High-Fidelity Modeling of Buoyancy-Driven Diffusion Flames
Towards Fire Suppression

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Buoyancy-driven diffusion flames have been widely studied as a canonical fire configuration due to practical and scientific interests. Numerical investigations are conducted in this dissertation to improve understandings of interactions and couplings among turbulence, chemistry, soot, and multiphase radiation in buoyancy-driven diffusion flames. A high-fidelity modeling framework based on OpenFOAM-5.x, including detailed models for chemistry, radiation, and soot, is developed to improve the numerical accuracy and the computational efficiency with scale-resolved simulations. A Monte Carlo ray tracing (MCRT) based radiation solver coupled with line-by-line databases is developed to describe gas and soot radiation. Detailed and efficient radiation models for water mists are developed and coupled with the MCRT solver. An adaptive hybrid integration chemistry solver is implemented to speed up finite-rate chemistry integration. A semi-empirical two-equation soot model is incorporated to describe soot dynamics.
The developed multi-physical platform is systematically verified through a series of combustion-radiation systems including a laminar ethylene diffusion flame and four laminar methane diffusion flames with good agreement. The developed platform is subsequently employed to investigate a laboratory-scale turbulent pool fire. Good agreement with experiments on radiative heat fluxes, and with theories on flame temperature, velocity and puffing frequency, is achieved. Detailed investigations on interactions among chemistry, soot, radiation, and turbulence are performed to gain physical insights on modeling chemistry, soot and radiation.

Drawn on the database from high-fidelity pool fire simulations, three physics-based reduced-order models including a flamelet model considering re-absorption, an optimized two-step mechanism for chemistry, and a simple soot model based on the laminar smoke point concept, are developed. Encouraging results are obtained using the reduced-order models with considerable savings in computational cost. Finally, to investigate radiative attenuation of water mists in fire suppression, a radiation model considering anisotropic scattering for water mists is developed and validated against theoretical values, and is adopted to obtain benchmark results for development of reduced-order radiation models.
High-Fidelity Modeling of Buoyancy-Driven Diffusion

Flames Towards Fire Suppression

Bifen Wu

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High-Fidelity Modeling of Buoyancy-Driven Diffusion Flames Towards Fire Suppression

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Chapter 1

Introduction

1.1 Motivation

Fire, as a means of converting the latent energy in flammable materials to sensible heat through the form of combustion, has been playing an important role in the human history. The energy released from fires through various configurations has boosted the development of early human civilization and many modern industries. The increasing understanding of fires and combustion phenomena and the advancement in combustion control technologies have further benefited human communities worldwide in various aspects.

Fires can occur as part of the natural cycle in the ecosystem, e.g., the wildland fires, which effectively remove dead materials and release nutrients back to the environment so that the wildland regains vigor in the post-fire environment. However, fire spurred by unwanted combustion of fuels and/or uncontrollable flame spreads is an ever-present danger [10] that challenges the entire society, including policy making, public infrastructures, construction industries, insurance industries, individual business,
and personal health care systems. In 2015, U.S. fire departments responded to an estimated total of 1,345,500 fires. These fires killed 3,280 civilians and caused 15,700 civilian injuries [1]. Beyond the obvious life-safety aspect, unwanted fires also cause extraordinary property damages. For example, the property loss due to fires in 2015 was about $14.3 billion dollars [1]. Into the new era of economical and technological skyrockets, fire safety faces new challenges, especially with increasing magnitudes of warehouse storage and growing usage of battery and plastic materials. Advancing the technologies in fire prevention, detection and suppression is much more needed than ever, to improve fire safety, life quality, and environmental health.

Development of effective and efficient fire detection and suppression systems requires an in-depth understanding of fundamental fire dynamics under various conditions. As shown in Fig. 1.1, real-world fires take place at vastly different conditions due to a variety of human and natural causes. For almost all the real-world fires, extremely complex physicochemical processes, typically involving multiphase flows, chemical reactions of real fuels (gas, liquid, and/or solid), and heat transfers in convective/conductive/radiative forms, are present. Understanding the underlying physics in these key processes is essential to improving the existing designs of fire detection and protection systems. Fundamental fire research on canonical fire configurations is of critical importance to provide a comprehensive picture of these physical processes and their interactions.

Motivated by these existing challenges in fire research, this dissertation focuses
on investigating buoyancy-driven diffusion flames, a canonical fire configuration, using high-fidelity numerical simulations. Special attention is paid to the development of accurate radiation models, to examine the sensitivity of radiation subject to chemistry, soot and turbulence, and to improved understanding of radiation effects on both flames and water mists.

1.2 Buoyancy-driven diffusion flames

Among various fire configurations, buoyancy-driven diffusion flames, such as turbulent pool fires at normal gravity and/or at wind-blown conditions, have been commonly employed to understand fundamental mechanisms of fire propagation and to develop scaling relationships from small- to large-scale fires for decades [11]. This dissertation
will specifically focus on a turbulent pool fire configuration under atmospheric condition. Buoyancy, induced by gravity and density gradient through combustion, propels the flow above a fuel pool and drives the growth of fire to form turbulent flames downstream. The fuel pool evaporates by absorbing radiative and conductive heat, supporting continuous burning. The presence of rich and complex physical processes makes this particular fire configuration an important field of study in fire safety engineering.

Experimental efforts have constantly advanced the understanding of buoyancy-driven diffusion flames \cite{12, 13, 14, 15}. Dating back to 1970s, McCaffrey \cite{16} measured flame temperatures and vertical velocities along the centerline of methane pool fires. Since then, the experimentally-derived empirical correlations for temperature and velocity have been widely used for verification and validation in pool fire studies \cite{17, 18}. To identify the mechanisms of periodic oscillation, Cetegen and Ahmed \cite{19} experimentally investigated the puffing phenomena of propane pool fires and helium plumes, and proposed that the puffing frequency is scaled by the square root of the pool diameter.

To explore the radiation features in turbulent pool fires, Klassen and Gore \cite{20} studied the burning rate, radiative loss, emissive and absorption temperatures, and flame heights for liquid pools with a diameter ranging from 4.6 to 100 cm. The measured radiation-relevant data have been widely adopted to assess the performance of radiation models \cite{21, 22}. However, spatially resolved measurements of combustion-relevant quantities, such as temperature and species concentrations, were not available in this
collection of experiments. Weckman and Strong [23] measured the radial velocity and temperature at different elevations downstream of a medium-scale methanol pool fire to investigate the mixing and entrainment patterns. The dynamics of these methanol pool fires is relatively less impacted by radiation, and they are often employed to validate sub-grid fluid dynamics models [24, 25]. Comprehensive reviews of suitable experiments for validating numerical methods are provided in [26, 27]. A more recent model validation framework and associated experimental and numerical databases are available in [28, 29].

With the aid of these experimental databases and the rapid advancement of high performance computing, large eddy simulations (LES) have been widely applied to turbulent diffusion flames to understand different pertinent physical processes and to evaluate the performance of different models since early 2000s [18, 21, 24, 25, 30, 31]. Table 1.1 presents a brief representative, but not exhaustive, summary of previous numerical studies on turbulent pool fires. Models with different levels of fidelity have been used for individual physical processes, including turbulence, combustion, radiation, and soot. For chemical kinetics modeling, the single-step chemistry based on either finite-rate or infinitely fast assumptions is commonly used in pool fire simulations. Despite the success of the single-step chemistry in many fire simulations, it suffers from several drawbacks, such as its strong dependence on the fuel-type, the flame configuration and the combustion model, and its difficulty in capturing flame extinction, soot formation, and radiation characteristics. The use of detailed chemistry
can largely overcome these difficulties, which is however computationally intractable until recently owing to the advancement in cyber infrastructure and to the development of computationally-efficient methods for accommodating finite-rate chemistry. Examples include the species-lumping (cell-clustering) [32] approaches and tabulation-based combustion models [32]. In LES, turbulence-chemistry interaction (TCI) has been accounted for using different closure models such as the eddy dissipation concept (EDC) model [33], probability density function (PDF) methods [34], and steady flamelet models [35]. To describe soot formation and oxidation, both empirical and non-empirical soot models have been developed and applied to simulate pool fires with strong soot propensities [32, 36]. For example, Snegirev et al. [32] compared the performances of several soot models, including the one-step model by Khan et al. [37], the two-step model by Tesner et al. [38], and the Moss-Brookes model [39], in a 30 cm pool fire fueled by methane and heptane, respectively. When applying different soot models, drastically different distributions of soot volume fraction were predicted both inside the flame and in the overfire region, suggesting that problem-dependent calibration is essential in these soot models.

As seen from the above discussion, uncertainties can arise from one or multiple models in these simulations. This dissertation strives to introduce higher fidelity models to fire modeling, with a particular emphasis on radiation modeling. Radiation and its modeling in fires are discussed next.
Table 1.1: A summary of relevant numerical studies of turbulent pool fires.

<table>
<thead>
<tr>
<th>Study</th>
<th>Turbulence</th>
<th>Combustion</th>
<th>Radiation</th>
<th>Spectral model</th>
<th>Soot</th>
<th>TRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xin et al. [21]</td>
<td>LES</td>
<td>Z-based combustion model</td>
<td>Fixed $X_R$</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Xin et al. [40]</td>
<td>LES</td>
<td>Z-based combustion model</td>
<td>Fixed $X_R$, FVM</td>
<td>Gray</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Almedia et al. [41]</td>
<td>LES</td>
<td>EDC with single-step kinetic model</td>
<td>fvDOM</td>
<td>WSGG</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Maragkos et al. [24]</td>
<td>LES</td>
<td>EDC with single-step kinetic model</td>
<td>Fixed $X_R$, fvDOM</td>
<td>Gray</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Cheung and Yeoh [42]</td>
<td>LES</td>
<td>Strained laminar flamelet single-step kinetic model</td>
<td>DOM</td>
<td>WSGG</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Chatterjee et al. [43]</td>
<td>LES</td>
<td>EDC with single-step kinetic model</td>
<td>fvDOM</td>
<td>WSGG</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Snegirev et al. [32]</td>
<td>LES</td>
<td>EDC with single-step kinetic model, Steady flamelet</td>
<td>DOM</td>
<td>WSGG</td>
<td>One-step, two-step, Moss-Brooke model</td>
<td>A simplified TRI model</td>
</tr>
<tr>
<td>Fraga et al. [44]</td>
<td>LES</td>
<td>EDC with single-step kinetic model, Lumped method</td>
<td>FVM</td>
<td>Gray+WSGG</td>
<td>/</td>
<td>Full-TRI, partial TRI</td>
</tr>
<tr>
<td>Sikic et al. [45]</td>
<td>LES</td>
<td>EDC with single-step kinetic model, Lumped method</td>
<td>FVM</td>
<td>Gray+WSGG</td>
<td>/</td>
<td>Full-TRI, partial TRI</td>
</tr>
</tbody>
</table>
1.3 Radiation in fires

Thermal radiation has significant impacts on the behaviors of fire systems. For large-scale fires, radiation accounts for the majority of the overall heat transfer to the ambient \[46\]. It is, however, challenging to perform simultaneous point measurements of multiple scalars in experiments for large-scale turbulent pool fires. Detailed simulations of these fire systems with increasing fidelity provide vital information on fire propagation, which can help prevent or alleviate consequences of large-scale fires. Therefore, an improved understanding of the heat transfer mechanisms in fires is of practical and scientific interests, and numerical simulations using high-fidelity models offer an alternative solution to explore the intrinsic interactions related to radiation.

Radiation modeling in fires is typically limited by the trade-off between accuracy and computational cost, instead of by the availability of radiation models. Radiation models of different fidelity have been extensively developed over the past few decades \[47\]. With the increasing availability of computational resources, modeling radiation in fires has gradually evolved beyond the fixed radiant fraction method and the assumption of optically-thin limit \[30, 45, 48\]. Solvers for the radiative transfer equation (RTE), such as the $P_1$ method, the finite volume method (FVM), the discrete ordinates method (DOM) \[49\], and DOM modified with a finite volume implementation (fvDOM) \[50\], have been routinely applied in conjunction with computational fluid dynamics (CFD) simulations of flames and fires. A range of spectral property models are also available, including global gray models, wide-band models optimized for fire
scenarios, narrow-band models, and line-by-line models. The accuracy of these RTE solvers and spectral models depends on the geometric configuration of a fire system, the characteristics of the participative media (i.e., optically-thick or thin, isotropic or anisotropic scattering, broad-band or spectral radiation, etc.), and the boundary conditions of the target systems. For example, Xin et al. [21] performed LES of a 7.1 cm methane pool fire using a mixture fraction based combustion model and a single-step chemical kinetic model. Radiation was modeled by a fixed radiant fraction method, where radiative loss is constantly proportional to the local chemical heat release rate. Subsequently, Xin et al. [40] extended the developed solver to a one-meter methane pool fire, and compared the performances of two radiation models, the aforementioned fixed radiant fraction method and the FVM method with gray radiative properties. They observed that ignoring radiative heat loss leads to an over-prediction of the vertical velocity. Consalvi et al. [30] adopted the decoupled method to assess different radiative property models using a 30 cm toluene pool fire with different levels of soot volume fraction. By comparing the Statistical Narrow Band Correlated $k$ method (SNBCK) with the Full Spectrum correlated $k$ model (FSCK), they reported that FSCK with a 5-point Gauss-Legendre quadrature scheme and $k$-distributions assembled from the 43 narrow band database could provide high accuracy with acceptable computation cost. Recently, Sikic et al. [45] used the fvDOM solver to evaluate the performance of different spectral models for gas radiation using a 30 cm methanol pool fire. Two gray models and three nongray implementations of weighted-sum-of-gray-gases (WSGG),
and a box model based on the exponential wide band model (EWB) were compared. They found that nongray WSGG models show better performance than their gray counterparts for the relatively low-sooting methanol flames, while the computation cost of the nongray models is approximately two to three times that of the gray models. These studies suggest that the accuracy of various spectral models strongly depends on the size of the pool and the sooting propensity of the fuel, while the optimal choice of the radiation models for different fire configurations remains unclear.

Another challenge in modeling radiation in combustion systems is the compatibility of radiation and combustion models. For example, combustion models that use tabulation to account for finite-rate chemistry, such as the flamelet approaches [51], do not directly and accurately evaluate radiative heat loss term to the flow solver. Consequently, the evaluation of spectral properties and the computation of the local energy loss requires further treatment when coupling radiation models with tabulation-based combustion models [52].

Other difficulties also exist when modeling thermal radiation in fires. The first arises from the inherent instabilities of fires and their transition to turbulent flames downstream. The transient evolution of important scalars, such as temperature, concentrations of radiative species, and soot volume fraction, can affect the evolution of local radiative heat sources. The second is due to the highly inhomogeneous nature of the radiative media including gaseous species, heterogeneous soot, and water droplets when fire suppression is considered.
Facing these challenges, to accurately capture radiative characteristics and to further understand radiation in turbulent pool fires, recent numerical studies have attempted to go beyond the empirical correlations from experiments and to incorporate more robust sub-models to capture transient dynamics in turbulence, chemistry, soot, etc., for improved fidelity of radiation modeling, as summarized in Table 11. For example, Cheung and Yeoh [42] conducted a fully-coupled LES of a large-scale methane pool fire. The strained laminar flamelet approach combined with a single-step reaction was used to account for turbulence-chemistry interactions (TCI). A two-equation soot model [53] that relates soot production to the local temperature and fuel mole fraction was adopted to describe soot dynamics. Radiation was solved by the DOM solver with the S4 quadrature scheme and a WSGG spectral property model. With these sub-models, they quantitatively captured velocity fluctuations and the pulsation frequency. More recently, Maragkos et al. [24] systematically studied a 30.5 cm methanol pool fire. A single-step kinetic model and the fixed radiant fraction model were used for chemistry and radiation, respectively. Through experimental validation and parametric studies, they concluded that the non-unity Lewis number has a discernible impact on predictions of the flame temperature. Prediction of the flow field is also improved with the dynamic turbulence model compared with the one-equation eddy viscosity model [54]. In a subsequent study, Maragkos et al. [25] incorporated the WSGG model for radiation, and compared their latest results against experimental data. The use of the WSGG model accurately reproduced the experimental radiant fraction, which sug-
gests the importance of more accurate radiation models. Besides the above submodels, appropriate modeling of soot dynamics becomes critical for heavily sooting pool fires. Chatterjee et al. [18] developed a combined sub-grid soot-radiation model, based on the laminar smoke point concept [55], and applied it to a 30 cm heptane pool fire. Good agreement with the McCaffrey correlation [16] was attained for the mean centerline temperature rise and velocity, due to the inclusion of soot and radiation. Very recently, Fraga et al. [44] adopted well-resolved LES to simulate a 0.5 m pool fire with methanol and ethanol. A single-step kinetic model was combined with EDC, while radiation was evaluated using FVM. Both gray and nongray spectral models were tested for assessing turbulence-radiation-interaction (TRI) with different spectral treatments. By resolving the Kolmogorov scale, they were able to evaluate the importance of interactions of turbulence and radiation under the RANS context and concluded that temperature fluctuations play a dominant role on TRI. To reliably predict mean radiative heat transfer, fluctuations in species concentrations still need to be accounted for.

Despite the significant progress, whenever new physics is introduced, robust radiation modeling in fires is still challenging. For instance, for the reduced ambient oxygen condition encountered in water suppression, models that do not physically account for extinction can easily break down. Even with a given RTE solver and a spectral model, it is important to determine the optimal combination of model parameters, for example, the number of discretization angles in the DOM solver and the number of bands in wide-band models. An assessment of the optimal number of discretization
angles for DOM is particularly important when scattering media and wall radiation are present for capturing radiation behaviors in fire suppression environments. Hence, determination of optimal radiation model combination for fire-inspired configurations is another focus of this dissertation.

1.4 Water mists in fire suppression

In fire suppression, water or water mist are often involved as a medium to extract heat from fires, to dilute the oxygen in combustible gases, to wet the potential “fuel” surfaces, and to attenuate radiative heat transfer through absorption and/or scattering [56]. Through coupled radiation/convection/phase-change processes with water in fires, the temperature of the fire can be significantly reduced, which eventually extinguishes the fire. At the same time, the dispersion of water or water mists can block the heat radiated to unburnt and/or burning surfaces from the fire, and thereby largely reduces the risk of flash-over that is often initiated by surface preheating in a compartment. Compared with other fire suppression techniques, water-based fire suppression systems are usually more environmentally friendly and less expensive, and thus are widely used over a broad range of conditions, such as in compartment fires.

Water mists, in contrast to the large-size water droplets produced by conventional sprinklers, are usually finer with diameters ranging from 10 to 400 µm [56], due to the higher operating pressures. Water mists are preferable whenever reduced water consumption or reduced water damage is warranted. The reduced size of water mists can
enhance the efficiency of heat transfer from the fire to water mists because of their larger overall surface areas per mass and their longer suspension time [57]. The short lifetime associated with fine droplets (due to the small mass) also significantly reduces the effective time for radiative attenuation. Meanwhile, finer mists are expected to follow the flow field more closely due to their relatively small Stokes numbers [58]. The distribution of water mists in space hence can be rather involved, which may lead to more frequent interactions with other participative media, such as soot and nongray gases. Such complicated multi-physical interactions result in highly nonlinear responses of fire to water mists, and these nonlinear responses often depend on the fuel types (i.e., gaseous versus liquid/solid) and the ambient conditions (i.e., enclosure or open space). Therefore, the design of a fire suppression system using water mists requires a quantitative approach to estimate and to predict the effectiveness/performance of water mists for various fire scenarios [56]. Radiative attenuation has been acknowledged as one of the dominant modes for fire suppression [59]. Therefore, an accurate description of water mist radiation is essential to facilitating performance assessment and design optimization of water mists systems.

Investigation of the intrinsic radiative attenuation characteristics of water mists is, however, challenged by the heterogeneous nature of fires. The hot combustion products produced from fires are typically composed of gaseous radiative species such as CO₂, H₂O, and CO. Heated wall is another type of radiative source in fire environments. All of these radiative sources actively interact with the injected water mists by affecting
the absorption and scattering behaviors in a nonlinear fashion. The optical properties controlling these radiative behaviors strongly depend on the incident wavelength and the size distribution of the droplets. Therefore, detailed spectral descriptions of radiative species and heated walls are required to obtain the optical properties of water mists. In addition, the presence of soot (hot or cold), especially in large-scale fires, may introduce additional effects on global radiative heat transfer characteristics. For example, Parent et al. [60] reported a lower extinction coefficient for a smoke/water-mist mixture than what was obtained for the water mists system alone. However, the mechanisms leading to this counter-intuitive observation have not been well understood. Liu et al. [61] numerically studied the impact of water vapor on soot formation. Radiative attenuation in the sooting flame was found significantly lower when water vapor is present. Dilution, thermal and chemical effects were found to be the three main mechanisms for soot reduction. Because multiphase transport and radiation effects were not considered in [61], the impact of the absorption and scattering from the droplets are still not clear. Additionally, most of the existing studies focus on experimental exploration of soot/water-mist interactions, while modeling studies with comprehensive radiation models are still quite limited. Numerical investigations have the unique advantage of decoupling various controlling parameters. Particularly in this dissertation, the effects of anisotropic scattering and soot-mist interactions are targeted. As an important step towards comprehensive simulations of water mists in fire systems, it is a worthwhile exercise to study the scattering effects through the development of detailed radiation
1.5 Objectives and structure of the dissertation

The work resulting in this dissertation was initially motivated by an experimental study of water suppression of fires of stored warehouse containers. The experiment was designed to establish a rational basis for assessing the effectiveness of water suppression systems, and to develop new standards in safety distance of warehouse containers with different goods. Two key measurements of this experimental study are concerned of practical interest: (i) the activation time of a water sprinkler, and (ii) the radiative heat flux from burning fires to the surrounding. Accurate predictions of both measurements are important to classify the hazards of commodities and for modeling fire growth in warehouse configurations. This dissertation seeks not only to develop accurate and efficient numerical tools to improve fundamental understandings of fires and water mists, but also to establish a numerical framework that is capable of modeling real-life fire and water mist interactions, thus enabling reliable numerical assessment of water suppression systems and saving tremendous amount of investments for fire experiments. A turbulent pool fire is selected as a representative configuration of the warehouse fires. Water mists with a designed size distribution is introduced to mimic the water droplets ejected from the sprinklers. Since the radiative heat flux is a key metric that is used to quantify overall radiative characteristics and to evaluate the risk of a fire, special emphasis is placed on the radiative heat flux in numerical simulations throughout this
dissertation. Specifically, the successful prediction of the radiative heat flux is one of important metrics to the quality of a radiation model/simulation.

The objectives of this dissertation are therefore threefold. The first is to improve the physical understanding of interactions among various sub-processes in turbulent pool fires, such as turbulence, combustion, soot, and radiation. This is achieved by developing a scale-resolved reacting flow numerical platform that has the capability of handling detailed chemistry and radiation. The numerical framework is then applied to simulate a laboratory-scale turbulent pool fire, and detailed data analysis is conducted to examine the intrinsic physics. Second, drawn on the database obtained from high-fidelity simulations of the turbulent pool fires, physics-based reduced-order models are developed for fire simulations with reasonable accuracy and acceptable computational cost. Lastly, to understand multiphase radiative interactions between water mists and fires, suitable radiation models to account for nongray radiation and scattering for water mists are also developed. To achieve these objectives, this dissertation is outlined as follows:

In Chapter 2, development of the high-fidelity numerical framework is presented in detail. The governing equations for reacting flows are introduced, followed by a detailed description of models for chemistry, soot, and radiation.

In Chapter 3, a laminar ethylene diffusion flame and a series of laminar methane diffusion flames are simulated to validate the developed numerical platform and to assess the performance of different sub-models under steady and flicking conditions.
In Chapter 4, a laboratory-scale turbulent pool fire is simulated using the developed numerical framework. Validations against experiments and theoretical relations are presented. Radiative interactions between soot and gas, interactions between chemistry and radiation, as well as turbulence-radiation interaction (TRI) are investigated.

In Chapter 5, physics-based reduced-order models are developed for gas-phase chemistry and soot for fire applications. Systematic validation and assessment of the developed reduced-order models are presented and discussed.

In Chapter 6, computationally-efficient detailed radiation models for water mists are developed and validated. A benchmark case is designed and simulated to provide database for developing reduced-order models for water mists. Physical effects of scattering and interactions between soot and mist radiation are assessed and discussed.

Finally, in Chapter 7, conclusions are drawn and recommendations for future research are provided.

1.6 Guide to appendices

A brief guide is provided for the appendices listed at the end of this dissertation:

Appendix A.1 The pressure correction equation in OpenFOAM presents a derivation of the pressure correction equation employed in fireFoam from the continuity and momentum equations for updating pressure.

Appendix A.2 Verification of the heptane chemical mechanism assesses the performance of the skeletal heptane chemical mechanism used in this dissertation in cap-
turing the behaviors of radiation-relevant species.

Appendix A.3 Validation using a laminar counter-flow diffusion flame presents the verification of the developed numerical platform in this dissertation using a laminar counter-flow diffusion flame along with a grid convergence study.

Appendix A.4 Derivation of the radiative solutions for a simple cylinder model presents a full derivation of the analytical solution to the radiative transfer equation based on the cylindrical coordinate system.

Appendix A.5 The Mie theory for spherical water mists presents a detailed derivation of the Mie theory for water droplets and discusses the computational challenges of directly applying the Mie theory to model radiation of water droplets.

Appendix A.6 Derivation of the analytical solution for linearly scattering media describes the one-dimensional slab configuration that is widely used for validating radiation models based on simple assumptions, and presents detailed derivations of the analytical solutions for isotropic and linearly anisotropic scattering media with gray property.

Appendix A.7 Chemical mechanisms used in this dissertation summarizes all the chemical kinetic models used in this dissertation.

1.7 List of journal publications


Chapter 2

Numerical models and solvers

A new numerical modeling framework (reactingDJFoam) is developed in this dissertation [62, 63], for high-fidelity simulations of general reacting flows considering radiative heat transfer. The reactingDJFoam is constructed based on the fireFoam solver within the open source CFD toolbox in OpenFOAM-5.x [50], which is an object-oriented C++-based second-order finite-volume solver, featuring advanced meshing capabilities (structured/unstructured polyhedral meshes) and the parallel computing capability using message passing interface (MPI) protocols. The reactingDJFoam solver allows for coupling of a variety of numerical solvers and physical models for turbulence, chemical kinetics, radiation, soot, etc., the details of which will be provided in this chapter.
2.1 Numerical solvers

Governing equations of mass, momentum, species, and sensible enthalpy, shown in Eqs. (2.1) to (2.4), are solved in a segregated manner in \textit{reactingDJFoam}.

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = S_\rho, \hspace{1cm} (2.1)
\]

\[
\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho uu) = -\nabla p + \nabla \cdot \tau + \rho g, \hspace{1cm} (2.2)
\]

\[
\frac{\partial \rho Y_k}{\partial t} + \nabla \cdot (\rho u Y_k) = -\nabla \cdot J_k + \rho \dot{\omega}_k, \hspace{0.5cm} k = 1, \ldots, N_s - 1, \hspace{1cm} (2.3)
\]

\[
\frac{\partial \rho h_s}{\partial t} + \nabla \cdot (\rho u h_s) = \frac{Dp}{Dt} - \nabla \cdot J_h + S_c + S_r. \hspace{1cm} (2.4)
\]

Here \( \rho \) is the density, \( S_\rho \) is the source term due to evaporation or other mass addition and/or extraction processes, \( u \) is the velocity vector, \( g \) is the gravitational acceleration, \( h_s \) is the sensible enthalpy, \( Y_k \) is the mass fraction of species \( k \), \( \rho \) is the hydrodynamic pressure, and \( N_s \) is the number of chemical species. The viscous stress tensor \( \tau \), and the diffusion fluxes for the \( k^{th} \) species \( J_k \), and for the sensible enthalpy \( J_h \) are expressed as follows,

\[
\tau = \mu [\nabla u + (\nabla u)^T - 2/3(\nabla \cdot u)I], \hspace{1cm} (2.5)
\]

\[
J_k = -\rho D_k (\nabla Y_k + \frac{Y_k}{M} \nabla M), \hspace{1cm} (2.6)
\]

\[
J_h = -\lambda \nabla T + \sum_{k=1}^{N_s} h_{s,k} J_k. \hspace{1cm} (2.7)
\]
I denotes the identity matrix, \( \mu \) denotes the dynamic molecular viscosity, and \( M \) denotes the molecular weight of the mixture. \( D_k \) is the diffusivity for species \( k \), and \( \lambda \) is the thermal conductivity of the mixture. \( \dot{\omega}_k \) is the chemical source term for the mass fraction of the \( k \)th species. \( S_c \) and \( S_r \) are the chemical heat release rate and radiative source term, respectively. Details on the solvers for these two source terms are provided in Secs. 2.2 and 2.3, respectively.

The reacting\( DJFoam \) solver is a pressure based solver, where the velocity is obtained from the momentum equation and the pressure field is solved using a pressure correction equation [64, 65]. In particular, the pressure correction equation is obtained by manipulating continuity and momentum equations. Note that the equation of state is not solved directly to get the pressure, but is used to derive the pressure correction equation, as is detailed in Appendix A.1. A pressure-implicit with splitting of operators (PISO) algorithm [66] is used.

Note that the species and energy transport equations are solved sequentially after the momentum equation in each PISO loop as shown in Fig. 2.1. Considering detailed species transport coefficients is critical for modeling diffusion flames with heavy hydrocarbon fuels using a grid near flame-resolved resolution [24]. To account for effects of the non-unity Lewis number and Schmidt number, a mixture-averaged molecular diffusion model [2] is also implemented into reacting\( DJFoam \), which is not available in the default \( fireFOAM \) solver.
Fig. 2.1: Flowchart of the multi-physical reactingDJFoam solver.
2.2 Thermal radiation modeling

2.2.1 Radiative transfer equation (RTE)

The radiative source term $S_r$ in Eq. (2.4) is obtained by solving the radiative transfer equation (RTE). For an emitting, absorbing and scattering medium, the radiative transfer equation is given by

$$s \cdot \nabla I_{\lambda}(s) = \kappa_{\lambda}I_{b,\lambda} - \beta_{\lambda}I_{\lambda}(s) + \frac{\sigma_{\lambda}}{4\pi} \int I_{\lambda}(s')\Phi_{\lambda}(s', s)d\Omega', \quad (2.8)$$

where $I_{\lambda}$ is the spectral intensity along direction $s$, $I_{b,\lambda}$ is the black-body intensity at wavelength $\lambda$, $\kappa_{\lambda}$, $\sigma_{\lambda}$, and $\beta_{\lambda} = \kappa_{\lambda} + \sigma_{\lambda}$ are wavelength-dependent absorption, scattering, and extinction coefficients, respectively. $\Phi_{\lambda}$ is the scattering phase function, and $\Omega'$ denotes the solid angle. When no scattering is considered, $\sigma_{\lambda} = 0$, and the extinction coefficient $\beta_{\lambda} = \kappa_{\lambda}$.

A few assumptions are made to derive Eq. (2.8), including that the medium is stationary compared to the speed of light, the medium is nonpolarizing and the state of polarization is neglected, and the medium has a constant index of refraction [49]. These assumptions are usually valid when describing thermal radiation in conventional fire systems.

For each spatial location $x$, once $I_{\lambda}(s)$ is determined, the volumetric radiative
source term can be determined as

\[ S_r(x) = \int_{\lambda=0}^{\lambda=\infty} \int_{4\pi} s \cdot \nabla I_\lambda(s; x) d\Omega d\lambda. \] (2.9)

To obtain \( S_r \), either the differential form in Eq. (2.8) or the integral form in Eq. (2.9) can be solved by a specific RTE solver with spectral models for \( \kappa_\lambda \) and \( \sigma_\lambda \). The RTE solver and spectral models are introduced next.

