The Pennsylvania State University
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NUMERICAL SIMULATION OF AXISYMMETRIC LAMINAR
DIFFUSION FLAMES WITH SOOT

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by
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Abstract

Detailed numerical modeling of combustion phenomena, soot formation, and radiation is an active area of research. In this work a general-purpose, pressure-based, finite volume code for modeling laminar diffusion flames has been incorporated into the CFD code OpenFOAM. The code uses a mixture-averaged model for the calculation of transport coefficients, and can be used to perform detailed modeling of multi-dimensional laminar flames using realistic molecular transport, and with detailed chemical mechanisms containing hundreds of chemical species and reactions. Two soot models have been incorporated into the code: a semi-empirical two-equation model, as well as a detailed Method of Moments with Interpolative Closure (MOMIC). An emission-only, optically-thin radiation model has also been included in the code to account for the radiative heat loss, and sophisticated radiation models with detailed calculations of spectral properties and radiative intensity have also been included. The flame code showed excellent scalability on massively distributed, high-performance computer systems. The code has been validated by modeling four axisymmetric, co-flowing laminar diffusion flames, and the results have been found to be mostly within experimental uncertainty, and comparable to results reported in the literature for the same and similar configurations. A number of parametric studies to study the effects of detailed gas-phase chemistry, soot models and radiation have also been performed on these flame configurations. It has been found that the flames considered in this work are all optically thin, and so the simple, emission-only, optically-thin radiation model can be used to model these flames with good accuracy and a reasonable computational effort. In particular, the detailed radiation models increase the computational cost by two orders of magnitude, and thus their applicability in a detailed calculation may be limited.

It was found that the two-equation soot model used in conjunction with a gas-phase mechanism that adequately describes the combustion of C₂ hydrocarbons
produces results in close agreement with experimental data for a 1-bar ethylene-air flame, a 10 bar methane-air flame, as well as an ethane-air flame at 10 bar. The detailed MOMIC soot model requires the use of a larger, more detailed gas-phase chemical mechanism containing polycyclic aromatic hydrocarbons (PAH) with four rings, and thus the computational cost associated with the MOMIC soot model is significantly higher. The detailed model was used to model the flames, and computed soot levels were within a factor of two of the experimental values, which is typically considered good agreement considering the complex physics involved. The last flame studied using both the soot models was a N₂-diluted ethylene-air flame, in which the predicted values of major gas-phase species were seen to be close to the experimental values, but the soot levels were off by an order of magnitude. Notwithstanding the lack of agreement with measurements for this flame, the flame solver with the soot models was demonstrated to be a robust, scalable, and general code with potential applications to a variety of laminar flames in the non-premixed, partially premixed and premixed regimes.
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To my dear wife Sudeshna,
and to my parents ...
Combustion is at the heart of our civilization. Like the invention of the wheel, learning to produce and in some sense control fire was one of the most important stepping stones for the progress of human civilization. In modern times almost all the power that we use is obtained from combustion—we use fuels to power our vehicles, to heat and light our homes and so on.

In recent years we have become increasingly aware of the fact that the burning of hydrocarbon fuels to power our civilization comes at a very high price—its effect on the environment. Burning of hydrocarbons produces carbon dioxide, which is a greenhouse gas, and over a long period of time the emission of CO$_2$ can have detrimental effects on the environment, and contribute to global warming. Also, there are other aspects of combustion that can produce more immediate risks to human health and well-being, which include pollutant formation. The notable ones among these pollutants are soot, the oxides of nitrogen that are formed at higher temperatures (sometimes referred to as NO$_x$), and carbon monoxide. Over the past three decades, a lot of attention has thus been paid to studying and understanding the phenomena of combustion and the production of the pollutants, especially soot. Yet, as regulations for pollutant emissions become stricter, understanding combustion phenomena at a very basic level remains a challenge for combustion researchers.
1.1 Soot

Soot is an important by-product of hydrocarbon combustion, especially under fuel-rich conditions. It is a major constituent of particulate matter. Particulate matter can be classified into two main subtypes:

1. Inhalable coarse particles, and
2. fine particles.

The former includes particles with diameters in the range of 10 $\mu$m and 2.5 $\mu$m. Smaller particles fall in the second category. Primary soot particles have diameters of the order of about 25 nm [7, 8], and thus soot can be classified as being fine particles.

1.1.1 Ill effects of soot

Typically, soot formation is an undesirable side-effect of hydrocarbon combustion. In gas turbines, and also in conventional engines, the formation of soot can lead to serious issues with maintenance and structural integrity of the system. Soot adversely affects the performance of energy-producing devices. Moreover, soot deposits inside the combustion chamber can lead to rapid wear of the components [9].

The major ill-effects of soot are its effects on human health, and the effect it has on a global scale as a potential agent responsible for climate change, and as one of the factors responsible for global warming [10]. Due to its small size, soot can enter the lungs when it is inhaled. Continued exposure to soot and other particulate matter can have detrimental effects on human health, such as asthma, and various heart and lung diseases.

Soot is thus a major pollutant, and the main driving force behind the study of soot formation and growth is to be able to eliminate, or at least to minimize the formation of soot in combustion systems. Soot does have some uses, such as in the manufacture of pigments for printing, and for making rubber tires.

Formation of soot is a highly complex process and our knowledge of the processes involved are limited; however in recent years our understanding of the pro-
cess of combustion has enabled us to gain a somewhat deeper understanding of the phenomena that lead to the formation of pollutants such as soot.

One major area in which the study and understanding of soot formation and growth processes is important is the field of propulsion. It is necessary to study and develop tools that can help us understand and predict the formation of soot in complex engineering devices.

1.1.2 Formation of soot from gas-phase species

In many combustion systems, the fuel is in either a gaseous state or in a liquid state. Soot is particulate matter, and nascent soot is possibly a blend of very fine particles and liquid droplets. The formation of solid soot particles from the gas-phase species is still not fully understood. Part of this lack of understanding stems from the fact that there is no precise definition of what constitutes an incipient soot particle, and how it differs from gas-phase species of similar molecular mass. In some works, polycyclic aromatic hydrocarbon (PAH) molecules above a certain size were considered to be soot. In terms of modeling approximations, different cut-off points have been suggested, for example, the formation of PAH dimers, notably of pyrene [11, 12]. Other cut-off points have been used in modeling studies, for example C$_2$H$_2$ [5, 13], and naphthalene [3].

In spite of the limited understanding of the processes leading to soot formation, it is now accepted that at some point in the chemical reaction pathways, the first soot particles are formed. These soot particles then react with the gas-phase species and grow in size. Soot can also be oxidized by oxidizing species in the gas phase. Soot particles can also grow by the process of coalescence with other soot particles as they undergo Brownian collisions.

Despite the fact that our understanding of soot has grown over the last several years, numerically simulating the formation of soot in complex devices is difficult due to the computational effort required. Soot models thus are often developed and applied to simpler laboratory flames for the initial validation of the models. Therein lies the importance of studying the formation and growth of soot in simple flame configurations. Once the models are seen to perform reasonably well for such flames, they can then be modified to suit complex engineering devices.
1.2 Soot modeling

Over the last several decades a significant body of literature has been devoted to the study of soot formation and associated phenomena. Numerous experimental and computational studies have been undertaken by different researchers, and this has contributed to our understanding of the processes in soot formation and growth. A summary of these processes has been provided by Richter and Howard [14]. Based on our understanding of these processes several soot models have been proposed [5, 11, 13, 15, 16]. A comprehensive review of the soot models has been performed by Kennedy [17].

Kennedy et al. [18] proposed a soot model based on the mixture fraction. In this model an equation for the soot volume fraction is solved, and the rates of formation and growth of soot is determined by the local mixture fraction.

Leung et al. [13] suggested the use of a simple C$_2$H$_2$-based model for the study of soot in non-premixed flames of ethylene. In their model, the soot precursor was taken to be acetylene, and surface growth of soot was by the reaction of soot with the gas-phase acetylene. Guo et al. [5, 19] used a semi-empirical soot model based on the work of Leung et al. to study laminar diffusion flames in co-flowing and opposed-flow configurations.

Frenklach and Wang [11] provided a detailed mechanism for the formation and growth of soot from the gas-phase species with a four ring aromatic (pyrene) as the soot precursor. In this work they proposed the hydrogen-abstraction-C$_2$H$_2$-addition (HACA) mechanism for the growth of aromatic species beyond the first ring. They argued that analogous reaction pathways are responsible for soot particle surface growth. Many of the simulations using detailed soot models in literature are based on some form of the HACA growth mechanism for soot surface growth [7, 20, 21, 4]. Dworkin et al.[4] used a sectional method for modeling soot in the simulation of laminar diffusion flames. The soot particle distribution function (PSDF) was divided into 35 sections, and two equations were solved for each section: one for the primary spherical number density, and the other for the soot aggregate density. The models for soot surface growth and inception were the same as those proposed by Frenklach and Wang [11].
1.3 Objectives of the present study

In this study the primary focus was on the development of a general-purpose numerical tool to study and quantify combustion phenomena in multi-dimensional laminar flames using realistic molecular transport, detailed chemistry calculations, soot models and radiation models. The focus of this work was on soot formation and growth, but the study of the gas-phase combustion process was also an integral part of the study. The main vehicle for this study was a solver for laminar diffusion flames that was built based on the open-source CFD code OpenFOAM [22]. A semi-empirical, two-equation soot model [5, 13] and a detailed soot model, the Method of Moments with Interpolative Closure (MOMIC) [15] were incorporated into the solver. Radiation from soot is an important parameter in sooting flames, and initially an optically thin radiation model [5, 6] was also included in the solver. Subsequently a number of detailed radiation models [23] were also coupled to the solver.

In this work the focus was on modeling axisymmetric, co-flowing laminar diffusion flames. The objective of this study was to study the formation and growth of soot in laminar flames with complex, multi-dimensional flow configurations. The choice of these axisymmetric flames was driven by the fact that these flame configurations allowed the numerical models to be applied to multi-dimensional flames with a tractable computational expense. In some sense, therefore, this work was intended to bridge the gap between the simulations of quasi one-dimensional laminar flames with soot [2], and the modeling of soot in turbulent flames. The main aspect of this study was to perform parametric studies to understand the effects of various parameters—the gas-phase chemistry, the soot models, and radiation models—on the problem. The flame configuration most extensively studied in this work was an atmospheric-pressure ethylene-air diffusion flame [24], for which an abundance of experimental data is available. Other studied flame configurations were a methane-air flame and an ethane-air flame, both at 10 bars, and a N\textsubscript{2}-diluted ethylene-air flame at 4 bar pressure.
1.4 Organization of the dissertation

The rest of this dissertation is organized into several chapters. A very brief outline of each chapter is given below:

**Chapter 2** describes the basic modeling aspects of the simulation of laminar diffusion flames.

**Chapter 3** provides an overview of soot in general, with a focus on modeling. This is followed by a description of the soot models used in the present work.

**Chapter 4** provides a general overview of the spectral models and RTE solvers used in radiation modeling, with a focus on the models used in the present work.

**Chapter 5** presents the results obtained in the simulations of the 1-bar ethylene-air laminar diffusion flames in the present work. Parametric studies using various gas-phase chemical mechanisms are shown, as is the effect of the soot models on the flame. A sensitivity study on the effect of inlet boundary conditions on temperature is also presented.

**Chapter 6** describes the study of higher pressure laminar diffusion flames undertaken as part of the present work. Results for three different flames are presented, along with a discussion on the reliability of the experimental measurements.

**Chapter 7** provides a summary of the parametric studies using different detailed radiation models, with a focus on the importance of radiative heat transfer in these flame configurations, and the effect of modeling reabsorption as opposed to modeling radiation with an emission-only model.

**Chapter 8** provides a summary of the present work, along with some possible future directions.
Modeling Laminar Diffusion Flames

A co-flowing laminar diffusion flame is a very important flame type for combustion research, as it provides a vehicle for the study and calibration of numerical tools to be used in combustion problems. A model developed for a laminar diffusion flame may subsequently be used to form flamelet tables that can be used for turbulent flame configurations [25]. The combustion process, as well as the formation of products and pollutants is strongly dependent on the rate of mixing of the fuel and the oxidizer; a proper handling of the transport phenomena, and in particular the differential diffusion of heat and mass is therefore critical to successfully modeling a laminar diffusion flame [26].

2.1 Diffusion in multicomponent systems

Diffusion gives rise to a diffusion velocity (or flux) which is usually modeled by a gradient-diffusion hypothesis; i.e., the diffusion flux for any quantity is proportional to its own gradient.

2.1.1 Mass diffusion

Mass diffusion is often modeled using Fick’s law; thus we usually write an equation for the diffusion velocity for species \( k \) as

\[
V_{k,i} = -\frac{D_{km}}{Y_k} \frac{\partial Y_k}{\partial x_i},
\]
where \( Y_k \) is the mass fraction of species \( k \), and \( D_{km} \) is its diffusivity with respect to the rest of the gas mixture. Typically for a multicomponent system \( D_{km} \) is different for each component, and thus the rates of diffusion are different for the components. This has an effect on the combustion process as the fuel, the oxidizer and the products diffuse in and out of the reaction zone at different rates.

### 2.1.2 Diffusion of energy

A similar approach can be used to model the diffusion of enthalpy, but an additional complication arises due to the fact that mass also carries enthalpy with it as it diffuses. This gives rise to the interdiffusion flux, in addition to the flux of energy driven by a temperature gradient. Thus the expression for the heat flux \( \mathbf{q} \) becomes

\[
\mathbf{q}_i = -\lambda \frac{\partial T}{\partial x_i} + \rho \sum_{k=1}^{N} h_k Y_k V_{k,i},
\]

where \( \lambda \) is the thermal conductivity of the mixture, and \( h_k \) is the mass-specific enthalpy of species \( k \).

If a Fickian model is used to model mass diffusion, the interdiffusion term introduces an extra term in the enthalpy equation. This term is sometimes neglected, especially in modeling turbulent combustion, but this introduces an inconsistency into the system. Even in turbulent multicomponent flows, this inconsistency shows up in the temperature field obtained as a solution of the energy equation [27]; if the term is neglected, the model will predict significant temperature changes even when the physical system involves mixing of two gases at the same temperature.

The effect of the interdiffusion flux can be alleviated somewhat by assuming unity Lewis number for all components—an assumption that sets the additional term in the energy equation to zero. This approach may work well for flames where the specific role of molecular diffusion is not very significant, as in turbulent flames. However, for laminar diffusion flames, since the rate of reaction depends strongly on the rates at which the different components diffuse, this assumption is clearly not an appropriate one.
2.1.3 Thermophoresis

Thermophoresis, or the Soret effect, refers to a diffusion of mass driven by a temperature gradient. The thermophoretic velocity for species $k$ is given as

$$W_{k,i} = -\frac{D^T_k}{\rho Y_k T} \frac{1}{T} \frac{\partial T}{\partial x_i},$$

where $D^T_k$ is the thermal diffusion coefficient for species $k$. To compute the thermophoretic velocity for species $k$, we define a thermal diffusion ratio $\Theta_k$ [28] so that the thermal diffusion velocity is defined as

$$W_{k,i} = -\frac{D_{km} \Theta_k}{X_k T} \frac{1}{T} \frac{\partial T}{\partial x_i},$$

where $X_k$ is the mole fraction for species $k$, and $T$ is the temperature. Typically the thermal diffusion effects are either completely ignored [29], or a light-species approximation is used, where this effect is computed for the gas-phase species having a molecular weight less than a cut-off [5, 28].

2.2 Modeling laminar flames in the present work

In this work a solver for laminar diffusion flames has been developed based on the open-source CFD solver **OpenFOAM** [22]. **OpenFOAM** is a code written in C++ with a number of solvers for different problems along with a selection of models in the form of libraries. Thus any model can be used by the solver by simply linking it to the proper libraries. The use of **OpenFOAM**-based codes for simulating laminar flames has been reported in the literature [30, 31].

The version of **OpenFOAM** selected for this work was 1.7.1 and the solver was based on **reactingFOAM**, which is a solver for turbulent diffusion flames available in **OpenFOAM**. However, being a solver for turbulent flames, the solver was lacking in some features that made modifications necessary in order to enable it to handle slow-flowing laminar diffusion flames.

The main features the laminar flame solver had to incorporate are:

- A realistic model for molecular transport, and
• an accounting for the interdiffusion flux.

2.2.1 Modeling transport properties

In order to model the effects of differential diffusion for the gas-phase species and enthalpy, the transport properties must be modeled. The most accurate way of doing this is to include a full multicomponent treatment, which is obviously the most accurate, but at the same time is computationally more involved as an additional set of equations has to be solved at each spatial location.

The other approach that works well for many cases [32] is to use what is known as a mixture-averaged model [28]. In this model, like the multicomponent model, the transport properties for the individual components are evaluated using molecular parameters, and then the properties for the mixture are computed using mixing rules. This approach has the advantage of being computationally less involved, and has been adopted in the present work.

The calculation of the transport properties and the mixing rules adopted in this work closely follow the approach of Kee et al. [28].

2.2.1.1 Viscosity

The viscosity of the gas-phase species $k$ is given by [33]

$$
\mu_k = \frac{5}{16} \sqrt{\frac{\pi m_k k_B T}{\pi \sigma_k^2 \Omega^{(2,2)*}}} ,
$$

where $T$ is the temperature, $\sigma_k$ is the Lennard-Jones collision diameter, $m_k$ is the molecular mass for species $k$, $k_B$ is Boltzmann’s constant, and $\Omega^{(2,2)*}$ is the reduced collision integral, which is a function of the reduced temperature $T_k^*$, given by

$$
T_k^* = \frac{k_B T}{\varepsilon_k},
$$

where $\varepsilon_k$ is the Lennard-Jones potential well depth for species $k$. The collision integrals are evaluated from curve-fits to the reduced temperature [34].
2.2.1.2 Binary diffusivities

The binary diffusion coefficient for gas-phase species \(j\) and \(k\) is given by [33]

\[
D_{jk} = \frac{3}{16} \frac{\sqrt{2\pi k_B^3 T^3/m_{jk}}}{p\pi \sigma_{jk}^2 \Omega^{(1,1)*}},
\]

where \(m_{jk}\) is the reduced molecular mass for species \(j\) and \(k\), defined as

\[
m_{jk} = \frac{m_j m_k}{m_j + m_k},
\]

\(p\) is the pressure, \(\sigma_{jk}\) is the reduced collision diameter, and the reduced collision integral \(\Omega^{(1,1)*}\) is a function of the reduced temperature \(T_{jk}^*\). These parameters are calculated based on whether the two molecules involved are both polar, both non-polar or one polar and the other non-polar.

For the case of two non-polar molecules or two polar molecules interacting, the reduced quantities are defined as

\[
\varepsilon_{jk} = \sqrt{\left(\frac{\varepsilon_j}{k_B}\right) \left(\frac{\varepsilon_k}{k_B}\right)},
\]

\[
\sigma_{jk} = \frac{1}{2} (\sigma_j + \sigma_k).
\]

For a non-polar molecule interacting with a polar one, we define the reduced polarizability \(\alpha_n^*\) and the reduced dipole moment \(\mu_p^*\) as

\[
\alpha_n^* = \frac{\alpha_n}{\sigma_n^3},
\]

\[
\mu_p^* = \frac{\mu_p}{\sqrt{\varepsilon_p \sigma_p^3}},
\]

where \(\alpha\) denotes the polarizability and \(\mu\) denotes the dipole moment; the subscript \(p\) refers to the polar species and the subscript \(n\) to the non-polar species. The reduced temperature \(T_{jk}^*\) is defined as

\[
T_{jk}^* = \frac{k_B T}{\varepsilon_{jk}}.
\]
The reduced quantities are calculated as

\[ \frac{\varepsilon_{np}}{k_B} = \zeta^2 \sqrt{\left( \frac{\varepsilon_n}{k_B} \right) \left( \frac{\varepsilon_p}{k_B} \right)}, \]

\[ \sigma_{np} = \frac{1}{2} (\sigma_n + \sigma_p) \zeta^{-\frac{1}{2}}, \]

where

\[ \zeta = 1 + \frac{1}{4} \alpha_n^* \mu_p^* \sqrt{\frac{\varepsilon_p}{\varepsilon_n}}. \]

### 2.2.1.3 Thermal conductivity

The thermal conductivity is assumed to have contributions from translational, rotational and vibrational components. The thermal conductivity of species \( k \) is given by [35]

\[ \lambda_k = \frac{\mu_k}{M_k} \left( f_{\text{trans}} C_{v,\text{trans}} + f_{\text{rot}} C_{v,\text{rot}} + f_{\text{vib}} C_{v,\text{vib}} \right), \quad (2.3) \]

where \( M_k \) is the molecular weight for species \( k \),

\[ f_{\text{trans}} = \frac{5}{2} \left( 1 - \frac{2}{\pi} \frac{C_{v,\text{rot}}}{C_{v,\text{trans}}} A \right), \]

\[ f_{\text{rot}} = \frac{\rho_k D_{kk}}{\mu_k} \left( 1 + \frac{2}{\pi} \frac{A}{B} \right), \]

\[ f_{\text{vib}} = \frac{\rho_k D_{kk}}{\mu_k}. \]

Here the self-diffusion coefficient \( D_{kk} \) is obtained by substituting \( j = k \) in equation (2.2), and the density of gas-phase species \( k \) is obtained as

\[ \rho_k = \frac{p M_k}{R_u T}, \]

where \( R_u \) is the universal gas constant. Further,

\[ A = \frac{5}{2} - \frac{\rho_k D_{kk}}{\mu_k}, \]
\[ B = Z_{\text{rot}} + 2 \left( \frac{5}{3} \frac{C_{v,\text{rot}}}{R_u} + \frac{\rho_k D_{kk}}{\mu_k} \right). \]

Here \( Z_{\text{rot}} \) is the rotational relaxation number and is given by

\[ Z_{\text{rot}}(T) = Z_{\text{rot}}(298) \frac{F(298)}{F(T)}, \]

where

\[ F(T) = 1 + \frac{\pi^2}{2} \left( \frac{\varepsilon/k_B}{T} \right)^{\frac{1}{2}} + \left( \frac{\pi^2}{4} + 2 \right) \left( \frac{\varepsilon/k_B}{T} \right) + \pi^2 \left( \frac{\varepsilon/k_B}{T} \right). \]

The translational and rotational components of the gas specific heat are dependent on the kind of molecule under consideration. For a linear molecule,

\[
\frac{C_{v,\text{trans}}}{R_u} = \frac{3}{2},
\]

\[
\frac{C_{v,\text{rot}}}{R_u} = 1,
\]

\[
C_{v,\text{vib}} = C_v - \frac{5}{2} R_u.
\]

For a non linear molecule

\[
\frac{C_{v,\text{trans}}}{R_u} = \frac{3}{2},
\]

\[
\frac{C_{v,\text{rot}}}{R_u} = \frac{3}{2},
\]

\[
C_{v,\text{vib}} = C_v - 3 R_u.
\]

For a single atom (for example H, O, etc.) there are no internal contributions to the specific heat. Hence

\[
\frac{C_{v,\text{trans}}}{R_u} = \frac{3}{2},
\]

\[
\frac{C_{v,\text{rot}}}{R_u} = 0,
\]

\[
C_{v,\text{vib}} = 0.
\]
The molecular parameters for the gas-phase species are obtained from the transport database that accompanies each chemical mechanism.

2.2.1.4 Fitting the transport coefficients

The calculation of transport properties for systems containing a large number of species is computationally very expensive. To speed up the calculations, the temperature-dependent parts of the transport properties for the individual species are fitted using the GNU Scientific Library [36], with the method of least squares. The logarithms of the properties are fitted to polynomials in the logarithm of temperature, as was done by Kee et al. [28].

For the viscosity of species \( k \) we have

\[
\ln \mu_k = \sum_{n=0}^{3} a_{n,k} (\ln T)^n.
\]

For the thermal conductivity we have

\[
\ln \lambda_k = \sum_{n=0}^{3} b_{n,k} (\ln T)^n.
\]

The viscosity and the thermal conductivity are functions of temperature only, while the binary diffusivities are functions of temperature and pressure. We fit the binary diffusivities of each pair of species \((j, k)\) at 1 bar pressure; the actual diffusivity is obtained by dividing the value thus obtained by the pressure in bars. Thus

\[
\ln D_{jk}^\circ = \sum_{n=0}^{3} d_{n,jk} (\ln T)^n,
\]

where the superscript \( \circ \) denotes that the quantity is evaluated at a pressure of 1 bar.

The fitting procedure needs to be carried out once for each chemical mechanism, and then any simulation using that mechanism can be performed using the coefficients thus obtained. Use of the fitting procedure for the large mechanisms used in this work (\( \sim 100 \) species) resulted in a speed-up of more than a factor of two compared to calculating the transport properties on the fly using the relations
described in Sec. 2.2.1.1 through Sec. 2.2.1.3.

2.2.1.5 The mixture-averaged properties

Once the individual species transport properties are calculated, we use mixing rules to estimate the transport properties for the mixture [28].

Mixture viscosity

The mixture viscosity is given by

\[ \mu = \sum_{k=1}^{N} \frac{X_k \mu_k}{\sum_{j=1}^{N} X_j \Phi_{kj}}, \]  

(2.4)

where

\[ \Phi_{kj} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_k}{M_j} \right)^{-\frac{1}{2}} \left[ 1 + \left( \frac{\mu_k}{\mu_j} \right)^{\frac{1}{2}} \left( \frac{M_j}{M_k} \right)^{\frac{1}{4}} \right]^2. \]  

(2.5)

Mixture thermal conductivity

The thermal conductivity of the mixture is given by

\[ \lambda = \frac{1}{2} \left( \sum_{k=1}^{N} X_k \lambda_k + \frac{1}{\sum_{k=1}^{N} X_k / \lambda_k} \right). \]  

(2.6)

Diffusion coefficients

The diffusion coefficient for species \( k \) with respect to the mixture is given by [5]

\[ D_{km} = \frac{1 - X_k}{\sum_{j \neq k} X_j / D_{jk}}. \]  

(2.7)

Thermal diffusion ratios

As described in section 2.1.3, a thermal diffusion ratio \( \Theta_k \) can be defined for species \( k \), so that the thermophoretic velocity is given by

\[ W_{k,i} = -\frac{D_{km} \Theta_k}{X_k} \frac{1}{T} \frac{\partial T}{\partial x_i}. \]  

(2.8)
We only consider the thermal diffusion effects for ‘light’ species; that is to say, we choose a molecular weight cut-off of 5. The thermal diffusion ratio for species \( k \) is given by

\[
\Theta_k = \sum_{j \neq k} \theta_{kj},
\]

(2.9)

where

\[
\theta_{kj} = \frac{15}{2} \frac{(2A^*_{kj} + 5)(6C^*_{kj} - 5)}{A^*_{kj}(16A^*_{kj} - 12B^*_{kj} + 55)} \frac{M_k - M_j}{M_k - M_j} X_k X_j.
\]

(2.10)

In Eq. (2.10), \( A^*_{kj}, B^*_{kj}, \) and \( C^*_{kj} \) are three ratios of collision integrals, and are defined as

\[
A^*_{kj} = \frac{1}{2} \frac{\Omega_{jk}^{(2,2)}}{\Omega_{jk}^{(1,1)}},
\]

\[
B^*_{kj} = \frac{1}{3} \frac{5\Omega_{jk}^{(1,2)} - \Omega_{kj}^{(1,3)}}{\Omega_{kj}^{(1,1)}},
\]

\[
C^*_{kj} = \frac{1}{3} \frac{\Omega_{kj}^{(1,2)}}{\Omega_{kj}^{(1,1)}}.
\]

For each chemical mechanism we fit the quantity \( \frac{\theta_{kj}}{X_k X_j} \) for each pair of species \((j, k)\) for which \( M_k \leq 5 \). Thus we have

\[
\frac{\theta_{kj}}{X_k X_j} = a_{kj} + b_{kj}T + c_{kj}T^2 + d_{kj}T^3.
\]

(2.11)

2.2.2 Modeling the interdiffusion flux

In this work the differential diffusion of heat and mass are accounted for by the inclusion of the interdiffusion flux in the enthalpy equation. As mentioned in section 2.1.2, ignoring the interdiffusion flux can lead to large inaccuracies in the temperature field. In the present work, it was found that these errors in temperature can be severe enough to produce completely unphysical solutions.
2.2.3 Modeling chemistry

Apart from the equations of flow and energy, reacting flow calculations involve the
calculation of chemistry—the effect of reactions on the flow. For a CFD calculation
of a reacting flow, this is typically the most expensive part of the computation.

