et al. [87] using thermocouple particle deposition (TPD), and Köylü et al. [86] by thermophoretic sampling (TS) and transmission electron microscope (TEM) images. It can be seen that the reversible model provides the best agreement; however, the 100% model is within a factor of three as well. The 1% model predicts very minimal soot volume fractions at lower axial heights.

Fig. 3.2 displays a comparison between the experimental values and those computed with the models for $d_p$ along a) the pathline of maximum soot along the wings, and b) the centerline. Experimental data along the wings is taken from Megaridis and Dobbins [84], and those along the centerline by Köylü et al. [86]. It can be seen once again that the reversible model displays the best agreement. The 100% model vastly over-predicts primary particle diameters. As expected, the 1% model predicts smaller, more reasonable, primary particle diameters as compared to the 100% model [43]; however, it is already shown that the 1% model fails to predict the correct soot volume fraction at low axial heights.

Fig. 3.3 displays a comparison of $N_p$ (primary particle number density) along the wings, with experimental data taken from Megaridis and Dobbins [85], and Puri et al. [50]. Measurement data for $N_p$ along the centerline are not available. Fig. 3.4 displays a comparison of $N_a$ (aggregate number density) along the a) wings and b) centerline, with experimental data taken from Santoro et al. [83], and Puri et al. [50]. In all of these figures, the 1% model displays comparable results to the reversible model; however, the 100% model generally fails to match the experimental results.
Figure 3.2: Comparison of experimental values and those computed with the Reversible, 100%, and 1% models for primary particle diameter ($d_p$) along a) the pathline of maximum soot on the wings and b) the centerline for the ethylene-air Santoro Flame [84,86].

Figure 3.3: Comparison of experimental values and those computed with the Reversible, 100%, and 1% models for primary particle number density ($N_p$) along the pathline of maximum soot on the wings for the ethylene-air Santoro Flame [50,85].

The reason for the drastically improved agreement when utilizing the reversible condensation model is due to more accurate partitioning of PAHs through the nucleation and condensation processes. The 100% model diverts too much PAH mass through condensation, and thus very large primary particles are predicted. As a consequence, in Fig. 3.1a), the 100% model is unable to predict soot burnout due to the very large, relatively low-surface-area particles that are formed, as oxidation rates are highly dependent on soot surface area. It should be noted that the numerical results are sensitive to which PAH(s) are selected to participate in the nucleation, and to a lesser degree, condensation processes, and highly sensitive to the PAH concentrations predicted by the chemical mechanism.
It has been demonstrated that when combined with a fundamental, fully reversible nucleation model, the only tested condensation model that can reasonably reproduce all relevant average soot morphological parameters along the wings and centerline is the one with efficiency based on equilibrium constants. In light of the results, it is clear that no single constant efficiency for condensation will give satisfactory results for all soot morphological parameters. Also, due to the lack of satisfactory results when implementing the model proposed in [95], in which condensation efficiency is a function of temperature and collision reduced mass, it is clear that there must be some functional dependence on the equilibrium constants as well if reasonable agreement with experimental measurements is to be obtained. Stated another way, reversibility of the condensation process must be explicitly accounted for if accurate particle morphology predictions are desired. Additionally, the results in this study reinforce the important relationship between nucleation and condensation. The proposed reversible model is able to produce good agreement, while reducing the number of arbitrary tunable parameters, and represents a significant advancement in improving the methods for fundamental modeling of soot formation.

3.4 Conclusions

A novel, fundamental reversible model for PAH-based soot nucleation and condensation has been developed with the use of statistical mechanics and the results from several recent investigations. This fundamental model removes the need for arbitrary constants for nucleation and condensation efficiency. It is shown that in order to accurately predict experimental data, both nucleation and condensation
models must explicitly account for reversibility.

For future work, PAHs within soot particles should be tracked, so the effect of soot carbonization may be investigated. The assumption as to which PAHs participate in the nucleation and condensation processes should be avoided. The reversibility of the HACA surface growth mechanism should be investigated as well. To further validate the proposed reversible model, comparisons should be made with particle size distribution (PSD) data sets or other data sets that contain detailed soot particle morphological information. The model should be applied to other data sets that include soot morphology data, including those at elevated pressures and under premixed conditions, to extend the validation of the model, although currently such data sets are very limited. The extended validation will allow investigations of soot formation with a model that is well supported by both the underlying physics present in the literature and comparisons to experimental data.
Chapter 4

Assessing relative contributions of PAHs to soot mass


4.1 Introduction

Reducing soot emissions from combustion processes is important due to the negative health and environmental effects of atmospheric soot. In order to achieve this goal, there has to be a fundamental understanding of the mechanisms of soot formation to allow for the determination of economically viable methods of reducing these emissions. Due to the highly complex nature of soot formation, detailed numerical models are employed to gain fundamental understanding of the factors that affect each mechanism of soot evolution. The recent European emission standard for land vehicles, EURO 6, includes regulations on particle number density in addition to total particle mass (and hence particle size), thus accurate modeling of particle number density and size is important. In a recent study [47], it was shown that the relative efficiency of nucleation versus condensation heavily influences soot primary particle diameter predictions. In order to accurately predict soot particle size for a wide range of conditions, numerical models must be able to accurately model nucleation and condensation, and their relative contributions to total soot mass, without reliance on tunable efficiencies for these processes.
4.1.1 PAH clustering during soot formation

There has been a significant amount of recent investigations into the nature of physical PAH nucleation and condensation. In work by Sabbah et al. [93], it was shown that at flame temperatures, the dimerization of two pyrene molecules was not thermodynamically favored. A temperature-dependent equilibrium constant for the dimerization of pyrene was proposed and based on its very small magnitude at flame temperatures, it was determined that dimerization must be highly reversible. It was asserted in that work that any proposed efficiency for the nucleation process should be a function of equilibrium ratios or constants. There has been some work into attempting to define an equilibrium constant for the dimerization of other PAHs as well. In a review article by Wang [15], statistical mechanics was utilized to define an equilibrium constant for the dimerization of pyrene, ovalene, and circumcoronene using binding energies taken from [94]. Some assumptions had to be made, with the most significant being the average frequency of the vibration modes created during the dimerization process. Investigations have been performed into the magnitude of these vibration modes in the work of Totton et al. [95] for pyrene, coronene, ovalene, hexabenzocoronene, and circumcoronene dimers. In Totton et al. [95], a more advanced model for determining the binding energies between PAHs was developed. Molecular dynamics simulations were utilized to propose a coagulation efficiency for PAH-PAH (nucleation) and PAH-PAH cluster (condensation) collisions that had dependencies on temperature and collisional reduced mass. Rapacioli et al. [96, 97] looked at the frequencies of the vibration modes for coronene stacks containing up to 8 coronenes and vibration modes for various PAH dimers. Their conclusion was that in general, as PAH stack sizes increase, as would occur during the condensation process, vibration frequencies are reduced. In Elvati and Violi [98], and Chung and Violi [99], it was determined that the addition of aliphatic chains, and not only a PAH’s size, influence whether or not a dimerization was favored. Finally, Lowe and Violi [107] expanded on the work by investigating heterogeneous dimer pair stability. Their work suggested that the reduced mass of the pair was the main factor in determining dimer stability. All of these works reached the conclusion that PAHs much larger than pyrene (ovalene and larger) would need to be present for physical PAH attraction to play a role in nucleation and condensation. This result was a significant finding as at the time most detailed soot formation models utilized the pyrene dimerization process to model soot nucleation.

