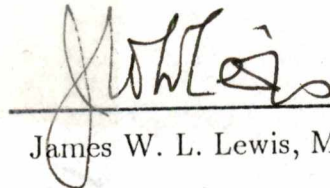
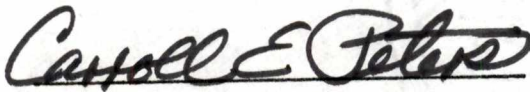


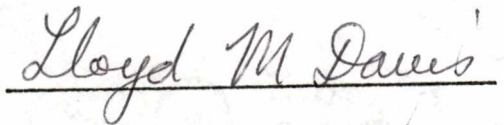
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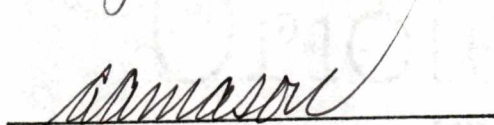
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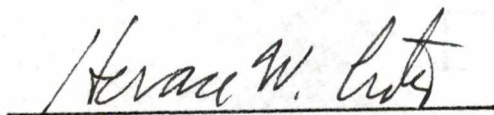

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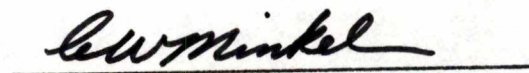








Accepted for the Council:



Vice Provost

and Dean of the Graduate School

**OPTICAL DETERMINATION OF HYDROCARBON PARTICLE
SIZES PRODUCED BY PYROLYSIS OF ACETYLENE**

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Dragan P. Petrovic

May 1991

To my children

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ABSTRACT

Optical determination of particle sizes produced by flames is complicated by uncertainties in the properties of the produced solid particulates which is a result of the complex reaction pathways which lead to their formation and growth. This work reports on the design and construction of an apparatus for the generation of hydrocarbon particles by thermal decomposition of acetylene in the drift-tube environment and the results of optical measurements leading to the determination of particle sizes and particle number densities.

The transmission measurements were performed in the ultraviolet portion of the electromagnetic spectrum and the applicability of the optical constants for soot which were obtained from the theoretical extrapolations has been verified for the wavelengths in the range from 260 to 400 *nm*. The determination of particle sizes and number densities was obtained by applying a novel method for the deconvolution of the results of multiwavelength transmission measurements.

For pressures of approximately 290 *Torr*, the temperature of 1350 *C*, and growth-time in the vicinity of 50 milliseconds, particle sizes were determined to be in the vicinity of 60 nanometers from the transmission-measurement results, while the diffusion-broadening measurements yielded values in the range from 35 to 40 nanometers in diameter. The agreement between the results of the two different optical particle-sizing techniques is acceptable considering the assumptions which entered the determination of particle sizes in each of the two measurement techniques.

The growth of particles was modeled by mapping of the essential features of the evolution of soot particles onto the two fractal-growth models. The applicability of the scaling theory to the solution of the coagulation (Smoluchowski) equation

under the conditions which existed in the apparatus was tested by evaluating the reaction-rate constants in the coagulation equation.

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CHAPTER I

INTRODUCTION

It is well-known that the burning of hydrocarbon fuels is accompanied by the production of soot particles. Although soot production is a familiar phenomenon, the understanding of the soot-formation process is far from complete. The primary reason for this lack of understanding is the complexity of the soot generation process. Also, there are limitations in conducting experimental investigations under the conditions in which soot occurs readily; *i.e.*, in flames.

The importance of this lack of understanding is reflected in the effects of soot on a variety of phenomena. The preservation of both local and global environments is a major problem of modern civilization. In spite of efforts to develop alternative sources of energy, hydrocarbon fuels continue to play a key role in energy production. Mostly of anthropogenic origin, soot is an important constituent of atmospheric aerosols, contributing to about thirteen percent [1]¹ of total suspended particulate material at urban locations. The presence of soot particles in the atmosphere has an adverse impact on health, reduces visibility, and alters the local and global climate. For example, soot produced in diesel engines has a tendency to absorb carcinogen materials and thus represents a health hazard. Atmospheric soot particles participate in the radiative transfer of solar energy which may lead to a significant reduction of local temperatures, as observed in some medium-scale fires [2]. Long-range transport of atmospheric soot, generated primarily in urban areas, to remote areas such as the Arctic and Antarctica has been observed [3] and may result in a change of the global climate. This is expected since the increased light absorption in the visible portion of the electromagnetic spectrum of soot-contaminated ice and snow have higher melting

¹Here and in the following, numbers within the square brackets refer to the numbered entries given in the References on page 181.

rates than the uncontaminated materials.

As an integral part of the combustion process, soot has a significant impact on the overall performance of combustors. Heat-transfer rates are influenced by the presence of the soot particles [4]. In most cases, soot increases the radiative power of the flame, which amounts to an increase of the heat transfer rates. This is important in some flame-heating applications, and in such cases, it is desirable to operate with a soot-laden flame. However, soot particles can also have detrimental effects since the presence of soot can shorten the lifetime of gas-turbine blades or cause burn-out of walls in cooled, liquid-propellant rockets [4]. Soot in jet-engine exhausts also participates in radiant energy-transfer with the result that engine exhausts have characteristic radiation signatures. This information is important for military applications. Fuel additives can alter the visibility of aircraft turbine engine exhausts [5], and it is of interest to investigate the origins of that phenomenon.

Experimental investigations of soot can be classified into two general groups. One class of studies is motivated directly by the improvement of the understanding of the soot formation process. A better understanding of mechanisms of the nucleation and growth of soot is necessary to gain a control over the production of soot. In some applications it may be advantageous to increase production of soot (flame-heating applications). However, in most cases increasing the soot production presents no difficulties. More frequently, it is desirable to suppress the soot production (*e.g.* environmental applications). Either way, an understanding of growth mechanisms provides an opportunity for controlling, and therefore optimizing the soot production in particular applications.

Another class of soot-related studies is concerned with the diagnostics of soot. Soot is often found in complex systems where it plays an active role in the overall dynamics of the system through its chemical reactivity and the radiative heat-transfer

processes. Combustion is an obvious example where the presence of soot has an impact on chemical processes in flames by depleting number densities of the species which participate in its formation and growth by providing sites for heterogeneous nucleation, and by having a significant impact in establishing the overall heat balance in the system. Since the kinetics of all reactions are temperature-dependent, soot plays a significant role in the overall dynamics of such complex systems. Similarly, atmospheric soot is just one of the constituents of the total particulate matter in the atmosphere which must be accounted for to characterize behavior of a system under consideration. Accurate determination of quantity and size of soot particles is therefore important for analysis of such complex systems.

Optical diagnostic techniques are convenient for *in situ*, non-intrusive measurements which is a crucial consideration for the study of chemically reactive systems. It is well known that optical diagnostic techniques depend on knowledge of the optical properties of particles under consideration [6,7]. Experimental data for soot [8] are scarce, and it is common practice to rely on the theoretical extrapolations for optical constants of soot in the visible and the ultraviolet (UV) portion of the spectrum. The sensitivity of a particle-sizing techniques based on the measurement of the intensity of light depends also on the size parameter². Since the size of particles under consideration is unknown, measurements at wavelengths for which the knowledge of optical properties is uncertain may be required to achieve adequate sensitivity with respect to particle size. The use of extrapolated values for optical constants from the literature [8-13] in the particle-sizing applications must then be verified. Another important aspect for the particle-sizing applications is the fact that experimentally studied soot samples frequently have a distribution in sizes [4,14]. The determination of the particle-size distribution function from optical

²The size parameter is defined as $x = \pi D/\lambda$, where D is the diameter of the particle, and λ is the wavelength of the incident light.

measurements is a difficult task, particularly if the form of that distribution is not known beforehand [6]. Therefore, it would be advantageous to develop and verify techniques for the determination of the particle-size distribution on a soot particles produced in a controlled manner, which lend itself to systematic investigation by several particle-sizing techniques.

The experimental part of this dissertation is comprised of particle-sizing measurements on pyrolysis-generated soot in a drift-tube environment, which have not been reported in the literature. As was mentioned earlier, most of the experimental data about soot originate from studies on a flame-generated soot, where the presence of oxygen may play a crucial role in the formation and growth of soot [14]. On the other hand, pyrolysis of hydrocarbons takes place in flames as well. Since soot can be formed by pyrolysis of hydrocarbons [4,14], it would be advantageous to create experimental conditions which would allow one to study soot formed in an oxygen-free environment. The elimination of oxygen from the system reduces the uncertainty with respect to the chemical composition of soot which, in turn reduces uncertainty in the optical properties of soot particles. The importance of isolating the soot formation and growth from chemical reactions involving oxygen will be discussed in more detail in Chapter II. In addition to this topic, that chapter presents a brief overview of main characteristics of soot, and an overview of the thermal decomposition of acetylene process. A drift-tube environment is a choice which provides grounds for studies of soot-growth *per se*, and for the verification of particle-sizing techniques.

The formation and growth of soot will be discussed in more detail in the next chapter, but it is necessary to mention here that it is generally recognized that the soot-formation process has three distinct stages. The first and least understood stage of the process is the nucleation of the soot particles. In the nucleation stage, the

complex sequence of chemical reactions transforms the molecular system into the larger-size particulates. The transition from a large molecule to an incipient soot nucleus is somewhat arbitrarily specified to occur for particulate masses of approximately 10^4 *amu*, which corresponds to a particle of about 3 *nm* in diameter. The second stage of the process is the growth of these nuclei from their initial size of a few nanometers in diameter to spherical particles with diameters in the range of several tens of nanometers. The final stage in the soot production is the agglomeration of these spherical entities into larger units. When examined under the electron microscope, these larger units frequently form chain-like structures [4,14,15].

Although the formation of incipient nuclei presents the greatest mystery, mechanisms of growth in the last two stages are also subject to discussion [16,17], and the study of soot in all three stages of growth needs further research. In addition to this, one intuitively expects that the last two stages of growth will be accompanied by the development of an appreciable distribution in sizes of soot particles. Therefore, the study of the last two stages of growth is important for both the soot-growth studies and the application of optical diagnostic techniques.

To perform the particle-sizing measurements on the pyrolysis-generated soot in the drift-tube environment, it was necessary to design and build an apparatus which would lend itself to such studies. The apparatus, which will be referred to as a *soot generator*, should meet several requirements:

1. The apparatus should produce soot in a system involving only carbon, hydrogen and inert gases.
2. The apparatus must permit one to apply optical diagnostic techniques with temporal resolution which is of interest in the soot-formation process.
3. The apparatus should have the capability of collecting soot samples which could

be analyzed with a scanning electron microscope.

Chapter III of this dissertation describes the development of an original apparatus for study of the final two stages of the soot formation process. The realization of such experimental conditions is a significant accomplishment of this effort. Inductive radio-frequency (RF) heating of graphite was chosen as the method of heating which is required for achieving high temperatures required for thermal decomposition of hydrocarbons. Acetylene was the obvious choice for the hydrocarbon material. Acetylene and polyacetylenes are important species for the soot formation process [14]. Moreover, the thermal decomposition of acetylene has been well-studied in the past [18-27], although the thermal decomposition process of acetylene by itself has eluded full understanding. As this type of experimental setup is new, the material presented in that chapter is necessarily descriptive in nature. The performance of the apparatus was evaluated qualitatively by applying different optical diagnostic measurements. Specifically, video-intensified microscopy and the transmission measurements have been used for a preliminary characterization of the apparatus performance.

Two different optical techniques were applied for the characterization of particle sizes in the particle field generated by the soot generator: multiwavelength transmission measurements and diffusion-broadening spectroscopy. The basic theoretical background of the determination of the particle-size distribution function (PSDF) from a multiwavelength transmission data is discussed in detail in Chapter IV. That chapter presents analysis of a numerical fitting procedure which is required for the determination of the mean diameter and the variance of the PSDF. The presented numerical technique was applied to the results of transmission measurements, which are described and presented in Chapter V.

Chapter VI presents the theoretical background, the experimental apparatus,

and the results of the particle sizing using diffusion-broadening spectroscopy. Since the data acquisition and processing scheme employed in this set of measurements is unusual, a significant portion of this chapter is devoted to a detailed description of those measurements.

Chapter VII is devoted to the characterization of the growth of soot-particles. It was shown that the essential features of the evolution of soot particles can be mapped on the fractal-growth models and that the time is, in general, a scaling variable. This allows one to capture essential features of the soot-particle growth. The quantitative description requires the introduction of some assumptions about the details of growth. The applicability of the scaling analysis to the growth of soot particles was investigated by assuming that neutral species control the growth.

The particle-sizing of pyrolysis-generated soot in a laminar flow using the combination of multiwavelength extinction measurements and diffusion-broadening spectroscopy techniques has not, to the author's knowledge, been performed in the past. The agreement between the obtained results with the results of the multiwavelength transmission measurements was acceptable considering the difficulties which accompanied the acquisition of data during the light-scattering measurements (diffusion-broadening spectroscopy). This result is particularly significant since it allows one to validate the use of UV-extrapolated values for optical constants of soot. The determination of particle sizes by a diffusion-broadening spectroscopy technique does not depend on the optical properties of particles. Since the data inversion of transmission required the use of the extrapolated values for the optical constants, the outcome of these measurements confirms the validity of such extrapolation.

Analysis of the determination of the particle-size distribution function parameters from multiwavelength transmission measurements is also, to the author's knowledge, an original work which sheds some light on the applicability of the pre-

sented numerical fitting procedure for that purpose.

Another important outcome of these measurements concerns the evaluation of the performance of this new type of experimental arrangement. Difficulties, the most significant one being related to the very nature of the acetylene decomposition process, and advantages of this apparatus are discussed in Chapter VIII. That chapter presents a summary of the work performed, and recommendations for further study.

CHAPTER II

CHARACTERISTICS OF SOOT

This chapter has four distinct sections which present various soot-related information which is pertinent to the present study. The first section gives a brief overview of the general properties of soot. The knowledge of the complex index of refraction of soot is a prerequisite for the determination of the particle-size distribution parameters from the multiwavelength transmission measurements, and the second section is devoted entirely to a review of the relevant published material. The third section discusses primarily the existing theories of the soot nucleation process. The main purpose of a brief review of the possible chemical reaction pathways in the nucleation is to show the significance of the soot-formation process in an oxygen-free environment. The last section discusses thermal decomposition of acetylene, with intention to outline a behavior that could be expected in a soot particle generator.

II.1 General properties of soot

As was mentioned in the Introduction, the mechanisms for the formation and growth of soot are not well understood. The lack of understanding of soot-formation does not imply that very little is known about soot. There is an abundance of experimental data obtained by a variety of experimental techniques which provide information on the chemical composition of soot and help in establishing the general time sequence of events in the soot generation process. Since most of the experimental data refer to soot studies in flames at atmospheric pressures, the following brief overview of the field refers primarily to such conditions, and quoted numbers illustrate order-of-magnitude values for specific quantities. A complete review of soot properties and the soot-formation process is beyond the scope of this work; the

interested reader is directed to existing review articles and books [4,14,15].

The term *soot* refers generally to irregularly shaped particles whose building-blocks are roughly spherical particles of several tens of *nm* in diameter. These spherical building-block particles are frequently referred to as soot particles since the formation of irregular, chain-like structures does not always occur [15]. Soot particles are comprised of a large number of crystallites, 2 – 3 *nm* in size, with graphitic, hexagonal structure. One characteristic of the graphite crystal is that it is comprised of parallel lattice planes with a honeycomb arrangement of carbon atoms [28]. These planes have a very specific ordering and relative orientation with the interplanar separation of 3.35 Å. Unlike graphite, crystallites found in soot have a random orientation of planes (five to ten planes per crystallite) with a honeycomb arrangements. Layer planes are still parallel to one another, but due to the random relative orientation, the inter-planar separation is larger (3.44 Å). The structure of soot has not been explained [15]. It is not clear whether the crystallites are growing from within an already formed particle, or the particle is formed by coagulation of growing nuclei.

The overall atomic carbon-to-hydrogen (*C : H*) ratio of soot is in the range from 8:1 to 12:1. Flame-generated soot may also contain significant amounts of other elements, like oxygen. Other elements that may have been present in the initial hydrocarbon fuel can be detected in soot particles as well [4]. Incidentally, it is quite common to find that the term *carbon* is used in the literature as a direct substitute for the term *soot*. Considering the complex chemical composition of soot particles, the use of the word “*soot*” is more appropriate. Hydrogen content depends on the particular conditions under which soot is formed. For example, acetylene black, which is formed by a thermal decomposition of acetylene, contains very small amounts of hydrogen [15].

Soot particles may also be electrically charged [14] with the fraction of charged soot particles changing during the soot-formation process. In the final stages of growth, 20 to 30 % of flame-generated soot carries one unit of electrical charge. Both positively and negatively charged particles are present in appreciable amounts [29]. It has been demonstrated that soot formation and luminosity of air/ethylene flames, which is an indicator of the presence of soot in flames, can be influenced by the application of the electric field. However, a similar effect was not observed in acetylene flame [15].

Effects of pressure, temperature, and chemical additives on the soot formation in flames have also been investigated as well [15]. In general, higher pressures result in an enhancement of the soot production. The effects of temperature are complex since the fuel composition has a strong influence on the determination of the dominating reaction pathways. Addition of non-metallic species to flame fuels can enhance or suppress the soot formation, and these effects are usually related to the changes in the effective air/fuel ratio, temperature, effective pressure (addition of inert gases), or particular chemical reactions. Addition of metallic additives generally amounts to an decrease in soot formation. The explanation is generally linked to the role of ions in the soot formation, but a detailed interpretation of these effects is not clear [15].

One of the difficulties in the explanation of soot formation process stems from its hydrogen content. For the initial, unburned hydrocarbon material, the atomic carbon-to-hydrogen ($C : H$) ratio is on the order of 1:1, and the chemical processes that lead to an order-of-magnitude increase of this quantity remain unclear. The chemical composition of soot is a very important issue for the soot particle-sizing problem. This is particularly significant if soot particles contain elements other than carbon or hydrogen. In this case, the possibility of having a resonant impurity state

may have diverse effects on optical properties of soot particles, and significant effects on the interpretation of the optical diagnostic measurements.

II.2 Optical properties of soot

Marchand [30] reviews optical properties of various forms of solid carbon which indicate that essential features of the absorption spectra for different types of carbon have great similarity with graphite. Quantitative differences may be large, however, and the determination of firm correlations for possible causes of differences is far from complete. Efforts by Pluchino *et. al.*[12] illustrate the importance and the magnitude of uncertainties. In a version of the Millikan oil-drop experiment, they have performed angular-scattering measurements on a single carbon particle. Using the Mie theory and the Marquardt's [31] nonlinear least square regression, they were able to determine particle sizes and attribute optical constants to individual particles. They reported measurements on two different carbon particles, supplied by the same manufacturer, having the same size of $3.75\mu m$. Recovered indices of refraction for both particles were nearly the same (1.7 and 1.6 at 488 nm), while the extinction coefficients differed by 60 percent (0.8 and 0.5). The magnitude of this discrepancy may not be unusual, nor cause a significant error in the determination of the particle sizes, but it may be important for the determination of the total amount of soot in the flame [8].

For soot, experimental, optical property data in the UV are scarce. In some portions of the spectrum, it is necessary to use the theoretical or extrapolated expressions. Although this may be convenient, there is no substitute for the experimental data. Recently, Bockhorn, Fetting and Heddrich [17] reported measurements which indicate that the optical properties of soot change during the growth of soot particles. This is may be attributed to the chemical constituency which changes during

the growth. Dalzell and Serofim [8] also conclude that optical properties depend on the $C : H$ ratio and note that there is no strong correlation between the optical properties and the molecular structure. They also developed an expression which is widely used for particle-sizing applications. The model is based on the dispersion relation where parameters are fitted to experimental data in the 400 nm to 1000 nm range. A similar model, with different parameters, has been proposed by Lee and Tien [9] and they point out that the temperature dependence of optical constants is present, but not significant.

Regardless of all the questions, it is the consensus that the model developed by Dalzell and Serofim is valid in the visible part of the spectrum. Therefore, in the absence of experimental data, it will be assumed here that an extrapolation to the near-UV and the UV part of the spectrum is also valid. Figure II- 1 shows the optical constants of soot that will be used in the data inversion procedure. The absorption peak at 250 nm , which is characteristic for all forms of carbon with graphitic structure [30], is a prominent feature in this model for soot as well.

II.3 Nucleation and growth of soot

The most striking features of the soot-growth process are the time scale of events and the chemical composition of the final product. The generation of soot in flames occurs typically within several tens of milliseconds, [14,4]. Initial incipient particles occur within a few milliseconds, then form spherical particles with diameters of 10 – 30 nm within 10 – 20 $msec$, and finally agglomerate after several tens of milliseconds into larger soot aggregates. Considering the initial molecular and atomic species which initiate the process, the magnitude of the size change over such short time intervals is remarkable. The characteristic particle size increases three orders of magnitude which is equivalent to an increase of nine orders-of-magnitude in the

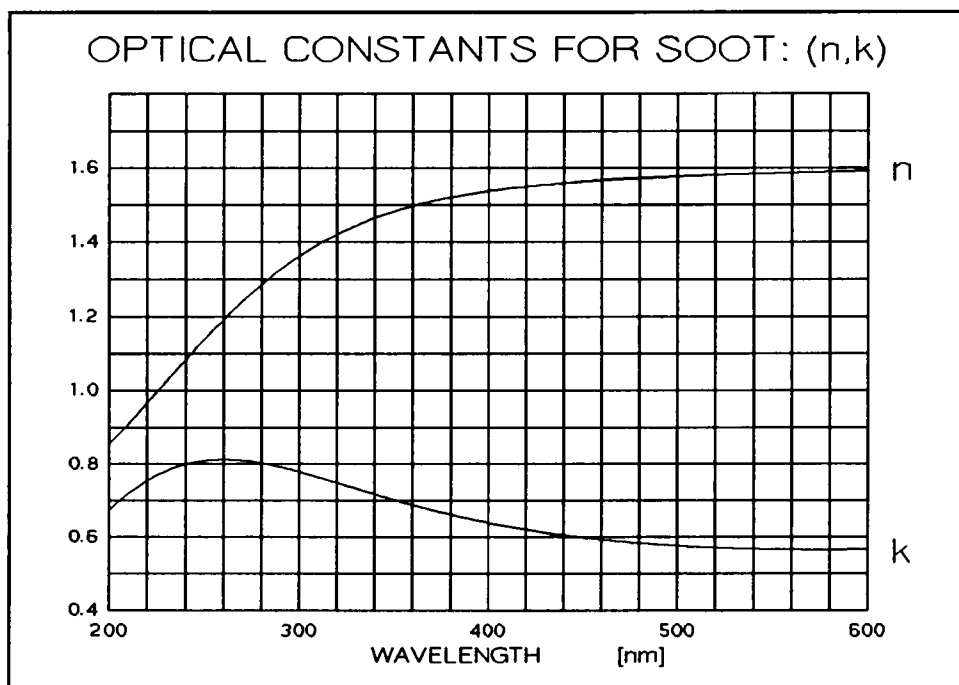


Figure II- 1: Optical constants of soot according to Dalzell and Serofim [8].

molecular weight. Identification of the governing chemical pathways that explain this dramatic transformation is one of the major problems that requires explanation. In addition to accounting for the time sequence of events, theoretical models should explain the graphitic structure and the chemical composition of soot particles. A brief overview of theoretical efforts to model the formation of soot will show the importance of the investigation of the soot-formation process in the oxygen-free environment.

Existing theories of the soot-formation process can be classified into two basic groups. One group of theories emphasizes the role of ions in the soot-formation process, while the other set of models gives preference to various chemical pathways involving neutral species. The number of reacting species that participate in the process is large and thus presents difficulties in the identification of the mechanism which controls the soot-formation. The number of possible reaction channels is even larger. Since experimental data for most of the reaction channels do not exist, theoretical studies [21] frequently involve complex chemical reaction systems where

most of the parameters are estimated. This makes it difficult to identify a single path responsible for the soot-formation phenomenon.

A comprehensive review of the field given by Calcote [14] is remarkable for many reasons. A compilation of published experimental data, primarily on sooting flames, allowed him to analyze many of the proposed theories and to propose a new model for the incipient soot-formation. A range of models based on neutral species have been essentially rejected by Calcote on various grounds. Reactions involving polyacetylenes are estimated to be too slow to explain the rapid formation of soot. The polyacetylene theory considers the addition of radicals forming a giant chain-molecule as the primary mechanism for the incipient soot-particle. This theory accounts for the $C : H$ composition change since radical addition is accomplished by the dehydrogenization of the large chain molecule. Apart from the objection to the characteristic time scale involved, the main obstacle in the polymerization theory is the inability to explain the graphitic structure of soot particles. The final product of this chain-reaction process is a giant chain molecule with essentially a linear structure rather than the polycyclic carbon structure which is characteristic of soot. Polycyclic aromatic hydrocarbons (PAH) are also observed in sooting flames, and since the formation of the cyclic structure is a problem in the polyacetylene chain reaction scheme, it is only natural to investigate the possibility of whether the PAH species play a significant role in soot-formation [26]. Experimental results show that the concentration of PAH species continues to increase well beyond the point at which the soot formation rate is negligible. A combination of reactions involving polyacetylenes and PAH species with free radicals may explain the soot-formation process through neutral-species reactions. However, such theories are not yet developed.

One theory which may be particularly suitable for the explanation of pyrolysis-

generated soot has a following scenario: the nucleation of initial particles is followed by a surface-growth and then growth proceeds by coagulation [15]. It is well known [32] that nucleation of particles occurs readily if nucleation sites such as ions of either sign, or even a large molecule already exist in the system if the vapor reaches supersaturation state. Therefore, once a surface in the form of a carbon particle is available, it will continue to grow. This growth results in a reduction of the vapor pressure and at some point the equilibrium is established. Subsequent growth takes place by coagulation which would result in formation of chains. Tesner [27] finds that the activation energy for the decomposition of acetylene on a solid carbon is close to zero, and thus supports this model in the case of the acetylene flames, or the soot generated by pyrolysis of acetylene. Gaydon [15] argues that this model does not explain the $C : H$ ratio.

Calcote [14] indicates that ionic theories are gaining in acceptance. A mechanism proposed by Calcote involves chemical reactions of ionic species with C_xH_y as the neutral building blocks³ rather than physical nucleation on ions. In this scheme, C_xH_y species interact with the primary ions which leads to the dehydrogenization and growth in size of ionic species. Such reactions are thermodynamically favorable exothermic reactions which are presumably fast enough to explain the rate of incipient soot formation. Larger hydrocarbon ions, such as $C_{13}H_9^+$ or $C_{19}H_{11}^+$, presumably rearrange into aromatic structures very rapidly since gaseous ions are considerably more stable in such structures. These larger aromatic ions continue to grow with continuous dehydrogenization process via further oxidation and reactions with C_xH_y species. It is conceivable that these ions and neutralized molecules continue to grow to molecular weights of about 10^4 *amu*. At that point, it is assumed that the huge molecules are essentially the incipient soot particles which continue to grow through

³ C_xH_y stands for different species including acetylene, polyacetylenes, and species such as C_2H , CH_2 , and C_4H .

the particle-particle agglomeration process. This is indicated by the fact that the total soot production rate approaches zero and the number density of soot particles starts decreasing while the average size of soot particles increases.

The scenario proposed by Calcote is appealing since it is based on the fast ionic reactions, which allows one to account for the rapid increase of molecular weights. Also, the $C : H$ ratio is expected to increase via the dehydrogenization process. This model is far from being accepted since it is merely a qualitative model which has the potential to account for various experimental observations. The key element in this model is the presence of the incipient ions. The assumption is that the primary ions in flames are produced by chemi-ionization reactions such as



The presence of oxygen supports the explanation for the high $C : H$ ratio since it is expected that the oxidation of large molecular ionic and neutral species contributes to the dehydrogenization of the soot. Therefore, the presence of oxygen is an important ingredient of ionic theories.

However, soot particles are also observed without the presence of oxygen in the thermal decomposition of hydrocarbons. The presence of ionic species in pyrolysis experiments have been confirmed by experiment as well, and according to Calcote [14] the reaction



is probably responsible for the production of the primary ions in the pyrolysis. As we are interested in the thermal decomposition of acetylene, it should be mentioned that the origin of ionic species in the pyrolysis of acetylene is unclear. Although acetylene is a relatively simple molecule, the thermal decomposition process of acetylene is not well understood. Regardless of the origin, it is plausible that ionic species in

pyrolysis play a significant role in the soot-formation process. However, the models involving ionic species depend on the presence of oxygen in flames. The explanation for the high $C : H$ ratio of soot in Calcote's ionic mechanism relies in part on the oxidation process. Therefore the experimental studies of the soot produced by the thermal decomposition of hydrocarbons has the potential of shedding some light on the soot-formation process. The pyrolysis of hydrocarbon takes place in flames as well. Therefore, the effect of the oxygen-free environment on the soot-formation process remains to be investigated.

The composition, or the $C : H$ ratio, of soot produced by the thermal decomposition of hydrocarbons may be different from the composition of soot occurring in flames. Also, the time scale of events in pyrolysis may differ appreciably from flame-generated soot, assuming that the fast ionic reactions are important. Therefore, the study of soot-formation in an oxygen-free environment should provide the opportunity to obtain one more piece of experimental evidence which may prove useful in the explanation of the long-standing problem of soot-formation⁴.

II.4 Thermal decomposition of acetylene

Thermal decomposition of acetylene is a well-studied, chemical phenomena [18-24,27]. The thermal behavior of the acetylene molecule, which has a linear structure $H - C \equiv C - H$, is rather complex. It has been studied experimentally in static systems [18], flow systems [19,20], and shock-tubes [22,24], and experimental data exist for temperatures in the range from 625 K to 2500 K. A detailed, theoretical kinetic-model of soot formation in shock-tube pyrolysis has also been proposed by Frenklach *et.al.* [21]. Accounting for approximately 600 elementary reversible reactions of 180 species, they showed that the soot formation in shock-tube pyrolysis

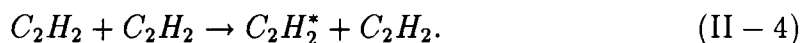
⁴It should be stated that the goal of this dissertation is not to answer the fundamental questions about the soot-formation process. That would be a very ambitious task indeed.

of acetylene can be explained by a detailed study of neutral-hydrocarbon reactions (ionic reactions were not considered). The model showed that the formation of species with the aromatic ring governs the overall kinetics of the system. It should be noted that species such as C_2 or ionic species were not considered. Most of the published work is concerned only with the chemical aspects of the decomposition. Tesner [27] reports sizes of particles formed by the thermal decomposition of natural gas ($0.05 \mu m$). Some information about soot particles produced by pyrolysis of acetylene originates from the research related to the production of acetylene-black. Acetylene-black is a product which is important for the carbon-black industry⁵. It is usually manufactured by a continuous pyrolysis at temperatures around $800^\circ C$, and it results in particles which are fairly small, $400 \text{ \AA}$ to $500 \text{ \AA}$.

Thermal decomposition of acetylene is a result of both homogeneous and heterogeneous processes, which gives it a temperature dependence whose interpretation is complex. At low temperatures ($T < 800K$), homogeneous reactions dominate the process, while at high temperatures ($T > 1900K$), heterogeneous decomposition of acetylene is the dominant process[20]. For a specified temperature, both heterogeneous and homogeneous reactions exist. The homogeneous reactions are of second order in acetylene concentration, while the heterogeneous decomposition is a first-order reaction. The heterogeneous reaction is dominated by the reaction [18,20]



The homogeneous process involves a complex sequence of reactions where the initial step is the excitation of the acetylene via



This reaction should dominate the process even in the presence of the inert gases [18]. Subsequent reactions of the excited state of the acetylene molecule, $C_2H_2^*$ (its

⁵The soot is used as a filler in a rubber-making, inks, paints, and microphones.

lowest-lying triplet state), may result in the deactivation of acetylene or participate in the addition-reaction



The $C_4H_4^*$ molecule interacts further with the acetylene molecule and either starts the polymerization process or produces various stable aromatic molecules (primarily benzene), which have been observed experimentally [23].

Since the products of the initial cracking of acetylene are different for homogeneous and heterogeneous reactions, overall products are a complex function of temperature. Products of the homogeneous reaction tend to undergo a long chain polymerization [18] with a chain length on the order of 100 reactions or more, while the heterogeneous reaction products are primarily carbon and CH_4 . Therefore, the surface decomposition of acetylene has a completely different nature from the homogeneous decomposition. In systems where the heterogeneous reactions dominate the kinetics, *i.e.*, in systems with a high surface-to-volume ratio, a heavy production of soot can be observed [18].

Chemical reactions following the decomposition of acetylene can be classified into two groups: chain-carrying reactions and chain-ending reactions. In chain-carrying reactions the addition of free radicals leads to the formation of long chain molecules, while chain-ending reactions result in the formation of stable aromatic molecules. The chain-ending reactions have a much stronger temperature dependence than the chain-carrying reactions. As a consequence, low temperatures favor formation of long chains, while at high temperatures, the kinetics of the chemistry are dominated by non-chain reactions.

For the design of the soot particle generator it is important to note the main trends of the pyrolysis process. At low temperatures, the formation of long chains is dominant, while chain-ending reactions producing aromatic products are favored

by higher temperatures. Also, heterogeneous reactions lead to a direct production of C_2 species.

Finally, it should be mentioned that the absorption spectra of hydrocarbons undergoing pyrolysis in a flow-tube have been studied [15]. Continuous absorption developed with the increase of temperature. At lower temperatures, absorption was strongest in the UV, and at the higher temperatures gases appeared yellow, and at highest temperatures (1300 K), a mist formed in the tube. Gaydon and Wolfhard find a similarity of that spectrum to the continuum spectrum of benzene at high temperatures. This type of spectrum would result from extinction of light by small particles as well but Gaydon and Wolfhard suggest that it could be attributed to PAH compounds.

CHAPTER III

SOOT PARTICLE GENERATOR

In this chapter a soot generator apparatus designed by the author is described in detail. The design objectives, the associated difficulties in the design, and limitations of the performance will be discussed as well. As a part of the apparatus description, the results of the numerical computations and additional results from flow visualization studies using video-intensified microscopy will be presented.

III.1 Apparatus

The experimental setup has three major components: the source of particles, the drift-tube with the soot-collection assembly, and the gas-handling system. The most significant part of the system is the source of particles, which will be referred to as the *source*. The source-design description starts by discussing the conceptual design and various, frequently conflicting, requirements which must be fulfilled by the design.

III.1.1 Particle source

A primary requirement is that the system be clean and oxygen-free during the operation while maintaining the high temperature required for thermal decomposition. Another requirement stems from the fact that one of the objectives is to investigate the growth of soot; *i.e.*, the temporal evolution of the particle size distribution function, along with the measurements of the total soot production. Optical techniques, being non-intrusive, are the most suitable for that purpose. Therefore, suitable viewing ports for such measurements must be provided. Finally, the apparatus should be capable of collecting soot samples for scanning-electron microscopy

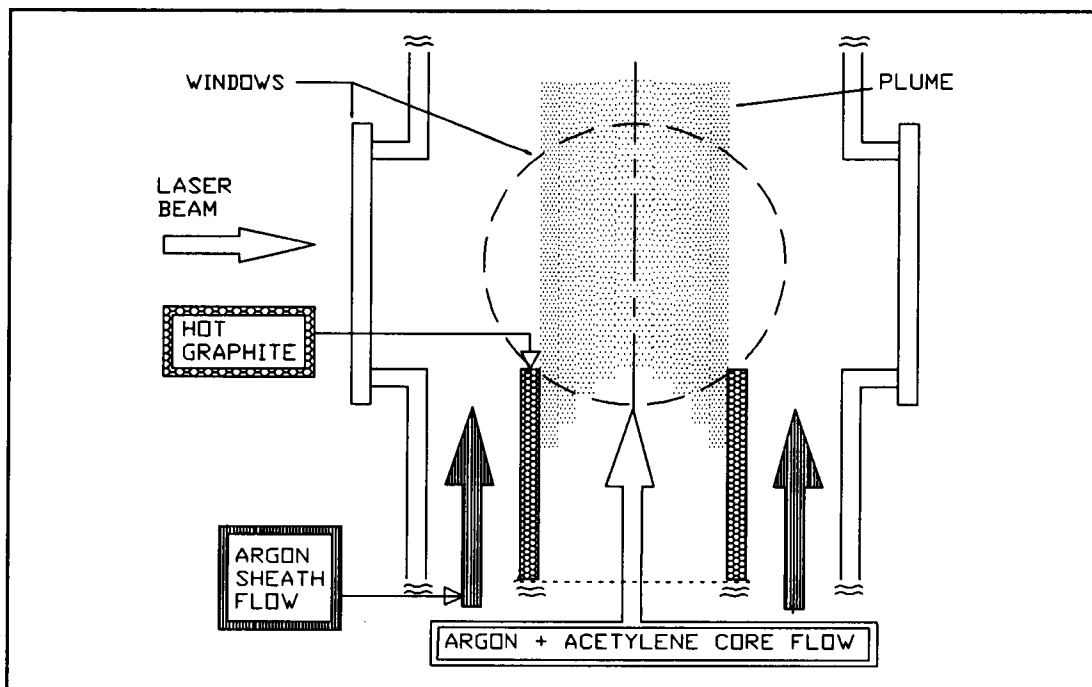


Figure III- 1: A schematic representation of the soot particle generator.

analysis.

To meet these requirements, radio-frequency (RF) induction-heating of a hollow, graphite rod in the drift-tube environment was used. The conceptual design of the source is shown in Figure III- 1. Flowing the acetylene over the heated, graphite surface provides sufficient cracking of the acetylene, and the subsequent soot production takes place within and downstream of the graphite rod.

Since one objective of this work was to provide the opportunity for the optical measurements, particulate contamination of windows was considered to be a major problem. This problem is most readily solved by using a cylindrical drift-tube which has at least two concentric, laminar-flow patterns, as shown in Figure III- 1. Velocity matching is required to avoid flowfield mixing and in principle, it is possible to have more than two concentric flows, but achieving a velocity match between the separate flows can be a difficult problem. Matching of the separate flows is particularly hard if the individual flow components have a complicated radial temperature distribution.

The outermost flow, labeled as the *sheath flow* in Figure III- 1, should confine the *core* flow which carries soot particles and thus protect the observation windows from contamination by soot particles.

The implementation of this conceptually simple idea turned out to be a difficult task. It is hard to overestimate the importance of the temperature requirements imposed on the source design. The design is dictated by the requirements for soot production and the provision of suitable viewing ports on the drift-tube, while maintaining a steady laminar flow-field pattern. To emphasize the design difficulties, the major requirements can be itemized as follows:

1. The source should maintain steady conditions over the periods of time required to perform measurements. The longest measurement times required are on the order of 10 to 20 minutes (extinction measurements).
2. The observation windows should remain clean of particle deposition during the measurements.
3. The observation point should provide sufficient freedom for performing extinction measurements, small-angle scattering measurements and 90-degree scattering or polarization measurements.
4. The observation point should be as close as possible to the point where the soot is created to allow monitoring of soot growth in its early stages.
5. The flowfield should be laminar (defined primarily by the pumping system, although buoyancy effects are inevitable). Turbulent flow and subsequent mixing of produced particles would contaminate the observation windows. Therefore, the maximum velocity is limited by the Reynolds number.
6. In order to facilitate the comparison of experimental data and growth calcula-

tions, it is necessary to assign a temporal reference point in the flowfield. As discussed in the previous section, heterogeneous soot production is a strong function of the temperature. Therefore, it is only logical to use the hottest point on the graphite rod as a reference point. In the present arrangement it would be desirable to arrange that the tip of the graphite rod (orifice) has the highest temperature. However, due to the heat transport (through radiation, convection, and conduction), the hot region necessarily has appreciable spatial extent. Thus, the determination of time sequence of events, particularly in the vicinity of the orifice, must be determined from a detailed flow analysis.

To meet all of the requirements, several different designs were considered. The first design⁶ involved a graphite rod with outside diameter of 12 *mm* and inner diameter of 10 *mm*. The initial design included two concentric sheath flows. Two sheath flows were required since it was necessary to place the RF-coil close to the graphite rod while keeping the observation windows at large distance. It turned out that this concept required the placement of the RF-coil that conflicted with either the flowfield or the heating requirements.

After a series of failed attempts, it was decided to accept the risk of contaminating the observation windows and to place the RF-coil outside the flowfield. The collection of soot was compromised severely by not locating the sampling point of the soot in the vicinity of the optical observation point. The final source design used in the experiment is shown in Figure III- 2.

Figure III- 2 depicts the part of the flow tube that includes the window section and the RF coil which was used for the induction heating. The soot-collection

⁶The very first design attempt actually involved a direct-current heating of the graphite. This heating method had problems with the design of electrodes within a drift-tube environment, including the erosion of electrodes. In addition to this, the required electrode cooling gave the highest temperatures at the central portion of the graphite rod. This resulted in the deposition of the soot on the walls with $T < T_{max}$ *within* the rod. Also, having the soot inception domain well within the rod implied that the observation of the early stages of soot-growth was not possible.

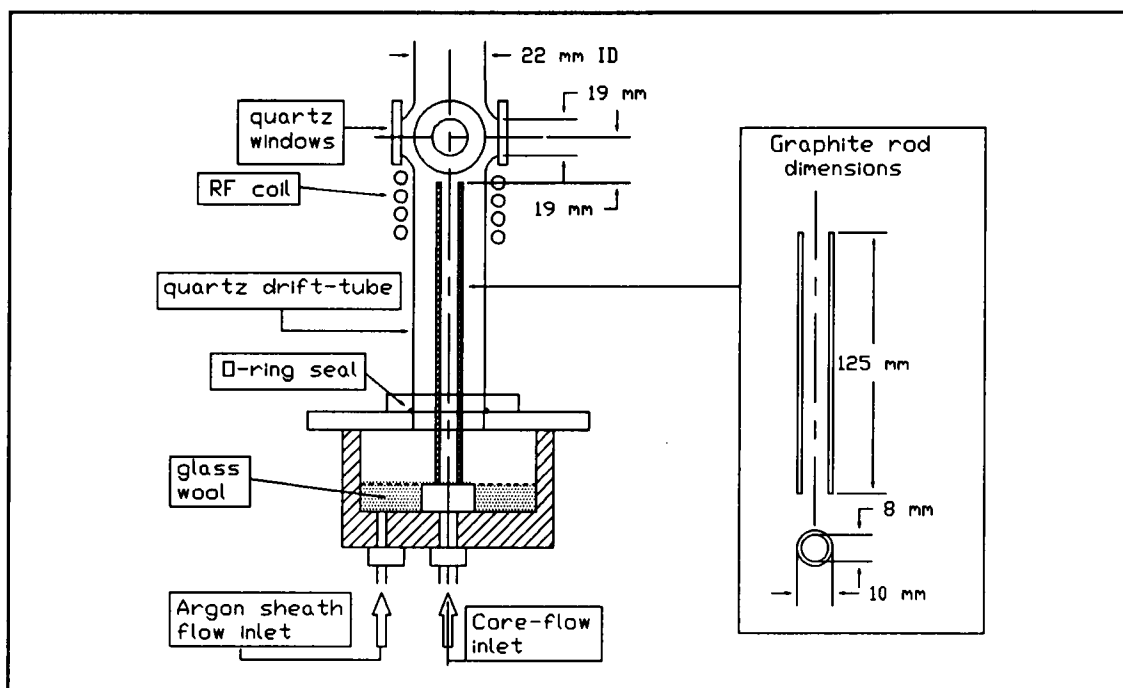


Figure III- 2: The source and the observation window section of the soot particle generator.

assembly will be presented later.

The graphite rod, which was a high-purity graphite (UF-4S) cylindrical rod supplied by Stackpole, was machined to the dimensions specified in Figure III- 2. The major impurity components were: Mg (3 ppm), Fe (3.7 ppm), and Si (0.5 ppm). The purity of the graphite rod was not critical however, since prior to the operation, the rod was kept at 1400 C at pressures of approximately 290 Torr for one to two hours in a pure, argon environment. This temperature is well above the recommended temperatures for cleaning of graphite (Dushmann, [33]).

The flow tube was made of quartz (manufactured by Labglass, Inc.). This quartz was not an optical-grade quartz, since the choice of material was dictated by the temperature requirements. In this design, the drift-tube walls experience temperatures which are higher than the softening point of pyrex. Some other design solutions, which would permit the use of a pyrex tube, were considered as well. For

example, RF heating can be accomplished by using a magnetic-flux-concentrator arrangement [34]. This type of design offers one feature which is highly desirable: heating can be localized in the relatively narrow part of the graphite rod near the orifice. Moreover, the observation windows would be removed from the core flow. Unfortunately, this approach requires a split-ring configuration, [34] and the design of the sheath-flow becomes a problem. The concentrator must be placed within a drift-tube, and consequently, it is necessary to have two concentric sheath flows which makes the velocity match requirement more difficult. Moreover, the concentrator must be cooled and this causes the difficulty due to the extreme, temperature-gradient requirements for the materials used for the definition of the sheath-flows. The sheath-flow serves its purpose only if it is uniform. The occurrence of small cracks in fitting which define the sheath-flow upon the exposure to the high temperature makes the sheath-flow design extremely difficult.

The cell windows consist of two pairs of parallel, mutually perpendicular, $1/4$ - *inch* thick, quartz-window flats (manufactured by Oriel). Windows were attached to the flow tube with a high-temperature sealant⁷, manufactured by GE. The attachment flanges were machined out of aluminum, where glass-to-metal sealing was accomplished with Viton O-rings. The RF coil was a 4-turn coil made of a $1/4$ -*inch* copper tubing with a coil inner-diameter of $1\frac{1}{8}$ *inches*. The Lindberg RF power-supply had a nominal output power of $3kW$, and was operated at the frequency of approximately 910 kHz . The resistivity of the graphite was specified by the manufacturer as $9.1\mu\Omega/m$ at $292K$, and for this particular coil-graphite geometric arrangement, coupling of the RF power was maximum at the nominal operating frequency.

⁷The sealant is a high-temperature sealant used in the automotive industry.

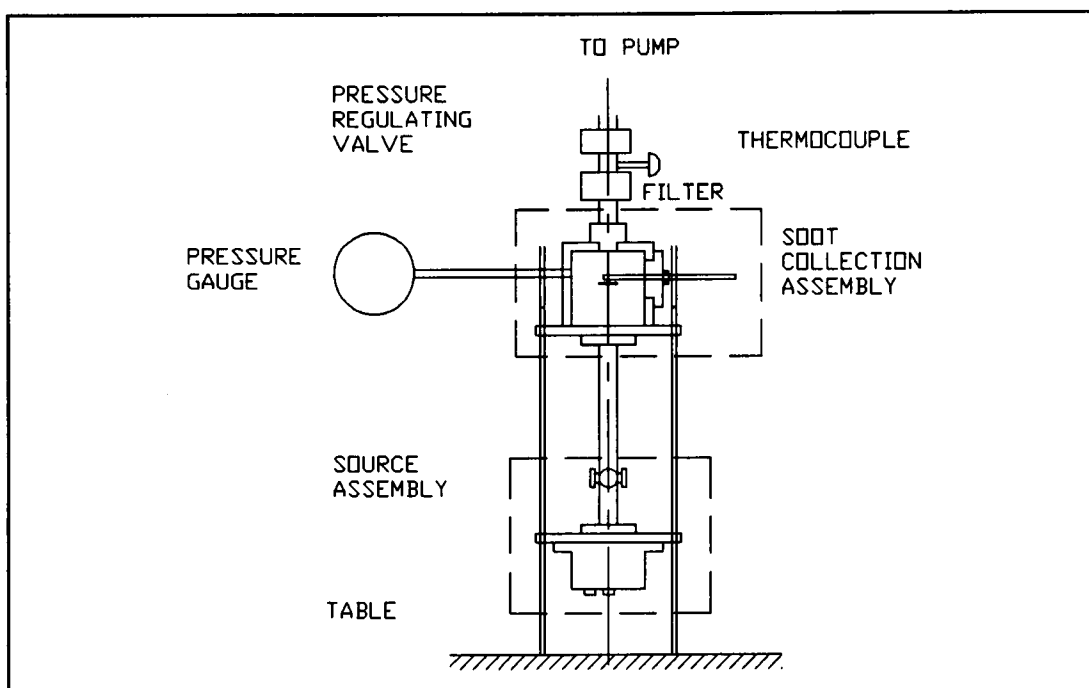


Figure III- 3: The soot-generator apparatus.

III.1.2 Drift-tube design

The soot collection assembly was placed at the end of the 40 *cm*-long drift-tube. Therefore, the soot was collected in the later stages of growth (on the order of one second, as will be shown later by numerical results). Figure III- 3 shows the full assembly of the apparatus.

The rather simple soot-collector section consisted of a $1/4$ - *inch* stainless steel rod that positioned an aluminum plate directly in the center of the flowfield. Axial and rotational motion of the stainless-steel holder was possible since the vacuum sealing of the holder was accomplished with the Ultra-Torr seal. This degree of freedom allows one to control partially the soot deposition on the aluminum plate by inserting the aluminum plate in the flow for the desired "exposure" time. Although this design does not allow collection at the same location as the observation windows, electron microscope study can provide information about shapes and sizes of parti-

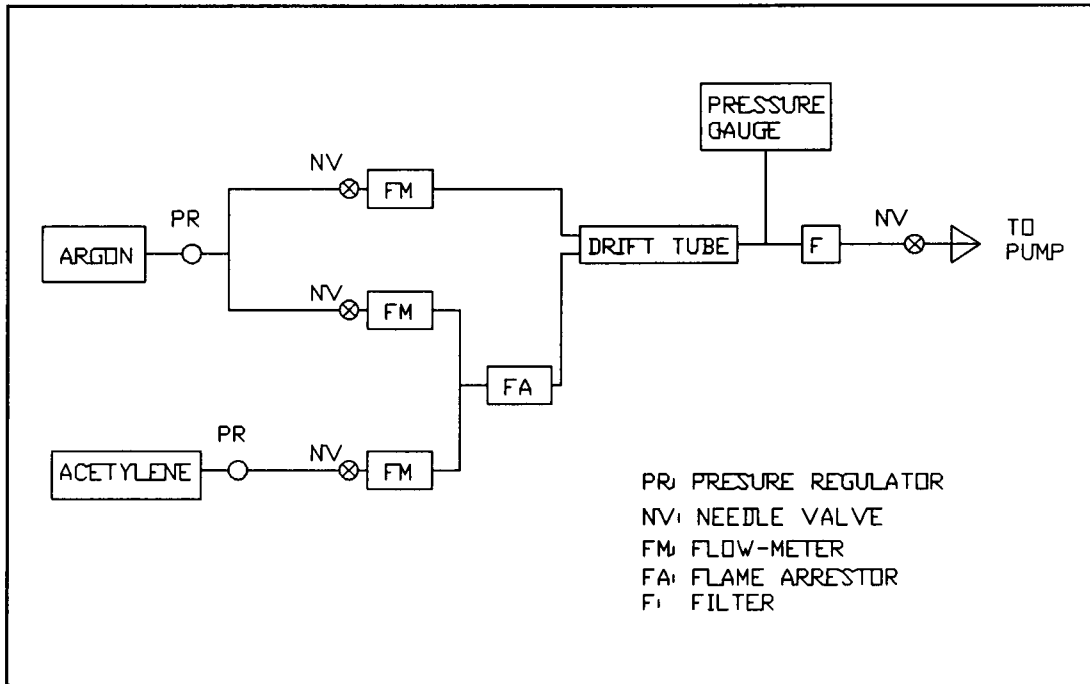


Figure III- 4: A schematic diagram of the experimental setup.

cles. Both types of information are useful for the verification of the particle-sizing techniques.