### 2.2.2 Spectral models

The Planck-mean absorption coefficient \( \kappa_{P,i} \) for the \( i^{th} \) gaseous species is defined as,

\[ \kappa_{P,i} = \frac{\int_0^\infty \kappa_{\eta,i} I_{b\eta} d\eta}{\int_0^\infty I_{b\eta} d\eta}, \] (2.10)

where \( \eta \) is the wavenumber, and \( I_{b\eta} \) is the blackbody emissive intensity evaluated at wavenumber \( \eta \). \( \kappa_{\eta,i} \) is the absorption coefficient at wavenumber \( \eta \) for species \( i \). When more than one participating gaseous species are present, the following additive form are adopted to obtain the gas-phase Planck-mean absorption coefficient \( \kappa_{P,g} \),

\[ \kappa_{P,g} = \sum_{i=1}^{n_r} \kappa_{P,i} p_i, \] (2.11)

where \( p_i \) is partial pressure of species \( i \), and \( n_r \) is total number of radiative species.

The pressure-based spectral absorption coefficients \( \kappa_{\eta,i} \) for the gas phase are ob-
tained from the line-by-line (LBL) database [67] generated from HITEMP2010 [68] and HITRAN2012 [69]. Five species, including CO$_2$, H$_2$O, CO, CH$_4$ and C$_2$H$_4$, are considered for temperatures from 300 K to 3000 K, and for various mole fractions of the participating species. It should be noted that the spectral databases for hydrocarbons such as CH$_4$ and C$_2$H$_4$ are constantly updated within the HITRAN community [69]. For the purpose of accounting for thermal radiation, the line-by-line databases are sufficiently accurate and have been regarded as the “truth” for spectral model development.

For soot, the Planck-mean absorption coefficient, $\kappa_{P,s}$, is evaluated using a similar method as illustrated in Eq. (2.10), where the spectral absorption coefficient $\kappa_{\eta,i}$ is replaced by $\kappa_{\eta,s}$. $\kappa_{\eta,s}$ is computed from the Rayleigh’s small particle limit [49] by neglecting the scattering effect,

$$
\kappa_{\eta,s} = C_{\eta} f_s \eta, \text{ and } C_{\eta} = \frac{36 \pi n_s k_s}{(n_s^2 - k_s^2 + 2)^2 + 4n_s^2 k_s^2},
$$

(2.12)

Here, $f_s$ is the soot volume fraction. $n_s$ and $k_s$ are the wavelength-dependent real and imaginary parts of the complex index of refraction, which are obtained from experimental measurements in [70] as,

$$
n_s = 1.811 + 0.1263 \ln(\lambda) + 0.027 \ln^2(\lambda) + 0.0417 \ln^3(\lambda), \quad (2.13)
$$

$$
k_s = 0.5281 + 0.1213 \ln(\lambda) + 0.02309 \ln^2(\lambda) + 0.01 \ln^3(\lambda). \quad (2.14)
$$

For a mixture with both soot and gas, the total Planck-mean absorption coefficient can
be computed as

$$\kappa_P = \kappa_{P,g} + \kappa_{P,s} .$$  \hspace{1cm} (2.15)

Note only \(\kappa_{P,g}\) has an explicit dependence on partial pressures.

The scattering coefficients need to be accounted for when particle diameters are comparable to the incident wavelengths, such as in the case of water droplets. Descriptions of their spectral properties are postponed to Chapter 6 to allow for a more coherent discussion on water mist radiation.

### 2.2.3 RTE solvers

The Monte Carlo ray tracing (MCRT) method is one of the most general solution procedures for solving Eq. (2.8) \[49\]. Physically, the radiative source term \(S_r\) is composed of a volumetric absorption component (\(\dot{Q}_{abs}\)) and a volumetric emission component (\(\dot{Q}_{emi}\)),

$$S_r = \dot{Q}_{abs} - \dot{Q}_{emi} = \dot{Q}_{abs} - 4\kappa_P \sigma T^4 ,$$  \hspace{1cm} (2.16)

where \(\kappa_P\) is the total Plank-mean absorption coefficient for participative media, and \(\sigma\) is the Stefan-Boltzmann constant (\(\sigma = 5.669 \times 10^{-8} \text{ W/(m}^2\text{K}^4)\)).

The MCRT method obtains solutions to the RTE by emitting and tracing a statistically large number of “energy rays” to account for their interactions with participating media. Each energy ray carries a specific amount of energy, and has a specific wavelength, direction, and origin. They are emitted everywhere within the computational
domain. The number of energy rays emitted by the host cell is proportional to its local emission potential [71]. The selection algorithms of the origin, propagation direction, and wavelength of each energy ray are based on random number relations and have been reported in [49, 67, 71]. A brief description of the mathematical formulation is provided here.

For a finite volume cell \( k \) with volume \( V_k \), the total emission from this cell is given by,

\[
E_{\text{tot}} = \int_{V_k} 4\kappa \rho \sigma T^4 dV ,
\]

(2.17)

where \( dV = dx dy dz \) for the Cartesian coordinates. Three uniformly distributed random numbers \( R_x, R_y, R_z \) between zero and unity are generated to obtain positions of emission through the following random number relations that are derived from importance sampling based on the local emissive power \( \kappa \rho \sigma T^4 \),

\[
R_x = \frac{\int_{0}^{x} \int_{0}^{y} \int_{0}^{z} \kappa \rho \sigma T^4 dz dy dx}{\int_{0}^{x} \int_{0}^{y} \int_{0}^{z} \kappa \rho \sigma T^4 dz dy dx} \text{ or } x = x(R_x) ,
\]

(2.18a)

\[
R_y = \frac{\int_{0}^{y} \int_{0}^{z} \kappa \rho \sigma T^4 dz dy}{\int_{0}^{x} \int_{0}^{y} \int_{0}^{z} \kappa \rho \sigma T^4 dz dy} \text{ or } y = y(R_y, x) ,
\]

(2.18b)

\[
R_z = \frac{\int_{0}^{z} \kappa \rho \sigma T^4 dz}{\int_{0}^{z} \kappa \rho \sigma T^4 dz} \text{ or } z = z(R_z, x, y) .
\]

(2.18c)
For CFD calculations where $\kappa P\sigma T^4$ remains constant throughout the cell, the distribution of emission point only depends on the geometry of the local computational cell.

All possible directions for emission from a point within the medium are contained within the solid angle of $4\pi = \int_0^{2\pi} \int_0^\pi \sin \theta d\theta d\psi$, where the polar angle $\theta$ and the azimuthal angle $\psi$ are measured from arbitrary reference axes. Thus, isotropic emission directions are determined by two additional random numbers $R_\psi$ and $R_\theta$,

$$R_\psi = \psi / 2\pi, \text{ or } \psi = 2\pi R_\psi ,$$  \hspace{1cm} (2.19a)

$$R_\theta = 0.5 \int_0^\theta \sin \theta d\theta, \text{ or } \theta = \cos^{-1}(1 - 2R_\theta) .$$  \hspace{1cm} (2.19b)

As for the selection of emission wavenumber, when accounting for nongray participating media, a hybrid wavenumber selection scheme [67] is adopted. Following the observation that there are no overlap effects for emission between different radiative species, emission from each species is considered separably in this hybrid scheme [67]. Hence, the emitting species $s$ is determined first and then the appropriate wavenumber is finalized within the selected emitting species. Therefore, the random number relationship is written as,

$$R_\eta = \frac{\sum_{i=1}^{s-1} E_i}{E_{tot}} + \frac{\int_0^\eta \kappa_{\eta,s} I_{b\eta} d\eta}{E_{tot}} ,$$  \hspace{1cm} (2.20)
where \( s \) is the index of the selected emitting species, and \( \kappa_{\eta,s} \) is the spectral absorption coefficient of the \( s \)th species. For a given random number \( R_{\eta} \), the emitting species is determined by

\[
s = j, \quad \text{if} \quad \frac{\sum_{i=1}^{j-1} E_i}{E_{tot}} < R_{\eta} \leq \frac{\sum_{i=1}^{j} E_i}{E_{tot}}.
\]

(2.21)

Once the emitting species is determined, \( R_{\eta} \) is re-scaled according to

\[
0 \leq R_{\eta,s} = \frac{R_{\eta}E_{tot} - \sum_{i=1}^{j-1} E_i}{E_j} < 1.
\]

(2.22)

To reduce the computational cost associated with handling a line-by-line spectral database, an inverted relation \( \eta - R_{\eta,i} \) is tabulated. The adopted LBL database has the form of

\[
\eta = f_{\eta,i}(R_{\eta,i}, T, x_i), \quad \kappa_{\eta,i} = f_{\kappa,i}(\eta, T, x_i), \quad i = 1, 2, ..., n_r,
\]

(2.23)

where \( x_i \) is the mole fraction of species \( i \), \( f_{\eta,i} \) and \( f_{\kappa,i} \) denote the two tabulated functions in the LBL database.

An “energy partitioning” scheme \([72]\) is used to account for absorption of energy rays within the participating medium. The energy \( (Q_j) \) carried by ray \( j \) is attenuated gradually and the energy is deposited to each finite volume cell along its path, until fully depleted or when it exits the computational domain \([71]\). For a finite volume cell
$k$, the absorptivity is given as \[49\]

$$\alpha_{\eta,k} = 1 - \exp(-\int_0^{\Delta t} \kappa_{\eta} ds). \quad (2.24)$$

where $\Delta t$ is determined according to the local cell geometry and the direction of incoming ray. $\kappa_{\eta}$ is obtained from the LBL database based on the local thermochemical state and the incoming wavenumber $\eta$. The absorbed energy of this cell from $j^{\text{th}}$ energy ray is given by,

$$\Delta Q_{\text{abs},k} = Q_j \alpha_{\eta,k}. \quad (2.25)$$

Therefore, after the ray tracing process, the volumetric absorption source term for the $k^{\text{th}}$ cell is computed as

$$\dot{Q}_{\text{abs}} = \sum_{j\in J'_k} \Delta Q_{\text{abs},k} / V_k, \quad (2.26)$$

where $J'_k$ denotes the collection of energy rays that interact with the $k^{\text{th}}$ cell. A complete description of the emission and absorption sub-processes can be found in [73, 74].

Finally, as each ray moves through the domain, it may change direction due to scattering along its travel path. The treatment of scattering due to the presence of water mists will be introduced in Chapter 6.
2.3 Chemistry solver

Accurate description of chemical kinetics is essential for predicting combustion dynamics such as ignition, extinction, and flame propagation. Within the operator-splitting framework, the local chemical kinetic system is governed by a set of ordinary differential equations (ODEs):

\[
\frac{d\phi}{dt} = S(\phi),
\]

(2.27)

where \(\phi\) is a vector of dependent variables of dimension \(n_\phi\), including temperature and species concentrations, and \(S\) represents the chemical source terms.

When highly reactive radicals and their associated short timescales are present, the local chemical system is stiff, thus requiring a stiff ODE solver to stably advance the transient chemistry integration. Among the widely used are backward differentiation formula (BDF) based solvers such as VODE [75] and DASAC [76], and extrapolation based solvers such as SEULEX [77]. By default, OpenFOAM uses i.e., the SEULEX solver for stiff chemistry integration. As reported in previous studies [78, 79], while the SEULEX solver can accurately capture auto-ignition behaviors for simple fuels such as methane, it fails to predict more involved events such as two-stage ignition and flame propagation, potentially due to its inability in tackling extremely small timescales, and its inadequate description of transport properties. To improve the accuracy and robustness for chemistry integration, in this dissertation, two additional stiff chemistry solvers are coupled into OpenFOAM in place of the default SEULEX solver. The first is the
a widely-used VODE solver, enhanced by analytical Jacobian using an in-house an-
alytical Jacobian generator [80]. The second is an adaptive chemistry solver AHI-S
[81], which is based on hybrid integration and sparse matrix techniques. Details of the
implementations are shown as follows.

2.3.1 VODE with analytical Jacobian

VODE is one of the most widely used stiff ODE solvers in the combustion community.
It is a variable-coefficient solver with an order of accuracy up to five. To successfully
couple VODE with OpenFOAM, a Fortran interface is developed allowing data com-
munication between the C++ based main CFD solver, and the Fortran-based chemistry
solver, as shown in Fig. 2.1. In particular, local thermochemical state of each computa-
tional cell, such as pressure, temperature, and species mass fractions, are provided to
the chemistry solver that feeds the chemical source terms back to the transport equa-
tions in CFD. Jacobian is a central piece of implicit ODE solvers. By default, VODE
uses finite differences to numerically evaluate the Jacobian. The computational cost of
this procedure typically scales as a quadratic function of the number of ODEs. Analyt-
ical Jacobian based on the intrinsic analytical rate description of the chemical kinetics,
on the other hand, can significantly reduce the computational cost by up to one order
of magnitude. The accuracy of implemented VODE solver in OpenFOAM was demon-
strated in Fig. 2.2 where the temperature profile from a homogeneous auto-ignition
system of the stoichiometric heptane and air mixture is compared with the reference
Fig. 2.2: Auto-ignition predicted by SENKIN and the implemented VODE solver.

solution from SENKIN in CHEMKIN [2]. A 40-species mechanism [82] is employed to describe heptane reaction kinetics. The inlet temperature and pressure are 1200 K and 1 atm, respectively. Solution from the implemented VODE solver exactly matches the reference solution.

2.3.2 The AHI-S solver

Conventional detailed chemistry solvers, such as VODE [75], solve all variables in Eq. (2.27) implicitly, and thus can be computationally expensive when the mechanism size is large. Hybrid methods that seek to reduce the size of the implicit core of the ODE solver have the potential to further improve the computational efficiency. To this end, a recently developed sparse stiff chemistry solver (AHI-S) [81] is further implemented within the OpenFOAM framework. The AHI-S method couples the dynamic adaptive hybrid integration (AHI) method [83] and the sparse matrix techniques to achieve re-
duced computational cost. Procedurally, fast species and reactions are first identified on-the-fly based on an analytical formulation of reaction timescales \cite{84} and user-defined timescale threshold. Fast chemistry is then solved implicitly, while the slow chemistry is solved explicitly. When solving the implicit part of the ODEs, the intrinsic sparsity of the Jacobian of fast chemistry is further explored to systematically eliminate the unimportant entries from the Jacobian, such that efficient sparse matrix techniques can be taken full advantage of \cite{81}.

The accuracy and efficiency of the AHI-S solver have been extensively validated in a previous study \cite{81} for simple zero-dimensional (0D) and one-dimensional (1D) test cases. The present study focuses on validation of the AHI-S solver within the OpenFOAM platform, while assessment of the performance of the developed solver in three dimensional (3D) turbulent flames is detailed in \cite{62}.

The AHI-S solver in OpenFOAM is first validated against predictions obtained using SENKIN from CHEMKIN \cite{2} using 0D homogeneous auto-ignition systems of propane/air mixtures. A skeletal propane mechanism with 31-species is employed \cite{62}. Figure 2.3(a) shows the ignition delay times calculated by AHI-S and CHEMKIN match exactly.

To further validate the implemented AHI-S solver with mixture-averaged transport properties, 1D unstrained laminar premixed flames are simulated. The 1D premixed flame calculation is initialized with the 1D steady state solution obtained from PREMIX in CHEMKIN \cite{85}. The premixed C$_3$H$_8$/air mixture with an inlet temperature
Table 2.1: Comparison of the calculated laminar flame speeds.

<table>
<thead>
<tr>
<th>φ</th>
<th>CHEMKIN</th>
<th>reactingDJFoam</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>31.21</td>
<td>30.17</td>
</tr>
<tr>
<td>0.78</td>
<td>27.16</td>
<td>27.72</td>
</tr>
<tr>
<td>0.76</td>
<td>25.84</td>
<td>25.12</td>
</tr>
<tr>
<td>ϵ_{RD}(%)</td>
<td>3.6</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.9</td>
</tr>
</tbody>
</table>

Fig. 2.3: Validation of the implemented AHI-S solver using (a) 0D autoignition system, (b) 1D unstrained laminar flame with φ = 0.78, T_0 = 300 K, and p_0 = 1 atm. Lines represent results obtained from CHEMKIN [2], and symbols indicate calculation using the implemented solver in OpenFOAM.

of 300 K and pressure of 1 atm enters the computational domain from the left boundary with an inlet velocity equal to the nominal laminar flame speed. The computational domain is [0, 3] cm with a uniform grid resolution of 20 µm, such that the flame thickness is well resolved. Figure 2.3(b) shows profiles of temperature and two important species (OH and CH\textsubscript{2}O) at φ = 0.78. Good agreement is observed between the results obtained by reactingDJFoam and those by CHEMKIN. The calculated laminar flame speeds, S_L, at three different equivalence ratios from the reactingDJFoam and CHEMKIN, are summarized in Table 2.1. Good agreement is obtained with relative errors less than 5%.

In addition, the overall computational cost of the AHI-S solver is significantly reduced compared to the built-in solvers in OpenFOAM and the VODE solver cou-
Fig. 2.4: Comparison of execution time for chemistry with chemistry solvers.

plied with analytical Jacobian. To illustrate the potential saving in the context of 3D LES simulation, the computational cost is assessed using a turbulent bluff-body stabilized flame with a mesh consisting of ten million cells [62]. The 31-species skeletal mechanism is adopted for the propane/air mixture [62]. A fixed time step of 40 µs is employed. Figure 2.4 compares the chemistry execution time per time step for the AHI-S and VODE solvers implemented in reactingDJFoam. When using analytical Jacobian, the cost of VODE solver is reduced by approximately 50% compared to that obtained with numerical Jacobian. With AHI-S solver, the computational cost is further reduced by 90%, mainly due to the elimination of internal sub-steps and the reduced size of implicit core. More significant saving in computational cost is expected when larger chemical mechanisms and/or larger meshes are used.
2.4 Semi-empirical two-equation soot model

A semi-empirical two-equation soot model [8, 9] is employed in this dissertation. This semi-empirical soot model attempts to capture the physical and chemical dynamics of soot formation, growth, and oxidization using two transport equations. Semi-empirical two-equation models are widely used in applications with significant amount of soot including engine simulations [86, 87, 88, 89, 90], and are increasingly being used in fire-related combustion systems [36, 91]. Along with the gas phase species conservation equations, it solves two additional modeled Eulerian transport equations: one for soot mass fraction $Y_s$ and the other for particle number density $N_{soot}$ (particles/kg), as expressed in Eq. (2.28).

$$\frac{\partial \rho Y_s}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j Y_s) = \frac{\partial}{\partial x_j} \left( \frac{\mu}{Sc} \frac{\partial Y_s}{\partial x_j} \right) + 0.54 \frac{\partial}{\partial x_j} \left( \frac{\mu}{T} Y_s \frac{\partial T}{\partial x_j} \right) + S_m , \tag{2.28a}$$

$$\frac{\partial \rho N_{soot}}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j N_{soot}) = \frac{\partial}{\partial x_j} \left( \frac{\mu}{Sc} \frac{\partial N_{soot}}{\partial x_j} \right) + 0.54 \frac{\partial}{\partial x_j} \left( \frac{\mu}{T} N_{soot} \frac{\partial T}{\partial x_j} \right) + S_N , \tag{2.28b}$$

where $\mu$ is the dynamic viscosity of the gas mixture, $Sc$ is a soot Schmidt number. It was found that a value of 60 for the Schmidt number worked well under laminar conditions [48].

Particle inception, surface growth, oxidation, and coagulation are represented as follows. Inception is assumed to rely on acetylene (C$_2$H$_2$). Surface reaction is modeled in two steps, one for growth and one for oxidization. In addition to oxidation by O$_2$ [8].
soot oxidation pathways are augmented by including OH and O, with the suggested reaction rates provided by [9]. It also considers agglomeration due to aging of the soot particles. The reaction steps are provided in Table 2.2.

Table 2.2: Soot formation and oxidation pathways in [8] (R1-R3), with augmented oxidation reactions described in [9] (R4-R5). \( §_j \) represents a soot particle with \( j \) carbon atoms.

<table>
<thead>
<tr>
<th>Reaction Step</th>
<th>Reaction</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Inception</td>
<td>( jC_2H_2 \rightarrow 2§_j + jH_2 )</td>
<td>( R_1 = k_1(T)[C_2H_2] )</td>
</tr>
<tr>
<td>2 Growth</td>
<td>( C_2H_2 + §<em>j \rightarrow §</em>{j+2} + H_2 )</td>
<td>( R_2 = k_2(T) \sqrt{A_s}[C_2H_2] )</td>
</tr>
<tr>
<td>3 Oxidation</td>
<td>( §<em>j + \frac{1}{2}O_2 \rightarrow §</em>{j-1} + CO )</td>
<td>( R_3 = k_3(T)A_s[O_2] )</td>
</tr>
<tr>
<td>4 Oxidation</td>
<td>( §<em>j + OH \rightarrow §</em>{j-1} + CO + H )</td>
<td>( R_4 = k_4(T)A_s[OH] )</td>
</tr>
<tr>
<td>5 Oxidation</td>
<td>( §<em>j + O \rightarrow §</em>{j-1} + CO )</td>
<td>( R_5 = k_5(T)A_s[O] )</td>
</tr>
</tbody>
</table>

Here, \( §_j \) denotes a soot particle with \( j \) carbon atoms. The representation of soot as \( §_j \) is approximate, and it has been argued [92] that this approximation is reasonable as long as surface reaction is the dominant process and less than 10% of the total soot mass is from the inception process. It also assumes that an incipient soot particle consists of 100 carbon atoms \( (C_{min} = 100) \) and has a radius of 1.24 nm, and argues that the final result is almost independent of the size of the first soot particle. The functional dependence on soot surface area per unit of volume is assumed to be \( f(A_s) = \sqrt{A_s} = a_p(\rho N_s) \), where \( a_p \) is the surface area of an individual particle. Parameters listed in Table 2.2 are defined as follows:
\[ d = \left( \frac{6Y_s}{\pi \rho_s N_{soot}} \right)^{1/3} [m], \quad (2.29) \]

\[ a_p = \pi d^2 [m^2], \quad (2.30) \]

\[ k_1 = 0.1 \times 10^5 \exp(-21100/T) [s^{-1}], \quad (2.31) \]

\[ k_2 = 0.6 \times 10^4 \exp(-12100/T) [m^{1/2} s^{-1}], \quad (2.32) \]

\[ k_3 = 0.1 \times 10^5 T^{1/2} \exp(-19680/T) [ms^{-1}]. \quad (2.33) \]

Other model constants, such as the agglomeration constant \( (C_a = 9) \), the density of soot \( (\rho_s = 1800 \text{ kg/m}^3) \), and the molar mass of soot \( (M_s = 12.011 \text{ kg/kmol}) \), follow the original specifications in [8].

Two-way coupling is employed, where the concentrations of gas species and gaseous temperature are affected by soot-related reactions. Note that one-way coupling is usually sufficient for \( \text{C}_2\text{H}_2 \)-based models, as suggested by [90, 93].

### 2.5 Boundary condition

For simulations with very small convective velocities, as commonly encountered in purely buoyant fires [17], the diffusive mass flux introduced by the differences between the cell-center and the inlet boundary face could become comparable to the convective flux, which thereby should be accounted for to accurately describe the boundary conditions for species mass fractions. The species flux correction for inlet boundary condi-
tions are implemented in OpenFOAM as the totalFlowRateAdveectiveDiffusive boundary condition [50]. For species \(i\), whose mass fraction is \(Y_i\) on the boundary face, the net flux at the boundary face is determined as,

\[
\rho^0 U^0 Y_i^0 = \rho U Y_i - \rho D_i \frac{\partial Y_i}{\partial x_j},
\]

(2.34)

where the superscript 0 indicates values specified by the users on the inlet boundaries. To simplify the derivation, the face norm of the boundary face is assumed to be aligned with the \(x_j\) coordinate. Assume at the cell center of the first layer of cells adjacent to the inlet boundary, density and velocity at the cell centers are identical to those at the inlet boundary, i.e., \(\rho = \rho^0\), and \(U = U^0\). By invoking first-order upwind discretization,

\[
Y_i^0 = Y_i - \frac{D_i (Y_c - Y_i)}{U} \Delta x,
\]

(2.35)

where \(\Delta x\) is the distance between boundary face and the corresponding cell center, and \(Y_c\) is the mass fraction at the cell center, the equation can be rearranged as,

\[
Y_i(1 + \frac{D_i}{U \Delta x}) = Y_i^0 + \frac{D_i}{U \Delta x} Y_c.
\]

(2.36)
By defining a weighting function, \( \omega = 1/(1 + D_i \Delta x/U) \), the actual inlet mass fraction of species \( i \) can be obtained by,

\[
Y_i = \omega Y_i^0 + (1 - \omega) Y_c.
\]  (2.37)

It is now clear that such a correction is necessary when the equivalent diffusive velocity \( D_i/\Delta x \) is comparable with the advective velocity \( U \) and when \( Y_i^0 \) is substantially different from \( Y_c \). It should be noted that the molecular diffusivity \( D_i \) need to be consistent with the underlying transport property models used for the internal computational domain. Mixture-averaged \( D_i \) is implemented in the totalFlowRateAdectiveDiffusive boundary condition in this dissertation to maintain the consistency between the boundaries and the interior fields.

### 2.6 Summary

A schematic flow-chart of the developed numerical framework is shown in Fig. 2.1. When multiphase reacting flows are considered, a Eulerian-Lagrangian framework can be further employed to describe the coupling between the gaseous flow fields and the dynamics of the discrete phases, as done in [73, 74]. Compared to the built-in fireFoam solver in OpenFOAM, the numerical platform developed in this study features the following improvements:

- Implementation and application of the AHI-S solver to accelerate the calculation
of finite-rate chemistry with improved accuracy.

- Inclusion of the capability to consider non-unity Lewis and Schmidt numbers.

- Development of detailed radiation solver (MCRT) and spectral property models to model multiphase radiation, involving coal particles and water droplets.

- Coupling with a semi-empirical two-equation model for soot modeling (leveraging existing work at [92]).

- Implementation of a total mass flow rate based boundary condition to consider the effect of differential diffusion.

These improvements are necessary to enable the subsequent scale-resolved detailed simulations of laminar diffusion flames and turbulent pool fires.
Chapter 3

Detailed simulation of laminar diffusion flames

In this chapter, laminar diffusion flames in co-flowing air are considered for model validation and assessment. Among various fire-related configurations, laminar diffusion flames are often adopted for assessing different radiation models, without introducing additional model uncertainties associated with subgrid turbulence and combustion models. Simulating laminar diffusion flames is, however, not an easy task, considering the need of resolving the fine reaction layers associated with radicals involved in detailed chemical kinetics, the need of capturing the flickering amplitude and frequency in unsteady flames, and the requirement of predicting soot dynamics in luminous flames. With such complexities, an appropriate choice of the radiation and combustion modeling strategy becomes critical. Improved understanding of sufficient and optimal model combinations, including both combustion-related models and radiation models, for simulating laminar diffusion flames is of vital importance.

A series of laminar diffusion flames comprising both steady and unsteady features [94] is targeted in this chapter, where experimentally measured radiative heat flux, radiant fraction, flame height and flame puffing frequency are available for compari-
son. In particular, less explored in radiation studies in the literature, flickering laminar flames are simulated here to examine modeling requirements. As fires often transition from laminar to unstable, and eventually to turbulent flames, detailed explorations of flickering laminar flames from a coupled combustion and radiation modeling viewpoint are essential for understanding sufficient and optimal model combinations for simulating laminar and/or turbulent diffusion flames. More validations towards turbulent pool fires are certainly warranted and will be presented in the next chapter. We consider this study as a vital first step for assessing the overall performance of the newly developed numerical platform in Chapter 2 on realistic flames.

The current study is, to the author’s best knowledge, one of the few laminar flame modeling studies where the coupling between radiation and combustion models is accounted for during radiation model comparison. In addition, physical insights gained through model comparison will be leveraged when generating reduced-order models. The rest of this chapter is organized as follows. Section 3.1 first presents validations on a laminar ethylene/air diffusion flame, where experimentally measured major species concentrations, temperature, and soot volume fraction are available for comparison. Next, four target laminar co-flowing methane/air flames are described in Sec. 3.2 including two small stationary flames and two larger flickering flames. The baseline results are compared with experimental measurements in Sec. 3.3. Parametric variations in thermal boundary conditions, RTE solvers, spectral models, chemical mechanisms, and soot models are also conducted in Sec. 3.3. Based on the observed
sensitivities, critical submodels and numerical parameters are finally recommended for modeling stationary and flickering laminar methane/air flames in Sec. 3.4.

3.1 A laminar ethylene diffusion flame

Only radiation-related quantities are reported for the four target flames [94]. Therefore, the solver introduced in Chapter 2 is first validated using a similar laminar diffusion flame, where species and temperature measurements are available. The atmospheric ethylene-air diffusion flame was experimentally studied by Santoro et al. [95], and numerically studied by [48, 96, 97, 98]. Pure ethylene is injected from a central brass tube with an inner diameter of 11.1 mm. The outer diameter of air co-flow is 101.6 mm. The fuel tube extends to a height of 4 mm beyond the inlet plane of the air co-flow. The experimental setup is enclosed in a 405 mm tall brass chimney to protect the flame from laboratory air currents. The fuel velocity is 3.91 cm/s, and the air velocity is 8.90 cm/s.

The targeted flame is a non-smoking flame where soot is completely oxidized within the flame. In the experiment [95], soot was measured using a laser extinction/scattering technique, while gaseous temperature was measured by a quartz microprobe. The measured samples were analyzed by a mass spectrometer (MS) and subsequently verified by gas chromatography (GC) to obtained species concentrations. The experimental uncertainty for the major species, i.e., CO$_2$, and for OH were estimated as $\pm20\%$ and $\pm50\%$, respectively.

Considering axisymmetry, a non-uniform wedge-like computational domain is
constructed, starting from approximately 30 mm upstream of the exit plane of the co-
flow, and extending to a height of 180 mm in the axial direction and a distance of
150 mm in the radial direction. Fuel and air streams are separated by a 10 mm long
fuel-tube wall. Uniform velocity profiles are prescribed for both fuel and air inlets with
a temperature of 300 K. Since the temperature of the fuel-tube wall was not measured in
the experiment, a fixed temperature of 300 K is assumed. The computational domain is
discretized by 52,580 non-uniform cells with finer resolution placed near the fuel nozzle
and the fuel-air mixing layer to resolve the flame and shear layer. Gravity is included
in the axial direction to account for buoyancy. A 32-species skeletal mechanism [99] is
adopted for ethylene chemistry. Radiation is modeled by the Monte Carlo ray tracing
method with line-by-line databases. The two-equation soot model is employed to de-
scribe soot dynamics. A soot Schmidt number of 60 is adopted as suggested by [48].
Note that the choice of the soot precursor, e.g., C_2H_2 versus polycyclic aromatic hy-
drocarbons (PAH), and of the chemical kinetic model can lead to large variations in
the prediction of soot volume fraction, as observed in previous studies [90, 100]. Such
variation is generally believed to be one of the largest uncertainties in the two-equation
soot model.

Figure [3.1] shows the temperature profiles at various heights. The uncertainty in
the measured temperature is reported as ±10%. Overall, the temperature field is well-
predicted by the simulation within the uncertainty range. The radial profiles of molar
concentrations of C_2H_2, CO_2, CO, and OH at H = 2.0 cm, are also compared with
Fig. 3.1: Temperature profiles at various heights for the $\text{C}_2\text{H}_4$-air flame: (a) 2 cm, (b) 3 cm, (c) 4 cm, (d) 7 cm.

experimental measurements, as shown in Fig. 3.2. Very good agreement is observed for the soot precursor $\text{C}_2\text{H}_2$. The simulation over-predicts the peak OH value, and the overall profile is shifted to a smaller radial location. Meanwhile, slightly lower CO and higher CO$_2$ concentrations are observed approaching the center of the fuel jet, indicating a slight over-prediction of CO-CO$_2$ conversion. A similar trend was reported in previous numerical studies [48], in which these discrepancies were attributed to the uncertainty associated with the chemical mechanism.

