Detailed soot modelling in laminar premixed flames

Jasdeep Singh

Churchill College

A dissertation submitted for the degree of Doctor of Philosophy at the University of Cambridge

July 2006
To thy Lord
Preface

The work presented in this dissertation was undertaken at the Department of Chemical Engineering, University of Cambridge, between October 2001 and July 2006. It is the original work of the author unless specifically acknowledged in the text. Neither the present dissertation, nor any part thereof, has been submitted previously for a degree to this or any other university. This thesis contains approximately 40000 words, 14 tables, and 43 figures in total. The author was funded by the Pochobradsky Studentship (Churchill College) and British Chevening Scholarship.

Some of the work in this dissertation has been published:


2. J. Singh, R. I. A. Patterson, and M. Kraft, (2005), Multi-variate modelling of soot particle distributions in laminar premixed flames, 7th *World Congress of Chemical Engineering*.


Other publications:


2. R. I. A. Patterson, **J. Singh**, and M. Kraft, (2006), Method of Moments with Interpolative closure for non-spherical particles, 11\textsuperscript{th} *International Conference on Numerical Combustion*.


Jasdeep Singh
July 2006.
Summary

This dissertation presents an improved soot model to predict soot formation in laminar premixed flames for all relevant pressure conditions. A novel stochastic algorithm is used to solve the equations that describe the soot model. The algorithm is computationally efficient and allows for modelling multi-dimensional distributions, such as the age and mass of soot particles.

The dynamics of an ensemble of soot particles, which are defined by a soot model, is described by the Smoluchowski equation with additional source terms for nucleation and surface reactions. This equation, which has a complicated form, is solved by the stochastic approach that uses a new majorant kernel applicable for all pressure regimes. This majorant kernel reduces the complexity of the problem from $O(n^2)$ to $O(n)$, where $n$ is the number of stochastic particles representing the soot ensemble. Additionally, variants of the stochastic algorithm are implemented where the surface reactions that account for more than 90% of the total events are treated deterministically. This reduces the computational time by up to three orders of magnitude.

The stochastic algorithm resolves the entire particle size distribution (PSD) without introducing closure assumptions. For the first time, the ability of a soot model to predict the evolution of a detailed PSD is tested by comparing the simulated results with the experimental measurements. The sensitivity of the soot PSD to the processes and parameters defining the soot model is investigated. A mixture of poly aromatic hydrocarbons for the inception process, size-based Van der Waals enhancement factors for the particle-particle coagulation, and a new particle age based model for the number of active sites on the surface of a soot particle available for reaction with the gaseous species, are introduced in the soot model to obtain an agreement between the simulated and experimental PSDs.
Acknowledgements

I would like to take this opportunity to thank my supervisor Dr. Markus Kraft for his continued guidance and constructive criticism, without which this thesis would not have been what it is. It has been a great pleasure working with Robert Patterson, Dr. Michael Balthasar and Dr. Amit Bhave at the Computational Group, Cambridge. I thank them for stimulating discussions and for sharing their time and insights with me. I am grateful to Prof. Hai Wang for providing the experimental results without which the present work would have been incomplete.

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I am grateful to the Churchill College and British Chevening for the financial support offered for the present work. I would also like to thank the Department of Chemical Engineering, Centre for Scientific Enterprise Ltd., the Combustion Institute, Cambridge Philosophical Society, and Society of Chemical Industry for extending financial help, enabling me to present my research findings at conferences and research meetings.

Finally, I am grateful to my parents, my brother Gurman, and my wife Ruby for their love, prayers and blessings which helped me stay focussed.
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<th>Description</th>
<th>Value</th>
<th>Units</th>
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</thead>
<tbody>
<tr>
<td>$c$</td>
<td>Speed of light</td>
<td>$3 \times 10^8$</td>
<td>m.s$^{-1}$</td>
</tr>
<tr>
<td>$C_{pyr}$</td>
<td>Concentration of pyrene</td>
<td></td>
<td>mol.cm$^{-3}$</td>
</tr>
<tr>
<td>$C_{ext}$</td>
<td>Extinction cross section</td>
<td></td>
<td>cm$^2$</td>
</tr>
<tr>
<td>$C_{sca}$</td>
<td>Scattering cross section</td>
<td></td>
<td>cm$^2$</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter of a soot particle</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>$d_{avg}$, $\bar{d}$</td>
<td>Average diameter of a soot particle</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>$d_1$</td>
<td>Diameter of a single carbon atom</td>
<td>$2.77 \times 10^{-10}$</td>
<td>m</td>
</tr>
<tr>
<td>$d_{pyr}$</td>
<td>Diameter of a pyrene molecule</td>
<td>$7.9 \times 10^{-10}$</td>
<td>m</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
<td>$6.626 \times 10^{-34}$</td>
<td>J.s</td>
</tr>
<tr>
<td>$k$</td>
<td>Wave number</td>
<td>$2\pi/\lambda$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>$1.3807 \times 10^{-23}$</td>
<td>J.K$^{-1}$</td>
</tr>
<tr>
<td>$Kn$</td>
<td>Knudsen number</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Kn_1$</td>
<td>Knudsen number calculated for $d_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{ext}$</td>
<td>Extinction coefficient</td>
<td></td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>$m$</td>
<td>Refractive index of a soot particle</td>
<td>$1.57 + 0.56i$</td>
<td></td>
</tr>
<tr>
<td>$E(m)$</td>
<td>Function of the refractive index, $m$</td>
<td>$0.2595$</td>
<td></td>
</tr>
<tr>
<td>$F(m)$</td>
<td>Function of the refractive index, $m$</td>
<td>$0.2173$</td>
<td></td>
</tr>
<tr>
<td>$n_{\infty}$</td>
<td>Refractive index of the surrounding gas</td>
<td>$1$</td>
<td></td>
</tr>
<tr>
<td>$m_1$</td>
<td>Mass of a single carbon atom</td>
<td>$2.004 \times 10^{-26}$</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{O{H}}$</td>
<td>Mass of a OH molecule</td>
<td>$2.839 \times 10^{-26}$</td>
<td>kg</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of stochastic particles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N$, $N_d$</td>
<td>Number density</td>
<td></td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$\bar{N}$</td>
<td>Normalization parameter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro number</td>
<td>$6.023 \times 10^{23}$</td>
<td>mole$^{-1}$</td>
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<tr>
<td>$Q_{vv}$</td>
<td>Scattering coefficient</td>
<td></td>
<td>cm$^{-1}.sr^{-1}$</td>
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### NOMENCLATURE

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<th>Description</th>
<th>Value</th>
<th>Units</th>
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<tbody>
<tr>
<td>( r )</td>
<td>Radius of a soot particle</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature of soot particles</td>
<td></td>
<td>K</td>
</tr>
<tr>
<td>( T_{\text{max}} )</td>
<td>Peak temperature in the flame</td>
<td></td>
<td>K</td>
</tr>
<tr>
<td>( U )</td>
<td>Internal energy</td>
<td></td>
<td>kg.m(^2).s(^{-2})</td>
</tr>
<tr>
<td>( x )</td>
<td>Number of carbon atoms in a soot particle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( y )</td>
<td>Number of carbon atoms in a soot particle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( z )</td>
<td>Dimensionless diameter</td>
<td>( \pi d/\lambda )</td>
<td></td>
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### Greek Symbols

<table>
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<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
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<tr>
<td>( \alpha )</td>
<td>Fraction of sites on a C atom that are active</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Coagulation kernel</td>
<td></td>
<td>m(^3).s(^{-1})</td>
</tr>
<tr>
<td>( \widehat{\beta} )</td>
<td>Majorant kernel</td>
<td></td>
<td>m(^3).s(^{-1})</td>
</tr>
<tr>
<td>( \chi )</td>
<td>Number of active sites on a soot particle</td>
<td></td>
<td>cm(^{-2})</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Efficiency of a majorant kernel</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength used in light scattering</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>( \lambda_m )</td>
<td>Gas mean free path</td>
<td></td>
<td>m</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Viscosity</td>
<td></td>
<td>kg.m(^{-1}).s(^{-1})</td>
</tr>
<tr>
<td>( \mu_i )</td>
<td>( i^{th} ) reduced moment for PDF based on ( x )</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>( \nu_i )</td>
<td>( i^{th} ) moment for a PSD</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>( \rho_s )</td>
<td>Density of soot</td>
<td>1800</td>
<td>kg.m(^{-3})</td>
</tr>
<tr>
<td>( \sigma_s )</td>
<td>Variance of a soot PSD</td>
<td></td>
<td>–</td>
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### Abbreviations

<table>
<thead>
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<th>Description</th>
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<tr>
<td>C/O ratio</td>
<td>Carbon to Oxygen ratio</td>
</tr>
<tr>
<td>DSA</td>
<td>Direct simulation algorithm</td>
</tr>
<tr>
<td>HACA</td>
<td>Hydrogen abstraction carbon addition</td>
</tr>
<tr>
<td>LSODE</td>
<td>Livermore solver for ordinary differential equations</td>
</tr>
<tr>
<td>MoM</td>
<td>Method of Moments</td>
</tr>
<tr>
<td>MoMIC</td>
<td>Method of Moments with interpolative closure</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly aromatic hydrocarbons</td>
</tr>
<tr>
<td>PDF</td>
<td>Probability density function</td>
</tr>
<tr>
<td>PSDs</td>
<td>Particle size distributions</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
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Chapter 1

Introduction

Soot: The Good, the Bad and the Ugly.

Soot affects contemporary life in many ways. On the positive side, carbon black—which is made from soot—is omnipresent in our daily uses. It is used mainly as a reinforcing agent in rubber products such as tires, tubes, cables and other mechanical rubber goods; used as a black pigment in printing, carbon paper, typewriter ribbon inks, paints, plastics, fibres and ceramics; leather finishes; manufacture of dry-cell batteries, electrodes and carbon brushes; conductive and antistatic rubber and plastic products; videodiscs and tapes; and high temperature insulating material. Also, the emergence of nanotechnology has opened up new avenues for the use of carbon in material development and applications such as the high efficiency fuel cells and catalyst support (Dicks, 2006). The production of carbon black for the use in the above mentioned applications requires a maximum yield of soot from the flame pyrolysis of a hydrocarbon feedstock. This aspect of carbon formation in flames has received extensive coverage in the carbon black literature (Donnet and Voet, 1976; Lahaye and Prado, 1978; Schwob, 1979; Wissler, 2006).

On the negative side, however, soot contributes to many serious problems. In addition to contributing to pollution, soot enhances the emission of other pollutants from flames (e.g., carbon monoxide), causes undesirable radiative heat loads to combustion chambers, enhances the spread of unwanted fires due to radiant emission, and hampers fire fighting efforts by obscuring flames.

Soot has been suggested to be a major contributor to global warming: its effect in raising the global surface air temperature is double to that of carbon dioxide (Hansen and Nazarenko, 2004). Also, smaller soot particles are suspected
to exhibit dangerous effects on human health as they penetrate easily into the respiratory tracts. The poly aromatic hydrocarbons (PAH) that make up a soot particle have been found to be carcinogenic and mutagenic (Siegmann and Siegmann, 1998; Iwai et al., 2000) with a molecular biological pathway linking one of them—benzo[a]pyrene—to human lung cancer (Denissenko et al., 1996). These studies have forced severe regulatory limit on emissions of particulates. The combustion engineers are, thus, faced with a pressing need to design systems in which the amount of soot is controlled. Therefore, it is imperative to understand the phenomena of soot formation and oxidation.

1.1 Background to Soot formation and Oxidation

Soot is mostly carbon; other elements such as hydrogen and oxygen are usually present in small amounts. It is produced during the high temperature pyrolysis or combustion of hydrocarbons. The emission of soot from a combustor or from a flame is determined by the competition between soot formation and oxidation. A comprehensive model of the soot process must include both phenomena.

If one starts with an aliphatic fuel, the fuel molecules are broken down into smaller hydrocarbon molecules and free radicals either by pyrolysis or oxidative pyrolysis reactions. The initial step in the production of soot is the formation of the first aromatic species from these aliphatic hydrocarbons. The details of the process have been the subject of some considerable debate over the years. The aromatic species grow by the addition of other aromatic and smaller alkyl species to form larger polyaromatic hydrocarbons (PAH). Continued growth of the PAHs leads eventually to the smallest identifiable soot particles with diameters of the order of 1 nm and with masses of around 1000 amu (Kennedy, 1997). A great deal of information has been obtained over the years with regards to the formation step of soot in shock tubes, laminar premixed flames and laminar diffusion flames. The reviews by Haynes and Wagner (1981) and Richter and Howard (2000) are amongst the best sources for a full description of this phenomenon.

The first soot particles are roughly spherical in shape and have a C/H ratio of about 2. Upon aging, soot particles can coalesce into larger spherical particles, undergo surface reactions with surrounding gaseous species, dehydrogenate,
oxidize, and coagulate. The soot that is emitted from combustion devices typically has C/H ratio of approximately 10 and an aggregate structure (Miller et al., 2005).

The production of soot particles in a flame is inherently a chemically-controlled phenomenon. Low molecular weight (gaseous) hydrocarbons are converted to essentially solid carbon in just a few milliseconds. Thermodynamics alone cannot describe this process since soot is formed beyond regimes where it is thermodynamically stable relative to the oxides of carbon. Hence, chemical kinetics play an important role in soot production. To capture the essence of soot formation and oxidation, soot models are developed.

1.2 Soot Models

The formation and oxidation of soot is a result of many different chemical and physical processes. A detailed kinetic model of soot formation can be considered to consist of two principal components: gas-phase chemistry and soot particle dynamics.

The gas-phase chemistry submodel constitutes a set of chemical reactions that can possibly take place in the combustion system under investigation. The number of chemical reactions can be quite large, e.g. the combustion of a C$_2$ hydrocarbon fuel in a laminar premixed flame might require more than 500 chemical reactions to describe it. Initially, modelling the detailed chemical mechanism was a big challenge as it often resulted in high computational efforts. Therefore, short mechanisms were developed specific to the fuel in the combustion process (Jensen and Wilson, 1975; Kennedy et al., 1996). This gradually led to the formation of chemical mechanisms for the combustion of C$_1$ to C$_3$ hydrocarbons (Leung et al., 1991; Smith et al., 1995). The rates of reaction were obtained, primarily, by assuming equilibrium chemistry (Kennedy et al., 1990; Honnery and Kent, 1992; Kollmann et al., 1994; Makel and Kennedy, 1994) or quasi-steady state kinetics which formed flamelet libraries (Fairweather et al., 1992b; Moss et al., 1995). The inherent assumption in the development of these mechanisms was fast chemical reactions with time scales much shorter than the time scales of convection and diffusion of the gaseous species. The chemical mechanisms were extended to include the combustion of higher hydrocarbons such as the natural gas (Fairweather
et al., 1992a; Smith et al., 1995), kerosene, and diesel (Kouremenos et al., 1990) and were used to model various systems, e.g. turbulent diffusion flames, laminar diffusion flames, rocket motor, diesel engine, gas turbine engines etc. However, with more computational power at disposal, the focus shifted to developing detailed chemical mechanisms with accurate reaction rates. Major contributions in this area were made by Frenklach and Wang (1991), Colket and Hall (1994) and Lindstedt (1994).

The soot particle dynamics submodel describes the interaction of soot particles with each other and the surrounding gaseous species. This can be classified into three subcategories: Inception model, surface reaction model, and the coagulation model. The inception model elaborates on the formation of the first soot particle from the gaseous species. Initially, the rate of particle formation was assumed to be a function of the pressure, the equivalence ratio of unburned gases, and the temperature (Khan et al., 1971; Takahashi and Glassman, 1984; Olson et al., 1985). These correlations were specifically developed to predict soot formation in gas turbines and diesel engines. Many other parameters such as the height of the flame front and the composition and velocity of the burned gases were also used to model soot formation in diffusion flames (Jones, 1980). As more information on the gas phase chemistry became available, single (Lindstedt, 1992; Appel et al., 2000) and multiple chemical reaction(s) between the gaseous species (D'Anna et al., 2001; Richter et al., 2005) were proposed to give the first soot particle.

The coagulation has been modelled as the coalescence (Frenklach and Harris, 1986; Appel et al., 2000; Singh et al., 2005) or and aggregation (Puri et al., 1993; Köylü, 1997; Kazakov and Frenklach, 1998; Balthasar and Frenklach, 2005a,b) of two soot particles. The probability of three or more soot particles colliding simultaneously is very low and has not been incorporated in any model until now. Also, fragmentation of soot particles has rarely been included alongside the coagulation models. However, fragmentation is a possibility in high shear and high pressure environments such as in the diesel engine. Harris and Maricq (2002) discussed the role of fragmentation in defining the size distribution of diesel soot.

The surface reaction model has been the subject of much discussion over the past 50 years (Thomas, 1962). Although acetylene addition has long known to be the primary source of soot growth, debate still continues on its exact rate of
reaction. The problem is compounded by the lack of experimental measurements and the uncertainties where the measurements are available. Presently, the most recognized pathway of acetylene addition to a soot particle is via a free radical mechanism: Hydrogen Abstraction Carbon Addition (HACA) (Frenklach et al., 1984; Frenklach and Wang, 1991). The oxidation of soot particles plays equally an important role in soot particle dynamics. Although, oxidation models were not incorporated in the earlier soot models on the premise of fuel rich conditions, the models developed by Lee et al. (1962) and Nagle and Strickland-Constable (1962) for O$_2$ oxidation and Neoh et al. (1981) for OH oxidation are used in detail surface reaction models. The reaction and condensation of aromatic species, such as pyrene, are also included in surface reaction models (Appel et al., 2000).

By combining the gas phase chemistry and soot particle dynamics, soot models were developed. A comprehensive review on the existing soot models was provided by Kennedy (1997). The soot models were categorized into three domains depending on the detail of the gas phase chemistry and the soot particle dynamics: a) With empirical correlations, b) Semi-empirical models, and c) with detailed chemistry and soot particle dynamics. Mehta and Das (1992) solved for exhaust soot concentration in diesel engines using an empirical soot model; Kennedy et al. (1996) and Young and Moss (1995) solved for soot volume fraction and particle number density in laminar and turbulent ethylene-air diffusion flames respectively using semi-empirical soot models; and Frenklach et al. (1984) and Yoshihara et al. (1994) solved for soot yield in shock tube and direct injection diesel engine using detailed chemistry models. In the case of laminar flames, detailed soot models have been developed for counterflow and co-flow flames (Lindstedt, 1994), diffusion flames (Balthasar et al., 1996; Smooke et al., 2005), and premixed flames (Colket and Hall, 1994; Appel et al., 2000).

To isolate various issues concerning soot inception and mass growth one is interested in investigating simple systems such as the laminar premixed flame. The advantages of studying a laminar premixed flame are manifold:

1. Cheaper to set up experimentally as compared to engines;
2. Provides discrete experimental data, e.g. number density, soot volume fraction, and soot particle size distribution, as a function of the height from the burner;
CHAPTER 1. INTRODUCTION

3. Fewer variables defining the flame as compared to turbulent flames, thus easier to study the effect of variables such as the temperature, C/O ratio, and cold gas velocity on soot formation and oxidation;

4. Laminar premixed flames are steady in nature, \textit{i.e.} the concentration of soot and gas species does not change with time.

5. Easier to simulate numerically, can be modelled as a 1 dimensional problem along the length of the flame, \textit{i.e.} the change in concentration of soot and gas species concentration along the width of the flame is not accounted for.

A comprehensive soot model applied to laminar premixed flames was developed by Appel \textit{et al.} (2000). It included a detailed gas phase chemistry of over 500 chemical reactions describing the combustion of C$_1$ and C$_2$ hydrocarbon fuels and covered the important submodels of the soot particle dynamics model. This soot model, abbreviated ABF soot model in this thesis, has been successful at predicting the concentration of gaseous species of major reactants and products and the average properties of the soot particle ensemble such as the soot volume fraction and number density. The details of the ABF soot model, its merits and demerits, are discussed in the next chapter.

To test the soot models, conventional engineering solutions through the development of numerous prototypes may no longer be either economically attractive or, perhaps, even feasible. Therefore, numerical techniques are developed to solve the soot models and simulate different systems such as the engines and flames.

1.3 Numerical Techniques

As the literature on the numerical techniques available to simulate combustion processes in engines, flames, and other combustion systems is vast, this section will focus on the techniques used to simulate laminar premixed flames. In order to obtain the concentration of gaseous species and soot particles in a laminar premixed flame, numerical techniques need to solve both the gas phase chemistry and the dynamics of soot particle interaction. It is important to bear in mind that, until recently, experimental data on only soot volume fraction and number density were available. Therefore, most of the modelling work concentrated on matching the numerical results with the mean properties of the soot PSDs.
To model the evolution of an ensemble of soot particles the appropriate population balance equation (von Smoluchowski, 1916; Ramkrishna, 2000) has to be solved. Different approaches have been proposed in the past. Frenklach et al. (Frenklach and Harris, 1986; Frenklach and Wang, 1994; Kazakov et al., 1995; Frenklach, 2002) applied the method of moments to study soot formation in premixed flames using a detailed kinetic soot model. A major feature of the method of moments is its computational efficiency, which enabled its application to more complex problems such as the soot formation in diesel engines and gas turbines (Pitsch et al., 1996; Magnusson et al., 1998; Balthasar et al., 2000). While the method of moments predicts ensemble averaged quantities, the exact shape of the size distribution is not known explicitly. These studies have led to a wide range of basic understanding concerning the chemistry and physics of soot formation, but many questions remain and debate continues. These questions include, for example, the nature and size of soot nuclei, the mechanism of soot inception, the nature and number of chemically active sites on soot surface available for gas-surface reaction, and the sticking probabilities of particle-particle and PAH-particle collision.

To answer some of the questions, numerical techniques such as the discrete sectional method (Smooke et al., 1999), galerkin method (Appel et al., 2001), and stochastic approach (Balthasar and Kraft, 2003) were applied to model the dynamics of soot particle interaction. Appel et al. (2001) and Balthasar and Kraft (2003) compared numerically calculated soot particle size distributions averaged over few size classes to the experimental observations by Bockhorn et al. (1988). These numerical techniques provided a better understanding of soot formation but lacked the following features for effective soot model development.

1. Computational efficiency: Both the Galerkin and the Direct simulation stochastic approach took enormous computational time, in the order of days, to calculate soot PSD.

2. Resolution: Although, stochastic method provides detailed soot PSD, galerkin and sectional methods provides soot PSD averaged over few size classes.

3. Pressure regimes: The stochastic method was applied to simulate only low pressure flames as the implementation of coagulation of soot particles was limited to the free molecular regime. Understanding soot formation at high
pressure is important as most of the practical combustion devices such as the gas turbines and engines operate at high pressures.

Recently, Singh et al. (2005) and Patterson et al. (2006a) implemented few computationally efficient variants of the stochastic method, extended the method to include coagulation of soot particles for all relevant pressure regimes (Singh et al., 2004; Patterson et al., 2006b), and compared numerically calculated soot PSDs to detailed soot PSDs observed experimentally (Singh et al., 2006; Zhao et al., 2003a). This is discussed in detail in this thesis. Also, implementation of the population balance equation in CFD code (Zucca et al., 2006) and joint scalar transported probability density function (PDF) modelling of soot formation in turbulent flames (Lindstedt and Louloudi, 2005) has been achieved.

The gas phase chemistry submodel can be solved by PREMIX (Kee et al., 1985) and by many other commercially available software, e.g. COSILAB (Soft-predict, 2006). Principally, these softwares solve conservation of energy and conservation of species equations and use the set of chemical reactions as input along with the transport and thermal properties of the species involved in the chemical reactions. Frenklach et al. (Kazakov et al., 1995; Appel et al., 2000) solved the gas phase chemistry and the soot particle dynamics submodels simultaneously by coupling the PREMIX with the Method of Moments. Whereas, Balthasar and Kraft (2003) used the output of gas species concentration from the coupled version of the Method of Moments as the input to the stochastic method and predicted the soot PSD. The soot particle dynamics solved by the stochastic method was thus not directly coupled to the gas phase chemistry submodel. The error introduced by solving the gas phase chemistry and soot particle interaction separately is discussed in this thesis.

1.4 Experimental Techniques

Non-intrusive optical and laser-based techniques such as light scattering, small angle X-ray scattering (SAXS) (Hessler et al., 2002), small angle neutron scattering (SANS) (Wang et al., 2002) and Laser Induced Incandescence (LII) experiments have found increasing interest within recent years. Schulz et al. (2006) provided a comprehensive review on modelling the LII signal and identified current gaps in understanding the LII technique associated with the experimental
implementation, model descriptions, and signal interpretation.

The recent developments of advanced soot measurement techniques, including probe sampling followed by detailed soot PSD measurements with a scanning mobility particle sizer (SMPS) (Maricq, 2004; Zhao et al., 2003a,b, 2005), have provided soot data beyond the mean properties of PSDs. The spatial and temporal evolution of soot PSDs resulting from these experimental developments offer some unique modelling opportunities and challenges.

Advances are also being made to accurately measure–

- flame temperature using LII;
- gas species concentration of higher PAHs and concentration of sub nanometer sized soot particles using gas and mass spectrometers;
- aggregate structure of soot particles via transmission electron microscope (TEM) (Bockhorn et al., 1988);
- C/H ratio of soot particles amongst many others.

The accurate measurements of these parameters will provide comprehensive experimental data to validate soot models.

A common problem associated to the experimental techniques is the transformation of the experimental observation to the comparable quantities such as the number density, soot volume fraction, and particle size distribution. These transformations use assumptions such as a presumed distribution for a soot PSD, an empirical formula relating mobility diameter to particle diameter, soot particles being very small as compared to the wavelength of light used for light scattering experiments etc. More information on the soot PSD through numerical experiments is likely to aid in solving this inversion problem.

1.5 Aims of this Work

As is evident from the previous sections, much debate continues on the details of soot formation and oxidation. In light of recent experimental measurements of detailed soot PSD (Zhao et al., 2003a), this thesis attempts to develop an advanced and robust numerical technique that will aid in the development of a detailed soot model. The aims for this thesis are the following:
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1. To develop a stochastic method that can solve the soot model accurately for all relevant pressure regimes and is computationally efficient.

2. To validate the stochastic method by comparing results to the experimental observations (soot volume fraction and soot PSD) and the results of other numerical techniques that produce a similar output, e.g. Method of Moments coupled to PREMIX.

3. To perform numerical sensitivity studies in order to understand the effect of soot model parameters on the soot PSD in light of recent experimental observations (Zhao et al., 2003a).

4. To draw inferences from the above aims and propose potential improvements to the soot model to resolve any discrepancy between the experiments and results obtained numerically.

1.6 Organization of the Thesis

This thesis is organized into seven chapters. After the introduction in Chapter 1, the prerequisites for the development of a stochastic method are provided. This includes details on the soot model employed, the choice of laminar premixed flames for the experimental data, and the programs used to obtain the flame conditions which is an input to the stochastic method. Chapter 3 describes the development of a new stochastic algorithm that solves the population balance equation for all relevant pressure regimes. The algorithm includes a new methodology to model the process of coagulation, one that reduces the complexity of the problem from $O(n^2)$ to $O(n)$, where $n$ is the number of stochastic particles representing the soot ensemble. The chapter also discusses the variants of the direct simulation algorithm that reduce the computational time by up to three orders of magnitude. The knowhow that the time scales between the surface reaction processes and coagulation vary by many orders of magnitude is exploited. The surface reaction processes are treated deterministically or their rates are reduced and its effect increased proportionately on the soot particle size distribution.

Chapter 4 validates the stochastic method by comparing the results with the experimental measurements and other well known numerical methods that solve
the population balance equation, e.g. Method of Moments (MoM) and Liver-
more Solver for Ordinary Differential Equations (LSODE). The reasons for the
difference in the predictions of the average properties of a soot ensemble between
the MoM and stochastic method are elaborated. This includes a thorough in-
vestigation of the implementation of the MoM and discerning the exact sources
of error. This is followed by the applications and advantages of the stochastic
method over other numerical techniques.

In Chapter 5 the experimental data of Zhao et al. (2005) are discussed in
detail and the points for comparison of experimental and numerically obtained
soot PSDs are outlined. The computational results obtained from the stochastic
method are compared to the experimental data and numerical sensitivity studies
are performed to understand the effect of soot model parameters on the soot
PSDs. Also, inferences are drawn from this analysis and potential improvements
to the soot model are proposed to resolve the discrepancies between the experi-
ments and the results obtained numerically.

Chapter 6 concentrates on the development of a new model for the number
of active sites on a soot particle. It discusses the possible relations between the
age of a soot particle and the number of active sites on it, and is based on the
physical understanding of the process. The new model is tested by comparing
the experimental soot volume fraction and the computational results. Also, the
sensitivity of soot volume fraction to the parameters of the new model is investi-
gated. A new model for the number of active sites on a soot particle is suggested
which is a function of the local temperature of the flame and the age of a particle.

Finally, conclusions from the present work are drawn in Chapter 7. On
the basis of the insight gained and the problems faced while understanding soot
formation using stochastic method, recommendations for future work are included
in the final chapter.
Chapter 2

Prerequisites

For the development and successful implementation of a new numerical technique that simulates soot formation and oxidation, a few basic elements are required:

1. A physical soot model that describes the interaction of soot particles with each other and the surrounding gaseous species.

2. Experimental data for comparison with the simulated results and validation of the numerical technique.

3. An appropriate set of input conditions for the flame, e.g. concentration of gaseous species as a function of distance from the burner, numerical parameters.