III.1.3 Gas-handling system

The gas-handling system and the particle generator are shown in Figure III-4.

Gas throughputs were measured by thermal mass-flowmeters manufactured by MKS Instruments with maximum throughputs listed in Table III-1. The DC output signals of the mass flowmeters were measured with a digital voltmeter.

Table III-1: Mass flowmeter specifications	
Gas flow component	Maximum throughput [sccm](N_2)
argon-sheath	50,000
argon-core	1,000
acetylene-core	100

A manometer with an accuracy of ± 10 Torr was used for the pressure measurement, and the temperature was measured with an optical pyrometer, which is designed for the temperature range between $700^{\circ} C$ and $3200^{\circ} C$. Research-grade argon and acetylene gas, supplied by AIRCO, were used without any further purifications. The rest of the flow system involved standard Swagelok needle valves (SS-R-21 for the core flow and SS-R-31 for the sheath flow) and copper and tygon tubing. The pump was a 14 cfm Sargent-Welch rotary-vane pump. The pressure in the drift tube was regulated by the needle-valve which was protected from the soot deposition with a paper filter (manufactured by Arrow). The mixing of the core-flow gases, acetylene and argon, was accomplished by flowing the mixture through the flame-arrestor and the 1.1 *m*-long tygon tubing.

III.2 Performance: preliminary observations

In this section, some general observations about the trends in the performance of the soot generator with respect to the fundamental parameters of the system are presented. These parameters are temperature, pressure, gas-flow velocities and the composition of the core-flow. Most of these observations were performed using the transmission-measurement, the experimental setup for which is described in the next chapter. Here, the intention is to discuss general features of the system behavior.

The maximum temperature that could be achieved in the apparatus was limited by the quartz-window seals. The RF power-supply with this coil and source geometry is capable of achieving temperatures⁸ in excess of $1700^{\circ} C$. However, achieving such temperatures with the present apparatus was not attempted. The system was operated at a maximum temperature of $1400^{\circ} C$ during the cleaning of the graphite rod.

⁸Temperatures as high as $1800^{\circ} C$ have been measured with this coil-graphite arrangement in some of the previous attempts.

Another restriction is imposed by the pumping speed limitations. The search for the optimal flowfield-source operating point is guided by the requirement to have appreciable soot production at the highest gas-flow velocities which could be achieved with temperatures below $1400^{\circ} C$. Since the observation point is approximately 2 cm downstream from the orifice, flow velocities on the order of 40 cm/sec are equivalent to about 50 msec of growth time, which is close to the beginning of the last stage of the soot-growth process in flames. The conductance of the flow system was strongly influenced both by placing the filter before the pressure-regulating valve, and by the valve itself. The cross-sectional area of the drift-tube is 3.8 cm^2 , the core-flow area is 0.5 cm^2 , and the area of the annular section is 3.0 cm^2 . Preliminary measurements were performed with the maximum pumping speeds (with the pressure-regulating valve fully open), and it was found that maximum bulk cold-gas velocities of approximately 10 cm/sec could be achieved.

Some general trends in the soot production process are described below. Increasing the graphite-rod temperature, while keeping other parameters constant, increases soot production dramatically. A similar effect, as expected from consideration of the acetylene decomposition process, was observed by changing the pressure and the fraction of acetylene in the core flow.

Since a heavy sooting condition is not desirable, it was decided to perform measurements for the two flow conditions which are summarized in Table III-2.

Table III-2: Gas throughputs [scc/sec]		
Component	Low	High
Argon - sheath	13.31	26.62
Argon - core	1.575	3.15
Acetylene - core	1.225	2.45

The pressure in most experiments was kept at 290 Torr, and the temperature profile of the graphite rod is shown in Figure III- 5. Under such conditions,

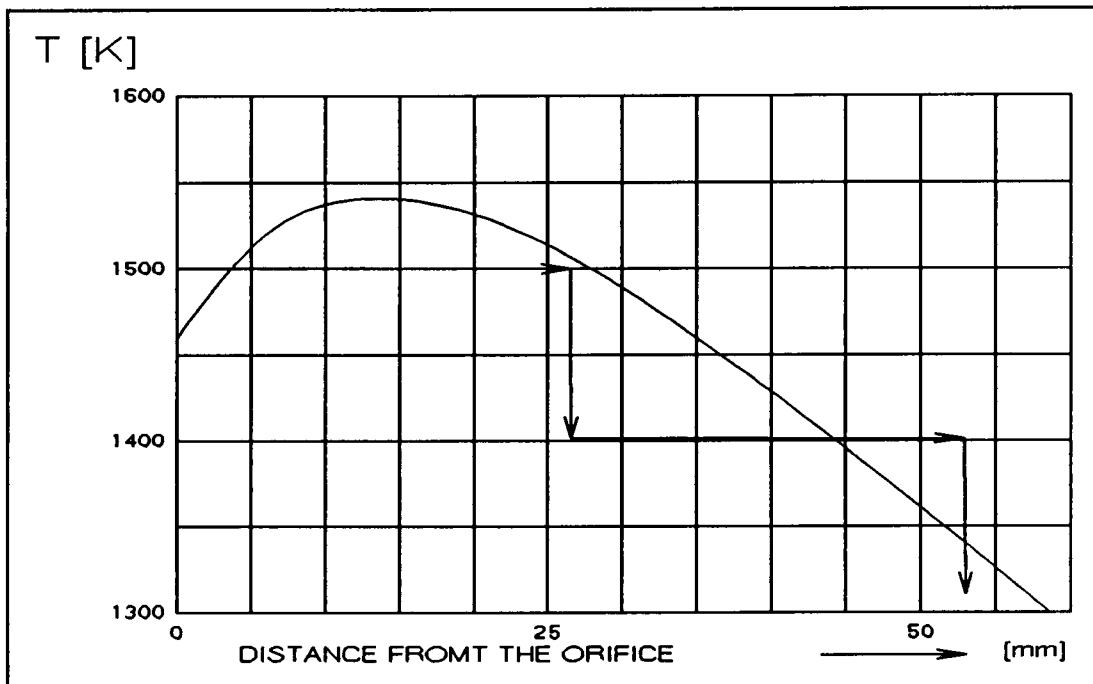


Figure III- 5: Graphite rod temperature distribution. Arrows indicate the distribution of temperatures which was used for the numerical flow analysis.

the source performance was stable, and the deposition rate on the window walls was small enough to allow unobstructed, repeatable measurements. In both cases, appreciable deposition of a light-brown, shiny film occurred 2 to 3 *cm* downstream from the window section. Similarly colored films were observed on the soot-collection assembly. Increasing the exposure time changed the color of the film to a dark-red, but it remained shiny. Increasing the temperature resulted in the production of layers of dark-black film. Further increases in the temperature produced the porous layers of acetylene-black soot particles. However, even under heavy-sooting conditions, thin layers of the material deposited on the drift-tube walls appears to have the same color as in the low-sooting conditions.

III.3 Flow analysis

This section presents the results of the numerical flowfield analysis. The numerical predictions of the flowfield have been used as an aid in the design of the apparatus and for the growth-rate calculations. The detailed numerical flowfield analysis of a chemically reactive system, two-phase flow is a difficult problem. Since the soot generator is in the exploratory stage, it was practical to make use of a commercial, computational fluid dynamics program (FLUENT, version 2.1, the product of Creare). The program was used to inspect the feasibility of the design presented in Figure III- 2. Since the FLUENT program is limited⁹ to the maximum of 10,000 finite flow-cells, the temperature of the graphite rod was approximated by the step-wise function as shown in Figure III- 5. The number of cells in the axial direction and radial directions was 40 and 24 respectively. The inlet-flow velocity was 10 *cm/sec*, and the gravitational acceleration was accounted for by assigning an acceleration of 9.81 *m/sec* in the negative *z*-direction. Using the physical properties of argon, the computations were performed assuming isothermal (300 K) drift-tube walls, and terminated after 1000 iterations. Figure III- 6 depicts the results of the flowfield velocities and the streamlines for the high-throughput case. The mixing zone shows the tendency to confine the core flow to smaller diameters. The drift-tube wall region shows the tendency for the formation of recirculation zones due to the large temperature gradients. The velocity profile within the graphite rod develops quickly. Figure III- 7 shows the contours of the axial velocity. This figure illustrates numerical values of the axial velocities in the mixing zone. The temperature distribution is shown in Figure III- 8. The most striking feature of the temperature profile is the flatness of the temperature distribution in the mixing region.

The essential features of both the high-throughput and low-throughput cases

⁹For other aspects of the capabilities of the FLUENT program, the interested reader is referred to the instruction manual.

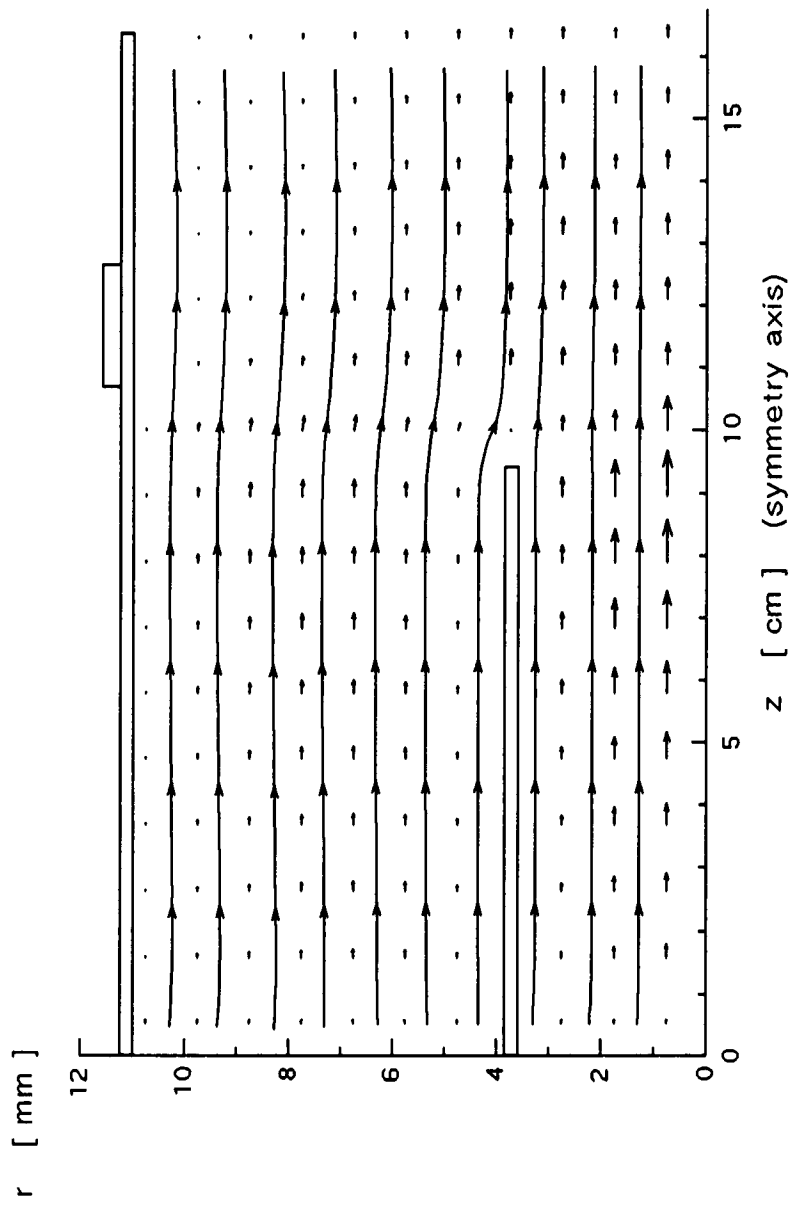


Figure III- 6: Velocity vectors and streamlines.

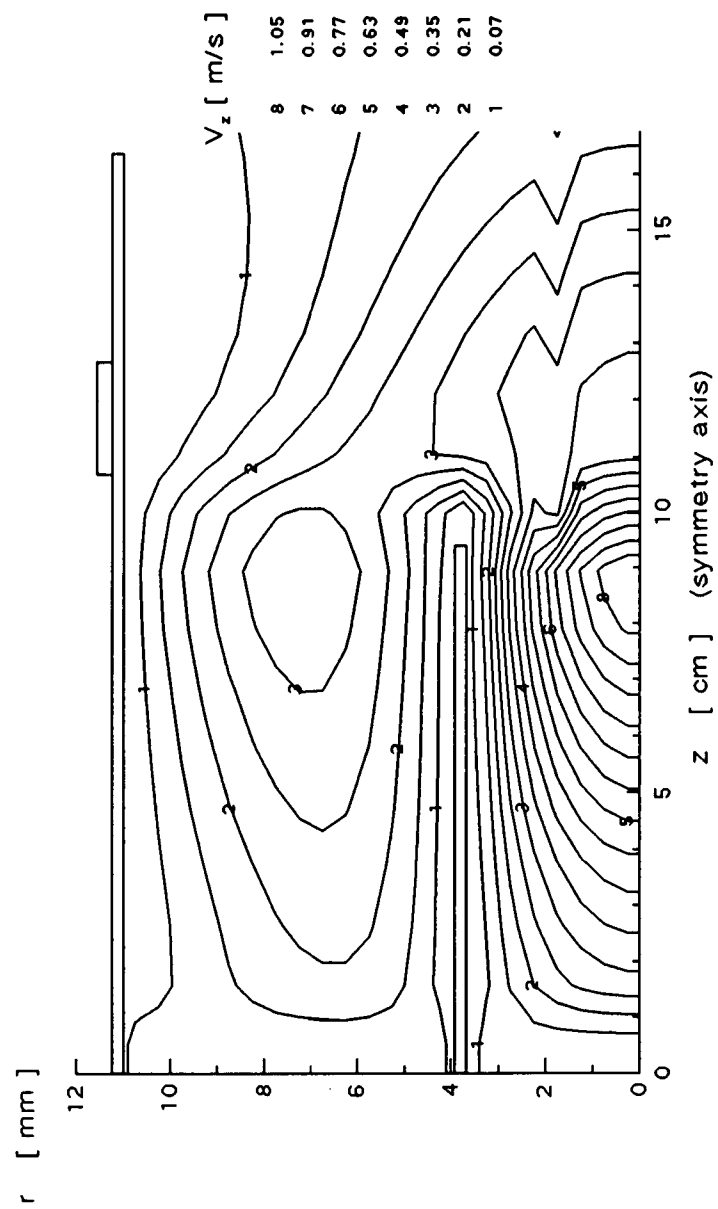


Figure III- 7: Axial velocity contours.

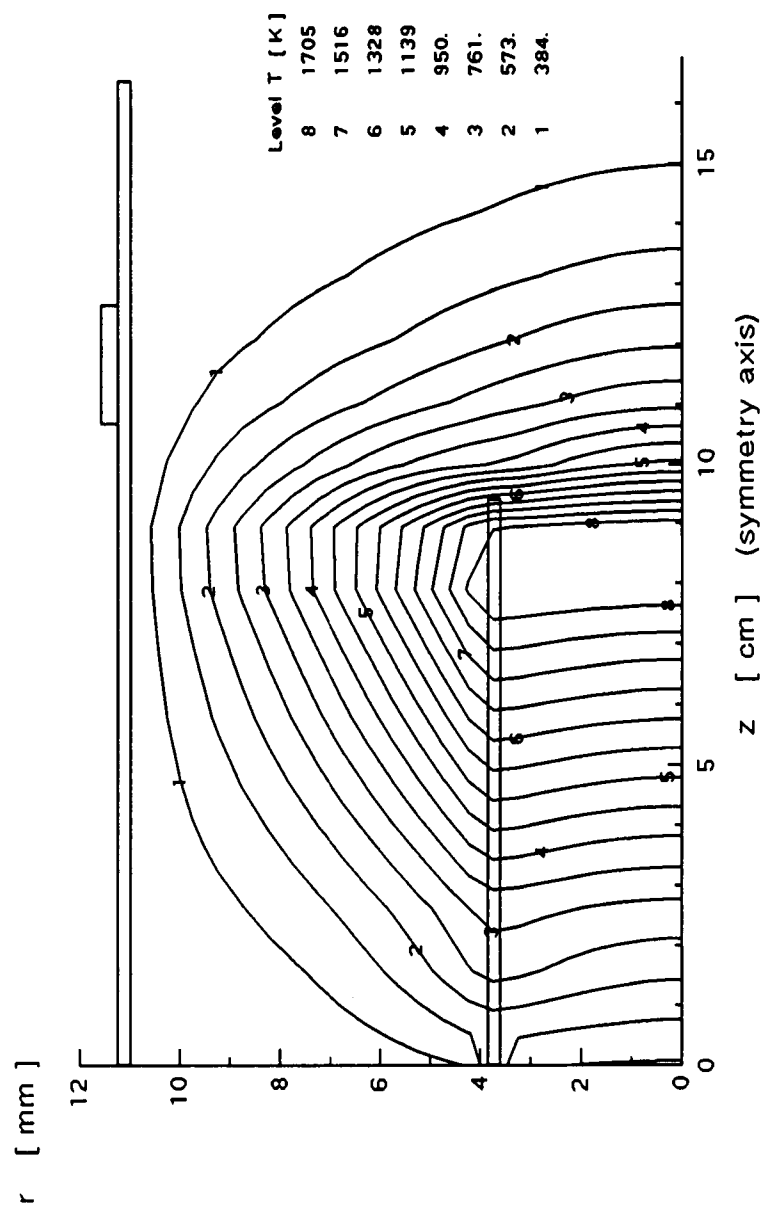


Figure III- 8: Temperature distribution.

are similar, with the difference being primarily in the magnitude of the velocities. Specifically, in the high-temperature region, at the observation point, the flow speeds for the two cases differ by only about 20 percent. Similarly, the differences in temperature distribution and the streamlines are not great. Additional computations were performed by assuming the adiabatic wall condition-restriction. The consequence of this restriction was primarily a sharp increase of the drift-tube wall temperatures (approximately 600 K in the mixing-zone region, just below the windows), and smoother streamlines along the walls of the drift-tube. However, general characteristics of the flow within the graphite rod and in the mixing zone remained very similar.

III.4 Radial distribution of the intensity of scattered light

Computational results discussed in the previous section are considered as only estimates of the actual flow pattern, and it was necessary to verify, at least qualitatively, the results of such computations. Scattering of light by particles can be used as an indicator of the flowfield pattern. Moreover, the radial distribution of the intensity of scattered light may prove useful in the interpretation of extinction measurement results. In principle, the total particle number density and the particle-size distribution function may depend on the radial position in the flowfield. Extinction measurements are line-of-sight measurements and the result is a spatially-integrated quantity. Therefore, point measurements are required if both the size distribution function and the total particle number-density are not spatially uniform. However, if one assumes that particle sizes are spatially uniform, then the radial dependence of the total number density may be inferred from the radial dependence of the scattered light.

The experiment for measuring the radial dependence of scattered light is depicted in Figure III- 9. Visualization of the particle flow was accomplished by

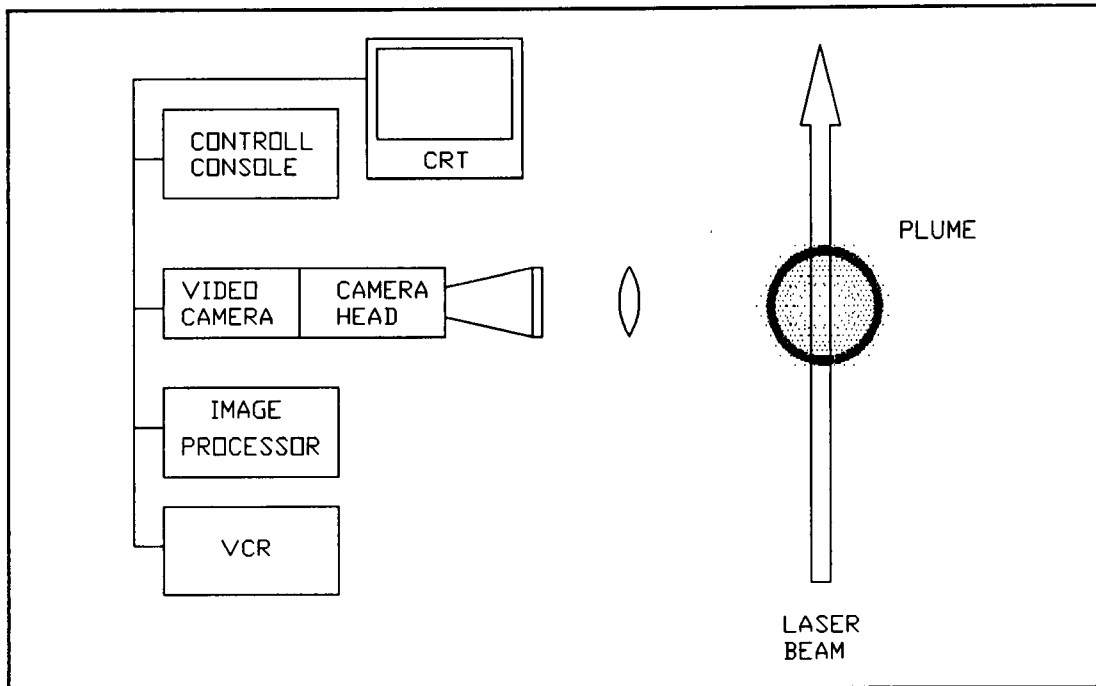


Figure III- 9: Schematic diagram of the experiment for the determination of the radial distribution of the scattered-light intensity.

observing the radiation scattered from an incident laser source. The incident laser-beam was the 488 *nm* line of an argon-ion laser, operating at a power of 100 mW, and the collimated beam diameter was 0.5 *cm*. A laser line-filter eliminated most of the undesirable background radiation, and the image of the scattered light was observed with a video-intensified microscope (VIM), manufactured by Hamamatsu, Model C1966-20. The laser beam was linearly polarized in the vertical direction, and the VIM was placed at 90 degrees in the plane containing the magnetic-field vector. The magnification of the optical system was calibrated by imaging a scale and the spatial resolution of the camera was found to be approximately 4.31×10^{-2} *mm*/pixel in both *x* and *y* directions. The intensity profiles of the scattered light for both flow conditions considered is shown in Figures III- 10 and III- 11. Figure III- 12 shows the intensity profile for the high-throughput case where the laser-beam, incident from the right-hand side was focused by a lens with a focal length of 7.5 *cm*.

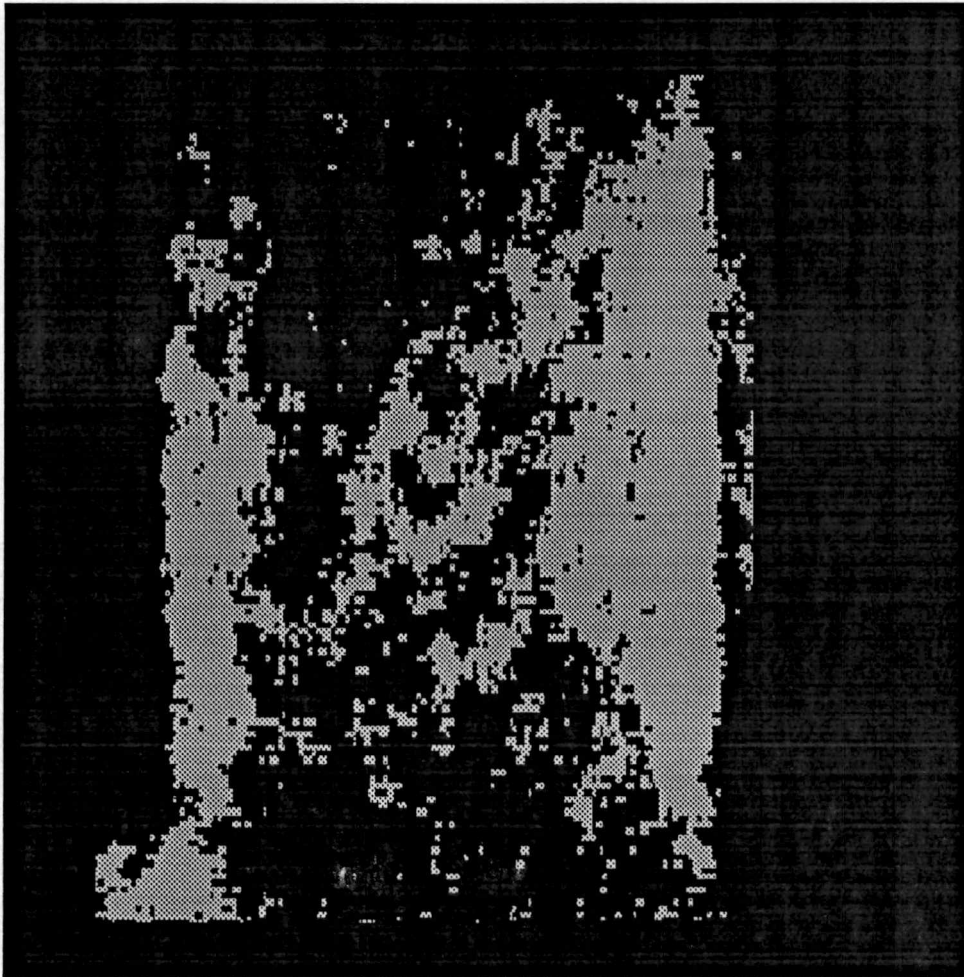


Figure III- 10: Intensity distribution - high throughput case. The collimated beam is incident from the right-hand side.

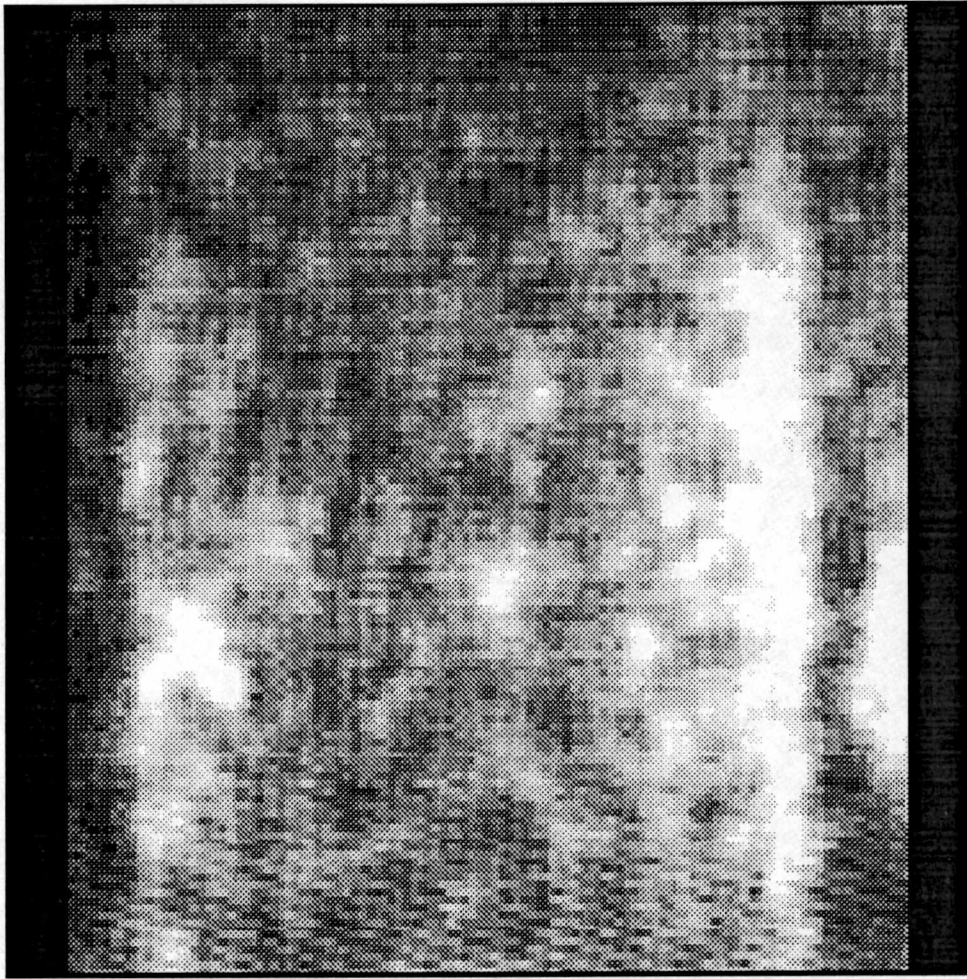


Figure III- 11: Plume distribution - low throughput case.

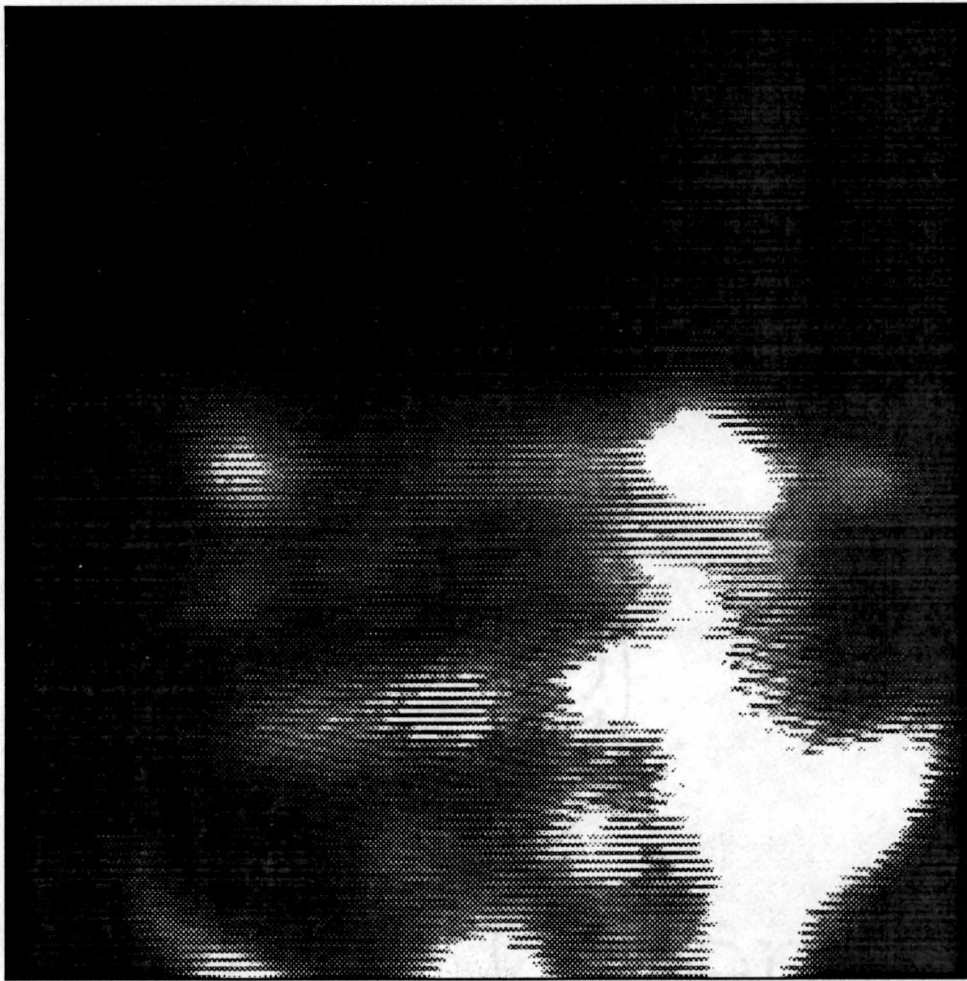


Figure III- 12: Intensity distribution - focused beam.

The bright area below the entrance point is due to the reflections from the windows. Finally, Figure III- 13 depicts the the case when the particle source ceases to be functional due to the changes within and at the orifice of the graphite rod.

The results indicate that in the high-throughput case the plume is concentrated primarily in the area where it was initially formed, *i.e.*, on the walls of the graphite rod, and forms a cylindrical layer of the particle field of 1.4 *mm* thickness and 7.6 *mm* in diameter. The beam diameter is only slightly smaller than the graphite rod diameter, which is not expected from the numerical computations.

It is important to note the comparative absence of scattered light in the sheath-flow area. Also, the center of the core flow has virtually no particles of larger sizes as evidenced by the absence of scattering from that part of the flow-field.

In contrast to that case, the low-throughput case shows the presence of scatterers in the central part of the core flow. The intensity of the scattered light is relatively constant in the core, suggesting a relatively uniform distribution in both sizes and number densities within the core flow. The difference in the flow conditions is reflected primarily in the acetylene residence times. The origin of the particulates in the center of the core flow can be attributed either to the homogeneous decomposition process, or diffusion of particles from the peripheral regions. Since the temperature distribution is nearly constant in the mixing zone past the orifice, one would expect that the diffusion process would take place towards the sheath flow at approximately the same rate. Therefore the lack of a scattering signal in the sheath flow area suggests that the particles in the central part of the core flow are due to the homogeneous nucleation process.



Figure III- 13: Intensity distribution - plugged source. Although the plume diameter is reduced, the presence of larger particles on the periphery is still dominant.

III.5 Discussion

In this chapter the design of a soot-generator apparatus is described which fulfills requirements for the study of soot formation in pyrolysis experiments. The major accomplishment of this apparatus is that it lends itself to particle-sizing measurements of pyrolysis-generated soot in a laminar flow environment, since such measurements have not been reported in the past. Moreover, the extension of the apparatus to include different chemical species would require only minor modifications of the present setup.

Window contamination due to particle deposition is an unavoidable problem in the present design. The severity of this problem depends on the particle deposition rate and the time required for performing the measurements. Multi-wavelength transmission measurements can require 5 to 20 minutes, depending on the number of measurements taken for the individual wavelength and the number of wavelengths. The transmission through the windows was measured before and after the system was in operation for 20-60 minutes, and it was found that the change in the transmission was negligible (within the error of the extinction measurements). Ironically, the diffusion-broadening-spectroscopy measurements, which last only about 2.5 minutes, turned out to be more critical with respect to the window contamination, as will be discussed in Chapter IV.

A low window contamination rate can be explained by analyzing the possible ways in which the particle deposition on the windows can take place. One way is the convective transport of particles. Assuming that the flowfield is laminar, this type of transport should be negligible. Moreover, the buoyancy effect on the flowfield in this design is actually beneficial. The sheath flow is also heated by the graphite rod, and the temperature profile in the mixing region is such that the buoyancy effect results in the reduction of the core-flow diameter in the window-section of the drift-tube.

This is certainly a favorable condition with respect to the window-contamination problem.

The diffusion of particles is another mechanism for the particle deposition. Assuming that the nucleation process takes place within 1 *msec*, it was estimated that the deposition rate in the window section of the tube through diffusion should be small. Considering the time-scales for the soot formation, one should expect the presence of larger particles in the core-flow past the orifice. Therefore, the major contamination of the windows may occur due to the molecular species with large molecular weights, and due to the potential particle formation within the sheath-flow which can occur due to the diffusion of acetylene decomposition products.

Therefore, as the experimental studies confirmed, window contamination is not a severe a problem. However, another significant difficulty emerged as a problem for the source operation. During operation, soot particles formed on the tip of the rod, which is approximately 20 *K* colder than the hottest part of the graphite. In addition to this, the heterogeneous reactions produced large amounts of carbon at the hottest area of the rod. This carbon is deposited on the interior walls of the rod (*i.e.*, at the hottest part of the rod). This resulted in a change of the source geometry which produced changes of the flow conditions over extended periods of time. The solution to this problem was not found since it is due to the very nature of the thermal decomposition of acetylene and the soot formation process. This problem restricts operating conditions to those for which the total soot production is small. Also, each measurement has to be taken with a "fresh" graphite rod. This measure of precaution does not eliminate the time-dependency of the source properties, but at least it does allow one to make comparisons on a relative basis. The magnitude of this problem could be reduced by increasing diameters of both the graphite rod and the drift-tube. This, in turn, would require major modifications in the design

and larger pumping speed capacities. Such arrangement would have larger heat losses due to the increase of the hot-surface area and a larger-capacity power-supply would probably be required.

The choice of operating conditions was made somewhat arbitrarily. The apparatus is new, and the choice of operating conditions can be made only after the some information about its performance is obtained. Moreover, the information on the particle sizes under these conditions can be used to determine the necessary modifications which would make this type of apparatus more useful. Therefore, it was necessary to obtain quantitative information about the soot produced in the existing apparatus and remove uncertainties associated with the operation of the apparatus. The information about the size of particles was obtained first from the transmission measurements. The next chapter presents a theoretical background and a numerical method for the determination of particle sizes from the results of transmission measurements, and the following chapter presents the results obtained on the present apparatus.

CHAPTER IV

PARTICLE SIZING FROM THE MULTIWAVELENGTH

TRANSMISSION MEASUREMENTS

This chapter presents a theoretical background for the transmission measurements which will be described in Chapter V. The first part of this chapter reviews the theory underlying the application of multiwavelength transmission measurements to the particle-sizing problem. The intention is to outline the derivation of the expressions which relate particle sizes to the results of the transmission, or extinction, measurements. A detailed presentation of the theory of scattering and absorption of light is beyond the scope of this effort, and this theory is discussed in detail in books on the light-scattering by small particles[6,7]. The emphasis will be placed on discussing the underlying assumptions of the particle-sizing technique based on multiwavelength extinction measurements.

The second part of this chapter presents and discusses a numerical procedure for the determination of the particle size distribution function (PSDF) parameters from multiwavelength extinction measurements. An investigation was performed to determine the feasibility and accuracy of using extinction measurements to determine the PSDF parameters by numerical deconvolution, or inversion of the relevant integral equation. A statistical analysis of the inversion results for a synthetic transmission spectra was performed. Results of these computations show that this approach can identify desired quantities provided that transmission measurements of sufficient accuracy have been performed at wavelengths appropriate for the PSDF. The data inversion approach presented in this chapter will be applied to results of multiwavelength transmission measurements described in the next chapter.

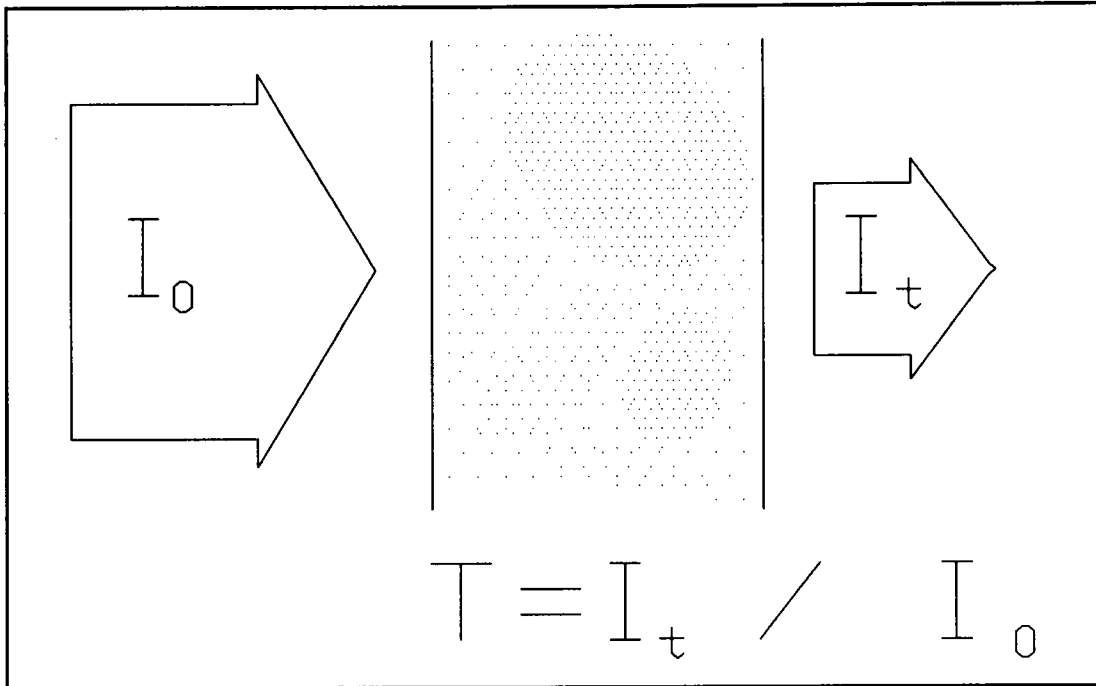


Figure IV- 1: Extinction of light through a medium containing particles.

IV.1 General assumptions

A beam of light propagating through a medium which contains small particles is attenuated due to the scattering and the absorption of light by particles, as shown in Figure IV- 1.

This removal of the electromagnetic energy from the direction of propagation of the incident light beam is called extinction. Therefore, the transmittance measurements contain information about the properties of particles in the medium. Establishing the relation between the transmittance measurements and particle sizes is complex since the extinction of light by a single particle depends on its size, shape, and its optical constants [6,7]. The most general case of a system of particles of arbitrary sizes, shapes, composition and spatial distribution is intractable, and the introduction of simplifying assumptions is in order.

There are three general assumptions which are prerequisite for most of the

particle-sizing techniques based both on extinction and scattering measurements. They are:

1. The scattering of light by a single particle is assumed to be an elastic process.
2. It is assumed that no correlation exists between the scattered fields of individual particles. This is usually quoted as the *independent scattering* assumption [6,7]. One interpretation of this assumption is that the total intensity of light scattered by an ensemble of particles is the sum of intensities of light scattered by each individual particle.
3. The optical density of the sample is assumed to be sufficiently low that *single-scattering* events dominate and that multiple scattering events can be neglected. This means that the total intensity of light reaching the detector after two or more scattering events can be neglected.

These assumptions are necessary for reducing the problem of interaction of light with an ensemble of particles to the problem of scattering and absorption of light by a single particle within the framework of the linear classical electromagnetic theory.

The validity of these assumptions has to be confirmed in each individual experiment. There are no firm rules for the independent scattering assumption. Van de Hulst [7] suggests that if the mean inter-particle separation is larger than 3 diameters of the particle, the independent scattering assumption should be valid. For an unknown sample, the criterion for the single-scattering assumption is based on the measurements of the extinction of light [7]; *i.e.*, it can be confirmed only after the initial measurements have been performed. The importance of this assumption for extinction measurements will be further discussed in the next section.

Although these assumptions represent a significant simplification of the problem, establishing the relationship between the transmission measurements and the particle size is still complex. Since the non-spherical particle case requires tedious computations [35], it is common practice in particle-sizing problems to assume that the particles are spherical. The relative importance of the validity of this assumption depends on other parameters in the problem; *i.e.*, the size parameter and the optical properties. At this point it will be assumed that soot particles are roughly spherical and that slight deviations from sphericity are statistically insignificant. This assumption allows one to consider the polydispersity effects in extinction measurements.

In most situations the ensemble of particles under consideration will have a distribution in sizes. Particle-sizing measurements on soot in flames [17,16,36], both intrusive and non-intrusive, indicate that the PSDF of soot particles in flames are polydisperse. It is common practice to assume that an analytical, two-parameter PSDF, $p(D; \langle D \rangle, \sigma)$, adequately describes the particle distributions. For the discussion of the determination of the PSDF parameters there is no need to specify which PSDF will be used for the actual data reduction. However, the use of the log-normal PSDF in particle-sizing problems is so common that the eventual use of that particular distribution should be anticipated. The log-normal PSDF is a particularly convenient choice since it is capable of describing broad size-distributions as well as narrow size-distributions. Naturally, it would be more satisfactory to justify the choice of the analytical form of the PSDF by the theoretical considerations of the growth process, which is in fact responsible for polydispersity of particles. Unfortunately, a sufficient theoretical support for any particular form of the PSDF does not exist. Alternatively, it is possible to describe the PSDF with a set of discrete points in diameter space and attempt to obtain a histogram [37] which fits the experimental results. This approach could be useful for a detailed study

of the growth mechanism, provided that the measurements have been performed with an extreme care and that the deconvolution procedure can be performed with a sufficient accuracy. However, in practice one rarely encounters situations where the deconvolution procedure can be performed with confidence for a general case. Therefore, this approach is somewhat local in nature, and the use of an analytical expression for the PSDF is perhaps more informative.

The particle field produced by the soot generator is spatially non-uniform. The cylindrical symmetry in the system exists, but this fact is not especially helpful. In principle, multiwavelength transmission measurements along different sections of the plume can be used to obtain the radial dependency of the PSDF parameters [38]. However, in the case of the particle field produced by the soot-generator, this approach is not yet feasible. The problem is in part due to the absolute dimensions of the flowfield of the soot generator: the plume diameter is relatively small, and only a few spatial positions could be measured. As shown by the VIM measurements in the last chapter, the spatial distribution can be approximated by a step-function in the high-throughput case. In the low-throughput case, the particle number density is nearly constant on the periphery of the plume. Similarly, the particle number density in the central part of the core-flow is constant as well. Prudent or not, this assumption must be used to determine the particle number densities within and on the periphery of the plume. This can be accomplished only with the aid of additional measurements (DBS). Therefore, for the theoretical considerations, it will suffice to consider the simplest case of the spatially uniform distribution of particles.

The extinction of light by a single particle depends on its optical properties. As discussed in Chapter II, optical properties of soot are somewhat uncertain. However, it is the consensus that the model developed by Dalzell and Serofim [8] is valid in the visible part of the spectrum. In the absence of experimental data, it will be

assumed here that an extrapolation to the near-UV and UV part of the spectrum is valid too, and this model and its extrapolation will be applied in the data inversion process.

IV.2 Extinction measurements: a synopsis

The list of assumptions discussed in the previous section is now sufficient to present the connection between transmission measurements and the parameters of the particle size-distribution function. For the previously discussed assumptions, the transmittance T of a monochromatic beam of light through a distance L of the particle field is described by the Lambert-Beer law [7]

$$T = \exp(-\kappa L), \quad (\text{IV} - 1)$$

where the attenuation per unit length, κ , is

$$\kappa = N \int_0^\infty \sigma_{ext}(D) p(D) dD. \quad (\text{IV} - 2)$$

The symbol N stands for the total particle number density, and $p(D)dD$ is the probability that a particle in a given ensemble of particles has a diameter in the interval $(D, D + dD)$. The quantity $\sigma_{ext}(D)$ is the optical-extinction cross section for a single particle of diameter D , and it is determined from the Mie theory [6,7] according to

$$\sigma_{ext}(D) = \frac{2\pi}{k^2} \sum_{l=1}^{\infty} (2l+1) \Re\{a_l + b_l\}. \quad (\text{IV} - 3)$$

In this equation, the symbol $\Re$ stands for the real part of the complex coefficients a_l and b_l . These coefficients are determined by

$$a_l = \frac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n(x) - \xi_n(x)\psi_n'(mx)}, \quad (\text{IV} - 4)$$

and

$$b_l = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n(x) - m\xi_n(x)\psi_n'(mx)}, \quad (\text{IV} - 5)$$

where m is the *relative refractive index*, and x is the *size parameter* of the particle which are defined by

$$m = \frac{n_p}{n_m}, \quad x = \frac{\pi n_m D}{\lambda}. \quad (\text{IV} - 6)$$

Here, n_p and n_m are complex indices of refraction for the particle and the surrounding medium, respectively, and λ is the vacuum wavelength. Functions $\psi_n(\rho)$ and $\xi_n(\rho)$ are the Ricatti-Bessel functions, which can be expressed in terms of the spherical Bessel functions ¹⁰ $j_n(\rho)$ and the spherical Hankel functions $h_n(\rho)$ as

$$\psi_n(\rho) = \rho j_n(\rho), \quad \xi_n(\rho) = \rho h_n(\rho). \quad (\text{IV} - 7)$$

This set of equations illustrates that even for the simplest particle shape (sphere), the required computations are relatively complex. However, computer programs exist for the efficient numerical evaluation of the extinction cross section [6,39].

This capability is crucial for the data-reduction process and the application of the minimization search technique. The unknown parameters which must be determined are the mean diameter, $\langle D \rangle$, the variance of the size-distribution, σ , and the product of the total particle number density and the optical path-length, NL . The determination of these parameters from a multiwavelength transmission measurements is an important topic that is discussed in detail in the next section.

Before proceeding with a presentation of a numerical technique, it is necessary to make a brief comment on the validity of the application of the Lambert-Beer law in the light of general assumptions discussed in the previous section. The independent particle scattering assumption is expected to be valid in most cases of practical interest. The validity of a multiple scattering assumption needs closer inspection since Van de Hulst estimates that a single particle scattering events prevail in cases where a transmission through a particle field exceeds 90 percent, and that

¹⁰The numerical evaluation requires application of *downward* recurrence, as suggested by Arfken [40].

for measured transmittances between 74 and 90 percent, a correction for a multiple scattering is required. Bohren and Huffman [6] on the other hand, argue that multiple scattering can be neglected if attenuation of light due to *total scattering only* is small. This is significantly less stringent requirement, especially if extinction is dominated by absorption. Horvath [41] recently reported experimental verification of the Lambert-Beer law on a monodisperse latex suspensions and atomized paraffin-oil, polydisperse particle field for extremely low transmittances (down to 0.0001). This indicates that the criterion quoted by van de Hulst is too conservative for the extinction measurements and the criterion of Bohren and Huffman will be used instead.

IV.3 Deconvolution of multiwavelength transmission measurements

The main topic that will be addressed in this section is a general method for determination of the PSDF parameters and the NL -product from multiwavelength transmission measurements using a numerical-fitting procedure. The method will be illustrated primarily with examples which are pertinent to the particular application of sizing particles produced by the soot generator. Nevertheless, the method can be potentially applied to an arbitrary set of transmittance values, $\{T_i\}$ measured at wavelengths $\{\lambda_i\}$. The optical properties of particles are assumed to be well-characterized by a set of complex refractive indices, $\{n(\lambda_i)\}$.

The intention is to design a numerical procedure which will identify a set of parameters $\{< D >, \sigma, NL\}_{fit}$, which results in the best fit to the measured transmission spectrum $\{T_i\}$. A measured transmittance is a complicated nonlinear function of all parameters, and one may be tempted to use some of the existing numerical fitting procedures for a nonlinear model to fit simultaneously all three parameters. However, this choice is not the best one since a set of measured trans-

mittances can be used to determine the PSDF parameters independently of the value of the NL product. Mathematically, the ratio

$$R(\lambda_i) \equiv R_i \equiv \frac{\tau_i}{\tau_{ref}} = \frac{\ln(T_i)}{\ln(T_{ref})} = \frac{\langle \sigma_i \rangle}{\langle \sigma_{ref} \rangle}, \quad (\text{IV} - 8)$$

where subscript "*ref*" indicates a measurement at some particular wavelength λ_{ref} , which will be called a *reference wavelength*, does not depend on the value of the NL -product.

