CHARACTERIZATION OF PRIMARY PARTICLE SIZE VARIATION AND ITS INFLUENCE ON MEASURABLE PROPERTIES OF AEROSOL SOOT

by

Ramin Dastanpour

B.A.Sc., Isfahan University of Technology, 2008
M.A.Sc., Isfahan University of Technology, 2010

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Mechanical Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

December 2016
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ABSTRACT

Accurate measurement of the properties, emission rates, and environmental impacts (i.e. climate forcing) of aggregated aerosols depend on precise measurement of their morphology (i.e. primary particle diameter, $d_p$, and its polydispersity).

For decades soot has been modeled as fractal-like aggregates of nearly equiaxed spherules. However, examination of the soot particles collected from different combustion environments shows that the larger aggregates contain larger primary particles and the variation in $d_p$ is much smaller within individual aggregates than between aggregates.

In addition to this size dependency, measurements of optical properties of mass-classified soot particles revealed that the mass-specific absorption cross section of soot also depends on particle mass. This along with the correlations observed between $d_p$ and aggregate size, suggest that these aggregates are formed in relatively homogeneous microscopic regions; after which particles with different formation, growth, and oxidation histories are mixed. This suggests that there is a need for accurate estimation of primary particle size distribution and refinement of assumptions commonly used in the conventional simulations and interpretation of the measurements.

Morphology characterization of the agglomerates is commonly performed by labor-intensive manual analysis of the images produced by transmission electron microscopy. A new method has been developed for automatic determination of $d_p$ based on the variation of the 2-D pair correlation function. Results obtained from this method approximately deviate ~4% from the manual method. Application of this method is not limited to the soot particles and it can be applied to any type of the agglomerates.

As an alternative approach, indirect in situ mass-mobility method proposed for the estimation of $d_p$ in zirconia particles has been tested and calibrated for soot particles. It was found that with some calibration, this method can provide results with useful accuracy.

Polydispersity of the primary particles has also been neglected in the previous investigations of the hydrodynamic properties of clusters. It was shown that the mobility-equivalent diameter and the overall size of the agglomerates not only depend on $d_p$ but also increase substantially with its
polydispersity. New correlations were developed for the free-molecular and continuum mobility diameters using stochastic projection and Stokesian Dynamics methods, respectively.
This integrated thesis is primarily based on four manuscripts that have been published in scholarly journals and an article prepared for publication. Permissions for reproduction of the previously published material are obtained from the publishers. Minor changes have been applied to the publications, e.g. numbering of the Figures and Tables, to make the thesis coherent.

A version of Chapter 2 has been published. Dastanpour, R., Rogak, S. N. (2014) “Observations of a correlation between primary particle and aggregate size for soot particles” Aerosol Science and Technology, 48(10), 1043–1049. doi:10.1080/02786826.2014.955565. Online supplementary information published with this article is presented in Appendix A of the dissertation. This chapter contains results obtained from the analysis of soot samples collected from a heavy-duty compression ignition engine, a gasoline direct injection engine, an inverted diffusion flame, and an aircraft jet engine.

- Inverted burner samples were collected and partly analyzed by Hugo Tjong, Arka Soewono, and Dr. Steve Rogak from UBC in collaboration with Rouzbeh Ghazi and Dr. Jason S. Olfert from University of Alberta. The author completed the production of the results and prepared appropriate sections for the manuscript.

- Aircraft jet engine samples were collected by Dr. Steven Rogak during the SAMPLE III.2 campaign conducted at the SR Technics turbine engine test facility in Zurich, Switzerland, from 23 April to 4 May 2012. TEM images were produced for these samples by Hugo Tjong at UBC. The author did the analysis of the images and prepared appropriate sections for the above mentioned manuscript under the supervision of Dr. Steve Rogak. Parts of the results obtained by the author for these samples, which were directly related to this research, were presented in the above mentioned manuscript. Rest of the results were published with collaborators in two other journal articles:


- Gasoline direct injection engine experiments were performed at the University of Toronto in collaboration with Dr. James Wallace, Phillip Mireault, and Manuel Ramos from University of Toronto, and Dr. Jason S. Olfert and Brian Graves from University of Alberta. The author performed the sample collection, analysis, and documentation of the results presented for this engine in chapter 2. These steps were conducted under the supervision of Dr. Steve Rogak. Other collaborators were responsible for running the engine and performing the effective density measurements. Collaborative results obtained from these experiments were presented in the 33rd Annual AAAR conference in Orlando, USA, October 2014.

- Heavy-duty compression ignition engine experiments were performed at UBC in collaboration with Bronson Patychuk from Westport Innovations Inc., and Dr. Jason S. Olfert and Brian Graves from University of Alberta. The author performed the sample collection, analysis, and documentation of the results presented for this engine in chapter 2. Other collaborators were responsible for running the engine and performing the effective density measurements. Collaborative results obtained from these experiments were published in the following article:


were developed by the author and his supervisor, Dr. Steve Rogak. Algorithm implementation was partly performed by the summer student, Jocelyne Boone, supervised by the author and his supervisor. Further development of the algorithm, calibration of the method, and documentation for publication were performed by the author under the supervision of Dr. Steve Rogak.

A version of Chapter 4 has been published. **Dastanpour, R., Rogak, S. N., Graves, B., Olfert, J., Eggersdorfer, M. L., & Boies, A. M. (2015) “Improved sizing of soot primary particles using mass-mobility measurements” Aerosol Science and Technology, 50(2), 101–109. doi:10.1080/02786826.2015.1130796.** Online supplementary information published with this article is presented in Appendix C of the dissertation. The author conducted this study by performing all the data analysis and prepared the manuscript under the supervision of Dr. Steve Rogak. Dr. Jason Olfert and Brian Graves helped in the collection of the experimental data. Dr. Maximilian Eggersdorfer helped by providing numerical aggregates used in the simulations. Dr. Adam Boies also helped with discussions led to the development of the method.

A version of Chapter 5 has been published. **Dastanpour, R., Rogak, S. N. (2016) “The effect of primary particle polydispersity on the morphology and mobility diameter of the fractal agglomerates in different flow regimes” Journal of Aerosol Science, 94, 22–32. doi:10.1016/j.jaerosci.2015.12.005.** Online supplementary information published with this article is presented in Appendix D of the dissertation. The author conducted this study by performing all the simulations and data analysis and prepared the manuscript under the supervision of Dr. Steve Rogak.

A version of Chapter 6 has been accepted to the 35th AAAR conference, Portland, Oct. 2016. **Dastanpour, R., Momenimovahed, A., Thomson, K., Olfert, J., Rogak, S. N. (2016) “Variation of the optical properties of laboratory generated soot with particles mass”**. Experiments were conducted at Measurement Science and Standards at National Research Council Canada in Ottawa. The author developed the experimental plan, analyzed the collected data, and prepared the manuscript under the supervision of Dr. Steve Rogak. Dr. Ali Momenimovahed and Dr. Kevin Thomson helped in the collection of the experimental data. Dr. Jason Olfert helped with discussions and provided insight for the development of the experiments and interpretation of the results.
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LIST OF SYMBOLS

\( a_p \)  Primary particles radius
\( P^* \)  Pair correlation function
\( d_a \)  Diameter derived from aggregate projected area
\( d_m \)  Mobility-equivalent diameter
\( D_f \)  Fractal dimension
\( E_m \)  Refractive index function = \( \text{Im} \left( \frac{(m^2-1)}{(m^2+2)} \right) \)
\( F_m \)  Refractive index function = \( \left| \frac{(m^2-1)}{(m^2+2)} \right| \)
\( K \)  Absorptive index in complex refractive index
\( k \)  Wave number (\( k = \frac{2\pi}{\lambda} \))
\( k_f \)  Fractal prefactor
\( L \)  Aggregate length
\( m \)  Complex refractive index
\( N_p \)  Number of primary particles in aggregate
\( n \)  Refractive index in complex refractive index
\( R_g \)  Radius of gyration
\( x_p \)  Particle size parameter
\( w_0 \)  Single scattering albedo
\( W \)  Aggregate width
\( \alpha_a \)  Absorption coefficient
\( \alpha_e \)  Extinction coefficient
\( \alpha_s \)  Scattering coefficient
\( \sigma_s^a \)  Total scattering cross section for aggregate
\( \sigma_a^a \)  Total absorption cross section for aggregate
\( \sigma_a^p \)  Absorption cross section of individual primary particles
\( \sigma_s^p \)  Scattering cross-sections of individual primary particles
\( \lambda \)  Incident light wavelength
\( \mu \)  Permeability
\( \varepsilon \)  Permittivity
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AIM</td>
<td>Aerosol Instrument Manager</td>
</tr>
<tr>
<td>AFM</td>
<td>Aerosol Flow Meter</td>
</tr>
<tr>
<td>CAPS</td>
<td>Cavity Attenuated Phase Shift</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation Particle Counter</td>
</tr>
<tr>
<td>CPMA</td>
<td>Centrifugal Particle Mass Analyzer</td>
</tr>
<tr>
<td>DDA</td>
<td>Discrete Dipole Approximation</td>
</tr>
<tr>
<td>DICI</td>
<td>Direct Injection Spark Ignition</td>
</tr>
<tr>
<td>DLA</td>
<td>Diffusion Limited Aggregation</td>
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<tr>
<td>DLCA</td>
<td>Diffusion Limited Cluster Aggregation</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analyzer</td>
</tr>
<tr>
<td>DDSCAT</td>
<td>Discrete Dipole Scattering Program</td>
</tr>
<tr>
<td>EGR</td>
<td>Exhaust Gas Recirculation</td>
</tr>
<tr>
<td>GDI</td>
<td>Gasoline Direct Injection</td>
</tr>
<tr>
<td>HPDI</td>
<td>High Pressure Direct Injection</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscope</td>
</tr>
<tr>
<td>IB</td>
<td>Inverted Burner</td>
</tr>
<tr>
<td>LII</td>
<td>Laser Induced Incandescence</td>
</tr>
<tr>
<td>MAC</td>
<td>Mass-specific Absorption Cross section</td>
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<tr>
<td>MEC</td>
<td>Mass-specific Extinction Cross section</td>
</tr>
<tr>
<td>MSC</td>
<td>Mass-specific Scattering Cross section</td>
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<tr>
<td>NNLS</td>
<td>Non-Negative Least Squares</td>
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<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
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<tr>
<td>PCM</td>
<td>Pair Correlation Method</td>
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<tr>
<td>RDG</td>
<td>Rayleigh-Debye-Gans theory</td>
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<tr>
<td>RDG-FA</td>
<td>Rayleigh–Debye–Gans Fractal Aggregate approximation</td>
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<tr>
<td>SMPS</td>
<td>Scanning Mobility Particle Sizer</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<tr>
<td>TPS</td>
<td>Thermophoretic Particle Sampler</td>
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<tr>
<td>UDAC</td>
<td>Unipolar Diffusion Aerosol Charger</td>
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ACKNOWLEDGEMENTS

I would first like to acknowledge my supervisor, Dr. Steve Rogak, for providing invaluable mentorship, technical expertise and encouragements throughout my studies. His inspiration, professional guidance and patience helped me enjoy every moment while working on this thesis. I would also like to thanks my supervisory committee: Dr. Partick Kirchen and Dr. Allan Bertram from UBC, and Dr. Kevin Thomson from National Research Council Canada (NRC), for providing expert opinion and evaluating different parts of this research.

As a part of this research, I was fortunate to collaborate with many researchers across Canada and globally in several measurement campaigns. I would therefore like to thank Dr. Jason Olfert (University of Alberta, Canada), Dr. Kevin Thomson (NRC, Canada), Dr. James Wallace (University of Toronto, Canada), Dr. Adam Boies (University of Cambridge, UK), Dr. Maximilian Eggersdorfer (Novartis Pharmaceuticals, Switzerland), Dr. Ali Momenimovahed (NRC, Canada), Brian Graves (University of Cambridge, UK), Phillip Mireault (General Motors, USA), Manuel Ramos (Ford Motor, Canada), Chris Mabson (UBC, Canada), and Bronson Patychuk (General Motors, Canada) for all their help in the measurement campaigns and related discussions. I also thank Derrick Horne and Bradford Ross (UBC BioImaging Facility) for assistance with the electron microscope; and NSERC CREATE–AAP program for training and two-year fellowship funding.

I am grateful to my lab mates and friends at Aerosol Lab and clean energy research centre, especially Amin Engarnevis, Pooyan Kheirkhah, Jeff Yeo, Jan Laesecke, Jeremy Rochussen, Rene Zepeda, Michael Karpinski-Leydier, Mahdiar Khosravi, and Alexander Sylvester for all their help and advice.

Challenges and difficulties of long days of research and PhD life could have not been conquered without encouragement and support of my lovely friends, Amir Pourmand, Nastaran Hajinazar, and Rajesh Rao.
Last but not least, I am thoroughly thankful to my lovely wife, Shaghayegh, for the enormous sacrifice she made joining me in this journey. Her support, encouragement, quiet patience and unwavering love were undeniably the bedrock upon which my life has been built. I deeply thank my parents for their love, support, and unwavering belief in me. They not only inspired me, but also inspired thousands of students over years of service as teachers. Without them, I would not be the person I am today. I also thank my brother, Reza, who was my strongest support in Vancouver, and my lovely sisters, Mozhgan and Mozhdeh, for their continuous encouragement and kindness.
DEDICATION

To my wife and parents, my inspiration and motivation
Chapter 1

Introduction

1.1 Background

1.1.1 Soot

Aerosol and colloidal aggregates are formed in many industrial and natural environments. Soot, for example, is a cluster of several primary particles formed by incomplete combustion of hydrocarbons. Primary particle and aggregate sizes are usually in the range of 10-60 nm and 20-500 nm [1], respectively. A sample soot particle is shown in Figure 1.1.

Formation and structure of these particles are affected by primary combustion parameters, such as fuel type, concentration, temperature, pressure, oxidizer, and residence time [2,3]. Considering the light absorbing behavior of soot, it is sometimes referred to as “black carbon”.

![Sample image of combustion generated soot particles. Scale bar is 100 nm.](image)

Figure 1.1: Sample image of combustion generated soot particles. Scale bar is 100 nm.

1.1.2 Soot impacts

Soot particles have significant adverse impacts on environment [4] and human health [5]. However, not all soot particles are unwanted. A variation of soot, carbon black, is manufactured
for use in ink and dark rubber industries; and uniform carbon particles are also used for tracking of intracellular processes [6].

With a radiative forcing ranging between 0.5 W m$^{-2}$ and 0.9 W m$^{-2}$, soot is considered as the greatest anthropogenic aerosol contributor to global warming [7–11]. These particles contribute to the climate forcing directly by absorbing part of the incoming solar radiation [12]; and indirectly by decreasing the temperature difference between the Earth's surface and the upper atmosphere, reducing the ambient relative humidity which suppresses the likelihood and shortens the livelihood of cloud formation [13], as well as decreasing snow or ice albedo [14]. Contrary to greenhouse gases, soot has a brief atmospheric lifetime of approximately 6 to 10 days [15] and reduction of its emissions could lead to rapid mitigation of the climate forcing in a short time scale. In spite of the numerous investigations, uncertainties of the net radiative forcing of atmospheric aerosols are still relatively large [12,16]. A large part of these uncertainties is due to the uncertainties in the measurements of the emission rates and properties of the particulate matters.

Carbonaceous particles are also of a great concern due to their negative impacts on health. These particles are known to contain carcinogenic compounds and are responsible for increased morbidity and mortality due to respiratory and cardiovascular disease [5,17,18]. Soot consists of polycyclic aromatic hydrocarbon (PAH) structures which can be mutagenic [19]. Studies have shown that the small particles penetrate deep into the human lung [20,21] and may translocate directly [22] or deliver carcinogenic material indirectly into the blood circulation [23].

### 1.1.3 Soot formation

Thermodynamic stabilization of hydrocarbon molecules is the driving force for soot formation. This process is influenced by fuel type, temperature, pressure, stoichiometry, and time. A combination of gas phase chemistry, coagulation, aggregation, surface growth, carbonization and oxidation occur during the formation and growth of the soot particles.

Soot formation starts with gas-phase chemistry during which the fuel is converted to large PAH molecules. These molecules form the particle nuclei and grow existing particles by deposition. During coagulation, two PAH nuclei intercept in a way that the original structure of one or both particles is lost. However, the structures of both particles are kept unchanged during aggregation which results in the formation of clusters.
In general, aggregation of colloidal particles occurs when particles contact with each other and short-range thermodynamic interactions lead to the attachment of two particles. Brownian diffusion is the main mechanism for the long-range movement of particles of approximately smaller than 100 nm. Depending on the “sticking coefficient”, also known as attachment efficiency, particles coming in contact may attach or repulse. When the sticking coefficient is smaller than one, particles attach to each other after several collisions and form denser and less branched structures. Short-range thermodynamic interactions that control the attachment of the colloidal particles can be understood in the context of Derjaguin-Landau-Verwey-Overbeak (DLVO) theory [24,25]. This theory simplifies thermodynamic surface interactions and predicts the probability of two particles sticking together by summing van der Waals and electric double-layer potentials. Particle collisions will be attractive or repulsive depending on the balance between these two forces. A detailed description of nanoparticle aggregation is available in [26].

Once aggregates are formed, PAH deposition on the surface of the particle may fill the vacant spaces between the primary particles and transforms the cluster into a smoothed primary particle of larger diameter. The rate of the surface deposition decreases as the particles grow.

Depending on the combustion environment, three types of particles may be produced: amorphous particles consisting of randomly oriented PAH molecules; curved particles containing highly curved PAH molecules; and graphitic particles consisting of parallel PAH molecules either in concentrically aligned or straight configurations. Vander Wal and Tomasek [27] and Teini et al. [3,28] found that most of the curved particles are formed in the high temperature combustion, which presumably has higher PAH concentration, and faster soot formation. During the fast formation process, high PAH concentration allows the inception of a large number of small particles. After the inception period, PAH concentration drops and most of the particle growth would be due to the agglomeration and coagulation of these particles. However, amorphous soot is produced in low temperature combustion in which PAH concentration is low and soot formation is slow. During the slow soot formation, a small number of amorphous nascent particle cores are formed. This would be followed by the production of additional PAH molecules which contribute in the growth of the particle cores mostly by surface condensation. Figure 1.2 summarizes the soot formation process.
In summary, structure and properties of soot particles are influenced by the combustion source, fuel type, local concentration of fuel and oxidizer, temperature, and pressure.

![Diagram of soot particle morphology](https://via.placeholder.com/150)

**Figure 1.2:** Cartoon representation of soot particle morphology for slow (left side) and fast (right side) PAH formation (© 2011 Paul Domenic Teini, adapted with permission) [3].

### 1.1.4 Soot morphology

Although soot particles possess different shapes, they are usually modeled as mass fractals. This concept was first introduced by Mandelbrot [29] and developed by Forrest et al. [30]. Fractal structures have self-similarity or scale invariance, based on which, within limits, they appear the same when viewed over a range of different scales. Mass fractal model has been used extensively in the development of simple mathematical descriptions for soot particles [31–35]. Number of the primary particles, $N_p$, can be correlated to the gyration radius, $R_g$, and primary particle radius, $a_p$, using the mass fractal correlation as follows [36]:

$$N_p = k_f \left( \frac{R_g}{a_p} \right)^{D_f} \tag{1.1}$$

where $D_f$ is fractal dimension, and $k_f$ is fractal prefactor. Fractal dimension is a measure of particle compactness, where it is 1 for long chains and has an upper limit of 3 for compact clumps of...
primary particles. $D_f$ and $k_f$ depend on the combustion source and operating condition; however for most cases values of 1.78 and 1.5 to 3.1 are reported for $D_f$ and $k_f$, respectively.

1.1.5 Transmission electron microscopy

Transmission electron microscopy is the most common and well-established measurement method used for direct visualization and characterization of the morphology of soot aggregates. In this method, soot samples are collected onto the small microscope grids. Then images are produced for the samples by either scanning electron microscope (SEM) or, most commonly, transmission electron microscope (TEM). Two dimensional structure of the collected particles can be quantified from these images. Primary particle diameter ($d_p$), aggregate maximum length ($L$) and width ($W$), projected-area equivalent diameter ($d_a$) and two dimensional gyration radius ($R_g$) can be measured from the images produced by TEM. $d_a$ is defined as the diameter of a sphere having the same projected area as the aggregate.

Three-dimensional structure of the aggregates can be resolved by electron tomography [37,38]; however, this method is extremely time-intensive; and also the stochastic nature of the aggregate structure limits the application of this method. As an alternative, three dimensional morphology parameters, e.g. number of primary particles in individual aggregates ($N_p$) and spatial arrangement of the primary particles, are commonly inferred from the 2D images using approximate models [36,39–41].

Soot properties are influenced by its morphology. For example, light scattering and absorption cross sections of soot particles of similar overall sizes are proportional to the 6th and 3rd powers of $d_p$ [34], respectively. Soot toxicity [42,43] is also proportional to its active surface area and consequently $d_p^2$. Its transport and deposition in the respiratory system is also often modeled by the aerodynamic diameter which is influenced by the primary particle diameter (as it influences the average projected area and mobility of these particles). Soot mass also correlates to $d_p^3$. Influence of the morphology on properties of fractal aggregates necessitates its accurate characterization. However, commonly used image processing methods are manual and extremely time-intensive. Development of a simple and robust method and open-source program for automatic determination of average diameter of the primary particles in individual aggregates from
TEM images benefits studies conducted in both fields of combustion generated nanoparticles and aerosol technology.

1.1.6 Emission regulations and soot properties

With the intention of reducing negative impacts of soot on health and environment, stringent regulations have been introduced to control particulate mass and number emissions [44,45]. Implementation of these regulations requires precise measurements, which necessitates good understanding of the soot properties, e.g. its morphology. As an example, a large group of emission measurements are based on the measurement of the light scattering which depends on the spatial arrangement and size distribution of the primary particles [46,47]; light attenuation methods are also sensitive to the primary particle diameter; mobility-based measurements also depend on the primary particle diameter and overall structure of the aggregates aerosols [48]. Consequently aggregate size, primary particle diameter, $d_p$, and its size distribution have strong influence on measurable properties and should be characterized accurately.

Radiative properties of soot [32,34,49–52] and its impact on atmosphere [53] are proportional to the diameters, size distribution, and spatial arrangement of its constitutive primary particles. For example, light scattering and absorption cross sections of soot particles of the same sizes (e.g. gyration diameter) are proportional to the 6th and 3rd powers of $d_p$ [34], respectively. Polydispersity of the primary particle diameter within individual aggregates also influences the overall structure of the particles (e.g. fractal dimension, pre-exponential factor, and gyration diameter) [54,55] and their light scattering behavior [52]. Soot toxicity [42,43,56,57] also correlates to the surface area of these particles and consequently $d_p^2$. Soot mass is also correlated to $d_p^3$. To emphasize more on the importance of the primary particle diameter, it can be shown that for a constant particle mass, 20% increase in the primary particle diameter results in 42% decrease in the number of the primary particles in each individual aggregate and 34% increase in the free molecular mobility diameter. Advanced data inversion and accurate measurement of concentration and size distributions of soot particles [48] also rely on accurate estimation of the primary particle diameter.
1.2 Motivation

Soot radiative and transport properties, and consequently emission measurements and climate models, are influenced by its morphology. As described in the previous section, primary particle diameter has a strong influence on measurable properties of aggregates (e.g. scattering and absorption). Previously, it was assumed that the average primary particle diameter is similar in all soot aggregates generated by a specific combustion source or at a specific operating condition [9,46,58–61]. In other words, aggregates were assumed to be produced from equal-sized primary particles regardless of the size of the aggregates. This assumption has been used extensively in the generation of numerical aggregates and estimation of soot properties such as light scattering. Consequently, in these studies, changes in the size of the particles in an ensemble of aggregates were only reflected by variations in the number of primary particles.

However, a few recent studies have reported the observation of very different average primary particle diameters in aggregates of different sizes. Barone and her coworkers [62] reported images of aggregates produced by a 2.0 liter 4-cylinder Direct Injection Spark Ignition (DICI) engine in which larger aggregates were composed of larger primary particles (see Figs. 6-7 in their article). A similar observation is reported for soot particles produced by a 0.55 liter single-cylinder Gasoline Direct Injection (GDI) engine [63]. Although, none of these studies either confirmed or provided quantitative analysis for the variation of \( d_p \) with the size of the aggregates, reported observations lead to a new plausible hypothesis described in the following paragraphs.

