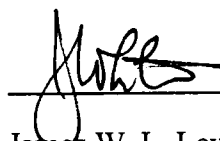


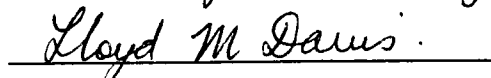
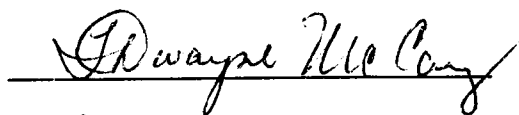
To the Graduate Council:

I am submitting herewith a dissertation written by Feng Sun entitled "**Optical Measurement of Particle Size Distribution Function Using Downhill Simplex Method: Theory and Experiment.**" I have examined the final copy of this dissertation for the form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of **Doctor of Philosophy**, with a major in **Physics**.

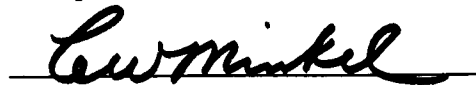


James W. L. Lewis, Major Professor

We have read this dissertation
and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

OPTICAL MEASUREMENT OF PARTICLE SIZE
DISTRIBUTION FUNCTION USING DOWNHILL SIMPLEX
METHOD; THEORY AND EXPERIMENT

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

Feng Sun

May, 1994

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Dedicated to:

谨献给:

My parents; 孙仲禹, 淑范,
我的双亲;

My wife; 凤娟, 及
我的妻子;

My children; 亦超, 亦星
我的孩子们;

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ABSTRACT

A new method is introduced for retrieving the particle size distribution function (PSDF) from optical measurements. Criteria are derived and demonstrated for assessing the validity of the multi-dimensional least-squares deconvolution results derived from experimental data. Using the covariance matrices **C** and the newly revealed **B**, stability of this deconvolution technique is discussed and compared with the linear inversion method. The relations of the variances of the PSDF parameters and the experimental errors have been derived and the effects and restrictions of the profiles for the PSDF have been discussed. All the theoretical predictions of this method are tested using Monte Carlo-simulated experimental data which consists of scattering and extinction measurements for water and soot particles, respectively. The results show that for water droplets of $1\mu m$ mean diameter, the method is good for $\pm 25\%$ random experiment error for scattering and $\pm 6\%$ for extinction. For the smaller soot particles $0.05\mu m$ mean diameter, the corresponding maximum error levels are $\pm 10\%$ and $\pm 6\%$, respectively. These differences in the scattering and extinction results are explained using information content analysis.

Experimental confirmation of these newly developed deconvolution technique was accomplished using multi-angle scattering measurements of a water droplet spray field. Sensitivity of the deconvolution to uncertainties in the index of refraction was determined using droplet compositions of water and laser-dye mixtures. The laser-dye concentration was varied to provide a variable and known imaginary term of the index

of refraction. A range of discrete laser wavelengths was used for this study to span the wavelength range of the variations of the index of refraction. The application of this deconvolution method yield, in addition to the PSDF parameters, the real and imaginary terms of the index of refraction which agreed with the computed values. A method was developed and verified for the proper treatment of the variation with observation angle of the scattering volume of the experiment, and the results were compared with those results using other correction methods for the experimental data of various optical configurations. Finally, the cause of the variation of the mean droplet size versus the concentration of laser-dye in the solution was investigated.

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LIST OF SYMBOLS AND ABBREVIATIONS

α	group of variables defined in Eq(2.2.1) or scale constant in Eq(3.2.10).
β	angle between the vectors of $\mathbf{d}$ and ϵ defined in Eq(3.3.3a) or scale constant in Eq(3.2.10) and Eq(5.2.7b).
β'	angle between the vectors $\mathbf{d}$ and ϵ defined in Eq(3.3.3b).
Γ	eigenvalue matrix for the dual-covariance matrix $\mathbf{B}$ as defined in Eq(2.4.2b).
γ	eigenvalue of $\mathbf{B}$ Eq(2.4.4), digital filter in linear inversion method [Eq(2.2.8)], or angular integration limits of the detector aperture [Eq(6.2.5a)].
ΔX	differentiation of X with respect to a variable.
$\delta(r)$	small deviation of kernel functions [Eq(5.2.8)].
ϵ, ϵ	measurement error vector or its component [Eq(2.3.1)].
ζ	angular integration limit defined in Eq(6.2.5b)].
η	view angle of detector as shown in Fig(6.2.1).
θ	scattering angle [Eq(3.2.12)].
Λ	eigenvalue matrix for the covariance matrix $\mathbf{C}$ [Eq(2.3.7b)].
λ	eigenvalue of the covariance matrix $\mathbf{C}$ [Eq(2.3.9a)] or light wavelength.
μ	one of the parameters of a log-normal distribution function [Eq(2.1.10)].
ν	degree of freedom in least square minimization [Eq(2.3.15)].
π_n	expansion coefficient of Mie kernels [Eq(2.1.8)].
σ	one of the parameters of a log-normal distribution function [Eq(2.1.10)] or the widths of various distribution functions as introduced in Chapter 3.
τ	intensity ratio of the scattered (or extinct) light and the incident light [Eq(2.1.5)] or the expansion coefficient of Mie kernels [Eq(2.1.8)].
χ	residual of the least square or deconvolution calculations [Eq(2.2.9)].
a	aperture sizes or the expansion coefficients of Mie kernels [Eq(5.1.7)].
$\mathbf{B}$	dual-covariance matrix [Eq(2.2.5a)].
$\mathbf{C}$	covariance matrix [Eq(2.2.7a)].

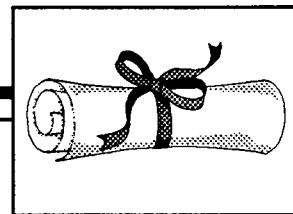
LIST OF SYMBOLS AND ABBREVIATIONS, continued

C	concentration of laser-dye solution [Eq(6.4.2)].
C_d, C_m	concentrations for dimmer or monomer laser-dye solution [Chapter 6].
C_e, C_s	extinction or scattering cross-sections [Eq(2.1.9)].
D	mean particle size [Eq(2.1.11)].
D_e	equilibrium constant of a laser-dye solution [Eq(6.4.2)].
$\mathbf{d}$	difference of the vectors $\mathbf{t}$ and $\mathbf{g}$ [Eq(2.3.1)].
d	particle size or diameter of a particle.
DHS	Downhill simplex deconvolution method.
$F(x)$	synthetic function for testing Gaussian quadrature method [Eq(3.2.7)].
$\mathbf{f}$	trial particle size distribution function (PSDF) in deconvolutions [Eq(2.2.10)].
$\mathbf{g}$	the true measurement data vector [Eq(2.2.9)].
$\mathbf{g}_e$	the error-added measurement data vector [Eq(2.2.9)].
GCM	Geometry Correction Method for scattering volume changing [Chapter 6].
$\mathbf{H}$	smooth matrix introduced in linear inversion method [Eq(2.2.8)].
K	Mie kernel functions [Eq(2.2.1)].
I	inner product of two functional vectors [Eq(5.1.1)].
k	optical constant (imagitive part of the index of refraction) [Eq(6.4.1)].
L	scattering or extinction length of the particle field [Eq(2.1.2)].
l	the integration variable of L [Eq(2.1.2)].
m	the number of integration points for particle size [Eq(2.2.2)], or the complex index of refraction [Eq(2.1.2)].
MC	Monte Carlo simulation method.
N	particle number density [Eq(2.1.3)].
N_1, N_2, N_3	N-numbers for violations of the criteria for deconvolutions [Eq(3.3.4)].
NL	number density times the scattering (or extinction) length [Eq(2.1.3)].
n	measurement number [Eq(2.2.1)] or real part of the index of refraction.
P	fraction number proportional to the magnitude of error [Eq(5.2.18)].

LIST OF SYMBOLS AND ABBREVIATIONS, continued

$p, p(r)$	true PSDF [Eq(2.1.10)].
PSDF	particle size distribution function.
R_D, R_V	relative variances of D, V [Eq(3.3.5)] or other quantity denoted by the subscript.
r	particle size or radius of a particle.
S_1, S_2	complex scattering matrix elements [Eq(2.1.8)].
t	trial vector in deconvolution [Eq(2.2.9)].
U	unitary transformation matrix for the covariance matrix C [Eq(2.3.7)].
u, u_i	eigenvector and its element of the covariance matrix C [Eq(2.3.7)].
V	unitary transformation matrix for the dual-covariance matrix B [Eq(2.4.2)].
V	variance of the log-normal PSDF [Eq(2.1.11)].
v, v	eigenvector and its element of the dual covariance matrix B [Eq(2.4.2)].
w_i	weight factor for Gaussian Quadrature integration algorithm [Eq(3.2.5)].
X	fraction of monomers in laser-dye solutions [Eq(6.4.1)].
x	size parameter of Mie theory [Eq(2.1.7)].
Y^2	control parameter for deconvolution calculations [Eq(3.3.1)].

Chapter 1



Introduction

It has long been a goal for researchers who deal with systems of small particles to acquire the ability to determine *in situ* the particles' size distribution function (PSDF), the local number density, and the complex index of refraction. The importance of these parameters to a broad range of fields^[1] such as astronomy, biophysics, chemistry, meteorology, remote sensing, environment monitoring, and combustion evaluation emphasizes the importance of developing a non-intrusive, accurate, and efficient method to achieve this goal.

The methods which have been developed and tested to obtain these parameters include optical scattering (or extinction), chemical dye solubilization, optical and electron microscopy, neural-networks, and sedimentation.^[2] Among these, the optical methods are the most commonly used because they do not need to take samples or place intrusive sensors in the system. The optical methods are absolute in the sense that the theory permits the reduction of the data directly to the final results. Other advantages of the optical methods compared to the other methods, include speed, accuracy, and convenience, and these advantages enable the optical methods to be most frequently applied to diverse particulate systems for *in situ* measurements, including some hostile environments such as a combustion chamber.

Among the many detecting methods for particle sizing are single particles counters and dual beam devices.^[2e,2f] These methods are restricted in nature to the study of dilute particle systems. They can not, in practice, be applied to the systems of high number density, systems of very small particles, such as soot particles in a flame, or those systems with large turbulent intensities such as some engine exhausts or combustion chambers. These methods will not be discussed in this dissertation.

Basically, there are two major categories optical methods for particle sizing; dynamical and static light-scattering methods. The dynamical scattering methods measure for the moving particles the scattered signals which are related to the velocity and position dynamical parameters of the particles. A typical method of dynamical scattering category is the diffusion-broadening spectroscopy (DBS) or Laser Doppler Spectroscopy (LDS).^[3] Specifically, DBS measures the auto-correlations of the light signals scattered by the moving particles in a flow field. The advantage of this type of method is that, in addition to the particle size information, the velocity of the particles can be determined. This method is suitable for small particles^[3a] (particle radius r smaller than the light wavelength λ), and the interpretation of the results is straightforward for monodisperse distributions. The other advantage of the DBS method is that the index of refraction of the particulate system is not needed. There are, however, some limitations for the DBS method. For example, the diffusion coefficient for each size group of the particle system must be known, deconvolutions are required for polydisperse distributions,^[3a] and the effects of non-spherical particles (such as rotational broadening) must be carefully evaluated.

The static optical methods will be simply referred to as the scattering method in this dissertation (extinction is just a special case of scattering with a zero scattering

angle). From hereafter, the word "scattering" means multi-angle scattering and "extinction" stands for multi-wavelength extinction throughout this dissertation and, because of the similarity of in mathematical form for scattering and extinction, most of the discussions and results are suitable to either of them. The scattering method,^[4] either the multi-angle scattering and multi-wavelength extinction method, are suitable for a diverse range of particle sizes ($r < \lambda$, or $r > \lambda$) and with such merits as simplicity in experiment set-up, speed in data acquisition, and applicability to *in situ* measurements for various hostile conditions. This method can be used for polydisperse particle size distributions. The results for a sample particle system discussed in Chapter 3 of this dissertation show that for a reasonably broad PSDF, this method can also yield a good result, using the data reduction method introduced in this dissertation. The major drawback of the scattering method is that the data reduction of the measurements is rather difficult, as will be discussed in this dissertation.

The goals of this dissertation are to develop and apply a method for the data reduction for the optical scattering techniques to obtain maximum information from the measurements, such as the particle size distribution function, number density, and the complex index of refraction of the particles. Although the discussion form hereafter is based on the static optical scattering method, the principles developed in this work can be applied to the dynamical optical method as well.

As will be seen in Chapter 2, the optical signal $g(\alpha_i)$ can be expressed as

$$g(\alpha_i) = \int_0^{\infty} K(\alpha_i, r) p(r) dr \quad i = 1, \dots, n \quad (1.1.1)$$

where $K(\alpha_i, r)$ is called Mie kernel function which has a complicated mathematical expression,^[4] α_i represents either the wavelength λ , for extinction case, or the scattering

angle θ_i for scattering case, and the radius r is used to denote a particle size. The integration over r sums the contributions from all particle sizes.

Equation (1.1.1) is a Fredholm integration equation of the first kind^[5,6] which has no known analytical solutions for the Mie kernels. It can be considered as a convolution of the kernel function $K(\alpha, r)$ with the PSDF $p(r)$. A direct problem is to calculate a set of $g(\alpha_i)$'s from a known PSDF $p(r)$ using (1.1.1), while any mathematical attempt of recovering the PSDF $p(r)$ from known g_i 's through (1.1.1) is called an inversion or deconvolution.

Although the experiments (for either scattering or extinction) are easily to be performed with relatively good precision, the data analysis for the scattering or extinction measurements is, unfortunately, very difficult^[6] to obtain the PSDF, and this is the major drawback of the optical methods. The major reason of this difficulty is because of the existence of the intrinsic correlations or inter-dependency of the optical signals,^[2a] as will be discussed in Chapter 5. Therefore, Mie equations like (1.1.1) gain the reputation of being ill-conditioned, which means the inversion or deconvolution of a Mie equation turns out to be difficult^[6]. Further, even for an ideal particulate system of spherical particles of uniform composition, the kernel function K in (1.1.1) still has a very complicated mathematical expression, and therefore the numerical calculation is lengthy and the physical insights are less obvious. Among the methods investigated to simplify the deconvolution of Eq.(1.1.1), a common approach is to approximate the Mie kernel function $K(\alpha, r)$ of Eq.(1.1.1) either in the large particle size limit^[7] (particle size r much larger than the wavelength λ of the light) or small particle size limit^[8] ($r \ll \lambda$). Some of the approximation methods treat Eq.(1.1.1) as special mathematical transformations. For example, reference [7a] uses the diffraction approximation (for

$r \gg \lambda$) and converts (1.1.1) into a Mellin transformation while Reference [8a] uses the Rayleigh-Gans approximation (for $r \ll \lambda$) for K and converts (1.1.1) into a Fourier transformation. As a consequence, the deconvolution of $p(r)$ can be performed and studied analytically, but these methods are not referred to as an inversion or deconvolution,^[9] as will be discussed in Chapter 5.

To seek a widely applicable deconvolution method which is suitable for the particles of any size range, however, the kernel function from Mie theory has to be used. The most widely used method for inverting Eq.(1.1.1) is called linear inversion method.^[6,9-12] Twomey and others have made tremendous contributions to this method and this method is adopted in many publications^[9-12] for particle sizing. The advantages of this method include: it is mathematically clear and direct, the functional form of the PSDF need not be known (or be guessed) beforehand, it can invert the particle size distribution in a histogram representation, and it can be used in diverse experimental data. As will be shown in chapter 2, a simple application of this method to experimental data will yield an unstable solution in $p(r)$. To remedy this deficiency of the linear inversion method, algorithms have been proposed to include a smoothing matrix and a digital filter,^[6] or other mathematical method involving lengthy derivations.^[9b-c] Even with these remedial algorithms, however, difficulties still exist to find the proper value of the digital filter for most cases and therefore the results may not be satisfactory.^[5] Generally, the magnitude of the digital filter is chosen on a trial and error basis.

From the discussion above, it is obvious that a widely applicable, rapid, accurate, and stable method for retrieval of the particle size distribution function from the optical measurements is needed.

A new method, which is called the Downhill Simplex (DHS) method, is introduced and developed in this dissertation for the retrieval of the PSDF for the optical measurements. As has been stated above, although the major procedure of this dissertation solves the full Mie equation (1.1.1) to obtain the PSDF $p(r)$ from the static optical scattering method, the principles of this method can be applied to the dynamic optical method.

To assess better the goodness of the new method, the following items are proposed which are the commonly acceptable criteria for the characterization of the method:

- (1) Information efficient — one can obtain the maximum amount of knowledge about the system with minimum input information.
- (2) Applicable to diverse situations — it should be valid for all related problems and to all other problems with similar mathematical formulation.
- (3) High accuracy and stability — the results must be quantitatively assessed based on mathematical relations and should yield accurate results even for large errors in the measurements.
- (4) Statistically faithful — the method should be capable of thorough simulation tests.
- (5) Predictable variances in final results — it should predict the uncertainties or confidence limits on the resultant parameters.
- (6) Information content evaluations — it should provide for the experimental system an evaluation of which combination of data points contains more information than others and which experiment is better for a certain system.
- (7) Provable by experiments — the predictions of the theory should be verified by the true experimental data with error bars.

To satisfy the requirements listed above, this dissertation includes both theoretical and experimental work and is divided into two parts: theory (chapters 2 to 5), and experiment (chapters 6 and 7).

The DHS method is based on a robust multi-dimensional curve fitting technique, and with the help of the least square analysis, can obtain accurate results for up to $\pm 25\%$ random errors in the experimental data. Because of the nature of the method, there are basically no input parameters required in addition to the experimental data and the method is applicable to any similarly formulated problems. Therefore, it satisfies criteria (1) and (2).

Chapter 2 demonstrates the satisfaction of criterion (3). Introducing the topics of scattering and extinction, a major relation for the DHS method is derived which specifies the relation between the fitted data and the experimental error. The stability of this method is discussed and compared with that of the linear inversion method. A matrix **B**, hereinafter called "dual-covariance matrix" is used for the first time in the discussion on the stability of a deconvolution method.

Chapter 3 demonstrates the satisfaction of criterion (4). By applying the Monte Carlo simulation technique to particle sizing, the statistical characteristics of the DHS method are obtained, and the predictions in Chapter 2 are verified. The conditions for the simulations and the details of the computation algorithm are discussed.

Chapter 4 exhibits that criterion (5) is satisfied. Starting from the major relation derived in Chapter 2, the relations are derived for the variances of the distribution parameters as a function of the experimental error ϵ . The restrictions set forth on the parameters of PSDF are discussed, and the related equations are given. These relations are also proved to be valid by the Monte Carlo simulation results.

Chapter 5 is provided to show that criterion (6) is satisfied. Beginning with the linear vector-space theory for the data of the optical signals, the information content for specific experimental data is discussed using the covariance $\mathbf{C}$. It is verified that, for the same number of the measurements, scattering has more information content than extinction. The criterion for information content is examined and tested. A detailed discussion is given for the first time on the dual-covariance matrix $\mathbf{B}$ which turns out to be able to tell, in principle, if a certain experimental set up could be used to retrieve PSDF for a certain system.

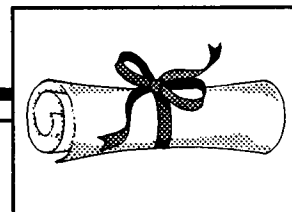
Chapter 6 and 7 show that criterion (7) is satisfied. In Chapter 6, scattering experiments are performed for pure water droplets to verify the DHS deconvolution method and the predictions in the previous chapters. A detailed discussion on the experimental conditions and data acquisition methods is described. The variation of the changes in the observed scattering volume with respect to the scattering angle is carefully examined, and a correction method is given. Three methods for the scattering volume correction are compared for the experimental data of different physical configurations, and the conditions for each method to be valid are discussed.

To extend the application of the DHS method to the absorbent particles, Chapter 7 studies the effects of the index of refraction of the particles on the retrieval of the PSDF. The index of refraction of the water droplets is systematically varied to see the effects of the physical properties of the particles on the results of the PSDF, by mixing laser-dye with water to form laser-dye solutions of different concentrations. A method for calculating the index of refraction of a solution of a known laser-dye concentration (within a certain concentration range) is revealed and tested by the experimental results. The cause of the observed systematic variation of the particle size as the index of

refraction of the particles is varied is also investigated. Simultaneous deconvolutions for 5 parameters including the particle size parameters, particle number density, and index of refraction yield very satisfactory results.

This dissertation is completed with a detailed summary of the major achievements of this work and the major conclusions are provided. Included also in this chapter are some further research topics that suggested for future study.

Chapter 2



Particle Sizing Using Downhill Simplex Method

In this chapter, a new method for obtaining particle size distribution function parameters from the optical scattering or extinction data is introduced. Section 1 briefly introduces the theory for light scattering by small particles. Section 2 discusses the inversion or deconvolution of PSDF, including the downhill simplex (DHS) non-linear multi-dimensional curve fitting algorithm. Section 3 derives the relations that a successful deconvolution using the DHS method should obey, and section 4 compares the stability of DHS method with other method.

§2.1 Light Scattering by an Ensemble Of Particles

Transmission and Scattering

A rigorous solution for the problem of light scattering by particles is based on Mie theory,^[4] as is commonly referenced. In order to comply with Mie theory, the following assumptions are made in this dissertation for all the particulate systems:

- (1) the particles are spherical in shape and uniform in composition,
- (2) the particles are randomly distributed in space, and
- (3) the number density of particles is moderate.

Assumption (1) enables the use of Mie theory of scattering and extinction; assumption (2) means that the scattering signals from different particles are independent

and therefore incoherent; and assumption (3) assures that single scattering events dominate the experimental data and there are always enough particles in the scattering volume so that the signal fluctuations are moderate.

From the Beer-Lambert law, the transmission formula for an incident light with wavelength λ , intensity I_0 (W/cm²) is:

$$\frac{I(\lambda)}{I_0(\lambda)} = \exp(-\tau_t), \quad (2.1.1)$$

where τ_t is called optical thickness. Let L be the optical length (the length of light beam intercepting the particle field); assumptions (1) and (2) allow τ_t to be written as

$$\tau_t = \int_0^L \int_0^\infty C_e(\lambda, r, l, m) n(r, l) dr dl. \quad (2.1.2)$$

Here, $C_e(\lambda, r, l, m)$ is the Mie extinction cross-section for each particle with radius r at spatial position l , $n(r, l)$ is the number density of particles with radius of $r - r+dr$ at the same location l , and m is the complex index-of-refraction (IOR) of the particles. The integration over r sums the contributions of all particles within the system. Using assumptions (2) and (3), the spatial dependence l can be ignored, and $n(r)$ can be expressed as

$$n(r) = Np(r),$$

where $p(r)$ is the particle size distribution function (PSDF) and N is the constant particle number density (cm⁻³). Now (2.1.2) can be written as

$$\tau_t = NL \int_0^\infty C_e(\lambda, r, m) p(r) dr. \quad (2.1.3)$$

Using the similar argument to the case of scattering yields

$$I_s(\Omega_0, \lambda, m) = I_0(\lambda) \tau_s(\Omega_0, \lambda, m) \quad (2.1.4)$$

$$\tau_s(\Omega_0, \lambda, m) = NL \int_0^\infty C_s(\Omega_0, \lambda, r, m) p(r) dr, \quad (2.1.5)$$

where C_s is the Mie differential scattering efficiency integrated over the solid angle subtended by the detector placed at direction of $\Omega_0 = (\theta_0, \phi_0)$. The integration in (2.1.2) over scattering length can not, in general, be replaced by simply multiplying by the length L . This issue will be addressed in Chapter 6.

Mie theory

The extinction and scattering cross-sections in equation (2.1.2) and (2.1.4) can be obtained from Mie theory and only the expressions for these cross-sections will be given here. Interested readers are referred to the books in [4] for detailed discussions.

A reference plane in scattering is defined as the plane contains the incident and scattering beams. The scattered field amplitudes at far zone for a spherical particle is

$$\begin{pmatrix} E_{\parallel s} \\ E_{\perp s} \end{pmatrix} = \frac{e^{ik(r_0 - z)}}{-ikr_0} \begin{pmatrix} S_2 & 0 \\ 0 & S_1 \end{pmatrix} \begin{pmatrix} E_{\parallel i} \\ E_{\perp i} \end{pmatrix}, \quad (2.1.6)$$

where the subscript i or s indicates incident or scattered electrical field component, respectively, and the subscript $\parallel$ or $\perp$ denotes the polarization direction of the electrical field of being parallel or perpendicular to the reference plane, respectively. The quantity r_0 is the distance between the scattering center and the detector, and $\mathbf{k}$ is the wave vector of the light.

The complex scattering matrix elements S_1 and S_2 depend on the complex index-

of-refraction m ($m = n + i k$ is wavelength dependent) of particles, scattering direction $\Omega_0 = (\theta_0, \phi_0)$, and size parameter x . For a particle with a radius r , the size parameter x is defined as:

$$x = \frac{2\pi r}{\lambda}. \quad (2.1.7)$$

S_1 and S_2 are given by:

$$\begin{aligned} S_1 &= \sum_{n=0}^{\infty} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n) \\ S_2 &= \sum_{n=0}^{\infty} \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n), \end{aligned} \quad (2.1.8)$$

where the expansion coefficients a_n , b_n , τ_n and π_n are functions of θ , ϕ , λ , m and r .

The scattering and extinction cross-sections are then

$$\begin{aligned} C_s(r, m, \theta_0, \phi_0, \lambda) &= \frac{1}{k^2} \int_{\Delta\Omega} d\Omega (|S_1|^2 \sin^2 \phi + |S_2|^2 \cos^2 \phi) \\ C_e(r, m, \lambda) &= \frac{2\pi}{k^2} \text{Re} \left[\sum_{n=0}^{\infty} (2n+1) (a_n + b_n) \right], \end{aligned} \quad (2.1.9)$$

where $\Delta\Omega$ is the solid angle subtended at the scattering center by the detector.

The profiles for the extinction and scattering efficiencies versus particle size parameter are plotted in Fig.(2.1.1) and (2.1.2) for two indices of refraction, respectively. The extinction (or scattering) efficiency for a particle is defined by the extinction cross section divided by the area of the particle. It is clear from the figures that the scattering curve has more structure than the extinction curve which results the difference in information content of scattering and extinction signals. This feature will be discussed in the subsequent chapters.