One may object that this procedure introduces a bias into the data inversion procedure by distinguishing between the measurement at λ_{ref} and other data. However, this is not true, since this relation between optical densities follows from a Lambert-Beer law. Therefore, assuming a sufficiently accurate measurement process, and a perfect accuracy in the deconvolution process, the choice of λ_{ref} should be completely irrelevant. But there are additional reasons to actually prefer the use of particular reference wavelength for the data inversion. For example, a known magnitude of the experimental error can be one of the selection criteria for choosing λ_{ref} . Also, the confidence in the knowledge of optical constants at particular wavelengths can be used as a guidance in the selection process. Most importantly, the numerical stability of the deconvolution procedure may indicate that the use of particular reference wavelengths may be preferred.

The deconvolution will be done in two distinct phases. The first phase of the data inversion is comprised of the determination of ratios $\{R_i\}$, $i = 1, \dots, N_t - 1$, where N_t is the number of points in the transmission spectrum. Using a set of trial values for the PSDF parameters $\langle D \rangle$ and σ , one attempts to minimize the quantity

$$\chi_R^2(\langle D \rangle_{trial}, \sigma_{trial}) = \sum_{i=1}^{i=N_t} [R_i(exp) - R_i(trial)]^2. \quad (\text{IV} - 9)$$

The second phase consists of the determination of the NL product using the mean diameter and the variance as obtained from the first stage of the data inversion.

Various numerical techniques for the minimization (maximization) of functions exist [31] for the first phase of the data inversion process. In the particular application presented here, a Nelder-Mead downhill-simplex method was applied. Using the trial parameters for the PSDF, the quantity $R_i(trial)$ is computed by evaluating the corresponding average extinction cross section, $\langle \sigma_{ext}(\lambda_i; \langle D \rangle_{trial}, \sigma_{trial}) \rangle$ at all wavelengths followed by the computation of the ratios according to the choice for the reference wavelength. The average extinction cross section is determined by a numerical integration over the diameter of

$$\sigma_{ext}(D; \lambda_i) p(D; \langle D \rangle_{trial}, \sigma_{trial}), \quad (IV - 10)$$

where $\sigma_{ext}(D)$ is computed according to the Mie theory for extinction of light by spherical particles, and the PSDF, $p(D)$, is a log-normal PSDF with trial parameters, computed as described in Appendix A. The quantity $R_i(exp)$ is computed from the experimental data.

The second phase of the deconvolution procedure is concerned with the determination of the NL -product. Assuming that the first stage of the data inversion resulted in an accurate estimate of the PSDF parameters, a value of the NL -product can be determined by noting that

$$\tau(\lambda_i) = NL \langle \sigma(\lambda_i) \rangle \quad (IV - 11)$$

for a constant $\langle D \rangle$ and σ at all λ_i , can be viewed as a linear equation

$$Y = A \cdot X + B, \quad (IV - 12)$$

where the independent variable X is the average extinction cross section, and constant $A = NL$ (theoretically, B should be 0). Therefore, the second stage of the data inversion procedure is just a least-squares fit of NL product to the transmission spectrum. With NL determined in this manner, the fit to the experimental spectrum

can be computed, and as an estimate of the quality of the fit, a quantity

$$\chi_T^2 \equiv \sum_{i=1}^{i=N_t} [T_{exp}(\lambda_i) - T_{fit}(\lambda_i)]^2 \quad (\text{IV} - 13)$$

can be defined.

The determination of unknown parameters by the minimization of χ_R^2 poses several questions. The most important questions are

1. Is the outcome of the minimization process guaranteed to lead to the correct answer?
2. Assuming that the numerical fitting technique is successful, what is the relation between experimental errors and outcome of the minimization process?
3. At what wavelengths¹¹ should the measurements be performed in order to provide the most accurate characterization of the particle field under consideration?

All three questions are in effect concerned with the same topic: how much information about the PSDF parameters is contained in a set of multiwavelength transmission measurements? The answer to this question is important regardless of the particular data inversion technique since this information can be used to choose a proper experimental arrangement in order to increase the accuracy in the determination of measured parameters. This issue has been discussed extensively in the literature [42,43,37,44]. Answers to these questions requires a detailed analysis of quantities which are important for the determination of the PSDF parameters from the multiwavelength measurements.

¹¹Similar question can be posed for the scattering measurements, substituting the *angle* for the wavelength.

IV.3.1 Information content analysis

Extinction of light by a single spherical particle is in general a complicated function of the size parameter, $x = \pi D/\lambda$ and optical properties of a particle. Therefore, if a sample is completely unknown, it is not possible to make an efficient analysis prior to gaining some additional information about the sample. For particles generated by the soot generator one can expect that particles are considerably smaller than $1\ \mu m$, and in all probability smaller than $0.2\ \mu m$. This conclusion can be reached from the reported soot particle sizes in flames [14]. Therefore, for the preliminary analysis it will suffice to consider particle diameters in that range, or to be conservative, from 0 to $500\ nm$.

As a first step it is necessary to identify and analyze the size dependency of quantities pertinent to extinction with wavelength as a parameter. This will account for the wavelength-dependent optical properties exactly, while giving some insight about the potential difficulties in the minimization procedure which uses integrated quantities.

As a starting point, one can compute the *extinction efficiency*

$$Q_{ext}(D) = \frac{4\sigma_{ext}(D)}{\pi D^2}, \quad (IV - 14)$$

as a function of a diameter for a certain selection of wavelengths in a diameter range of interest, as shown in Figure IV- 2. Extinction efficiencies for soot are relatively smooth functions of diameter due to the high absorption [6]. A more complex structure appears in the case of particles with small *extinction* (imaginary part of the complex index of refraction). Such particles typically show a prominent sequence of peaks which oscillate around $Q_{ext} = 2$, whose magnitude decreases with a particle diameter. Those peaks are the due to the interference of incident and forward-scattered light [6,7]. For a highly absorbing particle, such as soot, this structure is

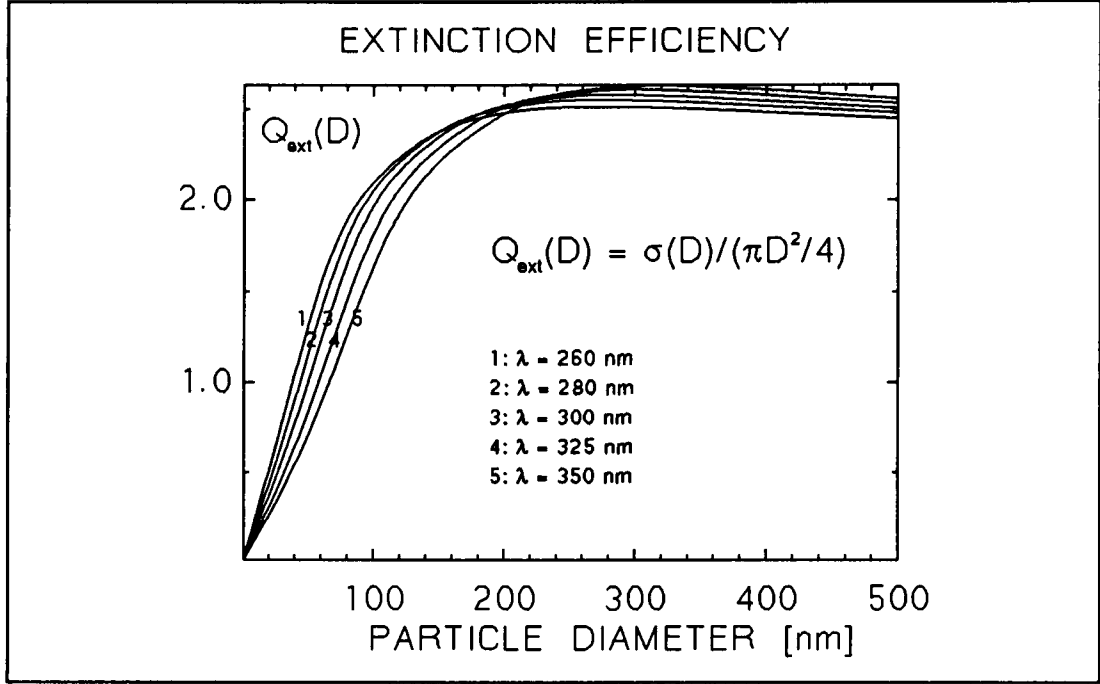


Figure IV- 2: Extinction efficiency for soot particles.

almost imperceptible: the extinction is dominated strongly by the absorption [6].

The size dependency of the extinction efficiency is perhaps not the most suitable quantity for displaying the effect which the selection of wavelengths will have on the measured transmission spectrum. A quantity which is more informative for that purpose can be identified by following considerations. For a monodisperse PSDF, the attenuation coefficient can be written as

$$\kappa = N\sigma_{ext}(D) = N \cdot v_p \cdot \frac{\sigma_{ext}(D)}{v_p} = f \frac{\sigma_{ext}(D)}{v_p}, \quad (IV - 15)$$

where v_p is the volume of the particle:

$$v_p = \frac{\pi D^3}{6}, \quad (IV - 16)$$

and f represents the volume fraction of particles. The *volume attenuation coefficient*, $\sigma_{ext}(D)/v_p$, is informative for particle sizing experiments for several reasons. For a fixed f , i.e., for the fixed total mass of particles, $\sigma_{ext}(D)/v_p$ shows the efficiency

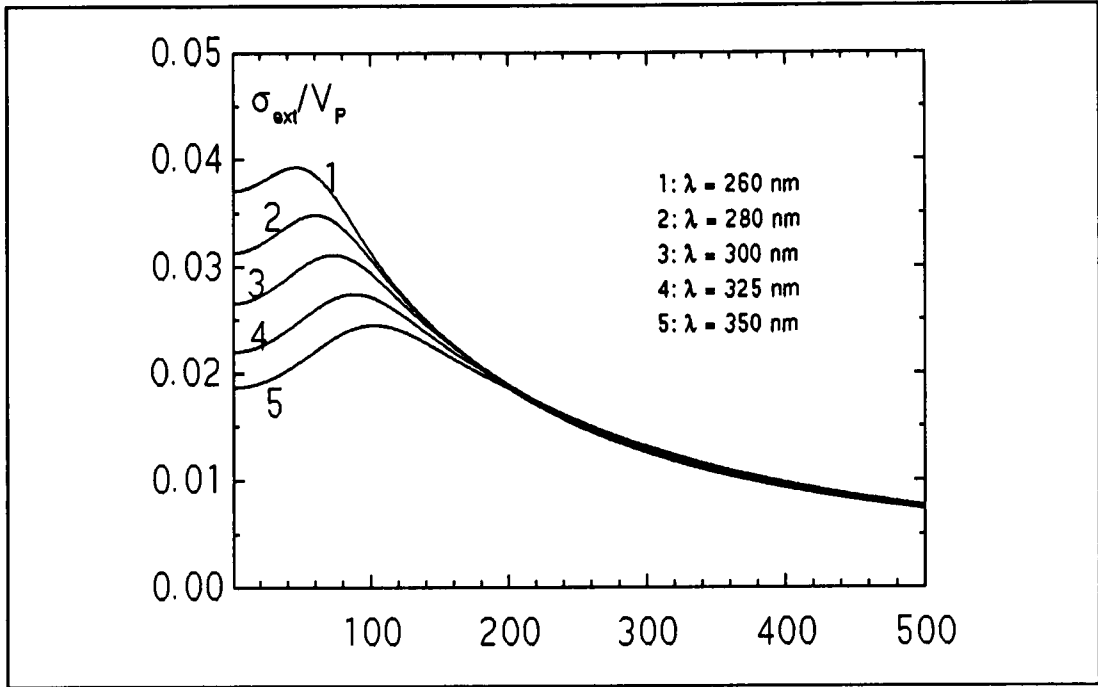


Figure IV- 3: Volume attenuation coefficient [nm^{-1}] for soot.

for extinction at particular wavelength if particles are of a given size. Therefore, it contains the information needed for the proper selection of wavelengths in the multiwavelength extinction measurements. The volume attenuation coefficient for soot is shown for the same set of wavelengths as in Figure IV- 3. Therefore, this figure indicates more clearly that the transmission spectra will be distinguishable if particles are smaller than approximately 150 nm in diameter for this given set of wavelengths. On the other hand, all curves approach constant values as the particle diameter approaches zero. This implies that the extinction in this diameter range is relatively insensitive to details of the PSDF. Consequently, a numerical-fitting data-inversion procedure should extract the information about the PSDF parameters from the transmission spectrum measured at those wavelengths indicated on Figures IV- 2 or IV- 3 if the particles are in the size range from approximately 30 to 150 nm . Figure IV- 2 shows that extremely accurate measurements, followed by an equally accurate deconvolution procedure, are required if one intends to determine particle

sizes in the vicinity of 150 nm, or larger, from measurements performed at these specified wavelengths.

Figure IV- 4 shows theoretical ratios of optical densities, from the same set of wavelengths presented in the previous two figures, for the case of soot particles. Each individual curve on these plots could be used for a graphical determination of the particle size, assuming a monodisperse particle distribution from two-wavelength measurements. Therefore, this type of plot can be used as an auxiliary aid in the selection of a range of diameters in which absolute minimum of χ_R^2 is most likely to occur. These plots reveal that although curves shown in Figures IV- 2 and IV- 3 appear to be smooth in a $D > 100$ nm range, ratios of cross sections show more significant changes in that diameter range. This size-dependent behavior would be even more pronounced for nonabsorbing particles and the occurrence of multiple solutions is easy to envision. If a form of the ratio $R_i(D)$ is complex, the effect of the PSDF is not easy to predict.

Plots shown in Figure IV- 4 provide a basis for an estimate of the anticipated error in the determination of the diameter in a particular diameter range based on the error in measurements. The simplest way to do this is to plot the experimentally found ratio

$$R(\lambda_1, \lambda_2) = \frac{\ln T(\lambda_1)}{\ln T(\lambda_2)}, \quad (\text{IV} - 17)$$

and the corresponding ratios which include the measurement errors

$$R_{\pm}(\lambda_1, \lambda_2) = \frac{\ln [T(\lambda_1) \pm \Delta T(\lambda_1)]}{\ln [T(\lambda_2) \pm \Delta T(\lambda_2)]}. \quad (\text{IV} - 18)$$

A large uncertainty in the diameter range implies that a particular wavelength combination is not informative for the particle sizing, and such wavelength combinations should be omitted.

This error can be determined numerically as follows. If the error in the transmission measurement is ΔT for a particular pair of wavelengths, λ_1 and λ_2 , and R_0

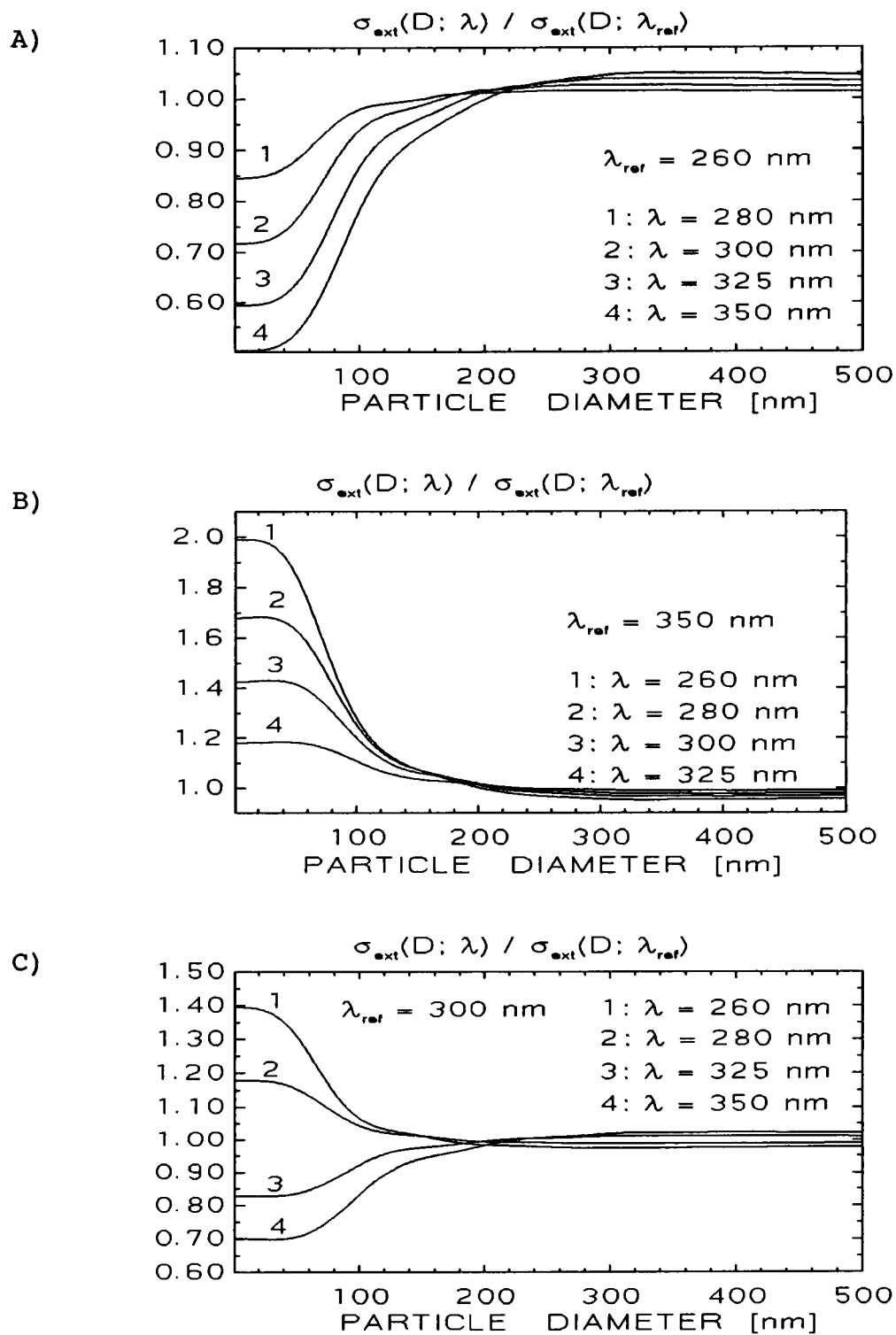


Figure IV- 4: Ratios of optical densities for soot using $\lambda_{\text{ref}} = 260, 300, \text{ and } 350 \text{ nm}$.

denotes

$$R_0 = \frac{\ln T(\lambda_1)}{\ln T(\lambda_2)}, \quad (\text{IV} - 19)$$

then

$$R = \frac{\ln [T(\lambda_1) + \Delta T(\lambda_1)]}{\ln T(\lambda_2)}. \quad (\text{IV} - 20)$$

Assuming that ΔT results in a small change in the ratio, this change can be estimated by

$$\Delta R = \left(\frac{dR}{dD} \right) \Delta D. \quad (\text{IV} - 21)$$

On the other hand,

$$R = \frac{\ln \{T(\lambda_1)[1 + \Delta T(\lambda_1)/T(\lambda_1)]\}}{\ln T(\lambda_2)} \approx R_0 + \frac{\Delta T(\lambda_1)}{T(\lambda_1)} \frac{1}{|\ln T(\lambda_2)|}, \quad (\text{IV} - 22)$$

which allows one to estimate the fractional error in the diameter as

$$\frac{\Delta D}{D} \approx \frac{[\Delta T(\lambda_1)/T(\lambda_1)]}{|\ln T(\lambda_1)|} \left| \frac{d \ln R}{d \ln D} \right|^{-1}. \quad (\text{IV} - 23)$$

Therefore, Equation (IV- 23) can be used to estimate the usefulness of the particular wavelength pair combination in the data inversion process and the precision of measurement for a required accuracy in the determination of the mean diameters. It should be emphasized that this analysis provides just an order-of-magnitude estimate of errors since it is based on the assumption that particles are monodisperse.

In addition to narrowing the average particle diameter range, the plots shown in Figure IV- 4 can be used to improve on the sensitivity of the minimization procedure. As an estimate about the sensitivity of the data inversion routine it is useful to plot the function $(1/R_i)(dR_i/dD)$, as shown in Figure IV- 5.

For nonabsorbing particles, such plots may reveal that some of the wavelength-pair combinations may actually have a sign reversal right in a diameter range where the PSDF may not be negligible. If possible, such wavelength ratios should be also

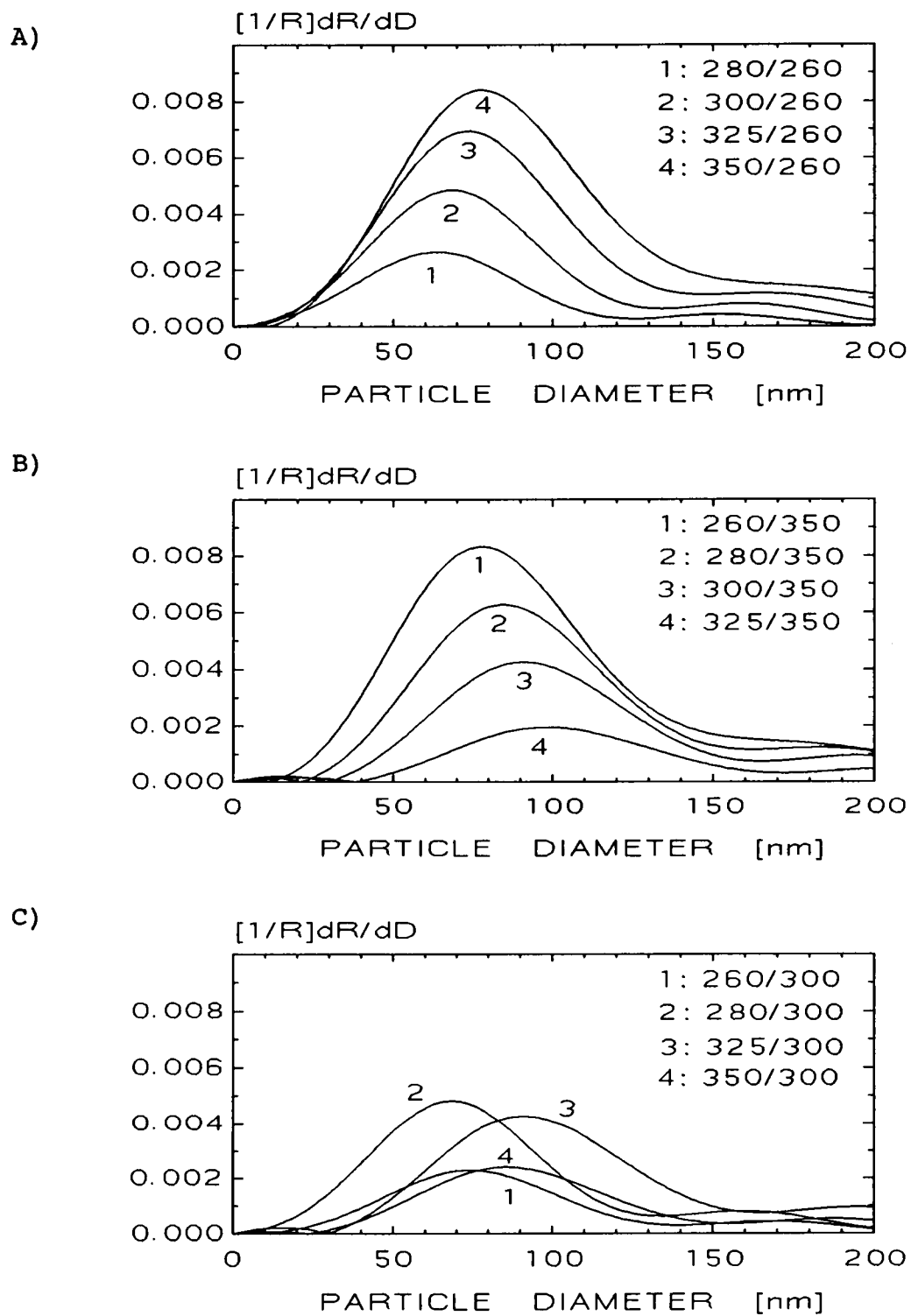
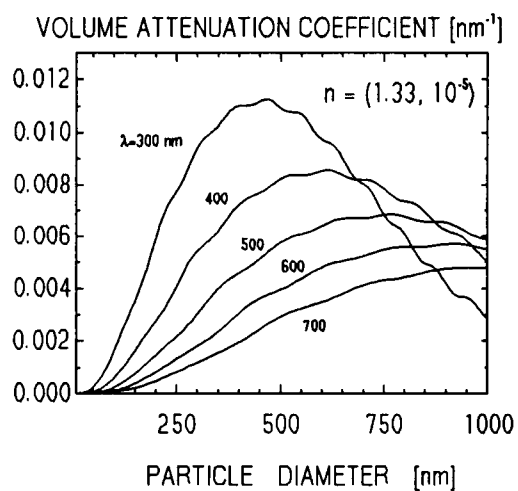


Figure IV- 5: The sensitivity of ratios to particle diameter.

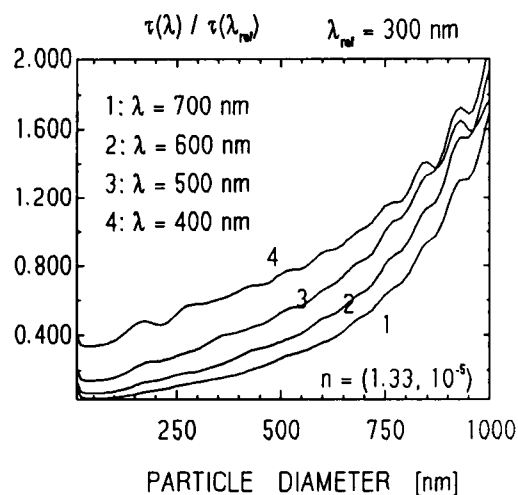
eliminated from the deconvolution procedure since those terms would change relatively slowly compared to other terms which comprise χ_R^2 . Figure IV- 5 shows that the sensitivity of the data reduction process from a multiwavelength measurement depends on the choice of the reference wavelength. For example, the use of $\lambda_{ref} = 260 \text{ nm}$ would be preferable if a preliminary analysis indicates that the average particle diameter is closer to 50 than to 100 nm. However, if the average particle diameter happens to be larger than 100 nm, the minimization procedure will be more efficient if $\lambda_{ref} = 350 \text{ nm}$ is used instead. For particle sizes at either end, the use of the 300 nm as a reference wavelength would be less practical since only two out of 4 ratios would undergo significant changes as the minimization procedure progresses. In spite of these comments, the simplex routine should be designed so that the ultimate answer does not depend on the reference wavelength choice.

To summarize the first phase of the deconvolution procedure, preliminary investigations should be performed to assure that the converged results correspond to an absolute minimum of χ_R^2 . Once a range for the most probable mean particle diameter has been determined, the minimization can proceed by a proper selection of the reference wavelengths and a set of wavelengths that gives the maximum sensitivity to the deconvolution procedure.

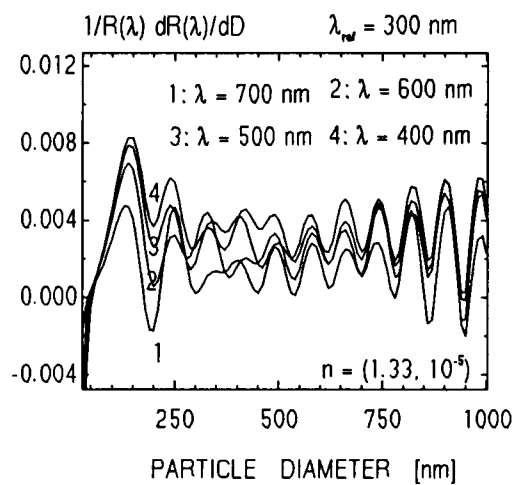
To illustrate the effects of the optical properties of particles on the minimization technique, a volume attenuation coefficient was computed for a hypothetical medium with a refractive index of 1.33 and extinction of 10^{-5} for the five wavelengths and shown by plot A in Figure IV- 6. Corresponding optical density ratios are shown by plot B of that figure.



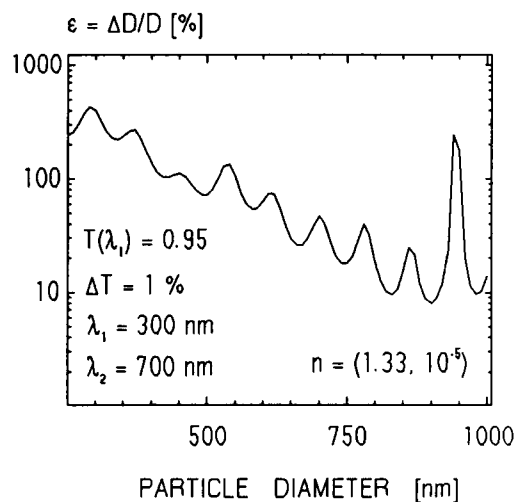
A)



B)



C)



D)

Figure IV- 6: The possibility of existence of multiple minima in χ_R^2 .

The sensitivity of particular wavelength pair combinations and an estimate of the error for the determination of a monodisperse diameter are shown by plots *C* and *D*, respectively. Figure IV- 6 clearly illustrates that a rough estimate of the particle diameters can be determined from plot *C*). However, the introduction of polydispersity makes further estimates difficult. Also, the existence of several local minima in such cases is inevitable.

The above analysis of important elements in the numerical fitting procedure is based largely on a procedure for the determination of particle sizes from a two-wavelength transmission measurement. The information about the PSDF parameters from the multiwavelength transmission measurements depends strongly on the proper choice of wavelengths at which the transmittance is measured. Existence of multiple local minima must be anticipated, and the data inversion process can be improved by making a judicious choice for the inclusion of particular experimental data for the deconvolution. Also, the sensitivity of the minimization procedure can be improved by making a proper choice for the reference wavelength, once a sufficiently narrow bracket can be placed on the mean diameter. The most significant difficulty in the data inversion may occur due to the existence of local minima and potentially large errors arising from experimental errors.

IV.3.2 Statistical data inversion procedure

The propagation of errors in the deconvolution process can be revealed by performing a suitable statistical analysis of results for a large number of experimental transmission spectra. Alternatively, the mean transmittance and the variance from the experimental results can be used to create a large number of synthetic data assuming a gaussian distribution of errors. Preliminary experience with a deconvolution technique indicated that displacing a single transmission point from the

correct value causes difficulty in convergence of the minimization process. This can be anticipated from the discussion in the previous section. If a derivative dR_i/dD for a measurement with a large systematic error is large compared to other ratios, the minimization process will be erratic. In this case, placing of a limitation on a variation of the transmittance offers a practical approach.

The statistical processing is expected to reveal the behavior of the deconvolution procedure with regard to the existence of local minima and the propagation of errors by estimating the accuracy of the results of the data-inversion. In addition to this, the anticipated behavior of the minimization process with respect to the choice for λ_{ref} should emerge. Therefore, it is important for the validation of the minimization approach, and for the interpretation of the obtained results. Perhaps the most important aspect is that one can see the effects of the presence of systematic errors. Of course, numerical errors will also amount to some distribution in values of deconvolved parameters. The effect of numerical errors was estimated to be negligible during the testing of the basic deconvolution routine. Using a synthetic spectrum for given parameters, the minimization routine would practically always produce correct results within one or two percent of the initial values. This was performed using optical properties of soot, which is in a way easier case since the occurrence of local minima is less likely to be a problem. Therefore, the effects of the numerical errors will be neglected. However, for the example shown in Figure IV- 6, accumulation of numerical errors would have significant impact on the data inversion. An outline of the computer program for the statistical fitting procedure is given in Figure IV- 7. The recorded results were processed separately since it allowed the processing of partial results.

The results of this processing will be now illustrated by one example. A primary purpose of this example is to demonstrate the significance of systematic

THE FLOW-CHART FOR THE DECONVOLUTION OF THE MULTI-WAVELENGTH TRANSMISSION MEASUREMENTS

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THE PROGRAM FOR THE DETERMINATION OF THE PARTICLE SIZE DISTRIBUTION FUNCTION PARAMETERS FROM THE MULTI-WAVELENGTH TRANSMISSION MEASUREMENTS.

GENERAL REMARKS:

- (a) All computations performed using a double precision arithmetic.
- (b) A log-normal particle size distribution function (PSDF) characterized by a mean diameter, $\langle D \rangle$, and a variance, σ^2 , is assumed.
- (c) The determination of the average extinction cross-section, $\langle \sigma_{ext} \rangle$ is obtained by integrating $(\pi D^2/4) Q_{ext}(D; \lambda, n(\lambda)) pdf(D; \langle D \rangle, \sigma)$, where D is a diameter of the particle, $Q_{ext}(D)$ is the extinction efficiency for that size particle, at a given wavelength λ (with the optical properties of particle characterized by a complex index of refraction $n(\lambda)$). The integration limits are determined by requiring that the exponential part of the PSDF is greater than 10^{-10} . The integration is performed by using the trapezoidal rule (Romberg integration scheme). Extinction efficiencies are computed by the interpolation from a set of $\{Q_{ext}(D_j)\}$, where $D_j = [1, 5000]$ nm in steps of 1 nm which are determined by a subroutine from Bohren & Huffman [6] for each wavelength for which the experimental data exists.



1. READ-IN EXPERIMENTAL DATA: $\{\lambda_i\}$, $\{n(\lambda_i)\}$, $\{T(\lambda_i)\}$, AND $\{\delta T(\lambda_i)\}$, $i=1, N_\lambda$ [N_λ is the number of wavelengths in the multi-wavelength measurements].



2. READ-IN THE DECONVOLUTION PARAMETERS:
 - (a) Three sets of the PSDF parameters $\{\langle D \rangle, \sigma\}$ which will be used as the initial guesses.
 - (b) The number of different data sets $\{T(\lambda_i)\}$ randomly to be processed.



3. THE DETERMINATION OF QUANTITIES WHICH ARE NECESSARY FOR THE DETERMINATION OF $Q_{ext}(D; \lambda, n(\lambda))$ BY INTERPOLATION:
 - (a) Check if files $QEXT.\lambda_i$, containing $Q_{ext}(D, \lambda, n(\lambda))$ for all λ_i already exist. If files exist, read-in $Q_{ext}(D)$. Else, compute $Q_{ext}(D)$ and create files $QEXT.\lambda_i$ for future use. Store extinction efficiencies in a two-dimensional array $QEXTS(I_\lambda, J)$ [$I_\lambda = 1, N_\lambda$, and $J = 1, 5000$].
 - (b) Compute the coefficients to be used for the interpolation for all λ_i and store them in a two-dimensional array $QSPLINS(I_\lambda, J)$ [$I_\lambda = 1, N_\lambda$, and $J = 1, 5000$].



Figure IV- 7: Algorithm of the program for the data inversion.

THE FLOW-CHART FOR THE DECONVOLUTION OF THE MULTI-WAVELENGTH TRANSMISSION MEASUREMENTS

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4. START A SET OF COMPUTATIONS USING $\lambda_{REF} = \lambda_1$ AS A REFERENCE WAVELENGTH [$i = 1, N_\lambda$].

Create files for storing intermediate results.



6. START THE SET OF COMPUTATIONS FOR $N_{SAMPLES}$ SETS OF TRANSMISSION DATA $\{T(\lambda_i)\}_{random}$ [$K=1, N_{SAMPLES}$].

Each $T(\lambda_i)_{random}$ is determined from the mean experimental values T_i and corresponding experimental errors δT_i assuming a Gaussian distribution of errors. For a given set $\{T(\lambda_i)\}_{random}$ determine a two-dimensional array

$R(i,j) = \ln(T(\lambda_i)_{random}) / \ln(T(\lambda_j)_{random})$
which presents the current "experimental" ratio of optical densities [$i, j = 1, N_\lambda$].



7. INITIALIZE PARAMETERS FOR THE SIMPLEX ROUTINE:

(a) Reset initial guesses.

(b) Compute the initial residuals $R_{initial}$ for initial parameters as a sum of

$$\{ [\langle \sigma_{ext}(\lambda_i) ; \langle D \rangle_{guess} \sigma_{guess} \rangle / \langle \sigma_{ext}(\lambda_{guess} ; \langle D \rangle_{guess} \sigma_{reference} \rangle] - R(i,j) \}^2$$

 which is necessary for the SIMPLEX routine.



8. MINIMIZE THE RESIDUAL FOR A CURRENT $\{T(\lambda_i)\}_{random}$ BY USING THE NELDER-MEAD DOWNHILL SIMPLEX PROCEDURE.



9. COMPUTE THE LEAST-SQUARE FIT TO DETERMINE THE NL-PRODUCT



9. STORE THE RESULTS. STATISTICAL ANALYSIS OF DATA PERFORMED SEPARATELY

Figure IV- 7: ... Continued.

errors in experimental data. The statistical deconvolution program was first applied to the input data file which contained the following data:

Table IV-1: Input parameters			
$\lambda[nm]$	refractive index	Transmittance [%]	error [%]
260	(1.1915, 0.8128)	74.67	0.5
300	(1.3620, 0.7792)	79.47	0.5
350	(1.4824, 0.7029)	84.96	0.5

The number of samples was 500, and the reference wavelength was 260 nm. Preliminary analysis showed that the mean diameter is in the vicinity of 60 nm, and the initial values for the average diameter were assumed to be: $\langle D \rangle = \{59, 59.5, 59.9\}$ [nm]. The initial values for the variance were assumed to be: $\sigma = \{.5, 0.15, 1\}$ [nm]¹². After this first set of computations was completed, the transmittance at $\lambda = 300$ nm was first *reduced* by nearly 0.5 % to 0.79 , while keeping other parameters unchanged, and the second set of computations was performed. In the third set of computations, the same data point was set to 0.80 (approximately 0.5 % *above* the original value).

Figure IV- 8 shows histograms of solutions for all three sets of computations. Solutions for the first set of data ($\delta T(\lambda = 300nm) = 0$) are marked by circles. Statistical results for all three cases are summarized in Table IV-2. Quantities ΔD ,

Table IV-2: Statistics of the results						
Case	$\langle D \rangle$	σ	NL	$\Delta \langle D \rangle$	$\Delta \sigma$	$\Delta(NL)$
	[nm]	[nm]	[cm ⁻²]	[nm]	[nm]	[cm ⁻²]
$\Delta T = 0$	57.56	0.028	4.00×10^{12}	1.43	0.024	4×10^{12}
$\Delta T = -0.5 \%$	59.31	0.046	2.34×10^{12}	1.44	0.039	1.42×10^{12}
$\Delta T = +0.5 \%$	38.77	2.34	8.8×10^{11}	15.29	1.7	1.68×10^{12}

¹²The Nelder-Mead downhill simplex method requires $n + 1$ estimates for the minimization of n parameters.

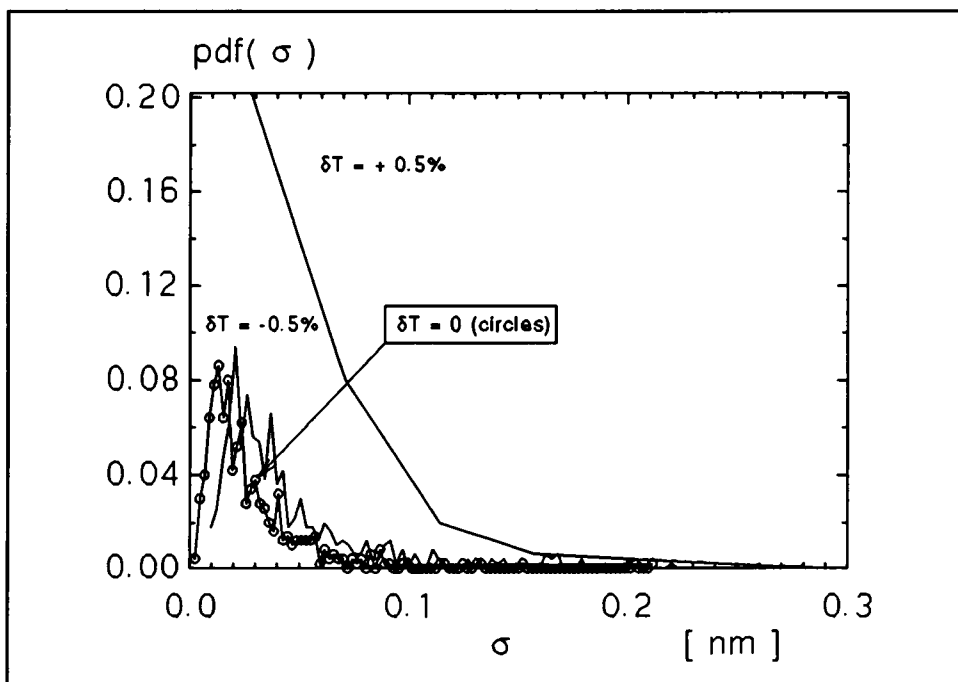
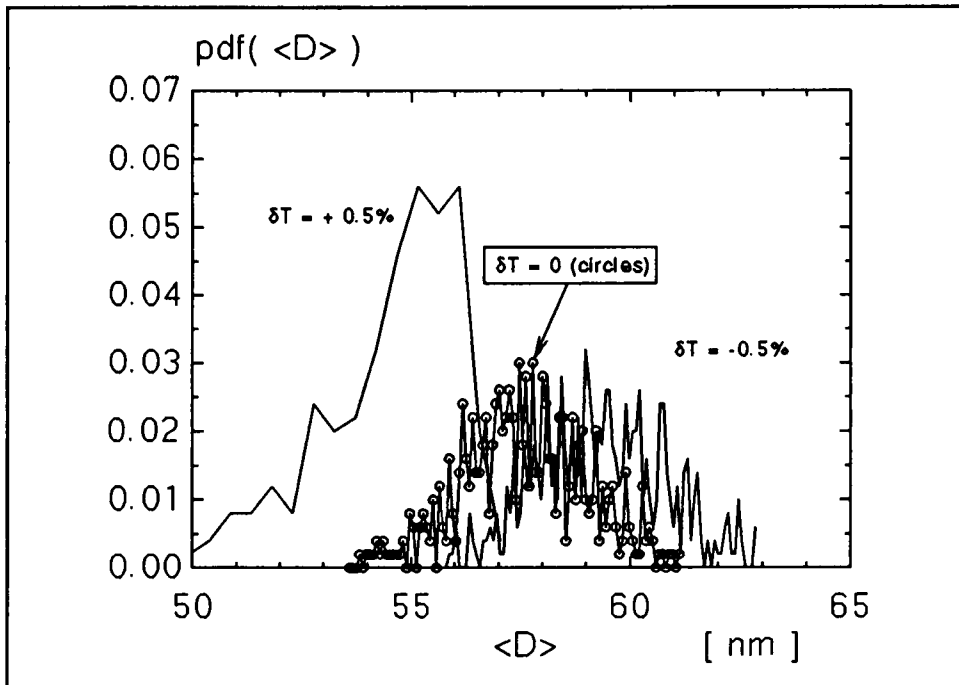


Figure IV- 8: The distribution of solutions for the three cases quoted in Table IV-1.

$\Delta\sigma$, and $\Delta(NL)$ denote standard deviations for the mean diameter, variance, and column-density respectively. Figure IV- 8 shows several important features of the minimization process. The histogram of solutions for the mean diameter indicates that the general trends of the minimization routine are as one could expect from the changes that were made in the transmittance at $\lambda = 300 \text{ nm}$. An increase in the transmittance should correspond to a decrease in the mean diameter and *vice versa*.

In the $\Delta T = 0$ case, the histogram is relatively symmetrical and the mean $\langle D \rangle$ and the most probable $\langle D \rangle$ (the peak of the histogram) nearly coincide. All 500 solutions were within 52.5 nm and 61 nm, indicating a relatively stable minimization process. Since for each of 500 samples the transmittances are drawn randomly from "experimental" error bars of 0.5 %, the mean diameter is determined as $57.6 \pm 1.4 \text{ nm}$!

Results for the $\Delta T = - 0.5 \%$ case exhibit a similar behavior. All solutions fall within $\langle D \rangle = 55$ and $\langle D \rangle = 63 \text{ nm}$, but the histogram is more skewed than in the $\Delta T = 0$ case. The mean diameter is larger by 1.75 nm, and the peak of the histogram is perhaps at a slightly lower value (the location of the most probable diameter can not be resolved accurately). The magnitude of the shift in $\langle D \rangle$ and the range of solutions could be anticipated from results of the $\Delta T=0$ case. The direction of the shift towards larger diameters is correct, since a higher absorption indicates larger particles.

Results for the $\Delta T = +0.5\%$ are somewhat surprising. The range of $\langle D \rangle$ is quite large: from 9.8 to 58 nm (the full range of diameters will be shown in the next figure; the range of diameters on the histogram was truncated in order to facilitate the comparison of the most prominent features in all three cases). This indicates a large instability of the minimization process. However, the most probable $\langle D \rangle$ is at approximately 55 nm, about 2.5 nm below its equivalent in the $\Delta T =$

0 case. The width of the peak in the histogram is also consistent with the other two cases. In spite of a large frequency of occurrence in the anticipated domain, a large fraction of solutions is dispersed over lower diameters. This behavior can be easily explained by noting that the sampled domains are as shown in Figure IV- 9. The

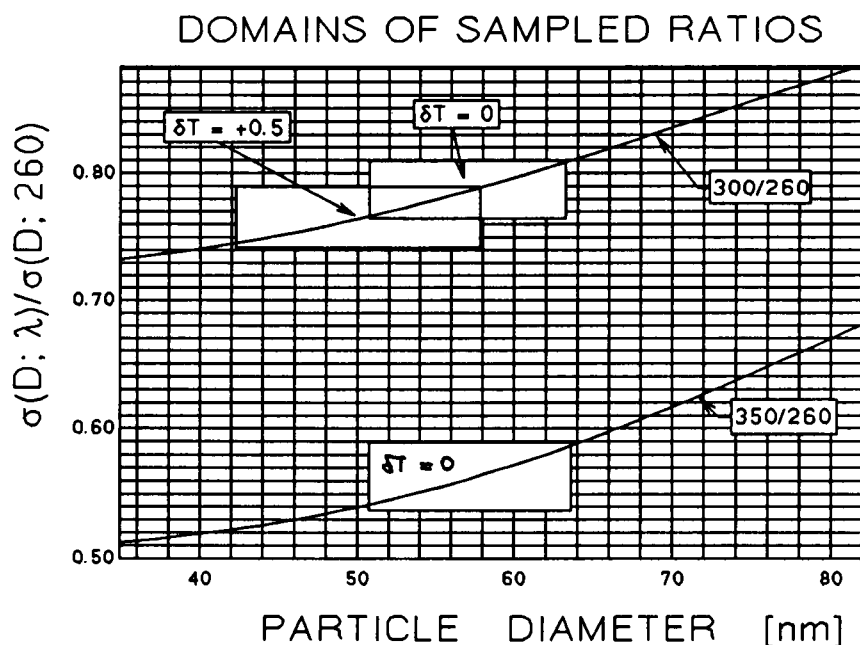


Figure IV- 9: Domain of sampling for $\Delta T = +0.5$. Program probes the size domain where a loss of sensitivity to size is appreciable.

entire range of solutions for the mean diameters is shown in Figure IV- 10, which shows *all* $500 < D > -\sigma$ solutions for all three cases. This figure shows that the minimization routine has a difficult task since there is a significant loss of sensitivity for diameters smaller than 50 nm. Therefore, the $< D > -\sigma$ results indicate that a decrease of the mean diameter is compensated by an increase in σ , as expected. A simultaneous reduction of both parameters in a region $D < 20$ nm is due to the sign reversal in $dR(300/260)/dD$ near 10 nm-range. Therefore, accumulation of numerical errors brings the solution in a range where the minimization routine will attempt

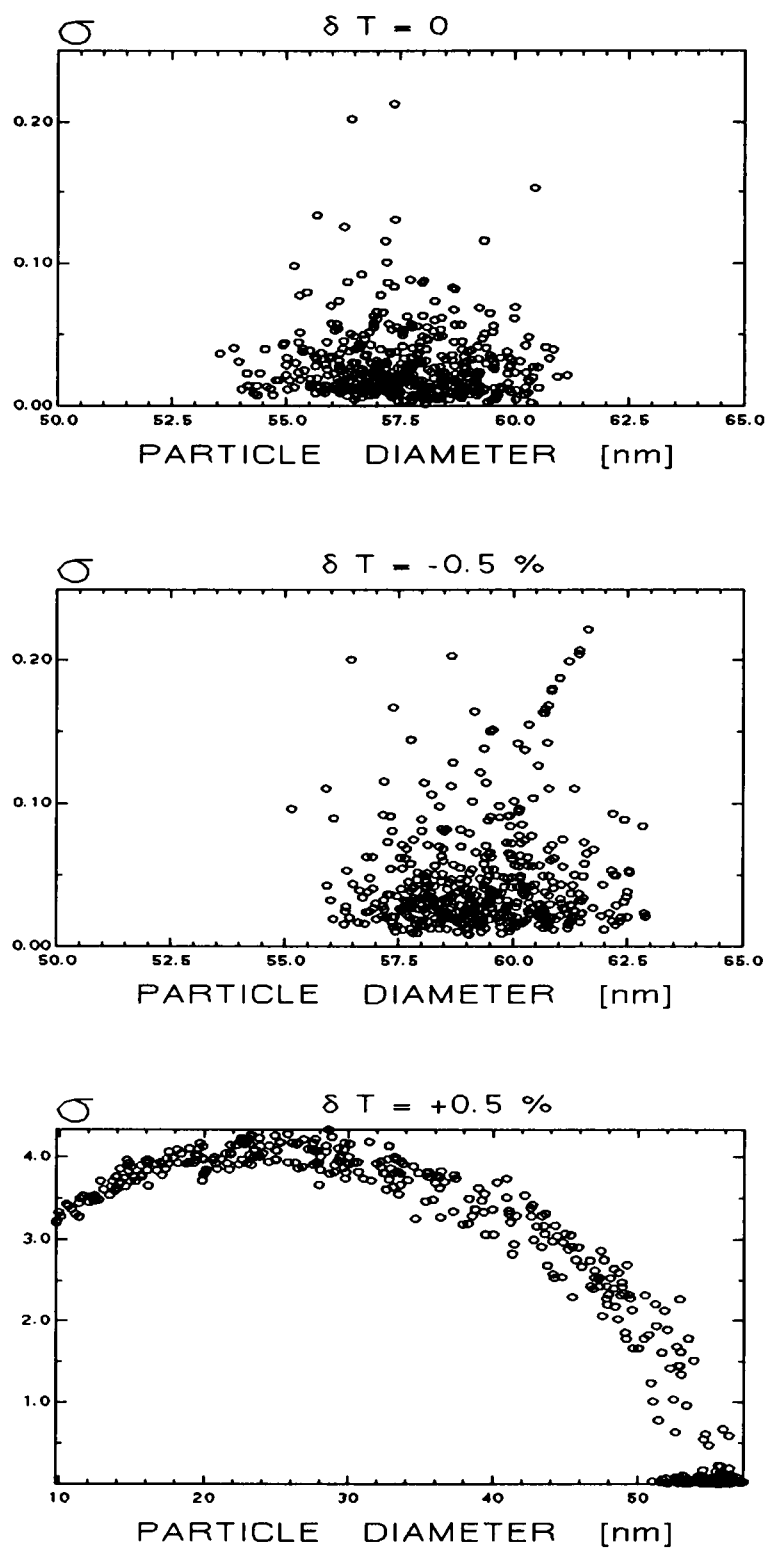


Figure IV- 10: Full scatter-plots of solutions for D and σ for all three cases.

to further reduce the mean diameter in order to minimize χ_R^2 . Therefore, when simplex solutions are driven below approximately 30 nm, continuing a minimization routine loses all sensitivity and should be terminated. This loss of the sensitivity is also indicated by the fact that for more than 60 percent of generated transmission spectra the convergence criterion was not reached in a fixed number of iterations (200). Figure IV- 11 shows scatter plots of $\chi_R^2(< D >)$ for the two indicated cases. There is an obvious correspondence between the histogram for the mean diameter and the smallest χ_R^2 . Also, the minimization is, on the average, worse in the $\Delta T = -0.5 \%$ case than in the $\Delta T = 0$ case. Otherwise, these plots demonstrate behavior that could be anticipated.