Figure 3.3 compares profiles of predicted soot volume fraction with the experi-
Fig. 3.2: Species profiles at a height of $H=2.0$ cm for the $C_2H_4$-air flame: (a) $C_2H_2$, (b) OH, (c) CO, (d) CO$_2$.

A higher soot yield is predicted near the fuel nozzle, while a lower soot volume fraction is observed further downstream ($H = 7$ cm). Good agreement is observed at the fuel-air mixing layer for $H = 2$ to 4 cm. Note that the inlet boundary conditions [101], the choice of chemical mechanisms [48] and the model constants [90] may significantly impact the prediction of soot. The baseline solver is considered to be satisfactory here, and will be employed next to assess the performance of radiation models using the target methane/air flames.
Fig. 3.3: Soot profiles at various heights for the C₂H₄-air flame: (a) 2 cm, (b) 3 cm, (c) 4 cm, (d) 7 cm.

3.2 Laminar methane diffusion flames

The series of methane-air laminar flames [94] is the main target in this chapter, which is selected by the Workshop on “Defining RTE Solution Methods for Multi-mode Transfer” [47]. The burner is a modified “Santoro” burner where the fuel injection tube is extended to \( L = 6.4 \) cm above the air injection tube to allow the measurement of the heat flux below the flame region, as shown in Fig. 3.4. The diameter of the fuel tube is \( d_{\text{fuel}} = 1.11 \) cm, and the outer diameter of the air annular coaxial tube is \( d_{\text{coflow}} = 10.16 \) cm. Available measurements include the visible flame length \( L_f \) ex-
tracted from photographs, radiant fractions, and radiative heat flux normal to the control surface at \( r = R \) (see Table 3.1 for values of \( R \)). Fuel is injected at different flow rates for the flames designated in [94] as flames ID-2, ID-4, ID-9, and ID-11. The inlet velocity (\( U \)), radiant fraction (\( X_R \)), flame length (\( L_f \)), as well as the measurement location \( R \) are summarized in Table 3.1. Due to their higher Reynolds numbers, flames ID-9 and ID-11 are unsteady flickering flames, and their flame heights were determined by averaging the visible flame lengths recorded in a sequence of 150 photographs with a short exposure time. The minimum and maximum mean flame heights were recorded [102], as listed in Table 3.1. Yellow luminosity is experimentally observed for all four flames indicating existence of soot, although no quantification of the soot volume fraction is available from the experiments. More details on the target flames can be found in [94, 102].

The computational domain is illustrated in Fig. 3.4. To minimize the boundary effect introduced by the entrainment of the ambient air, the radial direction of the computational domain is set to be larger than \( R = 11.4 \) cm for all four cases. The axial direction extends to more than three-fold of \( L_f \) (ID-11). A grid convergence study is first performed under the adiabatic condition using three different meshes. The meshes, denoted as M1, M2, and M3, consist of 0.11 million, 0.18 million, and 0.22 million cells, respectively. Note that additional grid points are embedded in the flame stabilization region near the rim of the nozzle wall for finer resolution. Figure 3.5 presents the radial profiles of OH mass fraction obtained using the three meshes on flames ID-4.
Table 3.1: Inlet conditions and flame characteristics for the simulated flame series.

<table>
<thead>
<tr>
<th>Flame ID</th>
<th>U, m/s</th>
<th>$L_f$ cm</th>
<th>$R$, cm</th>
<th>$X_R$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.0517</td>
<td>5.5</td>
<td>5.4</td>
<td>12.5</td>
</tr>
<tr>
<td>4</td>
<td>0.0689</td>
<td>7.6</td>
<td>5.4</td>
<td>14.1</td>
</tr>
<tr>
<td>9</td>
<td>0.121</td>
<td>15.0±0.5</td>
<td>11.4</td>
<td>17.6</td>
</tr>
<tr>
<td>11</td>
<td>0.155</td>
<td>17.4±1.2</td>
<td>11.4</td>
<td>18.0</td>
</tr>
</tbody>
</table>

and ID-11 at $H = 5$ cm. As shown, the difference between M2 and M3 is negligible, suggesting grid convergence. To balance the computational cost and accuracy, the M2 mesh is selected to conduct the subsequent simulations for the four flames.

The boundary conditions for velocity at the fuel nozzle are specified according to Table 3.1. A fixed velocity of 0.208 m/s is specified for the coflow air for all four cases, and an open boundary condition is specified for the ambient boundaries to allow of air-entainment. The nozzles for both the fuel inlet and the air coflow are included in the computational domain to eliminate inlet boundary effects. The flow profiles at the nozzle exit plane are verified to be fully-developed for both streams. The inlet temperatures are fixed at 298 K for both fuel and coflow nozzles. For pressure, a fixed value of 1 atm is specified for the side and outlet boundaries, while zero gradient is assigned to the nozzle inlets. The nozzle wall is assumed to be isothermal (298 K), following the suggestion in [47]. The above boundary conditions are used for the baseline simulations.

To investigate the chemical effects, a 16-species skeletal mechanism [103], referred to as “SK16”, and a more recent 25-species skeletal mechanism [104], referred
Fig. 3.4: Details of the computational domain.

to as “SK25”, are adopted for comparison. Simulations with SK16 are employed as the baseline. Note that SK25 contains soot-relevant species, such as C$_2$H$_2$, which enables the use of the two-equation soot model discussed in Sec. 3.1. Studies of the potential effects of soot radiation are performed with default model parameters [8].

Different radiation solvers including the MCRT introduced in Chapter 2, P1 and optically-thin (OT) models [49], as well as different radiation properties such as gray
Fig. 3.5: Comparison of the radial profiles of OH mass fraction obtained using three different meshes at $H = 5$ cm for flames (a) ID-4, and (b) ID-11.

and nongray treatments are further compared. The spectral property of soot in Chapter 2 is employed for soot radiation.

Table 3.2 summarizes the thermal boundary conditions of the fuel nozzle, chemical mechanisms, radiation models, and the inclusion of soot, for the eighteen cases investigated in this study.
Table 3.2: Cases investigated in this chapter. Flame ID and Name are combined to denote each case.

<table>
<thead>
<tr>
<th>No.</th>
<th>Flame ID</th>
<th>Boundary</th>
<th>Mechanism</th>
<th>Soot</th>
<th>Radiation</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>Adiabatic</td>
<td>SK16</td>
<td>No</td>
<td>MCRT/LBL</td>
<td>Adiabatic</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Non-adiabatic</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>Adiabatic</td>
<td>SK16</td>
<td>No</td>
<td>MCRT/LBL</td>
<td>Adiabatic</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Non-adiabatic</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>Adiabatic</td>
<td>SK16</td>
<td>No</td>
<td>MCRT/LBL</td>
<td>Adiabatic</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Non-adiabatic</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>Adiabatic</td>
<td>SK16</td>
<td>No</td>
<td>MCRT/LBL</td>
<td>Adiabatic</td>
</tr>
<tr>
<td>8</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Non-adiabatic, SK16, Reabs</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>$T_w=298$K</td>
<td>SK16</td>
<td>No</td>
<td>MCRT/Gray</td>
<td>NA</td>
</tr>
<tr>
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<td>4</td>
<td>$T_w=298$K</td>
<td>SK16</td>
<td>No</td>
<td>P1/Gray</td>
<td>NA</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>$T_w=298$K</td>
<td>SK16</td>
<td>No</td>
<td>OT</td>
<td>NA</td>
</tr>
<tr>
<td>12</td>
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<td></td>
<td></td>
<td></td>
<td>SK16, MCRT/Gray</td>
</tr>
<tr>
<td>13</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SK16, P1/Gray</td>
</tr>
<tr>
<td>14</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SK16, OT</td>
</tr>
<tr>
<td>15</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SK16, Norad</td>
</tr>
<tr>
<td>16</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SK25, Nosoot-OT</td>
</tr>
<tr>
<td>17</td>
<td>11</td>
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<td></td>
<td></td>
<td></td>
<td>SK25, Soot-OT</td>
</tr>
<tr>
<td>18</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SK25, Soot-Reabs</td>
</tr>
</tbody>
</table>
3.3 Results and discussion

The flame structures are first presented, followed by a comprehensive comparison with experiments. Parametric studies on boundary conditions, radiation models, chemical mechanisms, and soot radiation are discussed in detail. Finally, the pinch-off mechanism for the unsteady flame is briefly discussed.

3.3.1 Flame structures

The structures of flames ID-4 and ID-11 are first illustrated to facilitate subsequent discussion. As shown in Fig. 3.6, flame ID-4 has a typical diffusion flame structure where the peak of temperature or OH mass fraction can be considered as the flame sheet. Observed as a steady flame, flame ID-4 is stabilized slightly above the rim of the nozzle, as indicated by the contour of OH mass fraction. The Planck-mean absorption coefficient is approximately 0.6 m\(^{-1}\) within the flame, and increases to 1.2 m\(^{-1}\) beyond 10 cm downstream. Based on the flame length and the Planck-mean absorption coefficient within the flame, the optical thickness (\(\tau\)) is approximately 0.045, indicating that this flame is within the optically-thin limit (i.e., \(\tau \ll 1.0\)). The emission source term is strong near the flame front where temperature is high, while the radiative absorption is more uniformly distributed with a slight peak near the axis. Beyond two flame lengths, the temperature and CO\(_2\) mass fraction maintain at approximately 1000 K and 0.06, respectively, and the Planck-mean absorption coefficient is higher downstream than that near the flame front.
Fig. 3.6: Scalar fields of flame ID-4. From left to right are: T (1000 K), mass fraction of OH (10\(^{-3}\)), mass fraction of CO\(_2\), Planck-mean absorption coefficient \(\kappa_P\) (m\(^{-1}\)), emission source term (1MW/m\(^3\)), and absorption source term (1MW/m\(^3\)).

Figure 3.7 shows the instantaneous flame structure of flame ID-11. As the inlet flow rate increases, periodic “flame pinch-off” is observed near the centerline at 12 cm. The wrinkles of the flame surfaces seen in the temperature contour develop periodically with a frequency of 16.7 Hz, which is close to the observed frequency in the experimental study (i.e., 16.9 Hz [102]). Stronger flame absorption is noticed downstream comparing to flame ID-4, due to a combined effect of higher flame temperature, higher concentration of participative species, and a larger characteristic length scale. A larger optical thickness is expected for flame ID-11 where the flame length is up to 17 cm. Similar periodic behavior is observed for flame ID-9, and both flames will be referred to as the unsteady flames hereinafter. Flames ID-2 and ID-4, on the other hand, will be referred to as the steady flames.
Fig. 3.7: Scalar fields of flame ID-11. From left to right are: T (1000 K), mass fraction of OH ($10^{-3}$), mass fraction of CO$_2$, Planck-mean absorption coefficient $\kappa_P$ (m$^{-1}$), emission source term (1MW/m$^3$), and absorption source term (1MW/m$^3$).

3.3.2 Radiative heat flux

The radiative heat fluxes obtained from the numerical simulations are compared with experiments for the two steady flames in Fig. 3.8. To reduce its statistical variance, the radiative heat flux in Fig. 3.8 is obtained by postprocessing the steady-state solutions, using the same MCRT/LBL solver as used in the coupled simulations, where the ray tracing procedure is repeated 100 times to obtain statistics. For each solution, 0.6 million rays are emitted in total and the radiative heat flux is computed by averaging energy across each boundary cell surface.

The average heat fluxes for each computational cell along the measured location ($r = R$) are presented as lines in Fig. 3.8. The radiative heat fluxes are under-predicted...
Fig. 3.8: Comparison of the radiative heat fluxes along the $r = R$ boundary for flames ID-2 and ID-4.

by the baseline model for both flames. The under-prediction can result from uncertainties in thermal boundary conditions, chemical mechanisms, and lack of soot modeling. The latter two factors are discussed in Sec. 3.3.5, while the sensitivity to the thermal boundary conditions are examined here in Fig. 3.8. Results obtained using adiabatic boundaries can differ as much as 15% from the baseline results. The nozzle wall temperature has proven to be a critical boundary condition for predicting flame stabilization [105]. To reduce uncertainties arising from the thermal boundary conditions, temperature measurements along the nozzle wall or conjugate heat transfer treatment should be included for future studies.

The averaged radiative heat fluxes of two unsteady flames are compared with experiments in Fig. 3.9. For both flames, 200 snapshots at a time interval of 0.0025 s are employed for averaging, which mimics the experimental procedure of measuring heat flux under unsteady conditions. The vertical bars denote root mean square (r.m.s)
**Fig. 3.9:** Comparison of the radiative heat fluxes along the $r = R$ boundary for unsteady flames ID-9 and ID-11. The vertical bars on the numerical results denote r.m.s values due to unsteadiness.

**Table 3.3:** Comparison of radiant fractions in percentage (%).

<table>
<thead>
<tr>
<th>Flame</th>
<th>ID-2</th>
<th>ID-4</th>
<th>ID-9</th>
<th>ID-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>12.5</td>
<td>14.1</td>
<td>17.6</td>
<td>18.0</td>
</tr>
<tr>
<td>Simulation</td>
<td>11.2</td>
<td>14.8</td>
<td>18.7</td>
<td>18.5</td>
</tr>
</tbody>
</table>

values due to unsteadiness. The adiabatic boundary condition again predicts higher radiative fluxes than the baseline. A nearly constant gap between the numerical results and experiments is observed in the mean radiative flux profiles beyond $1.5L_f$ for both flames. One possible explanation, in addition to other modeling uncertainties to be discussed in Sec. 3.3.5 is the different data processing approaches used in experiments and simulations. The background noise is subtracted from the signal in experiments [102], while no such treatment is performed for the numerical results. The different treatments can lead to exaggerated discrepancies between simulations and experiments, especially at downstream locations where the absolute values of heat fluxes are low.
Table 3.3 compares the predicted radiant fractions to their experimental counterparts. The results are obtained from simulations with adiabatic nozzle walls. The radiant fractions differ by approximately 1% for both steady and unsteady flames. The differences are consistent with the discrepancies observed in Figs. 3.8 and 3.9. It should be noted that no flame-specific model turning was performed during the simulations of this series of target flames. Based on the comparison in this section, we consider the performance of the reacting DJFoam platform satisfactory.

3.3.3 Effects of radiation models on steady flames

In this section, the P1 radiation solver [106] and a Planck-mean based gray spectral model are compared to the baseline MCRT/LBL solver in coupled simulations. The P1 solver and the gray spectral model are selected for comparison, as they are the most widely available solver and spectral model in CFD packages [50, 107]. Therefore, such comparison may provide some general guidance to the choice of radiation models for laminar diffusion flames. An optically-thin model is also compared, where the radiative emission is computed using the Planck-mean absorption coefficients that are derived from the LBL database and flame re-absorption is neglected. The same set of Planck-mean absorption coefficients are also employed as the gray spectral model.

Four coupled simulations are conducted for flame ID-4, with variations only in the radiation models. Case “MCRT/Gray” features the MCRT solver with the gray model, to study the effect of the spectral property models. Subsequently, the P1 solver
Table 3.4: Comparison of four radiation models in accuracy and computational cost.

<table>
<thead>
<tr>
<th>Models</th>
<th>Frozen-analysis</th>
<th>Coupled-simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{emi}$, W</td>
<td>$Q_{abs}$, W</td>
</tr>
<tr>
<td></td>
<td>$Q_{emi}$, W</td>
<td>$Q_{abs}$, W</td>
</tr>
<tr>
<td>MCRT/LBL</td>
<td>1.80 0.348</td>
<td>1.59 0.327</td>
</tr>
<tr>
<td>MCRT/Gray</td>
<td>1.80 0.024</td>
<td>1.55 0.023</td>
</tr>
<tr>
<td>P1/Gray</td>
<td>1.80 0.020</td>
<td>1.55 0.017</td>
</tr>
<tr>
<td>OT</td>
<td>1.80 0</td>
<td>1.55 0</td>
</tr>
</tbody>
</table>

is employed with the gray model (“P1/Gray”) to illustrate the effect of RTE solvers. Lastly, the optically-thin (“OT”) simulation is designed to understand the effect of re-absorption. Note that four models predict the same emission source terms when the underlying thermal-chemical fields are identical.

The performance of different radiation models for flame ID-4 is also evaluated in Table 3.4. The total emission $Q_{emi}$, total absorption $Q_{abs}$, and the absorption fraction $\chi_{abs}$, as defined in Eq. (3.1), are compared.

$$Q_{emi} = \int_V \dot{Q}_{emi} dV, \quad Q_{abs} = \int_V \dot{Q}_{abs} dV, \quad \chi_{abs} = \frac{Q_{abs}}{Q_{emi}}.$$  \hspace{1cm} (3.1)

Here, $dV$ and $V$ denote the volumes of each cell and the entire computational domain, respectively. The three metrics are obtained from four coupled simulations and from frozen-field analyses of a snapshot without any radiation models. Significant differences in the predicted absorption fraction $\chi_{abs}$ are observed between MCRT/LBL and other models in both coupled and frozen-field analyses. This suggests the importance
of nongray spectral models in laminar diffusion flame simulations. Comparing results obtained from MCRT/Gray and from $P_1$/Gray, it is observed that the RTE solver plays a less significant role than the nongray spectral model. The coupled simulations and the frozen-field analyses predict similar model performances, although the absolute differences in $Q_{abs}$ become smaller in the coupled simulations. In addition, $Q_{emi}$ varies between different models in the coupled simulations, due to the feedback from the radiative sources to the thermochemical fields. The comparison here justifies the usage of frozen-field analysis in assessing radiation models. However, coupled simulations are required if differences in the thermochemical fields are concerned.

Although significant differences in $Q_{abs}$ are observed in Table 3.4, the fraction of absorption $\chi_{abs}$ is small in general. The cost of the MCRT/LBL solver is affordable for such coupled simulations, which however is still ten times that of the $P_1$ solver with simple gray model.

Figure 3.10(a) further compares the axial profiles of temperature and radiative source terms obtained from all models. The differences in the temperature profiles are minor, with a maximum difference of 25 K near the peak temperature between MCRT/LBL and OT. The MCRT/LBL predicts slight higher temperature than the other three models, because it accurately captures the nongray absorption indicated by the weak re-absorption peak in Fig. 3.6. The relative difference of the peak radiative source term is approximately 12.9% between MCRT/LBL and the other three models. Figure 3.10(b) shows the axial mass fractions of CO$_2$ and OH. Minor differences
Fig. 3.10: Comparison of (a) centerline temperature and radiative source term, and (b) mass fractions of CO\textsubscript{2} and OH for flame ID-4 with four radiation models. The vertical lines denote the normalized flame height.

are observed for OH as it is sensitive to temperature.

Compared to the differences observed by changing the nozzle-wall boundary in Fig. 3.8, the differences among different radiation models are negligible, which suggests that the prediction of radiative absorption plays a secondary role in these optically-thin laminar flames. The differences between MCRT/LBL and MCRT/Gray are larger than that between MCRT/Gray and P1/Gray, indicating again that spectral property models play a more important role than the RTE solvers.

Therefore, considering both accuracy and computational efficiency, the optically-thin model or a simple P\textsubscript{1} solver could provide a reasonable approximation to the radiation field for steady laminar flames with a small optical thickness. However, when pollutants such as soot and/or NO\textsubscript{x} are concerned, the small discrepancies observed in temperature and OH mass fraction may be sufficient to change the evolution of these pollutants.
3.3.4 Effects of radiation models on flickering flames

The performance of different radiation models for the flickering flame ID-11 is investigated using the coupled simulations, as summarized in Table 3.5. The absorption source is slightly higher compared to ID-4, because flame ID-11 has a larger optical thickness.

The differences between the MCRT/LBL and MCRT/Gray again indicate the importance of nongray spectral models. The differences between P1/Gray and MCRT/Gray are amplified compared to those in Table 3.4.

<table>
<thead>
<tr>
<th>Models</th>
<th>Emi, W</th>
<th>Abs, W</th>
<th>$\chi_{abs}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCRT/LBL</td>
<td>5.51</td>
<td>1.34</td>
<td>24.3</td>
</tr>
<tr>
<td>MCRT/Gray</td>
<td>5.32</td>
<td>0.11</td>
<td>2.0</td>
</tr>
<tr>
<td>P1/Gray</td>
<td>5.31</td>
<td>0.04</td>
<td>0.8</td>
</tr>
<tr>
<td>OT</td>
<td>5.31</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The performance of different radiation models on capturing flame characteristics is investigated in Fig. 3.11. The differences in the temperature profiles are slightly larger than those in flame ID-4, with a maximum difference of 42 K between MCRT/LBL and OT. A relatively large discrepancy of the radiative source term is observed between MCRT/LBL and the other three models in the peak values. Correspondingly, larger discrepancy is observed in the mean OH profiles in Fig. 3.11(b).

To further explore the effects of radiation, the instantaneous flame height and flame puffing frequency obtained from three radiation modeling approaches are com-
Fig. 3.11: Comparison of (a) axial temperature and radiative source term, and (b) mass fractions of CO$_2$ and OH for flame ID-11 with four radiation models. The vertical lines denote the mean flame height.

pared with experiments in Figs. 3.12 and 3.13 including the adiabatic limit, referred to as “SK16, Norad”, the optically-thin limit, referred to as “SK16, OT”, and the MCRT/LBL model, referred to as “SK16, Reabs”. Because no numerical definition is identical to the experimental metric, the instantaneous flame height in simulation is defined as the maximum vertical height of the stoichiometric isoline ($Z_{st}$). A fast Fourier transformation is applied to the instantaneous flame height to obtain the puffing frequency ($f$) for both simulations and experiments. Note that $f$ is independent of the definition of instantaneous flame height. The three simulations under-predict the instantaneous flame height, which may result from the uncertainties in the chemical mechanism, as demonstrated in Sec. 3.3.5. The adiabatic model predicts shorter flames after pinch-off compared to the models with heat loss. By comparing “Reabs” and “OT”, it is seen that the consideration of re-absorption has a negligible impact on the flame height.

Interestingly, as shown in Fig 3.13, three radiation models predict the same puff-
Fig. 3.12: Comparison of the instantaneous flame height between experiments and results obtained with three radiation models.

...ing frequency, which is approximately 16.7 Hz with a relative error of 1.2% compared with experiments (16.9 Hz). This implies that radiation treatment has a minor effect on $f$, which is consistent with previous studies of which concluded that state the flickering is mainly due to hydrodynamic entrainment [108].

3.3.5 Effects of chemical mechanism and soot on flickering flames

Parametric studies are conducted using two chemical mechanisms, with and without soot modeling in this section for flame ID-11.

Figure 3.14 shows contours of instantaneous flame structures at two time instances, one depicting a pinched flame, and the other before the pinch-off. The simulation was conducted using the 25-species mechanism (SK25) with the two-equation soot model. Soot is formed on the fuel-rich side near the flame tip, with a peak soot...
Fig. 3.13: Comparison of the puffing frequency between experiments and results obtained with three radiation models.

volume fraction of approximately 1.2 ppm. The Planck-mean absorption coefficient $\kappa_p$ is up to 3.6 m$^{-1}$ within high soot yield regions, and significant higher flame emission is observed compared to that without considering soot.

Figure 3.15 compares the mean radiative heat fluxes obtained from different chemical kinetic models, with and without soot modeling, and with and without flame re-absorption. Comparing results obtained from the two chemical mechanisms without soot (i.e., “SK16, OT” versus “SK25, Nosoot-OT”), it is clear that chemical mechanisms show minor impact on the radiative heat flux in this flame. When soot and its contribution to radiation are considered (i.e., “SK25, Soot-OT” and “SK25, Soot-Reabs”), larger radiative heat fluxes are predicted along the boundary. The effect of radiative re-absorption plays a minor role in predicting the radiative flux when soot is absent (i.e., “SK16, OT” versus “SK16, Reabs”), however, it plays a more significant
role when soot is present (i.e., “SK25, Soot-OT” and “SK25, Soot-Reabs”). In these coupled simulations, considering re-absorption with soot modeling leads to an approximately 13% increase in the total soot yield, compared to that from the optically-thin model. The flame temperature also slightly increases, and the combined effects of higher flame temperature and higher soot yield lead to higher radiative heat flux predicted along the boundary, as shown in Fig. 3.15. Although not quantified in experiments, soot clearly has a non-negligible contribution to the radiative flux in this flame and should be characterized for future studies.

Figure 3.16 compares the instantaneous flame height to the experiments. A closer agreement of the instantaneous flame height with experiments is predicted by SK25 than by SK16. When soot is present, the flame is further elongated due to the enhanced heat loss arising from soot radiation. The flame puffing frequency from SK25 remains unchanged (not shown), indicating that the flame puffing frequency is insensitive to the choice of chemical mechanisms, radiation models, and the consideration of soot. Since the puffing mechanism is mainly controlled by the hydrodynamic flow fields \[108, 109\], it is not surprising that chemistry and radiation play a secondary role for this weakly sooting flame.

### 3.3.6 Effects of re-absorption on soot dynamics

Finally, to assess effects of flame re-absorption on soot dynamics, the case using MCRT/LBL to capture flame re-absorption is compared to that with optically-thin assumption (OT)
Fig. 3.14: Scalar fields of flame ID-11 at two time instants (a) and (b), respectively. From left to right are: $T$ (1000 K), mass fraction of OH ($10^{-3}$), soot volume fraction $f_v$ (ppm), Planck-mean absorption coefficient $\kappa_p$ (m$^{-1}$). The black dash-dot lines denote $Z_{st}$. 
**Fig. 3.15:** Comparison of radiative heat fluxes obtained from the baseline model (SK16, Reabs), SK16 with optically-thin radiation (SK16, OT), SK25 with optically-thin radiation without soot (SK25, Nosoot-OT), SK25 with optically-thin radiation with soot (SK25, Soot-OT), and SK25 with MCRT/LBL with soot (SK25, Soot-Reabs). Results with background noise correction are presented.

**Fig. 3.16:** Comparison of instantaneous flame height obtained from experiments (Exp), SK16 with the optically-thin model (SK16, OT), SK25 with the optically-thin model without soot (SK25, Nosoot-OT), and SK25 with the optically-thin model with soot (SK25, Soot-OT).
for flame ID-11 in Fig. 3.17, where evolution of the total heat release, the total radiative heat loss, and the ratio \( X_R \) are compared. The \( X_R \), defined in Eq. (3.2), indicates the part of the heat release radiated from the flame and is of particular interest since it quantities the radiant power transferred to the environment. Note that the definition in Eq. (3.2) is distinct to the experimental radiant fraction, where the heat fluxes collected from the boundary were integrated. When considering flame re-absorption, the overall chemical heat release remains unchanged, while smaller radiative loss is observed. This leads to an absolute difference of approximately 4% for \( X_R \) between the two cases, which suggests that ignoring flame re-absorption would lead to an over-prediction of the radiant fraction.

\[
X_R = \frac{\int_V |\dot{S}_r|}{\int_V \dot{S}_c}. \tag{3.2}
\]

In addition, with flame re-absorption, the overall soot yield increases by approximately 13% compared with the OT limit. The flame temperature also slightly increases when re-absorption is considered. The combination of higher flame temperature and higher soot yield leads to higher radiative heat flux predicted along the boundary, as shown in Fig. 3.15.

### 3.3.7 Flame pinch-off

To investigate the pinch-off mechanism, Fig. 3.18 presents contours of strain rate, where the iso-levels of 15% of maximum OH mass fraction and of \( Z = Z_{st} \) are shown to represent the reaction layer and the flame sheet, respectively. Velocity streamlines are
Fig. 3.17: Evolution of (a) total heat release, (b) total radiative loss, and (c) ratio of total heat loss versus total heat release predicted with and without re-absorption, respectively.
also presented with green solid lines. Case eighteen in Table 3.2 is examined here. At 
$t = 0$, the flame is growing along the streamwise direction with a continuous flame sheet 
($Z_{sw}$) and a continuous reaction layer. A small vortex is observed at around $H = 10$ cm 
on the air side of the flame sheet. This vortex forms when the flame becomes unstable, 
as depicted by the corrugated streamline for $t = 0.02$ s at $H = 12$ cm. This is due 
to the presence of the upward buoyancy force that is established by the heat release 
from the flame. As time evolves, the vortex rolls and convects the flame towards the 
center in the radial direction and stretches it in the axial direction ($t = 0.03$ s). Flame 
pinch-off occurs as the upper flame segment separates from the main body of the flame 
($t = 0.05$ s). 

The strain rate at the tip of pinch-off flames is approximately $80–100$ s$^{-1}$, which 
is significantly lower than the extinction strain rate for the laminar methane-air contour-
flow flame ($385$ s$^{-1}$) measured by experiments [110]. In fact, as the flame is com-
pressed, the combustible mixture diminishes, which results in a discontinuous flame 
sheet (i.e., discontinuous $Z_{sw}$ isoline near the pinch-off location at 0.05 s). Therefore, 
for the current flame, it is more likely that the flame is pinched off by the cut-off of fuel 
supply to the neck of the flame rather than by strain-induced local extinction. Similar 
observations and conclusions have been reported in a previous experiment of laminar 
unsteady ethylene-air diffusion flames [109], where flame pinch-off was explained by 
the reduction in fuel supply to the neck of the flame.
3.4 Summary

Two steady and two unsteady laminar flames from the Workshop on “Defining RTE Solution Methods for Multi-mode Transfer” are simulated in this chapter using the developed numerical reacting flow solver coupled with detailed radiation models. Eighteen simulations are conducted for systematical parametric study and good agreement with experiments is achieved when all the necessary physical and chemical processes are adequately accounted for. To capture the flickering motion, the buoyancy forces need to be considered. The prediction of radiative heat flux for the target flames is most sensitive to soot modeling (that is, when soot is indeed present in the flame), the spec-
ification of the thermal boundary conditions, and modeling of radiative re-absorption when soot is present. The flame height prediction is sensitive to the choice of chemical mechanism and inclusion of soot, while the puffing frequency prediction is insensitive to all the chemical and radiation models tested in this study. The flame pinch-off is shown to be related to depletion of combustible mixtures rather than the strong strain on flame surfaces, which indicates that accurate prediction of strain-induced chemical extinction limit is not required when creating new chemical models for capturing flame pinch-off. To allow for more effective assessments of radiation models using this series of flames, it is recommended that soot and the thermal boundary conditions should be quantified in both experimental and numerical studies in the future.
Chapter 4

Detailed study of a laboratory-scale pool fire

4.1 Overview of pool fire simulations

Turbulent pool fires have been widely studied for decades [13], as one of the canonical configurations in fire science. Turbulent pool fires of different scales and with various fuels have been employed to investigate fire dynamics [13, 111], thermal radiation [112], fuel burning rate [27], and extinction [113, 114]. Despite the progress made in simulating and capturing the multi-physical interactions, robustly modeling pool fires remains challenging, when subjecting to environments involving extreme conditions. For example, reduced oxygen level due to evaporation of water suppression may break convectional models where extinction is generally simplified. In addition, significant uncertainties still persist in chemical kinetics and soot models, as discussed in [90, 100]. Lastly, appropriate turbulence-chemistry-radiation interaction models are currently under active development [44], posing further challenges for LES of turbulent pool fires. To mitigate these uncertainties and difficulties, turbulence-resolved simulations are employed in this chapter to study a laboratory-scale heptane pool fire. A
33-species chemical kinetic model [7] is employed to account for ignition, flame propagation and extinction. The simulation incorporates the most comprehensive physical details in modeling pool fires to date, the numerical instrumentation of which is also a challenge in order to maintain reasonable computational cost.