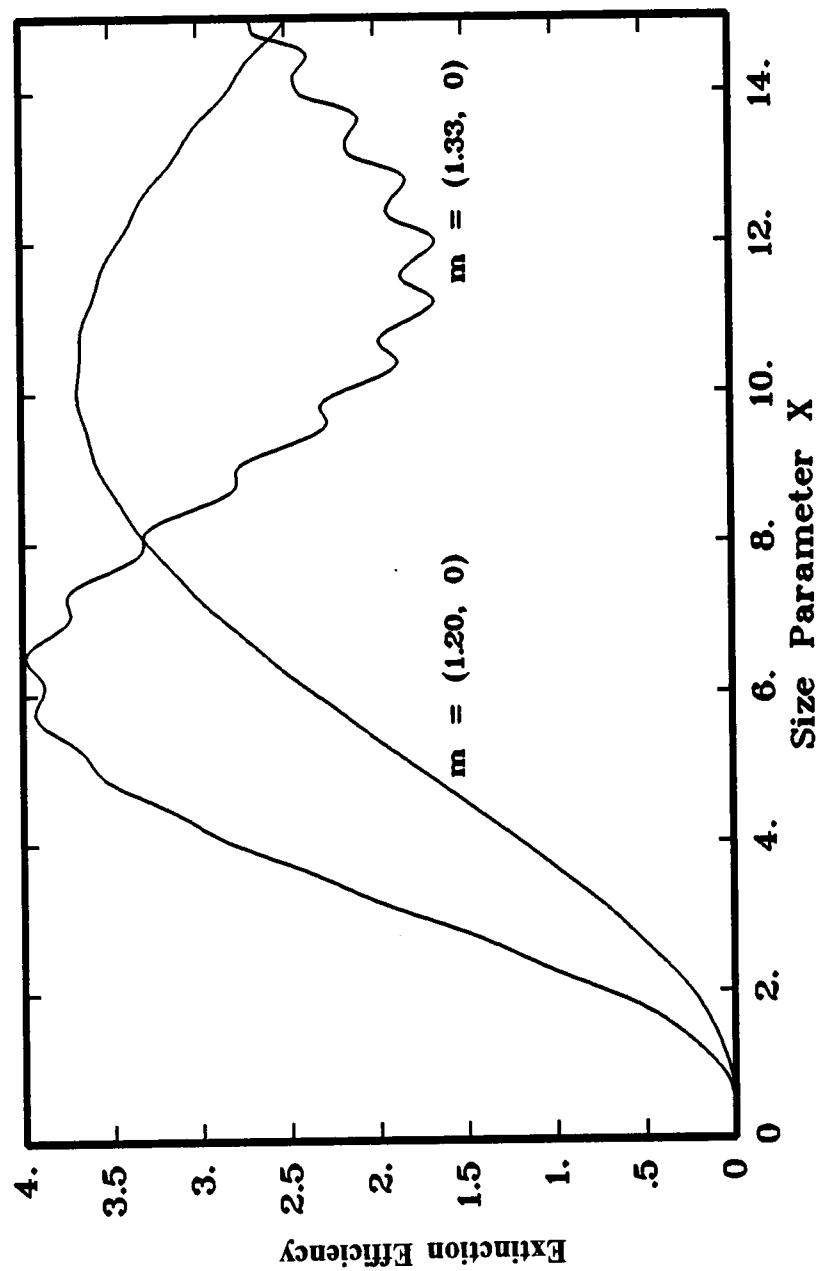


Figure 2.1.1 The extinction efficiencies vs. particle size parameters for materials with different index of refractions.

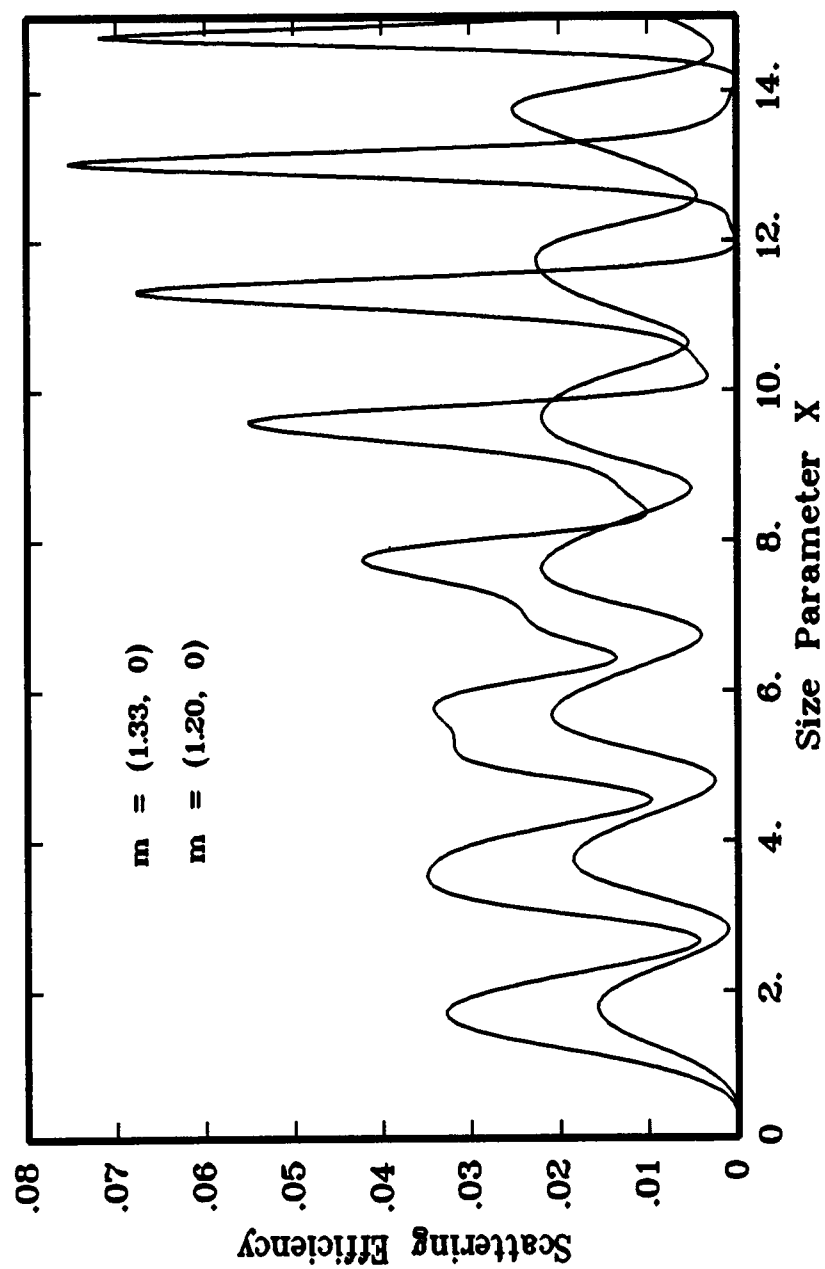


Figure 2.1.2 The scattering efficiencies at 90 degree for materials with different index of refraction. (1.33,0) upper curve and (1.20,0) lower curve.

Particle Size Distribution Function PSDF $p(r)$

The PSDF can be presented in different ways, such as histogram, tabular form, or analytically. The last form is utilized by many authors.^[5] The obvious advantage for a functional form of PSDF is the ease of evaluation without the need of interpolation or extrapolation. If needed, two or more analytical functions can be linearly combined to form a bimodal distribution.

The best known distribution function is the normal distribution, but it is rarely used because negative particle size is allowed there and the exact symmetry of the curve is not a good model for a natural particulate system.^[4a] A commonly used PSDF is the log-normal distribution of particle diameter d

$$p(d) = \frac{1}{\sqrt{2\pi}\sigma d} \exp\left[-\frac{(\log d - \mu)^2}{2\sigma^2}\right], \quad (2.1.10)$$

where the parameters μ and σ are related to the mean D and standard variance V by

$$\begin{aligned} D &= \exp\left(\mu + \frac{\sigma^2}{2}\right) \\ V^2 &= \exp(2\mu + \sigma^2)[\exp(\sigma^2) - 1]. \end{aligned} \quad (2.1.11)$$

An example of the log-normal distribution is plotted in Fig.(2.1.3). Although the log-normal distribution is adopted in the subsequent discussions, the results are, however, suitable to any other distribution function as well.

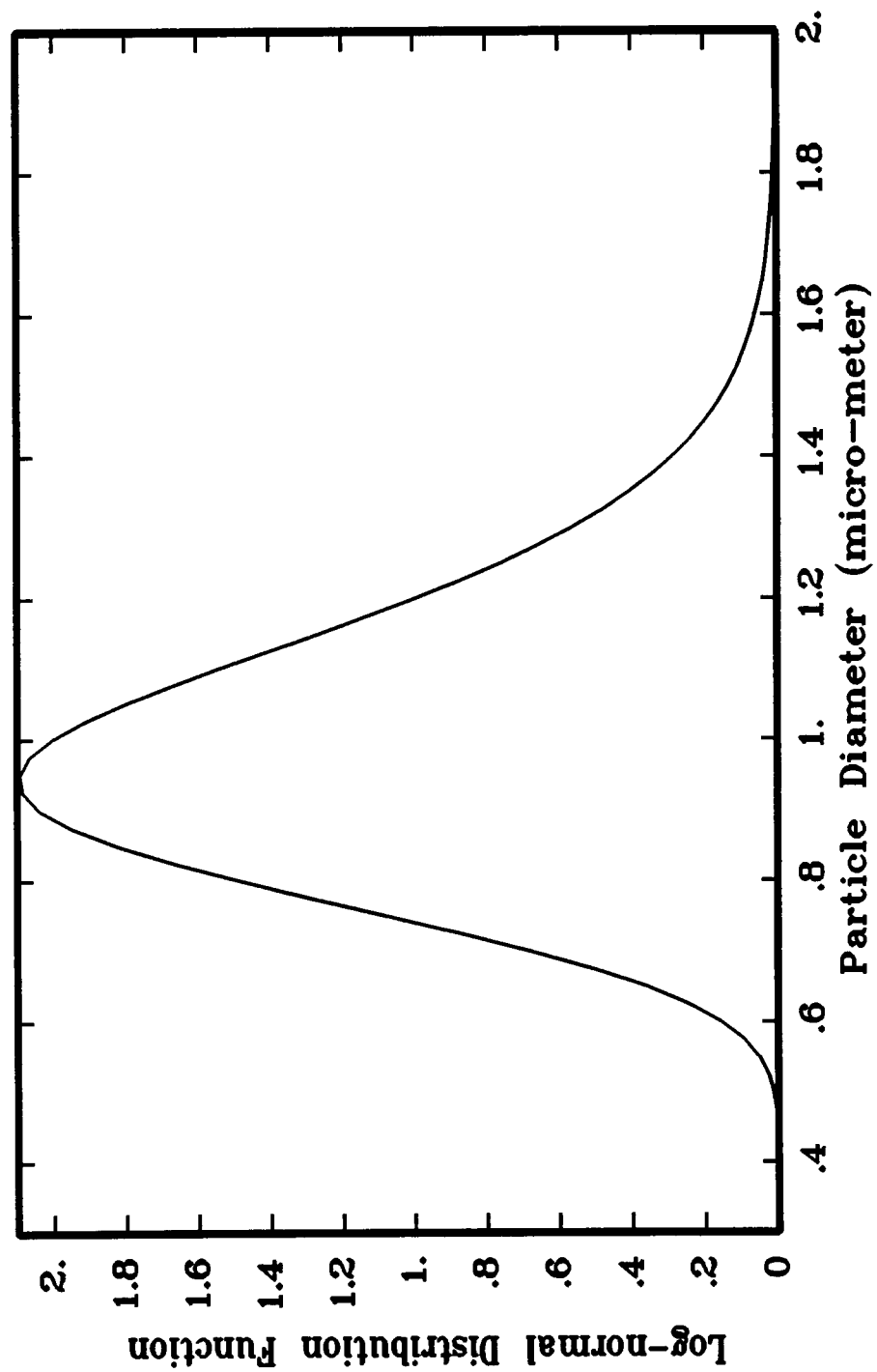


Figure 2.1.3 A log-normal distribution with $D = 1$ and $V = 0.2$.

§2.2 Deconvolution of Particle Size Distribution Functions (PSDF)

Omitting the constant N and L for the moment, the expressions of (2.1.3) and (2.1.5) can be written in a general form as has been seen in Chapter 1:

$$g(\alpha_i) = \int_0^{r_{\max}} K(\alpha_i, r) p(r) dr \quad i = 1, \dots, n \quad (2.2.1)$$

where $K(\alpha_i, r)$ is the kernel function, α_i represents the parameter groups of either (λ, m) or (Ω, λ, m) for extinction and scattering, respectively. Also, either radius r or diameter d is used to denote a particle size.

Linear Inversion

The most commonly used method to recover the PSDF $p(r)$ is called linear inversion. Twomey^[6,9,10] and others^[11-14] have made tremendous contributions to linear inversion method and this method seems to be mature and is widely used by many researchers.

The linear inversion algorithm, using linear space concepts, digitizes equation (2.2.1) as the dot product of two m component function vectors like:

$$g(\alpha_i) = \sum_{j=1}^m K(\alpha_i, r_j) p(r_j) \quad \text{or} \quad g_i = \sum_{j=1}^m K_{ij} p_j, \quad i=1, \dots, n \quad (2.2.2)$$

or in matrix notation

$$\mathbf{g} = \mathbf{K} \cdot \mathbf{p}, \quad (2.2.3)$$

where $\mathbf{g}$ is a $n \times 1$ column vector and $\mathbf{p}$ is a $m \times 1$ column vector. The $n \times m$ matrix $\mathbf{K}$, depending on the numerical algorithm, may contain a weight function. If $\mathbf{K}$ is a

square matrix ($n=m$) and its inverse K^{-1} exists, a direct solution would be

$$p = K^{-1} \cdot g.$$

If K is not a square matrix ($n \neq m$), the solution takes the form of

$$p = (K^+ K)^{-1} K^+ \cdot g,$$

or

$$p = B^{-1} K^+ \cdot g \quad (2.2.4)$$

where the $^+$ denotes matrix transpose. The real, positive definite, symmetric matrix B , which is defined to be the dual-covariance matrix and will be utilized in the next section for stability discussion, is:

$$B = K^+ \cdot K, \quad (2.2.5a)$$

where

$$B_{ij} = \sum_{k=1}^m K(\alpha_k, r_i) K(\alpha_k, r_j). \quad (2.2.5b)$$

Twomey *et. al.* pointed out that the solution in equation (2.2.3) or (2.2.4) is not stable because of the ill-conditioned nature of the Mie equations corresponding to the heavy inter-dependence between the kernels. In fact, for a finite measurement error vector ϵ (any experiments contain some error, of course), the error in $p(r)$ would be^[9]

$$|\delta p(r)|^2 = \sum_{i=1}^n \frac{\epsilon_i^2}{\lambda_i}, \quad (2.2.6)$$

where λ_i is the i th eigenvalue of the covariance matrix C which is defined as

$$C = K \cdot K^+, \quad (2.2.7a)$$

and

$$C_{ij} = \int_0^{r_{\max}} K(\alpha_i, r) K(\alpha_j, r) dr \approx \sum_{k=1}^m K(\alpha_i, r_k) K(\alpha_j, r_k). \quad (2.2.7b)$$

Because the Mie kernels are highly dependent on each other, the off-diagonal elements of $\mathbf{C}$ are therefore relatively large, which results in some very small eigenvalues of $\mathbf{C}$, e.g.^[10] $\lambda_{\min} \sim 10^{-6}$. These small eigenvalues will definitely magnify the measurement error ϵ in (2.2.6) and yield an unstable solution in $p(r)$. To solve this problem, one could introduce a smoothing matrix $\mathbf{H}$ and use a Lagrangian multiplier γ as a digital filter to eliminate the influence of small eigenvalues of the matrix $\mathbf{C}$. Equation (2.2.4) then becomes

$$\mathbf{p} = (\mathbf{B} + \gamma \mathbf{H})^{-1} \cdot \mathbf{K}^+ \cdot \mathbf{g}. \quad (2.2.8)$$

An inversion using equation (2.2.8) is a constrained linear inversion in which the value of γ represents the degree of constraint. An inconvenience of (2.2.8) is that $\mathbf{H}$ and γ must be chosen carefully in order to obtain good results. If γ is too large, one finds an over-constrained solution which gives a larger error than the overall error ϵ in $\mathbf{g}$ due to all causes (experimental error, quadrature error, etc.) because some of the useful information in the data might have been filtered out. If γ happens to be too small, one has an under-constrained solution in which part of error ϵ has been inverted back to $p(r)$ yielding oscillations in the solution. In general, γ is determined on a trial-and-error basis.

Downhill Simplex (DHS) Deconvolution Method

Aiming to use minimum input information, the DHS multi-dimensional curve fitting technique is applied to the particle sizing problem to invert the PSDF and other

parameters from the experimental data. Originating from Nelder and Meed^[15,16] this method finds the location of the minimum (or maximum) for a function by adjusting the M parameters (for a M -dimensional problem) in a certain way. Once the minimum location is found, the final set of parameters is the answer.

A simplex is a geometrical figure formed (for a M dimensional problem) by $M+1$ points in a M dimensional coordinate system including all polygonal faces and lines connecting the points. For a three dimensional problem, a simplex is a tetrahedron as shown in Fig.(2.2.1).

To start a simplex, one guesses any reasonable locations of $M+1$ points which constitute the initial simplex. The program then evaluates the function at each point and sorts them according to their values. It then makes a reflection from the highest point (with the largest function value) across the opposite face of the simplex to reach a lower point as shown in Fig.(2.2.1). The simplex would then be expanded or contracted in one or more directions according to the function value at each point. The computation is considered to be converged when the difference in function values between the maximum and minimum among the $M+1$ points of the final simplex is negligible. Consequently, the volume of the final simplex would be so small that it could be thought of as a single point. Interested readers are referred to references [15,16] for a detail description.

Let $\mathbf{g}_e = \mathbf{g} + \epsilon$ be the experimental data vector, $\mathbf{g}$ the true data, and ϵ the experiment error. Denoting $\mathbf{t}$ as the trial data, the function to be minimized in this work is

$$\chi^2 = (\mathbf{t} - \mathbf{g}_e)^2 = (\mathbf{t} - \mathbf{g} - \epsilon)^2, \quad (2.2.9)$$

with

$$\mathbf{t} = \mathbf{K} \cdot \mathbf{f}$$

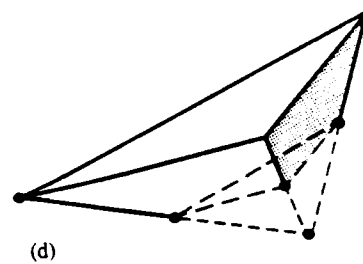
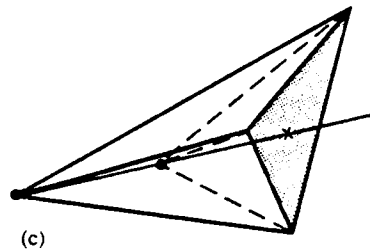
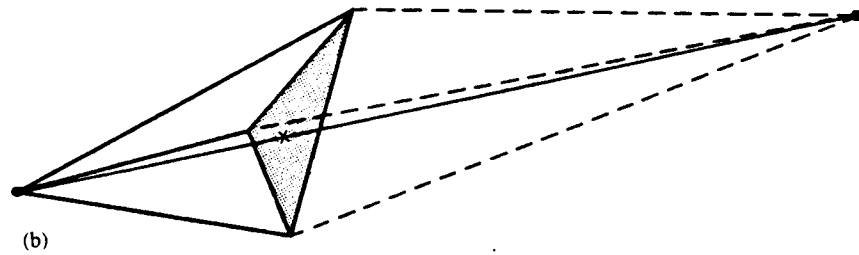
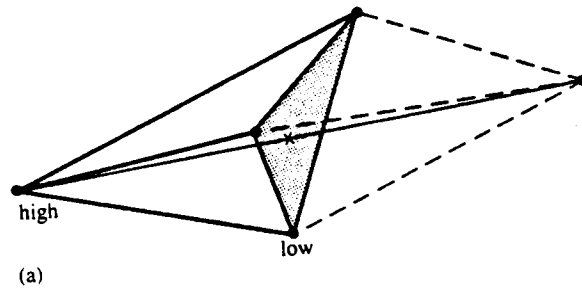


Figure 2.2.1 A sample of the adjustment for a 3-dimensional simplex, (a) a reflection away from a high point, (b) a reflection and expansion away from a high point, (c) a contraction along one dimension from the high point, or (d) a contraction along all dimensions toward the low point. Source, Reference [16].

$$\mathbf{g} = \mathbf{K} \cdot \mathbf{p}, \quad (2.2.10)$$

where $\mathbf{f}$ is the trial vector for the true PSDF $p(r)$. Equation (2.2.9) is the familiar least-square fit. In these deconvolutions, the trial vector $\mathbf{t}$ is changed by changing the trial distribution function vector $\mathbf{f}$, through adjusting the size distribution parameters μ and σ in (2.1.10), and therefore D and V in (2.1.11), to obtain the best fit. Other parameters such as number density N and complex index of refraction m can also be adjusted to obtain more information from a set of data, as will be seen later.

It is obvious that the judgement of goodness of fit is a key issue for any curve fitting technique. The next step is to investigate what is the condition that a good deconvolution must satisfy.

§2.3 Criteria for Goodness of Fit and Stability Analysis

Least Square Minimization

Hereafter, a matrix notation is used when possible to simplify the derivation. Vectors and matrices are in bold faces, and a dot represents a product between two vectors.

Equation (2.2.9) is now written as

$$\chi^2 = [\mathbf{K} \cdot (\mathbf{f} - \mathbf{p}) - \boldsymbol{\epsilon}]^+ \cdot [\mathbf{K} \cdot (\mathbf{f} - \mathbf{p}) - \boldsymbol{\epsilon}] = (\mathbf{d} - \boldsymbol{\epsilon})^+ \cdot (\mathbf{d} - \boldsymbol{\epsilon}) \quad (2.3.1)$$

where

$$\mathbf{d} = \mathbf{t} - \mathbf{g} = \mathbf{K} \cdot (\mathbf{f} - \mathbf{p}).$$

In searching for the minimum of (2.3.1), partial derivatives are applied to χ^2 with respect to the vector $\mathbf{f}$:

$$\partial \chi^2 / \partial \mathbf{f} = 0. \quad (2.3.2)$$

Vector $\mathbf{f}$ has m components $\mathbf{f} = \sum f_k \mathbf{e}_k$, $k = 1, \dots, m$, where $\mathbf{e}_k$ is the unit vector. From (2.3.2), one thus finds m equations of the form

$$\partial \chi^2 / \partial f_k = 0, \quad k = 1, \dots, m$$

$$\text{or} \quad \mathbf{e}_k^+ \cdot \mathbf{K}^+ \cdot \mathbf{K} \cdot \mathbf{f} + \mathbf{f} \cdot \mathbf{K}^+ \cdot \mathbf{K} \cdot \mathbf{e}_k - 2 \mathbf{e}_k^+ \cdot \mathbf{K}^+ \cdot \mathbf{K} \cdot \mathbf{p} - 2 \boldsymbol{\epsilon}^+ \cdot \mathbf{K} \cdot \mathbf{e}_k = 0. \quad (2.3.3)$$

Since each term in (2.3.3) is a real quantity and therefore the first two terms are equal. Equation (2.3.3) leads to

$$2 \mathbf{e}_k^+ \cdot (\mathbf{K}^+ \cdot \mathbf{K} \cdot \mathbf{f} - \mathbf{K}^+ \cdot \mathbf{K} \cdot \mathbf{p} - \mathbf{K}^+ \cdot \boldsymbol{\epsilon}) = 0.$$

Since $\mathbf{e}_k \neq 0$,

$$\mathbf{K}^+ \mathbf{K} \cdot (\mathbf{f} - \mathbf{p}) = \mathbf{K}^+ \boldsymbol{\epsilon} \quad (2.3.4)$$

$$\text{or} \quad \mathbf{K}^+ \cdot (\mathbf{t} - \mathbf{g}) = \mathbf{K}^+ \boldsymbol{\epsilon}. \quad (2.3.5)$$

Multiplying each side of (2.3.5) by its transpose results in

$$(\mathbf{t} - \mathbf{g})^+ \cdot \mathbf{K} \cdot \mathbf{K}^+ \cdot (\mathbf{t} - \mathbf{g}) = \boldsymbol{\epsilon}^+ \cdot \mathbf{K} \cdot \mathbf{K}^+ \cdot \boldsymbol{\epsilon}. \quad (2.3.6a)$$

It is seen that the $n \times n$ matrix $\mathbf{K} \cdot \mathbf{K}^+$ is just the covariance matrix $\mathbf{C}$ defined in (2.2.7). Equation (2.3.6a) can then be expressed as

$$(\mathbf{t} - \mathbf{g})^+ \cdot \mathbf{C} \cdot (\mathbf{t} - \mathbf{g}) = \boldsymbol{\epsilon}^+ \cdot \mathbf{C} \cdot \boldsymbol{\epsilon}. \quad (2.3.6b)$$

Assuming λ_i is the i th eigenvalue of $\mathbf{C}$ with an eigenvector $\mathbf{u}_i$, then the unitary matrix $\mathbf{U}$ will diagonalize $\mathbf{C}$ into its eigenvalue matrix Λ , where

$$\mathbf{U} = (\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_n), \quad \mathbf{U}^+ \cdot \mathbf{U} = \mathbf{U} \cdot \mathbf{U}^+ = \mathbf{I}. \quad (2.3.7a)$$

$$\Lambda = \mathbf{U}^+ \mathbf{C} \mathbf{U} = \begin{pmatrix} \lambda_1 & & \\ & \lambda_2 & \\ & & \ddots \\ & & & \lambda_n \end{pmatrix}. \quad (2.3.7b)$$

For n -dimensional vectors $\mathbf{y}$ and $\mathbf{y}^+$, their unitary transformations are

$$\mathbf{y}' = \mathbf{U}^+ \cdot \mathbf{y}, \quad (2.3.7c)$$

$$\mathbf{y}^{+'} = \mathbf{y}^+ \cdot \mathbf{U}. \quad (2.3.7d)$$

Inserting $\mathbf{U} \cdot \mathbf{U}^+ = \mathbf{I}$ before and after matrix $\mathbf{C} = \mathbf{K} \cdot \mathbf{K}^+$ on both sides of (2.3.6b)

and applying (2.3.7b - d), Eq.(2.3.6b) can be written as:

$$(\mathbf{t}' - \mathbf{g}')^+ \cdot \Lambda \cdot (\mathbf{t}' - \mathbf{g}') = \epsilon'^+ \cdot \Lambda \epsilon'. \quad (2.3.8)$$

Eq.(2.3.8) can be written explicitly as

$$\sum_{i=1}^n \lambda_i (t'_i - g'_i)^2 = \sum_{i=1}^n \lambda_i \epsilon_i^2, \quad (2.3.9a)$$

or

$$\sum_{i=1}^n \lambda_i [(t'_i - g'_i)^2 - \epsilon_i^2] = 0. \quad (2.3.9b)$$

Since $\mathbf{C}$ is a positive definite symmetrical matrix, its eigenvalues are all positive, $\lambda_1 > \lambda_2 > \dots > \lambda_n > 0$. Using the mean value theorem, one can always find a number $\lambda' > 0$ ($\lambda_1 > \lambda' > \lambda_n$) so that

$$\lambda' \sum_{i=1}^n [(t'_i - g'_i)^2 - \epsilon_i^2] = 0, \quad (2.3.9c)$$

or

$$\sum_{i=1}^n (t'_i - g'_i)^2 = \sum_{i=1}^n \epsilon_i^2. \quad (2.3.9d)$$

Because the unitary transformation (2.3.7) does not change the length of a vector, one can obtain

$$\sum_{i=1}^n (t_i - g_i)^2 = \sum_{i=1}^n \epsilon_i^2 \quad (2.3.9e)$$

or

$$d = |\mathbf{t} - \mathbf{g}| = |\boldsymbol{\epsilon}|. \quad (2.3.10)$$

Equation (2.3.10) says that for a successful deconvolution using the curve fitting method, the length of $\mathbf{d} = \mathbf{t} - \mathbf{g}$, the difference vector between fitted and true data vectors, must equal to the length of the error vector ϵ . For a special case $\epsilon = 0$, one has $\mathbf{t}=\mathbf{g}$ from (2.3.10) which leads to the obvious result of $\mathbf{f} = \mathbf{p}$.