A more interesting feature emerges if one plots χ_T^2 as a function of the mean diameter, as shown in figure IV- 12. If the input data file contains perfectly accurate values for the mean transmittances, one must expect that this procedure will lead to a distribution of χ_T^2 , which will exhibit a minimum in the same diameter range as the χ_R^2 . This figure shows that a deviation in coincidence in minima of χ_T^2 and the most probable diameter is an indicator that some sort of systematic error in a given data set exists.

A similar procedure was applied to a synthetic transmission spectrum for the case shown in Figure IV- 6 on page 66 for a mean diameter of 125 nm and corresponding variance of 25 percent (31.25 nm). Plots IV- 6 - C and D suggest that this would be a difficult case for the deconvolution from measurements at wavelengths as indicated in that figure. Indeed, this was the case, and the "experimental" error had to be confined to 0.05 percent in order to produce a distribution of results as shown in Figure IV- 13.

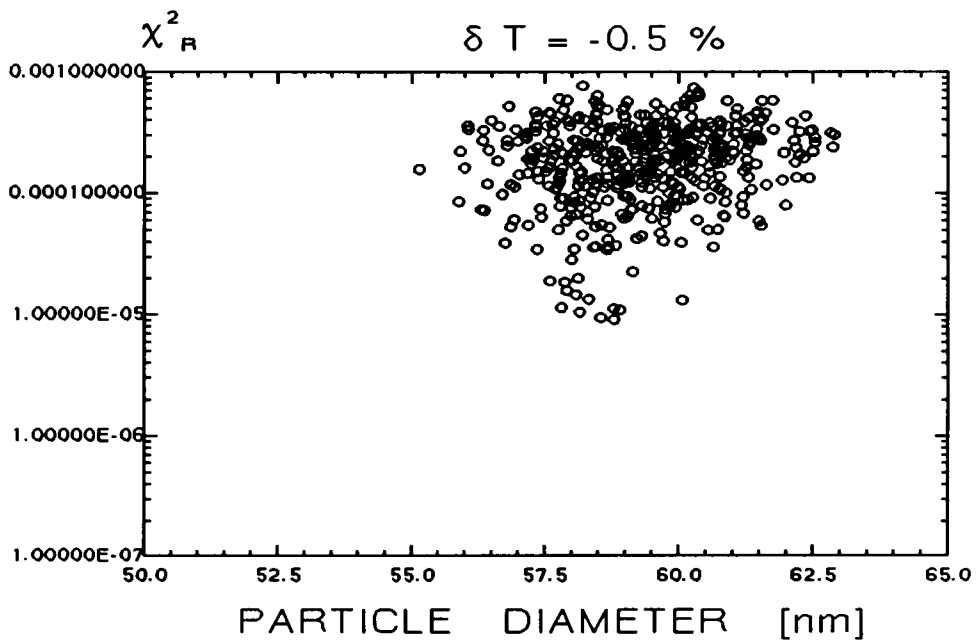
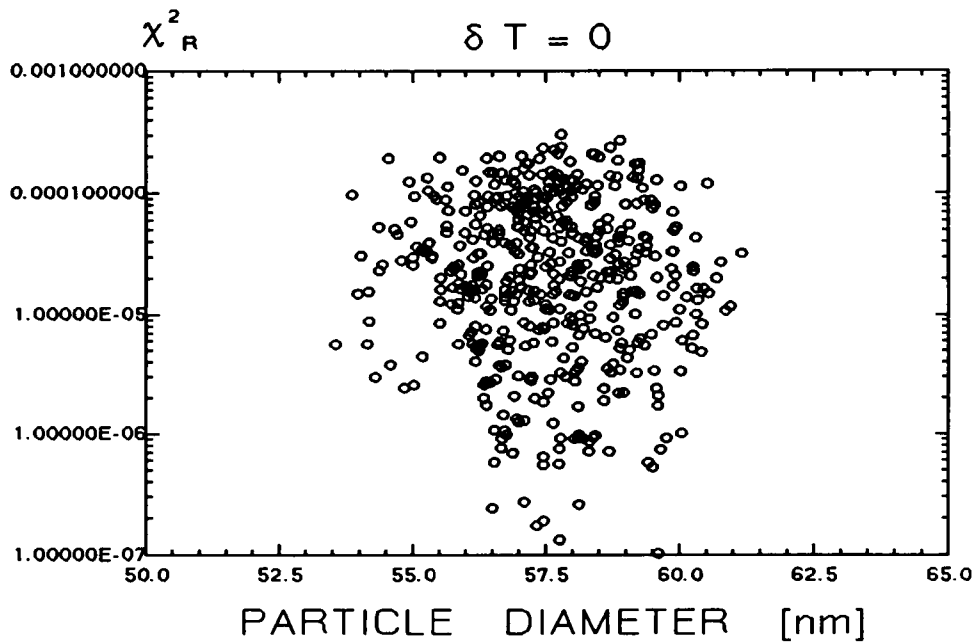


Figure IV- 11: The effects of ΔT on χ^2_R .

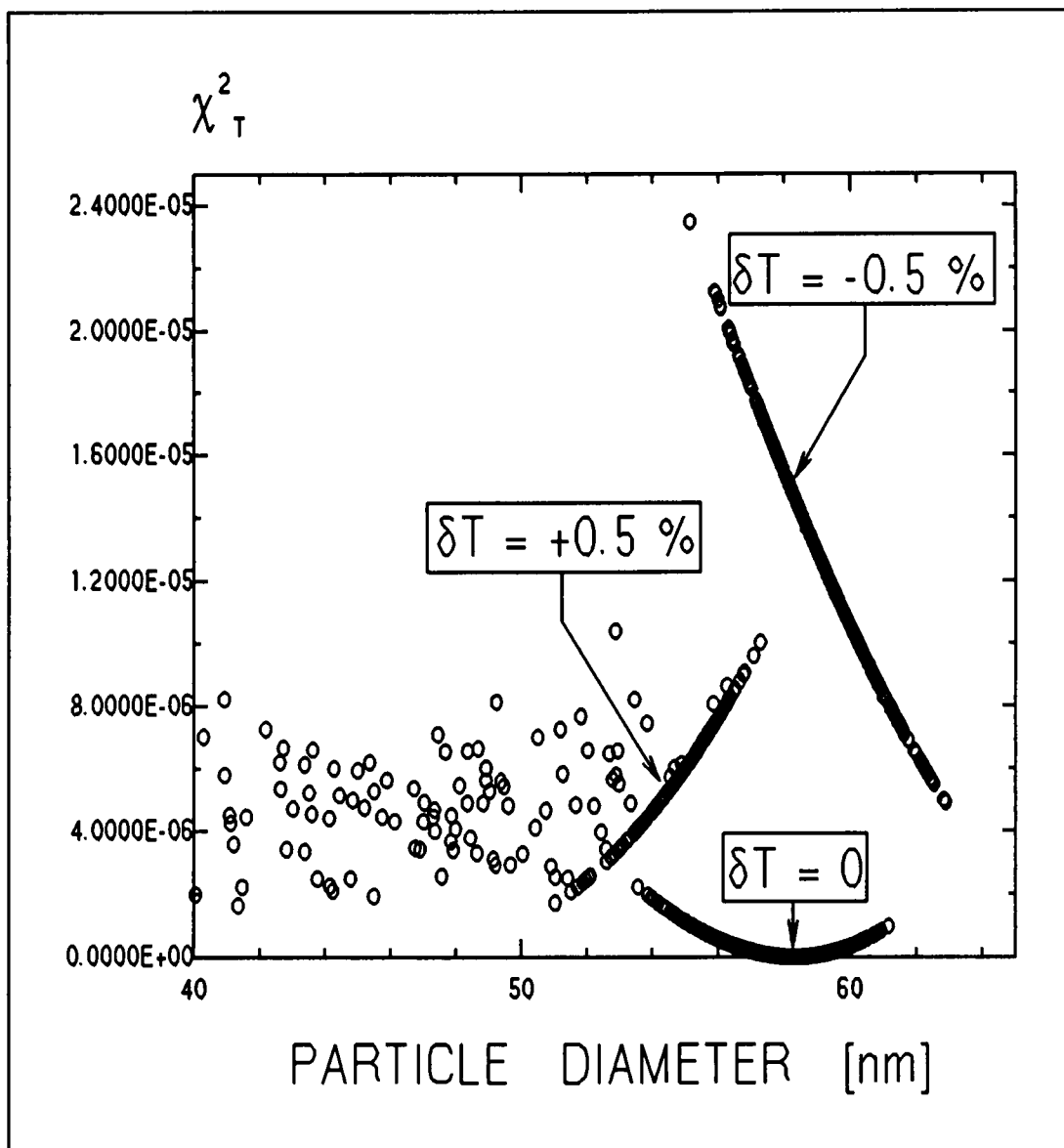


Figure IV- 12: The displacement of χ^2_T minima. The location for the most probable mean diameter indicates that systematic errors result in an under/over estimate of the mean diameter. This effect is even more pronounced for the χ^2_T -residual.

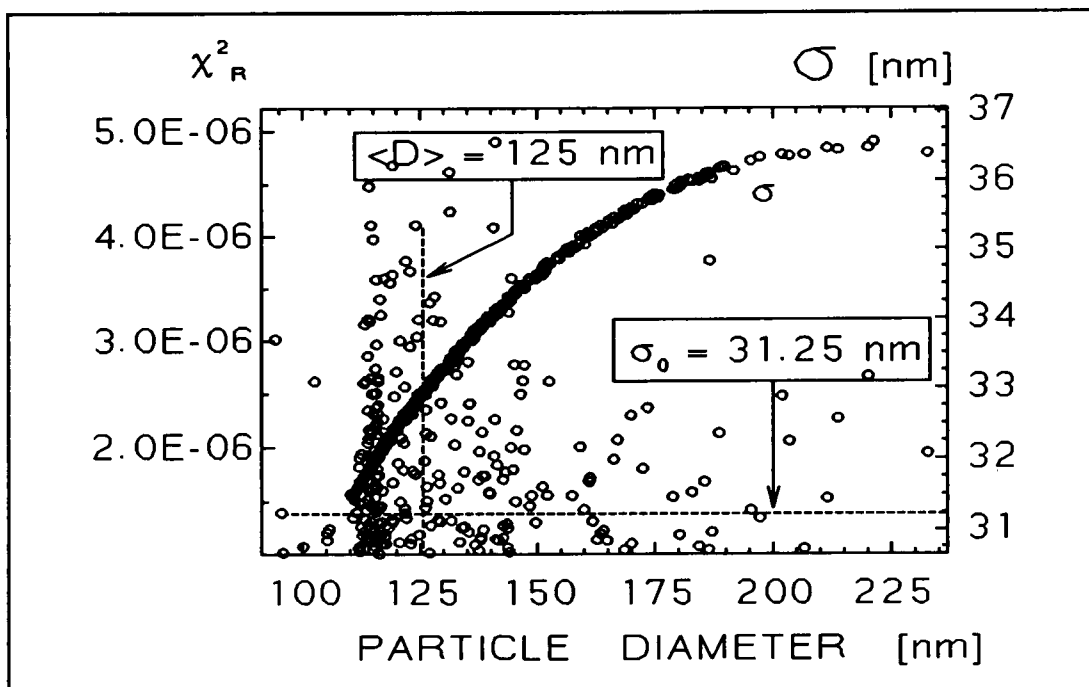


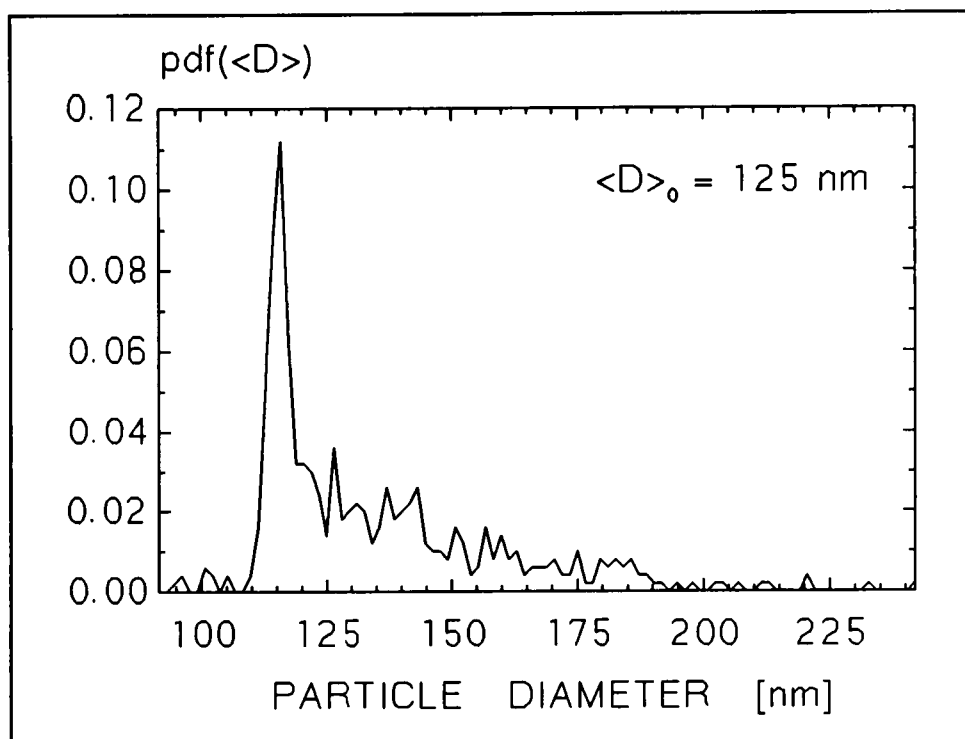
Figure IV- 13: Scatter plots for $D - \chi^2_R$ and $D - \sigma$ for the case shown in Figure IV-6 on page 66.

Histograms of solutions, shown in Figure IV- 14, indicate that the maxima in the distributions are shifted with respect to the true values. The exact origin of these shifts is not determined, since it could be attributed to numerical errors, or more likely, to a significant change in the sensitivity over the diameter range covered by a relatively broad PSDF.

IV.4 Conclusions

A numerical procedure for the determination of the PSDF parameters from the multiwavelength measurements was presented. An analysis of the information content for this purpose was performed. It was found that the desired information can be extracted provided that a set of measurements is performed at wavelengths which provide the sufficient information about particle sizes. The data inversion may require several iterations since elimination of data for some wavelengths may improve

A)



B)

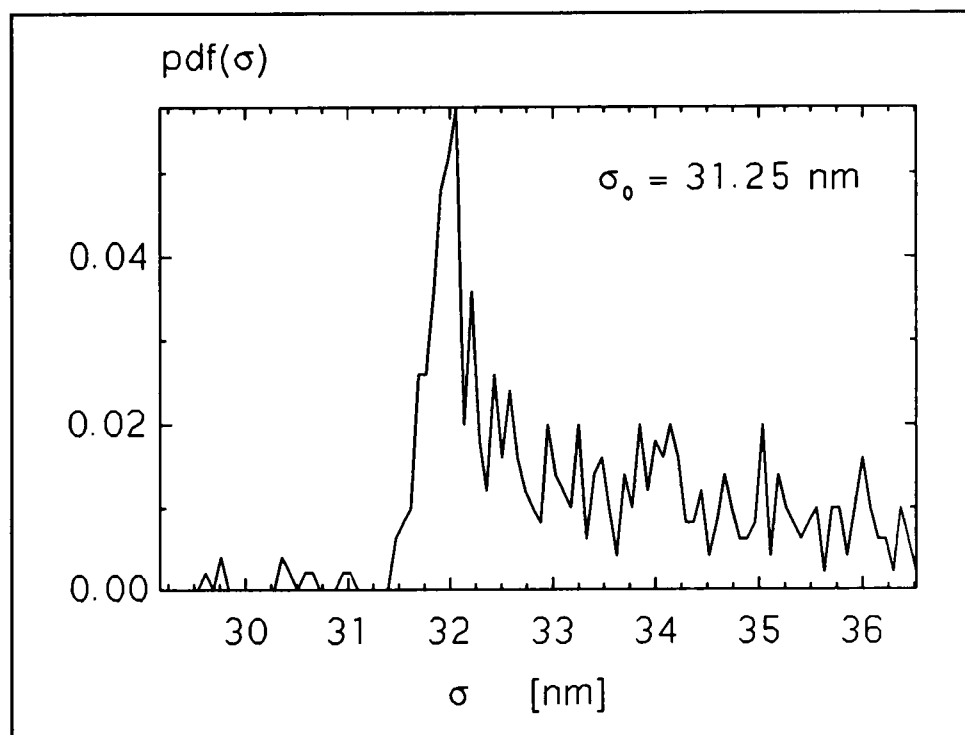


Figure IV- 14: Histograms of solutions for the case shown in Figure IV-6 on page 66.

the convergence and accuracy of the minimization procedure.

Scatter plots shown in Figures IV-9, IV-11, and IV-12 clearly illustrate that the minimization technique is not guaranteed to give a unique answer and that a statistical approach is necessary to obtain conclusive results. Moreover, the significance of experimental errors is best revealed through the statistical processing of data. An estimate of the relationship between the error in measurement and the error in the determination of particle sizes is given by Equation IV- 23. That expression and the corresponding plots (Figure IV-6 -D on page 66) are useful for the selection of wavelengths which should be included in the data inversion process for a given range of diameters.

Numerical errors in the deconvolution depend on the choice for the reference wavelength for a particular particle-field under consideration, but the significance of this effect is minimized by the statistical processing of data. This effect will be illustrated more clearly in the next chapter in a discussion of the data inversion of extinction measurement results for the particle-field produced by the soot generator.

CHAPTER V

EXTINCTION MEASUREMENTS AND DECONVOLUTION OF THE RESULTS

The first part of this chapter presents the experimental setup and the results of the multi-wavelength, transmission measurements for the two flow conditions which were discussed in Chapter III. The second part presents the results of the data inversion technique described in Chapter IV to experimental results.

V.1 Experimental setup

Extinction (transmission) measurements are in principle very easy to perform, but there are some aspects of the experimental arrangement that require particular attention. The Mie theory shows that forward scattering of light is strongly preferred for the scattering of light by particles larger than the wavelength. Consequently, extinction measurements should eliminate the possibility of collecting this forward-scattered light. The discrimination between the direct and the forward-scattered light is accomplished by keeping the detector's acceptance angle small. Strict rules prescribing the minimum acceptance angle do not exist. The restriction to less than 10% of the divergence angle of the principle lobe of the Fraunhofer diffraction for an aperture of diameter D (where D is the diameter of the particle) is recommended by Gougeon [45]. Since this angle is approximately

$$\theta_F = \frac{1.22\lambda}{D}, \quad (\text{V} - 1)$$

the acceptance angle should be smaller than

$$\theta_a = \frac{\lambda}{8.4D}, \quad (\text{V} - 2)$$

where θ is the divergence half-angle of the collection optics measured in radians. Therefore, the acceptance angle for small particles may be quite large. For example, for particles of 100 nm in diameter and wavelength $\lambda = 260 \text{ nm}$, this criterion for the acceptance angle gives an angle of approximately 18 degrees. Incidentally, Horvath [41], who reported the validity of the Lambert-Beer law for the extremely low transmittances of 0.0001, attributes the surprising outcome of his measurements to a small acceptance angle (0.01 radians). For the largest particle diameter and for the shortest wavelength in his measurements, Gougeon's criterion recommends an acceptance angle of approximately 0.025 radians. Therefore, Equation V- 2 appears to be an acceptable "rule-of-thumb" criterion.

In laboratory measurements it is possible to determine the acceptance angle by finding the range of angles for which the *transmittance* measurements are insensitive to the aperture settings. For the measurements described in the next section, this issue was not critical since the observed particles turned out to be small, as will be shown shortly.

The main characteristic of the arrangement is the use of the relative transmission measurements. The power output of the lamp is a function of time, and the same is true for the properties of the photomultiplier tube. To eliminate errors due to these uncertainties, and to measure the extinction of the plume alone, relative transmission measurements are recommended. The experimental arrangement is shown in Figure V- 1.

The relative transmission technique can be explained as follows. The incident light beam, 2 mm in diameter, is divided into two beams of nearly equal intensities by the beam splitter (BS-1). One beam, which will be called the *probe beam*, collimated by shutters AP1 and AP2 and chopped at frequency f_1 , is deflected by the mirror M2 and reaches the beam splitter BS-2 after passing through the set of the observation

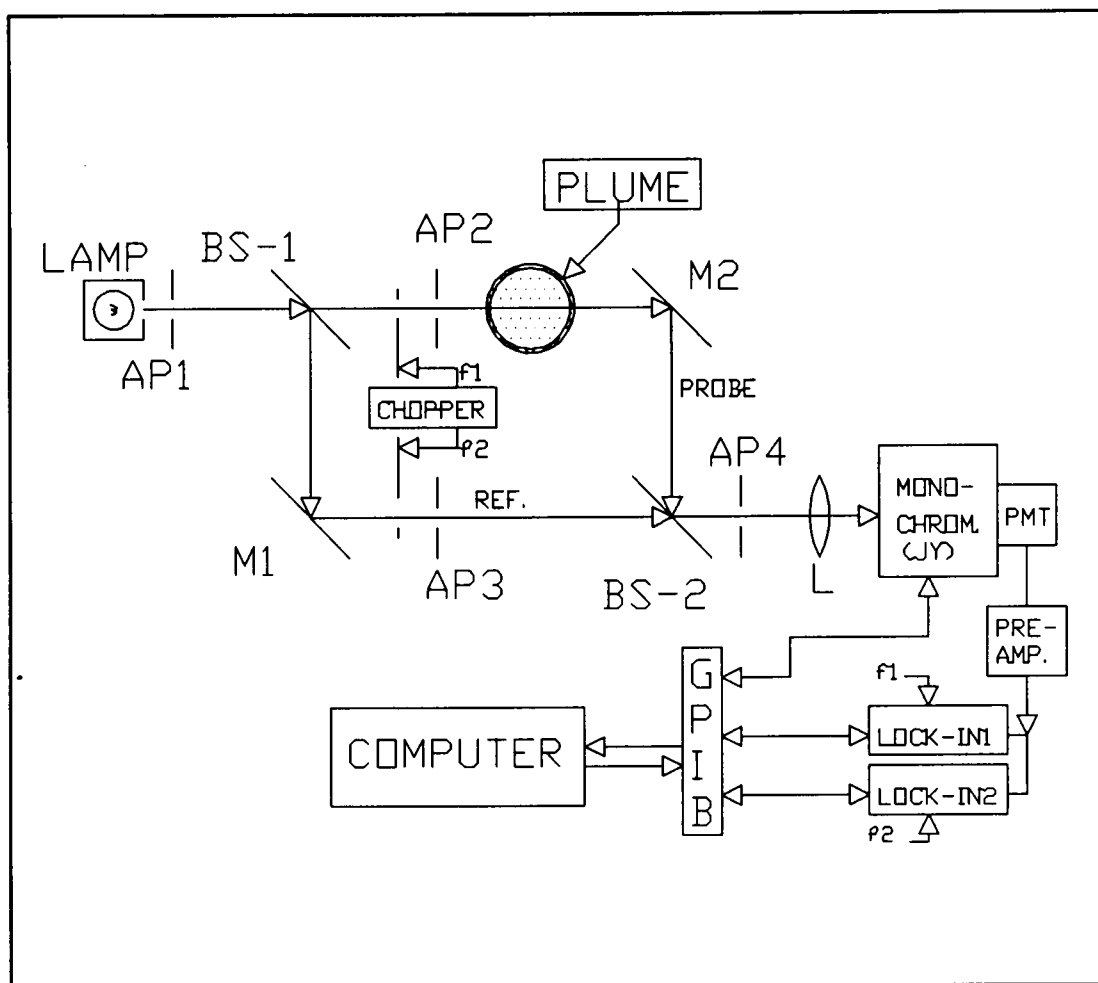


Figure V- 1: A schematic representation of the experimental arrangement.

windows. The other beam, which will be called the *reference beam*, collimated by shutters AP1 and AP3 and chopped at frequency f_2 , reaches the beam splitter BS-2 after passing approximately the same distance as the probe beam. Recombined on the beam splitter BS-2, both beams are apertured by the shutter AP4 and reach the photomultiplier (PMT) after the wavelength selection by the monochromator (JY), which had an acceptance angle of 0.8° . The photomultiplier output is integrated and amplified by the pre-amplifier and applied to two lock-in amplifiers which measure the intensities of the individual beams, by referencing appropriate chopper frequencies f_1 and f_2 . The lock-in amplifiers (model 5104 manufactured by EG&G) were

operated with 3-seconds integration time. The identical and broad-band beam splitters have 50 percent transmission in the visible portion of spectrum. The adjustment of shutters AP2 and AP3 allows one to make the intensities of both beams nearly equal over the whole range of wavelengths of interest. The transmittance is determined by performing measurements with and without the presence of the plume. The measurement without the presence of the plume gives the calibration constant

$$c(\lambda) = \left[\frac{I(\text{probe})}{I(\text{reference})} \right]_{\text{cal}} = \left[\frac{V1}{V2} \right]_{\text{cal}} \quad (\text{V} - 3)$$

which is used with the measured voltage of the reference beam signal to measure the instantaneous incident intensity on the particle field. Here, $V1$ and $V2$ are the voltages measured by the lock-in amplifiers. Therefore, the transmittance is determined as

$$T = \left[\frac{I_t(\text{probe})}{I_0(\text{probe})} \right]_{\text{plume}} = \left[\frac{I_t(\text{probe})}{c \cdot I(\text{reference})} \right]_{\text{plume}} = \frac{[V1/V2]_{\text{plume}}}{[V1/V2]_{\text{cal}}} \quad (\text{V} - 4)$$

Since all other optical elements are accounted for by the pre-calibration measurement, the reference beam provides the information about the instantaneous intensity of light incident on the particle field *alone*. This is important, since the measurement of the transmittance *after* the measurement with the plume gives the information about the extinction by the deposited substance on the window walls.

Besides the concern for the window-deposition, the time dependence of the source is of concern too. The software for the computerized control of the monochromator and the lock-in amplifiers existed to reduce the data acquisition time to a minimum. The total length of each transmission-spectrum scan was determined by the number of the transmission measurements at each wavelength and the number of points in the spectrum. For statistical purposes, the number of measurements at each wavelength was always larger than 30, and most of the measurements were performed with 40 data points for each wavelength. Measurements with a better

statistical quality (200 data points) required considerably longer measurement times since the data were acquired at a typical rate of 3 data points per integration time-constant. Since the temporal behavior of the source is critical, the number of data points was kept at a relatively low value (80). Statistical data-processing was performed on-line, and from the average voltages and their standard deviations, it was possible to determine the measurement precision of the transmittance T .

The transmission spectra were taken for the visible and the UV portion of the spectrum. For the transmission measurements in the visible and near-UV (350 nm to 550 nm), a xenon lamp was used as the light source. The results of the xenon-lamp measurements were informative only in the sense that they showed the particles to be smaller than $0.1\mu m$. However, the accessible spectral range was not suitable for the particle-sizing measurements with the low plume densities that caused neither window contamination nor drastic alteration of the operation of the source. Since all measurements with the xenon lamp showed the window-contamination problems, these measurements will not be discussed extensively. For the UV wavelengths in the range 220 nm to 400 nm, a deuterium lamp was used. The monochromator, manufactured by Jobin-Yvon (JY), has a focal length of 640 mm, an f -number of $f/5.7$, a 1200 grooves/mm grating, and a dispersion of 1.2 nm/mm . The entrance and the exit slits were kept at 200 μm during the measurements. The spectrometer is equipped with a drive system which can be controlled by the computer through a GPIB interface. The monochromator was calibrated in wavelength using a mercury lamp by scanning from the low towards the high λ , and this direction of scanning was maintained for all measurements reported here. The photomultiplier tube was operated at 900 V (EMI, RFI/S MK II). The chopper was a two-slit chopper, operating at a frequency of 309 Hz. The experimental arrangement was tested by making the transmission measurements on the set of the neutral-density filters at wavelengths

for which the calibration sheet was supplied by the manufacturer (Oriel).

Prior to performing the transmission measurements, the approximate steady-state distribution of the apparatus was achieved. This was accomplished by operating the soot generator for 45 to 60 minutes at the heated operating flow conditions but without the particle-producing acetylene flow. Each measurement was comprised of at least two pre-calibration scans in pure argon. This was done to confirm the temperature stabilization, and it also improved the statistics of the calibration constant. The introduction of the acetylene was achieved by shutting-off the RF power supply, setting the desired throughput of the acetylene flow, and gradually increasing the heating back to the operating temperatures. This was required since the introduction of the acetylene at the operating temperature could result in large perturbations in the flow pattern, which would usually result in the contamination of windows by soot. The transmission was continuously monitored at one fixed wavelength (usually 250 nm) to ascertain that the steady-state condition existed. After the transmission spectrum was acquired, the temperature of the graphite rod was gradually reduced to avoid window contamination. The acetylene flow was removed from the drift tube, and the RF generator was turned on again to heat the graphite to the same temperature. Then, one or two post-calibration scans were taken. In some cases, the plume-transmission scans were acquired several times, separated by intervening calibration scans. At the end of the sequence of measurements, the apparatus was evacuated, and the ultimate pressure reached (50 to 60 *mTorr*) was an indication of potential problems with the sealing. The window seals remained intact throughout these studies, and only after extensive thermal cycling of the window sealant (during the diffusion-broadening-spectroscopy measurements), did vacuum integrity problems occur.

V.2 Experimental results

This section presents transmission spectra measured under various flow conditions which illustrate the apparatus performance. Results shown in Figure V- 2 are particularly important since the diffusion broadening spectroscopy measurements were performed under the same flow conditions and the data inversion for this particular set of data will be presented in the next section. The data were acquired

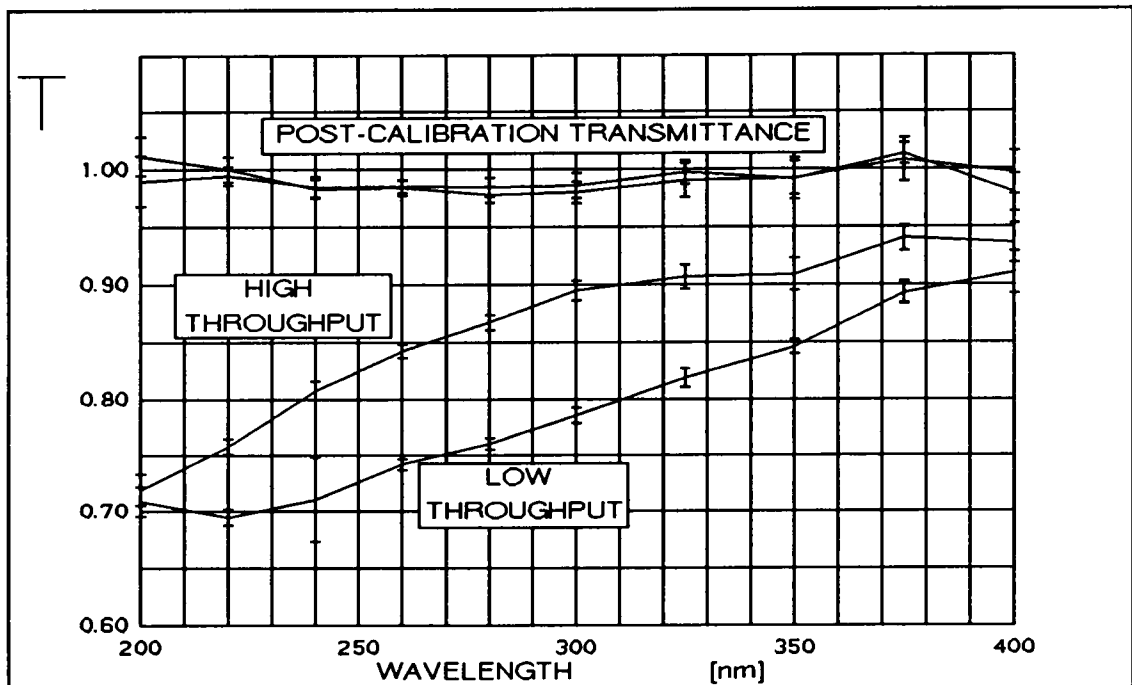


Figure V- 2: The transmission spectrum for the two flow conditions given in Table II-2.

by making two pre-calibration scans, followed by the scan for the high-throughput flow conditions and one post-calibration scan. Then, flow conditions were changed to the low-throughput case. After the system was thermally stabilized, the transmission scan was acquired for the low-throughput case, followed by the post-calibration scan. Transmissions were computed from the average values for the calibration scans. For each point in the spectrum errors of measurement for both beams were computed

Table V-1: Conditions - case 1				
Pressure	Temperature	sheath [Ar]	core [Ar]	acetylene
[Torr]	[°C]	$\text{atm} \cdot \text{cm}^3/\text{sec}$	$\text{atm} \cdot \text{cm}^3/\text{sec}$	$\text{atm} \cdot \text{cm}^3/\text{sec}$
340	1350	13.5	1.6	1.3

from the average values of the measured voltages and their standard deviations. The post-calibration transmittance was determined by referencing the first two pre-calibration scans only. This shows that the window contamination is small compared to the error of the extinction measurements. Figure V- 3, in contrast to Figure V- 2, presents one set of “bad” data which illustrates some problems with the long-run behavior of the apparatus. In this case, only pre-calibration measurements were

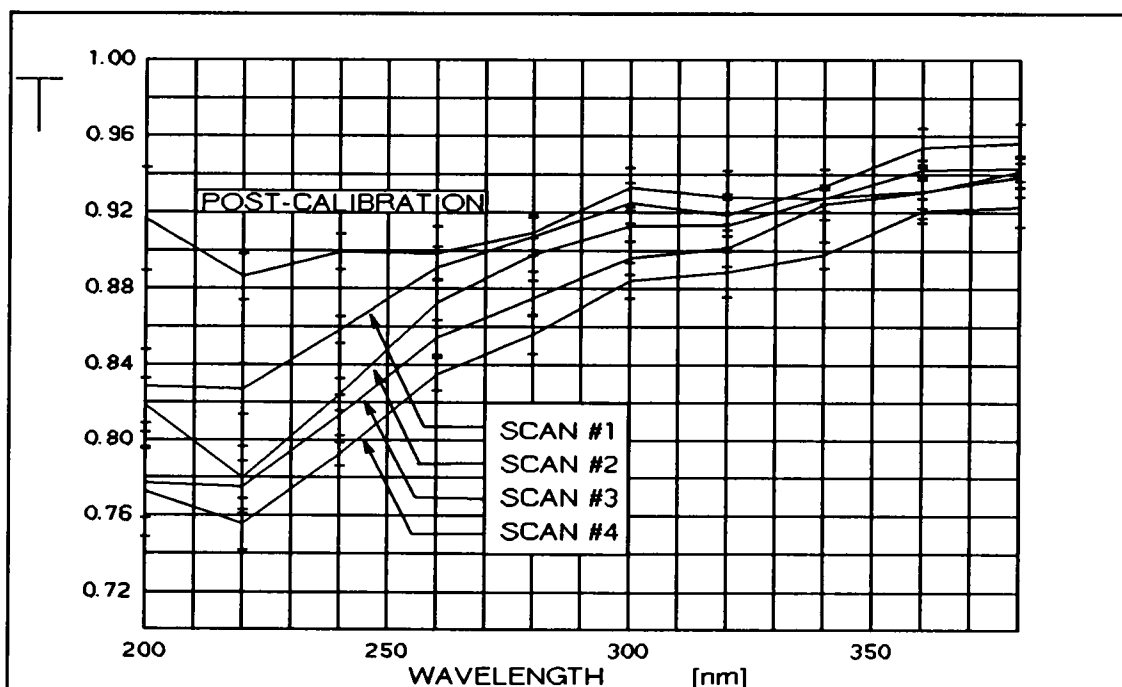


Figure V- 3: Transmission spectrum for the flow conditions given in Table V-1.

referenced for the determination of the transmittance. Spectra were acquired sequentially, with 20 minute intervals of continuous, plume-producing operation of the soot

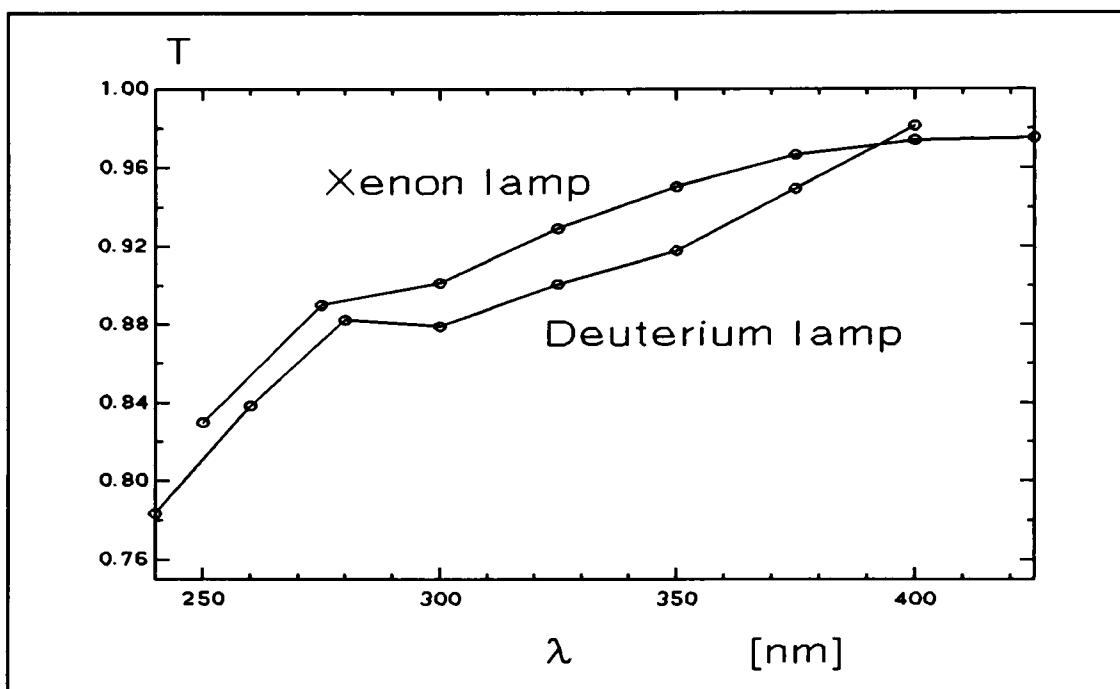


Figure V- 4: Transmission spectra for the flow conditions given in Table V-2.

Table V-2: Conditions - case 2				
Pressure	Temperature	sheath [Ar]	core [Ar]	acetylene
[Torr]	[°C]	$atm \cdot cm^3/sec$	$atm \cdot cm^3/sec$	$atm \cdot cm^3/sec$
375	1250	17.3	3.5	.95

generator between individual scans. This particular sequence of data was troubled with pressure regulation due to the malfunction of the soot-filter. The total duration of the operation was approximately 130 *min* (the duration of each individual scan was approximately 6.5 *min*). The differences in results for individual scans could be attributed to both the changes in the properties of the source and to the flow perturbations due to the malfunction of the filter.

Transmission spectra acquired with the xenon lamp, and the deuterium lamp are shown in Figure V- 4 and illustrate the repeatability of the source operation. The output of the xenon lamp is appreciably reduced for wavelengths below 350 *nm*,

exactly in the portion of the spectrum where the sensitivity to particle sizes is largest. For that reason, xenon-lamp measurements could not be used for these particle-sizing applications and were abandoned. Figure V- 5 is an even better illustration of the repeatability of the source operation. Each curve in this Figure was obtained

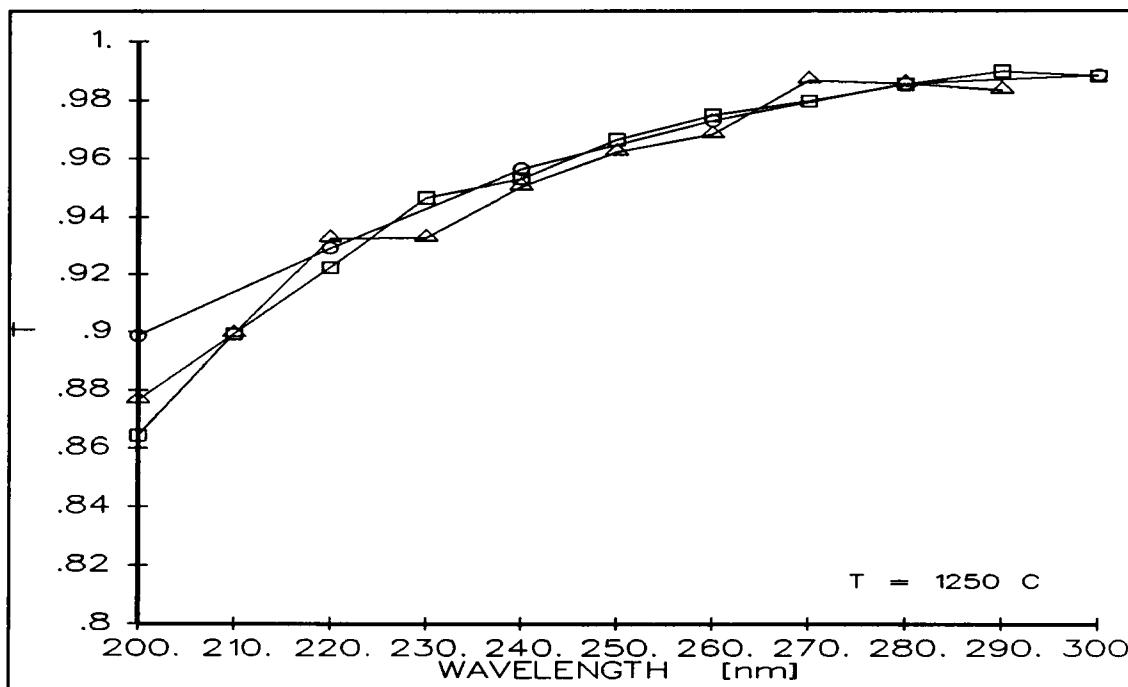


Figure V- 5: Transmission spectra for the flow conditions given in Table V-3.

Table V-3: Conditions - case 3				
Pressure	Temperature	sheath [Ar]	core [Ar]	acetylene
[Torr]	[°C]	$atm \cdot cm^3/sec$	$atm \cdot cm^3/sec$	$atm \cdot cm^3/sec$
290	1250	26.6	3.15	2.0

by completing an independent sequence of measurements using the deuterium lamp. These data represent the lowest temperature at which the transmission measurements indicated appreciable extinction.

The temperature dependence of extinction is shown in Figure V- 6, with the

flow conditions which were slightly changed from the high-throughput case. The temperature range was between 1250 and 1400°C. Since the complete sequence of measurements was rather long, it was necessary to reduce the throughput of acetylene in order to achieve the steady operation of the source over the long periods of time. The number of points in the spectrum is reduced for the same reason. This figure

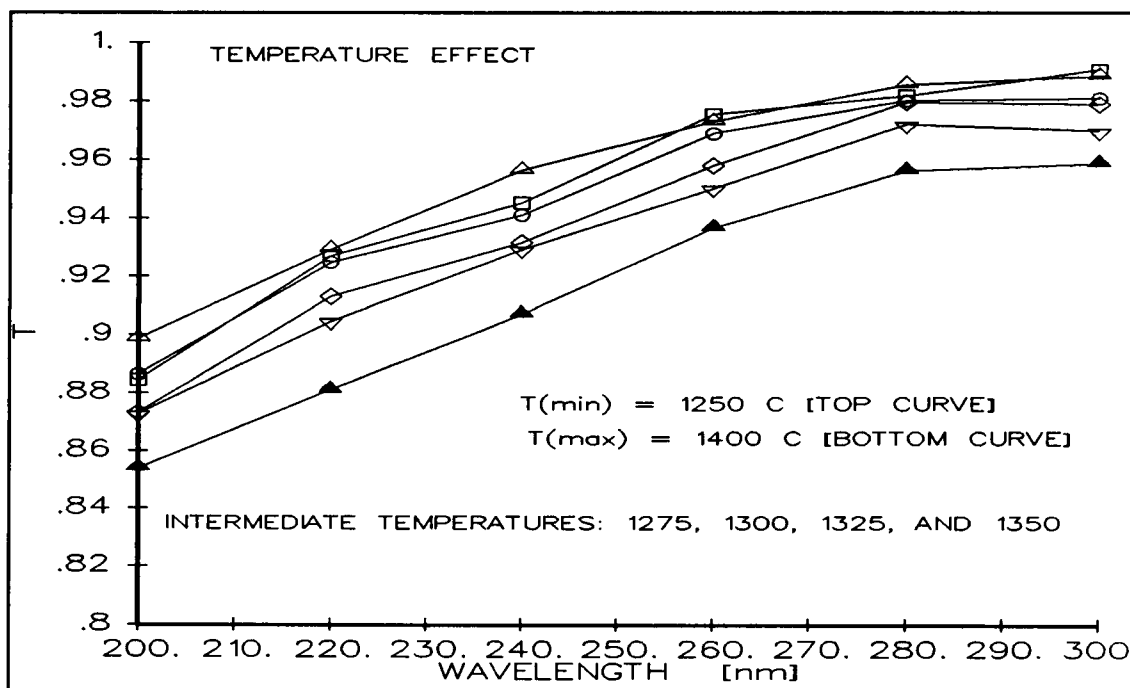


Figure V- 6: Transmission spectra for the flow conditions given in Table V-4.

Table V-4: Conditions - case 4				
Pressure	Temperature	sheath [Ar]	core [Ar]	acetylene
[Torr]	[°C]	$atm \cdot cm^3/sec$	$atm \cdot cm^3/sec$	$atm \cdot cm^3/sec$
290	1250	26.6	3.15	2.0
290	1275	26.6	3.15	2.0
290	1300	26.6	3.15	2.0
290	1325	26.6	3.15	2.0
290	1350	26.6	3.15	2.0
290	1400	26.6	3.15	2.0

shows that the transmission decreases with temperature increase, with the most pronounced change at the highest temperature settings (1350°C and 1400°C).

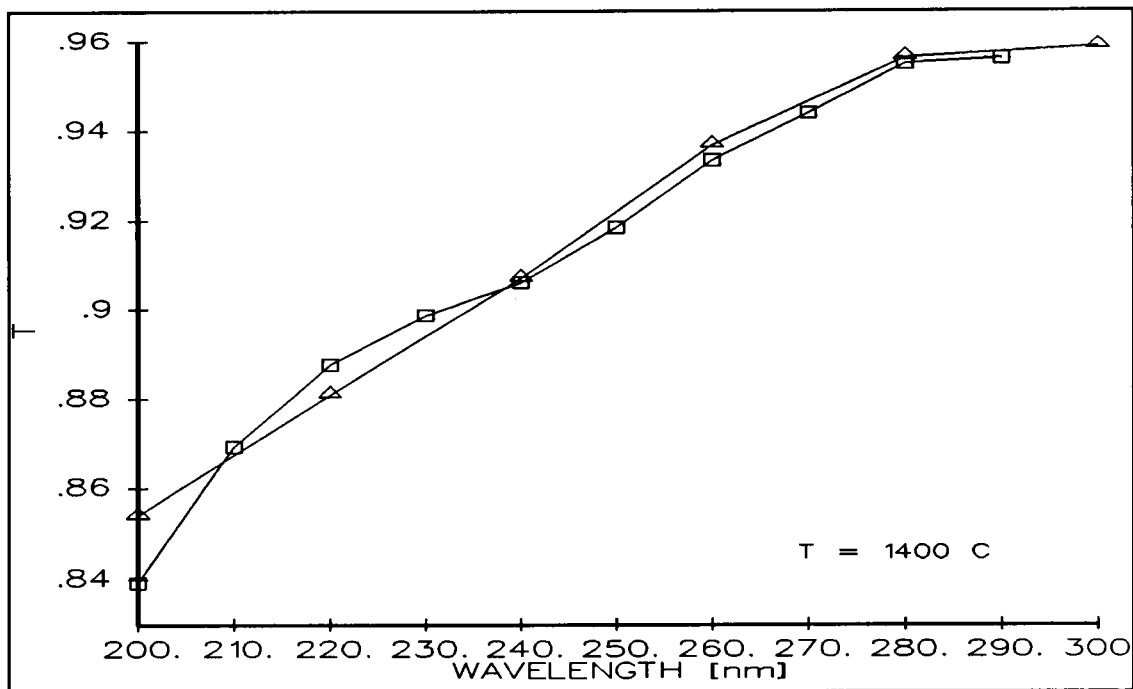


Figure V- 7: Transmission spectra for the flow conditions given in Table V-5.

Table V-5: Conditions - case 5				
Pressure	Temperature	sheath [Ar]	core [Ar]	acetylene
[Torr]	[$^{\circ}\text{C}$]	$\text{atm} \cdot \text{cm}^3/\text{sec}$	$\text{atm} \cdot \text{cm}^3/\text{sec}$	$\text{atm} \cdot \text{cm}^3/\text{sec}$
290	1400	26.6	3.15	2.0

At the end of the sequence of 5 temperature settings, it was found that the inner diameter of the graphite rod was reduced by approximately 1 mm over a length of 5-8 mm in the area where the temperature was the highest. The identical sequence of measurements was repeated and Figure V- 7 shows individual transmission spectra for two scans at high-temperature setting. The repeatability in this case shows that the changes in the source properties are at least reproducible, although the changes

in the graphite rod were appreciable.

This set of measurements shows that the residence-time of acetylene has an appreciable effect on the soot production (Figure V- 2). The reproducibility of results was confirmed, and the window contamination problem had a minimal impact on the extinction measurements. However, due to the nature of heterogeneous decomposition of acetylene, the source properties change over long periods of time.

V.3 Data inversion results

This section presents results of the deconvolution program applied to the low-throughput case shown in Figure V- 2. The most significant assumptions are:

1. The particle-field produced by the soot generator has a spatially-uniform size-distribution.
2. Carbon particles across the plume can be characterized by the same optical constants.

The validity of these assumptions will be discussed after the results of the deconvolution are presented. The low-throughput data set was chosen because the comparison with the diffusion-broadening-spectroscopy results for such flow conditions are possible. Deconvolution of results will simultaneously demonstrate the application of the numerical parameter-fitting approach which was described in the previous chapter. This will illustrate both the expected behavior, in accord with discussions of that approach in Chapter IV, and some additional properties of the numerical parameter-fitting approach.

The first step in the data-inversion process was establishing the most probable range for the mean diameter of particles. Preliminary inspection of data based on the ratios of optical densities for monodisperse distribution indicated clearly that the

particles are smaller than 100 nm, and therefore, much of the analysis presented in discussions of Figures IV-2 to IV-5 is directly applicable.