Several techniques are used to handle these chemical kinetic source terms in the
equations. Some researchers have used a Strang operator-splitting approach, where
the chemical kinetics are integrated using a stiff ODE solver, and then the transport
equations are solved [30]. The advantage of this method is to separate the effects
of the stiff chemical kinetics from the transport. Another approach is to linearize
the species mass-fraction equations, and then to solve them simultaneously at each
point in the domain [29, 32].

In the present work, a form of the operator splitting method has been used. At
any spatial location, we form a system of ODEs comprising the mass fractions \( Y_k \)
of the species and the temperature \( T \) as

\[
\frac{dY_k}{dt} = \frac{\dot{\Omega}_k M_k}{\rho}, \quad k = 1, 2, \ldots N
\]

\[
\frac{dT}{dt} = -\frac{1}{\rho C_p} \sum_{k=1}^{N} h_k \dot{\Omega}_k M_k,
\]

where \( \dot{\Omega}_k \) is the molar rate of production of species \( k \), \( C_p \) is the specific heat of the
mixture at constant pressure, and \( h_k \) is the specific enthalpy of species \( k \). Thus we
integrate the system of ODEs at constant pressure and enthalpy.

2.2.4 Summary of the governing equations

The governing equations for a flame are essentially statements of conservation of
mass, momentum and energy. There are multiple species present in a combustion
system, and so each species has its own conservation equation. The equations are:

1. **The equation of continuity**, expressing the global mass conservation prin-
ciple,

2. **The species mass fraction equations**, expressing the conservation for the
individual species,
3. **The momentum equation**, which is a statement of the principle of conservation of momentum, and

4. **The energy equation**, which is obtained from the principle of conservation of energy.

In addition to these equations there are also **equations of state**, which help to close the system. Typically the energy equation is solved for the energy variable, and then the temperature is obtained from the caloric equation of state.

**The Equation of Continuity**

The equation of continuity can be written as

\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} = 0. \tag{2.12}
\]

In the above equation, \( \rho \) is the gas-phase density and \( \mathbf{u} \) is the velocity.

**The Species Mass Fraction Equations**

The mass fraction of the gas-phase species \( k \) is governed by the following equation:

\[
\frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial (\rho u_i Y_k)}{\partial x_i} + \frac{\partial (\rho V^c_i Y_k)}{\partial x_i} + \frac{\partial (\rho W_{k,i} Y_k)}{\partial x_i} = \dot{\omega}_k + \frac{\partial}{\partial x_i} \left( \rho D_{km} \frac{\partial Y_k}{\partial x_i} \right), \tag{2.13}
\]

where \( \dot{\omega}_k \) is the rate of production of species \( k \) by chemical reactions, \( W_{k,i} \) is the thermophoretic diffusion velocity of species \( k \), and \( V^c_i \) is the correction velocity that is introduced to ensure that the diffusion velocities of all the species add up to zero.

**The momentum equation**

The momentum equations are the Navier-Stokes equations for compressible flow:

\[
\frac{\partial (\rho u_i)}{\partial t} + \frac{\partial (\rho u_i u_j)}{\partial x_j} = \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i. \tag{2.14}
\]
Here the stress tensor $\tau_{ij}$ is defined as
\[
\tau_{ij} = -p\delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial u_m}{\partial x_m} \delta_{ij} = -p\delta_{ij} + \sigma_{ij},
\]
where $\sigma_{ij}$ is the deviatoric stress, $g$ is the acceleration due to gravity and $p$ is the pressure.

**The energy equation**

The energy equation in terms of the sensible enthalpy $h_s$ is
\[
\frac{\partial (\rho h_s)}{\partial t} + \frac{\partial}{\partial x_i} \left( \rho u_i h_s + \rho V_c h_s \right) = \frac{Dp}{Dt} - \sum_{k=1}^{N} \dot{\omega}_k h_{c,k} + \frac{\partial}{\partial x_i} \left( \rho \alpha \frac{\partial h_s}{\partial x_i} \right)
\]
\[
+ \frac{\partial}{\partial x_i} \left[ \rho \sum_{k=1}^{N} \left( \frac{1}{Le_k} - 1 \right) h_{s,k} \frac{\partial Y_k}{\partial x_i} \right]
\]
\[
- \frac{\partial}{\partial x_i} \left[ \rho \sum_{k=1}^{N} h_{s,k} Y_k W_{k,i} \right] + \dot{Q},
\]
where $\alpha$ is the thermal diffusivity of the mixture, $Le_k = \frac{\alpha}{D_{g,m}}$ is the Lewis number for species $k$, $h_{s,k}$ is the sensible enthalpy for species $k$, $h_{c,k}$ is the chemical part of the enthalpy for species $k$, and $\dot{Q}$ is the heat source term, which includes radiation.

**Equations of state and other auxiliary relations**

For our problems we assume that the gas-phase species behave as ideal gases. Thus the thermal equation of state becomes
\[
p = \rho R_u T \sum_{k=1}^{N} \left( \frac{Y_k}{M_k} \right),
\]
where $M_k$ is the molecular weight of species $k$, and $R_u$ is the universal gas constant.

The mole fractions $X_k$ and the mass fractions $Y_k$ are related by:
\[
X_k = \frac{Y_k M}{M_k}
\]
\[
\frac{Y_k}{M_k} = \frac{Y_k}{\sum_{i=1}^{N}(Y_i/M_i)},
\]

where $\bar{M}$ is the average molecular weight for the mixture, defined as

\[
\bar{M} = \sum_{k=1}^{N} X_k M_k.
\]

The temperature $T$ is obtained from the caloric equation of state:

\[
h_s = \int_{T_{std}}^{T} C_p dT,
\]

where $C_p$ is the specific heat of the mixture at constant pressure, and $T_{std}$ is the standard temperature at which the formation enthalpies are defined. Typically $T_{std}$ is taken to be 25° C (298.15 K).

**Thermodynamic properties**

For ideal gases, the standard-state thermodynamic properties are functions of temperature only. Thus the standard molar specific heat at constant pressure for species $k$ is given by

\[
\frac{C_{p,k}}{R_u} = \sum_{n=0}^{4} a_{n,k} T^n,
\]

where the superscript $\circ$ denotes standard state. Similarly, for the standard-state values of the molar enthalpy $H_k^\circ$ and the standard-state molar entropy $S_k^\circ$ we have

\[
\frac{H_k^\circ}{R_u T} = \sum_{n=0}^{4} \frac{a_{n,k} T^n}{n+1} + \frac{a_{n,5}}{T},
\]

\[
\frac{S_k^\circ}{R_u} = a_{0,k} \log(T) + \sum_{n=0}^{4} \frac{a_{n,k} T^n}{n} + a_{6,k}.
\]

Further, for ideal gases, the specific heats and the enthalpy are functions of temperature only; thus the superscript $\circ$ can be dropped from $C_{p,k}$ and $H_k^\circ$ in Eqs.
(2.17) and (2.18). The thermodynamic properties are evaluated as

\[
\frac{C_{p,k}}{R_u} = \sum_{n=0}^{4} a_{n,k} T^n.
\]

\[
\frac{H_k}{R_u T} = \sum_{n=0}^{4} \frac{a_{n,k} T^n}{n + 1} + \frac{a_{n,5}}{T},
\]

\[
\frac{S_k^o}{R_u} = a_{0,k} \log(T) + \sum_{n=1}^{4} \frac{a_{n,k} T^n}{n} + a_{6,k}.
\]

The coefficients \(a_{0,k}\) through \(a_{6,k}\) for species \(k\) are obtained from the thermodynamic database that accompanies each mechanism.

Thus we have a fully determinable system from which we can solve for the flow field and also for the temperature and composition of the gas mixture.
Soot is formed as a by-product of hydrocarbon combustion. The formation of soot is a very complicated process, and even though major advances have been made in combustion technology and modeling, our understanding of the processes leading to the inception, growth and destruction of soot remain far from complete.

Soot is a major pollutant and human health hazard. Soot does have some uses, such as manufacture of pigments for printing, and for use in the manufacture of rubber tires. In some applications, such as in industrial furnaces, where the main objective is to attain high heat transfer rates, the formation of soot may be somewhat beneficial in promoting heat transfer by radiation [37]. But in these applications the system must ensure that almost all the soot is oxidized before the products of combustion leave the system and enter the atmosphere.

It is therefore important to understand and control the processes that lead to the formation, growth, and oxidation of soot during combustion.

Soot formed in combustion is composed mainly of carbon, and is black in color, but its composition is not uniquely defined. Soot particles may contain up to 10 mole percent of hydrogen, and this number is higher for young soot particles [37].

### 3.1 Processes in soot formation and oxidation

It is now generally accepted that soot formation occurs due to four major processes [38]:

1. Nucleation
2. Growth
3. Oxidation
4. Destruction
1. Nucleation or inception of soot particles,

2. particle growth by coagulation,

3. surface reactions (soot surface growth and oxidation, and PAH condensation on soot surface), and

4. agglomeration of soot particles.

### 3.1.1 Nucleation

Nucleation, or inception, of soot refers to the collection of processes that lead to the formation of soot from the gas-phase species in the combustion system. The exact mechanism of the formation of soot has long been a source of debate [17]; the possible pathways include [1, 17]

- the growth of the planar polycyclic aromatic hydrocarbons (PAH) into fullerine-like structures,
- the formation of soot from PAH molecules,
- the formation of soot from ionic species in combustion.

It is now believed that the main soot precursors are PAH species [1, 11].

To understand the formation of PAH, the important first step is the formation of the first aromatic ring (benzene, \( \text{C}_6\text{H}_6 \)) from the aliphatic molecules. Once the first aromatic rings are formed, they grow into PAH. Frenklach and Wang [11] proposed a mechanism for this process, which is known as the ‘Hydrogen-abstraction-C\(_2\)H\(_2\)-addition’ (HACA) mechanism. In their work, a representative reaction set for the HACA mechanism is given as

\[
A_i + H \rightleftharpoons A_i \cdot + H_2, \tag{3.1}
\]

\[
A_i \cdot + C_2H_2 \rightleftharpoons A_iC_2H_2 \cdot, \tag{3.2}
\]

\[
A_iC_2H_2 \cdot + C_2H_2 \rightarrow A_{i+1} + H. \tag{3.3}
\]

In this reaction scheme, \( A_i \) denotes a PAH molecule containing \( i \) aromatic rings, and \( A_i \cdot \) denotes a radical formed from the molecule by hydrogen-abstraction.
Then $A_iC_2H_2\cdot$ denotes a radical formed by $C_2H_2$-addition to the radical formed in reaction (3.1).

In oxidative environments the oxidation of the radicals formed in reaction (3.1) needs to be considered:

$$A_i \cdot + O_2 \rightarrow \text{products.}$$

(3.4)

In the presence of molecular oxygen, some of the key intermediate species (such as $C_2H_3$ and $C_4H_3$ radicals) react with $O_2$, thereby inhibiting the formation of the first aromatic ring. At the same time, $O_2$ also helps to build up the radical pool, which promotes the formation of the intermediates and H atoms. The net effect of $O_2$ is thus determined by a balance between the two processes.

The transition from the gas-phase species to the solid soot particles is possibly the least understood part of the mechanism. In some early works, the mass in PAHs above a certain size was treated as soot. Frenklach and Wang [11] suggested that soot is formed by the coalescence of two PAH species to form a dimer.

In addition to PAHs, other soot precursors have been used by modelers, notably $C_2H_2$ [5, 13] and benzene [16].

### 3.1.2 Coagulation

Once the soot particles are formed they collide with each other due to Browninan motion, and form larger soot particles. This process is called coagulation. The process of coagulation decreases the number of soot particles, and has no effect on the total mass of soot in the system.

### 3.1.3 Surface reactions

The mass of the soot particles depends on the reaction of the soot particles with the gas-phase species. There is some uncertainty in the exact nature of the chemical reactions that contribute to soot particle growth, but a general consensus seems to be that the soot growth mainly occurs by the reaction of the soot particle with acetylene [11].

It has been proposed that the surface growth reactions of soot with the gas-phase H, $C_2H_2$ and $O_2$ are analogous to the corresponding reactions for the PAH
molecules [39, 11]. The soot surface growth process is thus considered to be very similar to the HACA reaction pathway. A summary of the reactions leading to the surface growth (and oxidation) of soot particles is summarized in table 3.1.

Table 3.1. Summary of soot surface growth and oxidation reaction pathways

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( C_{\text{soot}} - H + H \rightleftharpoons C_{\text{soot}} \cdot +H_2 )</td>
<td>[12, 40]</td>
</tr>
<tr>
<td>2</td>
<td>( C_{\text{soot}} - H + \text{OH} \rightleftharpoons C_{\text{soot}} \cdot +\text{H}_2\text{O} )</td>
<td>[12, 41]</td>
</tr>
<tr>
<td>3</td>
<td>( C_{\text{soot}} \cdot +\text{H} \rightarrow C_{\text{soot}} - \text{H} )</td>
<td>[12]</td>
</tr>
<tr>
<td>4a</td>
<td>( C_{\text{soot}} \cdot +\text{C}_2\text{H}<em>2 \rightarrow C</em>{\text{soot}} - \text{H} + \text{H} )</td>
<td>[12]</td>
</tr>
<tr>
<td>4b</td>
<td>( C_{\text{soot}} \cdot +\text{C}_2\text{H}<em>2 \rightarrow C</em>{\text{soot}} \cdot +\text{H} )</td>
<td>[42]</td>
</tr>
<tr>
<td>5</td>
<td>( C_{\text{soot}} \cdot +\text{O}_2 \rightarrow 2\text{CO} + \text{products} )</td>
<td>[12]</td>
</tr>
<tr>
<td>6</td>
<td>( C_{\text{soot}} \cdot +\text{OH} \rightarrow \text{CO} + \text{products} )</td>
<td>[12]</td>
</tr>
</tbody>
</table>

In these reactions, \( C_{\text{soot}} - \text{H} \) represents a reactive site on the surface of the soot particle, and \( C_{\text{soot}} \cdot \) denotes the corresponding radical.

Reaction pathway 4a adds mass to the soot particle and depletes the soot radical, whereas pathway 4b preserves the radical. Wang and coworkers [42] noted that the use of reaction pathway 4a in their work led to a significant under-prediction of soot for laminar counter-flow diffusion flames, while use of the pathway 4b led to an over-prediction of the soot levels. They concluded that the reactions 4a and 4b occur simultaneously in the flame; the pathway 4a is more adequate to describe the soot surface growth in the high-temperature regions of the flame where there is likely to be an abundance of H radicals, while the pathway 4b is more important near the low-temperature stagnation plane. This also explains why the pathway 4a works better in laminar premixed flames: in these flames, locally the conditions are more similar to the high-temperature, high H concentration regions of diffusion flames.

Soot particle growth also occurs by the condensation of PAH molecules on the soot surface. This process is similar to particle coagulation, in the sense that the soot particles undergo collisions with the PAH molecules, and coalesce to form bigger soot particles [42].
3.1.4 Agglomeration

The initial soot particles formed are very nearly spherical in shape, but after a certain size, the spherical shape gives way to chain-like structures that can be treated as obeying fractal relationships [15, 43]. This phase of soot particle growth is called agglomeration into aggregates.

A schematic [1, 2] of the various processes is given in Fig 3.1

![Figure 3.1. Schematic of the different processes in soot formation and growth [1, 2].](image)

3.2 Soot models

One of the challenges in soot modeling is the fact that our understanding of the processes of soot formation, growth and oxidation is limited. In spite of this limitation, several soot models have been developed; they can broadly be divided into three classes [17]:

1. Empirical models,

2. semi-empirical models, and

3. detailed models.
Among these, the empirical models are correlation based, and are not computationally daunting. The semi-empirical models attempt to incorporate some of the physical and chemical processes of soot formation and growth into the model, and use a phenomenological approach to evaluate some model parameters to close the model. These models usually involve the solution of equations for one or more soot variables (the soot volume fraction, number density, mass fraction and so on), and so they do involve some computational complexity.

The detailed soot models attempt to include the details of the soot nucleation, growth and oxidation processes into the soot model with as little dependence on empirical parameters as possible. These models involve the solution of set of equations describing the soot particle size distribution. The global quantities such as the soot volume fraction and the total soot number density are calculated from the distribution obtained. Because of the typically larger number of equations solved, as well as the inclusion of details of the soot formation and growth phenomena, the detailed models are computationally challenging.

### 3.2.1 Empirical soot models

Empirical soot models typically do not involve the solution of additional equations to describe soot, but rather use correlations to relate the amount of soot to the other flame parameters. They find use in situations where the problem complexity makes the detailed or semi-detailed models computationally intractable. One major deficiency of the empirical models is that they cannot be reliably used to predict soot yields for conditions that are different from the conditions under which the model was calibrated.

Two important parameters in empirical soot models are a critical equivalence ratio ($\phi_c$) for premixed flames, and a threshold sooting height for diffusion flames. These correlations are dependent on the particular fuel under consideration. To remove the dependence on the particular system or burner, Calcote and Manos [44] defined a threshold sooting index (TSI) as

$$\text{TSI} = a - b\phi_c,$$  \hspace{1cm} (3.5)

where $a$ and $b$ are model constants, determined by calibration.
Khan et al. [45] proposed an empirical soot model for diesel engine combustion, which assumes that the rates of soot formation and growth are only dependent on the soot particle inception rate. The latter can be expressed as a function of the pressure, the temperature, and the equivalence ratio. The soot loading $C_s$ (kg m$^{-3}$) is given by

$$\frac{dC_s}{dt} = c \frac{V_u}{V_{NTP}} P_u \phi^n e^{\frac{E}{R_u T}},$$

(3.6)

where $c$ and $n$ are model parameters, $V_u$ is the volume of the soot formation zone (m$^3$), $V_{NTP}$ is the volume of the cylinder contents at normal temperature and pressure (NTP), $P_u$ is the partial pressure of the unburned fuel, $\phi$ is the local equivalence ratio of the unburned fuel, $E$ is an activation energy, $R_u$ is the universal gas constant, and $T$ is the local temperature.

### 3.2.2 Semi-empirical soot models

Semi-empirical soot models attempt to incorporate some of the known physical and chemical processes behind soot formation and growth, as opposed to the use of empirical correlations based on experimental evidence. This approach thus leads to a simple description of the chemical reactions of the soot precursors and of soot particle growth.

One important semi-empirical soot model is the one proposed by Leung et al. [13] and modified by Guo et al. [5]. In this model equations are solved for the soot number density and the soot mass fraction; the soot volume fraction is obtained from the soot mass fraction. The soot precursor is assumed to be acetylene (C$_2$H$_2$).

The soot surface growth is assumed to be via the reaction of the soot particles with C$_2$H$_2$. Leung et al. [13] considered oxidation by molecular oxygen (O$_2$) only, while Guo and co-workers [5, 19] added oxidation by O and OH to the model. The soot oxidation model is still an area of on-going research. Oxidation by OH radical is important in the post-flame regions, whereas O$_2$ is the oxidizing species at locations further upstream. However, no single soot oxidation model is known to produce good agreement across a broad range of flame conditions.
3.2.3 Detailed soot models

Detailed soot models attempt to resolve the particle size distribution, and are computationally more expensive. These models attempt to include a realistic description of the physical and chemical processes that lead to the formation and growth of soot particles.

One important detailed soot model is the Method of Moments with Interpolative Closure (MOMIC) [15, 11, 43]. In this method the problem is formulated in terms of the moments of the soot particle size distribution. We define the rth soot concentration moment (particles/m³) as

\[ M_r = \sum_{i=1}^{\infty} m_i^r N_i, \]  

where \( m_i \) is the number of carbon atoms in the soot particles of size class \( i \) and \( N_i \) is the number density of that size class. Equations are solved for the soot concentration moments, and then the soot volume fraction \( f_v \) is obtained from the first moment \( (M_1) \) as

\[ f_v = \frac{M_1 m_C}{\rho_{\text{soot}}}, \]

where \( m_C \) is the mass of a carbon atom (kg) and \( \rho_{\text{soot}} \) is the density of soot (kg m⁻³), assumed constant.

The method involves computing source terms due to particle nucleation, coagulation and surface reactions. The source terms involve the size moments or the reduced moments, defined as

\[ \mu_k = \frac{M_k}{M_0}, \]

where the index \( k \) can be fractional for some terms. These ‘fractional’ moments are obtained from the integer-order moments by interpolation. This step thus involves interpolative closure.

3.3 Soot models in the present work

In this work we have implemented in OpenFOAM two soot models: a semi-empirical model, and a detailed one.
3.3.1 Semi-empirical model

The semi-empirical soot model used in this work is based on the two-equation soot model used by Guo et al. [5], which in turn is obtained from an earlier model by Leung et al. [13] where some of the reaction rate coefficients were modified by Guo et al. to agree with experiments. In the present work, the model by Leung et al. has been retained in its entirety, and the additional oxidation steps suggested by Guo et al. have been appended to the model. Two transport equations are solved to describe the soot. The variables are:

1. soot number density \( N_s \) (particles/kg),

2. soot mass fraction \( Y_s \).

The transport equations are

\[
\frac{\partial \rho Y_s}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j Y_s) = \frac{\partial}{\partial x_j} \left( \mu \frac{\partial Y_s}{\partial x_j} \right) - \frac{\partial}{\partial x_j} (\rho V_{T,j} Y_s) + S_m, \tag{3.8}
\]

\[
\frac{\partial \rho N_s}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j N_s) = \frac{\partial}{\partial x_j} \left( \mu \frac{\partial N_s}{\partial x_j} \right) - \frac{\partial}{\partial x_j} (\rho V_{T,j} N_s) + S_N. \tag{3.9}
\]

In equations (3.8) and (3.9), \( \mu \) is the viscosity of the gas-phase mixture, \( Sc \) is a soot Schmidt number, and \( V_{T,i} \) is the thermophoretic diffusion velocity for soot (m/s), defined as

\[
V_{T,i} = -0.54 \frac{\mu}{\rho T} \frac{\partial T}{\partial x_i}.
\]

The original formulation by Guo et al. [5] does not have the molecular diffusion term for the equations; these were added for numerical stability. It is expected that the effective Schmidt number for soot should be large: \( Sc >> 1 \). It was found that a value of 60 for the Schmidt number worked well.

The term \( S_m \) is the source term for the soot mass fraction and contains contributions from soot nucleation (\( \dot{\omega}_n \)), soot growth (\( \dot{\omega}_g \)) and soot oxidation (\( \dot{\omega}_O \)). Thus,

\[
S_m = \dot{\omega}_n + \dot{\omega}_g - \dot{\omega}_O.
\]
The soot precursor is assumed to be acetylene (C$_2$H$_2$). Soot oxidation by molecular oxygen (O$_2$), oxygen radical (O) and hydroxyl radical (OH) are considered. The soot inception process is modeled as

$$\text{C}_2\text{H}_2 \rightarrow 2\text{C}(S) + \text{H}_2,$$  \hspace{1cm} (3.10)

where C(S) denotes soot. The surface growth is assumed to take place by reaction of soot with C$_2$H$_2$, and is given by

$$\text{C}_2\text{H}_2 + n\text{C}(S) \rightarrow (n + 2)\text{C}(S) + \text{H}_2.$$  \hspace{1cm} (3.11)

The reaction rates are given as

$$r_1 = k_1(T)[\text{C}_2\text{H}_2],$$
$$r_2 = k_2(T)f(A_s)[\text{C}_2\text{H}_2].$$

Here $[\cdots]$ represents a concentration (kmol/m$^3$). The function $f(A_s)$ denotes the effect of the soot surface area per unit volume. Guo et al. [5] assumed that the dependence of $f$ on $A_s$ is linear, that is, $f(A_s) = A_s$. However, in this work the square-root dependence of $f$ on $A_s$ was used, as described by Leung et al. [13]:

$$f(A_s) = \sqrt{\frac{\pi}{2}} \left(\frac{6M_s}{\pi \rho_s}\right)^{2/3} \left(\frac{\rho Y_s}{M_s}\right)^{1/3} (\rho N)^{1/6}.$$  \hspace{1cm} (3.12)

Here $\rho_s$ is the soot density, taken as 2000 kg/m$^3$ and $M_s$ is the molecular weight of carbon (12.01115 kg/kmol).

For the oxidation of soot, the following three reactions are considered [5]:

$$\frac{1}{2}\text{O}_2 + \text{C}(S) \rightarrow \text{CO},$$  \hspace{1cm} (3.13)

$$\text{OH} + \text{C}(S) \rightarrow \text{CO} + \text{H},$$  \hspace{1cm} (3.14)

$$\text{O} + \text{C}(S) \rightarrow \text{CO}.$$
The reaction rates for these three reactions are computed from the following relationships:

\[ r_3 = k_3(T)T^{1/2}A_s[O_2], \]
\[ r_4 = \phi_{OH}k_4(T)T^{-1/2}A_sX_{OH}, \]
\[ r_5 = \phi_Ok_5(T)T^{-1/2}A_sX_O. \]

Here \( \phi_O \) and \( \phi_{OH} \) are, respectively, the collision efficiencies for O and OH. A value of 0.13 was used for \( \phi_{OH} \) and a value of 0.5 for \( \phi_O \). The rate coefficients are summarized in table 3.2.

**Table 3.2. Rate coefficients for the two-equation soot model**

<table>
<thead>
<tr>
<th>( k_i )</th>
<th>( A_i )</th>
<th>( E_i )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI units</td>
<td>SI units</td>
<td>kcal/mol</td>
<td>-</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>10000.0</td>
<td>41.0</td>
<td>[13]</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>6000.0</td>
<td>24.0</td>
<td>[13]</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>10000.0</td>
<td>39.0</td>
<td>[13]</td>
</tr>
<tr>
<td>( k_4 )</td>
<td>106.0</td>
<td>0.0</td>
<td>[5]</td>
</tr>
<tr>
<td>( k_5 )</td>
<td>55.4</td>
<td>0.0</td>
<td>[5]</td>
</tr>
</tbody>
</table>

The reaction rate coefficients are then evaluated as

\[ k_i(T) = A_i e^{-\frac{E_i}{R_uT}}. \]

It should be noted that the reaction rates described above denote representative processes aiming to capture global behavior, and thus cannot be compared to detailed, elementary reactions. The source term \( S_N \) in Eq. (3.9) takes into account soot inception and agglomeration. It is given by

\[
S_N = \frac{2}{C_{\text{min}}}N_A r_1 - 2C_a \left( \frac{6M_s}{\pi \rho_s} \right)^{1/6} \left( \frac{6k_B T}{\rho_s} \right)^{1/2} \left( \frac{\rho Y_s}{M_s} \right)^{1/6} \left( \rho N_s \right)^{11/6},
\]

where \( N_A \) is Avogadro’s constant \((6.022 \times 10^{26} \text{ particles/kmol})\), \( C_{\text{min}} \) is the number of carbon atoms in the incipient soot particle \( (100) \), \( k_B \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J/K})\) and \( C_a \) is the agglomeration rate constant, for which a value of 9.0 is used [5].
3.3.2 Detailed soot model

The detailed soot model used in the present work is the Method of Moments with Interpolative Closure [15, 11, 43]. The soot particle size distribution is described by its first six moments, $M_0$ through $M_5$. The governing equation for the $r$th moment is

$$\frac{\partial M_r}{\partial t} + \frac{\partial}{\partial x_j} (u_j M_r) = \frac{\partial}{\partial x_j} \left( \frac{\mu}{Sc} \frac{\partial M_r}{\partial x_j} \right) - \frac{\partial}{\partial x_j} (V_{T,j} M_r) + \dot{M}_r,$$

where a soot Schmidt number of 60 was used, as in the two-equation soot model. $\dot{M}_r$ is the source term, and contains contributions from soot particle inception, particle coagulation, surface growth by the HACA mechanism, soot oxidation, and PAH condensation. This source term can be written as

$$\frac{dM_r}{dt} = R_r + G_r + W_r,$$

where $R$, $G$, and $W$ are the contributions from soot inception, coagulation, and surface growth (including PAH condensation).