The simplest explanation of the observed variation of \( d_p \) with the particle size is the “external mixing” hypothesis shown in Figure 1.3. Optical diagnostics of combustion process indicate that in a turbulent flame, velocities, temperatures and concentrations of reactants and soot are highly inhomogeneous [64–67]. These non-uniformities, along with the strong dependence of soot formation on local combustion properties described in section 1.1.4, suggest the production of soot with relatively different structures throughout the combustion domain, while similar structures are expected to form in microscopic regions of relatively uniform properties. In such a combustion environment, most of the soot is oxidized as it passes through the stoichiometric surface, and it would be emitted from the flame as small islands with “locally” uniform structures. Typically, coagulation rate of the aggregates decreases by post-flame dilution. As a result, a sample far
downstream of the combustion contains soot morphologies “A” and “B” in separate aggregates, with a small amount of “internal mixing”.

![Figure 1.3: External mixing hypothesis illustrated for a sample flame (© 2016 Steve Rogak, used with permission)](image)

The above-mentioned hypothesis substantially changes the aerosol measurements (e.g. inversion algorithms developed for mobility measurements) and interpretation of soot properties; and highlights the need for the development of new methods for probing the combustion. Existence of a correlation between $d_p$ and aggregate size also implies a need to adjust the traditional soot fractal model, because it would no longer be accurate to assume that aggregates are composed of equiaxed primary particles and their mass is only proportional to the number of primary particles.

The external mixing hypothesis along with the descriptions provided on the soot formation, also suggest performing investigations on the size-dependency of the properties of the soot particles. For example, so far, a constant mass-specific absorption cross section (MAC) has been assumed of soot particles of different diameters. However, external mixing hypothesis suggests different formation and growth histories for small and large particles, which ultimately may result in different graphitization and optical properties for particles of different sizes. This may lead to inaccurate estimation of soot contribution to climate forcing, its properties, and emission rates. Considering the importance of the above-mentioned hypothesis, its validity has to be investigated and quantized thoroughly for different combustion sources. The combined influence of this
hypothesis and the primary particle polydispersity on the hydrodynamic and radiative properties of soot particles has to be investigated.

Transmission Electron Microscopy (TEM) is an *ex situ* method commonly used for the measurement of \(d_p\) and aggregate size. Although this method provides visual observation of the soot particles, quantitative results can only be acquired from this method by time-intensive manual analysis of the micrographs [40]. Development of automated image processing programs or alternative methods for *in situ* estimation of \(d_p\), its size distribution, and aggregate size is essential in the investigation of the external mixing hypothesis. Application of these methods may not only be limited to the soot particles, but would also benefit investigations of all sort of the agglomerated aerosols.

### 1.3 Research objectives

Considering the motivations described in the previous section, this research aims to accomplish the following objectives:

- Investigating the correlation between primary particle size and the size of the aggregates for different combustion environments. This comprehensive study requires taking samples from several operating conditions of different pre-mixed and non-premixed combustion sources. Using TEM analysis, the variation of \(d_p\) with the particle size can be characterized.
- Developing an automated image processing program for accurate analysis of the TEM images and *ex situ* morphology characterization of aggregate properties.
- Developing an *in situ* method for the estimation of average primary particle diameter in aggregates.
- Investigating the effect of the primary particle polydispersity and its mixing state on the morphology and hydrodynamic properties of the agglomerates\(^1\) in different flow regimes.

\(^1\) Agglomerates are commonly defined as clusters of point touching primary particles while aggregates are defined as clusters of primary particles with some levels of monomer overlap. In spite of the definition differences, aggregate and agglomerate are used interchangeably in aerosol community.
• Investigating the size-dependent optical properties of soot particles. External mixing hypothesis suggests the existence of correlations between the primary particle diameter and radiative properties of soot particles with aggregate size.

1.4 Thesis outline

Motivated by the objectives mentioned in section 1.3, this dissertation is divided into six further chapters.

In chapter 2, the existence of a correlation between the primary particle and agglomerate diameters is confirmed through extensive analysis of TEM images produced for different combustion sources. The strength of this correlation and its influence on aerosol studies are discussed in this chapter. Polydispersity of the primary particles within individual agglomerates and ensembles of particles are also measured and compared.

Chapter 3 describes a new algorithm developed for automated measurement of the average primary particle diameters from TEM images. The accuracy of the method is investigated for both numerically generated agglomerates of point-touching primary particles and real soot particles. The influence of the primary particle overlap on the accuracy of the method is discussed and the method’s potential for the measurement of the this coefficient is described.

In chapter 4, the accuracy and validity of an in situ method developed for the measurement of the primary particle diameter of zirconia particles is investigated for carbon soot. This method is based on mass and mobility measurements and does not require time-intensive sample collection and production of the TEM images. This method is also calibrated for carbon soot and is shown to provide results with reasonable accuracy.

Chapter 5 describes the influence of the primary particle polydispersity and internal and external mixing scenarios on the structure and hydrodynamic properties of the fractal agglomerates. Numerically-generated clusters of point-touching primary particles with different levels of the primary particle polydispersity are used in this study. Variation of the gyration radius, surface area, mass, and mobility diameters in the free-molecular and continuum regimes are investigated numerically and new correlations are developed for the estimation of the mobility diameters based on the agglomerate morphology.
Chapter 6 describes experimental results obtained for the optical properties of the mass-classified particles generated by a laboratory flame. Variations of the mass-specified extinction, absorption, and scattering cross sections, as well as the single scattering albedo of the particles with mass are investigated in this chapter. Variation of the primary particle and agglomerate diameters are also investigated through TEM analysis.

Finally, Chapter 7 summarizes the results and provides recommendations for future work.
Chapter 2

Observations of a correlation between primary particle and aggregate size for soot particles

2.1 Introduction

For decades, soot has been modeled as fractal-like aggregates of nearly equiaxed spherules. Cluster-cluster aggregation simulations, starting from a population of primary particles, give rise to structures that closely match real aerosols of solid particles produced in flames. In such simulations, primary particle size is uncorrelated with aggregate size, as all aggregates contain primary particles drawn from the same population. Aerosol measurements have been interpreted with this geometric model. However, as described in section 1.2, TEM images of soot aggregates with larger primary particles within larger soot aggregates have been reported in a few studies [62,63]. Similar observations along with quantitative results have been reported for inverted burner soot; and it was also shown that if $d_p$ scales as $d_A^n$, the mass-mobility exponent of the particles, $D_m$ (defined from $m \propto d_m^{D_m}$), will be increased by approximately $n$ [68].

The effect of primary particle polydispersity on the fractal dimension of soot aggregates has been investigated before [69], but by the nature of the simulation, it was assumed that large and smaller primary particles were equally likely to be present in aggregates of all sizes. As far as the author knows, this is consistent with previous experimental and theoretical treatments of primary particle polydispersity. This is, however, inconsistent with two widely known features of soot formation. Firstly, in premixed systems, the primary particle size varies systematically with residence time and stoichiometry [70]. Secondly, in most engineered combustion systems, soot is formed only in

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1 A version of this chapter has been published: “Aerosol Science & Technology: Observations of a correlation between primary particle and aggregate size for soot particles.” 48(10): 1043-1049. Copyright 2014. Reston, VA. Reprinted with permission.” Online supplementary information published with this article is presented in Appendix A of the dissertation.
a tiny fraction of the system volume, usually in turbulent conditions with large fluctuations in local
stoichiometry and time spent in conditions favourable to soot formation. Particles formed in
different combustion regions experience different formation and growth patterns, e.g. local
equivalence ratio and residence time. The size of the primary particles and agglomerates forming
in a combustion process depends on the interplay of complex formation and evolution mechanisms
including nucleation, coagulation, surface growth, carbonization, oxidation, and sintering [71–74].
Typically, surface growth and coagulation prior to carbonization lead to larger more spherical
particles. Soot formation processes depend very strongly on both local equivalence ratio and local
temperature.

Here, TEM results obtained from the analysis of thousands of aggregates and primary particles
sampled from multiple operating conditions of three non-premixed and one (imperfectly) premixed
combustion environments are compiled. The variations of $d_p$ in aggregates of different sizes, the
effect of shielding on primary particle sizing from TEM images and the variations in primary
particle size are investigated.

## 2.2 Experimental setup for TEM sampling

Soot samples from two types of reciprocating engines, a jet engine, and the inverted burner were
collected on TEM grids using thermophoretic particle sampler (TPS).

Gasoline Direct Injection (GDI) engine: TEM samples taken from this engine (Ford 2.0 Liter,
inline 4 cylinder) cover two types of fuel (gasoline blended with 0% and 30% ethanol) and four
sets of operating conditions. Operating conditions include transient cold start and hot start tests,
simulated highway cruise condition (2600 RPM and 40 lb.ft of torque), and a higher speed and
lower torque setting (3000 RPM and 28 lb.ft). Exhaust was diluted using a TSI 379020A two-stage
rotary disk diluter. Detailed description of the experimental setup is described in [75]. Soot
samples were collected from either denuded or undenuded streams. In total 17 sets of soot samples
were considered in TEM analysis of soot particles for this source.

High Pressure Direct Injection (HPDI) natural gas engine: Particles were collected from a 15 liter,
6-cylinder, Cummins ISX engine operating with Westport Innovations HPDI natural gas
combustion system. HPDI uses a diesel-pilot to ignite jets of natural gas; performance and
emissions are closer to a diesel engine than a pilot-ignited fumigation engine. The engine was operated on a single cylinder (5 cylinders were deactivated) at 15 different conditions. Engine speed, load, EGR and fumigation were varied in these operating conditions. The exhaust gas was diluted with a ratio of approximately 10:1. In total 14 sets of soot samples were considered for this engine.

Aviation gas turbine (JE): Soot particles were generated by a 120 kN thrust General Electric CFM56-5B4-2P turbofan engine at various engine speeds. All samples were collected downstream of a long (12 m) heated tube at 160°C. In total, 11 sets of samples collected at engine speeds varying in the range of 1000 to 4500 rpm were considered for this engine. Detailed description of the experimental setup is described in [76,77]

Laminar Inverted Burner (IB): Soot samples were collected from an inverted burner fed with methane and operated at 8 different global equivalence ratios. Detailed description of the experimental setup is described in [68]. In total, 8 sets of soot samples were considered for this burner.

2.3 TEM imaging and image processing

TEM imaging was performed on the soot samples using a Hitachi H7600 transmission electron microscope operating at 80.0 kV and equipped with an AMT CCD camera. Images were taken at either high resolution or high contrast modes. Images considered in size characterisation were collected under optimum optical focus with nominal resolution of 0.2 nm and typical magnifications in the range of 100,000-500,000 times using QuartzPCI software.

Images were taken at different locations on the center and around the grid. Human bias was also reduced by a random selection of the individual aggregates for imaging.

TEM images were analyzed using a semi-automatic MATLAB-based image processing program described in the Appendix A. Aggregate size was characterized using the binary images produced from the grayscale TEM images with the thresholding technique, and primary particle diameters were measured manually.
2.4 Results and discussion

2.4.1 Qualitative observations

Sample TEM images of soot particles collected from the combustion sources considered in this research are illustrated in Figure 2.1. Each panel of this image corresponds to one combustion source operating in steady state. For each combustion source, aggregates with very different primary particle diameters are shown in this figure.

Figure 2.1: Sample TEM images of aggregates with different primary particle sizes. All scale bars are 100 nm.

In these images an increase in primary particle size with aggregate size can be observed. However, considering the statistical uncertainties, the existence of such a correlation can only be verified by quantitative analysis of thousands of aggregates and primary particles. Additionally, these images show that primary particle sizes may be more uniform in individual aggregates than an ensemble of the aggregates- but this too is to be verified statistically, as shown below.

2.4.2 Primary particle and aggregate sizing

The total number of the TEM images produced, and number of the aggregates and primary particles measured for each combustion source are summarized in Table 2.1.
Table 2.1: Number of TEM images and particles considered

<table>
<thead>
<tr>
<th>Source</th>
<th>Number of images produced</th>
<th>Number of aggregates analyzed</th>
<th>Number of primary particles analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDI engine</td>
<td>670</td>
<td>554</td>
<td>6516</td>
</tr>
<tr>
<td>HPDI engine</td>
<td>332</td>
<td>584</td>
<td>4030</td>
</tr>
<tr>
<td>Aviation gas turbine</td>
<td>351</td>
<td>292</td>
<td>1279</td>
</tr>
<tr>
<td>Inverted burner</td>
<td>144</td>
<td>180</td>
<td>$&gt;1608^1$</td>
</tr>
</tbody>
</table>

TEM results obtained from the analysis of these images are illustrated in Figure 2.2. Each point on this plot corresponds to the average diameter of primary particles and projected-area equivalent diameter of one aggregate. Variations within individual aggregates are discussed in the next section. To avoid complexity, results obtained from different operating conditions of each combustion source are grouped together.

Figure 2.2: The variation of average primary particle diameter (in individual aggregates) vs. aggregate projected-area equivalent diameter.

---

$^1$ - This number corresponds only to the primary particles counted in 89 (out of 180) aggregates. Inverted burner samples were analyzed prior to other samples and intermediate image processing results are not available for all equivalence ratios.
Although for each aggregate size range, a distribution of $d_p$ is present, in general the average primary particle size increases with aggregate size. As illustrated assumption of a constant average primary particle diameter for each of these combustion sources is a poor representation of data. For the GDI engine, the average $d_p$ in individual aggregates increases from approximately 5 nm to 40 nm with aggregate projected-area equivalent diameter increasing from 8 nm to 700 nm. Soot samples collected from HPDI engine, aviation gas turbine and inverted burner show similar trends. This confirms considerable increase in average primary particle size (for the cases investigated here, about 4-6 times increase in size) when aggregate size increases in an ensemble of aggregates (the aggregate size range is almost 10 times larger than primary particle size range). These differences are too large to be explained by artifacts of TEM resolution (image processing program used for these measurements enables operators to zoom on different sections of images for accurate measurements. Consequently, human detection errors are approximately similar for both large and small particles. Moreover, all images were produced at high magnifications providing resolutions better than 0.7 nm/pixel and much smaller than primary particle sizes). These differences cannot also be explained by the physical constraint that $d_p$ cannot exceed $d_a$ (most aggregates have many primary particles, so $d_a >> d_p$). Similar trends were observed for most individual operating conditions, but in each case the scatter is too large to develop accurate correlations.

### 2.4.3 Primary particle polydispersity

The geometric standard deviation of primary particles for the whole ensemble of aggregates ($\sigma_{g,p,ens}$) is defined here as:

$$\sigma_{g,p,ens} = \exp\left(\sqrt{\sum_{i=1}^{N_{p,ens}} \frac{(\ln \frac{d_{p,i}}{d_{pg,ens}})^2}{N_{p,ens}}}\right)$$

(2.1)

where $N_{p,ens}$ and $d_{pg,ens}$ are the total number and geometric mean diameter of all primary particles measured in an ensemble of aggregates, respectively. This measure of size variation does not consider whether primary particles may be connected within the same aggregate. For all aggregates from a sample, this measure of variation in an ensemble is in the range of approximately 1.25 to 1.7.
The polydispersity of the primary particles within individual aggregates ($\sigma_{g,p,agg}$) can be characterized by

$$\sigma_{g,p,agg} = \frac{1}{N_{agg}} \sum_{j=1}^{N_{agg}} \exp \left( \sqrt{ \frac{\sum_{i=1}^{N_{p,j}} (\ln \frac{d_{p,i}}{d_{pg,j}})^2}{N_{p,j}} } \right)$$

(2.2)

where $N_{p,j}$ and $d_{pg,j}$ are the total number and geometric mean diameter of all primary particles in $j$th aggregate. $N_{agg}$ is total number of aggregates measured in each ensemble of particles.

As illustrated in Figure 2.3, primary particles are more uniform in individual aggregates than ensembles of aggregates. In this figure, each symbol is the result of analysis of hundreds of images obtained for each combustion source and operating condition. This is consistent with the correlation of $d_p$ with $d_a$ shown in Figure 2.2.

Figure 2.3: Geometric standard deviation of primary particles in ensembles of aggregates vs. individual aggregates. Each point on this graph corresponds to $\sigma_{g,p,ens}$ and average $\sigma_{g,p,agg}$ for an individual operating condition. Solid line shows 1:1 ratio for the x axis and the y axis.

A higher level of primary particle polydispersity in ensembles of soot particles is attributed to the heterogeneous distribution of combustion charges in macroscopic scales of the combustion

$^1$ The average primary particle diameter of each individual aggregate is correlated to $d_{pg}$ and $\sigma_{g,p,agg}$ by $d_p = d_{pg} \exp(\ln^2 \sigma_{g,p,agg} / 2)$. 
domain. However, primary particles mainly form in microscopic scales where combustion charge is relatively homogeneous. Consequently, the observation of large aggregates composed of relatively uniform large primary particles might be correlated to the agglomeration of these primary particles in microscopic rich (and hot) regions favorable for primary particle formation. Similarly, smaller aggregates composed of smaller primary particles are formed in small lean regions of the combustion.

Average $\sigma_g$ of the primary particles in ensembles of aggregates was found to be approximately equal to 1.15 for particles produced by a premixed McKenna burner [78]. Although the different sampling, microscopy and analysis procedures in that work might make precise comparison with our work difficult, it is interesting that the premixed laboratory flame, with particles all sampled at a single residence time, show a far narrower primary particle size distribution than shown by any of the systems studied in our work.

2.4.4 Potential sampling and image analysis artifacts

Sampling and TEM imaging could produce several artifacts which would be investigated now. Firstly, the sampler may produce unrepresentative samples. All samples discussed here were collected from a heated stream directed at a cold TEM sample grid. The main mechanism of deposition is thermophoresis, but impaction is significant for large particle. In particular, for the jet engine and inverted burner samples, velocities were large enough to result in oversampling of aggregates with large aerodynamic diameters (those larger than about 200 nm). Conceivably this could bias large-aggregate sampling towards larger primary particles, but the other samples were collected with much lower velocities, and in any case, impaction cannot explain the observations related to Figure 2.3. For the HPDI and GDI samples, it is confirmed that TEM aggregate sizes are very close to those determined by mobility sizing, so samples are representative of the aerosol.

Several artifacts could arise in the microscopy. Operator bias in selecting aggregates for imaging might be a concern; this has been addressed by imaging all particles in randomly located portions of the grid. Variations in magnification might make smaller primary particles less visible when imaging large aggregates, but in our work, images are produced at high magnification which provides resolutions better than 0.7 nm/pixel and smaller than primary particle sizes. Moreover, primary particle sizing in large aggregates was done by breaking aggregates into smaller sections,
by zooming on different parts of the particles, which eliminates the effect of image magnification on the probability of the smaller primary particles being excluded from measurements.

Finally, a fundamental projection artifact will be considered. This might occur if smaller particles are more likely to be covered by large particles in images of large aggregates. This effect is investigated here using computer generated aggregates with non-uniform primary particle size; these aggregates were donated by Eggersdorfer and Pratsinis [69]. This effect is investigated using 1200 aggregates numerically generated by hierarchical cluster-cluster agglomeration algorithm described in [79]. These aggregates consist of 16, 32, 64, and 128 polydisperse primary particles with $\sigma_{g,p,agg} = 1.4$. For better simulation of polydispersity effect, the value assumed here for the geometric standard deviation of primary particles in individual aggregates is larger than what was measured for “individual” aggregates and is closer to values measured for “ensembles” of aggregates ($\sigma_{g,p,ens}$).

TEM images were simulated by projecting aggregates in three different orientations. Average diameter ($d_p$), geometric standard deviation ($\sigma_g$), and total number of the primary particles ($N_p$) in individual aggregates which can be detected and measured were calculated from the simulated TEM images. A detailed simulation of the TEM image formation resulting in a greyscale intensity being related non-linearly to soot thickness was not attempted here. Instead, simplified algorithms were used to estimate what would be observable by normal operators.

As an extreme case, primary particles are assumed to be opaque. This means that the area of a primary particle which is placed beneath other primary particles cannot be observed in projected images (complete shielding). Moreover, if more than 50% of the area of the primary particle is completely shielded it is assumed that the primary particle size cannot be measured. A second model assumes primary particles to be partially transparent and is further discussed in Appendix A.

Differences between the measured and actual $N_p$ and $d_p$ are measured by normalized parameters defined by equations 2.3 and 2.4. Aggregate size is indicated by projected area-equivalent diameter $d_a$, normalized by the mean primary particle diameter $d_p$. Results obtained for $\Delta N_p$ and $\Delta d_p$ are illustrated in Figures 2.4 and 2.5. Results acquired for these parameters and variations in $\sigma_g$ are compared for the two shielding criteria in Figures A.1 to A.3 in Appendix A.
As expected and shown in Figure 2.4, as the aggregate size increases, a larger fraction of the primary particles are shielded. Figure 2.5 shows that the size of the primary particles “measured” from projected images are slightly larger than actual values. This means that shielding results in slightly overestimation of the primary particle sizes from TEM images. However, even for large aggregates, this overestimation is about 2% of the actual size of the primary particles. This small shielding effect is negligible comparing to 4-6 times changes in primary particle size with aggregate size, as illustrated in Figure 2.2. It confirms that the trends illustrated in Figures 2.2 and 2.3 are not artifacts caused by shielding of the smaller primary particles with larger ones.

\[
\Delta N_p = \frac{N_{p,\text{meas}} - N_{p,\text{act}}}{N_{p,\text{act}}} 
\]  

(2.3)

\[
\Delta d_p = \frac{d_{p,\text{meas}} - d_{p,\text{act}}}{d_{p,\text{act}}} 
\]  

(2.4)

Figure 2.4: Effect of shielding on the number of primary particles detectable on projected images.
Figure 2.5: Effect of shielding on the average primary particle diameter in individual aggregates detectable on projected images.

2.5 Conclusions

Based on analysis of hundreds of TEM images from three non-premixed and one (imperfectly) premixed combustion systems, there is a correlation between primary particle and aggregate size. It was shown that although a range of the primary particle diameter was measured for each particle size, larger aggregates are mainly composed of larger primary particles. Moreover, the primary particles are more uniform in individual aggregates than in ensembles of aggregates. These results cannot be explained by the sampling, projection and image analysis artifacts considered here.

These variations in primary particle size are consistent with the aggregates being formed in relatively homogenous microscopic regions; after formation and growth, aggregates from different regions, with different soot formation patterns and/or residence time, are mixed.

Many aerosol properties depend non-linearly on both primary particle and aggregate size; therefore, it may not be appropriate to assume that all aggregates are formed from primary particles with the same size distribution. The correlation between primary particle size and aggregate size implies a need to adjust the traditional fractal model, because it would no longer be accurate to assume that aggregate mass is proportional to the number of primary particles.
It seems likely that the variations in primary particle size would be different for different sources, but the time involved in manual TEM analysis makes it difficult to provide quantitative measurements that can distinguish these sources.
Chapter 3

Automated primary particle sizing of nanoparticle aggregates by TEM image analysis

3.1 Introduction

Aerosol and colloidal aggregates are formed in many industrial and natural environments. These nanoparticle aggregates can be either useful or hazardous. Soot, for example, is formed by incomplete combustion of hydrocarbons; and has significant adverse impacts on human health [5] and climate [4,14]. The morphology of the aggregate influences its environmental impacts, and its transport and radiative properties; and primary particle diameter \(d_p\) is one of the most important morphological parameters of nano-clusters.