This chapter is organized as follows. The description of the target turbulent heptane pool fire is introduced in Sec. 4.2. Numerical details that are not discussed in Chapter 2 are described in Sec. 4.3. In Sec. 4.4 results obtained from detailed simulations are presented and discussed with a particular focus on the thermochemical characteristics of the target fire. Summaries are finally drawn in Sec. 4.5.

### 4.2 The target pool fire

A small (i.e., pool diameter $D = 2R_0 = 7.1$ cm) heptane pool fire [20] is simulated in this study. Based on the fuel and the pool diameter, the inlet power ($Q_{chem}$) is 4.0 kW. The target pool fire has strong sooting propensity, leading to a large radiant fraction ($X_R$) of approximately 29%. Abundant radiation-relevant experimental data are documented in [20], including the radiative heat flux along the boundaries, emissive and absorption temperatures, flame height, radiative transmittance, etc. To avoid additional uncertainty related to the evaporation model, the liquid heptane is modeled as pre-vaporized gas with a prescribed mass flow rate obtained from the experiments. The relatively small pool size enables a detailed simulation of the flame dynamics through high-fidelity models.
To inform the mesh resolution, the Kolmogorov scale for the target flame is first estimated. Based on an empirical scaling relationship [16] that relates the mean axial velocity to the fire power $Q_{chem}$, as shown in Eq. (4.1), the maximum velocity is estimated to be 2.5 m/s. The fluctuating velocity is then assumed to be 30% of the maximum mean axial velocity, as shown in Eq. (4.2). The integral length scale is assumed to be $L_f = 0.5D = 0.0355$ m. This results in an estimated turbulent Reynolds number of $Re_t = 267$, and an estimated Kolmogorov length scale of approximately 0.054 cm, according to Eq. (4.3) for the target pool fire.

$$\bar{u}_{CL,max} = 1.9 \times Q_{chem}^{1/5} = 2.5 \text{ m/s}, \quad (4.1)$$

$$u' \approx 0.3 \times \bar{u}_{CL,max} = 0.75 \text{ m/s}, \quad (4.2)$$

$$\eta_k \sim L_f(Re_t)^{-3/4} = 0.054 \text{ cm}. \quad (4.3)$$

The laminar flame thickness $\delta_f$ is evaluated to be $\delta_f = \sqrt{D_{th,st}/\chi_{st}} = 0.36$ cm, where $D_{th,st}$ and $\chi_{st}$ are the thermal diffusivity and scalar dissipation rate evaluated at the stoichiometric location of a laminar counterflow diffusion flame at the extinction limit. This definition of $\delta_f$ is frequently employed to assess resolution requirement for DNS of diffusion flames [14, 99]. Lastly, the thickness of the soot layer is observed to be approximately 2 mm in experiments [115], which poses the stringiest constraints on mesh resolution. Based on these estimations and consideration of computational cost, a mesh resolution of $\Delta = 0.5$ mm is selected. Turbulence can be considered as resolved by the present mesh, so no sub-grid stress model is applied to the momentum equation in this
Table 4.1: Physical and numerical parameters of the simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>( \text{C}<em>7\text{H}</em>{16} )</td>
</tr>
<tr>
<td>Pool diameter ( D ), cm</td>
<td>7.1</td>
</tr>
<tr>
<td>Inlet mass flow rate ( \dot{m} ), kg/m(^2)·s</td>
<td>0.0230</td>
</tr>
<tr>
<td>Inlet power ( Q_{\text{chem}} ), kW</td>
<td>4.0</td>
</tr>
<tr>
<td>Flame height ( H_f ), cm</td>
<td>34.5</td>
</tr>
<tr>
<td>Radiant fraction ( X_R ), %</td>
<td>29</td>
</tr>
<tr>
<td>Domain size ( R \times H ), cm</td>
<td>39.1 \times 60</td>
</tr>
<tr>
<td>Time step ( \Delta t ), ( \mu s )</td>
<td>2</td>
</tr>
<tr>
<td>Computational cells</td>
<td>9.6 million</td>
</tr>
<tr>
<td>Energy rays for radiation</td>
<td>48 million</td>
</tr>
<tr>
<td>Kolmogorov scale (pre-estimated), cm</td>
<td>0.054</td>
</tr>
<tr>
<td>Kolmogorov scale (post-estimated), cm</td>
<td>0.057</td>
</tr>
<tr>
<td>Thermal flame thickness, cm</td>
<td>0.36</td>
</tr>
<tr>
<td>Soot layer thickness, cm</td>
<td>0.2 [115]</td>
</tr>
</tbody>
</table>

simulation. Approximately seven grid cells are placed within one laminar flame thickness, and a laminar closure is adopted for the sub-grid combustion modeling. Based on the previous investigation of unstrained and strained laminar flames [62], we consider the laminar closure model to be adequately accurate for the grid resolution employed in the present study, especially when significant heat loss is present and prominent model uncertainty is involved with soot. The physical and numerical parameters of the simulation are summarized in Table 4.1.

A cylindrical computational domain is constructed as shown in Fig. 4.1. The radial direction of the computational domain extends to \( R = 11R_0 \), where the radiative heat flux was experimentally measured. Along the axial direction, the inlet of the
domain is aligned with the pool surface. Note that the fuel pan was elevated approximately 15 cm above ground level in the experiment, and the fuel level was constantly maintained at 3.5 mm below the rim of the fuel pan. These details are not captured by the current computational domain, which might have an impact on the prediction of air entrainment as discussed in similar configurations in [116]. To capture the radiation behaviors of the fire and the plume, the axial span extends to approximately $1.5H_f$, or 60 cm. The resolution is approximately 0.1 cm in the axial direction and 0.05 cm in the radial direction. As shown in Fig. 4.1(b) from the bottom view of the computational domain, the mesh is refined at the base of the fuel inlet and stretched towards the side boundary, resulting in approximately 9.6 million cells in total.

**Fig. 4.1**: Illustration of the computational domain and mesh. (a) Dimensions of the 3D computational domain. (b) Mesh details of the fuel inlet and ambient air inlet. The inner white circle indicates the rim of the pool pan.
4.3 Numerical configurations

The simulations are conducted using the developed numerical platform *reactingDJ-Foam*. The baseline models include the Monte Carlo ray tracing radiation solver coupled with the line-by-line database, and the semi-empirical two-equation soot model with default parameters. The chemical mechanism, the coupling strategy of combustion and radiation, and the boundary conditions are described in this section.

4.3.1 The chemical kinetic model

A 33-species, 227-reactions *n*-heptane skeletal mechanism \[7\] is employed to account for finite-rate chemistry. This model was reduced from JetSurf v1 \[6\] to predict both pyrolysis and oxidation of *n*-heptane for high-temperature applications. The skeletal mechanism showed good agreement with the detailed mechanism for ignition delay, laminar flame speed, and extinction residence time \[7\]. To further assess the accuracy of the skeletal mechanism in preserving the structures of radiation-relevant species, mass fractions of CO$_2$, H$_2$O, CO, CH$_4$ and C$_2$H$_4$, are computed from the detailed and skeletal mechanisms using a laminar counterflow diffusion flame, as shown in Appendix A.2. Profiles in the mixture fraction space are compared, and the maximum difference is approximately 6.8%, observed for the peak mass fraction of C$_2$H$_4$ at a mixture fraction of 0.234. Therefore, the skeletal mechanism is considered to be sufficiently accurate in capturing both chemistry and radiation-relevant species in this study.
4.3.2 Coupling strategy

In a coupled radiation-combustion simulation, the radiative source term $S_r$ must be provided to the energy transport equation, while the RTE solver requires the local state variables, i.e., temperature, pressure, and species molar concentrations to evaluate local emissive power and absorption. Consequently, the coupling frequency between the main flow solver and the RTE solver can significantly impact the accuracy and computational cost [117]. The time step from the main hydrodynamic combustion solver is constrained by the convective time scale and by the chemical time scales. When radicals such as OH, O, and H and/or soot are considered, the chemical time scales can become the limiting time scale in fire simulations. For radiation, since electromagnetic waves travel at the speed of light, which can be several orders of magnitude higher than the convective velocity, the transient term in the RTE is often neglected when coupled with combustion applications. Consequently, the appropriate radiative time scale in a combustion system is determined by the dynamics of the participating species and temperature, which is correlated with the convective time scale [117]. Different time scales involved in this pool fire are briefly investigated provided below to inform the choice of updating frequency for the radiative source term.

The convective time scale is defined as

$$\tau_{flow} = \Delta x_m/\bar{u},$$  \hspace{1cm} (4.4)
where $\bar{u}$ is the mean centerline axial velocity, and $\Delta x_m$ is the mean grid spacing. Based on Eq. (4.4), the convective time scale is approximately $2 \times 10^{-4}$ s. This definition was also employed in [117], where the bulk flow velocity was used for a momentum-driven flow.

The chemical time scales $\tau_{\text{chem}}$ of radiation-relevant species and soot are calculated based on the inverse of the diagonal terms in the corresponding chemical Jacobian evaluated analytically. The time scales presented in Fig. 4.2 are conditional on temperature. By comparing the four species at above 1000 K, it is observed that soot chemistry is the limiting scale, which ranges from $10^{-5}$ to $10^{-1}$ s.

Based on these analyses, the time step $\Delta t$ for the flow solver is selected such that the chemical time scales for soot and other critical minor species are well captured. The radiative source term $S_{r}$ is updated every $N_{it} \Delta t$, which is dictated by the convective time scale. Here, $N_{it}$ is referred to as the updating frequency for radiative source term, and...
a value of 100 is used as the baseline value accordingly. The performances between
the tight-coupling and loose-coupling simulations are compared in Fig. 4.3. \( t_{\text{rad}} = N_{it}\Delta t \), where \( N_{it} \) is referred to as the updating frequency for radiation. \( N_{it} = 1 \) denotes
tight-coupling simulation, and \( N_{it} = 100 \) and 1000 denote loose-coupling simulations.
Negligible differences are observed for the maximum temperature, the total heat release
rate, and the total absorption rate between \( N_{it} = 1 \) and \( N_{it} = 100 \). Relative errors are
within 0.3\% for all three variables. Larger errors are observed with \( N_{it} = 1000 \), where
the maximum error for total absorption is approximately 1.5\%. With \( N_{it} = 1000 \), the
coupling time scale exceeds the estimated convection time scale, thus leading to the
observed discrepancy. Therefore, \( N_{it} = 100 \) is adopted in this study. The effect of the
updating frequency has also been discussed in [117, 118], where \( N_{it} = 100 \) was also
recommended. It is worth noting that the computational cost for every 100\( \Delta t \) is only
26\% of that for the tightly-coupled simulation.

Fig. 4.3: A comparison of (a) maximum temperature, (b) total heat release rate, and
(c) total absorption energy rate for two updating frequencies. The left y-axis
indicates the absolute value and the right y-axis indicates the relative error.
4.3.3 Boundary conditions and computational setup

The temperature at the fuel inlet is set to be the boiling point of \( n \)-heptane at 1 atm \( (T_{in} = 371.6 \, \text{K}) \), while the ambient temperature and pressure are 300 K and 1 atm, respectively. All the boundaries of the computational domain are open, allowing air to be entrained. A mixed boundary condition is assigned for velocity at the side and at the outlet of the domain, setting zero gradient for any outward flow and calculating the inlet velocity from pressure for any inward flow. A fixed total pressure condition \[22\] is specified at the side boundary and at the outlet of the domain. A zero-gradient boundary condition is assigned for species and temperature at the open boundaries. Note that gravity is included in the axial direction as shown in Fig. \[4.1(a)\]. To accurately consider the diffusive mass flux at the fuel inlet, the modified total mass flux boundary in Chapter \[25\] is adopted for the inlet of each species as suggested in \[17\].

The transport equations are advanced in time using a first-order implicit Euler scheme with a fixed time step \( \Delta t = 2 \times 10^{-6} \, \text{s} \), which is determined based on discussions in Sec. \[4.3.2\]. This results in a maximum Courant-Friedrich-Lewy (CFL) number based on bulk flow velocity of less than 0.02. A second-order central difference scheme is adopted for the convective and diffusive terms.

A hierarchy of simulations are designed and conducted in this chapter for systematic parametric studies, as summarized in Table \[4.2\]. Case 5 has the most comprehensive set of sub-models, and is considered as the baseline case. The baseline case is initiated with a single-step chemistry without considering radiation for the first 0.2 seconds...
Table 4.2: Cases investigated in this chapter.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Soot</th>
<th>Radiation</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No</td>
<td>No</td>
<td>Gas-norad</td>
</tr>
<tr>
<td>2</td>
<td>No</td>
<td>MCRT/LBL</td>
<td>Gas-rad</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>No</td>
<td>Soot-norad</td>
</tr>
<tr>
<td>4</td>
<td>Yes</td>
<td>OT</td>
<td>Soot-OT</td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>MCRT/LBL</td>
<td>Gas-soot</td>
</tr>
</tbody>
</table>

to obtain a stably developing thermal flow field. Subsequently, radiation and detailed chemistry are turned on, and the solution is advanced for another 0.3 seconds to achieve a more realistic flame shape. After that, soot chemistry and soot radiation are further initiated to advance the solution to the statistically steady state. The total simulated physical time is approximately two seconds (equivalent to ten puffing periods), and statistics are collected based on the last one second.

4.4 Results and discussion

The simulation results are first verified and validated using empirical correlations and experimental measurements. The detailed flame structure, especially in the near-pool region, are explored next. After that, key results from these high-fidelity simulations are presented and discussed in detail with the following emphasis:

- Interactions between gas and soot radiation.
- Interactions between radiation and chemistry.
• Interactions between radiation and turbulence.

4.4.1 Validation of the puffing frequency and axial temperature

With limited experimental data on the flow and temperature fields, the simulation is first verified using theoretical and empirical relations for pool fires. The instantaneous axial velocity and temperature probed at \( H = 0.2 \text{ m} \) \( (0.58H_f) \) along the centerline of the pool are presented in Fig. 4.4(a) to show the global flame dynamics. Strong fluctuations are observed for both axial velocity and temperature at this location, due to the unsteadiness introduced by the flame and the buoyancy force. After Fourier transform, the power spectrum of velocity is presented in the frequency domain in Fig. 4.4(b). The theoretical puffing frequency is superimposed as the vertical black dashed line, which is derived to be \( f = 0.5 \sqrt{g/D} = 5.87 \text{ Hz} \) (equivalent to 0.17 s in time) [119]. The prominent peak in the power spectrum of velocity is close to the puffing frequency, indicating that the most significant dynamic time scale is captured by the current simulation.

The time-averaged temperature and axial velocity along the centerline are extracted from the last five puffing periods and are shown in Fig. 4.5. The vertical bars denote their respective root mean of square (r.m.s.) magnitudes. Comparison is made between the numerical solutions and empirical correlations that are derived based on experimental measurements of a collection of pool fires in [16]. Three different regions, i.e., continuous flaming, intermittent, and plume regions are separated by the vertical lines. These regions are demarcated by \( H/Q_{chem}^{2/5} \) equal to 0.08 and 0.2. The mean ve-
locity rapidly rises up from zero to the maximum value within the continuous flaming region and remains relatively constant in the intermittent and plume regions in McCaffrey’s correlations [16]. The numerical results exhibit similar scaling behaviors, where close agreement is observed for both temperature and velocity in the plume region. However, in the intermittent region, large deviations between the numerical and the empirical relations are observed, which, in addition to modeling uncertainty, can be partly attributed to the fact that the empirical relations were regressed using experimental data that were heavily weighted towards 14.4 kW pool fires. In addition, the over-prediction of temperature can arise from the uncertainties in the temperature measurements, since this scaling relation was generalized from experimental data that was not corrected for thermal-couple radiation [16]. Similar discrepancy was reported in [17], where LES was coupled with an infinitely-fast chemistry model and a fixed radiant fraction model to simulate a 0.3 meter square methane pool fire. Strong temperature and velocity fluctuations are observed in the numerical results for all three regions, as indicated by the large vertical bars, and they also contribute to the discrepancies between the numerical and theoretical relations.

The mean turbulent velocity intensity based on the ratio of r.m.s. and mean velocities is approximately 35%. Accordingly, using Eqs. (4.2) and (4.3), the Kolmogorov scale (i.e., post-estimated) can be estimated again using the actual fluctuating velocity, leading to a value of 0.057 cm, which is very close to the pre-estimated value listed in Table 4.1. This observation confirms that the grid resolution in this study is sufficient
4.4.2 Validation of the radiative heat flux

The radiative heat fluxes collected along the boundaries are compared with the experimental measurements in Fig. 4.6 to validate the simulation. The non-dimensional radiative heat fluxes, $q'' \times R^2/Q_{\text{chem}}$, are shown as a function of axial distance normalized for resolving turbulence length scales.
Fig. 4.5: A comparison of (a) mean temperature and (b) mean vertical velocity along the centerline with McCaffrey’s correlations. The vertical bars denote their respective r.m.s. $T_0$ refers to the room temperature (300 K).
by the flame height \((H/H_f)\). The radial radiative heat flux is measured near the pool surface and is normalized by the square of the distance from the pool center divided by the total chemical power of the flame, \(q'' \times (r - R_0)^2 / Q_{chem}\). The radial distance from the pool center is normalized by the flame height, \(r/H_f\). Frozen-field analyses are performed on eight snapshots selected within a puffing period at a time interval of 0.02 s. The mean and r.m.s. values are not altered when sixteen snapshots are employed (not shown). Numerical results of mean and r.m.s. are then computed based on the eight snapshots, presented in Fig. 4.6 as lines and vertical bars. The experimental error bar is estimated based on the reported uncertainties of 20% and 40% along the axial and radial directions, respectively.

As shown in Fig. 4.6, radiative heat fluxes are significantly under-predicted when soot is ignored. When soot is considered, the radiative heat flux shows good agreement with the experiments. This suggests that soot is a non-negligible contributor to the radiative flux, which is consistent with the experimental observations \([20]\). The magnitude of the r.m.s of the radiative heat flux is slightly higher in the “Gas-soot” case compared to the “Gas-rad” case, which can be attributed to the intermittent thin soot structures as discussed in Sec. 4.4.4. Moreover, better agreement with the experiment is observed for the radiative heat flux along the radial direction when soot is considered, which indicates that the existence of soot in the flame may also promote the radiative feedback to the fuel pool. As pointed out by the experimental study \([20]\), the uncooled burner may lead to an over-prediction of the radiative heat flux near the pool. This
argument possibly explains the larger discrepancy observed for the radiative flux in the radial direction.

The mean radiant fraction, which is defined using the “semi-infinite cylinder” assumption adopted in the experiment [120], is 25% based on the eight snapshots, which is 4% lower than the experimental measurement (29%). The under-prediction of radiative loss can possibly be explained by the uncertainties in predicting soot volume fractions. Figure 4.7 shows the radiative heat fluxes obtained from two parametric variations where the soot volume fractions are artificially increased and decreased by 50% with respect to the baseline case. The prediction obtained with 50% more soot agrees with the experiment very well along the axial direction. Improvement is also observed in the radial direction near pool. Figure 4.7 therefore suggests that the current simulation potentially under-predicts soot volume fraction over the entire domain, which can lead to the under-prediction of radiative loss. Similar under-prediction of soot volume fraction was also observed in the simulation of the ethylene-air diffusion flame in Chapter 3 using the same model parameters.

4.4.3 Line-of-sight spectral flame emission

With the line-by-line spectral model and the Monte Carlo solver, the line-of-sight spectral radiative flux can be extracted for comparison with experiments, as shown in Fig. 4.8. Consistent with the experimental measurement, the spectral radiative fluxes are collected at $r = 11R_0$ and $H = 1D$. Statistical mean is collected from the same
Fig. 4.6: A comparison of the radiative heat flux along the (a) axial and (b) radial directions. The red symbols indicate experimental results. The black and blue lines indicate results obtained with and without the soot model, respectively.

Fig. 4.7: A comparison of the radiative heat flux along the (a) axial and (b) radial directions. “fv×1.5” and “fv×0.5” respectively indicate 50% increase and decrease in soot volume fractions with respect to the baseline case (“fv×1.0”).
eight snapshots as discussed in Sec. 4.4.2. The r.m.s. values indicate the sample-to-sample variation in the mean spectral fluxes due to unsteadiness. Very good agreement between the computation and experiment is observed, especially at $\lambda = 4300$ nm where CO$_2$ emission dominates and at $\lambda = 2700$ nm where both CO$_2$ and H$_2$O emissions are significant. The good agreement in the wavelength and intensity is essentially a manifestation of the high-fidelity line-by-line spectral model and the radiation solver that are employed in this study. For wavelength smaller than 2000 nm, the emission is mostly contributed by soot, which is reflected by the broadband behavior in the spectral intensity profile.

Very good agreement is observed within the range of [1000, 2300] nm, however, an experimental peak near $\lambda = 3300$ nm is missed by the computation. The wavelength range of [3268, 3512] nm suggests that the discrepancy is potentially contributed by unaccounted for C-H stretching bonds in alkanes and alkenes [121] in the combustion mixture. The conjecture is supported by Fig. 4.9 where the molar concentration of CH$_4$ is artificially increased to five and fifty folds of the predicted value. Good agreement with the experimental peak is observed when fifty folds of CH$_4$ is applied, although an increase of fifty folds seems to be unreasonably high.

To have noticeable emission peak in the spectral intensity, the gas molecules with the C-H stretching bonds should also take on a reasonably high temperature. Clearly, the flame structure in the physical and phase spaces could provide further insights on the discrepancy, which will be discussed next in Sec. 4.4.4. With the verification and
Fig. 4.8: Spectral radiative flux collected along line-of-sight collected at $r = 11R_0$ and $H = 1D$ above the pool surface.

Fig. 4.9: Spectral radiative fluxes with different levels of CH$_4$ at $r = 11R_0$ and $H = 1D$ above the pool surface.
validation conducted in this section, we observe satisfactory agreement between the computation and the experiments, especially considering that no models are manually tuned to match the target condition. In particular, the radiation feature is well captured by the simulation. Subsequently, the focus will be shifted to discussions on the physical insights provided by the simulations.

4.4.4 Detailed flame structure and near-pool statistics

A snapshot of the instantaneous flame structure is shown in Fig. [4.10], where two-dimensional diametrical planes of relevant scalar fields are presented for the “Gas-soot” case. Flame sheets, indicated by the iso-line of stoichiometric mixture fraction, are observed to transition from a laminar-like smooth surface near the pool to slightly wrinkled surfaces and pinched-off pockets further downstream. Temperature and OH mass fraction (not shown) peak in the neighborhood of the stoichiometric mixture fraction, indicating a typical diffusion flame structure. The incomplete combustion product CO is concentrated inside the flame core on the fuel-rich side, while CO$_2$ and H$_2$O are distributed on both sides of the stoichiometric isoline and are convected further downstream. Soot is formed inside the flame core on the fuel-rich side as expected. The Planck-mean absorption coefficient $\kappa_P$ peaks in the same region, indicating the significance of soot radiation. It should be noted that when soot is absent in the “Gas-rad” case (not shown here), $\kappa_P$ is usually low along the flame sheet where temperature is high, due to the negative correlations between the gaseous absorption coefficients and
temperature.

Also shown in Fig. 4.10, the fuel is almost depleted by \( H = 0.1 \) m, whereas smaller hydrocarbons still prevail. A large amount of \( \text{C}_2\text{H}_4 \) is observed within the flame core and near the flame surface, serving as the *de facto* fuel of the diffusion flame. Compared to \( \text{C}_2\text{H}_4 \), the mass fractions of \( \text{CH}_4 \) and \( \text{C}_2\text{H}_2 \) are much lower in this region. To further investigate the mixture composition, a top view of these species at \( H/D = 1 \) is displayed in Fig. 4.11. A few fuel cracking products are observed at this location, including \( \text{C}_5\text{H}_{10}, \text{C}_4\text{H}_8, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2, \) and \( \text{CH}_4 \), with \( \text{C}_2\text{H}_4 \) being the most abundant species \( (Y_{\text{C}_2\text{H}_4,max} = 0.08) \). The larger hydrocarbons are more confined to the core, while the smaller hydrocarbons diffuse faster to get to the high-temperature flame sheet. Therefore, smaller molecules and radicals such as \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{CH}_4 \) and \( \text{CH}_2\text{O}, \) are more likely to contribute to the observed emissive peak in Fig. 4.9, compared to larger hydrocarbons such as heptane. Intermittent soot layers are formed between the stoichiometric mixture fraction and the peak \( \text{C}_2\text{H}_2 \), and concentrated in highly curved flame regions. From Fig. 4.10, it can be argued that more participating species need to be included in the radiation model, if the near-pool spectral radiative emission or absorption needs to be quantified. However, their contribution to overall heat loss is relatively weak.
Fig. 4.10: Contours of instantaneous flame structures. The first row from left to right are mass fractions of fuel, CO, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, and CH\textsubscript{4}. The second row from left to right are temperature (in 1000 K unit) and mass fractions of CO\textsubscript{2} and H\textsubscript{2}O, soot volume fraction, and $\kappa_P$. The iso-line of stoichiometric mixture fraction ($Z_{st} = 0.0622$) is superimposed on each contour as the black dashed line.
Fig. 4.11: Contours of instantaneous flame structures for top view at $H = 1D$. First row from left to right: mass fractions of fuel, $C_5H_{10}$, $C_4H_8-1$, $C_3H_6$, and $C_2H_6$. Second row from left to right: mass fractions of $C_2H_4$, $C_2H_2$, $CH_4$, soot volume fraction and temperature in 1000 K unit. The iso-line of stoichiometric mixture fraction ($Z_{st} = 0.0622$) is superimposed on each contour as the black dashed line.

4.4.5 Radiation characteristics

The chemical and radiative source terms in the energy transport equation are explored to assess their respective contributions to the dynamics of sensible enthalpy. In Fig. 4.12, the joint probability density functions (JPDF) of the source terms and mixture fraction are collected from the same eight snapshots that are discussed in Sec. 4.4.2. Only samples located within $r \leq 0.1$ m are considered. The superimposed blue lines on the JPDFs indicate the mean values of each source term conditional on $Z$. The statistics are shown till $Z = 0.4$, beyond which both source terms are negligible. Both the “Gas-rad” and the “Gas-soot” cases are presented to understand the impact of soot on chemistry and radiation. For the “Gas-rad” case, the exothermic chemical heat release rate peaks at the flame sheet. A negative heat release zone is observed from $Z = 0.1$ to $Z = 0.3$, as a result of endothermic fuel cracking reactions. Note that the endothermic zone is
Fig. 4.12: JPDFs of chemical power and radiative power in the phase space for (a) “Gas-rad”, and (b) “Gas-soot” cases. The blue line indicates the conditional mean, and the black dotted line marks the stoichiometric mixture fraction.

absent when the single-step chemical mechanism is employed. Peak radiative source also locates near the flame sheet and behaves as a heat sink in the energy transport equation. Similar trends of the chemical heat release rate are observed for the “Gas-soot” case, indicating that the effect of soot chemistry is minor in changing the overall heat release behaviors. However, the peak radiative loss slightly shifts to the fuel-rich side and to higher values, due to strong soot emission induced by the high soot yield and relatively high temperature in this region. The shift of the radiation peak away from the flame sheet indicates that the radiative heat loss cannot be conveniently related to the chemical heat release rate through a constant fraction.

To further distinguish radiative characteristics between gas and soot, the contributions of gas and soot to the absorption coefficient, emission and absorption source terms are investigated in temperature space. The Planck-mean absorption coefficients
in Fig. 4.13 and the mean quantities in Fig. 4.14 are collected from the same eight snapshots as in Fig. 4.12.

Figure 4.13 shows the gaseous ($\kappa_{P,g}$) and soot ($\kappa_{P,s}$) absorption coefficients. Two branches of $\kappa_{P,g}$ are observed for the gas phase below 1200 K. The higher branch is caused by accumulated combustion products and relatively lower temperature within the flame core. Towards the flame sheet, $\kappa_{P,g}$ decreases due to the negative correlation between $\kappa_{P,g}$ and temperature. $\kappa_{P,g}$ shifts to the lower branch moving into the plume region, where CO$_2$ and H$_2$O are diluted through mixing with air. On the contrary, $\kappa_{P,s}$ exhibits a single peak in temperature space around 1500 K, which results from the high yield of hot soot formed inside the flame sheet (see Fig. 4.10). Cold soot is observed at downstream locations of the plume. The different peaks in $\kappa_{P,g}$ and $\kappa_{P,s}$ suggest that radiation behaviors by gases and soot can dominate different regions of the flame.

Figure 4.14 further shows the conditional mean emitted and absorbed energy as functions of temperature for gases and soot, respectively. With the $T^4$ dependence,
Baseline results: Soot alters radiative characteristics

Fig. 4.14: Total emitted and absorbed power as functions of temperature, respectively.

Emissive energy peaks in the neighborhood of 1600 to 1800 K for both gases and soot, with the peak soot emission slightly shifting to the lower temperature side due to its presence in the fuel-rich side of the flame. The total emission from the gas mixture is stronger than that from soot, i.e., with a ratio of 3:2. For absorption, the gas phase has a much stronger contribution than soot, and the gas absorption is consistently around 20 W throughout the temperature window.

For temperature below 800 K, absorption exceeds emission, indicating a heating effect from radiation. Note that the total absorption is approximately 30% of the total emission in this pool fire when considering soot radiation.

4.4.6 Spectral interactions between soot and gas

With the available information on the origin of each energy ray from the radiation solver, the absorption behaviors of gas and soot are further differentiated by counting
Table 4.3: Frozen-field analyses of the absorbed energy portion for the “Gas-soot” case. Mean absolute value within a puffing period is shown. The mean total absorbed energy is $290 + 22 = 312$ W.

<table>
<thead>
<tr>
<th>Absorbed energy, W</th>
<th>Gas absorption</th>
<th>Soot absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emitter</td>
<td>Gas</td>
<td>Soot</td>
</tr>
<tr>
<td>Energy, W</td>
<td>283</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>16</td>
</tr>
</tbody>
</table>

Energy rays based on their emitters. As shown in Table 4.3, the gas absorption contributes to approximately 93% of the total absorption, and the soot absorption is only 7%, which again confirms the dominant role of gas absorption in this flame. In addition, out of the portion that is absorbed by gas, approximately 97% comes from gas emission, whereas only 3% is contributed from soot emission. This implies that self-absorption is the major mode of gas absorption. Similarly, for the soot absorption, approximately 73% comes from soot, and only 27% is contributed from gas emission.

Self-absorption from soot is slightly reduced compared to gases, which is further explained through the power spectra in Fig. 4.15. The emission power spectra for gases and soot are collected from the whole computational domain, as shown in Fig. 4.15(a). Figure 4.15(b) shows the power spectra collected along the boundary of the computational domain, which represents energy that reaches the boundary after being absorbed by the participative media. The wavelength distribution of CO is not shown as it only contributes to less than 2% of the total radiative energy. The distinct spectral and broadband emission behaviors from gases and soot are manifested by the intermittent
Fig. 4.15: Power spectra of (a) radiation emitted over the whole domain, and (b) radiative loss across the boundaries. Results are obtained from the same time instance as Fig. 4.10.

and continuous emissive spectra from CO$_2$/H$_2$O and from soot, respectively. The most intensive emission occurs at a wavelength of 4300 nm, which is a signature of CO$_2$ emission. At 2700 nm, emission from CO$_2$, H$_2$O and soot has comparable magnitudes. For wavelengths lower than 2700 nm, soot emission is dominant.