3.3.2.1 Soot inception

Soot inception is modeled as the coalescence of two PAH molecules to form a dimer. The rate of formation of all possible dimers is

$$R_r = \frac{1}{2} \sum_{i=3}^{\infty} \sum_{j=3}^{\infty} \beta^{PAH}_{i,j} (m_i + m_j)^r N_i^{PAH} N_j^{PAH},$$

where

$$\beta^{PAH}_{i,j} = \varepsilon \sqrt{\frac{\pi k_B T}{2\mu_{ij}}} (d_i + d_j)^2$$

is the frequency of PAH collisions, $\mu_{ij}$ is the reduced mass of the $i$th and the $j$th PAH species, $d_i$ and $d_j$ are the collision diameters of the $i$th and the $j$th PAH species, and $\varepsilon$ is the van der Waals enhancement factor, which has a value of 2.2.

A simpler expression for the inception rate has been suggested by Rezvan et
al. [41] as

\[ R_0 = \varepsilon \sqrt{\frac{4\pi k_B T}{m_C NC_{PAH}}} d_{PAH}^2 N_{PAH}^2, \]

\[ R_r = 2 NC_{PAH} R_{r-1} \quad r = 1, 2, \ldots, 5, \]

where \( NC_{PAH} \) is the number of carbon atoms per PAH molecule, \( m_C \) is the mass of a carbon atom (12.0 amu), \( N_{PAH} \) is the number density of the PAH molecules, and \( d_{PAH} \) is size of the PAH molecule (m). In this work it has been assumed that the PAH species for inception is pyrene (C\(_{16}\)H\(_{10}\)), so \( NC_{PAH} = 16 \), and a value of \( 7.11 \times 10^{-10} \) m has been used for \( d_{PAH} \) [41].

### 3.3.2.2 Soot coagulation

The coagulation of soot is modeled based on the theory of aerosol dynamics of soot particles. The starting point for the model is Smoluchowski’s equation

\[ \frac{dN_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{ij} N_j N_{i-j} - \sum_{j=1}^{\infty} \beta_{i,j} N_i N_j, \]

where \( N_i \) is the number density of particles of size class \( i \), and \( \beta_{i,j} \) is the collision coefficient between particles of size classes \( i \) and \( j \). The collision coefficient depends on the sizes of the colliding particles, and hence a closed-form solution to Eq. (3.20) cannot be obtained. In terms of the moments we can write

\[ \frac{dM_0}{dt} = -G_0 = -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{ij} N_i N_j, \]

\[ \frac{dM_r}{dt} = G_r = \frac{1}{2} \sum_{k=1}^{r-1} \binom{n}{k} \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{ij} m_i^k m_j^{r-k} N_i N_j \right), \quad r = 2, 3, \ldots, 5. \]

The exact form of the collision coefficient \( \beta \) depends on the coagulation regime as defined by the Knudsen number, \( K_n = 2 \lambda_f/d \), where \( \lambda_f \) is the mean free path for the gas-phase and \( d \) is the particle size [15]. In the present work, only the free-molecular regime \( (K_n > 1) \) is considered [20].
In the free-molecular regime we define a grid function of order \( l \) as

\[
f_{l}^{(x,y)} \equiv \frac{1}{M_{0}^{2}} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_{i} + m_{j})^l \left( m_{i}^{1/3} + m_{j}^{1/3} \right)^{2} m_{i}^{-\frac{1}{2}} m_{j}^{\frac{1}{2}} N_{i}N_{j},
\]

which may be simplified to give

\[
f_{l}^{(x,y)} = \sum_{s=0}^{l} \binom{l}{s} \left( \mu_{l+x-s} - \frac{1}{6} \mu_{s+y} + 2 \mu_{l+x-s} - \frac{1}{6} \mu_{s+y} - \frac{1}{6} \right).
\]

(3.24)

Here \( \mu_{k} \) is the reduced soot moment of order \( k \), defined as \( \mu_{k} \equiv \frac{M_{k}}{M_{0}} \). For non-integer values of \( k \), \( \mu_{k} \) is obtained by interpolation among the logarithms of the integer-order moments.

The coagulation terms can be written in terms of the grid functions as

\[
G_{0} = \frac{K_{f}}{2} M_{0} f_{\frac{1}{2}}^{(0,0)},
\]

(3.25)

\[
G_{r} = \frac{K_{f}}{2} M_{0}^{2} \sum_{s=1}^{r-1} \binom{r}{s} f_{\frac{1}{2}}^{(s,r-s)}, \quad r = 1, 2, \ldots, 5,
\]

(3.26)

where the coefficient \( K_{f} \) is given by

\[
K_{f} = \varepsilon \sqrt{\frac{6k_{B}T}{\rho_{s}}} \left( \frac{3m_{C}}{4\pi\rho_{s}} \right).
\]

The grid functions of order \( \frac{1}{2} \) are evaluated by interpolation among the logarithms of the integer-order grid functions. Evaluation of the coagulation terms in the free-molecular regime therefore involves a double interpolation: both the reduced moments and the grid functions need to be evaluated by interpolation. In this work an interpolating polynomial of the Lagrange form was used.

### 3.3.2.3 Soot surface growth

The soot surface growth is modeled using the HACA mechanism, summarized in table 3.1. The reaction rates are computed as \( k_{i} = A_{i}T^{3\delta}e^{-\frac{E_{a,i}}{RT}} \). The soot kinetic model parameters are given in table 3.3.
Table 3.3. Rate coefficients for the MOMIC soot model

<table>
<thead>
<tr>
<th>$k_i$</th>
<th>$A_i$</th>
<th>$\beta_i$</th>
<th>$E_i$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^3$mol$^{-1}$s$^{-1}$</td>
<td>kcal/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1$</td>
<td>$4.2 \times 10^{13}$</td>
<td>0.0</td>
<td>13.0</td>
<td>[12]</td>
</tr>
<tr>
<td>$k_{-1}$</td>
<td>$3.9 \times 10^{12}$</td>
<td>0.0</td>
<td>11.0</td>
<td>[40, 41]</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$1.0 \times 10^{10}$</td>
<td>0.734</td>
<td>1.43</td>
<td>[12]</td>
</tr>
<tr>
<td>$k_{-2}$</td>
<td>$3.68 \times 10^{8}$</td>
<td>1.139</td>
<td>17.1</td>
<td>[41]</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$2.0 \times 10^{13}$</td>
<td>0.0</td>
<td>0.0</td>
<td>[12]</td>
</tr>
<tr>
<td>$k_{4a}$</td>
<td>$8.0 \times 10^{7}$</td>
<td>1.56</td>
<td>3.8</td>
<td>[12]</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$2.2 \times 10^{12}$</td>
<td>0.0</td>
<td>7.5</td>
<td>[12]</td>
</tr>
<tr>
<td>$k_6$</td>
<td>$\gamma_{OH=0.13}$</td>
<td>0.0</td>
<td>0.0</td>
<td>[12]</td>
</tr>
</tbody>
</table>

The reactions with the gas-phase species are modeled as

\[
W_{r}^{C_2H_2} = k_{4a}[C_2H_2] \alpha \chi_{C_{soot} \bullet} \pi C_s^2 M_0 \sum_{l=0}^{r-1} \left( \frac{r}{l} \right) \mu_{l+\frac{2}{3}}(2)^{r-l}, \tag{3.27}
\]

\[
W_{r}^{O_2} = k_5[O_2] \alpha \chi_{C_{soot} \bullet} \pi C_s^2 M_0 \sum_{l=0}^{r-1} \left( \frac{r}{l} \right) \mu_{l+\frac{2}{3}}(-2)^{r-l}, \tag{3.28}
\]

\[
W_{r}^{OH} = \gamma_{OH}[OH] \sqrt{\frac{\pi k_B T}{2m_{OH}}} N_A C_s^2 M_0 \sum_{l=0}^{r-1} \left( \frac{r}{l} \right) \mu_{l+\frac{2}{3}}(-1)^{r-l}, \tag{3.29}
\]

where $\alpha$ is the steric factor, or the fraction of the soot surface sites available for reaction, $m_{OH}$ is the mass of the OH radical, $\gamma_{OH}$ is the collision efficiency for the OH radical, and

\[
C_s = \left( \frac{6m_C}{\pi \rho_s} \right)^{\frac{1}{3}}.
\]

$\chi_{C_{soot} \bullet}$ is the number density of the surface radicals, given by

\[
\chi_{C_{soot} \bullet} = \chi_{C_{soot} \bullet - H} \frac{k_1[H] + k_2[OH]}{k_{-1}[H_2] + k_{-2}[H_2O] + k_5[H] + k_{4a}[C_2H_2] + k_5[O_2]}, \tag{3.30}
\]

where $\chi_{C_{soot} \bullet - H}$ is the nominal number density of the soot radical sites, for which a value of $2.3 \times 10^{19}$ m$^{-2}$ is prescribed [11]. In the present work the reaction pathway 4$a$ from table 3.1 is considered. The code, however, provides an option to switch completely to 4$b$, or to a combination of 4$a$ and 4$b$.

The parameter $\alpha$ is difficult to quantify from a theoretical point of view. Dworkin et al. [4] used a constant value of 0.078 for $\alpha$ in their work, while Appel
et al. [12] used a temperature and size-dependent correlation for $\alpha$ as

$$\alpha = \tanh \left( \frac{a}{\log \mu_1} + b \right).$$  \hspace{1cm} (3.31)

where $a$ and $b$ are model parameters which are functions of temperature. They applied this model to a set of eight premixed flames, and the best-fit relations for $a$ and $b$ were found to be

$$a = 12.65 - 0.00563T,$$
$$b = -1.38 + 0.00068T.$$

In the absence of a rigorous theoretical justification for a choice of $\alpha$, it was left as a free parameter in the present work. It is possible that the appropriate value of $\alpha$ will depend on the conditions for the particular flame being investigated.

The contribution of PAH condensation on soot surface growth is modeled as [11]

$$W_{r_{PAH}} = 2.2 \sqrt{\frac{\pi k_B T}{2m_c}} \sum_{l=0}^{r-1} \binom{r}{l} \left( C_h^2 M_{r+l}^{PAH} M_{l}^{soot} + 2C_h C_s M_{r-l}^{PAH} M_{l}^{soot} + C_s^2 M_{r-l}^{PAH} M_{l}^{soot} \right).$$ \hspace{1cm} (3.32)

In Eq. (3.32),

$$C_h = d_A \sqrt{\frac{2}{3}},$$

where $d_A$ is the size of a single aromatic ring, taken to be equal to 1.395$\sqrt{3}$Å, since the length of an aromatic C-C bond is 1.395Å [11]. Also, $M_{r_{PAH}}$ is the $r$th concentration moment of the PAH species distribution, defined as

$$M_{r_{PAH}} = \sum_{i=i_0}^{\infty} m_i^r N_{i_{PAH}}^r,$$

where $i_0$ is the initial PAH size from which lumping begins, and the summation is taken over all PAH sizes equal to and above this size. To ensure consistency between the moments of the PAH species concentrations and the soot concentration moments, the mass $m_i$ of the PAH species of size $i$ is represented by the number
of carbon atoms in that species.

In the present work it is assumed that the soot precursor PAH is pyrene ($C_{16}H_{10}$), that all molecules larger than pyrene are considered to be part of soot, and that all PAH species smaller than pyrene are fully resolved by the gas-phase chemistry model. With these assumptions, Eq. (3.32) is simplified to give [41]

\[
W_{r}^{PAH} = 2.2 \sqrt{\frac{\pi k_B T}{2m_C}} [A_4] N_A M_0 \sum_{l=0}^{r-1} \binom{r}{l} \left( C_h n^{l+\frac{1}{2}} \mu_l + 2C_h C_s n^{r-l} \mu_{l+\frac{1}{2}} \right),
\]

(3.33)

where $A_4$ represents pyrene, $M_0$ is the zeroth soot concentration moment, and $n = 16$ is the number of carbon atoms in a pyrene molecule. In Eq. (3.33) it is assumed that all collisions between a soot particle and a PAH molecule lead to condensation. It was pointed out by Wang et al. [42] that a temperature-dependent probability for PAH sticking to the soot particle may be more realistic. Based on a sensitivity study, Dworkin et al. [4] and Zhang et al. [46] suggested the use of a PAH condensation efficiency of 50%. In this work, the same value of 0.5 for a PAH condensation efficiency was adopted. Thus we rewrite Eq. (3.33) as

\[
W_{r}^{PAH} = \eta_{condensation} 2.2 \sqrt{\frac{\pi k_B T}{2m_C}} [A_4] N_A M_0 \sum_{l=0}^{r-1} \binom{r}{l} \left( C_h n^{l+\frac{1}{2}} \mu_l + 2C_h C_s n^{r-l} \mu_{l+\frac{1}{2}} \right),
\]

(3.34)

where $\eta_{condensation}$ is the PAH condensation efficiency.
Combustion systems contain gases and soot at relatively high temperatures (\(\sim 2000\) K), and so radiation becomes an important phenomenon. In Eq. (2.15), the term \(\dot{Q}\) contains the contribution from radiation. In the energy equation, the effect of radiation shows up as the divergence of the radiative heat flux. The heat flux in such a case is given as

\[
q_i = -\lambda \frac{\partial T}{\partial x_i} + \rho \sum_{k=1}^{N} h_k Y_k V_{k,i} + q_{i,\text{radiation}},
\]

(4.1)

where \(\lambda\) is the thermal conductivity of the gas, \(T\) is the temperature, \(\rho\) is the gas density, \(h_k\) is the specific enthalpy of gas-phase species \(k\), \(Y_k\) is the mass fraction of species \(k\), and \(V_k\) is the diffusion velocity of species \(k\). As explained in appendix A.4, the first term on the right hand side of Eq. (4.1) is the heat flux due to conduction, and the second term is due to the interdiffusion flux. Evaluation of the radiative heat flux \(q_{\text{radiation}}\) is discussed in this chapter.

### 4.1 Optically thin model

In this work, an optically thin radiation model [5, 6] was used as the baseline model. This model is based on the emission-only radiation model from the TNF workshop [47]. The source term in the energy equation due to radiation in this
model is given by

\[ q_r = -\nabla \cdot \mathbf{q}_{\text{radiation}} = -4\sigma K_p(T^4 - T_b^4) - C f_v T^5. \quad (4.2) \]

Here \( \sigma \) is the Stefan-Boltzmann constant \((5.699 \times 10^{-8}\text{Wm}^{-2}\text{K}^{-4})\) and \( K_p \) is the Planck-mean absorption coefficient for the gas mixture. The background temperature \( T_b \) is used to make sure that the temperature of the gas does not fall below the ambient temperature. The negative sign indicates that radiative heat loss acts as a \textit{sink}, which is consistent with the emission-only model. Here \( f_v \) is the soot volume fraction, and \( C \) is a constant with a value of \( 3.334 \times 10^{-10} \) for a power density in \( \text{W/cm}^3 \) and temperature in Kelvins [5].

The Planck-mean absorption coefficient for the mixture is obtained as [6]

\[ K_p = \sum_i^M p_i a_{p,i}, \]

where \( p_i \) is the partial pressure (in atm) and \( a_{p,i} \) (in \( \text{m}^{-1}\text{atm}^{-1} \)) is the Planck-mean absorption coefficient for gas species \( i \). In this model only radiative contributions from soot, CO\(_2\), H\(_2\)O, CH\(_4\) and CO are considered. The \( a_{p,i} \) are expressed as functions of temperature (equations 4.3 and 4.4) and the curve fits in the temperature range \( 300 - 2500 \text{K} \) are summarized in Tables 4.1 and 4.2. For CO\(_2\) and H\(_2\)O the expression for the Planck-mean absorption coefficient is

\[ a_p = c_0 + c_1(1000/T) + c_2(1000/T)^2 + c_3(1000/T)^3 + c_4(1000/T)^4 
+ c_5(1000/T)^5, \quad (4.3) \]

and for CH\(_4\) and CO the expression becomes

\[ a_p = c_0 + c_1T + c_2T^2 + c_3T^3 + c_4T^4. \quad (4.4) \]
<table>
<thead>
<tr>
<th>Coefficient</th>
<th>H₂O</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>c₀</td>
<td>-0.23093</td>
<td>18.741</td>
</tr>
<tr>
<td>c₁</td>
<td>-1.12390</td>
<td>-121.310</td>
</tr>
<tr>
<td>c₂</td>
<td>9.41530</td>
<td>273.500</td>
</tr>
<tr>
<td>c₃</td>
<td>-2.99880</td>
<td>-194.050</td>
</tr>
<tr>
<td>c₄</td>
<td>0.51382</td>
<td>56.310</td>
</tr>
<tr>
<td>c₅</td>
<td>-1.86840 \times 10^{-5}</td>
<td>-5.8169</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>CH₄</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>c₀</td>
<td>6.6334</td>
<td>4.7869</td>
</tr>
<tr>
<td>c₁</td>
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</tr>
<tr>
<td>c₃</td>
<td>2.5611 \times 10^{-10}</td>
<td>-4.25732 \times 10^{-7}</td>
</tr>
<tr>
<td>c₄</td>
<td>-2.6558 \times 10^{-14}</td>
<td>2.02894 \times 10^{-10}</td>
</tr>
</tbody>
</table>

### 4.2 Detailed radiation models

The optically-thin radiation model does not account for the reabsorption of radiation by the gas mixture. Thus temperatures predicted using the model are likely to be lower. In order to account for the effects of radiation reabsorption, a detailed model must be used. This means that the radiative transfer equation (RTE) must be solved; additionally, the spectral dependence of the properties such as the absorption coefficient $\kappa_\eta$ must be accounted for.

#### 4.2.1 The Radiative Transfer Equation

The general form of the radiative transfer equation is [48]

$$
\frac{1}{c} \frac{\partial I_\eta}{\partial t} + \frac{\partial I_\eta}{\partial s} = \kappa_\eta I_{\eta b} - \kappa_\eta I_\eta - \sigma_{s\eta} I_\eta + \frac{\sigma_{s\eta}}{4\pi} \int_{4\pi} I_\eta(\hat{S}_i) \Phi_\eta(\hat{s}_i, \hat{s}) \, d\Omega_i, \quad (4.5)
$$

where $c$ is the velocity of light in vacuum, $I_\eta$ is the radiative intensity corresponding to a wave number $\eta$, $s$ denotes the directional coordinate, $I_{\eta b}$ is the blackbody radiative intensity corresponding to a wave number $\eta$, $\kappa_\eta$ is the absorption coeffi-
cient at the wave number $\eta$, $\sigma_{s\eta}$ is the scattering coefficient at the wave number $\eta$, $\Phi_\eta$ is the scattering phase function, and $\Omega_i$ is the solid angle around the direction $i$.

The velocity of light $c$ is much larger than any velocity scales encountered in engineering applications, and thus the first term in Eq. (4.5) drops out. The radiative transfer equation thus becomes

$$\frac{\partial I_\eta}{\partial s} = \kappa_\eta I_{b\eta} - \kappa_\eta I_\eta - \sigma_{s\eta} I_\eta + \frac{\sigma_{s\eta}}{4\pi} \int_{4\pi} I_\eta(\hat{s}_i) \Phi_\eta(\hat{s}_i, \hat{s}) d\Omega_i. \quad (4.6)$$

Equations (4.5) and (4.6) indicate that the intensity of radiation in a particular direction (at a given wave number) is augmented by emission in that direction, and is attenuated by absorption in that direction, and scattering away from that direction. The last term in Eq. (4.5) denotes the contribution of in-scattering, that is to say the radiative energy from other directions being directed into the given direction by scattering, and thus serves to augment the intensity in the given direction.

The RTE is therefore an integro-differential equation in five dimensions (three spatial coordinates, and two local directional ones), and also requires an integration over the spectrum.

### 4.2.2 Spectral models

In principle, the radiative transfer equation must be solved at each wave number location in the spectrum. Since this would mean solving the RTEs at millions of spectral locations, and also since in a reacting flow calculation radiation is simply one of the several processes considered, solving the RTEs in this way is not an option for practical problems.

The absorption coefficient $\kappa$ can be obtained by summing up the contributions from each wave number as

$$\kappa = \sum_\eta \kappa_\eta.$$ 

Various spectral models have been developed to compute the spectral quantities, and various RTE solvers have been coupled to the present flame solver. A brief summary of the features and capabilities of the detailed radiation model library
has been given by Cai et al. [23].

4.2.2.1 Line-by-line models

In a line-by-line (LBL) calculation, the contributions from individual spectral lines are considered, and a fine spectral resolution ($\sim 0.01 \text{ cm}^{-1}$) is used. The RTE must be solved at more than a million spectral locations, and the computational cost is prohibitively expensive if a deterministic RTE solver is used. The LBL method coupled with a statistical photon Monte Carlo method can be used [23].

4.2.2.2 Gray model

As the name suggests, in a gray model, the quantities are assumed to be independent of the wave number. The spectral quantities are computed apriori, and the resulting RTE has no spectral dependence. For a mixture of reacting gases, the equivalent gray absorption coefficient is usually taken to be the Planck-mean value. The optically thin radiation model outlined previously is an example of a radiation model using the gray-gas approximation.

4.2.2.3 Correlated k-distribution models

k-Distribution based models are used because they yield high accuracy, and at the same time are computationally less intense than the line-by-line models [23]. The absorption coefficient $\kappa_{\eta}$ typically varies widely over the spectral range; in fact $\kappa_{\eta}$ attains the same value at multiple spectral positions, and performing line-by-line calculations in such a case would lead to a significant duplication of effort. The k-distribution is a re-ordered absorption coefficient which is given as a function of an artificial wave number $g$. The re-ordered absorption coefficient ($k$) is a monotonic function of $g$, and thus the integration over the spectrum can be performed with relative ease. In a full-spectrum k-distribution (FSK) model, the absorption coefficient is weighted by the local Planck function $I_{b\eta}$, which varies across the spectrum.
4.2.2.4 Narrow-band databases

In the context of a k-distribution model, a narrow band is a small spectral band over which the Planck function may be assumed constant. Over such a narrow band the k-distribution is independent of the Planck function, and as such can be stored in a database. The narrow band k-distribution is obtained by interpolation between the thermodynamic state in the database and the arbitrary state. The full-spectrum k-distribution is then assembled as a sum of the narrow-band k-distributions weighted by the Planck function for each of the narrow bands.

4.2.2.5 Correlation tables

For some of the more important radiating species, the full-spectrum k-distribution can be approximated by functions which have been fitted to the actual k-distribution for the species. These functional forms are what are known as correlation tables. Use of these correlations to determine the k-distribution greatly speeds up the calculation of the spectral quantities with some loss of accuracy.

4.2.3 Mixing models

Once the k-distributions for the individual gas-phase species are known, the k-distribution for the mixture must be determined using some kind of a mixing rule. Two different mixing models were included in the radiation model: the multiplication model [49], and the uncorrelated mixture model [50].

4.2.3.1 Multiplication model

In the multiplication model it is assumed that the absorption coefficients of different species are statistically independent, and as such, can be treated like the probability of independent events. It is known that for two independent events, the probability of occurrence of both of them is given by the product of their respective probabilities. In a similar manner, the cumulative k-distribution for the mixture \( g(k) \) is given by [49]

\[
g(k) = \prod_i g_i(k), \tag{4.7}
\]

where \( g_i(k) \) is the cumulative k-distribution for gas-phase species \( i \).
4.2.3.2 Uncorrelated mixture model

In the uncorrelated mixture model, the cumulative k-distribution for the gas mixture is given in terms of the cumulative k-distributions of the individual gas-phase species as

\[ \mathcal{L}[f(k)] = \prod_i \mathcal{L}[f_i(k)], \tag{4.8} \]

where the operator \( \mathcal{L} \) denotes the Laplace transform.

4.2.4 RTE solvers

Several numerical methods are available to solve Eq. (4.6) in conjunction with any of the aforementioned spectral models. Some of the important methods for solving the RTE are [48]:

1. The method of spherical harmonics (\( P_N \) methods),
2. the discrete ordinates method (DOM),
3. the stochastic photon Monte Carlo method (PMC).

4.2.4.1 The method of spherical harmonics

Spherical harmonics are special functions that satisfy Laplace’s equation in spherical coordinates. These functions are also mutually orthogonal (or orthonormal, depending on the specific representation chosen), and thus are useful as basis functions. Thus the radiative intensity at any location \( \mathbf{r} \) can be expressed in terms of the spherical harmonics in the form of a generalized two-dimensional Fourier series representation as

\[ I(\mathbf{r}, \mathbf{s}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} I_l^m(\mathbf{r}) Y_l^m(\mathbf{s}), \tag{4.9} \]

where the \( I_l^m(\mathbf{r}) \) are coefficients depending on position only, and \( Y_l^m(\mathbf{s}) \) are the spherical harmonics. Equation (4.9) may now be substituted into Eq. (4.6). Since the spherical harmonics are mutually orthogonal, the resulting equation may be multiplied by \( Y_{k'}^n(\mathbf{s}) \), and a subsequent integration over all directions yields a set of infinite coupled partial differential equations in the position-dependent functions \( I_l^m(\mathbf{r}) \).
Now an approximation is made: Eq. (4.9) is truncated after a finite number of terms, and the number of terms retained determines the order of the resulting \( P_N \) method. The maximum value for \( l \) retained in Eq. (4.9) gives the method its name; for instance, in the \( P_1 \) method the series is truncated at \( l = 1 \), and \( l \) takes the values 0 and 1. Higher order methods are naturally possible, and the \( P_3 \) method is also used. Since it is known that the approximations of odd order are more accurate than the next even order approximations [48], the even order approximations (for example \( P_2 \), \( P_4 \), etc) are never used.

The accuracy of the method increases slowly with method order, while the mathematical complexity rapidly increases [48]. For this reason, approximations beyond \( P_3 \) are rarely ever used. It is possible to simplify the \( P_N \) formulation for a one-dimensional slab, and the resulting equations can be extended to three dimensions, forming the simplified \( P_N \) (SP\(_N\)) method [23]. The lower-order methods, SP\(_3\) and SP\(_5\) are similar in mathematical complexity to the \( P_1 \) method.

### 4.2.4.2 The discrete ordinates method

The discrete ordinates method attempts to use a discrete representation of the directional variation in the radiative intensity. In this method the integrals over direction are approximated by numerical quadrature. The RTE (Eq. (4.6)) is solved for a set of \( n \) different directions. The integral of any quantity over direction is calculated as [48]

\[
\int_{4\pi} f(\hat{s})d\Omega \approx \sum_{i=1}^{n} \omega_i f(\hat{s}_i),
\]

where \( \omega_i \) is the quadrature weight associated with the direction \( \hat{s}_i \). Thus Eq. (4.6) is replaced by a set of \( n \) partial differential equations.

The discrete ordinates method suffers from the effect of false scattering, which is due to discretization errors [48]. Like artificial diffusion in a finite difference discretization, this effect causes a radiation beam to widen as it moves through the medium. This ‘diffusion’ of radiative intensity can be reduced by using a finer mesh for the discrete ordinates.

The other effect that is seen in this method is what is called the ray effect [48]. If the method is used to model a radiation source emitting in all directions, the intensity is carried by a finite set of rays. As the rays move away from the source
the distance between the individual rays increases, and at a certain distance from
the source, there are large zones which fall entirely outside of any ray direction.
To alleviate this difficulty a higher order quadrature scheme can be used.