Criteria for Goodness of Fit

In the derivations above, the kernel function $\mathbf{K}(\alpha, r)$ was kept unchanged. In any numerical calculation, however, the upper limit of particle radius $r_{\max}$ in (2.3.1) is changed whenever the PSDF is modified because of the quadrature algorithm used. Any variation in $r_{\max}$ will cause a change in locations of abscissas and therefore, a change in the values of the kernel function and the trial PSDF $\mathbf{f}$. As a result, the vector which is actually varied in the fitting procedure is $\mathbf{d}$ rather than $\mathbf{f}$ in (2.3.1). If ϵ is a totally random error vector, the experimental data $\mathbf{g}_e$ will not form a smooth curve if the measurement points are sufficiently dense. The real and trial vectors $\mathbf{g}$ and $\mathbf{t}$, respectively, are, however, smooth curves which depend on Mie kernels. As a result of this character, the resultant optimum vector $\mathbf{t}$ is usually closer to $\mathbf{g}$ rather than to $\mathbf{g}_e$. This behavior will be shown in a plot of the simulation results in Section 3.3.

To visualize better the vectorial relations of all the previously introduced vectors, one can imagine a simple experiment in which only three measurements (g_1, g_2, g_3) have been made, with related errors ($\epsilon_1, \epsilon_2, \epsilon_3$), see the vector relations in Fig.(2.3.1) and Fig.(2.3.2). The measurements are assumed to be optimal in the sense that the corresponding kernel functions (K_1, K_2, K_3) are independent (orthogonal to each other).

Figure.(2.3.1) shows the 3-dimensional relations for the vectors of $\mathbf{t}$, $\mathbf{g}$, $\mathbf{g}_e$, etc. The 2-dimensional relation for the vectors of $\mathbf{t}$, $\mathbf{d}$ and ϵ is shown in Figure (2.3.2).

As will be discussed in Chapter 3, the simulation results show that in most cases, Eq.(2.3.10) should be re-written as

$$d = |\mathbf{t} - \mathbf{g}| < |\chi| \leq |\epsilon|. \quad (2.3.11)$$

Although a rigorous derivation of (2.3.11) is not readily obtainable from the previous discussions, an intuitive examination can lead to the same result. According to statistics, the mean value of a chi-square distributed quantity q^2 equals its degree of freedom.^[16] For a least-square curve fitting procedure through which j parameters are to be obtained, the mean value of q^2 (the parameter to be minimized) which consists of a summation of n terms, satisfies

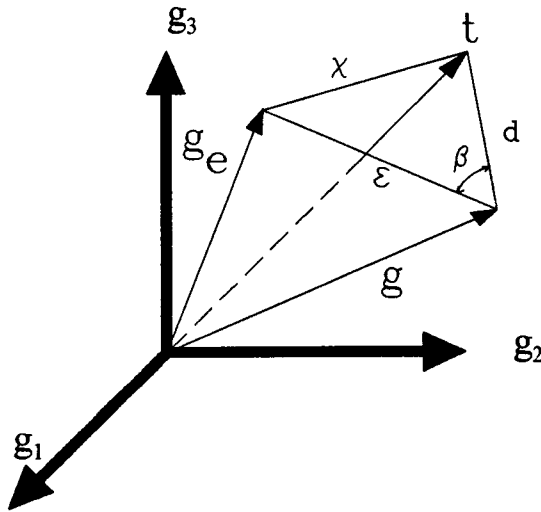


Figure 2.3.1 The geometrical relation of vectors $\mathbf{t}$, $\mathbf{g}_e$ and $\mathbf{g}$.

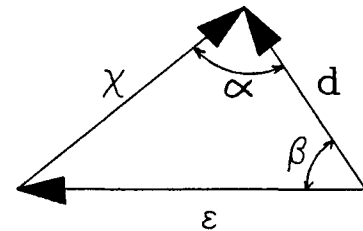


Figure 2.3.2 The geometrical relation of vectors $\mathbf{d}$, χ , and ϵ .

$$\overline{q^2} = \sum_{i=1}^n \left(\frac{t_i - g_{e_i}}{\epsilon_i} \right)^2 = n - j = v.$$

This is the same as the χ^2 in (2.3.1) except for a weight factor ϵ_i^{-1} . If $\epsilon_{\min}$ ($\epsilon_{\max}$) is the minimum (maximum) component of ϵ , a mean error $e^2 = \langle \epsilon^2 \rangle / n$ can always be found such that

$$\epsilon_{\min}^2 \leq e^2 \leq \epsilon_{\max}^2$$

and the expression for q^2 has the form of

$$\overline{q^2} e^2 = (n - j) e^2 = \frac{n - j}{n} \overline{\epsilon^2} \leq \overline{\epsilon^2}.$$

This equation is actually the relation between the mean values of χ and ϵ

$$\overline{\chi_{\min}^2} = \sum_{i=1}^n \overline{(t_i - g_{e_i})^2} = \frac{n - j}{n} \overline{\epsilon^2} \leq \overline{\epsilon^2}. \quad (2.3.12a)$$

which explains the second part of the simulation results indicated by Eq.(2.3.11).

The first part of Eq.(2.3.11) can be interpreted by considering Eq.(2.3.1) which can be alternatively expressed as

$$\chi^2 = (\mathbf{d} - \boldsymbol{\epsilon})^+ \cdot (\mathbf{d} - \boldsymbol{\epsilon}) = d^2 + \epsilon^2 - 2 d \epsilon \cos \beta, \quad (2.3.12b)$$

where β is the angle between vectors $\mathbf{d}$ and $\boldsymbol{\epsilon}$. As has been mentioned, the quantities that is varied in the deconvolution is $\mathbf{t}$ (or $\mathbf{d}$) and this will lead to the changes in the quantities d and β in the above expression. Because of Eq.(2.3.13), the restriction imposed on β can be expressed as

$$\beta < \alpha$$

where α is the angle between the vectors χ and ϵ , as shown in Fig.(2.3.2). Introducing a Lagrangian multiplier λ , the equivalent function (replacing χ^2) to be minimized is given by

$$Y = d^2 + \epsilon^2 - 2d\epsilon\cos(\beta) + \lambda(\beta - \alpha + \delta^2),$$

and the constraint for β has been assumed to be

$$\beta - \alpha - \delta^2 = 0,$$

where the positive quantity δ^2 was introduced to make the constraint an equality.

The minimum of Y can be obtained by setting

$$\begin{cases} \frac{\partial Y}{\partial d} = 0 \\ \frac{\partial Y}{\partial \beta} = 0 \\ \frac{\partial Y}{\partial \delta} = 0, \end{cases} \quad (2.3.13a)$$

and one finds from (2.3.13a) using (2.3.12b)

$$\begin{cases} d = \epsilon \cos(\beta) \\ \chi = \epsilon \sin(\beta) \\ \delta \rightarrow 0_+ \\ \beta \rightarrow \alpha_- \end{cases} \quad (2.3.13b)$$

which implies that d , χ and ϵ form a right triangle with ϵ the hypotenuse ($\beta' \leq 90^\circ$). The last relation in above expression means that angle β will not be larger than α , the angle between the vectors χ and ϵ . If β is sufficiently large (close to α), one finds

$$d^2 < \chi^2_{min} \leq \epsilon^2, \quad (2.3.14a)$$

which is exactly the same as Eq.(2.3.11). For an experiment in which d is not known, the last part of (2.3.14a) can be used to assess the quality of the deconvolution, or

$$\chi^2_{exp} \leq \epsilon^2_{exp}. \quad (2.3.14b)$$

The derivation for (2.3.13b) is for an individual deconvolution case with the aid of Eq.(2.3.12a) (as the constraint) which is held for the mean values of χ and ϵ . Therefore, the resultant equations (2.3.14ab) are always true only in the sense that all the quantities should be replaced with the appropriate mean values, within certain error margins.

In the computer simulations (detailed in Chapter 4), there do exist some very good individual deconvolutions in which that $d \ll \chi$ Equation (2.3.14a) was observed for non-averaged values of d , χ , and ϵ . For all successful deconvolutions, the mean values observe Eq.(2.3.14a) very well. A table for all relevant quantities will be given in Chapter 3 to show the details.

Equation (2.3.14b) is appropriate to use for the realistic experimental data for which d is not available. It says that a good deconvolution should give such a result in which the difference between the fitted and experiment data should be very close to the overall random measurement error. Another interesting fact is that (2.3.14a) gives an upper limit for the angle β' between $\mathbf{d}$ and ϵ ($\beta' < 90^\circ$). From a deconvolution of synthetic data for which all $\mathbf{d}$, χ , and ϵ are known, one can calculate and compare the angles β and β' through (2.3.12b) and (2.3.13b).

In all the above derivations, the kernel functions of Eq.(2.3.1) were assumed

to be independent each other and each could provide independent information about the PSDF. In fact, unfortunately, the Mie kernels ($K_1, K_2, \dots$) of the optical scattering or extinction signals are highly interdependent and hence form a skewed coordinate system. This character will definitely restrict the information content in the optical measurements. This topic will be discussed in Chapter 5.

The minimization results (2.3.13ab) and the subsequent derivations, as well as the results obtained so far, are suitable for any form of PSDF, such as log-normal distributions. Because a log-normal PSDF has been adopted in the discussion, adjusting the components f_k of the trial PSDF $\mathbf{f}$ in searching for the minimum in χ^2 can now be accomplished through changing the two parameters D and V , and the results should also obey the general criteria (2.3.14a,b). A detailed discussion of such procedures is given in Chapter 3.

§2.4 Stability Comparison and Covariance Matrices C and B

To test the stability of the DHS method and to compare it with the linear inversion results (2.2.6), one needs an expression for the error in PSDF $p(r)$.

Beginning with (2.3.4) and multiplying each side by its transpose, one can obtain

$$(\mathbf{f} - \mathbf{p})^+ \cdot \mathbf{K}^+ \cdot \mathbf{K} \cdot \mathbf{K}^+ \cdot \mathbf{K} \cdot (\mathbf{f} - \mathbf{p}) = \boldsymbol{\epsilon}^+ \cdot \mathbf{K} \cdot \mathbf{K}^+ \cdot \boldsymbol{\epsilon}, \quad (2.4.1a)$$

$$\text{or} \quad (\mathbf{f} - \mathbf{p})^+ \cdot \mathbf{B} \cdot \mathbf{B} \cdot (\mathbf{f} - \mathbf{p}) = \boldsymbol{\epsilon}^+ \cdot \mathbf{C} \cdot \boldsymbol{\epsilon}. \quad (2.4.1b)$$

Here, matrix $\mathbf{B} = \mathbf{K}^+ \mathbf{K}$ is nothing but the dual-covariance matrix, which was employed in (2.2.8). Just like matrix $\mathbf{C}$, $\mathbf{B}$ is a real, symmetric and positive definite matrix with

all positive eigenvalues.

Using the same treatment as for $\mathbf{C}$ in (2.3.6) and assuming γ_i to be the i th eigenvalue of $\mathbf{B}$ with the eigenvector $\mathbf{v}_i$, the unitary matrix $\mathbf{V}$ can diagonalize $\mathbf{B}$ into its eigenvalue matrix $\mathbf{\Gamma}$, where

$$\mathbf{V} = (\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_n), \quad \mathbf{V}^+ \cdot \mathbf{V} = \mathbf{V} \cdot \mathbf{V}^+ = \mathbf{I}, \text{ and} \quad (2.4.2a)$$

$$\mathbf{\Gamma} = \mathbf{V}^+ \mathbf{B} \mathbf{V} = \begin{pmatrix} \gamma_1 & & & \\ & \gamma_2 & & \\ & & \ddots & \\ & & & \gamma_n \end{pmatrix}. \quad (2.4.2b)$$

Applying the same diagonalization procedures to (2.4.1) as was performed for Eq.(2.3.7), one can obtain

$$(\mathbf{f}' - \mathbf{p}')^+ \cdot \mathbf{\Gamma}^2 \cdot (\mathbf{f}' - \mathbf{p}') = \epsilon'^+ \cdot \mathbf{\Lambda} \cdot \epsilon'. \quad (2.4.3)$$

Writing (2.4.3) explicitly, one finds

$$\sum_{j=1}^m \gamma_j^2 (f'_j - p'_j)^2 = \sum_{i=1}^n \lambda_i \epsilon_i'^2. \quad (2.4.4)$$

Define the weighted average values for $\mathbf{f}' - \mathbf{p}'$ and ϵ as

$$\langle (f-p)^2 \rangle = \frac{\sum_{j=1}^m \gamma_j^2 (f'_j - p'_j)^2}{\sum_{j=1}^m \gamma_j^2} \quad (2.4.5a)$$

$$\langle \epsilon^2 \rangle = \frac{\sum_{i=1}^n \lambda_i \epsilon_i^2}{\sum_{i=1}^n \lambda_i}, \quad (2.4.5b)$$

Equation (2.4.4) can now be written as

$$\langle (f-p)^2 \rangle = \langle \epsilon^2 \rangle \frac{\sum_{i=1}^n \lambda_i}{\sum_{j=1}^m \gamma_j^2}. \quad (2.4.6)$$

Although the covariance matrix **C** does not equal its dual matrix **B**, even when they have the same dimension, their traces are identical:

$$\begin{aligned} \text{tr}(\mathbf{C}) &= \text{tr}(\mathbf{K}\mathbf{K}^+) = \sum_{i=1}^n (\mathbf{K}\mathbf{K}^+)_{ii} = \sum_{i=1}^n \left(\sum_{j=1}^m K_{ij} K_{ji}^+ \right) \\ &= \sum_{j=1}^m \left(\sum_{i=1}^n K_{ji}^+ K_{ij} \right) = \sum_{j=1}^m (\mathbf{K}^+ \mathbf{K})_{jj} = \text{tr}(\mathbf{K}^+ \mathbf{K}) = \text{tr}(\mathbf{B}). \end{aligned} \quad (2.4.7a)$$

Since a unitary transformation does not change the trace of a matrix, one can obtain from (2.3.7b) and (2.4.2b)

$$\sum_{i=1}^n \lambda_i = \sum_{j=1}^m \gamma_j. \quad (2.4.7b)$$

Applying the Chebyshev inequality

$$\sum_{j=1}^m \gamma_j^2 \geq \frac{\left(\sum_{j=1}^m \gamma_j \right)^2}{m}$$

and (2.4.7b) to (2.4.6), one finds

$$|\delta p|^2 = \langle (f-p)^2 \rangle \leq \langle \epsilon^2 \rangle \frac{m}{\sum_{j=1}^m \gamma_j} \approx \epsilon^2, \quad (2.4.8)$$

where the fact that m , the dimension of $\mathbf{B}$, is the same order of magnitude of $\text{tr}(\mathbf{C})$ or $\text{tr}(\mathbf{B})$ has been used.

Equation (2.4.8) shows clearly that for a successful deconvolution using the curve fitting method, the difference between the fitted and true distribution is about the same order of magnitude as the experimental error. The method is thus stable in comparison to equation (2.2.6).

The cause of the stability difference between the downhill simplex curve fitting technique (2.4.8) and linear inversion (2.2.6) is easily understood; DHS avoids the direct inversion for an ill-conditioned matrix and uses an optimum selection of parameters and thus is stable. For the special case of $\epsilon = 0$, one finds $\mathbf{f} = \mathbf{p}$ which is, again, the obvious result. More discussions on the reliability properties of DHS method will be seen in Chapter 4.

In the previous discussions, two co-variance matrixes $\mathbf{C}$ and $\mathbf{B}$ have been introduced. Their important roles in evaluating the stability of a deconvolution method have been shown through Eq(2.4.4) to Eq(2.4.8). In fact, the most important feature of the two matrices is that the distributions of their matrix elements represent the information content of the system. To show this clearly, the elements of $\mathbf{C}$ and $\mathbf{B}$ can be written as

$$\begin{cases} C_{ij} = \sum_{k=1}^m K(\lambda_i, r_k) K(\lambda_j, r_k) \\ B_{ij} = \sum_{k=1}^n K(\lambda_k, r_i) K(\lambda_k, r_j) \end{cases} \quad (2.4.10)$$

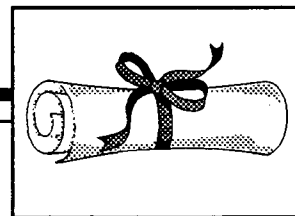
where λ represents wavelength for extinction measurements (scattering angles for scattering measurements) and r represents particle size.

The physical meaning of C_{ij} is that it represents the correlation between the kernels of the i th and the j th wavelengths (or scattering angles for scattering situations) throughout the whole size range of particles. The correlation relationship between the Mie kernels K_i 's are represented in the particle size r domain for different wavelength λ_i 's. The covariance matrix $\mathbf{C}$ takes an important role in the theory of linear inversion and is widely used by Twomey *et al.* [9,10]; in stability evaluation and information content analysis. From the view point of information content, an experimental configuration with relatively large non-diagonal elements of matrix $\mathbf{C}$ indicates less information content can be obtained, as will be discussed in Chapter 5. One thus needs to choose some other more independent measurement points to acquire more information on the particle system.

By comparison, the dual matrix $\mathbf{B}$ has drawn little attention and has not yet been singled out for discussion. Regarding its physical meaning, from the expression of (2.4.10), one can deduce (analogously to C_{ij}) that B_{ij} indicates the correlation between the signals from a particle with radius r_i and another with r_j over all measurements points. These correlation relationships of the Mie kernels K_i 's are represented in the wavelength λ domain for different particle size r_i 's. If the two kernels overlap each

other within some wavelength range, which results in relatively large B_{ij} , one can not detect the size information using that experiment no matter how many measurements are made. B_{ij} thus, in principle, tells if an experiment is suitable for a specific particulate system. More detailed discussion about the information content issue will be given in Chapter 5.

Chapter 3



Monte Carlo Simulation and Results

In this chapter, the Monte Carlo (MC) simulation method is applied to the deconvolution of PSDF from optical measurement and all the predictions of Chapter 2 are verified. Section 3.1 introduces the applications of MC method to the deconvolution of PSDF; section 3.2 describes the details of numerical treatment for the calculations in the simulations; and finally, section 3.3 performs the simulations for a relatively large particle system (absorbent water droplets, $D = 1\mu m$, $V = .2\mu m$) for the multi-angle scattering and multi-wavelength extinction cases. A complete discussion is given for the simulation results for the scattering case, and the results are then compared with the theoretical predictions in Chapter 2. Section 3.4 performs simulations similar to those of section 3.3 but for small soot particles ($D = .05\mu m$ and $V = .02\mu m$), and the results are compared with those of the large particles. Some discussion is given on the accuracy of the results for the two experimental methods (scattering vs. extinction).

§ 3.1 Monte Carlo Method in the Deconvolution of PSDF

To verify the validity of the DHS method and its predictions (2.3.14a) or (2.3.14b) that were introduced in Chapter 2, it is practical to simulate an experimental data set and perform the deconvolutions using this data set for different measurement

errors and under different conditions. Through the analysis of the results of simulations and deconvolutions, the parameters of PSDF can be obtained, and the predictions made in chapter 2 can be verified. Some new knowledge about the DHS method, such as the distribution functions for the PSDF parameters and information content of the experimental data, can also be obtained. This method for acquiring information through simulations is referred to as the Monte Carlo method and has seen widespread used.

A good description on the MC method is given by Shreider:^[17] " The Monte Carlo method (or method of statistical trials) consists of solving various problems of computational mathematics by means of the construction of some random process for each such problem, with the parameters of the process equal to the required quantities of the problem. These quantities are then determined approximately by means of its statistical characteristics, which are approximately equal to the required parameters."

Because the task of this dissertation is to obtain the distribution parameters of PSDF from the experimental data with some measurement errors, the random process mentioned above should correspond to the experiment error ϵ . To use the MC method to simulate a real experiment and generate statistical relations, the following procedures are adopted:

- (1) generate a set of synthetic data $\mathbf{g}$, as described in Chapter 2 by Eq.(2.2.3), with a certain set of parameters (e.g., $D_0 = 1.0$, $V_0 = 0.2 \mu m$ and $NL_0 = 1.111 \times 10^{10} cm^{-2}$).
- (2) add to each data value g_i some random error ϵ_i according to some prescribed error level σ_ϵ to obtain a set of noisy data $\mathbf{g}_\epsilon$.
- (3) use the noisy data as the experimental data, perform a deconvolution to get the resultant parameters D , V and/or NL as well as other parameters such as d^2 , χ^2 , ϵ^2 , β and β' as defined in (2.3.11) through (2.3.14b).

(4) repeat steps (2) and (3) for many times (200 to 500) to obtain the statistical distribution of the parameters in (3).

It is apparent from Shreider's statement that a random error generator with the same statistics of the real experimental data error is needed in order to apply the Monte Carlo method to perform simulations. Assuming there is no systematic error in the data, the error for each data value should be Gaussian distributed around the true value (or the mean for a real experiment data). Thus ϵ must be Gaussian distributed with a zero mean and σ_ϵ width (denoted as $[0, \sigma_\epsilon]$).

The first task is to find a random number generator which is Gaussian distributed. Most ready-to-use random number generators give, however, random bits which are uniformly distributed as $[0,1]$. Reference [16] gives, through transformation theory, a Gaussian random number generator with zero mean and unit standard deviation from a uniform random deviate. It is necessary to generalize this generator from $[0,1]$ to $[0, \sigma_\epsilon]$ following a similar procedure as in Ref. [16]. The uniform random deviate must have a probability function $p(x)$ which is defined as

$$p(x)dx = \begin{cases} dx & 0 < x < 1 \\ 0 & \text{otherwise.} \end{cases} \quad (3.1.1)$$

The probability distribution $p(x)$ is normalized so that

$$\int_{-\infty}^{\infty} p(x)dx = 1. \quad (3.1.2)$$

If y is a function of the random deviate x ,

$$y = y(x),$$

then the probability distribution of y , denoted by $p(y)dy$, is determined by the

fundamental transformation law of probabilities,

$$|p(y)dy| = |p(x)dx|$$

or

$$p(y) = p(x) \left| \frac{dx}{dy} \right|. \quad (3.1.3)$$

If $x_1, x_2, \dots$ are random deviates with a joint probability distribution $p(x_1, x_2, \dots)dx_1dx_2\dots$, and if $y_1, y_2, \dots$ are each functions of all the x 's, then (3.1.3) can be generalized as

$$p(y_1, y_2, \dots) = p(x_1, x_2, \dots) \left| \frac{\partial(x_1, x_2, \dots)}{\partial(y_1, y_2, \dots)} \right| \quad (3.1.4)$$

where the term with partial derivative is the Jacobian determinant of the x 's with respect to the y 's.

The functional form of $p(y)$ needed for simulations is a Gaussian form with standard deviation σ_e . For a two-dimensional situation, the expected distribution function is

$$p(y_1, y_2) = \frac{1}{2\pi\sigma_e} \exp \left[-\frac{y_1^2 + y_2^2}{2\sigma_e^2} \right]. \quad (3.1.5)$$

For a more general situation, assume $\bar{y}_1$ and $\bar{y}_2$ are the mean values of random deviates y_1 and y_2 with the widths of e_1 and e_2 , respectively. Consider the following transformations between the pairs of $\{x_1, x_2\}$ and $\{y_1, y_2\}$

$$\begin{aligned} y_1 - \bar{y}_1 &= \sigma_1 \sqrt{-2\ln x_1} \cos 2\pi x_2 \\ y_2 - \bar{y}_2 &= \sigma_2 \sqrt{-2\ln x_1} \sin 2\pi x_2 \end{aligned} \quad (3.1.6)$$

or

$$\begin{aligned}
x_1 &= \exp \left[-\frac{1}{2} \left(\frac{(y_1 - \bar{y}_1)^2}{\sigma_1^2} + \frac{(y_2 - \bar{y}_2)^2}{\sigma_2^2} \right) \right] \\
x_2 &= \frac{1}{2\pi} \arctan \frac{(y_2 - \bar{y}_2)\sigma_1}{(y_1 - \bar{y}_1)\sigma_2}
\end{aligned} \tag{3.1.7}$$

The Jacobian determinant can be calculated as

$$\left| \frac{\partial(x_1, x_2)}{\partial(y_1, y_2)} \right| = \left| \begin{array}{cc} \frac{\partial x_1}{\partial y_1} & \frac{\partial x_1}{\partial y_2} \\ \frac{\partial x_2}{\partial y_1} & \frac{\partial x_2}{\partial y_2} \end{array} \right| = \frac{1}{2\pi\sqrt{\sigma_1\sigma_2}} \exp \left[-\frac{(y_1 - \bar{y}_1)^2}{2\sigma_1^2} - \frac{(y_2 - \bar{y}_2)^2}{2\sigma_2^2} \right] \tag{3.1.8}$$

Eq.(3.1.8) is the product of two independent Gaussian distributions with $[\bar{y}_1, \sigma_1]$ and $[\bar{y}_2, \sigma_2]$ respectively. It is the most general form of a Gaussian random deviate transformation formula. Setting the two means to zero and two widths equal in (3.1.8) and substituting it into (3.1.4), one can obtain the expected relation (3.1.5).