Data for the full transmission spectrum for the low-throughput case shown in Figure V- 2 is listed in Table V-6. Symbols $\Re(n)$ and $\Im(n)$ in that table denote the real and imaginary parts of the refractive index, n .

Table V-6: Low-throughput transmission				
λ [nm]	$\Re(n)$	$\Im(n)$	T	ΔT
200	0.8546	.6741	7.077165E-01	1.300398E-02
220	0.9656	.7552	6.965477E-01	7.650975E-03
240	1.0821	.7997	7.197694E-01	3.880884E-02
260	1.1915	.8128	7.477317E-01	5.118410E-03
280	1.2858	.8029	7.691368E-01	5.031471E-03
300	1.3620	.7792	7.919001E-01	6.356030E-03
325	1.4331	.7414	8.267711E-01	7.498616E-03
350	1.4824	.7029	8.499688E-01	1.008476E-02
375	1.5159	.6685	8.917881E-01	8.033888E-03
400	1.5385	.6397	9.153498E-01	1.615278E-02

The range of wavelengths at which the transmission could be measured with the deuterium lamp with an acceptable accuracy was between 200 and 350 nm, and the best signal levels were in the wavelength range from 210 to 250 nm. However, the optical properties of soot indicate that the real part of the refractive index changes sign in the vicinity of 230 nm. This fact *per se* would not be a reason for concern if optical properties of carbon particles were known with certainty. The use of wavelengths for which a real part of refractive index is less than one is not recommended for particle-sizing applications since the extinction becomes very sensitive to optical properties. For example, for particles in a Rayleigh regime ($x \ll 1$), extinction is dominated by absorption [6], and in that case the absorption efficiency is determined

according to [6]

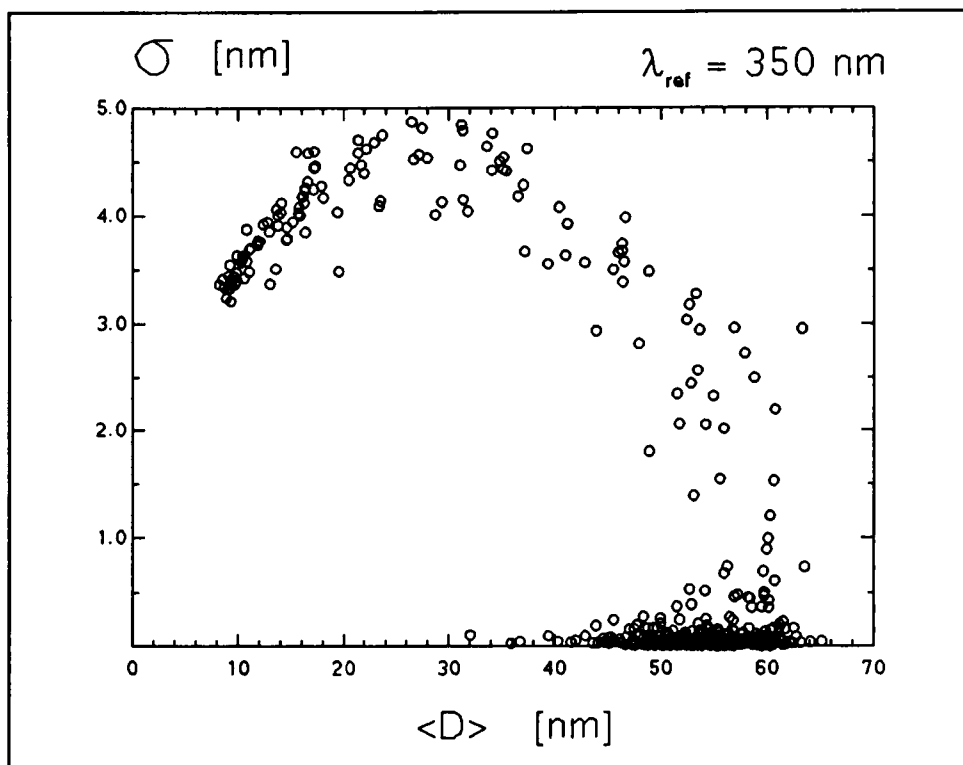
$$Q_{abs} \equiv \frac{4\sigma_{abs}}{\pi D^2} = 4x\Im\left\{\frac{n^2 - 1}{n^2 + 2}\right\}. \quad (V - 5)$$

The denominator of this expression becomes small when $\Re(n)$ becomes smaller than one. It is easy to anticipate existence of resonant-like behavior when $\Re(n^2) \rightarrow -2$. For particles which are not small compared to the wavelength, occurrence of these resonances, which are referred to as *surface modes* of small particles, are also size-dependent. As was discussed in Chapter II, optical properties of soot are not well-known in this wavelength regime. Therefore, in transmission measurements for wavelengths lower than 240 nm, knowledge of the optical constants is more critical for particle-sizing applications than for longer wavelengths.

On the other end of spectrum, measurements at 375 and 400 nm are not reliable due to second-order effects and the low signal levels. Therefore, measurements at 260, 280, 300, 325, and 350 nm were chosen for the particle sizing. Moreover, an appreciable size-sensitivity exists for the deconvolution in the particle size domain of interest at those wavelengths. Thus, results for the above-mentioned wavelengths are used as input parameters for the statistical processing of results which will be shown shortly. It should also be mentioned that for all presented cases the number of samples was 500. Finally, trial values for the minimization procedure for a mean diameter and its variance were in the vicinity of 22.5 and 5 nm, respectively.

Figure V- 8 shows final results in a $\langle D \rangle - \sigma$ plane for reference wavelengths of 350 nm (plot A) and 260 nm (plot B). The distribution of solutions with respect to χ_R^2 -residuals for both cases is shown in Figure V- 9. Corresponding scatter plot for χ_T^2 -residuals is depicted in Figure V- 10.

A)



B)

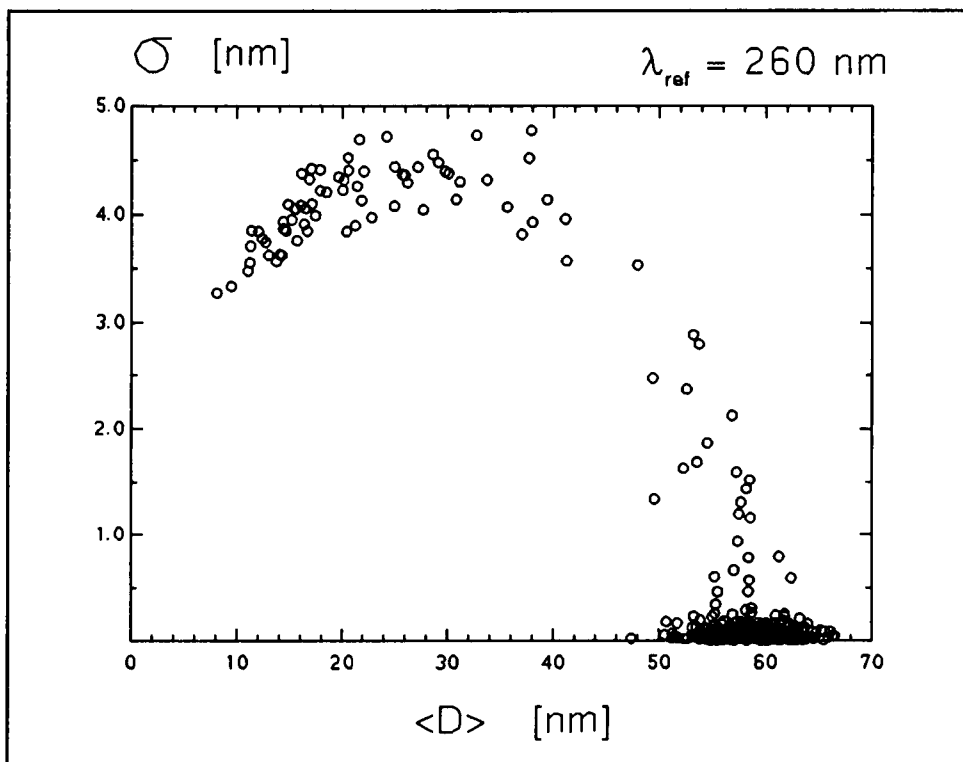
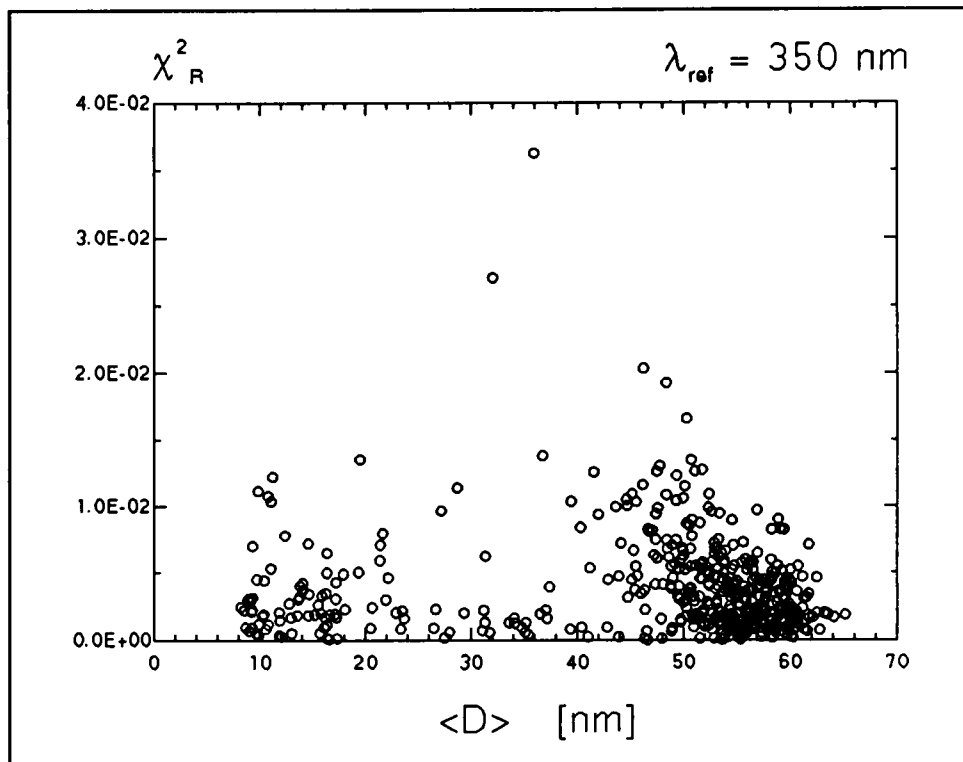


Figure V- 8: Scatter plot of the results.

A)



B)

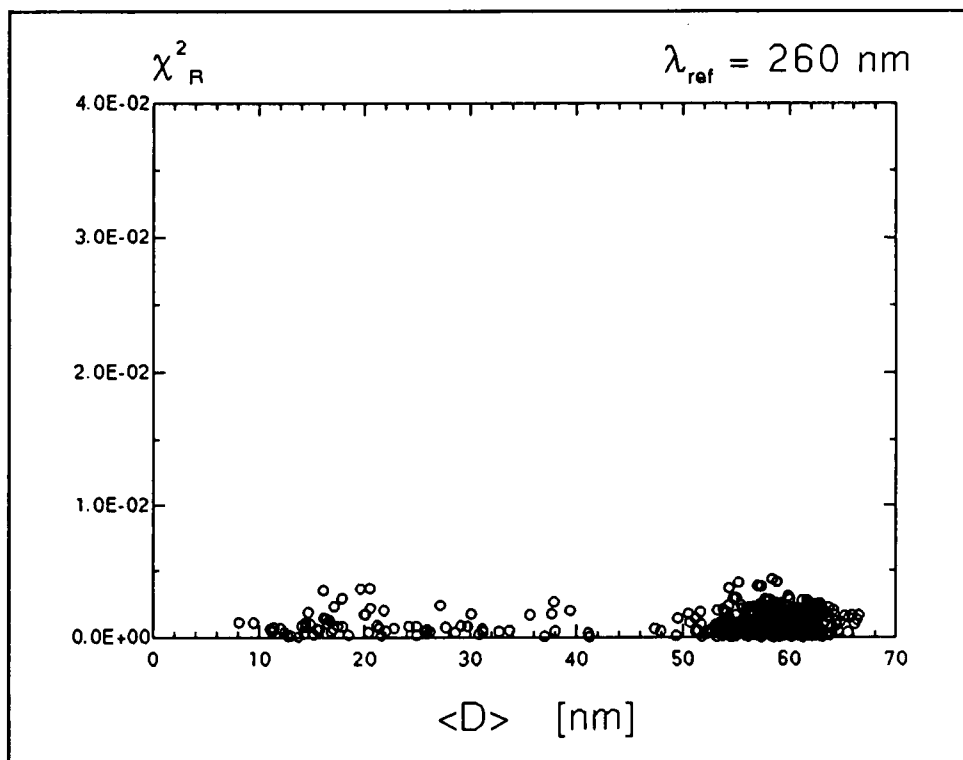
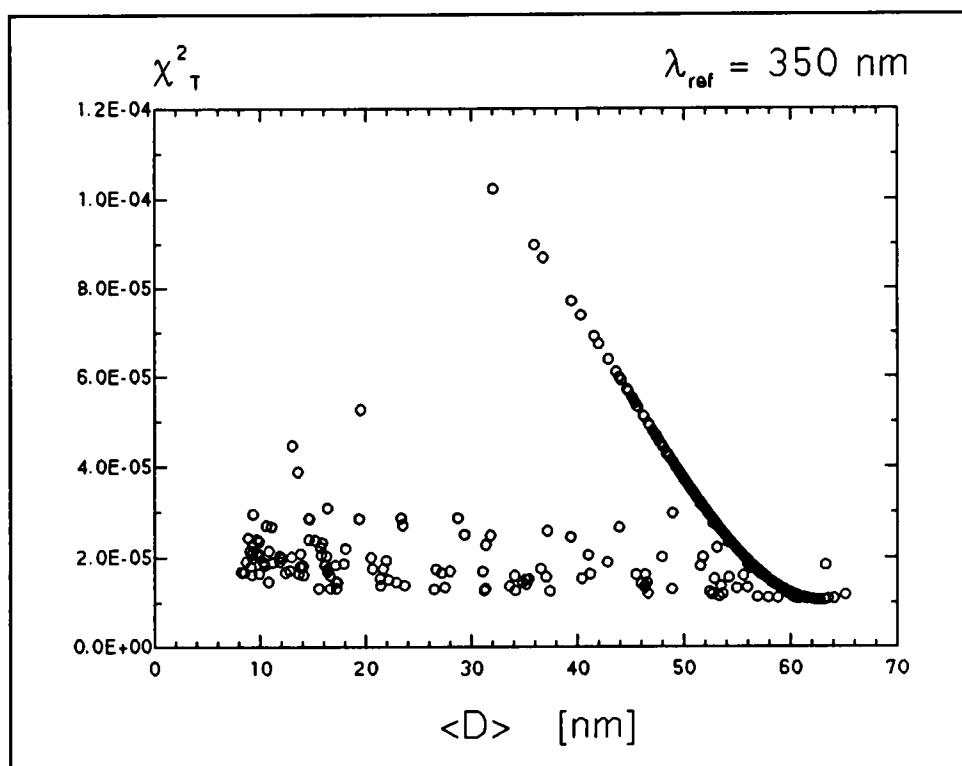


Figure V- 9: The $D - \chi^2_R$ distribution for two reference wavelengths.

A)



B)

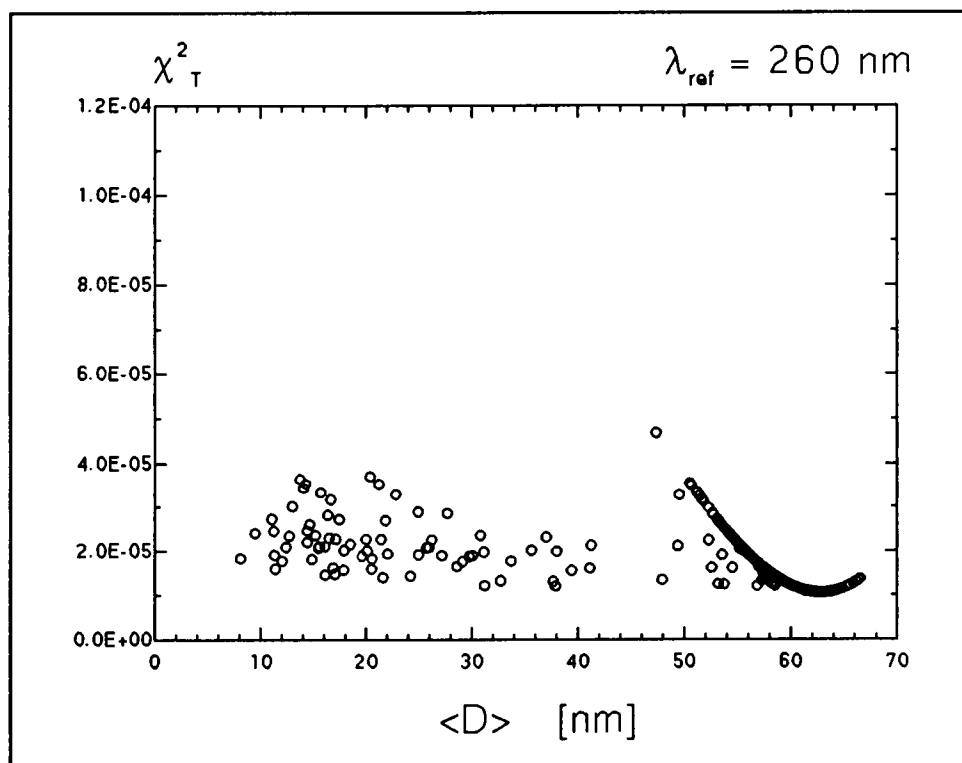


Figure V- 10: The $D - \chi^2_T$ distribution for two reference wavelengths.

Plots A and B in Figure V- 9 show clearly that the minimization procedure does not produce a unique answer: the χ_R^2 -residual of the same magnitude results in a broad range of solutions for the mean and the variance of the size-distribution function. These plots also demonstrate the importance of choice for the reference wavelength: the residual χ_R^2 is about one order of magnitude lower for $\lambda_{ref} = 260nm$ than for $\lambda_{ref} = 350nm$. More importantly, plot B of Figure V- 8 shows a perceptibly smaller frequency of solutions with small mean diameter and large variance. Similar conclusions follow from plots shown in Figure V- 10. The accumulation of solutions in the range between $\langle D \rangle = 55 nm$ and $\langle D \rangle = 60 nm$ is obvious in Figure V-8, but the range of solutions is quite broad. Of course, such scattering in results could be expected, since this is a diameter region for which the sensitivity to size becomes marginal for this choice of wavelengths. However, plots shown in Figure V- 10 are particularly intriguing, since they show three distinct classes of solutions. One set of solutions forms a curve showing a distinct minima, as expected from the program described in Chapter IV, while the rest of the solutions is distributed without a particular regular pattern. However, comparing the results of Figures V-8 and V-10, one finds a second set of solutions which exhibit appreciable frequency for mean diameters in the vicinity of 5 nm and variances of approximately 4 nm. The third group of solutions is comprised of solutions with relatively large diameters (larger than 30 nm) and very low χ_T^2 -residual. This group of solutions is especially intriguing, since solutions with small mean diameters (less than 30 nm) could be expected from the analysis discussed in Chapter IV.

For such large diameters, variance is generally small, as can be seen on plots in Figure V- 8. However that figure also shows that there is a number of solutions with a variance σ larger than 1 nm with large mean diameters. The ratio $\sigma / \langle D \rangle$ is however, still small for all σ due to a large mean diameter. This is important, since

it allows one to correlate this peculiar behavior to the properties of the log-normal particle-size distribution function. For small $\sigma / \langle D \rangle$, the form of the argument in the exponential of the PSDF¹³ is quadratic in quantity

$$\ln \left(\frac{D}{\langle D \rangle} \right) + \ln \left[1 + \left(\frac{\sigma}{\langle D \rangle} \right)^2 \right] \approx \ln D + 2 \ln \sigma - 3 \ln \langle D \rangle. \quad (\text{V} - 6)$$

Therefore, it was of interest to display the distribution of χ_R^2 as a function of $\ln \langle D \rangle / \ln \sigma$, which is shown by plots A and B in Figure¹⁴ V- 11.

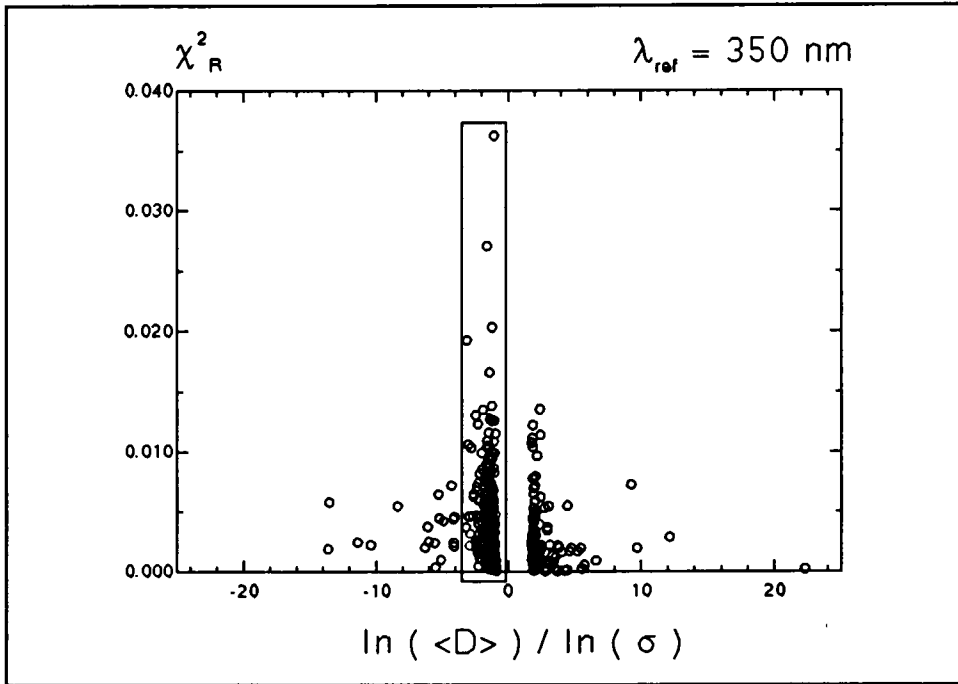
These plots suggest that the minimization routine was not capable of distinguishing between the two sets of solutions due to the integration over a small range of diameters. However, most of the solutions fall into the boxed area shown in plot A, or in the area with a negative $\ln(\langle D \rangle) / \ln(\sigma)$ in plot B of Figure V- 11. Therefore, such solutions have been selected, and plots corresponding to Figures V- 8 to V- 10 of those selected solutions are shown in Figures V- 12, V- 13, and V- 14.

Plots in Figure V- 12 show that this restriction selects solutions in a considerably smaller range of $\langle D \rangle$ and σ . Figures V- 13 and V- 14 again show that the numerical stability of the minimization procedure is better for $\lambda_{ref} = 260 \text{ nm}$. Moreover, Figure V- 14 shows that only solutions which form the expected type of distribution in χ_T^2 -residual are selected. So, for small variances, the minimization process is complicated by the requirement for integration over small ranges of diameters where the form of the log-normal distribution may lead the minimization process to ambiguous answers. This behavior should be eliminated by replacing the log-normal PSDF with a monodisperse distribution in cases when $\sigma / \langle D \rangle$ becomes sufficiently small.

¹³For more details about the log-normal PSDF, the reader is referred to Appendix A.

¹⁴Plots A and B in this figure display a majority (about 80 percent) of all solutions.

A)



B)

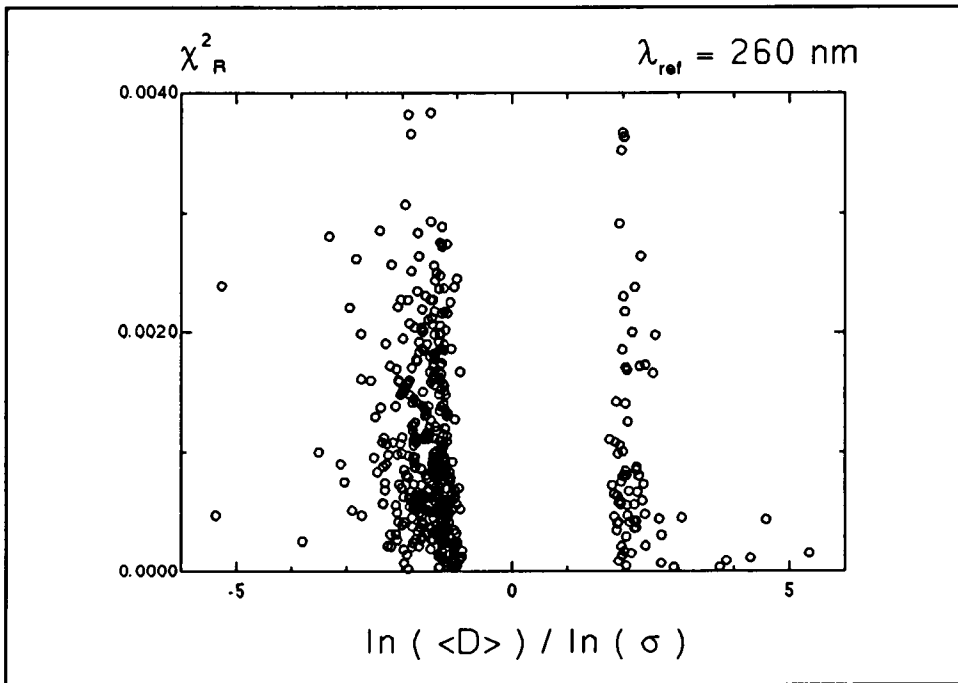
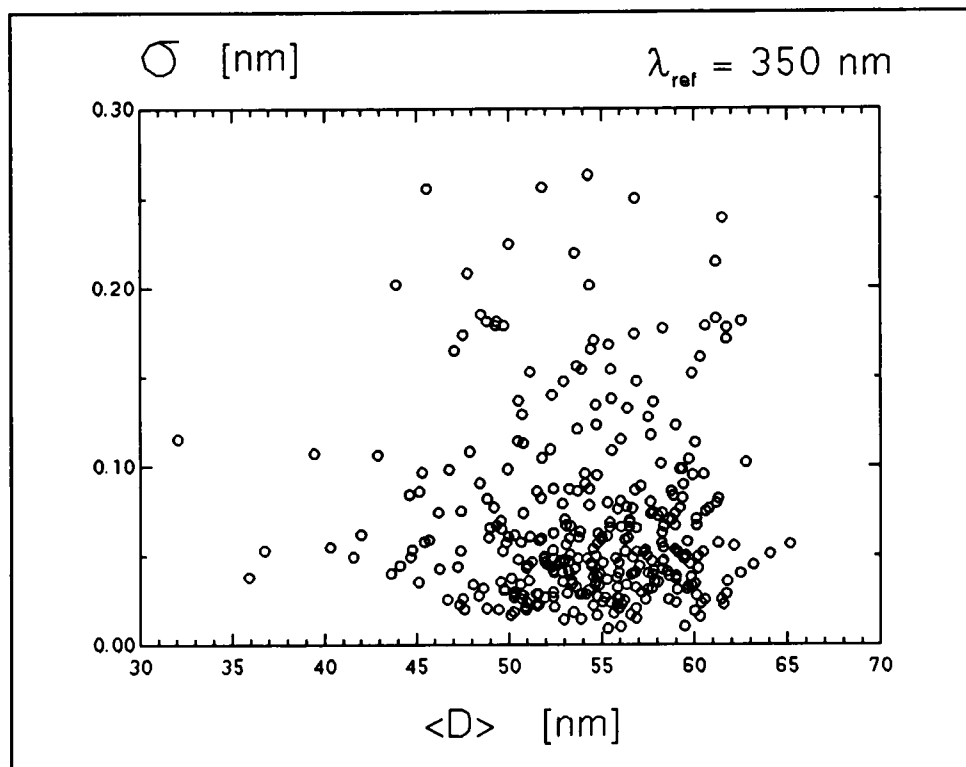


Figure V- 11: The effect of the quadratic form in the argument of the PSDF.

A)



B)

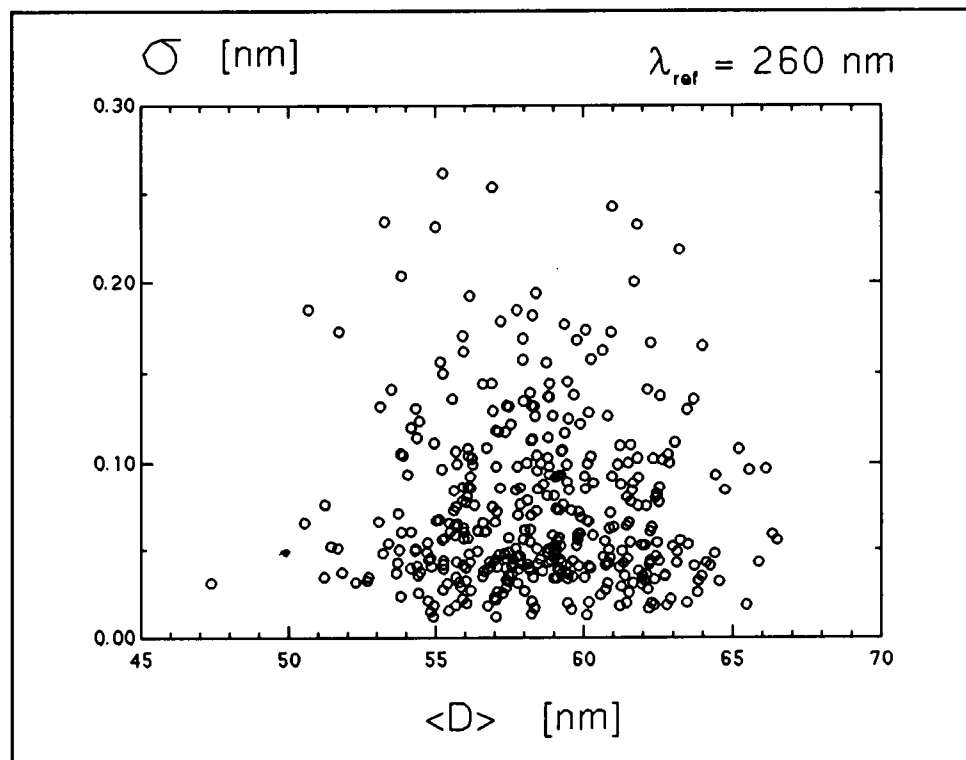
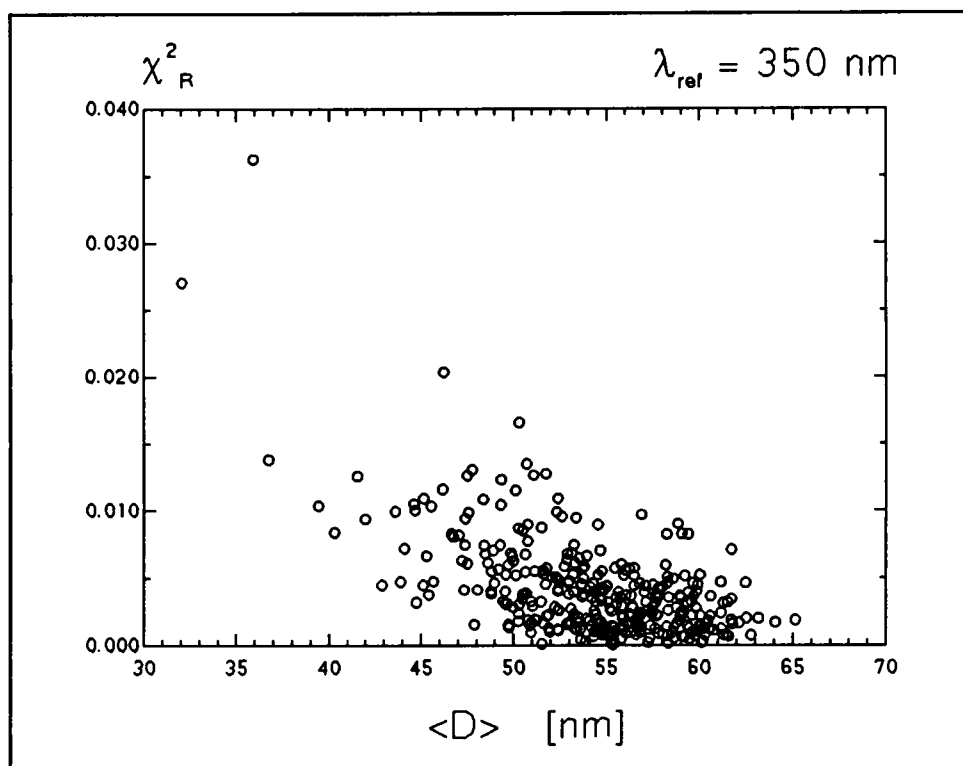


Figure V- 12: Scatter plot of the $D - \sigma$ results for selected solutions.

A)



B)

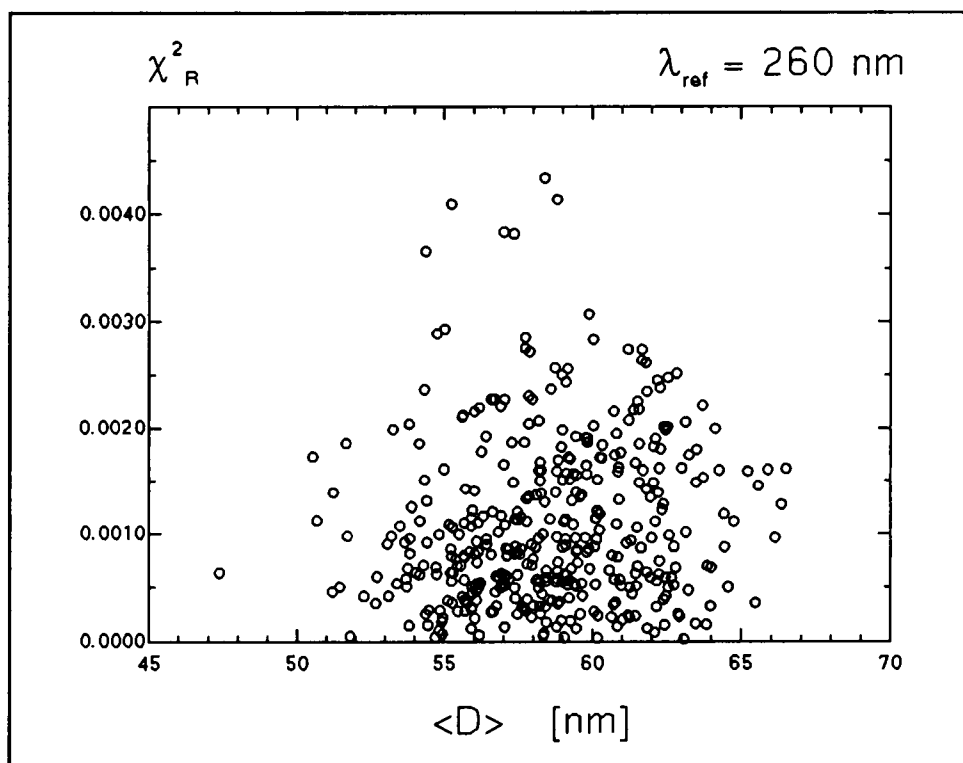
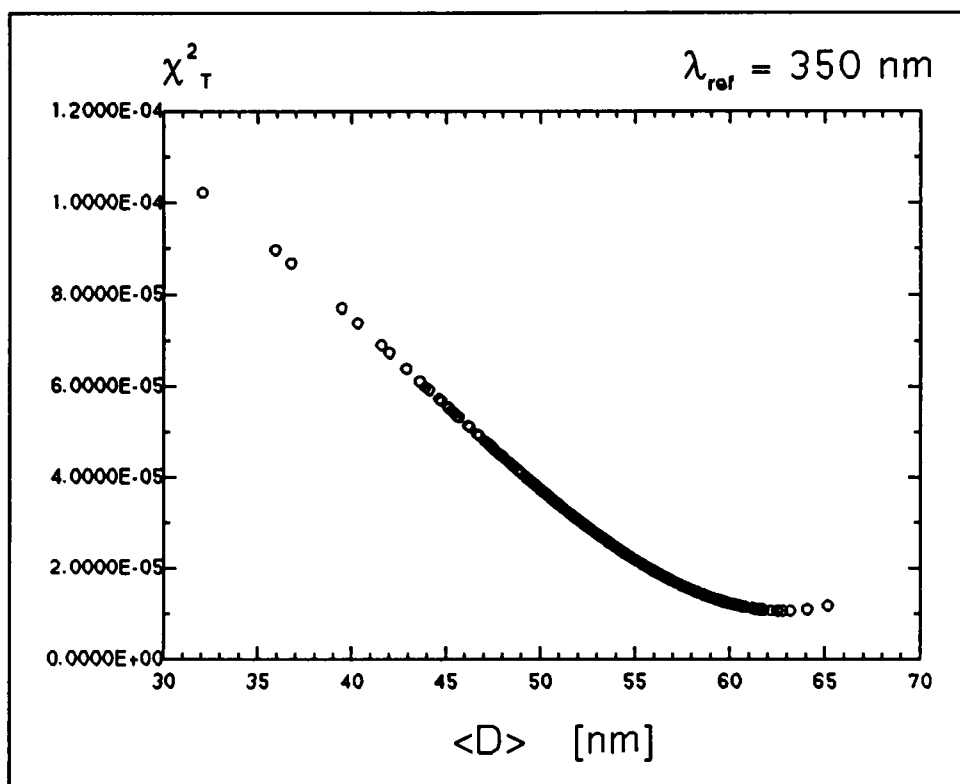


Figure V- 13: Distribution of χ^2_R - D for selected solutions.

A)



B)

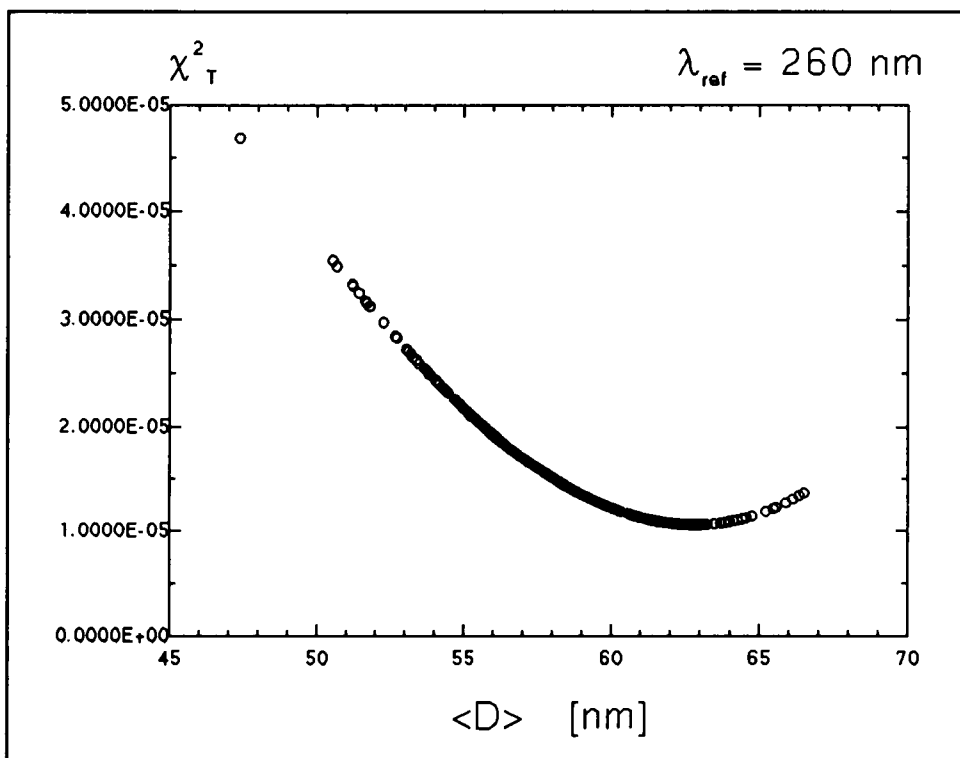


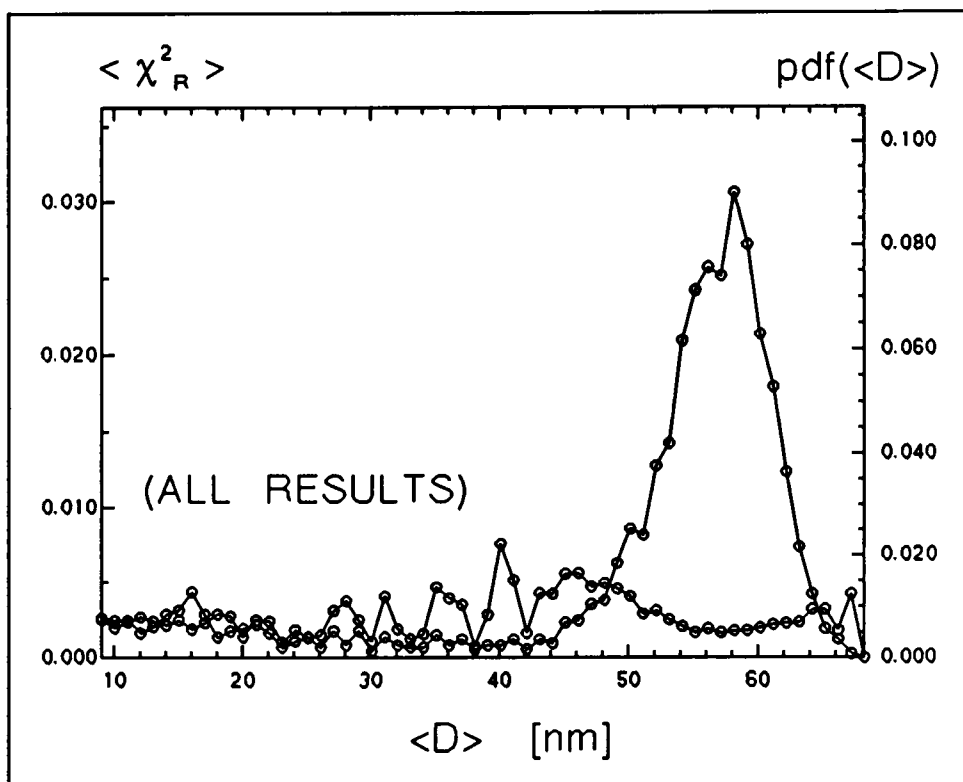
Figure V- 14: Distribution of χ^2_T - D for selected solutions.

Histograms of the solutions are shown in Figure V- 15. Plot A in that Figure shows also the average χ_R^2 -residual in the diameter range between $\langle D \rangle$ and $\langle D + \Delta D \rangle$, where $\Delta D = 1 \text{ nm}$. Plot B shows corresponding curves for solutions selected according to the value for $\ln(\langle D \rangle)/\ln \sigma$, as discussed above. Both plots are obtained by processing solutions for all reference wavelengths, *i.e.*, for 2500 solutions (5 reference wavelengths $\times$ 500 sample points for each λ_{ref}). The average $\chi_R^2(D)$ -residual were plotted in an attempt to emphasize that, on the average, the χ_R^2 -residual does exhibit some sort of minima in the portion of the largest frequency of solutions, as expected from the parameter-fitting concept based on the minimization of that residual.

Plot A in Figure V- 16 shows the computed transmission spectrum using the most probable values for the mean and the variance of the size-distribution function. Obviously, the minimization process leads to a transmission spectrum which is well within experimental errors. The solid curve in that plot is the average transmission from computations using $\lambda_{ref} = 260 \text{ nm}$, and the dashed curve is a result for $\lambda_{ref} = 350 \text{ nm}$.

Figures V- 10, V- 14, and V- 15 suggest that the experimental data of Figure V-2 contain systematic errors, as can be also noticed on plot A of Figure V- 16. The most probable mean diameter and the minima in χ_T^2 do not coincide (approximately 57 and 63 nm , respectively), and from the analysis of Chapter IV, it can be concluded that the most probable mean diameter is slightly underestimating the actual mean diameter, but not to a large extent.

A)



B)

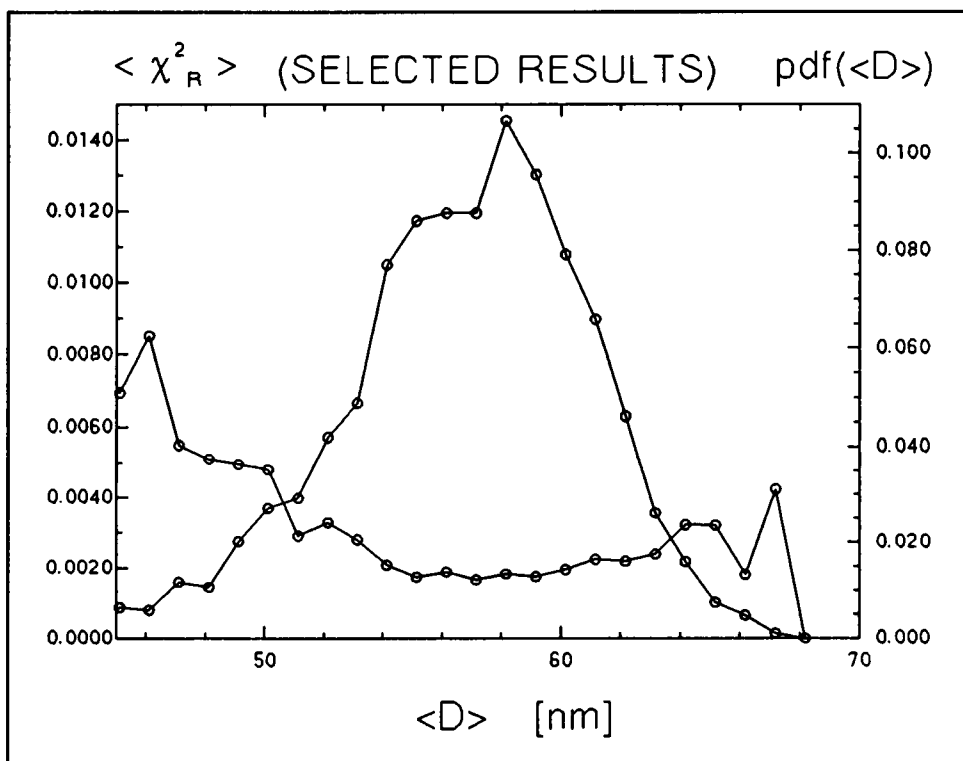
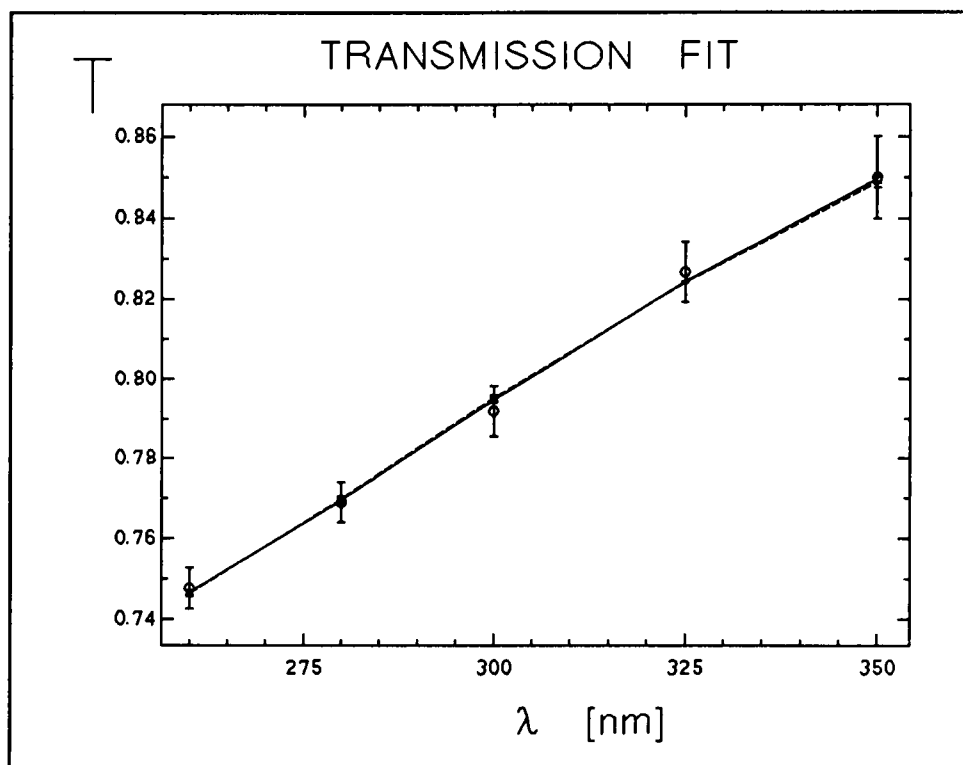


Figure V- 15: The frequency of solutions and $\langle \chi_R^2(D) \rangle$.

A)



B)

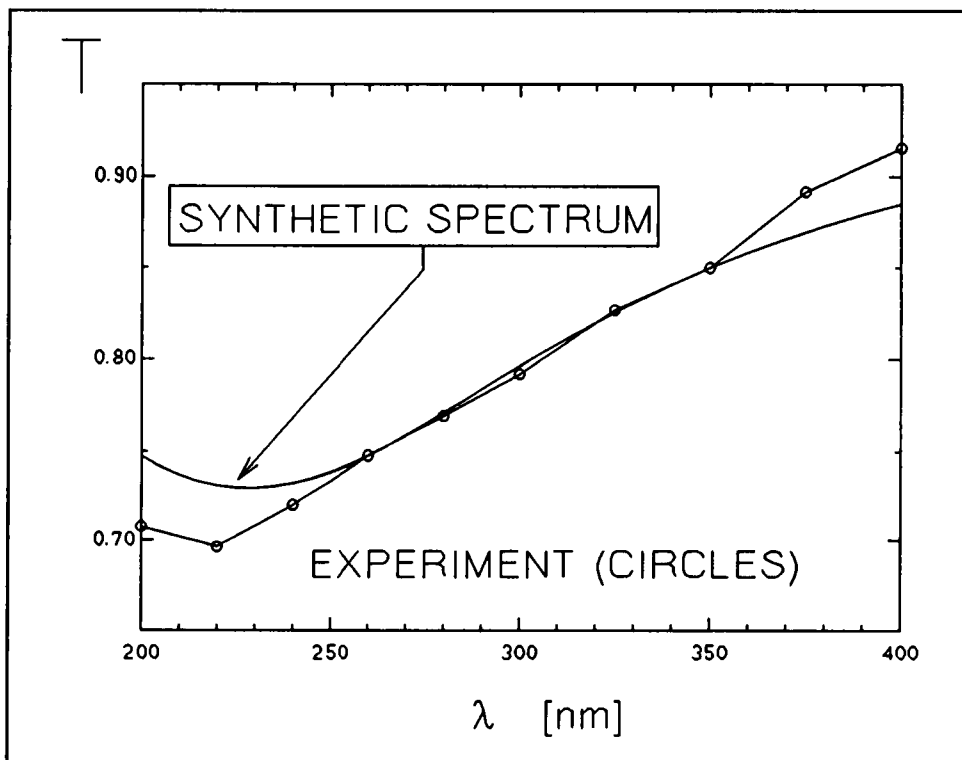


Figure V- 16: The fit to the experimental transmission spectrum.