This chapter discusses the choice of a soot model, the selection of laminar premixed flames for experimental data, and a methodology to obtain the input flame conditions for the stochastic method. Therefore, the three objectives for this chapter are:

1. To elaborate on the choice of the ABF soot model (Appel et al., 2000) for modelling the soot formation and oxidation. Both the merits and demerits of each submodel of the ABF soot model are discussed.

2. To list the properties of and criteria for the choice of laminar premixed flames that are analyzed in this thesis.

3. To introduce PREMIX originally developed by Kee et al. (1985). PREMIX is a tool used to calculate the time variation of the temperature and gaseous species profiles in a laminar premixed flame.
2.1 ABF Soot Model

A soot model consists of two principal components: gas phase chemistry which determines the flame structure, and soot particle dynamics which describe the evolution of the soot particle ensemble. Various soot models have been proposed depending on the type of the flame (premixed, diffusion), the Reynolds number (laminar, turbulent), and the system under observation (Engines, shock tubes, burners). A review on the soot models and their applications have been discussed in the previous chapter. Therefore, this section will concentrate on the details of the ABF soot model.

The ABF soot model as used in this thesis is exactly as documented in Appel et al. (2000). It has been broadly successful at predicting: (a) the concentration of gaseous species of major reactants and products, and (b) the average properties of an ensemble of soot particles, such as the soot volume fraction and number density, in laminar premixed flames. This has partially validated both the gas phase chemistry submodel and the particle dynamics submodel. The ABF soot model has been widely used in recent years. The gas phase chemistry submodel has been used to predict the poly aromatic hydrocarbons (PAH) formation in different types of flames and systems: Heptane combustion in an engine (Babushok and Tsang, 2004), non-premixed methane flames (D’Anna and Kent, 2003), diffusion flames (Violi et al., 2003), laminar premixed flames (Appel et al., 2001) etc. The particle dynamics submodel has also been used to predict the average properties of a soot ensemble (Kazakov et al., 1995; Appel et al., 2000, 2001), aggregate structure of a soot particle (Balthasar and Frenklach, 2005a,b), and fully resolved soot particle size distribution (Balthasar and Kraft, 2003; Singh et al., 2006).

The following sections describe the details of the gas phase chemistry and the particle dynamics submodels. Their merits and demerits are discussed below:

Gas-Phase Chemistry

The role of the gas-phase chemistry model is to predict the profiles of the gaseous species accurately. The gas-phase chemistry of the ABF soot model is largely based on that of Wang and Frenklach (1997) for PAH formation in C$_2$ hydrocarbon flames. It includes the pyrolysis and oxidation of C$_1$ and C$_2$ species, the
formation of higher, linear hydrocarbons up to C\textsubscript{6} species, the formation of benzene and further reactions leading to pyrene, as well as the oxidation pathways of the aromatic species. The description of the small hydrocarbon reactions is founded on GRI-Mech 1.2 (Smith \textit{et al}., 1995), one of the consistent and reliable descriptions of C\textsubscript{1} combustion chemistry. The formation of benzene and phenyl is described by the reactions of C\textsubscript{4}H\textsubscript{x} species with acetylene, by the cyclization reactions of C\textsubscript{5}H\textsubscript{x} species, and the combination of propargyl radicals. The formation path of pyrene starting with benzene follows the “hydrogen-abstraction-carbon-addition” (HACA) reaction sequence along with the ring-ring condensation (Frenklach \textit{et al}., 1984). The reaction channels and rate coefficients for the even-carbon atom aromatics formation and the HACA growth are those of Wang and Frenklach (1997), augmented with a consistent set of thermodynamic data (Wang and Frenklach, 1993) and transport properties (Wang and Frenklach, 1994) of aromatic species.

It is important to note that the correctness of output from the particle dynamics model relies, first of all, on the accuracy of the species profiles supplied by the gas-phase submodel, in particular those that define the soot particle nucleation and surface growth rates. Therefore, if one is interested in a predictive description of soot evolution, the accuracy of the model for the flame structure must be confirmed first. The gas-phase chemistry of Wang and Frenklach (1997) under-predicted the concentration of acetylene and pyrene. Therefore, rate constants were modified for few reactions and additional reactions were proposed to the Wang and Frenklach (1997) gas phase chemistry (Appel \textit{et al}., 2000). The ABF gas phase mechanism consists of 101 chemical species and 550, 544, and 546 reactions at 120 mbar, 1 bar, and 10 bar pressure respectively.

**Soot particle dynamics**

The particle dynamics submodel includes reactions between the surface of the soot particle and the surrounding gaseous species; coagulation, aggregation, and inception to list the important ones. Each of these processes has been studied in detail in either flame environment or otherwise and submodels have been developed. Depending on the problem under investigation, a collection of submodels gives us a soot model.

The ABF model, which has three types of processes namely the inception,
Figure 2.1: Schematic description of a laminar premixed flame with the processes in the ABF soot model highlighted. Starting from the burner front, a mix of gaseous species is observed that includes the formation of smaller PAHs. This is followed by the inception of a soot particle (shown here as a dimerization of pyrene). The other processes, i.e. coagulation, condensation of PAHs, and surface reaction of gaseous species, all take place simultaneously and throughout the flame. The size of larger PAHs and soot particles represented by black dots are not to scale and are for schematic purpose only.
coagulation, and surface reactions, has been successful in predicting the macro
scale properties of a soot ensemble, e.g. soot volume fraction and particle number
density, in laminar premixed flames (Appel et al., 2000; Balthasar and Kraft,
2003). The inception is modelled solely as the collision of two gaseous pyrene
molecules, coagulation is modelled as the coalescence of two soot particles, and
the surface reactions include the reactions of pyrene, acetylene, oxygen, and OH
with the surface of a soot particle. Much work on particle dynamics submodel
was earlier done by Frenklach and Wang (1991) and Kazakov et al. (1995). The
merits and shortcomings of each submodel are discussed in detail in the following
sections:

2.1.1 Inception model

In the ABF soot model, the smallest soot particle is incepted upon the collision
of two gaseous pyrene molecules and no other type of inception occurs. It
has long been realised that the precursor to soot must have special properties
(Thomas, 1962). They must be stable enough thermodynamically to withstand
severe, high-temperature combustion environments, yet they must be sufficiently
reactive to promote the growth of larger molecules on fairly short time scales.
Richter and Howard (2000) indicate that Rummel and Veh (1941) were the first
to propose a major role for PAHs because of their thermodynamic stability. De-
tailed investigations in order to elucidate higher PAHs formation pathways have
been conducted (Bittner and Howard, 1981; Frenklach et al., 1984; Colket, 1986;
Ahrens et al., 1994; Violi et al., 2001). Various groups, since, have adopted incep-
tion models to include PAH growth beyond pyrene (Mauß et al., 1994; D’Anna
et al., 2000; Richter et al., 2005). Although there is a considerable evidence that
the PAHs are the key reactants in soot formation and that the PAH growth is
through free radical intermediates, e.g. conjugated polyene and polybenzenoid
radicals (Bonne et al., 1965; Homann and Wagner, 1967; Crittenden and Long,
1973; Glassman, 1979; Vlasov and Warnatz, 2002); historically other species have
also been considered key soot formation reactants. Roles, at least under certain
conditions, for ionic (Calcote, 1981) and aliphatic species (Homann and Wagner,
1967; Oktem et al., 2005) have also been suggested.

The inception of a soot particle has been studied from various angles: the first
reaction steps; formation of the first aromatic ring; roles of acetylene, fullerenes
and higher PAHs in the growth process; impact of thermodynamics etc. This is because the chemical details of the formation of a nascent soot particle are relatively poorly understood, mostly because of the experimental difficulties. The efficient identification of species produced at different stages of the growth process is limited to molecular masses less than 300 amu using gas chromatography, while the observation and counting of soot particles by the high resolution electron microscopy has been limited to particle diameters of larger than about 1.5 nm. The analysis of larger PAHs by means of liquid chromatography and mass spectrometry as well as the increase of the resolution of electron microscopic techniques are objectives of ongoing research. Additional information has been obtained using optical techniques and this contributes to an increasing body of experimental data.

In his 1988 plenary article, Glassman (1989) states that “incipient particle formation determines the volume fraction of soot and is controlled by the rate of formation of the first aromatic species containing one to two rings”. As most of the initial experimental data was available for the number density and soot volume fraction, the inception models were designed to correctly predict the mean properties of the soot ensemble. It was shown by Yoshihara et al. (1994) that from the standpoint of predicting mean particle properties, e.g., soot volume fraction, inclusion of PAH growth beyond pyrene yields practically the same result as assuming pyrene dimerization as the only step of particle inception. The ABF soot model thus restricts itself to a simple inception model that has been quite effective in predicting the mean properties of the soot ensemble. It is to be noted that the capacity of the ABF soot model to predict soot PSD could not be realised earlier because of the absence of experimental measurements and the numerical techniques. This is discussed in detail in chapter 5.

### 2.1.2 Coagulation model

Coagulation is modelled as the **coalescence of two soot particles**. The rate of collision of two soot particles is defined by the coagulation kernel which takes a different form in each pressure regime. The kernels are determined by the physics involved in the interaction of pairs of particles. In general, the main drivers of particle transport are brownian motion, gravitational settling and turbulence, the latter two being not important in the context of laminar premixed flames.
Coagulation models have been extended to include aggregation, a phenomena well documented. Experimentalists have mostly used aggregation models to translate the optical properties observed for the soot ensemble into soot volume fraction, number density (Köylü and Faeth, 1992; Puri et al., 1993; Köylü, 1997), and PSDs. On the other hand, modelers have used aggregation models to better match experimental measurements and in soot model development (Kazakov et al., 1995; Balthasar and Frenklach, 2005a,b).

The numerical implementation of the coagulation model is probably the most challenging and computationally expensive out of all the other processes. This is because the criteria to select the particles for the coagulation event are governed by the coagulation kernel, which has a complicated dependence on the mass of soot particles. With the inclusion of aggregation in the coagulation model, the coagulation kernel has an additional dependence on the shape of soot particles. This increases the complexity of the coagulation kernel and is a cause of significant increase in the computational time to simulate the coagulation process. It is important to bear in mind that in the ABF soot model, the soot particles are considered spherical which defines the surface area of a soot particle in terms of the volume or mass.

Also, it is observed experimentally that the soot particles are spherical in the range 25 − 30 nm, are nearly spherical in the range of 40 − 45 nm, and take on an aggregate form beyond 50 nm (di Stasio and Massoli, 1997; Köylü et al., 1997; Vander Wal et al., 1999). In regards to the soot model development (see table 2.2 and chapter 5), the flames under analysis have maximum particle diameter of 60 nm. All these reasons obviate the need to include aggregation in the coagulation model. Therefore, coagulation is modelled as the coalescence of two spherical soot particles only.

The coagulation kernels for the different flow regimes are classified on the basis of Knudsen number ($Kn_x = 2\lambda_m/d_x$, where $\lambda_m$ is the gas mean free path and $d_x$ is the diameter of a soot particle containing $x$ carbon atoms). Figure 2.2 indicates the operating regime for a soot particle given the pressure of the flame, the temperature of the surrounding gas, and the size of the soot particle. For example, a particle of diameter 30 nm at a temperature of 1400 K in a 1 bar flame will be in the free molecular regime, whereas a particle of diameter 90 nm at a temperature of 2100 K in a 10 bar flame will be in the transition regime. The
values of the temperature and soot particle diameters for the figure have been chosen to represent conditions in different parts of flames.

**Continuum regime** \((Kn \leq 0.1)\)

This regime is applicable when the size of a particle is large relative to the mean free path of the gas molecules. In such a case, the fluid acts as a continuum with the movement of the molecules given by the diffusion theory. The derivation of the coagulation kernel, \(\beta\), assumes a Stokes’ law drag coefficient and takes the following form for two soot particles containing \(x\) and \(y\) carbon atoms respectively:

\[
\beta_{x,y} = K_0 \left( x^{-1/3} + y^{-1/3} \right) \left( x^{1/3} + y^{1/3} \right),
\]

where

\[
K_0 = \frac{2k_BT}{3\mu},
\]

\(k_B\) is the Boltzmann constant, \(T\) is the temperature, and \(\mu\) is the viscosity of the fluid.
Slip flow regime \((0.1 < Kn \leq 1)\)

The diffusion theory model is extended to \(Kn = 1\) by modifying the Stokes’ law with a factor \(C\), which is a function of \(Kn\). As in (Kazakov et al., 1995), the factor \(C\) is taken to be:

\[
C_x = 1 + 1.257 \times Kn_x.
\]

The coagulation kernel in the slip flow regime takes the following form:

\[
\beta^{sf}_{x,y} = K_0 \left( \frac{C_x}{x^{1/3}} + \frac{C_y}{y^{1/3}} \right) (x^{1/3} + y^{1/3}),
\]

\[
= K_0 \left( x^{1/3} + y^{1/3} \right) \left[ (x^{-1/3} + y^{-1/3}) + (x^{-2/3} + y^{-2/3}) \right] U,
\]

where

\[
U(T, P) = 1.257 \times Kn_1 (T, P).
\]

It should be noted that in the limit of low Knudsen numbers the correction factor \(C \to 1\), thus approaching the continuum regime kernel.

Free molecular regime \((Kn > 10)\)

This regime applies when a particle is small relative to the mean free path of the gas molecules. This usually occurs when the pressure of the flame is atmospheric or lower. The collision rate is calculated through statistical mechanics by averaging over the velocity distribution in the fluid. The rate is augmented by including the Van der Waals forces and a correction for sticking probability of the soot particles (Huang et al., 1991; Harris and Kennedy, 1988). This leads to the following form for the kernel:

\[
\beta^{fm}_{x,y} = A \left( x^{-1} + y^{-1} \right)^{1/2} \left( x^{1/3} + y^{1/3} \right)^2,
\]

where

\[
A = 2.2 \left( \frac{3m_1}{4\pi \rho_s} \right)^{1/6} \left( \frac{6k_B T}{\rho_s} \right)^{1/2},
\]

\(m_1\) is the mass of a single carbon atom, and \(\rho_s\) is the density of the soot particle. Their values are given in the Nomenclature.
Transition regime \((1 < Kn \leq 10)\)

The Boltzmann equation and diffusion theory model, applicable in the free molecular and continuum regimes respectively, cannot be extended into the transition regime, which lies in between. Therefore, Pratsinis (1988) developed an approximate kernel valid for the transition regime, which was motivated by the Fuchs kernel (Fuchs, 1964; Kazakov et al., 1995):

\[
\beta_{t_{x,y}} = \beta_{sf_{x,y}} \left[ 1 + \frac{\beta_{sf_{x,y}}}{\beta_{fm_{x,y}}} \right]^{-1}. \tag{2.4}
\]

The kernel, which is twice the harmonic mean of the slip flow and the free molecular kernels, is a complicated function of the soot particle size.

The numerical implementation of the coagulation model in different pressure regimes is discussed in chapter 3. To reiterate, aggregation is not included in the coagulation model.

### 2.1.3 Surface reaction model

The surface reaction model is probably the least understood and the most important part of the soot model for predicting the soot volume fraction. In the ABF soot model, there are four surface reactions with the surrounding gaseous species:

1. condensation of Pyrene, which adds 16 carbon atoms to the soot particle;
2. surface growth by Acetylene through the Hydrogen Abstraction Carbon Addition (HACA) mechanism (Frenklach et al., 1984), which adds 2 carbon atoms to the soot particle;
3. oxidation by \(O_2\), which removes two carbon atoms from the soot particle; and
4. oxidation by \(OH\), which removes a single carbon atom from the soot particle.

Table 2.1 describes the reaction scheme between the gaseous species and soot particles. The kinetics of the surface reactions is described in terms of surface sites. In the present formalism, these are carbon atoms either saturated with
Table 2.1: Surface growth mechanism

\[
k = AT^n \exp(-E/RT)
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(A) (cm(^3)mol(^{-1})s(^{-1}))</th>
<th>(n)</th>
<th>(E) (kcal/mol)</th>
<th>(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{\text{soot}} \cdot H + H \rightarrow C_{\text{soot}}^* + H_2)</td>
<td>(4.2 \times 10^{13})</td>
<td>13.0</td>
<td>(k_1)</td>
<td></td>
</tr>
<tr>
<td>(C_{\text{soot}} \cdot H + H \leftarrow C_{\text{soot}}^* + H_2)</td>
<td>(3.9 \times 10^{12})</td>
<td>11.0</td>
<td>(k_1)</td>
<td></td>
</tr>
<tr>
<td>(C_{\text{soot}} \cdot H + \text{OH} \rightarrow C_{\text{soot}}^* + H_2O)</td>
<td>(1.0 \times 10^{10})</td>
<td>0.734</td>
<td>1.43</td>
<td>(k_2)</td>
</tr>
<tr>
<td>(C_{\text{soot}} \cdot H + \text{OH} \leftarrow C_{\text{soot}}^* + H_2O)</td>
<td>(3.68 \times 10^8)</td>
<td>1.139</td>
<td>17.1</td>
<td>(k_2)</td>
</tr>
<tr>
<td>(C_{\text{soot}}^* + H \rightarrow C_{\text{soot}} \cdot H)</td>
<td>(2.0 \times 10^{13})</td>
<td></td>
<td></td>
<td>(k_3)</td>
</tr>
<tr>
<td>(C_{\text{soot}}^* + C_2H_2 \rightarrow C_{\text{soot}} \cdot H + H)</td>
<td>(8.0 \times 10^7)</td>
<td>1.56</td>
<td>3.8</td>
<td>(k_4)</td>
</tr>
<tr>
<td>(C_{\text{soot}}^* + O_2 \rightarrow \text{products})</td>
<td>(2.2 \times 10^{12})</td>
<td>7.5</td>
<td></td>
<td>(k_5)</td>
</tr>
<tr>
<td>(C_{\text{soot}} \cdot H + \text{OH} \rightarrow \text{CO} + \text{products})</td>
<td>Neoh et al. (1981) model, (\gamma_{\text{OH}} = 0.13)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hydrogen, \(C_{\text{soot}} \cdot H\), or dehydrogenated, \(C_{\text{soot}}^*\). The dehydrogenated carbon atoms are involved in the acetylene addition and \(O_2\) oxidation reactions. Pyrene condensation is modelled as the coagulation between a soot particle and a particle of diameter that comprises of 16 carbon atoms. In the absence of a clear mechanism of \(\text{OH}\) reaction with soot particle, Neoh et al. (1981) empirically found the reaction probability (\(\gamma_{\text{OH}}\)) of \(\text{OH}\) collision with a soot particle to estimate the \(\text{OH}\) oxidation rate. In addition, a parameter \(\alpha\)—the fraction of surface sites available for reactions with gaseous species, was introduced to account for the observed decay in the surface rates with time.

\[
\alpha = \tanh \left( \frac{a}{\log(\nu_1/\nu_0)} + b \right), \tag{2.5}
\]

where \(\nu_1/\nu_0\) is the first reduced moment of the soot particle size distribution and is a measure of the average particle diameter of the soot PSD. It is important to note that the value of the average particle diameter is continuously updated during simulations and thus no \(a\) \(a\) priori assumptions have to be made for its estimation. ‘\(a\)’ and ‘\(b\)’ are fitted parameters based on the data from 8 laminar premixed flames.

\[
a = 12.65 - 0.00563\ T, \tag{2.6}
\]
\[
b = -1.38 + 0.00068\ T, \tag{2.7}
\]

where \(T\) is the local temperature in Kelvin. The value of \(\alpha\) is between 0 and 1 and is the same for all the soot particles at a given time in the flame. All of the
eight laminar premixed flames that were used to obtain the parametric function for $\alpha$ are chosen for the analysis in this thesis and cover a range of C/O ratio and pressure (see table 2.2). The parametric function has been developed solely keeping in mind the match between the experimental and numerically obtained values of soot volume fraction. The function lacks any physical description of the decay of the active sites on the surface of the soot particle. Hence, it has limitations in predicting the number density, soot PSD and other experimentally measurable quantities.

Surface ageing, a phenomenon observed experimentally where the reactivity of surface sites decrease with increasing particle growth or age (Haynes and Wagner, 1982; Harris and Weiner, 1985), has gathered much attention in the literature. This is because of the following reason. Surface reactions account for more than 90% of the total processes in the flame and therefore any small change in modelling the process affects the soot volume fraction and PSDs enormously.

Frenklach and Wang (1991) introduced the notion of active sites on the soot particle surface. In conjunction with a decrease in concentration of H-radicals (Frenklach and Wang, 1994), it was used as an explanation for the experimental observation of surface ageing. Surface ageing has also been attributed to the formation of defects on the particles’ surface generated during surface growth (Frenklach, 1996; Frenklach et al., 1998) and reversibility of the acetylene addition step in a HACA surface growth scheme (Mauß et al., 1994; Mauß and Bockhorn, 1995). While initially a constant number of active sites were used with the kinetic soot model, it was expressed as a function of flame temperature and subsequently as a function of flame temperature and mean particle size (Kazakov et al., 1995). A global expression for the mean fraction of surface sites that are active ($\alpha$) for a series of laminar premixed flames was established by Appel et al. (2000). Particle ageing will be discussed in detail in chapter 6, where a new approach enables each soot particle to carry its individual number of active sites (Singh et al., 2005).

### 2.2 Flame Database

Developing a new numerical technique to predict the properties of a soot ensemble loses half its purpose if it can not be validated against experimental measurements. The experimental techniques to measure properties of a soot population
have developed enormously over the years. Initially, the average properties of a soot population, such as the soot volume fraction and number density, were available through light scattering experiments. Presently, Laser Induced Incandescence (LII) provides spatially resolved soot volume fraction and number density; mass spectrometers give the elemental composition of soot particles, e.g. C/H ratio; and electron microscopes make available the aggregate structure of soot particles. Also, soot particle size distributions are available from small angle X-ray scattering, small angle neutron scattering, and scanning mobility particle sizer (SMPS).

The accuracy with which each experimental technique obtains the properties of a soot ensemble is still hotly debated in literature. Moreover, the measurements from an experimental technique often need to be inverted to obtain the properties of a soot ensemble, e.g. the extinction and absorption coefficients measured in a light scattering experiment are inverted to obtain the soot volume fraction and number density. The theoretical assumptions underlying the inversion process are sometimes questionable and are under review. This is discussed in detail in chapter 4. Furthermore, it is important to bear in mind that the experimental measurements are made in a variety of systems, e.g. laminar premixed flames, turbulent flames, diffusion flames, engines etc. This restricts a consistent set of experimental data from the same experimental technique for a particular system.

In summary, the experimental techniques now offer measurements that provide more than the average properties of a soot ensemble. However, the range of experimental conditions covered is still very limited and in particular there is a need for more studies in which detailed measurements are collected while parameters are systematically varied. In this thesis, the focus is on simulating the soot particle dynamics in laminar premixed flames. Under these constraints, a set of 14 flames were chosen that were burnt by different experimental groups where light scattering experiments were used to obtain the soot volume fraction and the SMPS was employed to obtain the normalized soot particle size distribution.

Table 2.2 and 2.3 outlines the properties of the laminar premixed flames that are analyzed in this thesis. The flames are carefully chosen to represent a range of C/O ratios, peak temperatures, and pressures. The mole fraction illustrated in the table is that of the feed gas, $T_{\text{max}}$ represents the maximum temperature in the flame, and the velocity is the cold gas velocity of the feed gas.
Table 2.2: Properties of the laminar premixed flames

<table>
<thead>
<tr>
<th>Flame designation</th>
<th>% Mole fraction</th>
<th>C/O ratio</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (K)</th>
<th>Velocity (cm/s)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>24.2 37.9 37.9/0</td>
<td>0.64</td>
<td>1790</td>
<td>7.0</td>
<td>1</td>
</tr>
<tr>
<td>A2</td>
<td>24.2 37.9 37.9/0</td>
<td>0.64</td>
<td>1820</td>
<td>7.85</td>
<td>1</td>
</tr>
<tr>
<td>A3</td>
<td>24.2 37.9 37.9/0</td>
<td>0.64</td>
<td>1920</td>
<td>10.0</td>
<td>1</td>
</tr>
<tr>
<td>B1</td>
<td>24.2 37.9 0/37.9</td>
<td>0.64</td>
<td>1790</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>B2</td>
<td>24.2 37.9 15.1/22.8</td>
<td>0.64</td>
<td>1810</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>B3</td>
<td>24.2 37.9 37.9/0</td>
<td>0.64</td>
<td>1840</td>
<td>8.0</td>
<td>1</td>
</tr>
<tr>
<td>XSF1.78</td>
<td>14.0 18.0 0/68.0</td>
<td>0.78</td>
<td>2110</td>
<td>4.0</td>
<td>1</td>
</tr>
<tr>
<td>XSF1.88</td>
<td>15.5 17.4 0/67.1</td>
<td>0.88</td>
<td>1930</td>
<td>6.5</td>
<td>1</td>
</tr>
<tr>
<td>XSF1.98</td>
<td>17.0 17.4 0/65.6</td>
<td>0.98</td>
<td>1910</td>
<td>5.4</td>
<td>1</td>
</tr>
<tr>
<td>JW1.69</td>
<td>12.7 18.3 0/69.0</td>
<td>0.78</td>
<td>2104</td>
<td>5.9</td>
<td>1</td>
</tr>
<tr>
<td>JW10.60</td>
<td>11.2 18.7 0/70.1</td>
<td>0.60</td>
<td>2017</td>
<td>6.0</td>
<td>10</td>
</tr>
<tr>
<td>JW10.673</td>
<td>12.4 18.4 0/69.2</td>
<td>0.673</td>
<td>1895</td>
<td>3.0</td>
<td>10</td>
</tr>
<tr>
<td>JW10.68</td>
<td>12.5 18.4 0/69.1</td>
<td>0.68</td>
<td>1880</td>
<td>6.0</td>
<td>10</td>
</tr>
<tr>
<td>WBF12.3</td>
<td>22.6 12.4 55.0/0</td>
<td>1.30</td>
<td>1980</td>
<td>20.1</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*10% water vapor was added to the fuel stream. The fuel was C<sub>2</sub>H<sub>2</sub>.

Table 2.3: References of the laminar premixed flames

<table>
<thead>
<tr>
<th>Flame</th>
<th>Nature of measurements</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1–B3</td>
<td>Normalized soot PSDs</td>
<td>Zhao et al. (2005)</td>
</tr>
<tr>
<td>XSF</td>
<td>Soot volume fraction</td>
<td>Xu et al. (1997); Faeth and Kim (2004)</td>
</tr>
<tr>
<td>JW</td>
<td>Soot volume fraction</td>
<td>Appel et al. (2000)</td>
</tr>
<tr>
<td>WBF</td>
<td>Soot volume fraction</td>
<td>Bockhorn et al. (1984)</td>
</tr>
</tbody>
</table>

The data on the soot volume fraction from the XSF, WBF, and JW flames formed the basis for the parametric function (2.5) describing the number of active sites on the surface of a soot particle.

2.3 Flame Modelling using PREMIX

PREMIX is part of the CHEMKIN family of programs, published by Sandia National Laboratories (Kee et al., 1985). PREMIX is a tool used to calculate the temperature and species profiles as a function of distance from the burner in a laminar premixed flame. The lateral variation in the temperature and concentration of species is not accounted for, i.e. it is a one dimensional model. The 1-D flame model is able to predict the adiabatic flame speeds for a freely propagating
flame and calculate the temperature and species profiles for a burner-stabilized flame. The PREMIX program uses a reaction mechanism data file as an input along with the thermal and transport properties of each of the species involved in the mechanism. This input is the same as the gas phase chemistry submodel in a soot model.

The governing equations of the problem solved by PREMIX are the conservation of energy and the conservation of species. These equations allow for the time variation of temperature and species concentration profiles, but not of mass flow. The problems solved by PREMIX are steady, i.e. the solution does not change with time at a particular distance from the burner. A Newton algorithm is used to attempt solution from an initial guess. The Newton algorithm operates on the steady part of the equations, i.e. the time derivative is neglected. If the Newton algorithm fails, the time derivative is added and a time integration is performed. Upon completion of a certain number of time-steps, the Newton algorithm again attempts to solve the problem. The time integration has the effect of giving the Newton algorithm a different starting point, one that may lie in the domain of convergence. Often it is found that the initial guesses have to be fine-tuned by the user to obtain a converged solution. This involves modifying the input flame parameters such as the inlet temperature of the mixture gas, the peak temperature of the flame, the product mole fractions, and the absolute and relative tolerances of the error. These parameters are sometimes modified simultaneously and sometimes individually. It can often happen that no converged solution is obtained even after fine-tuning the initial guesses. This is because the number of grid points at which the solution is sought is large. Therefore, it is recommended to first obtain a solution at a low resolution and gradually add grid points.

For a burner stabilized flame, the mass flow rate of the gases is specified along with the burner exit gas temperature. At the downstream end of the domain all the gradients are assumed to be zero. The upstream boundary conditions specify the species composition of the gaseous mixture along with the gas temperature. While solving the equation for the conservation of energy, it is difficult to quantify heat losses from radiation. The temperature profile thus calculated from the energy equation can be quite different from that experimentally observed. In the case where the temperature profile as a function of distance from the burner is known from experimental measurements, the conservation of energy equation
need not be solved. In this way, the need to quantify the heat losses due to the radiation is removed and more accurate profiles for the gaseous species are obtained.

For greater detail about the algorithms used, the discretization employed, and other computational aspects of PREMIX, the reader is referred to the Sandia Report referenced Kee et al. (1985).

**Modifications to PREMIX**

As explained in the previous section, PREMIX outputs the profiles of gaseous species as a function of distance from the burner. However, the reaction mechanism which is an input to the PREMIX does not include reactions of gaseous species with the soot particles, or the formation of an incipient soot particle. Therefore, PREMIX does not account for the consumption of gaseous species due to the presence of soot particles. The profiles of the gaseous species, thus, were not entirely accurate. Therefore, PREMIX was modified to account for the consumption of gaseous species due to the reaction with and formation of the soot particles.