Production rate and properties of synthetic particles, and accurate measurement of emission rate and size distribution of fractal aggregates depend on accurate estimation of the morphology of these particles and sizing of their constitutive primary particles. Radiative properties of soot [32,34,49,50,80] and its impact on atmosphere [53] are not only influenced by the overall size of the particles, but are also non-linearly proportional to the diameters and size distribution [47] of its constitutive primary particles. For example, light scattering and absorption cross sections of soot are proportional to the 6\(^{th}\) and 3\(^{rd}\) powers of \(d_p\) [34], respectively. Soot toxicity [42,43] is also correlated to its active surface area, and consequently \(d_p^2\). Its mass is also correlate to the 3\(^{rd}\) power of \(d_p\). Additionally, the overall size of the particles is also influenced by the primary particle diameter and its size distribution [54,55]. Advanced data inversion and accurate measurement of concentration and size distributions of soot particles using Scanning Mobility Particle Spectrometers (SMPS) [48] rely on accurate estimation of the primary particle diameter.

\[d_p^2\]

Combined light scattering and absorption measurements were used by Sorensen et al. [81] to estimate $d_p$. However, this approach requires prior information on the fractal dimension and optical properties, e.g. refractive index, of soot particles. Light depolarization has also been used for the measurement of $d_p$; however, the method has been shown to be sensitive to the fractal dimension, refractive index, and a few other morphology parameters of soot [82]. Laser-Induced Incandescence (LII) is another method which uses cooling rate of the soot particles to measure primary particle size [80,83]. This model is also highly sensitive to soot chemical composition and morphology. Eggersdorfer et al. [84,85] have proposed a method for sizing of the primary particles in Zirconium aggregates using particle mass and mobility diameter. This method is extended to carbon soot particles by Dastanpour et al. [86] (chapter 4 of this dissertation).

Transmission Electron Microscopy (TEM) of particles collected on a microscope grid provides visual observation of the soot particles and is commonly used for morphology characterization of nano-particles [1,36,43,75–77,87–91]. Statistically reliable results can only be acquired from this method when a great number of images are analyzed. Primary particle diameters are commonly measured manually [40,87] from digitized TEM images; and this manual sizing is an exceedingly time-intensive process.

Grishin et al. [92] have used Hough transform in the analysis of the TEM images for automatic determination of primary particle size distribution in individual aggregates. However, accurate results can only be acquired when prior information on the size range of the primary particles in each aggregate is known. This model can only detect primary particles touching the edge of the aggregate and relies on the assumption of perfectly spherical structures for primary particles. Testing this method on samples from a Gasoline Direct Injection (GDI) engine (described below), we found that the accuracy of this model is extremely sensitive to the fitting parameters. For example, by changing the engine operating condition an increase of approximately 4 nm in primary particle diameter was measured from manual analysis of the TEM images; however the automatic method only showed an increase of less than 1 nm in primary particle size. Accurate measurement of the primary particle diameter by this method requires algorithm calibration for each individual TEM image.

In another automated sizing algorithm [93], the Euclidian Distance Mapping Surface-Based Scale Analysis (EDM-SBS) was used for automatic sizing of the primary particles. However, the
influence of particle size on the accuracy of the method has not been investigated. De Temmerman et al. [94] have developed a semi-automatic image processing method in which the primary particles are detected on binarized TEM images by watershed segmentation and their sizes are measured using EDM. Their method is not limited by the assumption of spherical structures for primary particles and monomers should not necessarily be located on the perimeter of the clusters.

A simple and robust method for automatic determination of average diameter of the primary particles in individual aggregates has been developed here and then tested on numerical agglomerates of point touching primary particles and soot aggregates formed at different operating conditions of two reciprocating engines. This method can be used as an alternative approach for automatic measurement of the primary particle diameters in individual\(^1\) and ensembles\(^2\) of agglomerates.

### 3.2 The Pair Correlation Method (PCM)

This method uses the 2-D pair correlation function to estimate \(d_p\). The pair correlation function \(P(r)\) is a weighted average of the particle density at a given radius \(r\) [95]. For binary images, this function estimates the probability of finding another pixel at a distance \(r\) from a reference pixel:

\[
P(r) = \lim_{dr \to 0} \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\theta(r_{ij})}{2\pi r dr}
\]

where \(\theta(r_{ij}) = 1\) for \(r_{ij} < r + dr\) and \(\theta(r_{ij}) = 0\) elsewhere, \(r_{ij}\) is the distance between pixels \(i\) and \(j\), and \(N\) is total number of the pixels within the projected region of the particle. At small distances, \(P(r) \to 1\); at distances comparable to the aggregate dimensions it falls to zero.

Simple Pair Correlation Method (PCM) developed here is based on the assumption that \(P^* = P(d_p/2)\) is nearly constant for all soot particles. First, the value of \(P^*\) is measured for aggregates with known primary particle diameter. To this end, synthetic TEM images were produced by random projections of straight chains of monodisperse primary particles and numerical fractal

\(\text{\textsuperscript{1}}\) Average primary particle diameter for each aggregate.

\(\text{\textsuperscript{2}}\) Average primary particle diameter in the whole ensemble of aggregates. This is the average of the mean primary particles measured for each individual aggregate.
agglomerates with different levels of primary particle polydispersity and overlap. This parameter was also measured for real TEM images using manually measured primary particle radius. $P(r)$ was calculated for all synthetic and real TEM images, and its value at the known primary particle radius ($P^*$) was measured. Finally, a constant value was selected for $P^*$ by averaging $P(d_p/2)$ measured for individual synthetic and real TEM images.

Once $P^*$ is known, PCM can be used for the calculation the average diameter of the primary particles in both synthetic and real TEM images. This method consists of three main steps. First, the portion of the image corresponding to the projection of each individual aggregate should be detected. To this end, real TEM images were automatically binarized using Otsu’s algorithm for thresholding [96] and rolling ball transformation [92]; and synthetic images were scanned pixel-by-pixel. Second, $P(r)$ should be calculated for each aggregate. In order to reduce computational costs, but still preserve the structure of the aggregates, values of the pair correlation function (PCF) were computed at different distances $r$ from the reference points on the skeleton of the particles. The particle’s skeleton was detected using MATLAB built-in function “bwmorph” and operation algorithm “thin”. This operation removes pixels on the boundaries of the projected binary image without breaking the particle. Skeleton and $P(r)$ curve of a sample TEM image are illustrated in Figure 3.1. Finally, average radius of the primary particles will be the radius at which $P(r)$ is equal to $P^*$ (Fig. 3.1, panel d).

Figure 3.1: (a) Sample TEM image of real soot; (b) its skeleton; (c) $P(r)$; (d) detail of $P(r)$ around $P^*$ and $r_p$. 

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3.3 Images used for PCM development and validation

3.3.1 Numerical agglomerates

The PCM was first developed using numerical particles including straight chains and three-dimensional fractal agglomerates. Straight chains were composed of monodisperse primary particles of point-touching primary particles (overlap coefficient\(^1\) \(C_{ov}=0\)). The total number of the primary particles \((N_p)\) in chains was varied between 1 and 100. Fractal agglomerates were generated by Eggersdorfer and Pratsinis [69]. The agglomerates were produced by a cluster-cluster agglomeration algorithm [69,79] and consisted of 16, 32, 64, 128, 256, and 512 primary particles. Fractal prefactor, \(k_f\), of the generated particles was approximately constant and equal to 1.4 while the fractal dimension, \(D_f\), decreased from 1.78 to 1.73 as the primary particles polydispersity increased from 1 to 1.6, consistent with the results obtained by Eggersdorfer and Pratsinis [55] for particles generated by the DLCA algorithm. Diameters of the primary particles were selected randomly from log-normal distributions with \(\sigma_g\) values of 1.0, 1.2, 1.4, and 1.6. Considering the range of the values reported for the overlap coefficient of soot in literature [36,97,98], three different cases of \(C_{ov}=0\) (point-touching primary particles), \(C_{ov}=0.1\), and \(C_{ov}=0.3\) were considered for each \(N_p\) and \(\sigma_g\). The range of the parameters considered here covers a large group of fractal structures ranging from gold nanochains to zirconia and soot aggregates. Ten aggregates were generated for each \(N_p, \sigma_g\), and \(C_{ov}\), and 50 random synthetic TEM images were produced for each aggregate, a total of 36,000 synthetic images. A sample numerical agglomerate and the corresponding synthetic TEM image is illustrated in Figure 3.2.

\(^1\) \(C_{ov} = \frac{(d_{p,ij} - D_{ij})}{\bar{d}_{p,ij}}\), where \(\bar{d}_{p,ij}\) and \(D_{ij}\) are the average diameter and center-to-center separation distance of two adjustment primary particles of \(i\) and \(j\), respectively.
3.3.2 Images of engine exhaust particulate

Soot particles were collected from several operating conditions of two reciprocating engines. A Ford 2.0 Liter, inline 4-cylinder GDI engine was run with three types of fuel (gasoline blended with 0%, 10%, and 30% volumetric ratio of ethanol: E0, E10, and E30, respectively). Operating conditions of this engine include transient cold start (CS) and hot start (HS) tests, simulated highway cruise (C) condition (2600 RPM and 58 N.m torque), and a higher speed and lower torque (S) setting (3000 RPM and 38 N.m torque). Another set of samples was collected from a 15 liter, 6-cylinder (5 cylinders were deactivated), Cummins ISX High Pressure Direct Injection (HPDI) engine operating with Westport Innovations HPDI natural gas combustion system. This engine was run at five different operating modes including 25, 37, 50, and 75 percent of maximum load at an engine speed of 1500 rpm (B25, B37, B50, and B75). Lower load test points were operated at 20% exhaust gas recirculation (EGR) while the highest load (B75) test point was ran at 25% EGR. Engine was also run at 63% maximum load and a lower speed of 1200 RPM at 0% EGR (A63). Soot samples were deposited thermophoretically on TEM grids and images were produced by a Hitachi H7600 transmission electron microscope operated at 80 kV under high resolution mode. Details of the experiments and sampling procedures are further discussed in [75,99]. Several studies have shown that soot from combustion sources, unless it has been collapsed by substantial coatings (not the case here) has a fractal dimension, \( D_f \), close to 1.8 [100,101]. Soewono studied the fractal dimension from one of the test engines here (the HPDI engine) and found only subtle variations in \( D_f \) [102,103].
3.4 Results and discussion

3.4.1 Numerical aggregates

Each of the numerically-generated chains and fractal agglomerates were projected randomly into 50 different orientations\(^1\) (500 images for each set of \(N_p\), \(\sigma_g\), and \(C_{ov}\) for fractal aggregates and 50 images for each chain size). Synthetic binary images were produced by Monte Carlo approach: each particle was scanned by rays in Z direction emerging from every single point on the X-Y plane. Once the binary images were produced, skeleton of the projected particle was detected and pair correlation function was computed at distances \(r\) from the skeleton of each image using Eq. (3.1); and values of \(P^*\) were calculated at the known average \(\bar{r}_p\).

Variation of the average \(P^*\) with the particle size \((N_p)\) is illustrated in Figure 3.3 (left panel) for chains and fractal agglomerates of point-touching primary particles \((C_{ov}=0)\). The effect of the overlap coefficient on \(P^*\) of the fractal aggregates is reported in Table 3.1 and illustrated in Figure 3.4. In Figure 3.4, the horizontal axis is the ratio of the projected area-equivalent diameter to the gyration diameter, \(d_a / d_g\). This ratio decreases with \(N_p\) for \(D_f < 2\), and unlike the fractal dimension, is obtained directly from the image without any assumptions.

As illustrated in Figures 3.3 (left panel) and 3.4, \(P^*\) increases with \(N_p\), \(\sigma_g\) and \(C_{ov}\). As particles become larger, a greater portion of the primary particles are shielded by other primary particles which ultimately results in slower decrease of the value of the pair correlation function with \(r\) and a larger value for \(P^*\). As \(C_{ov}\) increases, the average thickness (distance between the skeleton and the edge) of the projected particle also increases; which ultimately results in an increase in the value of \(P^*\).

\(^1\) To insure the accuracy of the algorithm, ten particles were selected and projected randomly into 50 different orientations. Measured average \(P^*\) was consistent (<0.01 deviation) with those obtained from 20 projections.
Figure 3.3: $P^*$ of straight chains and agglomerates of point-touching primary particles with different sizes and polydispersity (left panel); measurement error of PCM (right panel). Each point represents the average of the desired parameter over 50 synthetic images for chains and 500 synthetic images for agglomerates.

Table 3.1: $P^*$ for agglomerates of different $N_p$ and $\sigma_g$

<table>
<thead>
<tr>
<th>$\sigma_g$</th>
<th>$C_{ov}$</th>
<th>$N_p=16$</th>
<th>$N_p=32$</th>
<th>$N_p=64$</th>
<th>$N_p=128$</th>
<th>$N_p=256$</th>
<th>$N_p=512$</th>
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$^1$ Standard deviation of the reported $P^*$ varies between 0.01 and 0.05 for large and small $N_p$, respectively.
Figure 3.4: Effect of $C_{ov}$ on $P^*$ of aggregates of different sizes and polydispersity.

As $N_p$ increases, $P^*$ approaches 0.7 ($N_p \leq 100$) for chains of monodisperse primary particles. Average $P^*$ varies between 0.84 to 0.95 for aggregates of different $N_p$, $\sigma_g$ and $C_{ov}$. Its average varies between 0.89 and 0.93 for aggregates of $\sigma_g \approx 1.2$ and $C_{ov}$ in the range of 0.1 and 0.3; which are the most probable primary particle polydispersity (Fig.3 of [87]) and overlap coefficients [36,97,98] for real soot aggregates. Compared to chains, fractal agglomerates have a branched structure and more particle overlap in projected images, which might explain the larger $P^*$.

As reported by Dastanpour and Rogak [54] (chapter 5 of this dissertation), the gyration diameter of the fractal agglomerates increases with the polydispersity of the primary particles. Accordingly, $P^*$ is also expected to increase with $\sigma_g$, but results here show that the effect is small for large aggregates. The effect of $\sigma_g$ on $P^*$ can be estimated for numerical agglomerates of point-touching primary particles using the following correlation ($R^2=0.99$):

$$P_{avg}^* = 0.78 + 0.022 \exp(\sigma_g)$$  \hspace{1cm} (3.2)
Next, the constant values of $P^*$ obtained for chains (0.7), and fractal agglomerates of different polydispersity (right column of Table 3.1) were used to estimate $d_p$ from the pair correlation functions, $P(r)$, calculated for each synthetic image. The deviation of the estimated diameter $d_{p,PCM}$ from the real average primary particle diameter $d_{p,real}$ was estimated using Eq. (3.3) and is illustrated in Figure 3.3 (right panel). For simplicity, only results obtained for $C_{ov}=0$ are illustrated.

$$\Delta d_p = 100 \left| \frac{d_{p,PCM} - d_{p,real}}{d_{p,real}} \right|$$ (3.3)

This method resulted in an average primary particle sizing error of approximately 7% for straight chains of $N_p > 10$ and less than 14% error for fractal agglomerates of different sizes and polydispersity. Maximum error occurs for single spheres and is approximately 27%.

If the aggregated-optimized value of $P^*$ is used for analysis of straight chains, the error is approximately 18% (Fig. B.1, Appendix B).

3.4.2 Real soot aggregates

First, primary particle size was measured manually for 11 operating conditions of two reciprocating engines. On average 35 aggregates were analyzed for each operating condition. Then, Otsu’s algorithm and rolling ball methods were used for automatic detection of the aggregate projected area; and the corresponding pair correlation functions $P(r)$ were calculated. Using $P^*=0.85$ obtained from the simulation of the numerical agglomerates of point-touching primary particles with $\sigma_g \approx 1.2$ (approximate polydispersity for real soot aggregates according to Fig. 3 in [87]), the average diameter of the primary particles was measured for individual aggregates. As shown in Figure B.2 (Appendix B) the average sizing error of the model using $P^*=0.85$ is approximately 20%. Real aggregates often have partially fused primary particles, and primary particle overlap coefficients in the range of 0-0.3 which suggest that the optimum $P^*$ for soot should be larger than 0.85, which indeed was found to be the case.

To further improve the accuracy of the method for carbon soot, $P^*$ was measured for 132 aggregates randomly selected from the library of the TEM images taken at 5 different operating conditions of the GDI engine. Since the number of the primary particles cannot be directly
measured from 2-D TEM images, $P^*$ is plotted as a function of $d_a/d_g$ in Figure 3.5, as in Figure 3.4. The average $P^*$ obtained from the analysis of the TEM images of the GDI engine is $0.913 \pm 0.02$. This is within the range of the $P^*$ values determined for numerically-generated aggregates with $1.2 \leq \sigma_g \leq 1.4$ and $0.1 \leq C_{ov} \leq 0.3$.

Using $P^* = 0.913$ obtained from the analysis of the TEM images produced for the GDI engine, average primary particle size was measured for 390 aggregates captured on TEM images of both GDI and HPDI engines. As summarized in Table 3.2 and Figure 3.6, the size of the primary particles measured manually varies between approximately 10 nm and 50 nm for individual particles; and its ensemble-average varies between 15 nm and 26 nm in different operating conditions. This shows that the proposed method is not limited to a narrow range of the primary particle size. PCM estimates the average diameter of the primary particles in individual aggregates ($d_{p,\text{agg}}$) with an average error of approximately $13\%$ for all operating conditions. Considering the nature of the manual sizing which is highly time-intensive, PCM provides results with useful level of accuracy in a very short processing time (less than 5 seconds for binarization and primary particle sizing on a Core(TM) i7-3770 CPU @ 3.40 GHz, 8 GB RAM). The ensemble average diameter of the primary particles can be estimated for each operating condition ($d_{p,\text{ens}}$) with an average error of $4\%$.

The accuracy of the PCM is sensitive to the $P^*$ value; decreasing $P^*$ from 0.913 to 0.82, $\Delta d_{p,\text{ens}}$ increases to from $4\%$ to $10\%$. However, as described earlier, the optimum value of $P^*=0.913$ is determined here by extensive analysis of thousands of synthetic and real TEM images and is shown to provide good accuracy for simulated and real soot particles.

The model accuracy was estimated using Eq.(3.3) assuming that the manual measurements were perfect. In reality, manual measurements are influenced by human perception and also involve statistical uncertainty, so not all of the reported error is attributable to flaws in the PCM. As an illustrative calculation, suppose that 16 primaries are measured manually for a large aggregate with $N_p \gg 16$. The standard deviation is typically $8$ nm (Table 3.2), yielding a standard error of $8/\sqrt{16}=2$ nm on a typical mean diameter of $20$ nm ($10\%$ error). Thus, roughly half of the reported error could be related the statistics of the manual sizing.
Figure 3.5: P* of real soot aggregates (“TEM”) as well as synthetic images of chains and fractal agglomerates.

Figure 3.6: Average $d_p$ for 390 individual aggregates by PCM vs. manual sizing (“TEM”). Solid line is a 1-by-1 line, and dashed lines are ±20% error boundaries.
Table 3.2: Average primary particle diameters obtained from manual image processing and PCM

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Diameters (nm)</th>
<th>Errors (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Manual $d_{\text{p,ens,manual}}$</td>
<td>PCM $d_{\text{p,ens,PCM}}$</td>
</tr>
<tr>
<td>GDI_E0_C</td>
<td>26(±7)⁴</td>
<td>24(±9)</td>
</tr>
<tr>
<td>GDI_E0_S</td>
<td>26(±9)</td>
<td>24(±7)</td>
</tr>
<tr>
<td>GDI_E0_CS</td>
<td>12(±4)</td>
<td>11(±2)</td>
</tr>
<tr>
<td>GDI_E10_C</td>
<td>21(±6)</td>
<td>22(±7)</td>
</tr>
<tr>
<td>GDI_E10_S</td>
<td>16(±4)</td>
<td>15(±5)</td>
</tr>
<tr>
<td>GDI_E10_HS</td>
<td>15(±4)</td>
<td>16(±6)</td>
</tr>
<tr>
<td>GDI_E30_C</td>
<td>17(±4)</td>
<td>16(±4)</td>
</tr>
<tr>
<td>GDI_E30_S</td>
<td>18(±4)</td>
<td>18(±5)</td>
</tr>
<tr>
<td>GDI_E30_CS</td>
<td>21(±8)</td>
<td>21(±9)</td>
</tr>
<tr>
<td>HPDI_B50</td>
<td>19(±5)</td>
<td>18(±6)</td>
</tr>
<tr>
<td>HPDI_B25</td>
<td>20(±8)</td>
<td>19(±9)</td>
</tr>
<tr>
<td>HPDI_A63</td>
<td>26(±7)</td>
<td>21(±6)</td>
</tr>
<tr>
<td>HPDI_B37</td>
<td>17(±4)</td>
<td>17(±5)</td>
</tr>
<tr>
<td>HPDI_B75</td>
<td>17(±4)</td>
<td>17(±5)</td>
</tr>
</tbody>
</table>

1 $d_{\text{p,ens}}$ is the average diameter of the primary particles in the ensemble of images produced for each operating condition.
2 Values in parenthesis are standard deviations.
3 $\Delta d_{\text{p,ens}}$ is the average error of the automatic method for ensembles of aggregates; and is equal to $100 \cdot (d_{\text{p,ens,PCM}} - d_{\text{p,ens,manual}})/d_{\text{p,ens,manual}}$.
4 $\Delta d_{\text{p,agg}}$ is the average error for individual aggregates $= \frac{100}{N_{\text{agg}}} \sum_{i}^{N_{\text{agg}}} \left| \frac{d_{\text{p,PCM,i}} - d_{\text{p,TEM,i}}}{d_{\text{p,TEM,i}}} \right|$, where $N_{\text{agg}}$ is the total number of the aggregates analyzed at each operating condition.

An attempt was made to correlate $P^*$ with features that can be obtained directly from the image, such as $d_a/d_g$ which were shown earlier to affect $P^*$. As shown in Figures B.3 and B.4 (Appendix B), a simple correlation between the parameters described above and the value of the $P^*$ cannot be easily derived. Although this “generalized” method can handle a wide range of particle types (e.g. chains to aggregates) better than the simple PCM with constant $P^*$, for normal soot the more complex method provides no improvement. A possible explanation is that one of the most important structural features, the overlap coefficient, is not easily extracted from the image.
When either versions of the PCM are used, errors associated with the human biases and manual analysis of the TEM images are eliminated. As illustrated in Figure B.6 (Appendix B), both versions of this method are capable of capturing a size correlation between the primary particle and aggregate sizes, consistent with the trends reported by Dastanpour and Rogak [87] from the manual analysis (chapter 2 of this dissertation).

Primary particle overlap coefficient can also be measured by the PCM approach. If primary particle size is known from other methods (e.g. manual measurement or combined mass-mobility experiments), the value of $P^*$ corresponding to the known primary particle diameter can be calculated. Overlap coefficient can be estimated using $P^*$ and $d_a/d_g$ (Figure 3.4).

To facilitate the application of this method by interested researchers, developed open source program is uploaded online and can be downloaded for free [104].

### 3.5 Conclusions

A new method, the Pair Correlation Method (PCM), was developed for automatic estimation of the average primary particle size from binary images of aggregates. The key assumption is that the pair correlation function drops to a critical value $P^*$ at the primary particle size. Unfortunately $P^*$ is not the same for all classes of aggregates, and is not a simple function of geometric parameters such as aspect ratio or the number of primary particles. Fortunately, for broad classes of particles, such as engine soot, $P^*$ is nearly constant.

Although this method does not provide information on the size distribution of the primary particles in individual aggregates, it provides useful results for real soot. Ensemble-average size distribution of the primary particles can also be calculated by this method. $P^*$ was tuned for a portion of the images from one engine and then tested on soot images from two types of reciprocating engines. Using a constant value of $P^*$ resulted in an average error below 13% (relative to manual sizing) for individual aggregates and 4% for ensemble of the aggregates. This accuracy is comparable to the best available algorithms for primary particle sizing, and importantly, the PCM can be used for analysis of TEM images of agglomerates without a priori knowledge of the primary particle size.
Chapter 4

Improved sizing of soot primary particles using mass-mobility measurements

4.1 Introduction

The properties and impacts of aggregated aerosol particles (i.e. soot, metal oxide fumes) depend on their morphology, as characterized by fractal dimension, prefactor and primary particle diameter. The morphology may be measured directly by time consuming ex situ microscopy or rapid but indirect in situ methods. As an alternative approach to labor-intensive ex situ TEM sample collection and analysis, Eggersdorfer et al. [84,85] proposed an indirect method for the measurement of the average primary particle diameters of flame-made zirconia particles using mass and mobility measurements and two constants, projected area exponent $D_\alpha$ and prefactor $k_a$. It was shown that the primary particle diameter of the flame-made zirconia particles can be estimated with a reasonable accuracy with this method. Additionally, this method is mainly based on mass and mobility measurements, which are commonly performed in combustion measurements, and eliminates the need for complicated and more expensive approaches, e.g. Laser Induced Incandescence (LII). This model was validated for aggregates with quite uniform primary particle sizes. Additionally, the model was developed for cluster-cluster aggregates formed by coagulation and is also shown to work for sintered structures. However, carbon soot does not sinter; and mainly grows by cluster-cluster collisions and surface growth. The validity of this method is investigated in this chapter for soot particles emitted from two reciprocating engines. Here, it is shown that using previously-published values of $D_\alpha$ and $k_a$ [84,85], soot primary

1 A version of this chapter has been published: “Aerosol Science & Technology: Improved sizing of soot primary particles using mass-mobility measurements.” 50(2): 101–109. Copyright 2016. Reston, VA. Reprinted with permission.” Online supplementary information published with this article is presented in Appendix C of the dissertation.
particle diameters estimated from mass and mobility measurements are inconsistent with those obtained directly from the analysis of TEM images.