The experimental work performed by Teini et al. [100], in which High Resolution Transmission Electron Microscopy (HRTEM) was used to investigate the types of particles found within nascent soot, conflicted with the results of these recent thermodynamic investigations. The HRTEM showed that the sizes of particles within nascent soot were fairly constant at the core and edges, and consistent
with PAHs containing approximately 20 carbon atoms, or 5-rings. Even though these smaller PAHs are not thermodynamically favored to physically bond, they have been found within the cores and edges of nascent soot particles, leading to the assertion that species of this size are important to nucleation and condensation processes. This finding is consistent with the much earlier work of [101], where laser micro-probe mass spectrometry (LMMS) was used to determine the mass of PAHs found within nascent soot particles. The masses were found to be consistent with PAHs consisting of approximately 20 to 21 carbons. It should be noted that in [101], PAHs containing as many as 38 carbons were detected in more mature soot particles. To reconcile the experimental observations with the theoretical works, it has been suggested that PAH-based nucleation and condensation may not be controlled by equilibrium, but rather kinetics, for which accounting for reversibility is highly important. The work of Schuetz and Frenklach [102] supports this notion, as molecular dynamics simulations displayed that the short lifetime of a pyrene dimer may be sufficiently long to experience a subsequent collision and thus support subsequent growth.

Given this evidence, in Eaves et al. [45] as detailed in the previous chapter, the present authors asserted that the nucleation and condensation processes should be modeled as reversible events. A novel, fundamental, reversible PAH clustering (RPC) model was developed which utilized the recent studies into physical PAH stacking and statistical mechanics to derive the reverse rates of nucleation and condensation. It was demonstrated that when considering nucleation as a reversible event, condensation should be considered reversible (as opposed to being efficiency-based) as well, to give best agreement with experimental data. While the development of this model was a significant advancement, there were three limitations of the model as originally conceived. The model only considered one homogeneous dimerization event (of benzo-a-pyrene, or A5-A5), assumed that once a cluster larger than two PAHs formed that it rapidly became amorphous, mature soot, and was very computationally intensive.

4.1.2 Agenda

In this present work, the RPC model is expanded to include nucleation and condensation from a wide range of PAH size groups. The surface PAH tracking model is replaced with a total soot PAH tracking model to allow for less computational effort and provide the ability to account for PAH reactions, or carbonization, within soot particles. The performance of the new model is assessed and the new model is utilized to elucidate the key PAH contributors to the nucleation and condensation processes.
4.2 Problem formulation

The flame chosen for this investigation is the steady, non-smoking, co-flow laminar diffusion ethylene-air flame originally investigated in [82], and since exhaustively studied by multiple groups. This flame has published experimental data for soot aggregate and primary particle size and number densities. These characteristics make it an excellent choice for comparisons of various soot models. This flame has been extensively studied both experimentally and numerically, thus the details of the burner and flame may be viewed in [50,83,84].

For the gaseous phase, the fully coupled elliptical conservation equations for mass, momentum, energy, and species mass fraction are solved. CoFlame [108], a parallelized sooting laminar flame solver, utilizes the axi-symmetrical nature of the flame, and equations are solved in the two-dimensional ($z$ and $r$) cylindrical co-ordinate system. Conjugate heat transfer between the solid fuel tube and the fuel and air streams is modeled using the harmonic mean method [42,72]. The chemical kinetic mechanism that is used for this investigation is the one originally presented in [11], with modifications described in [12,40]. Soot particle dynamics are described using a fixed sectional method, in which soot particle mass ranges are divided logarithmically into discrete sections. The soot sectional model includes several processes, those being nucleation, PAH condensation, HACA surface growth, surface oxidation, coagulation, fragmentation, particle diffusion, and thermophoresis.

Nucleation and condensation are modeled as the physical binding of PAHs to other PAHs (nucleation), or clusters of PAHs or soot particles (condensation). The nucleation and condensation model employed is referred to as the reversible PAH clustering (RPC) model. The nucleation process is treated as fully reversible, while the condensation process is treated reversibly although net negative condensation rates are disallowed to maintain numerical stability. Statistical mechanics is utilized to determine the enthalpy and entropy of the nucleation and condensation processes for any arbitrary PAH-PAH or PAH-PAH cluster or soot collision event. These values can in turn be used to determine an equilibrium constant [15,95] and subsequently reverse rate coefficients [45]. The enthalpy and entropy change are given by [103]:

$$\Delta H = -E_0 - 4k_B T + \sum_{i=1}^{6} \left( 1 + \frac{1}{e^{hcv_i/(k_B T)} - 1} \right) hcv_i$$  (4.1)

$$\frac{\Delta S}{R_u} = \ln \left[ \left( \frac{m_3 h c B_1 B_2}{2m_1 m_2 B_3} \right) \frac{h^3 P}{\pi^2 (k_B T)^4} \frac{\sigma_2 \sigma_3}{\sigma_1} \right] - 4 + \sum_{i=1}^{6} \frac{[hcv_i/k_B T]}{e^{[hcv_i/(k_B T)]} - 1} - \ln[1 - e^{-hcv_i/(k_B T)}]$$  (4.2)

where $\Delta H$ is the enthalpy change, $\Delta S$ is the entropy change, $R_u$ is the universal gas constant, $k_B$ is the
boltzmann constant, $T$ is the gas temperature, $h$ is Plank’s constant, $c$ is the speed of light, $m_1$ and $m_2$ are the masses of the two colliding entities, $m_3$ is the combined mass of the two entities, $\sigma_i$ are the symmetry numbers, and $B_i$ are the rotational constants. The dimers and soot primary particles are assumed to have no symmetry ($\sigma_i = 1$). The values for $B_i$ are determined utilizing the correlation presented in [104]. Additionally, it is assumed the rotational constants of a dimer are half of a monomer PAH [15] and that the rotation constants of the soot primary particle are unaffected by the condensation process ($B_2 = B_3$). Values for the binding energies are taken from Totton et al. [95], along with the scaling relationship for binding energies and collisional reduced mass developed in [94]. The vibrational mode frequencies for the nucleation and condensation processes are the same as in [45]. Once the enthalpy and entropy change is determined, it is straight-forward to find the Gibbs free energy change, equilibrium constants, and thus the reverse rate coefficients given the forward rate constants utilized in [45]. The reverse rates for nucleation and reverse rates of condensation for the $i^{th}$ section are given by:

$$R_{\text{nuc, rev}} = k_{\text{rev, nuc}} [\text{Dimers}]$$  \hspace{1cm} (4.3)

$$R_{\text{cond, rev, i}} = k_{\text{rev, cond}} [\text{PAH}_{\text{Soot, i+1}}]$$  \hspace{1cm} (4.4)

where $[\text{Dimers}]$ is the concentration of dimers, and $[\text{PAH}_{\text{Soot, i+1}}]$ is the concentration of PAH molecules on the surface of the soot particles in the $(i+1)^{th}$ section. A detailed description of the development of the reversible nucleation and condensation model is available in [45] and the previous chapter. All other soot processes, including nucleation, surface growth, PAH surface condensation, surface oxidation, coagulation, fragmentation, particle diffusion, thermophoresis, and particle radiation are modeled in the same fashion as in [26, 36, 38, 40–49, 71]. A detailed description of the governing equations, boundary conditions, solution methodology, and chemical mechanism can be found in previous works [108] and chapter 2.