4.2.4.3 The photon Monte Carlo method

The photon Monte Carlo method (PMC) uses ray tracing to directly account for
the different processes that take place in radiation: emission, absorption, and
scattering. A representative photon bundle is used to track a ray in particular
direction. The ray moves through the domain and undergoes absorption, scattering
and reflection until all its energy is absorbed, or until it leaves the computational
domain. For smaller problems the PMC method is more expensive than the other
methods mentioned, but for larger problems an increase in problem complexity
does not significantly increase the computational effort. The direction and spectral
properties of each photon bundle is governed by a set of random numbers, and thus
if a large enough sample size is considered, radiative heat transfer can be modeled
to any degree of accuracy.

These detailed radiation models were part of the external library [23] that was
coupled to the flame code. In the present work the k-distribution model with the
narrow-band database was used for the calculation of spectral quantities, and the
P₁ and the SP₅ RTE solvers were used. The discrete ordinates method is often used
in the study of these laminar co-flowing diffusion flames [4, 21]. However in the
present work it was found that the application of the method in the axi-symmetric
wedge geometry would lead to large errors in the radiation calculations, unless a
very fine resolution was used. Hence the method was not used in the present work.
Chapter 5

Application to Atmospheric-Pressure Co-Flowing Laminar Diffusion Flames

The laminar flame solver was extensively tested on atmospheric-pressure co-flowing laminar diffusion flames. The primary goal of this exercise was to develop a numerical tool to model multi-dimensional laminar flames with detailed soot and radiation models.

As mentioned in Sec. 2.2, the laminar flame solver was built on top of OpenFOAM, which is an object-oriented CFD code written in C++. It is thus possible to make use of many of OpenFOAM’s native features: different solvers for solving the linear systems arising from the discretization of the partial differential equations, the discretization schemes, and the ODE solvers to integrate the chemistry. The laminar flame solver utilizes a mixture-averaged approach for calculating the transport properties, an ignition model based on equilibrium calculations at constant pressure and enthalpy, and various radiation models. In this chapter, a gray optically thin radiation model is used. The components of the gravitational acceleration can be prescribed with respect to the chosen coordinate system. This framework makes the solver general, and in principle it can be used to model flames in complex configurations, and allows for the use of detailed chemical mechanisms containing hundreds of species and thousands of elementary reactions.

The diffusion terms in the partial differential equations were discretized by
a second-order central difference method, the convection terms were discretized using an upwind scheme for the scalars, while a blended scheme was used for the momentum equation. Starting from an initial estimate, the solution was advanced in time using a first-order Euler scheme.

The PBiCG (Preconditioned Bi-Conjugate Gradient) solver was used for all equations except for pressure, which used a PCG (Preconditioned Conjugate Gradient) solver. The preconditioner used for the PBiCG solver was DILU (Diagonal Incomplete LU), while the PCG solver used a DIC (Diagonal Incomplete Cholesky) preconditioner. An absolute tolerance of $10^{-8}$ was used for the simulation, while the relative tolerance was specified as 0 to force the solver to converge to the absolute tolerance at each time-step.

5.1 Study of a CH$_4$-air flame

The code was first used to model a co-flowing laminar methane-air flame in the classical Burke and Schumann configuration [51], which was first studied experimentally and numerically by Mitchell et al. [52] and numerically by Smooke et al. [53], and Katta and Roquemore [54]. The fuel flows through a central tube of diameter 12.7 mm, and the outer co-flow diameter is 50.8 mm. The burner is enclosed by a Pyrex glass cylinder, and so the outer boundary in the radial direction is modeled as a no-slip wall in the present work. The flow rates of the fuel and air are 5.7 cc/s and 187.7 cc/s respectively. The inlet velocity of the fuel is thus 4.5 cm/s, while the co-flow velocity is 9.88 cm/s.

Mitchell et al. [52] used a flame-sheet assumption to model the flame. The governing equations for momentum, species mass fractions, and energy were solved in an iterative fashion using an alternating-direction implicit (ADI) technique.

Smooke et al. [53] used a stream function-vorticity based method, along with the flame sheet approximation to model the flame. An initial estimate for the variables was obtained on a coarse mesh using a time-dependent numerical method. Grid points were then inserted adaptively, and the problem was solved iteratively by Newton’s method.

Roquemore and Katta [54] used the time-dependent code UNICORN (Unsteady Ignition and Combustion with ReactioNs) to model this flame. The code
solves the equations for momentum, species mass fractions, and enthalpy using a finite-difference discretization. Three different gas-phase chemical mechanisms were used to model the flame, and good agreement with experiments was achieved in the simulations.

In the present work, the computational domain started just downstream of the burner, and extended to a distance of 300 mm in the axial and 25.4 mm in the radial direction. The domain was divided into $171 \times 60$ control volumes. A non-uniform mesh was used, with the mesh finer near the inlet, and inside the flame zone. Two gas-phase mechanisms were used for modeling the flame, as summarized in table 5.1.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Number of species</th>
<th>Number of reactions</th>
<th>Reference</th>
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</thead>
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<tr>
<td>SC16</td>
<td>16</td>
<td>42</td>
<td>[55]</td>
</tr>
<tr>
<td>GRI Mech 3.0</td>
<td>53</td>
<td>325</td>
<td>[56]</td>
</tr>
</tbody>
</table>

Thermal diffusion for the gas-phase species was not considered in the simulations. The preheating of the fuel was ignored, as was the presence of the fuel tube wall. Uniform velocity profiles were prescribed for the fuel and air inflow. Radiation was modeled by the optically-thin radiation model [5, 6]. Gravity was included in the axial component of the momentum equation.

Figure 5.1 shows the temperature profiles at three different heights from the burner. The agreement with experiment is generally good, particularly in view of the fact that the experimental uncertainties are not quantified. Also, this flame was experimentally determined to be a luminous flame, and so some soot is present in the flame. Soot was not modeled in this flame, since no experimental data were available. The soot can affect the temperature field due to heat loss by radiation, and so a simulation using a soot model would be a more accurate depiction of this flame.

Figure 5.2 shows the profiles of some of the major gas-phase species at a height of 12 mm from the burner. As for the temperature, the overall shape of the profiles is captured by the simulation. The experiments indicate that a small but detectable concentration of $O_2$ is present near the core of the flame, and the simulation using the GRI Mech 3.0 mechanism is able to capture this phenomenon. The centerline
levels of CO and CO$_2$ are under-predicted by the simulation, as are the centerline H$_2$ levels. H$_2$ is difficult to track accurately in a flame simulation because of its very low molecular weight, and high diffusivity. Further, thermophoretic diffusion for hydrogen was not considered in the simulation; during the course of the present study of C$_2$H$_4$-air flames (Sec. 5.2) it was found that the centerline H$_2$ levels can vary by a factor of two depending on whether thermal diffusion is included or not. The main objective behind modeling the methane-air flame was to see if the laminar flame solver could capture the experimental trends qualitatively, and so a detailed investigation of this flame with soot models and more detailed gas-phase mechanisms was not undertaken. In any case, the experimental uncertainties were not known, and so it is difficult to say if there would have been a better match with experiments if such a study had been undertaken.
Figure 5.2. Major gas-phase species profiles at a height of 12 mm from the burner for the 1-bar CH$_4$-air flame: (a) O$_2$ (b) CO$_2$ (c) CO (d) H$_2$.

5.2 Study of a C$_2$H$_4$-air flame

The flame solver with the soot models was tested on an atmospheric-pressure ethylene-air flame which was studied experimentally by Santoro et al. [24], and modeled by Kennedy et al. [57], D’Anna et al. [3], and Dworkin et al. [4]. The fuel was pure ethylene which flowed through a central brass tube of inner diameter 11.1 mm. The outer co-flow had a diameter of 101.6 mm. The fuel passage contained glass beads to provide a uniform exit velocity and the tube extended to a height of 4 mm beyond the inlet plane of the air co-flow. The experimental set up was enclosed in a 405 mm tall brass chimney to protect the flame from laboratory air currents. Slots were machined on the chimney to provide optical access for the experiment. The fuel flow rate was 3.85 cc/s, while the air flow rate was 713.3
cc/s. The fuel velocity was thus 3.98 cm/s, and the air velocity was 8.90 cm/s. This set of conditions corresponds to the non-smoking flame of Santoro et al. [24], where the soot is completely oxidized within the flame.

The soot particle measurements were carried out by a laser extinction/scattering technique, while the temperature measurements were performed using thermocouples. Radial profile measurements of the gas-phase species in the flame were obtained by a quartz microprobe [57]. The samples were analyzed by a mass spectrometer (MS) and subsequently verified by gas chromatography (GC). An experimental uncertainty of ±20% was noted for the major gas-phase species, while the uncertainty for OH was estimated at ±50% [57].

Kennedy et al. [57] modeled the flame using a boundary-layer form of the governing equations; starting from the inlet, the solution was ‘marched’ downstream using a spatial stepsize \( \Delta x \), which was chosen to satisfy accuracy requirements. The governing equations were solved in cylindrical coordinates, and axial diffusion was ignored in the simulation. Soot was modeled using a semi-empirical, \( \text{C}_2\text{H}_2 \)-based two-equation model, which was based on the model used by Fairweather et al. [58]. Soot radiation was modeled by an optically-thin model, and radiation from the gas-phase species was ignored.

D'Anna et al. [3] modeled the same flame using a sectional model [59, 60] for soot inception, growth and oxidation. The soot precursor was assumed to be naphthalene \( \text{C}_{10}\text{H}_8 \). The governing equations were solved in cylindrical polar coordinates on a computational domain that extended to a height of 100 mm in the axial direction, and to a radial distance of 48 mm. Radiation was modeled by the discrete transfer method [61], and the absorption coefficient of soot was tuned to match the simulation results to the experimental temperature profile. Figures 5.3 and 5.4 show the comparisons of their simulations with the experimental data.

Dworkin et al. [4] used a sectional soot dynamics model in their study of this flame. The soot particle size distribution function was divided into 35 discrete sections, and two equations were solved for each section: one equation for the primary spherical particle number density, and the other for soot aggregate density. Thus the soot model involved the solution to 70 additional equations. The soot precursor was taken to be pyrene \( \text{C}_{16}\text{H}_{10} \), and soot surface growth was modeled by the HACA mechanism [11]. Radiation was modeled by the discrete ordinates
method with a statistical narrow-band correlated k-distribution (SNBCK) for spectral properties. Figures 5.5 and 5.6 show some of the results obtained by Dworkin et al. .

In the present work, two sets of simulations were performed for this flame: one where the fuel tube geometry was considered, and the other where the geometry was not considered.

### 5.2.1 Simulations with the fuel tube

In the first set of simulations, the computational domain started at the exit plane of the co-flow, and so a 4 mm section of the fuel-tube wall was considered (Fig. 5.7). Uniform velocity profiles were prescribed for both the fuel and air and an inlet temperature of 300 K was used for both streams. Since the computational domain included a small part of the fuel tube, this was expected to account for fuel preheating, which was demonstrated to be important in a work by Guo and
Figure 5.4. Soot profiles predicted by D’Anna et al. [3] for the 1-bar ethylene-air flame.

Figure 5.5. Radial profiles predicted by Dworkin et al. [4] for the 1-bar ethylene-air flame.
coworkers [5]. The temperature of the fuel-tube wall was not available, and so as a first approximation, an adiabatic condition was assumed.

The computational domain extended from the air flow inlet to a height of 200 mm in the axial direction, and up to a distance of 51 mm in the radial direction. This domain was divided into $160 \times 78$ non-uniform control volumes. A schematic of the computational domain is shown in Fig. 5.7. A no-slip boundary condition was applied at the outer radial boundary, which corresponds to the brass chimney used in the experiments. The two-equation soot model was used to model the flame, and a soot Schmidt number of 60 was used in the simulations. Gravity was included in the solution of the axial momentum equation. Radiation was modeled by the optically-thin model [5, 6]; thermal diffusion for the gas-phase species was not considered. Five different gas-phase mechanisms were used.

A summary of the chemical mechanisms is given in table 5.2. Among these five mechanisms, the ABF31, the QLY70, and the QLY33 mechanisms were used in a comprehensive study of soot and gas-phase chemistry in ethylene-air flames by Mehta et al. [67]. The parent mechanism for ABF31 is the 100-species mechanism (ABF100) developed by Appel at al. [12], which in turn is modified from an
Figure 5.7. Computational domain for the 1-bar C$_2$H$_4$-air flame with the nozzle included. Figure not to scale.

Table 5.2. Gas-phase mechanisms used to model the C$_2$H$_4$-air flame

<table>
<thead>
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<th>Mechanism</th>
<th>Number of species</th>
<th>Number of reactions</th>
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<td>LYR32</td>
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<td>206</td>
<td>[63]</td>
</tr>
<tr>
<td>QLY33</td>
<td>33</td>
<td>205</td>
<td>[64]</td>
</tr>
<tr>
<td>QLY70</td>
<td>70</td>
<td>463</td>
<td>[65]</td>
</tr>
<tr>
<td>WL75</td>
<td>75</td>
<td>529</td>
<td>[66]</td>
</tr>
</tbody>
</table>

earlier 99-species mechanism (WF99) developed by Wang and Frenklach [68]. The ABF100 mechanism was reduced to a 31-species mechanism using MECHMOD [62]. Qin et al. [65] proposed a mechanism for C$_2$ chemistry with 70 species (QLY70), which includes species up to benzene. This mechanism was reduced by Law [64] to a 33-species mechanism (QLY33) using the Direct Relational Graph (DRG) technique.
5.2.1.1 Temperature and gas-phase species

Figure 5.8 shows the temperature profiles at various heights from the nozzle obtained using the mechanisms ABF31, LYR32, and QLY33. The corresponding profiles obtained using the mechanisms QLY70 and WL75 are shown in Fig. 5.9.

![Temperature profiles](image)

Figure 5.8. Temperature profiles at various heights for the 1-bar C\textsubscript{2}H\textsubscript{4}-air flame using the two-equation soot model and including the nozzle in the simulation: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

Overall, the temperature field is well-predicted by the simulation. The fuel-tube wall was modeled as being adiabatic in the simulation, so near the inlet the temperature and the velocity fields are likely to be affected by the boundary condition; at the flame heights shown in the figures, however, the effect of the boundary condition for the fuel-tube wall is expected to be small [57]. The uncertainty in the measured temperatures is taken to be ±10%, and the temperatures obtained using all the five chemical mechanisms agree to within this uncertainty band. The
centerline temperatures are captured by all five simulations, as is the width and shape of the temperature profile. Therefore, as far as the predicted temperatures are concerned, it is not possible to determine if any one chemical mechanism is necessarily performing better or worse than others.

An optically-thin radiation model was used in these simulations. Since the reabsorption of radiation is ignored in the optically-thin model, the temperatures are expected to be somewhat lower than what we would obtain from a radiation model that accounts for both emission and reabsorption. The fact that the optically-thin model gives temperatures so close to the experimental values suggests that the flame in question is optically thin.

The radial profiles of C$_2$H$_2$, CO$_2$, CO and OH at a height of 20 mm from the
Figure 5.10. Species profiles at a height of 20 mm from the nozzle for the 1-bar C$_2$H$_4$-air flame using the two-equation soot model and including the nozzle in the simulation: (a) C$_2$H$_2$ (b) CO$_2$ (c) CO (d) OH.

nozzle are plotted for the mechanisms ABF31, LYR32, and QLY33 in Fig. 5.10. All three chemical mechanisms in Fig. 5.10 predict a higher concentration of C$_2$H$_2$ at the centerline, compared to the experimental values. The computed profiles are seen to be narrower than the experimental profile, a feature that is also seen for CO$_2$ and CO. The predicted values lie within experimental uncertainty near the centerline, but the narrower profile means that in the wings the mole fractions go to zero at a shorter radial distance than the experiments suggest. A similar narrowing of the radial OH profile is also noted, and the computed OH peak is higher than the experimentally obtained value. This trend is seen to consistent with trends observed in other modeling studies, as shown in Fig. 5.5.

Figure 5.11 shows the radial profiles for the same gas-phase species at a height
of 20 mm, as predicted by the simulations using the chemical mechanisms QLY70 and WL75. The agreement with experiment using these two larger mechanisms is seen to be similar to Fig. 5.10. The profiles are narrower than the experimentally obtained ones, but the agreement of the centerline \( \text{C}_2\text{H}_2 \) mole fractions seem to be better. Since the simulations using the various mechanisms were set up in an identical fashion, the differences in results can only be due to differences in the chemical mechanisms. While it is not possible to say with certainty which chemical mechanism gives ‘better’ results, it appears that the larger chemical mechanisms seem to be performing slightly better in as far as matching the results with experiments is concerned. This may simply be due to the fact that the larger mechanisms incorporate more detail into the chemistry model, in the form of additional reaction products and pathways. However, the larger mechanisms also add considerably to the computational expense of the simulation, with the computational cost increasing as the square of the number of gas-phase species considered, or even more.

5.2.1.2 Soot volume fractions

The two-equation soot model was used to model the flame in this configuration. The soot volume fraction profiles obtained from the simulations using the mechanisms ABF31, Lyr32 and QLY33 at different heights from the nozzle are shown in Figure 5.12. The peak soot levels are well-captured by the simulations, particularly in view of the simple soot model used, and our lack of a complete understanding of the processes involved. The soot model is based on \( \text{C}_2\text{H}_2 \), which is a major intermediate species in hydrocarbon combustion. Hence we might expect to see soot being produced at places where the experiments would indicate no soot to be present. This is also seen in the model, especially near the centerlines at the lower axial heights, in Fig. 5.12(a). Overall the agreement with experiment is comparable to that in other modeling studies [4, 3], and the three chemical mechanisms produce similar results. This is not surprising, since the same soot model parameters were used in all these three simulations, and the differences would therefore be due to the gas-phase species predictions only. As seen in Figs. 5.8 and 5.10, the results for the major gas-phase species and temperature are very similar for the three mechanisms. This feature of the results also illustrates an important point
Figure 5.11. Species profiles at a height of 20 mm from the nozzle for the 1-bar C$_2$H$_4$-air flame using the two-equation soot model and including the nozzle in the simulation: (a) C$_2$H$_2$ (b) CO$_2$ (c) CO (d) OH.

in soot modeling: the soot model predictions are only as good as the predictions for the gas-phase species.

The soot volume fractions obtained using the mechanisms QLY70, and WL75 are shown in Fig. 5.13. The results are similar for the two mechanisms. The soot levels using these two mechanisms are slightly lower than those predicted in Fig. 5.12. It can be seen from Figs. 5.10 and 5.11 that the C$_2$H$_2$ levels are somewhat over-predicted by the mechanisms ABF31, Lyr32, and QLY33. Since the two-equation soot model relates the rate of formation of soot to C$_2$H$_2$, we would expect to see somewhat lower soot levels using the mechanisms QLY70 and WL75.
Figure 5.12. Soot volume fraction profiles at various heights for the 1-bar C\textsubscript{2}H\textsubscript{4}-air flame using the two-equation soot model and including the nozzle in the simulation: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

5.2.1.3 Effect of the fuel-tube wall

One of the challenges of modeling a co-flowing laminar diffusion flame is to account properly for the boundary conditions at the inlet, for which experimental measurements are typically not available. It was demonstrated by Guo et al. [19] in their study of a different ethylene-air co-flowing laminar diffusion flame, that the fuel undergoes significant preheating prior to reaching the reaction zone, and room-temperature boundary conditions at the fuel-tube exit plane cannot capture this preheating. In their work they included a portion of the fuel tube in the simulation, similar to what was done in the present work. The prescription of appropriate temperature boundary conditions on the wall of the tube is problematic. For the flame studied by Guo et al., a linear temperature variation was prescribed.
Figure 5.13. Soot volume fraction profiles at various heights for the 1-bar C₂H₄-air flame using the two-equation soot model and including the nozzle in the simulation: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

along the tube wall: the temperature varied from 300 K to 403 K over a distance of 4 cm.

Dworkin et al. [69] used a different approach to model the conditions near the fuel-tube wall. Instead of prescribing a boundary condition on the fuel-tube wall, the heat conduction equation was solved inside the solid wall. A zero-flux condition was prescribed for the gas-phase species at the interface between the solid and the fluid, while the heat flux at the interface was matched.

Eaves et al. [70] performed a conjugate heat transfer analysis to model the fuel-tube wall for modeling ethylene-air flames at pressures ranging from 2 to 33 atmospheres. They observed that the temperature and soot volume fractions depend strongly on the handling of the fuel-tube wall and the fuel preheating,
particularly for flames which are anchored to the tube wall. Not surprisingly, the adiabatic wall assumption predicted the highest temperatures near the wall, while the room-temperature wall assumption produced the lowest temperatures. These two scenarios present the two extreme cases, and reality lies in between the two. The conjugate heat transfer analysis attempted to properly account for this effect, even though it required the use of a much finer mesh, and a correspondingly higher computational effort.

In the present work, an attempt was made to account for the fuel preheating by including a 4 mm length of the fuel tube in the simulation. In the initial studies, an adiabatic condition was assumed for the fuel-tube wall. To investigate the effect of the adiabatic wall, another simulation was performed with the ABF31 mechanism, where a linear temperature profile was prescribed on the fuel-tube wall. The temperature was assumed to vary from 300 K to 400 K over a 4 mm length of the tube wall. While such a steep temperature gradient is likely to be unrealistically high, the goal of this simulation (hereafter referred to as simulation 2) was to see the effects of the assumed temperature profile, and to compare it to the adiabatic case (hereafter called simulation 1).

Figure 5.14 shows the resulting temperature profiles at various heights above the nozzle. Since the aim of this study was to compare the effect of the inlet temperature boundary conditions on the computed, temperature and soot fields, the experimental uncertainties are not indicated. In general, simulation 2 produces lower temperatures than simulation 1, and the difference is more pronounced close to the nozzle. At the heights of 3 and 5 mm, the peak temperature is lower by a hundred degrees or even more. At a height of 20 mm, the temperatures from simulation 2 are lower, but the difference is not so marked. The lower temperatures at the lower flame heights would be expected to affect the soot inception process, and subsequently the centerline soot levels.

Figure 5.15 shows the soot volume fraction profiles at various heights from the nozzle. The soot levels are in general lower for simulation 2, and the most prominent effect seems to be at the centerline. At the heights of 10 and 15 mm, there is almost no soot at the centerline, which is consistent with the experimental measurements. It is believed that the centerline soot levels are affected by the soot inception rates in the lower regions of the flame; the lower temperatures in
Figure 5.14. Effect of fuel-tube wall boundary condition on the temperature profiles at various heights for the 1-bar C$_2$H$_4$-air flame: (a) 3 mm (b) 5 mm (c) 15 mm (d) 20 mm. Simulation 1 is the one using the adiabatic nozzle, while in simulation 2 the nozzle wall has a linear prescribed temperature.

simulation 2 lower the soot inception rates, leading to lower soot levels at the centerline.

5.2.2 Simulations without the fuel tube

Due to the difficulty in modeling the fuel-tube wall in a flame simulation it is common practice to ignore the presence of the fuel-tube wall altogether, i.e., to begin the computational domain just downstream of the fuel tube. The preheating of the fuel is often neglected, or is accounted for by prescribing an elevated temperature for the fuel stream.

Dworkin et al. [4] modeled the same C$_2$H$_4$-air flame using a sectional soot model.
Figure 5.15. Effect of fuel-tube wall boundary condition on the soot volume fraction profiles at various heights for the 1-bar C$_2$H$_4$-air flame: (a) 10 mm (b) 15 mm (c) 20 mm (d) 30 mm. Simulation 1 is the one using the adiabatic nozzle, while in simulation 2 the nozzle wall has a linear prescribed temperature.

and a computational domain that started just downstream of the fuel tube. The fuel stream temperature was raised to 400 K, while the co-flow inlet temperature was taken to be 300 K. The fuel stream temperature was determined by matching the temperature profile to experiments at a location just downstream of the fuel tube. The results were seen to be insensitive to the choice of the velocity profile for the fuel stream, and so a flat velocity profile was prescribed for both the fuel and the co-flow.

The flame was set up in a fashion similar to Dworkin et al. [4] using a new mesh where the domain started just downstream of the tube. The computational domain extended from just downstream of the nozzle to a height of 150 mm in the axial direction, and to a distance of 51 mm in the radial direction. The do-
main was divided into $192 \times 88$ non-uniform control volumes. A schematic of the computational domain is shown in Fig. 5.16. A temperature of 400 K and a flat velocity profile was prescribed for the fuel stream, while the co-flow temperature was prescribed as 300 K. Thermophoretic diffusion for the light ($M_k < 5$) gas-phase species was included in the simulation. Simulations were performed using both the two-equation soot model and the MOMIC model.

### 5.2.2.1 Two-equation soot model

The ABF31, LYR32 and the QLY70 mechanisms were used to model the flame in the new configuration. These three mechanisms were chosen as they represent three different families of chemical mechanisms for $C_2$ chemistry [2, 67].

Figure 5.17 shows the resulting temperature profiles at various heights above the nozzle. Once again, the computed values lie within the experimental uncertainty. The centerline temperatures are well predicted, and the locations of the
peak temperature, and the shape of the temperature profiles are well captured by all three mechanisms. Comparing the results to those in Figs 5.8 and 5.9 it is seen that at the heights investigated, the temperature predictions are similar to those obtained using an adiabatic nozzle wall in the simulation. We would expect the differences in temperature due to the boundary conditions to be important only in a small region near the inlet [57], and the simulation results show that this indeed is the case.

Figure 5.17. Temperature profiles at various heights for the 1-bar C\textsubscript{2}H\textsubscript{4}-air flame using the two-equation soot model, with the nozzle excluded: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

Figure 5.18 shows the soot volume fraction profiles at various heights from the nozzle. Similar to Figs. 5.12 and 5.13, the maximum soot volume fractions are within a factor of 2. However, the location of the peak soot volume fraction is shifted towards the centerline in the simulations. The peak soot volume fraction
in the wings is determined mainly by the surface growth rates; the model seems to capture the peak soot levels, and the general shape of the soot profiles, especially at the lower heights. This indicates that the surface growth process is adequately modeled by the two-equation soot model.

![Soot volume fraction profiles at various heights for the 1-bar C₂H₄-air flame using the two-equation soot model, with the nozzle excluded: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.](image)

**Figure 5.18.** Soot volume fraction profiles at various heights for the 1-bar C₂H₄-air flame using the two-equation soot model, with the nozzle excluded: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

Near the flame tip, the agreement with experiment is not as good as at the lower heights. This part of the flame is dominated by the oxidation of soot, and the discrepancy points to a deficiency in modeling the oxidation process. The oxidation model used in the present work is based not on the Nagle-Strickland Constable (NSC) model [71], but rather on the oxidation model proposed by Leung et al.[13]. They noted that the NSC model significantly under-predicted the soot oxidation rate, and so they proposed a new mechanism for soot oxidation. Liu
et al. [72] used the two-equation soot model to study a smoking C_2H_4-air flame and concluded that the NSC oxidation model over-predicts the oxidation rate for soot, which also means that Leung et al.’s model [13] would also over-predict the oxidation rate for soot. Liu et al. [72] concluded that the smoking flame cannot be successfully modeled unless the oxidation model is modified. In the present work, the two-equation soot model predicts a maximum soot volume fraction of about 7 ppm, which is close to but lower than the experimental value of about 9.5 ppm.

Figure 5.19 shows the radial profiles for the major gas-phase species at a height of 20 mm. The agreement with experiment is good, and comparing with Figs. 5.10 and 5.11 we conclude that the inlet boundary conditions seem to have a very small effect on the gas-phase species profiles. Any differences due to the choice of the inlet boundary conditions would show up only in a small region near the inlet; for a tall flame such as this (∼88 mm), the effects would be negligible for most of the flame. However, for shorter flames, typical of smaller geometries and higher pressures, the effect of the inlet boundary conditions would not be negligible. This makes the modeling of ‘shorter’ flames more difficult.