In most engineered combustion systems, soot particles are typically formed in turbulent conditions with large variation in local stoichiometry [64] and time spent in conditions affecting soot formation, growth and oxidation [72,73]. Dastanpour and Rogak [87] (chapter 3 of this dissertation) have recently shown that the average diameter of the primary particles changes with the aggregate size in many combustion sources. They have also shown that the primary particles are more uniform in individual aggregates compared to ensembles of aggregates. These findings are consistent with the aggregates being formed in relatively homogenous microscopic regions; after formation and growth, aggregates formed in different regions, with different residence time and/or formation and growth patterns, are mixed. Although this explanation is plausible (indeed, there is no doubt that there are substantial spatial variations in soot formation conditions in combustion devices) [64], it is exceedingly difficult to model the impact of these variations on soot structure. In fact, quantitative predictions of soot mass and mean particle size remain very challenging [105].

Considering this size variation, it is shown in Appendix C that using the model constants $D_\alpha$ and prefactor $k_\alpha$ determined by Eggersdorfer et al. [85] results in inaccurate estimation of the primary particle size for carbon soot. Here, it is shown for the first time that their power-law correlation is also true for clusters grown by surface growth (instead of sintering) if correct values of parameters $D_\alpha$ and $k_\alpha$ are used. These parameters are determined for a broad range of experimental conditions of two reciprocating engines. Although values of $D_\alpha$ and $k_\alpha$ are found to be sensitive to the operating conditions, soot primary particle diameter can still be estimated with reasonable accuracy by mass-mobility measurements using new constant values for $D_\alpha$ and $k_\alpha$.

4.2 Experimental

Two types of reciprocating engines were considered for this study. The first was a High Pressure Direct Injection (HPDI) natural gas compression-ignition engine operating with Westport Innovations HPDI natural gas combustion system. Natural gas ignition is provided by a diesel pilot. The engine was operated on a single cylinder at seven different operating conditions according to the European Stationary Cycle (ESC-13; EU Directive 1999/96/EC). Most test points
were operated at 15% exhaust gas recirculation (EGR) while the lower-load test points were operated at 20% EGR. The engine was run at 25, 37, 50, and 75 percent of maximum load at an engine speed of 1500 RPM (denoted as B25, B37, B50, and B75, respectively). The highest load (B75) test point was run at 0%, 20%, and 25% exhaust gas recirculation. The HPDI engine was also run at 63% maximum load and a lower speed of 1200 RPM at 0% EGR (denoted as A63). At this operating condition, the majority (~80%) of the natural gas was injected into the combustion chamber during the intake stroke, allowing the bulk of the gas to premix before ignition. The second engine used Gasoline Direct Injection (GDI) and was operated at simulated highway cruise condition (2600 RPM and 58 N.m of torque), and a higher speed and lower torque setting (3000 RPM and 38 N.m), denoted by Highway and Speed thereafter, respectively. The GDI engine was fueled by mixtures of gasoline and 0% (E0), 10% (E10), and 30% (E30) ethanol by volume.

All measurements were carried out downstream of a thermodenuder operating at approximately 200°C [106]. For HPDI tests, higher thermodenuder temperatures were also tested and no significant change was observed in particle number and size distributions. This is not a precise way to determine the mass of organics on the soot, but a change in the size distribution [75] will be observed for semi-volatile mass fractions of 10% or more. Even if 10% of the particle mass was composed of volatile material, primary particle diameter would have approximately decreased by only 5% under the vacuum condition of the TEM (considering densities of the particle core and coating to be 1800 kg/m³ and 1200 kg/m³, respectively).

A TSI 379020A two-stage rotary disk diluter was also used upstream of the thermodenuder in GDI campaign [99]. The first and second stages of the diluter were heated to 80°C and 300°C, respectively. The thermodenuder and heated dilution removed volatile components from the particulate sample, and what remained were non-volatile particles, predominantly composed of elemental carbon. More information on the effects of denuding and heated dilution on particle volatility is presented in Appendix C.

Soot samples were collected on TEM grids using a thermophoretic precipitator and images were produced by a Hitachi H7600 transmission electron microscope operating at 80 kV under high resolution mode. Soot particles were size-classified using a TSI differential mobility analyser (Model 3081) and their masses were measured by a Cambustion Centrifugal Particle Mass Analyser (CPMA) [107] which mass-classifies particles based on the balance between the
electrical mobility, centrifugal forces, and translational velocity of charged particles. Details of the experimental methods are further described in [75,99].

### 4.3 Theory

As discussed in [85], the average projected area \( (a_a) \) of fractal-like aggregates can be related to the number of their constituent primary particles \( n_{va} \) by the following power law (Medalia 1967) correlation:

\[
n_{va} = k_a \left( \frac{a_a}{a_{va}} \right)^{D_\alpha} \tag{4.1}
\]

where \( a_{va} = \pi d_{va}^2 / 4 \) is the projected area of a primary particle with surface area mean (Sauter) diameter of \( d_{va} \), and \( k_a \) and \( D_\alpha \) are the prefactor and projected area exponent which depend on aggregate morphology and collision type. For aggregates of monodisperse point-touching primary particles, \( n_{va} \) and \( d_{va} \) are the actual number and diameter of the primary particles in the cluster, respectively. However, real soot aggregates are composed of polydisperse primary particles and are partially coalesced. Surface-area equivalent diameter \( (d_{va}) \) and number \( (n_{va}) \) of the primary particles in polydisperse aggregates are defined as following [108],

\[
d_{va} = \frac{6v}{a} = \frac{\sum_i d_{p,i}^3}{\sum_i d_{p,i}^2} \tag{4.2}
\]

\[
n_{va} = \frac{6v}{\pi d_{va}^3} \tag{4.3}
\]

where \( v \) and \( a \) are volume and surface area of the aggregate, \( d_{p,i} \) is the diameter of the \( i \)th primary particle, and \( k_a \) and \( D_\alpha \) are usually extracted from fitting Eq. (4.1) to the results obtained from numerical simulations [1,84,109–112] or experimental measurements [1,113]. Values reported in literature for \( k_a \) and \( D_\alpha \) are in the range of 1.0 to 1.18, and 1.07 to 1.15, respectively (summary of the reported values is reported in Table 4.1). These values were obtained for cases where average \( d_{va} \) is statistically independent of the aggregate size.

The number of the primary particles in individual aggregates can also be correlated to the mass of the aggregate, \( m \), by,
\[ n_{va} = \frac{m}{m_{va}} \tag{4.4} \]

where \( m_{va} = \pi \rho d_{va}^3 / 6 \), and \( \rho \) is the material density. Different values in the range of 1770 kg/m\(^3\) to 2100 kg/m\(^3\) are reported for soot density [40,114,115][114,115]; here \( \rho = 1800 \) kg/m\(^3\) is used.

### Table 4.1: \( D_\alpha \) and \( k_a \) values reported in literature

<table>
<thead>
<tr>
<th>Authors (Year)</th>
<th>( D_\alpha )</th>
<th>( k_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eggersdorfer et al. (2012) [84]: agglomerates</td>
<td>1.08±0.002(^a)</td>
<td>1.11±0.015(^a)</td>
</tr>
<tr>
<td>Eggersdorfer et al. (2012) [84]: aggregates(^b)</td>
<td>1.07±0.03(^a)</td>
<td>1.0±0.04(^a)</td>
</tr>
<tr>
<td>Pierce et al. (2006) [111]</td>
<td>1.07(^c)</td>
<td>-</td>
</tr>
<tr>
<td>Al Zaitone et al. (2009) [112]</td>
<td>1.08</td>
<td>1.07</td>
</tr>
<tr>
<td>Medalia (1967) [110]</td>
<td>1.15(^d)</td>
<td>-</td>
</tr>
<tr>
<td>Köylü et al. (1995) [1]: numerical simulation</td>
<td>1.10</td>
<td>1.16</td>
</tr>
<tr>
<td>Köylü et al., (1995) [1]: TEM micrographs</td>
<td>1.09±0.02(^a)</td>
<td>1.15±0.18(^a)</td>
</tr>
<tr>
<td>Köylü and Faeth (1992) [113]</td>
<td>1.08</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) confidence interval; \(^b\) agglomerates sintered by viscous flow and grain boundary diffusion simulations; \(^c\) estimated by the authors from the correlation \( a_a = N_{va}^{0.92} \) reported in the article; \(^d\) estimated by the authors from the correlation \( a_a = m^{0.87} \)

The mobility diameter (\( d_m \)) of aggregates in the free molecular [109] and transition [39] regimes is approximately equal to the projected-area equivalent diameter (\( d_a \)) of the aggregates (\( d_a = 2\sqrt{a_a / \pi} \)) [85]. Park et al. [40,114] showed that this approximation is accurate for diesel aggregates of up to \( d_a = 220 \) nm. Considering this approximation, and by combining Eqs. (4.1) and (4.2), \( d_{va} \) can be written in terms of \( m \) and \( d_m \) [85]:

\[
d_{va} = \left( \frac{\pi k_a \rho}{6m} \right)^{1/2} \left( d_m \right)^{2D_\alpha - 3} \tag{4.5} \]

Substituting Eq. (4.4) into Eq. (4.1) and taking the natural logarithm, Eq. (4.6) can be derived. This equation can be used for the estimation of \( D_\alpha \) and \( k_a \) from combined mass, mobility, and electron microscopy measurements.
\[
\ln \left( \frac{m}{m_{va}} \right) = 2D_{a} \ln \left( \frac{d_{m}}{d_{va}} \right) + \ln(k_{a})
\]

As shown by Dastanpour and Rogak [87] (chapter 3 of this dissertation), primary particle diameter scales with aggregate size in many soot sources, including those considered here. Based on examination of individual aggregates, there is substantial variation about the mean trend, so it is difficult to determine an exact functional relation between the primary particle and aggregate diameters. A power law relation similar to Eq. (4.7) is consistent with the measurements (see Figures C.2-C.3 and Tables C.1-C.2 in Appendix C), and is mathematically convenient.

\[
d_{va} = k_{TEM} d_{a}^{D_{TEM}}
\]

Sauter diameters of the primary particles \(d_{va}\) estimated by power-law correlations are used for mass and mobility diameter normalizations in Eq. (4.6).

### 4.4 Results and discussion

#### 4.4.1 TEM analysis

Sample TEM images produced in this study are shown in Figure 4.1. Particles were stable under the electron beam for all cases considered here. Images shown here are samples of the images taken for each operating condition and their characteristic dimensions do not necessarily represent the averaged parameters obtained from the analysis of tens to hundreds of images produced for each test point.

Average Sauter diameters of the primary particles were estimated at different mass-mobility test points using the prefactor and projected area exponent parameters obtained by Eggersdorfer et al. [84] \((k_{a} = 1.0 \pm 0.04 \text{ and } D_{a} = 1.07 \pm 0.03)\) and Eq. (4.5). These diameters are compared with those directly obtained from the analysis of the TEM images as shown in Figures C.2 and C.3 in Appendix C. On average, primary particle diameters determined by this algorithm were 41% and 21% different from those obtained from the analysis of TEM images produced for HPDI and GDI engines, respectively. TEM analysis provides scattered and discrete information on the primary particle and aggregate sizes which may be mainly due to the heterogeneity of the combustion environment. Consequently, TEM-based Sauter diameters of the primary particles corresponding
to each mobility diameter, $d_{va,TEM}$, were estimated using Eq. (4.7) fitted to TEM results obtained at different operating conditions. Details of this procedure and values obtained for $k_{TEM}$ and $D_{TEM}$ are discussed in Appendix C (section C.2).

![Sample TEM images](image)

Figure 4.1: Sample TEM images taken from different operating conditions of HPDI and GDI engines. Images are selected randomly. Illustrated images have the same magnification. Scale bar is 100 nm.

As shown in Figures C.2 and C.3, although this model predicts an increase in primary particle size with aggregate size, qualitatively consistent with TEM measurements [87], it does not estimate primary particle size accurately, especially for large aggregates.

### 4.4.2 Estimation of $D_{a}$ and $k_{a}$ for soot particles using experimental measurements and optimization

The accuracy of primary particle size measurement from mass-mobility measurements is sensitive to model parameters $D_{a}$ and $k_{a}$. Here, two approaches are used for the calculation of these parameters at different operating conditions of the engines considered in this study.

First, TEM-determined Sauter diameters of the primary particles were estimated for all mass-mobility measurement test points with the application of Eq. (4.7) on TEM analysis data. Optimum values of $D_{a}$ and $k_{a}$ (referred to as $D_{a,\text{opt}}$ and $k_{a,\text{opt}}$ thereafter) were calculated using regression
to minimize the difference between TEM-determined $d_{\text{va}}$ and the results of Eq. (4.5). Using this method, the average primary particle sizing error was reduced to approximately 11% and 5% for HPDI and GDI soot samples, respectively. These primary particle sizing errors are the minimums that could be achieved from mass-mobility measurements; these include measurement uncertainties of instruments, TEM image processing uncertainties, and regression accuracy.

Second, mass-mobility data (obtained from CPMA and differential mobility analyser measurements) and TEM-obtained $d_{\text{va}}$ (and $m_{\text{va}}$) were used in Eq. (4.6); and model parameters $D_{\alpha,\text{meas}}$ and $k_{\alpha,\text{meas}}$ were determined at each operating condition using regression.

Model constants derived from both approaches are reported in Table 4.2; prefactor and projected area exponent change considerably (up to 22% for $D_{\alpha}$ and 82% for $k_{\alpha}$) from one test point to another. Additionally, averages of these parameters are different for the combustion sources considered here. Consequently, accurate estimation of the primary particle diameter requires this model to be calibrated for each operating condition or at least soot source. Furthermore, both approaches used for the estimation of $D_{\alpha}$ and $k_{\alpha}$ (“optimized” and “measured”) from combined mass-mobility and TEM measurements result in approximately similar parameter values.

It should be mentioned that the variation of the primary particle diameter with the mobility diameter of the aggregate has to be considered when Eq. (4.6) is used. Assuming average $d_{\text{va}}$ to be constant and independent of the mobility diameter (set to the arithmetic mean TEM-based sauter primary particle diameter), normalized particle mass ($m/m_{\text{va}}$) can be measured from Eq. (4.6) using $k_{\alpha}$ and $D_{\alpha}$ parameters suggested by Eggersdorfer et al. [84,85]. As shown in Figure 4.2, for many test points negative values are measured for logarithms of normalized mass and mobility diameters. This means that the aggregates had mass and/or mobility diameters smaller than a single primary particle, which is physically impossible. The assumption of a constant average $d_{\text{va}}$ for the whole size distribution of the aggregates is erroneous for systems having a considerable variation in average primary particle diameter with aggregate size.

Considering correlation between primary particle and aggregate sizes as described by Eq. (4.7), $d_{\text{va}}$ was measured for each mobility diameter. Results obtained for the normalized mass and mobility of soot aggregates with this adjustment are shown in Figure 4.3. As illustrated, logarithms
of normalized mass and mobility diameter are no longer negative for most points (except for three points, which could be ascribed by the measurement uncertainties).

Table 4.2: Prefactor and projected area exponent measured with different methods

<table>
<thead>
<tr>
<th>Engine</th>
<th>Mode*</th>
<th>$D_{\alpha, opt}$</th>
<th>$D_{\alpha, meas}$</th>
<th>$k_{a, opt}$</th>
<th>$k_{a, meas}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPDI</td>
<td>B25</td>
<td>1.01</td>
<td>1.18</td>
<td>1.40</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>B37</td>
<td>1.13</td>
<td>1.15</td>
<td>1.20</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>B50</td>
<td>1.13</td>
<td>1.14</td>
<td>1.13</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>B75 20% EGR</td>
<td>1.08</td>
<td>1.13</td>
<td>0.83</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>B75 0% EGR</td>
<td>1.20</td>
<td>1.21</td>
<td>0.79</td>
<td>0.81</td>
</tr>
<tr>
<td>HPDI</td>
<td>A63 80% Premixed</td>
<td>1.10</td>
<td>1.14</td>
<td>1.19</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>B75 25% EGR</td>
<td>1.05</td>
<td>1.16</td>
<td>1.40</td>
<td>1.20</td>
</tr>
<tr>
<td>GDI</td>
<td>E0-Highway</td>
<td>1.21</td>
<td>1.21</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>E0-Speed</td>
<td>1.23</td>
<td>1.23</td>
<td>0.77</td>
<td>0.74</td>
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<tr>
<td></td>
<td>E10-Highway</td>
<td>1.19</td>
<td>1.17</td>
<td>0.84</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>E10-Speed</td>
<td>1.10</td>
<td>1.11</td>
<td>1.17</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>E30-Highway</td>
<td>1.20</td>
<td>1.19</td>
<td>0.82</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>E30-Speed</td>
<td>1.19</td>
<td>1.20</td>
<td>0.80</td>
<td>0.77</td>
</tr>
</tbody>
</table>

* Detailed description of the test points and their naming are described in the experimental section. ** $D_{\alpha, opt}$ and $k_{a, opt}$ values are calculated with ±0.005 uncertainty.
Figure 4.2: Logarithmic plot of normalized aggregate mass in relation to the mobility-equivalent diameter when average $d_{va}$ is constant and independent of the aggregate size. Left panel: HPDI engine, Right panel: GDI engine.

Figure 4.3: Logarithmic plot of normalized aggregate mass in relation to the mobility-equivalent diameter when average $d_{va}$ is correlated to the aggregate size. Left panel: HPDI engine, Right panel: GDI engine.

4.4.3 Modified model parameters

Average $D_{a,\text{opt}}$ ($D_{a}^*$) and $k_{a,\text{opt}}$ ($k_{a}^*$) measured for the HPDI engine were used for the calculation of the primary particle sizes in both engines. Using $D_{a}^* = 1.1 \pm 0.02$ and $k_{a}^* = 1.13 \pm 0.08$ instead of $D_{a} = 1.07 \pm 0.03$ and $k_{a} = 1.0 \pm 0.04$ [85], the mean error in the estimation of the
primary particle size was reduced from 41% and 21% to 19% and 12% for different operating conditions of HPDI and GDI engines, respectively. The accuracy of the model using these “modified parameters” is compared to cases where optimized parameters (minimum error) and parameters governed by Eggersdorfer et al. [85] were used; results are reported for individual operating conditions in Figure 4.4.

Figure 4.4: Average $\Delta d_{va}$ measured for different sets of $k_a$ and $D_{a}$ at multiple operating conditions. Eggersdorfer et al. [85] model uses $k_a=1.0$ and $D_a=1.07$; $k_{a,opt}$ and $D_{a,opt}$ parameters are determined for each operating condition separately. Modified model uses $k_{a}^{*}=1.13$ and $D_{a}^{*}=1.1$.

In Figure 4.5, primary particle diameter estimated from Equation (4.3) (for the original and modified values of $D_a$ and $k_a$) for a particular mobility diameter is plotted against the TEM-obtained diameter, $d_{va,TEM}$, for the same particle projected-area equivalent diameter (i.e., assuming $d_m = d_a$). $d_{va,TEM}$ is measured from the application of Equation (4.6) where $k_{TEM}$ and $D_{TEM}$ are determined from regressions to the whole TEM analysis data. As shown, using newly proposed values of $D_{a}^{*} = 1.1$ and $k_{a}^{*} = 1.13$, the difference between estimated Sauter diameters and those obtained from TEM analysis, especially at large mobility diameters, was reduced at all operating conditions of both soot sources. At each operating condition, primary particle size has a considerable wide size distribution which is associated with variations in the aggregate size. Note that in all cases, the original parameters ($D_a = 1.07$ and $k_a = 1.0$) resulted in the primary particle diameter increasing faster with $d_m$ than indicated by TEM. As shown in Figure 4.5, for some
operating conditions such as B75 20% EGR, and B75 0% EGR, neither the old nor the new model agrees well with TEM measurements. After re-examining these measurements, it appears that they are similar to other points except for especially low values of $D_{\text{TEM}}$ – that is, primary particle diameter has a weak correlation with aggregate size. However, a clear trend was not observed between the accuracy of the model and $D_{\text{TEM}}$.

Figure 4.5: Sauter primary particle diameter measured from Eq. (5) using parameters suggested by Eggersdorfer et al. [84] and newly obtained parameters vs. TEM data for both HPDI and GDI engines.
4.5 Conclusions

Models developed for \textit{in situ} estimation of Sauter diameters of the primary particles with mass-mobility measurements were compared with TEM measurements. It was found that good agreement between TEM and \textit{in situ} estimations can be obtained using model parameters that depend on source and operating conditions. Variation of the primary particle diameter with aggregate size is also taken into account in the estimation of the new model parameters. Consideration of this size correlation is essential in order to obtain physically realistic mass and mobility. It was also found that for nearly all cases, agreement can be improved with the application of new, constant values for the model parameters $k_a$ and $D_a$, but it remains to be seen whether these values will work for a broad range of soot sources.
Chapter 5

The effect of primary particle polydispersity on the morphology and mobility diameter of the fractal agglomerates in different flow regimes

5.1 Introduction

Aerosol and colloidal agglomerates of smaller primary particles are formed in many industrial and natural environments. While some nanoparticle aggregates are potentially useful, soot aggregates formed by incomplete combustion of hydrocarbons are known responsible for adverse health effects [18] and climate forcing [14].

Production rate and properties of synthetic particles, aerosol residence time in atmosphere, and its dispersion rate and motion under different flow regimes are influenced by the morphology and hydrodynamic properties of these particles. Reliable measurement of the emission rate and size distribution of fractal aggregates also depend on accurate estimation of the morphology and mobility of these particles.

Great effort has been devoted to the estimation of the hydrodynamic properties of straight chains and fractal agglomerates in different flow regimes. The mobility of the aerosols of different structures is usually expressed by an equivalent mobility diameter ($d_m$). This diameter is equal to the diameter of a virtual sphere experiencing the same drag force under the same flow condition. Experimental measurements have been performed to correlate the mobility diameter of the fractal

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aggregates to the structure, e.g. radius of gyration ($R_g$), primary particle diameter ($d_p$), and projected area of these particles [39,101,116–120].

Several simulations have also been carried out to calculate the mobility diameter of clusters in different flow regimes. In the free molecular regime, the mobility diameter of the fractal aggregates, $d_{m,fm}$, is approximately equal to their average projected area equivalent diameter, $d_a$, [39]. This is consistent with the results obtained from Monte Carlo simulations of momentum transfer rate of chains and fractal aggregates in this regime [121–123]. Consequently, if primary particle size variation is to influence particle mobility in this regime, it should be limited to the geometric relation between the number of primary particles and the projected area.

Calculation of the effect of morphology on continuum regime mobility is not as simple as the free molecule regime. Several methods have been developed for the assessment of the mobility diameter of aggregates in this regime. A group of these methods treats aggregates as porous spheres of homogeneous [124] or variable permeability [125]. The Lattice Boltzmann Method (LBM) has been used for the investigation of hydrodynamic properties of fractal aggregates by many researchers [126–128]. Brownian dynamics approach has also been used in several studies [123,129–131] for the estimation of the collision kernels of particles and surrounding gas molecules, and mobility diameters of particles of irregular shapes in the continuum regime. As an another approach the Finite Element Method (FEM) has also been used for the investigation of the hydrodynamic properties of clusters in this regime [127,132]. Although these methods provide high accuracy, they are usually computationally expensive. Kirkwood–Riseman theory of hydrodynamic interaction of particles is another method commonly used for the calculation of the drag force on clusters of spherical particles [33,133–135].