In writing the working program, Reference [16] makes a transformation to transfer the unit square of $[x_1, x_2]$ domain into a two dimensional Gaussian distribution within which the radius R can be used as x_1 and the angle with respect the to abscissa can serve as the random angle $2\pi x_2$. By making appropriate adjustments, a very good Gaussian random number generator is obtained with the distribution parameters of $[0, \sigma_e]$. To verify the goodness of the generalized random number generator, a program was developed to generate the desired random numbers, which were compared with a real Gaussian distribution function with the same mean and width. The distribution functions of the random numbers generated by the random number generator agree very well with the expected distribution.

§ 3.2 Mathematical Treatment in Simulations

As was mentioned in Chapter 2, the DHS method utilizes the least-square minimization technique. It is well known that the least-square method assumes that each data point must be Gaussian distributed around its mean. Therefore, the statistical character of the experimental signals need to be known to assure the least square is suitable for use.

It is well known that for sufficiently long integration intervals, the scattered photons by a random particulate system are Possionian distributed

$$p(k, \alpha) = \frac{\alpha^k e^{-\alpha}}{k!} \quad (3.2.1)$$

where k is the number of photons and α is the mean.

If k is sufficiently large, the Possion distribution (3.2.1) approaches a Gaussian distribution.^[16] This allows one to use the least-squares method in analyzing scattering signals which involve a sufficiently large number of photons.

The least-square is considered as a maximum likelihood estimator. In general, a ν -dimensional least-square problem is to minimize

$$\sum_{i=1}^N \left[\frac{y_i - y(x_i; \alpha_1, \dots, \alpha_\nu)}{\sigma_i^2} \right]^2 \quad (3.2.2)$$

by adjusting the ν parameters. Here y_i is the experimental data with the error of σ_i , and $y(x, \alpha_1 \dots \alpha_\nu)$ is a known function. It is straightforward to show^[16] that for data with Gaussian-distributed errors, the least-square minimization does maximize the likelihood of the estimation of the parameters, as shown in the following. Because each data has an independent Gaussian-distributed error, the probability distribution function of the

data set is just the product of the probability of each point,

$$P = \prod_{i=1}^N \left\{ \exp \left[-\frac{1}{2} \left(\frac{y_i - y(x_i)}{\sigma_i} \right)^2 \right] \Delta y \right\}. \quad (3.2.3)$$

Maximizing (3.2.3) is equivalent to maximizing its logarithm, or minimizing the negative of its logarithm, namely

$$\left[\sum_{i=1}^N \frac{[y_i - y(x_i)]^2}{2\sigma_i^2} \right] - N \lg \Delta y \quad (3.2.4)$$

Clearly, minimizing (3.2.4) is equivalent to minimizing (3.2.2) since N , σ , and Δy are constants.

What is seen from the above is that the least-square fitting is a maximum likelihood estimation of the fitted parameters if the measurement errors are independent and normally distributed. It does not require that the data values themselves are independent. There are, actually, some possibilities that the data points themselves are not totally independent. In fact, as pointed out by many researchers^[9-12] and from Figs.(2.2.1) and (2.2.2), the optical scattering signals, especially the extinction signals, are highly intertwined. The existence of the interdependency among the signals will definitely affect the information content of the data. This topic will be discussed in Chapter 5.

Another subject that needs to be addressed is the calculation of the improper integration of the Mie kernels as defined in (2.2.1). Due to the non-linear nature of the fitting function, the accuracy of the integration is crucial since even a small error in calculation would lead the deconvolution in a false direction and the results might be unpredictable.

Like most numerical treatments, the infinite limit of the integration of size of the

particles is replaced with a maximum diameter $d_{\max}$ which depends on the parameters of the PSDF. Since $d_{\max}$ is changed each time when the parameters of the PSDF are changed, one cannot use the last integration results to implement current calculation because the locations of the function evaluation have been changed. Therefore, Gaussian quadrature is better than Romberg integration to use in this work because Gaussian Quadrature needs fewer evaluations than Romberg's scheme does, even though the latter one has the advantage of using previous evaluations. The detailed discussion on the Gaussian quadrature will be omitted in this dissertation (see, *e.g.*, Reference [16] for details).

Briefly, Gaussian quadrature digitizes an infinite integration into a weighted summation

$$g = \int_0^{\infty} f(x) dx \approx \sum_{i=1}^N f(x_i) w(x_i) \quad (3.2.5)$$

where x_i is the i th root of some polynomial and $w(x_i)$ is the appropriate weight. The "approximate equality" sign can be replaced by an equal sign if $f(x)$ is a $2N$ order polynomial. The choice of the polynomial (*e.g.* Hermite, Legendre, Laguerre *etc.*) depends on the agreement of the profiles between the weight and the integrand. A wise selection of the weight could also remove the integrable singularities in the integrand!^[16] Armed with this technique, the integration of (2.2.1) takes the form of

$$g(\alpha_i) = \sum_{k=1}^m K(\alpha_i, d_k) p(d_k) w(d_k) \quad i=1,2,\dots,n \quad (3.2.6)$$

Because the integration of Mie kernels in (2.2.1) has no closed form, it is hard to test the validity of using Gaussian quadrature to replace the integration. To make sure

that (3.2.6) is an appropriate substitution for (2.2.1), an analytical function $F(x)$ can be used to replace the kernel in (3.2.6). Evidently, the test function $F(x)$ must satisfy the following requirements:

- (1) The profile is similar to the Mie kernel within the integration domain, and
- (2) The integration has a known analytical form.

The Mie kernels for scattering or extinction increase as the particle size parameter increases, with more or less oscillations in case of non-absorbing particles, see Figs.(2.2.1) and (2.2.2). A substitute function like

$$F(x) = x^{\alpha} [1 + \gamma \cos(\beta \ln x)] \quad \gamma < 1, \quad (3.2.7)$$

is chosen to simulate this behavior. The advantages of this function is that one can adjust the parameters α , β and γ to simulate the kernel function's behavior. For example, increasing α can raise the baseline of the whole profile, raising β can oscillate the curve at any frequency, and changing γ can regulate the amplitude of oscillation. Fig.(3.2.1) shows the profile of $F(x)$ for $\alpha = 0.1$, $\beta = 50$ and $\gamma = 0.5$. From this figure it is clear that the curve has a very high ripple frequency, which is very similar to the scattering signals from a non-absorbing material (pure water) as shown in the upper curve of Fig.(2.2.1). Replacing the Mie kernel in (2.2.1) by $F(x)$, the integration has the form of

$$I = \int_0^{\infty} f(x) F(x) dx = \int_0^{\infty} \exp\left[-\frac{(\ln x - \mu)^2}{2\sigma^2}\right] x^{\alpha} [1 + \gamma \cos(\beta \ln x)] \frac{dx}{\sqrt{2\pi}\sigma x}. \quad (3.2.8)$$

Making a transformation of variable

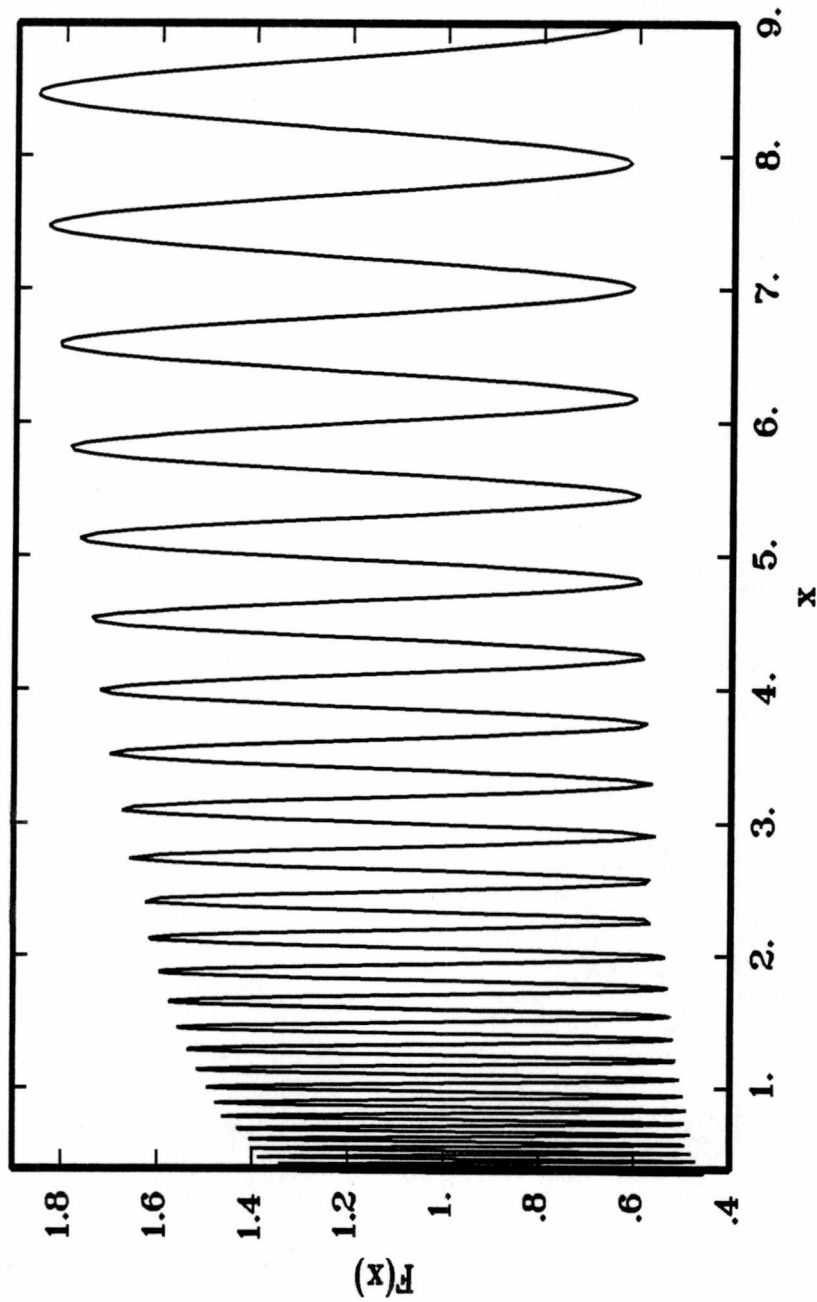


Figure 3.2.1 The profile of test function $F(x)$. It is very similar to the scattering efficiency as shown in Fig.(2.2.2). The parameters are $\alpha = 0.1$, $\beta = 50$, and $\gamma = 0.5$.

$$x = \exp(\sqrt{2}\sigma z + \mu), \quad (3.2.9)$$

the integration can be calculated analytically

$$\begin{aligned} I &= \frac{e^{\alpha\mu}}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-z^2 + \sqrt{2}\alpha\sigma z) \cos[\beta(\sqrt{2}\sigma z + \mu)] dz \\ &= \exp\left[\alpha\mu + \frac{\sigma^2(\alpha^2 - \beta^2)}{2}\right] \cos[\beta(\alpha\sigma^2 + \mu)]. \end{aligned} \quad (3.2.10)$$

Using (3.2.10), the integration for the fixed set parameters of $F(x)$ was calculated and listed in the Appendix, along with a comparison of those obtained by the Gaussian quadrature method for different numbers of integration points. All the values are from computer results with double precision. From Table (A.1), it is clear that the error between the two is as small as 10^{-4} with only 100 integration points. The calculations of integrations in particle size diameter in the simulations and deconvolutions can therefore be trusted.

Whenever the PSDF parameters are adjusted during the deconvolutions, the upper limit of the integration particle size d should be changed according to the width of the PSDF. In general, the wider the PSDF is, the larger the upper will be. Because the number of the integration points is fixed, the locations of the integration points will be changed at each vertex of a simplex during deconvolution to make the integration points distribute evenly in the domain. This is performed by scaling every integration point each time to extend the points throughout the entire domain using a linear transformation for the size parameter. As the result of scaling of the integration variable, the whole integration should be multiplied by the same scaling factor.

Armed with the above treatment, one can write out the final deconvolution formula for the simulations. For the extinction case, the expression is given by Eqs.(2.1.1-2.1.3)

and the formula is relatively simple. The optical thickness τ_e can be written as

$$\tau_e(\lambda) = \frac{NL\pi}{4} \int_0^{\infty} Q_e(d, \lambda, m) d^2 p(d) d(d) \quad (3.2.11a)$$

where the extinction efficiency Q_e is related to the extinction cross-section through $C_e = \text{area} \times Q_e$ which is defined by Eq.(2.1.9). Using Gaussian quadrature, the above expression can be digitized as

$$\tau_e(\lambda) = \frac{NL\pi}{4} \sum_{k=1}^{k_{\max}} Q_e(d_k, \lambda, m) d_k^2 p(d_k) w_k \quad (3.2.11b)$$

where $k_{\max}$ is integration number and the subscript k corresponds to the k th root of the appropriate polynomials and w_k is the corresponding weight. In the simulations of this dissertation, Laguerre polynomials were adopted.

The formula for scattering signals is a little more complicated. For a linear polarized incident light, the light scattered by a spherical particle in the (θ, ϕ) direction is

$$A^2 = \frac{i(d, \theta, \phi)}{k^2 r^2} = \frac{|S_1(d, \theta)|^2 \sin^2 \phi + |S_2(d, \theta)|^2 \cos^2 \phi}{k^2 r^2} \quad (3.2.12a)$$

where S_1 and S_2 as defined by (2.1.8) are also functions of particle diameter d , light wavelength λ , and the complex index of refraction m .

Since the detector has a finite aperture, it is necessary to integrate the scattering signal over the solid angle subtended by the aperture at the center of the particle field and finally, integrate over the particle size d to include all contributions from all the particles with distribution function $p(d)$. Equation (2.1.5) then becomes

$$\tau_s = \frac{1}{k^2} \int_0^{d_{\max}} \int_{\Delta\Omega} [|S_1(d, \theta)|^2 \sin^2 \phi + |S_2(d, \theta)|^2 \cos^2 \phi] p(d) d(d) d\Omega \quad (3.2.12b)$$

For a circular aperture with half angle $\delta\theta$ located at (θ_0, ϕ_0) , τ_s has the form of^[18]

$$\begin{aligned} \tau_s = & \frac{1}{k^2} \int_0^{d_{\max}} p(d) d(d) \times \\ & \times \int_{\theta_0 - \delta\theta}^{\theta_0 + \delta\theta} \left[(|S_1|^2 + |S_2|^2) \phi(\theta) - \frac{1}{2} (|S_1|^2 - |S_2|^2) \cos 2\phi_0 \sin 2\phi \right] \sin \theta d\theta \end{aligned} \quad (3.2.12c)$$

where

$$\phi(\theta) = \cos^{-1} \left(\frac{\cos(\delta\theta) - \cos\theta \cos\theta_0}{\sin\theta \sin\theta_0} \right). \quad (3.2.12d)$$

Applying the Gaussian-Laguerre and Gaussian-Jacobi formulae for particle size and angular integrations, Eq.(3.2.12c) becomes

$$\tau_s(\theta_0) = \frac{D_c}{k^2} \sum_{i=1}^k p(d_i) [h_1(d_i, \theta_0) + h_2(d_i, \theta_0)] w_L(d_i), \quad (3.2.13)$$

where

$$h_{1,2}(d_i, \theta_0) = A_c \sum_{j=1}^J |S_{1,2}(d_i, \eta_j)|^2 \left[\phi(\eta_j) \mp \frac{\cos 2\phi_0 \sin 2\phi(\eta_j)}{2} \right] w_J(\eta_j). \quad (3.2.14)$$

Here the D_c and A_c are scaling factors for diameter and angular integrations and d_i and η_j are the scaled integration variables, respectively. The quantities of w_L and w_J are weights for Gaussian Laguerre and Gaussian-Jacobi integrations.

With all of the previous preparation, the simulations are performed. The Mie extinction and scattering efficiencies are calculated using the subroutine by Wiscombe^[19]

and the DHS routine comes from [16].

§ 3.3 Monte Carlo Simulations for Absorbent Water Droplets

Synthetic Data Generation

The system is assumed to be an absorbent water droplet spray in air with a complex index of refraction of $(1.33, +i0.02)$ for wavelength $6328 \text{ \AA}$. The PSDF is a log-normal distribution with a mean diameter $D_0 = 1.0 \text{ }\mu\text{m}$ and standard derivation $V_0 = 0.2 \text{ }\mu\text{m}$.

First, the scattering case is examined in detail because it contains more information than the extinction case.^[10] This means that the scattering signals are less interdependent than those of extinction ones. Therefore, the analysis of scattering data can be better utilized to verify all previous predictions since those derivations are based on the assumptions that each measurement is independent. Actually, it can be seen in the following discussion that the extinction measurements can also be used to obtain the PSDF if it is provided with more accurate measurement than scattering. The information content issue will be discussed in Chapter 5.

To simulate data as close to a real experiment as possible, the following steps have been made:

- (1) A finite aperture size of the detector is assumed with a solid angle of 2.4×10^{-4} steradian subtended at the scattering center (aperture angle of 1°). The scattering kernels in (3.2.12b) are then integrated with respect to that solid angle.
- (2) Gaussian quadrature^[16] is used to perform all integrations. The $d_{\max}$ in (3.2.12c) is changed according to the change in PSDF to make sure the integrations over particle size converge.

- (3) The data are normalized at a specific angle to eliminate the influence of large values in number density in (2.1.5). This method is shown to be very efficient and able to reduce some systematic error in data (if all errors are positive or negative by some percentage).
- (4) The error ϵ is calculated using a Gaussian random number generator with zero mean and standard derivation σ_e . The σ_e is chosen as some percentage of true data, and the error bar b of the synthetic data equals $2\sigma_e \times (\text{data value})$.

To reduce the influence of big differences in scattering signals between small and large angles, the quantity being minimized is defined by

$$Y^2 = \sum_{i=1}^n \left[\log \left(\frac{t_i/t_0}{g_{e_i}/g_{e_0}} \right) \right]^2. \quad (3.3.1)$$

where all data values, denoted by a subscript 0, have been normalized by the data at the scattering angle of 80° . The advantage of such normalization is that it can reduce some systematic measurement errors such as all positive or negative errors which are proportional to the data. The final results of d_i , χ_i and ϵ_i are divided by g_i to scale them to moderate values for comparison among the three quantities; that is:

$$d^2 = \sum_{i=1}^n \frac{(t_i - g_i)^2}{g_i^2}, \quad \chi^2 = \sum_{i=1}^n \frac{(t_i - g_{ei})^2}{g_i^2} \quad \text{and} \quad \epsilon^2 = \sum_{i=1}^n \frac{(g_{ei} - g_i)^2}{g_i^2}. \quad (3.3.2)$$

To show the equivalency of using Y^2 of (3.3.1) in place of χ^2 of (3.3.2), the differentiation of Y^2 with respect to t_i can be expressed as

$$\Delta(Y^2) = 2 \sum_{i=1}^n \frac{\Delta t_i}{t_i}. \quad (3.3.3a)$$

Performing the same operation to χ^2 , keeping in mind that t_i approaches g_i , yields

$$\Delta(\chi^2) = 2 \sum_{i=1}^n \frac{t_i - g_{ei}}{g_i} \frac{\Delta t_i}{g_i} \bigg|_{t_i = g_i} = 2 \sum_{i=1}^n R_i \frac{\Delta t_i}{t_i} ; \quad R_i = \frac{\epsilon_i}{g_i}. \quad (3.3.3b)$$

It is obvious that both Y^2 and χ^2 approach to zero at the same rate except for a factor of R_i which is just the relative error of each data point.

For a real experimental data set in which the true data $\mathbf{g}$ is never known, $\mathbf{d}$ is not available and Eq.(3.3.2) is still valid if one replaces the denominators by g_{ei} and the numerator in ϵ_i by the corresponding experimental error bar. In fact, the similar results were obtained in the simulations when the denominators were replaced with g_{ei} in (3.3.1b). To simplify the notation, the quantity σ_e , the width of Gaussian distribution of the random error, is referred to the percentage of appropriate measurement data value. For example, $\sigma_e = 20\%$ actually means $\sigma_e = 20\% \times (\text{data value})$.

Deconvolution and Results

To obtain the statistical relations, 200 deconvolutions were performed for error level σ_e varying from $\pm 2\%$ to $\pm 50\%$, each gives a set of parameters of $(D, V, d^2, \chi^2$ and $\epsilon^2)$. Then the 200 parameter sets for each error level were sorted according to the increasing values of d^2 . The six averages ($\langle D \rangle$, $\langle V \rangle$, $\langle d^2 \rangle$, $\langle \chi^2 \rangle$, $\langle \epsilon^2 \rangle$) are plotted in Fig.(3.3.1) and their standard deviations (STD) (σ_D , σ_V , σ_{d^2} , σ_{χ^2} , σ_{ϵ^2}) are listed in Table (3.3.1) with respect to error levels σ_e , respectively. The results with four digits came directly from the computer print out and it is shown that the calculation error in the

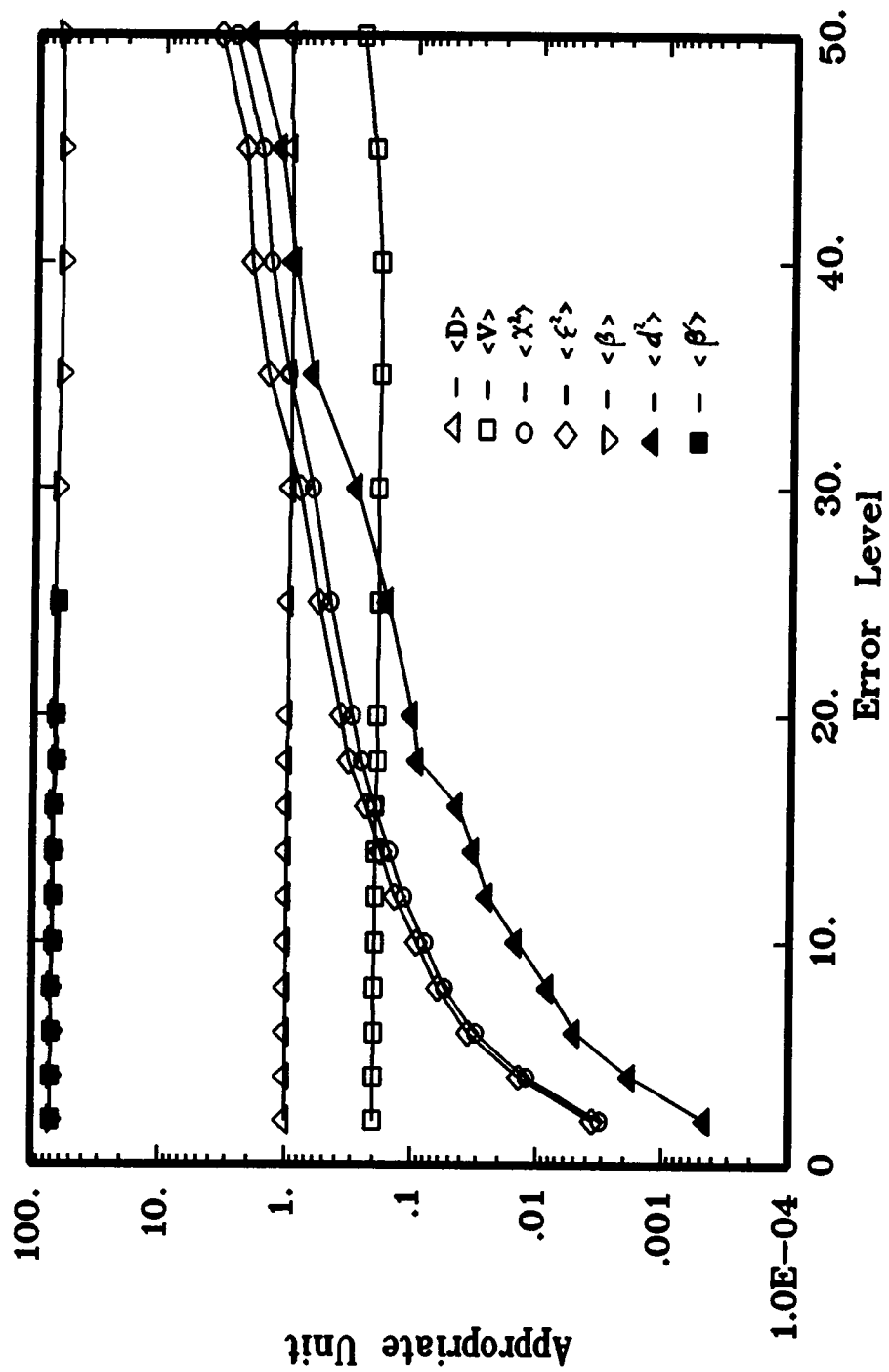


Figure 3.3.1 Deconvolution results vs. error levels (water/scattering).

Table 3.3.1 The deconvolution results for water scattering case: standard deviations of various parameters vs. error levels. The error level σ_e is from $\pm 2\%$ up to $\pm 50\%$, each with 200 deconvolutions. The horizontal dashed lines separate the four groups, as discussed in the text.