5.2.2.2 MOMIC soot model

The flame was also modeled using the MOMIC soot model. This is a detailed soot model, and the role of PAH species in the soot formation and growth are accounted for. The soot precursor is taken to be pyrene, and so the chemical mechanism used must account for the growth of aromatics up to four rings. This precludes the use of any of the five chemical mechanisms used to simulate the flame using the two-equation soot model. This increases the computational effort considerably; not only is the soot model more complex and requires the solution to a larger number of scalars, the accompanying gas-phase chemistry model is also much larger than before. For this reason, a direct comparison of the computational cost of the two soot models is not straightforward.

Three gas-phase chemistry mechanisms were used to model the flame. The mechanisms are summarized in table 5.3.

The simulations were performed without considering the fuel-tube nozzle, and the same mesh was used for the simulations. The original form of the MOMIC soot model [15, 11, 43] was used with two important modifications.
Figure 5.19. Species profiles at a height of 20 mm from the nozzle for the 1-bar C$_2$H$_4$-air flame using the two-equation soot model, with the nozzle excluded: (a) C$_2$H$_2$ (b) CO$_2$ (c) CO (d) OH.

Table 5.3. Gas-phase mechanisms used in the MOMIC soot model

<table>
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<th>Mechanism</th>
<th>Number of species</th>
<th>Number of reactions</th>
<th>Reference</th>
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<tr>
<td>CalTech176</td>
<td>176</td>
<td>1095</td>
<td>[73, 74, 75]</td>
</tr>
</tbody>
</table>

The first modification was made to the surface growth rate in the model. The reaction rate for the reaction 4a in table 3.1 was increased by a factor of two. This was done to get a better agreement with the peak soot volume fractions in the wings, since the original model significantly under-predicted the peak soot in the flame. This is similar to the approach of Guo et al. [76], where the reaction rate had to be increased by a factor of five to get a good agreement with experiment.
The MOMIC soot model was originally formulated for laminar premixed flames [15], and for diffusion flames the model parameters need to be suitably modified. For this reason, a multiplying factor was added to the reaction-rate calculation for reaction 4a; the factor defaults to unity, but depending on the flame being investigated, the user has the option of choosing a value that best describes the situation.

The second modification was made to the PAH condensation model. In the original MOMIC model [11, 41] it was assumed that all collisions between a soot particle and a PAH molecule lead to a condensation reaction. Zhang et al. [46] used a PAH condensation efficiency of 50%, as was used by Dworkin et al. [4]. This value was used in the present work. The efficiency was also left as a free parameter in the code, with a default value of unity.

One model parameter with a marked influence on the soot levels is the steric factor $\alpha$, which is defined as the fraction of the reactive sites (‘armchair’ sites) on the soot particle surface that are available for surface growth or oxidation reactions. Various values and functional forms for $\alpha$ are found in literature. Frenklach and Wang [39] used a constant value of 0.1 in their work, while in a later work [11] the value of 0.35 was used. Guo et al. [77] used the following temperature-dependent functional form:

$$
\alpha = 0.0045 \exp\left(\frac{9000}{T}\right).
$$

Appel et al. [12] used a fitted correlation for $\alpha$, where $\alpha$ was a function of the local temperature and the average soot particle size, quantified by the reduced soot moment $\mu_1$. In their work, $\alpha$ was calculated as

$$
\alpha = \tanh\left(\frac{a}{\log \mu_1} + b\right),
$$

where the fitted parameters $a$ and $b$ were given by

$$
a = 12.65 - 0.00563T,
$$

$$
b = -1.38 + 0.00068T.
$$

Guo et al. [20, 7] used a correlation of the same form, but they modified the model
parameters $a$ and $b$ to

$$a = 3.0 \times (12.65 - 0.00563T),$$

$$b = -1.38 + 1.02 \times 10^{-2}T.$$  

The correlation used by Appel et al. [12] was obtained from a study of eight premixed flames, and it is difficult to provide a general expression for $\alpha$ that works for all flame conditions. For this reason, Dworkin et al. [4] used a constant value of 0.078 for $\alpha$. In the present work a value of unity for $\alpha$ was seen to work well for all three mechanisms. A value of 1 for $\alpha$ indicates that all radical sites on the surface of the soot particle are available for reaction with C$_2$H$_2$ or O$_2$.

Figure 5.20 shows the resulting temperature profiles at various heights above the nozzle. The temperatures near the centerline are well within experimental error. However, in the wings, the simulations predict lower temperatures compared to experiment. This is likely to be due to the combination of the soot model and the chemical mechanisms used. A similar under-prediction of the temperature in the wings was also observed by Dworkin et al. [4] and D’Anna et al. [3].

Figure 5.21 shows the radial profiles for the major gas-phase species at a height of 20 mm. For the aliphatic species and OH, the computed profiles are seen to be narrower than the experimentally obtained profiles. The centerline levels of C$_2$H$_2$ and CO are well predicted by all three mechanisms, while the CO$_2$ levels are somewhat over-predicted. The centerline benzene levels are well-predicted by the ABF100 and the CalTech176 mechanisms, while the BPP148 mechanism over-predicts the centerline benzene levels. D’Anna et al. [3] noted that the experimental benzene profiles have an additional uncertainty due to the fact that some of the benzene may condense in the sampling line, and therefore may not show up in the GC analysis. Thus all three chemical mechanisms are able to predict the benzene concentrations to within an acceptable range of accuracy.

Pyrene is an important species because it is taken to be the soot precursor in the MOMIC soot model. For the flame under study, experimental data on pyrene is not available, and so only the simulation results are shown in Fig. 5.21(f). At the centerline, the mechanisms ABF100 and BPP148 predict lower levels of pyrene compared to the CalTech176 mechanism. In the absence of experimental data, it
is difficult to say if the simulations capture the pyrene profiles at the various axial heights.

Figure 5.22 shows the temperature and C\(_2\)H\(_2\) profiles along the centerline. The temperature profile along the centerline is accurately captured by all three mechanisms. This is also seen in Fig. 5.20, where the differences with experiment are near the wings, but the centerline values of temperature are close to experiments. The acetylene profile is also mostly within experimental error, with the simulations predicting a slightly broader axial profile.

Figure 5.23 shows the profiles of benzene and pyrene along the centerline. The benzene profiles agree to within a factor of two, while the pyrene profiles show more dispersion. This can be attributed to the PAH growth pathways in the mechanisms.
Figure 5.21. Species profiles at a height of 20 mm from the nozzle for the 1-bar C$_2$H$_4$-air flame using the MOMIC soot model, with the nozzle excluded: (a) C$_2$H$_2$ (b) CO$_2$ (c) CO (d) OH (e) benzene (f) pyrene.
The ABF100 mechanism only accounts for PAH growth via the HACA pathway [11], while the BPP148 mechanism contains additional reaction pathways. The CalTech176 mechanism is more modern, and it attempts to include all known pathways of PAH growth. Thus the pyrene levels predicted by the CalTech176 mechanism are the highest.

Figure 5.24 shows the resulting soot volume fraction profiles at various heights above the nozzle. The peak soot volume fraction in the wings is captured by all three chemical mechanisms. The soot volume fractions in the wings are governed mostly by the soot surface growth process; the combination of the modified surface growth rate and a steric factor of unity can thus capture the soot volume fractions in the wings. At the centerline, the soot levels are underpredicted, especially in the upper part of the flame. The soot volume fraction at the centerline is governed by the soot inception model. The under-prediction of the centerline soot in the present work could be due to a deficiency in the chemical mechanisms, the soot model itself, or a combination of the two factors.

Dworkin et al. [4] pointed out that the HACA mechanism for PAH growth, as in the mechanism ABF100, cannot adequately describe the formation of the PAH species. Since the PAH species are treated as precursors of soot, the soot inception process is suppressed due to a lower concentration of pyrene in the simulated combustion products. To alleviate this difficulty, they used a chemical mechanism with additional PAH growth pathways, which was modified from a mechanism used

![Figure 5.22](image-url)
Figure 5.23. Centerline profiles of benzene and pyrene for the 1-bar C₂H₄-air flame using the MOMIC soot model, with the nozzle excluded.

by Slavinskaya and Frank [78]. Using this mechanism, they were able to predict the centerline soot volume fractions to within an order of magnitude.

This chemical mechanism could not be used in the present work due to numerical stiffness, but the BPP148 and CalTech176 mechanisms used do account for additional pathways of PAH formation and growth. It was seen that, even though the centerline pyrene levels were much higher with the CalTech176 mechanism as compared to the ABF100 or the BPP148 mechanisms, the effect on the centerline soot levels was not significant. The peak soot levels at the centerline are of the order of 4 ppm, and none of the three mechanisms were able to capture the soot levels in this region. Dworkin et al. [4] reported a peak centerline soot volume fraction of about 1 ppm, which is larger than that in the present work, but still significantly lower than the experimental value. This inability of the modeling studies to correctly capture the soot levels at the centerline points to a drawback in the soot model itself, and needs to be further investigated.

Comparing the results obtained using the semi-empirical model and the detailed soot model, it is seen that the two soot models produce similar results for the ethylene flame. The centerline soot levels are actually somewhat better predicted by the two-equation model, even though this is possibly an artifact of the C₂H₂-based soot model, rather than suggesting that the model is an accurate depiction of the actual processes. The two-equation model was calibrated to model non-premixed ethylene flames [13], and so it works very well for the ethylene-air diffusion flame.
Figure 5.24. Temperature profiles at various heights for the 1-bar C₂H₄-air flame using the MOMIC soot model, with the nozzle excluded: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

The MOMIC soot model attempts to incorporate the details of the processes of soot formation and growth, but since our understanding of the different processes is limited, the submodels of soot formation and growth are unable to fully capture the physics of the problem. There seems to be no clear advantage in choosing one the soot models over the other; in terms of computational cost, the two-equation model is much more attractive, but for a different flame configuration the MOMIC soot model might produce results in closer agreement with experiments.
5.3 Summary

In this chapter, the laminar flame solver and the soot models were applied to two different co-flowing diffusion flames. The first flame studied was a co-flowing, 1-bar methane-air diffusion flame studied experimentally by Mitchell et al. [52] and numerically by Smooke et al. [53]. The temperature and major species profiles were seen to agree with experimental data.

The models were then applied to an ethylene-air flame at 1 bar pressure. This flame had been studied experimentally by Santoro et al. [24], and modeled by Kennedy et al. [57], D’Anna et al. [3], and Dworkin et al. [4]. Initially a set of simulations was performed using the flame solver and the two-equation soot model, in which the fuel-tube wall was modeled as being adiabatic. Five gas-phase mechanisms were used in this study, and the computed and measured profiles of temperature, and major species profiles were seen mostly to agree to within experimental error. The soot volume fraction profiles were also well captured, particularly in light of the fact that a semi-empirical soot model was used, and also that our understanding of the processes involved in the formation, growth and oxidation of soot are far from complete. Another study was then performed using the same two-equation soot model, in which the effect of the boundary conditions on the fuel-tube wall was investigated. In a second set of simulations using the two-equation model, the nozzle wall was no longer considered as part of the domain; instead, the fuel stream was preheated to 400 K. The results from this set of simulations also agreed with experiments.

The ethylene flame was then modeled using a detailed soot model, the Method of Moments with Interpolative Closure (MOMIC). The fuel-tube wall was ignored in these simulations, and the fuel stream was preheated. Three different gas-phase mechanisms, containing aromatic species up to pyrene (C_{16}H_{10}) were used. The soot precursor was assumed to be pyrene, and the surface growth and oxidation model followed the HACA mechanism of Wang and Frenklach [11]. However, in order to get good agreement with the soot volume fractions in the wings, the reaction rate for the addition of C_{2}H_{2} to soot was increased by a factor of two. The temperature and the major gas-phase species were seen to agree with the experiments, and the soot levels in the wings were also well captured. However, at
the centerline, the simulations predicted soot levels lower from experimental values by an order of magnitude for all the three chemical mechanisms. This is consistent with the findings reported in the literature for this and other similar flames, and is likely due to a fundamental deficiency in the soot model.
Chapter 6

Application to higher-pressure flames

In chapter 5, the laminar flame code and soot models were applied to atmospheric-pressure co-flowing laminar diffusion flames. The major gas-phase species profiles, and temperature were mostly within experimental error, while the soot volume fraction showed an agreement comparable to those found in the literature [17, 4, 3]. As a next step, the code and models were applied to higher-pressure flames. The target flames were chosen from the International Sooting Flame Workshop [79] datasets.

6.1 Study of a 10-bar methane-air flame

The first high-pressure flame that was studied was from a family of methane-air flames, studied experimentally by Joo and Gülder [80], and modeled by Liu et al. [81].

These experiments were conducted at pressures from 1.0 to 6.0 MPa. The fuel was pure methane, and it flowed through a central tube at 0.55 mg/s. The fuel tube was tapered for a distance of 5 mm on either side; the fuel tube inner diameter before the taper was 2.29 mm, while at the end of the fuel tube, the inner diameter increased to 3.06 mm (Fig. 6.1). The outer diameter of the fuel tube decreased from 4.76 mm to 3.06 mm over the same distance. The co-flow was air with a mass flow rate of 0.4 g/s for the lower pressures, and 0.8 g/s for the higher pressures.
The co-flow diameter was 25 mm. Sintered foam was used to obtain a uniform flow just prior to the beginning of the fuel-tube taper. Sintered foam was also used within the co-flow passage at a distance of 14.7 mm below the exit plane of the fuel tube. Both the fuel and the air streams were at a temperature of 294 ± 3 K. The entire setup was enclosed in a high-pressure chamber designed for a pressure of up to 110 atm. Optical access in to the chamber was provided through three slots machined at 0°, 90° and 180° locations. Soot volume fraction and temperature measurements were carried out by the spectral soot emission technique.

Liu et al. [81] used a two-equation soot model to simulate the methane-air flames at pressures between 5 and 40 atm. The two-equation model used in their work is similar to the one used in the present work, with one notable difference being that the oxidation model for soot is based on the Nagle-Strickland Constable (NSC) model [71]. The NSC soot oxidation model was modified by Liu et al. [72] to account for the fact that the NSC model over-predicted the soot oxidation rate for smoking flames. For these high-pressure flames, Liu et al. [81] modified the NSC oxidation model to account for the higher pressures. Radiation was modeled by a statistical narrow-band correlated k-distribution (SNBCK) based model.

In the present work, the 10-bar methane-air flame was simulated using the two-equation soot model. The chemical mechanism used was GRI Mech 3.0 [56], from which all reaction pathways and species leading to NOx were removed. The resulting mechanism comprises 36 species and 219 reactions. The computational domain starts at a distance of 10 mm below the exit plane of the fuel tube, and so the tapered fuel tube wall was included in the simulation. The fuel-tube temperature was assumed to vary linearly from 294 K at the inlet to 794 K at the fuel-tube exit. The reason behind this choice of temperatures was that the gas temperature near the nozzle lip was found to be close to 800 K by Eaves et al. [70], who used a conjugate heat transfer method to model ethane-air diffusion flames using the same burner configuration. The computational domain extends to a height of 6 cm in the axial direction and to a distance of 12.5 mm in the radial direction. The domain was discretized into 160 × 90 non-uniform control volumes. Thermophoretic diffusion for ‘light’ (MW < 5) species was included in the simulation. A soot Schmidt number of 60 was used. Uniform inlet velocities corresponding to the prescribed mass flow rates were used for both the fuel and
the air co-flow. Radiation was modeled by the optically thin, emission-only model used for the 1-bar flames [5, 6]. Inlet temperatures for both the fuel and air were assumed to be 294 K. The effect of gravity was included in the axial component of the momentum equation. As in the case of the 1-bar flames, the diffusion terms in the governing equations were discretized by a central difference scheme, while the convective terms were discretized by an upwind scheme for the scalars. A blended scheme was used to discretize the convective terms in the momentum equation. A first-order Euler scheme was used to march the solution in time. A schematic of the computational domain is shown in Fig. 6.1.

6.1.1 Temperature and soot profiles

Figure 6.2 shows the temperature profiles at various heights from the fuel tube as compared to experiments. The agreement with experiment is seen to be within about 10%. In all the profiles, the experimental temperatures are seen to rapidly decrease at a certain radial distance. As explained later, this is due to a deficiency
in the measurement technique, and is therefore not seen in the simulation results.

![Figure 6.2](image-url)

**Figure 6.2.** Temperature profiles at various heights for the 10-bar CH\(_4\)-air flame using the two-equation soot model: (a) 3 mm (b) 4 mm (c) 5 mm (d) 6 mm.

The spectral soot emission technique has several limitations [80]. First, the measurement is based on the emission of radiation from soot, and so temperature measurements can only be performed in regions where soot is present in sufficiently high concentrations. Second, it has been seen that the technique predicts a temperature decrease in the outer regions of the flame annulus that is not seen in numerical models or even in other measurement techniques. This can lead to an underprediction of measured temperatures in the primary reaction zone. This effect is likely due to errors introduced into the inversion algorithm when inverting the rapidly decaying signal from soot near the edge of the flame. Further, near the flame core, the soot volume fractions are typically much lower than the
peak soot levels in the wings, and this can also lead to inaccuracies in the temperature measurements. Joo and Gülder [80] performed multiple measurements at the same spatial location on different occasions, and found that the temperature curves thus obtained agreed to within 2%, indicating a high level of repeatability. While such a procedure would certainly eliminate any ‘random’ measurement errors, any systemic errors would still show up in the measurements. For this reason, experimental uncertainties are not shown in Fig. 6.2.

The level of agreement between the measured and computed temperatures also indicates that the flame is optically thin, since the emission-only model is able to resolve the temperature profile. It may seem counterintuitive that a flame at a higher pressure would be optically thin, but the flame geometry is much smaller for this flame compared to the 1 bar flame; not only is the fuel passage much narrower, but the visible flame height, as estimated from the soot radiation, is only about 9 mm [80], as opposed to about 88 mm for the 1-bar ethylene-air flame.

Figure 6.3 shows the soot volume fractions at various heights from the fuel tube exit plane. The peak soot volume fractions in the wings are well captured by the model. The centerline soot levels are also of the same order as in experiments. Experimental uncertainties in the measured soot volume fractions were not quantified by Joo et al. [80], but a later work by Eaves et al. [21] modeling an ethane-air flame at high pressures using the same burner indicated that the errors associated with the spectral soot emission method can be as high as 30 – 40%. In Fig. 6.3, the soot volume fractions are plotted against experimental data, and the maximum uncertainty of 40% is shown with the data. The peak soot volume fractions are seen to occur at the wings at the lower axial heights, and the centerline soot levels are negligible. At higher axial locations, the soot profiles shift towards the centerline, and the peak soot at the centerline is about 10 ppm.

Comparing the soot profiles with the results for the 1-bar C\textsubscript{2}H\textsubscript{4}-air flame described in chapter 5, we see that even at the elevated pressure of 10 bar, the level of agreement with experiment is similar to the 1-bar flame. It is to be noted that the two-equation soot model was used as in chapter 5, and no special treatment was introduced to account for higher pressures. This is different from the work of Liu et al. [81], where the soot oxidation model was modified to account for the higher pressures.
The two-equation model used in the present work is based primarily on the simplified model for soot formation that was proposed by Leung et al. [13]. The model is calibrated to predict soot in non-premixed flames, and the soot precursor is taken to be $\text{C}_2\text{H}_2$, which is a major intermediate species in hydrocarbon combustion. As seen in chapter 5, the flame solver is able to accurately model the flame conditions for these non-premixed flames, and the gas-phase mechanisms are able to resolve the major gas-phase species (including $\text{C}_2\text{H}_2$). This in part explains the success of this relatively simple soot model in our studies.

![Soot volume fraction profiles at various heights for the 10-bar CH$_4$-air flame using the two-equation soot model: (a) 3 mm (b) 4 mm (c) 5 mm (d) 6 mm.](image)

**Figure 6.3.** Soot volume fraction profiles at various heights for the 10-bar CH$_4$-air flame using the two-equation soot model: (a) 3 mm (b) 4 mm (c) 5 mm (d) 6 mm.
6.2 Study of a 10-bar ethane-air flame

The next high-pressure flame that was modeled was chosen from a set of ethane-air diffusion flames at pressures of 0.2\textendash{}3.34 MPa studied experimentally by Mandatori and Gülder [82], and modeled by Eaves et al. [70, 21]. The burner geometry is the same as that used to study the methane-air flames in Sec. 6.1. In this case, pure ethane flows through the central tube at 0.52 mg/s, and the co-flow is air flowing at 0.12 g/s for pressures of 0.2 \textendash{} 2.53 MPa, and 0.24 g/s for pressures of 3.04 \textendash{} 3.34 MPa. As in the previous setup, sintered metal foam was used in the air-flow passage to obtain a uniform velocity profile at a distance of 14.7 mm below the fuel-tube exit plane. Sintered foam was also used in the fuel tube just prior to the start of the taper. Measurements of temperature and soot volume fraction were carried out by the spectral soot emission technique.

Eaves at al. [21] numerically studied the ethane flames for pressures of 2 \textendash{} 15 atm. Soot was modeled by a sectional method, wherein the soot particle distribution function was divided into 35 discrete sections. Two transport equations were solved per section: one equation for the primary spherical particle number density, and another for soot aggregate density. Thus the soot model required the solution to 70 additional equations. Soot inception was assumed to be due to the dimerization of pyrene (C_{16}H_{10}, A_4), and the soot particle surface growth was modeled by the HACA mechanism [11]. Radiation was modeled by the discrete ordinates method and a statistical narrow-band correlated k-distribution (SNBCK) based model. The computational domain started just downstream of the fuel-tube exit plane. Flat velocity profiles were prescribed for the inlet, and both the fuel and air streams were assumed to be at 300 K. Flames at pressures above 15 atm were not modeled, since there is known to be significant attachment of the flame to the fuel tube at these high pressures, which requires the specification of proper inlet boundary conditions.

To overcome the difficulty in specifying temperature boundary conditions on the nozzle wall, in a more recent work Eaves et al. [70] modeled the heat transfer between the fuel tube wall and the fluid streams using a conjugate heat transfer analysis. In their simulations, the fuel-tube wall was considered as part of the computational domain, and not a boundary. Within the fuel-tube wall, a very
high viscosity value was assigned while solving the momentum equations in order to mimic the solid wall. The values of the thermal conductivity and specific heat capacity of steel were used within the tube wall while solving the energy equation. Using this method Eaves et al. were able to model flames at pressures above 15 atm, and up to 33 atm. The major drawback with the use of a conjugate heat transfer method is that a very fine mesh is required near the fuel-tube wall, and the computational cost is correspondingly higher.

In the present work, the 10-bar ethane flame was modeled. The two-equation soot model was used, and the chemical mechanism used was LYR32 [63], since the fuel is a C$_2$ hydrocarbon. The chemical mechanism contains 32 species and 206 reactions. As in the case of the methane-air flame, the computational domain started at a distance of 10 mm below the fuel-tube exit plane, and so the tapered nozzle geometry was included in the simulation. The computational domain extended to a height of 6 cm in the axial direction and up to a distance of 12.5 mm in the radial direction; this was divided into 160 × 90 non-uniform control volumes.

The fuel and the air streams were assumed to be at 300 K, and the temperature of the nozzle wall was assumed to increase linearly from 300 K at the inlet to 800 K at the fuel-tube exit plane. This value is consistent with the results obtained using the conjugate heat transfer analysis [70]. Uniform flow velocities corresponding to the mass flow rates were prescribed at the fuel and air flow inlets. Thermophoretic diffusion for ‘light’ species was included in the simulation. A soot Schmidt number of 60 was used in the calculations. The optically thin, emission-only radiation model was used in the simulations.

### 6.2.1 Temperature and soot profiles

Figure 6.4 shows the temperature profiles at various heights from the nozzle. Since the spectral soot emission method was used in the measurements, the measured temperatures suffer from the same issues as explained before. The total uncertainty in the measured temperature was reported to be about 3.5% [82], but because of the inherent sources of inaccuracies in the measurement technique, the uncertainties are not shown in Fig. 6.4. The calculated and measured temperatures mostly lie within about 5% of each other. However, the experimental temperature profiles
show the same sudden, rapid drop as we move radially out into the wings.

The temperatures computed using the optically thin radiation model agree with the experimental values. This suggests that the flame is optically thin, as was the 1 bar ethylene flame and the 10 bar methane flame. Even though the pressure is higher than the ethylene flame, the flame is smaller in size: the visible flame height is only about 10 mm.

Figure 6.4. Temperature profiles at various heights for the 10-bar C\textsubscript{2}H\textsubscript{6}-air flame using the two-equation soot model: (a) 3 mm (b) 4 mm (c) 5 mm (d) 7 mm.

Figure 6.5 shows the soot volume fractions at various heights from the fuel-tube exit plane. Eaves et al. [21] pointed out that the errors associated with the spectral soot emission method can be as high as 30–40%. In Fig. 6.5 the experimental data are plotted along with the maximum (40%) uncertainties. As expected, the peak soot levels are larger than those for the methane flame. At the lower axial heights, the peak soot volume fraction occurs in the wings, and the peak shifts towards
the centerline at the higher axial positions. The peak centerline soot is about 30 ppm. The model is able to capture this trend in the soot volume fraction, even though at the lower heights, the model predicts a non-zero soot volume fraction at the centerline. This is likely due to the fact that an acetylene-based soot model is in use; as seen in the earlier studies, since C$_2$H$_2$ is an important intermediate product in hydrocarbon combustion, the soot model produces soot in parts of the flame where experiments indicate no soot to be present. Even then, the level of agreement between the experiment and the model is encouraging. As for the methane-air flame, the two-equation soot model was used as in the case of the 1 bar flame, with no modifications to account for the higher pressures. An indirect effect of the higher pressures comes in because of higher concentrations of the gas-phase species because of the larger density values. However, the soot model still solves the same equations to calculate the rates, and the higher soot levels are simply due to the fact that the soot precursor and growth species (here C$_2$H$_2$) are present in higher concentrations than in a 1 bar flame.

6.3 Study of a 4-bar ethylene-air flame

The next flame was chosen from a set of laminar, co-flowing ethylene-air flames from the International Sooting Flame workshop. These are a set of several experiments conducted at pressures from 4 to 16 atm. The soot measurements were done at pressures between 4 to 16 atm, the temperatures were measured at pressures between 1 to 4 atm, and the measurements of the gas-phase species were done at pressures from 1 to 16 atm. The fuel-tube inner diameter was 4 mm, and the fuel stream comprised ethylene flowing at the rate of 1.37 mg/s, and nitrogen flowing at 6.41 mg/s. The fuel-tube wall was tapered for a distance of 5 mm; the outer diameter of the fuel tube before the start of the taper was 6.1 mm for the measurement of soot, while for the experiments measuring temperature or the gas-phase species the outer diameter was 6.35 mm. The co-flow diameter was 50 mm, and the co-flow was air flowing at 1.25 g/s for the 4 atm case, 2.51 g/s at the pressure of 8 atm, 4.01 g/s at a pressure of 12 atm, and 4.42 g/s at the highest pressure of 16 atm.

Steel wool or carbon foam was used inside the fuel tube, at a distance of 8
mm below the exit plane of the tube. On the air side, honeycomb structures or aluminum foam was used 5 mm below the exit plane of the fuel tube. Soot measurements were done by a line of sight attenuation (LOSA) technique, while the temperatures were measured by a thermocouple. The concentrations of the gas-phase species were measured by extraction via a quartz probe, and subsequently analysing the samples by a GC method. Details of the experimental measurements for temperature and the gas-phase species is described in the works of Kailasanathan et al. [83, 84].

In the present work, the pressure of 4 bar was selected for the simulation. The burner that was modeled corresponds to the one used for the soot measurements: the fuel-tube inner diameter was 4 mm, and the outer diameter of the fuel tube varied from 6.1 mm to 4 mm over a height of 5 mm. The fuel stream comprised

Figure 6.5. Soot volume fraction profiles at various heights for the 10-bar C_2H_6-air flame using the two-equation soot model: (a) 3 mm (b) 4 mm (c) 5 mm (d) 7 mm.
Figure 6.6. Computational domain for the 4-bar, N$_2$-diluted C$_2$H$_4$-air flame. Figure not to scale.