One of the most accurate methods commonly used for the simulation of the hydrodynamic interactions between aggregates and flow field in the limiting case of low Reynolds number, creeping flow, is referred to as Stokesian Dynamics (SD) [126,127,136–140]. In this method the flow disturbance caused by the non-overlapping primary particles in clusters is modeled through the superposition of point forces on the surface of the primary particles. The multipole expansion of the flow velocity in a series of spherical harmonics is used and the hydrodynamic interactions are simulated by a combination of far-field mobility and pairwise additive resistance calculations. Hydrodynamic interactions of two equal [141] and unequal [142,143] spheres in different flow
patterns are modeled by the Stokesian Dynamics method through the construction of resistance and mobility matrices which purely depend on the diameter and relative arrangement of primary particles in regards to the flow field. Application of SD to N-body clusters was pioneered by Brady & Bossis (1988) and Durlofsky et al., (1986). As confirmed by rigorous numerical simulations of Gwaze et al. (2006) and Schlauch et al. (2013), SD provides good accuracy with modest computational time.

In large clusters, it is commonly assumed that the hydrodynamic radius becomes proportional to the radius of gyration [35]:

$$R_{m,c} = \beta R_g$$  \hspace{1cm} (5.1)

This proportionality was first investigated by [33,135]. Using Kirkwood-Riseman theory, they obtained $\beta = 0.875$ for particles generated by Diffusion Limited Cluster-cluster Aggregation (DLCA) composed of 50 to 400 monodisperse primary particles. Studies performed by Rogak and Flagan [146], Wang and Sorensen [120] (1999), Wiltzius [147], and Sorensen [35] suggested $\beta$ to be in the range of 0.68 to 0.78 for DLCA aggregates with a fractal dimension ($D_f$) of 1.78. However, as it will be discussed later in this chapter, a wide range of values are reported in literature for $\beta$.

Although an extensive body of literature is already available for the simulation of the hydrodynamic properties of the fractal aggregates in different flow regimes, previous studies are limited to the clusters composed of monodisperse primary particles. However, particles formed in different environments are shown to be composed of primary particles of different levels of polydispersity [87,148]. Eggersdorfer and Pratsinis [55] have shown that the fractal dimension of aggregates decreases with primary particle polydispersity. The influence of the primary particle polydispersity on the morphology (i.e. surface area, mass, and radius of gyration), and hydrodynamic behavior of particles in the free molecular and continuum regimes are investigated in this chapter.

5.2 Methods

Algorithms used for the generation of numerical aggregates and calculation of the mobility diameters of these particles in free molecular and continuum flow regimes are described in the
following sections. The transition regime case is not discussed here because an established interpolation approach [131] can be used for the calculation of the mobility diameter at arbitrary Knudsen number, given the two limiting cases of free molecular and continuum regimes. Application of the interpolation to averages for the limiting regime cases is not identical to interpolating first, then averaging over individual aggregates, but this effect is not considered in this chapter.

5.2.1 Generation of the numerical agglomerates

Mobility calculations were performed on numerical particles including straight chains and three-dimensional fractal agglomerates of point-touching spheres. Straight chains were composed of 1 to 1000 monodisperse primary particles and were only used for validation purposes.

Fractal agglomerates were generated by Eggersdorfer & Pratsinis [69] using a hierarchical cluster-cluster agglomeration algorithm [79]. Aggregates were composed of 16, 32, 64, 128, 256, and 512 point-touching primary particles. The primary particle size distribution of aggregates generated by different sources can usually be well represented by a lognormal size distribution [47, 75–77, 80, 87, 149]. Detailed comparison of normal and lognormal fits to primary particle size distributions obtained from the analysis of real soot images produced by transmission electron microscopy (section D.1 in Appendix D) confirms the suitability of the lognormal assumption. Considering the experimental results obtained from the analysis of a large group of the TEM images reported in chapter 2, primary particle diameters were selected randomly from lognormal distributions with geometric standard deviations ($\sigma_g$) of 1.0, 1.2, 1.4, and 1.6. The polydispersity of the primary particles was also checked for the generated particles to compensate the stochastic errors rising from the limited number of the primary particles in small aggregates. One hundred aggregates were generated for each $\sigma_g$ and number of primary particles ($N_p$) for a total of 2400 aggregates.

5.2.2 Free molecular regime

In the free molecular regime, the average mobility diameter of an arbitrary shaped particle is approximately equal to its average projected-area equivalent diameter, $d_a$: 
\[ d_{m, fm} \approx \bar{d_a} = 2 \frac{\bar{a_a}}{\sqrt{\pi}} \]  

(5.2)

where \( \bar{a_a} \) is the arithmetic mean of the particle’s projected area. \( \bar{a_a} \) was computed using a Monte Carlo approach. Each particle was rotated randomly in the three-dimensional space and the particle was “scanned” by rays in Z direction emerging from every single point on the X-Y plane. Counting the rays “hitting” the particle, the total projected area of the particle was computed.

### 5.2.3 Stokes regime

The dependency of the drag force on the structure of the fractal aggregates in the limiting case of zero Reynolds number can be investigated by Stokesian Dynamics (SD) [144,145]. SD is based on the solution of the Stokes equation for a point force given by the Oseen tensor. The linearity of the Stokes equation allows the superposition of the flow disturbance caused by the point forces distributed on the surfaces of the particles. Considering the spherical structure of the primary particles, a multipole expansion of the force field is used. The general formulation of the SD includes force, torque, and stresslet (F-T-S model); and covers translational velocity, angular velocity, and rate of strain interactions. For a cluster of \( n \) primary particles, the general formulation of the SD can be presented as follows:

\[
\begin{bmatrix}
F_n \\
T_n \\
S_n
\end{bmatrix}
= \mathcal{R} \cdot
\begin{bmatrix}
U_n - U^\infty \\
\Omega_n - \Omega^\infty \\
-\dot{E}^\infty
\end{bmatrix}
\]  

(5.3)

where \( F_n, T_n, \) and \( S_n \) are the force, torque, and stresslet\(^1\) acting on the primary particles. \( U_n \) and \( \Omega_n \) are translational and angular velocities of the primary particles, respectively. \( U^\infty \) and \( \Omega^\infty \) are the translational and angular velocities of the far-field flow. \( \dot{E}^\infty \) is the rate of strain tensor of far-field flow at the centre of mass of the primary particles. The number of the lines over the parameters in Eq. (5.3) shows the order of the tensor (however, it represents average values in the rest of this

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\(^1\) symmetric part of the first moment of the surface stress
chapter). Finally, $\mathcal{R}$ is the grand resistance matrix which solely depends on the relative position and diameters of the primary particles.

In case of the rigid-body clusters where the relative velocities of any two primary particles are zero, the lubrication correction can be ignored [126,127,139,140] and SD formulation will be reduced to F-T model. Here, the grand resistance matrix was constructed using the algorithm described by Durlofsky et al. [144]; and the exact two-body resistance functions of unequal primary particles suggested by Jeffrey & Onishi [143] and Kim & Karrila [150] were used.

Considering the linearity of the Stokes equations, the total drag force acting on an agglomerate is equal to the summation of the drag forces acting on its constituent primary particles. The arithmetic mean drag force acting on an individual aggregate is computed for 50 random rotations of the grand mobility matrix in the three dimensional space.

Upon the measurement of the total drag force, the mobility equivalent diameter of the aggregates in the continuum regime ($d_{m,c}$) can be calculated using the following equation,

$$d_{m,c} = \frac{F}{3\pi \mu U} \quad (5.4)$$

where $F$ is the magnitude of the drag force, $\mu$ is the dynamic viscosity of the medium, and $U$ is the relative velocity of the particle and the medium.

### 5.3 Results and discussion

#### 5.3.1 Agglomerate structure characterization

The average fractal dimension, $D_f$, and prefactor, $k_f$, of numerical agglomerates were calculated from Eq. (5.5):

$$N_p = k_f \left( \frac{R_g}{R_{pg}} \right)^{D_f} \quad (5.5)$$

Here $R_{pg}$ is the median radius of the primary particles; and $R_g$ is the three-dimensional radius of gyration of the particles given by:
\[ R_g^2 = \frac{1}{\sum R_i^3} \sum R_i^3 (a_i^{2-\text{CM}} + R_{g,i}^2) \]  

(5.6)

where \( R_i \) is the radius of the \( i^{\text{th}} \) primary particle, \( a_{i-\text{CM}} \) is the separation distance of the \( i^{\text{th}} \) primary particle from the center of the mass of the particle; and \( R_{g,i} \) is the radius of gyration of the \( i^{\text{th}} \) primary particle (\( R_{g,i}^2 = 0.6 R_i^2 \)).

Figure 5.1 shows that the average gyration diameter (\( d_g = 2R_g \)) of the agglomerates at each \( N_p \) increases with \( \sigma_g \). Throughout this article \( d_{pg} \) is the median diameter of the primary particles in individual agglomerates.

Figure 5.1: The effect of \( \sigma_g \) on normalized \( d_g \) in agglomerates of different size, \( N_p \).

Applying linear regression to the logarithms of \( N_p \) and \( R_g/R_{pg} \) showed that the fractal dimension decreases from 1.78 to 1.73 as the primary particles polydispersity increases from 1 to 1.6, consistent with the results obtained by Eggersdorfer & Pratsinis [55] for particles generated by the DLCA algorithm. However, \( k_f \) was approximately constant and equal to 1.4. Although numerical aggregates used in this study were not generated by a DLCA algorithm, their fractal structure is similar to the DLCA particles.
For the simulated aggregates, the mass and area were computed and the average values of these parameters were found to be within 1% of the expected values for lognormally distributed particles [151], that is

\[ m_{\text{agg}} = \exp(4.5 \ln^2 \sigma_g) \frac{\pi}{6} \rho d_{pg}^3 N_p \]  

(5.7a)

\[ s_{\text{agg}} = \exp(2 \ln^2 \sigma_g) \pi d_{pg}^2 N_p \]  

(5.7b)

These results do not depend on the structure of the aggregates, but the radius of gyration and mobility diameters do depend on structure and thus cannot be obtained analytically. The accuracy of these equations for agglomerates composed of a finite number of primary particles is discussed in the next section.

### 5.3.2 Mobility diameter of the fractal agglomerates in the free molecular regime

Agglomerates of different sizes and polydispersity were projected into 50 random orientations and their projected areas were measured. Arithmetic average mobility equivalent diameter \((d_{m, fm})\) is equal to the average projected-area-equivalent diameter of the particles \((d_a)\).

The mobility diameter in the free molecular regime can be correlated to \(N_p\) and \(d_{pg}\) in the following form:

\[ d_a = d_{m, fm} = k_{m, fm} d_{pg} N_p^{D_{m, fm}} \]  

(5.8)

The normalized mobility diameter of the fractal agglomerates in the free molecular regime is plotted as a function of \(N_p\) for different \(\sigma_g\) in Figure 5.2 (solid lines). Variation of \(d_{m, fm}/d_{pg}\) with \(\sigma_g\) for different \(N_p\) is also illustrated in Figure D.3 (Appendix D). Regression shows that \(D_{m, fm}\) is almost independent of \(\sigma_g\); however, \(k_{m, fm}\) increases up to 26% when \(\sigma_g\) reaches 1.6. For simplicity, \(D_{m, fm}\) was kept constant and equal to 0.46 and \(k_{m, fm}\) was measured for different \(\sigma_g\) (Table 5.1, which also includes the continuum regime results discussed in the next section). For aggregates of monodisperse primary particles, \(d_{m, fm} = 0.97 d_{pg} N_p^{0.46}\) is within 3% deviation from \(d_{m, fm} = d_{pg} N_p^{0.46}\) suggested in [35].
Figure 5.2: The effect of $\sigma_g$ on normalized $d_{m,\text{fm}}$ and $d_{m,c}$ in agglomerates of different size, $N_p$.

Table 5.1: Regression-obtained parameters for agglomerates of different polydispersity

<table>
<thead>
<tr>
<th>$\sigma_g$</th>
<th>$D_{m,\text{fm}}$</th>
<th>$k_{m,\text{fm}}$</th>
<th>$D_{m,c}$</th>
<th>$k_{m,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.46</td>
<td>0.970 (±0.011)</td>
<td>0.52</td>
<td>0.887 (±0.005)</td>
</tr>
<tr>
<td>1.2</td>
<td>0.46</td>
<td>1.006 (±0.010)</td>
<td>0.52</td>
<td>0.917 (±0.004)</td>
</tr>
<tr>
<td>1.4</td>
<td>0.46</td>
<td>1.095 (±0.010)</td>
<td>0.52</td>
<td>0.987 (±0.010)</td>
</tr>
<tr>
<td>1.6</td>
<td>0.46</td>
<td>1.226 (±0.012)</td>
<td>0.52</td>
<td>1.086 (±0.005)</td>
</tr>
</tbody>
</table>

All fits have $R^2 > 0.99$.

Variation of $k_{m,\text{fm}}$ with $\sigma_g$ can also be formulated by $k_{\text{fm}} = 0.94 + 0.03 \sigma_g^{4.8}$ (R-square=0.99). Substituting this into Eq. (5.8), free molecular mobility diameter of the fractal agglomerates can be calculated using the following correlation:

$$d_{m,\text{fm}} = (0.94 + 0.03 \sigma_g^{4.8}) d_{\text{pg}} N_p^{0.46}$$

This result is numerically about 1% higher than using the surface-area-equivalent diameter, $d_{ps}$, (measured from the application of Eq. 5.7b) in $d_{m,\text{fm}} = 0.97 d_{ps} N_p^{0.46}$.

The relation between mobility diameter and mass (Eqs. 5.8 and 5.9) is often expressed in the inverse manner, $m \sim d_{m}^{6.06}$ [68,152–154]. The normalized mass of the individual simulated
aggregates (measured directly from $\sum m_i$ where $m_i$ is the mass of an individual primary particle) is plotted as a function of the normalized free molecular mobility diameter in Figure 5.3 (continuum results are illustrated in Figure D.4 in Appendix D). The ratio of the actual mass of the agglomerates (illustrated in Figure 5.3) to the masses estimated from the application of Eq. (5.7a) are also illustrated in Fig D.5 (Appendix D) for different normalized free molecular mobility diameters. As illustrated in Figures 5.3 and D.4-D.5, aggregates with the same $N_p$ have a wide range of mass and mobility diameters. The relative variations increase with $\sigma_g$ and decrease with $N_p$. These Figures also show that particles of the same mobility have a wide range of mass which cannot fully be captured by Eq. 5.7a. The mass-mobility exponent of particles of the same primary particle polydispersity and different $N_p$ was determined from the slope of the lines in Figure 5.3. Our results showed that the mass-mobility exponent increased slightly from 2.15 to 2.23 as $\sigma_g$ increased from 1.0 to 1.6 (substantially consistent with constant $D_{m, fm}$ discussed earlier). Although the present work focusses on average values of mass and mobility, Figures 5.3 and D.4-D.5 show that individual aggregates can deviate substantially from the average mass-mobility relation – a fact that should be considered in models of instrument transfer functions.

Figure 5.3: The effect of $\sigma_g$ on the mass-mobility correlation of numerically-generated particles in the free molecular regime. Continuous lines are regressions to the data in the forms of $m/m_p = A d_{m, fm}^{\beta_{m, fm}}$. Dotted lines are extrapolation of the fitted lines to slightly larger $d_{m, fm}/d_{pg}$. 
5.3.3 Mobility diameter of straight chains and fractal agglomerates in the continuum regime

5.3.3.1 Validation of computational method

First, SD was applied to doublets and straight chains of monodisperse primary particles (Table D.1, Appendix D). These calculations agreed with analytical results to better than 5% - about as good as the Lattice Boltzman Method (LBM) for doublets [126]. Our results for straight chains also agree to within 4% error of results reported by [121,137,155] (Figure D.6, Appendix D).

Next, fractal agglomerates of monodisperse primary particles were subjected to uniform flow fields in 50 random directions and mobility-equivalent diameter was computed. Average results are plotted as a function of $N_p$ in Figure 5.4; and agree well with literature [35,123,126,127,132,134,137]. Slight discrepancies between the results could be due to the differences in the particle structures (the whole structure may not necessarily be fully captured by only $D_f$ and $k_f$), sample size and averaging artifacts, and errors in the calculation of the approximate mobility diameters.

![Figure 5.4: Variation of normalized $d_{m,c}$ with $N_p$ in fractal agglomerates of monodisperse primary particles. Values in parenthesis are $(D_f, k_f)$.](image)

For aggregates of monodisperse primary particles, regression yields $d_{m,c} = 0.887 d_{pg} N_p^{0.52}$, approximately consistent with the equations suggested by Sorensen [35].

Three-dimensional radii of gyration $R_g$ were also calculated and the ratio of average continuum mobility radius to $R_g$ was computed. As illustrated in Figure 5.5, for fractal agglomerates of monodisperse primary particles $\beta$ is $0.89 \pm 0.02$ in the range of $N_p=64$ to 512 consistent with the values reported by Chen et al. [33] and Meakin et al. [135] where the Kirkwood-Riseman method was used. Earlier studies [33,35,101,132,134,135,146] suggested that the value of $\beta$ converges to a constant value as $N_p$ increases. However, as shown in Figure 5.5, a relatively wide range of $\beta$ is reported in literature. These differences cannot be all attributed to the differences in the simulation models since similar methods resulted in different $\beta$ (e.g. [33,126,134,137]). These differences may mainly be attributed to the differences in the structures of the fractal agglomerates used in these studies. It worth noting that the whole structure of the particles may not necessarily be fully captured by $D_t$ and $k_t$.

![Figure 5.5: Variation of $R_{m,c}/R_g$ with $N_p$ in fractal agglomerates of monodisperse primary particles. Values in parenthesis are ($D_t$, $k_t$). Results presented for [123] and [126] are obtained by the authors applying Eq. (5.5) to the reported mobility results.](image-url)
5.3.3.2 Effect of primary particle polydispersity on $d_{m,c}$

A correlation between the mobility equivalent diameter in continuum regime ($d_{m,c}$) with total number and median diameter of the primary particles is formulated similar to the equation suggested by Sorensen [35],

$$d_{m,c} = k_{m,c} d_{pg} N_p^{d_{m,c}}$$  \hspace{1cm} (5.10)

Normalized continuum mobility diameter of the fractal agglomerates is plotted as a function of $N_p$ for different $\sigma_g$ in Figure 5.2 (dashed lines). Variation of normalized $d_{m,c}$ with $\sigma_g$ for different $N_p$ is also illustrated in Figure D.7 (Appendix D). As for the free molecular regime, $D_m,c$ does not change significantly with $\sigma_g$; however, $k_{m,c}$ is approximately 22% higher at $\sigma_g=1.6$ compared to $\sigma_g=1$. For simplicity, $D_m,c$ was kept constant and equal to 0.52 and $k_{m,c}$ was measured for different $\sigma_g$ (Table 5.1).

Variation of $k_{m,c}$ with $\sigma_g$ can be formulated as $k_{m,c} = 0.85 + 0.03 \sigma_g^{4.4}$ (R-square=0.99). Substituting this into Eq. (5.10), the average continuum mobility diameter is

$$d_{m,c} = (0.85 + 0.03 \sigma_g^{4.4}) d_{pg} N_p^{0.52}$$  \hspace{1cm} (5.11)

The influence of the primary particle polydispersity on $\beta = R_{m,c}/R_g$ was also investigated. Our results show that, although both $R_{m,c}$ and $R_g$ increase with $\sigma_g$, their ratio $\beta$ increases by only 3% as $\sigma_g$ increases from 1 to 1.6 (Table 5.2).

<table>
<thead>
<tr>
<th>$\sigma_g$</th>
<th>1.0</th>
<th>1.2</th>
<th>1.4</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>0.89 (±0.02)*</td>
<td>0.88 (±0.02)</td>
<td>0.90 (±0.03)</td>
<td>0.92 (±0.04)</td>
</tr>
</tbody>
</table>

* values in parenthesis are the standard deviations.

The influence of the primary particle polydispersity on the mobility of agglomerates fully aligned in an external flow field, i.e. differential mobility analyzer, was also investigated. As shown in Figure D.8 (Appendix D), the ratio of the mobility diameter of particles aligned in an external field to their orientation-averaged mobility diameter is approximately independent of the primary particle polydispersity.
5.3.4 Effect of “internal” and “external” mixing of primary particle size variations on the mass of the mobility-classified particles

Dastanpour and Rogak [87] (chapter 2 of this dissertation) found that the ensemble-based geometric standard deviation of the primary particle size distribution $\sigma_{g,\text{ens}}$, is typically about 1.4 while it is less than 1.4 for individual agglomerates in the same ensemble ($\sigma_{g,\text{agg}} < 1.4$). This means that, much of the primary particle size variation is “externally mixed”. Here, we consider the implications of this in a hypothetical experiment in which particles are classified based on their mobility. For a constant ensemble-based geometric standard deviation of $\sigma_{g,\text{ens}} = 1.4$ and geometric mean primary particle size ($d_{pg,\text{ens}}$), three different cases are considered here (Figure 5.6).

![Diagram showing different cases of agglomerates](image)

**Figure 5.6:** Different sets of agglomerates having the same ensemble-average primary particle polydispersity ($\sigma_{g,\text{ens}}=1.4$). Red circles are centered at the center of mass of the particles, with diameters equal to $d_{m,\text{fm}}$ of the particles.

I. Individual agglomerates are composed of monodisperse primaries ($\sigma_{g,\text{agg}} = 1.0$) and primary particle size variations are “externally mixed” ($d_{pg}$ is not similar in different

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1 Geometric standard deviation of all primary particles regardless of the agglomerates they belong to.
agglomerates); here it is simulated with two distinct agglomerate types such that $\sigma_{g,\text{ens}} = 1.4$.

II. Individual agglomerates are composed of polydisperse primaries with $\sigma_{g,\text{agg}} = 1.325^1$; but primary particle size variations are “internally mixed” ($d_{pg}$ is similar for all agglomerates of the same mobility); this is effectively the situation considered in the previous sections of this paper.

III. Individual agglomerates are composed of polydisperse primaries with $\sigma_{g,\text{agg}} = 1.2$ and $d_{pg}$ varies between agglomerates (it changes in a way that $\sigma_{g,\text{ens}} = 1.4$).

Depending on the situation, each of these cases may be observed in practice. Case III is the most realistic case for soot particles [87].

Figure 5.7 illustrates the variation of normalized mass with free molecular mobility diameter of mixtures of aggregates according to the 3 cases. Mobility classification corresponds to a vertical line on the graph. Continuum mobility results are excluded for simplicity. Comparing case I with Case II, agglomerates of the same mobility diameter have 20.2±3% and 24.4±3% smaller mass in the free molecular and continuum regimes, respectively. Case III is between Cases I and II.

The importance of discriminating between $\sigma_{g,\text{agg}}$ and $\sigma_{g,\text{ens}}$ in simulations and analysis of experimental data is further elaborated in Table 5.3 for a hypothetical mobility classification experiment. For each case, more than a thousand agglomerates were generated; a lognormal size distribution was assumed for the ensembles of the primary particles; and the geometric mean primary particle diameter of each individual agglomerate was selected from this distribution.

Normalized free molecular and continuum mobility diameters of the size classified particles were set to 5 in the simulated experiment. Table 5.3 also reports geometric mean number of the primary particles in individual agglomerates and normalized mass $(m/m_{pg,\text{ens}}$, where $m_{pg,\text{ens}}$ is the mass of the median-diameter particle $d_{pg,\text{ens}}$ considering all primaries in the whole ensemble of the agglomerates). Depending on $\sigma_{g,\text{ens}}$ and $\sigma_{g,\text{agg}}$, particles of the same mobility diameter will have significantly different median $N_p$ and $m/m_{pg,\text{ens}}$. These results elaborate that the differences

---

1 $\sigma_{g,\text{agg}}$ and $\sigma_{g,\text{ens}}$ cannot be exactly equal.
between $\sigma_{g,\text{ens}}$ and $\sigma_{g,\text{agg}}$ should be considered and appropriate values of these parameters should be used in the simulations and interpretation of the experimental data.