$\sigma_e\%$	$N_p N_2 N_3$	σ_D	σ_V	σ_d	σ_x	σ_e	σ_{β}°	σ_{β}°	$R_D\%$	$R_V\%$
± 2	1, 0, 0	4.137×10^{-3}	2.735×10^{-3}	4.597×10^{-4}	1.791×10^{-3}	1.974×10^{-3}	9.198	9.163	0.4	1.4
± 4	0, 0, 0	7.841×10^{-3}	5.260×10^{-3}	2.163×10^{-3}	6.305×10^{-3}	7.279×10^{-3}	8.892	8.870	0.8	2.6
± 6	0, 0, 0	1.222×10^{-2}	8.870×10^{-3}	5.239×10^{-3}	1.811×10^{-2}	2.069×10^{-2}	8.774	8.688	1.2	4.4
± 8	2, 0, 1	1.604×10^{-2}	1.132×10^{-2}	9.792×10^{-3}	2.968×10^{-2}	3.322×10^{-2}	9.939	9.705	1.6	5.7
± 10	0, 0, 0	2.059×10^{-2}	1.477×10^{-2}	1.751×10^{-2}	4.365×10^{-2}	5.156×10^{-2}	9.693	8.887	2.1	7.4
± 12	2, 0, 0	2.440×10^{-2}	1.822×10^{-2}	4.147×10^{-2}	6.755×10^{-2}	8.648×10^{-2}	10.17	9.265	2.4	9.1
± 14	3, 0, 1	2.905×10^{-2}	2.098×10^{-2}	4.619×10^{-2}	9.254×10^{-2}	.1143	10.52	9.564	2.9	10.5
± 16	3, 0, 0	3.061×10^{-2}	2.405×10^{-2}	6.954×10^{-2}	.1209	.1446	10.73	9.150	3.1	12.0
± 18	14, 0, 1	3.676×10^{-2}	3.076×10^{-2}	.1618	.1610	.2319	14.23	11.95	3.7	15.5
± 20	11, 0, 1	4.186×10^{-2}	3.121×10^{-2}	.2061	.1847	.2819	14.01	11.23	4.2	15.6
± 25	10, 0, 4	4.962×10^{-2}	4.119×10^{-2}	.4175	.3294	.5474	—	12.29	5.0	20.6
± 30	19, 4, 3	7.192×10^{-2}	6.054×10^{-2}	.6778	.5062	.8147	—	12.45	7.2	30.5
± 35	37, 3, 3	9.692×10^{-2}	6.824×10^{-2}	1.152	.6198	1.259	—	13.94	9.7	34.0
± 40	37, 2, 7	.1333	9.741×10^{-2}	1.314	1.136	1.775	—	13.27	13.3	48.7
± 45	38, 5, 15	.2999	.1985	2.675	1.817	2.478	—	13.89	30.0	99.5
± 50	39, 9, 17	.4813	.3115	4.307	3.109	4.176	—	13.70	48.1	115.8

computer is negligible in comparison with experimental error.^[13] To evaluate the effect of each error level on the deconvolution results according to (2.3.14a), three N numbers (N_1, N_2, N_3) were introduced in Table(3.3.1) , where

$$N_1 = \text{times of which } \chi^2_{\min} \leq \epsilon^2 \text{ is violated,} \quad (3.3.4a)$$

$$N_2 = \text{times of which } d^2 \leq \chi^2_{\min} \text{ is violated,} \quad (3.3.4b)$$

$$N_3 = \text{times of which } d^2 < \epsilon^2 \text{ is violated.} \quad (3.3.4c)$$

Other quantities in Table(3.3.1) and Fig.(3.3.1) are β , β' , R_D and R_V . The pair of (β , β') are calculated in accordance with (2.3.12) and (2.3.13b) respectively by:

$$\left\{ \begin{array}{l} \beta = \cos^{-1}(d^2 + \epsilon^2 - \frac{\chi^2_{\min}}{2d\epsilon}) \\ \beta' = \cos^{-1}(\frac{d}{\epsilon}) \end{array} \right. \quad (3.3.5a)$$

$$\left\{ \begin{array}{l} \beta = \cos^{-1}(d^2 + \epsilon^2 - \frac{\chi^2_{\min}}{2d\epsilon}) \\ \beta' = \cos^{-1}(\frac{d}{\epsilon}) \end{array} \right. \quad (3.3.5b)$$

and the pair of (R_D, R_V) are defined as

$$\left\{ \begin{array}{l} R_D = \frac{\langle \sigma_D^2 \rangle}{\langle D^2 \rangle} \times 100\% \\ R_V = \frac{\langle \sigma_V^2 \rangle}{\langle V^2 \rangle} \times 100\% \end{array} \right. \quad (3.3.6a)$$

$$\left\{ \begin{array}{l} R_D = \frac{\langle \sigma_D^2 \rangle}{\langle D^2 \rangle} \times 100\% \\ R_V = \frac{\langle \sigma_V^2 \rangle}{\langle V^2 \rangle} \times 100\% \end{array} \right. \quad (3.3.6b)$$

Table (3.3.1) or Fig.(3.3.1) can be divided into four groups according to the N numbers:

- (1) ($N_1 = 0 \sim 1, N_2 = N_3 = 0$) for the errors within $\pm 10\%$ of the true data,
- (2) ($N_1 = 3 \sim 5, N_2 \approx N_3 \approx 0$) for the error of $\pm 12\%$ to $\pm 16\%$,
- (3) ($N_1 = 10 \sim 14, N_2 = 1 \sim 4, N_3 = 0$) for error of $\pm 18\%$ to $\pm 30\%$, and
- (4) ($N_1 = 19 \sim 39, N_2 = 3 \sim 17, N_3 = 3 \sim 9$) for errors of $\pm 30\%$ to $\pm 50\%$.

To see the statistics clearly, 500 extra deconvolutions were performed for each error level. The data were again sorted according to increasing value of d^2 and the quantities of D , V , d^2 , χ^2 , etc., are plotted in the figures as will be discussed, with

respect to the ordering number N ($= 500$) which indicates the value of d^2 .

One can see from Table (3.3.1) that in group (1), the criteria for goodness of fit (2.3.14a) is perfectly observed for all deconvolutions except for occasional occurrences of systematic-like error (with all-positive or all-negative random errors) which yield violations of (3.3.4a). The recovery of both data curve $g(\theta)$ and PSDF $p(r)$ is excellent and $R_D \leq 7.4\%$, $R_V \leq 10.3\%$ indicating a safe error range. Figs.(3.3.2) and (3.3.3) show the result for $\sigma_e = \pm 6\%$ and $\sigma_e = \pm 10\%$ respectively.

In group (2), the criteria (2.3.14a) is still observed for most of the deconvolutions. The recovery of data curve $g(\theta)$ and PSDF $p(r)$ are still good with $R_D \leq 7.7\%$ and $R_V \leq 14.1\%$. The violations of (3.3.4a) in this group, however, imply some 1% - 3% deconvolutions would give noticeable error in the result. Figs.(3.3.4A,B) show the results for $\sigma_e = \pm 16\%$.

Group (3) includes more violations of (3.3.4a) and even violations of (3.3.4b) ($N_2 = 1 \sim 4$) appears. Although the resultant data curve $g(\theta)$ and PSDF $p(r)$ are fairly good with $R_D \leq 8.7\%$ and $R_V \leq 20.7\%$, the violations of (2.3.14b) in this group mean the results might not satisfy some strict experiments in which PSDF is critical. Figs.(3.3.5A,B) shows the result for $\sigma_e = \pm 25\%$.

The big numbers in N_1 ($= 19 \sim 39$) and N_2 ($= 3 \sim 17$) in Group (4) represent unstable deconvolutions and the occurrence of $N_3 = 3 \sim 9$ indicates some faulty result might appear. If one has to deal with the data with such large error, multiple deconvolutions are advised to get average values because here $R_D \leq 43.6\%$ and $R_V \leq 116.8\%$. Trying different starting simplex may also help. Figs.(3.3.6A,B) shows the result for $\sigma_e = \pm 50\%$

Parameters such as $(\langle\beta\rangle, \langle\beta'\rangle)$ and (R_D, R_V) which suffer relatively big changes

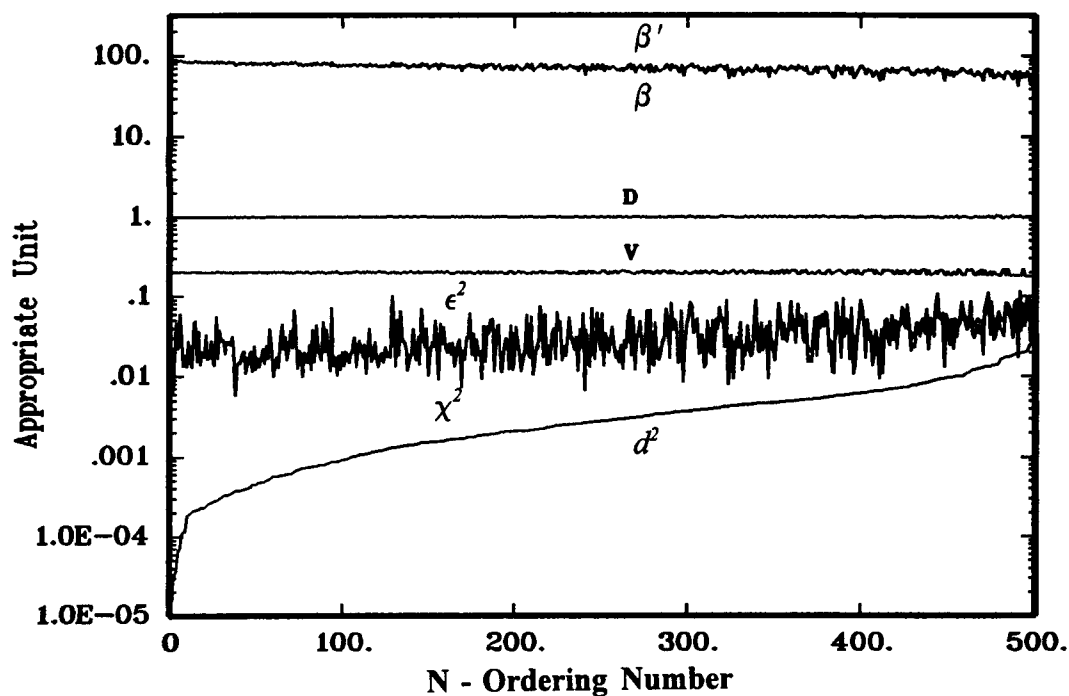


Figure 3.3.2: Deconvolution results for $\pm 6\%$ error (Water/scattering).

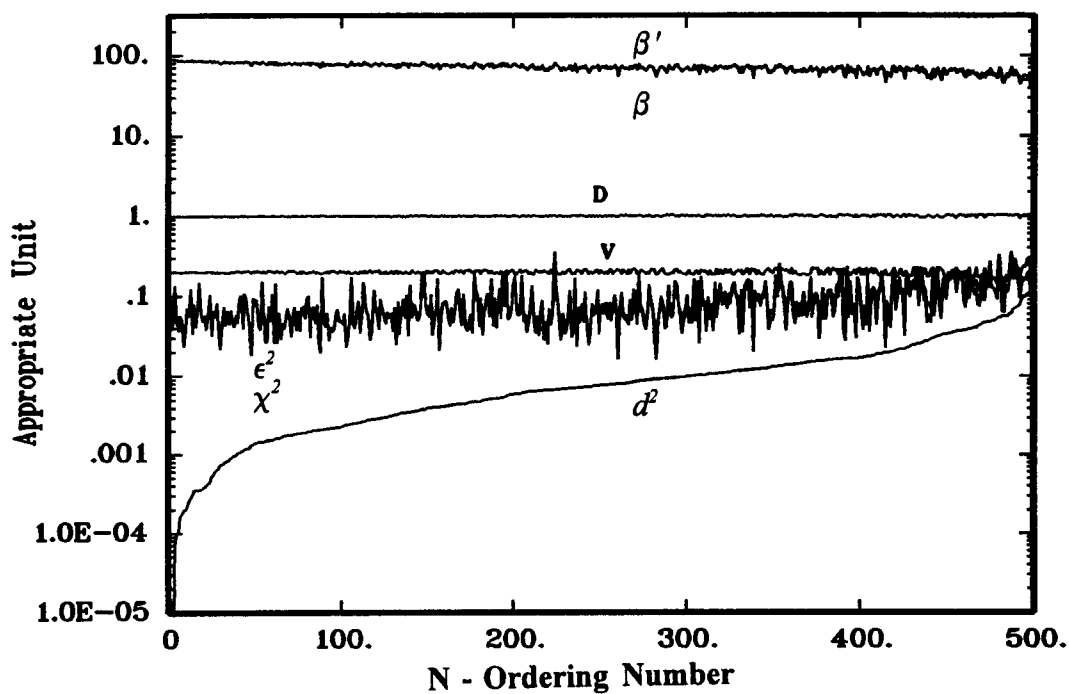


Figure 3.3.3: Deconvolution results for $\pm 10\%$ error (Water/scattering).

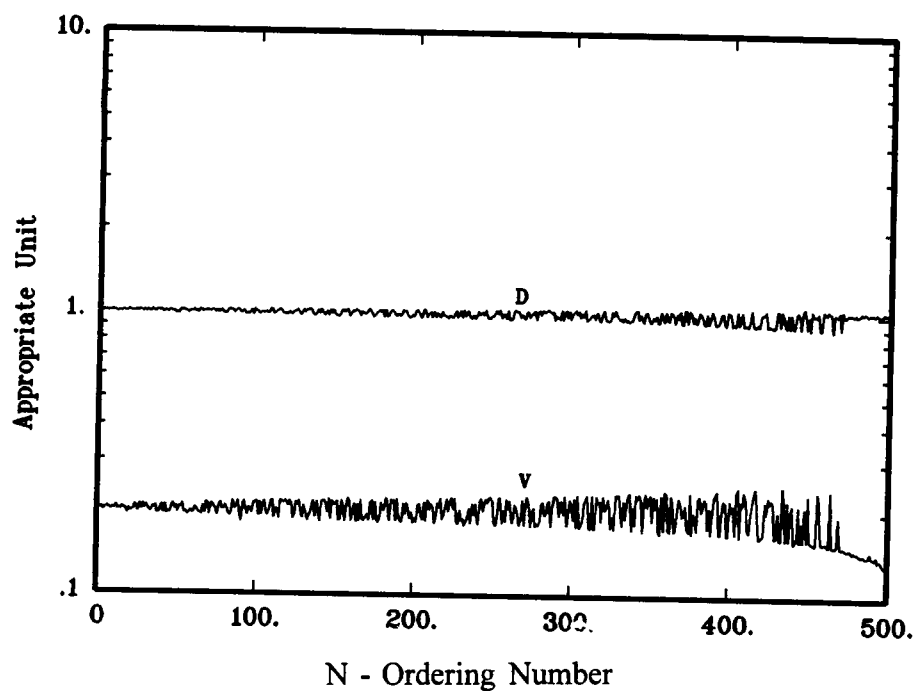


Figure 3.3.4A For D and V .

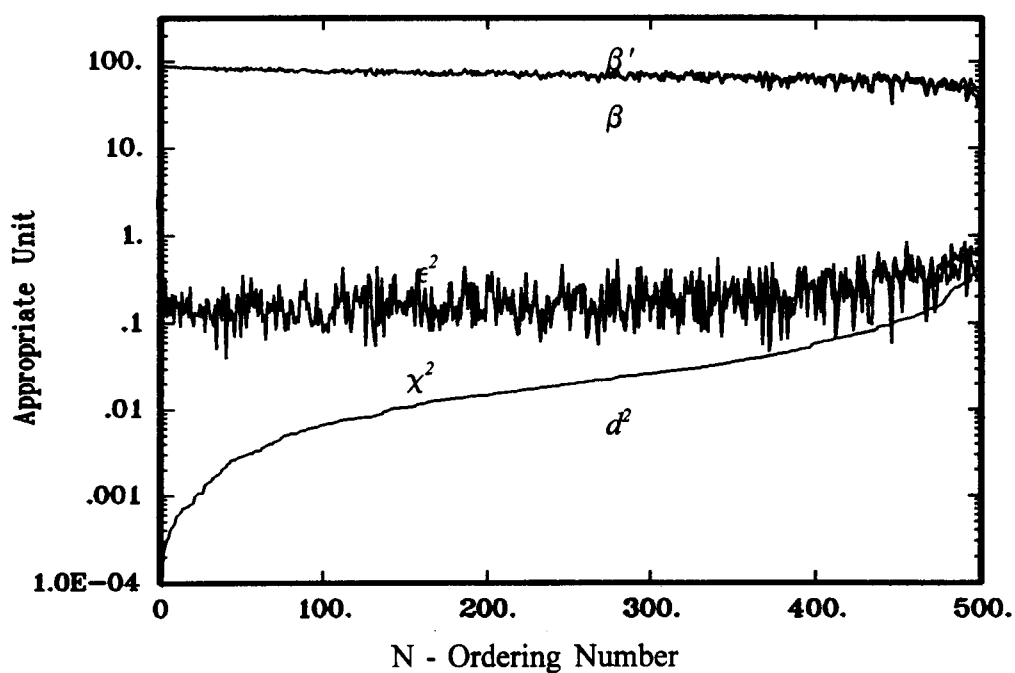


Figure 3.3.4B For d^2 , χ^2 , ϵ^2 , β , and β' .

Figure 3.3.4 Deconvolution results for $\pm 16\%$ error (water/scattering).

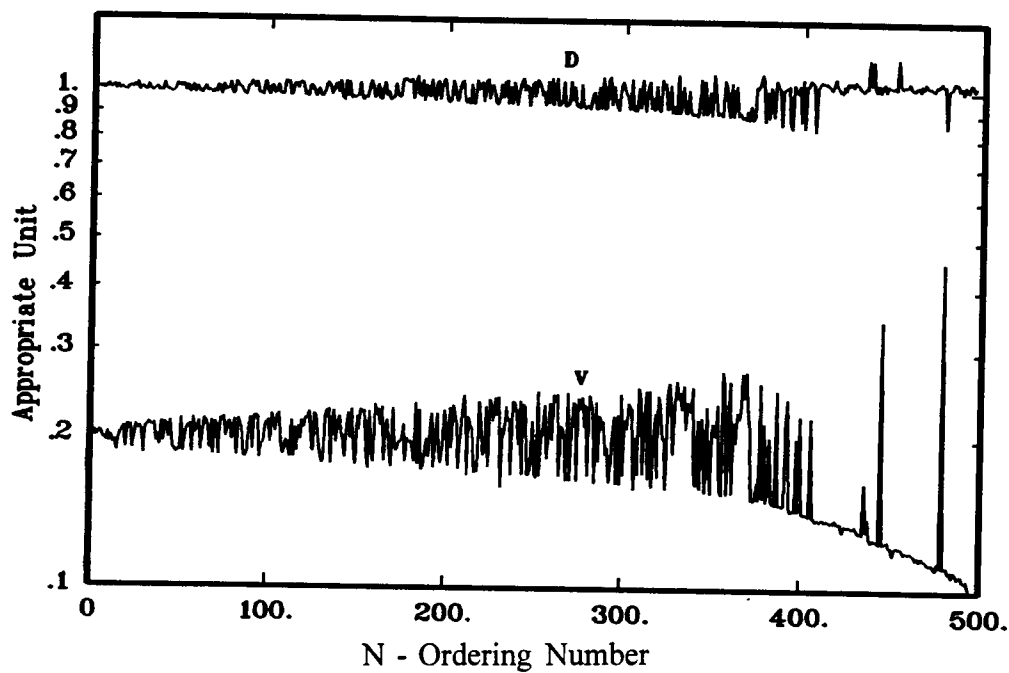


Figure 3.3.5A For D and V .

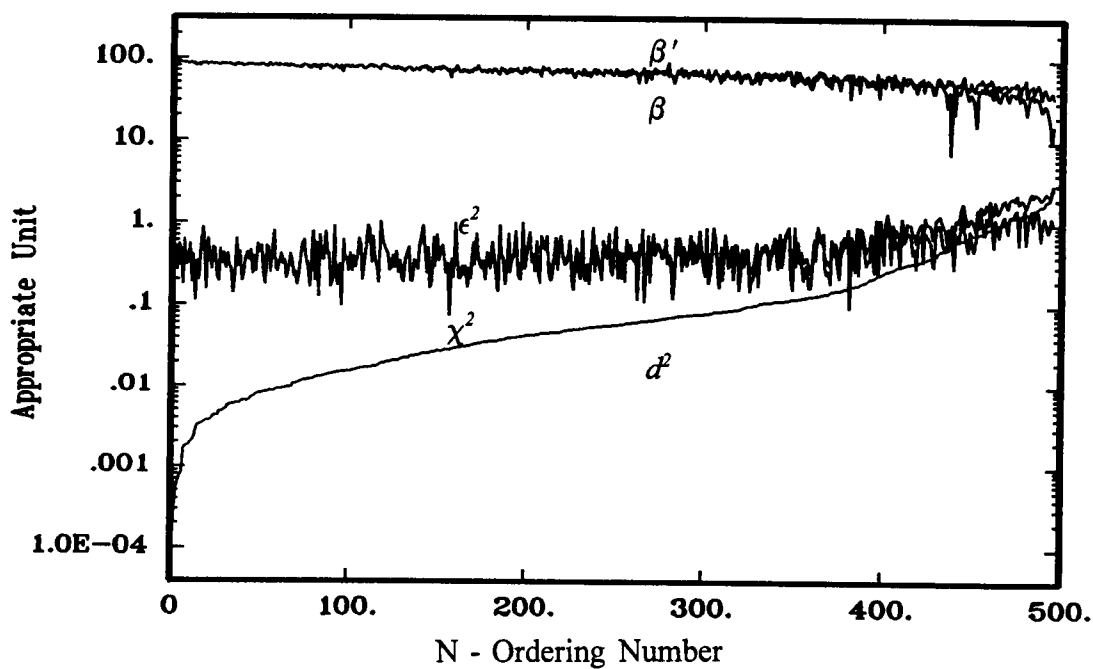


Figure 3.3.5B For d^2 , χ^2 , ϵ^2 , β , and β' .

Figure 3.3.5 Deconvolution results for $\pm 25\%$ error (water/scattering).

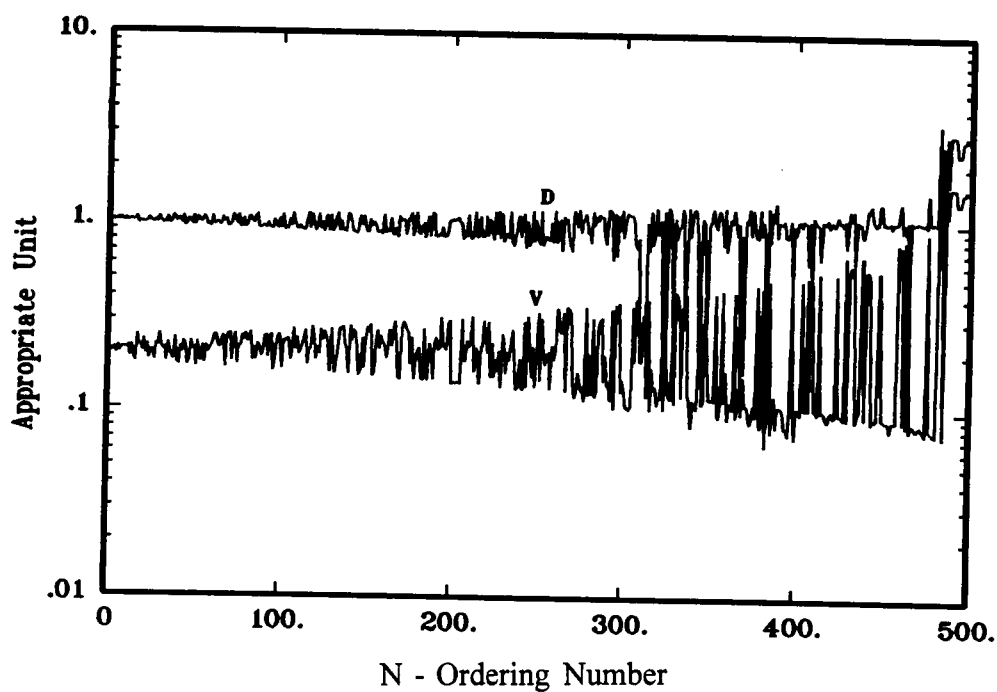


Figure 3.3.6A For D and V .

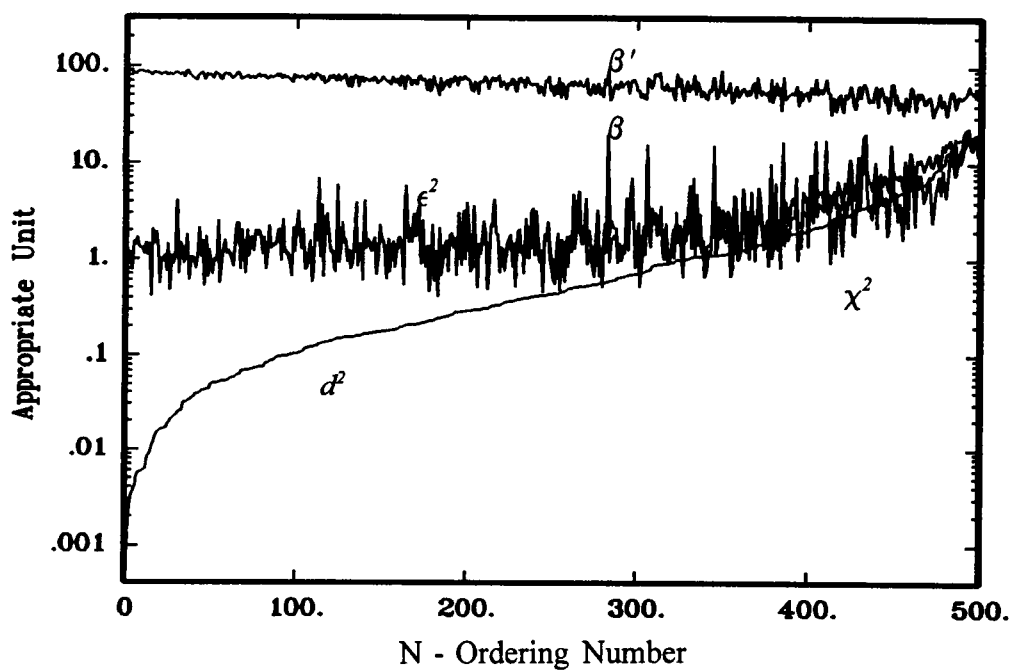


Figure 3.3.6B For d^2 , χ^2 , ϵ^2 , β , and β' .

Figure 3.3.6 Deconvolution results for $\pm 50\%$ error (water/scattering).

at the beginning of group(3), may also be used to assess the goodness of fit. Instead of being close to zero, $\langle\beta\rangle$ is around $71^\circ - 72^\circ$ for group (1) and group(2) with a STD about 10° as shown in Table (3.3.1). An apparent fall to $68^\circ - 69^\circ$ happens at the beginning of group(3) with a wider STD of $12^\circ - 13^\circ$. The fact that $\langle\beta'\rangle$ is always slightly larger than that of $\langle\beta\rangle$ proves that the treatment of (2.3.13) is appropriate. In other words, the DHS deconvolution achieves final results by minimizing d (through adjusting d and β), the difference between the fitted vector $\mathbf{t}$ and true vector $\mathbf{g}$, as predicted by (2.3.14). The relatively big changes in the pairs (R_D, R_V) and (β, β') occurring at the end of group (3) confirms that $\sigma_e \leq \pm 16\%$ is a safe region for deconvolution for this particulate system.