### 4.3 Model development

The RPC model, originally proposed in [45] and in the previous chapter, is modified to allow nucleation or condensation to occur from a wide range of PAH size groups. The RPC model is expanded to include soot nucleation and condensation from the dimerization of 6 different PAH size groups, those being PAHs containing 10 (A2), 12 (A2R5, P2), 14 (A3), 16 (A4), 18 (BGHIF, A4C2H), or 20 (BAPYR, the largest PAH in the mechanism) carbons (representative PAHs are in parenthesis). Multiple homogeneous and heterogeneous dimer pairs are tracked. The equations utilized to track surface PAHs are replaced
by those for tracking PAHs contained within soot particles so that the effects of carbonization can be
investigated and possible reductions in computation time. In total, the enhanced RPC model solves 322
equations at each control volume to resolve soot morphology and composition, with 21 dimer sections
containing 2 equations per section (chemically and non-chemically bonded dimers), and 35 aggregate
sections with 7 equations per section (primary particles, and 6 groups of internal PAHs).

4.3.1 PAH dimers

Given the 6 different size groups, there are 21 unique combinations possible for a dimerization, or
nucleation, event. To accurately track each combination, the first 21 sections of the particle dynamics
model are treated as dimer sections. In these sections, there are only two equations per section, those
being the number density of aggregates and the number density of dimers, as the primary particle
and PAH number densities of these sections are prescribed. The equation for the number density of
aggregates for these dimer sections are the same as originally described in [38] for the first section. The
number density of dimers equation is similar; however, an additional source term from the effect of
carbonization is included. By including the effect of carbonization, the rate at which physically bonded
PAH dimers reverse into PAH monomers is reduced as the carbonization rate will reduce the number
density of dimers. The difference between the number density of aggregates and number density of
dimers in the first 21 sections would represent PAH dimers that are chemically- rather than physically
bonded. Table 4.1 below lists the 21 dimer pairs considered by the enhanced RPC model.

The binding energies for the various dimer pairs are calculated based on the binding energy for pyrene
from Totton et al. [95] and the linear scaling of binding energy with collisional reduced mass developed
by Herdman and Miller [94]. The frequencies of the six vibration modes that are created during a
dimerization event are taken from [45] and are kept the same for all possible dimerization events. It
is shown in previous works, and the previous chapter, that the average vibration frequency does not
change significantly between different homogenous dimers [45]. While there are very limited studies
on heterogeneous dimerization, Lowe et al. [107] did demonstrate that the difference in free energies of
dimerization for heterogeneous pairs are primarily due to alterations in binding energies, rather than
entropic, or vibrational frequency, effects. Thus, the assumption that the average vibration frequency
for heterogeneous dimers is constant and equal to that of homogeneous dimers is applied.
Table 4.1: PAH dimers in the enhanced RPC model

<table>
<thead>
<tr>
<th>Dimer Number</th>
<th>PAH Size Group 1</th>
<th>PAH Size Group 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 (A2)</td>
<td>10 (A2)</td>
</tr>
<tr>
<td>2</td>
<td>10 (A2)</td>
<td>12 (A2R5)</td>
</tr>
<tr>
<td>3</td>
<td>10 (A2)</td>
<td>14 (A3)</td>
</tr>
<tr>
<td>4</td>
<td>10 (A2)</td>
<td>16 (A4)</td>
</tr>
<tr>
<td>5</td>
<td>10 (A2)</td>
<td>18 (BGHIF)</td>
</tr>
<tr>
<td>6</td>
<td>10 (A2)</td>
<td>20 (A5)</td>
</tr>
<tr>
<td>7</td>
<td>12 (A2R5)</td>
<td>12 (A2R5)</td>
</tr>
<tr>
<td>8</td>
<td>12 (A2R5)</td>
<td>14 (A3)</td>
</tr>
<tr>
<td>9</td>
<td>12 (A2R5)</td>
<td>16 (A4)</td>
</tr>
<tr>
<td>10</td>
<td>12 (A2R5)</td>
<td>18 (BGHIF)</td>
</tr>
<tr>
<td>11</td>
<td>12 (A2R5)</td>
<td>20 (A5)</td>
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<td>12</td>
<td>14 (A3)</td>
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<td>13</td>
<td>14 (A3)</td>
<td>16 (A4)</td>
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<tr>
<td>14</td>
<td>14 (A3)</td>
<td>18 (BGHIF)</td>
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<tr>
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<td>20 (A5)</td>
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<td>17</td>
<td>16 (A4)</td>
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<td>18</td>
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<td>19</td>
<td>18 (BGHIF)</td>
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<tr>
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<td>18 (BGHIF)</td>
<td>20 (A5)</td>
</tr>
<tr>
<td>21</td>
<td>20 (A5)</td>
<td>20 (A5)</td>
</tr>
</tbody>
</table>

4.3.2 Soot PAH number density

In order to utilize the RPC model, there must be information about the PAH content of the soot particles in each section such that the reverse condensation rates can be determined. Therefore, an additional conservation equation is solved per section for the PAH number density for each PAH group included in the condensation process in a similar fashion as primary particles are tracked in each section [32,62].

The general PAH number density conservation equation is given by:

\[
\rho v \frac{\partial N_{i}^{pah}}{\partial r} + \rho u \frac{\partial N_{i}^{pah}}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho D_{i}^{a} \frac{\partial N_{i}^{pah}}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho D_{i}^{a} \frac{\partial N_{i}^{pah}}{\partial z} \right) - \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho N_{i}^{pah} V_{Ts,r} \right) - \frac{\partial}{\partial z} \left( \rho N_{i}^{pah} V_{Ts,z} \right) + \frac{\partial N_{i}^{pah}}{\partial t} \bigg|_{co} + \frac{\partial N_{i}^{pah}}{\partial t} \bigg|_{sg} + \frac{\partial N_{i}^{pah}}{\partial t} \bigg|_{ox} + \frac{\partial N_{i}^{pah}}{\partial t} \bigg|_{fr} + \frac{\partial N_{i}^{pah}}{\partial t} \bigg|_{ca} \\
(i = DN + 1, 2, ..., SN)
\]

where \( \rho \) is the gas phase density, \( v \) and \( u \) are the radial and axial velocities respectively, \( N_{i}^{pah} \) is the number density of a given PAH size group in the \( i \)th section, \( D_{i}^{a} \) is the diffusion coefficient for aggregates in the \( i \)th section, \( V_{Ts,x} \) is the thermophoresis velocity in the \( x \) direction, \( DN \) is the number of dimer
sections, \( SN \) is the total number of sections, and the remaining terms are the rate of change of the number density of PAHs due to PAH condensation and HACA surface growth (\( sg \)), surface oxidation (\( ox \)), coagulation (\( co \)), fragmentation (\( fr \)), and carbonization (\( cb \)).