Analysis of the presented data inversion process leads to the conclusion that the particle field in the low-throughput case is comprised of nearly monodisperse particles of diameter $58\text{ nm} \pm 4\text{ nm}$. The specification of the variance is practically meaningless, since the variance is less than 0.1 nm , as can be seen from plots in Figure V- 12.

Plot B in Figure V- 16 allows one to compare experimental results and a synthetic transmission spectrum for 58-nm soot particles. This plot demonstrates the difficulties that would be encountered by the use of experimental results at either side of the measured spectrum, as was discussed previously.

V.4 Conclusions

This chapter presented the results of transmission measurements on the particle-field generated by the soot-generator under various flow conditions, and illustrated the general behavior of the apparatus. Measurements showed a good repeatability of the results in spite of difficulties due to changes in the particle-source properties. The time scale of changes in the properties of the particle-source precluded the possibility of acquiring high-resolution transmission spectra and made the interpretation of results more difficult.

Transmission measurement results for the low-throughput case have been subjected to the data inversion procedure which was described in Chapter IV. The assumption was that the particle-field has spatially uniform properties in both its size-distribution and optical properties. Under such circumstances, it was found that particles are nearly monodisperse, with a diameter in the vicinity of 58 nm . Using this result, the NL -product is approximately $7.4 \times 10^9\text{ cm}^{-2}$. Since the nominal plume diameter is 8 mm , this would correspond to a total particle number-density of approximately $9.2 \times 10^9\text{ cm}^{-3}$ and a soot volume-fraction of $f = 9.4 \times 10^{-7}$. This allows

one to make an estimate for the mean inter-particle separation, which is important for the validation of the independent scattering assumption, of approximately 30 soot-particle diameters. If the assumption of spatial uniformity in particle sizes and optical properties is valid, the independent scattering assumption should be valid in both the core and the outer regions of plume.

The validity of assumptions regarding spatial uniformity can not be confirmed since transmission measurements are line-of-sight measurements. Therefore, it is necessary to have a point-measurement of particle sizes to confirm the results of this chapter. However, some qualitative analysis of the particle field can be made in the following way.

The main characteristic of the particle-field in the apparatus is the distinct effect of the heterogeneous reactions on the hot walls of the graphite rod. This is important for both the thermal decomposition process and the particle formation. One possible scenario follows from the acetylene decomposition process. Heterogeneous decomposition on hot walls should promote formation of aromatic species and liberation of carbon in the form of C_2 (Chapter II). Liberated carbon can either participate in the particulate formation or re-graphitize on the graphite-rod surface. The graphitization path implies an increase in H_2 concentration in a flow, and this should result in suppression of soot formation [14,4,15]. Aromatic species, on the other hand, should promote soot formation [15,14]. At the same time, it is known [4,15] that fuels with an increased content of aromatic species exhibit a tendency to produce *coke*, spherical particles, frequently referred to as cenospheres, which are much harder than soot and which have adverse impact on the operation of diesel engines. Thus, an increased production of aromatic species can result in the production of carbon particles which are quite different from soot. According to Glassman [4], very little is known about the growth of such particles. The optical properties of

such particles could be very different from that of soot due to different $C : H$ ratios and to the lack of graphitic structure in cenospheres.

As a consequence, the resultant particle-field at the observation point may be comprised of soot particles in the core and an appreciable number density of cenospheres in the outermost portions of the plume. This would certainly complicate the interpretation of the experimental transmission spectra. The application of a spatially resolving, particle-sizing technique which is not sensitive to the optical properties of the particles, such as diffusion-broadening spectroscopy, satisfies this requirement.

CHAPTER VI

PARTICLE SIZING FROM DIFFUSION-BROADENING SPECTROSCOPY MEASUREMENTS

The diffusion-broadening spectroscopy (DBS) technique is reported in the literature as an extremely efficient method for the characterization of particle sizes if particles are in the Rayleigh-regime (size parameter $x \ll 1$) [46,45,47,48]. Conventional ¹⁵ particle-sizing techniques frequently do not have sufficient sensitivity in this regime, and the DBS technique is then practically the only non-intrusive experimental technique indicated for the measurement of the size of such particles. It is particularly advantageous to use this technique for the study of soot-formation in flames [49,50,51] since the determination of particle sizes does not require knowledge of the optical constants of particles[47]. Strictly speaking, the DBS technique measures the diffusion coefficient of the particle in the host medium, and the size of particle can be inferred from that quantity[47]. The DBS technique has been used for the determination of the PSDF [45,46] in the past, but the knowledge of the optical properties for that purpose is required [49].

This chapter presents theoretical background for particle size determination using the DBS technique and describes a procedure for deconvolution of experimental results. A brief overview of the DBS method is followed by the presentation of the theoretical background of the method. Assumptions required for the development of theoretical expressions will be illustrated, when appropriate, by order-of-magnitude estimates for conditions which existed in actual measurements.

A review of the theoretical background is followed by the description of the experimental arrangement and the data-acquisition scheme which was applied in

¹⁵Term *conventional* refers to experiments based on measuring the *average intensity* of light.

the measurements. The chapter concludes with the presentation and discussion of results.

VI.1 Introduction

An assumption of conventional particle-sizing techniques is that the photon-particle scattering event is an elastic process. However, frequency shifts in the scattered light will be always present due to the inelastic scattering from the translational and rotational degrees of freedom of a particle. For this reason, the DBS method is sometimes referred to as Laser-Doppler Spectroscopy (LDS) [45]. Names such as photon correlation spectroscopy, dynamic light-scattering, or light-beating spectroscopy are also used to describe investigations of properties of light scattered in a quasi-elastic Rayleigh scattering process.

Frequency shifts of the scattered light contain information about the state of motion of scattering objects. Motion of small particles is described by the theory of Brownian motion, which may require corrections due to the directed motion of particles in a laminar flowfield. The theory of the Brownian motion, and the theory of scattering of light by a single particle establish the connection between the statistical properties of the scattered light and the diffusion coefficient of a particle. The size of the particle is then determined through the relationship between the diffusion coefficient and the diameter of the particle. For that reason, the particle diameter obtained by the DBS measurement is frequently referred to as the *hydrodynamic diameter* of the particle [47].

Light scattered from an ensemble of particles suspended in the ambient gas simultaneously contains information about both gas molecules and particulates. Therefore, it is necessary to determine if scattered light contains the information which can be unambiguously attributed to particles alone. The simplest argument

is based on the fact that particles, although much smaller than the wavelength of visible light, are much larger than gas molecules. The polarizability of particles is therefore much larger than the polarizability of gas molecules, and since the intensity of scattered light is proportional to the square of the polarizability¹⁶, particles are several orders of magnitude more efficient scatterers than gas molecules. This is not sufficient to ensure that the measured signal is dominated by particle-scattering since intensity of the scattered light is also proportional to the number-density of light-scatterers. So, a criterion for discriminating the light scattered by particles from that scattered by molecules can be written as

$$n_p \alpha_p^2 \gg n_m \alpha_m^2, \quad (\text{VI} - 1)$$

where n_p , n_m are number densities, and α_p , α_m are polarizabilities of particles and molecules, respectively.

However, this intensity-based discrimination criterion is not absolutely required for the application of the DBS technique. Being much larger than gas molecules, particles move more slowly than gas molecules. Therefore, particles contribute to fluctuations of scattered light on a much longer time-scale. Thus, besides the intensity of the scattered light, the temporal resolution can be also used to identify without ambiguity properties of light scattered by particulates. Of course, this issue can be easily resolved experimentally if the application allows one to conduct measurements with and without the presence of particles.

The intensity of scattered light from Rayleigh scatterers is small and consequently, an intense light source must be used to obtain measurable signal levels. Furthermore, the frequency content of the scattered light has a bandwidth which is much smaller than the frequency of the incident light. Accurate measurement of small frequency changes requires that the incident light is nearly monochromatic.

¹⁶ Assuming that particles are in the Rayleigh-regime.

These two requirements explain why the experimental work in this field was intensified with the advent of lasers.

A brief history of the field given by Berne and Pecora [47] shows that the theoretical foundations of the DBS technique have been known since the early decades of this century. In 1964, Cummins *et.al.* [48] showed that the optical-mixing technique can be used to resolve the spectrum of light scattered from the dilute suspensions of polystyrene spheres. The optical-mixing technique shifts the interesting portion of the spectrum to low frequencies, where the signals can be processed more accurately than by using a direct filter-technique. For example, a diffraction grating used in monochromators is a filter which is capable of resolving processes which are faster than approximately $0.1ns$. Characteristic time scales of interest in the DBS applications are in the range from $0.1\mu s$ to $1s$. Therefore, a diffraction grating can not be used in the DBS measurements. A Fabry-Perot interferometer can resolve processes whose characteristic time is in the range $10^{-6} - 10^{-10}$ seconds. Therefore, for studies of fluctuations with a characteristic time in the range from 1 microsecond to 1 second, the optical-mixing technique must be used. Although a Fabry-Perot interferometer may be applicable in some situations, the optical mixing is more versatile, more accurate, and simpler. Thus, modern DBS measurements use exclusively the optical-mixing technique [47].

A schematic representation of the basic DBS setup is shown in Figure VI-1. The angle between the propagation directions of the incident laser beam and the scattered signal is the scattering angle ϑ . A focusing lens (FL), and a collection lens and aperture (CL and AP2) define the scattering volume (V_{scat}). The polarizer and the analyzer define the state of polarization of the incident light and the scattered light, respectively. The purpose of the laser line-filter is to eliminate background radiation.

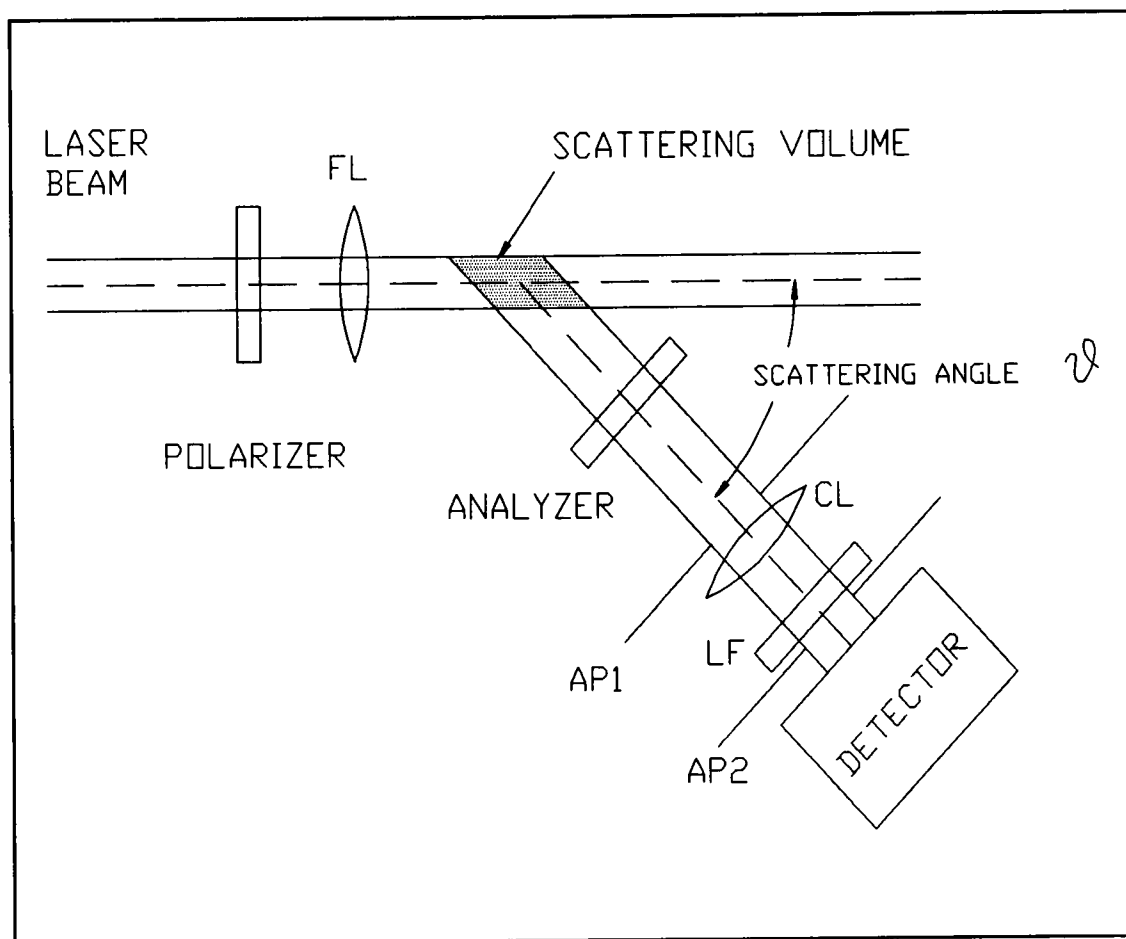


Figure VI- 1: A schematic representation of the diffusion-broadening experiment.

The detector is usually a photomultiplier tube. The photoelectric current, which is proportional to the intensity of the scattered light, is processed electronically. There are two different signal-processing techniques: analog and digital [47]. The analog signal-processing may be accomplished by either an analog autocorrelator, which measures the time-autocorrelation function, or a spectrum analyzer, which produces a power spectrum of the intensity of scattered light since the power spectrum and the autocorrelation function are Fourier-transform pairs [47]. The digital signal-processing is based on a photon-counting detection technique. One measures the number of photo-counts in a given time interval and computes the

time-correlation function from the number of these photo-counts.

Although the two methods of signal processing are theoretically equivalent, the digital autocorrelation technique has some practical advantages. Spectrum analyzers and associated electronics have a finite frequency bandwidth. The shortest bandwidth, which is usually set by an analog filter, sets also the limitation on the frequency content of the signal. Since the frequency span of the measured signal is not known *a priori*, there is a possibility of aliasing, which can not be corrected. The digital autocorrelation technique avoids this problem by integrating over this high-frequency noise by counting the number of photons in given time intervals. The only consequence of the presence of high-frequency noise in the digital signal-processing is the reduction of the signal-to-noise ratio[47]. Therefore, the use of a digital-processing method is more appropriate if the measured signal levels are low. For high signal levels, the analog signal-processing is preferred because the pulse-pair resolution time of the photomultiplier tube becomes inadequate to resolve and count individual photons, and the photon-counting technique becomes difficult.

The experimental arrangement presented in Figure VI-1 is known as the *homodyne* method, since the optical mixing is accomplished by the mixing of the scattered light with itself. Alternatively, for the *heterodyne method*, one accomplishes the frequency down-conversion by mixing the scattered light and a portion of the incident laser-light on a photomultiplier tube. The homodyne optical mixing technique was applied in measurements reported in this chapter.

VI.2 Theory

This section presents the theoretical relations which are necessary for the determination of particle sizing from the DBS measurements. The first part of this section is devoted to a monodisperse PSDF case. Since both analog and digital

signal-processing had been attempted in the experiment, review of the theoretical background includes expressions which are applicable to both types of experimental approach. A more complete analysis of the DBS technique, including the effects of polydispersity, effects of a directed particle motion in a laminar flowfield, and effects of sample illumination by a non-uniform, gaussian-profile laser beam, will be presented in the second part of this section.

VI.2.1 General assumptions

One of the fundamental assumptions, as for the extinction measurements, is the independent-particle-scattering assumption. The transmission measurements indicated that the volume fraction of particles for all conditions is approximately 10^{-6} . This implies that the mean separation between particles is about two orders-of-magnitude larger than a particle diameter. Therefore, the independent-particle-scattering condition¹⁷ exists for the two particular flow conditions in the soot generator. Another important assumption is that the measured, scattered light reaches the surface of the detector after a single-scattering event. The criterion for the validity of this assumption, which is given by van de Hulst [7], calls for the use of the extinction measurements at $488nm$ (wavelength used in the present DBS measurements). Under all circumstances of interest, the transmission in the vicinity of that wavelength was always near or above 90 percent. Therefore, the optical density, for a beam traversing the plume field across the long diameter was always less than 0.1. The rule of thumb, recommended by van de Hulst [7], is that the optical density should be less than 0.1 in order to consider a single-scattering assumption to be valid. Hence, it can be concluded that this condition is satisfied for the two specific flow conditions investigated in the transmission and the DBS measurements.

¹⁷According to van de Hulst [7], a mean separation of about 3 diameters is sufficient to justify the validity of this assumption.

Also, it will be necessary to assume that the scattering volume contains a large number of spherical particles. It will be assumed, without further considerations, that the optical response of the system under consideration is linear. A large number of scattering centers is required for the application of the central limit theorem from probability theory, as will be discussed later. This requirement normally is easy to meet by the experimental arrangement since the scattering volume can be adjusted by a focusing lens and the collection optics. The magnitude of a particle number density indicated by transmission measurements is such that even a small scattering volume would contain a large number of particles. For example, a cylindrical volume of $40\text{ }\mu\text{m}$ in diameter and $350\text{ }\mu\text{m}$ in length would contain approximately 3000 soot-particles. Finally, it is assumed that the incident laser-light is well-represented by a monochromatic, linearly polarized, plane-wave of wavevector $\mathbf{k}_i$.

VI.2.2 Preliminary definitions

To simplify future discussion of both analog and digital signal-processing, it will be useful at this point to introduce some quantities and establish mathematical relationships between them.

The total, scattered electric field, $E_s(t)$ at the location of a detector, has frequency components

$$E_s(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{+\infty} E_s(t) \exp(i\omega t) dt. \quad (\text{VI} - 2)$$

The detector actually measures the intensity of light which is proportional to [52]

$$R_i(\omega) \equiv |E_s(\omega)|^2 = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} E_s^*(t) E_s(t + \tau) \exp\{i\omega(\tau)\} dt d\tau. \quad (\text{VI} - 3)$$

Here and in the following, the asterix denotes a complex-conjugate quantity. Therefore, the spectral content of light can be obtained from statistical analysis of the

temporal behavior of the fluctuating light. Equation VI- 3 describes an unnormalized power spectrum that would be measured with a spectrum analyzer.

An analog autocorrelator measures the photocurrent autocorrelation function

$$R_i(\tau) \equiv \frac{1}{T} \int_T E_s^*(t) E_s(t) E_s^*(t + \tau) E_s(t + \tau) dt, \quad (\text{VI} - 4)$$

where the integration time, T , is assumed to be large compared to the characteristic time-scale of the fluctuations of the light. Since Brownian motion is a Markoffian process, 0 and τ will be used instead of t and $t + \tau$. The frequency down-conversion in the homodyne arrangement is accomplished by mixing the scattered light with itself and for that reason $R_i(\tau)$ is called the *homodyne correlation function*.

Establishing the relation between the diffusion coefficient and the photocurrent will require the use of electric-field correlation function which is defined by

$$R_E(\tau) \equiv \langle E_s^*(0) E_s(\tau) \rangle = \frac{1}{T} \int_T E_s^*(0) E_s(\tau) dt. \quad (\text{VI} - 5)$$

According to Berne and Pecora [47], $R_E(\tau)$ and $R_i(\tau)$ are related by

$$R_i(\tau) = | R_E(0) |^2 + | R_E(\tau) |^2. \quad (\text{VI} - 6)$$

This important relation is valid if the scattered light is a gaussian-random variable. This is the case if particles move independently of each other, and if the scattering volume contains a large number of particles, which was one of the assumptions. The scattered field is then a sum of independent random variables, and the application of the central limit theorem [53] implies that the total scattered field is also a gaussian variable. Since $R_E(\tau)$ is the second moment, and $R_i(\tau)$ is the fourth moment of the gaussian distribution, the relation between higher moments of that distribution establishes the relationship given by Equation(VI- 6) [53]. Experimental arrangement must ensure the validity of the gaussian approximation because the simplicity of the

final expressions for the data inversion by the DBS method assumes that Equation (VI- 6) is valid.

In the digital signal-processing method, one counts the number of the photon-pulses detected by the photomultiplier in a given time interval $\Delta\tau$. If the intensity of light at the location of the detector is $I(\mathbf{r}, t)$, then the number of photons registered by the detector is

$$n(\tau) = \kappa \int_{S_{det}} d^2\mathbf{r} \int_{\tau}^{\tau+\Delta\tau} I(\mathbf{r}, t) dt, \quad (\text{VI} - 7)$$

where the proportionality constant κ is related to the quantum efficiency of the detector having a surface area S_{det} .

The correspondence between the number of photons and the intensity of light exists [52] and a digital autocorrelation function, $G(\tau)$ is defined as [47]

$$G(\tau) \equiv \langle n(0)n(\tau) \rangle. \quad (\text{VI} - 8)$$

Since sampling times are digitized and number of photons is an integer-valued quantity, the more appropriate form for a digital autocorrelation function is [47]

$$G(\tau) = \frac{1}{M} \sum_{j=1}^M n_j n_{j+k}, \quad (\text{VI} - 9)$$

where

$$\tau = k \cdot \Delta\tau, \quad (\text{VI} - 10)$$

and the total averaging time T is given by

$$T = M \cdot \Delta\tau. \quad (\text{VI} - 11)$$

VI.2.3 Elementary relations - monodisperse PSDF

The objective of this section is to establish the connection between the measured quantities (power spectrum or correlation function) and the diffusion coefficient

of particles, assuming that particulates are monodisperse spheres. The scattering vector, $\mathbf{q}$, is defined by the geometry of Figure VI- 1 on page 116 as

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s, \quad (\text{VI} - 12)$$

where $\mathbf{k}_s$ is the wavevector of the light scattered at the polar angle ϑ . Since the magnitude of the frequency shift is negligible, it follows that

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\vartheta}{2}\right), \quad (\text{VI} - 13)$$

where n is the index of refraction of the surrounding medium ($n = 1$ was assumed in the present measurements) and λ is the vacuum wavelength of the incident light.

The total electric-field that is observed at the surface of the detector is a linear superposition of scattered fields of individual particles. The electric field due to scattering by the j -th particle is

$$E_j(t) = E_s \exp[i(\mathbf{q} \cdot \mathbf{r}_j(t) - \omega_0 t)], \quad (\text{VI} - 14)$$

where E_s is the amplitude of the scattered field by a single particle, and ω_0 is the angular frequency of the incident light. The total field at the location of the detector is

$$E_s(t) = E_s \sum_{j=1}^N \exp[i(\mathbf{q} \cdot \mathbf{r}_j(t) - \omega_0 t)], \quad (\text{VI} - 15)$$

where N is the total number of particles in the scattering volume.

Substituting equation (VI- 15) into the equation (VI- 6) gives

$$R_E(\tau) = E_s E_s^* e^{-i\omega_0 \tau} \left\langle \sum_{j=1}^N \sum_{i=1}^N e^{i\mathbf{q} \cdot \Delta \mathbf{r}_i(\tau)} \right\rangle, \quad (\text{VI} - 16)$$

where

$$\Delta \mathbf{r}_i(\tau) = \mathbf{r}_i(0) - \mathbf{r}_i(\tau). \quad (\text{VI} - 17)$$

Angular brackets stand for averaging over ensemble of Brownian particles. Since particles move independently, the cross-particle terms vanish in the correlation function computation. Further simplification follows from the assumed monodispersity of

particles. Being identical, all particles contribute the same way to the total scattered field. Since the total intensity of the scattered light, I_s , is

$$I_s = N E_s^* E_s, \quad (\text{VI} - 18)$$

then

$$R_E(\tau) = \langle \exp(i\mathbf{q} \cdot \Delta\mathbf{r}(\tau)) \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(\Delta\mathbf{r}, \tau) \exp[i\mathbf{q} \cdot \Delta\mathbf{r}(\tau)] d^3\Delta\mathbf{r}(\tau), \quad (\text{VI} - 19)$$

where $P(\Delta\mathbf{r}, \tau)$ is the probability that the particle which was at $\mathbf{r}(t)$ at time t , moves to a location $\mathbf{r} + \Delta\mathbf{r}$ in a time interval τ . This probability distribution function for a Brownian particle is given by

$$P(\Delta\mathbf{r}, \tau) = (4\pi D\tau)^{-\frac{1}{2}} \exp\left\{-\left(\frac{\Delta r^2}{4D\tau}\right)\right\}, \quad (\text{VI} - 20)$$

where D is a diffusion coefficient of the particle. Therefore, the correlation function can be written as [46]

$$R_E(\tau) = I_s e^{-i\omega_0\tau} \exp(-q^2 D\tau). \quad (\text{VI} - 21)$$

This result can be substituted into Equation (VI- 6) to yield the homodyne correlation function

$$R_i(\tau) = I_s^2 [1 + \exp(-2q^2 D\tau)]. \quad (\text{VI} - 22)$$

Since the spectral density and autocorrelation function are Fourier-transform pairs, the spectral density for a monodisperse particle case is

$$R_i(\omega) = \frac{\langle n_s \rangle^2}{\pi} + \langle n \rangle^2 \delta(\omega) + \frac{\langle n \rangle^2}{\pi} \left[\frac{2q^2 D}{\omega^2 + (2q^2 D)^2} \right], \quad (\text{VI} - 23)$$

where a shot-noise term, $\langle n_s \rangle$, was added after the integration. Therefore, the power spectrum in an idealized particle-sizing application has a Lorentzian profile.

The expression for a digital correlation function which corresponds to Equation (VI- 22) is

$$G(\tau) = \langle n_{\Delta\tau} \rangle^2 [1 + \exp(-2q^2 D\tau)], \quad (\text{VI} - 24)$$

where $\langle n_{\Delta\tau} \rangle$ denotes the average number of photons per sampling interval.

Equations (VI- 22), (VI- 23), and (VI- 24) establish the connection between the experimentally measured quantity, the homodyne correlation function (power spectrum), and the diffusion coefficient of particle. The particle size can be inferred from the relation between the diffusion coefficient and the size of the particle through the Einstein relation

$$D = \mu k_B T, \quad (\text{VI} - 25)$$

where k_B is the Boltzmann's constant, T is the temperature of the medium, and μ is the mobility of the particle. The mobility is given by [50]

$$\mu = \frac{1 + A \frac{\lambda_m}{R_p} + Q \frac{\lambda_m}{R_p} \exp(-b \frac{R_p}{\lambda_m})}{6\pi\eta R_p}, \quad (\text{VI} - 26)$$

where λ_m is the mean-free path of molecules in the surrounding gas, η is the dynamic viscosity of the ambient gas, and R_p is the radius of the particle. A, Q , and b are reasonably well-known constants which determine the slip correction factor ($A = 0.86, Q = 0.29, b = 1.25$).

One of the subtle points in the derivation above concerns the interpretation of τ in the probability distribution function for the Brownian particle. The motion of the Brownian particle of mass M can be described by the Langevin equation

$$M \frac{d\mathbf{v}}{d\tau} = -\zeta \mathbf{v} + \mathbf{F}_{stoch}, \quad (\text{VI} - 27)$$

where ζ is the friction constant, $\mathbf{v}$ is the velocity of the Brownian particle and $\mathbf{F}_{stoch}$ is the stochastic force, *i.e.*, the force due to the collisions of particles with surrounding gas molecules. Being a stochastic variable, $\mathbf{F}_{stoch}$ is a quantity which has a finite correlation time of its own, which is on the order of the characteristic collision time for a molecule-particle collision event. Therefore, τ is a coarse-grained time which can not be specified with a resolution on time-scale comparable to the characteristic

collision time. This is so because the particle motion differs appreciably from the pure diffusion process if the correlations in the motion of particles over short time intervals exist. A strict analysis by Berne and Pecora [47] show that

$$\langle \Delta r^2(t) \rangle = 6Dt - \frac{6Mk_B T}{\zeta^2}. \quad (\text{VI} - 28)$$

Berne and Pecora also quote

$$\frac{6Mk_B T q^2}{\zeta^2} \ll 1 \quad (\text{VI} - 29)$$

as a criterion for using the Equation (VI- 20) in the given form. An order-of-magnitude estimate for typical conditions in the drift-tube at the observation point region can be made by assuming the temperature in the soot generator at the observation point to be¹⁸ 1050 *K* and computing the transport properties of the gas as described in Appendix B. With the viscosity estimated to be 5.1×10^{-4} *poise*, for a particle of 50 *nm* in diameter, the friction factor $\zeta = 2\pi\eta D \approx 8 \times 10^{-9}$ *gm/sec*. Assuming the particle mass density of 2 *gm/cm*³, the quantity in Equation (VI- 29) is approximately 1.2×10^{-3} for the scattering angle of 16.7 degrees and for the 90 degrees measurements, its value is about 0.029. The expression for the power spectrum given by Equation (VI- 23) contains a shot-noise term which is added empirically, while the homodyne correlation function given by Equation (VI- 22) does not include the shot-noise. Noise of this origin is referred to as a *pre-detection noise*, whereas other noise (*e.g.* noise originating in associated electronic equipment, photomultiplier dark-current) is referred to as a *post-detection noise*. Berne and Pecora [47] show that the concept of *coherence area* is important for signal-to-noise ratio (SNR) considerations in optical-mixing experiments. Equation (VI- 15) assumes that the scattered light is spatially coherent over the entire surface of the detector. In contrast to that, a lack of a spatial coherence would result in addition of signals with

¹⁸This is a typical number for the temperature at the observation point according to FLUENT computations.

random phases, and therefore, a combined signal would be random. Coherence area is a quantity which indicates the area over which the electric fields, originating from an extended source, are spatially correlated. Coherence area can be estimated by [47]

$$A_{coh} \approx \frac{\lambda^2}{\Omega}, \quad (\text{VI} - 30)$$

where Ω is the solid angle subtended by the source at the location of the detector. Berne and Pecora showed that pre-detection SNR increases linearly with the area of the photomultiplier, A_{PMT} , if $A_{PMT} < A_{coh}$, and that SNR is constant if $A_{PMT} > A_{coh}$. Therefore, large coherence areas are indicated for experimental conditions which is usually accomplished in practice by focusing of the incident laser beam to reduce Ω and consequently, increase A_{coh} .

Therefore, a digital correlation function is usually written as [47]

$$G(\tau) = \langle n \rangle^2 \left[1 + s \exp(-2q^2 D\tau) \right], \quad (\text{VI} - 31)$$

where s is a number between 0 and 1, usually between 0.1 and 0.9. The value of s is controlled by the collection optics, geometry, and sampling time $\Delta\tau$ [47] and is determined from the experimental data. Finally, the relative error due to the experiment's finite averaging-time T is given by [47]

$$\left(\frac{2\tau_c}{T} \right)^{1/2}, \quad (\text{VI} - 32)$$

where τ_c is the correlation time

$$\tau_c = \frac{1}{2Dq^2}. \quad (\text{VI} - 33)$$

VI.3 Additional effects and a polydisperse PSDF

The objective of this section is to discuss modifications which are required to account for the effects of polydispersity, directed motion of particles in a flowfield,

and the sample illumination by a non-uniform laser beam. The extension to systems involving polydisperse particles is a straightforward operation. It is common practice to use a *discrete* PSDF form by specifying a number of particles in each size group according to a chosen analytical form of a two-parameter PSDF. To account for the size-dependence of the scattering efficiency, the details of the experimental arrangement must be considered. In the present experiment, the incident laser light was linearly polarized, perpendicular to the scattering plane which is the defined by the incident laser beam, and the scattering direction. The scattered light is then also polarized perpendicular to the scattering plane, and it is necessary to scale each size group of the PSDF by multiplying it with the Mie function $i_1(\vartheta; D_j)$ [7]. Assuming that each group of particles of size D_k moves with a uniform velocity $\mathbf{v}_k$, the resulting power spectrum is given by[51]

$$R_i(\omega) = \frac{\langle n_s \rangle^2}{\pi} + \langle n \rangle^2 \delta(\omega) + \frac{\langle n \rangle^2}{\pi} \sum_j \sum_k a_j a_k \left[\frac{q^2(D_j + D_k)}{[\omega - \mathbf{q} \cdot (\mathbf{v}_j - \mathbf{v}_k)^2 + [q^2(D_j + D_k)]^2]} \right]. \quad (\text{VI} - 34)$$

Factors a_k account simultaneously for the particle number density in the k - *th* size group and for the scattering efficiency of such particles.

This expression indicates that the homodyne spectrum does not change its profile as long as particles of all sizes move with the same velocity. It should be noted that only the velocity component along the scattering vector $\mathbf{q}$ is significant. For the two flow conditions in the soot generator, extinction measurements showed that particles were sufficiently small to ensure that all particles moved with the bulk velocity of the gas in the drift-tube¹⁹.

The particle field is illuminated by a non-uniform laser beam and since the Equation (VI-16) implicitly assumes that illumination of particles in a scattering volume is uniform, a correction for this effect may be required. The intensity of

¹⁹However, for large particles of significant polydispersity, this may not be the case.

the TEM_{00} mode exhibits gaussian symmetry with respect to the beam propagation axis. Accounting for the beam profile results in a Voigt profile of the power spectrum, as shown by Penner *et al.* [51]. The waist of the gaussian beam-waist, w and the bulk-velocity of the gas define a transit time,

$$\tau_t = \frac{2w}{|\mathbf{v}|}, \quad (\text{VI} - 35)$$

and the characteristic diffusion time is

$$\tau_{diff}^{-1} = 2 |\mathbf{q}|^2 D \quad (\text{VI} - 36)$$

where D is the diffusion coefficient of the particle. For the flow conditions in the soot generator, the characteristic diffusion time is on the order of one microsecond while the transit time is on the order of 100 microseconds. Therefore, each particle executes a Brownian motion under essentially constant illumination conditions, and the correction for a gaussian beam-profile is not required. Otherwise, the exponential in the correlation function (VI-24,33) becomes [51]

$$\exp \left\{ - \left[\left(\frac{t}{\tau_t} \right)^2 + 2q^2 Dt \right] \right\}. \quad (\text{VI} - 37)$$

VI.4 Determination of particle sizes

The determination of particle sizes from the DBS measurements ultimately relies on the correlation between the diffusion coefficient and the particle size. Since the experimental data for the physical conditions existing in the drift-tube are not known, computational estimates are required. Diffusion coefficients for each size group were computed using the Lennard-Jones interaction potential parameters for argon and acetylene as given by Reid *et al.* [54] and expression (VI-28). The determination of the gas-mixture properties is presented in detail in Appendix B. For the flow conditions which existed during the measurements, the diffusion coefficient

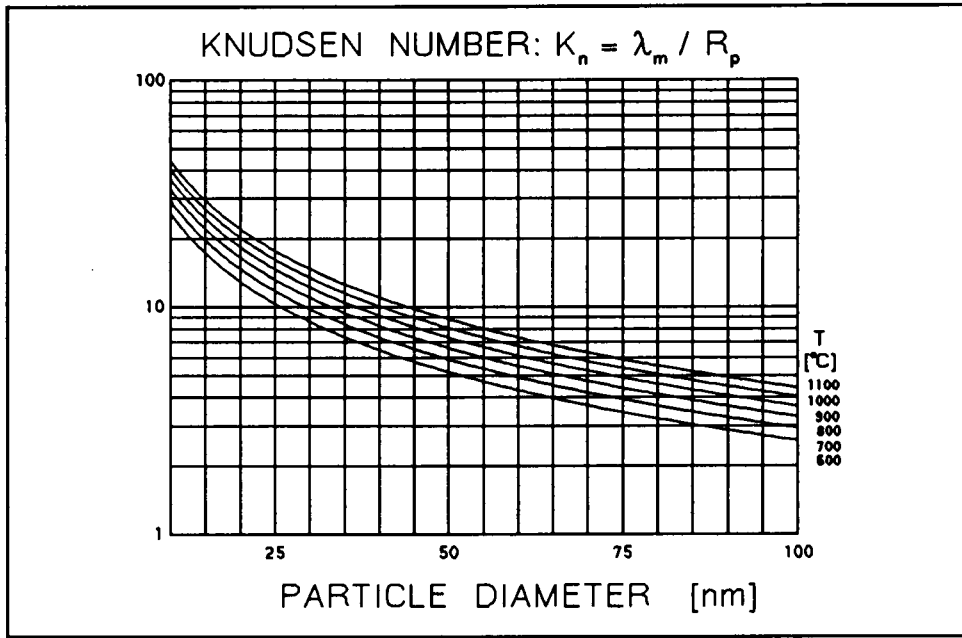


Figure VI- 2: Knudsen number for pressure of 290 *Torr*.

depends strongly on the mean-free path, λ_m of the ambient gas. Figure VI- 2 depicts the computed Knudsen number, defined by

$$K_n = \frac{\lambda_m}{R_p}, \quad (\text{VI} - 38)$$

where R_p is the radius of a particle. Figure VI- 3 shows corresponding diffusion coefficients for particles in the size range of interest in the present measurements.

Assuming a scattering angle of 16.7 degrees, which was chosen since that was one of the angles for which the measurements have been performed, a characteristic diffusion time was computed and results are shown in Figure VI- 4. Figure VI- 4 illustrates the most elementary determination of particle sizing with the DBS method. At the same time, Figure VI- 4 shows that the bandwidth of the associated electronics imposes severe limitations on the scattering angle. For example, in order to measure 50 *nm*-particles, the associated electronics must have a bandwidth of at least 1 *MHz*. This is a fairly stringent requirement, and for analog signal-processing

a choice of smaller scattering angles is indicated. Finally, Figure VI- 4 shows that the DBS method is not extremely sensitive to temperature of the ambient gas: for 50-nm particles an error in temperature of $\pm 100\text{ K}$ results in a relative error of less than 20 ± 10 percent.

Therefore, the determination of particle size assuming a monodisperse distribution is straightforward. The determination of the PSDF parameters, however, is considerably more complicated. The form of Equation(VI- 34) indicates the main difficulty in the determination of PSDF parameters from DBS measurements. Hinds and Reist [46] describe the procedure for measuring the mean and the variance of the log-normal PSDF by using measurements at two angles. Such measurements require a steady particle-flowfield, and because the soot-generator flowfield is not sufficiently steady over long periods of time, such measurements were not possible.

The only alternative approach is to use a numerical-fitting procedure similar to the one which was used for the inversion of the transmission data. This is

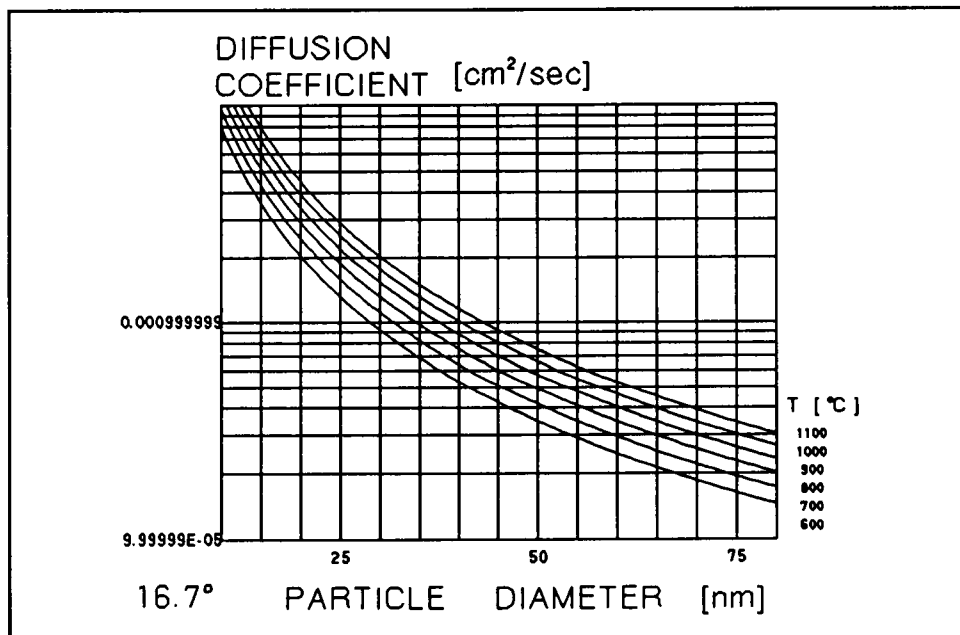


Figure VI- 3: Diffusion coefficient of soot particles[cm^2/sec].

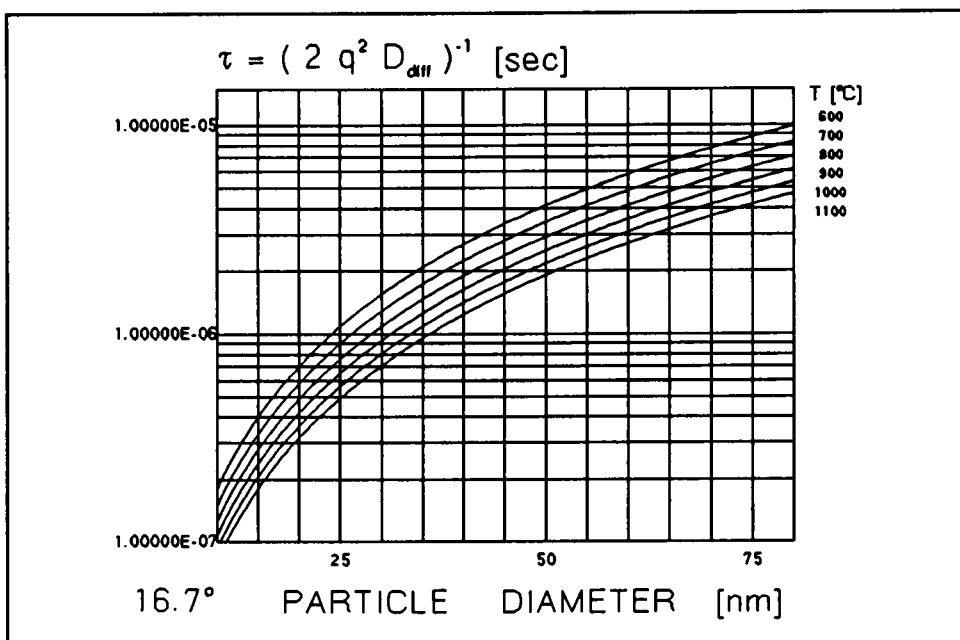


Figure VI- 4: Characteristic diffusion time.

generally a difficult task and most of the literature reports the average particle size, assuming a monodisperse distribution for particle sizes. It should be emphasized that the monodispersity-assumption leads to large errors in the case of a broad size-distribution because the scattering efficiency is size-dependent. Another reason for concern in the interpretation of the results of the DBS measurements is the numerical determination of the ambient-gas properties. The actual environment involves different species (some of them may be charged) and the determination of a diffusion coefficient is subject to question. Since the data for the experimental conditions are not precisely known, data reduction was performed as described above, and it must be stated that the uncertainty of the measurements is limited by this approximate determination of physical properties.

VI.5 Experimental

This section describes the experimental arrangement, data acquisition and processing and presents the experimental results of the DBS measurements. A homodyne-mixing technique with digital-signal processing was employed. This was accomplished without the use of a photon-correlator, which is usually used for DBS measurements by digital signal-processing [47]. Since the employed signal-processing scheme was unusual, it is discussed in detail after the description of the experimental arrangement. The section concludes with the presentation of experimental results.

VI.5.1 Experimental setup

The experimental arrangement is shown in Figure VI-5. This figure depicts only the 90-degree scattering configuration, although measurements at small scattering angles were performed as well. The excitation source was the 488 nm line of the argon-ion laser (Excell 5000-5) with a maximum power (nominal) of 1.6 W at that wavelength. The laser was equipped with an etalon which ensured single-mode, TEM_{00} operation. Single-mode operation is important to avoid oscillations between longitudinal modes which would modulate the measured autocorrelation function. The laser beam was steered with mirrors M1, M2²⁰, M3, and M4 to the polarizer (labeled POL in Figure VI-5), and focused at the particle field by the focusing lens (FL).

The laser-beam divergence at 488 nm was specified to be 0.569 mrad and the beam propagation distance was 189 cm. For the focusing lens of 7.5 cm focal length, the focal volume diameter and Rayleigh range were estimated to be 40×10^{-4} cm and 0.48 cm, respectively. The focusing lens and the mirror M4 were mounted on a translational stage which enables one to direct the laser beam to different locations

²⁰Mirrors M1 and M2 were actually used to raise the beam to the level of the windows.

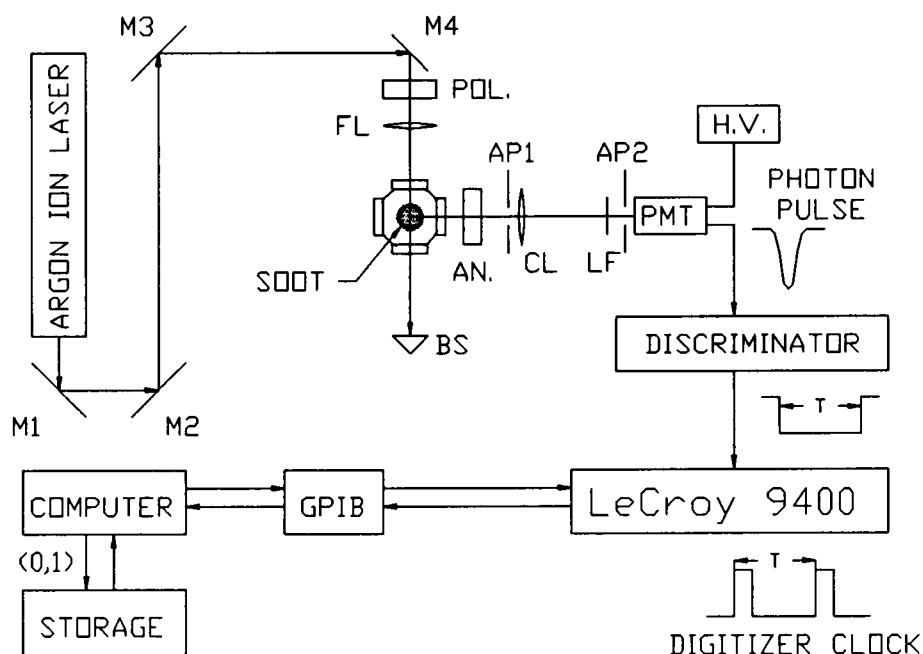


Figure VI- 5: A schematic diagram of experimental arrangement.

of the plume-field.

The collection optics consisted of the collection lens (CL) with 20 *cm* focal length, apertures AP1 (2 *mm* diameter) and AP2 (2 *mm* diameter), a 488 *nm* line-filter (LF), and a polarization analyzer (AN). The plume was imaged onto AP2 with 1:1 magnification. Thus, CL together with AP2 served to define a 2 *mm* diameter region from which scattered light was collected, while AP1 served as an *f*-stop which defines the coherence area of the light at AP2. The detector was a high-gain photon-counting photomultiplier tube (PMT). The discriminator used was the Tennenec TC455. The digital oscilloscope was the LeCroy 9400 with a minimum sampling time of 10 *ns* and a digitizing window of 5 *ns*; the LeCroy 9400 was controlled via the GPIB interface by a personal computer. The digital oscilloscope could be programmed to sequentially measure and store signals in predetermined time intervals.

The maximum number of stored data points by the LeCroy 9400 is 32000.

VI.5.2 Signal processing

The most interesting aspect of this experimental arrangement was the signal processing. The digital oscilloscope, which was capable of sampling and storing the detector signal at high sampling-rates, provided the opportunity to perform either the digital or the analog signal-processing technique. The advantage of digital signal-processing relative to analog signal-processing has been discussed in the previous sections. In the present application, digital processing was required. The main problem in applying the analog signal-processing is the requirement that all associated electronics must have a sufficiently large bandwidth. The frequency content of the scattered light depends on the scattering angle. In many applications one can choose a sufficiently small scattering-angle to adjust the frequency range of the signal to the bandwidth of the equipment. The results shown in Figure (VI- 4) indicate that scattering angles of 5 degrees or less are required to compress the frequency content below the 100 *kHz*-range. The soot-generator and drift-tube design makes measurements at such small scattering angles extremely difficult. In addition to this design problem, the signal level, particularly for the high throughput conditions, was not very strong, which suggested that the application of the digital technique would be advantageous. However, it should be mentioned that the analog signal-processing approach has been tested on a dilute suspension of latex spheres in distilled water in a 90-degree scattering angle configuration since the resulting power-spectrum for the particular size of latex spheres of 0.087 μm , was in a *kHz*-range. For a of viscosity of water at room temperature, the characteristic diffusion time was determined and an estimate for the size was obtained. The result was about 20 percent larger than the nominal particle diameter. In this case however, it was possible to achieve

signal-levels which were considerably larger than in the case of soot particles.

The design problem can be explained by describing a procedure for optical alignment that was used for the small-angle scattering measurements. A stationary scatterer would be placed in the drift-tube at the location of the intended measurement, which was either at the center of the plume, or at a point on the periphery of the plume. The drift-tube had to be rotated slightly with respect to the incident beam in order to avoid multiple reflections from the windows, which were not anti-reflection-coated because of the high temperature of the environment. However, this alignment prior to conducting the measurement proved to be of little value since the temperature increase during the measurement changed slightly the beam propagation direction and the pre-measurement alignment was lost. Window contamination was an additional complication since a detected signal was frequently due to particle deposition on the window. This was evidenced by the presence of a large signal without the plume while keeping the apparatus under the same operating temperature. Under such circumstances, measurements with scattering angles less than 10 degrees were impossible. Even measurements at larger angles (10.5 and 16.7 degrees) proved to be difficult to conduct. With this restriction on the minimum scattering angle, the application of digital signal-processing was in order.

To facilitate the discussion of the signal processing, a diagram depicting the relevant timing sequences is given in Figure VI- 6. The PMT photon-pulses were converted into pulses of fixed duration T_d by the discriminator and the digital oscilloscope measures the voltages in time intervals T_s .