It might be appropriate to look into a typical deconvolution result to have a direct visualization of how (2.3.14) is obeyed (for good deconvolutions) or violated (for poor deconvolutions). Table (3.3.2) gives some sections of data for Fig.(3.3.5) which is for $\sigma_e = \pm 25\%$. As mentioned above, all parameters have been sorted according to an increasing d^2 . Fig(3.3.7A) plots the resultant curves for $\mathbf{t}$, $\mathbf{g}_e$, and $\mathbf{g}$ which shows clearly that the fitted curve $\mathbf{t}$ is closer to the true data $\mathbf{g}$ than to the error data $\mathbf{g}_e$, as pointed in §2.3. Fig(3.3.7B) shows the original PSDF ($D_0 = 1.0 \mu\text{m}$, $V_0 = 0.2 \mu\text{m}$) and fitted PSDF ($D = 1.04$, $V = 0.1876$) for one of the 200 deconvolutions for $\sigma_e = \pm 25\%$.

The common features of Fig.(3.3.2) to (3.3.6) are that for the deconvolutions with small d^2 corresponding to good deconvolutions (ordering number N below 300), χ^2 and ϵ^2 are so close that they basically overlap each other (χ^2 is always lower than ϵ^2) and so are β and β' (β is always lower than β'). The overlap of χ^2 and ϵ^2 occasionally contributes 1 or 2 counts to N numbers for group(1). As d^2 becomes larger and larger, the overlaps between χ^2 and ϵ^2 begin to split while χ^2 is always below ϵ^2 . The same

Table 3.3.2 Some of the 200 decovolution results for $\sigma_e = \pm 25\%$. The 4 shaded blocks are those which violate (2.3.14b) and the areas surrounded by dotted lines are for those which violate (2.3.14a).

N	$\langle D \rangle$	$\langle V \rangle$	d^2	χ^2	ϵ^2	β'	β
1	1.004	.1984	2.5298×10^{-4}	.1866	.1874	87.89	85.30
2	1.011	.1963	1.4344×10^{-3}	.3201	.3225	86.18	84.84
3	1.001	.2055	1.4646×10^{-3}	.2387	.2404	85.52	85.18
4	.9950	.1960	1.6031×10^{-3}	.3116	.3135	85.90	85.47
5	.9904	.2043	2.0280×10^{-3}	.4654	.4653	86.21	88.23
11	.9833	.2039	5.8953×10^{-3}	.3409	.3401	82.43	86.75
148	1.087	.1959	.1387	.7212	.7113	63.80	78.18
164	1.098	.1550	.2170	.1115	.2384	17.42	40.89
175	1.037	.1380	.3395	.3378	.6619	44.26	45.58
178	1.007	.1351	.3869	.1997	.5477	32.81	37.04
179	1.144	.1674	.3946	.4922	.4776	24.64	64.05
191	1.041	.1247	.6950	.6925	1.265	42.16	47.48
192	1.171	.1238	.7419	.6869	.8669	22.32	54.92
196	1.047	.1154	1.153	.6338	1.458	27.19	40.32
197	1.036	.1111	1.458	1.071	1.930	29.66	46.33
198	1.026	.1100	1.586	.6500	1.900	24.00	35.23
199	1.047	.1078	1.668	.9956	2.321	32.02	40.48
200	1.028	.1065	1.932	.7238	2.094	16.17	34.82

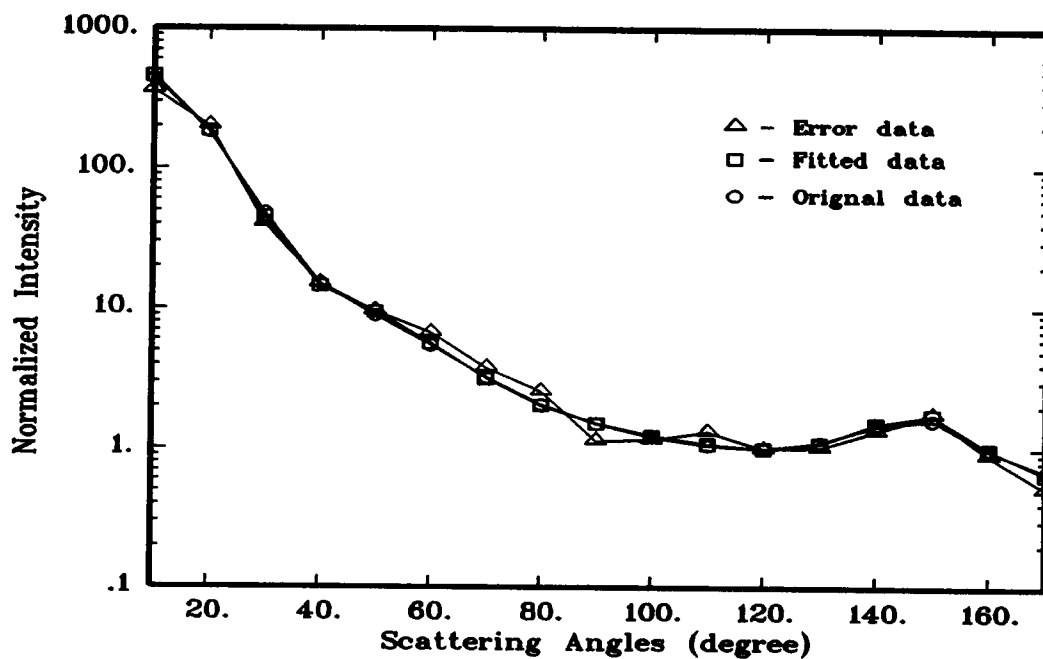


Figure 3.3.7A A typical deconvolution results.

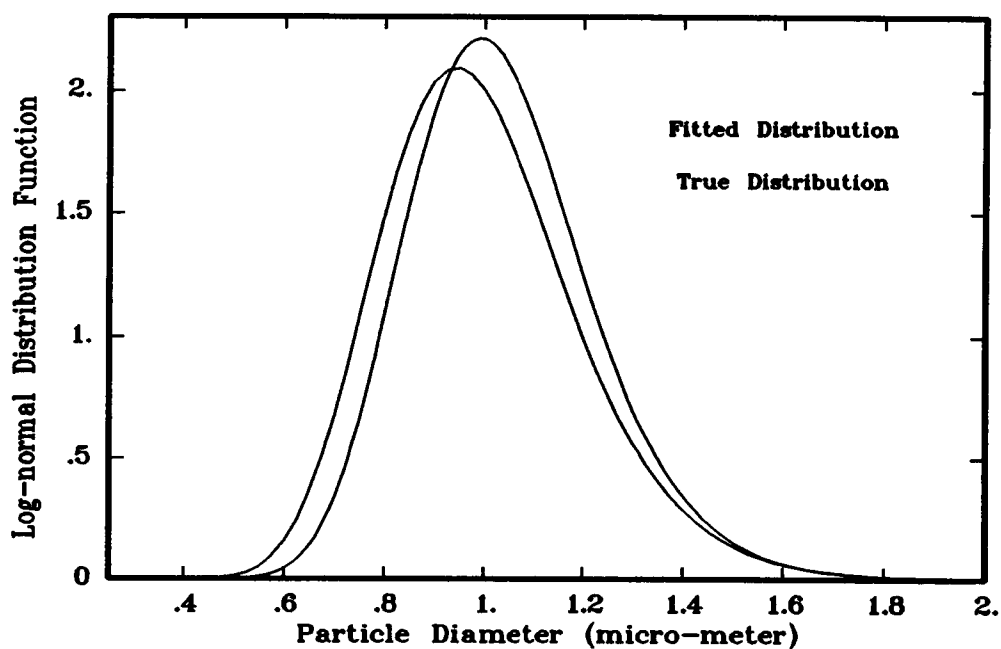


Figure 3.3.7B Corresponding fitted PSDF with $D=1.04$ and $V=0.1876$.

Figure 3.3.7 Typical deconvolution results for $\pm 25\%$ error (water/scattering).

thing happens to the decreasing pair of β and β' (with $\beta \leq \beta'$) only when N is close to 500. Because of violations of (2.3.14b), β' is not available for groups (3) and (4).

For the multi-wavelength extinction case, one must know more information about the response of the particle system to the incoming light before doing deconvolutions, *i. e.*, one needs the spectra of both the real and imaginary components of index of refraction. For comparison, it was assumed that the particle system is the same as that of scattering with the index of refraction listed in Table (3.3.3). To compare with Figs.(3.3.2) - (3.3.7AB), 500 deconvolutions were performed for each error level of $\pm 6\%$, $\pm 10\%$, $\pm 16\%$, $\pm 25\%$ and $\pm 50\%$, respectively. Because the interdependence of the extinction kernels, the " N numbers" introduced in the scattering case can not be used to assess the goodness of fit. For the same reason, the angles β and β' are not available either since the violations of (2.3.14a) or (2.3.14b) appear even for adding some small error to the data.

The 5 typical error level results for the extinction cases are plotted in Figs.(3.3.8) - (3.3.12AB) and each curve consists of 500 deconvolution results which are similar as those in Figs.(3.3.2) - (3.3.6AB) for scattering case. From Fig(3.3.8), one can see the $\pm 6\%$ error case is safe for deconvolution because the big fluctuations in V occur only on the very last order numbers. The fluctuation level in V is close to that of the $\pm 16\%$ error in scattering situation. Fig(3.3.9) shows that $\pm 10\%$ error in extinction measurement can be deconvolved provided multi-deconvolution be performed to get a reliable result in V . For the error levels of $\pm 16\%$ to $\pm 25\%$, the results in V usually contain big errors but the results for D are reasonably good, see Figs.(3.3.10A,B) and Figs.(3.3.11A,B). In the higher error levels, the results would be unbelievable because some big fluctuations occur in both D and V , see Figs.(3.3.12A,B).

Table 3.3.3 Index of refraction of
absorbent water

$\lambda(nm)$	n	k
460	1.299	1.784×10^{-2}
470	1.295	3.107×10^{-2}
480	1.294	5.997×10^{-2}
490	1.323	8.147×10^{-2}
500	1.374	9.600×10^{-2}
510	1.375	7.005×10^{-2}
520	1.360	4.777×10^{-2}
530	1.360	4.415×10^{-2}
540	1.364	3.895×10^{-2}
550	1.366	2.392×10^{-2}
560	1.364	1.630×10^{-2}
570	1.360	1.040×10^{-2}
580	1.357	6.63×10^{-3}
590	1.354	4.13×10^{-3}
600	1.352	2.42×10^{-3}
610	1.346	1.65×10^{-3}
627	1.341	8.8×10^{-4}

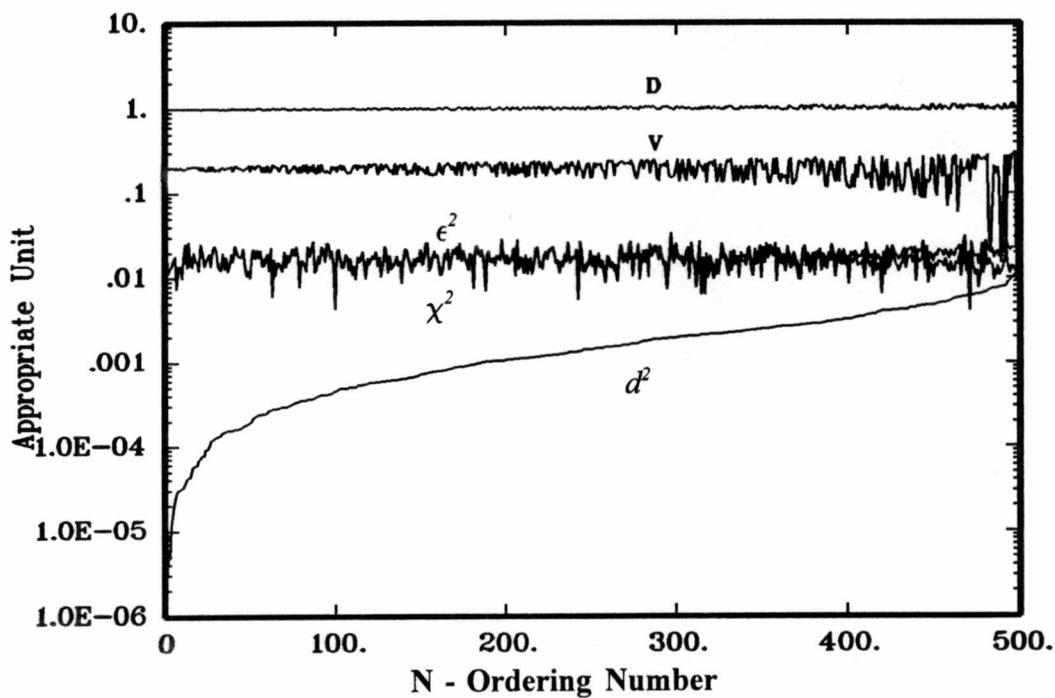


Figure 3.3.8: Deconvolution results for $\pm 6\%$ error (water/extinction).

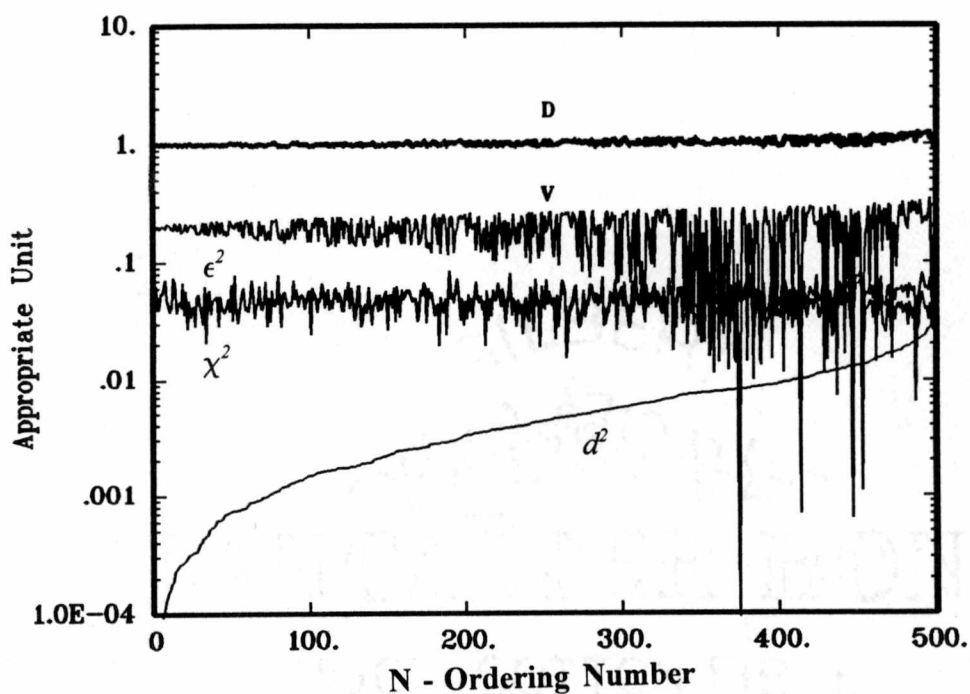


Figure 3.3.9: Deconvolution results for $\pm 10\%$ error (water/extinction).

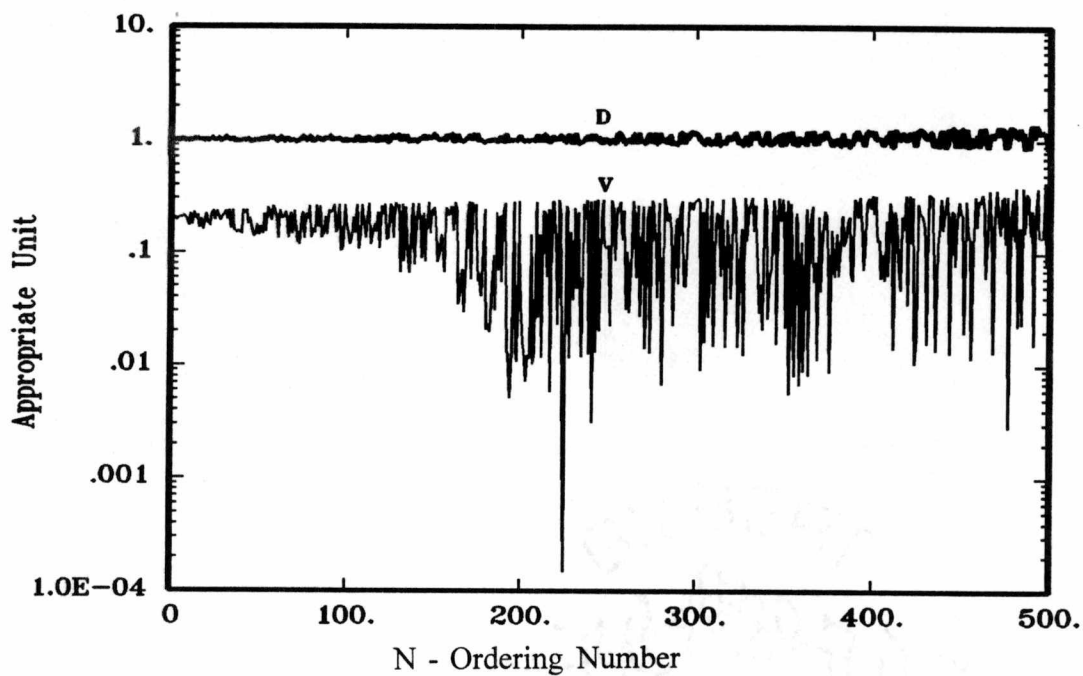


Figure 3.3.10A For D and V .

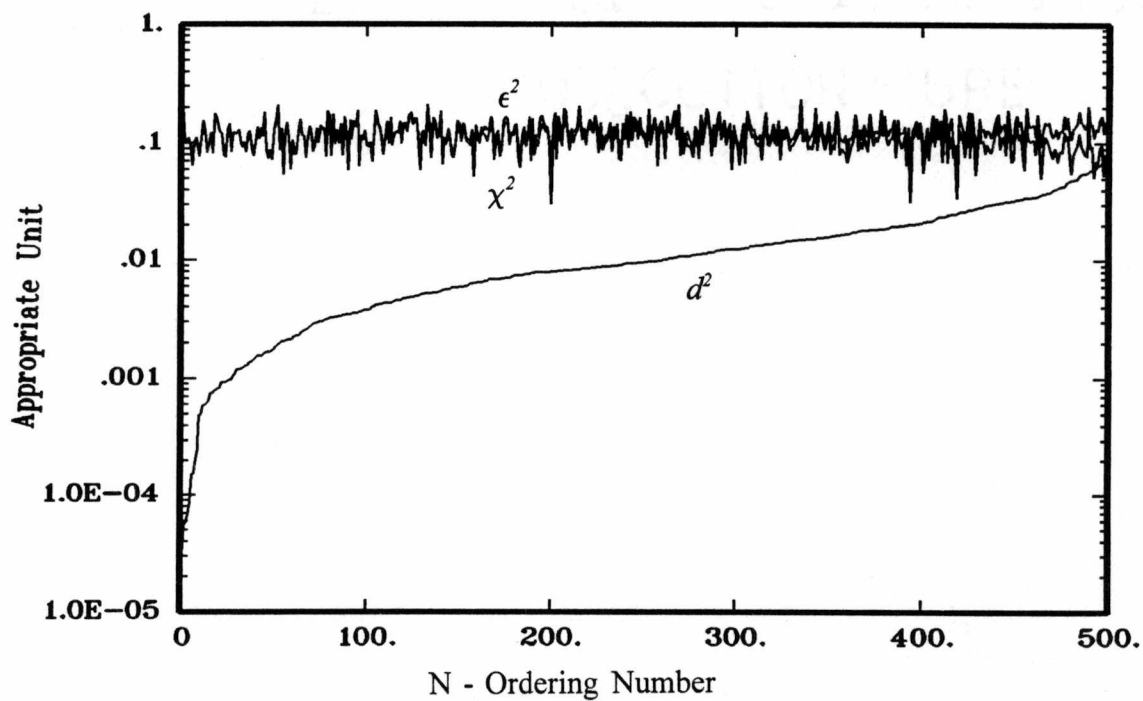


Figure 3.3.10B For d^2 , χ^2 , ϵ^2 , β , and β' .

Figure 3.3.10 Deconvolution results for $\pm 16\%$ error (water/extinction).

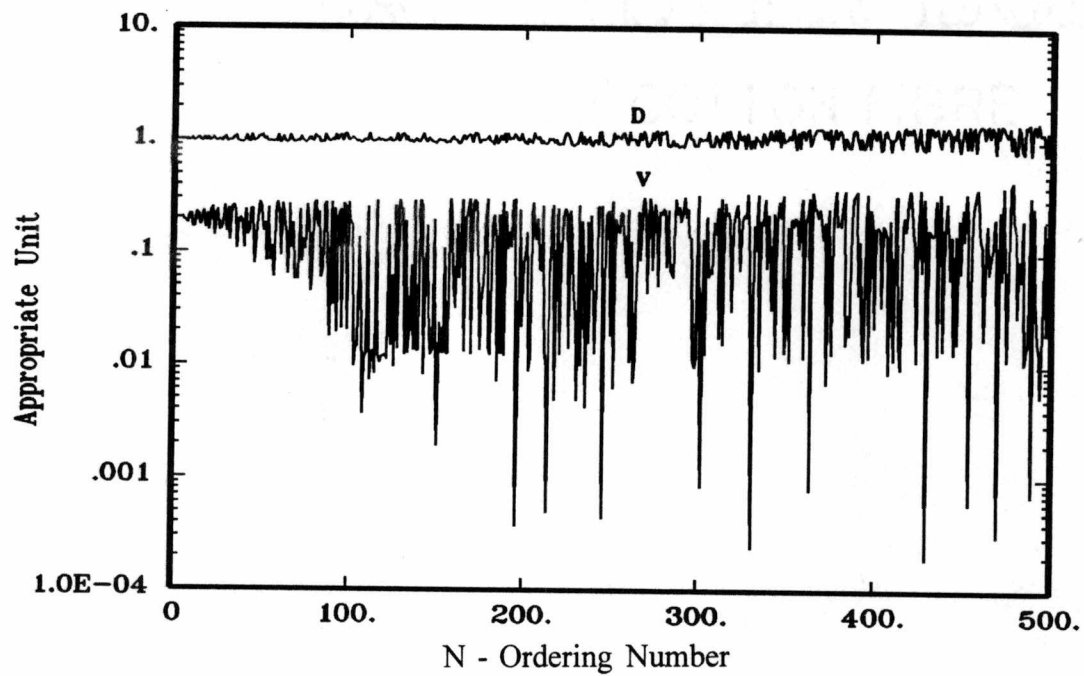


Figure 3.3.11A For D and V .

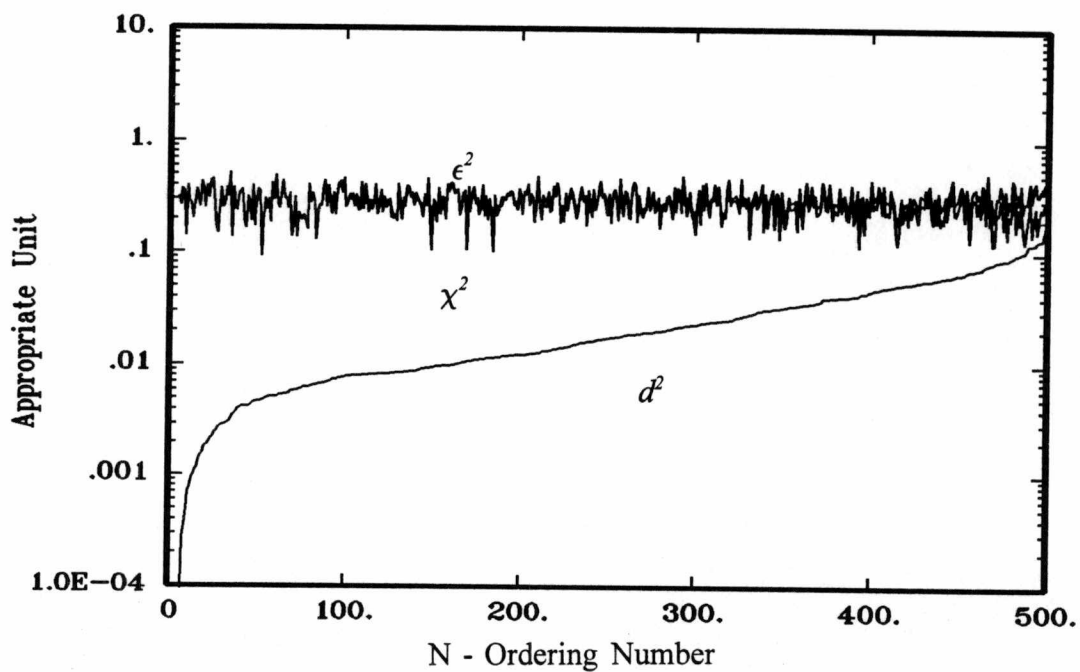


Figure 3.3.11B For d^2 , χ^2 , ϵ^2 , β , and β' .

Figure 3.3.11 Deconvolution results for $\pm 25\%$ error (water/extinction).