The source term due to surface growth is given by:

\[
\frac{\partial N_{pah}^i}{\partial t} \bigg|_{sg} = \left\{ \begin{array}{ll}
- \frac{I_{g,i}}{m_{i+1}-m_i} n_{pah,i} & \text{if } i = DN+1 \\
\frac{I_{c,DNtoDN+1}}{m_{i+1}-m_i} n_{pah,i} - \frac{I_{g,i}}{m_{i+1}-m_i} n_{pah,i} + \frac{I_{c-pah,DNtoDN+1}}{m_{pah}} & \text{if } i = DN+2 \\
\frac{I_{c,i-1}}{m_{i}-m_{i-1}} n_{pah,i-1} \quad & \text{if } i = DN+3, \ldots, SN-1 \\
\frac{I_{c,i-1}}{m_{i}-m_{i-1}} n_{pah,i-1} + \frac{I_{c-pah,i-1}}{m_{pah}} & \text{if } i = SN
\end{array} \right.
\]

where \( I_{g,i} \) is the total of all PAH condensation and HACA surface growth rate for the \( i^{th} \) section in units of g/cc/sec and is always positive, \( I_{c,i} \) is the total of all PAH condensation rates for the \( i^{th} \) section, \( I_{c-pah,i} \) is the PAH condensation rate for the particle PAH size group being tracked in the \( i^{th} \) section, \( m_i \) is the representative mass of aggregates in the \( i^{th} \) section, \( n_{pah,i} \) is the number of PAHs per aggregate in the \( i^{th} \) section, and \( m_{pah} \) is the mass of one PAH from the size group. By employing the equations in this manner, it is assumed that when an aggregate moves to a higher section due to HACA surface growth, the aggregate no longer has any internal PAHs. This assumption is arrived at by assuming the amount of HACA growth required to move an aggregate to a higher section would cause sufficient bonding such that no physically bonded PAHs would remain.

The source term due to oxidation is given by:

\[
\frac{\partial N_{pah}^i}{\partial t} \bigg|_{ox} = \left\{ \begin{array}{ll}
\frac{I_{ox,i}}{m_i} n_{pah,i} - \frac{I_{ox,i+1}}{m_{i+1}-m_i} n_{pah,i} + \frac{I_{ox,i+1}}{m_{i+1}} n_{pah,i+1} & \text{if } i = DN+1 \\
\frac{I_{ox,i}}{m_i} n_{pah,i} - \frac{I_{ox,i+1}}{m_{i+1}-m_i} n_{pah,i+1} + \frac{I_{ox,i+1}}{m_{i+1}} n_{pah,i+1} & \text{if } i = DN+2, \ldots, SN-1 \\
\frac{I_{ox,i}}{m_i} n_{pah,i} & \text{if } i = SN
\end{array} \right.
\]

where \( I_{ox,i} \) is the oxidation rate for the \( i^{th} \) section in units of g/cc/sec and is always negative.

The source term due to coagulation is given by:

\[
\frac{\partial N_{pah}^i}{\partial t} \bigg|_{co} = \sum_{m_{i-1} \leq m_j + m_k \leq m_{i+1}} \left( 1 - \frac{\delta_{j,k}}{2} \right) \eta_{ij} \beta_{j,k} \xi_{j,k} \eta_{ij}^a N_{j} \eta_{ij}^a N_{k} - \eta_{ij} \xi_{j,k} \eta_{ij}^a N_{j} \eta_{ij}^a N_{k} \sum_{k=1}^{35} \beta_{i,k} \xi_{i,k} \eta_{ij}^a N_{j} \eta_{ij}^a N_{k}
\]

where \( \delta \) is the Kronecker delta function, \( \beta_{j,k} \) is the collision kernel of two aggregates in the \( j^{th} \) and
$k^{th}$ sections \[57\], $\eta_{pah,i}$ is the number of PAHs of the given size group per aggregate in the $i^{th}$ section, and $\xi_{j,k}$ is the coagulation efficiency of two aggregates in the $j^{th}$ and $k^{th}$ sections and is set to 0.20 in this work \[39\]. The factor $\eta_{pah}$ assigns PAHs to two adjacent sections so that PAH number density and number of PAHs per aggregate are conserved and is calculated as:

$$\eta_{pah} = \frac{m_i}{m_j + m_k} (n_{pah,j} + n_{pah,i})$$ (4.9)

The source term for fragmentation is given by:

$$\left. \frac{\partial N_{pah}^{i}}{\partial t} \right|_{fr} = \begin{cases} \frac{\Gamma_{i+1} S_{i+1} N_{i+1} a n_{pah,i+1}}{J_s} & \text{if } i = DN + 1 \\ (\Gamma_{i,i} - 1) S_i N_i^a n_{pah,i} + \frac{\Gamma_{i,i} S_{i+1} N_{i+1} a n_{pah,i+1}}{J_s} & \text{if } i = DN + 2, ..., SN - 1 \\ (\Gamma_{i,i} - 1) S_i N_i^a n_{pah,i} & \text{if } i = SN \\ \end{cases}$$ (4.10)

Once the soot PAH number density is determined, the amount of surface PAHs is still required to determine the reverse rates of condensation. In order to determine the concentration of surface PAHs, it is assumed that the distribution of PAHs within soot particles at any given instant is approximately uniform. This assumption implies that internal re-ordering is much faster than the rate at which PAHs condense on the surface of soot particles, which is supported by the studies of Chen et al. \[109\]. The concentration of surface PAHs $[\text{PAH}]_{Soot,i}$ in the $i^{th}$ section is given by:

$$[\text{PAH}]_{Soot,i} = \frac{N_{pah}^{i} \rho C_{pah} C_{mass} A_{Soot,i}}{m_i A_{pah}}$$ (4.11)

where $\rho$ is the density, $C_{pah}$ is the number of carbons in the considered PAH, $C_{mass}$ is the mass of a carbon atom, $A_{Soot,i}$ is the total surface area of soot in the $i^{th}$ section, and $A_{pah}$ is the area of the considered PAH.

One additional term in the soot PAH number density equation is the carbonization rate, which is given by:

$$\left. \frac{\partial N_{pah}^{i}}{\partial t} \right|_{ca} = A \exp \left( \frac{E_A}{R_a T} \right)$$ (4.12)

where $A$ is the pre-exponential term, and $E_A$ is the activation energy. The value of $E_A$ is taken from \[101, 110\]. The value of $A$ in the literature varies by six orders of magnitude; however, in this study it is set to $1.78 \times 10^{10}$, which is in the range of the values reported in literature \[101, 110, 111\].
and provides the best agreement with experimental data. It should be noted that without modeling the carbonization process, soot volume fractions are underpredicted by several orders of magnitude. This result is consistent with all recent studies on PAH clustering processes, which demonstrate that physical bonding alone cannot be the sole mechanism of soot formation and that chemical processes must be involved [95,107,109]. A detailed study of the effect of varying the carbonization rates on predicted soot morphology is left for future work.

4.4 Results and discussion

4.4.1 Model performance

Computational cost

The original RPC model, starting from an initial guess containing an accurate temperature field and major species concentrations, takes approximately 420,000 CPU-Hours utilizing 384 Intel Xeon processors to reach a converged solution for the co-flow laminar diffusion ethylene-air flame originally investigated in [82]. The original RPC model only considered two PAH size groups and 140 soot transport equations. For the same flame, computational domain, and number of processors, the enhanced RPC model takes approximately 101,000 CPU-Hours, while considering 6 PAH size groups and solving 322 soot transport equations. Since computational time is approximately proportional to the number of equations to the power of 2 for the CoFlame code, the enhanced RPC model computationally costs approximately 20 times less than the original RPC model for an equal number of conservation equations. This reduction in cost is attributed to tracking the total PAH number density within soot particles, rather than attempting to track soot surface PAH number density, which was numerically cumbersome.

Soot morphology predictions

The performance of the enhanced RPC model is assessed based on comparisons to data available for the co-flow laminar diffusion ethylene-air flame originally investigated in [82] and results for the original RPC model [45].