Figure 5.7: Variation of normalized $m_p$ with $d_{m,\text{fm}}$ for three polydispersity cases.

Table 5.3: Effect of $\sigma_{g,\text{agg}}$ and $\sigma_{g,\text{ens}}$ on median $N_p$ and $m/m_{pg,\text{ens}}$ for a hypothetical mobility classification experiment.

<table>
<thead>
<tr>
<th>Case</th>
<th>$\sigma_{g,\text{agg}}$</th>
<th>$\sigma_{g,\text{ens}}$</th>
<th>$d_{m}/d_{pg,\text{ens}}$</th>
<th>$N_p$</th>
<th>$m/m_{pg,\text{ens}}$</th>
<th>$N_p$</th>
<th>$m/m_{pg,\text{ens}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.0</td>
<td>1.4</td>
<td>5</td>
<td>35</td>
<td>35.19</td>
<td>28</td>
<td>28.10</td>
</tr>
<tr>
<td>II</td>
<td>1.4</td>
<td>1.4</td>
<td>5</td>
<td>27</td>
<td>42.29</td>
<td>23</td>
<td>34.96</td>
</tr>
<tr>
<td>III</td>
<td>1.2</td>
<td>1.4</td>
<td>5</td>
<td>32</td>
<td>38.26</td>
<td>26</td>
<td>31.34</td>
</tr>
</tbody>
</table>

5.4 Conclusions

For a fixed number of primary particles $N_p$ and median primary particle diameter $d_{pg}$, the physical size of the aggregate increases substantially with primary particle polydispersity $\sigma_g$. Arithmetic average primary particle diameter, surface area, and total mass of aggregates increase with $\sigma_g$. Consequently, the effect of primary particle polydispersity should be considered carefully in the analysis of transmission electron micrographs or combined mass and electron microscopy analysis.
Correlations are developed here to link number, size, and polydispersity of the primary particles to the surface area, mass, and projected area of the fractal agglomerates.

The first effect of primary particle polydispersity on mobility diameter is simply that the physical size of the aggregate increases with polydispersity. This effect can be substantial (~26%) in the free molecule regime for $\sigma_g=1.6$ and $N_p=512$; in this regime we cannot say whether or not primary particle size variation has any effect other than the geometric one described above, for we have assumed that the arithmetic average mobility equivalent diameter is equal to the average projected-area-equivalent diameter of the particle.

In the continuum regime, we have used Stokesian Dynamics computations that should be capable of resolving the effect of structure accurately. As for the free molecular regime, the mobility diameter of fractal agglomerates increases with primary particle polydispersity in the continuum regime. This effect can be substantial (~23%) in this regime for $\sigma_g=1.6$ and $N_p=512$. Nearly all of this effect is due to the change in radius of gyration; the average ratio $\beta = R_{m,c}/R_g$ increases by ~3% as $\sigma_g$ increases from 1 to 1.6. We have found that the considerable variation of $d_{m,c}/d_g$ in the literature cannot all be ascribed to calculation or measurement error: different cluster aggregation mechanisms yield different structures that affect $d_{m,c}/d_g$. Correlations are derived for the estimation of the mobility diameter based on the size, number, and polydispersity of the primary particles in fractal agglomerates in both free molecular and continuum regimes.

It is shown that particles of the same fractal structure and number of primary particles may have different mass and mobility diameter. The spread of the mass and mobility distributions increase with primary particle polydispersity while the mass-mobility exponent is not strongly affected by $\sigma_g$.

Having developed models for the mobility of fractal aggregates it is possible to consider the implication of primary particle size variability in experiments, e.g. when mass and optical properties are estimated for mobility classified particles. It is important to discriminate between the variations of the primary particle diameters within individual agglomerates and the variations within ensembles of aggregates.
Chapter 6

Variation of the optical properties of laboratory generated soot with particles mass

6.1 Introduction

As described in chapter 1, mass-specific absorption cross section (MAC), mass-specific scattering cross section (MSC), and single scattering albedo ($\omega_0$) are important parameters required for accurate measurement of the emission rates and modeling of the climate forcing.

For decades, MAC of soot particles has been assumed to be independent of particle size and mass. Values approximately in the range of 3.5 ($m^2g^{-1}$) to 8.3 ($m^2g^{-1}$), at a wavelength of 660 nm, have been reported in literature for MAC [9,156–165]. Published values of MAC, MSC, and $\omega$ are summarized in Tables 6.1 to 6.3.

Based on the observation of a correlation between $d_p$ and $d_a$, soot particles are most likely formed in relatively homogeneous microscopic regions; after formation and growth, aggregates from different regions are mixed. Particles experiencing different formation and oxidation patterns and/or residence time may have different internal structures and optical properties. The variation of the optical properties and morphology of the soot particles with size is investigated in this chapter.

6.2 Experimental

Measurements reported here can be classified in three distinct groups as indicated in Figure 6.1. These include (1) size measurement and particle collection for electron microscopy (Figure 6.1, panel a), (2) effective density measurement (Figure 6.1, panel b), and (3) measurement of the optical properties and size distributions of mass-classified particles (Figure 6.1, panel c).

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6.2.1 Particle generation and treatment

Soot particles have been produced by an inverted coflow methane/air diffusion flame. This type of flame was first introduced by Stipe et al. [166]. The inverted design prevents the flame from flickering and provides a stable source for soot with a wide range of size distribution [167–169]. The inverted burner was run at two setpoints: (1) HighEC with an air-fuel mass ratio of 16.4, and (2) N₂-diluted with an air-fuel ratio of 24.4 and N₂-fuel mass ratio of 0.82. Combustion air was added as a coflow entering from behind the flame base. Primary dilution air flow rates of 200 lpm.
and 150 lpm were used for HighEC and N₂-diluted operating conditions, respectively. The primary particle free dilution air at 60°C was added to the system at approximately 10-20 cm downstream of the flame tip to prevent the condensation of semi-volatile material. In both operating conditions, soot aerosols were passed through a catalytic denuder (often called a catalytic stripper) operated at 350°C. This temperature was selected in accordance with the Particle Measurement Program for automotive particulate emissions based on which particles remaining after heating to 300°C to 400°C at a sufficient residence time are considered non-volatile [170]. To confirm the removal of organic material, the mass ratio of the elemental carbon to total carbon, EC/TC, was measured downstream of the catalytic stripper based on thermal-optical technique using Sunset OC-EC analyzer, run on a thermaloptical transmittance protocol. Measured EC/TC ratios were greater than 97% in both operating conditions.

The sample was drawn from the main exhaust line, approximately 1.5 meter downstream of the flame tip. In order to increase the measured scattering intensities, a secondary unheated dilution air was mixed with the sample. A sample line with the length of five meter was employed to transfer the sample from sampling point to the measurement instruments.

For all measurements conducted here, excess aerosol flow was extracted upstream of the catalytic stripper by mass flow controllers in order to maintain a flowrate of 1.5 lpm for size measurement and particle collection experiments, 3 lpm for effective density measurements, and 3.2 lpm for optical measurements through the instrument. For all cases, the denuded stream was then passed through a dryer column to remove remaining water and organic vapors.

### 6.2.2 Electron microscopy

Soot particles were collected for electron microscopy by a point-to-plane electrostatic precipitator (electric field of ~5 kV), ESPnano from DASH Connector Technology [171]. Carbon substrate 300 mesh Cupper was used for electron microscopy. TEM images were produced using a Hitachi H7600 transmission electron microscope operated at 80 kV under high-resolution mode. Images were taken at the center and four other locations around the grid; and at optimum optical focus with nominal resolution of 0.2 nm. An open-source automatic image processing program [172] was used for the characterization of the morphology parameters from the TEM images.
6.2.3 Size distribution

Size distributions and concentrations were measured by TSI scanning mobility particle sizer (SMPS) consisting of a condensation particle counter (CPC 3776), and a classifier (model 3080) equipped with a 3077A neutralizer and a differential mobility analyzer (DMA 3081). SMPS measures the size distribution and concentration of the soot particles based on the balance between the electrical mobility migration velocity and translational velocity of these particles. Inversion of the collected data to size distributions were performed by TSI aerosol instrument manager (AIM) program and an in-house developed non-negative least squares (NNLS) program. NNLS inversion algorithm uses a similar kernel function and results in similar mobility size distributions compared to AIM [173,174]; however, it provides options for: (1) consideration of the variation of the primary particle diameter with agglomerate size in the calculation of the surface area and mass distributions, and (2) application of the effective density results in the calculation of the mass distributions.

6.2.4 Effective density

Effective density of the particles can be determined by the following correlation.

\[ \rho_{\text{eff}} = \frac{m}{\frac{4}{3} \pi d_m^3} \]  

(6.1)

where \( m \) and \( d_m \) are the mass and mobility-equivalent diameter of the particles determined by CPMA and SMPS, respectively.

The mass of a particle is often found to scale with \( d_m \) in a power-law relationship.

\[ m = C d_m^{D_m} \]  

(6.2)

where \( C \) is a prefactor, and \( D_m \) is the mass-mobility exponent. Inserting equation 6.2 into equation (1), effective density can be correlated to the mass-mobility exponent by equation 6.3.

\[ \rho_{\text{eff}} = k d_m^{D_m - 3} \]  

(6.3)

where \( k \) is a prefactor.
Effective density measurements were made using a DMA, CPC, and a centrifugal particle mass analyzer (CPMA, Cambustion Ltd). Particles were first classified based on their electrical mobility-equivalent diameter using a DMA column. Multiple charging probability was greatly reduced by using a second neutralizer (soft-x-ray neutralizer, TSI Inc.) downstream of the DMA column. Then particles were passed through the CPMA. This instrument consists of two concentric rotating electrodes. Based on the balance between the centrifugal and electrostatic forces acting on the charged particles, only particles of a narrow range of the mass to charge ratio will exit the instrument [107]. The resolution of the CPMA was set between 3.15 and 8. This resolution is defined as the mass to charge ratio divided by the full width of the CPMA transfer function determined where the transmission efficiency is half the maximum value [175].

6.2.5 Optical properties

The experimental setup used for the measurement of the light scattering and extinction is illustrated in Figure 6.1, panel c. The conditioned aerosol was first charged by a unipolar diffusion aerosol charger (UDAC, Cambustion Ltd.) [176] operated at a flowrate of 3.2 lpm. Particles passing through this instrument gain high net-positive charge. Charged particles were then classified by the CPMA at sample flowrate of 3.2 lpm. The CPMA was run at different mass-to-charge ratios in the ranges of 0.05 to 0.5 and 0.03 to 0.2 fg per elementary charge for HighEC and N₂-diluted operating conditions, respectively. An aerosol flow meter (AFM; Cambustion Ltd.) was used downstream of the CPMA for measurement of the sample flow rate. The concentration of uncharged particles was also checked occasionally downstream of the CPMA by an electric precipitator and a CPC. Previous studies have shown that the majority of the uncharged particles passing through a UDAC-CPMA setup are smaller than 12 nm in mobility-equivalent diameter [177]. Concentration of the particles smaller than this size threshold is negligible for the operating conditions considered in this study. Uncharged particle number concentration was found to be less than 5 cm⁻³.

Mass concentration, size distribution, and optical properties of particles were measured simultaneously downstream of the CPMA. Mass concentration of the mass-classified particles was measured using a Faraday cup aerosol electrometer operated at a flowrate of 2 lpm. Size distributions were measured by SMPS. Extinction and scattering coefficients of particles were measured using a cavity attenuated phase shift spectrometer (CAPS-PMssa monitor, Aerodyne
Research Inc.) operated at a wavelength of 660 nm. The extinction measurement is based on cavity-attenuated phase shift (CAPS) technique, while scattering is measured using integrating nephelometry by incorporating a Lambertian integrating sphere within the sample cell. The precision of both extinction and scattering measurements is better than 1 Mm\(^{-1}\) (1s, 1σ). CAPS-PMssa scattering was calibrated with non-absorbing polystyrene latex particles (PSLs) prior to the experiments. Measured extinction, \(\alpha_{\text{ext}}\), and scattering, \(\alpha_{\text{scat}}\), coefficients were corrected for the actual pressure and temperature of the measuring cell using equation 6.4.

\[
\frac{\alpha_{\text{ext/ scat}}}{\alpha_{\text{ext/scat},0}} = \frac{P_0 T}{P T_0} \tag{6.4}
\]

where \(P_0\) is the ambient pressure, \(T_0\) is 5 Kelvins above ambient temperature, and \(P\) and \(T\) are real-time pressure and temperature of the measuring cell.

Given that extinction is the sum of the absorption and scattering, Mass-specific absorption cross section (MAC, m\(^2\) g\(^{-1}\)), Mass-specific scattering cross section (MSC, m\(^2\) g\(^{-1}\)), and single scattering albedo, \(w_0\), can be calculated from Equations 6.5-6.7, respectively.

\[
\text{MAC} = \frac{\alpha_{\text{abs}}}{m_p N} = \frac{\alpha_{\text{ext}} - \alpha_{\text{scat}}}{m_p N} \tag{6.5}
\]

\[
\text{MSC} = \frac{\alpha_{\text{scat}}}{m_p N} \tag{6.6}
\]

\[
w_0 = \frac{\text{MSC}}{\text{MSC} + \text{MAC}} \tag{6.7}
\]

where \(N\) and \(m_p\) are the number density, and average mass of the particles, respectively. \(\alpha_{\text{abs}}\) is also the absorption coefficient.

### 6.3 Results and discussion

Inverted burner was run at both HighEC and N\(_2\)-diluted operating conditions. Three sets of data were collected for effective density and optical properties at each operating condition.
6.3.1 Morphology and primary particle diameter

On average, 45 images were produced for each test point. Diameters of the primary particles, $d_p$, and projected area equivalent diameters of the aggregates, $d_a$, were measured for more than 90 particles at each operating condition.

Sample TEM images produced for HighEC and N$_2$-diluted operating conditions are illustrated in Figure 6.2. Soot structures observed on TEM images are typical of the soot produced in different combustion environments [87]. Qualitative observation of the TEM images shows higher coalescence and less clear boundaries between the primary particles at N$_2$-diluted operating condition (Figure 6.2, panel d).

![Sample images of the soot particles collected from the inverted burner. Scale bars are 100, 200, 100, and 50 nm in panels a, b, c, and d, respectively.](image)

Average primary particle diameters measured from the analysis of the TEM images are plotted against the projected-area equivalent diameters of the aggregates in Figure 6.3. As illustrated, although the average primary particle diameter is smaller at N$_2$-diluted test point, on average, it increases with $d_a$ in both operating conditions. First-order power law correlations were fitted to
the measured data. Regression results show that the slope of the fitted correlations are approximately similar for both operating conditions. The variation of the primary particle size with aggregate size can also be observed in the sample TEM images shown in Figure 6.2. The observed correlation of $d_p$ with $d_a$ is consistent with the results reported for different types of the reciprocating engines [87,178,179] and a jet engine [76,77,87]. The observed correlation suggests that the primary particles and aggregates are mainly formed in small zones where combustion conditions are relatively homogeneous; after formation and growth, aggregates from different regions, with different soot formation patterns and residence times, are mixed.

Figure 6.3: Primary particle diameter versus projected-area equivalent diameter of particles measured from TEM images.

6.3.2 Size distributions

To ensure the stability of the burner, size distributions were measured before and after the measurements of the effective density and optical properties. Size distributions of the particles produced in both operating conditions are illustrated in Figure 6.4. As shown, particles produced at HighEC operating condition are larger than the N$_2$-diluted test point. Measured geometric mean mobility equivalent diameters are approximately 240 nm and 140 nm for HighEC and N$_2$-diluted
operating conditions, respectively. As illustrated in Figure 6.4, mobility distributions calculated by non-negative least squares (NNLS) program are in agreement with the outputs of AIM software.

![Plot of size distributions](image)

Figure 6.4: Size distributions obtained with NNLS compared to TSI AIM software.

### 6.3.3 Effective density

As discussed in the experimental section, a tandem-neutralizer configuration was used in order to reduce the multiple charging probability. Sample mass distributions of the mobility-classified particles measured with CPMA downstream of a single neutralizer are compared with those obtained with the application of tandem-neutralizer and NNLS predictions in Figure 6.5. Panels a and d show the CPMA scans for 80 nm and 280 nm mobility-classified particles using single neutralizer configuration, respectively. Panels b and e represent CPMA scans for 80 nm and 280 nm mobility-classified particles using tandem neutralizer configuration, respectively. Finally, panels c and f represent the estimated mass distributions produced by NNLS for 80 nm and 280 nm mobility-classified particles, respectively. These distributions are calculated combining size distribution and effective density results with the application of Fuchs charging probabilities [180]. First and second numbers in the legends of panels c and f correspond to the number of the elementary charges particles carry downstream of the first and second neutralizers, respectively.
Effective densities were obtained here using the largest peak of the mass distributions measured from the tandem-neutralizer configuration (corresponding to particles carrying a single elementary charge downstream of both neutralizers).

![Figure 6.5: Mass distribution of size classified particles produced in N₂-diluted operating condition using single and tandem neutralizer, and derived from combined size distributions and effective density information using NNLS program.](image)

Results of the effective density measurements performed for HighEC and N₂-diluted operating conditions are illustrated in Figure 6.6. As expected, effective density decreases with particle size in both operating conditions. This is due to the fact that the fractal particles incorporate more open space as they grow in size. Particles produced at HighEC operating condition have higher effective densities.

Conventional first-order power law correlations (Eq. 6.3) were fitted to the effective density data and mass-mobility exponents were calculated. The shaded region represents an uncertainty of ±20% in effective density. As illustrated in Figure 6.6, the power law regression overestimates the effective densities of larger particles at HighEC operating condition. As an alternative, a second order polynomial equation was fitted to the HighEC effective density (Figure 6.7). However, as it will be discussed later, application of either power law or polynomial regressions for the
representation of the effective density has minor impacts on the results obtained for optical properties. Consequently, unless if mentioned otherwise, power law correlations are used for the estimation of the effective density of both HighEC and N\textsubscript{2}-diluted particles in the following sections.

Figure 6.6: Effective density versus mobility-equivalent diameter. First-order power law regressions were used for both operating conditions.

Figure 6.7: Effective density versus mobility-equivalent diameter. First-order power law and second-order polynomial regressions were used for N\textsubscript{2}-diluted and HighEC operating conditions, respectively.
6.3.4 Mass distribution

Inserting the effective density and size distribution results in equation (6.1), mass distributions of the particles produced at HighEC and N$_2$-diluted operating conditions were calculated with the non-negative least squares (NNLS) program. Count median mass, CMM, values of 3.6 fg and 0.5 fg were measured for HighEC and N$_2$-diluted operating conditions. In a similar approach, size distributions measured for the mass-classified particles using experimental setup shown in panel c of Figure 6.1 were also converted to mass distributions. Variation of the calculated CMM with the mass to charge ratio setting of the CPMA is illustrated in Figure 6.8.

![Figure 6.8: Variation of CMM with CPMA mass to charge ratio. The continuous lines are only eye guides.](image)

As shown in Figure 6, CMM increases with mass to charge ratio; however, particles produced at N$_2$-diluted operating condition have higher mass at each mass to charge set point of the CPMA.

6.3.5 Mass-specific absorption cross section

Mass-specific absorption cross sections were measured for different mass-to-charge ratios at HighEC and N$_2$-diluted operating conditions. The results in Figure 6.6 were then used to find the
MAC values reported in literature are recalculated for the 660 nm wavelength, $\lambda$, used in this study considering $\lambda^{-1}$ dependence for absorption. As shown, results obtained in this study are well within the range of the published data.

Our results show that the MAC values increase substantially with particle mass for both burner conditions. Considering this along with the correlation observed between the primary particle and aggregate diameters it may be speculated that the small and large particles have different nanostructure and may have different levels of graphitization. This is consistent with the
hypothesis that the aggregates are mainly formed in microscopic scales; after which particles with different formation, growth, and oxidation histories are mixed to form the ensemble emissions.

Interestingly, results obtained for both operating conditions follow a similar trend and can be represented by a single first order power law correlation ($R^2=0.89$).

Table 6.1: Review of the MAC numbers reported in literature for different sources and different measurement techniques.

<table>
<thead>
<tr>
<th>Party source</th>
<th>MAC (m$^2$/g)</th>
<th>λ (nm)</th>
<th>MAC (m$^2$/g) at λ=660 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond &amp; Bergstrom [9]</td>
<td>7.5±1.2</td>
<td>550</td>
<td>6.25±1.0</td>
</tr>
<tr>
<td>Schnaiter et al. [161]</td>
<td>5.2±0.3</td>
<td>700</td>
<td>5.52±0.31</td>
</tr>
<tr>
<td>Moosmüller et al. [157]</td>
<td>8.47</td>
<td>532</td>
<td>6.83</td>
</tr>
<tr>
<td>Scherrer [163]</td>
<td>9.05</td>
<td>550</td>
<td>7.54</td>
</tr>
<tr>
<td>Radney et al. [158]</td>
<td>5.69±0.83</td>
<td>405</td>
<td>3.49±0.51</td>
</tr>
<tr>
<td>Cross et al. [159]</td>
<td>7.45 to 8.68</td>
<td>532</td>
<td>6.0-7.0</td>
</tr>
<tr>
<td>Zhang et al. [156]</td>
<td>8.7</td>
<td>532</td>
<td>7.01</td>
</tr>
<tr>
<td>Schnaier et al. [160]</td>
<td>5.5</td>
<td>550</td>
<td>4.58</td>
</tr>
<tr>
<td>Horvath [162]</td>
<td>10</td>
<td>550</td>
<td>8.33</td>
</tr>
<tr>
<td>Suo-Anttila et al. [165]</td>
<td>-</td>
<td>-</td>
<td>4.0</td>
</tr>
<tr>
<td>Liu et al. [164]</td>
<td>6.2</td>
<td>628</td>
<td>6.37</td>
</tr>
</tbody>
</table>

Sensitivity of the results to effective density measurements was investigated with the consideration of ±20% uncertainty in the first order power law correlations obtained for effective densities (dotted lines in Figure 6.9). Results obtained with the application of the second order polynomial correlation for effective density of HighEC particles (dashed line) are also compared with those obtained with the utilization of the power law regression (continuous line) in Figure 6.9. $R^2$ of the regressions presented in Figure 6.9 are all greater than 0.82. As shown in this figure, the observed
increase of MAC with particle mass is not influenced substantially with the regression uncertainties for effective density.

Using the calculated first-order power law correlation between MAC and particle mass (\( \text{MAC} = 6.6 \text{ mass}^{0.125} \)), mass distributions (obtained from combined size distribution and effective density information) were converted into MAC distributions; and arithmetic mean values of 7.5 (m\(^2\)g\(^{-1}\)) and 6.5 (m\(^2\)g\(^{-1}\)) (at \( \lambda = 660 \) nm) were calculated for HighEC and N\(_2\)-diluted operating conditions, respectively.

Results presented in Figure 6.9 for the size dependency of the MAC number along with different arithmetic mean MAC values reported in Table 6.1 imply a major limitation of climate models in terms of radiative forcing of black carbon, and emphasize the need to differentiate the relative roles of black carbon particles of different sizes and origins.

### 6.3.6 Mass-specific scattering and extinction cross sections

Mass-specific scattering and extinction cross sections measured at HighEC and N\(_2\)-diluted operating conditions are plotted against the CMM values in Figure 6.10.

![Figure 6.10](image)

Figure 6.10: Right panel: MSC results obtained from experiment compared with simulations. Dotted lines are extrapolation of the modeling data to larger mass. Left panel: MEC results vs. particle mass.
Contentious lines illustrated in this figure are calculated from the simulation results reported by Liu and Mishchenko [164]. In their study, variation of the MSC with the number of the primary particles, $N_p$, was calculated using the superposition T-matrix method. Fractal dimension, $D_f$, and prefactor, $k_f$, of the agglomerates used in their simulations were 1.82 and 1.19, respectively. Their simulations were performed at a wavelength of 625 nm, $d_p=20$ nm (approximately consistent with the average primary particle diameter in our study), and two refractive indexes of $m=1.75+0.435i$ and $m=2+i$. Here, $N_p$ is converted to mass using the material density and primary particle diameter considered in their simulations, and results are corrected for a wavelength of 660 nm considering $\lambda^{-4}$ dependence for scattering. It worth mentioning that the confirmation of our results with Liu and Mishchenko [164] simulations does not necessarily mean that the particles produced at HighEC and N2-diluted operating conditions have refractive indexes of $m=2+i$ and $m=1.75+0.435i$, respectively.