C$_2$H$_4$ flowing at 1.37 mg/s and N$_2$ at 6.41 mg/s. The co-flow diameter was 50 mm, and the air flow rate was 1.25 g/s. The computational domain started at a distance of 8 mm from the fuel-tube exit plane on the fuel-side, while on the air side, the domain started at a distance of 5 mm below the fuel tube exit plane. Thus the tapered fuel-tube wall geometry was included in the simulations. The domain extends to a distance of 8 cm in the axial direction, and to a radial distance of 25 mm. The domain is divided into 84 cells in the radial direction, and into 130 cells in the axial direction on the fuel side. On the air side the number of cells in the axial direction is 120. The total number of non-uniform control volumes is 10320. A schematic of the computational domain is shown in Fig. 6.6.

A linear temperature distribution is prescribed on either side of the fuel tube; on the fuel side, the temperature varies from 400 K at the domain inlet to 450 K at the fuel-tube exit plane, while on the co-flow side, the temperature is 300 K at the air inlet plane (which corresponds to a location 3 mm downstream of the fuel inlet plane), and increases to 450 K at the fuel tube exit plane. A uniform
velocity profile corresponding to the inlet fuel composition and mass flow rate was prescribed, and a uniform temperature of 400 K was prescribed at the fuel inlet. It was checked by a sensitivity calculation that the centerline temperature profiles could not be captured with a room-temperature boundary condition at the fuel inlet plane, but a value of 400 K worked well. For the co-flow inlet, a uniform temperature of 300 K and a uniform velocity profile corresponding to the air flow rate was prescribed.

As in the case of the other simulations, the diffusion terms in the governing equations were discretized by a second order, central difference scheme, while an upwind scheme was used for the convective term for the scalars. The convective term in the momentum equation was discretized by a blended scheme. A first-order Euler scheme was used to march the solution in time. This flame was simulated using both the two-equation soot model and the MOMIC soot model. For both the models, a soot Schmidt number of 60 was used. Radiation was modeled using the same optically thin model as was used previously [5, 6].

### 6.3.1 Simulations with the two-equation soot model

The flame was first modeled using the ABF31 mechanism [62] and the two-equation soot model. The ABF31 mechanism contains 31 species and 179 reactions. The profiles of soot volume fraction and temperature along the centerline are shown in Fig. 6.7.

Kailasanathan et al. [83] experimentally studied the effects of diluents on the temperature and soot precursors in this burner configuration. The simulated conditions correspond to the 4 atm ethylene flame diluted at 82.5% by volume of nitrogen. The temperature was measured by an uncoated, 75 µm thermocouple. Multiple measurements were taken at each spatial location, and after correcting for radiation effects, the uncertainties in temperature were reported as ±15 K around the true values. However, these uncertainties are not shown in Fig. 6.7(a), since a 30 K temperature difference would be almost impossible to discern on the plot. Also, the uncertainties were estimated by repeating the measurements at each spatial location, and not by a rigorous analysis, or by comparing data obtained independently from multiple measurement methods. The general shape of
Figure 6.7. Centerline profiles of (a) temperature, (b) soot volume fraction, (c) $C_2H_4$, and (d) $C_2H_2$ for the 4-bar $N_2$-diluted $C_2H_4$ flame using the two-equation soot model.

The axial temperature profile and the location of the peak centerline temperature is captured by the model. However the peak temperature is seen to be lower in the simulations than in the experiment, especially between the heights of 20 and 30 mm.

The soot volume fraction measurements were carried out by the LOSA method. Uncertainties in soot volume fraction were not available. From Fig. 6.7(b) it is seen that the centerline soot levels are well represented by the model. The location of the peak centerline soot volume fraction is captured, and the peak value is also within 70% of the experimental value.

The gas-phase species concentrations were measured by extraction using a quartz probe, and subsequent analysis by a GC-MS+FID [84]. As in the case of temperature, multiple measurements were performed at each spatial location,
and the average of these values was reported as the final data. The peak standard deviations were used to quantify the uncertainties. The highest standard deviation of ±12% was reported for propane, while toluene gave a standard deviation of ±9%. The other C\textsubscript{3} species gave a standard deviation of ±6%, while for all other species the standard deviation was less than ±3%. Among the species concentrations reported by Kailasanathan et al. [84], the ABF31 mechanism only contains the species C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2}. Centerline profiles of these two species are shown in Figs. 6.7(c) and 6.7(d). The uncertainties are not shown in the figure. Ethylene is the fuel species, and its centerline profile is well captured by the simulation. The centerline profile of the fuel is directly governed by the rate of burning, and this is a strong function of the inlet boundary conditions. Specifications of the inlet boundary conditions are not always precise. In the simulation it was seen that the temperature at the inlet boundary had to be rasied to 400 K in order to capture the centerline temperature profile. This indicates that heat transfer by conduction to the inlet fuel stream was not negligible. In such circumstances, it is likely that the fuel species (C\textsubscript{2}H\textsubscript{4}) may have already started to pyrolyze before it even reached the start of the computational domain. Since the full effect of this fuel pyrolysis is not accounted for, the simulated centerline profile of the fuel can deviate from the experimentally reported values. In light of this limitation, the agreement in the centerline values of C\textsubscript{2}H\textsubscript{4} is encouraging.

The computed centerline profile of C\textsubscript{2}H\textsubscript{2} shows very good agreement with the centerline values up to a height of about 15 mm above the fuel-tube exit plane. Above this height the experimental values indicate a rapid decay in the centerline C\textsubscript{2}H\textsubscript{2} levels. This trend is not captured by the simulation; rather, the C\textsubscript{2}H\textsubscript{2} levels continue to rise until a height of about 17 mm, and then the levels go down. This is possibly an artifact of the particular gas-phase chemical mechanism in use.

Figure 6.8 shows the temperature profiles at various heights from the nozzle exit plane. At the heights of 15 and 19 mm from the nozzle exit, the centerline temperature is well predicted; at the heights of 21 and 23 mm, the centerline temperature is seen to be lower than the experimental values. This is consistent with the results in Fig. 6.7(a), where the simulated centerline temperature follows the experimental values up to a height of about 20 mm, and then the computed temperature profile is lower than the experimental profile between the heights of
20 and 30 mm. The computed radial temperature profiles are seen to be wider than the experimental ones at all heights above the nozzle. Due to the reasons described before, the uncertainties (±15 K) are not indicated in the figure.

Figure 6.8. Temperature profiles for the 4-bar \( \text{N}_2 \)-diluted \( \text{C}_2\text{H}_4 \) flame using the two-equation soot model at various heights above the nozzle: (a) 15 mm (b) 19 mm (c) 21 mm and (d) 23 mm.

Figure 6.9 shows the computed and experimental soot volume fraction profiles at the same heights from the nozzle. It is seen that at all of these four heights, the centerline soot levels are about 70% of the experimental value. However, in the wings, the simulations predict a much higher soot peak value than the experiments.

6.3.2 Simulations with the MOMIC soot model

The 4-bar flame was also modeled using the ABF100 chemical mechanism [12] and the MOMIC soot model. This mechanism is the parent mechanism for ABF31,
Figure 6.9. Soot volume fraction profiles for the 4-bar N₂-diluted C₂H₄ flame using the two-equation soot model at various heights above the nozzle: (a) 15 mm (b) 19 mm (c) 21 mm and (d) 23 mm.

and contains 100 species and 542 reactions including PAH species up to four ring aromatics (pyrene, C₆H₁₀). The growth of the PAH molecules is assumed to occur by the HACA mechanism [11]. The MOMIC soot model was used as in the case of the 1 bar flame; a Schmidt number of 60 was used, the surface growth rate due to C₂H₂ addition to the soot surface was multiplied by a factor of two, and an efficiency of 50% for the condensation of PAH on soot was used. The inception of soot was assumed to occur by the dimerization of two pyrene molecules. Figure 6.10 shows the computed temperature and some of the gas-phase species profiles along the centerline.

The centerline temperature profile is very similar to the one obtained from the simulation with the two-equation soot model and the ABF31 mechanism; up to a
height of about 20 mm from the nozzle, the computed temperature closely follows the experimental temperature profile. Then between the heights of 20 and 30 mm, the simulation predicts a lower temperature than the experiment. The visible flame height was reported to be about 27 mm [83], and it is thus seen that in the post-flame region, the computed temperatures are higher than the experimental values.

The centerline soot profiles are not shown in the figure because the combination of the MOMIC soot model with the ABF100 mechanism produces very low concentrations of soot along the flame centerline. This feature of the soot model was also seen in the simulations of the 1-bar flames. Dworkin et al. [4] suggested that the ABF100 mechanism produces lower levels of PAH species, and thus the centerline soot levels are under-predicted. A similar under-prediction of the centerline soot was also seen in the simulations using more modern gas-phase chemical mechanisms, and it appears that the centerline soot levels are affected by a combination of uncertainties in the predicted PAH levels, as well as a possible deficiency in the soot inception submodel itself.

Figure 6.10(b) shows the profile of benzene along the centerline. Benzene is an important species for soot modeling since it marks the beginning of aromatic chemistry; the aliphatic compounds form the first aromatic ring, and then the growth to PAH species occurs. The computed benzene profile agrees with the experimental profile to within a factor of two, but the simulated profile is seen to be wider than the measured profile. Considerable uncertainties exist as to the precise pathways of formation of benzene from aliphatic species, and also the measurement of these aromatic species is more difficult due to possible condensation in the sampling lines. Unfortunately this also means that the uncertainties in the predicted PAH species is large. The detailed soot models attempt to relate the soot formation process to the concentrations of the PAH species, and thus introduce a large uncertainty in the computed soot levels, especially in the centerline regions, where inception is dominant.

The centerline profile of C_2H_2 shows the same characteristics as for the earlier simulation with the two-equation soot model: up to a height of about 15 mm, the computed profile is very close to the experimental profile, and after this height, the computed values continue to rise until a height of about 22 mm, followed by
a rapid decrease. Since the ABF100 mechanism is the parent mechanism for the
ABF31 mechanism, it is expected that the major reaction pathways to form C\textsubscript{2}H\textsubscript{2}
are similar. The centerline profile of C\textsubscript{2}H\textsubscript{4} is well predicted by the model, as are
the profiles of propadiene and 1,3 butadiene.

Figure 6.11 shows the temperature profiles at different heights above the fuel
nozzle using the MOMIC soot model and the ABF100 mechanism. The tempera-
ture profiles are similar to the ones obtained using the two-equation soot model.
At the lower axial heights (15 and 19 mm in Fig. 6.11), the centerline temperatures
are well captured by the model, while at the higher axial locations, the computed
centerline temperatures are lower than the those reported experimentally. In the
wings, at all the four locations the computed temperature profiles are seen to be
broader than the experimental profiles.

Figure 6.12 shows the radial profiles of soot volume fraction at the same axial
heights. In all of these profiles we note that the simulation produces negligible soot
at the centerline, which is consistent with the results obtained using the MOMIC
soot model for the 1 bar ethylene flame. As explained before, the possible causes
for this under-prediction of the centerline soot levels are an underprediction of
PAH species when aromatic growth is modeled in the chemical mechanisms, and
an inherent deficiency in the soot inception model itself.

The computed soot profiles show that there is an over-prediction of soot in
the wings of the flame. The soot levels in the wings are dependent on the surface
growth model in use, as was seen for the 1 bar flame. The surface growth rate is
governed by the steric factor \( \alpha \), which is a measure of the fraction of the sites on
the soot particle surface where reaction can occur. In the absence of a universal
expression for \( \alpha \), a value of unity was used in this simulation. It is possible that
such a value of \( \alpha \) is unrealistically high for this flame, leading to an over-prediction
of soot in the wings.

Another parameter that governs the soot surface growth rate is the multiplying
factor used in the surface growth model. This factor is used to multiply the reaction
rate for C\textsubscript{2}H\textsubscript{2} addition to the soot particle surface. For the 1 bar flame it was found
that the reaction rate had to be multiplied by a factor of two to get good agreement
with the soot volume fractions in the wings. Such an approach has been reported
by Guo et al. [76], who had to multiply the reaction rate by five. In the present
work it was seen for the 1 bar flame that the effect of these two parameters on the soot volume fraction was significant; the peak soot levels in the wings was seen to be almost directly proportional to the product of $\alpha$ and the reaction rate multiplying factor.

The uncertainty in the predicted soot volume fraction when using the MOMIC soot model serves to highlight our limited understanding of the processes of soot formation, growth and oxidation. The detailed soot model does attempt to account for all the known physical and chemical processes that take place; however, since our knowledge of these processes is limited, these submodels often have to be hand-tuned to get good agreement with a certain set of conditions. The steric factor $\alpha$, the reaction rate multiplying factor, and the PAH condensation efficiency $\eta_{\text{condensation}}$ are the free parameters in the MOMIC soot model. The set of values for these parameters which produced a good agreement with experimental data for one flame was seen to be inadequate for a different flame condition. A set of value for these parameters obtained from basic, first-principle calculations will improve the computed results, but such an approach will require us to have a more complete knowledge about the soot formation processes, and will almost certainly produce a soot model which may not be practical for use in a flame calculation.

### 6.4 Summary

In this chapter, the laminar flame solver and the soot models were applied to three laminar diffusion flames at elevated pressures. The first one was a co-flowing, laminar methane-air flame at 10 bar studied experimentally by Joo and Gülder [80], and numerically by Liu et al. [81]. In the experiments, the spectral soot emission technique was used, which has some drawbacks. The measurement is based on the emission of radiation from soot, and thus the temperature can only be measured at a location if there is a sufficiently high soot concentration. The method also suffers from an inversion error, leading to an unphysical drop in the temperature values near the outer edge of the flame annulus. In the present work, the two-equation soot model was used in conjunction with the GRI Mech 3.0 [56] chemical mechanism (excluding all reactions and paths that lead to NO$_x$ formation). The temperature profiles matched closely with the experimental profiles, and in view
of the uncertainties in the measurement technique, the agreement is satisfactory. The soot volume fraction profiles also showed good agreement with experiments.

The next flame that was studied was a 10-bar ethane-air flame studied experimentally by Mandatori and Gülder [82], and modeled by Eaves et al. [70, 21]. The burner for this flame is identical to the burner used for the 10-bar methane-air flame. The flame was modeled using the LYR32 mechanism [63] and the two-equation soot model. The computed temperature values were found to lie within about 5% of the experimental values. The calculated soot volume fractions were also seen to agree with the experiments.

The next flame studied in this work was a 4-bar N₂-diluted ethylene-air flame studied by Kailasanathan et al. [83, 84]. This flame was initially modeled using the ABF31 chemical mechanism [62] and the two-equation soot model. The computed profiles of temperature, soot and some of the gas-phase species showed good agreement with experiment.

The 4-bar flame was also simulated using the ABF100 chemical mechanism [12] and the MOMIC soot model. The profiles of temperature and major gas-phase species showed a good agreement with experiment. However, the soot profiles are affected by the uncertainties and limitations of the MOMIC soot model, and so a good agreement with experiment could not be obtained. However, it is very likely that a good agreement could be obtained by changing some of the model parameters in the MOMIC soot model such as the surface growth enhancement factor, and the steric factor $\alpha$, and the PAH-soot condensation efficiency. The MOMIC soot model is a detailed model that attempts to take into account the different processes in the formation, growth, and oxidation of soot. In the absence of rigorously obtained model parameters, some parts of the model have to be used with hand-tuned model coefficients, and though a given set of these coefficients may produce a very good agreement with some experimental conditions, the trends predicted by the soot model are not universal.
Figure 6.10. Centerline profiles of (a) temperature, (b) benzene, (c) C\textsubscript{2}H\textsubscript{4}, (d) C\textsubscript{2}H\textsubscript{2}, (e) propadiene, and (f) 1,3 butadiene for the 4-bar N\textsubscript{2}-diluted C\textsubscript{2}H\textsubscript{4} flame using the MOMIC soot model.
Figure 6.11. Temperature profiles for the 4-bar \( \text{N}_2 \)-diluted \( \text{C}_2\text{H}_4 \) flame using the MOMIC soot model at various heights above the nozzle: (a) 15 mm (b) 19 mm (c) 21 mm and (d) 23 mm.
Figure 6.12. Soot profiles for the 4-bar N₂-diluted C₂H₄ flame using the MOMIC soot model at various heights above the nozzle: (a) 15 mm (b) 19 mm (c) 21 mm and (d) 23 mm.
Chapter 7

Effect of radiation in co-flow,
sooting laminar diffusion flames

In chapters 5 and 6, the flames were modeled using our baseline, emission-only optically thin model [5, 6, 47]. In this model the reabsorption of radiation by the gas-phase species and soot is ignored, and thus the temperatures calculated using this model can be used to estimate the lower-bound temperatures in such configurations. To investigate the effect that the radiation model has on the simulation results, some of the calculations were repeated using more detailed radiation models [23].

7.1 Radiation in the 1-bar $\text{C}_2\text{H}_4$-air flame

The non-smoking, atmospheric pressure ethylene-air flame of Santoro et al. [24] was revisited to study the effect of radiation on the flame, especially on the computed temperature and soot fields. The first goal of the study was to determine if radiation was at all an important effect to consider for this flame. As shown in the results in chapter 5, the computed temperature and soot volume fraction profiles showed good agreement with experimental data when the optically-thin radiation model was used, and this agreement suggests that the flame may be optically thin.
7.1.1 Simulations without a radiation model

To further quantify the effect of radiation in the C\textsubscript{2}H\textsubscript{4}-air flame, the calculations were repeated using the ABF31 chemical mechanism [62], the two-equation soot model and with the radiation term turned off in the energy equation.

![Temperature profiles at various heights for the 1-bar C\textsubscript{2}H\textsubscript{4}-air flame with and without radiation: (a) 20 mm (b) 30 mm (c) 40 mm (d) 50 mm.](image)

Figure 7.1 shows the computed temperature profiles at four different heights from the burner. At all the axial heights, the temperatures computed using the optically-thin radiation model are significantly lower than the ones computed without radiation. This indicates that heat loss due to radiation is an important aspect of this flame, and for successful modeling of this flame, some kind of radiation model must be used. More importantly, the two simulations establish upper and lower bounds on the temperature field: the temperatures computed without any radiation model sets an upper bound on the predicted temperatures, while the sim-
ulation using the optically-thin radiation model establishes a lower bound. These two cases represent the two extremes as far as the radiation is concerned, and the use of a detailed radiation model which accounts for spectral radiation properties and reabsorption of radiation should produce temperatures in between the two extremes.

An important feature of these temperature profiles is that the difference between the temperatures from the two simulations is of the order of about $\sim 500$ K at the flame centerline, and this difference decreases towards the wings, specially at the higher axial locations, as shown in Figs. 7.1(c) and 7.1(d). At the flame centerline, the temperatures calculated using the optically-thin model show a very good agreement with experimental data, and this suggests that in this region the flame is optically thin. In the wings the optically-thin model predicts temperatures which are closer to the lower end of the uncertainty band, and at some heights the predicted temperatures are below the experimental uncertainty band. This suggests that some reabsorption effects may become important as we move radially outwards.

The adiabatic simulation over-predicts the temperature both in the wings and at the centerline. However, in the wings, the temperature difference is not as large as that at the centerline.

Figure 7.2 shows the computed soot volume fraction profiles at the same heights above the burner. Overall, the calculation without the radiation model produces more soot in the flame. It is interesting to note that the simulation without radiation predicts higher soot levels than the optically-thin model at locations close to the burner in the flame, but at higher axial locations, this trend is reversed. This can be explained in terms of the predicted temperature profiles which show higher temperature for the simulation without radiation; at the lower axial heights, the soot levels are dominated by the formation and growth of soot particles, and the higher temperatures in the adiabatic simulation speeds up both the formation and growth of soot. The higher axial locations are the soot oxidizing regions, and the high temperatures speed up the oxidation of soot in these regions. The result is that in the oxidative environment the soot disappears faster when the temperature is higher.
Figure 7.2. Soot profiles at various heights for the 1-bar C$_2$H$_4$-air flame with and without radiation: (a) 20 mm (b) 30 mm (c) 40 mm (d) 50 mm.

7.1.2 Simulations with detailed radiation models

The ethylene flame was also modeled using detailed radiation models. The ABF31 chemical mechanism was used along with the two-equation soot model. The k-distribution model with narrow-band databases along with the uncorrelated mixture model [50] were used for the calculation of spectral quantities, and the P$_1$ and SP$_5$ RTE solvers were used. Since the flame is expected to be optically thin, it was expected that reabsorption effects would be small. To reduce the computational time, radiation calculations were performed every 1000 time steps, and a total of 90,000 time steps of step size $1 \times 10^{-5}$ seconds were used. Radiation calculations were thus performed 90 times during the course of the simulations. Radiation from CO$_2$, H$_2$O, CO, CH$_4$, and C$_2$H$_4$ was considered, while soot radiation was calculated using the model for soot refractive index as suggested by Chang and
7.1.2.1 Simulations using the P₁ RTE solver

Figure 7.3 shows the computed temperature profiles at various heights from the burner. The RTE solver used in this case is the P₁ solver. At the lower axial heights, the temperature difference between the optically-thin model and the P₁ model are of the order of about 25 K, which indicates that at these heights, the reabsorption effects are small. At the later axial heights, the centerline temperature difference grows to about 50 K.

![Temperature profiles](image)

**(a)**

**Figure 7.3.** Temperature profiles at various heights for the 1-bar C₂H₄-air flame using the P₁ RTE solver: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

Figure 7.4 shows the soot volume fraction profiles at the same heights above the burner. The soot levels predicted by the detailed radiation model are slightly higher than those computed using the optically-thin model. This feature of the results can
be explained if we take into account the fact that the computed temperatures are slightly higher when the P$_1$ model is used; at higher temperatures, the rates of soot formation and growth are enhanced. At the same time, the higher temperatures are also expected to increase the soot oxidation rate, and so the soot levels should decrease faster in the oxidation-dominated post-flame region. Figure 7.5 shows the profiles of soot and temperature along the flame centerline. As seen in the figure, up to a height of about 20 mm the two simulations produce almost identical soot levels at the centerline, and then the simulation using the detailed radiation model produces a higher value of the peak soot. Then, as we move further downstream, and into the oxidation regime, lower soot levels are predicted by the simulation using the detailed radiation model.

**Figure 7.4.** Soot profiles at various heights for the 1-bar C$_2$H$_4$-air flame using the P$_1$ RTE solver: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.
7.1.2.2 Simulations using the \(SP_5\) RTE solver

The ethylene flame was also simulated using the simplified \(P_5\) (\(SP_5\)) RTE solver. Figure 7.6 shows the computed temperature profiles at various heights from the burner. The temperature profiles calculated using the \(SP_5\) model are seen to be similar to those obtained using the \(P_1\) solver. At the lower axial heights, the difference in temperatures predicted by the optically-thin model and the detailed model are of the order of about 10 K, while at the higher axial locations the difference is larger, growing to about 50 K.

Figure 7.7 shows the computed soot profiles at the same axial heights. As in the case of the simulations using the \(P_1\) model, the soot levels are higher when the detailed radiation model is used. The reason for this is also easily explained: since the temperatures are slightly higher when the detailed radiation model is used, and this increases the rates of soot formation and growth. It also follows that in the oxidative region the higher temperatures would also speed up soot oxidation, leading to a faster decrease in soot levels in the post-flame regions. Figure 7.8 shows the profiles of temperature and soot along the flame centerline computed using the \(SP_5\) RTE solver. It is seen that the soot is oxidized faster in the post-flame region.
Figure 7.6. Temperature profiles at various heights for the 1-bar C$_2$H$_4$-air flame using the SP$_5$ RTE solver: (a) 20 mm (b) 30 mm (c) 40 mm (d) 70 mm.

7.2 Radiation in higher pressure flames

The detailed radiation models were also used to simulate the higher-pressure laminar diffusion flames described in chapter 6. The two-equation soot model was used, and as in the case of the 1-bar ethylene-air flame, the narrow-band databases along with the uncorrelated mixture model [50] were used for the calculation of spectral quantities, in conjunction with the P$_1$ and the SP$_5$ RTE solvers. As before, in order to speed up the calculations, the RTEs were solved about 90 times during the course of the simulation, instead of carrying out the expensive radiation calculations at every time step.
7.2.1 The 10-bar methane-air flame

The first high-pressure flame simulated with a detailed radiation model was the 10-bar methane-air flame, described in Sec. 6.1 [80, 81]. As before, the chemical mechanism used was GRI Mech 3.0 [56], from which all species and reactions leading to the formation of NO\textsubscript{x} were removed. As mentioned in Sec. 6.1, the resulting mechanism consists of 36 species and 219 reactions. The P\textsubscript{1} RTE solver was used with the narrowband k-distribution model.

Figure 7.9 shows the computed temperature profiles at various heights above the burner. The temperatures computed using the detailed radiation model are slightly higher than those from the simulation using the optically-thin model. This is consistent with what we would expect: accounting for radiation reabsorption will increase the temperature of the gas-phase. The temperature difference is highest
Figure 7.8. Centerline profiles of temperature and soot for the 1-bar $\text{C}_2\text{H}_4$-air flame using the SP$_5$ RTE solver.

at the centerline, and drops off in the wings. The temperature difference is about 10 K at the lower axial locations, while at the higher locations it increases to about 25 K.

It may seem somewhat counter-intuitive that the effects of radiation reabsorption in this 10-bar flame are not as prominent as those encountered for the 1-bar ethylene flame. However it is to be noted that the 1-bar flame uses a different fuel ($\text{C}_2\text{H}_4$), and the characteristic dimensions are much larger for the 1-bar flame; the fuel tube has a diameter of 3.06 mm for the 10-bar flame, while the ethylene flame has a fuel tube diameter of 11.1 mm. The visible flame height for the 1-bar ethylene flame is also larger: about 88 mm [24], as opposed to the much smaller 9 mm flame in the case of the 10-bar methane flame [80]. The optical thickness of the medium determines to what extent the reabsorption of radiation is important, and even at the elevated pressure of 10 bar, the small dimensions of the flame can make the methane flame optically thin.

Figure 7.10 shows the profiles of soot volume fraction at the same heights from the burner. As in the case of the 1-bar flame, the soot levels are higher for the simulation with the detailed radiation model. The reason for this has already been discussed: higher temperatures lead to an increase in the soot formation and growth rates.
7.2.2 The 10-bar ethane-air flame

The next high-pressure flame that was modeled with a detailed radiation model was the 10-bar ethane-air flame described in Sec. 6.2 \cite{21, 70, 82}. The LYR32 chemical mechanism \cite{63} was used to model this flame. The RTE solver used for this simulation was the simplified P$_5$ or the SP$_5$, while the same narrowband k-distribution model was used for calculating the spectral quantities.

Figure 7.11 shows the computed temperature profiles at various heights above the burner. It is seen that the temperatures calculated using the detailed radiation model are slightly higher than the ones obtained using the optically-thin model. However the differences are much smaller in this flame, of the order of 10 K or less. This suggests that the flame is optically thin, and so the baseline emission-only, optically-thin model is sufficient to capture the radiation effects.
Figure 7.10. Temperature profiles at various heights for the 10-bar CH_4-air flame using the P_1 RTE solver: (a) 3 mm (b) 4 mm (c) 5 mm (d) 6 mm.

Figure 7.12 shows the soot volume fraction profiles at the same heights above the burner. As expected, the soot levels predicted using the detailed model are very close to the ones obtained using the optically-thin model. The detailed radiation model produces slightly more soot, but the difference is almost imperceptible, as the lines lie essentially on top of each other. This is also consistent with the behavior in the other studied flames.

### 7.2.3 The 4-bar ethylene-air flame

The last flame studied using the detailed radiation model was the 4-bar N_2-diluted C_2H_4-air flame, described in Sec. 6.3 [83, 84]. The flame was modeled using the ABF31 mechanism [62] and the two-equation soot model. The P_1 RTE solver was used along with the narrowband k-distribution model.
Figure 7.11. Temperature profiles at various heights for the 10-bar C$_2$H$_6$-air flame using the SP$_5$ RTE solver: (a) 3 mm (b) 4 mm (c) 5 mm (d) 7 mm.