Fig. 4.1 displays a comparison between the experimental values and those computed with the CoFlame code with the original RPC model from Eaves et al. and enhanced RPC model in the present work for soot volume fraction along the pathline of maximum soot along the wings (left), and the centerline (right). Both models produce very similar results along the wings and centerline of the flame. The predictions are within the experimental uncertainty along the wings, although there are underpredictions of the
Figure 4.1: Comparison of experimental values and those computed with the CoFlame code for soot volume fraction along the pathline of maximum soot on the wings (top) and the centerline (bottom) for the ethylene-air Santoro Flame [82, 86, 87].

Fig. 4.2 displays a comparison between the experimental values and those computed with the CoFlame code for the original RPC model from Eaves et al. and enhanced RPC model in the present work for primary particle diameter ($d_p$) along the pathline of maximum soot along the wings (left), and the centerline (right). Experimental data along the wings is taken from Megaridis and Dobbins [84], and those along the centerline by Köylü et al. [86]. The enhanced RPC model predicts larger primary particles along the wings and centerline, although the differences along the centerline are minimal. Both models underpredict primary particle size along the centerline. Given that centerline soot volume fraction is on the low end of the experimental uncertainty along the centerline, the underprediction of primary particle diameters can be attributed to an insufficient amount of surface growth, either by the HACA mechanism or PAH condensation. For a given number density, soot volume fraction will scale with $d_p^3$. Due to low radical pools, the centerline of a diffusion flame is PAH condensation dominated [40–42]; therefore, the underpredictions are attributed to insufficient PAH condensation, or missing chemical soot surface growth pathways.

Fig. 4.3 displays a comparison of $N_a$ (aggregate number density) along along the wings (left), and the centerline (right). While the original RPC model predictions are not within experimental uncertainty, the enhanced RPC model is within uncertainty for the majority of axial height locations along the wings and centerline. The enhanced RPC model provides improved predictions at lower axial heights. This improved prediction is discussed in section 4.4.2.
Chapter 4. Assessing relative contributions of PAHs to soot mass

Figure 4.2: Comparison of experimental values and those computed with the CoFlame code for primary particle diameter ($d_p$) along the pathline of maximum soot along the wings (left), and the centerline (right) for the ethylene-air Santoro Flame [84,86].

Figure 4.3: Comparison of experimental values and those computed with the CoFlame code for aggregate number density ($N_a$) along the pathline of maximum soot along the wings (left), and the centerline (right) for the ethylene-air Santoro Flame [50,83].

Fig. 4.4 displays a comparison of $N_p$ (primary particle number density) along the wings, with experimental data taken from Megaridis and Dobbins [85], and Puri et al. [50]. Measurement data for $N_p$ along the centerline are not available. The enhanced RPC model predicts a lower primary particle number density; however, both models are within experimental uncertainty.

Finally, Fig. 4.5 displays a comparison of $n_p$ (average number of primaries per aggregate) along the pathline of maximum soot along the wings (left), and the centerline (right), with experimental data taken from Iyer et al. [89], Puri et al. [50], and Köylü et al. [86]. It can be seen that the enhanced RPC model provides improved predictions along the wings and centerline.
4.4.2 Contribution of each PAH size group to nucleation and condensation

Due to the uncertainties associated with the carbonization rate, the contribution of each PAH to nucleation and condensation is investigated for four different carbonization rates with different orders of magnitude for the pre-exponential term. Model C11 has a pre-exponential of $1.78 \times 10^{11}$, Model C10 $1.78 \times 10^{10}$ and so on.

Fig. 4.6 displays the total path integrated contribution to soot nucleation for each of the 21 dimer pairs along the pathline of maximum soot along the wings (top), and the centerline (bottom), for the four models. Along the wings and centerline, the dimer pairs that contribute the most to nucleation...
are pair 1 (two 10 carbon PAHs, or A2-A2) and 7 (two 12 carbon PAHs, or A2R5-A2R5), which are the smaller dimer pairs. Along the centerline, pair 1 is dominant for the greatest range of carbonization rates, while pair 7 is dominant for the greatest range on the wings. The improved predictions for aggregate number density along the centerline in Section 4.4.1 can be attributed to including smaller dimer pairs in the nucleation process. As the carbonization rate is decreased, there is a trend of larger dimer pairs having a greater contribution to the nucleation process. Along the wings, Model C08 shows significant contributions from dimer pair 11 (10-20, or A2R5-BAPYR) and dimer pair 21 (20-20, or BAPYR-BAPYR). However, Model C08 has poor agreement with experimental soot primary particle diameters on the centerline. Fig. 4.7 displays a comparison between the experimental values and those computed with the CoFlame code for the original RPC model from Eaves et al. and the previous chapter, the enhanced RPC model in the present work (C11 Model), and the present work with the Model C08 for primary particle diameter ($d_{pp}$) along the centerline. It can be seen that the C08 Model displays poor agreement with the experimental data.
Figure 4.7: Comparison of experimental values and those computed with the CoFlame code for primary particle diameter ($d_p$) along the centerline for the ethylene-air Santoro Flame [84,86].
Fig. 4.8 displays the total path integrated contribution to PAH condensation for each of the 6 PAH size groups along the pathline of maximum soot along the wings (top), and the centerline (bottom) for the four models. Along the wings and centerline, both the relatively small and large PAHs play a significant role in the condensation process with the highest contributions from PAHs with 12 carbons (A2R5) and those with 18 carbons (BGHIF). Similar to nucleation, as the carbonization rate is reduced, larger PAHs have greater contributions to the condensation process.

**Figure 4.8: Total path integrated contribution to PAH condensation for each of the 6 PAH size groups for four models along the pathline of maximum soot along the wings (top), and the centerline (bottom) for a co-flow ethylene-air diffusion flame.**

In summary, the results display that smaller PAHs are dominant for the nucleation process, while a broad range of PAHs are important for the condensation process. To understand this result, an additional calculation is performed with Model C10 with all condensation rates equal to zero, or in other words, PAHs are only able to undergo a nucleation process. Fig. 4.9 displays the total path integrated contribution to soot nucleation for each of the 21 dimer pairs, for Model C10 without condensation, along the pathline of maximum soot along the wings (top), and the centerline (bottom). In the absence of condensation, the importance of larger dimer pairs to nucleation is greater than when condensation is permitted. On the wings, dimer pair 19 is dominant (18-20, or BAPYR-BGHIF), which is the third...
largest dimer pair considered. While on the centerline a smaller dimer pair, pair 7 (A2R5-A2R5), is dominant, significant contributions are seen from dimer pair 19 as well.

![Figure 4.9: Total path integrated contribution to soot nucleation for each of the 21 dimer pairs, for Model C10 without condensation, along the pathline of maximum soot along the wings (top), and the centerline (bottom) for a co-flow ethylene-air diffusion flame.](image)

From these results in Fig. 4.9, the reason for the observed importance of smaller dimer pairs in Fig. 4.6 is due to the presence of condensation. In the RPC model, the condensation process is less reversible than the nucleation process due to two factors: increased binding energies, and lower frequencies of the vibration modes created [45]. While there is uncertainty in the frequency of the vibrational modes, a lower frequency is consistent with literature [96,97]. Additionally, the enhanced RPC model demonstrates good agreement for primary particle diameter, displaying that the ratio of nucleation to condensation strength is reasonable, as primary particle size predictions are very sensitive to the relative strengths of these two processes [47]. Thus, once a dimer, or cluster, is formed from an initial pool of PAHs, it is more probable that remaining free PAHs will condense on the existing cluster, rather than form a new cluster or dimer. Since smaller PAHs are formed prior to larger PAHs on a given streamline in diffusion flames, the initial clusters are formed from these smaller PAHs. Subsequently, any larger PAHs forming in the gas phase preferentially condense rather than dimerize, leading to the low contribution of larger
PAHs to the nucleation process.