For the power spectra in Fig. 4.15(b), the magnitude of the 4300 nm CO$_2$ peak is reduced by 20%, due to the strong self-absorption from CO$_2$. Below 2700 nm, the peak power for soot, CO$_2$ and H$_2$O are not significantly reduced, indicating weaker self-absorption in this spectral window. There is a dip in the soot spectrum at 4300 nm,
indicating that a discernable amount of soot emission is re-absorbed at 4300 nm by CO$_2$. The differences in the absorption behaviors of gas and soot can be explained by the flame structure and by their characteristic thicknesses ($L_c$). As shown in Fig[4.10], the characteristic thickness of CO$_2$ layers is on the order of the pool diameter, while the characteristic thickness of soot is much smaller, on the order of a few millimeters. The optical thickness $\tau$ is proportional to the characteristic thickness (i.e., $\tau = \kappa L_c$), when the absorption coefficients are comparable between soot and gas. Consequently, the re-absorption effect is more prominent with CO$_2$ than with soot. In addition, the relative locations of the radiative layers also determine the amount of re-absorption. For example, soot is enclosed by hot combustion products such that soot emission at 4300 nm is clearly absorbed by the gases. On the other hand, radiation emitted from the lean side of the flame is outside the stoichiometric surface, and is largely lost to the boundary because no significant participative media exist between the outer surface of the flame and the boundary.

It is interesting to note that optically-thick and optically-thin behaviors co-exist in the current fire system. For example, the gas phase features significant re-absorption (i.e., significant optical thickness), while soot exhibits optically-thin behavior. In addition, although the overall soot radiation is optically-thin, it is optically-thick (i.e., significant re-absorption is observed) at 4300 nm because of the presence of CO$_2$. Such spectral interactions between gas and soot indicate the importance of accounting for the nongray behaviors when both gas and soot are contributing significantly to radiation.
4.4.7 Turbulence-radiation interactions (TRI)

As seen in previous sections, it is important to consider soot radiation in fire simulations. Prediction of soot is very sensitive to temperature which may be affected by the prediction of subgrid turbulence-radiation interactions (TRI). TRI for radiative emission arises from the inequality when evaluating the mean of the emission source term $Q_{emi} \propto \kappa_p T^4$:

$$\bar{\kappa_p T^4} \neq \kappa_p(\bar{T}, \bar{X}_i, \bar{P}) \bar{T}^4 . \tag{4.5}$$

The overbar ($\bar{\cdot}$) represents either time averaging in the Reynolds Navier-Stokes Averaged (RANS) context, or spatial filtering in the LES context. In this section, we focus on the investigation of emission TRI in the LES framework, namely, LES-TRI.

The emission TRI can be measured by the ratio of the two terms in Eq. (4.5) as

$$R_{emi} = \frac{\bar{\kappa_p T^4}}{\kappa_p(\bar{T}, \bar{X}_i, \bar{P}) \bar{T}^4} = R_{\kappa_p}(R_{T^4} + R_{Ib}) , \tag{4.6}$$

where $X_i$ refers to the molar concentration of $i^{th}$ radiative species. The three contributions on the right hand side of Eq. (4.6), $R_{\kappa_p}$, $R_{T^4}$, and $R_{Ib}$, indicate the self-correlation of absorption coefficient, self-correlation of temperature, and the cross-correlation between temperature and absorption coefficient, respectively. By assuming $\bar{T'}$ and $\bar{\kappa}_p'$ to
be negligible, the three quantities can be written as

\[ R_{\kappa P} = \frac{\overline{\kappa P}}{\kappa_P(T, X_i, P)} , \]

\[ R_{T^4} = 1 + 6 \frac{T'^2}{T} + 4 \frac{T'^3}{T^3} + \frac{T'^4}{T^4} , \]

\[ R_{Ib} = 4 \frac{\kappa'_P T'}{\kappa_P T} + 6 \frac{\kappa'_P T'^2}{\kappa_P T^2} + 4 \frac{\kappa'_P T'^3}{\kappa_P T^3} + \frac{\kappa'_P T'^4}{\kappa_P T^4} . \]

(4.7) \hspace{1cm} (4.8) \hspace{1cm} (4.9)

To obtain these quantities for LES-TRI, an \textit{a priori} analysis is performed by applying a box filter to the data from the detailed pool fire simulation. For a given quantify, \( Y \), filtered value \( \overline{Y} \) is obtained by taking the mean of all the values in the filter box, while the subgrid fluctuation \( Y' \) is calculated as the difference between the exact value (i.e., that from the detailed simulation) and the filtered value, such that \( Y = \overline{Y} + Y' \). Based on \( \overline{Y} \) and \( Y' \), all the terms in Eqs. (4.7)-(4.9) can be subsequently evaluated.

Figures 4.16 and 4.17 show contours of the emission TRI and its three contributing terms on the center plane from an instantaneous time snapshot when considering soot radiation, with a filter size of \( 8\Delta x \) and \( 16\Delta x \), respectively. Lines denoting 10% of the maximum radiative emissive loss are superimposed on all figures. All the quantities, except \( R_{\kappa P} \), are confined to the range of \([0.8, 2]\). Clearly, values away from unity are observed for all the terms, and the TRI is stronger with a larger filter size. \( R_{\kappa P} \) shows small positive and negative values on the fuel-rich side and the fuel-lean side, respectively. \( R_{Ib} \) and \( R_{T^4} \) are larger than unity along the flame front where flame temperature and fluctuations of radiative species and temperature are both high. A slight attenu-
Fig. 4.16: Emission TRI with a filter size of $8\Delta x$ on the center plane with soot radiation. (e) Emission source term in MW/m$^3$, and the green line denotes 10% of the maximum emissive loss.

A strong effect of TRI is observed in the downstream region where flame temperature is relatively low.

By comparing the location with strong TRI and the location with high radiative emission, it is clear that majority of the high-TRI region locates at the outer edge of the flame, where strong flame intermittency is present. This is consistent with the findings from a recent TRI study in the RANS context [122].

When only gas radiation is considered, as shown in Figs. 4.18 and 4.19, similar dependency of TRI on the filter size is observed. Negative $R_{kP}$ is also seen along the flame fronts. Distinct from the case with soot radiation (Figs. 4.16 and 4.17), the region with strong TRI is aligned with the flame fronts, where the radiative loss is relatively high (e.g., larger than 10% of the maximum radiative loss) due to both high flame temperature and high concentrations of radiative species. This is because, for flames with
**Fig. 4.17:** Emission TRI with a filter size of $16\Delta x$ on the center plane with soot radiation. The green line denotes 10% of the maximum emissive loss.

Soot radiation, the radiative loss is tightly coupled with soot, and thereby the region of strong TRI is shifted to locations with both high soot yield and high flame temperature. The different TRI behaviors between flames with and without soot radiation suggest that cautions should be taken when developing LES-TRI models for fires with different sooting propensities. This is part of future research.

### 4.5 Summary

A laboratory-scale turbulent heptane pool fire is simulated using the developed numerical platform in Chapter 2. The turbulent flow field is resolved by the mesh, finite-rate chemistry is accounted for by a 33-species skeletal mechanism, radiation is solved by the Monte Carlo ray tracing solver with the line-by-line spectral database (MCRT/LBL) for five participating species, and soot is modeled by the semi-empirical two-equation
Fig. 4.18: Emission TRI with a filter size of $8\Delta x$ on the center plane with soot radiation. The green line denotes 10% of the maximum emissive loss.

Fig. 4.19: Emission TRI with a filter size of $16\Delta x$ on the center plane with soot radiation. The green line denotes 10% of the maximum emissive loss.
model. Detailed investigations are conducted to fundamentally understand interactions and couplings among chemistry, soot, radiation, and turbulence. Encouraging agreement is achieved for the flame temperature and vertical velocity along the axis, when comparing to the empirical scaling relations. Good agreement with experiment is achieved in predicting the radiative heat fluxes along the axial and radial directions, while the computed radiative flux is shown to be sensitive to the prediction of soot volume fraction. With MCRT/LBL, the spectral distribution of the emissive power can be easily collected along line of sight and directly compared with experiments. Excellent agreement with experimental data is observed, especially for the 4300 nm emissive peak. Another emissive peak around 3300 nm is under-predicted by the simulation, suggesting that possible contributions from species that contain C-H stretching bond are not accounted for in the current models.

The instantaneous flame contours show a peak temperature near the stoichiometric mixture fraction, following a typical diffusion flame structure. Significant fuel cracking is observed near the pool surface, with small hydrocarbon species, such as C₂H₄, acting as the de facto fuel of the diffusion flame. The total radiative re-absorption is found to be approximately 30% of the total radiative emission. Gas and soot have comparable contributions to emission, whereas gas dominates over soot in re-absorption.

Soot significantly alters the radiative characteristics compared to the non-sooting condition. Soot is abundant in the fuel-rich side of the mixture, shifting the maximum Planck-mean absorption coefficient from the product-abundant low-temperature down-
stream to the high-temperature reaction-intensive upstream of the flame. The presence of soot also shifts the peak radiative emissive power to the fuel-rich side, whereas both chemical heat release and radiative emission peak near the stoichiometric mixture fraction when soot is absent. The radiative source term is clearly disproportionate to the chemical source term, indicating that the common treatment of radiative heat source as a fixed fraction of the chemical source may fail to represent the local energy balance, especially when soot is present.

The analyses of the spectral power spectra show strong CO$_2$ emission and self-absorption near 4300 nm. Soot emission concentrates in the shorter wavelength range, i.e., below 2000 nm, and insignificant self-absorption is observed for soot due to its small optical thickness. Within the 4300 nm CO$_2$ band, a dip of the soot emissive spectra collected along the boundaries indicates strong interaction of soot and CO$_2$ at this wavelength. The detailed spectral power spectra in this study, for the first time, numerically quantify how soot and nongray gases interact within pool fires.

Finally, it is worth noting that the observations addressed in the present study are based on a laboratory-scale pool fire with low levels of turbulence intensity and soot volume fraction in an open environment. Some of the conclusions are sensitive to the spatial structures of the flame. Accordingly, caution should be taken in extrapolating the results reported here to larger-scale pool fires. To simulate practical fires, it is critical and necessary to derive physics-based reduced-order models with acceptable computational cost, which will be discussed in the next chapter leveraging the insights
obtained from this well-resolved laboratory-scale fire simulation.
Chapter 5

Development of reduced-order models

As seen from previous chapters, detailed description of turbulence-chemistry-radiation-soot interactions remains an outstanding challenge in fire modeling even at laboratory scales under idealized conditions. When simulating real-time fires to predict in situ fire hazards, detailed models, such as those used in previous chapters, are computationally prohibitive. On the other hand, if not guided by the proper physics, empirical models can have limited applicability. Drawn on the high-fidelity pool fire simulation database in Chapter 4, reduced-order models on chemistry, soot, and turbulence-chemistry interaction (TCI) are developed here. Specifically, Sec. 5.1 first examines the distribution of radiative source terms using a flamelet extraction method. A simple flamelet model considering radiative re-absorption is proposed. After that, a multi-objective optimization method is employed to construct a two-step reaction mechanism for heptane in Sec. 5.2. The optimized mechanism is validated using the laboratory-scale heptane pool fire. Finally, a simple soot model based on the laminar smoke point concept is constructed in Sec. 5.3. This simple soot model combined with the two-step mechanism is then examined in the same pool fire. A summary is finally provided in Sec. 5.4.
5.1 Development of a flamelet model accounting for re-absorption

Flamelet based models for diffusion flames have been widely employed to describe combustion in fires in recent years \[32, 42, 116, 123, 124, 125\], due to its reduced computational cost while accounting for finite-rate chemistry and turbulence-chemistry interaction (TCI).

While previous investigations recognized the importance of accurate radiation modeling in combination with flamelet models \[123, 125\], only the radiative emission in the optically-thin limit has been incorporated into some of the advanced flamelet models \[126\]. Radiative re-absorption effects are rarely considered or simply treated as a constant proportion of the emissive sources \[51\].

Given these considerations, we examine the distribution of radiative source terms within the framework of Lagrangian flamelets. A flamelet model that considers the re-absorption effect is subsequently proposed based on the flamelet analysis. The non-adiabatic case where both nongray gas and soot radiations are considered (Case “Gas-soot”) and the adiabatic case with neither soot nor radiation models (Case “No-rad”) introduced in Chapter 4 are employed in this section.

5.1.1 Diagnostics using Lagrangian flamelet extraction

The Lagrangian flamelet extraction method \[127, 128\] is employed to examine the radiation characteristics in the mixture fraction space. The mixture fraction $Z$ is defined following Bilger’s definition \[129\] using the gaseous species. The transport equation
for $Z$ that is derived from the species transport equations is written as

$$\rho \frac{\partial Z}{\partial t} + \nabla \cdot (\rho u Z) = \nabla \cdot (\rho D_Z \nabla Z) + \epsilon, \quad (5.1)$$

where $\epsilon$ encapsulates the preferential diffusion correction [127]. $u$ is the instantaneous velocity vector, $\rho$ is density, and $D_Z$ is the thermal diffusivity. The scalar dissipate rate $\chi$ is a key parameter in the flamelet formulation, and is defined as, $\chi = 2D_Z|\nabla Z|^2$.

To extract instantaneous flamelet solutions from the unsteady pool fire simulations, an orthogonal coordinate system is introduced and is spanned by the covariant basis vector $\hat{n}$, $\hat{s}$, and $\hat{t}$, which are defined as [127]:

$$\hat{n} = \frac{\nabla Z}{|\nabla Z|}, \quad \hat{s} = \frac{\hat{n} \times \hat{e}}{|\hat{n} \times \hat{e}|}, \quad \hat{t} = -\hat{n} \times \hat{s}, \quad (5.2)$$

where $\hat{n}$ is the normal unit vector of the mixture fraction isosurface pointing towards the fuel side, and $\hat{e}$ is an auxiliary unit vector that is not aligned with $\hat{n}$.

In the flamelet formulation, all quantities and derivatives along the flame aligned direction $\hat{n}$ are associated with the flamelet-structure and all orthogonal contributions along the plane that is spanned by the vector $\hat{s}$ and $\hat{t}$ are considered as high-order terms. The spatial flamelet-structure can then be extracted by integrating the following equation:

$$dx = \hat{n} \, dZ/|\nabla Z|. \quad (5.3)$$
This relation maps the mixture fraction space to the physical space, and is employed to extract flamelet profiles from the pool fire database. As an example, Fig. 5.1 shows the mean temperature contour along the mid-plane for Case “Gas-soot”. The red solid line indicates the mean stoichiometric mixture fraction (i.e., $Z = Z_{st}$), and the black dashed line denotes an instantaneous isoline of $Z_{st}$. The flamelets are extracted from three elevations marked by blue-solid lines. The right panels in Fig. 5.1 show the top view of ten instantaneous flamelets at each location, superimposed on the instantaneous temperature field.

Using the collection of extracted flamelets, a budget analysis of the temperature equation is performed, to examine the distribution of radiative source terms and their relations to other source terms. The temperature equation in physical space is written as:

$$\rho c_p \left( \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = \nabla \cdot \left( \lambda \nabla T \right) + \dot{\omega}_c + \dot{\omega}_r - \left( \sum_{k=1}^{N_k} \rho c_{p,k} Y_k V_k \right) \cdot \nabla T, \quad (5.4)$$

where $\dot{\omega}_c$ and $\dot{\omega}_r$ account for contributions from chemical reaction and radiation, respectively. $\lambda$ is the thermal conductivity, and $Y_k V_k$ is the diffusive flux induced by species $k$. The pressure fluctuation term is omitted according to the low Mach number approximation in the pool fire simulations. Hence, terms on the RHS of Eq. (5.4) are, respectively, the heat conduction, the chemical heat release rate, the radiative heat loss rate, and the species-diffusion induced enthalpy flux.

The temperature equation can be transformed from the physical space to the mix-
Fig. 5.1: Left: contour of the mean temperature field. The red-solid line and black-dashed line denote the mean and instantaneous stoichiometric mixture fraction ($Z_{st} = 0.0622$), respectively. Right: top-view of instantaneous temperature field at three locations. Ten extracted flamelet solutions are marked by the black solid lines. The black-dashed line denotes the corresponding instantaneous $Z_{st}$.
ture fraction space using the following mapping method,

\[(t, x) \rightarrow (\tau, Z(t, x), Z_2(t, x), Z_3(t, x))\]  \hspace{1cm} (5.5)

where \(Z_2\) and \(Z_3\) are the coordinates that are aligned with \(\hat{s}\) and \(\hat{t}\), respectively. The corresponding transformation operators can be written as \([127]\),

\[\frac{\partial}{\partial t} \rightarrow \frac{\partial}{\partial \tau} + \frac{\partial Z}{\partial t} \frac{\partial}{\partial Z} - (u - (u \cdot \hat{n})\hat{n}) \cdot \nabla,\]  \hspace{1cm} (5.6)

\[\nabla \rightarrow \nabla Z \frac{\partial}{\partial Z} + \nabla_\perp,\]  \hspace{1cm} (5.7)

where \(\tau\) is the Lagrangian flamelet time and \(\nabla_\perp\) indicates the gradient in the flame-orthogonal direction. The last term on the RHS of Eq. (5.6) represents the Lagrangian flamelet velocity along the mixture fraction isosurface.

After applying operators in Eq. (5.6) to Eq. (5.4), the Lagrangian flamelet equation is obtained,

\[\frac{\partial T}{\partial \tau} = (J_1 + J_{2c} + J_{2R} + J_3 + J_4 + J_5) + J^\perp.\]  \hspace{1cm} (5.8)

The terms on the RHS are expressed as,

\[J_1 = \chi_z \frac{\partial^2 T}{\partial Z^2} ,\]  \hspace{1cm} (5.9a)
\[ J_{2, C} = \omega_c / (\rho c_p), \quad J_{2, R} = \omega_r / (\rho c_p), \]  

\[ J_3 = \frac{XZ}{2c_p} \left( \frac{\partial c_p}{\partial Z} + \sum_{k=1}^{N_i} c_{p,k} \frac{\partial Y_k}{\partial Z} \frac{\partial T}{\partial Z} \right), \]  

\[ J_4 = \frac{XZ}{2c_p D_Z} \left\{ \frac{1}{\rho} \sum_{k=1}^{N_i} h_{s,k} \left[ \frac{\partial (\rho(D_Z - D_k))}{\partial Z} \cdot \frac{\partial Y_k}{\partial Z} \right] + \sum_{k=1}^{N_i} h_{s,k}(D_Z - D_k) \frac{\partial^2 Y_k}{\partial Z^2} \right\}, \]  

\[ J_5 = -\varepsilon Z \frac{\partial T}{\partial Z}. \]  

The preferential diffusion correction term \( \varepsilon \) is decomposed into a flame-aligned \((\varepsilon^Z)\) and a flame-orthogonal component \((\varepsilon^\perp)\). A detailed expression of the flame-orthogonal term \( J^\perp \) is available in [127]. The \( J^\perp \) term denotes the contributions that are perpendicular to the flame-aligned direction, and are commonly neglected in the flamelet limit [127].

As evident from Eq. (5.9), the flamelets extracted from the target fire database comprise effects of scalar mixing \((J_1)\), chemical reaction \((J_{2,C})\), radiative heat transfer \((J_{2,R})\), effects of species-diffusion \((J_3)\), enthalpy-flux due to non-unity Lewis number \((J_4)\), and preferential diffusion correction \((J_5)\) on flame-aligned direction. Furthermore, the unsteady effects in Eq. (5.6) are also contained in the database and subsequently in the extracted flamelets. Here, only the radiative source terms \( J_{2,R} \) are analyzed to provide physical guidance to the model development.

Numerically, a fourth-order central difference is used to calculate spatial gradient of scalars, and a second-order central difference scheme is used to compute the diver-
gence terms. Statistics from two puffing periods (equivalent to 0.34 s) at a time interval of 0.01 s are analyzed. At each time instant, 40 instantaneous flamelet solutions are extracted at each axial location as shown in Fig. 5.1, leading to a total of 1360 flamelets for analysis.

5.1.2 Structures of radiative emission and absorption

The total radiative source term $J_{2,R}$ can be decomposed into a local emission component and a non-local absorption component. To understand the distributions of the two components in composition space, conditionally-averaged emission and absorption sources obtained from the “Gas-soot” case are shown in Fig. 5.2, where the vertical bars denote the r.m.s of each variable. The large r.m.s. value of the emission source at $H/D = 3$ results from the unsteady intermittent soot layers in the turbulent plumes. Since the size of the pool fire is relatively small in this study, the absorption source only represents a small fraction of the emission source near the flame front. However, the emission source quickly reduces away from the flame front, while the absorption source maintains a relatively constant profile over the entire Z-space and can even exceed the emission in the fuel-rich and fuel-lean regions acting as a heating source for the local mixture. This implies that radiation not only contributes to heat loss, but also preheats the fuel and air streams. To accurately account for such behaviors, the non-local absorption term needs to be carefully modeled. The relative constant profile of the absorption source term in the Z-space indicates that a constant proportionality between
emission and absorption is inadequate in capturing the effect of re-absorption. Meanwhile, the relatively flat profiles of absorption source terms inspire the development of an absorption model for the flamelet approach, as described next.

### 5.1.3 A simple conceptual radiation model in the mixture fraction space

With the observations in Sec. 5.1.2, we seek to find a simple and robust conceptual model to explain the radiative behaviors in the mixture fraction space. In particular, the conceptual model focuses on description of the non-local re-absorption processes, because the emission source term can be fully described by the local radiative species composition and temperature. Moreover, the re-absorption effects have been conventionally neglected [126] or simplified as proportional to the local emission source [51] when building flamelet tables for modeling purposes in the literature. The conceptual model is expected to improve modeling of re-absorption in such studies.

![Fig. 5.2: Comparison of mean emission (Emi) and absorption (Abs) source terms for “Gas-soot”. The vertical bars denote the r.m.s values. Values are normalized by their respective maximum heat release rate at each location. The vertical lines denote Z_{st}.](image)
To incorporate the non-local absorption behaviors of a laminar/turbulent pool fire, a cylindrical configuration is introduced, as shown in Fig. 5.3. The proposal of the cylindrical configuration is inspired by two observations: 1) radiative energy decays exponentially as a function of the optical thickness \((\tau_P = \kappa L)\), i.e., Beer’s Law \([49]\) dictating that remnant radiative energy \(I_o\) after passing through a mixture with optical thickness \(\tau_P\) is

\[
I_o = I_i \exp(-\tau_P), \tag{5.10}
\]

and 2) the power of the radiative emission is proportional to \(T^4\). The two observations indicate that 1) a closer radiative source has a much larger impact on the local re-absorption than a source that is far away in the optical thickness coordinates; 2) the high temperature flame front has a much stronger emissive power than the relatively lower temperature region, e.g., emission is five time stronger for \(T = 1800\) K than \(T = 1200\) K when everything else is equal.

With these observations, a laminar flame profile is employed to initialize the composition and temperature within the cylinder. The red-dashed surface indicates the location of \(Z_{st}\), with the fuel and air streams located inside and outside the \(Z_{st}\) surface, respectively. The laminar solution is mapped along the azimuthal and axial directions so that the composition in cylinder is effectively one dimensional (i.e., change only along the \(r\) direction). Such a one-dimensional configuration builds in the geometric information through the cylindrical flame surfaces, and can potentially enable analytical solutions (detailed derivations are presented in Appendix \(A.4\)) of the re-absorption term.
Fig. 5.3: Left: a schematic of cylinder configuration. Right: Profiles of temperature and mixture fraction in the mixture fraction space (top) and along the radial direction (bottom) for $H/D = 0.14$.

The assumption of the cylindrical configuration is first assessed by comparing with the pool fire database. The extracted pool fire temperature and species along the flamelets at $H/D = 0.14$ and 2 are employed to construct the cylinder in Fig. 5.3. The temperature and Planck-mean absorption coefficients in the mixture fraction space and along the radial direction at $H/D = 0.14$ are provided for reference. The $\kappa_p$ obtained from the LBL data is used to calculate the emissive source term. The mapping between
the physical location and the mixture fraction space location is obtained by

\[ r = \int_0^r dr' = -\int_0^{Z(r)} \sqrt{\frac{2D_z}{\chi}} dZ. \]  

(5.11)

The Monte Carlo ray tracing solver detailed in Chapter 3 is employed to obtained the modeled re-absorption source term, which is compared with the results from the fire simulations in Fig. 5.4. Encouraging agreement on the magnitude and the profiles is observed between the analytical cylinder model and the pool fire data at both locations, which implies that the cylinder configuration provides an effective approximation for the pool fire.

**Fig. 5.4:** Comparison of idealized cylinder absorption model with pool fire simulations at \( H/D = 0.14 \) (denoted as \( H = 10 \) mm) and \( H/D = 2 \) for the “Gas-rad” case, referred to as “GR”.

By introducing the cylindrical flame configuration, the analytical description of the radiative absorption source term is available. Detailed description and derivation of the radiative absorption source term are provided in Appendix A.4. Based on above
discussion, the absorption source term is expressed as

\[ \dot{Q}_{abs} = \kappa(r)G(r), \quad (5.12) \]

where the absorption coefficient \( \kappa \) and the incident radiative intensity \( G \) are function of local radius, \( r \). Note that for a given flamelet, \( G(r) \) depends on the information of all grid points in the mixture fraction space.

The procedure of constructing the flamelet library considering absorption source term is detailed in the following. In calculation of a diffusion flamelet with a given scalar dissipation rate \( \chi \), for each iteration or time step:

- The emission source is evaluated based on the local temperature \( T \) and local Planck-mean absorption coefficient \( \kappa_P(p, T, X_i) \).
- The absorption source term is evaluated using the proposed cylindrical absorption model based on the thermochemical states at all grid points in \( Z \).
- The flame solution is advanced to next iteration or time step with the emission and absorption source terms obtained from Steps 1 and 2.

The developed flamelet re-absorption model can be directly applied to consider gray radiation; additional models for \( \kappa(r) \) are needed if nongray modeling of the absorption source terms is involved.
5.2 Development of a two-step mechanism

In numerical simulations of combustion systems involving real fuels, detailed description of chemical kinetics is typically required to capture important combustion and emission characteristics. High computational cost associated with detailed chemical mechanisms becomes a numerical challenge, especially when large scale unsteady flame are conducted using large eddy simulation (LES). A large-size ODE systems must be solved at each time step to advance the conservation equations of temperature and species concentrations.

Simplified chemical mechanisms based on fuel-specific global reaction steps provide an alternative method to accommodate real fuel chemistry and have been widely used in fire simulations due to its low computational cost. Westbrook and Dryer [130] showed long ago that one- to four-step chemical mechanisms have the capability to predict adiabatic flame temperature and laminar flame speed, in particular for lean mixtures, using constant, but fuel-specific, rate coefficients to match experimental measurement of flame speed at stoichiometric and atmospheric condition. Large errors were observed for rich mixtures due to the absence of fuel pyrolysis and dissociation effects. Varatharajan et al. [131] developed two-step mechanisms of jet fuels for detonation applications using the theory of chain-branching thermal explosions. To improve accuracy for global mechanisms, approaches based on equivalence ratio (\( \phi \)) dependent rate coefficients, instead of constant values, have been proposed [132, 133] to cover a wider range of flame conditions, e.g., for partially premixed combustion [132]. Although not
included as targets for model construction, reasonable prediction of the extinction strain rate and ignition delay were reported in Ref. [132] and [133]. More systematic methods for optimizing single-step mechanisms have been reported by Erraiy et al. [134], targeting at flame temperature, flame speed and flame thickness.

Most of the simplified mechanisms were developed by targeting at only one category of flame features such as adiabatic flame temperature, ignition delay time, or laminar flame speed. Therefore, in practical combustion systems involving more than one flame features, the accuracy of these simplified mechanisms are not well controlled, or at least not well quantified. To address this difficulty, multi-objective optimization is adopted in this section to design a simple two-step chemical mechanism for heptane fires at atmospheric conditions.

In the following, the general formulation of the two-step heptane mechanism is first introduced, followed by a brief description of the optimization procedure. The optimized two-step mechanism and its performance are presented and discussed in Secs. 5.2.3 and 5.2.4.

5.2.1 Formulation of the two-step mechanism

The two reactions involved in the two-step mechanism for heptane are shown in Eq. (5.13).
\[ C_7H_{16} + 7.5O_2 \rightarrow 7CO + 8H_2O \quad (5.13) \]

\[ CO + 0.5O_2 + H_2O \iff CO_2 + H_2O \quad (5.14) \]

The first reaction partially oxidizes fuel with air into CO and H\(_2\)O, while the second reaction further converts CO to CO\(_2\). The corresponding reaction rates for the two reactions are formulated based on the Arrhenius form as,

\[
k_1 = A_1 \exp(-\frac{Ea_1}{RT})[C_7H_{16}][O_2], \quad (5.15)
\]

\[
k_{2f} = A_{2f} \exp(-\frac{Ea_2}{RT})[CO][O_2]^{0.25}[H_2O]^{0.5}, \quad (5.16)
\]

\[
k_{2b} = A_{2b} \exp(-\frac{Ea_2}{RT})[CO], \quad (5.17)
\]

where \(A_{2f} = 3.98 \times 10^{14}\), \(A_{2b} = 5 \times 10^6\), \(Ea_2 = 40\) kcal/mol. These coefficients as well as the reaction orders for CO, O\(_2\), and H\(_2\)O in the second reaction are taken from Ref. [130]. For the first reaction, unity reaction orders for both fuel and oxygen are assumed to avoid numerical instability which may arise from non-unity reaction orders. The pre-exponential coefficient \(A_1\) and the activation energy \(Ea_1\) were usually assumed to be fuel dependent constants, while large \(\phi\)-dependence has been observed in Ref. [132]. In the following, \(Ea_1\) is fixed to be 30 kcal/mol, and \(A_1\) is selected as
the independent variable for mechanism optimization. Two objective functions, \( e(x) = [f_1(x), e_2(x)] \), are constructed,

\[
e_1(A_1) = \sum_{j=1}^{N_T} (w_j (\tau_j^{\text{sim}} - \tau_j^{\text{exp}})/(\tau_j^{\text{exp}}))^2 ,
\]

\[
e_2(A_1) = \sum_{j=1}^{N_T} (w_j (v_j^{\text{sim}} - v_j^{\text{exp}})/(v_j^{\text{exp}}))^2 ,
\]

where \( w_j \) is the weighting assigned as unity, \( \tau_j^{\text{exp}} \) and \( \tau_j^{\text{sim}} \) are the predicted ignition delay times using the detailed mechanism and the global mechanism, respectively, under the \( j^{th} \) thermochemical state. The \( v_j^{\text{exp}} \) and \( v_j^{\text{sim}} \) are predicted laminar flame speed using detailed mechanism and the global mechanism, respectively. The states are chosen from the feasible range constrained by the inlet temperature \( T_0 \) and equivalence ratio \( \phi \). \( N_T \) is the total number of states tested in the optimization process. The laminar flame speed is calculated using the 1D unstrained premixed flame configuration and the ignition delay is obtained from 0D constant-pressure auto-ignition systems, using the PREMIX and SENKIN programs from CHEMKIN II [2], respectively.