Results illustrated in Figure 6.10 show that the particles produced at HighEC operating condition have higher MSC. Both modeling and experiment show an increase in MSC with particle mass. This is mainly due to the increase in the number of the primary particles as the scattering cross section varies with $N_p^2$ while the particle mass varies with $N_p$. Standard deviations of the measured MSC is considerably larger at very small mass. This is due to the low concentration and weak scattering signal at these measurement points. This shows that the increase observed in MSC for smaller particle mass may be an artifact of the measurement uncertainties.

Summary of the MSC values reported in literature for different fuels and combustion sources [158,161,165,181] is provided in Table 6.2. As shown here, results obtained in this study are well within the range of the published data.

Considering the MEC results illustrated in Figure 6.10 (right panel), in an extreme case MSC should increase from approximately zero to 5 in order to obtain a constant MAC over the whole range of the mass distribution; which is impossible.

As mentioned earlier, extinction and scattering coefficients are measured independently by CAPS-PMssa.
Table 6.2: Review of the MSC values reported in literature for different sources and different measurement techniques.

<table>
<thead>
<tr>
<th></th>
<th>MSC (m$^2$/g)</th>
<th>$\lambda$ (nm)</th>
<th>MSC (m$^2$/g) at $\lambda$=660 nm</th>
<th>Particle source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perera et al. [181]</td>
<td>5.5</td>
<td>520</td>
<td>2.12</td>
<td>Diesel</td>
</tr>
<tr>
<td>Schnaiter et al. [161]</td>
<td>0.8±0.2</td>
<td>700</td>
<td>1.01±0.25</td>
<td>Diesel</td>
</tr>
<tr>
<td>Suo-Anttila et al. [165]</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>Resin cakes, Jet-A fuel, and suitcase (warehouse burning)</td>
</tr>
<tr>
<td>Radney et al. [158]</td>
<td>6.51</td>
<td>405</td>
<td>0.92</td>
<td>Santoro-style ethylene diffusion flame, contained high OC content</td>
</tr>
</tbody>
</table>

6.3.7 Single scattering albedo

Results obtained for the single scattering albedo at HighEC and N$_2$-diluted operating conditions are plotted in Figure 6.11. Similar to MSC, measurement uncertainties increase substantially at small mass. Summary of the values reported for single scattering albedo in literature for different fuels and combustion sources [156,158,161,163,164,182–184] is also provided in Table 6.3. As shown in this table, values measured here at $\lambda$=660 nm are within the range of 0.15 to 0.3 reported in literature for the wavelengths in the range of 532 nm to 700 nm.

![Figure 6.11: Single scattering albedo versus mass.](image)
Contrary to the previously published data, it is shown here that the single scattering albedo increases with particle mass. This is similar to the trend observed for MAC increasing with mass.

Table 6.3: Review of the single scattering albedos reported in literature for different sources and measurement techniques.

<table>
<thead>
<tr>
<th>Source</th>
<th>( w )</th>
<th>( \lambda ) (nm)</th>
<th>Particle source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scherrer [163]</td>
<td>0.17±0.05</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>Colbeck et al. [182]</td>
<td>0.3</td>
<td>632</td>
<td>Diesel</td>
</tr>
<tr>
<td>Schnaiter et al. [161]</td>
<td>0.17±0.01</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>Mulholland [185]</td>
<td>0.19 &amp; 0.25</td>
<td>633</td>
<td>Laminar &amp; turbulent acetylene and ethylene flames</td>
</tr>
<tr>
<td>Schnaiter et al. [160]</td>
<td>0.22±0.01</td>
<td>700</td>
<td>CAST co-flow propane diffusion flame, contained ~30% OC</td>
</tr>
<tr>
<td>Zhang et al. [156]</td>
<td>0.1</td>
<td>532</td>
<td>Santoro-type propane diffusion burner</td>
</tr>
<tr>
<td>Radney et al. [158]</td>
<td>0.5±0.03</td>
<td>405</td>
<td>Santoro-style ethylene diffusion flame, contained high OC content</td>
</tr>
<tr>
<td>Kim et al. [183]</td>
<td>0.7</td>
<td>530</td>
<td>miniCAST propane diffusion flame, contained EC/TC=0.77</td>
</tr>
<tr>
<td>Colbeck et al. [184]</td>
<td>0.28±0.25</td>
<td>632</td>
<td>LPG combustion</td>
</tr>
<tr>
<td>Liu et al. [164]</td>
<td>0.15</td>
<td>628</td>
<td>Simulation (mass=1.51 fg, ( d_p=20 ) nm, ( D_f=1.8, k_f=1.19, m=1.75+0.435i ))</td>
</tr>
</tbody>
</table>

6.4 Conclusions

Based on measurements of optical properties of mass-classified soot particles produced by an inverted burner, there is a correlation between Mass-specific Absorption Cross section and particle mass. It was shown that MAC increases substantially with particle mass. Moreover, analysis of the samples collected for \textit{ex situ} transmission electron microscopy also show an increase in primary particle diameter with the projected-area equivalent diameter of the soot particles. Measured single scattering albedo was also increased with particle mass.

Variations in primary particle diameter and MAC are consistent with the previously proposed hypothesis based on which aggregates are formed in relatively homogeneous microscopic regions; after which particles with different formation, growth, and oxidation histories are mixed and formed the total emission. These results suggest that the particles formed in a single operating
condition may have experienced different graphitization processes and have differences in their nanostructure and/or fringe morphology.

According to the results discussed here, it is not appropriate to assume that all aggregates formed in a combustion environment have the same optical properties. Consideration of the observed variations in optical properties of soot is essential in accurate estimation of the emission rates, specially using optical methods. Accuracy of the climate models would also be enhanced with the consideration of these variations.
Chapter 7

Summary of conclusions, contributions and recommendations

In this chapter, a summary of the results obtained in this research is presented, and contributions and limitations of the research are highlighted. Finally, recommendations are described for the implementation of the results obtained in this study and future work.

7.1 Conclusions and contributions

The first objective of this research was achieved in chapter 2. Examination of transmission electron micrographs of soot samples collected from various non-premixed and premixed combustion sources showed that primary particle sizes are not well mixed within an aerosol population. For the first time, it was shown that a correlation exists between primary particle and aggregate sizes. Analysis of the TEM images revealed that the larger aggregates are mainly composed of larger primary particles, and the primary particles are more uniform in individual aggregates than in ensembles of aggregates. Therefore, it may not be appropriate to assume that all aggregates are formed from primary particles drawn from the same size distribution. These imply a need to adjust the traditional fractal model, because it would no longer be accurate to assume that aggregate mass is proportional to the number of the primary particles. This correlation also implies that the inversion algorithms commonly used for the measurement of aerosol properties, e.g. those based on scattering, attenuation, or mobility classification, need to be adjusted accordingly. For example, underestimation of the primary particle diameter of aggregates of a specific size (mobility diameter or mass) results in substantial underestimation of the scattering cross section of these aerosols.

The observed variations in primary particle size can be explained if soot aggregates are formed and grew by coagulation in small zones of the combustion chamber, prior to dilution and transport (with minimal coagulation) to the sampling system. Results presented in this chapter showed that the variation of the primary particle diameter with aggregate size is different for different sources;
however, the time involved in manual TEM analysis makes it difficult to provide quantitative measurements that can distinguish these sources.

Results obtained in Chapter 2 along with the dependence of the agglomerate properties on primary particle diameter elaborate the importance of accurate measurement of the primary particle diameter and its size distribution for fractal particles. Considering this, chapters 3 and 4 describe new approaches for the \textit{ex situ} and \textit{in situ} measurement of the primary particle diameter (second and third objectives of this study). Chapter 3 describes a new method, the Pair Correlation Method (PCM), for automatic estimation of the average primary particle diameter from TEM images. Using numerically generated agglomerates of point touching primary particles and agglomerates with different levels of the primary particle overlap, as well as TEM images of real soot, it was shown that the pair correlation function drops to a critical value $P^*$ at the average primary particle radius. Although different types of particles were found to have different $P^*$ values, it was shown that $P^*$ is nearly constant for a broad type of particles, e.g. engine soot. Using PCM, average primary particle diameter within \textit{individual} particles as well as \textit{ensembles} of particles can be calculated with average errors (relative to manual sizing) of 13\% and 4\%, respectively. This accuracy is comparable to the best available algorithms for primary particle sizing; and importantly, the PCM can be used for analysis of TEM images of agglomerates without a priori knowledge of the primary particle size. Correlation of the primary particle and aggregate diameters was also captured by this method. Results presented in this chapter show the potential of the PCM algorithm for the estimation of the primary particle overlap. This automated method eliminates the need for tedious and labor-intensive manual processing of the TEM images and benefits researchers studying not only the soot morphology, but also all forms of agglomerated particles. An approximation of the primary particle polydispersity cannot yet be determined from this method.

Even with the development of automated PCM image processing program, TEM-based primary particle sizing still requires sample collection on microscope grids and image production. These \textit{ex situ} steps make TEM method time-consuming. Chapter 4 investigates the applicability of an alternative \textit{in situ} method originally developed for the estimation of the average primary particle diameters of the zirconia agglomerates for carbon soot. This method is based on mass and mobility measurements and has two constants. Since the formation and growth of zirconia aggregates are
different from carbon soot, the primary particle diameters of soot particles measured directly from transmission electron microscopy were compared with the diameters estimated from mass-mobility measurements. Two reciprocating engines and a wide range of operating conditions were considered in this study. Contrary to the zirconia particles, it was shown that no universal model constants can be found for carbon soot. Good agreement between TEM and in situ estimations can be obtained for carbon soot only if the model parameters are adjusted for different sources and operating conditions. This suggests that with some calibration, in situ sizing of the primary particle diameter, using mass and mobility measurements, can provide useful accuracy. However, it remains to be seen whether these values will work for a broad range of soot sources. The variation of the primary particle diameter with particle size was also taken into consideration and was shown to be essential to obtain physically realistic results.

Chapter 5 describes the results obtained for the forth objective of this research. In chapter 5, the effect of the primary particle polydispersity on morphology and hydrodynamic properties of agglomerates was investigated. It was shown that for a fixed number of primary particles \( N_p \) and median primary particle diameter \( d_{pg} \), arithmetic average primary particle diameter, radius of gyration, surface area, and total mass of aggregates increase with \( \sigma_g \). Correlations were developed for the estimation of surface area, mass, and projected area of the fractal agglomerates using \( N_p \), \( d_{pg} \), and \( \sigma_g \). Using projection and Stokedian Dynamics methods it was shown that the mobility diameter of fractal agglomerates increases with primary particle polydispersity in free-molecular and continuum regimes, respectively. This increase is substantial (\(-26\%\) and \(-23\%\) for \( \sigma_g = 1.6 \) and \( N_p = 512 \) in the free-molecular and continuum regimes, respectively). Nearly all of these effects are due to the changes in overall size and radius of gyration of agglomerates. Correlations are derived for the estimation of the mobility diameter based on \( N_p \), \( d_{pg} \), and \( \sigma_g \) in fractal agglomerates in both free-molecular and continuum regimes. Application of the newly developed correlations improves the estimation of the dispersion rate and transport behavior of agglomerated aerosols in different environments, e.g. atmosphere or suspensions in liquids; and also improves the accuracy of emission measurements obtained by mobility-based spectrometers.

Results presented in chapter 5 also show the importance of discriminating between the variations of the primary particle diameters within individual agglomerates and the variations within ensembles of aggregates; which is important in the interpretation of size and mass measurements.
Finally, the last objective of this study was investigated in chapter 6. This chapter describes experimental measurements of optical properties of mass-classified soot particles produced by an inverted burner; and shows that the mass-specific absorption cross section increases substantially with particle mass. The observed correlation is consistent with the hypothesis proposed in Chapter 2, based on which aggregates are formed in relatively homogeneous microscopic regions; after which particles with different formation, growth, and oxidation histories are mixed and formed the total emission. These results suggest that the particles formed in a single operating condition may have experienced different graphitization processes and have differences in their nanostructure and/or fringe morphology. Consequently, it is not appropriate to assume that all aggregates formed in a combustion environment have the same optical properties.

Accurate measurement of the primary particle diameter from either automated \textit{ex situ} or approximate \textit{in situ} methods developed in this study benefits agglomerate studies in different fields. Consideration of the effects of the primary particle polydispersity on structure and hydrodynamic properties of particles also not only benefits soot studies and measurements, but also benefits a broad range of studies related to agglomerate dispersion and transport in different medium. Consideration of the size dependency of the primary particle diameter and agglomerate size along with the correlation of the optical properties of the soot particles with their mass provides insight into the formation and mixing of the agglomerates in combustion environments. The accuracy of the emission measurement and climate models will also improve substantially with the consideration of these dependencies.

At this point, it can be stated that the primary objectives of the thesis have been achieved. In particular,

- The correlation between the primary particle size and the size of the aggregates is investigated. The existence of the correlation was confirmed. An external mixing hypothesis was developed based on this size dependency.
- An automated image processing program was developed for \textit{ex situ} measurement of the primary particle diameter from TEM images.
- An \textit{in situ} method was developed for the estimation of the average primary particle diameter from mass and mobility measurements.
- Effects of the primary particle polydispersity and its mixing state on the morphology and mobility diameter of the agglomerates in different flow regimes were investigated and appropriate correlations were developed.
- Size-dependent optical properties of the soot particles were investigated. It was shown that the larger particles have higher mass-specific absorption. This is consistent with the external mixing hypothesis.

7.2 Recommendations

7.2.1 Recommendations for use of the present results in aerosol science

The automated image processing algorithm or the in situ mass-mobility approach introduced in chapters 3 and 4 can easily be used for accurate measurement of the primary particle diameter of agglomerated aerosols including soot.

Correlations confirmed for the variation of the primary particle diameter and MAC with particle size emphasize the necessity for refining aerosol measurements. The variation of the primary particle diameter with particle size has to be considered in the interpretation of the mobility measurements. For instance, size distributions obtained from SMPS inversion algorithms can be corrected considering this correlation. The influence of this correction would be substantial especially in the estimation of the surface area and volume/mass distributions commonly obtained from size measurements.

These measurements and data inversion algorithms can be further improved with the application of the new equations suggested in chapter 5. The influence of the primary particle polydispersity on mobility diameter is considered in these equations.

Finally, accuracy of the optical-based mass emission measurements and climate models can be enhanced with the consideration of the correlation between MAC and particle mass suggested in chapter 6.

7.2.2 Recommendations for future research

Programs could also be developed for the estimation of the primary particle overlap from the PCM algorithm described in Chapter 3. Calibrations should also be carried out for the constant
parameters used in the *ex situ* primary particle sizing method described in Chapter 4. Applicability of the proposed method to different sources should still be confirmed.

Variations of the primary particle diameter and mass-specific absorption cross section of soot with particle mass suggests differences in the formation, growth, and oxidation history of the particles which may result in different nano-structures. Fundamental combustion phenomena which leads to the observed properties still requires further research. Investigation of the graphitization level of either mass- or size-classified soot particles with Raman spectroscopy and analysis of the fringe length, separation, and tortuosity with high resolution TEM provides qualitative and quantitative insight into the combustion process and differences observed in the properties and structures of soot particles.

Furthermore, analysis of the soot samples collected at different height above burner (HAB) or experienced different treatments, e.g. oxidation, with high resolution TEM or Raman spectroscopy also provides more insight into the correlations confirmed in this research. This can be followed further by the development of advanced methods for rapid collection of soot samples from different regions of more complicated environments and analysis of these samples with the methods mentioned earlier.

This study investigated the size-dependency of the optical properties of soot particles produced by inverted burner and showed that the mass-specific absorption cross section increases with mass. Existence and strength of this trend should still be investigated for particles produced in more complex environments, e.g. engine. Interestingly, the correlation of the MAC number with particle mass was found to be approximately independent of the operating condition for the source considered here. Further investigation is required to study the source dependency or independency of this trend. This benefits the accuracy of the optical-based emission measurements, improves estimations of the soot properties, provides more reliable inputs for the climate forcing models, and provides improved insight into the combustion process.
BIBLIOGRAPHY


[170] “UNECE Regulation No. 83 (Emissions of M1 and N1 categories of vehicles).”


Appendix A

Supplemental information for chapter 2

A.1 Linear and power fits to \(d_p-d_a\) data presented in Figure 2.2 of chapter 2

Results obtained from fitting correlations in the forms of \(d_p = c\) (constant average primary particle size for all aggregate sizes) and \(d_p = a \cdot d_a^b\) (power fit) to the data presented in Figure 2.2 of chapter 2 are summarized in Table A.1.

According to these results, assuming a constant average primary particle size for the whole ensemble of the aggregates in each combustion source is erroneous. Instead, power fits all resulted in better fits and all have lower bounds (95% confidence) greater than 0.2 for \(b\) (\(b\) is the slope of a linear fit in log-scale).

Figures A.1 and A.2 compare \(\Delta N_p\) and \(\Delta d_p\), defined by equations 2.4 and 2.5 in chapter 2, for the two shielding cases assumed in this model. Shielding effect on the measurement of primary particle polydispersity is also investigated by the normalized parameter defined by equation A.1 and is illustrated in Figure A.3.

\[
\Delta \sigma_g = \frac{\sigma_{g,\text{meas}} - \sigma_{g,\text{act}}}{\sigma_{g,\text{act}}} \tag{A.1}
\]

As shown in these figures, the difference between “measured” and “actual” \(N_p\), \(d_p\), and \(\sigma_g\) in practical measurements (case 2) is smaller than the extreme case (case 1). This conforms that the effect of shielding on practical measurement of primary particle size from TEM images results in a slight overestimation of \(d_p\). However, this overestimation is less than 1% of the actual primary

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1 This section has been published as the online supplemental information for the following article: “Aerosol Science & Technology: Observations of a correlation between primary particle and aggregate size for soot particles.” 48(10): 1043-1049. Copyright 2014. Reston, VA. Reprinted with permission.”
particle diameter; and is negligible comparing to 4-6 times changes in primary particle size with aggregate size, as illustrated in Figure 2.2 (chapter 2).

Table A.1: Curve fitting results for data presented in Fig. 2.2.

<table>
<thead>
<tr>
<th>Source</th>
<th>Fit type</th>
<th>$d_p = c$</th>
<th>$d_p = a \cdot d_a^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$c = 19.93$ (19.26, 20.6)*</td>
<td>$a = 5.22$ (4.32, 6.12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R-square: -2.22e-16</td>
<td>b = 0.30 (0.26, 0.33)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-square: 0.349</td>
</tr>
<tr>
<td>GDI</td>
<td></td>
<td>$c = 24.45$ (23.84, 25.06)</td>
<td>$a = 6.49$ (5.46, 7.52)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R-square: 1.776e-15</td>
<td>b = 0.29 (0.26, 0.32)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-square: 0.327</td>
</tr>
<tr>
<td>HDPI</td>
<td></td>
<td>$c = 27.21$ (25.8, 28.63)</td>
<td>$a = 5.01$ (3.36, 6.66)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R-square: -2.22e-16</td>
<td>b = 0.39 (0.32, 0.46)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-square: 0.282</td>
</tr>
<tr>
<td>Aviation gas turbine</td>
<td></td>
<td>$c = 31.19$ (29.54, 32.85)</td>
<td>$a = 6.05$ (2.94, 9.17)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R-square: -2.22e-16</td>
<td>b = 0.29 (0.20, 0.38)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R-square: 0.195</td>
</tr>
</tbody>
</table>

* Values in all brackets are 95% confidence bounds.

Figure A.1: Effect of shielding on the number of primary particles detectable on projected images.
Figure A.2: Effect of shielding on the average primary particle diameter in individual aggregates detectable on projected images.

Figure A.3: Effect of shielding on the polydispersity of the primary particles in individual aggregates measured from projected images.
A.2 Notes for image processing program

In order to extract morphological parameters of soot particles from TEM images, a semi-automatic image processing program was developed in MATLAB. The first version of this program was developed in our group by Arka Soewono [102]. Its performance has been enhanced for accurate measurement of soot morphology at different magnifications.

The operation of this program can be divided into three sections. First, images are loaded and morphological parameters are extracted from these images in units of pixel (or squared pixel). Then, these measured parameters are scaled with the size of the pixels (nm/pixel) to acquire desired units (nm for length and nm² for area). Finally, these results are exported and further processed to produce the desired representations.

TEM images are loaded by the program (Fig. A.4, panel a). The user crops each image to select the desired aggregate (Fig. A.4, panel b). The aggregate’s morphological parameters are measured by transforming the cropped grayscale image into a binary image by setting a threshold level for the brightness of the image. To compensate for the effect of high levels of background intensity fluctuations usually present in images taken at high magnifications, the operator can draw a freehand boundary around the aggregate, but not necessarily close to it (Fig. A.4, panel c). The threshold level will only be changed in the selected region and after a background intensity correction is applied to the cropped image. Projected area, maximum length and width, gyration radius, and projected-area equivalent diameter of the aggregates are measured from the final binary image (Fig. A.4, panel d). Particle perimeter is also measured using the aggregate edge obtained from the binary image. The detected particle edge is super-imposed onto the cropped image and is used to make sure that the binary image is produced accurately (Fig. A.4, panel e). Primary particle sizing is performed manually. The accuracy of the primary particle sizing is enhanced by breaking large aggregates into multiple sections. Considering that the primary particle is not a perfect sphere, its diameter is measured by averaging its size in two different directions (Fig. A.4, panel f).

Image scale is determined either automatically, using automatic detection of the image magnification, or by using the scale bar. All measured parameters are stored in a spreadsheet. Size distribution parameters (mean, geometric mean, standard deviation, and geometric standard
deviation) of the primary particles and aggregates are calculated and histograms are plotted by the post processing part of the program.

![Figure A.4: TEM image processing steps.](image)

Upon request, this image processing program can be shared with other researchers for morphology characterization of soot particles from TEM images.
Appendix B

Supplemental information for chapter 3

B.1 PCM error using $P^*$ obtained from simulations

PCM error when average $P^*$ obtained from the simulation of the fractal agglomerates is used for straight chains:

Figure B.1: Primary particle sizing error of PCM for chains and aggregates of different sizes and polydispersity. Chain results are governed with the application of $P^*=0.84$ (corresponding to fractal agglomerates of monodisperse primary particles $\sigma_g=1$).

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1 This section has been published as the online supplemental information for the following article: Dastanpour, R., Boone, J. M., Rogak, S. N. (2016) “Automated primary particle sizing of nanoparticle aggregates by TEM image analysis” Powder Technology, 295, 218–224. doi:10.1016/j.powtec.2016.03.027.
B.2 Comparison of the manual and automated primary particle sizing results using $P^*$ obtained from simulations

Comparison of the manually measured average diameters of the primary particles in individual aggregates with PCM, when average $P^*$ obtained from the simulation of the fractal agglomerates is used for the analysis of the TEM images:

![Graph](image)

Figure B.2: Average diameter of the primary particles estimated by PCM (using $P^*$=0.85, obtained for point-touching agglomerates with $\sigma_g$=1.2) vs. TEM (manual) sizing. Solid line is a 1-by-1 line (0% error), and dashed lines are ±20% error boundaries. Figure consists of 390 data points.