The result of smaller PAHs being important to the nucleation process is consistent with the literature. Teini et al. [100] utilized HRTEM to investigate the sizes of PAHs within nascent soot particles by analyzing fringe lengths. It was shown that the average size of PAHs were those containing 20 carbons; however, the mode of the distribution were PAHs with 12 carbons (A2R5). Apicella et al. [112] utilized HRTEM to investigate PAHs with soot particles. Based on the diameters of the basic structure units (BSU) from nascent soot (low axial heights) reported in the supplemental material, the results indicate nascent soot primarily contained PAHs with 12 carbons as well. While the results of Adkins and Miller [113] for optical band gap (OBG) measurements suggest that PAHs containing 14 rings, or 42 carbons, are important to the nucleation process, the work of Commodo et al. [114, 115] suggests that the resulting OBG measurements are a stronger function of the number of PAHs within BSU stacks, rather than the size of the individual PAHs within soot particles. While theoretical studies suggest that small PAH dimerization is not thermodynamically favored, unfavored does not mean impossible. Also, these theoretical studies neglect the possibility of chemical bonding. The enhanced RPC model utilizes parameters derived by these theoretical studies and includes the effect of chemical bonding, thus the conclusions of this study are congruent with previous theoretical studies [15,94–99,107].

4.5 Conclusions

The original reversible PAH clustering (RPC) model is enhanced to include 21 dimerization events and tracking of internal PAHs within soot particles. The enhanced RPC model shows improved agreement with experimental measurements for an ethylene-air coflow diffusion flame. Even though there is uncertainty in the carbonization rate, when investigating rates that span four orders of magnitude, the conclusions of this work are consistent. Smaller PAHs contribute the most to nucleation processes due to condensation being less reversible than nucleation and the step-wise nature of PAH growth in diffusion flames, while small and large PAHs are important for the condensation process. While the exact contribution from each PAH size group will depend on the predictions of gas phase PAHs from the chemical mechanism, the general trends observed in this study are not expected to change as the trends can be explained based on the fundamental knowledge of the nucleation and condensation processes. Future work should focus on developing a fundamental model for the carbonization process.
Chapter 5

Influence of pressure on near nozzle flow field and soot formation

N. A. Eaves, S. B. Dworkin, and M. J. Thomson. Influence of pressure on near nozzle flow field and soot formation in laminar co-flow diffusion flames. To be submitted

5.1 Introduction

Soot formation during combustion processes is a concern due to several negative health and environmental effects of elevated atmospheric soot levels. Due to these negative effects, there is a desire to reduce soot emissions from practical combustion devices, which tend to operate at elevated pressures. Thus, studying the effect of pressure on soot formation is important.

There have been a number of recent experimental investigations on the effect of pressure on soot formation in a laminar co-flow flame configuration [116–132]. This configuration is utilized due to the simplified geometry, yet still allowing for investigation of the possible effects of diffusion and mixing. These studies concluded that maximum soot volume fraction increased with increasing pressure; however, the study by Joo and Gülder [121] had the interesting result of soot volume fraction reaching a peak at 55 atm, then monotonically declining as pressure was raised further. A brief communication by Mandatori and Gülder [133] demonstrated another unique phenomenon where at 36.5 atm the entire ethane fuel stream converted to soot.

To compliment these experimental investigations, multiple numerical studies have been performed to attempt to understand the reasons for the experimentally observed influence of pressure on soot
formation. Most studies relied on simplified soot models that had limited ability to understand how the mechanisms of soot formation are influenced \[92,131,134–138\]; however, others have used the more advanced method of moments \[132\] or sectional soot formation models \[41,42,130\] that utilize PAH-based soot nucleation and condensation models. One sectional soot formation code, CoFlame \[108\], discussed in detail in chapter 2, has been validated and extensively used to investigate soot formation under a wide range of conditions, including high pressure. These advanced studies concluded that the experimentally observed increase in soot formation with increasing pressure was due to the positive feedback nature of soot formation, instigated by density increases. In addition, the study in \[42\] demonstrated the importance of extending the computational domain to model below the exit plane of the fuel tube and including a conjugate heat transfer (CHT) model within numerical simulations of high pressure sooting diffusion flames. However, there still has been no adequate explanation of the reason for the complete conversion of ethane at 36.5 atm observed in \[133\], even with the investigations of Eaves et al on these flames \[41,42\].

To date, there are limited studies on the effect of pressure on the flow field of co-flow diffusion flames and the subsequent effect of the flow field on soot formation. In a very recent work, Xiong et al. \[139\] experimentally and numerically displayed that recirculation zones can form near the nozzle of atmospheric pressure co-flow laminar diffusion flames when the fuel density is greater than that of air. Additionally, they concluded that in order to numerically predict the recirculation zones, the computational domain should extended into the fuel tube, similar to the conclusions of \[42\]. Xiong et al. \[139\] asserted that the cause of the recirculation zones was due to the negative buoyancy effects exerted on fuels with density greater than air. The results from \[139\] raise the question if recirculation zones could be responsible for the complete conversion of ethane to soot observed in \[133\].

Since ethane is approximately the same density as air, there may be another mechanism that causes the observed recirculation zones in high pressure laminar diffusion flames. It should be noted that in the study by Xiong et al. \[139\], constant mass flow rates for air and for fuel were used for all flames, thus fuels with higher densities would have lower flow velocities. Other researchers have noted the importance of selecting fuel and air mass flow rates such that the resultant flow velocities are matched to minimize shear effects \[140,141\]; however, it is not known to what extent minimizing shear effects is necessary.

### 5.1.1 Agenda

In this present work, the CoFlame soot formation code \[108\], extensively validated at atmospheric pressure, and previously validated for soot volume fraction at elevated pressure against the data of
Mandatori and Gülder [124], is utilized to investigate the potential of recirculation zones causing the observed complete conversion of ethane to soot. The influence of pressure on the size of any potential recirculation zones is explored, along with an explanation of the cause of the recirculation zone observed in this work and in [139].

5.2 Flame and model description

The flames chosen for this investigation are the steady, non-smoking, co-flow laminar ethane/air diffusion flames at pressures of 2 to 33 atm, studied experimentally by Mandatori and Gülder [124, 125]. Fuel and air mass flow rates are kept constant as pressure is varied, with values of 0.0052 g/s for the fuel stream and 0.12 g/s for 15 atm and below, and 0.24 g/s at higher pressures for the air stream. The Reynolds number for the fuel stream for these flames is 20.2. The computational domain used extends 3.45 cm in the axial direction and 1.18 cm in the radial direction, and is divided into 416 \((z)\) x 172 \((r)\) control volumes. A non-uniform mesh is used to save computational cost while still resolving large spatial gradients. The first 0.5 cm in the \(z\) direction is below the fuel tube exit plane. This distance is sufficient to ensure the temperature gradients at \(z = 0.0\) (the bottom of the computational domain) are negligible.