The photon counting was accomplished by adjusting $T_d \approx T_s$. To illustrate the photon-counting scheme, let us first consider the ideal conditions; *i.e.*, a perfect match in timing with an infinitely fast digitizing process. For this case, the digital oscilloscope would record only two distinct voltage-values. Transferring the

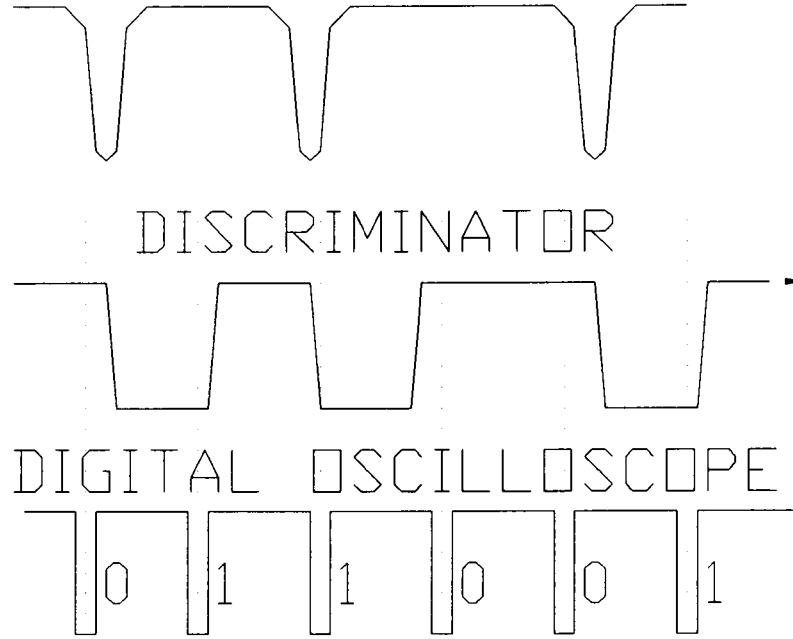


Figure VI- 6: Discriminator - digital oscilloscope timing.

recorded values to the computer, one can attribute to each high voltage a value of 1 (photon present) or 0 (no photon). That means that all photons recorded by the PMT would be recorded with the oscilloscope and counted by post-processing of the recorded signal by a computer. Post-processing of the recorded signal determines the autocorrelation function given by Equation (VI- 31) or

$$G(\tau) = \frac{1}{N_{max}} \sum_{j=1}^{N_{max}} n_j n_{j+k}, \quad (VI - 39)$$

where n_j is 1 or 0, depending on whether the photon was detected or not at the $j - th$ time interval. The upper limit, N_{max} is not necessarily equal to 32000 for the following reason. The definition of the autocorrelation function and the minimization of a relative error (Equation VI-33 on page 127) indicate the preference for long integration-times. Therefore, the upper limit of the summation, N_{max} , in the Equation (VI- 39) should be as large as possible. On the other hand, averaging of the high-frequency noise and the timing-mismatch effects, which are discussed below,

can be optimized by adding several sequential data points to represent the number of photo-counts, n_j in a sampling interval of duration

$$\Delta\tau = N_p T_s, \quad (\text{VI} - 40)$$

where N_p denotes the number of added data points. Moreover, $G(\tau)$ can be normalized to give

$$g^{(2)}(\tau) = \frac{1}{\langle n_{\Delta\tau} \rangle^2} G(\tau), \quad (\text{VI} - 41)$$

This normalized form of the correlation function is useful for the numerical-fitting procedure since

$$g^{(2)}(\tau) - 1 = s \exp(-2q^2 D\tau) \quad (\text{VI} - 42)$$

contains the information about the diffusion coefficient of the particle.

One important aspect of this data acquisition scheme is the fact that the match in timing is not perfect. The photon arrival is a random process, and this fact will be used for analysis of various aspects of the experimental arrangement. If $T_d < T_s$, then a fraction of photons

$$1 - \frac{T_d}{T_s}, \quad (\text{VI} - 43)$$

would not be counted. Since photons arrive randomly, the effect of missing some photons is the same as if a photomultiplier tube had a lower quantum efficiency. If the timing is set so that $T_s < T_d < 2T_s$, every photon would be counted twice. This condition is not desirable since the oscilloscope has a capability of storing only 32,000 data points. This results in a decrease of the integration time which reduces statistical averaging significantly. However, condition $T_s < T_d < 2T_s$ is useful for the timing adjustment procedure. With a constant intensity light source, the transition of $T_d = T_s$ condition to $T_d > T_s$ is followed by a marked increase in the number of registered photons. This facilitates achieving the $T_d \approx T_s$ condition. In measurements, $T_s =$

20 ns was used, while T_d was adjusted to 19 ns. The rise-time of the discriminator pulse was measured to be 1.5 ns.

The deviation from the perfect square profile of the discriminator pulse and the finite digitizing time (5ns) amount to measuring voltages in the range $V(0)$ to $V(1)$. Therefore, it is necessary to introduce the cut-off voltage to discriminate photons. This was accomplished by adjusting the offset voltage on the digital oscilloscope just below the noise level of the $V(0)$ state. Since the photon arrival is random, the probability of misrepresenting a signal level is estimated as

$$\left[\frac{\Delta T_d}{T_d} + \frac{T_{digitizing}}{T_s} \right] \frac{V_{offset} - V(0)}{V(1) - V(0)} P_p, \quad (VI - 44)$$

where P_p is the probability of a photon arriving during the time interval T_s (or T_d). The quantity in equation (VI- 44) is estimated to be much lower than 1 %.

The only remaining question with regard to the timing issue is what is the optimum number of counts per sampling interval? The most efficient way of using the limited storage capabilities of the digital oscilloscope suggests that on the average, one photon per two sampling intervals would be the most useful for statistical purposes. Therefore, the autocorrelation function was computed by requiring that the average number of photons per point, which consisted of N_p data points, is close to 0.5 for each individual scan²¹. A flow-chart of the data acquisition program is given in Figure VI-7. A block-diagram of the data processing program is depicted in Figure VI-8. This signal processing concept was tested by exposing the PMT to a light-emitting diode light-source driven by a signal generator at 1 MHz. Data were acquired, and processed on the computer. The autocorrelation function was computed and it is shown in Figure VI-9. The top curve, which represents the average $G(\tau)$ for 10 scans, is offset by a constant value for clarity from $G(\tau)$ for the single, 32000 data-points scan. It should be mentioned that the correlation function was

²¹The term *scan* refers to a data acquisition of 32000 sequential data points.

THE DATA ACQUISITION PROGRAM



Get the number of LeCroy 9400 data sets to be acquired, N_s .

Initialize the communication with GPIB/LeCroy.



Start acquiring and transferring N_s LeCroy data sets.

Each set of 32,000 data points is acquired, transferred via GPIB, and stored in the computer memory in the integer*1 format. After 10 data sets have been acquired and stored in the computer memory, store all acquired data in a single data file. Resume with the data acquisition until all N_s data files are acquired.



END

Figure VI- 7: Flow-chart of the data acquisition program.

DATA PROCESSING PROGRAM



Compute the correlation function for
each individual LeCroy data set of
32000 data points.



Compute the average correlation
function from all
individual data sets. Determine the
diffusion time for each individual
data set and the average of diffusion
times.



Compute the synthetic correlation
function



END

Figure VI- 8: Block-diagram of the data processing program.

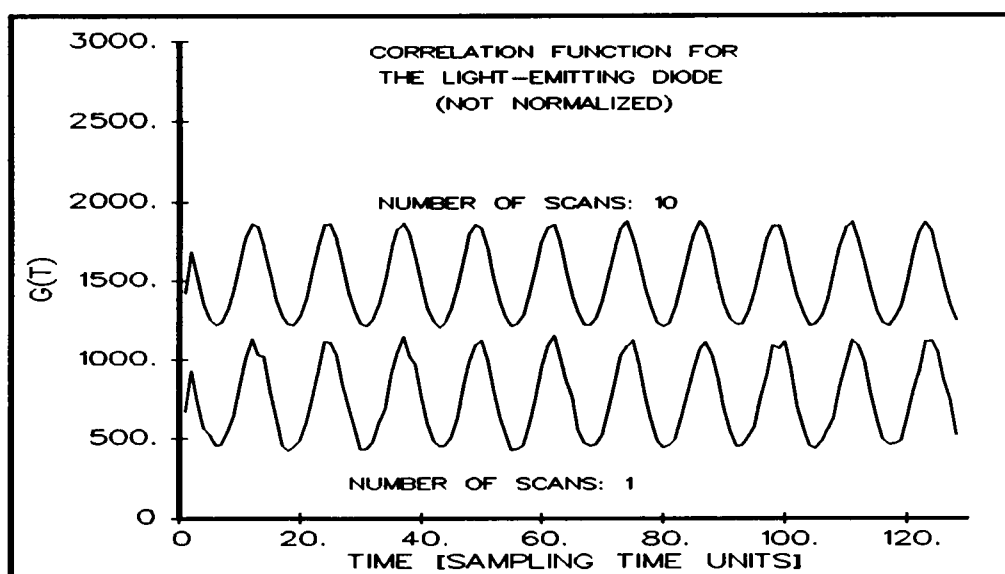


Figure VI- 9: The test of the data processing scheme. The correlation function of the light-emitting diode driven by the signal generator. This experiment confirmed that this signal processing technique works well.

computed without the addition of adjacent data points, *i.e.* $N_p = 1$, which results in a poor time-resolution. Also, $G(1)$ shows anomalous behavior, which is a result of timing and offset problems combined. This behavior diminishes if one performs the integration over several sequential data points.

The discussion of the signal-processing can be summarized as follows. The basic concept of the data-acquisition technique works well, as shown by results in Figure VI- 9. The most important limitation of this data-acquisition scheme occurs due to the storage-limitations of the LeCroy 9400 oscilloscope which sets the limitation on the integration time. If addition of a large number of data points is required, then the relative error in the specification of time increases as $\sqrt{N_p}$. In the data inversion process, a numerical fitting routine was used to determine the characteristic diffusion time for each individual scan, and a synthetic autocorrelation function was

computed using

$$\langle \tau_{diff} \rangle = \frac{1}{N_{scans}} \sum_{i=1}^{N_{scans}} (2q^2 D_{fit,i}) \quad (VI - 45)$$

and compared relative to

$$\langle g^{(2)} - 1 \rangle = \frac{1}{N_{scans}} \sum_{i=1}^{N_{scans}} g_i^{(2)} - 1 \quad (VI - 46)$$

which is determined from the experimental data. This comparison is meaningful only if the particle-source exhibits a steady operation during the acquisition of sequential scans. One indicator of the particle-source behavior in time is the average number of photons per sampling time interval, $\langle n_{\Delta\tau} \rangle$. For that reason, the averaging was performed only for data sets for which $\langle n_{\Delta\tau} \rangle$ was approximately constant.

VI.6 Results

The DBS measurements have been conducted for three different scattering angles: 90, 16.7, and 10.5 degrees. The two flow conditions studied correspond to the two flow conditions studied with the extinction measurements which are also given in Table VI-1. The pressure was kept at the fixed value of 290 Torr. The temperature at the tip of the graphite rod was kept at 1350°C. In all cases the

Table VI-1: Gas throughputs [scc/sec]		
Component	Low	High
Argon - sheath	13.31	26.62
Argon - core	1.575	3.15
Acetylene - core	1.225	2.45

sampling time of the digital oscilloscope was 20 nanoseconds. The photo-count rate during measurements was typically in the range from 1.5 to 2.5×10^6 counts per second. The count rate prior to the measurement was on the order of 70 counts per second. The standard data acquisition procedure included the acquisition of a sequence of 60 scans.

The two most significant complications in conducting the present DBS measurements were due to difficulties in obtaining results for small-angle scattering and, even more importantly, due to the temporal variations of the signal on a time-scale comparable to a single-scan data acquisition time. Figure VI- 10 shows the temporal variation of the average number of photon-counts per sampling time. As a consequence, individual autocorrelation functions change from scan-to-scan. Figure VI- 11 shows $g^{(2)} - 1$ computed for several individual scans for which the average number of photons per sampling point was approximately constant. Large noise is a direct consequence of the constraint upon the maximum integration time.

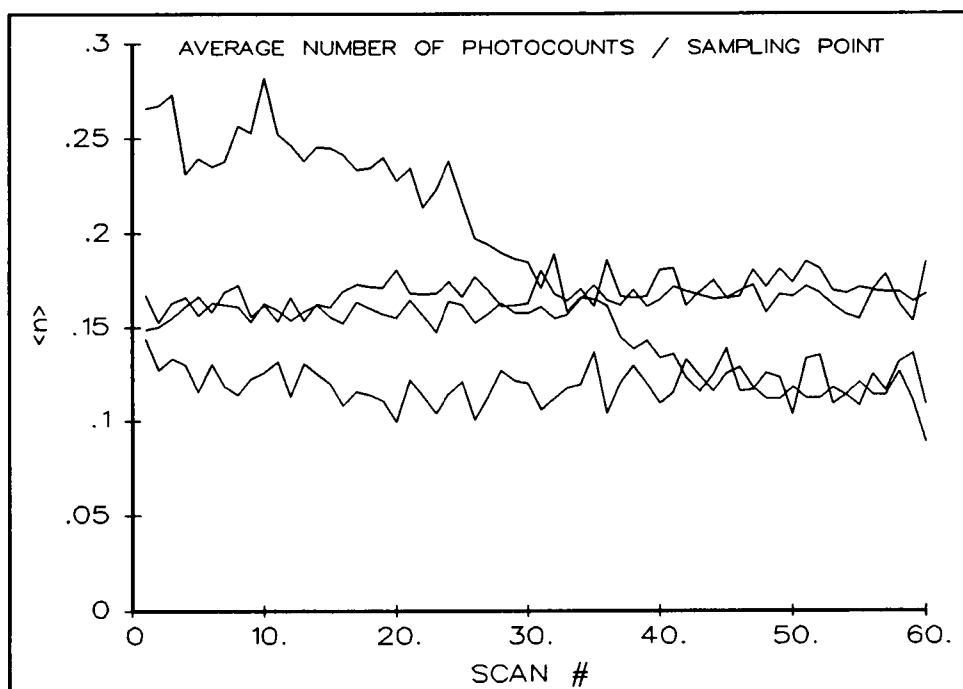


Figure VI- 10: Temporal variations of the average number of photo-counts. The figure shows the results for four sequences of 60 data-acquisition scans.

VI.6.1 Measurements at 90-degree scattering-angle

Measurements for the 90-degree scattering angle have been the least difficult to conduct. The results shown by plots in Figure VI- 12, which have been obtained with the laser-beam focused on the circumference of the soot-particle field, illustrate some of the typical features of the DBS measurements with the present data-acquisition scheme. Plot (a) shows that the average number of photons was relatively constant throughout the sequence of 60 scans, although a small drift towards larger photo-count rates is perceptible. Plot (b) shows the magnitude of the noise, which is a result of the limited integration time. Plot (c) in Figure VI- 12 depicts the average $g^{(2)}(\tau) - 1$, computed from all 60 scans illustrating the effect of the addition of data-points in the computation of the autocorrelation function, particularly for small τ . The temporal resolution is poor as evidenced by a small number of points

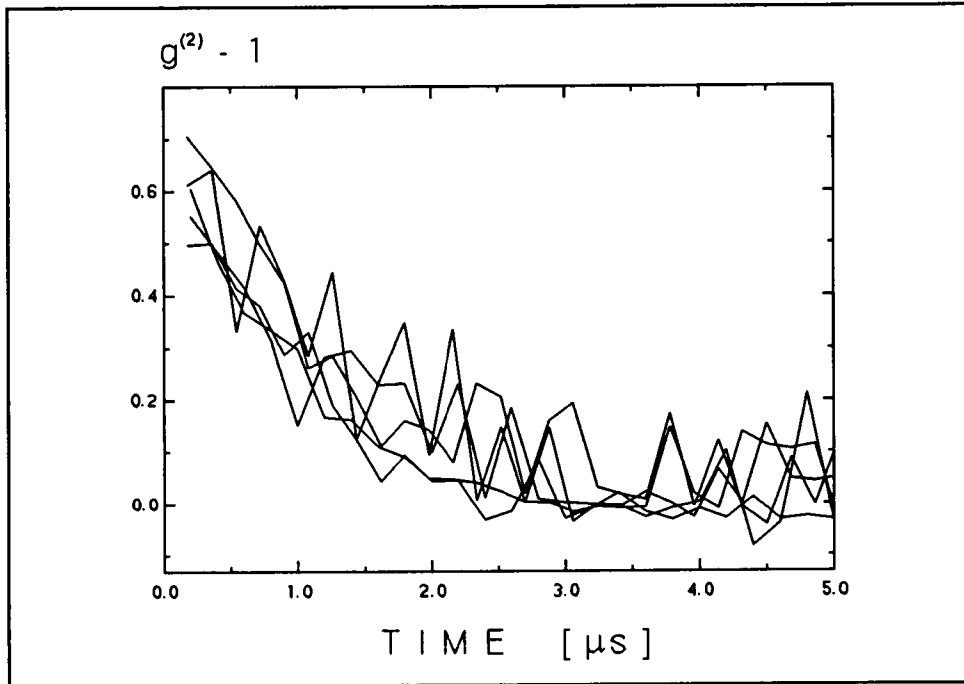
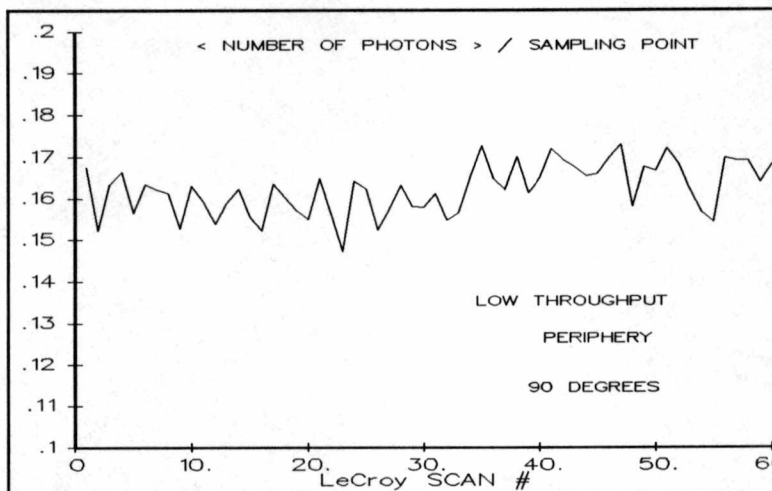


Figure VI- 11: Typical individual $g^{(2)}(\tau) - 1$. The data sets of approximately constant intensity of the scattered light were selected.

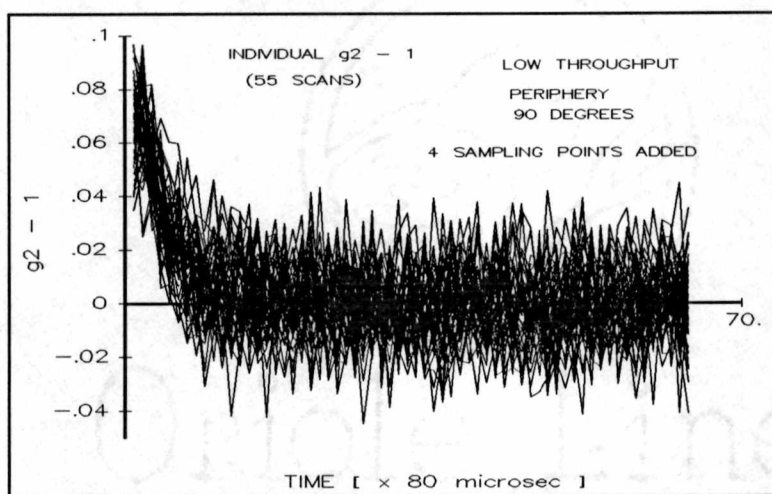
for times less than $0.25 \mu s$ (less than 13 sample-points). Large noise of individual autocorrelation functions precludes accurate determination of the characteristic diffusion time. However, the signal-level was relatively constant, and the average $g^{(2)} - 1$ can be used to estimate the upper limit on the diffusion time to be approximately of $0.1 \times 10^{-6} s$. This characteristic time corresponds to $2.37 \times 10^{-6} s$ for 16.7-degree scattering and using the plot for characteristic diffusion times shown in Figure VI-4 on page 131, a particle size of 45 nm could be inferred (assuming the temperature of 800 °C). Of course, plot VI- 12-c clearly indicates that the error is large. Results for the low-throughput, center of the plume case and for the high-throughput (laser beam focused on the circumference) were not more informative for the particle-sizing application either. The measurements in a 90-degree configuration clearly indicated the need for measurements at smaller scattering-angles.

VI.6.2 Measurements at 16.7-degree scattering-angle

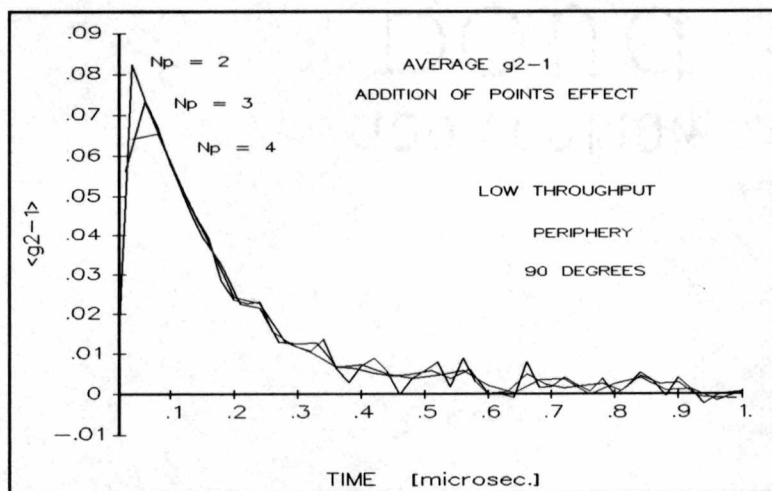
Measurements at small scattering angles were more difficult to perform due to the geometry of the drift-tube design-problem as was discussed in the previous sections. For the 16.7-degree scattering-angle, all measurements have failed except for the low-throughput case, with a laser-beam focused at the center of the plume. The same data processing routine was applied and Figure VI- 13 shows $g^{(2)}(\tau) - 1$ which were computed by integrating over 4 data-points. The resulting curves show large noise, and this resulted in a large spread of the individually-fitted diffusion times. Figure VI- 14 shows that the best-fit diffusion times varied between approximately one and 1.6 microseconds. The average characteristic diffusion time for all 60 scans was determined as 1.24 microseconds. The distribution of solutions is shown in Figure VI- 15. A synthetic $g^{(2)}(\tau) - 1$ was computed using a parameter $s = 0.804$, and the result is compared to individual scans, as shown in Figure VI- 16.



a) The average number
of photo-counts/80 ns.



b) $g^{(2)} - 1$ for each individual
scan.



c) The effect of addition of
sampling points.

Figure VI- 12: The DBS results for low-throughput, 90-degree scattering angle.

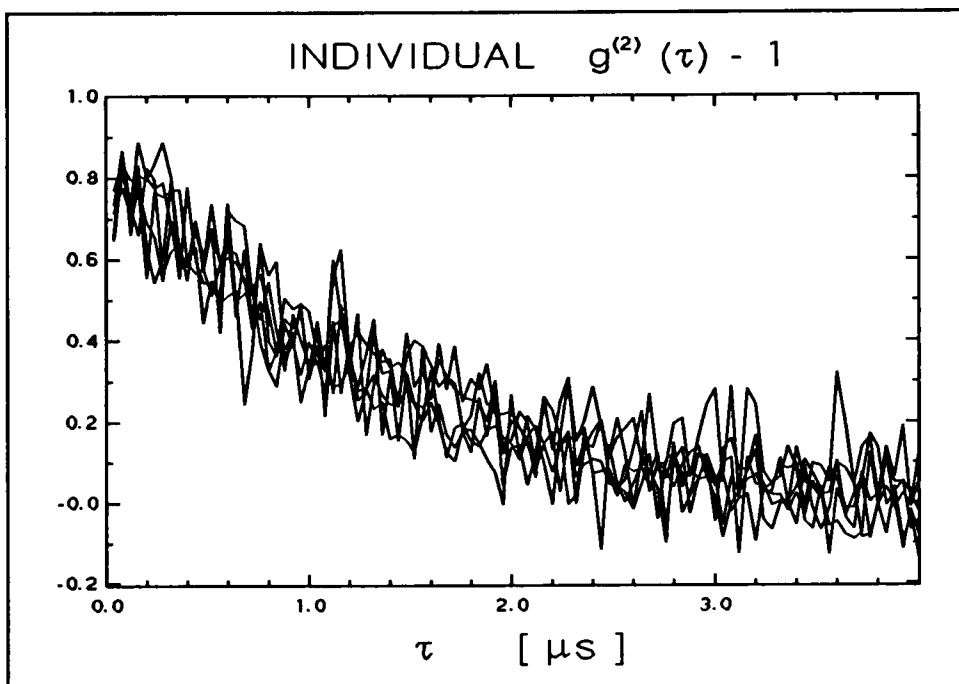


Figure VI- 13: Low throughput, 16.7 degrees scattering, center of the plume.

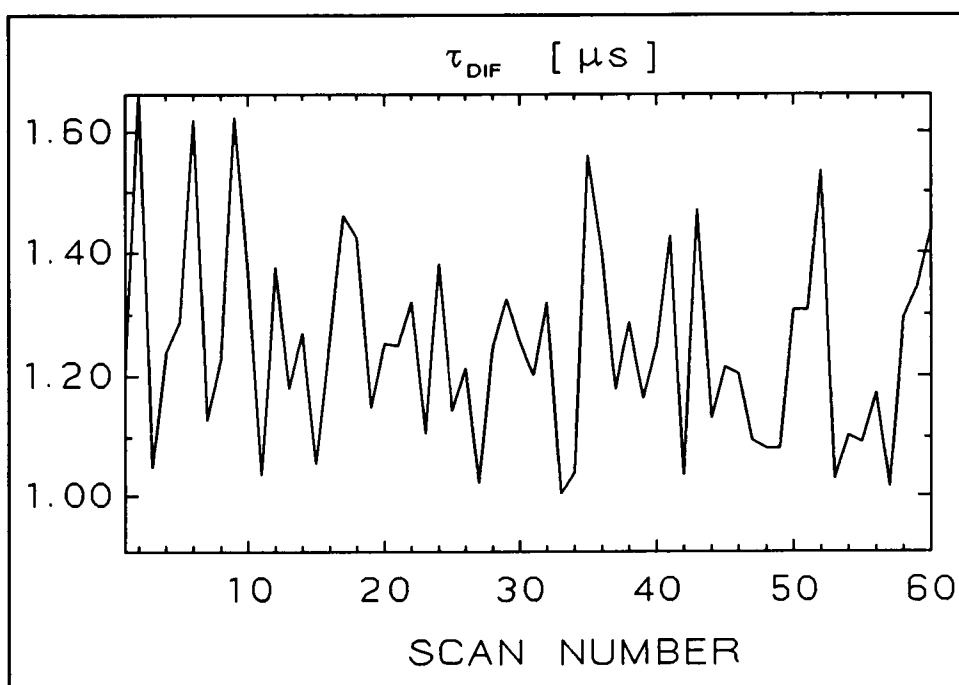


Figure VI- 14: The fit to individual scans.

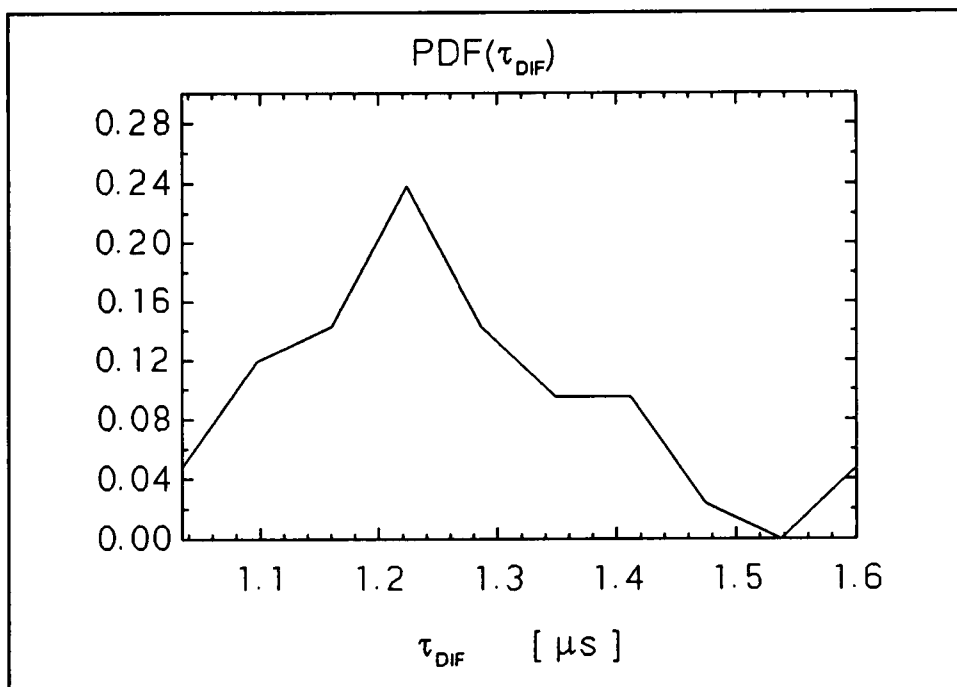


Figure VI- 15: The histogram of characteristic diffusion times for individual scans.

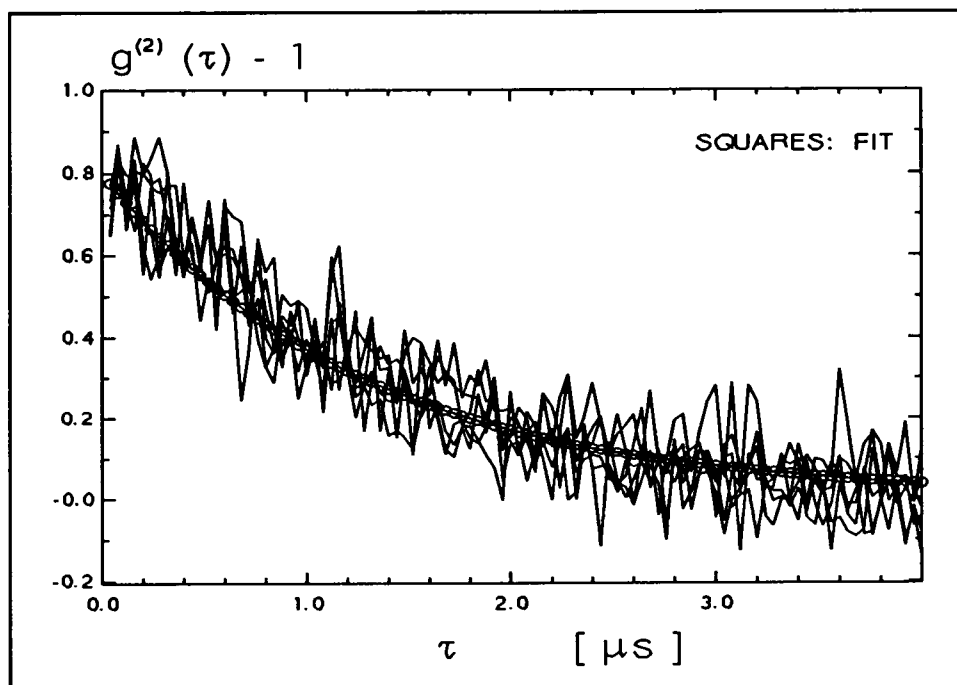


Figure VI- 16: Comparison of individual $g^{(2)}(\tau) - 1$ and the best-fit. $\tau_{dif} = 1.24 \mu s$ was used for the fit.

The same fit was compared to the average $g^{(2)}(\tau) - 1$ for a complete sequence of 60 scans. The result is shown in Figure VI- 17. Assuming the temperature of 800 °C, these results indicate that the particle size is in the vicinity of 35 to 40 nm.

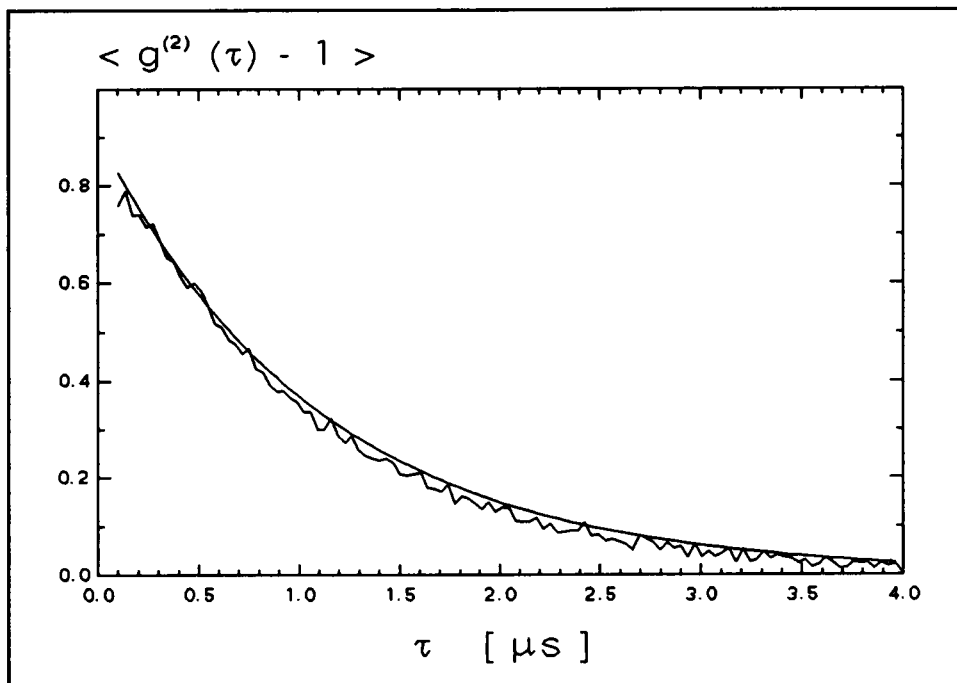


Figure VI- 17: The average $g^{(2)}(\tau) - 1$ compared to the best-fit.

VI.6.3 Measurements at 10.5-degree scattering-angle

The measurements in a 10.5-degree configuration have been extremely difficult to perform and after a series of failed attempts, marginally successful set of measurements has been performed for a high-throughput condition with a laser-beam focused on the circumference of the plume. The average number of photons per data point and the distribution of the solutions for the individual characteristic correlation times are shown in Figures VI-18 and VI-19.

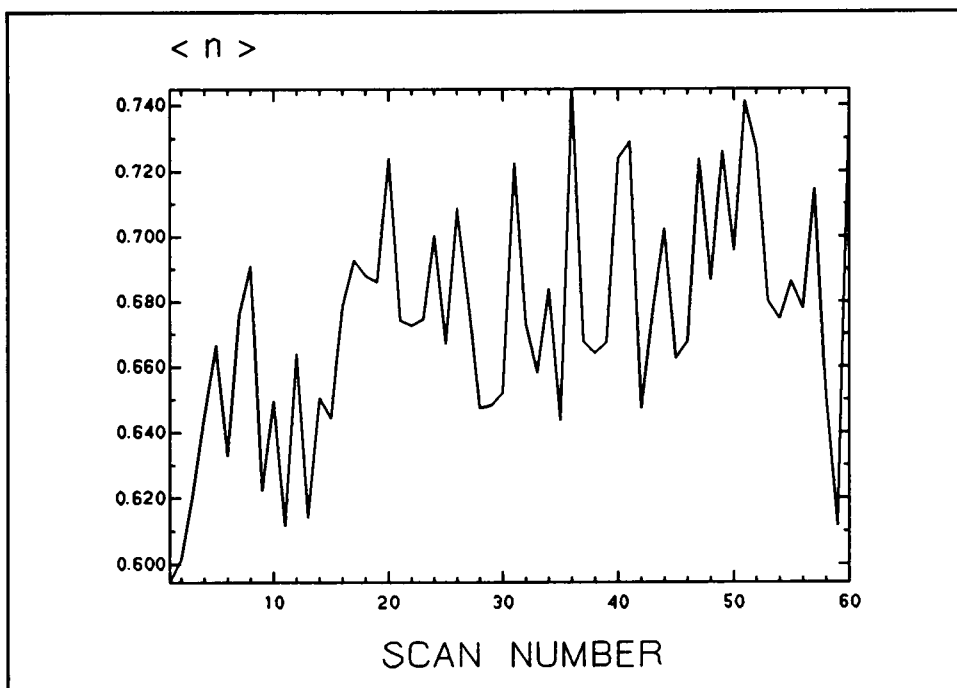


Figure VI- 18: High throughput, 10.5 degrees, circumference of the plume.

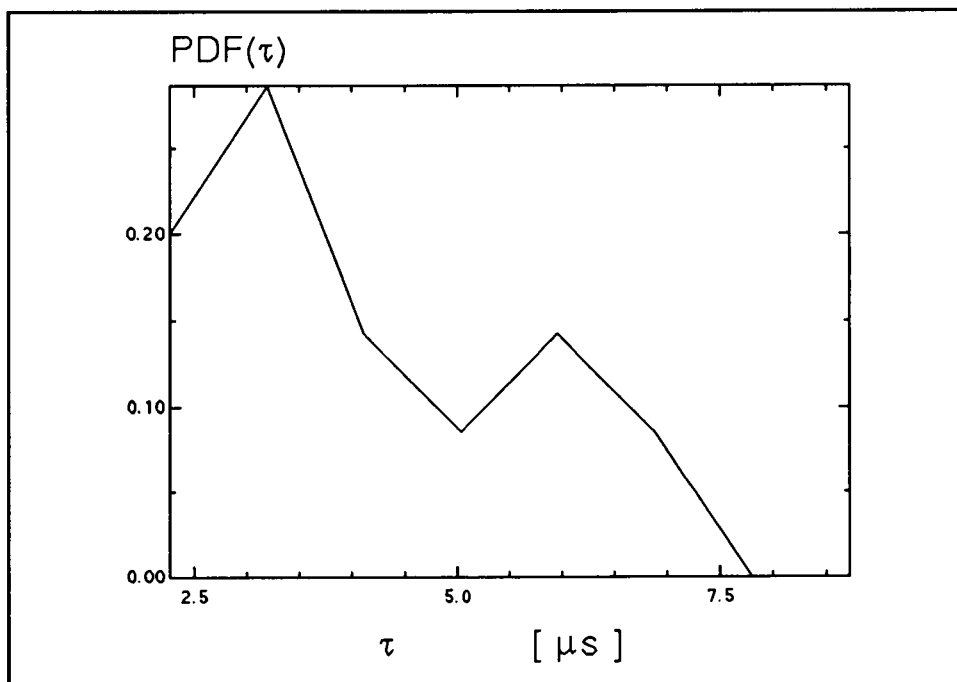


Figure VI- 19: The distribution of the correlation times giving an average of $3.42 \mu s$.

However, computed autocorrelation functions were extremely noisy, as shown in Figure VI- 20. As a result, characteristic correlation times have a broad distribution. The average of $3.42 \mu s$ was scaled to $1.37 \mu s$ at 16.7 -degrees, and this is in an acceptable agreement with the results obtained in the 16.7 -degree configuration.

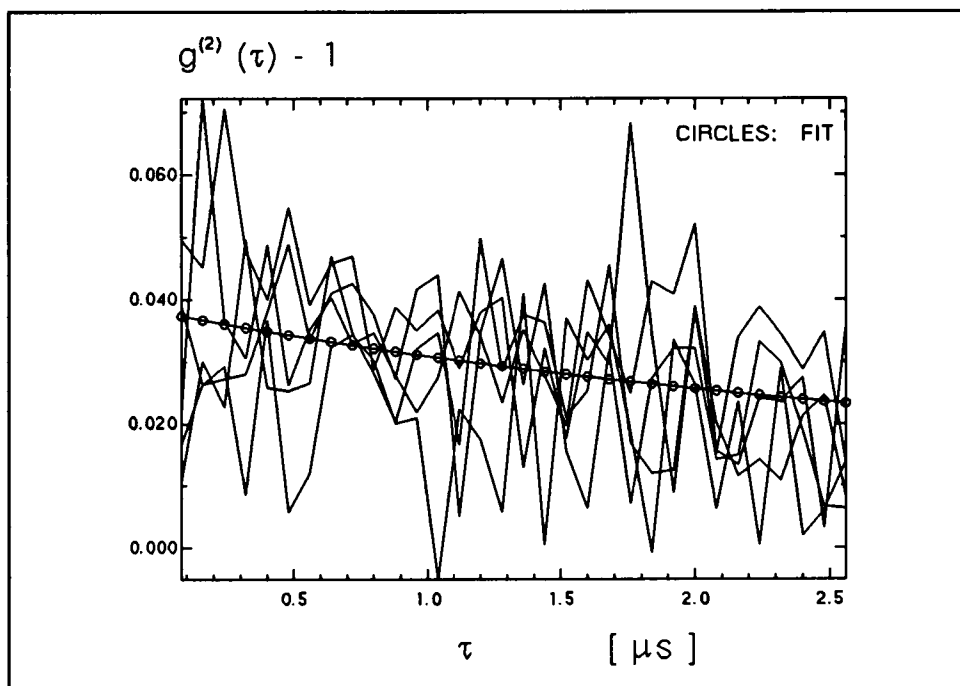


Figure VI- 20: The fit to individual scans, 10.5 degrees configuration.

Figure VI-20 shows the best-fit using $\tau=3.42 \mu s$.

VI.7 Discussion

The DBS measurements had complications related to the design of the apparatus, data-acquisition, and the determination of particle sizes. The most serious difficulty is related to the unsteady operation of the particle-source, which can be improved only by the modification in the design of the apparatus. The data-acquisition was limited severely by a limited averaging time, which resulted in noisy data, although the data-acquisition concept *per se* is functional. Finally, the determination

of particle sizes is subject to question since the determination of gas properties was achieved by computation. This approach certainly needs improvement, but the effects of the limited integration time and the resulting noise is more important.

This chapter will be concluded by stating that the DBS measurements in the present arrangement could not determine particle sizes with accuracy. The results indicate that the mean particle diameter is in the range between 30 and 35 *nm* for the low-throughput conditions, at the center of the plume. The results for the high-throughput conditions were too noisy to claim the determination of particle sizes with confidence. However, the lack of a long-exponential tail in the correlation function indicates that particle diameters are smaller or in the same size-regime as in the low-throughput case.

The DBS measurements revealed that the temporal behavior of the particle-source on a short-time scale (milliseconds) is unsteady. This is the consequence of heterogeneous reactions on the walls of the graphite-rod and low pumping speeds. These effects can be minimized by applying higher pumping speeds and by minimizing the surface-to-volume ratio in the graphite-rod design. For more accurate measurements, the drift-tube and the observation windows assembly must be designed to make low-angle scattering measurements accessible.

CHAPTER VII

GROWTH OF SOOT-PARTICLES

The importance of understanding and modeling the formation and growth of soot particles was discussed in previous chapters. For the optical particle-sizing applications the importance of the knowledge of the particle-size distribution function, which can be obtained from a growth model, was demonstrated in Chapter IV. The log-normal distribution function was a pragmatic choice since that distribution describes well either a polydisperse or a monodisperse system. Polydispersity is a result of the growth process, and theoretical justification for the particular form(s) of the PSDF must be obtained from the study of the growth process.

The modeling of the evolution of soot particles is difficult since questions with regard to the nucleation process, the role of ions in all stages of growth, and the structure of soot particles remain without answer. This chapter describes the application of fractal geometry for the characterization of soot-particle growth. In addition to this, the applicability of the scaling theory for the modeling of soot-particle growth will be investigated, assuming that neutral species dominate the growth process.

This chapter starts with a brief overview of theoretical approaches in the aerosol study of formation and growth. This is followed by a review of theoretical background to the application of scaling laws in the rate-equation approach to particle-growth phenomena. Results of this analysis is then applied to the system of rate-equations, assuming that neutral particles dominate the growth of soot-particles. Then, the basic features of the soot-particle growth are mapped onto two types of random, fractal-growth models. This chapter concludes with a discussion of the presented numerical results.

VII.1 Background theory

The modeling of soot-particle growth is particularly complex, but that does not imply that the modeling of the evolution of a much simpler aerosol system is an easy task. The nucleation stage of growth, which may be homogeneous or heterogeneous, involves a relatively large number of particles, and accounting for the interactions between constituents is one of the major issues in the theory. Once formed, particles continue to grow by condensation of molecular species and the coagulation or aggregation of larger particles into large aggregates. The difficulties in modeling of these stages in the aerosol evolution are related to the size of particles in the course of growth. Initially, the particle size is small compared to the mean-free path, λ_m , of the inert, carrier-gas molecules. Therefore, a particle behaves essentially as a large molecule. In the final stages of growth, particle size is typically comparable, or much larger than λ_m and its motion is well-described by the theory of Brownian motion. The Knudsen number, which is defined as

$$K_n = \frac{\lambda_m}{R_p}, \quad (\text{VII} - 1)$$

where R_p is the radius of the particle, indicates if the particle is in the free-molecular regime ($K_n \gg 1$) or continuum regime ($K_n \ll 1$). A transition-regime, which is characterized by Knudsen numbers in the range from 0.1 to 10, is the most difficult for a theoretic treatment.

Brock [55] classifies all theories dealing with the evolution of aerosol particles into three general categories: macroscopic, mesoscopic, and microscopic. The starting point in macroscopic theories are the conservation laws for mass and energy. One of the difficulties in such an approach is that the use of various coefficients is required, and in most cases the determination of these coefficients is phenomenological. One example of macroscopic theory is the model for droplet growth by condensation developed by Kang [56].

Kang studied thermal and mass-transfer effects on the growth of a droplet by condensation of molecular species from a supersaturated vapor in an inert-gas environment. Kang's model is based on conservation laws for mass and energy. Mass-balance and energy-balance can be determined in the free-molecular limit and in the continuum regime, and the main difficulty arises if the droplet size is in the transition regime. To surmount this difficulty, Kang introduces, as a mathematical construct, a sphere whose center coincides with the center of a growing, spherical droplet. The sphere, chosen to be larger than the droplet, divides the space surrounding the growing droplet into two regions. For the interior of the sphere, mass and energy transfers can be determined considering free-molecular mechanisms. It was assumed that the continuum-limit approximation holds for the space beyond the surface of that sphere. This approximation implies that the radius of a dividing sphere, R_s , must be larger by approximately one mean-free-path than the radius of the droplet, R_d . Kang also assumed that the radius of the sphere for the mass-balance equation does not necessarily coincide with the radius of the sphere for the energy-balance equation. Therefore, he introduced into the problem two, free parameters which characterize the exact location of such spheres:

$$R_s = R_d + \xi_i \lambda_m, \quad (i = m, E) \quad (\text{VII} - 2)$$

where ξ_i are free parameters which are chosen separately for the mass-balance and energy-balance equations. Typical values for ξ_i are usually in the range between 1 and 10, and the choice has a strong impact on the solution only in the transition regime [56].

The mass-balance and energy-balance equations require the use of quantities such as the sticking coefficient of the vapor molecules and the thermal accommodation factors for the vapor and inert-gas molecules. Combining the mass-balance equations and energy balance equations, while assuming constant properties of the

surrounding gas, one obtains an exact analytical expression which describes the droplet-size evolution and the temperature of the droplet. Using only the leading terms in the solution, Kang's model predicts that the particle size increases as

$$D \sim t^{\frac{1}{2}}. \quad (\text{VII} - 3)$$

A more exact version of Kang's model accounts for the changing properties of the carrier-gas conditions, but the solution must be obtained numerically. The solution becomes a function of the concentration of droplets, but in a dilute limit, the behavior does not differ significantly from the solution for the non-changing fluid conditions.

Kang's model accounts for the condensation of species from the vapor phase only, but not for the coalescence. The advantage of this type of approach is that it provides more detailed information about the particle (*i.e.* its size, temperature, and concentration effects). The disadvantage is that the values for various coefficients are not always known with accuracy, which is a characteristics of macroscopic models [55].

Mesoscopic theories can be related ultimately to the master-equation formulation. For example, a coagulation process can be described by a system of rate-equations

$$\frac{\partial n_i}{\partial t} = \frac{1}{2} \sum_{j+l=i} K(j,l)n_j n_l - n_i \sum_j K(i,j)n_j, \quad (\text{VII} - 4)$$

where n_i represents a number-density of particles comprised of i monomers²², and $K(i,j)$ represents the reaction-rate constant for the aggregation of particles of size i and j . The set of rate-equations (VII- 4), which is usually referred to as the Smoluchowski equation, can be related directly to the stochastic, master-equation formulation [57,58] by making the correspondence between the reaction-rate constants and transition probabilities between "states" i and j . The first term in the

²²The term *monomer* here denotes loosely a molecule or a smallest particle size participating in the particle growth process.

Smoluchowski equation represents the rate of formation of particles of a given size, and the second term represents the decrease in a number-density of particles due to coagulation which results in the formation of larger aggregates. The Smoluchowski equation can be extended to account for an external source of monomers or the effects of sedimentation in a gravitational-field [55]. The solution of the system of rate-equations (VII- 4) depends on the form of the kernels $K(i, j)$ and on the initial conditions. The determination of rate constants usually requires the introduction of some approximations, particularly in the transition-regime.

Microscopic theories are concerned with the nucleation stage of growth. A Monte-Carlo or molecular-dynamics approach [32] is used to extract information about interactions between molecules which form the nucleation center. Such methods require the knowledge of the form of the interaction potential between constituents.

For the evolution of soot-particles, the rate-equation formulation given by Equation (VII- 4) is of particular interest since the recent development of random, fractal-growth models allow one to obtain insight into the general features of the solution without actually obtaining the solution. Under certain circumstances, the form of the kernels $K(i, j)$ permits the application of the scaling laws for the prediction of growth of particles. The basic concepts of the application of the scaling theory to the Smoluchowski equation are discussed in the next section.

VII.2 Scaling: basic concepts

Scaling implies that a system of N particles of unit-size in a box of length L can be described by N particles of size $\langle R \rangle$ in a box of length $L \langle R \rangle$. Therefore, one is interested in the behavior of the solution to the Smoluchowski equation under the coarse-graining procedure, and the main idea is that this procedure leaves the

form of the solution to the Smoluchowski equation invariant. In other words, the solution of the Smoluchowski equation is not sensitive to the initial conditions [60,61] and some essential features of the solution can be obtained by applying the scaling theory.

The scaling analysis will require some assumptions about the system under consideration. One of the assumptions is that the total mass in the system is conserved. Also, it is assumed that, at each instant, the system can be characterized by *only one* characteristic size $s(t)$. Here, the term *size* is used to refer to the number of monomers in a particle. It can be argued [62] that the solution of the Smoluchowski equation (VII- 4) behaves as

$$n_j \sim j^\theta \phi(j/s(t)), \quad (\text{VII} - 5)$$

where $\phi(x)$ is an arbitrary function which decays rapidly for large x . This postulated form of the solution reflects the scaling-assumption through the dependence on $x = j/s$ in the “unknown” function $\phi(x)$, while the factor j^θ reflects the conservation of mass in the system. Daoud [61] showed that the application of the mass-conservation law

$$\sum j n_j(t) = \text{const.} \quad (\text{VII} - 6)$$

leads to a quite general result $\theta=-2$ for the exponent in Equation (VII- 5). It is postulated [62] that the characteristic particle size, which is defined by

$$s(t) = \frac{\sum j^2 n_j(t)}{\sum j n_j(t)} \quad (\text{VII} - 7)$$

behaves as

$$s(t) \sim t^z. \quad (\text{VII} - 8)$$

Therefore, the general form for $n_j(t)$ is given by

$$n_j(t) \sim j^{-2} \phi(j t^{-z}). \quad (\text{VII} - 9)$$

It can be seen that for j comparable to the characteristic size of the distribution,

$$n_j(t) \sim j^{-2}, \quad (\text{VII} - 10)$$

since $\phi(x \sim 1)$ is nearly constant. This result is valid for arbitrary form of kernels $K(i, j)$.