The conservation of species equations were coupled to the equations describing the time evolution of the moments of the soot particle size distribution (Frenklach, 2002). This ensured that the gas species participating in the formation, growth, and oxidation of a soot particle were approximately accounted for.

There were closure problems associated with obtaining soot moment equations and approximations were made alongside the use of interpolation routines. The Method of Moment with Interpolative Closure often abbreviated MoMIC in the literature will be abbreviated MoM for the purpose of this thesis. The approximations and the error introduced by MoM are investigated in section 4.2.1. However, of the methods available, the program that couples the PREMIX and MoM makes notably few assumptions to predict the concentration of gas species. In summary, the experimental temperature measurements and the modified PREMIX program provides a reasonably accurate input of the flame conditions for the stochastic method, which is described in the next chapter.
Chapter 3

Stochastic Method

This chapter details the development of a stochastic method that solves the equations describing the ABF soot model exactly. Here, “exactly” means that the effects of all approximations have been shown (with high probability) to be negligible. This is important because other numerical techniques used for validation of soot models do contain approximations as discussed in Chapter 4.

The differential equation describing the temporal evolution of the soot population, inline with the soot model, is the following:

\[
\frac{\partial}{\partial t} c(t, x) = I(t) c^{in}(x) + \sum_{\ell=1}^{4} \left[ \beta_{x-\delta\ell}^{\ell}(x) c(t, x - \delta\ell) - \beta_{x}^{\ell}(x) c(t, x) \right] + \frac{1}{2} \sum_{y=1}^{x-1} \beta_{x-y,y} c(t, x-y) c(t, y) - \sum_{y=1}^{\infty} \beta_{x,y} c(t, x) c(t, y),
\]

and

\[
\delta\ell = \begin{cases} 
16 & \text{for } \ell = 1 : \text{Condensation,} \\
2 & \text{for } \ell = 2 : \text{Acetylene addition,} \\
-2 & \text{for } \ell = 3 : \text{O}_2 \text{ oxidation,} \\
-1 & \text{for } \ell = 4 : \text{OH oxidation,} 
\end{cases}
\]

\[
c^{in}(x) = \begin{cases} 
1 & \text{for } x = 32, \\
0 & \text{otherwise,}
\end{cases}
\]
CHAPTER 3. STOCHASTIC METHOD

\[ \delta(x) = \begin{cases} 
0 & \text{if an oxidation process results in } x < 32, \\
1 & \text{for rest of the cases,} 
\end{cases} \]  

(3.4)

with the initial condition

\[ c(0, x) = c_0(x) = 0 \quad \text{for all } x, \]

where \( c(t, x) \) is the concentration of soot particles composed of \( x \) carbon atoms at a time, \( t \). \( I \) is the nucleation rate and \( \beta_x^\ell \) is the rate of the \( \ell \)th surface reaction for a particle composed of \( x \) carbon atoms. The coagulation kernel, \( \beta_{x,y} \), takes a different form in each pressure regime, as elaborated in section 2.1.2.

Equation 3.1 is a more general form of the basic discrete Smoluchowski coagulation equation with additional source terms for inception and surface reactions. The Smoluchowski coagulation equation (SCE) has been solved analytically for simple kernels, \( i.e. \) for \( \beta = 1 \) (von Smoluchowski, 1916), \( x+y \) (Golovin, 1963), \( x.y \) (McLeod, 1964), and reviewed by Aldous (1999). The complexity of the calculations required for these relatively simple forms of the kernel does not encourage the hope that complete analytical solutions can be obtained for more realistic forms of the kernel. Gillespie (1975) developed an exact method for numerically simulating the coalescence process for general forms of the kernel by using a direct simulation Monte carlo algorithm. This stochastic method was based on the joint probability function which is derived from the coagulation kernel describing the interaction of the particles and the mass distribution of the particles at the current time. Using the same principle, more efficient algorithms were developed by employing majorant kernels to solve the SCE (Eibeck and Wagner, 2000, 2003). The concept of majorant kernels will be discussed in detail in this chapter.

Solving equation 3.1 to obtain the properties of a soot particle population has attracted the attention of many modelers. Most often, only few features of the soot particle size distribution are needed to provide the information required about the soot particle ensemble, \( e.g. \) number density, soot volume fraction, and mean diameter of the particles. These are also the quantities which are accessible by experimental measurements. Basically, two different approaches have been used to solve the soot PSD without prescribing a particular form to it \( a \) \( priori \). The first is based on the Method of Moments (MoM) developed by Frenklach (2002), and the second is a discrete sectional method (Gelbard
and Seinfeld, 1980; Colket and Hall, 1994; Pope and Howard, 1997; Smooke et al., 1999; Appel et al., 2001). The MoM solves for the moments of the soot PSD and thus predicts the ensemble averaged quantities. A major feature of the MoM is its computational efficiency which enables its application to more complex problems such as soot formation in diesel engines and gas turbines. However, the exact shape of the size distribution is not known explicitly and it gives limited information for detailed soot modelling. On the other hand, the sectional techniques provide low resolution insight into the soot PSD and require significant computational time.

The stochastic method, details of which are covered in this chapter, has previously been used to solve the Smoluchowski equation. Balthasar and Kraft (2003) obtained fully resolved soot PSD for a low-pressure laminar premixed flame and compared it to experimentally determined distributions. The experimental measurements were obtained from molecular beam sampling of the soot flame and TEM micrographs of the soot particles (Bockhorn et al., 1988).

In this chapter, an algorithm is developed to solve the soot model for all the relevant pressure regimes (see section 2.1.2) previously limited to low-pressure flames only. Before providing details on this direct simulation algorithm, the importance of modelling all the relevant pressure regime, specifically the transition regime, needs to be justified.

3.1 Importance of the Transition Regime

A study was conducted to observe the flow regimes for soot particles at various flame pressures. The chemical conditions of the flame JW10.68 were chosen for this study because a range of particle sizes (20 – 150 nm) are observed on examining its soot PSD (figure 4.13). With such a broad span of soot particle sizes, a range of Knudsen numbers are observed for the particles in the flame. This translates into soot particles interacting in different flow regimes. Further, so as to solely observe the effect of flame pressure on the percentage of particles interacting in different flow regimes, the pressure input to the stochastic method was varied from 1 to 100 bar whilst leaving the flame chemistry unaltered, and equal to that predicted by PREMIX for the 10 bar flame.

The flow regime of particles that coagulated was recorded throughout the
Figure 3.1: Percentage of soot particles in the Free molecular regime (⋯), Transition regime (- - -), and Slip flow regime (—) at operating pressures of 1, 10, and 100 bar.

flamm. Figure 3.1 illustrates the percentage of coagulating particles in each regime for varying operating pressures in the flame. It is observed that these soot particles are predominantly in the free molecular regime at 1 bar, transition regime at 10 bar, and slip flow regime at 100 bar. However, with the change in initial conditions of the flame, i.e. C/O ratio, operating pressure, and cold gas velocity, the probability of particles in the transition regime is quite high for both low and high pressure flames.

From the study above and knowing that the pressures in a practical combustion devices range from atmospheric to 100 bar, it can be inferred that the interaction of soot particles will be defined by multiple coagulation kernels over a period of time for a system under study. This warrants development of a kernel that encompasses the interaction of soot particles in different flow regimes. The transition regime kernel (2.4), which in the limits of low and high Knudsen number equals the slip flow and free molecular kernel, is a suitable choice for such a kernel.

As discussed in the previous chapter, the transition regime kernel has a complicated dependance on the size of a soot particle. To efficiently simulate the interaction of soot particles in this regime, the concept of a majorant kernel is used. The following section explains this in more detail.
3.2 Majorant Kernel

The majorant kernel was a tool developed to reduce the computational time taken to simulate a process without introducing any approximation. This was first developed and used by Eibeck and Wagner (2000) to simulate the coagulation process defined by the SCE. They reduced the complexity associated with solving the coagulation process from \( O(n^2) \) to \( O(n) \), thus significantly increasing computational efficiency. This is explained in detail below.

In the stochastic method described in the next section, there are two steps which are critical to the implementation of the algorithm.

1. Calculation of the rates of processes, e.g. coagulation.

2. Selection of particles to perform the process, e.g. selection of two particles to coagulate from the collection of stochastic particles representing the soot ensemble.

Large computational time may be required for the simulation of either of these steps. It will be seen later in this chapter that the rate of coagulation is calculated as:

\[
R_{\text{coag}} = \frac{N}{2} \sum_{1 \leq i \neq j \leq n} \beta_{x_i,x_j},
\]  

where \( n \) is the number of stochastic particles representing the soot ensemble and \( i \) and \( j \) are the indices of these particles. \( x_i \) and \( x_j \) give the mass of the soot particles with the indices \( i \) and \( j \) respectively and \( N \) is the normalization parameter to balance the rate of coagulation and the rate of inception (see section 3.5.1). The factor of \( 1/2 \) is introduced because coagulation is not sensitive to the ordering of the two participating particles.

In a non-mathematical terminology, the rate of coagulation is the summation of the coagulation kernel, \( \beta_{x_i,x_j} \), over all pairs of soot particles. This requires \( n^2 - n \) operations and is of \( O(n^2) \) complexity. The computational time required is therefore high for large \( n \). For simple kernels, the rate of coagulation can be expressed as the summation of a finite set of moments of the size distribution. For example, in the case of continuum kernel, (2.1), the rate of coagulation is,

\[
R_{\text{coag}} = K_0 N \left[ n(n - 2) + \sum_{i=1}^{n} x_i \frac{n}{2} \sum_{i=1}^{n} x_i^{\frac{n}{2}} \right]
\]
CHAPTER 3. STOCHASTIC METHOD

This reduces the computational time significantly as only a few moments of the size distribution need to be tracked; an operation of $O(1)$ complexity. However, obtaining the rate of coagulation in the form of equation 3.6 is not possible for the free molecular and transition regime kernels.

Similarly, the selection of two particles out of the ensemble of stochastic particles for the coagulation process may also require up to $n^2 - n$ operations. However, if the rate of coagulation can be expressed in terms of the moments of the size distribution, (3.6), the number of operations are reduced to a maximum of $2n$ operations. Mathematically, this is equivalent to reducing the complexity of the problem from $O(n^2)$ to $O(n)$.

To achieve a similar reduction in the complexity of performing the coagulation process in the cases of the free molecular and transition regime kernels, the concept of a majorant kernel is introduced. A majorant kernel, $\hat{\beta}_{x,y}$, has the following properties:

1. it must be greater than or equal to the coagulation kernel $\beta_{x,y}$ for all $x, y$, i.e. $\hat{\beta}_{x,y} \geq \beta_{x,y} \forall x, y$;

2. the majorant kernel should facilitate the expression of the rate of coagulation in terms of the moments of the PSD, c.f. (3.6);

3. it should have a high efficiency, i.e. $\beta_{x,y}/\hat{\beta}_{x,y}$ should be as close to 1 as possible.

The last point needs more explanation. The introduction of a majorant kernel increases the simulated rate of coagulation as compared to the actual rate of coagulation implied by the model. This means that extra coagulation events will be simulated. To correct for this, a coagulation event is accepted with the probability $\beta_{x,y}/\hat{\beta}_{x,y}$, i.e. some of the coagulation events will be fictitious in nature and the particles will not coalesce. An efficient kernel will therefore reduce the number of fictitious events.

It is important to note that for a given kernel, there is no unique majorant kernel. For example, two majorant kernels for the free molecular regime are illustrated in table 3.1. Both majorant kernels satisfy the criteria 1 and 2. However, as can be observed from the figure 3.2 and table 3.1, the efficiency of the majorant kernels varies. The majorant kernel with the lower efficiency takes more fictitious jumps and requires more computational time as compared to the
majorant kernel with the higher efficiency. The left plot in figure 3.2 does not have the Eibeck and Wagner majorant kernel plotted. This is because the values of the majorant kernel were too high to be within the domain of the ordinate axis. However, a logarithmic scale was used for the ordinate axis in the second plot of figure 3.2 to compare the majorant kernels. The majorant kernel developed by Goodson and Kraft (2002) for the free molecular kernel will be used to develop a majorant kernel for the transition regime. The derivation for the Goodson and Kraft (2002) majorant kernel is detailed in Appendix A.1 in order to elucidate the functionality of a majorant kernel.

**Table 3.1: Majorant kernels for the free molecular regime kernel**

<table>
<thead>
<tr>
<th>Kernel / Majorant kernel</th>
<th>Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta A (x^{-1} + y^{-1})^{1/2} (x^{1/3} + y^{1/3})^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tilde{\beta} 2\sqrt{2} A (x + y)$</td>
<td>Low</td>
<td>Eibeck and Wagner (2001)</td>
</tr>
<tr>
<td>$\hat{\beta} 1.4178 A (x^{-1/2} + y^{-1/2}) (x^{2/3} + y^{2/3})$</td>
<td>High</td>
<td>Goodson and Kraft (2002)</td>
</tr>
</tbody>
</table>

**Figure 3.2:** Efficiency of the majorant kernels for the free molecular regime described in table 3.1. The left and right plot are for $y = 4096x$ and $y = x$ respectively.

### 3.2.1 Majorant kernel for the transition regime

To solve the dynamics of soot particles in the transition regime accurately and in a reasonable computational time, a majorant kernel is required. It is not possible
to easily satisfy all the three properties of the majorant kernel mentioned in the previous section for the transition regime, so a majorant rate is introduced. This is a slight generalization of the majorant kernel concept. This concept will enable us to simulate the coagulation process in the flames for all pressures through the use of a transition regime kernel (Singh et al., 2004; Patterson et al., 2006b).

First, a majorant for (2.4) is derived that meets criteria 1 and 3. It should be noted that no majorant is required for the slip flow regime because the rate of coagulation can be expressed as the sum of moments of the PSD (3.17). The majorant for the free molecular regime is defined in table 3.1. So, following the harmonic mean idea (2.4), we define:

\[
\frac{1}{\tilde{\beta}_{x,y}^t} := \frac{1}{\hat{\beta}_{x,y}^{fm}} + \frac{1}{\hat{\beta}_{x,y}^{sf}}.
\]

Since, \(\hat{\beta}_{x,y}^{fm} \geq \beta_{x,y}^{fm}\) we have:

\[
\frac{1}{\frac{1}{\tilde{\beta}_{x,y}^t}} \leq \frac{1}{\frac{1}{\hat{\beta}_{x,y}^{fm}}} + \frac{1}{\frac{1}{\hat{\beta}_{x,y}^{sf}}} = \frac{1}{\beta_{x,y}^t},
\]

which implies

\(\frac{1}{\tilde{\beta}_{x,y}^t} \geq \beta_{x,y}^t\) \hspace{1cm} (3.7)

However, \(\tilde{\beta}^t\) is not suitable for use as a majorant because it does not satisfy criterion 2. We proceed to a slightly larger majorant kernel with the definition:

\[
\hat{\beta}_{x,y}^t := \min \left(\hat{\beta}_{x,y}^{fm}, \hat{\beta}_{x,y}^{sf}\right) \geq \beta_{x,y}^t \geq \beta_{x,y}^t.
\]

Evaluating \(R_{coag}\) using \(\hat{\beta}^t\) is still slow - \(O(n^2)\) since every pair of particles has to be considered. The present author and colleagues then introduced a “majorant rate” (Singh et al., 2004; Patterson et al., 2006a). Defining \(\hat{R}_{coag}\) as the value of \(R_{coag}\) resulting from setting \(\beta = \hat{\beta}^t\) in (3.5), we have a majorant rate \(\hat{R}_{coag}\) for the transition regime given by (note that there is no \(\hat{\beta}^t\)):

\[
\hat{R}_{coag}^t := \min \left(\hat{R}_{coag}^{fm}, \hat{R}_{coag}^{sf}\right) \geq \hat{R}_{coag}^t \geq R_{coag}^t.
\]

If \(\hat{R}_{coag}^{fm} \leq R_{coag}^{sf}\) the time step proceeds using \(\hat{\beta}^{fm}\) as a majorant kernel, otherwise
\( \beta^s \) is used. The probability of acceptance of the coagulation event is given by

\[
p = \begin{cases} 
\frac{\beta^t}{\hat{\beta}^m} & \text{if the time step proceeds using } \hat{\beta}^m, \\
\frac{\beta^t}{\beta^s} & \text{if the time step proceeds using } \beta^s.
\end{cases}
\]

This simple majorant rate is used in this thesis.

**Efficiency of the majorant kernel**

The efficiency of the majorant kernel was calculated as the ratio of number of coagulation events simulated to the number of coagulation events implied from the increased coagulation rate due to the majorant kernel. This was recorded for four flames (see *Table 3.2*), which constituted both 1 and 10 bar flames, low and high sooting flames, and unimodal and bimodal PSD flames.

**Table 3.2:** Average efficiency of the majorant kernel for the transition regime

<table>
<thead>
<tr>
<th>Flame</th>
<th>Pressure (bar)</th>
<th>Sooting</th>
<th>PSD shape</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>High</td>
<td>Bimodal</td>
<td>0.846</td>
</tr>
<tr>
<td>A3</td>
<td>1</td>
<td>Low</td>
<td>Unimodal</td>
<td>0.917</td>
</tr>
<tr>
<td>JW 10.60</td>
<td>10</td>
<td>Low</td>
<td>Unimodal</td>
<td>0.646</td>
</tr>
<tr>
<td>JW 10.673</td>
<td>10</td>
<td>High</td>
<td>Unimodal</td>
<td>0.616</td>
</tr>
</tbody>
</table>

The efficiency of the majorant is very high in the cases where the soot particles lie mostly in the free molecular regime, e.g. flames A1 and A3. The flames A1 and A3 are both 1 bar flames and, in accordance with figure 3.1, most of the soot particles are in the free molecular regime. However, as the soot particles grow larger, they are likely to be in the transition regime. This decreases the efficiency of the majorant kernel. Because the soot particles are larger for flame A1 than A3, it can be observed from *figure 3.3* that the efficiency of the majorant kernel for flame A1 is less than A3.

The behavior of the efficiency of the majorant kernel for the 10 bar flames is completely different to the 1 bar flames, as can be observed from the *figure 3.4*. The efficiency sharply decreases to a minimum of 0.4 – 0.5 and then increases steadily to a value in the range of 0.7 – 0.8. For the 10 bar flames, the small size soot particles are in the free molecular regime in the early part of the flame resulting in high efficiency. As the particles grow larger and are in the transition regime, there is a phase when the coagulation kernels for the free molecular and
Figure 3.3: Efficiency of the transition regime majorant kernel for 1 bar flames.

Figure 3.4: Efficiency of the transition regime majorant kernel for 10 bar flames.
the slip flow regimes are equal. Mathematically, if $\beta^{sf} = \beta^{fm}$, the transition regime kernel and its efficiency take the following form:

$$\beta^t = \frac{\beta^{fm} \beta^{sf}}{\beta^{fm} + \beta^{sf}} = \frac{\beta^{sf}}{2} = \frac{\beta^{fm}}{2},$$

(3.10)

$$p = \begin{cases} 
\frac{\beta^t}{\beta^{fm}} = \frac{\beta^{fm}}{2\beta^{fm}} < 0.5 & \text{if the time step proceeds using } \beta^{fm}, \\
\frac{\beta^t}{\beta^{sf}} = \frac{1}{2} & \text{if the time step proceeds using } \beta^{sf}.
\end{cases}$$

(3.11)

The efficiency of the majorant kernel is minimum in the region where the free molecular and slip flow coagulation kernels are equal. However, as one kernel becomes larger than the other, the efficiency of the majorant kernel increases with the distance from the burner. It is to be noted that the particles are still in the transition regime which is why the efficiency plateaus between 0.7 and 0.8. The efficiency would have increased had the particles grown large enough to be in the slip flow regime. However, it is indicated from figure 3.1 that this is only possible at very high pressures (~50 – 100 bar).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.5.png}
\caption{Efficiency of the majorant kernel and positioning of soot particles for different flames for all relevant pressure regimes: Illustrative.}
\end{figure}

Figure 3.5 summarizes the interaction of soot particles for different flames on the Knudsen number scale. Also, plotted is the efficiency of the majorant kernel. It is to be noted that the data in the figure 3.5 is for illustrative purposes only and indicates the general trend. In essence, with the introduction of the
majorant kernel, the complexity of performing the coagulation process is reduced from $O(n^2)$ to $O(n)$ resulting in a significant reduction in computational time. For the purpose of this thesis, any algorithm using a majorant kernel will also be termed DSA, as it introduces no approximation. The proof of this exists in (Eibeck and Wagner, 2000).

3.3 Direct Simulation Algorithm

This section will illustrate a stochastic approach to solve equation 3.1 for the model described and presents a direct simulation algorithm (DSA). DSA is a computationally expensive numerical technique. However, variants of the DSA can be developed (see section 3.6) that might introduce no, negligible, or a considerable error.

The Algorithm

The stochastic algorithm for solving the Smoluchowski equation is:

1. Generate the initial state: for all the flames simulated in this thesis, the initial condition is 0 particles.

2. Wait an exponentially distributed time step $\tau$, with parameter

$$
R(p) = R_{\text{coag}}(p) + R_{\text{pin}}(p) + R_{\text{cond}}(p) + R_{\text{sg}}(p) + R_{O_2 \text{ ox}}(p) + R_{\text{OH ox}}(p),
$$

$$
\tau = -\frac{\ln(y)}{R(p)},
$$

(3.12)

where $y$ is a uniformly distributed random number between 0 and 1, $R_i$ for each regime is defined in section 3.4, and $R_{\text{coag}}$ is calculated based on the majorant kernels where applicable.

3. With probability

$$
\frac{R_\omega(p)}{R(p)},
$$

go to step $\omega$, where $\omega = 4$ is Particle inception, $\omega = 5$ is Surface growth by C$_2$H$_2$, $\omega = 6$ is Oxidation by O$_2$, $\omega = 7$ is Oxidation by OH, $\omega = 8$ is Coagulation, and $\omega = 9$ is Condensation. $\omega$ may be generated using
the standard inverse transform method, see for example algorithm ‘DI’ in section 3.2.4 of (Fishman, 1996).

4. **Perform inception**, *i.e.*
   
   (a) Add a particle of size 32 to the ensemble and go to step 2.

5. **Perform surface growth by** $\text{C}_2\text{H}_2$, *i.e.*
   
   (a) Select a particle of size $x$ uniformly after weighting each particle by its surface area;
   
   (b) Remove the particle of size $x$ and add a particle of size $x + 2$ to the ensemble;
   
   (c) Go to step 2.

6. **Perform oxidation by** $\text{O}_2$, *i.e.*
   
   (a) Select a particle of size $x$ uniformly after weighting each particle by its surface area;
   
   (b) Remove the particle of size $x$ and,
   
   i. add a particle of size $x - 2$, if $x \neq 32$ or $x \neq 33$;
   
   ii. if $x = 32$ or $x = 33$, then the model treats the particle as oxidized back to the gas phase and it is not replaced in the ensemble;
   
   (c) Go to step 2.

7. **Perform oxidation by** $\text{OH}$, *i.e.*
   
   (a) Select a particle of size $x$ uniformly after weighting each particle by its surface area;
   
   (b) Remove the particle of size $x$ and,
   
   i. add a particle of size $x - 1$, if $x \neq 32$;
   
   ii. if $x = 32$, then the model treats the particle as oxidized back to the gas phase and it is not replaced in the ensemble;
   
   (c) Go to step 2.

8. **Perform coagulation**, *i.e.*

   If operating in the transition regime go to step 8f, else go to step 8a.
(a) With probability
\[ \frac{Y_i}{\sum_{i=1}^{4} Y_i}, \]

go to step 8b for \( i = 1 \), step 8c for \( i = 2 \), step 8d for \( i = 3 \), and step 8e for \( i = 4 \). \( Y_i \) are defined for each regime in section 3.4.

(b) The particles are selected by observing the terms in the expression \( Y_1 \):
   
   i. Select a particle of size \( x \) uniformly from the ensemble;
   
   ii. Select a particle of size \( y \) uniformly from the ensemble for the continuum and the slip flow regimes and weighted by mass to the power one-sixth for the free molecular regime;
   
   iii. If the same particle gets selected, then go to step 8b, otherwise go to step 8g.

(c) The particles are selected by observing the terms in the expression \( Y_2 \):
   
   i. Select a particle of size \( x \) weighted by mass to the power one-third for the continuum and the slip flow regimes and by mass to the power one-sixth for the free molecular regime;
   
   ii. Select a particle of size \( y \) weighted by mass to the power minus one-third for the continuum and the slip flow regime and by mass to the power minus one-half for the free molecular regime;
   
   iii. If the same particle gets selected, then go to step 8c, otherwise go to step 8g.

(d) The particles are selected by observing the terms in the expression \( Y_3 \):
   
   i. Select a particle of size \( x \) uniformly from the ensemble for the slip flow regime;
   
   ii. Select a particle of size \( y \) weighted by mass to the power minus one-third for the slip flow regime;
   
   iii. If the same particle gets selected, then go to step 8d, otherwise go to step 8g.

(e) The particles are selected by observing the terms in the expression \( Y_4 \):
   
   i. Select a particle of size \( x \) weighted by mass to the power minus one-third for the slip flow regime;
ii. Select a particle of size \( y \) weighted by mass to the power minus two-third for the slip flow regime;

iii. If the same particle gets selected, then go to step 8e, otherwise go to step 8g.

(f) **Procedure for the transition regime.**

Evaluate the rate of coagulation, \( R_{\text{coag}} \), for the free-molecular (\( R_{\text{coag}}^{\text{fm}} \)) and the slip flow (\( R_{\text{coag}}^{\text{sf}} \)) regimes. These are defined in section 3.4.

i. If \( R_{\text{coag}}^{\text{fm}} \leq R_{\text{coag}}^{\text{sf}} \), then go to step 8a with \( Y_1, Y_2 \) from the free-molecular regime and \( \hat{\beta}^t = \hat{\beta}^{\text{fm}} \) else,

ii. go to step 8a with \( Y_1, Y_2, Y_3, Y_4 \) from the slip flow regime and \( \hat{\beta}^t = \beta^{\text{sf}} \).

(g) Perform the (possibly fictitious) coagulation:

i. With probability

\[
q = 1 - \frac{\beta_{x,y}}{\hat{\beta}_{x,y}},
\]

perform the fictitious event and do not alter the particle ensemble and go to step 8(g)iii else,

ii. remove the particles of size \( x \) and \( y \) and add a particle of size \( x+y \),

iii. go to step 2.

9. **Perform a condensation step, i.e.**

If operating in the transition regime go to step 9e, otherwise go to step 9a.

(a) With probability

\[
Z_i / \sum_{i=1}^{3} Z_i,
\]

go to step 9b for \( i = 1 \), step 9c for \( i = 2 \), step 9d for \( i = 3 \). \( Z_i \) is defined for each regime in section 3.4.

(b) Select a particle of size \( x \) uniformly from the ensemble and go to step 9f.

(c) Select a particle of size \( x \) weighted by mass to the power one-third and go to step 9f.
(d) Select a particle of size \( x \) weighted by the surface area of the particle for the free molecular regime and by mass to the power minus one-third for the slip flow and the continuum regimes. Go to step 9f.

(e) **Procedure for the transition regime.**

Evaluate the rate of condensation-\( R_{\text{cond}} \) for the free molecular (\( R_{\text{cond}}^{\text{fm}} \)) and the slip flow (\( R_{\text{cond}}^{\text{sf}} \)) regimes. These are defined in section 3.4.

i. If \( R_{\text{cond}}^{\text{fm}} \leq R_{\text{cond}}^{\text{sf}} \), then go to step 9a with \( Z_1, Z_2, Z_3 \) from the free-molecular regime and \( \hat{\beta}_{t,\text{cond}} = \beta_{t,\text{fm,cond}} \) else,

ii. Go to step 9a with \( Z_1, Z_2, Z_3 \) from the slip flow regime and \( \hat{\beta}_{t,\text{cond}} = \beta_{t,\text{sf,cond}} \).

(f) Perform the (possibly fictitious) condensation event:

i. If the original regime was anything except transition go to step 9(f)iii else,

ii. with probability

\[
q = 1 - \frac{\beta_{t,\text{cond}}}{\hat{\beta}_{t,\text{cond}}},
\]

the event is fictitious so do not alter the particle ensemble and go to step 9(f)iv else,

iii. remove the particle of size \( x \) and add a particle of size \( x + 16 \),

iv. Go to step 2.

The above algorithm uses the input of the numerical parameters and flame conditions to provide the soot particle size distribution.

### 3.4 Rates of Processes

Consider a stochastic particle system \( x_i(t), \ i = 1, 2, \ldots n(t) \) \( t \geq 0 \), where \( x_i(t) \) represents the size of particle with index \( i \) at time \( t \) and \( n(t) \) is the time varying number of stochastic particles in the system. The rate of the processes, which are used to calculate the probability of the occurrence of each process and the time step for the Markov process, are as follows:
Chapter 3. Stochastic Method

Particle Inception

The rate of particle inception, \( R_{\text{pin}} \), uses the coagulation kernel calculated for two particles having a size equivalent to 16 carbon atoms each, \( \beta_{16,16} \). The value of the kernel, \( \beta_{16,16} \), varies with the pressure regime and can be obtained from equations 2.1, 2.2, and 2.3 for the continuum, slip flow, and free molecular regime respectively.

\[
R_{\text{pin}} := \frac{1}{2N} \beta_{16,16} (C_{\text{Pyr}}N_A)^2,
\]

(3.13)

where, \( C_{\text{Pyr}} \) is the concentration of pyrene molecules (mol/cm\(^3\)) in the gas phase, \( N_A \) is the Avogadro number, and \( N \) is the normalization parameter.