### 5.2.2 Multi-objective optimization

A decoupled methodology is employed in this work, combining the non-dominated sorting genetic algorithm (NSGA-II) [135] and the CHEMKIN library to optimize the reaction rate constant, namely, \( A_1 \), in an automated manner. NSGA-II has been widely
used in various engineering optimization problems due to its high computational efficiency. A schematic of the optimization procedure is shown in Fig. 5.6. The goal of NSGA-II is to find a series of Pareto optimal solutions or the “Pareto front”. In NSGA-II, each solution is first assigned a rank based on the number of other solutions it dominates over. The more solutions a solution dominates over, the lower rank it is assigned. The crowding distance of Solution \( x_i \) is the average length of the dashed cuboid illustrated in Fig. 5.5. Solution \( x_i \) can defeat Solution \( x_j \) in a selection tournament when it satisfies one of the following criteria. First, Solution \( x_i \) has a lower rank than Solution \( x_j \) or, \( r_i < r_j \), where \( r \) indicates the rank. Second, Solution \( x_i \) has a larger crowding distance than Solution \( x_j \) or, \( d_i > d_j \), when they share the same rank. In this way, similar solutions are avoided and the diversity of the solutions is retained.

The NSGA-II procedure comprises several key sub-process, i.e., population creation, genetic operation including crossover and mutation, and selection operation. Here, the most important selection operation, i.e., the sorting algorithm, follows [135]. A probability \( p_c \) is used as the crossover parameter, while \( p_m \) is used as the mutation operating factor. The overall algorithm is implemented in MATLAB. Key parameters involved in this study are listed in Table 5.1.

As the final two-step mechanism is intended for fire simulations at the atmospheric condition, optimization is targeted for the inlet pressure of 1 atm, and the inlet temperature of 300 K for flame speed calculations and 700–1500 K (with an interval of 100 K) for auto-ignition calculations. The equivalence ratio ranges from 0.5 to 1.5 with
Fig. 5.5: Schematic representation of the rank and the crowding distance in NSGA-II [3].

Table 5.1: Important parameters of NSGA-II.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Crossover probability, $p_c$</th>
<th>Crossover distribution index, $\eta_c$</th>
<th>Mutation probability, $p_m$</th>
<th>Mutation distribution index, $\eta_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference range</td>
<td>0–1.0</td>
<td>5–20</td>
<td>0–1.0</td>
<td>5–50</td>
</tr>
<tr>
<td>Real value</td>
<td>0.5</td>
<td>20</td>
<td>1</td>
<td>20</td>
</tr>
</tbody>
</table>
Fig. 5.6: A schematic of the multi-objective optimization procedure.
an interval of 0.05. In total, 21 inlet conditions for flame speed calculation, and 189 initial conditions for ignition delay calculations, are targeted to optimize the two-step mechanism.

### 5.2.3 Optimization results

Figure [5.7] shows the distribution of the two objective functions, i.e., the relative errors in flame speed and ignition delay time, at different equivalence ratios. A clear trade-off between these two objectives is observed for all equivalence ratios, indicating that flame speed and the ignition delay time cannot be accurately predicted simultaneously with simple two-step mechanism. Since the laminar flame speed is probably correlated with the rate of flame spread in fires, the optimization solution that minimizes the relative error in flame speed is employed for pool fire simulations in the following.

![Figure 5.7: Error in laminar flame speed versus error in ignition delay. Each line represents an individual equivalence ratio.](image)

Figure [5.8] compares flame speed predicted by the optimized two-step mechanism
Fig. 5.8: Prediction of laminar flame speed from different chemical mechanisms.

and the detailed mechanism (SK33). The results predicted by the conventional two-step mechanism with constant rate coefficients [130] are also shown. The optimized two-step mechanism is shown to accurately predict the flame speed for different equivalence ratios, while the conventional two-step mechanism fails on the fuel-rich side.

5.2.4 Performance in the pool fire simulation

The performance of the optimized two-step mechanism is further assessed using the turbulent pool fire configuration introduced in Chapter 4. For simplicity, no radiation and soot modeling is considered in this section. Results from the 33-species detailed mechanism (from case “Gas-norad” in Chapter 4) are used for comparison.

Figure 5.9 compares the mean temperature, mean mass fractions of CO₂ and CO on the center plane from the two mechanisms. Overall good agreement is observed in the prediction of the major flame structure on the temperature contour. Larger discrepancies are observed near the flame center for two major combustion products CO and
**Fig. 5.9:** Contours of temperature, and CO$_2$ and CO mass fractions from detailed and two-step mechanisms.

CO$_2$. Figure 5.10 compares the radial profiles of mean temperature and mean CO$_2$ and CO mass fractions at four downstream locations. Clearly, the mean temperature shows good agreement between two mechanisms. The maximum relative error for temperature is approximately 33% at $r = 0$ and $H/D = 1$. A slight over-prediction is observed for the mean CO$_2$ profiles. In contrast, the two-step mechanism significantly under-predicts the CO, especially near the centerline, with a maximum relative error of 58% at $r = 0$ and $H/D = 2$. These observations indicate that the two-step mechanism over-predicts the conversion of CO to CO$_2$ compared with the detailed mechanism, which is consistent with the findings in [133]. Therefore, if flame temperature is the major concern, the optimized two-step mechanism can provide a reasonable approximation, while a chemical mechanism with added complexities is necessary to better predict CO.

To investigate effects of inadequate prediction of CO to CO$_2$ conversion on ra-
Fig. 5.10: Radial profiles of mean temperature, and CO$_2$ and CO mass fractions from detailed and two-step mechanisms at four downstream locations.
diation modeling, Fig. 5.11 compares the Planck-mean absorption coefficient and the radiative source term conditional on mixture fraction, using the two mechanisms. Compared with the detailed mechanism, the two-step mechanism predicts lower $\kappa_p$ at $Z = [0.2, 0.5]$ and larger $\kappa_p$ at $Z = [0.5, 0.9]$. These discrepancies, combined with the difference of temperature prediction, lead to an over-prediction of radiative loss on the fuel-rich side using the two-step mechanism. Interestingly, similar $\kappa_p$ distribution is obtained using the two mechanisms, while larger radiative loss is predicted using the two-step mechanism with a relative error of 14%. This is mainly due to the higher flame temperature predicted by the two-step mechanism. Further comparison of radiative heat flux is shown in Fig. 5.12. To calculate the mean heat flux, eight snapshots are selected as described in Chapter 4 and are employed for frozen-field analysis for both two cases. The two-step mechanism shows good agreement with the SK33 on the radiation heat flux, with an overall over-prediction within 25%.

The combined effects of temperature and radiative species on the radiation fields suggest that the ratio of CO to CO$_2$ mass fractions can be another potential objective function for mechanism optimization when radiation characteristics are concerned. This will merit further investigation in future research.

5.3 Development of a reduced-order soot model

For large-scale fire simulations, computationally-efficient yet accurate soot models are desirable. Most of the detailed soot models are impractical for use in fire safety en-
**Fig. 5.11:** Conditional mean of $\kappa_p$ and $S_r$.

**Fig. 5.12:** Comparison of radiative heat fluxes along side boundary in the left y-axis. The relative error corresponds to the right y-axis.
engineers due to their complexity, large computational cost, or large number of fuel-specific and/or condition-specific parameters that require extensive manual calibrations. While semi-empirical soot models, e.g., the two-equation soot model introduced in Chapter 2, can overall provide adequate accuracy for fire configurations with the presence of ppm-level soot, they typically rely on the description of the soot precursor, such as C₂H₂ or PAH, which are, however, not available in general when global chemical mechanisms such as the two-step mechanism in the previous section are employed.

The primary aim of this section is to develop a reliable soot model that can be generalized to an arbitrary hydrocarbon fuel with acceptable accuracy and low computational cost, targeted for buoyancy-driven diffusion flames. In particular, a soot model that uses the concept of laminar smoke point (LSP) to characterize sooting propensity of an arbitrary fuel is implemented [136]. Methodology of the LSP soot model is introduced in Sec. 5.3.1. Preliminary results based on the LSP soot model are presented and discussed in Sec. 5.3.2.

5.3.1 LSP concept for soot modeling

Lautenberger et al. [136] developed a simple soot model that can be generalized to arbitrary hydrocarbon fuels using the laminar smoke point height. In this model, soot inception, nucleation, coagulation, and agglomeration, are not explicitly accounted for. Instead, they are lumped into two global processes: soot formation and soot oxidation.
Only the soot mass fraction, \( Y_s \), is solved by the following transport equation:

\[
\frac{\partial \rho_2 Y_s}{\partial t} + \mathbf{u} \cdot \nabla \rho_2 Y_s + \rho_2 Y_s \nabla \cdot \mathbf{u} = 0.55 \nabla \cdot \frac{Y_s \mu}{T} \nabla T + \dot{\omega}_s^\prime', \tag{5.20}
\]

where the net soot formation rate is given by \( \dot{\omega}_s^\prime = \dot{\omega}_{sf} + \dot{\omega}_{so} \). The soot formation rate, \( \dot{\omega}_{sf} \), and oxidation rate, \( \dot{\omega}_{so} \), are expressed as the product of polynomial functions of mixture fraction (\( Z \)) and temperature (\( T \)), respectively,

\[
\dot{\omega}_{sf} = f_{sf}(Z)g_{sf}(T), \quad \dot{\omega}_{so} = f_{so}(Z)g_{so}(T). \tag{5.21}
\]

Here, \( f_{sf}, g_{sf}, \) and \( f_{so} \) are selected as cubic polynomials, whereas \( g_{so} \) is assumed to a linear function. The coefficients of the four polynomial functions are determined by solving a set of algebraic equations by specifying the values and slopes of the polynomials at three locations in \( Z \) (\( Z_L, Z_P, \) and \( Z_H \)), and three locations in \( T \) (\( T_L, T_P, \) and \( T_H \)), respectively. The subscripts \( L \) and \( H \) refer to the lower and upper limits of the soot formation/oxidation processes, whereas the subscript \( P \) refers to the location for peak rates. Figure 5.13 shows the profiles of the polynomial functions corresponding to the two formation and oxidation source terms in the mixture fraction and temperature spaces, respectively. Note that polynomial coefficients for Fig. 5.13 were calibrated to match experimental data for the 212 W Santoro ethylene diffusion flame [136]. The point at which soot formation peaks (at \( Z_P \)) is defined as the laminar smoke point, referred to as “LSP”.
Based on the LSP concept, a simple soot model for heptane is developed. Specifically, the same functional forms of both the formation and oxidation source terms are employed, while the lower and upper limits for soot formation in $Z$ and $T$ spaces are adjusted according to the stoichiometric level of the heptane/air mixture. More importantly, the peak rate of soot formation is tuned to match the laminar smoke height for the heptane fuel according to,

$$
\dot{\omega}_{sf,P} = 1.1 \left( \frac{0.106}{l_s} \right) \left( \frac{28}{M_F} \right)^{\nu} \left( \frac{p_0}{p'} \right)^2 .
$$

where $p'$ is the reference pressure of 1 bar, $l_s$ is the smoke point flame height for a pure fuel measured in experiments, $M_F$ is the fuel molecular weight, and $n = 1$ as suggested in [136]. The smoke point flame height for heptane is 0.123 m [55], resulting in a peak formation rate of $\dot{\omega}_{sf,P}$ of 0.265 kg/(m$^3$·s). In addition, for the sake of numerical stability, the individual source terms are limited according to local fuel and oxygen

Fig. 5.13: (a) Mixture fraction polynomials. (b) Dimensionless temperature polynomials.
levels and integration time step as follows,

\[
\dot{\omega}_{sf} \leq -\rho Y_{\text{fuel}}/\Delta t - \dot{\omega}_{\text{gas,fuel}},
\]

\[
\dot{\omega}_{so} \leq -\rho Y_{\text{O}_2}/\Delta t - \dot{\omega}_{\text{gas,O}_2},
\]

where \(\dot{\omega}_{\text{gas,fuel}}\) and \(\dot{\omega}_{\text{gas,O}_2}\) represent reaction source terms due to gas-phase chemical kinetics. As a result, the functional form of the formation rate in mixture space for heptane is denoted by the black bash-dot line in Fig. 5.13, while the other three functional forms remain unchanged.

### 5.3.2 Performance in the pool fire simulation

The LSP soot model is coupled with the two-step mechanism developed in Sec. 5.2, referred to as “the simplified model”, while the two-equation soot model is coupled with the 33-species skeletal mechanism, referred to as “the detailed model”, as summarized in Table 5.2. The simplified model is tested in the same laboratory-scale turbulent pool fire using the same computational setup as described in Chapter 4. Simulations are conducted at the optically-thin limit and the radiative loss from both gas and soot is accounted for. Assessment of the LSP soot model is achieved by comparing results of the simplified model with the detailed model (i.e., the “Soot-OT” case in Chapter 4).

Figure 5.14 first compares the scatter of soot formation and oxidization source terms from the simplified and detailed models in the mixture fraction space and the tem-
Fig. 5.14: Soot formation and oxidization source terms in the mixture fraction and temperature spaces, respectively. Top row denotes results from the detailed case, and bottom row denotes synthesized results using the simplified case.

Overall, good agreement is achieved for the soot formation source term in both the mixture fraction and temperature spaces, while the soot oxidization source term exhibits large deviations. This can be explained by the fact that only the formation rate is adjusted in the current LSP model for heptane with the oxidation rate intact. Further model adjustment on the soot oxidation rate is needed for future research.

The radiative heat fluxes on the side boundary from the two models are compared...
Fig. 5.15: Comparison of radiative heat fluxes along side boundary in the left y-axis. The relative error corresponds to the right y-axis.

in Fig. [5.15] The simplified model shows good agreement with the detailed model, with a relative error within 20%. This implies that although large discrepancy may exist in the global quantities, the prediction of radiative heat flux using the simplified model is promising. Table [5.2] further compares the computational cost between the two models. By coupling the LSP soot model with the optimized two-step mechanism, the simplified model reduces overall computational cost by approximately 86%. Overall, this simple LSP model shows promising results with significantly reduced computational cost when coupled with the two-step mechanism, while additional improvements on the oxidization source term are needed for better prediction of the soot yield.
Table 5.2: Computational cost

<table>
<thead>
<tr>
<th>Case</th>
<th>Chemistry model</th>
<th>Soot model</th>
<th>Cost $/per step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detailed</td>
<td>SK33</td>
<td>Two-equation</td>
<td>24.2</td>
</tr>
<tr>
<td>Simplified</td>
<td>Two-step</td>
<td>Modified LSP</td>
<td>3.5</td>
</tr>
</tbody>
</table>

5.4 Summary

The pool fire database generated from high-fidelity simulations is adopted in this chapter to provide physical insights for developing reduced-order models on radiation, chemistry, and soot. By extracting Lagrangian flamelets, the non-proportionality between absorption and emission sources are noticed. A simple flamelet model accounting for re-absorption is proposed, where a cylinder concept is introduced to obtain analytical formulation for absorption source terms along the flamelets. The simple flamelet re-absorption model is evaluated by comparing results with the pool fire database at two downstream locations. Good agreement between the model and the database suggests that the proposed flame re-absorption model is capable of capturing re-absorption effects. Future research will be focused on incorporating the re-absorption model into run-time flamelet calculations.

To further reduce the computational cost associated with detailed chemistry, a multi-objective optimization method is developed to construct a two-step global reaction mechanism for heptane. A trade-off between the prediction of laminar flame speed and the prediction of ignition delay is observed. Due to the potential relevance of lam-
inar flame speed in fire spreading, a two-step mechanism optimized for flame speed is
developed and tested in the laboratory-scale heptane pool fire. Comparing with the de-
tailed mechanism, the optimized two-step mechanism provides good prediction on the
overall flame structure such as the mean flame temperature, although an over-prediction
of the conversion from CO to CO$_2$ is observed compared. Therefore, if flame temper-
ature is the major interest, the optimized two-step mechanism can provide reasonable
accuracy, while a chemical mechanism with added complexities is necessary to accu-
rately predict spatial profiles of chemical species such as CO and CO$_2$. The combined
effects of temperature and radiative species (i.e., CO and CO$_2$) on the radiation fields
suggest that the ratio of CO to CO$_2$ can be another potential objective function for
mechanism optimization which will merit further investigations.

Finally, a reduced-order soot model based on the laminar smoke point concept is
constructed for heptane pool fires. The simple soot model combined with the two-step
mechanism predicts a relatively higher soot yield and higher radiant fraction than that
with detailed models, which suggests that a better description of the oxidization rate
with careful calibrations is necessary. Approximately 86% saving in computational
cost is achieved with the coupled LSP model and two-step mechanism. Systematic
parametric adjustments or a data-driven optimization procedure will be required in the
future to improve the accuracy of the LSP soot model.
Chapter 6

Radiation characteristics of water mists

6.1 Overview of radiation modeling for water mists

Water mists/droplets are often involved in various fire suppression scenarios as a medium to mitigate fire spreads. For example, injected through water sprinkler at relatively high pressure, water mists may penetrate flame core and extract heat from fire, and/or wet the potential “fuel” surfaces. When heated by fires, the water vapor can replace oxygen content in the combustible gases. Both water mists and water vapor would act as radiative media, and attenuate radiative heat transfer through absorption and/or scattering [56]. Therefore, improving designs of water mist systems are of practical interest, and has attracted attentions and research effects over the past few decades.

Numerical simulations provide a powerful tool to understand the radiative attenuation of water mists and to improve designs of fire suppression systems due to its capability of capturing dynamics of water droplets over a wide range of time and length scales. In particular, the radiative effects of water mists have been extensively investigated numerically to determine the effective size distribution of water droplets, among
various other factors [59, 137]. An accurate description of water radiation is essential to facilitating design assessment and optimization for water mists systems.

To model radiative attenuation from water mists/droplets, the optical properties from all participative media should be considered. The Mie theory [49] describes the spectral and size dependence of spherical particles theoretically, and is typically considered as one of the most accurate theories for the calculation of the optical properties of water droplets [138]. However, due to the prohibitive computational cost associated with the Mie theory, simplifications are often made to accelerate the computation. Simple gray models with Planck-mean absorption and scattering efficiency functions were examined by Consalvi et al. [139] for a monodispersed system of water droplets to investigate the limitation of the gray assumption. They found that improvement is needed for media with an optical thickness of more than two. Viskanta et al. [140] developed empirical equations for water droplets of different sizes, and the efficiency factor for extinction in the small particle size limit of the Mie theory was used for scaling. More recently, Godoy et al. [141] introduced a scaling procedure, which requires pre-calculated properties of three monodispersed systems, to avoid numerical integration of the functions involved in the Mie theory. Several orders of magnitude of savings in computational cost is achieved through the tabulation/interpolation technique. However, the computational cost is still excessively high when coupled with transient CFD simulations, and a priori knowledge of the droplet size distribution is required to establish the tables.
The solver for the radiative transfer equation (RTE) is also crucial in capturing water radiative processes including the absorption and the anisotropic scattering processes. A hierarchy of RTE solvers has been employed to account for the scattering behavior in the literature, including the Lambert-Beer law [142], two-flux model [143], six-flux model [144], finite volume method (FVM) [139], discrete ordinates method (DOM) [145], and Monte Carlo (MC) based methods [146] as summarized in Table 6.1. The RTE solvers are often coupled with various models of radiative properties to investigate the physical behaviors of water radiation. For example, Berour et al. [147] coupled the Mie theory with a DOM solver to investigate the effectiveness of water curtains in fire protection by two-dimensional (2D) frozen-field analyses on both monodispersed and polydispersed water systems. Similar coupling was adopted by Collin et al. [145], where they employed a 43-band correlated-K (C-K) model for the gaseous radiative properties and solved the RTE for each band in a 2D domain to investigate the effects of the droplet concentration and the spray size, for example, on the transmissivity of water curtains. Besides that, many numerical studies have attempted to deal with the anisotropic scattering feature of water droplets. Hao et al. [148] investigated the radiative heat fluxes and temperatures under the assumption of isotropic scattering in a 2D stationary rectangular configuration. By comparing the FVM results against benchmark solutions [149], they concluded that the relative error between the linearly and non-linearly anisotropic scattering models increases with increasing forward scattering ratio. The capability to account for scattering by FVM and DOM was
further investigated by Boulet et al. [150] in purely scattering medium. They compared the solutions with reference solutions from Monte Carlo based method and found that an underestimation of the effective attenuation by scattering is produced with the DOM method.

Previous numerical studies have substantially advanced the understanding of water radiation. However, all of the above models have limited applicability for practical fire simulations. Radiation under the practical fire scenarios is mainly three-dimensional. Although the one and two-dimensional analyses [148] have been performed to compare against the available benchmark [151] and to save computational cost, they failed to provide three-dimensional radiative statistics, especially when the anisotropic scattering is dominant and needs to be accounted for. In addition, reduced-order spectral models for the gas phase [139] may lead to over- or under-prediction of the radiative attenuation caused by water mists, because of the strong spectral variations of the optical properties of water mists. The coupling of the Mie theory and the RTE solver should simultaneously consider the whole spectrum of thermal radiation and distribution of different droplet sizes. The validity of the scattering treatment for radiation of water mists, when subjecting to various irradiation sources, i.e., a combination of nongray gases and solid walls, has not been sufficiently investigated. The interactions between soot and water droplets are rarely addressed by existing models. To bridge the gap, high-fidelity models are developed in this dissertation to investigate the interactions among the nongray gas, nongray wall, soot, and water mists in fire
This chapter is organized as follows. The radiative properties models for water mist are described in Sec. 6.2. The calculations of radiative properties are first detailed on the basis of the Mie theory, followed by the description of the scattering model. Then, the coupling of the radiative property model with the MCRT solver is discussed. Section 6.3 describes the test configuration and numerical details. Verification and validation of the coupled solver are demonstrated in Sec. 6.4, and benchmark results are provided to facilitate comparison with reduced-order models. Parametric studies are performed to study the radiative attenuation of water mists in presence of soot. Conclusions are drawn in the end. Throughout this chapter, the spectral dependence is described on a basis of wavelength $\lambda$ (in microns), the size dependency can be interpreted as diameter dependence, and the droplets are assumed to be spherical.
<table>
<thead>
<tr>
<th>Year</th>
<th>Ref.</th>
<th>RTE solver</th>
<th>Gas phase</th>
<th>Liquid phase</th>
<th>Scatter</th>
<th>DIM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989</td>
<td>[142]</td>
<td>Lambert-Beer law</td>
<td>/</td>
<td>Approximation expression [152]</td>
<td>Approximation expression [152]</td>
<td>2D</td>
</tr>
<tr>
<td>1993</td>
<td>[143]</td>
<td>Two-flux model</td>
<td>/</td>
<td>Approximations for different absorption indices</td>
<td>/</td>
<td>2D</td>
</tr>
<tr>
<td>2000</td>
<td>[144]</td>
<td>Six-flux model</td>
<td>/</td>
<td>Wavelength independent</td>
<td>/</td>
<td>3D</td>
</tr>
<tr>
<td>2003</td>
<td>[139]</td>
<td>FVM</td>
<td>/</td>
<td>Mie theory</td>
<td>HG theory</td>
<td>2D</td>
</tr>
<tr>
<td>2003</td>
<td>[148]</td>
<td>FVM</td>
<td>/</td>
<td>Mie theory</td>
<td>Different phase function</td>
<td>2D</td>
</tr>
<tr>
<td>2004</td>
<td>[147]</td>
<td>DOM</td>
<td>Band model</td>
<td>Mie theory</td>
<td>Unnormalized phase function</td>
<td>2D</td>
</tr>
<tr>
<td>2005</td>
<td>[145]</td>
<td>DOM</td>
<td>C-K model</td>
<td>Mie theory</td>
<td>Mie-scattering phase function</td>
<td>2D</td>
</tr>
<tr>
<td>2006</td>
<td>[153]</td>
<td>FVM</td>
<td>Wide band</td>
<td>Mie theory</td>
<td>Scattering integral</td>
<td>3D</td>
</tr>
<tr>
<td>2007</td>
<td>[150]</td>
<td>FVM and DOM</td>
<td>/</td>
<td>Mie theory</td>
<td>HG theory Normalized phase function</td>
<td>3D</td>
</tr>
<tr>
<td>2008</td>
<td>[154]</td>
<td>MC based model</td>
<td>C-K model</td>
<td>Mie theory</td>
<td>Cumulative function</td>
<td>3D</td>
</tr>
<tr>
<td>2020</td>
<td>[137]</td>
<td>fvDOM</td>
<td>Band model</td>
<td>Band model based on Mie theory</td>
<td>HG theory Normalized phase function</td>
<td>3D</td>
</tr>
</tbody>
</table>
6.2 Radiation models

6.2.1 Radiative properties of water mists

Assuming that the droplets are spherical, and the radiation hits the droplet as plane un-polarized waves, the Mie theory provides an accurate solution to the Maxwell equation, and is adopted here to calculate the radiative properties of droplet clouds with arbitrary size distributions. Three quantities are needed as inputs for the Mie theory: (i) the droplet radius \( a \), (ii) the incident wavelength \( \lambda \), and (iii) the complex index of refraction \( \mathbf{m} = n_r - ik \), where the optical properties \( n_r \) and \( k \) are the real and imaginary components of the complex index of refraction of the water droplet. The first two quantities provide the dimensionless size parameter, \( x = 2\pi a/\lambda \), to measure the relative size of the droplet to the incident wavelength. Therefore, for a single water droplet of radius \( a \), the scattering efficiency factor \( Q_{\text{scat},\lambda} \) and extinction efficiency factor \( Q_{\text{ext},\lambda} \) are described by the Mie theory as,

\[
Q_{\text{ext},\lambda} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1) Re(a_n + b_n), \tag{6.1}
\]

\[
Q_{\text{scat},\lambda} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1) (|a_n|^2 + |b_n|^2), \tag{6.2}
\]

where the absorption efficiency \( Q_{\text{abs},\lambda} \) is determined as,

\[
Q_{\text{abs},\lambda} = Q_{\text{ext},\lambda} - Q_{\text{scat},\lambda} . \tag{6.3}
\]
$a_n$ and $b_n$ are the Mie scattering coefficients that are function of $x$. $n$ is the index of terms involved in the infinite series, and the evaluation of the infinite series is terminated when

$$n \approx 1.5x + 3 , \quad (6.4)$$

as suggested by [49]. Equation (6.4) suggests that more terms need to be retained in the evaluation as the size parameter $x$ increases.

The azimuthally averaged single-particle phase function is computed as

$$\Phi(\theta_s) = \frac{2(|S_1(\theta_s)|^2 + |S_2(\theta_s)|^2)}{x^2 \cdot Q_{scat,\lambda}} , \quad (6.5)$$

where the $S_1(\theta_s)$ and $S_2(\theta_s)$ are the complex amplitude functions. Based on $\Phi(\theta_s)$, an asymmetry factor $g$ is defined to characterize the angular distribution of scattered energy, which is defined as,

$$g(x) = 1/2 \int_{-1}^{+1} \Phi(\theta_s) \cos(\theta_s) d(\cos(\theta_s)) . \quad (6.6)$$

The asymmetry factor can often be employed to simplify the evaluation of the phase functions [138]. More detailed derivations and explanations of the Mie theory that are pertinent to this study are provided in Appendix A.5.

For clouds of water droplets of non-uniform sizes, once the efficiency factors for a single droplet are determined, the Eulerian bulk absorption and scattering coeffi-
cients, and asymmetry factor (indicated as $g_{\lambda}$ for clarification) of the water mists can be obtained by

\[ \kappa_{\lambda} = \pi \int_{0}^{\infty} Q_{\text{abs},\lambda} a^2 f(a) da , \]
\[ \sigma_{\lambda} = \pi \int_{0}^{\infty} Q_{\text{scat},\lambda} a^2 f(a) da , \]
\[ g_{\lambda} = \frac{\int_{0}^{\infty} g \times Q_{\text{scat},\lambda} a^2 f(a) da}{\int_{0}^{\infty} Q_{\text{scat},\lambda} a^2 f(a) da} , \]

where the $f(a)$ is the droplet size distribution function.

For a typical combustion system with irradiant wavelength ranging from 0 to 50 $\mu$m, the size parameter $x$ falls between 1 and 1000 for a water droplet with a diameter of 200 $\mu$m. With $x$ approaching 1000, on-the-fly calculations of the scattering and extinction efficiencies can be extremely time-consuming due to the large number of terms retained in the infinite series, according to Eq. (6.4). Meanwhile, a polydispersed system with a wide range of droplet diameters is inevitable, due to the absorption and subsequent evaporation processes for each droplet in the system. If the time scale of the dynamics of droplet is comparable with the time step, updating the radiative properties at each time step is necessary, which further increase the computational cost. The large computational demands render it prohibitive to directly couple the Mie theory with transient CFD simulations of practical interest. Therefore, the radiative properties consisting of the spectral and size dependence are pre-tabulated here to reduce the computational cost associated with the repetitive on-the-fly calculation. The table is
Table 6.2: Resolutions of the pre-tabulated spectral properties of water droplets.

<table>
<thead>
<tr>
<th>d space (µm)</th>
<th>Resolution (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 ~ 1</td>
<td>0.01</td>
</tr>
<tr>
<td>1 ~ 100</td>
<td>0.1</td>
</tr>
<tr>
<td>100 ~ 1000</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>λ space (µm)</th>
<th>Resolution (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66 ~ 2</td>
<td>0.02</td>
</tr>
<tr>
<td>2 ~ 20</td>
<td>0.1</td>
</tr>
<tr>
<td>20 ~ 50</td>
<td>10</td>
</tr>
</tbody>
</table>

constructed for droplet diameter ranging from 0 to 1000 µm with different resolutions, as shown in Table 6.2. For each tabulated diameter, calculations are performed for the range of wavelength that is frequently encountered in a typical combustion system (i.e., 0.66 to 50 µm in terms of wavelength, or 200 to 15,000 cm$^{-1}$ in terms of wavenumber). The resolutions of the wavelength space, as listed in Table 6.2, are determined by two factors: (i) the level of variation of the efficiency factors in the spectral space, and (ii) the available data of the complex indices of refraction of water droplets. The experimental measurement on the complex indices of refraction in [4], is adopted for database construction. The complex indices of refraction in the interested spectral range of the present study are shown in Fig. 6.1.

Figures 6.2(a) and (b) show the tabulated absorption and scattering efficiencies. Strong fluctuations of the absorption and scattering efficiencies are observed for short-wavelengths when droplet sizes are small, while the absorption and scattering efficiencies are close to unity for large droplets in the long-wavelength region. Similarly, Fig. 6.2(c) shows the contour of the asymmetry parameter for water droplets with different diameters subject to different wavelengths. For large droplets, $g$ remains close to unity throughout the spectral range, indicating the dominance of forward scattering. It
can be inferred that simple isotropic scattering assumption would fail to represent the scattering effects of water droplets in those ranges.

An important assumption made in the development of the spectral property model for the water mists is that the effect of liquid temperature on its optical properties is negligible for both the Mie theory and the tabulation method [155]. The tabulated spectral properties are compared with those calculated from the Mie theory, and the errors are below 2%, which will be discussed in detail in Sec. 6.4.1.

### 6.2.2 Radiative scattering

The MCRT solver detailed in Chapter 2 is adopted for modeling radiation of water droplets. A complete description of wall radiation can be found in [156]. Here, the treatment of scattering due to the presence of water mists is introduced. A ballistic scheme is used to determine the point of scattering. A ray is scattered whenever its
Fig. 6.2: The pre-tabulated spectral properties of water droplets: (a) absorption efficiency, (b) scattering efficiency, and (c) asymmetry factor.

optical thickness exceeds the maximum scattering optical thickness determined through the random number relationship given by Eq. (6.10),

$$opt_{scat,max} = \ln(1/R_{\sigma}) \ ,$$

(6.10)

where $R_{\sigma}$ is a random number uniformly distributed between zero and unity.

Once a scattering event is registered, the ray is redirected into a new direction. The scattering angles can be determined by the scattering phase function. Here, the Henyey-Greenstein (HG) phase function [49] is employed and the phase angle can be expressed as a function of the asymmetry factor $g$,

$$\Phi_{HG}(\theta_s) = \frac{(1 - g^2)}{[1 + g^2 - 2g \cos \theta_s]^{3/2}} \ .$$

(6.11)

The HG phase function provides a functional form that can be integrated easily. It has been demonstrated that the HG phase function provides accurate predictions for
Fig. 6.3: Comparison of the scattering phase functions obtained from (a) the Mie theory and (b) the HG theory for 20 µm droplet. Each line represents the phase function corresponding to a different incident wavelength.