In order to validate the model, the methane-air and propane-air co-flow laminar diffusion flames at atmospheric pressure studied by Xiong et al [139] are simulated. The air flow velocity is 6.2 cm/s, with methane and propane flow velocities of 4.45 and 1.40 cm/s respectively. Therefore, the velocity ratio, or shear between the fuel and air streams, is not constant between the different fuels, with the propane-air case having a higher air-fuel velocity ratio. The Reynolds number for fuel stream for the methane flame is 30.4 and for propane is 37.0. The computational domain used extends 12.54 cm in the axial direction and 3.95 cm in the radial direction, and is divided into 320 \((z)\) x 135 \((r)\) control volumes. The first 1.0 cm in the \(z\) direction is below the fuel tube exit plane. For all flames, top-hat velocity profiles are utilized for the air and fuel stream boundary conditions.

For the gaseous phase, the fully coupled elliptical conservation equations for mass, momentum, energy, and species mass fraction are solved. CoFlame [108] utilizes the axi-symmetrical nature of the flame, and equations are solved in the two-dimensional \((z\) and \(r)\) cylindrical co-ordinate system. Conjugate heat transfer between the solid fuel tube and the fuel and air streams is modeled using the harmonic mean method [42, 72]. The chemical kinetic mechanism that is used for this investigation is the one originally presented in [11], with modifications described in [12, 40].

Soot particle dynamics are described using a fixed sectional method, in which soot particle mass
ranges are divided logarithmically into 35 discrete sections. The soot sectional model includes several processes, those being nucleation, PAH condensation and HACA surface growth, surface oxidation, coagulation, fragmentation, particle diffusion, and thermophoresis. In a recent work [47], soot nucleation and condensation were modified to result from 5-ring aromatic (A5) collisions, specifically benzo[a]pyrene (BAPYR), secondary benzo[a]pyrenyl (BAPYR*S), and benzo(ghi)fluoranthene (BGHIF), as opposed to from pyrene, with a non-unity nucleation efficiency, which resulted in better centerline soot predictions. All other soot phenomena, including nucleation, surface growth, PAH surface condensation, surface oxidation, coagulation, fragmentation, particle diffusion, thermophoresis, and particle radiation are modeled in the same fashion as in [26,36,38,40–49,71].

5.3 Results and discussion

5.3.1 Flow field validation

Validation computations are performed for the methane-air and propane-air diffusion flames. Fig 5.1 displays the flow streamlines near the fuel tube exit plane for the two flames. The CoFlame code predicts the same results as in [139]. The methane flame results display no recirculation zone, while the propane-air flame results display a recirculation zone along the center axis of the flame. The CoFlame model is able to capture the qualitative trend of the formation of a recirculation zone for propane, and non-formation for methane.
5.3.2 Effect of pressure on flow field

With the flow field predicted by the CoFlame code being validated, it is now applied to the ethane-air high pressure co-flow diffusion flames. For flames at 10 atm and above, a flow phenomenon is computationally observed at the exit plane of the fuel tube near the centerline region. Fig. 5.2 displays streamlines for the 10, 15, 20, 25, 30, and 33 atm flames, zoomed in near the exit of the fuel tube (black region), which show the presence of a recirculation zone. This recirculation zone is not predicted at 2 atm or 5 atm flames; however, it is present for all other flames. It can be seen that the recirculation zone increases in size with increasing pressure. Additionally, as pressure increases, the streamlines near the fuel tube tip become increasingly more horizontal, directed towards the centerline. This flattening of the streamlines is due to the thinning of the flame cross sectional area as pressure increases due to reductions in flame thickness with increasing pressure [41], thus the flow is accelerated inwards.

In order to gain an understanding as to why these recirculation zones were predicted, two cold flow cases (where no flame is present and the entire domain is at 300 K), utilizing the inlet flow conditions for the 10 atm and 33 atm flame respectively, are computed. For the two cold flow cases, in which no flame is present, the recirculation zones do not appear. These results indicate that the recirculation zone is being predicted due to the influence of the high temperature flame on the flow field, which is consistent with the results in [139]. Table 5.1 displays the ratio of the air flow velocity to the fuel flow velocity at the exit plane of the fuel tube near the tube tip. The velocity for the fuel and air is taken at a location that is sufficiently far away from the fuel tube to no longer be in the boundary layer. As pressure is increased, the ratio of air to fuel velocity increases. Since the viscosity of gases is only a function of temperature, and temperature is relative constant in the region near the fuel tube tip for all pressures, this result indicates the shear between the air and fuel streams in the vicinity of the fuel tube increases with increasing pressure. The increase in the velocity ratio can be attributed to the high temperatures.
Figure 5.2: Computed flow streamlines with the CoFlame code near fuel tube tip for an ethane-air diffusion flame at 10 (top-left), 15 (top-middle), 20 (top-right), 25 (bottom-left), 30 (bottom-middle), and 33 (bottom-right) atm.
on the air side of the fuel tube (Ref [42] displayed temperatures of approximately 1700-1800 K), causing the air velocity to increase. This effect is combined with the streamlines becoming more horizontal due to the change in flame cross sectional area, thus lowering the fuel velocity in the fuel tube tip region as well. The result is an increasing shear between the air and fuel streams as pressure increases. The increase in shear is accompanied by an increase in the size of the recirculation zone as well.

<table>
<thead>
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<th>Pressure (atm)</th>
<th>Velocity Ratio</th>
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<tbody>
<tr>
<td>2</td>
<td>2.12</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
</tr>
<tr>
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<td>3.42</td>
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<td>30</td>
<td>4.44</td>
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<tr>
<td>33</td>
<td>4.68</td>
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</table>

Given these two analyses, the following assertion with regards to the cause of the recirculation zones is made. The recirculation zones are caused by the increasing acceleration of the air near the fuel tube tip as pressure increases, due to high temperatures, combined with the thinning of the flame cross sectional area and subsequent flattening of the flow streamlines. These two effects cause significant shear between the air and fuel streams, causing the fuel stream to accelerate in the region near the fuel tube tip. In order for continuity to be upheld, there must be a corresponding deceleration of the fuel stream in the centerline region. Eventually, this required deceleration is sufficiently large to cause the flow to reverse, and a recirculation zone forms.

Experimentally, it would be very difficult to detect the presence of these recirculation zones, as they are located in the center of the flame, inside the fuel tube. This location of the recirculation zones is contrary to the recirculation zones discovered in [139], as in that study the recirculation zones were fully above the exit plane of the fuel tube and detectable. It should be noted that while it would seem that simply reducing the air flow rate for experiments would reduce or eliminate the recirculation zones, there has to be consideration of flame stability as well. Most experiments at high pressure already utilized the minimum co-flow air required to obtain a stable flame [121,125], thus eliminating these recirculation zones may not be possible in some cases.

Based on the role of shear in the presence of the recirculation zones, it should be possible to induce a recirculation zone simply by increasing the air flow velocity, or reducing the fuel flow velocity. Since in the experiments in [139] a constant mass flow rate was used for all fuels, the fuel flow velocity was
smaller for heavier fuels (propane) than lighter fuels (methane). This constant mass flow rate means that for the heavier fuels, the shear between the air and fluid streams was higher, and thus the recirculation zones for the heavy fuel flames were influenced by the increased shear rather than directly due to the increases in the fuel’s density.

Another simulation is performed for the methane-air flame, except the air flow velocity is increased so that the ratio of the fuel to air velocities is the same as for the propane air case. For this simulation, a recirculation zone is not formed; however, upon increasing the air velocity by an additional factor of 2.25, a recirculation zone forms. This result supports the theory that the recirculation zones are formed due to high local shear between the air and fuel fluid streams in the vicinity of the fuel tube.