Coagulation

The rate of coagulation, \( R_{\text{coag}} \), for the free molecular (3.15), continuum (3.16), and slip flow regimes (3.17) is as follows:

\[
R_{\text{coag}} := \frac{N}{2} \sum_{1 \leq i \neq j \leq n} \beta_{x_i,x_j},
\]

(3.14)

\[
= 1.4178 \ AN \left[ (n-1) \sum_{i=1}^{n} x_i^\frac{1}{3} + \left( \sum_{i=1}^{n} x_i^\frac{2}{3} \sum_{i=1}^{n} x_i^{-\frac{1}{3}} - \sum_{i=1}^{n} x_i^{-\frac{2}{3}} \right) \right].
\]

(3.15)

\[
= K_0N \left[ \frac{n(n-1)}{\gamma_1} + \sum_{i=1}^{n} x_i^\frac{1}{3} \sum_{i=1}^{n} x_i^{-\frac{1}{3}} - n \right],
\]

(3.16)

\[
= K_0N \left[ \frac{n(n-1)}{\gamma_1} + \sum_{i=1}^{n} x_i^\frac{1}{3} \sum_{i=1}^{n} x_i^{-\frac{1}{3}} - n + \right.
\]

\[
\left. \frac{U(n-1) \sum_{i=1}^{n} x_i^{-\frac{2}{3}} + U \left( \sum_{i=1}^{n} x_i^\frac{1}{3} \sum_{i=1}^{n} x_i^{-\frac{2}{3}} - \sum_{i=1}^{n} x_i^{-\frac{1}{3}} \right) }{\gamma_3} \right].
\]

(3.17)
The majorant kernel is used to calculate the coagulation rate in the free molecular regime. Note the definition of the $Y_i$ by means of the under-braces. The steps to obtain (3.15) from (3.14) is detailed in Appendix A.2.

Pyrene condensation

The rate of condensation, $R_{\text{cond}}$, uses the coagulation kernel with one particle fixed to a size equivalent to 16 carbon atoms, $\beta_{x_{i,16}}$. It takes the following form for the free molecular (3.19), continuum and slip flow regimes (3.20):

$$R_{\text{cond}} = C_{\text{Pyr}} N_A \sum_{i=1}^{n} \beta_{x_{i,16}},$$

$$= C_{\text{Pyr}} N_A \sqrt{\frac{\pi k_B T}{2m_1}} \left[ \frac{C_1 n + C_2 \sum_{i=1}^{n} x_i^{\frac{1}{3}} + C_3 \sum_{i=1}^{n} x_i^{-\frac{1}{3}}}{Z_2} \right],$$

$$= C_{\text{Pyr}} N_A K_0 \left[ \frac{C_1 n + C_2 \sum_{i=1}^{n} x_i^{\frac{1}{3}} + C_3 \sum_{i=1}^{n} x_i^{-\frac{1}{3}}}{Z_2} \right],$$

where,

<table>
<thead>
<tr>
<th>Regime</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free molecular</td>
<td>$0.55 d_1^2$</td>
<td>$4.4 d_1 d_{\text{Pyr}}$</td>
<td>$8.8 d_{\text{Pyr}}^2$</td>
<td>Eq. 3.19</td>
</tr>
<tr>
<td>Continuum</td>
<td>2</td>
<td>$(16)^{-\frac{1}{3}}$</td>
<td>$(16)^{\frac{1}{3}}$</td>
<td>Eq. 3.20</td>
</tr>
<tr>
<td>Slip flow</td>
<td>$2 + \frac{U}{(16)^{\frac{1}{3}}}$</td>
<td>$(16)^{-\frac{1}{3}} \left(1 + \frac{U}{(16)^{\frac{1}{3}}} \right) U + (16)^{\frac{1}{3}}$</td>
<td>Eq. 3.20</td>
<td></td>
</tr>
</tbody>
</table>

Note the definition of the $Z_i$ by means of the under-braces. The calculation of $\beta_{x_{i,16}}$ uses the reduced mass ($m_r$) of the coagulating particles, which is approximated in the following way:

$$\frac{1}{m_r} = \frac{1}{m_x} + \frac{1}{m_{\text{Pyr}}} = \frac{1}{m_x} + \frac{1}{16} \approx \frac{1}{16}.\quad (3.21)$$

This is because the selection of a soot particle for the condensation event is largely...
based on the surface area of particles in the ensemble \((Z_3 \gg Z_2 > Z_1)\), which results in \(m_x \gg 16\).

**Acetylene addition and Oxygen oxidation**

Table 2.1 describes the reaction scheme between the gaseous species and soot particles. To obtain the rates of surface growth, the concentration of dehydrogenated carbon atoms \(\left[ C_{\text{soot}}^* \right] \) was required. In equilibrium conditions,

\[
\begin{align*}
(k_1[H] + k_2[OH]) \left[ C_{\text{soot}}^* \right] &= \left( \hat{k}_1[H_2] + \hat{k}_2[H_2O] + k_3[H] + k_4[C_2H_2] + k_5[O_2] \right) \left[ C_{\text{soot}}^* \right], \\
\left[ C_{\text{soot}}^* \right] &= \frac{(k_1[H] + k_2[OH])}{(\hat{k}_1[H_2] + \hat{k}_2[H_2O] + k_3[H] + k_4[C_2H_2] + k_5[O_2])} \left[ C_{\text{soot}} \cdot H \right], \\
\left[ C_{\text{soot}}^* \right] &= K_r \left[ C_{\text{soot}} \cdot H \right].
\end{align*}
\]

Thus, the rate of reaction for acetylene addition, \(R_{\text{sg}}\), and oxygen oxidation, \(R_{\text{O}_2 \text{ ox}}\), is

\[
\begin{align*}
R_{\text{sg}} &= k_4[C_2H_2] \left( K_r \left[ C_{\text{soot}} \cdot H \right] \right), \\
R_{\text{O}_2 \text{ ox}} &= k_5[O_2] \left( K_r \left[ C_{\text{soot}} \cdot H \right] \right).
\end{align*}
\]

Here, \(\left[ C_{\text{soot}} \cdot H \right]\) is the number of sites on the surface of a soot particle available for reactions with the gaseous species. This is calculated based on the surface area provided by an ensemble of soot particles.

\[
\left[ C_{\text{soot}} \cdot H \right] = \chi (\text{cm}^{-2}) \alpha \left( \pi \sum_{i=1}^{n} d_i^2 \right),
\]

where \(\alpha\) quantifies the surface ageing and \(\chi\) provides the number of active sites per square centimeter.

**OH oxidation**

This event is modelled in a similar manner to the pyrene condensation, except that the expression for the rate of OH oxidation does not vary with the pressure regimes. Neoh et al. (1981) found empirically that the collision efficiency of OH
molecules with soot particles was 0.13 on average. This provides us with the following expression for $R_{\text{OH} \text{ ox}}$:

$$R_{\text{OH} \text{ ox}} := 0.13 C_{\text{OH}} N_A \sqrt{\frac{\pi k_B T}{2m_{\text{OH}}}} \sum_{i=1}^{n} d_i^2.$$  \hspace{1cm} (3.28)

A similar approximation to (3.21) is used to give the reduced mass in the calculation of the rate of OH oxidation.

## 3.5 Computational Efficiency of DSA

Besides the use of a majorant kernel, there are other techniques to reduce the computational time required to simulate a flame using the DSA. These are described below:

### 3.5.1 Normalization parameter

The normalization parameter, $N$, is used to normalize the rates of inception and coagulation. The purpose of this is to reduce the computational time significantly. In the absence of the normalization parameter, inception rates are very large in the early part of the flame. The rate of inception can be as high as $10^{17}$ mol.cm$^{-3}$.s$^{-1}$, which gives time steps of the order $10^{-17}$ s. For a flame simulation lasting 100 ms, it can take $10^7$ s or 115 days even if each event took only a nano-second to simulate. The equations below illustrate how the normalization parameter balances the rate of inception and coagulation.

The original Smoluchowski equation is:

$$\frac{\partial}{\partial t} c(t, x) = I(t) c_{\text{in}}(x) + \sum_{\ell=1}^{4} \left[ \beta_{x-y} \delta(x) c(t, x - \delta t) - \beta_{y} c(t, x) \right]$$

$$+ \frac{1}{2} \sum_{y=1}^{x-1} \beta_{x-y} c(t, x - y) c(t, y) - \sum_{y=1}^{\infty} \beta_{x+y} c(t, x) c(t, y),$$  \hspace{1cm} (3.29)

with the initial condition

$$c(0, x) = c_0(x) = 0 \quad \text{for all } x.$$
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Introducing a normalization parameter $N$ such that,

$$\tilde{c}(t, x) := \frac{1}{N} c(t, x).$$

(3.30)

Substituting the above equation into (3.29), we get

$$\frac{\partial}{\partial t} N \tilde{c}(t, x) = I(t) c^\text{in} (x) + \sum_{\ell=1}^{4} \left[ \beta_{\ell}^x \delta (x) \ N \tilde{c}(t, x - \delta \ell) - \beta_{x}^x \ N \tilde{c}(t, x) \right]$$

$$+ \frac{1}{2} \sum_{y=1}^{x-1} \beta_{x-y,y} N \tilde{c}(t, x - y) \ N \tilde{c}(t, y) - \sum_{y=1}^{\infty} \beta_{x,y} N \tilde{c}(t, x) \ N \tilde{c}(t, y),$$

(3.31)

with the initial condition

$$\tilde{c}(0, x) = \tilde{c}_0(x) = \frac{1}{N} c_0(x) = 0 \quad \text{for all } x.$$

Simplifying the equation, we obtain:

$$\frac{\partial}{\partial t} \tilde{c}(t, x) = \frac{1}{N} I(t) c^\text{in} (x) + \sum_{\ell=1}^{4} \left[ \beta_{\ell}^x \delta (x) \ \tilde{c}(t, x - \delta \ell) - \beta_{x}^x \ \tilde{c}(t, x) \right]$$

$$+ N \left[ \frac{1}{2} \sum_{y=1}^{x-1} \beta_{x-y,y} \tilde{c}(t, x - y) \ \tilde{c}(t, y) - \sum_{y=1}^{\infty} \beta_{x,y} \tilde{c}(t, x) \ \tilde{c}(t, y) \right].$$

(3.32)

By observing (3.32), it is inferred that by introducing a normalization factor, the inception rate and coagulation rate are reduced and enhanced respectively by the normalization factor. It is important to note that the surface reaction rates are not altered. The choice of normalization factor is based on meeting the following conditions:

1. The rate of inception and coagulation should be of the same order of magnitude.

2. The resulting values of $n$, the number of stochastic particles representing the soot ensemble, in the simulation should be more than the minimum value required to obtain a converged solution. The relation between $n$ and the converged solution is discussed in the next section.
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It is advisable to keep the normalization factor constant while comparing results of the DSA with the new numerical techniques discussed in section 3.6.

3.5.2 Variance reduction techniques

The deviation from a converged solution is composed of a systematic error and a statistical error. The numerical techniques hope to obtain a converged solution whilst minimizing these errors by the proper choice of relevant parameters. In the algorithm described in the previous section, the statistical error can be minimized by increasing the number of repetitions $L$, and the systematic error reduced by having large values of $n$ to represent the soot ensemble.

Depending on the flame conditions and the varying rates of processes in the flame, $n$ changes with the distance from the burner. Where the coagulation rates are very high, $n$ can take small values, e.g. $100 - 500$. This is because for every coagulation event, $n$ decreases by 1. This, sometimes, results in a large systematic error.

Similarly, in the case where the inception rates are high, $n$ can take large values, e.g. $10,000 - 20,000$. This is because for every inception event, $n$ increases by 1. This results in large values for the rates of processes that yields very small time steps (3.12) and huge computational expense. The large values of $n$ result in low systematic errors. However, it is to be noted that beyond a certain value of $n$, the systematic error can not be further reduced. It is when both the systematic error and the statistical error can not be further minimized that the solution is considered a converged solution. This is done only in the absence of an analytical solution and once the numerical technique has been validated. The validity of the DSA is discussed in the next chapter.

In summary, small and large values of $n$ are the sources of the systematic error and computational expense respectively. In order to overcome these problems, particle doubling and Constant-n methods are used (Lina et al., 2002).

Particle doubling

In this technique, the lower limit of $n$ is fixed to a value, e.g. 4,000, that ensures minimum systematic error. As soon as the value of $n$ reaches the lower limit, $n$ is doubled. This doubles the rate of processes and therefore the normalization
parameter has to be adjusted accordingly. Mathematically,

\[ n_{\text{new}}(t) = 2n(t), \quad (3.33) \]
\[ N_{\text{new}} = 2N. \quad (3.34) \]

At the time of particle doubling, the properties of each stochastic particle representing the soot ensemble are replicated. Particle doubling is equivalent to zooming out to a larger volume of the flame with the assumption that the properties of the soot ensemble do not change. Particle doubling, thus, solves the issue of systematic error resulting from the low values of \( n \).

**Constant-n**

In this technique, the top limit of \( n \) is fixed to a value, \( e.g. 8,000 \), that ensures low computational expense. As soon as the value of \( n \) reaches the top limit, one stochastic particle is uniformly removed from the ensemble of stochastic particles. In this way, the distribution is preserved statistically. Mathematically,

\[ n_{\text{new}}(t) = n(t), \quad (3.35) \]
\[ N_{\text{new}} = \frac{n}{n+1} N. \quad (3.36) \]

### 3.6 Development of New Numerical Techniques

This section elaborates on the development of new numerical techniques that take less computational time to simulate a flame as compared to that using the Direct Simulation algorithm (DSA). It is observed from table 3.4 that the computational time taken to fully simulate a flame by DSA is very large, sometimes days to obtain results for a single run. Such large simulation times render the DSA useless for complex applications, \( e.g. \) turbulent combustion, engine simulations, and detailed chemistry soot models. To apply the stochastic methods to the applications mentioned above, and for the soot model development, faster numerical techniques are desired.

The simulations in table 3.4 were made on a 2.0 GHz AMD Athlon Processor and computational times were adjusted such that at least 4200 stochastic particles represented the soot ensemble.
Table 3.4: Computational time taken to simulate flames using Direct Simulation Algorithm

<table>
<thead>
<tr>
<th>Flame designation</th>
<th>Computational time / run</th>
<th>Order of magnitude for rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{C}_2\text{H}_2$ addition</td>
</tr>
<tr>
<td>JW1.69</td>
<td>1.5 h</td>
<td>$10^9$</td>
</tr>
<tr>
<td>JW10.60</td>
<td>45.3 h</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>JW10.68</td>
<td>198.0 h</td>
<td>$10^{12}$</td>
</tr>
<tr>
<td>JW10.673</td>
<td>914.4 h</td>
<td>$10^{12}$</td>
</tr>
</tbody>
</table>

While investigating the causes of the large computational time in DSA, it was observed that the rates of acetylene addition and OH oxidation were very large, at least three orders of magnitude larger than any of the other processes (see table 3.4). This resulted in significantly small time steps (3.12), a large number of events, and thus large computational times. However, this difference in the rates of processes provided opportunity to develop newer algorithms that will reduce computational time significantly and introduce manageable, sometimes negligible, error.

The rest of the chapter will expand on the new algorithms and quantify the error introduced by comparing the results with the DSA.

3.6.1 Weighted algorithm

This is a natural choice in the event when the difference between the rates of processes is significant. This algorithm introduces negligible error and brings the computational time down to a few hours per run.

In this algorithm, the rates of the process(es) with large rates are reduced such that the importance of each process is maintained, i.e. if acetylene addition is the dominant process, it will remain so even after its rate is reduced. The reduction of the rate of a process leads to a corresponding increase in the effect of one event on the chosen particle, i.e. if the rate of acetylene addition is decreased by a factor of 10, the number of carbon atoms added to a particle on the selection of the process is 20 instead of 2. The basis of the weighted algorithm is that within a small time frame a number of identical events acting on a particle can be grouped, i.e. if a particle undergoes 10 successive acetylene additions in a short time period, the same effect can be accounted for in a single step by decreasing the rate of acetylene addition and correspondingly increasing
the effect of the process. The assumption of 10 successive acetylene additions on a particle holds true only when acetylene addition rates are significantly larger than other processes, which is the case under discussion. The advantage, in such a case, is in saving the computational time taken to perform 9 acetylene addition steps.

The same principle can be applied to all the processes as long as the importance of each process is maintained. However, caution has to be exercised to not decrease the rates significantly as that can then have a disproportionate effect on the particle size distribution.

Another variation to the weighted algorithm is the selection of more than one particle once a process is chosen. To elaborate on this, in the weighted algorithm the effect of the reduced rate of a process is reciprocated by a corresponding increase or decrease in the number of carbon atoms on a single particle. In the variation described henceforth, the effect of the reduced rate is distributed on to more than one particle. The criterion for selecting the particles remains the same and as outlined in the algorithm before. This mimics the DSA in the selection of particles, but differs in the calculation of the sum of rates of all the processes after every time step. For example, if the rate of acetylene addition was reduced by factor of 10 and 5 particles are selected when the process is chosen, each of the particles adds 4 carbon atoms to it instead of 20 carbon atoms had only 1 particle been selected (see previous paragraph). Such a simulation will be represented as “SG 10 (5)” where the letters represent the process for which the rate is reduced, the number following it quantifies the reduction in the rate of the process, and the numeral in the bracket shows the number of particles selected when a process is selected. Although selection of particles consumes the most computational time, the decrease in the rate of the process(es) leads to an increase in the time step which reduces the computational time.

To discuss the efficiency of the weighted algorithm, two flames were chosen: (a) JW 10.60 which has five orders of magnitude difference between the rate of acetylene addition/OH oxidation and coagulation, with the rate of acetylene addition slightly larger than the OH oxidation; and (b) JW 1.69 with the rate of coagulation, OH oxidation, and the acetylene addition varying from each other by roughly an order of magnitude. The order of magnitude for the rates of different processes is summarized in table 3.4. The error between the new numerical
technique and the DSA, and the speedup factor are defined as follows:

\[
\text{%age Error} = \frac{| \text{New Numerical Technique} - \text{DSA} |}{\text{DSA}} \times 100,
\]  

(3.37)

\[
\text{Speedup factor} = \frac{\text{Time taken to simulate by the DSA}}{\text{Time taken to simulate by the New numerical technique}}.
\]  

(3.38)

For the flame JW 10.60, it can be observed from table 3.5 that a speedup factor of 20 was achieved by introducing error within the limits of statistical error (\(\pm 5\%\)). The rates of acetylene addition and OH oxidation were reduced by up to a factor of 100, which still kept the difference between the rate of coagulation and acetylene addition/OH oxidation to almost three order of magnitudes. In order to minimize error, 10 particles were chosen for the case where rates were reduced by factor of 100 so that only 20 C atoms were added to each particle instead of 200 C atoms on a single particle.

For the flame JW 1.69, the rates of acetylene addition, OH oxidation, and pyrene condensation were reduced by different factors. This was possible because of the difference between their respective rates and that of coagulation. Due to the relatively small difference between the rates of these processes, the maximum reduction in rate was limited to a factor of 15 for acetylene addition. A speedup factor of 10 was achieved with 10% error in the first moment. All the simulations were made with the same initial condition, \(i.e.\ N = 500, \ L = 3\) to enable a direct comparison with the DSA and ensure a converged solution. However, reduction of \(N\) by a factor of 5 increased the speedup factor by 5. This did not introduce any additional error, for the given conditions, as can be seen by comparing the results of the last two simulations in table 3.6.

By observing the data from the two flames, certain conclusions can be derived:

1. The weighted algorithm is successful in decreasing the computational time while introducing negligible error in the cases where the difference between the surface rates and coagulation is large.

2. As the DSA is run with large \(n\) to ensure the minimum number of particles representing the ensemble and a converged solution, the parameter \(N\) can be altered to obtain a higher speedup factor by introducing negligible error.
### Table 3.5: Numerical efficiency of different algorithms for flame JW 10.60

<table>
<thead>
<tr>
<th>Numerical technique</th>
<th>Details of simulation</th>
<th>Time / run</th>
<th>Speedup</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Simulation</td>
<td>SG 1 (1) OH 1 (1) Cond 1 (1)</td>
<td>45.3 h</td>
<td>1.0</td>
<td>0.0 0.0 0.0</td>
</tr>
<tr>
<td>Weighted Algorithm</td>
<td>SG 5 OH 4 (1) SG 15 OH 12 (3) SG 25 OH 20 (5) SG 100 OH 100 (10)</td>
<td>10.0 h 6.6 h 5.9 h 2.6 h</td>
<td>4.5 6.9 7.6 17.6</td>
<td>0.6 1.1 0.5 1.6 4.5 1.9 1.6 2.7</td>
</tr>
<tr>
<td>Operator Splitting</td>
<td>N = 125 L = 18 N = 75 L = 30 N = 50 L = 45</td>
<td>1.0 h 0.35 h 0.15 h</td>
<td>45.8 129.7 292.8</td>
<td>3.0 3.1 2.8 25.5 24.2 21.4 54.9 51.6 52.6</td>
</tr>
</tbody>
</table>

### Table 3.6: Numerical efficiency of different algorithms for flame JW 1.69

<table>
<thead>
<tr>
<th>Numerical technique</th>
<th>Details of simulation</th>
<th>Time / run</th>
<th>Speedup</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Simulation</td>
<td>SG 1 (1) OH 1 (1) Cond 1 (1)</td>
<td>3.07 h</td>
<td>1.0</td>
<td>0.0 0.0 0.0</td>
</tr>
<tr>
<td>Weighted Algorithm</td>
<td>SG 3 (1) OH 3 (1) SG 9 (3) OH 3 (1) SG 9 (2) OH 3 (1) SG 9 (1) OH 3 (1) SG 15 (1) OH 5 (1) Cond 2 (1)</td>
<td>1.34 h 1.04 h 0.86 h 0.67 h 0.38 h</td>
<td>2.8 3.6 4.4 5.6 9.8</td>
<td>3.1 2.9 3.0 4.0 5.5 0.3 0.3 3.0 9.4 10.8 1.5 1.8 8.1 23.0</td>
</tr>
<tr>
<td>Age Algorithm</td>
<td>N = 9000 L = 10 N = 4500 L = 20 N = 1500 L = 60 N = 500 L = 180 N = 150 L = 600 N = 50 L = 1800</td>
<td>2.98 h 0.63 h 0.06 h 43.4 s 12.5 s 3.9 s</td>
<td>1.3 6.0 61.3 312.6 1088.0 3456.1</td>
<td>3.8 3.9 4.0 4.0 4.0 4.0 22.8 22.9 23.0 23.0 23.3 23.7 48.5 48.6 48.9 48.7 48.8 48.6</td>
</tr>
<tr>
<td>Operator Splitting</td>
<td>N = 250 L = 9 N = 125 L = 18 N = 50 L = 45</td>
<td>2.42 h 0.61 h 0.09 h</td>
<td>1.6 6.2 42.3</td>
<td>5.3 5.4 5.9 7.8 7.4 7.0 7.8 18.5 17.0</td>
</tr>
</tbody>
</table>

### 3.6.2 Operator splitting

In this version of the algorithm, all the surface reactions are performed deterministically over a fixed interval of time ($\Delta t$) on all of the stochastic particles.
representing the soot ensemble. The processes that are used to calculate the waiting time are the nucleation and coagulation. As the rates of coagulation and nucleation are small compared to the rates of surface reaction processes, the waiting time steps are considerably larger than in the DSA. This reduces the computational time but introduces a systematic error. In order to decrease the systematic error, the operator splitting time step should be decreased. However, a decrease in the operator splitting time step ($\Delta t$) increases computational time considerably. For every operator splitting process, each particle adds the net amount of carbon atoms based on the sum of the rates of surface reaction processes over that time interval. The whole particle ensemble is then updated which is computationally very expensive, especially for large values of $n$.

The efficiency of the operator splitting algorithm is detailed for flames JW 10.60 and JW 1.69 in tables 3.5 and 3.6 respectively. For the flame JW 10.60, it can be observed that the error does not decrease with the change in the normalization parameter, which influences $n$, and the number of repetitions $L$. The error introduced is the systematic error. It is important to note that a speedup factor of up to 300 is achievable by predicting the second moment of the soot PSD within a factor of 2. For the flame JW 1.69, the error increases and then stabilizes to the value of systematic error with the decrease in the normalization parameter. This error is much smaller than in the flame JW 10.60 because the sum of the nucleation and coagulation rates is much higher in the case of flame JW 1.69. This decreases the waiting time, increases the accuracy and the computational expense. Thus, the speedup factor is limited to 40 if the error in predicting the second moment is to be less than 20%. Higher speedup factors are achievable by compromising the accuracy. However, in the case of the flames analyzed here, the numerical parameters were kept the same. This was done to see the effect of the nature of the flame on the error. It can be inferred from the discussion above that the flame JW 1.69, which has a bimodal soot PSD (figure 4.11), has a lower systematic error than the flame JW 10.60 which has a unimodal soot PSD (figure 4.13).

3.6.3 Age algorithm

The age algorithm is one of the most powerful numerical techniques to obtain the soot PSD in a few seconds. In order to illustrate the efficacy of this algorithm,
it is important to define the residence time of a particle in the flame. It is the
time spanned by a particle in the flame before it coagulates with another soot
particle. Therefore, the residence time of a particle is set to zero under two
conditions: the first when a new particle is incepted, and the second when two
particles coagulate. In the latter case, the history of the two particles coagulating
disappears and the coalesced particle is treated as a new particle.

As each stochastic particle that represents the soot ensemble is tracked in
the stochastic method, it is easy to follow the time spanned before a particle
coagulates. Before a particle coagulates, the surface reaction events are added
deterministically for the time equivalent to its residence time. The rate of surface
processes are averaged over the time interval. The particle with the added or sub-
tracted mass, which depends on the net rate of surface processes, then coagulates
with another particle to give a new coalesced particle. The residence time of this
new coalesced particle is set to zero as explained in the previous paragraph.

The waiting time ($\tau$) in the algorithm is calculated by the summation of
the rate of inception and coagulation only as opposed to including the rate of
surface reactions in the DSA (3.12). This increases the waiting time by orders of
magnitude and decreases the computational time by a similar order of magnitude.

The error in this numerical technique results from the high residence time of
particles. This is because the net surface reaction rates are obtained by averaging
over the residence time of a particle. In other words, the surface reaction rates are
calculated at the time when the residence time of the particle is set to zero and
at the time just before it coagulates. If the residence time of a particle is high,
the averaging does not capture the trend of surface reaction rates during that
time period. The averaging, thus, acts as a source of approximation. However,
if the residence time of a particle is low, the averaging is likely to provide a
more accurate representation of the surface reaction rates. In order to have low
residence time for the particles, the rates of coagulation and inception should be
reasonably high. The success of this algorithm thus depends on the magnitude
of the rates of inception and coagulation.

It was observed that while tracking the residence time of each stochastic
particle, the age of each particle was being captured as well. It is important to
differentiate between the age and the residence of a particle. Although, both the
age and residence time of a soot particle is set to zero when a new particle is
incepted, the difference arises when the two particles coagulate. The residence
time of the coalesced particle is set to zero, whereas the surface weighted average
is taken to calculate the new age of the coalesced soot particle.

\[ A_{i+j} = \frac{A_i S_i + A_j S_j}{S_i + S_j} \quad (3.39) \]

where, \( A \) and \( S \) correspond to the particle’s age and surface area. Until the time
a particle meets another particle to coagulate, the age of the particle increases
equivalent to the time spent in the flame. This is exactly the same way the
residence time of the particle increases.

The age of the particle was tracked to provide a physical meaning to the decay
in number of active sites on the surface of a soot particle, which was otherwise
modelled empirically (2.5). This provided the motivation to take the surface
weighted average for the age of a soot particle as compared to the mass weighted
average. This is discussed in detail in Chapter 6.

It can be observed from the table 3.6 that a speed up factor of up to 3500
is achievable for simulating the soot particle dynamics in flame JW 1.69. The
computational time reduces to around 4 s for a single run and the results are
within a factor of 2. This, as will be seen later in the chapter 4, is better than
what the Method of Moments can predict.

In summary, this algorithm introduces a systematic error but reduces computa-
tional time by almost three orders of magnitude and can be used as a source of
first estimate of PSD and mean properties of the ensemble such as soot volume
fraction and number density. This algorithm when coupled with the operator
splitting (Patterson et al., 2006a) reduces the systematic error significantly and
achieves similar reduction in the computational time.
Chapter 4
Validation of the Stochastic Method

This chapter discusses the validity of the stochastic method, which was introduced in chapter 3, through comparison with experimental measurements and other well-known numerical methods that solve the Smoluchowski equation. Although, in the limit $n \to \infty$, the results obtained by the stochastic method can be proven to converge to the true solution (Eibeck and Wagner, 2003), it is of significant interest that the solutions obtained from the feasible choices of $n$ and $L$ in the stochastic method match with the other numerical techniques.

The Livermore Solver for Ordinary Differential Equations (LSODE) (Radhakrishnana and Hindmarsh, 1994), solves the population balance equation (PBE) for each size class of soot particle (Patterson et al., 2006a). This provides a precise solution and an absolute benchmark for the validity of the stochastic method. Because LSODE solves the PBE for each size class, it is computationally intractable to use this method to solve real flame conditions due to the large number of size classes involved. Therefore, the Method of Moments (MoM) and experimental measurements are used as additional sources of validation, more so by observing the trends of number density and soot volume fraction.