Figure 7.13 shows the computed temperature profiles at various heights above the burner. The temperatures calculated using the detailed radiation model are slightly higher than those obtained using the optically-thin model. This flame is also confirmed to be optically thin, since the temperatures from the two simulations differ by about 15 K at the lower axial heights, while further downstream the difference is about 20 K. Even though this flame is at a higher pressure (4 bar) compared to the ethylene-air flame, the small physical dimensions of the flame make it optically thin. Thus the reabsorption effects are small.

Figure 7.14 shows the soot volume fraction profiles at the same heights above the burner. The simulation with the detailed radiation model produces more soot than the one using the optically-thin radiation model. This is consistent with the behavior seen for the other flames, and is due to the fact that the higher
temperatures speed up the soot formation and growth processes.

7.2.4 The radiant fraction

Of particular interest in radiative heat transfer calculations in reacting flows is to estimate the radiant fraction. The radiant fraction is the fraction of the energy input to the system that is emitted as radiation. For steady-state flow conditions, the energy input to a system $\dot{E}_{in}$ can be calculated as

$$\dot{E}_{in} = \sum_{inlets} \int \left( h_{inlet} + \frac{V_{inlet}^2}{2} + g z_{inlet} \right) \rho_{inlet} u_{inlet} \cdot dA,$$

Figure 7.12. Soot profiles at various heights for the 10-bar C$_2$H$_6$-air flame using the SP$_5$ RTE solver: (a) 3 mm (b) 4 mm (c) 5 mm (d) 7 mm.
where $u_{\text{inlet}}$ is the inlet velocity, $h_{\text{inlet}}$ is the enthalpy of the fluid entering the system through the inlet, $z_{\text{inlet}}$ is the elevation of the inlet above a reference level, and $g$ is the acceleration due to gravity. For the flames studied in this work, the flow velocities are small, and so the kinetic energy term $u_{\text{inlet}}^2$ in Eq. (7.1) can be neglected. If we take the reference level to be at the fuel-tube exit plane, the potential energy term $gz$ can also be neglected. Thus the energy entering the system can be approximated as

$$\dot{E}_{\text{in}} \approx \sum_{\text{inlets}} \int h_{\text{inlet}} \rho_{\text{inlet}} u_{\text{inlet}} \cdot dA.$$  

(7.2)

The source term in the energy equation due to radiation has contributions from

Figure 7.13. Temperature profiles for the 4-bar N$_2$-diluted C$_2$H$_4$ flame at various heights above the nozzle using the P$_1$ RTE solver: (a) 15 mm (b) 19 mm (c) 21 mm and (d) 23 mm.
both emission and absorption. Thus the net source term can be written as

\[ \dot{Q}_{\text{radiation}} = \dot{Q}_{\text{absorption}} - \dot{Q}_{\text{emission}}. \]

An estimate of the total rate of energy radiated for the computational domain \( E_{\text{emission}} \) is given by

\[ \dot{E}_{\text{emission}} = \iiint_V \dot{Q}_{\text{emission}} \, dV, \]

where the integration is performed over the entire volume. The radiant fraction may then be calculated as

\[ f = \frac{\dot{E}_{\text{emission}}}{\dot{E}_{\text{in}}}. \]

Table 7.1 shows the calculated radiant fractions for the flames using the detailed
radiation models.

Table 7.1. Radiant fractions calculated for the simulations with the detailed radiation models

<table>
<thead>
<tr>
<th>Flame</th>
<th>RTE solver</th>
<th>$E_{in} \ (W)$</th>
<th>$E_{emission} \ (W)$</th>
<th>$f(%)$</th>
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</thead>
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<tr>
<td>C$_2$H$_4$, 1 bar</td>
<td>P$_1$</td>
<td>1.9272235</td>
<td>0.586101</td>
<td>30.4117</td>
</tr>
<tr>
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<td>30.5790</td>
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<td>P$_1$</td>
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<td>0.0406603</td>
<td>8.6568</td>
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<tr>
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<td>0.0595768</td>
<td>12.1981</td>
</tr>
<tr>
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<td>P$_1$</td>
<td>0.8506494</td>
<td>0.073646</td>
<td>8.6576</td>
</tr>
</tbody>
</table>

It can be noted that this way of calculating a radiant fraction is somewhat different than what is typically used. The inlet energy to the system is commonly approximated as

$$\dot{E}_{in} \approx \dot{m}_{fuel} \Delta h_{c,fuel},$$

where $\dot{m}_{fuel}$ is the mass flow rate of the fuel, and $\Delta h_{c,fuel}$ is its lower heating value. Further, often the net radiation $\dot{Q}_{radiation}$ is used to estimate the radiant fraction instead of the emission. However, for the air stream at room temperature the contribution of the co-flow to the energy $\dot{E}_{in}$ is expected to be small. Further these flames were seen to be optically thin, and for such flames, the reabsorption contribution to $\dot{Q}_{radiation}$ is small. Hence even though these quantities are defined slightly differently, the value of $f$ based on the two different approaches would be close.

The calculations show that for the 1-bar flame about 30% of the energy of the fuel is lost to radiation, while at higher pressures the value drops to about 10%. Even though all the studied flames are optically thin, at higher pressures the relative importance of radiative heat loss decreases.

7.3 Summary

In this chapter, the detailed radiation models were applied to the co-flowing laminar diffusion flames studied in chapters 5 and 6. For all the flames, the simulation with the detailed radiation model produced slightly higher temperatures compared to the optically-thin radiation model. The soot levels were also seen to be higher for the simulation using the detailed radiation model. This can be attributed to
the higher temperatures predicted by the radiation model; the higher temperature enhances the rates of soot formation and growth, leading to higher soot levels in the inception and growth dominated regions. In the post-flame oxidation region, the soot disappears faster because the higher temperatures also facilitate the oxidation of soot.

The radiative heat transfer calculations using the detailed spectral models were seen to be two orders of magnitude more expensive than the rest of the flame code with soot, and so instead of calculating the radiation source terms at every time step, the calculations were performed no more than 90 times during the course of the entire simulation. For a steady state problem, such as the ones studied in this work this should not affect the final results, but for a true transient problem we would need to compute the radiative heat transfer more frequently. This will significantly increase the computational time.

It was also found that the flames studied in this work are optically thin; the simple, emission-only optically-thin radiation model produced temperatures which lie close to experimental values. Use of the detailed radiation models produced slightly higher temperatures due to reabsorption effects, but the differences in temperature are still smaller than the uncertainties in the experimental data. For these optically thin flames, the use of a detailed radiation model does not significantly alter the results, and in such cases it would be a better option to simply use the emission-only model.
Conclusions and future directions

In this work a pressure-based, general-purpose, finite volume laminar flame code was developed in the OpenFOAM [22] framework. The code uses a realistic representation of molecular transport by using a mixture-averaged approach for calculating the transport coefficients, and stiff ODE solvers for detailed chemistry calculations. A semi-empirical two-equation soot model as well as a detailed soot model, the Method of Moments with Interpolative Closure have been added to the flame solver. An optically-thin, emission-only radiation model was used as the baseline model for computing the radiative heat transfer, and subsequently a number of detailed radiation models have also been coupled to the code. The flame solver was run with 8 different chemical mechanisms ranging in size from 31 species up to 176 species, and was tested with both the semi-empirical and the detailed soot models. The code was also used to study the effects of various aspects of modeling such as gas-phase chemistry, soot and radiation in co-flowing laminar diffusion flames. In this chapter a summary of the simulations along with the key findings, and conclusions are given, followed by some areas where further investigation is required.

8.1 Atmospheric-pressure laminar diffusion flames

The flame solver was first used to model an atmospheric-pressure, co-flowing laminar methane-air diffusion flame which had been studied experimentally and numerically by Mitchell et al. [52] and numerically by Smooke et al. [53], and by Katta
and Roquemore [54]. The flow rate of the fuel is 5.7 cc/s while the co-flowing air flows at the rate of 187.7 cc/s. The predicted profiles of temperature and major gas-phase species showed good agreement with experimental data. Since experimental data for the flame did not include any soot measurements, these simulations did not include any soot models, and served to validate the main flame solver with detailed transport calculations, the optically-thin radiation model, and detailed chemistry.

As a next step the flame solver was used to model a 1-bar ethylene-air flame that had been studied experimentally by Santoro et al. [24], and modeled by Kennedy et al. [57], D’Anna et al. [3], and Dworkin et al. [4]. The fuel flow rate was 3.85 cc/s, while the air flow rate was 713.3 cc/s. The fuel velocity was thus 3.98 cm/s, and the air velocity was 8.90 cm/s. This set of conditions correspond to the non-smoking flame of Santoro et al. [24]. The first set of simulations was performed using an adiabatic boundary condition for the fuel-tube wall, and the two-equation soot model was used. Five gas-phase mechanisms, as summarized in table 5.2 were used in this study. The predicted profiles of temperature, major gas-phase species, and soot showed good agreement with experiments, with the computed profiles generally falling within experimental uncertainty.

A parametric study on the effect of the thermal boundary condition on the fuel-tube wall was also performed for this flame. It was found that the boundary conditions specified on the fuel-tube wall have a significant effect on the computed temperature profiles, especially near the fuel-tube exit plane.

A second set of simulations was performed for the ethylene-air flame using a computational domain that started just downstream of the fuel-tube exit plane, and thus the nozzle wall was not included in the simulation. To account for the fuel preheat, the inlet temperature of the fuel stream was raised to 400 K, as had been done by Dworkin et al. [4]. The results from this set of simulations also were within the experimental error of the measurements used for comparison.

The ethylene-air flame was then modeled using three detailed gas-phase mechanisms containing species up to four ring aromatics (pyrene). The fuel-tube wall was ignored in these simulations, and instead a temperature of 400 K was assumed for the fuel stream. The MOMIC soot model was used in these simulations. Soot was assumed to form by the dimerization of pyrene, and the soot surface growth
and oxidation followed the HACA mechanism of Wang and Frenklach [11]. The peak soot volume fraction in the wings was seen to be dependent mainly on the soot surface growth rate, and to get a good agreement with experimental data the rate of growth of soot particles by the attack of \( \text{C}_2\text{H}_2 \) on the soot particle surface had to be increased by a factor of two. This approach is somewhat arbitrary, but is not without precedent: in their simulations Guo et al. [76] had to increase this reaction rate by a factor of five. A constant steric factor \( \alpha \) of unity was used, and PAH species were assumed to condense on the soot particle surface with an efficiency of 50%. While the temperature and major gas-phase species showed an agreement with experiment comparable to those reported in the literature, the centerline soot levels were under-predicted by the MOMIC soot model by an order of magnitude or more. This is possibly due to a fundamental deficiency in the soot model itself.

8.2 Laminar diffusion flames at elevated pressures

Next the flame solver and soot models were applied to higher pressure laminar diffusion flames. The first flame studied was a 10-bar methane-air flame studied experimentally by Joo and Gülder [80], and numerically by Liu et al. [81]. The fuel flowed at the rate of 0.5 mg/s, while the air flow rate was 40 mg/s. The computational domain included the fuel-tube wall, and a linear temperature variation was prescribed on the fuel-tube wall. The two-equation soot model was used in this simulation. The computed soot profiles were seen to be within a factor of two of the experimentally obtained values. A quantitative comparison with the temperature profiles was not straight-forward, mainly due to the inherent limitations of the spectral soot emission technique used to measure temperature, as mentioned in Sec. 6.1.

The next flame studied in this work was a 10-bar ethane-air flame studied experimentally by Mandatori and Gülder [82], and modeled by Eaves et al. [70, 21]. The fuel flow rate was 0.52 mg/s, while the air flowed at a rate of 12 mg/s. As for the methane-air flame, a linear temperature profile was specified on the fuel-
tube wall. The two-equation soot model was used for this study. Once again, the agreement with experimental data was seen to be good; the simulation results were seen to be within experimental uncertainty. The measured temperatures also suffered from the same deficiencies as in the case of the methane-air flame.

The last flame studied in this work was a 4-bar $N_2$-diluted ethylene-air flame. The fuel stream comprised a mixture of ethylene flowing at the rate of $1.37 \text{ mg/s}$, and nitrogen flowing at $6.41 \text{ mg/s}$. A linear temperature profile was prescribed on the fuel-tube wall. This flame was simulated using the two-equation soot model as well as with the detailed MOMIC soot model. In both cases, the shape of the centerline temperature profile is well represented, but the peak centerline temperature from the simulations is lower than in the experimental values by about 200 K. The location of the centerline peak in the soot volume fraction is also captured by two-equation soot model, and the peak value is within 70% of the experimental values. The centerline soot levels cannot be predicted by the MOMIC soot model. The soot levels in the wings is larger than experiments for both the simulations. The two-equation model is a $C_2H_2$-based model, and since $C_2H_2$ is an important species in hydrocarbon combustion, the soot levels can be expected to be higher. In the case of the MOMIC soot model it may be recalled that the surface growth factor was multiplied by a factor of two, and a steric factor of unity was used. It is possible that the set of model parameters that produced good agreement with experimental data for the 1-bar flame caused the soot levels to be over-predicted in this flame.

8.3 Simulations with detailed radiation models

The baseline simulations in this work used an emission-only, optically-thin radiation model [5, 6]. To determine the importance of radiative heat transfer on the computed temperature, soot and gas-phase species, a study was undertaken with the 1-bar ethylene-air flame [24], where the radiation model was completely turned off. A comparison of the temperature and soot profiles thus obtained with the baseline simulation clearly showed that in order to successfully model the flame, the radiative heat transfer must be properly accounted for.

A detailed radiation model library [23] was coupled with the code in order
to run parametric studies. This library includes detailed spectral calculations and RTE solvers for the intensity field. This detailed radiation model was also used to simulate the flames studied in this work. The k-distribution model with narrow-band databases along with the uncorrelated mixture model [50] was used for the calculation of spectral quantities. Two variants of the method of spherical harmonics method [48], the P₁ and the SP₅ method were chosen for use in these calculations.

The 1-bar ethylene flame was modeled using both of these RTE solvers. It was found that the temperatures computed using the detailed radiation model were higher than that for the baseline calculations. The differences ranged from 25 K to 50 K, and since these differences are smaller than experimental uncertainty, it was concluded that the radiative heat transfer from the flame could be adequately described by the optically-thin radiation model.

The 10-bar methane-air flame [80, 81] was modeled using the P₁ RTE solver. The temperatures obtained using the detailed radiation model were seen to be even closer to the baseline case; the difference in the computed temperatures varied from about 10 K to 25 K. Thus it can be concluded that this flame is optically thin.

The 10-bar ethane-air flame [21, 70, 82] was modeled using the simplified P₅ or the SP₅ RTE solver. For this flame the differences between the temperatures obtained using the radiation model and the baseline simulation were seen to be of the order of 10 K or less.

The 4-bar C₂H₄-N₂-air flame [83, 84] was modeled using the P₁ RTE solver. The difference in temperatures between the baseline model and the detailed radiation model was seen to vary between about 15 K to 20 K.

Thus for all the flames studied in this work, it was found that the baseline optically-thin radiation model adequately accounted for the radiation heat loss. The flames were all optically thin; the 1 bar flame was larger in terms of physical dimensions, but was at a lower pressure, while for the other flames even though the pressures were higher, the small physical dimensions meant that the flame ended up being optically thin. In such a scenario it would be advisable to continue to use the baseline model for the calculation, since the radiation models add considerably to the cost of the simulation.

The effect of the detailed radiation model on the soot yield was also noted.
It was found that with the detailed radiation model the soot levels were slightly higher compared to the baseline calculations. This is explained when we recall that the temperatures computed using the detailed radiation model are slightly higher, leading to a faster rate of soot formation and growth. The higher temperatures also speed up the soot oxidation process, and thus even though the peak soot levels are higher, the soot levels decrease faster in the oxidation-dominated post-flame regions.

### 8.4 Scalability

An important factor in the use of a detailed multi-dimensional code is its scalability. A strong-scaling study was performed using the 32-species chemical mechanism on 8, 16, 32, and 64 cores. Due to the computational cost of the simulations, these tests were not run to a full steady state; rather each case was run for a specified amount of physical time, and the corresponding wall time was noted. Of interest in these tests is the ratio of the wall time using 8 processors to the wall time using \( n \) processors. For this problem, the speedup using 64 processors is seen to be about 6.2, and the parallel efficiency is more than 80% for \( n \leq 64 \). Because the computational cost increases with the size of the chemical mechanism used, for larger mechanisms (\( \sim 100 \) species) the speedup (relative to 8 processors) is expected to be even more.

![Figure 8.1. Strong scaling results for a relatively small axisymmetric laminar flame problem](image)
8.5 Conclusions

It was found that the flame solver with the two-equation soot model is able to adequately describe the gas-phase species, temperature and soot volum fraction fields for the 1-bar ethylene-air as well as the ethane and methane flames, when used in association with a gas-phase chemical mechanism that provides a detailed description of the major species in C\textsubscript{2} hydrocarbon combustion, and the associated reaction pathways. The detailed MOMIC soot model requires the use of larger chemical mechanisms, with more detailed description of the reaction pathways, and including PAH molecules up to pyrene.

The combination of the soot models, along with the base flame solver and the optically-thin radiation model was found to be adequate for the flames studied in this work with the exception of the 4-bar N\textsubscript{2}-diluted flame. Overall a robust, scalable, and efficient numerical tool has been developed which can be used to perform detailed modeling of laminar flames in a variety of configurations.

8.6 Future directions

In the present work several models were used to simulate axisymmetric laminar diffusion flames. Two soot models were used in this work, each with its advantages and disadvantages. There are, however, some areas where more work is required in order to gain a comprehensive understanding of the processes involved in soot modeling.

8.6.1 Prediction the centerline soot levels

In the simulations of the 1-bar ethylene-air using the MOMIC soot model, the soot levels in the wings were correctly predicted by the use of a steric factor of unity and a multiplying factor for the soot surface growth. The centerline soot levels cannot be predicted by the soot model in its current form. According to Dworkin et al. [4], the under-prediction of soot at the flame centerline is due to the underprediction of the PAH concentrations in the flame by the gas-phase mechanism. In this work several chemical mechanisms were used in conjunction
with the MOMIC soot model, but none of them resulted in the successful prediction of the centerline soot levels.

The centerline soot levels are believed to be dependent on the soot inception process, while the soot surface growth processes determine the soot levels in the wings. The soot inception process used in the MOMIC soot model is not necessarily a realistic depiction of the soot formation process. Indeed, the model assumes that two pyrene ($C_{16}H_{10}$) molecules undergo dimerization to form the nascent soot particles. Thus the incipient soot particles are assumed to contain only 32 carbon atoms. In reality the actual number of carbon atoms in the initial soot particle is likely to be much higher. The inception model attempts to link the physics of soot with the gas-phase chemical mechanism, and pyrene is little more than a convenient point where the gas-phase chemistry model ends, and the soot model takes over.

A more realistic soot inception model is likely to improve the predictions of the centerline soot levels.

### 8.6.2 Modeling of smoking flames

The flames modeled in chapters 5 and 6 were all non-smoking flames. In these flames, significant amounts of soot are produced, but the soot is completely oxidized within the flame. Most modeling studies of soot have focused on non-smoking flames. Modeling soot burnout remains one of the major challenges in soot modeling.

Liu et al. [72] used a two-equation soot model to simulate a non-smoking as well as a smoking ethylene flame [24] at one atmosphere pressure. They found that the model used to describe soot oxidation had a large influence on the smoking flame, while for the non-smoking flame the effect was not significant.

A soot oxidation model commonly used in the literature in conjunction with the two-equation soot model [81, 86] is the Nagle-Strickland Constable (NSC) model [71]. In this model, the oxidation of soot by molecular oxygen is assumed to proceed as

$$\frac{1}{2}O_2 + C(S) \rightarrow CO.$$  

(8.1)
The oxidation rate per unit surface area of soot (kg m\(^{-2}\)s\(^{-1}\)) is given by

\[
\dot{\omega}_{NSC} = 120 \left\{ \frac{k_a X_{O_2} \chi}{1 + k_z X_{O_2}} + k_b X_{O_2} (1 - \chi) \right\},
\]

where

\[
\chi = \left(1 + \frac{k_T}{k_b X_{O_2}}\right)^{-1},
\]

\(X_{O_2}\) is the mole fraction of O\(_2\), and the model parameters are calculated as [87]

\[
k_a = 20 \exp\left(\frac{-15098}{T}\right),
\]

\[
k_b = 4.46 \times 10^{-3} \exp\left(\frac{-7650}{T}\right),
\]

\[
k_T = 1.51 \times 10^5 \exp\left(\frac{-48817}{T}\right),
\]

\[
k_z = 21.3 \exp\left(\frac{2063}{T}\right).
\]

Leung et al. [13] mentioned in their work that the NSC oxidation model significantly under-predicts the soot oxidation by O\(_2\). They suggested the use of a different oxidation model, given on a unit area basis (kg m\(^{-2}\)s\(^{-1}\)) by

\[
\dot{\omega}_{Leung} = k_{Leung}[O_2],
\]

where the reaction coefficient \(k_{Leung}\) is given by

\[
k_{Leung} = 1 \times 10^4 T^{-\frac{1}{2}} \exp\left(\frac{-19680}{T}\right).
\]

Liu et al.[72] found that the NSC oxidation model over-predicts the oxidation rate in the ethylene-air diffusion flames. For a non-smoking flame it did not make a big difference, since the soot was oxidized inside the flame. However, for a smoking flame, the model predicted a complete soot burnout, which is not realistic for the given flow conditions. In the present work an attempt was made to model a smoking flame using the soot oxidation pathway suggested by Leung et al. [13], and the model produced a non-smoking flame. This is consistent with the observation of Liu et al., since the Leung oxidation model predicts a higher rate of soot oxidation by O\(_2\). To overcome this difficulty in modeling smoking diffusion flames, Liu et al.
[72] modified the oxidation model, and the new soot model was able to successfully capture the characteristics of the smoking flame.

As a next step of this work, the soot model can be modified to enable it to predict the sooting characteristics of the smoking flame.
Appendix A

Governing Equations for a Non-Sooting Flame

A.1 The Equation of Continuity

The equation of continuity can be written as

\[ \frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} = 0. \]  \hspace{1cm} (A.1)

In the above equation, \( \rho \) is the gas-phase density and \( u \) is the velocity.

A.2 The Species Mass Fraction Equations

The mass fractions of the \( N \) gas-phase species are governed by the following equation:

\[ \frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial [\rho Y_k (u_i + V_{k,i})]}{\partial x_i} = \dot{\omega}_k, \]  \hspace{1cm} (A.2)

\[ \alpha = 1, 2 \ldots N, \]

\[ \sum_{k=1}^{N} Y_k = 1. \]  \hspace{1cm} (A.3)

In this equation, \( Y_k \) is the mass fraction of species \( k \), \( V_k \) is the diffusion velocity corresponding to species \( k \), \( N \) is the number of gas-phase species and \( \dot{\omega}_k \) is the rate
of production of species \( k \) by chemical reactions. Mass diffusion is assumed to be of Fickian type, so that

\[
V_{k,i} = -\frac{D_k}{Y_k} \frac{\partial Y_k}{\partial x_i},
\]

where \( D_k \) is the diffusivity of species \( k \) with respect to the rest of the gas mixture. But this leads to one problem. Conservation of mass requires that summing equations (A.2) over all species yield the equation of continuity (A.1). However, if we directly add the equations (A.2) we obtain

\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} + \frac{\partial}{\partial x_i} \left( \rho \sum_{k=1}^{N} V_{k,i} Y_k \right) = 0.
\]

To make the third term on the left vanish, we therefore require that

\[
\sum_{k=1}^{N} V_{k,i} Y_k = 0.
\]

To alleviate this problem we adopt what is called the correction-velocity method. That is to say, we add a correction velocity to the Fickian diffusion velocity calculated above, and force it to satisfy the above relation. We thus have

\[
V_{k,i} = \hat{V}_{k,i} + V_i^c,
\]

where

\[
\hat{V}_{k,i} = -\frac{D_k}{Y_k} \frac{\partial Y_k}{\partial x_i},
\]

and

\[
V_i^c = \sum_{k=1}^{N} D_k \frac{\partial Y_k}{\partial x_i}.
\]
It is easy to show that now the condition \( \sum_{k=1}^{N} Y_k V_{k,i} = 0 \) is satisfied. Thus the transport equation for the gas-phase species becomes
\[
\frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i Y_k) + \frac{\partial}{\partial x_i} (\rho V_{c,i} Y_k) = \dot{\omega}_k + \frac{\partial}{\partial x_i} \left( \rho D_k \frac{\partial Y_k}{\partial x_i} \right). \tag{A.4}
\]

### A.3 The Momentum Equation

The momentum equations are the Navier-Stokes equations for compressible flow:
\[
\frac{\partial (\rho u_i)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_i u_j) = \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i. \tag{A.5}
\]

Here the stress tensor \( \tau_{ij} \) is defined as
\[
\tau_{ij} = -p \delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial u_m}{\partial x_m} \delta_{ij} = -p \delta_{ij} + \sigma_{ij},
\]
where \( \sigma_{ij} \) is the deviatoric stress, \( g \) is the acceleration due to gravity and \( p \) is the pressure.

### A.4 The Energy Equation

The energy equation is the most complex of the transport equations, as it can be written in many different forms. The basic form of the energy equation can be written in terms of the total energy per unit mass, \( e_t \), which is the sum of the

\[
\sum_{k=1}^{N} V_{k,i} Y_k = \sum_{k=1}^{N} V_{c,i} Y_k + \sum_{k=1}^{N} \dot{V}_{k,i} Y_k = \sum_{k=1}^{N} D_k \frac{\partial Y_k}{\partial x_i} - \sum_{k=1}^{N} D_k \frac{\partial Y_k}{\partial x_i} = 0.
\]

\(^1\)Indeed,
internal energy and the kinetic energy. Thus
\[ e_t = e + \frac{1}{2} u_i u_i. \]

The basic form of the energy equation is
\[ \frac{\partial (\rho e_t)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j e_t) = -\frac{\partial q_j}{\partial x_j} + \dot{Q} + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \rho u_i g_i, \tag{A.6} \]
where \( q \) is the heat flux and \( \dot{Q} \) is the heat source term, which includes radiation. It may be noted that the heat release due to chemical reactions is not a part of the term \( \dot{Q} \) since the chemical energy is part of \( e_t \).