Comparison of the scattering phase functions obtained from the Mie theory and the HG theory for the 20 µm droplet is shown in Fig. 6.3. Good agreement is observed especially when $\mu = \cos \theta_s$ is close to unity. Further quantification of the difference between the HG phase function and Mie scattering phase function in terms of the prediction of the radiative heat transfer pattern would be part of the future work.

With the phase function chosen, the scattering angles can be calculated through relationships of another two random numbers $R_{\psi_s}$ and $R_{\theta_s}$ as,

$$R_{\psi_s} = \psi_s/2\pi \quad (6.12)$$

$$R_{\theta_s} = \frac{1 - g^2}{2g} \times [(1 + g^2 - 2g)^{0.5} - (1 + g^2 - 2g \cos \theta_s)^{0.5}]. \quad (6.13)$$

Here, $R_{\psi_s}$ and $R_{\theta_s}$ respectively represent the azimuthal angle and polar angle for scat-
tering. The relationship of Eq. (6.13) is obtained by integrating the HG phase function in the range of $\theta_s \in [0, \theta_s]$ and then by normalizing the results with a full integration of $\theta_s$ from 0 to $\pi$. The scattering behavior is assumed azimuthally independent as shown in Eq. (6.12). With $g$ asymptotically approaching zero, Eq. (6.13) is reduced to

$$R_{\theta_s} = \frac{1}{2}(1 - \cos \theta_s), \quad (6.14)$$

which is consistent with those derived directly from isotropic scattering assumption.

Therefore, Eqs. (6.13)-(6.14) can be employed to account for either anisotropic or isotropic scattering, depending on the values of $g$. It should be noted that the scattering events in the MCRT solver only change the traveling directions of rays and no change in the intensity or the wavelength incurs during the scattering processes.

A schematic of the scattering treatment implemented in the MCRT solver is shown in Fig. 6.4. When an energy ray intersects with a new Eulerian cell, the transverse distance from the entering point to the bounding surface, $\Delta_l$, is first computed based on the geometry of the cell [158]. After that, the total absorption and scattering coefficients $\kappa_t$ and $\sigma_t$ are calculated based on the local properties of the mixture,

$$\kappa_t = \kappa_d + \kappa_g, \sigma_t = \sigma_d, \quad (6.15)$$

where $\kappa_g$ is the absorption coefficient of the gas-soot mixture. Here, the subscript of $d$ denotes the properties for the water droplets, and the contribution of the scattering co-
efficient only comes from the water droplets. The optical thicknesses due to absorption and scattering are respectively determined by,

\[ \Delta l_a = \kappa_t \times \Delta l, \Delta l_s = \sigma_t \times \Delta l. \]  \hfill (6.16)

The cumulative optical path due to scattering \((l_s + \Delta l_s)\) is first compared with the pre-determined maximum scattering optical thickness \(opt_{scat,max}\). If it is smaller than the maximum value, a comparison between \((l_a + \Delta l_a)\) and the pre-determined maximum absorption optical thickness, \(opt_{abs,max}\), is made to check whether the current ray is completely absorbed by the current cell. If the cumulative absorption optical thickness is greater than \(opt_{abs,max}\), the tracing of the ray is terminated, and the remaining energy carried by the ray is deposited to the current cell. If the cumulative absorption optical thickness is less than \(opt_{abs,max}\), the ray continues to be tracked to the next cell after losing the specific amount energy to the current cell.

Meanwhile, if \((l_s + \Delta l_s)\) is greater than \(opt_{scat,max}\), the exact scattering path and the corresponding absorption thickness need to be re-calculated by,

\[ \Delta n = (opt_{scat,max} - l_s)/\sigma_t, \Delta l'_a = \Delta n \times \kappa_t. \] \hfill (6.17)

The same determination procedure of the absorption state is performed again by replacing the original \(\Delta l_a\) with the new \(\Delta l'_a\). If after absorption, the ray is still alive, the new scattering angles are assigned to the ray according to Eqs.(6.13) and (6.14). The
scattered ray will be tracked until the remaining energy is completely depleted or until the ray exits the computational domain. After resetting the accumulated optical thickness of scattering to zero, the ray is then moved to the next cell and another loop of the “scattering-or-absorbing event” checking is repeated until its energy is completely absorbed by the participative media or it hits and/or exits the computational boundaries.

Once ray tracing is completed, the radiative source terms can be collected for each participating phase and for each computational cell, respectively. A Eulerian-Lagrangian system is employed to describe the flow field of the gas and liquid phases, and the radiative source terms (i.e., absorption - emission) are collected on a per-parcel basis for the Lagrangian water droplets and a per-cell basis for the Eulerian gas phase. The distributions of the absorbed energy across the gas and the water droplets follow [73] and are not discussed here.

### 6.3 The test configuration and computational details

#### 6.3.1 Three-dimensional cubic box

Verification of the newly developed scattering solver is first conducted using a one-dimensional homogeneous slab in Appendix A.6. Good agreement with theoretical derivation is observed with different scattering albedos. In this section, as shown in Fig. 6.5, a three-dimensional (3D) cubic enclosure is constructed to further validate the coupled MCRT solver in 3D settings. Due to its relative simplicity and repeatability in various software packages, the results can be employed as the benchmark for reduced-
Fig. 6.4: Flowchart of checking “scattering-or-absorbing event” within a finite volume cell during ray tracing.
order model development, such as that in [159].

The cubic configuration has been the subject of several numerical investigations, for examining both the models of the radiative properties and the RTE solvers. For example, Boulet et al. [150] used the three-dimensional form to investigate the ability of the FVM and the DOM methods to model strongly forward anisotropic scattering solid particles. A two-dimensional form of the configuration is adopted by Trivic et al. [160] to develop a coupled FVM solver for multiphase radiation. After that, they also extended it to a 3D configuration to develop radiation models for gray particles of anisotropic scattering [161].

The 1 m³ domain is discretized uniformly in the three directions. All six boundary surfaces are initially treated as cold black walls. If wall radiation is considered, the back surface, as indicated by the shadowed area in Fig. 6.5 is used as the emitting wall with a constant temperature. The media inside the enclosure are varied according to different objectives for parametric studies. When multiple radiative heat sources are involved, the symbol $E_w$ denotes the blackbody emissive power from the hot wall, and $E_g$ represents the blackbody emissive power from the gas. They are defined as,

$$E_w = A\epsilon\sigma T_w^4, E_g = 4\kappa_g\sigma T_g^4V,$$

where $T_w$ and $T_g$ are the temperatures of the emitting wall and the gas, respectively. $A$ is the area of the emitting wall, and $V$ is the volume of the emitting gas. $\epsilon$ is the emissivity of the black wall, which is equal to unity. Quantities used for comparison
in the subsequent sections are the dimensionless heat rate \((F^*)\) through a surface of a finite-volume cell, \(\Delta A\), and the dimensionless heat rate \((q^*)\), through a volume of a finite-volume cell, \(\Delta V\), defined respectively as,

\[
F^* = \frac{F \times \Delta A}{(E_w + E_g)}, \quad q^* = \frac{q \times \Delta V}{(E_w + E_g)}.
\]  

(6.19)

Here, \(F\) is computed using the radiative heat fluxes on the front face \((X = 1\ m)\) and \(q\) is obtained as the volumetric radiative heat source terms along the dashed line in Fig. 6.5 originating from \(Y = 0.5\ m, Z = 0.5\ m\) along the \(X\)-direction. Hence, \(F^*\) and \(q^*\) indicate the percentage of the net energy rate received per boundary face on the wall and per cell by the participative media, respectively.

Fig. 6.5: Schematic representation of the cubic box.

A Rosin-Rammler distribution is used to describe the size distribution of the polydispersed water mists system inside the cubic box. The minimum and maximum
Fig. 6.6: Cumulative density function (CDF) of the diameter of water droplets.

diameters of the distribution function are 10 and 1000 µm, with an ensemble-averaged value of 100 µm, and the spread of the distribution is equal to unity. The model parameters are selected to create a water mist cloud with more than 80% of droplet diameters smaller than 200 µm [56], as shown in Fig. 6.6. The total number of the water droplets is approximately 6.4 million and the Sauter mean diameter is 193 µm. The number of particles per parcel is fixed to be 1000. Therefore, as the sizes of water droplets vary, the volume fractions of water droplets also vary in the cubic box among different cells. The total volume fraction of the polydisperse water mist system in the cubic box is approximately 218 ppm. Two monodispersed systems with diameters of 20 µm and 193 µm are also examined in this study, whose total volume fractions are 0.27 ppm and 241 ppm, respectively.
6.3.2 Computational details

To eliminate the compounding effects of the coupled evaporation, movement, and heat transfer processes for water mists, frozen-field analyses are performed for all the simulations in this chapter. Therefore, no governing equations are solved for the gas phase, and thermophysical states (temperature for both phases, diameters of droplets, etc.) are unaltered during the simulations. The temperature of water droplets is set to be 293 K at atmospheric pressure. Radiative source terms are obtained by the Monte Carlo solver. The dynamic coupling between the evaporation and heat transfer, and other important sub-processes for water droplets are left as a future research avenue.

6.4 Results and discussion

Fourteen benchmark results using the 3D cubic box are provided. The effect of different scattering models on the heat flux is discussed next. Finally, using the newly developed models, the interactions between water mists and cold soot (i.e., non-emitting) are investigated for a fire-inspired mixture.

6.4.1 Validation of the scattering MCRT solver

The MCRT solver with scattering treatment is first validated against the analytical solutions obtained in Appendix A.6. Here, the validation focuses on the scattering modules. Two test cases are simulated, one with a linearly anisotropic scattering phase function and the other with an isotropic scattering phase function. The scattering albedo of the
Fig. 6.7: Comparison of the radiative heat source terms for (a) linearly anisotropic scattering with $A_1 = 1$, and (b) isotropic scattering when $A_1 = 0$. The solid lines and symbols represent analytical solutions and MCRT solutions, respectively, for water (blue), gas (black), and total radiation source terms (red).

Water droplets in the two cases are equal to 0.8 (i.e., scattering dominant). The total radiative heat sources as well as those for the individual phases, are shown in Fig. 6.7 indicated by the symbols with error bars. The exact solutions, represented by the solid lines, are also shown in the same figures. For a clear comparison, all the source terms are normalized by the total emissive power, along the central line. In both cases, the results obtained from MCRT agree well with the analytical solutions.

To assess the accuracy of the tabulated droplet properties, results obtained from the exact Mie theory and tabulation are compared when only radiation from walls and polydisperse water mists are involved. The relative difference, $\epsilon_{RD}$, is used to quantify the difference on the prediction of radiative heat source terms along the central line. It is defined as

$$
\epsilon_{RD} = \frac{(F_{tab} - F_{mie})}{F_{mie}},
$$

(6.20)
Fig. 6.8: (a) Comparison of radiative heat fluxes predicted by different optical models and their relative difference on the front face. (b) Comparison of the probability distribution function (PDF) of radiative source terms for water droplets with different optical models.

where $F_{\text{tab}}$ is predicted by tabulated properties and $F_{\text{mie}}$ is provided by the Mie theory (considered to be the “truth” here). Almost identical predictions of the radiative heat fluxes and source terms of water mists are obtained by the Mie theory and the tabulation method. The relative differences between the two predictions are comparable with the statistical errors in this case. A more detailed comparison of the probability density function of the absorbed energy by water mists, as shown in Fig. 6.8(b), indicates that the tabulation method can also capture the radiative behaviors of individual particles as the Mie theory does.

6.4.2 Computational performance of the tabulation method

A comparison of the computational efficiency is presented in Table 6.3 showing the ratio of the computational cost required by the tabulation method (denoted as “tab”) to that required by the Mie subroutine (denoted as “mie”). Five representative cases are
reported here, as shown in Table 6.3. The cost of the Mie theory depends on the size parameter, thereby the level of acceleration is also size-parameter dependent. For large droplets, e.g., 193 $\mu$m, the per-step calculation can be accelerated by a factor of $10^2$. For a polydisperse system that contains a significant amount of large droplets (i.e., the Sauter mean diameter of the polydisperse system is 193 $\mu$m), similar acceleration is observed. For smaller droplets, the speedup factor maintains above two. The execution time is implicitly influenced by temperature through the shift of emissive wavelengths. In fact, the tabulation method is more advantageous whenever the distribution of the size parameter shifts towards the larger side (i.e., the evaluation through the Mie theory goes up) or the radiative medium is optically thinner (i.e., the duration of ray-tracing goes up). Since the calculation of radiative properties is tightly coupled with the ray tracing scheme, the computational time of radiative properties is approximately one fourth of the overall execution time per statistical run for the tabulation method in all cases. The ray-tracing scheme has been shown to be one of the major contributors for the high computational cost of the MCRT method [67].

### Table 6.3: Computational performance of the tabulation method.

<table>
<thead>
<tr>
<th>Time ratio (%)</th>
<th>20 $\mu$m $T_w$, 1000 K</th>
<th>193 $\mu$m $T_w$, 1000 K</th>
<th>Poly $T_w$, 1000 K</th>
<th>Poly $T_w$, 2000 K</th>
<th>Poly $T_w$, 2000 K, $T_g$, 2000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{tab}/t_{mie}$</td>
<td>2.8</td>
<td>0.5</td>
<td>0.9</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>$t_{tab}/t_{total}$</td>
<td>23.4</td>
<td>25.9</td>
<td>25.6</td>
<td>25.6</td>
<td>25.1</td>
</tr>
</tbody>
</table>
6.4.3 Convergence study on the number of rays

The statistical errors are first quantified to determine the necessary numbers of rays used in the subsequent studies. Given that the convergence of the statistics may depend on the optical thickness and/or size parameters of the participating media, three representative cases are considered here. They are referred to as the vacuum case, the gas/wall case, and the gas/water/wall case. The temperature of the gases and the water droplets is set to be 293 K. For the convergence study, only the emission from the back wall at 2000 K is considered, and the emission from the gas phase $E_g$ is considered to be zero. Note that for all the simulations below, the standard deviations for all the quantities of interest are collected based on 50 independent statistical runs.

The dimensionless radiative energy rate along the central line on the front face are investigated for the three representative cases in Fig. 6.9, with the normalized standard deviations, $F_{std} \times \Delta A/E_w$, indicated as the error bars. As shown in Fig. 6.9, the ratios of the standard deviations to the predicted heat fluxes fluctuate around 6.5%, 5%, and 3% for two, four and eight million rays, respectively, following the $\sqrt{N}$ scaling rule for Monte Carlo methods [49]. For the gas/wall and gas/water/wall cases, both the gaseous radiative source term and/or the water radiative source term along the centerline are shown in Fig. 6.10 to examine the ray effect on predictions of three-dimensional quantities. Again, a decrease of the standard deviations of the radiative source terms is observed with increasing rays for both phases. Larger standard derivations are seen for gaseous source terms compared to that for the radiative heat fluxes. Figures 6.9-6.10
Fig. 6.9: Comparison of $F^*$ (top row) and the ratio of $F_{\text{std}}$ to $F$ (bottom row) obtained from two million, four million, and eight million of the total number of energy rays (abbreviated as NR) per statistical run for (a) the vacuum case, (b) the gas/wall case, and (c) the gas/water/wall case. The heights of the error bars indicate the values of the normalized standard derivations.

clearly demonstrate that different numbers of rays are required to maintain the same statistical error for different media and different quantities of interest. Therefore, in the subsequent studies, the number of rays is employed to maintain a standard deviation below approximately 5%.

6.4.4 Benchmark results

Three groups are simulated to study the radiative attenuation by water mists and their interactions with the radiative sources including: (i) only radiation of wall is considered; (ii) only radiation of gas is used; and (iii) radiation from both wall and gas are accounted for. For all three groups, a constant atmospheric pressure is used. A list
Fig. 6.10: Comparison of (a) $q^*_g$ for the gas/wall case, (b) $q^*_g$ for the gas/water/wall case, and (c) $q^*_d$ for the gas/water/wall case obtained from two million, four million and eight million of the total number of energy rays (abbreviated as NR) per statistical run. The heights of the error bars indicate the values of the normalized standard derivations. The ratios of $q_{std}$ to $q$ are displayed in the bottom row.
of key parameters, including the temperatures of wall ($T_w$) and gas phase ($T_g$) are presented in Table 6.4. The gas mixture is selected to be the complete combustion products (e.g., CO$_2$ and H$_2$O) that are available in most fire simulations. The radiative properties of gas phase strongly depend on the molar fractions of the radiative species, hence the molar fractions of the gas mixture are also reported in Table 6.5. The corresponding Planck-mean absorption coefficients are equal to 1.149 m$^{-1}$ and 0.233 m$^{-1}$ when $T_g$ is 1000 K and 2000 K, respectively. For the cases involving water mists, the anisotropic scattering model is used to account for the scattering behaviors.

The radiative interaction between wall and water mists is investigated by comparing the dimensionless radiative energy on the front face within Group 1 in Fig. 6.11(a). Comparing B1 with B2, or B3 with B4, it can be seen that higher percentage of energy is retained on the target wall when smaller droplets are involved. The global energy conservation analysis shows that 1%, 55%, 1%, and 33% of total emitted energy is absorbed by the droplets for B1 to B4, respectively. Clearly, more energy is retained by the larger droplets than by smaller droplets at both high and low temperatures levels, due to the larger absorption efficiencies associated with larger droplets.

In addition, the droplets tend to absorb more energy when the emission temperature is lower, by comparing the pair of B2 and B4. This can be possibly explained by the PDFs of the emissive wavelengths as shown in Fig. 6.12. The probability density function (PDF) of the emitted wavelength obtained from the wall at 1000 K shifted towards longer wavelength compared to that obtained from the wall at 2000 K. As
Table 6.4: Key parameters for the benchmark cases. B1 to B4 are referred to as Group 1, B5 to B8 are referred to as Group 2, and B9 to B14 are referred to as Group 3.

<table>
<thead>
<tr>
<th>Droplet size (µm)</th>
<th>Gas</th>
<th>$T_g$, K</th>
<th>$T_w$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1 20</td>
<td>No</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>B2 193</td>
<td>No</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>B3 20</td>
<td>No</td>
<td>0</td>
<td>2000</td>
</tr>
<tr>
<td>B4 193</td>
<td>No</td>
<td>0</td>
<td>2000</td>
</tr>
<tr>
<td>B5 20</td>
<td>Yes</td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>B6 193</td>
<td>Yes</td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>B7 20</td>
<td>Yes</td>
<td>2000</td>
<td>0</td>
</tr>
<tr>
<td>B8 193</td>
<td>Yes</td>
<td>2000</td>
<td>0</td>
</tr>
<tr>
<td>B9 20</td>
<td>Yes</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>B10 193</td>
<td>Yes</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>B11 20</td>
<td>Yes</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>B12 193</td>
<td>Yes</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>B13 20</td>
<td>Yes</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td>B14 193</td>
<td>Yes</td>
<td>2000</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 6.5: Composition (in mole) of the gas mixture when gas radiation is considered.

<table>
<thead>
<tr>
<th>Species</th>
<th>CO₂</th>
<th>H₂O</th>
<th>O₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar fraction, %</td>
<td>3.20</td>
<td>7.84</td>
<td>12.26</td>
<td>76.70</td>
</tr>
</tbody>
</table>
shown in Fig. 6.13 in general the scattering albedo coefficients decrease with increasing wavelength. Therefore, for the same droplets, absorption plays a greater role when the incident wavelength is longer and more incident energy is absorbed by the droplets. For the 20 µm droplets, the scattering albedo remains close to unity for both temperatures, hence not much difference is observed when comparing B1 and B3. Similar trend is also observed in Group 2, when examining the dimensionless quantity, $F^*$ as plotted in Fig. 6.11(b). However, the peak of the PDFs in cases B5 to B8 (i.e., spectral gas emission) is less sensitive to the change of temperature compared to cases B1 to B4 (i.e., blackbody emission), as shown in Fig. 6.12(b). For Group 2, the increase in temperature results in a decrease in the Planck-mean absorption coefficients that leads to reduced optical thicknesses. Therefore, less radiative energy is re-absorbed by the media when temperature is higher and higher flux on the back wall can be observed.

When both the radiation of gas and wall are considered, smaller droplets consistently absorb less than the large droplets, which results in a higher heat flux on the receiving wall (B9>B10, B11>B12). This behavior is the same as what is shown in
Benchmark results

Droplet size (um)

Gas composition(൚, ൪, ൫)

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>20</td>
<td>No gas</td>
</tr>
<tr>
<td>B2</td>
<td>193</td>
<td>No gas</td>
</tr>
<tr>
<td>B3</td>
<td>20</td>
<td>No gas</td>
</tr>
<tr>
<td>B4</td>
<td>193</td>
<td>No gas</td>
</tr>
<tr>
<td>B5</td>
<td>20</td>
<td>CO2+H2O</td>
</tr>
<tr>
<td>B6</td>
<td>193</td>
<td>CO2+H2O</td>
</tr>
<tr>
<td>B7</td>
<td>20</td>
<td>CO2+H2O</td>
</tr>
<tr>
<td>B8</td>
<td>193</td>
<td>CO2+H2O</td>
</tr>
<tr>
<td>B9</td>
<td>20</td>
<td>CO2+H2O</td>
</tr>
<tr>
<td>B10</td>
<td>193</td>
<td>CO2+H2O</td>
</tr>
</tbody>
</table>

Tw means wall temperature, Tg means gas temperature

\[ Y_{CO2} = 0.05, \quad Y_{H2O} = 0.05, \] anisotropic scattering

Fig. 6.12: Probability of the emissive wavelength distribution conditional on the 0 to 10 µm range for (a) wall, and (b) gas at 1000 K and 2000 K.

Fig. 6.13: Scattering albedo and asymmetry factor of (a) 20 µm, and (b) 193 µm water droplets. Dashed lines indicate locations of peak emissive wavelengths obtained in Fig. 6.12

Fig. 6.11(a). For the same diameter, the temperature pair \((T_g, T_w) = (2000, 2000)\) predicts higher flux than the combination of \((T_g, T_w) = (1000, 1000)\), which can be combined as a superimposition of the effects shown in Fig. 6.11(a) and (b). However, we also show that if the wall and gas are at different temperatures, the prediction of the front wall is not a linear combination of the findings in Fig. 6.11(a) and (b) anymore.
The relative strength of the emissive power, the optical thickness of the nongray gases, as well as the scattering albedo of droplets are all contributing factors to the distribution of the heat flux on the front wall, and the interactions of these factors are nonlinear, as indicated by B13 and B14 cases. Under these scenarios, detailed radiative models are necessary to provide robust predictions.

6.4.5 Impact of anisotropic scattering models

The anisotropic scattering model can be difficult to implement, depending on the underlying code structures and the compatibility of other sub-models. Therefore, the necessity and significance of the anisotropic scattering model are investigated here. The polydispersed water mists are employed because they are more representative of the practical applications compared to the monodispersed system. Five cases with different combinations of the radiative heat sources and scattering models are listed in Table 6.6. In Table 6.6 “Noscat” denotes no scattering model, “Iso” denotes isotropic scattering model, and “Aniso” denotes the anisotropic model described in Sec. 6.4.5. To quantify the anisotropy of the emissive sources, a ratio $r$ is defined as shown in the last column of Table 6.6. Because the gaseous emission is more isotropic due to its volumetric nature and the wall emission is more directional in the current configuration, their relative strength indicates the level of anisotropy of the emissive sources.

Table 6.7 shows the relative difference between the target scattering models and
Table 6.6: A summary of the conditions of the test cases.

<table>
<thead>
<tr>
<th>$T_g$, K</th>
<th>$T_w$, K</th>
<th>Scattering model</th>
<th>$r = E_g/(E_w + E_g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0</td>
<td>Noscat/Iso/Aniso</td>
<td>0</td>
</tr>
<tr>
<td>M2</td>
<td>1000</td>
<td>Noscat/Iso/Aniso</td>
<td>0.2231</td>
</tr>
<tr>
<td>M3</td>
<td>2000</td>
<td>Noscat/Iso/Aniso</td>
<td>0.4826</td>
</tr>
<tr>
<td>M4</td>
<td>2000</td>
<td>Noscat/Iso/Aniso</td>
<td>0.9372</td>
</tr>
<tr>
<td>M5</td>
<td>2000</td>
<td>Noscat/Iso/Aniso</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6.7: Energy absorbed by the front face using different scattering models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Aniso (W)</th>
<th>$\epsilon_{RD}$ (Noscat to Aniso)</th>
<th>$\epsilon_{RD}$ (Iso to Aniso)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>9.626E+04</td>
<td>12.77</td>
<td>-58.85</td>
</tr>
<tr>
<td>M2</td>
<td>9.887E+04</td>
<td>10.19</td>
<td>-54.68</td>
</tr>
<tr>
<td>M3</td>
<td>1.435E+05</td>
<td>4.31</td>
<td>-38.83</td>
</tr>
<tr>
<td>M4</td>
<td>5.566E+04</td>
<td>-8.65</td>
<td>-6.38</td>
</tr>
<tr>
<td>M5</td>
<td>5.260E+04</td>
<td>-9.38</td>
<td>-3.30</td>
</tr>
</tbody>
</table>

the anisotropic scattering model, which is defined as,

$$
\epsilon_{RD} = \frac{(F_{model} - F_{aniso})}{F_{aniso}} \times 100. 
$$

(6.21)

Radiation in M1 only comes from the back wall ($X = 0$ m), and the “Iso” model shows larger discrepancy than the “Noscat” model. This is due to the acute forward scattering feature of water mists, as discussed in Fig. 6.2(c). When such optical characteristics are combined with a highly directional emissive source, no scattering model
Fig. 6.14: Contours of radiative heat flux predicted with different scattering models of the front face for M1 (on the top row) and M5 (on the bottom row).

is actually a better approximation to the reality than the isotropic scattering model (i.e., M1 to M3). In general, when the emissive sources approach the isotropic limit (i.e., \( r \) approaches unity in this case), the difference of the prediction obtained from isotropic scattering and from anisotropic scattering reduces, e.g., from -59% to -3.3% as \( r \) approaches unity. For the no scattering model case, the minimum difference is around the statistical uncertainty, and it remains significant for either the purely wall or purely gas emission. The nonlinear trend in \( \epsilon_{RD} \) results from the combined effects of the anisotropy of the emissive sources and the relative importance of scattering with respect to absorption.

Figure 6.14 compares the distribution of fluxes predicted by different scattering
models for the M1 and M5 sets. The effect of the scattering model on the prediction of the local heat fluxes is clearly seen for the two extremes. For M1, a clear under-prediction of the radiative heat flux on the target face is observed when using the isotropic scattering model, and an under-prediction is observed when using no scattering models for the M5 case. Clearly, the effectiveness of different scattering models are highly case-dependent. Hence, it is necessary to apply high-fidelity radiation models to achieve robust predictions in various fire environments.

6.4.6 Interactions between soot and water mists

The interaction of soot and water droplets is investigated in this section using the poly-dispersed system with the fixed number density described in Sec. 6.3.1. Emission from the back wall at 2000 K is the only emissive source here. Different volume fractions of cold soot are added in the cube uniformly. The soot is treated as purely absorbing media in gas phase. The water droplets are modeled as nongray media with anisotropic scattering behaviors. The tested soot volume fractions are 0.1, 0.5, 1.0, 2.0, 4.0 and 8.0 ppm, of which the Planck-mean absorption coefficients range from 0.0308 m$^{-1}$ to 2.462 m$^{-1}$. Based on the same levels of soot, cases with and without water mists are compared to investigate the effect of soot on water radiation.

The energy distributions among the three participative media, i.e., soot, wall, and water mists, are shown in Fig. 6.15. For all the test cases, the total emitted energy is kept the same, so the sum of the energy absorbed by soot, water and wall remains constant.
Fig. 6.15: Percentage of absorbed energy by soot, wall, and water mists under different soot volume fractions.

The absorption of the cold soot increases as the soot volume fraction increases, hence less energy is received by walls and water mists. Given the fixed volume fraction of the water mists in this study, when the volume fraction of soot is higher than a specific threshold, which is approximately 0.5 ppm with the Planck-mean absorption coefficient of 0.154 m$^{-1}$, soot may overtake water mists in absorption. Soot becomes the major absorber under optically thick condition. The reduced absorption by water mists suggests the possibility of reduced evaporation rates in a dynamic simulation, depending on the competition between convection and radiation. If radiation is dominant in supplying heat for evaporation, the results in Fig. 6.15 suggest a negative impact of cold soot on the effectiveness of water mists, because cooling and dilution by the evaporated vapor are suggested to be two main mechanisms for fire suppression [61].

The integrated absorption along the $Y - Z$ plane at each specific $X$ location is
Fig. 6.16: Totally absorbed energy by soot and water along the wall emitting direction. The dashed lines indicate the results without water mists, while the solid lines represent the results with water mists.

presented in Fig. 6.16 When soot volume fraction is lower than 1 ppm, the total radiative attenuation increases accordingly as shown in Fig. 6.16 by adding the water mists. Opposite attenuation trends, however, are observed when the volume fractions of cold soot are larger than 2 ppm. The total absorption by the two phases decreases when water mists are added. Since soot is treated as cold media without emission, a possible explanation is that the added water mists behave as a scattering medium instead of absorbing medium. Hence, part of the incident energy, instead of being absorbed, is redistributed, which might enhance the total number of rays that escape the domain through the boundaries.

6.5 Summary

The MCRT solver is extended to account for water mist radiation in this study. The effect of anisotropic scattering is modeled by a combination of the Mie theory and the
Henyey-Greenstein relation. A tabulation method is established for water droplets to reduce the computational cost associated with the evaluation of the nongray optical properties using the Mie theory. The accuracy of the tabulation method is compared with that of the Mie theory, and excellent agreement has been achieved. The computational efficiency of the MCRT-Mie/Tab solver is demonstrated. The developed solver is first validated against theoretical solutions that are derived for a one-dimensional slab with gray gas and isotropic/anisotropic scattering media. After validation, the solver is employed to perform parametric simulations of a cubic enclosure with participating media with increasing complexity. The distribution of the radiative heat flux on the receiving face as well as along the centerline of the geometry is presented and compared. With a fixed distribution of water mist system, different volume fractions of soot are added to the cubic enclosure, and the absorption/scattering behavior of water droplets in presence of soot is studied.

When a highly directional emissive source is applied to water mists, results obtained without any scattering models prove to be better than those obtained using isotropic scattering model. However, when the emissive sources approach the isotropic limit, both isotropic and anisotropic scattering models predict comparable results. These trends are also observed on the prediction of local quantities such as the distribution of local radiative heat flux. A high-fidelity scattering model is therefore necessary to robustly evaluate radiation of a fire-inspired environment where various emissive sources may be involved. The addition of cold soot in a fixed distribution
of water mists system shows that soot may overtake droplets to become the main absorber. Water mists can reduce the radiation attenuation by redistributing the energy. Only cold soot is considered to investigate its effect on the effectiveness of water mists through frozen-field analyses; coupled simulations considering the soot as both emissive and absorbing media, as well as the feedback of soot formation to water radiation are planned for the future.
Chapter 7

Summary and future work

7.1 Summary

The understanding of multi-physical interactions in buoyancy-driven diffusion flames is advanced through high-fidelity modeling in this dissertation.