B.3 Generalized model

An attempt was made to develop a general method for particles of all shapes and structures. To this end, the variation of $P^*$ with four sets of parameters was investigated (Figure B.3): i) aspect ratio of the projected particles ($L/W$), where $L$ and $W$ are the maximum length and width of the projected particle, respectively; ii) slope of the pair correlation function at two-dimensional gyration radius, $dP(R_g)/dr$; iii) ratio of $d_a/d_g$; iv) ratio of $d_a/L_{skele}$ where $L_{skele}$ is the length of the particle skeleton. The first three parameters are correlated to the fractal structure of the particles while the last one is a measure of the average particle thickness. As shown in Figures B.3 and B.4,
a simple correlation between the parameters described above and the value of the $P^*$ cannot be easily derived. The following more complex two-parameter regression was obtained for $P^*$ as a function of $dP(R_g)/dr$ and $L/W$ ($R^2=0.94$):

$$P_{gen} = \left(\frac{P_{avg}(\sigma_g)}{0.84}\right) \left[0.7 + 0.003 \left(\frac{dP}{dr}|_{R_g}\right)^{-0.24} + 0.2 \left(\frac{L}{W}\right)^{-1.13}\right]$$  \tag{B.1}

where $P_{avg}$ should be calculated from Eq. (3.2) for point-touching agglomerates and is equal to 0.913 for real soot aggregates.

Figure B.3: Variation of $P^*$ with i) aspect ratio ($L/W$) where $L$ and $W$ are the maximum length and width of the projected particle, respectively; ii) slope of the pair correlation function at two-dimensional gyration radius, $dP(R_g)/dr$; iii) ratio of $d_a/d_g$; iv) ratio of $d_a/L_{skel}$ where $L_{skel}$ is the length of the particle skeleton.

As shown in Figure B.5, while the generalized model has the advantage of using a single correlation for all particles, its accuracy is slightly lower than the simple PCM with a value of $P^*$ optimized for a particular class of particle. Using the generalized model for the analysis of the TEM images, ensemble-average diameter of the primary particles and average $d_p$ for individual aggregates can be calculated with approximately 5% and 15% error, respectively.
The generalized version of the PCM is advantageous when the structures of the particles under investigation are substantially different (e.g. when the sample contains both chains and fractal clusters to the approximately same extent); however, for most collections of the images, particle structures are not enormously different and simple PCM is preferable.

When either versions of the PCM is used, errors associated with the human biases and manual analysis of the TEM images are eliminated. As illustrated in Figure B.6, both versions of this method are capable of capturing a size correlation between the primary particle and aggregate sizes, consistent with the trends reported by Dastanpour and Rogak [87] (chapter 3 of this dissertation) from the manual analysis.

![Figure B.4: Variation of $P^* L/W$ and $dP(R_g)/dr$; and corresponding surface fit.](image)

Figure B.4: Variation of $P^* L/W$ and $dP(R_g)/dr$; and corresponding surface fit.
Figure B.5: Generalized model error for chains and agglomerates composed of point-touching primary particles, and real TEM images of carbon soot. Solid line is a 1-by-1 line (0% error), and dashed lines are ±20% error boundaries.

Figure B.6: Variation of average primary particle diameter (in individual aggregates) vs. aggregate-projected area equivalent diameter. Diameters measured by PCM.
Appendix C

Supplemental information for chapter 4

C.1 Effects of thermodenuder and heated dilution on particle volatility

Heated dilution and a thermodenuder remove any volatile components of the particulate, resulting in a conditioned sample of purely non-volatile particles. By measuring the mass at a given mobility-equivalent diameter after denuding (i.e. the mass of a particle’s non-volatile component, \( m_{\text{denuded}} \)) as well as without denuding (i.e. the combined volatile and non-volatile mass of the particle, \( m_{\text{undenuded}} \)), the relative amount of present volatility can be determined. The mass volatile fraction (\( f_m \)) can be calculated as:

\[
f_m = 1 - \frac{m_{\text{denuded}}}{m_{\text{undenuded}}}
\]

This represents the portion of a particle’s mass that can be attributed to volatile material. The mass volatile fraction as a function of mobility-equivalent diameter for the GDI engine is shown in Figure S1, and includes measurements from all three fuels (E0, E10, and E30), and both engine conditions. A similar figure of \( f_m \) for the HPDI engine is reported in [75]. The mass volatile fraction plotted here is seen to be relatively independent of particle size, at approximately 5%. The volatility is thus very low, with particles comprised mostly of elemental carbon; however it is still clear that the heated dilution and thermodenuder have removed a portion of the particulate mass.

\[1\] This section has been published as the online supplemental information for the following article: Dastanpour, R., Rogak, S. N., Graves, B., Olfert, J., Eggersdorfer, M. L., & Boies, A. M. (2015) “Improved sizing of soot primary particles using mass-mobility measurements” Aerosol Science and Technology, 50(2), 101–109. doi:10.1080/02786826.2015.1130796.
Figure C.1: Mass volatile fraction for GDI engine, including measurements from three fuel blends and two engine conditions.

C.2 TEM analysis and Sauter diameters obtained by different methods

TEM sampling, and mass-mobility measurements were carried out for 7 and 6 operating conditions of the HPDI and GDI engines, respectively. In total, data was collected from 98 measurement points.

Arithmetic mean and Sauter diameters of the primary particles obtained by TEM analysis of the samples collected from these operating conditions are summarized in Table C.1.

As shown in Table C.1, \( d_{va} \) is usually greater than \( d_p \). According to the Eq. (4.2), Sauter or surface area mean primary particle diameter \( (d_{va}) \) is defined as: \( d_{va} = 6v/a \) or equivalently \( d_{va} = \frac{\sum_i d_{p,i}^3}{\sum_i d_{p,i}^2} \). For systems of polydisperse primary particles with a lognormal size distribution (as considered in this work) this correlation can be written as:

\[ d_{va} = \frac{\sum_i d_{p,i}^3}{\sum_i d_{p,i}^2} \]

1 Only 5 (out of 98) measurement points had mobility diameters larger than 220 nm.
\[ d_{va} = \frac{\sum_i d_{p,i}^3}{\sum_i d_{p,i}^2} = \frac{\sum_i d_{pg,i}^3}{\sum_i d_{pg,i}^2} \exp[4.5\ln^2(\sigma_g)] = d_{pg} \exp[2.5\ln^2(\sigma_g)] \]  

(C.2)

As shown in the above correlation, for a fixed median primary particle diameter, \( d_{va} \) increases with primary particle polydispersity.

Sauter diameters obtained from TEM analysis, application of Eq. (4.5) with the application of model parameters suggested by Eggersdorfer et al. [84,85] and the improved parameters derived in this study are illustrated in Figures C.2 and C.3.

Table C.1: Summary of TEM results for primary particle sizing.

<table>
<thead>
<tr>
<th>Engine</th>
<th>Mode</th>
<th>( N^a )</th>
<th>( d_p^b )</th>
<th>( d_{va} )</th>
<th>( a )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPDI</td>
<td>B25</td>
<td>238</td>
<td>20.99</td>
<td>30.95</td>
<td>3.23</td>
<td>0.45 (0.31,0.59)c</td>
</tr>
<tr>
<td></td>
<td>B50</td>
<td>833</td>
<td>14.42</td>
<td>18.97</td>
<td>3.06</td>
<td>0.39 (0.27,0.50)</td>
</tr>
<tr>
<td></td>
<td>B37</td>
<td>529</td>
<td>13.46</td>
<td>16.17</td>
<td>6.86</td>
<td>0.20 (0.12,0.28)</td>
</tr>
<tr>
<td></td>
<td>B75 20% EGR</td>
<td>1368</td>
<td>25.7</td>
<td>30.42</td>
<td>14.92</td>
<td>0.13 (0.08,0.19)</td>
</tr>
<tr>
<td></td>
<td>B75 0% EGR</td>
<td>727</td>
<td>18.59</td>
<td>22.86</td>
<td>12.01</td>
<td>0.13 (0.04,0.21)</td>
</tr>
<tr>
<td></td>
<td>A63 80% Premixed</td>
<td>823</td>
<td>19.85</td>
<td>29.22</td>
<td>5.40</td>
<td>0.31 (0.24,0.38)</td>
</tr>
<tr>
<td></td>
<td>B75 25% EGR</td>
<td>1027</td>
<td>16.08</td>
<td>18.67</td>
<td>5.00</td>
<td>0.27 (0.21,0.33)</td>
</tr>
<tr>
<td></td>
<td>E0-Highway</td>
<td>397</td>
<td>24.80</td>
<td>32.59</td>
<td>10.01</td>
<td>0.18 (-0.03,0.38)</td>
</tr>
<tr>
<td></td>
<td>E0-Speed</td>
<td>182</td>
<td>22.32</td>
<td>25.98</td>
<td>9.00</td>
<td>0.16 (-0.10,0.41)</td>
</tr>
<tr>
<td></td>
<td>E10-Highway</td>
<td>586</td>
<td>19.65</td>
<td>22.89</td>
<td>5.78</td>
<td>0.27 (0.17,0.38)</td>
</tr>
<tr>
<td></td>
<td>E10-Speed</td>
<td>608</td>
<td>16.58</td>
<td>20.11</td>
<td>2.07</td>
<td>0.45 (0.33,0.56)</td>
</tr>
<tr>
<td></td>
<td>E30-Highway</td>
<td>369</td>
<td>17.62</td>
<td>21.08</td>
<td>7.10</td>
<td>0.21 (0.09,0.33)</td>
</tr>
<tr>
<td></td>
<td>E30-Speed</td>
<td>769</td>
<td>16.02</td>
<td>19.40</td>
<td>5.19</td>
<td>0.26 (0.18,0.34)</td>
</tr>
<tr>
<td>GDI</td>
<td>E0-Highway</td>
<td>397</td>
<td>24.80</td>
<td>32.59</td>
<td>10.01</td>
<td>0.18 (-0.03,0.38)</td>
</tr>
<tr>
<td></td>
<td>E0-Speed</td>
<td>182</td>
<td>22.32</td>
<td>25.98</td>
<td>9.00</td>
<td>0.16 (-0.10,0.41)</td>
</tr>
<tr>
<td></td>
<td>E10-Highway</td>
<td>586</td>
<td>19.65</td>
<td>22.89</td>
<td>5.78</td>
<td>0.27 (0.17,0.38)</td>
</tr>
<tr>
<td></td>
<td>E10-Speed</td>
<td>608</td>
<td>16.58</td>
<td>20.11</td>
<td>2.07</td>
<td>0.45 (0.33,0.56)</td>
</tr>
<tr>
<td></td>
<td>E30-Highway</td>
<td>369</td>
<td>17.62</td>
<td>21.08</td>
<td>7.10</td>
<td>0.21 (0.09,0.33)</td>
</tr>
<tr>
<td></td>
<td>E30-Speed</td>
<td>769</td>
<td>16.02</td>
<td>19.40</td>
<td>5.19</td>
<td>0.26 (0.18,0.34)</td>
</tr>
</tbody>
</table>

\(^a\) \( N \) is total number of the primary particles measured for each mode; \(^b\) arithmetic mean primary particle diameter; \(^c\) numbers in parenthesis are 95% confidence intervals.
Figure C.2: Comparison of TEM-obtained $d_{va}$ to the diameters obtained from mass-mobility measurements with the application of parameters suggested by Eggersdorfer et al. [85] and improved parameters obtained in this study. Correlations in the forms of $d_{va} = a d_a^b$, $d_{va} = a d_a + b$ and $d_{va} = c$ are fitted to TEM data are also shown in the figure. All data are for HPDI engine.
Figure C.3: Comparison of TEM-obtained $d_{va}$ to the diameters obtained from mass-mobility measurements with the application of parameters suggested by Eggersdorfer et al. [85] and improved parameters obtained in this study. Correlations in the forms of $d_{va} = a d_a^b$, $d_{va} = a d_a + b$ and $d_{va} = c$ are fitted to TEM data are also shown in the figure. All data are for GDI engine.
C.3 Estimation of $d_{va,TEM}$ for particles of mobility diameter $d_m$

Variation of the Sauter diameter $d_{va}$ with the aggregate size was taken into account using equations in the form of $d_{va} = a d_a^b$ fitted to TEM results obtained at different operating conditions of both engines. Regression results are summarized in Table C.1. As discussed in the main article, mobility diameter is assumed to be equal to $d_a$.

As shown in Table C.1, the slope of the size correlation in logarithmic scale, $b$, is positive for all test points ($d_{va}$ increases with $d_a$). Minimum 95% confidence intervals of $b$ are all positive for the HPDI engine; however a few of them are negative for the GDI engine which means that the proposed correlation between $d_{va}$ and $d_a$ is weaker for these test points. As discussed in [87] and [75], the strength of this size correlation might be influenced by the formation and growth history of soot particles; and mixture and combustion heterogeneity. Root-mean-square error was also measured for regressions in the forms of $d_{va} = a d_a^b$, $d_{va} = a d_a + b$ (linear fit) and $d_{va} = c$ fitted to TEM data for all test points. As shown in Figures C.2-C.3 and Table C.2, the variation of the primary particle size with aggregate size is better represented by a power fit.

C.4 Model parameters $k_a$ and $D_\alpha$ derived from combined mass, mobility, and TEM measurements

Using experimental data in Eq. (4.6), model parameters $k_a$ and $D_\alpha$ were measured for both cases of constant average $d_{va}$ and variable $d_{va}$ for all operating conditions of both engines. Results are summarized in Figure C.4 and C.5.
Table C.2: RMSE of different fit types for $d_{va} - d_a$ size correlation.

<table>
<thead>
<tr>
<th>Engine</th>
<th>Mode</th>
<th>$d_{va} = a \ d_a^b$</th>
<th>$d_{va} = a \ d_a + b$</th>
<th>$d_{va} = c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPDI</td>
<td>B25</td>
<td>5.11</td>
<td>13.84</td>
<td>5.51</td>
</tr>
<tr>
<td></td>
<td>B37</td>
<td>4.93</td>
<td>10.84</td>
<td>5.13</td>
</tr>
<tr>
<td></td>
<td>B50</td>
<td>3.64</td>
<td>7.74</td>
<td>4.01</td>
</tr>
<tr>
<td></td>
<td>B75 20% EGR</td>
<td>5.51</td>
<td>9.27</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>B75 0% EGR</td>
<td>5.47</td>
<td>11.07</td>
<td>7.52</td>
</tr>
<tr>
<td></td>
<td>A63 80% Premixed</td>
<td>2.85</td>
<td>4.53</td>
<td>3.67</td>
</tr>
<tr>
<td></td>
<td>B75 25% EGR</td>
<td>2.72</td>
<td>6.96</td>
<td>3.74</td>
</tr>
<tr>
<td>GDI</td>
<td>E0-Highway</td>
<td>9.36</td>
<td>12.85</td>
<td>9.64</td>
</tr>
<tr>
<td></td>
<td>E0-Speed</td>
<td>8.47</td>
<td>12.29</td>
<td>8.53</td>
</tr>
<tr>
<td></td>
<td>E10-Highway</td>
<td>3.32</td>
<td>7.44</td>
<td>4.35</td>
</tr>
<tr>
<td></td>
<td>E10-Speed</td>
<td>2.82</td>
<td>5.36</td>
<td>4.69</td>
</tr>
<tr>
<td></td>
<td>E30-Highway</td>
<td>3.53</td>
<td>7.54</td>
<td>4.34</td>
</tr>
<tr>
<td></td>
<td>E30-Speed</td>
<td>3.19</td>
<td>7.55</td>
<td>4.14</td>
</tr>
</tbody>
</table>

Figure C.4: $k_a$ measured at different operating conditions of the HPDI and GDI engines for constant and variable $d_{va}$. 

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Figure C.5: $D_\alpha$ measured at different operating conditions of the HPDI and GDI engines for constant and variable $d_{va}$.

As shown, $D_\alpha$ parameters calculated for both engines are considerably smaller when the variation of $d_{va}$ with $d_m$ is taken into account. Consequently, after applying this adjustment less compact structures were predicted for the soot particles studied here.
Appendix D

Supplemental information for chapter 5

D.1 Comparison of normal and lognormal fits to experimentally measured primary particle size distributions

Chapter 5 computes the mobility of aggregates composed of lognormally distributed primary particles. The justification of the lognormal assumption is presented here. Primary particle size distributions were measured for different operating conditions of two types of reciprocating engines: High Pressure Direct Injection (HPDI) natural gas compression-ignition engine operating with Westport Innovations HPDI natural gas combustion system, and Gasoline Direct Injection (GDI) engine. Detailed description of the experiments and operating conditions are available in (Dastanpour et al., 2015; Graves et al., 2015). For the purpose of this study, three and four operating conditions were selected randomly for HPDI and GDI engines, respectively. For each operating condition an average of 600 primary particle diameters were measured manually from the images produced by transmission electron microscopy.

Three approaches were used for the comparison of the accuracy of the normal and lognormal fits to the primary particle size distributions. First, mean and median of $d_p$ and $\log(d_p)$ were compared. Primary particles are normally distributed if mean and median of $d_p$ are equal, and lognormally distributed if mean and median of $\log(d_p)$ are equal. Our image processing results showed that the mean and median of $d_p$ were approximately 6% different while mean and median of $\log(d_p)$ were equal ($O(10^{-3})$). Second, normal and lognormal distributions were fitted to the primary particle size distributions and Root Mean Square Errors (RMSE) of the fits were

\[ \text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2} \]

\[ \text{RMSE}_{\text{normal}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_i - \mu)^2} \]

\[ \text{RMSE}_{\text{lognormal}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_i - \mu \exp(\sigma^2/2))^2} \]

\[ \text{RMSE}_{\text{lognormal}} < \text{RMSE}_{\text{normal}} \]

1 This section has been published as the online supplemental information for the following article: Dastanpour, R., Rogak, S. N. (2016) “The effect of primary particle polydispersity on the morphology and mobility diameter of the fractal agglomerates in different flow regimes” Journal of Aerosol Science, 94, 22–32. doi:10.1016/j.jaerosci.2015.12.005.
measured. Our results showed that the normal distributions have approximately 20% higher RMSE. Finally, Empirical Cumulative Distribution Functions (ECDF) were measured for $d_p$ and $\log(d_p)$ and compared with ECDF of a standardized normally distributed data set (Figures D.1 and D.2). For simplicity, only four operating conditions are plotted here.

Figure D.1: ECD of the size distributions of $d_p$ for different operating conditions. Continuous lines are for actual data while dashed lines represent ECD for a standardized normally distributed data.

Figure D.2: ECD of the size distributions of $\log(d_p)$ for different operating conditions. Continuous lines are for actual data while dashed lines represent ECD for a standardized normally distributed data.
As illustrated, the difference between the ECD of log($d_p$) and the standardized normally distributed data is smaller compared to the ECD of $d_p$.

Considering the results provided here and in literature (Boies et al., 2015; Dankers & Leipertz, 2004; Dastanpour & Rogak, 2014; Graves et al., 2015; Johnson et al., 2015; Liu et al., 2006; Wu et al., 2015), the assumption of a lognormal size distribution for the primary particle diameter was used in this study.

**D.2. Effect of primary particle polydispersity on free molecular mobility diameter**

Variation of the normalized free molecular mobility diameter of fractal agglomerates, $d_{m, fm}/d_{pg}$, with $\sigma_g$ is illustrated in Figure D.3. Although $d_{pg}$ is nearly constant for different $\sigma_g$, the mobility diameter of the particles increases with polydispersity. This increase in about 27% at $\sigma_g$=1.6.

![Figure D.3: Variation of normalized $d_{m, fm}$ with $\sigma_g$ in aggregates of different sizes.](image_url)
D.3 Effect of primary particle polydispersity on mass-mobility correlation in the continuum regime

Figure D.4: The effect of $\sigma_g$ on the mass-mobility correlation of numerically-generated particles in the continuum regime. Continuous lines are regressions to the data in the forms of $m/m_p = A d_{m,c}^{D_m}$. Dotted lines are extrapolation of the fitted lines to slightly larger $d_{m,c}/d_{pg}$.

D.4 Comparison of actual and approximate masses of particles of different primary particle polydispersity for different normalized free molecular mobility diameters

Actual mass of an individual agglomerate was measured from the summation of the masses of its constituting primary particles, while its approximate mass is measured from the application of Eq. 5.7a.
Figure D.5: The ratio of actual and approximate masses of particles of different primary particle polydispersity for different normalized free molecular mobility diameters.

D.5 Validation of Stokesian Dynamics algorithm for doublets and straight chains of monodisperse primary particles

A doublet of monodisperse primary particles was generated and subjected to uniform flow in four different directions (primary particles aligned in Z axis). Results obtained from SD are compared to those obtained from Lattice Boltzman Method (LBM) and analytical solutions reported by Binder et al. (2006) in Table D.1. Drag forces, $F_d$, reported in this Table are normalized with the magnitude of the drag force acting on a single primary particle in the same flow regime ($6\pi \mu d_p$). Results obtained from SD method are less than 5% different from other methods.

Table D.1: Comparison of normalized drag forces acting on doublets in the continuum regime measured from the SD simulations with analytical solutions and LBM.

<table>
<thead>
<tr>
<th>Flow</th>
<th>Normalized $F_d$</th>
<th>Binder et al. (2006)</th>
<th>Relative difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SD</td>
<td>Analytical</td>
<td>LBM</td>
</tr>
<tr>
<td>xyz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>001</td>
<td>1.23</td>
<td>1.29</td>
<td>1.27</td>
</tr>
<tr>
<td>101</td>
<td>1.33</td>
<td>1.36</td>
<td>1.36</td>
</tr>
<tr>
<td>100</td>
<td>1.43</td>
<td>1.43</td>
<td>1.4</td>
</tr>
<tr>
<td>111</td>
<td>1.37</td>
<td>1.36</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Straight chains of monodisperse primary particles ($N_p=1$ to 1000) were also generated. Each chain was subjected to uniform flow fields in 50 random directions and SD simulation was performed. Mobility diameters of the chains in the continuum regime obtained from SD simulation are illustrated in Figure D.6. Our results are in great agreement with those reported by Chan & Dahneke (1981), Filippov (2000), and Horvath (1974), confirming that there was no computational errors.

![Figure D.6: Normalized $d_{m,c}$ vs. $N_p$ for straight chains.](image)

**D.6 Effect of primary particle polydispersity on continuum mobility diameter**

Variation of the normalized continuum mobility diameter of fractal agglomerates, $d_{m,c}/d_{pg}$, with $\sigma_g$ is illustrated in Figure D.7. Similar to the free molecular regime, continuum mobility diameter increases with primary particle polydispersity. This increase is approximately 5% at $\sigma_g=1.2$ and 23% at $\sigma_g=1.6$. 
D.7. Effect of primary particle polydispersity on the mobility of agglomerates fully aligned in the continuum regime

Aggregates migrating in an electric field, e.g. in differential mobility analyzer, orient in a way that their smallest principle axis of inertia parallels the migration direction. The influence of the particle alignment is also simulated by rotating the grand resistance matrix to a reference system defined by the directions of the principle axis of inertia. Directions of the principle axis of inertia are equal to the principle eigenvectors of the inertia tensor defined as follows:

\[
\bar{I}_{x,y,z} = \begin{bmatrix}
\sum_{i=1}^{N_p} ((y_i - y_{cm})^2 + (z_i - z_{cm})^2) & -\sum_{i=1}^{N_p} ((x_i - x_{cm})(y_i - y_{cm})) & -\sum_{i=1}^{N_p} ((x_i - x_{cm})(z_i - z_{cm})) \\
-\sum_{i=1}^{N_p} ((y_i - y_{cm})(x_i - x_{cm})) & \sum_{i=1}^{N_p} ((x_i - x_{cm})^2 + (z_i - z_{cm})^2) & -\sum_{i=1}^{N_p} ((y_i - y_{cm})(z_i - z_{cm})) \\
-\sum_{i=1}^{N_p} ((z_i - z_{cm})(x_i - x_{cm})) & -\sum_{i=1}^{N_p} ((z_i - z_{cm})(y_i - y_{cm})) & \sum_{i=1}^{N_p} ((x_i - x_{cm})^2 + (y_i - y_{cm})^2)
\end{bmatrix}
\] (D.1)

where \(x_i, y_i, \) and \(z_i\) are the coordinates of the \(i^{th}\) primary particle; and \(x_{cm}, y_{cm}, \) and \(z_{cm}\) are the coordinates of the center of the mass of the agglomerate.

As shown in Figure D.8, continuum mobility diameter of fractal agglomerates fully aligned in an external field \(d_{m,c1}\) is approximately 0.94 of the average \(d_{m,c}\) and almost independent of \(\sigma_g\).
Figure D.8: Variation of $d_{m,c,l}/d_{m,c}$ with primary particle polydispersity.