We multiply the momentum equation (2.14) by \( u_i \) to obtain the kinetic energy equation. Multiplication of equation (2.14) by \( u_i \) yields
\[ u_i \frac{\partial (\rho u_i)}{\partial t} + u_i \frac{\partial}{\partial x_j} (\rho u_i u_j) = u_i \frac{\partial \tau_{ij}}{\partial x_j} + u_i \rho g_i. \]
We define the kinetic energy as \( k = \frac{1}{2} u_m u_m \), and after some simplifications, the kinetic energy equation becomes
\[ \frac{\partial (\rho k)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j k) = \frac{\partial (u_i \tau_{ij})}{\partial x_j} - \tau_{ij} \frac{\partial u_i}{\partial x_j} + \rho u_i g_i. \tag{A.7} \]
Subtracting the kinetic energy equation (A.7) from equation (A.6), we obtain the thermal energy equation.
\[ \frac{\partial (\rho e)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j e) = -\frac{\partial q_j}{\partial x_j} + \dot{Q} - p \frac{\partial u_m}{\partial x_m} + \sigma_{ij} \frac{\partial u_i}{\partial x_j}. \tag{A.8} \]
Now we define the viscous dissipation function as
\[ \Phi \equiv \sigma_{ij} \frac{\partial u_i}{\partial x_j}. \]
For low-Mach-number flows, \( \Phi \) is negligible. Further using the definition of the
material derivative,
\[
\frac{D\zeta}{Dt} = \frac{\partial\zeta}{\partial t} + u_j \frac{\partial\zeta}{\partial x_j},
\]
the thermal energy equation can be written as
\[
\rho \frac{De}{Dt} = -\partial q_j \frac{\partial}{\partial x_j} + \dot{Q} - p \frac{\partial u_m}{\partial x_m}.
\tag{A.9}
\]
We now introduce the enthalpy, defined as
\[
h = e + \frac{p}{\rho},
\]
or
\[
e = h - \frac{p}{\rho},
\]
or
\[
\frac{De}{Dt} = \frac{Dh}{Dt} + \frac{p}{\rho^2} \frac{D\rho}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt}.
\]
Now using the definition of the material derivative, we can rewrite the equation of continuity (A.1) as
\[
\frac{D\rho}{Dt} + \rho \frac{\partial u_j}{\partial x_j} = 0,
\]
or
\[
\frac{p}{\rho^2} \frac{D\rho}{Dt} = -\frac{p}{\rho} \frac{\partial u_j}{\partial x_j}.
\]
Thus we have
\[
\rho \frac{De}{Dt} = \rho \frac{Dh}{Dt} - \frac{Dp}{Dt} - p \frac{\partial u_j}{\partial x_j}.
\]
Thus the energy equation (A.8) can be written in terms of enthalpy \(h\) as
\[
\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} - \frac{\partial q_j}{\partial x_j} + \dot{Q},
\tag{A.10}
\]
or in conservative form as
\[
\frac{\partial (\rho h)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j h) = \frac{Dp}{Dt} + \dot{Q} - \frac{\partial q_j}{\partial x_j}.
\tag{A.11}
Now we can write the enthalpy $h$ as the sum of sensible and chemical enthalpies, $h = h_c + h_s$, where

$$h_s = \int_{T_0}^{T} Cp(T) \,dT,$$

and

$$h_c = \sum_{k=1}^{N} h_{c,\alpha} Y_k.$$

Here $h_{c,\alpha}$ is the enthalpy of formation of species $k$ and $C_p$ is the specific heat (in terms of mass) at constant pressure for the mixture. If $C_{p,\alpha}$ is the specific heat for the $\alpha^{th}$ species, then we have

$$C_p = \sum_{k=1}^{N} C_{p,\alpha} Y_k.$$

In terms of the sensible enthalpy $h_s$, equation (A.11) can be written as

$$\frac{\partial(\rho h_s)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j h_s) + \sum_{k=1}^{N} h_{c,\alpha} \left[ \frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial}{\partial x_i} (\rho Y_k u_i) \right] = \frac{Dp}{Dt} + \dot{Q} - \frac{\partial q_j}{\partial x_j}.$$

Using the species-mass-fraction equation (A.2), we have

$$\sum_{k=1}^{N} h_{c,\alpha} \left[ \frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial}{\partial x_i} (\rho Y_k u_i) \right] = \sum_{k=1}^{N} h_{c,\alpha} \left[ \dot{\omega}_k - \frac{\partial}{\partial x_i} (\rho V_{k,i} Y_k) \right].$$

Thus we can write

$$\frac{\partial(\rho h_s)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j h_s) - \sum_{k=1}^{N} h_{c,\alpha} \frac{\partial}{\partial x_j} (\rho V_{k,j} Y_k) =$$

$$\frac{Dp}{Dt} + \dot{Q} - \sum_{k=1}^{N} h_{c,\alpha} \dot{\omega}_k - \frac{\partial q_j}{\partial x_j}. \quad \text{(A.12)}$$
Now the heat flux $\mathbf{q}$ is defined as

$$
q_i = -\lambda \frac{\partial T}{\partial x_i} + \rho \sum_{k=1}^{N} h_k Y_k V_{k,i}
$$

(A.13)

$$
= -\lambda \frac{\partial T}{\partial x_i} + \rho \sum_{k=1}^{N} h_{s,\alpha} Y_k V_{k,i} + \rho \sum_{k=1}^{N} h_{c,\alpha} Y_k V_{k,i},
$$

(A.14)

where $\lambda$ is the thermal conductivity of the mixture. Now

$$
h_s = \sum_{k=1}^{N} Y_k h_{s,\alpha} = \sum_{k=1}^{N} Y_k \int_{T_0,\alpha}^{T} C_{p,\alpha} dT'.
$$

Differentiation yields

$$
\frac{\partial h_s}{\partial x_j} = \sum_{k=1}^{N} Y_k \frac{\partial h_{s,\alpha}}{\partial x_j} + \sum_{k=1}^{N} h_{s,\alpha} \frac{\partial Y_k}{\partial x_j}.
$$

We can evaluate the first derivative on the right-hand side using Leibniz’s rule for differentiating under the integral sign:

$$
\frac{\partial h_{s,\alpha}}{\partial x_j} = \frac{\partial}{\partial x_j} \int_{T_0,\alpha}^{T} C_{p,\alpha} dT' = C_{p,\alpha}(T) \left( \frac{\partial T}{\partial x_j} \right) - C_{p,\alpha}(T_0,\alpha) \left( \frac{\partial T_0,\alpha}{\partial x_j} \right) + \int_{T_0,\alpha}^{T} \left( \frac{\partial C_{p,\alpha}}{\partial x_j} \right) dT'.
$$

Rearranging, we have

$$
-\lambda \frac{\partial T}{\partial x_j} = -\rho \alpha \frac{\partial h_s}{\partial x_j} + \rho \sum_{k=1}^{N} h_{s,\alpha} \frac{\partial Y_k}{\partial x_j},
$$

where $\alpha = \frac{\lambda}{\rho C_p}$ is the thermal diffusivity of the mixture.

Using the definition of $\mathbf{q}$ (equation A.14), we can write

$$
q_i = -\rho \alpha \frac{\partial h_s}{\partial x_i} + \rho \sum_{k=1}^{N} h_{s,\alpha} \frac{\partial Y_k}{\partial x_i} + \rho \sum_{k=1}^{N} h_{c,\alpha} Y_k V_{k,i} + \rho \sum_{k=1}^{N} h_{c,\alpha} Y_k V_{k,i}
$$
\[-\rho \frac{\partial h_s}{\partial x_i} + \rho \sum_{k=1}^{N} h_{s,\alpha} \frac{\partial Y_k}{\partial x_i} + \rho \sum_{k=1}^{N} h_{s,\alpha} Y_k V_{i}^c + \rho \sum_{k=1}^{N} h_{c,\alpha} Y_k V_{k,i} \]
\[- \rho \sum_{k=1}^{N} h_{s,\alpha} \left( D_k \frac{\partial Y_k}{\partial x_i} \right) \]
\[= -\rho \alpha \frac{\partial h_s}{\partial x_i} + \rho \sum_{k=1}^{N} h_{s,\alpha} \frac{\partial Y_k}{\partial x_i} \left( 1 - \frac{1}{Le_k} \right) + \sum_{k=1}^{N} h_{c,\alpha} \rho Y_k V_{k,i} + \rho V_i^c h_s, \]

where \( Le_k = \frac{\alpha}{D_c} \) is the Lewis number for species \( k \). Substituting this expression for \( q \) into the sensible enthalpy equation (A.13) and simplifying, we get the final form of the energy equation in terms of sensible enthalpy:

\[ \frac{\partial (\rho h_s)}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i h_s) + \frac{\partial}{\partial x_i} (\rho V_i^c h_s) = \frac{D_p}{Dt} - \sum_{k=1}^{N} \dot{\omega}_k h_{c,\alpha} \tag{A.15} \]
\[ + \frac{\partial}{\partial x_i} \left( \rho \alpha \frac{\partial h_s}{\partial x_i} \right) + \frac{\partial}{\partial x_i} \left[ \rho \alpha \sum_{k=1}^{N} \left( \frac{1}{Le_k} - 1 \right) h_{s,\alpha} \frac{\partial Y_k}{\partial x_i} \right] + \dot{Q}. \]
Governing Equations for a Sooting Flame

For a sooting flame, the gas-phase species and the soot chemically react, and thus an additional contribution comes into the equation of gas-phase mass-fractions. The equation of continuity is also modified\(^1\), as mass can move from the gas-phase to soot and vice versa.

\section*{B.1 Gas-Phase Mass Fraction Equations}

The species mass-fraction equations become

\[ \frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial}{\partial x_i} [\rho Y_k (u_i + V_{k,i})] = \dot{\omega}_k + \dot{\omega}_{k,\text{soot}}. \]  
\[(B.1)\]

Here as in equation (A.1), \(\rho\) is the gas-phase density and \(u\) is the velocity of the gas-phase. The new term \(\dot{\omega}_{k,\text{soot}}\) is the source term due to the soot-gas reactions.

It is to be noted that the gas-phase mass fractions \(Y_k\) are given with respect to the total \textit{gas-phase} mass, as opposed to the total mass. In this way if \(m_g\) is the total mass of the gas-phase species, and \(m_s\) is the mass of soot, we define the soot mass fraction as

\[ Y_s \equiv \frac{m_s}{m_g + m_s}, \]

\(^1\)To our knowledge, this has not been taken into consideration in any other modeling study.
and the gas-phase mass fractions are defined as

\[ Y_k \equiv \frac{m_k}{m_g}, \]

where \( m_k \) is the mass of gas-phase species \( k \). This ensures that

\[ \sum_{k=1}^{N} Y_k = 1. \]

The mole fractions of the gas-phase species are also defined in terms of the total number of moles of the gas-phase, and so the relationships given in section 2.2.4 remain unchanged.

### B.2 The Equation of Continuity

When we add all the equations (B.1), the source terms for the gas-phase reactions cancel out, but the contribution of the soot-gas sources is non zero. Accordingly, the equation of continuity is obtained as

\[ \frac{\partial \rho}{\partial t} + \frac{\partial \rho u_j}{\partial x_j} = \gamma_{\text{soot}}, \tag{B.2} \]

where \( \gamma_{\text{soot}} \) is the net effect of the soot-gas reactions, and is given by

\[ \gamma_{\text{soot}} = \sum_{k=1}^{N} \dot{\omega}_{k,\text{soot}}. \]

A similar consideration is needed for the diffusion velocity \( V_k \). As before we require the term \( \sum_{k=1}^{N} Y_k V_{k,i} \) to vanish; using the correction-velocity approach we arrive at the same result obtained earlier for the non-sooting case, namely

\[ V_{k,i} = \hat{V}_{k,i} + V_{i}^{c}, \]

where

\[ \hat{V}_{k,i} = -\frac{D_k}{Y_k} \frac{\partial Y_k}{\partial x_i}, \]
and

\[ V_i^c = \sum_{k=1}^{N} D_k \frac{\partial Y_k}{\partial x_i}. \]

The species mass-fraction equations thus become

\[ \frac{\partial (\rho Y_k)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j Y_k) + \frac{\partial}{\partial x_j} (\rho V_i^c Y_k) = \dot{\omega}_k + \dot{\omega}_{k,\text{soot}} + \frac{\partial}{\partial x_j} \left( \rho D_k \frac{\partial Y_k}{\partial x_j} \right). \quad (B.3) \]

### B.3 The Momentum Equation

The momentum equation remains the same as for the non-sooting case\(^2\), namely

\[ \frac{\partial (\rho u_i)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_i u_j) = \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i, \quad (B.4) \]

and as before, \( \tau_{ij} \) is the stress tensor, defined as

\[ \tau_{ij} = -p \delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial u_m}{\partial x_m}. \]

### B.4 The Energy Equation

Similar to the non-sooting case, we start from the general form of the energy equation. The energy variable is the stored energy \( e_t \) defined as

\[ e_t = e + \frac{1}{2} u_m u_m = e + k. \]

The energy equation in terms of \( e_t \) is identical to equation (A.6), namely

\[ \frac{\partial (\rho e_t)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j e_t) = -\frac{\partial q_j}{\partial x_j} + \dot{Q} + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \rho u_i g_i. \quad (B.5) \]

Once again we derive the kinetic-energy equation by multiplying the momentum equation (B.4) with \( u_i \). However, we have extra terms in this case as the left-hand side of the continuity equation (B.2) is not zero. Multiplyng equation (B.4) by

\(^2\)We assume there to be no drag force due the presence of soot particles in the flow.
Using the definition of the material derivative, we finally obtain the kinetic energy equation as

\begin{equation}
\rho \frac{Dk}{Dt} + 2k \gamma_{soot} = \frac{\partial}{\partial x_j} (u_i \tau_{ij}) - \tau_{ij} \frac{\partial u_i}{\partial x_j} + \rho u_i g_i.
\end{equation}

Now the energy equation can be written in terms of the material derivative. We start from the basic form (B.5):

\begin{equation}
\rho \frac{De_t}{Dt} + \rho u_j \frac{\partial e_t}{\partial x_j} + e_t \left[ \frac{\partial p}{\partial t} + \frac{\partial \rho u_j}{\partial x_j} \right] = -\frac{\partial q_j}{\partial x_j} + \dot{Q} + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \rho u_i g_i.
\end{equation}

Thus the energy equation becomes

\begin{equation}
\rho \frac{De_t}{Dt} + e_t (\gamma_{soot}) = -\frac{\partial q_j}{\partial x_j} + \dot{Q} + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \rho u_i g_i.
\end{equation}

Subtracting equation (B.6) from equation (B.7), we obtain an equation for the internal energy $e$:

\begin{equation}
\rho \frac{De}{Dt} + (e - k) \gamma_{soot} = -\frac{\partial q_j}{\partial x_j} + \dot{Q} + \tau_{ij} \frac{\partial u_i}{\partial x_j}.
\end{equation}

Once again the stress tensor is defined as

\[ \tau_{ij} = -p \delta_{ij} + \sigma_{ij}. \]
For a low-Mach-number flow, the viscous dissipation is neglected, and thus we have
\[
\rho \frac{De}{Dt} + (e - k)\gamma_{soot} = -\frac{\partial q_j}{\partial x_j} + \dot{Q} - p \frac{\partial u_m}{\partial x_m}.
\] (B.8)

We use the definition of enthalpy \( h = e + \frac{p}{\rho} \) and the equation of continuity (B.2) to obtain an equation for the enthalpy. We have
\[
e = h - \frac{p}{\rho},
\]
or \[
\frac{De}{Dt} = \frac{Dh}{Dt} - \frac{1}{\rho} \frac{DP}{Dt} + \frac{p}{\rho^2} \frac{D\rho}{Dt}.
\]

Now from the equation of continuity (B.2) we get
\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_j)}{\partial x_j} = \gamma_{soot},
\]
or \[
\frac{D\rho}{Dt} + \rho \frac{\partial u_j}{\partial x_j} = \gamma_{soot},
\]
or \[
\frac{p}{\rho^2} \frac{D\rho}{Dt} = \gamma_{soot} \frac{p}{\rho^2} - \frac{p \partial u_j}{\rho \partial x_j}.
\]

Thus the enthalpy equation becomes
\[
\rho \frac{Dh}{Dt} + (h - k)\gamma_{soot} = \frac{Dp}{Dt} - \frac{\partial q_j}{\partial x_j} + \dot{Q}.
\] (B.9)

In conservative form the equation becomes
\[
\frac{\partial (\rho h)}{\partial t} + \frac{\partial (\rho u_j h)}{\partial x_j} = \frac{Dp}{Dt} + \dot{Q} + k\gamma_{soot} - \frac{\partial q_j}{\partial x_j}.
\] (B.10)

Once again, we split the enthalpy into the sensible part and the chemical (formation) part as
\[
h = h_s + h_c,
\]
where

\[ h_s = \int_{T_0}^{T} C_p(T') dT' = \sum_{k=1}^{N} Y_k \int_{T_0}^{T} C_{p_k}(T') dT', \]

and

\[ h_c = \sum_{k=1}^{N} h_{c,\alpha} Y_k. \]

Substituting this into equation (B.10), we get

\[
\frac{\partial \rho h_s}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j h_s) + \sum_{k=1}^{N} h_{c,\alpha} \left[ \frac{\partial \rho Y_k}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j Y_k) \right] = D_p \frac{\partial h_c}{\partial t} + \dot{Q} + k \gamma_{soot} - \frac{\partial}{\partial x_j} \left( \rho \alpha \frac{\partial h_s}{\partial x_i} \right). \tag{B.11}
\]

Now from equation (B.3) we have

\[
\frac{\partial \rho Y_k}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j Y_k) = \dot{\omega}_k + \dot{\omega}_{k,soot} - \frac{\partial}{\partial x_j} (\rho V_{k,i} Y_k). \]

Substituting this relation and the definition of the heat flux \( q \) (equation A.14) into equation (B.11) and simplifying, we get the final form of the energy equation for a sooting case as

\[
\frac{\partial (\rho h_s)}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i h_s) + \frac{\partial}{\partial x_i} (\rho V_{i}^c h_s) = D_p \frac{\partial h_c}{\partial t} - \sum_{k=1}^{N} (\dot{\omega}_k + \dot{\omega}_{k,soot}) h_{c,\alpha}
\]

\[
+ \frac{\partial}{\partial x_i} \left( \rho \alpha \frac{\partial h_s}{\partial x_i} \right) + \frac{\partial}{\partial x_i} \left[ \rho \alpha \sum_{k=1}^{N} \left( \frac{1}{Le_k} - 1 \right) h_{s,\alpha} \frac{\partial Y_k}{\partial x_i} \right] + \dot{Q} + k \gamma_{soot}. \tag{B.12}
\]

Comparing with the non-sooting case (equation A.16), we see that this equation has two extra terms due to soot, \( \dot{\omega}_{k,soot} \) and \( \gamma_{soot} \). It is easy to show that if we set \( \gamma_{soot} \) and \( \dot{\omega}_{k,soot} \) to zero in all the equations described in this chapter, we recover the equations for a non-sooting flame (appendix A).
The MOMIC soot model

The Method of Moments with Interpolative Closure (MOMIC) [15, 11, 43] was used in this work. This appendix gives a brief discussion of the equations arising from the application of the method.

C.1 Coagulation

C.1.1 Brownian collisions

Brownian collisions among a population of particles is described by Smoluchowski’s equations, Eq. (3.20)

\[
\frac{dN_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{j,i-j} N_j N_{i-j} - \sum_{j=1}^{\infty} \beta_{i,j} N_i N_j, \tag{C.1}
\]

where \(N_i\) is the number density of particles of size class \(i\), and \(\beta_{i,j}\) is the collision coefficient between particles of size classes \(i\) and \(j\). The collision coefficient \(\beta\) depends in a non-linear manner on the sizes of the colliding particles, and so a closed-form solution to the above equation cannot be found.

In the MOMIC soot model, the \(r\)th moment of the soot particle size distribution function are defined as in Eq. (3.7)

\[
M_r = \sum_{i=1}^{\infty} m_i^r N_i.
\]
In terms of the moments, Smoluchowski’s equations can be written as

\[
\frac{dM_0}{dt} = -G_0 = -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{ij} N_i N_j, \tag{C.2}
\]

\[
\frac{dM_r}{dt} = G_r = \frac{1}{2} \sum_{s=1}^{r-1} \left( \frac{r}{s} \right) \left( \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{ij} m_i^s m_j^{r-s} N_i N_j \right), \quad r = 2, 3, \ldots, 5. \tag{C.3}
\]

The specific form of the collision coefficient \( \beta \) depends on the coagulation regime, which is characterized by the Knudsen number, \( K_n = 2\lambda_f/d \), where \( \lambda_f \) is the mean free path for the gas-phase and \( d \) is the particle diameter. In our work we focus on the free-molecular regime, characterized by \( K_n >> 1 \). In this limit, the collision coefficient for spherical soot particles is given as \([11, 15]\)

\[
\beta_{ij} = K_f \sqrt{\frac{1}{m_i} + \frac{1}{m_j} \left( m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}} \right)^2}, \tag{C.4}
\]

where \( m_i \) and \( m_j \) are the masses of the colliding particles, and

\[
K_f = \varepsilon \sqrt{\frac{6k_B T}{\rho_s}} \left( \frac{3m_C}{4\pi \rho_s} \right),
\]

where \( \varepsilon \) is the van der Waals enhancement factor, which has a value of 2.2. It may be noted that the mass of the particle of class \( i \) is characterized by the number of carbon atoms in that particle.

Substituting Eq. (C.4) into Eq. (C.2) we obtain

\[
G_0 = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} K_f \sqrt{\frac{1}{m_i} + \frac{1}{m_j} \left( m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}} \right)^2} N_i N_j,
\]

\[
= \frac{K_f}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left( m_i + m_j \right)^{\frac{1}{2}} m_i^{-\frac{1}{2}} m_j^{-\frac{1}{2}} \left( m_i^{1/3} + m_j^{1/3} \right)^2 N_i N_j,
\]

\[
= \frac{K_f}{2} M_0^2 f^{(0,0)}_i, \]

where \( M_0 \) is the mass of the soot particle.
where the grid function $f_t^{(0,0)}$ is as defined in Eq. (3.23):

$$f_t^{(x,y)} \equiv \frac{1}{M_0^2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i + m_j)^l (m_i^{1/3} + m_j^{1/3})^2 m_i^{x-\frac{1}{2}} m_j^{y-\frac{1}{2}} N_i N_j.$$

Similarly, substituting Eq. (C.4) into Eq. (C.3) we obtain

$$G_r = \frac{1}{2} \sum_{s=1}^{r-1} \binom{r}{s} \left[ \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} K_f \sqrt{\frac{1}{m_i} + \frac{1}{m_j}} \left( m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}} \right)^2 m_i^{r-s} N_i N_j \right]$$

$$= \frac{K_f}{2} \sum_{s=1}^{r-1} \binom{r}{s} \left[ \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i + m_j)^{\frac{1}{3}} \left( m_i^{\frac{1}{3}} + m_j^{\frac{1}{3}} \right)^2 m_i^{s-r} m_j^{r-s} N_i N_j \right],$$

$$= \frac{K_f}{2} M_0^2 \sum_{s=1}^{r-1} \binom{r}{s} f_t^{(s,r-s)}.$$

### C.1.2 The grid function

To evaluate the grid functions we use the binomial theorem for a positive integral index:

$$(a + b)^n = \sum_{s=0}^{n} \binom{n}{s} a^{n-s} b^s. \quad (C.5)$$

Now we have,

$$f_t^{(x,y)} = \frac{1}{M_0^2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (m_i + m_j)^l (m_i^{1/3} + m_j^{1/3})^2 m_i^{x-\frac{1}{2}} m_j^{y-\frac{1}{2}} N_i N_j.$$

Using the binomial theorem (Eq. (C.5)) we have

$$f_t^{(x,y)} = \frac{1}{M_0^2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ \sum_{s=0}^{l} \binom{l}{s} m_i^{l-s} m_j^s \right] (m_i^{1/3} + m_j^{1/3})^2 m_i^{x-\frac{1}{2}} m_j^{y-\frac{1}{2}} N_i N_j,$$

$$= \frac{1}{M_0^2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ \sum_{s=0}^{l} \binom{l}{s} m_i^{l+x-s-\frac{1}{6}} m_j^{s+y-\frac{5}{6}} (m_i^{\frac{2}{3}} + 2 m_i^{\frac{1}{3}} m_j^{\frac{1}{3}} + m_j^{\frac{2}{3}}) \right] N_i N_j,$$

$$= \frac{1}{M_0^2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left[ \sum_{s=0}^{l} \binom{l}{s} \left\{ m_i^{l+x-s-\frac{1}{6}} m_j^{s+y-\frac{5}{6}} + m_i^{l+x-s-\frac{1}{6}} m_j^{s+y+\frac{1}{6}} + 2 m_i^{l+x-s-\frac{1}{6}} m_j^{s+y-\frac{5}{6}} \right\} \right] N_i N_j,$$
\[ = \sum_{s=0}^{l} \binom{l}{s} \left( \mu_{l+x-s+y} + \mu_{l+x-s-y} + 2\mu_{l+x-s} \right), \]

where \( \mu_k \) is the reduced soot moment of order \( k \), defined as \( \mu_k \equiv \frac{M_k}{M_0} \). The fractional-order moments are obtained from the integer-order moments by interpolation.

The grid function of order \( \frac{1}{2} \) is obtained from the grid functions of integer order by interpolation. Frenklach and Wang [11] and Frenklach [15] proposed the following interpolation schemes for numerical efficiency and accuracy: to obtain \( f_{1}^{(x,y)} \), the recommended interpolations are

1. among \( f_{0}^{(x,y)}, f_{1}^{(x,y)}, f_{2}^{(x,y)} \), and \( f_{3}^{(x,y)} \) for \((x,y) = (0,0), (1,1), (2,2), (3,3)\),
2. among \( f_{0}^{(x,y)}, f_{1}^{(x,y)}, f_{2}^{(x,y)} \) for \((x,y) = (1,3), (2,3), (3,3)\),
3. between \( f_{0}^{(x,y)} \), and \( f_{1}^{(x,y)} \) for \((x,y) = (1,4)\).

### C.2 The transport equations

The transport equations for the \( r \)th soot concentration moment are given in literature as [2, 20]

\[
\frac{\partial M_r}{\partial t} + \frac{\partial}{\partial x_j} \left( u_j M_r \right) = \frac{\partial}{\partial x_j} \left( D_{p,1} \frac{\partial M_r}{\partial x_j} \right) - \frac{\partial}{\partial x_j} \left( V_{T,j} M_r \right) + \dot{M}_r, \tag{C.6}
\]

where \( V_T \) is the thermophoretic velocity for soot, given by

\[
V_{T,i} = -0.55 \frac{\nu}{T} \frac{\partial T}{\partial x_i},
\]

where \( \nu \) is the kinematic viscosity of the gas mixture, \( \dot{M}_r \) is the source term, and \( D_{p,1} \) is the diffusion coefficient for the smallest soot particle, given by

\[
D_{p,1} = \frac{3}{2\rho} \sqrt{\frac{mk_BT}{2\pi}} \left( 1 + \frac{\pi \alpha T}{8} \right) \frac{1}{d_1},
\]

\( ^1 \mu_k \) is also referred as the size moment. In fact, \( \mu_1 = \frac{M_1}{M_0} \) can be considered as a measure of the average size of a soot particle.
where $\bar{m}$ is the mean mass of the gas molecules, $\alpha_T$ is the thermal accommodation factor (0.9), and $d_1$ is the diameter of the smallest soot particle.

Instead of using the Eq. (C.6), we ignore the molecular diffusivity of the soot, and start with the equation of number density from the two-equation soot model:

$$\frac{\partial \rho N_s}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j N_s) = -\frac{\partial}{\partial x_j} (\rho V_{T,j} N_s) + S_N.$$  

It is to be noted that the number density in the two-equation model has the units of particles/kg, whereas in the MOMIC model the appropriate unit is particles/m$^3$. If $\tilde{N}$ is in units of particles/m$^3$, we have

$$N_s = \frac{\tilde{N}}{\rho}.$$  

The transport equation for $\tilde{N}$ can be written as

$$\frac{\partial \tilde{N}}{\partial t} + \frac{\partial}{\partial x_j} (u_j \tilde{N}) = -\frac{\partial}{\partial x_j} (V_{T,j} \tilde{N}) + S_\tilde{N}. \hspace{1cm} (C.7)$$  

We assume that an equation similar to Eq. (C.7) holds for the number density for each particle size class; the transport equation for the number density of particles of size class $k$ is therefore written as

$$\frac{\partial \tilde{N}_k}{\partial t} + \frac{\partial}{\partial x_j} (u_j \tilde{N}_k) = -\frac{\partial}{\partial x_j} (V_{T,j} \tilde{N}_k) + S_\tilde{N}_k. \hspace{1cm} (C.8)$$  

Taking the moments of Eq. (C.8), we write the equation for the $r$th moment as

$$\frac{\partial M_r}{\partial t} + \frac{\partial}{\partial x_j} (u_j M_r) = \frac{\partial}{\partial x_j} \left( \mu \frac{\partial M_r}{\rho \partial x_j} \right) - \frac{\partial}{\partial x_j} (V_{T,j} M_r) + \dot{M}_r, \hspace{1cm} (C.9)$$  

where the term $\frac{\partial}{\partial x_j} \left( \mu \frac{\partial M_r}{\rho \partial x_j} \right)$ has been added to make the numerical solution stable. The soot Schmidt number is taken as 60 in this work.
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