Furthermore, this chapter discusses the advantages of the stochastic method over other numerical techniques and elucidates on the difference between the results obtained from the stochastic method and the MoM.
CHAPTER 4. VALIDATION OF THE STOCHASTIC METHOD

4.1 Validity by LSODE

This study was done by Patterson et al. (2006a). Some specially constructed test cases were chosen such that high quality numerical solutions to (3.1) were readily obtainable using LSODE and all the features of our stochastic algorithm were tested. This was done by devising a set of chemical and physical conditions for each pressure regime that led to each of the four surface reactions, described in section 2.1.3, having rates of a similar order of magnitude (unlike most physical cases where they vary by many orders of magnitude).

An important acceleration of LSODE was achieved by redefining the $\delta \ell$ of (3.2) as follows:

$$\delta \ell = \begin{cases} 
16 & \text{for } \ell = 1 : \text{Condensation,} \\
4 & \text{for } \ell = 2 : \text{Acetylene addition,} \\
-8 & \text{for } \ell = 3 : \text{O}_2 \text{ oxidation,} \\
-4 & \text{for } \ell = 4 : \text{OH oxidation,} 
\end{cases}$$

so we only had to solve (3.1) for $i = 32, 36, 40, \ldots$, one quarter of the number of size classes needed for the physically realistic cases. It was ensured that the number of size classes used enabled LSODE to handle the largest particles that were observed in the stochastic simulations and which led to negligible number densities for the largest size classes. The results were found to be stable under the variations of this parameter.

LSODE uses an adaptive stepping method to advance the solution over time. For the error control, the estimated relative error introduced in each time step was restricted to $1 \times 10^{-6}$ for every component of the solution. This was intended to ensure that the relative error in all components of the final solution was small, altering this relative tolerance by a factor of 10 was not found to affect the results.

We used a range of settings to collect the stochastic simulation results shown here, as for LSODE we experimented with the parameter values to check that the results were independent of the values used. All the results shown are averaged over at least 20 repetitions of the simulations, with the number of computational particles, $n$, greater than 32768 except in the initial phases. The errors were less than $\pm 2\%$ for the first few size classes.
Figure 4.1: Comparison of the soot particle size distribution between the LSODE (—) and the Direct Simulation Algorithm (□).

Figure 4.1 shows the solution to (3.1) obtained in the test cases as described above. As can be seen in the figure, the simulations were run long enough to develop a range of particle sizes. The figure provides a clear illustration of the convergence results given in Eibeck and Wagner (2003), which explicates that the data obtained from the direct simulation algorithm (DSA) should converge to a solution of (3.1) as the number of computational particles used tends to infinity. This gives us the confidence that the results presented in future chapters are accurate solutions of (3.1) for the relevant input data. It is assumed here that the \( n \) and \( L \) are varied until a converged solution is obtained, i.e. the solution
does not change on the variation of parameters $n$ and $L$.

The issues surrounding the convergence of DSA were discussed in the previous chapter. In the next section, (3.1) is solved for real flame conditions and the validity of the stochastic method is discussed against experimental measurements and the results obtained from the Method of Moments.

### 4.2 Validity by the Method of Moments

In order to further the development of a soot model, the performance of the stochastic method in the real flame conditions needs to be tested against the other numerical techniques and experimental measurements. The Method of Moments has been used most prolifically for soot model development and is remarkably efficient computationally. It solves for the moments of the soot particle size distribution and makes a few assumptions to close the system of moments. There are different techniques in the literature to close the system of moments and the one presented here uses interpolation techniques. This Method of Moment with Interpolative Closure, often abbreviated MoMIC in literature, will be abbreviated MoM for this thesis. The comparison of the stochastic method with the MoM and experimental measurements will be used as a secondary source of validation for the numerical technique.

Six flames were simulated using the stochastic method and the MoM. These six flames were chosen to cover 1 and 10 bar flames (XSF 1.78 and JW 10.60), low and high sooting flames (JW 1.69 and JW 10.673), and flames with bimodal and unimodal particle size distributions (A1 and A3). The experimental data is thus obtained from different experimental groups. The properties of the flames are described in table 2.2. It is observed from figures 4.2, 4.3, and 4.4 that the trends of number density and soot volume fraction predicted by the DSA and MoM match with those from the experimental measurements. Furthermore, the order of magnitude of the results is the same for the simulations and experiments barring an exception in flame JW 10.673 where the experimental soot volume fraction is an order of magnitude greater than the simulated values. The trends for the flames XSF 1.88 and XSF 1.98 were similar to that of the flame XSF 1.78 and trends for the flame JW 10.68 were similar to that of the JW 10.673. Similarly, flames A1 and A3 represent the range offered from the set of flames A1 to A3.
CHAPTER 4. VALIDATION OF THE STOCHASTIC METHOD

and B1 to B3.

The number of active sites on the surface of a soot particle was modelled by the empirical relation (2.5) developed by Appel et al. (2000). As the sample points to develop the empirical relations were obtained from the flames analyzed above using MoM, one can observe the proximity of the simulated results from the MoM with the experimental measurements. Nonetheless, the figures confirm the success of the ABF soot model in predicting the average properties of the soot ensemble. It also shows the computational efficiency of MoM in solving the Smoluchowski equation.

With the approximations used in simulating flame by the MoM (discussed in next section) and uncertainties in the experimental measurements, the stochastic method predicts the soot volume fraction fairly well. This supports the validity of the stochastic method proved in the previous section.

Although, the DSA and MoM solve the same equation with the same soot model, considerable difference is observed in the soot ensemble properties predicted by the two numerical techniques, see figures 4.2, 4.3, and 4.4. The soot volume fraction and number density from the two numerical techniques can differ by a factor of 2 − 3 (note the log-scale for number density in the figures). This provided us with the motivation to investigate the sources of error within MoM and the conditions under which the errors were large. To quantify the error, flames A1 and A3 are chosen for reasons evident in the next section.

4.2.1 Error analysis

In order to make direct comparison between the MoM and the stochastic method, the Method of Moments was modified. The results shown in the previous section use the coupled version of MoM, i.e. the moment equations of the soot particle size distribution are coupled to the gas phase chemistry and are solved simultaneously (Kee et al., 1985; Revzan et al., 1995). The profile of the gaseous species obtained from the coupled version of the MoM is then used as the input to the stochastic method. The stochastic method is thus uncoupled from the gas phase chemistry. Therefore, in order to make direct comparison, an ordinary differential equation solver was developed that solved for the moments of the soot particle size distribution using the same input as provided to the stochastic method. The equations for the moments of the soot PSD were exactly the same as used in
Figure 4.2: Comparison of the number density and soot volume fraction between the Stochastic method (—), Method of Moments (- - -), and experimental measurements (●) for the 1 bar flames: JW 1.69 and XSF 1.78.
Figure 4.3: Comparison of the number density and soot volume fraction between the Stochastic method (—), Method of Moments (---), and experimental measurements (•) for the 10 bar flames: JW 10.60 and JW 10.673. The values of experimental measurement in the flame JW 10.673 are reduced by a factor of 8.
Figure 4.4: Comparison of the number density and soot volume fraction between the Stochastic method (—) and Method of Moments (- - -) for flames A1 and A3.
the coupled version of the MoM. It has to be noted that the results of the soot volume fraction and number density from the MoM for the coupled and uncoupled version are almost the same for the flames A1 and A3 (figure 4.5). This shows that the timescales of the gas phase chemistry and the processes involving soot formation and oxidation are very different. This implies that, for the given operating conditions, uncoupling the gas phase chemistry and the soot formation processes introduces negligible error. By the same argument, it follows that the coupling of the stochastic method to the gas phase chemistry is not likely to enhance the accuracy of the results.

In summary, for the purposes of quantifying the error, both the MoM and the stochastic method are uncoupled from the gas phase chemistry and use the same input. This is done so that whatever negligible error is introduced due to the uncoupling of the gas phase chemistry is not counted towards the difference between the two numerical techniques. The error between the MoM and stochastic method is defined as:

\[
\text{Percentage Error} = \frac{|\text{MoM} - \text{Stochastic}|}{\text{Stochastic}} \times 100
\]

To quantify the error, two flames were chosen: the first had nucleation prevalent throughout the flame and thus had a bimodal soot PSD (A1) and the second had nucleation for the initial part of the flame and had a unimodal PSD (A3). The other properties of the flame are given in the tables 2.2 and 5.1. The reason for choosing the two flames was to understand if the nature of the PSD had any effect on the error. Numerical simulations were designed such that the effect of each process in soot formation and oxidation was quantified and the exact source of error located.

Table 4.1 shows the maximum of error (4.1) in predicting the 0th, 1st, and 3rd moment of the soot PSD by the MoM for the flames A1 and A3. The first column describes the processes included in the simulation. All simulations were performed with at least 4096 stochastic particles representing the soot ensemble with a minimum of 10 repetitions. It was ensured that the results obtained from the stochastic method converged on varying \( n \) and \( L \). The increase in parameters \( n \) and \( L \) did not change the result. It was observed from figures 4.2, 4.3, and 4.4 that MoM over predicts the moments of the PSD. Following the error analysis, three further key observations may be made:
Figure 4.5: Comparison of the number density and soot volume fraction between the Method of Moments solved coupled (—) and uncoupled (□) to the gas phase chemistry for the flames A1 and A3.
Table 4.1: Percentage error in predicting integer moments by the Method of Moments for flame A1 and A3 at $H = 12 \, \text{mm}$

<table>
<thead>
<tr>
<th>Nature of events</th>
<th>Flame A1</th>
<th>Flame A3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0th</td>
<td>1st</td>
</tr>
<tr>
<td>Nuc only</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Nuc + SG</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Nuc + SG + Cond</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Nuc + SG + Cond + Oxid</td>
<td>23.7</td>
<td>25.9</td>
</tr>
<tr>
<td>Nuc + SG + Cond + Coag</td>
<td>196.8</td>
<td>14.0</td>
</tr>
<tr>
<td>All events</td>
<td>180.1</td>
<td>28.4</td>
</tr>
</tbody>
</table>

1. Nucleation (Nuc), surface growth by acetylene addition (SG), and pyrene condensation (Cond) contribute to no or negligible error (within the domain of statistical error).

2. Oxidation by $O_2$ and OH is a source of significant error in both flames A1 and A3. The magnitude of error is roughly the same for both the flames.

3. Coagulation is also a significant source of error in both A1 and A3 flames; however, the magnitude of error is much more pronounced in the flame A1 than in the A3.

Each of the processes are analyzed in detail to provide explanation for the magnitude of error each contributes towards the total error.

1. **Nucleation, Surface growth by acetylene, and Pyrene condensation**

The modelling of the nucleation process by the MoM involves no approximations and thus the results exactly match those obtained from the stochastic method (see first row of table 4.1).

The implementation of the surface growth by acetylene addition and pyrene condensation in the MoM uses fractional moments such as $\nu_z$, $z = \frac{1}{3}, \frac{2}{3}, \frac{4}{3}, \ldots$, where

$$\nu_z = \sum_{i=1}^{n} x_i^z.$$  \hspace{1cm} (4.2)

The differential equations in the MoM are written for the first six integer moments of soot PSD, i.e. $z = 0, 1, \ldots, 5$ in the above equation. Fractional moments, for the MoM, are then obtained by interpolation between the integer moments. The
quadratic interpolation technique described in Frenklach and Harris (1986) is employed to obtain the fractional moments. The stochastic method, which has information on the soot PSD, provides accurate fractional moments by performing the summation in (4.2).

<table>
<thead>
<tr>
<th>Interpolation domain</th>
<th>Extrapolation domain (−)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>$\nu_{-1/6}$</td>
</tr>
<tr>
<td>$\nu_{5/3}$</td>
<td>$\nu_{-1/3}$</td>
</tr>
<tr>
<td>$\nu_{7/3}$</td>
<td>$\nu_{-1/2}$</td>
</tr>
<tr>
<td>$\nu_{8/3}$</td>
<td>$\nu_{-2/3}$</td>
</tr>
</tbody>
</table>

The first column of table 4.2 shows the error due to the quadratic interpolation technique employed to obtain the fractional moments. It can be observed that the fractional moments obtained from the interpolation are sufficiently accurate. This supports the earlier observation that surface growth by acetylene addition and pyrene condensation contribute negligibly to the error (see second and third row of table 4.1).

2. Oxidation

Although, oxidation by $O_2$ and OH are modelled similarly to the acetylene addition and pyrene condensation respectively (see section 2.1.3), inclusion of the oxidation processes results in a significant error when the MoM is used. To calculate the rates of the oxidation processes, $\nu_{2/3}$ is used which is obtained from the same interpolation technique used before. This should result in little or no error.

On investigating further, it was observed that the error rose sharply in the initial part of the flame and remained steady thereafter, see figure 4.6. This observation was common to both the flames and suggested that the source of error was in the early part of the flame. This provided the motivation to monitor the surface rates and absolute number densities in the initial part of the flame. As the C/O ratio and the magnitude of error for both the flames were similar, flame A1 was chosen for this analysis.
On observing the surface rates in the early part of flame A1 (figure 4.7), it was seen that the summation of the oxidation rates were larger than the summation of the rates of acetylene addition and pyrene condensation between 0.25 and 0.35 mm above the burner. In other words, the net surface rate was less than zero which implies a reduction in the soot particle size. The soot particles are of very small size or are just incepted in the early part of the flame. Any soot particle that is subject to oxidation in this part of the flame is likely to oxidize completely into gas phase. This will result in the reduction of number density of the soot particles. It can be observed from figure 4.7 that the number density of soot particles decreases exactly when the net surface rate is less than zero. However, this observation is true only for the stochastic method where soot particles are tracked individually. On the contrary, in the case of Method of Moments where the average properties of the soot ensemble are followed, the phenomenon of soot particles getting oxidized back into the gas phase can not be accounted for. This
Figure 4.7: Surface rates and comparison of number densities for the flame A1 in the early stages of the flame.
is why the number density does not dip when simulated by the MoM. The failure to account for the oxidation of the smallest soot particle by the MoM introduces the error in the early part of the flame, as observed earlier in figure 4.6.

It is to be noted that another reason for dip in the number density can be coagulation of soot particles. However, the coagulation rate was almost zero in the early part of the flames ruling out the possibility of its role in reducing the number density. It is worthwhile commenting that the magnitude of the error is comparable for both flames A1 and A3, as the flames are similar in their early stages. Also, the error for the 0th, 1st, and 3rd moments for both the flames is roughly the same, as the initial error gets translated until the end of the flame (see row 4 of the table 4.1).

3. Coagulation

Coagulation is a source of significant error and it can be inferred from table 4.1 that the nature of PSD affects the magnitude of the error. Before proceeding with the analysis, it is meaningful to understand the implementation of the coagulation process by the MoM. This will give an insight into the potential sources of error.

In the MoM, differential equations describing the change in moments ($M_x$) with time on account of the coagulation process are illustrated below:

\[
\begin{align*}
\frac{dM_0}{dt} &= -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \beta_{x_i,x_j} = -\frac{1}{2} \langle \phi_{0,0} \rangle M_0^2, \\
\frac{dM_1}{dt} &= 0, \\
\frac{dM_2}{dt} &= \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i x_j \beta_{x_i,x_j} = \langle \phi_{1,1} \rangle M_0^2, \\
\frac{dM_3}{dt} &= 3 \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i^2 x_j \beta_{x_i,x_j} = 3 \langle \phi_{1,2} \rangle M_0^2,
\end{align*}
\]

\[\vdots\]

etc., where

\[
\langle \phi_{a,b} \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i^a y_j^b \beta_{x_i,x_j}.
\]
For the free molecular regime kernel,

\[
\langle \varphi_{a,b} \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (x_i + x_j)^{\frac{1}{2}} \left( \frac{x_i^{1/3} + x_j^{1/3}}{\sqrt{x_i x_j}} \right)^2 x_i^a y_j^b.
\]  \hspace{1cm} (4.8)

As the term \((x_i + x_j)^{\frac{1}{2}}\) cannot be expanded in equation 4.8, Frenklach and Harris (1986) introduced grid function, \(r f_{a,b}\), such that,

\[
\langle r f_{a,b} \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (x_i + x_j) r \left( \frac{x_i^{1/3} + x_j^{1/3}}{\sqrt{x_i x_j}} \right)^2 x_i^a y_j^b,
\]  \hspace{1cm} (4.9)

where \(r\) takes whole number values only. Using Lagrangian quadratic interpolation between the logarithms of \(f_{0,b}^0, f_{1,b}^1, f_{2,b}^2, \ldots\), Frenklach and Harris (1986) obtained the values of \(\langle \varphi_{a,b} \rangle\). For instance,

\[
\langle \varphi_{0,0} \rangle = (f_{0,0}^0)^{3/8} (f_{0,0}^1)^{3/4} (f_{0,0}^2)^{-1/8}.
\]  \hspace{1cm} (4.10)

A few observations relating to the implementation of the coagulation process by the MoM are as follows:

1. The coagulation process has no effect on the first moment of the PSD. This is why the error in the first moment \((\approx 10\%)\) due to coagulation is significantly less than in the zeroth \((30 - 200\%)\) and the third moment \((20 - 80\%)\). More precise values are in table 4.1.

2. Same particle coagulation: It can be observed from the equations (4.3) through to (4.6) that the summation is over all particle indices \(i\) and \(j\), not excluding the terms \(i = j\). This approximation introduces negligible error when the PSD is developed in the later part of the flame, as the summation of \(i = j\) terms will add little to the coagulation rate. Nevertheless, in the early part of the flame where there are few soot particles, the coagulation rate is overestimated. Considering that there are a few coagulation events in the early part of the flame, this is not likely to add significantly to the error. Also, excluding the \(i = j\) terms from the summation involves fractional moments that are in the extrapolation domain, e.g. \(\nu_{16/3}, \nu_{17/3}, \nu_6\).
Moments, fractional or integer, below the zeroth moment\(^1\) and above the fifth moment are in the extrapolation domain as the MoM only solves for the first six integer moments of the PSD. In the absence of an extrapolation technique, the exclusion of the \(i = j\) terms is likely to add more error when using the Method of Moments than the inclusion of the terms. Studies later in this section, will substantiate the above statement.

3. The calculation of \(\langle \varphi_{a,b} \rangle\) requires interpolation between \(r f_{a,b}\) (see equations 4.7 through to 4.10). Also, the calculation of \(r f_{a,b}\) uses fractional moments which are obtained from the interpolation of solid moments. This results in a **double interpolation**. The lagrangian quadratic interpolation technique employed by the MoM provides accurate results as observed in the analysis of oxidation process.

4. The calculation of \(r f_{a,b}\) (4.9) uses both negative and positive fractional moments, *e.g.*

\[
\langle 0 f_{0,0} \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \frac{\left(x_i^{1/3} + x_j^{1/3}\right)^2}{\sqrt{x_i x_j}},
\]

\[
= \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left(x_i^{1/6} x_j^{-1/2} + x_j^{1/6} x_i^{-1/2} + 2 x_i^{-1/6} x_j^{-1/6}\right),
\]

\[
= 2 \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left(x_i^{1/6} x_j^{-1/2} + x_i^{-1/6} x_j^{-1/6}\right). \tag{4.11}
\]

The MoM uses the same interpolation technique to obtain both the positive and negative fractional moments. However, negative fractional moments fall into the extrapolation domain. The ability of the interpolation technique to predict the negative fractional moments is rather poor. The second column in Table 4.2 shows that the error can go up to 80%. It is also observed that the errors are much smaller for flame A3 than for flame A1. The flames with the unimodal distribution, *e.g.* flame A3, B3, can be fitted to a log-normal distribution (see Figure 4.8) which increases the predictive ability of the interpolation technique to extrapolate. However, for flames with bimodal distribution (Flame A1), the errors are much larger as no particular trend

\(^1\text{negative fractional or integer moments}\)
can be established.

Figure 4.8: Comparison of experimental measurements (○) and a fitted lognormal distribution for flame B3 at a distance of 12 mm from the burner.

To confirm that the negative fractional moments are the major source of error, further investigations were conducted. The error in number density (figure 4.9) and negative fractional moments (figure 4.10) were plotted as a function of distance from the burner to observe any similarity. It can be observed from the figures 4.9 and 4.10 that the errors in number density and negative fractional moments follow the same trend for both the flames A1 and A3. As the miscalculation of the negative fractional moment can significantly affect the coagulation rates and the rate of change in moments, the difference in the results from the MoM and stochastic method is unsurprising.

It is difficult to comment on the collective error arising from excluding the oxidation of the smallest soot particle into the gas phase and an inaccurate calculation of negative fractional moments and thus the coagulation rate. The exclusion of oxidation of the smallest soot particle generally results in over prediction of the number density and other moments of the soot PSD by the MoM. However, the
coagulation rate can be both under and over predicted, depending on the nature of soot PSD and the suitability of the interpolation technique to extrapolate.

It can be observed from figures 4.2 to 4.4 that the MoM always over predicts the number density and the soot volume fraction. In summary, the Method of Moments uses a few approximations to obtain the moments of the soot PSD, however, it is computationally efficient and can be used for preliminary tests for soot model development. On the other hand, the stochastic approach provides an accurate solution to the Smoluchowski equation and can offer detailed information on soot PSD and other higher dimensional distributions for soot model development. Some of the applications and advantages of the stochastic method are discussed in the next section.

Figure 4.9: Error propagation in Number density with distance from burner for the flames A1 and A3: Effect of coagulation.
Figure 4.10: Error in predicting negative fractional moments at different distances from burner by the lagrangian interpolation technique.
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4.3 Applications and Advantages of the Stochastic Method

The advantages of using the stochastic method can be summarized as following:

1. No closure assumptions, no approximations, and thus an exact solution to the equation describing the model.

2. Ability to model multi dimensional distributions such as the age, surface area, and mass of the soot particle.

3. Manageable computational times to obtain a solution, \textit{i.e.} in the order of few minutes.

4. Better comparison with the experimental measurements as a consequence of the exact solution. This helps in soot model development.

4.3.1 Multi-dimensional particle size distributions

The objective of this section is to highlight the advantage of the stochastic method over the existing numerical techniques in predicting detailed multi-dimensional particle distributions. It is well known that the Method of Moments can only predict the moments of the soot PSD. A clear advantage of tracking soot particles in the stochastic method is the insight into the soot particle distributions, even multi-modal ones. Depending on the soot model; surface area, mass, age, and composition of the soot particles can be tracked. In the ABF soot model, where the soot particles are spherical, the surface area and the mass of the soot particle are correlated. In this thesis, both the mass and the age of soot particles are tracked. The soot particle age distribution is discussed in the chapter 6, where the number of active sites on each soot particle is related to its age.

\textbf{Figures 4.11, 4.12, and 4.13} depict different representations of soot particle size distributions as observed in literature. Figure 4.11 is plotted to obtain the temporal evolution of the soot PSD, whereas figures 4.12 and 4.13 are plotted for comparison with the experimental measurements and detailed readings at a number of distinct times. The bimodality in the soot PSD can be clearly observed in the flames JW1.69 and B1 (HW1.64) with the rest of the flames showing unimodal soot PSDs. The ordinate axis in the figures 4.12 and 4.13 is normalized.
by the logarithm of the abscissa to observe log-normal like distributions. The information on the nature of the soot PSD can aid in soot model development, estimation of flame temperature, and prediction of optical properties amongst many others. The assumption of a log-normal distribution for a soot PSD can be challenged even for flames with a unimodal soot PSD. Having the complete form of the soot PSD from a stochastic simulation aids also in the interpretation of concepts such as the variance which gives an indication on the dominant processes in the flame, i.e. coagulation, inception, or surface reactions.

Going back to the figures 4.2 to 4.4, it can be observed that the Method of Moment and the stochastic method differ only slightly in predicting number densities for flames with the unimodal distribution. However, they differ markedly for flames with bimodal distributions. This affects the prediction of optical properties for which accurate information on the soot PSD is required.

4.3.2 Optical properties

The objectives of developing a numerical technique to solve the soot population dynamics are manifold. A major one is to validate soot models by comparison with experimental measurements. Often the experimental measurements shown in the literature are transformed from what is actually measured. For example, absorption, scattering, and extinction coefficients are measured in a light scattering experiment and are then transformed into soot volume fraction and number density (Bohren and Huffman, 1983). Similarly, black body emissions which are measured in a Laser Induced Incandescence experiment are transformed to obtain the average properties of the soot ensemble (Melton, 1984; Vander Wal and Jensen, 1998; Axelsson et al., 2000).

Most of the transformations require certain approximations. This adds to the error in the experimental data often shown in literature. To avoid this error, numerical techniques such as the stochastic method are capable of calculating pre-transformation parameters. This enables a more direct comparison between the experiments and the numerics which provides better information on the accuracy of a soot model. Below is an example that illustrates the sources of error which arises from transforming the experimentally observed data to that which is published in the literature.
Figure 4.11: Temporal evolution of soot PSD for the flames JW 1.69 and JW 10.673.
Figure 4.12: Temporal evolution of soot PSD for the flames B1 (HW 1.64) and XSF 1.78.
Figure 4.13: Temporal evolution of soot PSD for the flames JW10.60 and JW10.68.
Light scattering

The particle number density and the soot volume fraction of a soot particle ensemble can be obtained from the scattering \((Q_{vv})\) and extinction \((K_{ext})\) coefficients which are obtained experimentally. In the process of obtaining the number density and the soot volume fraction, a few assumptions have to be made.

1. Mie Theory: Mie theory discusses the scattering and absorption of light by only spherical particles. It makes strings of assumptions such as the elastic scattering of light, single scattering, incoherent scattering, homogeneous and isotropic particles, and a non-absorbing and homogeneous surrounding medium. More details on each of the assumptions can be obtained in Appendix B.1.

2. Rayleigh scattering: In this regime, particles are small compared to the wavelength of light that is used to obtain the scattering and absorption coefficients.

3. Mono disperse particle size distribution.

With all the assumptions above, the experimental data on soot volume fraction and number density can have a varying degree of error. The following relations can be derived between the experimentally measured parameters and the properties of a soot ensemble:

\[
Q_{vv} = \frac{z^6}{k^2} F(m) N_d, \quad K_{ext} = \frac{4\pi z^3}{k^2} E(m) N_d, \quad (4.12)
\]

where, \(k = 2\pi/\lambda\) is the wave number, \(z = \pi d/\lambda\) is the dimensionless particle diameter, \(d\) is the particle diameter, \(N_d\) is the number density, \(\lambda\) is the wavelength used for scattering experiments, and \(E(m)\) and \(F(m)\) are functions of the refractive index of a soot particle.
The soot volume fraction \( f_v \), particle diameter, and particle number density are thus estimated from experimental measurements by:

\[
\begin{align*}
  f_v &= \frac{\lambda}{6\pi E(m)} K_{\text{ext}}, 
  \quad \text{(4.13)} \\
  d &= \lambda \left( \frac{4 E(m) Q_{vv}}{\pi^2 F(m) K_{\text{ext}}} \right)^{1/3}, 
  \quad \text{(4.14)} \\
  N_d &= \frac{F(m)}{4Q_{vv}} \left( \frac{K_{\text{ext} \lambda E(m)}}{} \right)^2.
  \quad \text{(4.15)}
\end{align*}
\]

The derivation of equations 4.13 to 4.15 is detailed in Appendix B.1. Continuing within the regime of Rayleigh scattering and extending the study to any particle size distribution, we obtain

\[
\begin{align*}
  Q_{vv,i} &= \frac{z_i^6}{k^2} F(m) N_i \quad K_{\text{ext},i} = \frac{4\pi z_i^3}{k^2} E(m) N_i \\
  Q_{vv} &= \sum_{i=1}^{\infty} Q_{vv,i} \quad K_{\text{ext}} = \sum_{i=1}^{\infty} K_{\text{ext},i} \\
  Q_{vv} &= \frac{\mu_6}{k^2} F(m) N_d \quad K_{\text{ext}} = \frac{4\pi \mu_3}{k^2} E(m) N_d.
  \quad \text{(4.16)}
\end{align*}
\]

where, \( \mu_i \) are the \( i \)-th reduced moment of the distribution \( P(z) \) of the size parameter \( z \). With this new formulation, the soot volume fraction can still be calculated by equation 4.13, however the number density and the average particle diameter can not be estimated without making further assumptions. These assumptions are as follows:

1. **Nature of the PSD:** Usually a log-normal distribution is assumed for laminar premixed flames.

2. **Variance of the the PSD:** A physically motivated variance is chosen, e.g. \( \sigma = 0.34 \) derived from the coagulation theory for aerosols in the free molecular regime, where coagulation is the dominant process (Wieschnowsky et al., 1988).

In the absence of the approximations mentioned above, it is impossible to obtain the soot particle size distribution and its reduced moments. This is also known as the **inversion problem**. To overcome the inversion problem, the experimentally observed optical properties of the soot ensemble are compared to the theoretically
calculated optical properties. In this way, inverting the scattering and absorption coefficients to obtain the mean properties of the soot ensemble and the soot PSD can be avoided. With an accurate numerical technique (stochastic method), a soot model (ABF soot model), and an optical theory (Mie theory), it is simple to calculate the theoretical optical properties of a soot ensemble. Mie theory is used here as the ABF soot model assumes soot particles to be spherical. The rest of the assumptions in the Mie theory carry through to any optical theory that deals with aggregates. It can be shown that the theoretical optical properties are functions of the fractional moments of the soot PSD, the wavelength used for scattering experiments, and the refractive index of a soot particle. In mathematical terms,

\[ Q_{vv} = f(\nu_i, \lambda, m), \]  
\[ K_{abs} = f(\nu_i, \lambda, m). \]  

The details of the derivation of the absorption and scattering coefficients as a function of fractional moments, wavelength, and refractive index are elaborated in the Appendix B.1. Equations B.18 and B.16 give the expanded form of the function for equations 4.17 and 4.18 respectively.