5.3.3 Relationship between recirculation zones and soot formation

To determine the relationship between the recirculation zones and soot formation, the 5 atm flame is re-simulated with the co-flow air velocity increased by a factor of ten. This increase is sufficiently large to induce a recirculation zone, although not excessively large to induce turbulence (an increase by a factor of five did not induce a recirculation zone). Fig. 5.3 displays the predicted soot volume fraction along the centerline of the flame with the experimental air flow rates and ten times the experimental rate and the experimental measurements [124]. There is a discrepancy between the experimental data and the computations at low axial heights; however, this discrepancy can be attributed to the model not differentiating between nascent and mature soot. The experimental technique used to determine soot volume fraction is only sensitive to mature soot; however, the model lumps both nascent and mature soot into one entity [142]. Nascent soot tends to form in the lower temperature (less than 1300-1600 K) regions of flames, prior to formation of mature soot, thus the predicted large soot volume fraction at low axial heights is mostly nascent soot [143]. When the recirculation zone is present, there is an increase in soot volume fraction near the exit plane of the fuel tube (axial height 0.5 cm in the figure); however, at larger axial heights the difference between the peak soot volume fraction for the two cases is very minimal.

Fig. 5.4 displays the predicted soot volume fraction along the centerline of the 10 and 33 atm ethane-air flames with the experimental air flow rates and the experimental measurements [124]. It can be seen that the calculations for the 33 atm flame predict a higher soot volume fraction in the recirculation zone than for the 10 atm flame. As pressure is increased, the recirculation intensity increases, and a larger soot volume fraction is predicted in the zone. The results point to an explanation for the experimentally observed complete conversion of the flame to soot at 36.5 atm [133]. Calculations for the 36.5 atm
flame were attempted; however, a converged steady state could not be resolved. As the computations progressed, the predicted recirculation zone spanned the entirety of the fuel tube exit plane with a very large \(O(10^3)\) soot volume fraction in the zone, which eventually lead to divergence. This result leads to the assertion that the complete conversion to soot is caused by the recirculation zone. While the CoFlame code is not a transient solver, nor can it handle a bulk solid phase, the trend of increasing soot in the recirculation zone as pressure increases and being unable to obtain a converged solution for the 36.5 atm flame support the stated assertion. To summarize, the effect of the recirculation zones on centerline soot formation is minimal up until the point the zone is sufficiently large to cause a complete conversion to soot.
5.4 Conclusions

The effect of pressure on near nozzle flow field and soot formation in laminar diffusion flames is investigated numerically using the CoFlame code. The code is validated against previous experimental data for methane and propane diffusion flames in its ability to correctly predict the formation of recirculation zones. From 10 atm and greater, recirculation zones are predicted to form along the centerline of the flame near the exit plane of the fuel tube for ethane-air diffusion flames previously investigated experimentally and numerically. The recirculation zones are shown to be caused by the increased local shear between the fuel and air fluid streams, and not solely due to density differences between the fuel and air. The formed recirculation zones are therefore able to explain the experimentally observed complete conversion of ethane to soot at 36.5 atm, although the effect of the recirculation zones on soot formation is shown to be minimal otherwise. Future work should focus on verifying the effect of shear experimentally for atmospheric diffusion flames where the recirculation zone would be more easily detected.
Chapter 6

Closure

6.1 Summary and conclusions

This thesis research has lead to the successful development of a novel model for the nucleation and condensation process that includes fundamental physics considering the reversible nature of both phenomena. This research is the first time that the reversible nature of these processes has been explored and implemented into a soot formation model. Additionally, the project has successfully determined the reason for the complete conversion of fuel to soot at very high pressures in a coflow flame. The five major findings of the studies presented in this thesis are summarized below:

1. A novel, fundamental reversible model for PAH-based soot nucleation and condensation has been developed with the use of statistical mechanics and the results from several recent investigations. This fundamental model removes the need for arbitrary constants for nucleation and condensation efficiency. It is shown that in order to accurately predict experimental data, both nucleation and condensation models must explicitly account for reversibility.

2. The original reversible PAH clustering (RPC) model is enhanced to include 21 dimerization events, tracking of internal PAHs within soot particles, and the effects of carbonization. The enhanced RPC model shows improved agreement with experimental measurements for an ethylene-air coflow diffusion flame.

3. Smaller PAHs contribute the most to nucleation processes due to condensation being less reversible than nucleation and the step-wise nature of PAH growth in diffusion flames, while small and large PAHs are important for the condensation process. While the exact contribution from each PAH
size group will depend on the predictions of gas phase PAHs from the chemical mechanism, the general trends observed in this study are not expected to change as the trends can be explained based on the fundamental knowledge of the nucleation and condensation processes.

4. The effect of pressure on near nozzle flow field and soot formation in laminar diffusion flames is investigated numerically. From 10 atm and greater, recirculation zones are predicted to form along the centerline of the flame near the exit plane of the fuel tube for ethane-air diffusion flames previously experimentally and numerically investigated. The recirculation zones are shown to be caused by the increased local shear between the fuel and air fluid streams, and not solely due to density differences between the fuel and air. The formed recirculation zones are therefore able to explain the experimentally observed complete conversion of ethane to soot at 36.5 atm, although the effect of the recirculation zones on soot formation is shown to be minimal otherwise.

5. The computational cost of utilizing detailed numerical models that including modeling of soot internal PAH structure is substantial and markedly higher than previous simulation efforts. The total number of equations that must be solved to resolve internal structure when using a sectional method is very high, leading to large computational costs. Resolving the structure of each individual PAH within soot particles is intractable using the current sectional model.

6.2 Recommendations for future work

Soot formation is a very complex and still ill-defined process. There are still many studies that need to be performed to gain a full understanding of soot formation mechanics, particularly at elevated pressures. Based on observations from the detailed modeling studies performed in this thesis, the following future studies are recommended:

1. Developing a fundamental model for the carbonization process. The enhanced RPC model includes the effects of carbonization; however, the rate is derived by matching numerical results with experimental data. The determined carbonization rate is likely to have limited general applicability due to this limitation. In order to alleviate this concern, a model that considers the fundamentals of the carbonization process should be developed, allowing for enhanced predictive capability.

2. Validation of the RPC model over a wide-range of conditions. While the RPC model did display improved results for the Santoro ethylene-air diffusion flame, it must be applied to a wider range of experimental conditions to judge its predictive capability.
3. Validation of soot particle and soot aggregate parameters at elevated pressure. While the CHT Model does give quantitatively accurate results for soot volume fraction at elevated pressures, no validation has been performed of soot particle or aggregate parameters. Primary particle number density, soot aggregate number density, and primary particle diameter all require validation at elevated pressures. Currently, this objective is hindered by the lack of available experimental data for these parameters.

4. Improvement of code efficiency and scalability. As the detail of the model increases, the ability to perform parametric studies with the detailed code in a timely manner is diminished due to the increased computational cost. Increasing the code’s parallel efficiency and scalability will allow numerical results to be obtained in a shorter time frame. Implementing adaptive mesh refinement and higher order discretization approaches will allow for higher accuracy solutions in a reduced time frame as well. Additionally, this enhanced capability would increase the feasibility of modifying the detailed code for turbulent flame simulations, as in the code’s current state, such solutions would be likely intractable.
Bibliography