A numerical framework was developed by coupling solvers for detailed radiation, detailed chemistry, and soot with scale-resolved flow solvers. The new framework is built on the open-source platform OpenFOAM and features a variety of new model development, model implementation and enhancement, including a MCRT/LBL solver for multiphase radiation, fast and accurate solvers for detailed chemistry, differential molecular transport, and an anisotropic scattering radiation model. The new numerical framework is designed to enable scale-resolved detailed simulations for buoyancy-driven diffusion flames, targeting at fire suppression conditions. The ultimate objective is to leverage the physical understanding from the detailed simulations, and create computationally-efficient physics-based reduced-order models.

A series of laminar diffusion flames were modeled in Chapter 3, serving as a val-
idation step of the developed numerical framework. Simulation of a laminar ethylene flame showed improved agreement with the experiment on flame temperature, mass fractions of major species, and the soot yield. Laminar methane diffusion flames containing steady and flickering conditions were then studied. Simulations not only accurately predicted the flame structure in steady flames, but also captured the puffing dynamics in flickering flames. Sensitivities to thermal boundary conditions of the nozzle wall, chemical mechanisms, soot models, and radiation models were systematically investigated for both steady and unsteady flames. For the flickering flame with largest radiant fraction, the prediction of radiative heat flux on the open boundary is most sensitive to the soot model, the specification of the thermal boundary conditions, and radiative re-absorption model when soot is present. The prediction of flame height is sensitive to the choice of chemical mechanism and whether or not soot is considered, while the prediction puffing frequency is insensitive to either the chemical mechanism or the radiation model.

With the insights and confidence attained through investigations of the unsteady laminar diffusion flames, the numerical platform was further employed to simulate a laboratory-scale turbulent heptane pool fire in Chapter 4. Results from the simulation was compared with experiments and theoretical relations. Good agreement was observed for the centerline mean temperature and velocity, the radiative heat flux along the open boundary, and the spectral radiative heat flux collected along a line-of-sight near the pool base. In particular, using the MCRT/LBL method, the spectral distribu-
tion of the emissive power collected along a line-of-sight exhibits excellent agreement with experimental data, especially for the 4300 nm emissive peak. Another emissive peak around 3300 nm was under-predicted by the simulation, potential due to the lack of additional radiative species that contain C-H stretching bonds.

Detailed analyses were then conducted to provide in-depth understanding of the multiple physical processes involved in turbulent pool fires. With the detailed chemical model, near pool flame characteristics were explored, where significant fuel cracking was observed near the pool surface, with small hydrocarbon species, such as C$_2$H$_4$, acting as the *de facto* fuel of the diffusion flame. For radiation, gas and soot have comparable contributions to emission, whereas gas dominates the re-absorption. Soot was found to significantly alter the radiative characteristics. Specifically, the presence of soot shifts the peak radiative emissive power to the fuel-rich side, whereas both chemical heat release and radiative emission peak near the stoichiometric mixture fraction when soot is absent. The radiative source term is clearly disproportionate to the chemical source term, indicating that the common treatment of radiative heat source as a fixed fraction of the chemical source may fail to represent the local energy balance, especially when soot is present. The analyses of the power spectra showed strong CO$_2$ emission and self-absorption near 4300 nm. Soot emission concentrates in the shorter wavelength range, i.e., below 2000 nm, and insignificant self-absorption was observed for soot due to its small optical thickness. Within the 4300 nm CO$_2$ band, a dip of the soot emissive spectra collected along the boundaries indicates strong interaction of soot
and CO$_2$ at this wavelength. The detailed spectral power spectra in this study, for the first time, numerically quantified how soot and nongray gases interact within pool fires.

By applying explicit filter to the original solutions, the importance of turbulence-radiation-interaction (TRI) at subgrid scale are explored. Distinct TRI behaviors are observed between flame with and without soot radiation, which suggests that caution should be taken when developing subgrid-scale TRI models for LES of fires with different sooting propensities.

The pool fire database was subsequently employed to develop reduced-order models for chemistry, soot, and turbulence-chemistry interaction in Chapter 5. Flamelet extraction and budget analysis were conducted on the pool fire database to assess the distribution of radiative source terms in flamelet coordinate. Absorption source terms exhibited an interesting near uniform distribution along the flamelets, which inspired the proposal of a simple re-absorption model for flamelet models using a cylindrical geometry. The simple flamelet re-absorption model was assessed through comparison with the pool fire database and promisingly good agreement was shown. The implementation of the cylinder model in a flamelet model is part of the future work.

A multi-objective optimization method was implemented to construct a global chemical mechanisms for capturing key chemical attributes of the system and to reduce computational cost simultaneously. A two-step mechanism is developed fitting the laminar flame speed and validated using the laboratory-scale heptane pool fire. The simple mechanism showed good prediction on overall flame structures such as the mean
flame temperature, but over-predicted of the convection of CO to CO\textsubscript{2} compared with the detailed mechanism. Radiative heat fluxes were also compared between two mechanisms, and their relative errors were within 20%. For radiation consideration, the ratio of CO to CO\textsubscript{2} mass fractions can be another objective function for future mechanism optimizations.

A soot model based on laminar smoke point (LSP) concept was introduced and constructed for heptane fires. The simple soot model combined with the two-step mechanism predicted good agreement on the radiative heat flux with the detail models. When coupled with the two-step mechanism, the LSP soot model achieves approximately 86% saving in computational cost.

In Chapter 6, computationally efficient radiation models for water droplets were developed and validated. The effect of anisotropic scattering was modeled by a combination of the Mie theory and the Henyey-Greenstein relation. A tabulation method was established for water droplets to reduce the computational cost while maintaining comparable accuracy as the Mie theory. A benchmark case was designed and simulated to provide benchmark database for developing reduced-order models for water droplets. When a highly directional emissive source is applied to water mists, results obtained without any scattering models prove to be better than those obtained using isotropic scattering model. However, when the emissive sources approach the isotropic limit, both isotropic and anisotropic scattering models predict comparable results. These trends are also observed on the prediction of local quantities such as the distribution
of local radiative heat flux. The addition of cold soot to a frozen water droplet system showed that soot may compete with droplets to become the main absorber of the radiative energy. Meanwhile, scattering by water droplets reduced the overall radiation attenuation.

7.2 Final perspectives and future work

The dissertation presents a few detailed simulations of laboratory-scale buoyancy-driven diffusion flames, with preliminary construction and validation of a few reduced-order models leveraging the physical insights obtained from the detailed simulations. Future research directions to further advance the progress are recommended in the following.

First, with progressive development of numerical models and computational infrastructure, high-fidelity modeling of larger-scale diffusion flames is a possibility for the near future. Such simulations can be of practical interest, enabling studies such as scaling-law mapping from small-scale to large-scale fires. The abundant data provided by such simulations can further facilitate development of robust numerical sub-models for practical fire simulations.

Second, improvement of soot-related modeling, including soot oxidation, soot radiation, and turbulence-radiation interactions in heavy-sooting environments, is critical for predictive fire modeling. Robust optimization of the laminar smoke point based soot model is pursued as part of the future work to achieve such a goal. Rigorous validation of the model using detailed simulation results and/or experiments remains
critical for such an effort.

Third, robust reduced-order models are essential for large-scale fire simulations. In particular, turbulence-radiation interactions, turbulence-chemistry interactions, and turbulence-soot interactions are needed and they can be further developed leveraging the database obtained from the laboratory-scale turbulent diffusion flame simulations here.

Finally, the radiation models for water mists that are proposed in this dissertation should be coupled with the fire simulations to investigate the flame-water-soot dynamics. The role of water radiation still needs to be further elucidated using such dynamic simulations (as opposed to frozen field analyses).
Bibliography


Appendix A

Supplementary materials

A.1 The pressure correction equation in OpenFOAM

As most solvers in OpenFOAM, *fireFOAM* is a pressure-based low-Mach number flow solver. A pressure correction equation is derived from the continuity and the momentum equations. A modified pressure, \( p_{rgh} = p - \rho g \cdot x \), which subtracts the hydrostatic pressure \( \rho g \cdot x \) from the total pressure \( p \), is employed when solving the pressure correction equation. A simplified version of the derivation is shown in the following.

The momentum equation (Eq. (2.2)) can be rewritten as:

\[
\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho uu) = -\nabla p_{rgh} - (g \cdot x) \nabla \rho + \nabla \cdot \tau ,
\]

where for simplification no other body forces except gravity is considered. Eq. (A.1) can be further expressed in a semi-discretized form as:

\[
A_P \cdot U_P - H \cdot U = -\nabla p_{rgh} - (g \cdot x) \nabla \rho ,
\]

where \( A_P \) and \( H \) are the diagonal and off-diagonal components of the coefficient matrix for velocity, and \( U_P \) and \( U \) are the new and old velocity vectors at all cell centers for one iteration step. Based on Eq. (A.2), the velocity vector \( U_P \) is obtained by

\[
U_P = A_P^{-1} H \cdot U - A_P^{-1} \cdot \nabla p_{rgh} - A_P^{-1} \cdot (g \cdot x) \nabla \rho .
\]

This expression for \( U_P \) then is plugged into the semi-discretized continuity equation as,

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot [\rho(A_P^{-1} H \cdot U - A_P^{-1} \cdot \nabla p_{rgh} - A_P^{-1} \cdot (g \cdot x) \nabla \rho)] = S_\rho .
\]

To obtain an equation for pressure, the equation of state is employed, which reads

\[
\rho = \psi p = \psi(p_{rgh} + \rho g \cdot x) ,
\]

where \( \psi = \partial \rho/\partial p \) signifies the compressibility of the flow. When the ideal gas law is used, \( \psi = 1/RT \) where \( R \) is the gas constant and \( T \) is the temperature. Direct substitution of \( \rho \) with Eq. (A.5) into Eq. (A.4), however, results in a non-linear equation for the
pressure due to the second term on the left hand side of Eq. \((A.4)\).

With the low-Mach number assumption, density from the previous iteration \(\rho^*\) can be taken as a reasonable approximation of the density at the current iteration step \(\rho\), and thus Eq. \((A.4)\) can be reorganized into Eq. \((A.6)\) by applying Eq. \((A.5)\) to the time-derivative term only.

\[
\frac{\partial \psi (p_{rough} + \rho^* g x)}{\partial t} + \nabla \cdot [\rho^* (A_F^{-1} H \cdot U - A_p^{-1} \cdot \nabla p_{rough} - A_F^{-1} \cdot (g \cdot x) \nabla \rho^*)] = S_p. \quad (A.6)
\]

Equation \((A.6)\) is the final form of the pressure correction equation for the modified pressure \(p_{rough}\). The total pressure is subsequently obtained with \(p = p_{rough} + \rho g \cdot x\), and the density is calculated from Eq. \((A.5)\). This pressure correction equation is then solved with momentum, species, and energy transport equations in an iterative procedure, referred to as the outer iteration in OpenFOAM \([65]\). A complete derivation of these equations can be found in \([64, 162]\).

### A.2 Verification of the heptane chemical mechanism

The performance of the 33-species skeletal mechanism for \(n\)-heptane \([7]\) in predicting species relevant to radiation and soot chemistry are compared with the detailed mechanism \([6]\). Figure A.1 shows species profiles in the mixture fraction space for mass fractions of CO, CO\(_2\), H\(_2\)O, CH\(_4\), C\(_2\)H\(_4\), and C\(_2\)H\(_2\), respectively. Solutions are obtained from a 1D laminar counter-flow diffusion configuration at the atmospheric pressure using the OPPDIF program in CHEMKIN-II \([2]\). Inlet temperatures of the fuel and air streams are 371.6 K and 300 K, respectively, which are chosen to match those used in the target pool fire simulation in Chapter \([4]\).

![Fig. A.1: Comparisons of profiles of (a) major radiative species, and (b) C\(_2\)H\(_4\), CH\(_4\), and C\(_2\)H\(_2\) between the detailed mechanism (referred to as “KK123” \([6]\)) and the skeletal mechanism (referred to as “KK33” \([7]\)).](image-url)
locities and the separation distance is approximately $2 \text{s}^{-1}$. Good agreement is observed between the two mechanisms for the three major radiative species (Fig. A.1). The skeletal mechanism slightly over-predicts $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2$ mass fractions on fuel-rich side (the stoichiometric mixture fraction is 0.0622). The error in peak $\text{C}_2\text{H}_4$ mass fraction is 6.8% located at around $Z = 0.234$. The differences may slightly affect the prediction of soot dynamics, but is considered satisfactory for this study.

### A.3 Validation using a laminar counter-flow diffusion flame

The *reactingDJFoam* solver has been verified using 0D auto-ignition system, 1D unstrained laminar flame in [62]. Here, the solver is further applied to another canonical configuration, which is constructed as a 2D simulation in OpenFOAM. The $n$-heptane/air laminar counter-flow diffusion flame and compared with the solution obtained from OPPDIF [163].

![Graphs showing velocity, mass fraction, temperature, and concentration profiles](image)

**Fig. A.2**: Comparison with CHEMKIN for a heptane laminar counter-flow diffusion flame at a stable burning condition.

The fuel and air inlet temperatures are 371.6 K and 300 K, respectively. The inlet velocities for the fuel and air are 10 cm/s and 16.8 cm/s, respectively, which leads to a global strain rate of $20 \text{s}^{-1}$. Such strain rate results in a stable burning solution located at the upper branch of the widely-known S-Curve. Figure A.2 shows the profiles of
velocity, temperature, and major species including fuel, O\textsubscript{2} and CO\textsubscript{2}. Good agreement is observed between results obtained from the reacting DJFoam solver and OPPDIF. Slight discrepancies are observed for intermediate species such as CO, OH and H\textsubscript{2}. The profile of OH is slightly improved when a finer grid of 0.2 mm is used, however, the results are converged for the major species for the mesh with a grid of 0.4 mm.

A.4 Derivation of the radiative solutions for a simple cylinder model

A detailed derivation specific to the cylindrical laminar diffusion flame configuration in Chapter 5.1 is presented below, following [164].

Two sets of coordinates are considered: a cylindrical coordinate system \((r', \psi', z')\) and a spherical coordinate system with respect to each of the point of interest \(P(r, \theta, \psi)\). Figure A.3 shows a schematic of the one-dimensional cylindrical configuration [164], and the coordinate system for a targeted point \(P\) and its projection on the \(r - \psi\) plane. For a specific radius \(r\), the incident radiation ray with an orientation of \((\theta, \psi)\) is derived. The formula is subsequently integrated over the whole \((\theta, \psi)\) space.

The cylindrical coordinate system is used to facilitate the computation of the incident intensity, where the coordinates \((r', \psi', z')\) are measured on the plane that is normal to the axis of the cylinder. Here, the temperature and radiative properties are assumed to vary only in the radial direction \(r\). The radiative intensity at an arbitrarily targeted point \(P\) is denoted as \(I(r, \theta, \psi)\), where the polar angle \(\theta\) is measured from the positive \(z\) axis and the azimuthal angle \(\psi\) is measured in the \(r - \psi\) plane perpendicular to it.

The radiative transfer equation (RTE) for an emitting, absorbing and scattering medium is given by

\[
s \cdot \nabla I_\lambda(r, s) = \kappa_\lambda I_{b,\lambda}(r) - \beta_\lambda I_\lambda(r, s) + \frac{\sigma_\lambda}{4\pi} \int S_\lambda(r, s')\Phi_\lambda(s \cdot s')d\Omega',
\]

where \(I_\lambda\) is the spectral intensity, \(I_{b,\lambda}\) is the black-body intensity, \(\kappa_\lambda, \sigma_\lambda, \) and \(\beta_\lambda = \kappa_\lambda + \sigma_\lambda\) are wavelength-dependent absorption, scattering, and extinction coefficients, respectively, and \(\Phi_\lambda\) is the scattering phase function. When no scattering is considered, \(\sigma_\lambda = 0\) such that extinction coefficient \(\beta_\lambda = \kappa_\lambda\). For the sake of simplicity, we assume that all the properties are independent of the wavelength \(\lambda\).

Equation (A.7) can be integrated along a path \((s)\) to yield the integral form of radiative intensity

\[
I(\tau_s, s) = I_w exp(-\tau_s) + \int_0^{\tau_s} S(\tau'_s, s) exp[-(\tau_s - \tau'_s)]d\tau'_s,
\]

(A.8)
where, by considering no scattering medium, the source function \( S \) is simplified as

\[
S(\tau_s', s) = I_b(\tau_s').
\]  

(A.9)

Here, \( I_w \) the intensity emanating from the cylinder boundary. It is assumed that \( I_w \) comes from the fresh air side (i.e., no emission from the cylinder boundary) where the air temperature is approximately 300 K.

Using the simple trigonometric relations shown in Fig. A.3, the optical thickness of \( \tau_s \) is expressed as

\[
\tau_s = \frac{\tau}{\sin \theta} \left[ \cos \psi + \sqrt{\left(\frac{\tau_0}{\tau}\right)^2 - \sin^2 \psi} \right] = \frac{1}{\sin \theta} \left[ \tau \cos \psi + \sqrt{\tau_0^2 - \tau^2 \sin^2 \psi} \right].
\]  

(A.10)

When \( \psi' \geq \pi/2 \),

\[
\tau_s' = \frac{1}{\sin \theta} \left[ \sqrt{\frac{\tau_0^2 - \tau^2}{\tau}} - \sqrt{\frac{\tau_0^2 - \tau^2 \sin^2 \psi}{\tau}} \right]
\]  

(A.11a)

\[
\tau_s - \tau_s' = \frac{1}{\sin \theta} \left[ \tau \cos \psi + \sqrt{\tau_0^2 - \tau^2 \sin^2 \psi} \right]
\]  

(A.11b)

\[
d\tau_s' = -\frac{\tau' / \tau}{\sin \theta \sqrt{(\tau' / \tau)^2 - \sin^2 \psi}} \, d\tau'.
\]  

(A.11c)
When \(\psi' < \pi/2\),
\[
\tau' = \frac{1}{\sin \theta} \left[ \sqrt{\tau'^2_0 - \tau'^2 \sin^2 \psi} + \sqrt{\tau'^2 - \tau'^2 \sin^2 \psi} \right]
\]  \hspace{1cm} (A.12a)
\[
\tau - \tau' = \frac{1}{\sin \theta} \left[ \tau \cos \psi - \sqrt{\tau'^2 - \tau'^2 \sin^2 \psi} \right]
\]  \hspace{1cm} (A.12b)
\[
d\tau' = -\frac{\tau' / \tau}{\sin \theta \sqrt{(\tau' / \tau)^2 - \sin^2 \psi}} d\tau'. \hspace{1cm} (A.12c)
\]

Note that \(\psi' \geq \psi\). Therefore, when \(\psi \leq \pi/2\),
\[
\int_0^\tau S(\tau, s) \exp[-(\tau - \tau')] d\tau' = \int_0^{\tau_0} S(\tau', \theta, \psi) \frac{\tau' / \tau}{\sin \theta \sqrt{(\tau' / \tau)^2 - \sin^2 \psi}} \exp \left[ -\frac{1}{\sin \theta} \left( \tau \cos \psi + \sqrt{\tau'^2 - \tau'^2 \sin^2 \psi} \right) \right] d\tau'
\]  \hspace{1cm} (A.13)

When \(\psi \geq \pi/s, \psi' \geq \pi/2\), the radiative source is simplified as
\[
\int_\tau^{\tau_0} S(\tau', \theta, \psi) \frac{\tau' / \tau}{\sin \theta \sqrt{(\tau' / \tau)^2 - \sin^2 \psi}} \exp \left[ -\frac{1}{\sin \theta} \left( \tau \cos \psi + \sqrt{\tau'^2 - \tau'^2 \sin^2 \psi} \right) \right] d\tau'. \hspace{1cm} (A.14)
\]

According to Eq. (A.9), the radiative intensity can be integrated separately based on \(\psi\). When \(-\pi/2 \leq \psi \leq \pi/2\),
\[
I(\tau, \psi, \theta) = I_0 \exp \left[ -\frac{\tau}{\sin \theta} \left( \cos \psi + \sqrt{(\tau_0 / \tau)^2 - \sin^2 \psi} \right) \right] + \int_{\tau_0}^\tau I_b(\tau', \theta, \psi) \frac{\tau' / \tau}{\sin \theta \sqrt{(\tau' / \tau)^2 - \sin^2 \psi}} \exp \left[ -\frac{1}{\sin \theta} \left( \tau \cos \psi + \sqrt{\tau'^2 - \tau'^2 \sin^2 \psi} \right) \right] d\tau' + \int_{\tau_0}^\tau I_b(\tau', \theta, \psi) \frac{\tau' / \tau}{\sin \theta \sqrt{(\tau' / \tau)^2 - \sin^2 \psi}} \exp \left[ -\frac{1}{\sin \theta} \left( \tau \cos \psi - \sqrt{\tau'^2 - \tau'^2 \sin^2 \psi} \right) \right]. \hspace{1cm} (A.15)
When $\pi/2 \leq \psi \leq 3\pi/2$,

$$I(\tau, \psi, \theta) = I_w \exp \left[ -\frac{\tau}{\sin \theta} \left( \cos \psi + \sqrt{\left(\frac{\tau_0}{\tau}\right)^2 - \sin^2 \psi} \right) \right] +$$

$$\int_\tau^{\tau_0} I_b(\tau', \theta, \psi) \frac{\tau'}{\sin \theta \sqrt{\left(\frac{\tau'}{\tau}\right)^2 - \sin^2 \psi}} \exp \left[ -\frac{1}{\sin \theta} \left( \tau \cos \psi + \sqrt{\left(\frac{\tau'}{\tau}\right)^2 - \tau^2 \sin^2 \psi} \right) \right].$$

(A.16)

Note that $\tau = \beta r$ is the optical distance along the radial direction, and $\tau_0$ is the total optical distance from the center to the boundary of the cylinder.

By integrating $I(\tau, \psi, \theta)$ along $\psi$ and $\theta$ directions, the radiative incident intensity can be obtained,

$$G(\tau) = \int_0^\pi \int_0^{2\pi} I(\tau, \psi, \theta) \sin \theta d\psi d\theta. \quad \text{ (A.17)}$$

Given that $I_w = 0$, the radiative incident intensity is simplified as,

$$G(\tau) = \int_0^\pi \int_{-\pi/2}^{\pi/2} \left\{ \int_{\tau/|\sin \phi|}^{\tau_0} I_b \frac{\tau'}{\sqrt{\left(\frac{\tau'}{\tau}\right)^2 - \sin^2 \psi}} \exp \left[ -\frac{1}{\sin \theta} \left( \tau \cos \psi + \sqrt{\left(\frac{\tau'}{\tau}\right)^2 - \tau^2 \sin^2 \psi} \right) \right] d\tau' + \int_\tau^{\tau_0} I_b \frac{\tau'}{\sqrt{\left(\frac{\tau'}{\tau}\right)^2 - \sin^2 \psi}} \exp \left[ -\frac{1}{\sin \theta} \left( \tau \cos \psi - \sqrt{\left(\frac{\tau'}{\tau}\right)^2 - \tau^2 \sin^2 \psi} \right) \right] d\tau' \right\} d\psi d\theta.$$

(A.18)

The absorption source term in the energy transport equation is given by,

$$Q_{abs} = \kappa G. \quad \text{ (A.19)}$$

The non-uniform gas emission and/or absorption can be considered by introducing the following functional form

$$\tau(r) = \int_0^r \kappa_p(r) dr, I_b = I_b(T(r)). \quad \text{ (A.20)}$$

Finally, the absorption source term is obtained with,

$$Q_{abs}(r) = \kappa(r)G(r). \quad \text{ (A.21)}$$
A.5 The Mie theory for spherical water mists

The radiation incident on a spherical particle is partly absorbed and partly scattered. The scattering is a dispersion of part of the incident radiant energy in different directions. The mathematical description of the interaction between incident radiation and a single spherical particle is presented with Maxwell’s wave equations. The solution to this problem is named as the “Mie theory”. The basic equations and functions of Mie theory are summarized below [49].

The fraction of the energy that is scattered into any given direction, defined by scattering angle $\theta_s$, is described by the Scattering phase function:

$$\Phi(\theta_s) = \frac{2}{x^2} i_1 + i_2 Q_{\text{scat}}.$$  \hspace{1cm} (A.22)

The quantities $i_1$ and $i_2$ are the non-dimensional polarized intensities, which are calculated from

$$i_1(x, \mathbf{m}, \theta_s) = |S_1(\theta_s)|^2, \quad i_2(x, \mathbf{m}, \theta_s) = |S_2(\theta_s)|^2.$$  \hspace{1cm} (A.23)

The $S_1(\theta_s)$ and $S_2(\theta_s)$ are the complex amplitude functions, expressed as

$$S_1(\theta_s) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos(\theta_s)) + b_n \tau_n(\cos(\theta_s))],$$  \hspace{1cm} (A.24)

$$S_2(\theta_s) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [b_n \pi_n(\cos(\theta_s)) + a_n \tau_n(\cos(\theta_s))].$$  \hspace{1cm} (A.25)

The direction-dependent functions, also called angular functions, $\pi_n$ and $\tau_n$ are related to the Legendre Polynomials $P_n(\cos(\theta_s))$ as

$$\pi_n(\cos(\theta_s)) = \frac{dP_n(\cos(\theta_s))}{d\cos(\theta_s)},$$  \hspace{1cm} (A.26)

$$\tau_n(\cos(\theta_s)) = \cos(\theta_s)\pi_n(\cos(\theta_s)) - \sin^2(\theta_s) \frac{d\pi_n(\cos(\theta_s))}{d\cos(\theta_s)}.$$  \hspace{1cm} (A.27)

The Mie scattering coefficients $a_n$ and $b_n$ are complex functions of $x$ and $y$,

$$a_n = \frac{\psi'_n(y)\psi_n(x) - m\psi_n(y)\psi'_n(x)}{\psi'_n(y) - \xi_n(x) - m\psi_n(y)\xi'_n(x)},$$  \hspace{1cm} (A.28)

$$b_n = \frac{m\psi'_n(y)\psi_n(x) - \psi_n(y)\psi'_n(x)}{m\psi'_n(y) - \xi_n(x) - \psi_n(y)\xi'_n(x)}.$$  \hspace{1cm} (A.29)

where $\mathbf{m} = n_r - ik$ is complex index of refraction, $x = 2\pi a/\lambda$ is particle size parameter and $y = \mathbf{m}x$. The functions $\psi_n(z)$ and $\xi_n(x)$ are the Ricatti-Bessel and Ricatti-Hankel
functions, respectively. They can be written as,

$$\psi_n(z) = z j_n(z), \xi_n(z) = iz j_n(z),$$

(A.30)

where $j_n(z)$ and $y_n(z)$ are spherical Bessel functions of the first and second kinds, respectively. The efficiency factors for extinction, scattering and absorption, $Q_{\text{ext}}$, $Q_{\text{scat}}$ and $Q_{\text{abs}}$ are given by

$$Q_{\text{ext}} = \frac{2}{\chi^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n),$$

(A.31)

$$Q_{\text{scat}} = \frac{2}{\chi^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2),$$

(A.32)

$$Q_{\text{abs}} = Q_{\text{ext}} - Q_{\text{scat}}.$$  (A.33)

The evaluation of the infinite series in the relations is terminated when $n \approx 1.5x+3$ [49].

A.6 Derivation of the analytical solution for linearly scattering media

The 1D slab configuration consisting of radiative media of constant optical properties is usually employed to validate radiation solvers/models because the analytical solutions can be obtained. The configuration is employed here to verify the developed anisotropic scattering solver. The 1D slab is bounded by two cold black walls 0.1 m apart. Water mist is distributed uniformly in the finite volume cells in a way that a desired spatial distribution of bulk Eulerian water extinction coefficient can be prescribed. All droplets are identical and have a diameter of 5 $\mu$m. The number of water droplets per computational cell is adjusted to obtain a constant extinction coefficient $\beta_d = 72.9$ m$^{-1}$. The gas mixture is chosen to have a homogeneous distribution with an absorption coefficient of $\kappa_g = 30$ m$^{-1}$.

The temperatures for gas and water mist are kept constant at 2000 K and 293 K, respectively. The grid resolution for this case is $\Delta = 4$ mm. Radiative source terms along the centerline are computed and compared with analytical solutions.

To verify the implementation of the scattering models as well as the tracing algorithm, both the isotropic scattering model and the linearly anisotropic scattering model for water droplets are tested. A brief derivation of the analytical solution is presented here. For linearly anisotropic scattering, the phase function is expressed as,

$$\Phi(\mu) = 1 + A_1 \mu.$$  (A.34)

$A_1$ is a fixed coefficient ranging from 0 to 1, $\mu = \cos \theta$ with $\theta$ as the polar angle.
A\(_1 = 1\), strongly forward scattering is expected. The source function is then given by,

\[ S(\tau, \mu) = (1 - \omega)I_b(\tau) + \frac{\omega}{4\pi}G(\tau) + \frac{A_1\omega}{4\pi}q\mu = S_1(\tau) + \frac{A_1\omega}{4\pi}q\mu, \] (A.35)

which is coupled with the incident radiation \(G\), and radiative heat flux, \(q\). \(\omega\) is the scattering albedo, and \(\tau\) is the optical thickness based on the total extinction coefficient \((\kappa_g + \beta_d)\). \(I_b\) can be calculated by \(E_b/\pi\), where \(E_b\) is the blackbody emissive power.

Equations for \(G\) and \(q\) are derived and expressed as,

\[ G(\tau) = 2J_1E_2(\tau) + 2J_2E_2(\tau_L - \tau) \]
\[ + 2\pi[\int_0^\tau S_1(\tau')E_1(\tau - \tau')d\tau' + \int_\tau^{\tau_L} S_1(\tau')E_1(\tau - \tau')d\tau'] \] (A.36)
\[ + \frac{A_1\omega}{2}[\int_0^\tau qE_3(\tau - \tau')d\tau' + \int_\tau^{\tau_L} qE_3(\tau - \tau')d\tau'], \]
\[ q(\tau) = 2J_1E_3(\tau) + 2J_2E_3(\tau_L - \tau) \]
\[ + 2\pi[\int_0^\tau S_1(\tau')E_2(\tau - \tau')d\tau' - \int_\tau^{\tau_L} S_1(\tau')E_2(\tau - \tau')d\tau'] \] (A.37)
\[ + \frac{A_1\omega}{2}[\int_0^\tau qE_4(\tau - \tau')d\tau' - \int_\tau^{\tau_L} qE_4(\tau - \tau')d\tau'], \]

Detailed derivations of Eqs. (A.36) and (A.37) can be founded in [49], and notations shown here are briefly described. \(E_n(x)\) refers to the exponential integral of order \(n\), and it is expressed as,

\[ E_n(x) = \int_0^1 \mu^{n-2}e^{-x/\mu}d\mu. \] (A.38)

\(J_1\) and \(J_2\) denote the emissive intensities from the two bounded walls, respectively. \(\tau_L\) is the maximum optical thickness that \(\tau\) can attain. In the presence of linearly anisotropic scattering, numerical integration is employed to obtain the radiative source term \(q\) at each \(\tau\). Subsequently, the calculated \(q\) is substituted into Eq. (A.36) to obtain \(G\). The absolute and relative tolerances of \(10^{-6}\) and \(10^{-6}\), are adopted to get converged results of \(G\) using MATLAB, respectively. When the fixed coefficient \(A_1\) is equal to zero, the equations are reduced to the isotropic scattering case. In that case, a decoupled relationship of \(G\) and \(q\) is expected.

### A.7 Chemical mechanisms used in this dissertation

A summary of the chemical mechanisms employed in this dissertation is provided in Table. [A.7]
Table A.1: Gas-phase chemical mechanisms for different fuels

<table>
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<th>Fuel</th>
<th>Number of species</th>
<th>Number of reactions</th>
<th>Ref.</th>
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</thead>
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<td>41</td>
<td>[103]</td>
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<td>[104]</td>
</tr>
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<td>Ethylene</td>
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