It is important to note that the assumptions of a mono-disperse distribution, Rayleigh scattering, nature of the PSD, and the variance of the soot PSD are not made to obtain equations 4.17 and 4.18. The advantage of the stochastic method is in predicting the fractional moments more accurately than the existing numerical techniques. This is because a complete information on the particle size distribution is available from the stochastic method. This enables the stochastic method to predict the theoretical optical properties more accurately than the MoM. The difference between the MoM and stochastic method has been quantified in the previous sections in this chapter.

A similar analysis can show the advantages of using the stochastic method over the other numerical methods to analyze the data from the Laser Induced Incandescence experiments (Appendix B.2). Also, experimental data for the soot PSD available from the scanning mobility particle sizer (SMPS), small angle X-ray scattering, and small angle neutron scattering can be compared with the soot PSD available from the stochastic method. The comparison of experimental and numerically evaluated soot PSDs can provide valuable information for soot model development. This is discussed in the next chapter.
Chapter 5

Soot Model Development

In the previous chapters, a stochastic method has been developed and validated to solve the Smoluchowski equation, given a soot model. The soot model employed was developed by Appel et al. (2000). It was observed that the ABF soot model, irrespective of the choice of a numerical technique, predicted the mean properties of the soot ensemble, e.g. soot volume fraction, number density, fairly well. Most of the predictions were within a factor of 2 – 3, which is quite good considering the uncertainties in obtaining experimental measurements.

To date most of the modelling work in the literature has concentrated on matching the numerical results with mean properties of soot PSDs. These studies have led to a broad but basic understanding of the chemistry and physics of soot formation, but many questions remain and debate continues. These questions include, for example, the nature and size of soot nuclei, the mechanism of soot inception, the nature and number of chemically active sites on the soot particle surface available for gas-surface reaction, and the sticking probabilities of particle-particle and PAH-particle collision. Over the last decade, progress has been somewhat limited partly because further understanding of these issues requires experimental information about soot PSDs beyond their mean properties.

The recent development of advanced soot measurement techniques, including probe sampling followed by detailed PSD measurements with a Scanning Mobility Particle Sizer (SMPS) (Maricq, 2004; Zhao et al., 2003a,b, 2005), Small Angle X-ray Scattering (Hessler et al., 2002) and Small Angle Neutron Scattering (Wang et al., 2002) have provided soot data beyond the mean properties of PSDs. The spatial and temporal evolution of soot PSDs resulting from these experimental
developments offer some unique modelling opportunities and challenges. The various issues concerning soot inception and mass growth may now be investigated on the basis of the new and more detailed experimental data and the recent advancements in numerical techniques for solving the dynamics of soot formation (Balthasar and Kraft, 2003; Singh et al., 2005, 2004; Patterson et al., 2006a).

To isolate various issues concerning soot inception and mass growth, one is interested in investigating the spatial and temporal evolution of the soot particle size distribution in simple systems, e.g., laminar premixed flames. In a recent study, Zhao et al. (2005) presented experimental data on the variations of soot particle size distributions as a function of the maximum flame temperature. These measurements yielded normalized particle size distributions at several heights from the burner for a series of burner-stabilized, laminar, premixed ethylene-oxygen-argon flames at a pressure of 1 bar. The purpose of this chapter is to present an attempt at modelling these PSDs and test the sensitivity of soot PSDs with respect to processes and parameters in the soot model. This information will help to provide insights to improve our understanding of the fundamental sooting processes and to refine the available models of soot formation.

The base soot model used in the current study is identical to that documented in chapter 2. The computational method used to obtain the soot PSD is a stochastic one (Balthasar and Kraft, 2003; Singh et al., 2004, 2005; Patterson et al., 2006a) which gives the exact solution to the population balance equation describing the dynamics of the particle population, see chapters 3 and 4.

This chapter is organized in the following manner. In section 5.1 the experimental data of Zhao et al. (2005) are discussed in detail and the points for comparison of experimental and numerically obtained soot PSDs are outlined. In sections 5.2 and 5.3, computational results are compared to the experimental data and numerical sensitivity studies are performed to understand the effect of model parameters on the soot PSDs. Also, inferences are drawn from this analysis and potential improvements are proposed to resolve the discrepancies between the model and experiments.
5.1 Experimental Data Analysis

The ethylene-oxygen-diluent flames in Zhao et al. (2005), described in table 5.1, were chosen for the current study. The experimental details, particle sampling and measurement techniques have been discussed elsewhere (Zhao et al., 2003a,b, 2005). In the unburned gas, the fuel and oxygen composition was held fixed (24.2%-mol C$_2$H$_4$ and 37.9%-mol O$_2$), but the maximum flame temperature differed due to variations in the cold gas velocity (series A) or the inert composition (series B). The two sets of flames were designed to provide conditions leading to both unimodal and bimodal PSDs within the range of particle diameters measurable by SMPS. The PSDs were measured as a function of distance, $H$, from the burner surface and usually cover the range of $H = 5$ to 12 mm.

Table 5.1: Summary of flame conditions and its PSD characteristics

<table>
<thead>
<tr>
<th>Flame code</th>
<th>Mol% diluent</th>
<th>Cold gas vel. (cm/s)</th>
<th>$T_{\text{max}}$ (K)</th>
<th>PSD characteristics for $H = 7/10$ mm$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar/N$_2$ $^a$</td>
<td></td>
<td></td>
<td>$D_{p,a}$ (nm)$^d$</td>
</tr>
<tr>
<td>A1</td>
<td>37.9/0</td>
<td>7.0</td>
<td>1790</td>
<td>4.3/4.1</td>
</tr>
<tr>
<td>A2</td>
<td>37.9/0</td>
<td>7.85</td>
<td>1820</td>
<td>3.3/3.2</td>
</tr>
<tr>
<td>A3</td>
<td>37.9/0</td>
<td>10.0</td>
<td>1920</td>
<td>–/–</td>
</tr>
<tr>
<td>B1</td>
<td>0/37.9</td>
<td>8.0</td>
<td>1790</td>
<td>4.2/3.6</td>
</tr>
<tr>
<td>B2</td>
<td>15.1/22.8</td>
<td>8.0</td>
<td>1810</td>
<td>–/2.9</td>
</tr>
<tr>
<td>B3</td>
<td>37.9/0</td>
<td>8.0</td>
<td>1840</td>
<td>–/–</td>
</tr>
</tbody>
</table>

$^a$ Unburned gas contains 24.2%-mol C$_2$H$_4$ and 37.9%-mol O$_2$. $^b$ Maximum flame temperature measured by a thermocouple and corrected for radiation. See Zhao et al. (2005) for details.

$^c$ See Fig. 5.1, $H$ is the distance from the burner surface. $^d$ Accurate to within 0.5nm.

The Scanning Mobility Particle Sizer is based on the principle of the mobility of a charged particle in an electric field. Particles entering the system are neutralized (using a radioactive source) such that they have a Fuchs equilibrium charge distribution. They then enter a Differential Mobility Analyser (DMA) where the aerosol is classified according to electrical mobility, with only particles of a narrow range of mobility exiting through the output slit. This monodisperse distribution then goes to a Condensation Particle Counter (CPC) which determines the particle concentration at that size. The DMA consists of a cylinder, with a negatively charged rod at its center, the main flow through the DMA being particle free ‘sheath’ air. It is important that this flow is laminar. The particle flow is injected at the outside edge of the DMA, particles with a positive charge move across the sheath flow towards the central rod, at a rate determined
by their electrical mobility. Particles of a given mobility exit through the sample slit at the top of the DMA, while all other particles exit with the exhaust flow. A major advantage of SMPS is its ease of portability and significantly lower power consumption as compared to Differential Mobility Particle Sizer (DMPS). The disadvantage of a SMPS comes from its CPC unit. These have a slow response time and their handling can be complicated because of the condensation liquid. It also has a limitation in predicting 2 to 5 nm sized particles.

In Zhao et al. (2005), the SMPS mobility diameter was corrected to yield real diameters on the basis of a recently developed nanoparticle transport theory (Li and Wang, 2003a,b), which supersedes the Stokes-Cunningham formula of electric mobility. More recent studies (Li and Wang, 2005, 2006) show that the momentum accommodation function of the aforementioned theory must depend critically on the particle material and that the change from specular-to-diffusion scattering occurs somewhat slower for carbon-like material than for silver or copper oxide data analyzed by Li and Wang (2003b). As a result, a new relationship between real and mobility particle diameter for spherical carbonaceous particles was proposed:

$$\frac{D_p}{D_{p,SMPS}} = \tanh(1.3582 + 0.0122 \cdot D_{p,SMPS}) - 0.42877 \cdot D_{p,SMPS},$$  \hspace{1cm} (5.1)

for air at room temperatures and 2 nm < $D_{p,SMPS}$ < 100 nm. In the above equation, $D_{p,SMPS}$ is the mobility diameter (nm) directly measured by SMPS. This correlation replaces the one presented in figure 2 of Zhao et al. (2005). The PSDs in this chapter are calculated from the SMPS mobility diameter using the above relation. The changes in the revised experimental PSDs are insignificant compared to those shown by Zhao et al. (2005).

The basic hypothesis of Zhao et al. (2005) is that the features of PSD, and especially the bimodality observed earlier (Zhao et al., 2003a), are strongly dependent on temperature. In particular, this determines whether the PSD is bimodal or unimodal within the particle size range detectable by SMPS. Low temperature flames tend to produce bimodal PSDs because of persistent particle inception and the competition between particle inception and particle-particle coagulation (Zhao et al., 2003a). For high temperature flames, the thermal dissociation of PAHs becomes significant at later stages (see e.g. Wang and Frenklach (1997);
Zhao et al. (2005)). This effectively stops the particle inception process and eliminates the competition between inception and coagulation. As a result, in the high temperature flames, the PSDs tend to be unimodal.

For flames where bimodal distributions are observed, the evolution of PSDs may be characterized by an initial, power-law type PSD for incipient soot, which evolves into a bimodal PSD upon particle size and mass growth. The second mode of the PSD is of log-normal type, whereas the first mode remains a power-law function. The basic features of measured bimodal PSDs are schematically shown in figure 5.1. For the purpose of comparing PSDs, the following three characteristic points on a PSD may be identified: (a) the trough applicable to bimodal PSDs only; (b) the “maximum”, normalized number density $nnd$, and (c) the “largest” detected particle diameter, conveniently defined here as the greatest diameter for which $nnd = 10^{-2}$. Here the normalized number density is defined as

$$nnd = \frac{1}{N} \frac{dN}{d \log D_p}.$$  \hfill (5.2)

Each of these features may be quantified by their corresponding particle diameter and $nnd$ values. For example, $D_{p,a}$ and $nnd_a$ denote the diameter and normalized number density at the bottom of the bimodal PSD trough, as seen in figure 5.1.

The following observations apply to all bimodal PSDs. The size of the smallest soot particle obtained from the SMPS measurement is 2.5 nm. Smaller particles obviously exist in the flame, but they were not detected because of the instrument limitation. The diameters at points (b) and (c), see figure 5.1 and table 5.1, both increase with $H$. The diameter $D_{p,a}$ remains almost constant for a flame. However, its $nnd$ decreases as $H$ increases. Not all features are common to all the flames. Therefore, the flames were also analyzed for variations with the flame conditions. The PSDs for flames A1 and B1 are bimodal, whereas flames A3 and B3 have unimodal PSDs. Flames A2 and B2 are intermediate cases with one of the two modes less significant. The flames with higher peak temperatures (A3 and B3) give unimodal PSDs and have $D_{p,c}$ values smaller than those of other flames, as seen in table 5.1.
Normalised Number Density (nnd) \[ \frac{dn}{d \log(D_p)} \]

Particle Diameter \(D_p\) (nm)

(a) Trough
(b) Peak
(c) "Largest" particle

Width

**Figure 5.1**: Characteristic particle diameters and their corresponding normalised number densities.

### 5.2 Numerical Results

Before comparing the simulated soot PSDs with the experimental observations, we first focus at the effects of probe perturbation on the soot PSDs. Such effects arise primarily from flame cooling due to the probe and the changes in gas velocity and thus the particle history (Zhao et al., 2003b). This will also account for particle-particle coagulation in the sample probe. These effects usually result in a need to spatially shift the numerical results to achieve appropriate comparison between models and experiments\(^\ddagger\). The soot PSDs of flames A3 and B3 were examined first. These two flames were chosen as they are most likely to match the experimental observations, considering that they have unimodal distributions and thus a smaller number of PSD parameters to be compared. Also, the higher

\(^\ddagger\)Another reason for a possible shift is in the discrepancy of defining the zero coordinate for a flame. The flame distance is measured sometimes from the burners’ front and sometimes from the uplifted flame front.
peak temperatures of these two flames and smaller measured particle sizes suggest little to no soot aggregation. This is in line with the assumption of spherical soot particles in the current soot model.

For flame B3, the experimental data and two sets of simulation data are plotted in figure 5.2. For proper comparison with the experimental data, the simulated number density is normalized by the total number density of particles with $D_p > 2.5 \text{ nm}$\(^\dagger\). This is done because the smallest soot particle recorded by the SMPS is of size 2.54 nm. The resulting simulated $nnd$’s are represented by the dashed lines without height offset, whereas the solid lines were shifted by $-3.5 \text{ mm}$ to match the PSD profile at $H = 5 \text{ mm}$. It is seen that the numerical results match the measurements very well upon application of this height offset. By similarly matching the PSD profile at $H = 5 \text{ mm}$ for flame A3, it was observed that the offset appears to be proportional to the inlet velocity of the unburnt gas mixture. Therefore, an offset of 4 mm for flame A3 and 3.25 mm for flame A1 was used, again, by matching the PSD profile at $H = 5 \text{ mm}$. The comparisons are illustrated in figures 5.3 and 5.4. From this point onwards, all plots of simulated PSDs are based on the data shifted in this way. As seen in figures 5.2 through 5.4, a reasonably good agreement was observed between the experimental measurements and simulations, especially at smaller distances from the burner surface. For the flames A2, B1 and B2, the results are comparable to those presented in figures 5.2 through 5.4. In this regard, the computational results are encouraging: with only a spatial shift, the evolution of the PSDs computed for each flame can be plotted on the same plot as the experimental data without having to adjust model parameters. As can be seen from these figures, unimodal distributions can be predicted to fairly good accuracy. The real challenge, however, lies in predicting bimodal distributions. This is because bimodal distributions do not fit into a family of parametric distributions such as the log-normal or gaussian distributions. Whereas, unimodal distributions can be fitted to log-normal distributions, see figure 4.8. The parameters of a unimodal distribution can be calculated if the moments of the soot PSD are known. As most of the development of soot models was concentrated on predicting the moments of the soot PSD, it is unsurprising that the simulated results for flames with the unimodal distribution matches to the experimental measurements. Therefore,

\(^\dagger\)The total number density for $D_p > 2.5 \text{ nm}$ is about a factor $2 - 3$ lower than for $D_p > 0.9 \text{ nm}$.
Figure 5.2: Normalized number density distribution of flame B3. The symbols represent the experimental measurements at distance $H$ mm, (---) represents numerical result as is without height offset, and (—) represents numerical results at $H - 3.5$ mm.
Figure 5.3: Normalized number density distribution of flame A3. The symbols represent the experimental measurements at distance $H$ mm, and (—) represents numerical results at $H − 4$ mm.
Figure 5.4: Normalized number density distribution of flame A1. The symbols represent the experimental measurements at distance $H$ mm, and lines represents numerical results at $H - 3.25$ mm: (—) PSD normalization uses the total number density $N$ for particles with $D_p > 2.5$ nm, (-----) normalization uses $N$ for $D_p > 0.9$ nm, and (---) increased the fraction of active surface site density by 30%.
the flame A1 which has a bimodal soot PSD will be the subject of the major part of the remaining discussion.

For large $H$ values of flame A1, the model under-predicts the particle diameters. One explanation for this difference is the absence of accurate models for the surface processes. This problem will be studied in detail later in the chapter. It is also observed in figure 5.4 that the bimodality of flame A1 and its development are qualitatively well predicted (cf., experimental data and the dashed lines), but the bottom of the PSD trough occurs at a particle diameter smaller than the observed size. The simulated $D_{p,a}$ (defined in figure 5.1) is 3 nm and about 1.5 nm smaller than that observed in the experimental measurements. Likewise, the $D_{p,b}$ and $D_{p,c}$ values are both under-predicted.

5.3 Numerical Sensitivity Analysis

Drawing motivation from the discrepancies between simulated and observed PSDs shown in figure 5.4 and considering the nonlinear response of the PSD characteristics with respect to the model parameters, numerical experiments were performed to identify parameters of the soot model that affect the detailed PSD features. The model parameters considered here include the size of the “smallest” particle $N_{c,0}$, i.e., 32 carbon atoms in the base case due to the assumption of pyrene-pyrene coalescence, the sticking probability of PAH-PAH (pyrene) collision ($\gamma_{PAH-PAH}$), the sticking probability of PAH-particle collision ($\gamma_{PAH-P}$), the average Van der Waal’s enhancement factor $\varepsilon = 2.2$, and the active surface site density $\alpha$ as defined by Appel et al. (2000). Unless otherwise indicated, the base case numerical experiment mentioned henceforth uses the soot model (Appel et al., 2000) unaltered. A new description of the surface active sites, proposed more recently by Singh et al. (2005), is employed occasionally and its use will be specifically indicated.

5.3.1 Sticking probability of Pyrene-Pyrene collision

Binary collisions between PAH molecules to give a dimer have been an area of investigation (Schuetz and Frenklach, 2002). The understanding that the dimer might not be stabilized in the time before it reverts to two pyrene molecules has
led us to examine the influence of non-unity sticking probability on the predicted PSDs.

**Figure 5.5:** Sensitivity of pyrene mole fraction profile with respect to the pyrene-pyrene sticking probability, $\gamma_{\text{PAH-PAH}}$, computed for flame A1. Secondary X axis is the spatially shifted distance.

In figure 5.5, it is observed that the gas-phase pyrene concentration increases as the sticking probability $\gamma_{\text{PAH-PAH}}$ is decreased. This is unsurprising as the pyrene molecules, which were initially consumed to form soot particles, are now present in the gas phase. The increase in the gas phase concentration of pyrene has two effects:

1. More pyrene is available for the condensation on soot particles, i.e. the rate of pyrene condensation increases as it is proportional to the concentration
of pyrene in the gas phase, see equations 3.19 and 3.20. Figuratively,

$$R_{\text{cond}} \propto \gamma_{\text{PAH}-p} C_{\text{PAH}}.$$  \hspace{1cm} (5.3)  

\[\uparrow \leftrightarrow \uparrow\]

It is to be noted that \(\gamma_{\text{PAH}-p}\), the sticking probability of a pyrene molecule with a soot particle, is used in (5.3). The \(\gamma_{\text{PAH}-p}\) does not get affected by the choice of \(\gamma_{\text{PAH}-\text{PAH}}\), which is altered here. In the equation above, it can be observed that with the increased concentration of pyrene available (\(\uparrow\)) and no change in \(\gamma_{\text{PAH}-p}\) (\(\leftrightarrow\)), the rate of condensation of pyrene on the soot particles increases (\(\uparrow\)).

2. The sum of the rates of condensation and inception is lesser than the base case (\(\gamma_{\text{PAH}-\text{PAH}} = 1\)). If the sum of the rates of condensation and inception was greater than the base case, the net consumption of pyrene by the two processes would be larger than the base case. This would have resulted in the net decrease in the concentration of pyrene in the gas phase which is contrary to the observation. It is also known that the rate of condensation increases with the increase in the concentration of pyrene in the gas phase. This implies that the rate of inception decreases more than the rate of condensation increases in order to have a net decrease in the sum of the rates. The rate of inception is proportional to the square of concentration of pyrene in the gas phase and the sticking probability of pyrene molecules. Figuratively,

$$R_{\text{in}} \propto \gamma_{\text{PAH}-\text{PAH}} C_{\text{PAH}}^2.$$ \hspace{1cm} (5.4)  

\[\downarrow \downarrow \uparrow\]

From the understanding that the rate of inception decreases (\(\downarrow\)) with the increase in concentration of pyrene in the gas phase (\(\uparrow\)), the magnitude of decrease in the sticking probability of pyrene molecules (\(\downarrow\downarrow\)) can be estimated. It is noteworthy to mention that for the case where \(\gamma_{\text{PAH}-\text{PAH}} = 0\) (figure 5.5), there is no inception or condensation. This is because, in the absence of inception, no soot particles are formed on which the condensation process can occur.
Figure 5.6: Sensitivity of PSD ($H = 10$ mm, Flame A1) with respect to $\gamma_{PAH-PAH}$. The symbols represent experimental measurements.

In figure 5.6, we compare the PSDs resulting from different $\gamma_{PAH-PAH}$ values. Qualitatively, it can be seen that with the decrease in $\gamma_{PAH-PAH}$, the PSD trough shifts to smaller soot particle sizes. The effect of the increase in the rate of condensation is a lateral shift in the PSD towards larger sizes. This is more pronounced for the part of the PSD associated with large soot particles, because larger soot particles with greater surface area are more likely to collide with pyrene molecules in the gas phase. However, the decrease in the rate of inception shifts the PSD to smaller sizes with a larger corresponding $nnd$. The lowering of the inception rate produces PSDs similar to the earlier distances/times in the flame.

The net effect, where the rate of inception decreases more than the rate at which condensation increases, is the shift of the PSD to marginally smaller sizes with larger corresponding $nnd$. Quantitatively, this shift and the $nnd_n$ is not commensurate to the shift in magnitude of $\gamma_{PAH-PAH}$ which is changed by an
order of magnitude for each simulation. For a change of two orders of magnitude in the sticking probability, the position of the trough changes by a little more than a nanometer and the maximum particle size by 5 nm. Moreover, the shift is in the direction opposite to the one desired to match the experimental measurements. It is also possible to consider an increased collision cross section of pyrene-pyrene molecules due to Van der Waals interactions (Harris and Kennedy, 1988), by a factor of up to 2. The ABF soot model uses average Van der Waals enhancement factor of 2.2. The values of enhancement factor can vary between 1.2 and 2.4 depending on the size of particles coagulating, thus the maximum factor of 2. The sensitivity of soot PSD to the variation in the enhancement factor is discussed in section 5.3.5. However, looking at results shown in figure 5.6 and the quantitative analysis, one can infer that a factor of 2 would not make much difference to the PSD. Similar trends were observed for the flame B1, which also has a bimodal distribution.

5.3.2 Sticking probability of PAH-Particle collision

In line with the previous study, the sticking probability of pyrene condensing on a soot particle was investigated.

It is observed from figure 5.7 that the gas-phase pyrene concentration increases with a decrease in the sticking probability of PAH-particle collisions, $\gamma_{PAH-p}$. This leads to an increase in the rate of inception but of a lesser magnitude than the decrease in the rate of condensation. The increase in the rate of inception is evident from the slight increase in the $nnd$ for the smallest soot particle and shift of the trough towards larger particle sizes with a corresponding lower $nnd$, as seen in figure 5.8. The decrease in the rate of condensation laterally shifts the PSD towards the smaller soot particles. As mentioned in the previous section, this is more visible in the part of the PSD which constitutes larger soot particles. Had the condensation rate not decreased, the largest soot particle would have been even larger due to the increased rate of inception. However, the decrease in the rate of condensation reduces the size of the largest particle, in comparison with the base case. As explained before, the smaller sized particles in the PSD do not get affected by the decrease in the rate of condensation.

The trends observed for the change in PSD due to decreasing $\gamma_{PAH-p}$ is directly opposite to that observed for $\gamma_{PAH-PAH}$ (see, figure 5.6). It is hard to
envisage a physical justification for changing the two $\gamma$'s in opposite directions. An adjustment to one is likely to require a similar adjustment to the other and, on the basis of figures 5.6 and 5.8, the overall effect is likely to be too small.

5.3.3 Density of active surface sites

Numerous sets of reaction mechanisms and kinetic parameters have been proposed for soot surface growth (Frenklach and Wang, 1991; Appel et al., 2000; Mauß et al., 1994), illustrating the fact that the exact surface growth kinetics are far from being understood. A recent photoionization aerosol mass spectrometry study (Oktem et al., 2005) on a similar ethylene flame showed that, in the late stage of their mass growth, soot particles contain a large amount of aliphatics. Depending on the equivalence ratio and possibly temperature, the aliphatic
content can be as large as the aromatic content. The mass growth through the reaction of soot with aliphatics is not accounted for in the current soot model. Hence, the under-prediction of particle size especially in the log-normal part of the PSDs at large values of $H$ (see figure 5.4) may be the consequence of inaccurate surface reaction rate as well as the lack of appropriate mass growth paths.

In this study, the numerical sensitivity analysis is carried out by uniformly increasing the fraction of active sites on the surface of the soot particles, $\alpha$, – one of the most empirical parameters in the soot model (2.5)- by 30%. This effectively increases the overall surface reaction rate by the same percentage value, without an explicit indication, for the time being, of the mechanism by which such an increase may be justified. Within the framework of the current soot model, acetylene addition is responsible for most of the mass added into the system ($> 90\%$); hence, the impact of this parameter on the soot PSD was expected to
be significant. Indeed, we observe from figure 5.4 (dash-dotted-dash line), that all characteristic particle diameters, \( D_{p,a}, D_{p,b} \) and \( D_{p,c} \), become uniformly and notably larger for all \( H \) values. Similarly, for large \( H \) values the shift of the simulated PSDs to larger particle sizes would appear to provide better agreement between experimental and simulated PSD profiles. Yet one cannot conclude that the increase in the surface reactivity is, even partially, a solution to the problem. Recall that the simulated PSD profiles were spatially shifted to compensate for the probe effects. Since the degree of this shift is empirical, the increase of particle size brought about by an increased \( \alpha \) can be compensated for by adjusting the spatial shift of the computed profiles. Meanwhile, the trough in bimodal PSDs deepens significantly as compared to the observed PSDs, especially for large \( H \) values. In addition, a uniform increase of surface reactivity fails to broaden the log-normal part of the PSDs sufficiently to match the experimental profiles.

Figure 5.9: Sensitivity of PSD \((H = 10 \text{ mm}, \text{Flame A1})\) with respect to the surface site model.

A new model is developed where the number of active sites on an individual
particle is a function of the local flame temperature and its residence time in the flame. The new model will be termed the “Age model” and its development is explained in the next chapter. Mathematically, the rate of decay of active surface sites on each particle is given by,

$$\frac{d}{dt} \alpha(t) = -\tilde{C} \, T(t) \, [\alpha(t) - a] \quad \alpha(0) = 1,$$

(5.5)

where it is assumed that the fraction of active sites at any time, $\alpha(t)$, never becomes zero. The values of $a = 0.2$ is the minimum fraction of active sites on a soot particle and $\tilde{C} = 0.1$ are both motivated from Singh et al. (2005) and are explained in chapter 6.

Upon coalescence of two soot particles, the density of active sites on the new soot particle is set to the surface area weighted mean of the densities for the coalescing particles. Here, the use of local temperature provides a more realistic and a physically motivated description for the particle ageing. This is still a simplistic model, but the prediction appears to be improved compared with the base soot model. A comparison of the two surface site models is presented in figure 5.9. Though the prediction with equation 5.5 is far from being perfect, the spacing between the bottom of the PSD trough and the diameter of PSD peak, $D_{p,b} - D_{p,a}$, is much better predicted. For the remaining studies, the base case will include the above “Age model”.

### 5.3.4 Assumption of “Smallest” model particle

Prior to the work by Yoshihara et al. (1994), particle inception was generally assumed to involve the dimerization of PAHs ($\geq$ pyrene) of different sizes. This may be implemented in soot models with a linear lumping algorithm (Frenklach and Wang, 1991). Various groups have also adopted inception models to include PAH growth beyond pyrene (D’Anna et al., 2000; Mauß et al., 1994; Richter et al., 2005; Vlasov and Warnatz, 2002). It was shown by Yoshihara et al. (1994) that from the standpoint of predictions of mean particle properties, e.g., volume fraction, this assumption yields practically the same result as assuming pyrene dimerization as the only step of particle inception. To predict the detailed soot PSDs, however, particle inception from pyrene dimerisation only may not be adequate because the position of the PSD trough can be very sensitive to the
size of the first particle. Therefore, the inception model is examined here by increasing the size of the first soot particle to 224 carbon atoms from 32 atoms. Incipient particles of 224 carbon atoms correspond to spherical particles of 1.68 nm in diameter, which is still below the detection limit of the SMPS. These large incipient particles could be formed by dimerisation of higher PAHs or coalescence of higher and lower PAHs.

The study was divided into two sections: (a) the size of the first particle was increased to 224 carbon atoms without changing the particle inception rate; and (b) the inception rate for case (a) was reduced by a factor of 7 to ensure that the amount of carbon added to the system was equal to that in the base case. We observe from figure 5.10 that the case (a) shifts the bottom of the trough significantly to larger sizes with higher corresponding \( n_{nd} \) than the base case, and the case (b) shifts the position of the minima significantly to smaller soot particle sizes, but with even higher corresponding \( n_{nd} \).