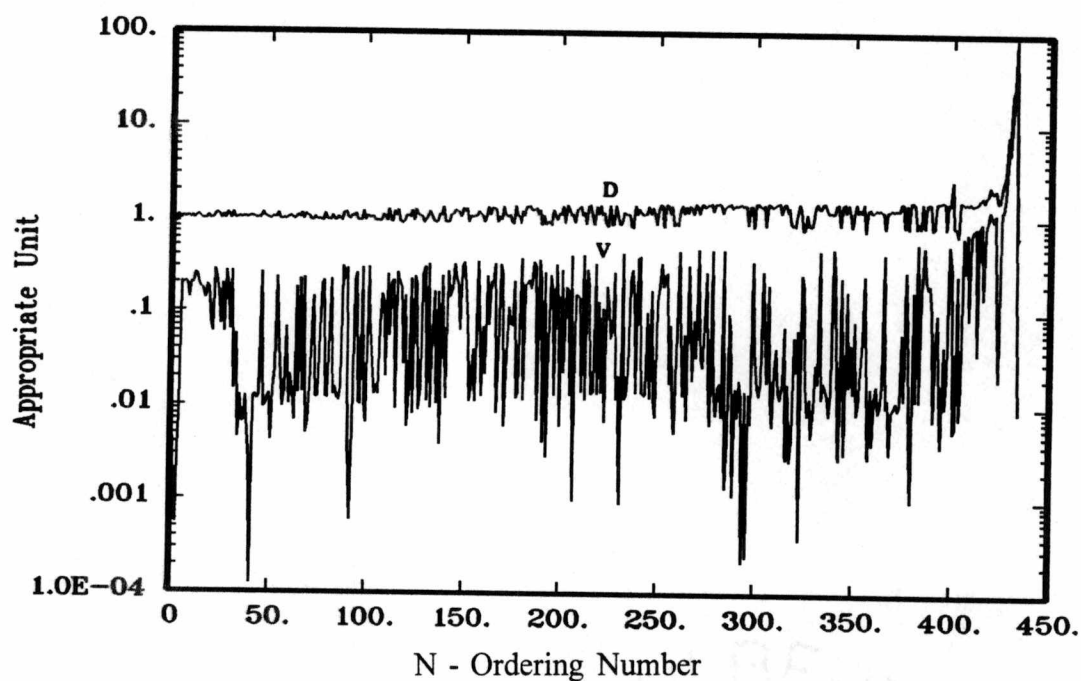


Figure 3.3.12A For D and V .

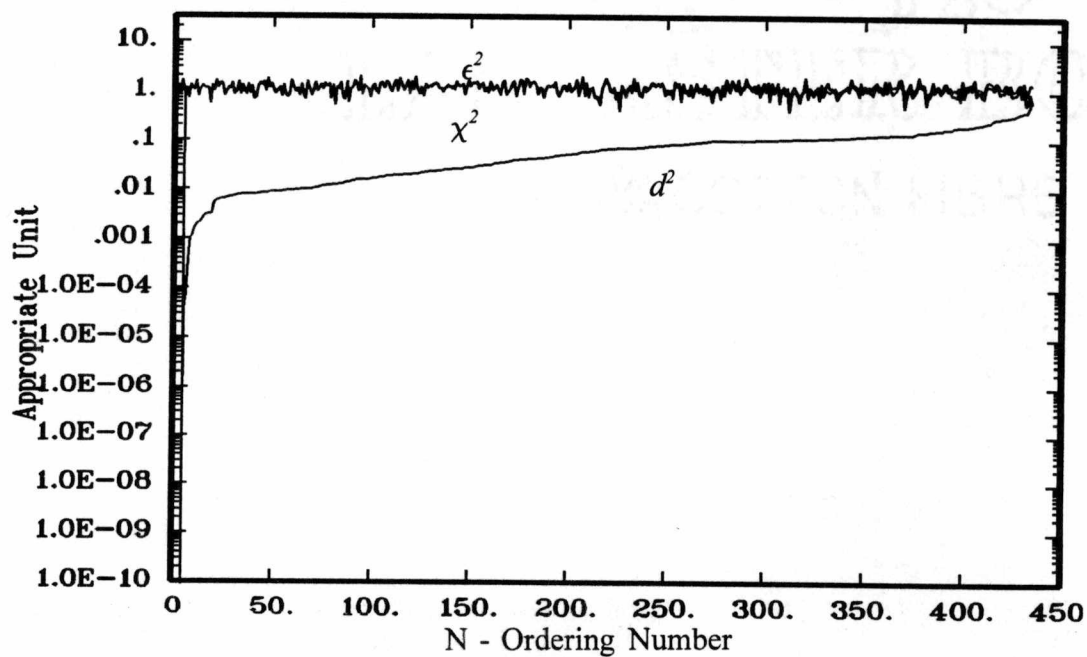


Figure 3.3.12B For d^2 , χ^2 , ϵ^2 , β , and β' .

Figure 3.3.12 Deconvolution results for $\pm 50\%$ error (water/extinction).

The relatively poor results that appear in the simulation for the extinction case are not surprising because the information content is quite limited in the extinction kernels, as pointed out by Twomey who performed information content analysis using the covariance matrix C , as defined and discussed in Chapter 2. The information content in extinction is so low that some of the measurements are totally redundant, *i.e.* they can be approximately linearly expressed by the combination of others. The inclusion of these dependent measurements in deconvolution provides nothing but noise which came from the limited experiment precision. In the simulations, the same index of refraction in the original data and trial data were used. In fact, any measured or calculated spectra of index of refraction contain some error. Taking this factor into consideration, the information is further limited in the extinction measurement because of the less accuracy in the index of refraction and the result would be worse.

From Fig.(3.3.5B) or (3.3.6B) , one might have noted two interesting changes in the distribution parameter pair D and V for the ordering number N below 300. The first is that whenever D goes up, V will go down a little bit accordingly and *visa versa*. This is reasonable because from the distribution (2.1.10) or (2.1.11), when one of the two parameters changes, the other one must change in the opposite direction to compensate the scattering signals. The second is that V always has a larger oscillation than D does, *i. e.* $R_V > R_D$. This is due to the nature of the log-normal distribution (2.1.10) and (2.1.11): *i.e.*, it is more sensitive in D than V for a narrow distribution. Although a detail discussion for distributions of D and V vs error ε will not be discussed here, it is informative to consider how the errors in D and V are related to the errors in μ and σ .

From (2.1.11) it is easy to show that for small changes $\Delta\mu$ and $\Delta\sigma$, the relative

changes in D and V are

$$\begin{cases} R_D = \frac{\Delta D}{D} = \Delta\mu + \sigma \Delta\sigma \\ R_V = \frac{\Delta V}{V} = \frac{D \Delta D(e^{\sigma^2} - 1) + D^2 e^{\sigma^2} \sigma \Delta\sigma}{V^2} \end{cases} \quad (3.3.7)$$

The deconvolution results show that for $\mu_0 = -1.96 \times 10^{-2}$ and $\sigma_0 = 0.198$ (for $D_0 = 1$, $V_0 = 2$) the ratio of R_V over R_D is larger than unit, *i.e.*,

$$\left| \frac{R_V}{R_D} \right|_{\substack{D_0 \\ V_0}} = \left| 1 + \frac{D_0^2 e^{\sigma_0^2} \sigma_0}{V_0^2} \frac{\Delta\sigma}{\Delta\mu + \sigma_0 \Delta\sigma} \right| = \left| 1 + 5.149 \frac{\Delta\sigma}{\Delta\mu + \sigma_0 \Delta\sigma} \right| > 1. \quad (3.3.8)$$

It is obvious that (3.3.8) is obeyed if $\Delta\mu$ and $\Delta\sigma$ are all positive or all negative no matter what values they are. If $\Delta\mu$ and $\Delta\sigma$ have different signs, the condition that (3.3.8) is valid will be:

$$5.149 \left| \frac{\Delta\sigma}{\Delta\mu + \sigma_0 \Delta\sigma} \right| > 2, \quad \text{or} \quad \frac{|\Delta\mu|}{|\Delta\sigma|} < \left(\sigma_0 + \frac{5.149}{2} \right) = 2.773 \quad (3.3.9)$$

Relation (3.3.9) is a very loose requirement and is observed for most of the deconvolutions. Actually, if μ and σ are changed by same fraction one finds

$$\left| \frac{\Delta\sigma}{\sigma_0} \right| \approx \left| \frac{\Delta\mu}{\mu_0} \right| \quad \text{will lead to} \quad \frac{|\Delta\mu|}{|\Delta\sigma|} \approx \frac{|\mu_0|}{\sigma_0} \approx 9.9 \times 10^{-2} \quad (3.3.10)$$

which far enough satisfies (3.3.9). Again, Eq(3.3.8) is just an intuitive interpretation for the larger relative fluctuations in V . Obviously, the complete expressions for the changes in D and V should be proportional to the experiment error ε , as will be discussed further in Chapter 4.

§ 3.4 Monte Carlo Simulations for Small Soot Particles

In order to examine the validity of the DHS method for other particle systems, simulations were also performed on small soot particles with PSDF parameters of $D=0.05\mu m$, $V=0.02\mu m$ for six typical error levels (*i. e.* $\pm 2\%$, $\pm 6\%$, $\pm 10\%$, $\pm 16\%$, $\pm 25\%$ and $\pm 50\%$, respectively) like for water droplets. The 17 wavelengths and the indices of refraction are listed in Table (3.4.1). To compare with the results from the water droplets, all conditions were set the same as those for water droplets except the wavelengths λ used here for both scattering and extinction simulations are shorter in order to compensate for the small particle size, because the Mie kernels depend on the size parameter $x = \pi d/\lambda$ (d particle size).

The deconvolution results are plotted in Figures (3.4.1) - (3.4.6AB) for the results of scattering and (3.4.7) - (3.4.12AB) for the results of extinction. One can see from the plots that the deconvolution results are acceptable for the error level up to $\pm 10\%$ for the scattering case compared to $\pm 16\%$ for water droplet scattering case discussed in §3.3. One can also estimate that the safe error level for the extinction of small soot particles is only around $\pm 6\%$ compared with $\pm 10\%$ for the big water droplets.

The fact that the extinction results are usually not as precise as those for scattering for the same particulate system indicates clearly that the information content about PSDF in extinction measurements is usually less than that in scattering for the conventional light wavelength range (from near ultra-violet to near-infrared). An intuitive explanation of this fact is that the extinction data only reflects how much of the light is "blocked" by the particles for a specific wavelength but no more details are revealed. For example, it is impossible to distinguish whether the extinction is due to

Table 3.4.1 Index of refraction of soot.

$\lambda(nm)$	n	k
230	1.0240	.7818
250	1.1384	.8097
270	1.2409	.8101
290	1.3262	.7923
310	1.3934	.7646
330	1.4445	.7335
350	1.4824	.7029
370	1.5102	.6749
390	1.5305	.6505
410	1.5453	.6299
430	1.5563	.6128
450	1.5644	.5991
470	1.5706	.5882
490	1.5754	.5800
510	1.5793	.5739
530	1.5825	.5698
550	1.5852	.5673

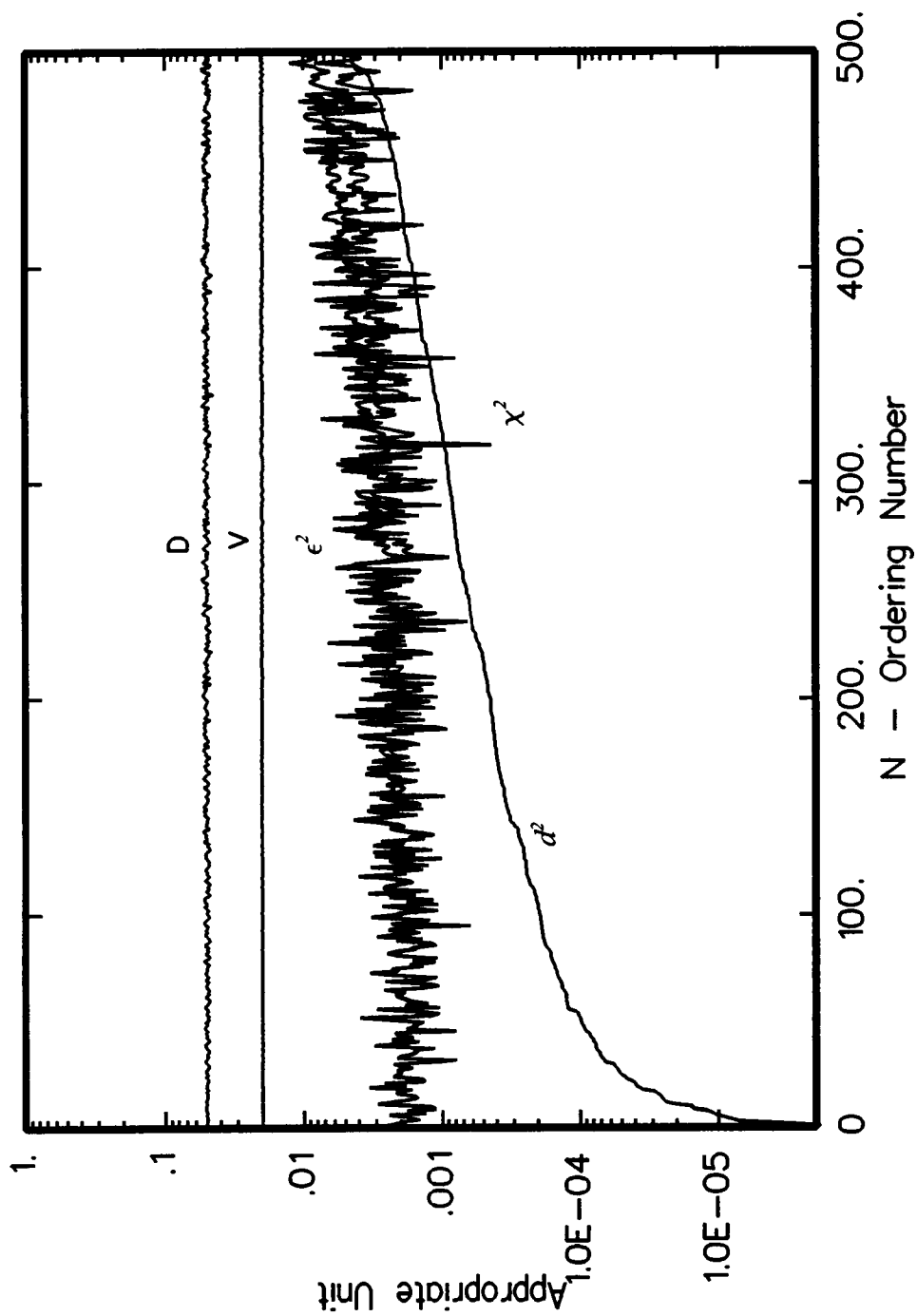


Figure 3.4.1 Deconvolution results for $\pm 2\%$ error (soot/scattering).

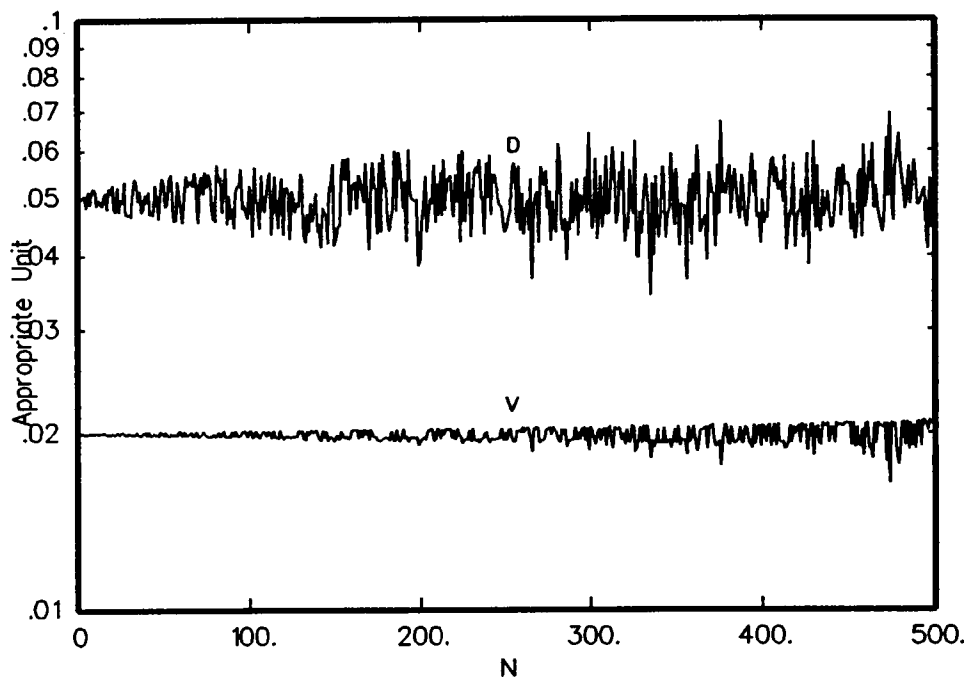


Figure 3.4.2A For D and V .

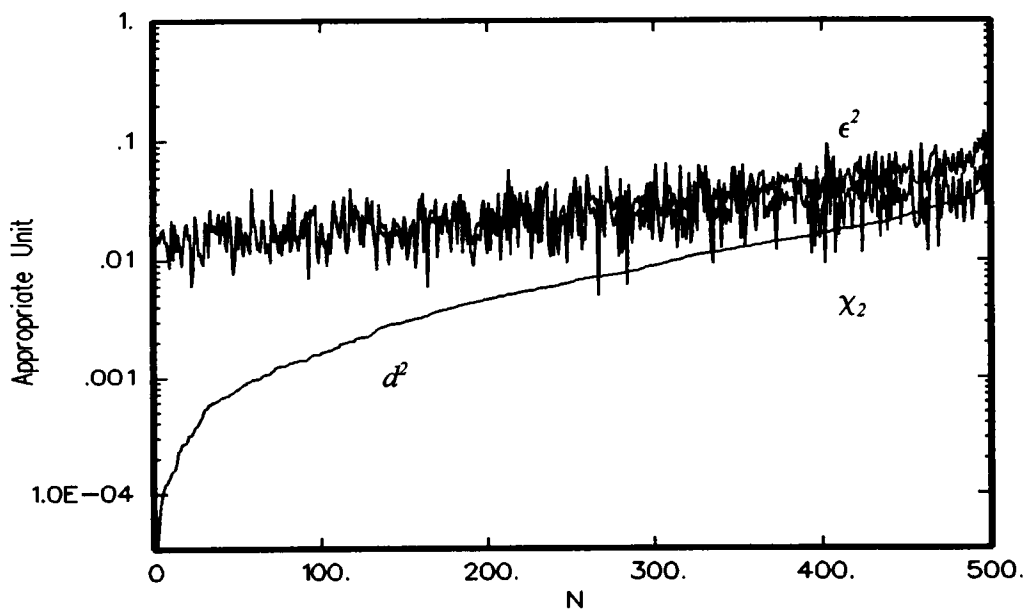


Figure 3.4.2B For d^2 , χ^2 and ϵ^2 .

Figure 3.4.2 Deconvolution results for $\pm 6\%$ error (soot/scattering).

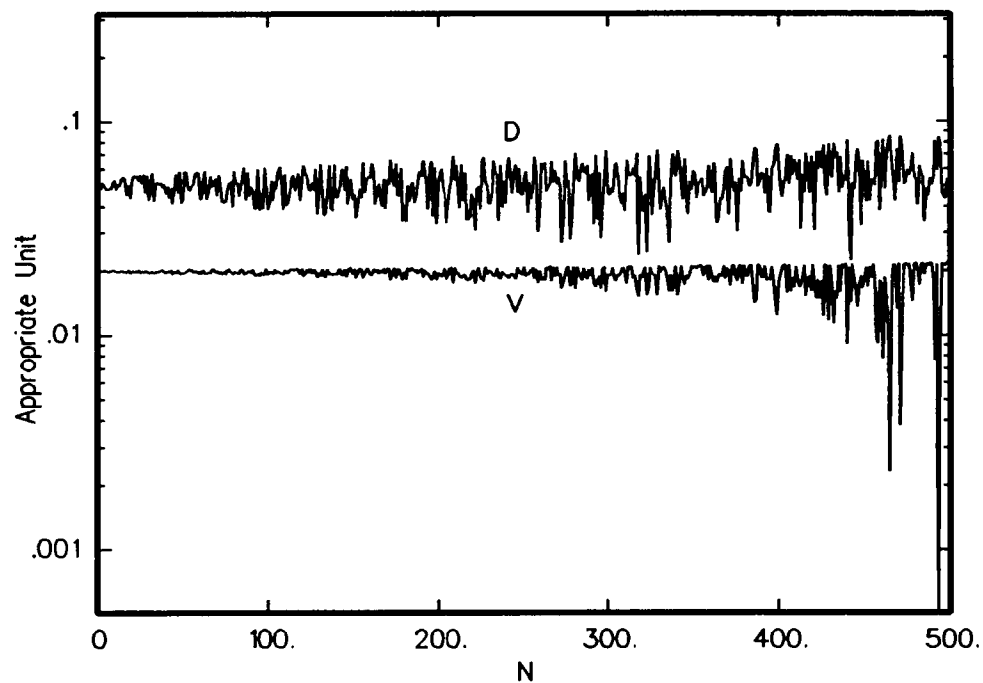


Figure 3.4.3A For D and V .

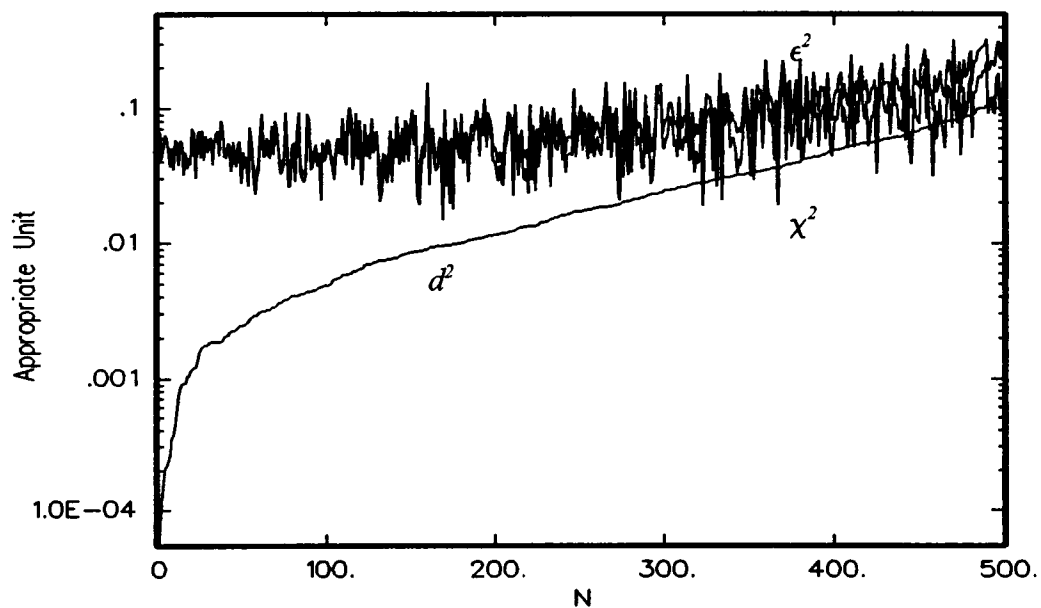


Figure 3.4.3B For d^2 , χ^2 and ϵ^2 .

Figure 3.4.3 Deconvolution results for $\pm 10\%$ error (soot/scattering).

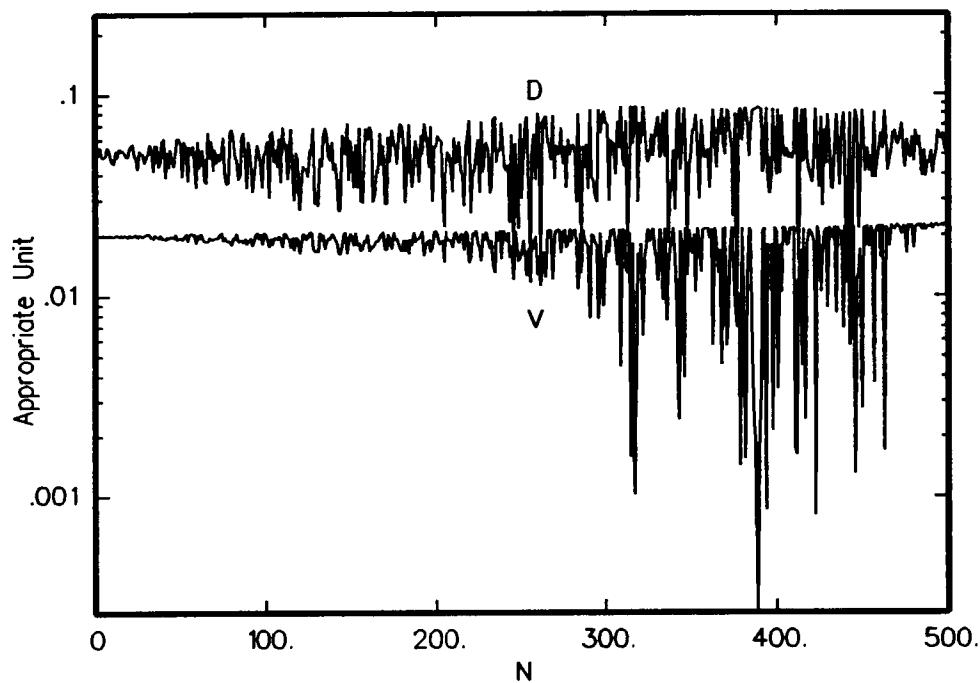


Figure 3.4.4A For D and V .

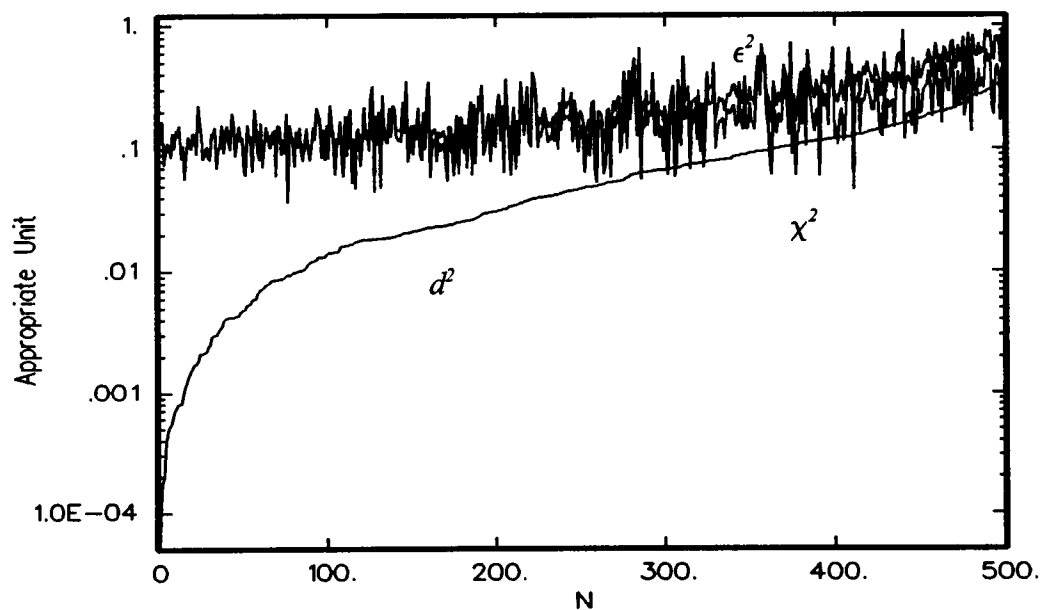


Figure 3.4.4B For d^2 , χ^2 , and ϵ^2 .