Besides the average particle size, $s(t)$, it is of interest to examine the behavior of the size-distribution variance. Leyvraz [60] showed that

$$\sum j^\rho n_j(t) \sim s(t)^{\rho-1}. \quad (\text{VII} - 11)$$

Since the variance is proportional to

$$\sum j^2 p(j, t) = \sum j^2 \frac{j n_j}{M_{total}} \sim \sum j^3 n_j, \quad (\text{VII} - 12)$$

then the variance has the same time dependence as the square of the average particle size, *i.e.*

$$\text{Var}(j) \sim s(t)^2. \quad (\text{VII} - 13)$$

This implies that the ratio of the standard deviation in size to the average size is constant in time, which is a very useful, general result of the scaling theory. This result is valid, however, only if the interactions among particles of a typical size dominate the behavior of the system. This means that the form of the “unknown” function $\phi(x)$ must be such that for both $x \ll 1$ and $x \gg 1$, $\phi(x)$ rapidly decays to zero. For the upper-limit, $x \rightarrow \infty$, this behavior is plausible, but the behavior of the solution for $\phi(x \rightarrow 0)$ must be considered. If the distribution can be described by a power-law [60]

$$\phi(x) \sim x^{\frac{w}{z}}, \quad x \ll 1, \quad (\text{VII} - 14)$$

then

$$n_j(t) \sim j^{-\tau} t^{-w}, \quad (\text{VII} - 15)$$

where exponent τ is given by

$$(2 - \tau)z = w. \quad (\text{VII} - 16)$$

In such case,

$$\sum j^\rho n_j(t) \sim t^{-w}. \quad (\text{VII} - 17)$$

Therefore, the variance is dominated either by small particles, in which case it decays as t^{-w} , or by large particles, in which case it is proportional to $s^2(t)$. The domination of the monomer-cluster (MC) addition reactions implies a strong monodispersity, while the domination of cluster-cluster (CC) reactions implies that the variance of the distribution diverges at the same rate as the characteristic size of particles.

The goal of the analysis is, of course, to determine the z -exponent on the basis of the specific form of the kernels $K(i, j)$. This will be facilitated by introducing further generalizations in the theory. Scaling theory assumes that the kernels can be characterized by only two exponents λ and ν , which are defined by requiring a homogeneity for the reaction-rate constants

$$K(aj, al) = a^\lambda K(j, l) \quad (\text{VII} - 18)$$

and postulating that

$$K(1, j) \sim j^\nu. \quad (\text{VII} - 19)$$

The validity of the postulated behavior in equations (VII- 18) and (VII- 19) can be inspected after a particular form for reaction-rate constants is determined, but for Brownian particles, the form of equations (VII- 18) and (VII- 19) is generally satisfied [60]. The homogeneous equation (VII- 18) defines the exponent λ , which is related to the scaling properties of the system, while the exponent ν reflects the importance of reactions involving monomers.

Exponent λ is related to the z -exponent, which was introduced by Equation (VII- 8). If a unique, characteristic particle size $s(t)$ exists, then the evolution of the

average particle size is dominated by interactions of particles of that size and

$$\frac{ds(t)}{dt} \sim K(s, s) \sim s^\lambda, \quad (\text{VII} - 20)$$

which follows from the definition of the λ -exponent. The time dependence of the average particle size from Equation (VII- 8) requires that

$$z = \frac{1}{\lambda - 1}. \quad (\text{VII} - 21)$$

The ν -exponent characterizes the importance of the MC addition process. The importance of the MC reactions relative to the CC reactions is best revealed by defining an additional exponent

$$\mu = \lambda - \nu. \quad (\text{VII} - 22)$$

It was shown [62,60] that the overall qualitative behavior of the system can be classified into three distinct groups according to the value of the μ -exponent:

1. $\mu > 0$: In this case CC reactions dominate the behavior of the system, and since larger clusters preferentially react among themselves, a large polydispersity results.
2. $\mu < 0$: In this case the average particle size grows primarily at the expense of smaller clusters, and therefore, the system retains a monodisperse character.
3. $\mu = 0$: This is a complicated case since the assumption about the existence of a characteristic particle-size is now questionable.

This approach requires that $K(i, j)$ kernels are constant in time and independent of the particle size. Combustion aerosols are subject to a significant changes in the ambient temperature which is accompanied by large changes in the particle sizes. Therefore, kernels $K(i, j)$ are subject to change in time and are size-dependent.

Meakin [63] studied this type of problem for Brownian kernels by assuming that the diffusion coefficient of a particle of size N , $D(N)$ depends on the size as

$$D(N) \sim N^\gamma, \quad (\text{VII} - 23)$$

where γ is some constant. He found that for $\gamma < -1/3$ the system behaves as in the $\mu < 0$ case, and for $\gamma > -1/3$, the solution behaves as in the $\mu > 0$ case.

This concludes the review of the scaling theory analysis of the reaction-rate aggregation models. In the next section, the results of this analysis will be applied to reaction kernels $K(i, j)$ which are appropriate for soot-particles.

VII.3 Rate-constant evaluation

This section presents the determination of the kernels $K(i, j)$ which are applicable for the soot-particle growth. The intention is to investigate the applicability of the scaling theory for the growth of soot particles for conditions comparable to the conditions which existed in the soot generator. The kernels $K(i, j)$ were computed assuming a Hamaker [68] interaction potential between neutral, spherical Brownian particles. The computed kernels were used to evaluate scaling exponents and the applicability of the scaling-analysis for the characterization of growth of soot-particles.

The determination of $K(i, j)$ is relatively simple if the Knudsen number for interacting species is such that both reactants are in the free-molecular regime, or if one particle is in the continuum limit while the other is in the free molecular regime. For particles in the transitional regime, some approximations must be introduced. For soot-particles, a method proposed by Rodger and Sceats [66,67] will be followed. It will be assumed that the interaction potential between constituent, hydrocarbon, spherical particles of a variable radii R_i and R_j , can be described via a Hamaker

potential, $V(R)$, given by

$$V(R) = -\frac{A'}{12} \left\{ \left[\left(\frac{R}{R_1 + R_2} \right)^2 \right]^{-1} + \left(\frac{R}{R_1 + R_2} \right)^{-2} + 2 \ln \left[1 - \left(\frac{R_1 + R_2}{R} \right)^2 \right] \right\}, \quad (\text{VII} - 24)$$

where R is the distance between the spheres. A' is the reduced Hamaker constant

$$A' = \frac{A}{k_b T} \frac{4R_1 R_2}{(R_1 + R_2)^2}, \quad (\text{VII} - 25)$$

and A is the characteristic well-depth of the interaction potential. Symbols k_b and T denote the Boltzmann constant and the temperature of the ambient gas, respectively. For hydrocarbons, $A/k_b T$ has a value in the range from 5 to 60 [67].

Rodger and Sceats recently proposed a method for the determination of $K(i, j)$ for neutral particles with this type of interaction potential, which is, in principle, valid regardless of the Knudsen-number value for either reactant. They showed that the problem of motion of two, spherical particles of masses m_i and m_j , mutually interacting with a long-range, spherical interaction potential $V(R)$ and with the thermal bath can be reduced to a problem of the motion of a single particle of reduced mass

$$m_{ij} = \frac{m_i m_j}{m_i + m_j}, \quad (\text{VII} - 26)$$

moving in the effective potential

$$V_{eff}(R) = V(R) - 2k_b T \ln(R). \quad (\text{VII} - 27)$$

The interaction with the thermal bath of individual reactants is characterized by a friction term

$$\zeta_i = \frac{k_b T}{D_i}, \quad (\text{VII} - 28)$$

where D_i is the diffusion coefficient of particle i . The friction factor of the reduced particle is then [66]

$$\zeta_{ij} = \left(\frac{m_i}{m_i + m_j} \right)^2 \zeta_j + \left(\frac{m_j}{m_i + m_j} \right)^2 \zeta_i. \quad (\text{VII} - 29)$$

The expression for $K(i, j)$ is then given by

$$K(i, j) = \pi(R_i + R_j)^2 \left(\frac{8k_b T}{\pi \mu_{ij}} \right)^2 W_{ij}(\infty)^{-1} \{ \sqrt{[1 + (t_{ij}/2)^2]} - t_{ij}/2 \}, \quad (\text{VII} - 30)$$

where

$$t_{ij} = \frac{\zeta_{ij}(R_i + R_j)}{\sqrt{2\pi k_b T \mu_{ij}}} \frac{W_{ij}(0)}{W_{ij}(\infty)}. \quad (\text{VII} - 31)$$

Parameters $W_{ij}(\infty)$ and $W_{ij}(0)$ which account for the interactions between particles are given by [66]

$$W_{ij}(\infty) = \left(\frac{R_i + R_j}{R_m} \right)^2 \exp [V(R_m)/k_b T], \quad (\text{VII} - 32)$$

and

$$W_{ij}(0) = (R_i + R_j) \int_{R_i+R_j}^{\infty} \frac{1}{R^2} \exp [V(R)/k_b T] dR, \quad (\text{VII} - 33)$$

where R_m denotes the location of the minima in the interaction potential $V(R)$. The quantity t_{ij} indicates if the particle is in the continuum regime ($t_{ij} \gg 1$) or the free-molecular regime ($t_{ij} \ll 1$), in which case the correct form of the answer is recovered [66].

It was assumed here that this model is applicable to growth of soot-particles for the entire range of particle sizes of interest. Details of the internal structure of soot-particles are ignored, and particles enter the collision events as spheres. The model of Rodger and Sceats is applicable to free-molecular, transition, and continuum-limit regimes. The exact, lower-limit for size is subject to question both with regard to the applicability of the theory and with respect to the definition of a "monomer" size. The size of microcrystallites in soot is in the range of one to three nm [14,15], however, it was assumed here that a "monomer" size is one nm as a reasonable choice.

Assumming the applicability of the Hamekar interaction potential implies that only neutral-species reactions are considered. Several constant values for the reduced

Hamekar constant were used, and this step is subject to question since particle evolution occurs over a range of temperatures. Also, the carbon-to-hydrogen ratio is changing during the growth and, therefore, it is plausible that the well-depth of the interaction potential changes during the growth. However, the intention is to extract the information about the characteristic behavior of growth. Therefore, the application of various well-depths for the interaction potential (estimated from thermal energies, to be approximately 2.6 electron-volts) provides information about the applicability of the scaling-analysis with respect to kernels which are not conventional Brownian-kernels ($K(i, j) = \text{constant}$, as is usually considered [60]). Considering a range of values for interaction-potential well-depths provides qualitative information about the effects of the chemical constituency of particles, but changes in the constituency with time are ignored since the Smoluchowski equation in a given form does not reflect these changes. Properties of the inert, carrier-gas have been computed as described in Appendix B, assuming a pressure of 290 Torr and a temperature of 1000°C . Finally, the mass-density of particles was assumed to be $1.5\text{g}/\text{cm}^{-3}$.

Using this approach, kernels $K(1, j)$ and $K(i, i)$ were computed for a range of particle diameters and results are shown in Figure VII- 1. Figure VII- 1 shows that the of MC reactions can be expected to dominate the behavior of the solution of the Smoluchowski equation. Also, Figure VII- 1 shows that the probability for the monomer-monomer reaction is small compared to the monomer-cluster reaction. Corresponding scaling-exponents were computed and results are shown in Figures VII- 2 through VII- 5.

The size-dependence of λ and ν exponents indicates that the homogeneity requirements specified by Equation (VII-18) and (VII-19) are not satisfied rigorously. In both cases, however, a trend to a constant value for large particle diameters is indicated, as could be expected from the values of the corresponding Knudsen numbers.

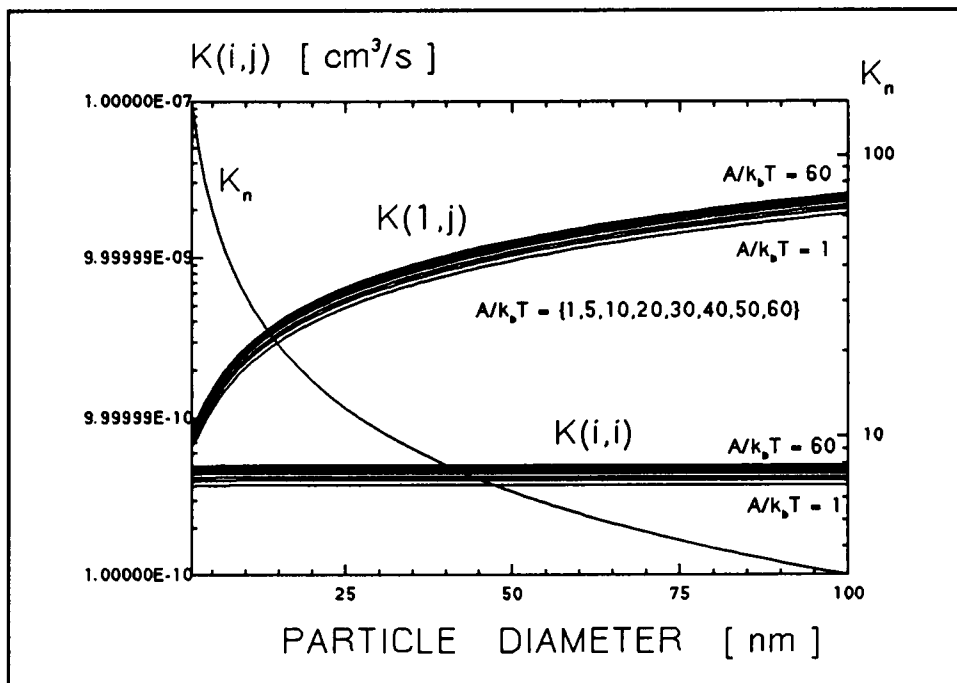


Figure VII- 1: Reaction-rate constants and Knudsen numbers.

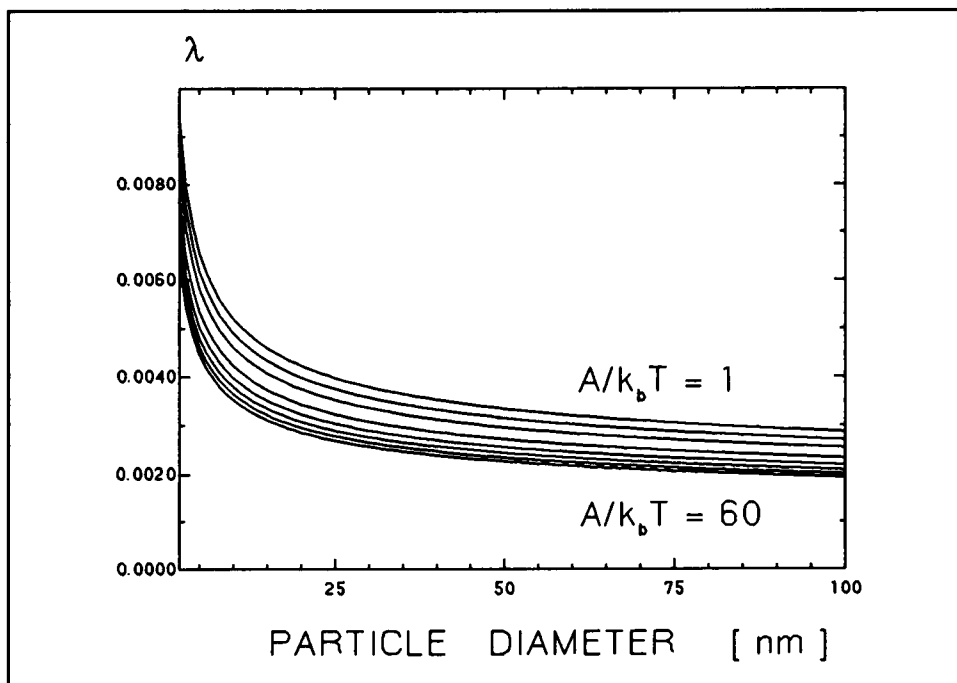


Figure VII- 2: Scaling exponent λ .

The Knudsen numbers indicate that the transition from a free-molecular regime to

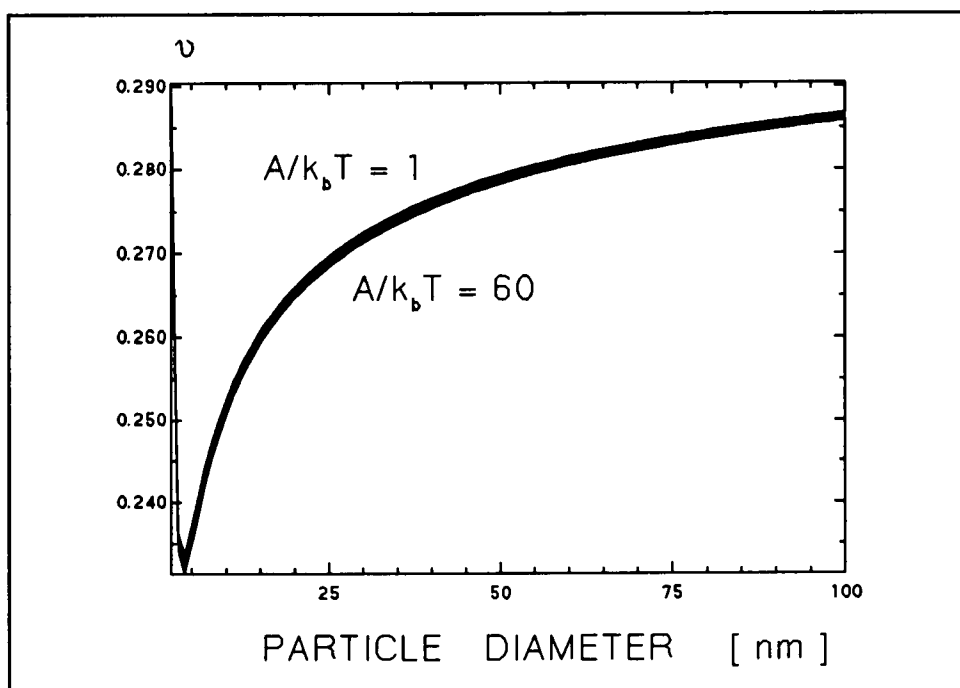


Figure VII- 3: Scaling exponent ν .

continuum regime occurs for particle of diameters larger than approximately 50 nm.

Since the diameters of interest are mostly in the free-molecular regime, it is of interest to compare the computed scaling exponents to the theoretical limiting values for λ and ν , using a kinetic-theory expression for the encounter rates for hard-spheres

$$K(i, j) \sim \frac{(R_i + R_j)^2}{\sqrt{m_{ij}}}. \quad (\text{VII} - 34)$$

Since the radius of the particle $R^3 \sim i$,

$$K(i, i) \sim R^{\frac{1}{2}} \sim i^{\frac{1}{6}} \quad (\text{VII} - 35)$$

and

$$K(1, i) \sim R^2 \sim i^{\frac{1}{3}}, \quad (\text{VII} - 36)$$

and consequently, the scaling exponents are $\lambda = \frac{1}{6}$ and $\nu = \frac{1}{3}$. Therefore, the values for scaling exponents $\mu = -\frac{1}{6}$ and $z = \frac{4}{3}$ follow. A discrepancy with the computed exponents exists due to the application of the Rodger-Sceats-model for

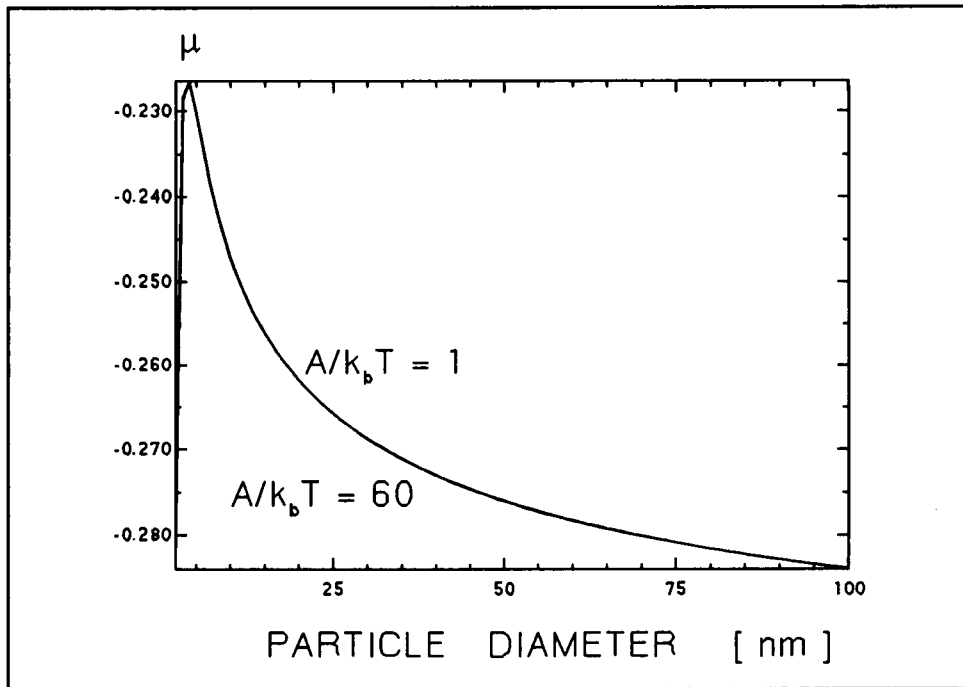


Figure VII- 4: Scaling exponent μ .

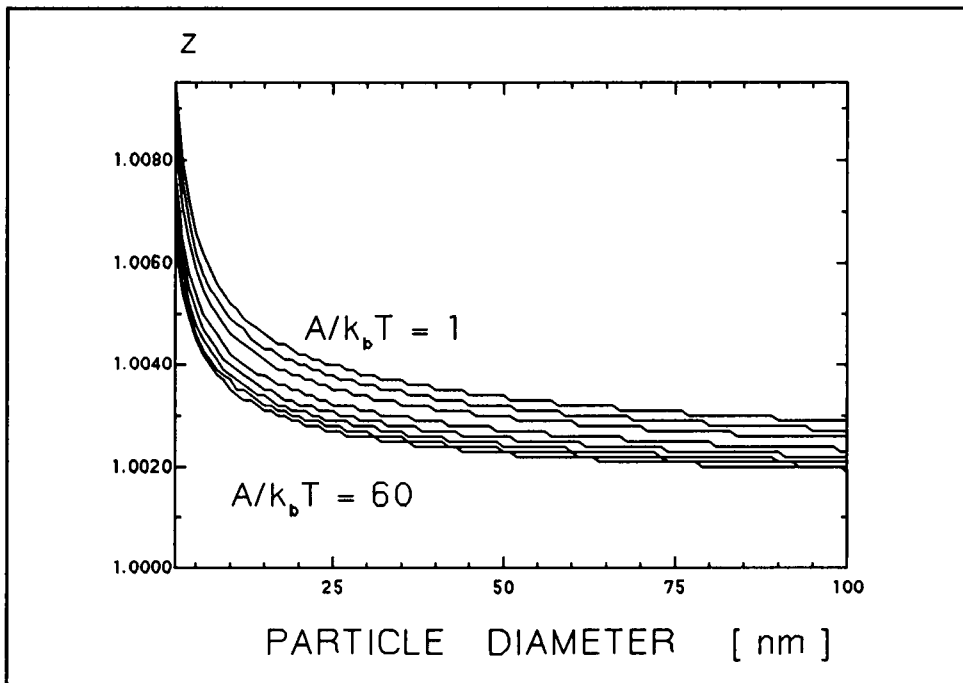


Figure VII- 5: Scaling exponent z .

the computation of the encounter rates. Rodger and Sceats [66] point-out that the

effect of the interaction-potential on the encounter rates is more important for the smaller particles and that this effect is always enhanced for the collision partners of the same size. This is manifested by the fact that the ν exponent is closer to the hard-sphere limit since the discrepancy in size of collision partners minimizes the effect of the interaction potential, while the deviation from a hard-sphere limit for the λ -exponent is more appreciable. Surprisingly, the result for the z -exponent is very close to the exact value for constant Brownian kernels [60] over the entire range of diameters. The results also show that scaling exponents are not strongly influenced by the choice for the Hamaker constant. Therefore, the effect of the interaction-potential on the encounter rates is fairly strong, even for small well-depths.

The scaling analysis, strictly speaking, can not be applied for the modeling of soot-particle growth since the assumed form of the reaction kernels do not satisfy the homogeneity requirement (VII-19). However, the computed kernels, and corresponding scaling exponents indicate the main trends in the evolution of soot-particles. In early stages of growth, if the supply of monomers is sufficient, the growth results in the formation of nearly spherical, compact particles since the MC-reactions dominate the growth. The production of monomers lasts for a short period of time, and the system will remain in the monomer-cluster regime as long the number-density of monomer species is sufficiently high so that monomer-addition reactions dominate the growth. After the monomer number-density is exhausted, the growth makes a transition to a cluster-cluster aggregation regime. In the cluster-cluster regime however, one must expect that physical conditions change due to the internal structure of soot particles. The above-described kernels and the scaling-analysis assume that the cluster-cluster reactions result in a coalescence of particles, and this would imply that the same growth-behavior would continue regardless of the size of "monomers". However, assuming that larger particles solidify rapidly, the growth is

in the monomer-cluster regime as long the monomer number-density is high. Therefore, a characteristic size of particles for which the transition to CC-growth occurs depends on the length of time during which a system sustains a large number-density of monomers. The effect of additional terms in the Smoluchowski equation has been studied by Viscek *et al.* [69], but they have investigated systems in which production of monomers was accompanied by the removal of particles from the system.

VII.4 Fractal-growth models

The main characteristic of fractal objects is their self-similarity on various length scales [64]. Such self-similarity for soot-particles can be established by looking at the structure of soot particles. The largest soot particle aggregates generally appear as random, porous, chain-like structures. Depending on the overall size of the aggregate, this structure has an obvious self-similarity on length scales in the range from approximately 100 nm to above 1 μm . Larger magnifications reveal that these aggregates are actually comprised of a large number of nearly spherical, compact particles. These particles are, in turn comprised of a large number of nearly spherical, microcrystalites, which are aggregates of primarily carbon atoms. Therefore, the self-similarity of soot particles is manifested by at least two different characteristic topologies. The structure of smaller particles is characterized by a relatively large compactness and by nearly spherical shapes. Larger particles are characterized by irregular, ramified, self-similar structures.

Various fractal-growth models have been introduced recently for the modeling of random structures like soot-particles. The Eden model and the diffusion-limited aggregation (DLA) model are two that can be applied for the characterization of soot-particle growth.

A complete review of the application of fractal geometry for the characteri-

zation of growth is beyond the scope of this effort since the intention here is only to outline the basic approach of fractal-growth models. Particular attention will be devoted to the above-mentioned models, which can capture the essential features of soot-particle evolution.

Characterization of fractal objects with a set of parameters is useful since it gives one a power of predicting their behavior without reference to details of the object's complex nature. All random, fractal-growth models represent a numerical-experiment type of study of complex growth phenomena which occur in nature. Fractal objects are usually created on some sort of lattice, usually a square or a cubic lattice. One particular lattice site is designated as a *seed* lattice site and some lattice sites are assigned as a *growth-sites*. Growth sites are selected according to the *fixed* rules of the model which is one essential feature of the model. The second part of the model consists of prescribed rules for the population of growth-sites by new members of a growing cluster. The rules for cluster growth represent a theoretician's effort to describe experimental conditions for which the model is developed. This, however, does not imply that the application of a particular fractal-growth model is applicable exclusively to specific experimental conditions. For example, the set of rules for the Eden model was proposed by Eden in an attempt to describe growth of cell colonies [63].

VII.4.1 Eden model

The Eden model has perhaps the simplest set of growth-rules. The empty, nearest-neighbor sites are labeled as growth-sites, and a new cluster member is chosen with a uniform probability from those sites. Actually, there are several variations of the Eden model, but all variants result in a formation of compact, roughly spherical objects. The growth continues until a cluster reaches a predetermined size. The

object is then analyzed for specific quantities (*e.g.* the radius of gyration), and a new object is grown in order to provide grounds for a statistical analysis. Hermann [65] showed that the average cluster of N monomers has an average radius-of-gyration, $R_g(N)$, which behaves as

$$N \sim R_g(N)^{D_f}, \quad (\text{VII} - 37)$$

where D_f is a *fractal dimension* which for the Eden model has a value of three. In other words, this fractal-growth model leads to a formation of random, compact, nearly spherical objects. These properties are also the properties of the soot-particle evolution in the first two stages of growth: nucleation, and growth of nuclei.

VII.4.2 Diffusion-limited cluster-cluster aggregation model

The diffusion-limited, cluster-cluster aggregation model is an extension of a single-cluster, diffusion-limited aggregation (DLA) model. Therefore, the simpler DLA model will be considered first. The DLA model was developed with the intention of modeling the growth of aggregates formed by Brownian motion of constituents. As in the Eden-model case, the seed particle is placed at the origin of a square or a cubic lattice and nearest-neighbor sites are labeled as growth-sites. A new particle starts a random-walk motion from a randomly chosen location away from the seed. The random-walk proceeds until the particle reaches one of the available growth-sites. However, there is a probability that the particle will move away from the seed, and if so, the random walk is terminated and a new particle is released. There are fixed rules for the determination of starting locations and for the termination of unsuccessful, random-walks; these rules are based on estimates from the probability theory and are not an essential part of the model. The addition of a new member of the cluster implies the occupation of that location, all empty nearest-neighbor sites of that location become new members of the list for the po-

tential growth-sites. This process is repeated until a cluster of the desired size is formed.

The diffusion-limited, cluster-cluster aggregation model is an extension of the DLA model in the sense that, instead of single-cluster growth, one investigates the growth of many clusters simultaneously. This is accomplished by distributing N particles on the lattice and allowing them to execute a Brownian, random-walk on the lattice. The contact of two particles results in the formation of larger clusters, which are allowed to diffuse and participate in the further growth.

Finally, it should be mentioned that the DLA model can be modified by assigning a sticking probability less than 1, which was an implicit assumption. In the limit of low sticking probabilities, the DLA-growth model reduces to the Eden model [63].

In conclusion to this section, it can be stated that the growth of soot particles can be mapped onto the two, above-mentioned fractal-growth models, since both fractal-growth models reflect the directional growth described by the Smoluchowski equation. The first two stages of growth result in the formation of compact, roughly spherical particles which can be described by the Eden-model, while the last stage of growth can be described by the cluster-cluster aggregation model. Obviously, there must be a transitional phase of growth, where the particles cease to follow the Eden-model and start to behave according to the cluster-cluster aggregation model.

VII.5 Comparison with experimental results

Up to this point, the discussion of the growth was concerned with the qualitative behavior of the soot-particle evolution. A direct application of the scaling theory is not possible since time-resolved measurements of particle sizes were not performed. Therefore, the introduction of additional assumptions is required. How-

ever, some numerical estimates can be obtained as follows. It will be assumed that the nucleation occurred in the flowfield at the location with the highest temperature. From the numerical analysis of flow (Chapter III), it is possible to estimate the growth-time, from the region with the highest temperature to the observation point to be approximately 50 milliseconds. This estimate is based on the radially-averaged axial components of the velocities. Figure III-7 on page 35 clearly indicates that this is just a crude approximation. A comparison with typical times from the flame-generated soot from a review by Calcote [14] supports this estimate.

The scaling theory predicts that the particle diameter increases as approximately $t^{\frac{1}{3}}$ since z is approximately one. If one uses as the characteristic times from flames [14], then particle sizes of approximately five nm are formed in about four milliseconds. Thus, the scaling analysis predicts particle sizes of approximately 10 nm in 50 milliseconds. Therefore, the scaling analysis predicts growth-rates which are too slow to explain the observed particle sizes, even if one allows for large margins of error on the estimate for the growth-time. The size-dependency of the scaling exponents is not sufficient to explain the magnitude of this failure either. The existence of a unique, characteristic particle-size, applicability of the Rodger-Sceats model, or the method of computation of gas-properties are possible reasons for the failure of the scaling-theory analysis.

Some estimates for the growth-rates can be obtained by introducing some additional assumptions. It will be assumed that the growth occurs by a direct decomposition of acetylene on the surface of the particles since this mechanism appears to be plausible for the growth of soot in pyrolysis of acetylene [15]. Therefore, an estimate about the number-density of acetylene molecules is required. For the pressure and the temperature which existed in the flow, the number-density of acetylene is less than approximately 10^{18} cm^{-3} . Furthermore, it will be assumed that the

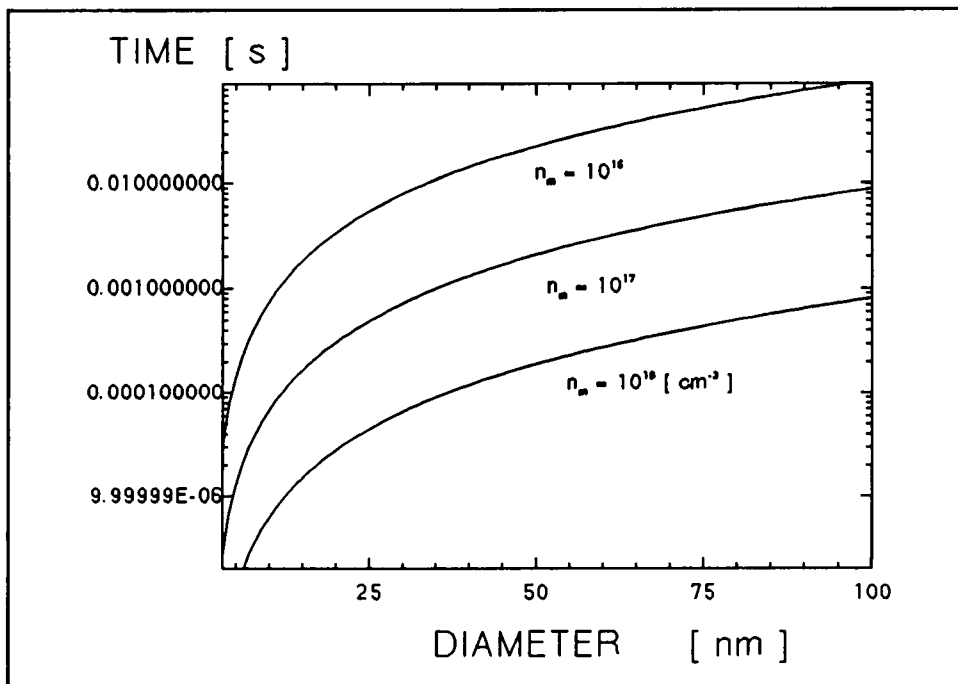


Figure VII- 6: An estimate of the growth of particles.

number-density of particles is $7.4 \times 10^9 \text{ cm}^{-3}$, as determined by the transmission measurements. Therefore, an extremely simplified version of the growth-model is that the MC reactions dominate the growth and that the initially-formed nuclei grow at the expense of small particles. If this point of view is adopted, the rate of loss of monomers is

$$\frac{\partial n_m}{\partial t} = -K(1, l)n_m n_p, \quad (\text{VII} - 38)$$

where l is the number of monomers in the particle; n_m and n_p denote the number-densities of monomers and particles, respectively. This equation was solved numerically for three initial number-densities of monomers, as indicated on Figure VII-6

This figure shows that a simple model which assumes the growth by the decomposition of acetylene directly on the surface of particles is within order-of-magnitude agreement with the experimental results, if one assumes that the number density of acetylene is about two orders-of magnitude lower than it can be esti-

mated from the flow conditions. This discrepancy could be possibly attributed to the conversion of acetylene to stable, non-reactive hydrocarbon species, losses to the walls, and the deposition on the walls of the graphite rod. Also, the computed rate-constants depend on the properties of the diffusion constants in an environment of a complex composition.

Therefore, this section is concluded by a remark that detailed modeling of the growth requires a much better characterization of the conditions of growth than is available. Therefore, the simplified model exploits a proposed mechanism for the growth of pyrolysis-generated soot particles and the results shown in Figure VII- 6 show that an order-of-magnitude agreement with experimental results can be reached.

VII.6 Discussion

Fractal geometry and the scaling-approach have been used for a qualitative description of the growth of soot-particles based on neutral-species only. Essential features of growth can be mapped on two fractal-growth models. Early stages of growth are dominated by monomer-addition processes, resulting in a formation of spherical particles. This stage of growth can be modeled by the Eden fractal-growth model. The depletion of monomers results in a transition to a cluster-cluster aggregation mechanism, which can be mapped on the DLA cluster-cluster growth model.

The above-described fractal-growth model is conceptually similar to the "nucleation-and-growth"-model, and to a certain extent, to Kang's droplet model. The difference is that the "nucleation-and-growth" considers energetics of growth in detail, assuming that the system is in equilibrium in application of the conservation laws. Fractal-growth is far-from the equilibrium model, and only the conservation of mass law is used. The application of this law can be questioned for the soot-particles, due

to the changes in the chemical composition of particles in the course of growth. In principle, the Smoluchowski equation can be extended by labeling each cluster by numbers of carbon and hydrogen atoms. This would imply that the Smoluchowski equation should contain additional terms which reflect a dehydrogenization of particles. However, for long-times, chemical constituency does not change with time, and the coarse-graining procedure would result in the elimination of such terms from the scaling-analysis.

The comparison of the growth-rates with the experimental results requires a detailed characterization of both flowfield and particle-field in the soot-generator. Since such information is not available, simplifying assumptions based on the proposed mechanism for growth of soot-particles was used for the comparison with the experimental results. It was shown that an order-of-magnitude agreement with the experimental results can be achieved in spite of the lack of information about the details of growth.

CHAPTER VIII

SUMMARY

This effort described the design and construction of an apparatus which lends itself to experimental studies of the formation of carbon particles generated by pyrolysis of acetylene. Experimental measurements could be compared to theoretical models with partial success. The transmission-measurement results and the light-scattering measurements revealed essential features of the present apparatus design. The results of transmission measurements showed that the application of the extrapolated values for the optical properties from Dalzell-Serofim model for wavelengths in the range from 250 *nm* to 400 *nm* is justified. The difficulties in conducting the light-scattering measurements clearly indicated certain drawbacks of the apparatus. The feasibility of future studies of carbon particles generated in a pure pyrolysis process requires the consideration of the necessary modifications of the present apparatus or completely different methods for the production of carbon particles.

Pyrolysis of hydrocarbon fuels in a drift-tube environment sets requirements with respect to the design of the particle-source assembly, drift-tube design, and the observation window and soot-collection assembly. The difficulties in meeting all requirements should not be underestimated, but are not insurmountable, as was demonstrated by the measurements on the present apparatus. However, the difficulties arising from the nature of the pyrolysis present problems which are more difficult to solve. The pyrolysis of hydrocarbons simultaneously involves both homogeneous and heterogeneous decomposition reaction mechanisms, and consequently it is difficult to create conditions which would permit one to distinguish between the two reaction pathways with ease. A more serious objection to the present design is also related to

the nature of the heterogeneous decomposition of hydrocarbons. The released carbon is deposited on the walls of the particle-source which results in unsteady operation of the apparatus, as evidenced by the results of light-scattering measurements.

The effects of the heterogeneous decomposition can be minimized by decreasing the surface-to-volume ratio of the particle-source assembly. The particle-source assembly is the crucial element of the apparatus and the change in the graphite rod would require modifications of all other elements of the apparatus. The increase of the graphite-rod diameter would improve the spatial resolution of scattering measurements, but the extent of modification is restricted by the radio-frequency, power-supply limitations. In contrast to the inductive heating, a direct-current, hot-filament arrangement can be considered instead. As a matter of fact, a hot-filament has a number of advantages over the present design. The design of all elements (drift-tube, observation windows, and soot-collection) would be simplified in that configuration. However, the impact of heterogeneous reactions on the temporal properties of the particle-source would probably be even worse than in the present design.

One of the accomplishments of this effort is the development of the method for the deconvolution of multiwavelength transmission measurements for particle-sizing applications. The method presented in Chapter IV is based on the fitting of the particle-size distribution function parameters to the experimental results. An alternative to the described data-inversion method can be recommended for future research. The new method can be outlined as follows. The ratio of optical densities defines one or more diameters for which the variance of the particle-size distribution is an exact zero. Assuming a small variance, $\delta\sigma$, the quantity χ_R can be computed for a range of mean-diameters in the vicinity of the solution for the monodisperse particle size. The minimum of χ_R can be identified (not minimized) for a certain diameter

D_1 , and the pair $(D_1, \delta\sigma)$ recorded. The procedure can be repeated by increasing the variance in steps of $\delta\sigma$, and this exploration of the $D - \sigma$ plane will result in a set of values $(D_i, i\delta\sigma)$ which traces some curve in that plane. This procedure can be repeated for several wavelength-pairs, and in the ideal case one expects to see that the intersection of individual curves results in an unambiguous determination of the particle-size distribution parameters. The advantage of this method would be that it provides the opportunity for a systematic search for the solution for the absolute minimum. A graphical presentation of individual curves may aid the identification of the solution and the choice of wavelength-pairs. Moreover, the impact of the experimental errors can be presented graphically as well. The method would require extensive computations, but it is conceivable that it would be more practical than the one described in Chapter IV.

The complexity of the formation and evolution of soot-particles is best described by the fractal-growth models. However, the form of the reaction kernels, which assumes neutral-species reactions only, does not satisfy the fundamental assumptions of the scaling theory and therefore a detailed solution of the Smoluchowski equation is required. In the case of soot-particles, however, the coagulation equation may require modification in order to describe the chemical constituency of particles. Perhaps the most significant application of the modified Smoluchowski equation would be in the nucleation stage of growth. The system of rate-equations can be solved using a stochastic simulation of chemical reactions, providing the information about fluctuations in the system which is, of course, significant for the nucleation phenomena. In addition to the chemical constituency aspect of the problem, the effects of charged species on the growth must be considered.

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APPENDICES

APPENDIX A

THE LOG-NORMAL DISTRIBUTION FUNCTION

The log-normal distribution function is frequently used for the characterization of particle sizes since its skewed profile closely resembles actual measured particle size distributions. This appendix presents the log-normal particle size distribution function which is convenient for computational purposes. This clarification is needed since the log-normal distribution is frequently quoted in forms which are not convenient for the computation, or the meaning of the parameters appearing in the expression is not sufficiently clear.

A random variable D is said to have a log-normal distribution if its logarithm, $\ln(D)$, is distributed according to a normal distribution. A normal distribution of a random variable X with a mean μ_n and the standard deviation σ_n is given by

$$p(x)dx = \frac{1}{\sqrt{2\pi}\sigma_n} \exp\left[-\frac{1}{2}\left(\frac{x - \mu_n}{\sigma_n}\right)^2\right]dx, \quad -\infty < x < +\infty, \quad (\text{A} - 1)$$

where μ_n is the expectation, $E\{X\}$, of the normal distribution (mean), and σ_n is the standard deviation which is defined as

$$\sigma_n \equiv \sqrt{\text{Var}\{X\}} = \sqrt{E\{X^2\} - (E\{X\})^2}. \quad (\text{A} - 2)$$

Substituting

$$x = \ln(D) \quad (\text{A} - 3)$$

in Equation (A- 2), the distribution for D can be written as:

$$p(D)dD = \frac{1}{\sqrt{2\pi}\sigma_n} \exp\left[-\frac{1}{2}\left(\frac{\ln D - \mu_n}{\sigma_n}\right)^2\right] \frac{dD}{D}, \quad 0 < D < +\infty. \quad (\text{A} - 4)$$

Expression (A- 4) is one of the frequently quoted forms of the log-normal distribution. The potential confusion due to the presence of the $\ln(D)$ term in the argument of the exponential function can be resolved by defining a quantity D^* by

$$\mu_n \equiv \ln(D^*), \quad (\text{A} - 5)$$

but this quantity is not the mean diameter, although it is referred to as a *geometric mean diameter* of the distribution. The parameters of the normal distribution, μ_n and σ_n , are related to the mean diameter, D_{mean} and the variance, $Var\{D\}$ by [70]

$$D_{mean} = E\{D\} \equiv \int_0^\infty Dp(D)dD = \exp(\mu_n + \frac{1}{2}\sigma_n^2), \quad (\text{A} - 6)$$

and

$$Var\{D\} = \exp(2\mu_n + 2\sigma_n^2) - \exp(2\mu_n + \sigma_n^2). \quad (\text{A} - 7)$$

For particle sizing applications it is convenient to specify the mean diameter and the standard deviation, $\sigma \equiv \sqrt{Var\{D\}}$. Equations () and () can be combined to express σ_n in terms of D_{mean} and σ as

$$\sigma_n = \sqrt{\ln[1 + \left(\frac{\sigma}{D_{mean}}\right)^2]} \equiv a. \quad (\text{A} - 8)$$

Also, the mean of the normal distribution can be written as

$$\mu_n = \ln(D_{mean}) - \frac{1}{2}\sigma_n^2. \quad (\text{A} - 9)$$

Therefore, the log-normal distribution can be expressed as

$$p(D)dD = \frac{1}{\sqrt{2\pi}aD} \exp\left\{-\frac{1}{2}\left[\frac{\ln(D/D_{mean}) + a^2/2}{\sigma_n}\right]^2\right\}, \quad 0 < D < \infty \quad (\text{A} - 10)$$

where

$$a \equiv \sqrt{\ln[1 + \left(\frac{\sigma}{D_{mean}}\right)^2]} \equiv \sigma_n. \quad (\text{A} - 11)$$

The probability density function, $p(D)$, is therefore completely specified in terms of quantities of physical interest, the mean diameter of the particle and the variance of the distribution. Moreover, that expression is useful for computational purposes since it involves evaluation of natural logarithms of dimensionless quantities. In applications of the log-normal distribution it is customary to use the symbol a for the quantity σ_n to avoid confusion with the quantity σ .

In particle sizing applications it is of interest to determine the average volume of the particle as well. For that purpose, a general relation for the $n - th$ moment of the log-normal distribution

$$D^{(n)} \equiv \int_0^\infty D^n p(D) dD = D_{mean}^n \exp\left(\frac{n(n-1)a^2}{2}\right) \quad (A-12)$$

can be used.

APPENDIX B

GAS-MIXTURE TRANSPORT PROPERTIES

This appendix presents the procedures used for the determination of transport properties of gas mixtures which were used in the interpretation of the diffusion-broadening spectroscopy measurements. The quantity of interest is the characteristic relaxation time for a particle of a given size. This characteristic time depends on the scattering angle and the diffusion constant. In turn, the diffusion constant depends on the gas transport properties. As we have a mixture of the gases for which experimental data are not available, gas properties were determined by using the Lennard-Jones interaction potential parameters for argon and acetylene as given by Reid *et al.* [54]. Used parameters are given in Table B-1 The molar fractions of acetylene and argon

Table B-1: Lennard-Jones parameters		
gas	ϵ/k_B [K]	σ [nm]
argon	93.3	0.3542
acetylene	231.8	0.4003

used in the computation correspond to the actual flow conditions. We assumed that the fraction of the decomposed acetylene can be neglected which allows us to estimate the molar fractions from the mass flow rates. The validity of this assumption can be questioned. However, at this point we mention that the ultimate deconvolution procedure does not depend strongly on the gas composition. Since the experimental data for this particular application are not available, a computational approach with some drastic simplifications is the only viable approach.

Viscosity determination

We used the Chapman-Enskog viscosity equation

$$\eta = \frac{26.69\sqrt{MT}}{\sigma^2\Omega_v}, \quad (\text{B} - 1)$$

where η is the dynamic viscosity [μP], M is the molecular weight [g/mol], T is the temperature [K], σ is the Lennard-Jones diameter [$\text{\AA}$], and Ω_v is the collision integral. Ω_v is computed by

$$\Omega_v = [A(T^*)^{-B}] + C[\exp(-DT^*)] + E[\exp(-FT^*)]. \quad (\text{B} - 2)$$

Here, T^* is the reduced temperature

$$T^* = \frac{k_B T}{\epsilon}, \quad (\text{B} - 3)$$

$A = 1.16145$, $B = 0.14874$, $C = 0.52487$, $D = 0.7732$, $E = 2.16178$, and $F = 2.43787$. This empirical determination of the collision integral is applicable from $0.3 \leq T^* \leq 100$ with an average standard deviation of only 0.064 percent [54].

Equation (B- 1) determines the dynamic viscosity of a pure gas. The viscosity of the gas mixture was computed by using the method of Reichenberg [54]. The rigorous kinetic theory of Chapman-Enskog can be extended to determine the viscosity of the mixture, but the final expressions are quite complicated and are rarely used in practice. There are several simplifying expressions in the literature that are used in practice. Reichenberg's equations are the most complex, but the most consistently accurate [54]. For a binary gas mixture of 1 and 2 the mixture viscosity equation is:

$$\eta_{mix} = K_1(1 + H_{12}^2 K_2^2) + K_2(1 + 2H_{12}K_1 + H_{12}^2 K_1^2). \quad (\text{B} - 4)$$

With η_i the viscosity of pure i , M_i the molecular weight of i , and y_i the mole fraction

of i in the mixture ($i = 1, 2$),

$$K_1 = \frac{y_1 \eta_1}{y_1 + \eta_1 \{y_2 H_{12} [3 + (2M_2/M_1)]\}}, \quad (\text{B} - 5)$$

$$K_2 = \frac{y_2 \eta_2}{y_2 + \eta_2 \{y_1 H_{12} [3 + (2M_1/M_2)]\}}, \quad (\text{B} - 6)$$

$$U_1 = \frac{[1 + 0.36 T_{r1} (T_{r1} - 1)]^{1/6}}{\sqrt{T_{r1}}}, \quad (\text{B} - 7)$$

$$U_2 = \frac{[1 + 0.36 T_{r2} (T_{r2} - 1)]^{1/6}}{\sqrt{T_{r2}}}, \quad (\text{B} - 8)$$

$$U_{12} = \frac{[1 + 0.36 T_{r12} (T_{r12} - 1)]^{1/6}}{\sqrt{T_{r12}}}, \quad (\text{B} - 9)$$

$$T_{ri} = \frac{T}{T_{ci}}, \quad (i = 1, 2), \quad (\text{B} - 10)$$

$$T_{r12} = \sqrt{T_{r1} T_{r2}}, \quad (\text{B} - 11)$$

$$H_{12} = \frac{\sqrt{M_1 M_2 / 32}}{(M_1 + M_2)^{3/2}} U_{12} (C_1 + C_2)^2, \quad (\text{B} - 12)$$

$$C_i = \frac{M_i^{1/4}}{\sqrt{\eta_i U_i}}. \quad (\text{B} - 13)$$

The critical temperatures T_c for argon and acetylene are 150.8 K and 308.3 K, respectively [54]. Rechenberg's method is complicated, but an accurate determination of the dynamic viscosity of the mixture is essential for the determination of the mobility of soot particles.

Mean-free path determination

The determination of the slip correction factor requires knowledge of the mean free path in the ambient gas. We have used the elementary relation:

$$D = \frac{v \lambda}{3}, \quad (\text{B} - 14)$$

where λ is the mean free path, and

$$v = \sqrt{\frac{8k_B T}{\pi m_1} + \frac{8k_B T}{\pi m_2}}, \quad (\text{B} - 15)$$

where m_1 and m_2 are molecular masses. The diffusion constant of the gas mixture was determined by

$$D_{12} = \frac{0.00266 T^{3/2}}{P \sqrt{M_{12}} \sigma_{12}^2 \Omega_D}. \quad (\text{B} - 16)$$

where D_{12} is the diffusion constant of the mixture [cm^2/sec], P is the pressure [bar],

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad [\text{\AA}], \quad \epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}, \quad T^* = \frac{k_B T}{\epsilon_{12}}, \quad (\text{B} - 17)$$

and Ω_D is given by analytical approximation [54]

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp DT^*} + \frac{E}{\exp FT^*} + \frac{G}{\exp HT^*}. \quad (\text{B} - 18)$$

Here, $A = 1.06036$, $B = 0.1561$, $C = 0.193$, $D = 0.47635$, $E = 1.03587$, $F = 1.52996$, $G = 1.76474$, and $H = 3.89411$.

VITA

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