It is generally true that with each addition of an aromatic ring, the concentration of PAHs decreases by about one order of magnitude (Homann, 1984). One might therefore expect the concentration of higher PAHs, such as the ones containing 112 carbon atoms, to be considerably lower than the concentration of pyrene. Thus, a significantly lower inception rate would be expected from higher PAHs than from pyrene. However, it is important to keep in mind that the typical ratio of pyrene used in condensation to that utilized for inception is 10 to 1 for bimodal flames and 1000 to 1 for unimodal flames. This implies that one could achieve similar amounts of particle inception with an order or two orders of magnitude lower concentration of pyrene if the condensation process were not occurring. Therefore, if we assume that the higher PAHs are not involved in condensation in the same way as the smaller PAHs, it is possible to envisage similar inception rates as are obtained in the base case. The case (a) listed above is thus justified by these assumptions.

In summary, the assumption about the first particle size, coupled with particle inception rates, has a large influence on the soot PSD predicted. To account for details of soot PSDs in these flames, a detailed chemistry model is therefore preferable which predicts concentration of gaseous species larger than pyrene. Furthermore, a mixture of small and large PAHs should be considered in soot inception. Analysis of the path of formation for pyrene and higher PAHs is not
Figure 5.10: Sensitivity of PSD \((H = 10 \text{ mm, Flame A1})\) with respect to size of the smallest soot particle \(N_{c,0}\) and nucleation rate. The symbols represent experimental measurements.

within the scope of this thesis.

5.3.5 Particle-Particle coagulation: Effect of Van der Waals enhancement factors

For the current flames, where most of the particle interactions occur in the free molecular regime, the probability of small and large soot particles coagulating is much larger than that of small-small or large-large coagulations. The differential collision kernels, therefore, must exert an effect on the particle size distribution. Though these kernels are exactly implemented in the soot model, the van der Waals enhancement factor was assumed to be a constant, 2.2, an average over the range of soot particle sizes (Harris and Kennedy, 1988). The enhancement factors for small-large soot particles coagulating vary between 1.2 and 1.8, which is well
below the average value of 2.2. For this reason, we tested the effect of a particle-size dependent enhancement factor on the soot PSDs. Mean enhancement factors were obtained from Harris and Kennedy (1988) by sectioning data into six classes: \( d < 6 \ \text{nm} \) treated as small particles, \( 6 \leq d < 12 \ \text{nm} \), \( 12 \leq d < 18 \ \text{nm} \), \( 18 \leq d < 24 \ \text{nm} \), and \( 24 \leq d < 30 \ \text{nm} \) forming intermediate size classes, and \( d \geq 30 \ \text{nm} \) classified as large particles (see table 5.2).

<table>
<thead>
<tr>
<th>d (nm)</th>
<th>&lt; 6</th>
<th>6 – 12</th>
<th>12 – 18</th>
<th>18 – 24</th>
<th>24 – 30</th>
<th>&gt; 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 6</td>
<td>2.40</td>
<td>1.65</td>
<td>1.40</td>
<td>1.25</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>6 – 12</td>
<td>1.65</td>
<td>2.35</td>
<td>2.00</td>
<td>1.85</td>
<td>1.80</td>
<td>1.80</td>
</tr>
<tr>
<td>12 – 18</td>
<td>1.40</td>
<td>2.00</td>
<td>2.30</td>
<td>2.20</td>
<td>2.10</td>
<td>2.10</td>
</tr>
<tr>
<td>18 – 24</td>
<td>1.25</td>
<td>1.85</td>
<td>2.20</td>
<td>2.25</td>
<td>2.15</td>
<td>2.15</td>
</tr>
<tr>
<td>24 – 30</td>
<td>1.20</td>
<td>1.80</td>
<td>2.10</td>
<td>2.15</td>
<td>2.20</td>
<td>2.20</td>
</tr>
<tr>
<td>&gt; 30</td>
<td>1.20</td>
<td>1.80</td>
<td>2.10</td>
<td>2.15</td>
<td>2.20</td>
<td>2.20</td>
</tr>
</tbody>
</table>

It can be observed from figure 5.11 that the position of the PSD trough shifts towards larger sizes with a higher corresponding \( nnd_a \) when the more detailed enhancement factors are used. This is because fewer smaller particles are being absorbed by the large particles, increasing their relative number density compared to the base case. The post minima distribution is not significantly affected.

### 5.4 Summary

For the first time, the ability of the soot model, presented by Appel et al. (2000), to predict the evolution of detailed soot PSDs is tested by comparing the simulated results with the experimental measurements. A stochastic particle method was used to obtain particle size distributions. The key features of the measured and simulated particle size distributions were identified and used as a simple way of comparing PSDs. The sensitivity of the soot PSD to the processes and the parameters defining the ABF soot model, such as the soot inception model, Van der Waals enhancement of particle-particle coagulation, and the surface activity model was investigated.

The qualitative effects of the parameters of the soot model on soot PSD are summarized in figure 5.12. It is clear that a closer prediction of the experimental PSDs may be achieved by an increase in the size of nucleating PAHs.
coupled with a somewhat reduced particle inception rate, an increase in the surface growth rates, and/or the use of a size dependent van der Waals enhancement factor and a consideration of the sticking probability for particle-particle coagulation. These parameters might have to be varied in different quantities for different flames. The scope of this thesis and the various coupled experimental and model uncertainties do not allow fixed numerical value for these parameters to be established, but the work establishes the baseline of comparison between the experimental and simulated soot PSDs and their evolution. It also provides insights into the qualitative and quantitative behaviors of soot PSDs with respect to a large number of model parameters.

Specifically, an increase in the incepting particle size was shown to have a very significant effect on the lower end of the PSDs, especially the trough of a bimodal PSD. This, whilst known previously, was quantified by estimating the size of poly...
Normalised Number Density (nnd)

\[ \frac{dn}{d\log(D_p)} \]

Particle Diameter \( D_p \) (nm)

- Increase nucleation size
- Increase nucleation rate
- Increase surface growth
- Size-dependent enhancement factor

**Figure 5.12:** Summary of effects of parameters of soot model on soot PSD.

aromatic hydrocarbons used in the inception process. This result suggests that to predict the details of soot PSDs and their evolution, the chemistry for higher PAHs and a more elaborate inception model are needed. The inception model could include interaction of different sized PAHs to give a range of sizes for the incepting particle.

A new model for the decay in the surface activity in which the activity of the soot particle depends only on the history of that particle and the local temperature of the flame, is shown to provide better predictions for soot PSDs than the empirical formula developed by Appel et al. (2000). The details of modelling active sites on the surface of soot particle are discussed in the next chapter.
Chapter 6

Surface Active Sites Modelling

It was established in the previous chapter that modelling of the active sites on the surface of a soot particle is amongst the most important factors for the success of a soot model. The rates of acetylene addition and $O_2$ oxidation have a primary dependance on the number of active sites available on the surface of a soot particle ($\alpha$). Similarly, the rate of other processes get affected by the change in $\alpha$, although indirectly. The number of active sites, thus, play a major role in defining the shape of the PSD.

The notion of active sites on the soot particle surface was introduced into kinetic soot modelling by Frenklach and Wang (1991). In conjunction with a decrease in concentration of the H-radicals (Frenklach and Wang, 1991, 1994), it was used as an explanation for the experimental observation of surface ageing. Experimentalists have reported that the reactivity of surface sites decreases with increasing particle growth or age (Haynes and Wagner, 1981, 1982; Harris and Weiner, 1983, 1985). Hence this process is often called surface ageing. It was attributed to a decrease in the number of active surface sites, i.e. sites that are accessible for reaction. On a mechanistic basis, surface ageing was attributed to the formation of defects on the particles’ surface generated during surface growth (Frenklach, 1996; Frenklach et al., 1998). It has also been attributed (Colket and Hall, 1994; Mauß and Bockhorn, 1995; Mauß et al., 1994) to the reversibility of the acetylene addition step in the HACA (hydrogen abstraction - carbon addition) surface growth scheme (Frenklach and Wang, 1991, 1994).

In the earlier soot models, constant fraction of active sites were assumed (Frenklach and Wang, 1991, 1994). Later, $\alpha$ was expressed as a function of
flame temperature (Kazakov et al., 1995) and subsequently as a function of flame temperature and mean particle size (Appel et al., 2000). A global expression for the mean fraction of active surface sites for a series of laminar premixed flames was established by Appel et al. (2000).

$$\alpha = \tanh \left( \frac{a(T)}{\log(\nu_1/\nu_0)} + b(T) \right),$$  \hspace{1cm} (6.1)

where \(a(T)\) and \(b(T)\) are parameters depending on the local flame temperature \((T)\):

\[
a = 12.65 - 0.00563 T, \hspace{1cm} (6.2)\\
b = -1.38 + 0.00068 T, \hspace{1cm} (6.3)
\]

The first reduced moment of the PSD,

$$\frac{\nu_1}{\nu_0} = \frac{\sum_{i=1}^{n} x_i}{n},$$  \hspace{1cm} (6.4)

gives the average mass of the soot particle in number of carbon atoms.

The aim of the present study is twofold. Firstly, a definition of particle age is proposed and particle age distributions are calculated. This is possible as a stochastic particle method is used, which can carry local information associated with the dynamics of each stochastic particle. Hence a unique value for the fraction of active surface sites can be assigned to each particle. Secondly, using this approach, a probable correlation between the number of active sites and particle age is investigated. The fact that each particle can carry its individual fraction of active surface sites means that not only laminar premixed flames, but also other classes of problems where the history of each particle might differ, can be described. This is the first attempt to investigate such an approach.

### 6.1 Soot Particle Age Distributions

Two flames, JW 10.673 and JW 1.69, were studied in detail as they differ markedly in their particle size distribution and soot growth characteristics. To facilitate the investigation of any correlation between \(\alpha\) and the age of individual particles
(A_p), the age of a particle is defined as follows: If a particle with index \( i \) and size \( x_i \) is incepted, its age is initialized to zero. After every event, or time step, the age of the particle is incremented with the actual waiting time \( (\tau, \text{equation 3.12}) \). If the particle is selected for coagulation with a particle of size \( x_j \), the age of the new particle of size \( x_i + x_j \) is set to the surface weighted average of the ages of particles with indices \( i \) and \( j \):

\[
A_p(t, x_i + x_j) = \frac{S_i(t) A_p(t, i) + S_j(t) A_p(t, j)}{S_i(t) + S_j(t)}, \tag{6.5}
\]

where \( A_p(t, i) \) and \( S_i(t) \) are the age and surface area of particle with index \( i \) at time \( t \) respectively. The reactivity of large particles can thus be altered by collisions with young particles.

Calculated age distributions are shown for flames JW 10.673 and JW 1.69 in figure 6.1. The age distributions reflect the basic features of the size distributions shown in figure 4.11. The age distribution for flame JW 1.69 is bimodal throughout the entire flame due to continuous nucleation. In contrast, in flame JW 10.673 the age distribution is bimodal for a short period in the main nucleation zone only. The main difference between size and age distributions however is the width in their large size or, in case of the age distribution, in their large age regions. While the size distribution develops a log-normal shape, the width of the age distribution decreases with increasing time. Thus the range of particle ages in flame JW 10.673 at large residence times is rather small.

The flames that exhibited a unimodal particle size distribution have a delta function like distribution for the age of particles at later times in the flame. This implies that the number of active sites on each particle is almost independent of its size. This matches the MoM in so far as, in that method, all the particles in the soot ensemble, irrespective of their size, have an average number of active sites given by the empirical relation (6.1). The observation of delta function like age distributions can be explained in the following manner. The particles which are freshly incepted and have smaller age preferentially coagulate with the particles of large size and considerably greater age. This is because the coagulation probability for two particles, one of which is of smaller size and the other larger (small-big), is much greater than the small-small or big-big combination. With a similar physical argument, a delta function like size distributions should be
Figure 6.1: Calculated soot particle age distributions at different residence times for flames JW 1.69 and JW 10.673.
observed too. However, where the coagulating particles add sizes, the surface weighted average is taken for the age of coagulating particles. This is why a log-normal like distribution is observed for the size distributions and delta function like distribution is observed for the age distributions.

It is important to note that the age of any particle will always be less than the global time at which the ages are observed. For example, the age of most of the particles at $t = 210$ ms is slightly less than 200 ms for the flame JW 10.673.

### 6.2 Age Dependence of Active Sites

To find a suitable function to correlate the age and the fraction of active surface sites on a particle, the expression in (6.1) used in the Method of Moments was investigated. The upper panel of the figure 6.2 shows the evolution of the mean $\alpha$ with the residence time for flames JW 1.69 and JW 10.673. It can be seen that $\alpha$ is unity initially and decreases markedly once soot particles start to grow. It levels off to a final value that is different for each of the investigated flames, i.e. 0.4 for flame JW 1.69 and 0.2 for flame JW 10.673.

As mentioned before, the shapes of the size distributions in the two flames are noticeably different. In flame JW 1.69 small, newly incepted particles are present throughout the entire flame. These particles should have a high surface reactivity as compared to the larger, older particles. This motivates attributing the difference in the final $\alpha$ to the continuous presence of young particles in flame JW 1.69.

### 6.2.1 Step-function

As a first attempt, the dependence of $\alpha$ on the particle age $A_p$ was expressed in terms of a step-function:

$$\alpha (A_p) = \begin{cases} 1 & \text{for } A_p \leq \theta, \\ 0.2 & \text{for } A_p > \theta, \end{cases}$$

(6.6)

where $\theta$ is the critical age defining the boundary between the two step values. The value of 0.2 for $A_p > \theta$ is motivated by the final value for the flame JW 10.673. It is thought that, for a flame where the particles are of significantly large size
Figure 6.2: Upper panel: The fraction of active sites on the soot particle surface, $\alpha$, as function of residence times for flames JW10.673 and JW1.69. Shown are values obtained with (6.1) used in the method of moments (- - -). Also shown is the surface weighted $\alpha$ obtained from the age distribution (—) depicted in figure 6.1 using the step function defined in (6.6) with $\theta = 12$ ms. Lower panel: Comparison of calculated soot volume fractions using the step-function approach with experimental values.
(> 100 nm) and age (≈ 200 ms), the number of active sites remaining on the surface of soot particles at the end of the simulation is likely to be the minimum number of active sites on the particle. It is assumed here that the number of active sites do not pass through an interior minimum and the function of $\alpha$ versus time is monotonically decreasing.

In the step-function, a high reactivity is assigned to young particles and a low reactivity to old particles. Figure 6.2 shows a comparison of surface weighted values of $\alpha$ obtained with the step-function approach using $\theta = 12$ ms are compared to the $\alpha$ used in the simulations with the MoM. The evolution of mean $\alpha$ obtained with the step-function closely resembles the original approach for both the flames. The sudden decrease in $\alpha$ is also well captured.

The simulations of the particle size distributions were repeated using the step-function approach to express the age dependence of $\alpha$. A comparison of measured and calculated soot volume fractions using the step-function approach in combination with the stochastic algorithm is shown in the lower panel of figure 6.2. It can be seen that the calculated volume fractions are within a factor of 2 as compared to the measured values despite the simplicity of the correlation between the age and the $\alpha$.

### 6.2.2 Exponential-function

It has also been suggested that the fraction of active surface sites on a particle decreases exponentially with its age (Haynes and Wagner, 1982; Woods and Haynes, 1991). This idea was adopted by using an exponential function to correlate age and fraction of active sites:

$$\alpha = a + (1 - a) \exp^{-CA_p},$$

(6.7)

where $a$ is a constant, $C$ the inverse of a typical decay time and $A_p$ the age of a particle.

Using (6.7), simulations were performed for four flames: JW 1.69, JW 10.673, JW 10.68, and WBF.12.3. WBF.12.3 is a low pressure (120 mbar) acetylene flame and has a bimodal PSD (Balthasar and Kraft, 2003). The properties of the flames are discussed in section 2.2. The constant $C$ was adjusted individually for each flame such that the calculated soot volume fraction matched the measured
values. The values of $C$ obtained in this manner are shown in Table 6.1. A comparison between the calculated and measured volume fractions along with surface weighted values of $\alpha$ is depicted in Figure 6.3.

**Table 6.1:** Parameter $C$ used in correlation $\alpha = 0.2 + 0.8 \exp(-CA_p)$ and maximum flame temperature for all simulated flames

<table>
<thead>
<tr>
<th></th>
<th>WBF.12.3</th>
<th>JW1.69</th>
<th>JW10.673</th>
<th>JW10.68</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$</td>
<td>200</td>
<td>20</td>
<td>25</td>
<td>130</td>
</tr>
<tr>
<td>$T_{\text{max}}$ (K)</td>
<td>1980</td>
<td>1711</td>
<td>1895</td>
<td>1880</td>
</tr>
</tbody>
</table>

From Table 6.1 it can be seen that the values for the parameter, $C$, varies markedly between the four calculated flames. Large values of $C$ were obtained for the WBF.12.3 and JW 10.68 flames corresponding to a strong decrease in $\alpha$ with increasing particle age. In contrast, a much smaller value of $C$ was found to provide a good match to the measured volume fractions for flames JW 1.69 and JW 10.673. This implies that, for these two flames, the decrease in $\alpha$ with particle age is much slower.

It has been suggested that the process of surface deactivation depends on flame temperature (Haynes and Wagner, 1982). Also, in their study, Appel et al. (2000) successfully correlated the parameters used in (6.1) with the maximum flame temperature. Thus, the values of parameter $C$ used in (6.7) were plotted as function of the maximum temperature of the respective flames, as shown in Figure 6.4.

It is seen that $C$ can be correlated to the maximum flame temperature for three out of the four calculated flames, i.e. flames JW 1.69, JW 10.68 and WBF.12.3. For these flames, the parameter $C$ increases linearly with increasing maximum flame temperature. A large value of $C$ corresponds to a fast depletion of active surface sites with increasing particle age. With the exception of flame JW 10.673, the results thus reproduce the trend that deactivation of surface reactivity proceeds faster at higher temperatures.

It is unclear why the value of $C$ in flame JW 10.673 differs so markedly to flame JW 10.68 despite the maximum flame temperatures being similar. Aggregation, which is not included in the current model, could affect the age dependence of $\alpha$. Total surface areas might be altered differently depending on the degree of aggregation in the different flames. For future work it is thus crucial to include aggregation and to investigate a larger set of premixed flames.
Figure 6.3: Upper panel: The fraction of active sites on the soot particle surface, \( \alpha \), as function of residence times. Shown are values obtained from the age distribution depicted in figure 6.1 using an exponential correlation between \( \alpha \) and the particle age as shown in (6.7). Parameter \( C \) in (6.7) was chosen individually for each flame, see table 6.1. Lower panel: Comparison of calculated and measured soot volume fractions as function of residence time.
Figure 6.4: Parameter $C$ used in the exponential correlation between the fraction of active surface sites and particle age ($\alpha = 0.2 + 0.8 \exp(-CA_p)$) as a function of maximum flame temperature. The line is a linear fit through the three data points for flames JW 1.69, JW 10.68 and WBF.12.3.

6.2.3 Numerical sensitivity analysis

This section gives details of the sensitivity of soot volume fraction to the parameters $a$ and $C$ in (6.7) for the following three flames: JW 1.69, JW 10.673, JW 10.68. The objective of this study is to investigate any correlations that may exist between these parameters and the local conditions of the flame.

It can be observed from the lower panels of figures 6.5, 6.6, and 6.7 that the soot volume fraction is sensitive to the exponential decay constant, $C$. This is unsurprising since any change in $C$ will exponentially affect the $\alpha$, and thus the soot volume fraction. However, the same can not be observed for $a$, see upper panels of the figures 6.5, 6.6, and 6.7. The change in values of $a$ will make a difference to $\alpha$ only if the exponential term approaches zero, thereby
nullifying the effect of the $1 - a$ term. The exponential term approaches zero for large values of $C$, such as in flame JW 10.68 where $C = 135$. For low values of $C$, any decrease in $a$ is reciprocated by a similar increase in $1 - a$. Although, the term $1 - a$ is multiplied by the exponential term, the effect of change in $a$ on $\alpha$ is minimized. The same is observed for flames JW 10.673 and JW 1.69 where $C = 25$. Therefore, for flames with high maximum temperature, the soot volume fraction is sensitive to both the pre-exponential and the exponential decay parameter. Whereas, for flames with low maximum temperature, the soot volume fraction is sensitive only to the exponential decay parameter.

In order to have a more consistent value for the exponential decay parameter across all the flames, the number of active sites can be expressed as a function of the local temperature of the flame. Using (6.7), one can obtain the rate of decay of $\alpha$ in the following way:

$$\frac{d}{dt} \alpha(t) = -C \ (1 - a) \ exp^{-CAp}$$

$$= -C \ [\alpha(t) - a].$$ \hfill (6.8)

By closely observing (6.8) and recalling from the above discussion that the parameter $C$ has a linear correlation with the flames maximum temperature, a parameter $\hat{C}$ can be chosen such that:

$$\hat{C} \ T(t) \approx C \ T_{\text{max}}.$$ \hfill (6.9)

The equation 6.8 can be rewritten to include the local temperature and the parameter $\hat{C}$:

$$\frac{d}{dt} \alpha(t) = -\hat{C} \ T(t) \ [\alpha(t) - a], \ \alpha(0) = 1.$$ \hfill (6.10)

The above equation is used to model the number of active sites on the surface of a soot particle and has been applied in Chapter 5 for soot model development.

## 6.3 Summary

The capabilities of the stochastic approach were utilized to calculate particle age distributions. With the obtained age distributions it was investigated whether particle age could be correlated with the fraction of active surface sites. Cor-
relations of two different functional forms were employed. First a step function was used to allocate a high surface activity to young particles and a low activity to old particles. In the second approach surface activity was expressed as an exponential function of particle age. Measured soot volume fractions could be well reproduced with both methods. The decay constant, which corresponds to the inverse of a typical deactivation time, used in the exponential approach was found to be a linear function of maximum flame temperature for three of the four calculated flames. This compares well with the experimental findings.

The results indicate that the fraction of active surface sites could indeed be expressed as a function of particle age. However, one of the calculated flames did not fit the trend found for the other flames. It is thus necessary to extend the present investigation to a larger set of flames. Also, aggregation of soot particles affecting the particles’ surface should be taken into account.
Figure 6.5: Sensitivity of parameters $a$ and $C$ in (6.7) for flame JW 10.673. The experimental measurements are plotted as ($\bullet$). The bold line (—) in the upper panel is for $a = 0.20$. 
Figure 6.6: Sensitivity of parameters $a$ and $C$ in (6.7) for flame JW 10.68. The experimental measurements are plotted as ($\bullet$).
Figure 6.7: Sensitivity of parameters $a$ and $C$ in (6.7) for flame JW 1.69. The experimental measurements are plotted as (●).
Chapter 7

Conclusions

This dissertation presents an improved soot model to predict soot formation in laminar premixed flames for all relevant pressure conditions. A novel stochastic algorithm is used to solve the equations that describe the soot model. The algorithm is computationally efficient and allows for modelling multi-dimensional distributions, such as the age and mass of soot particles.

The dynamics of an ensemble of soot particles, which are defined by a soot model, is described by the Smoluchowski equation with additional source terms for nucleation and surface reactions. The soot model employed in this thesis was developed by Appel et al. (2000). In this soot model, the nucleation was restricted to the collision of two gaseous pyrene molecules, the coagulation was modelled as the coalescence of two soot particles, and the surface reactions included the reaction of soot particles with pyrene, acetylene, oxygen, and OH. The Smoluchowski equation, which has a complicated form, is solved by the stochastic approach that uses a new majorant kernel applicable for all pressure regimes. This majorant kernel reduces the complexity of the problem from $O(n^2)$ to $O(n)$, where $n$ is the number of stochastic particles representing the soot ensemble.

Additionally, variants of the stochastic algorithm were implemented that reduced the computational time by up to three orders of magnitude. In these algorithms, the surface reactions that account for more than 90% of the total events were treated differently. In one of the variants, termed weighted algorithm, the rate of surface reactions were reduced and correspondingly the effect of surface processes on the soot PSD was increased proportionately. This was done when the difference between the timescales of the surface reaction processes and coag-
ulation process were quite large. The weighted algorithm introduced negligible error and reduced computational time by up to two orders of magnitude. In the other variants of the direct simulation algorithm, the surface reaction processes were treated deterministically over a time period. The time interval chosen was either fixed (Operator splitting) or based on the residence time of each soot particle (Age algorithm). A systematic error was introduced and the results were predicted within a factor of 2 to the DSA, however the computational time was reduced by up to three orders of magnitude.

The stochastic method was validated by comparing the results to the experimental measurements and the results from other well-known numerical techniques, such as the Method of Moments and the Linear Solver for Ordinary Differential Equations. The experimental measurements of the soot volume fraction and normalized particle size distribution (PSD) were obtained from fourteen laminar premixed flames that were burnt by different experimental groups.

The stochastic algorithm resolves the entire particle size distribution (PSD) without introducing closure assumptions. For the first time, the ability of a soot model to predict the evolution of a detailed PSD was tested by comparing the simulated results with the experimental measurements. Comparison of experimental and simulated PSDs for flames with unimodal PSD showed fairly good agreement. For the flames with bimodal PSDs, the sensitivity of the soot PSD to the processes and parameters defining the soot model was investigated. A mixture of poly-aromatic hydrocarbons for the inception process and size-based Van der Waals enhancement factors for the particle-particle coagulation were introduced in the soot model to obtain an agreement between the simulated and experimental PSDs. Also, a new model for the number of active sites on the surface of a soot particle was introduced. The model incorporated an exponential decay of the active sites as a function of the age of a particle and the local temperature of the flame. The sensitivity of soot volume fraction to the parameters defining the relations between the number of active sites on the surface of a soot particle and its age was examined.

In summary, a computationally efficient stochastic algorithm that enabled comparison of experimental and simulated PSDs, supported by comprehensive sensitivity studies, have provided the important steps towards soot model development.
CHAPTER 7. CONCLUSIONS

Future directions in soot modelling

Successful development of a stochastic method for simulating the soot model that describes the soot formation and oxidation was realized in this work. With the present work as a foundation, progress in the following areas could be made:

1. Modelling active sites on the surface of a soot particle
   
   (a) Aggregation models: The importance to accurately model the number of active sites on the surface of a soot particle has been shown in this thesis. The surface area available on a soot particle for reaction with the gaseous species is a key element in this model. Aggregation of soot particles can significantly change the surface area available on a soot particle from if the particles were assumed to only coalesce. Therefore, it is important to include aggregation models in the coagulation submodel especially for highly sooting flames. Advances in developing aggregation models are being made (Köylü, 1997; Kazakov and Frenklach, 1998; Balthasar and Frenklach, 2005a,b; Patterson et al., 2006c), however there is a need for more experimental measurements to validate these models.

   (b) Surface ageing: The surface ageing model proposed in this thesis needs to be validated in other types of systems, e.g. diffusion and turbulent flames.

2. The experimental data to validate the soot models are inadequate:
   
   (a) The lack of information on the concentration of larger PAHs and the PSD for small soot particles compromises the development of inception and gas phase chemistry submodels.

   (b) Additional data on the properties of soot particles, such as the C/H ratio and transmission electron microscope (TEM) pictures, are likely to provide indications to the physical processes leading to the formation of soot particles.

   (c) A consistent set of experimental data from a single system, e.g. gas phase species concentrations, number density and soot volume fraction of soot particles, soot PSD, C/H ratio etc. for a laminar premixed flame are required.
Appendix A

A.1 Majorant Kernel

In order to obtain a majorant kernel for the free molecular regime, we focus on the form of the coagulation kernel ($\beta^{fm}$) (Goodson and Kraft, 2002):

$$
\beta_{x,y}^{fm} = A \left( x^{-1} + y^{-1} \right)^{1/2} \left( x^{1/3} + y^{1/3} \right)^2.
$$

(A.1)

It is known that $(x^{-1} + y^{-1})^{1/2}$ cannot be expanded such that its summation results in the form of moments of a PSD. Therefore, a new expression greater than $(x^{-1} + y^{-1})^{1/2}$ is sought with aim that its summation yields term, which are in the form of moments of a PSD.

To prove that:

$$
(a + b)^n \leq (a^n + b^n) \quad 0 < n < 1, \quad a, b > 0,
$$

(A.2)

so that

$$
(x^{-1} + y^{-1})^{1/2} \leq \left( x^{-\frac{1}{2}} + y^{-\frac{1}{2}} \right).
$$

(A.3)

We require:

$$
(1 + r)^n \leq 1 + r^n,
$$

(A.4)

where $r = \frac{b}{a}$.

We have, for $0 < n < 1$ and $0 < r < 1$:

$$
(1 + r)^n \leq 1 + r, \quad (A.5)
$$

$$
1 + r^n \geq 1 + r. \quad (A.6)
$$
Therefore:

\[
(1 + r)^n \leq 1 + r^n, \quad (A.7)
\]
\[
(x^{-1} + y^{-1})^{1/2} \leq \left( x^{-\frac{1}{2}} + y^{-\frac{1}{2}} \right). \quad (A.8)
\]

It is also known that the expansion of \((x^{1/3} + y^{1/3})^2\) will result in three terms. If this can be reduced to two terms, fewer moments will be needed to express the summation in the form of moments of PSD. To prove that:

\[
(a + b)^n \leq 2^{n-1} (a^n + b^n) \quad n > 1, \quad a, b > 0, \quad (A.9)
\]
such that,

\[
(x^{1/3} + y^{1/3})^2 \leq 2 \left( x^{2/3} + y^{2/3} \right). \quad (A.10)
\]

Consider the function:

\[
\begin{align*}
\frac{df}{dr} &= n(2r)^{n-1} - n(1 + r)^{n-1} = 0 \quad \text{at } r = 1. \quad (A.13) \\
\frac{d^2 f}{dr^2} &= 2n(n-1)(2r)^{n-2} - n(n-1)(1 + r)^{n-2} \\
&= n(n-1)2^{n-2} > 0 \quad \text{at } r = 1. \quad (A.14)
\end{align*}
\]

This implies a global minimum at \(r = 1\), or \(a = b\). At \(r = 1\), the minimum value of \(f\) is:

\[
f(1) = (2^{n-1} \times 2) - 2^n = 0 \quad (A.15)
\]

This proves

\[
(x^{1/3} + y^{1/3})^2 \leq 2 \left( x^{2/3} + y^{2/3} \right). \quad (A.16)
\]
APPENDIX A.

The summation of the two new terms is shown in the next section.

A.2 Rate of Coagulation

The rate of coagulation shown in the section 3.4 is obtained from the summation of the coagulation kernel for the slip flow (3.17) and continuum regime (3.16). However, a majorant of the coagulation kernel is used in the case of free molecular regime (3.15). Shown below is the process to obtain the summation for the majorant kernel used in the free molecular regime.

To show that the rate of coagulation is,

\[ R_{\text{coag}} = \frac{N}{2} \sum_{1 \leq i \neq j \leq n} \hat{\beta}_{x_i, x_j}, \]  

\[ = 1.4178 \ AN \left\{ (n - 1) \sum_{i=1}^{n} x_i^{-\frac{1}{2}} + \left( \sum_{i=1}^{n} x_i^{\frac{3}{2}} \sum_{i=1}^{n} x_i^{-\frac{1}{2}} - \sum_{i=1}^{n} x_i^{\frac{1}{2}} \right) \right\} \]  

Note that from table 3.1,

\[ \hat{\beta}_{x_i, x_j} = 1.4178 \ A \left( x_i^{-\frac{1}{2}} + x_j^{-\frac{1}{2}} \right) \left( x_i^{\frac{3}{2}} + x_j^{\frac{3}{2}} \right). \]  

To calculate the rate of coagulation, the following summation needs to be evaluated:

\[ \sum_{1 \leq i \neq j \leq n} \left( x_i^{-\frac{1}{2}} + x_j^{-\frac{1}{2}} \right) \left( x_i^{\frac{3}{2}} + x_j^{\frac{3}{2}} \right). \]

Expanding the terms of the above equation, we get

\[ \sum_{1 \leq i \neq j \leq n} \left( x_i^{-\frac{1}{2}} + x_j^{-\frac{1}{2}} \right) \left( x_i^{\frac{3}{2}} + x_j^{\frac{3}{2}} \right) = \sum_{1 \leq i \neq j \leq n} \left[ \left( x_i^{\frac{1}{2}} + x_j^{\frac{1}{2}} \right) + \left( x_i^{\frac{3}{2}} x_j^{-\frac{1}{2}} + x_j^{\frac{3}{2}} x_i^{-\frac{1}{2}} \right) \right]. \]  

(A.20)
Separating the summations on the right hand side of (A.20), we get

\[
\sum_{1 \leq i \neq j \leq n} \left( x_i^{1_2} + x_j^{1_2} \right) = (x_1^{1_2} + x_1^{1_2}) + (x_2^{1_2} + x_1^{1_2}) + \ldots + (x_n^{1_2} + x_1^{1_2}) + \\
(x_1^{1_2} + x_2^{1_2}) + (x_2^{1_2} + x_2^{1_2}) + \ldots + (x_n^{1_2} + x_2^{1_2}) + \\
\vdots + \vdots + \ldots + \vdots + \\
(x_1^{1_2} + x_n^{1_2}) + (x_2^{1_2} + x_n^{1_2}) + \ldots + (x_n^{1_2} + x_n^{1_2}),
\]

\[
= (n - 1)x_1^{1_2} + \left( \sum_{i=1}^{n} x_i^{1_2} - x_1^{1_2} \right) + \ldots + (n - 1)x_n^{1_2} + \left( \sum_{i=1}^{n} x_i^{1_2} - x_n^{1_2} \right),
\]

\[
= (n - 2)x_1^{1_2} + \left( \sum_{i=1}^{n} x_i^{1_2} \right) + \ldots + (n - 2)x_n^{1_2} + \left( \sum_{i=1}^{n} x_i^{1_2} \right),
\]

\[
= (n - 2) \left( \sum_{i=1}^{n} x_i^{1_2} \right) + n \left( \sum_{i=1}^{n} x_i^{1_2} \right),
\]

\[
\sum_{1 \leq i \neq j \leq n} \left( x_i^{1_2} + x_j^{1_2} \right) = 2(n - 1) \sum_{i=1}^{n} x_i^{1_2},
\]

and

\[
\sum_{1 \leq i \neq j \leq n} \left( x_i^{2_2} x_j^{1_2} + x_j^{2_2} x_i^{1_2} \right) = 2 \sum_{1 \leq i \neq j \leq n} x_i^{2_2} x_j^{1_2},
\]

\[
= 2 \left( x_1^{2_2} x_1^{1_2} + x_1^{2_2} x_2^{1_2} + \ldots + x_1^{2_2} x_n^{1_2} \right) + \\
2 \left( x_2^{2_2} x_1^{1_2} + x_2^{2_2} x_2^{1_2} + \ldots + x_2^{2_2} x_n^{1_2} \right) + \\
\vdots + \vdots + \ldots + \vdots + \\
2 \left( x_n^{2_2} x_1^{1_2} + x_n^{2_2} x_2^{1_2} + \ldots + x_n^{2_2} x_n^{1_2} \right),
\]

\[
= 2 \left[ (x_1^{-1_2} \sum_{i=1}^{n} x_i^{2_2} - x_1^{1_2}) + \ldots + (x_n^{-1_2} \sum_{i=1}^{n} x_i^{2_2} - x_n^{1_2}) \right],
\]

\[
\sum_{1 \leq i \neq j \leq n} \left( x_i^{2_2} x_j^{1_2} + x_j^{2_2} x_i^{1_2} \right) = 2 \left[ \sum_{i=1}^{n} x_i^{2_2} \sum_{i=1}^{n} x_i^{1_2} - \sum_{i=1}^{n} x_i^{1_2} \right].
\]

The terms highlighted in the red color are not counted towards the summation.
as they are the result of \( i = j \). Therefore,

\[
\sum_{1 \leq i \neq j \leq n} \left( x_i^{-\frac{1}{3}} + x_j^{-\frac{1}{3}} \right) \left( x_i^{\frac{2}{3}} + x_j^{\frac{2}{3}} \right) = 2 \left[ (n - 1) \sum_{i=1}^{n} x_i^{\frac{1}{3}} + \left( \sum_{i=1}^{n} x_i^{\frac{2}{3}} \sum_{i=1}^{n} x_i^{-\frac{1}{3}} - \sum_{i=1}^{n} x_i^{\frac{1}{3}} \right) \right].
\]

(A.21)

Substituting equations A.19, A.20, and A.21 into A.17 gives us A.18. The same methodology is applied to obtain summation for the slip flow and continuum regime kernels.
Appendix B

B.1 Optical Properties

When particles interact with light, two different types of processes can occur. The energy received can be re-radiated, usually in different directions with different intensities, which is called scattering. Alternatively, the radiant energy can be transformed into other forms of energy, such as heat or radiation of different wavelength. These processes are called absorption. The extinction energy, which is the total energy lost by an incident plane wave, is equal to the scattered energy plus the absorbed energy.

\[ W_{\text{ext}} = W_{\text{sca}} + W_{\text{abs}}. \] (B.1)

In 1908, Gustav Mie developed the theory of absorption and scattering by small particle for a sphere of arbitrary diameter \(d\) and refractive index \(m = n + in'\), where \(n\) and \(n'\) are nonnegative. The imaginary part of the complex refractive index indicates the extent of attenuation of the incident wave as it propagates through the particle, and is thus the measure of absorption\(^1\), and the real part indicates the phase difference between the wavelets, and is thus the measure of scattering. If the particle is small compared to the wavelength, all secondary wavelets are approximately in phase; for such a particle, variation of scattering with direction is not expected. In addition, the phase relation among the scattered wavelets depend on geometrical factors: scattering direction, size, and shape.

To derive optical properties of an ensemble, a few assumptions are made in

\(^1\)For nonabsorbing materials, \(n' = 0\)
APPENDIX B.

the Mie theory. They are as follows:

1. Elastic scattering: The frequency of the scattered light is the same as that of the incident light.

2. Single scattering: The number of particles is sufficiently small and their separation sufficiently large that, in the neighborhood of any particle, the total field scattered by all the particles is small compared with the external field. With this assumption the total scattered field is just the sum of the fields scattered by individual particles, each of which is acted on by the external field in isolation from the other particles.

3. Incoherent scattering: The particles are many and their separations random, i.e. there is no systematic relation among the phases of the waves scattered by the individual particles; thus, the total irradiance scattered by the collection is just the sum of the irradiances scattered by the individual particles. However, even in a collection of randomly separated particles, the scattering is coherent in the forward direction.

4. The spherical particle is isotropic and homogeneous.

5. The medium surrounding the spherical particle is nonabsorbing and homogeneous.

6. The permeability of the spherical particle is equal to that of the surrounding medium.

With the above assumptions in place, the scattering cross section, $C_{sca}$ and the extinction cross section, $C_{ext}$ for a particle of nondimensional diameter, $z$ is as follows:

\[
C_{sca}(cm^2) = \frac{W_{s}}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) (|a_n|^2 + |b_n|^2), \tag{B.2}
\]

\[
C_{ext}(cm^2) = \frac{W_{ext}}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n), \tag{B.3}
\]
where

\[
\begin{align*}
a_1 &= -\frac{i^2}{3} P z^3 - \frac{i^2}{5} PQ z^5 + \frac{4}{9} P^2 z^6 - \frac{i}{175} PR z^7 + \frac{8}{15} Q P^2 z^8 + \mathcal{O}(z^9), \\
b_1 &= -\frac{i}{45} V z^5 - \frac{i}{945} W z^7 + \mathcal{O}(z^9), \\
a_2 &= -\frac{i}{15} S z^5 + \frac{i}{21} T z^7 + \mathcal{O}(z^9), \\
b_2 &= -\frac{i}{1575} V z^7 + \mathcal{O}(z^9), \\
a_3 &= -\frac{i4}{1575} U z^7 + \mathcal{O}(z^9), \\
&\vdots \\
k &= \frac{2\pi}{\lambda} \quad \ldots \text{Wave number,} \\
z &= \frac{\pi d}{\lambda} \quad \ldots \text{Non dimensional diameter,}
\end{align*}
\]

and the constants\(^2\), which are functions of the refractive index \(m\), are:

\[
\begin{align*}
P &= \frac{m^2 - 1}{m^2 + 2}, \\
Q &= \frac{m^2 - 2}{m^2 + 2}, \\
S &= \frac{m^2 - 1}{2m^2 + 3}, \\
T &= \frac{m^2 - 1}{(2m^2 + 3)^2}, \\
U &= \frac{m^2 - 1}{3m^2 + 4}, \\
V &= m^2 - 1, \\
R &= \frac{m^6 + 20m^4 - 200m^2 + 200}{(m^2 + 2)^2}, \\
W &= (m^2 - 1)(2m^2 - 5).
\end{align*}
\]

The coefficients \(a_1, b_1, a_2, b_2, a_3, \ldots\) are derived from the power series expansions of spherical Bessel functions. The expansions for higher order scattering coefficients involve terms of order \(z^9\) and higher and are neglected.

It is important to note that the scattering cross section evaluated in the (B.2) is based on unpolarized light. However, the measurements reported in the soot literature are based on vertically polarized light. In such a case, the scattering cross section is:

\[
C_{sca}(cm^2) = \frac{3\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right). \quad (B.4)
\]

The factor \(\frac{3}{2}\) is explained in section B.1.3. In order to obtain \(Q_{vv}\) and \(K_{ext}\), which

---

\(^2\)See section B.1.3 for values of constants at \(m = 1.57 + 0.56i\).
are experimentally measurable quantities and are published in the soot literature, certain modifications are made to $C_{sca}$ and $C_{ext}$:

\[ Q_{vv}(cm^{-1}sr^{-1}) = \frac{1}{4\pi}(sr^{-1}) \sum_{i=1}^{\infty} C_{sca,i}(cm^2)N_i(cm^{-3}), \quad (B.5) \]

\[ K_{ext}(cm^{-1}) = \sum_{i=1}^{\infty} C_{ext,i}(cm^2)N_i(cm^{-3}), \quad (B.6) \]

where $i$ is the index of a particular size of soot particle and $N_i$ its number density. Thus, for a monodisperse distribution,

\[ Q_{vv}(cm^{-1}sr^{-1}) \approx \frac{3N_d}{4k^2} \sum_{n=1}^{\infty} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right), \quad (B.7) \]

\[ K_{ext}(cm^{-1}) = \frac{2\pi N_d}{k^2} \sum_{n=1}^{\infty} \text{Re}(a_n + b_n), \quad (B.8) \]

where $N_d$ is the total number density per $cm^3$.

**B.1.1 Rayleigh scattering**

If we were interested only in the scattering and absorption by spheres, we would need to go no further than the Mie theory. However, in order to get an insight into the underlying physics, some limiting cases are discussed to give meaning to an otherwise semi-infinite strip of computer output. In Rayleigh scattering, the particles are small compared to the wavelength such that $|m|z \ll 1$, i.e. $(|a_1| \gg |b_1|, |a_2|, \ldots)$. In such a case, the scattering cross sections and other optical properties can be obtained by expanding the $a_1$ term. Thus, for a monodisperse distribution,

\[ Q_{vv}(cm^{-1}sr^{-1}) \approx \frac{3}{4k^2} (3|a_1|^2) N_d \]

\[ = \frac{3}{4k^2} \left( 3 \times \frac{4z^6}{9} \frac{|m^2 - 1|^2}{m^2 + 2} \right) N_d \]

\[ = \frac{z^6}{k^2} \frac{|m^2 - 1|^2}{m^2 + 2} N_d = \frac{z^6}{k^2} F(m) N_d, \quad (B.9) \]
\[ K_{\text{ext}}(\text{cm}^{-1}) \approx \frac{2\pi}{k^2} (3\text{Re}(a_1)) N_d \]
\[ = \frac{2\pi}{k^2} 2z^3 \text{Im} \left( \frac{m^2 - 1}{m^2 + 2} \right) N_d \]
\[ = \frac{4\pi z^3}{k^2} E(m) N_d. \]  
(B.10)

To obtain soot volume fraction, \( f_v = \frac{1}{6} \pi d^3 N_d \), \( z \) and \( k \) in (B.10) are expanded.

\[ K_{\text{ext}}(\text{cm}^{-1}) = \frac{4\pi z^3}{k^2} E(m) N_d \]
\[ = \frac{\pi^2 d^3}{\lambda} E(m) N_d \]
\[ = \frac{6\pi}{\lambda} f_v E(m), \]
\[ f_v = \frac{\lambda}{6\pi E(m)} K_{\text{ext}}. \]  
(B.11)

Reshuffling (B.9) and (B.10), particle diameter, \( d \) and number density, \( N_d \) can be estimated:

\[ d = \lambda \left( \frac{4}{\pi^2} \frac{E(m) Q_{vv}}{F(m) K_{\text{ext}}} \right)^{1/3}, \]  
(B.12)
\[ N_d = \frac{F(m)}{4Q_{vv}} \left( \frac{K_{\text{ext}}}{\lambda E(m)} \right)^2. \]  
(B.13)

Equations B.11 and B.12 are as derived in \( \text{(Axelsson et al., 2000)} \).

Continuing within the regime of Rayleigh scattering and extending the study to any particle size distribution, we obtain

\[ Q_{vv,i} = \frac{z_i^6}{k^2} F(m) N_i \quad K_{\text{ext},i} = \frac{4\pi z_i^3}{k^2} E(m) N_i \]
\[ Q_{vv} = \sum_{i=1}^{\infty} Q_{vv,i} \quad K_{\text{ext}} = \sum_{i=1}^{\infty} K_{\text{ext},i} \]
\[ Q_{vv} = \frac{\mu_6}{k^2} F(m) N \quad K_{\text{ext}} = \frac{4\pi \mu_3}{k^2} E(m) N, \]  
(B.14)

where, \( \mu_i \) are the \( i \)-th reduced moment of the distribution \( P(z) \) of the size parameter \( z = \pi d/\lambda \). Equation B.14 is the same as derived in \( \text{(Wieschnowsky et} \)
With this new formulation, the soot volume fraction can still be calculated by equation B.11.

The problems associated with the Rayleigh scattering are as follows:

1. Validity of $|m|z \ll 1$: For a soot particle with $m = 1.57 + 0.56i$, $|m| = 1.67$ and for $\lambda = 488$ nm, a common wavelength used in the studies of light scattering, the $|m|z \ll 1$ relation holds true for $d < 10$ nm. In the scope of our study, the particles are much larger and this assumption is seriously challenged.

2. Inversion problem:
   
   (a) Soot volume fraction: It can be calculated by equation B.11.
   
   (b) Number density: It can be only calculated if an assumption is made on the nature of PSD. The most common assumptions are monodisperse or lognormal distributions. For lognormal distributions, one has to assume a physically motivated variance, e.g. $\sigma_* = 0.34$ derived from coagulation theory for aerosols in free molecular regime, where coagulation is the dominant process (Wieschnowsky et al., 1988). In the case where variance is assumed, one solves for two variables: Number density and the mean diameter with two equations available. It is shown in (Bockhorn et al., 1988) that assuming lognormal distribution decreases the error in predicting number density by 45% and mean diameter by 35% as compared to monodisperse distribution. It can be observed from figure B.1 that the values of parameter, $\sigma_*$, in the range of 0.35 – 0.40 for a lognormal distribution are a good estimate to fit unimodal PSDs.
   
   (c) Particle size distribution: The PSD can be constructed if a PSD is assumed with a single unknown parameter.

However, it is important to keep in mind that the assumption of the nature of the PSD and the appropriate variance is not trivial. Moreover, recent experimental (Zhao et al., 2005) and computational techniques (Singh et al., 2004, 2006) have shown flames with bimodal distributions and where...

---

3Equation 3 in (Wieschnowsky et al., 1988) has a factor of $\lambda$ missing
the dominant soot event is its reaction with acetylene in the gas phase (Patterson et al., 2006a).

\[ K_{\text{ext}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n) \]

\[ = \frac{2\pi}{k^2} (3\text{Re}(a_1 + b_1) + 5\text{Re}(a_2 + b_2) + 7\text{Re}(a_3)). \]

\[ (B.15) \]

**Figure B.1:** Comparison between experimental measurements (○) and fitted lognormal distribution for the flames B2 and B3 at 12 mm from the burner.

In order to minimize the error in predicting soot ensemble properties, i.e. number density and soot volume fraction, numerical simulations allow more informed selections to be made for the variance of a PSD. The advantage of the stochastic method over the method of moments is that the nature of PSD is known. Both techniques, otherwise, are equally apt for calculating the variance of a distribution. It is however clear that using a lognormal distribution with a presumed variance based on a theory can lead to erroneous results.

### B.1.2 Expansion of terms in the Mie theory

As inversion problem is very difficult to tackle even in the Rayleigh scattering regime, one can attempt to predict optical properties to great accuracy, given a PSD, by expanding terms in the Mie theory. The PSDs can be calculated by numerical techniques, given a soot model.

For a single spherical particle, \( K_{\text{ext}} \) takes the form:

\[ K_{\text{ext}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}(a_n + b_n) \]

\[ = \frac{2\pi}{k^2} (3\text{Re}(a_1 + b_1) + 5\text{Re}(a_2 + b_2) + 7\text{Re}(a_3)). \]
For any particle size distribution, the above equation is summed over all the particles to give

\[ K_{\text{ext}} = \frac{\pi}{k^2} (K_3 \mu_3 + K_5 \mu_5 + K_6 \mu_6 + K_7 \mu_7) N, \] (B.16)

where

\[
\begin{align*}
K_3 &= 4 \text{Im}(P), \\
K_5 &= \frac{12}{5} \text{Im}(PQ) + \frac{2}{15} \text{Im}(V) + \frac{2}{3} \text{Im}(S), \\
K_6' &= \frac{8}{3} \text{Re}(P^2), \\
K_7 &= \frac{6}{175} \text{Im}(PR) + \frac{2}{315} \text{Im}(W) - \frac{10}{21} \text{Im}(T) + \frac{2}{315} \text{Im}(V) + \frac{8}{225} \text{Im}(U),
\end{align*}
\]

Similarly, for a single particle, \( Q_{\text{vv}} \) takes the form:

\[
Q_{\text{vv}} = \frac{3}{4k^2} \sum_{n=1}^{\infty} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right) = \frac{3}{4k^2} \left( 3(|a_1|^2 + |b_1|^2) + 5|a_2|^2 \right). \] (B.17)

For any particle size distribution, the above equation is summed over all the particles to give

\[ Q_{\text{vv}} = \frac{3}{4k^2} (K_6 \mu_6 + K_8 \mu_8 + K_9 \mu_9 + K_{10} \mu_{10}) N, \] (B.18)

where

\[
\begin{align*}
K_6 &= \frac{4}{3} |P|^2, \\
K_8 &= \frac{8}{5} \left[ \text{Re}(P)\text{Re}(PQ) + \text{Im}(P)\text{Im}(PQ) \right], \\
K_9 &= \frac{16}{9} \left[ \text{Re}(P^2)\text{Im}(P) - \text{Im}(P^2)\text{Re}(P) \right], \\
K_{10} &= \frac{4}{175} \left[ \text{Re}(P)\text{Re}(PR) + \text{Im}(P)\text{Im}(PR) \right] + \frac{12}{25} |PQ|^2 + \frac{|V|^2}{675} + \frac{|S|^2}{45}.
\end{align*}
\]

Equations B.16 and B.18 can be compared to equations 10.38\(^4\) and 10.37 re-

\(^4\)A factor of \(\lambda\) is missing in Eq. 10.38 in (Frenklach and Wang, 1994)
respectively in (Frenklach and Wang, 1994). The values of $K_7$ and $K_{10}$ are more accurate in this thesis than in (Frenklach and Wang, 1994) as the terms of higher order are included in the expansion of Mie theory coefficients.

B.1.3 Notes

Values of refractive index based constants

For $m = 1.57 + 0.56i$, a commonly used value for the refractive index of a soot particle (Smyth and Shaddix, 1996), the values of refractive index based constants are as follows:

\begin{align*}
P &= 0.387 + 0.260i, & Q &= 0.183 + 0.346i, & S &= 0.222 + 0.134i, \\
T &= 0.032 + 0.003i, & U &= 0.155 + 0.090i, & V &= 1.151 + 1.758i, \\
\end{align*}

Change in optical properties due to polarization of light

A difference can be observed in the scattering cross section between the equation B.2 (Bohren and Huffman, 1983) and B.4. The difference arises because equation B.2 is derived from assuming unpolarized light of intensity $i$, which is composed of perpendicular ($i_\perp$) and parallel ($i_\parallel$) components. Whereas, equation B.4 is derived when only vertically polarized light ($i_\perp$) is used for scattering experiments. Below is derived the ratio, $(i_\perp/i)$:

\begin{align*}
i_\perp &= X \\
i_\parallel &= X \cos^2 \theta \\
i &= \frac{i_\perp + i_\parallel}{2} \\
\frac{i_\perp}{i} &= \frac{\int_0^\pi \sin \theta \, d\theta}{\int_0^\pi \left( \frac{1+\cos^2 \theta}{2} \right) \sin \theta \, d\theta} = \frac{3}{2}
\end{align*}

Here, theta ($\theta$) is the angle between the $x$ axis of the incoming light (propagating in the $+z$ direction) and the transmission axis of the linear polarizer.
B.2 LII Modelling

Laser-induced incandescence is an effect based on the heating of soot particles by a short intense laser pulse. The radiation of the heated particle is then time resolved detected during the cooling phase. The particle heating is described by an absorption term. The cooling of the particle is mainly due to vaporization of the particle, heat conduction (and convection) to the surrounding gas, and black body radiation of energy. This leads to an energy balance

\[
\frac{dU}{dt} = \dot{Q}_{\text{abs}} - \dot{Q}_{\text{vap}} - \dot{Q}_{\text{con}} - \dot{Q}_{\text{rad}}. \tag{B.23}
\]

The term \(dU/dt\) describes the change of the internal energy of the particles with

\[
\frac{dU}{dt} = m_p c_s \frac{dT}{dt} = \frac{4}{3} \pi r(t)^3 \rho_s c_s \frac{dT}{dt}. \tag{B.24}
\]

Soot particles are heated up by laser intensity \(I_L(t)\) and the absorption term \(\dot{Q}_{\text{abs}}\) can be described as a function of absorption coefficient \(K_{\text{abs}}(r, \lambda_0)\) at the wavelength \(\lambda_0\):

\[
\dot{Q}_{\text{abs}} = K_{\text{abs}}(r, \lambda_0) I_L(t). \tag{B.25}
\]

The vaporization term \(\dot{Q}_{\text{vap}}\) takes the temporal change of mass into account:

\[
\dot{Q}_{\text{vap}} = -\Delta H_v(T) \frac{dm_p}{dt}, \tag{B.26}
\]

where \(W_v\) is the molecular weight of the vapor and \(\Delta H_v(T)\) is the temperature-dependent enthalpy of vaporization.

The heat loss due to conduction and convection \(\dot{Q}_{\text{con}}\) is determined by the particle surface area and the temperature difference with respect to the ambient gas temperature \(T_\infty\) and the heat transfer coefficient \(h'\):

\[
\dot{Q}_{\text{con}} = 4\pi r(t)^2 h' \frac{T - T_\infty}{r}. \tag{B.27}
\]

The detected Planck radiation is one of the main paths of heat loss and can be described as

\[
\dot{Q}_{\text{rad}} = 4 \int_0^\infty K_{\text{abs}}(r, \lambda) \frac{c_1 n_\infty^2}{\lambda^5(e^{c_2/\lambda T} - 1)}, \tag{B.28}
\]
where $c_1$, $c_2$ are first and second constant in Planck’s formula and $n_\infty$ is the refractive index of surrounding gas.

The mass balance of the soot particle is given by

$$-\rho_s \frac{dr}{dt} = \rho_v U_v,$$

(B.29)

where $\rho_v$ is the density of the vaporized soot and $U_v$ is the langmuir evaporation rate.

The mathematical model is explained in detail in (Melton, 1984; Vander Wal and Jensen, 1998). In order to solve the equations, particles are assumed spherical and of small size. The temporal decay of the radius of soot particle and the LII signal are shown in figures B.2 and B.3.

For a single particle of radius $r$,

$$I(t, T, r, \lambda_{em}) = \frac{2\pi c^2 h}{\lambda_{em}^5} \left[ \exp \left( \frac{hc}{\lambda_{em} kT(t)} \right) - 1 \right]^{-1} K_{abs}(\lambda_{em}, r).$$

(B.30)

The total signal can be obtained by:

$$I(t) = N_d \sum_{j=1}^{\infty} p_j I_j(t, T, r)$$

(B.31)

where, $N_d$ is the total number density and $p_j$ is the probability density for $j^{th}$ size class. Accurate values of $K_{abs}$ can be obtained from (B.15). The total signal can be obtained by making few assumptions which are as follows:

1. Temporal decay of temperature is independent of the radius: This assumption can be challenged for a bi-modal distribution where the range of particle sizes is rather large for which the temporal decay of temperature would vary as is observed in figure B.4. However, with the assumption in place, the total signal $I(t)$ is,

$$I(t) = \frac{2\pi c^2 h}{\lambda_{em}^5} \left[ \exp \left( \frac{hc}{\lambda_{em} kT(t)} \right) - 1 \right]^{-1} \int_0^\infty P(x) K_{abs}(\lambda_{em}, x) dx$$

$$= \frac{2\pi c^2 h}{\lambda_{em}^5} \left[ \exp \left( \frac{hc}{\lambda_{em} kT(t)} \right) - 1 \right]^{-1} \frac{\pi}{k^2} (K_3 \mu_3 + K_5 \mu_5 + K_6 \mu_6 + K_7 \mu_7) N_d.$$

(B.32)
2. Rayleigh scattering: This assumption is valid when the particles are small and the condition of $\pi d/\lambda \ll 1$ is satisfied.

$$I(t) = \frac{2\pi c^2 h}{\lambda_{em}^5} \left[ \exp \left( \frac{hc}{\lambda_{em} k T(t)} \right) - 1 \right]^{-1} \frac{\pi}{\kappa^2} K_3 \mu_3 N_d$$

$$= \frac{c^2 h}{2 \lambda_{em}^3} \left[ \exp \left( \frac{hc}{\lambda_{em} k T(t)} \right) - 1 \right]^{-1} E(m, \lambda_{em}) \mu_3 N_d. \quad \text{(B.33)}$$

3. Lognormal distribution: This assumption holds good for the unimodal PSDs. For a lognormal distribution with mean diameter $\tilde{d}$ and variance $\sigma^*$

$$I(t) = \frac{c^2 h}{2 \lambda_{em}^3} \left[ \exp \left( \frac{hc}{\lambda_{em} k T(t)} \right) - 1 \right]^{-1} E(m, \lambda_{em}) \left( \frac{\pi \tilde{d}}{\lambda_{em}} \right)^3 e^{4.5 (\sigma^*)^2} N_d. \quad \text{(B.34)}$$

Usually, all the three assumptions are made to obtain the soot volume fraction while transforming the LII signal $I(t)$. This introduces significant error. In the case of scattering experiments, only the first assumption is not made because low energy light does not change the temperature.

![Figure B.2: Temporal decay of the LII signal.](image)
Figure B.3: Temporal decay of a soot particle of radii 20 nm.

Figure B.4: Temporal decay of temperature for different particle sizes.