Figure 3.4.4 Deconvolution results for $\pm 16\%$ error (soot/scattering).

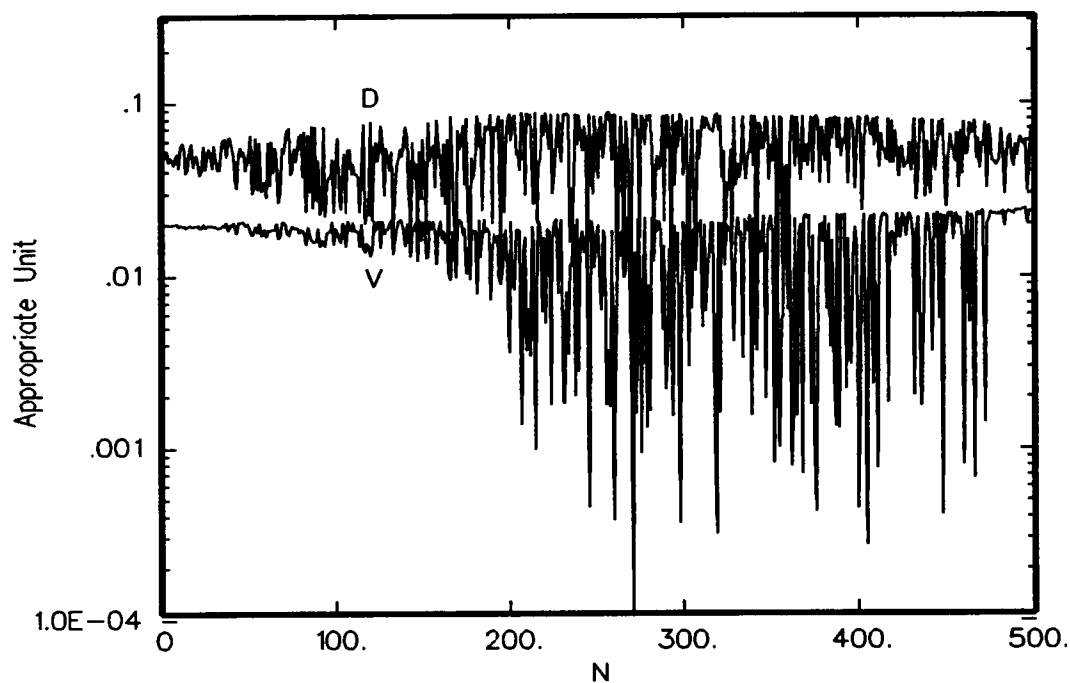


Figure 3.4.5A For D and V .

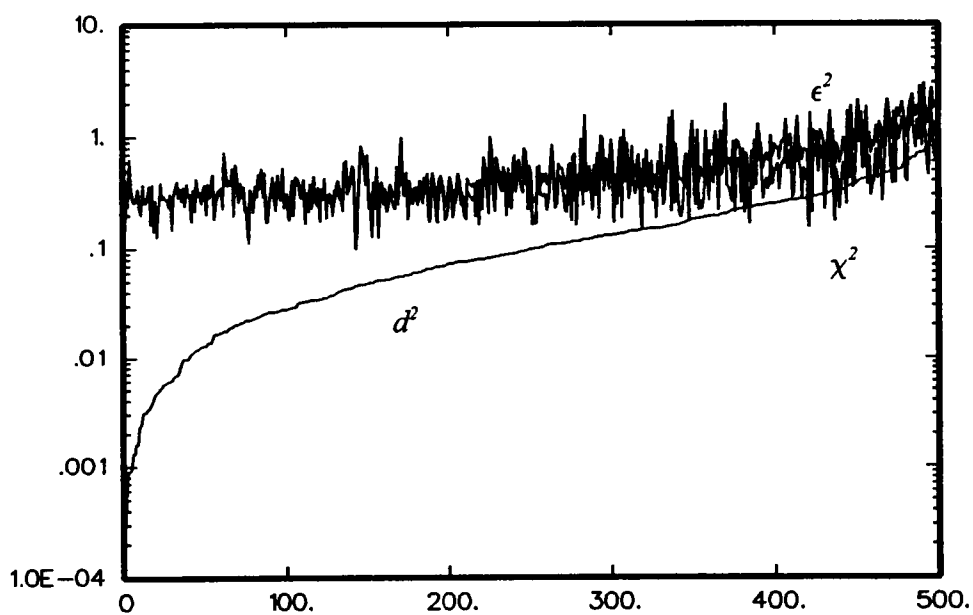


Figure 3.5.5B For d^2 , χ^2 and ϵ^2 .

Figure 3.4.5 Deconvolution results for $\pm 25\%$ error (soot/scattering).

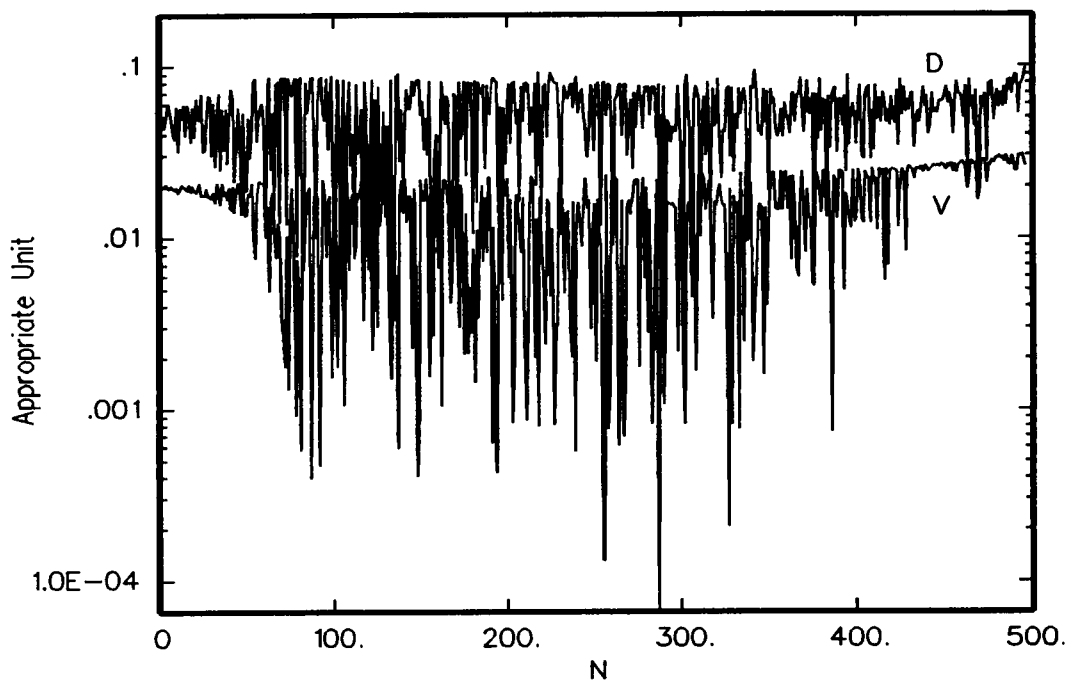


Figure 3.4.6A For D and V .

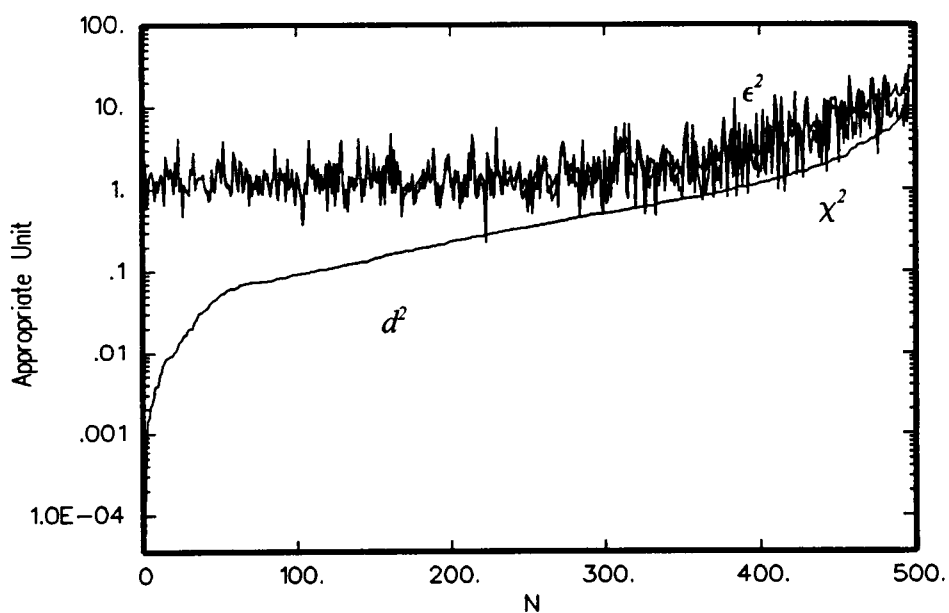


Figure 3.4.6B For d^2 , χ^2 , and ϵ^2 .

Figure 3.4.6 Deconvolution results for $\pm 50\%$ error (soot/scattering).

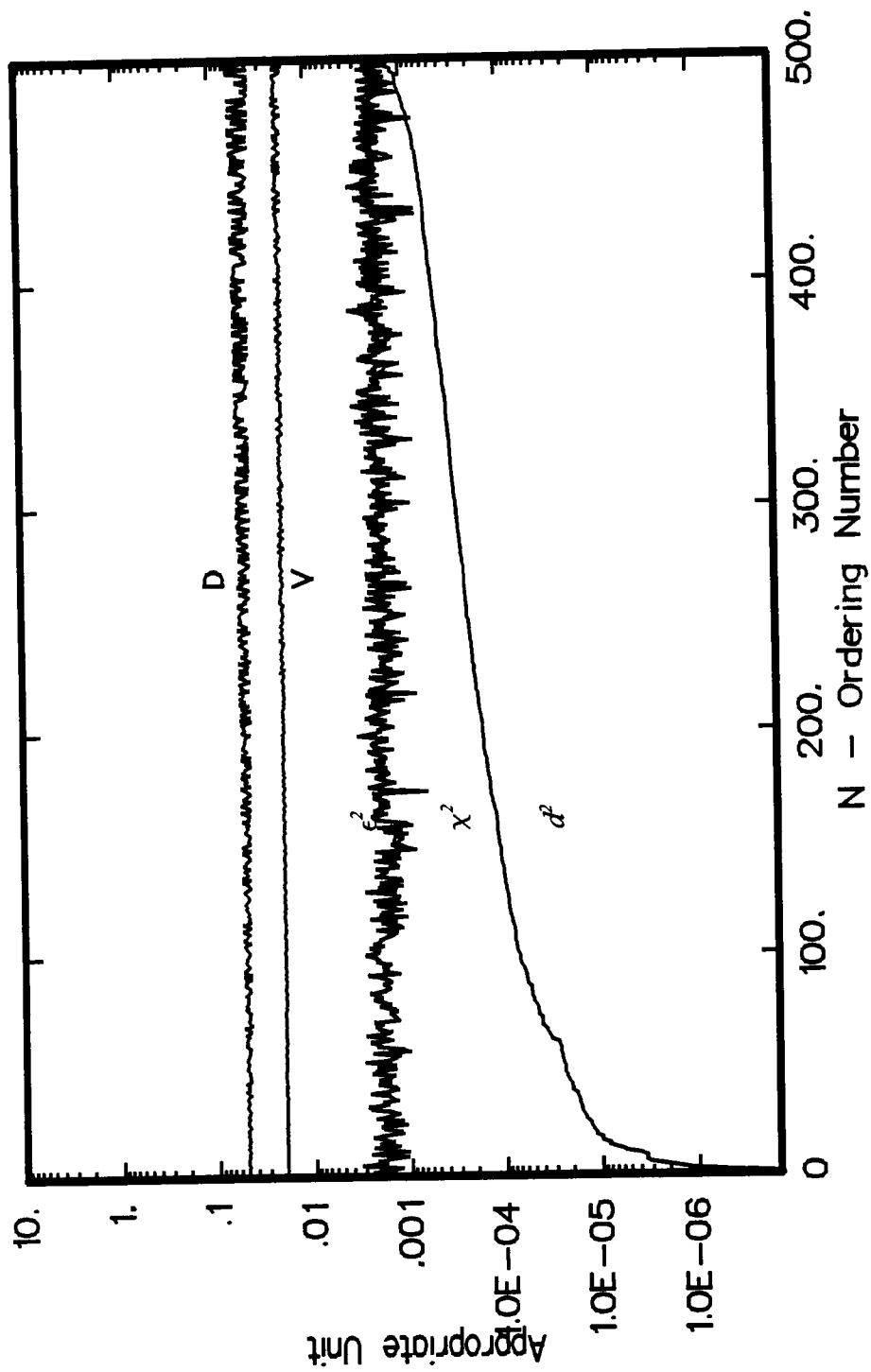


Figure 3.4.7 Deconvolution results for $\pm 2\%$ error (soot/extinction).

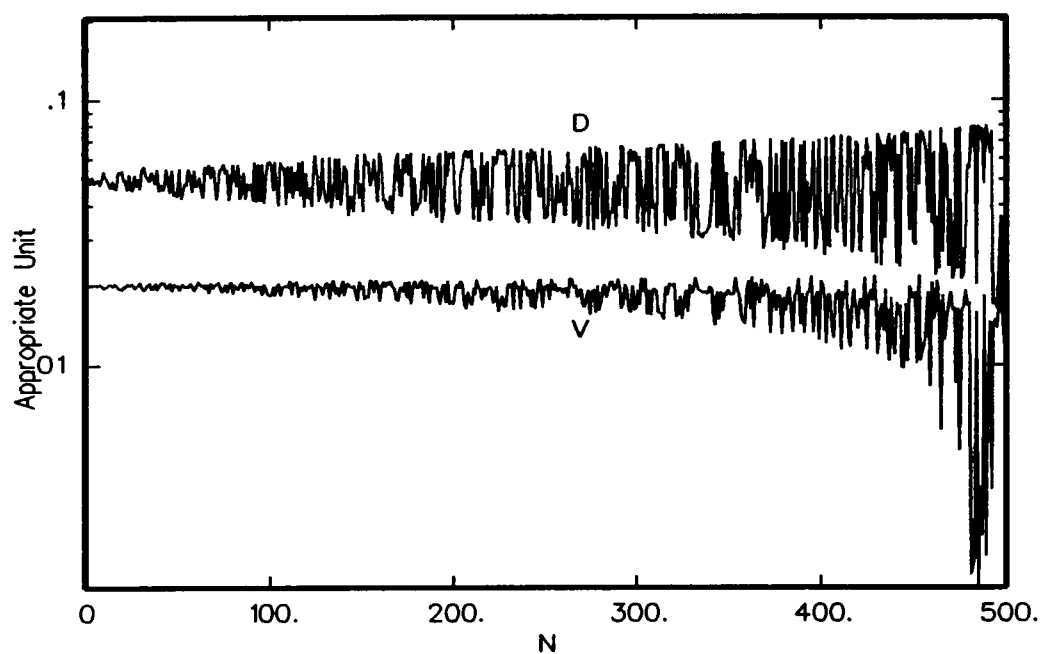


Figure 3.4.8A For D and V .

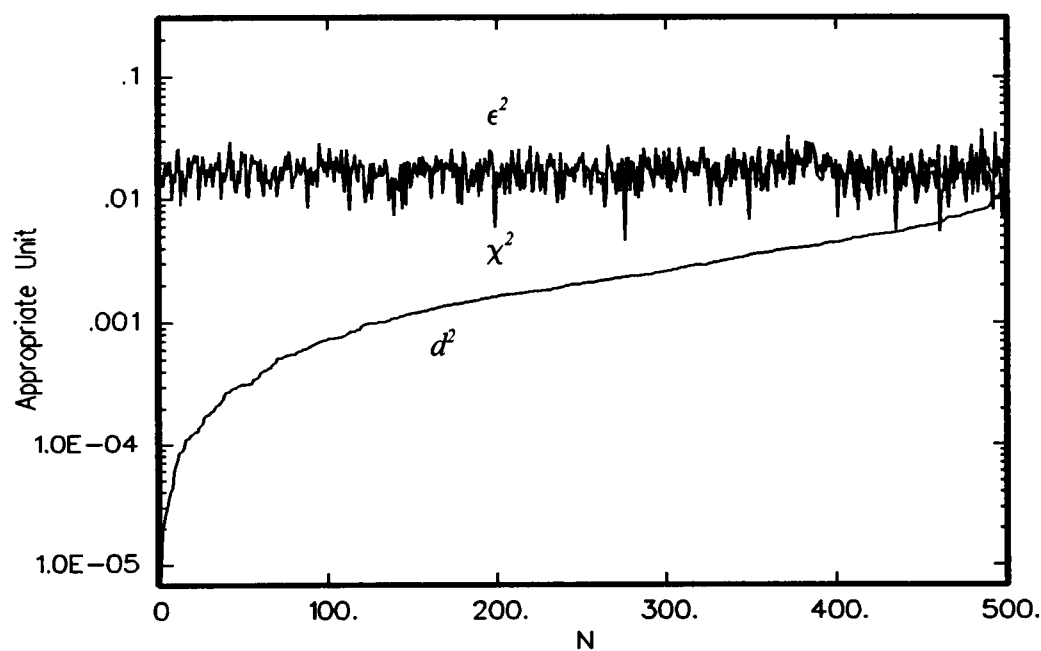


Figure 3.4.8B For d^2 , χ^2 , ϵ^2 .

Figure 3.4.8 Deconvolution results for $\pm 6\%$ error (soot/extinction).

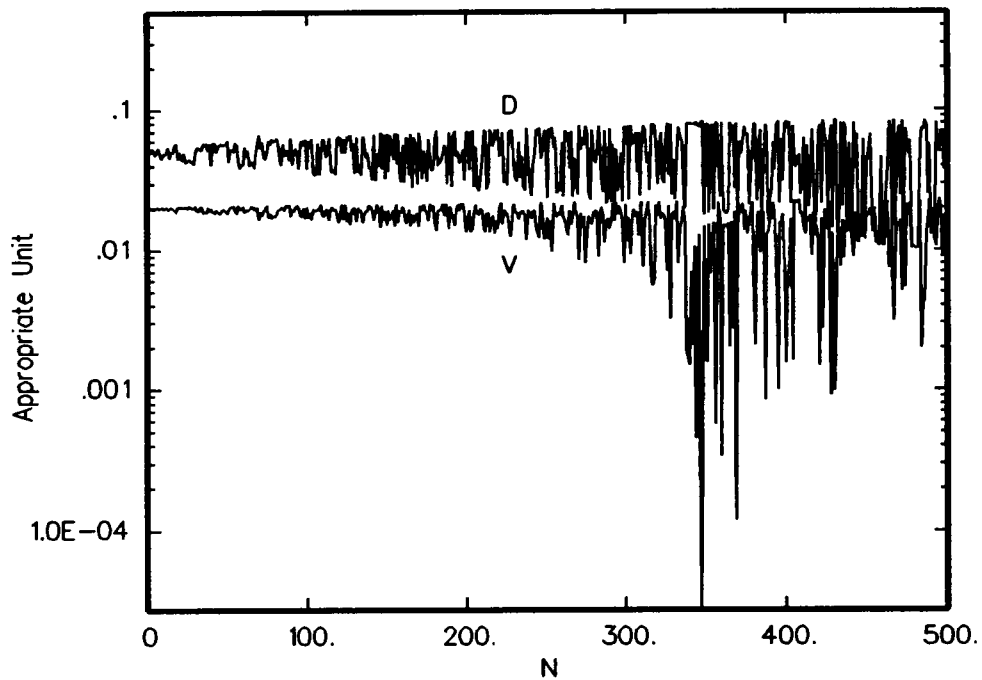


Figure 3.4.9A For D and V .

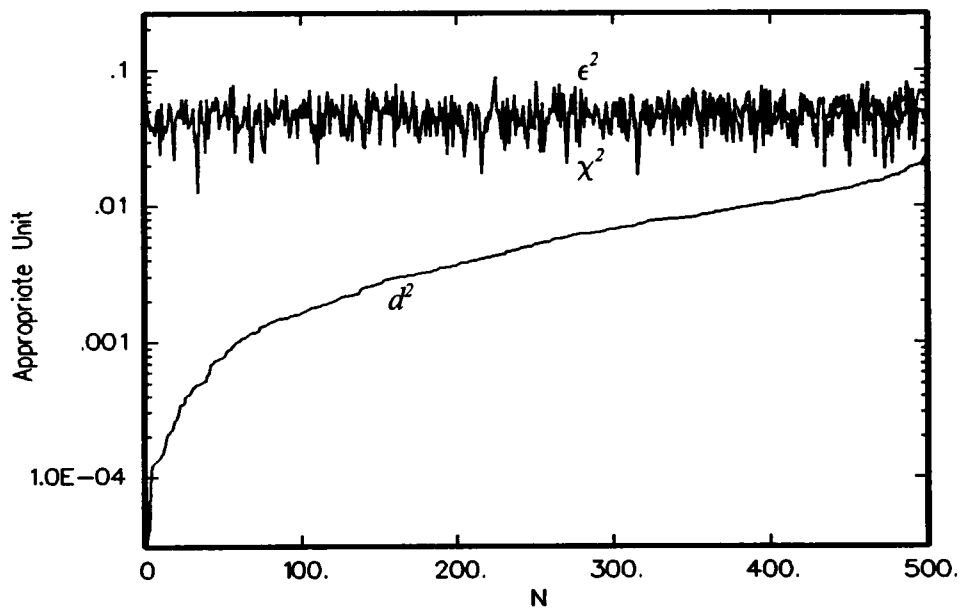


Figure 3.4.9B For d^2 , χ^2 , ϵ^2 .

Figure 3.4.9 Deconvolution results for $\pm 10\%$ error (soot/extinction).

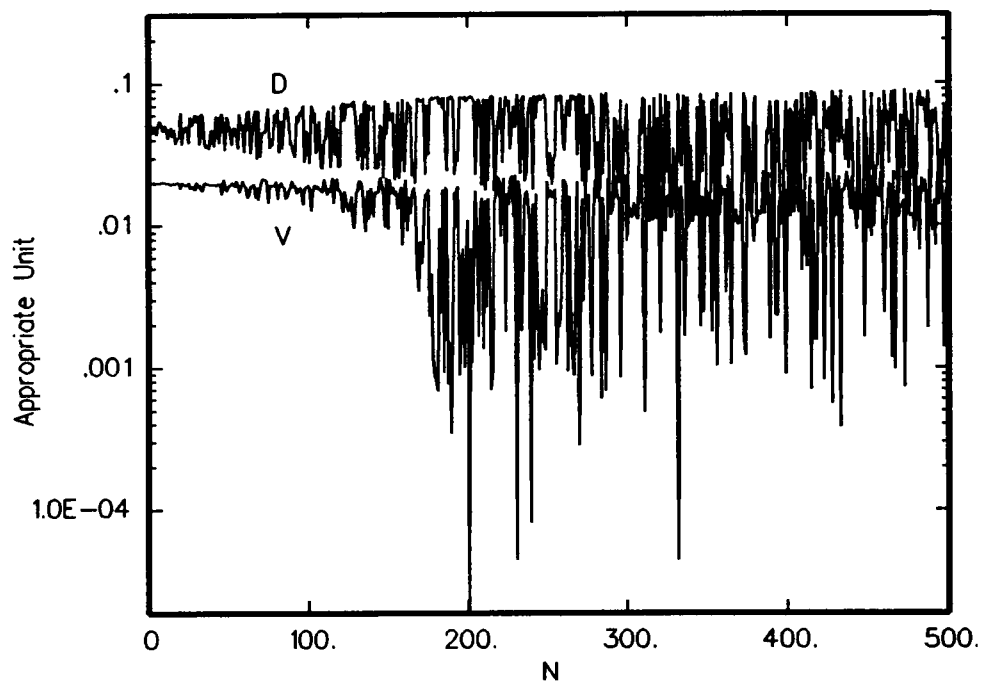


Figure 3.4.10A For D and V .

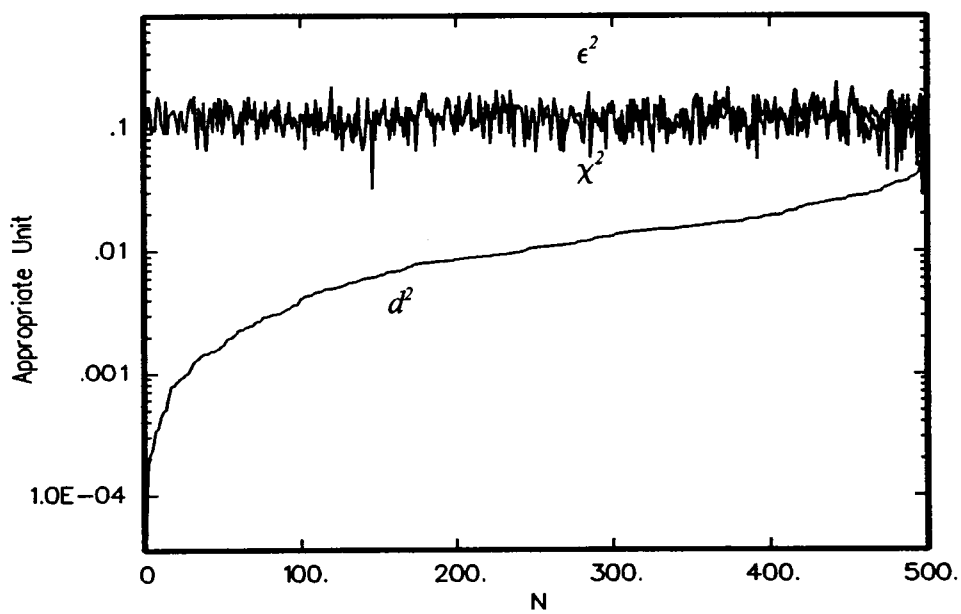


Figure 3.4.10B For d^2, χ^2, ϵ^2 .

Figure 3.4.10 Deconvolution results for $\pm 16\%$ error (soot/extinction).

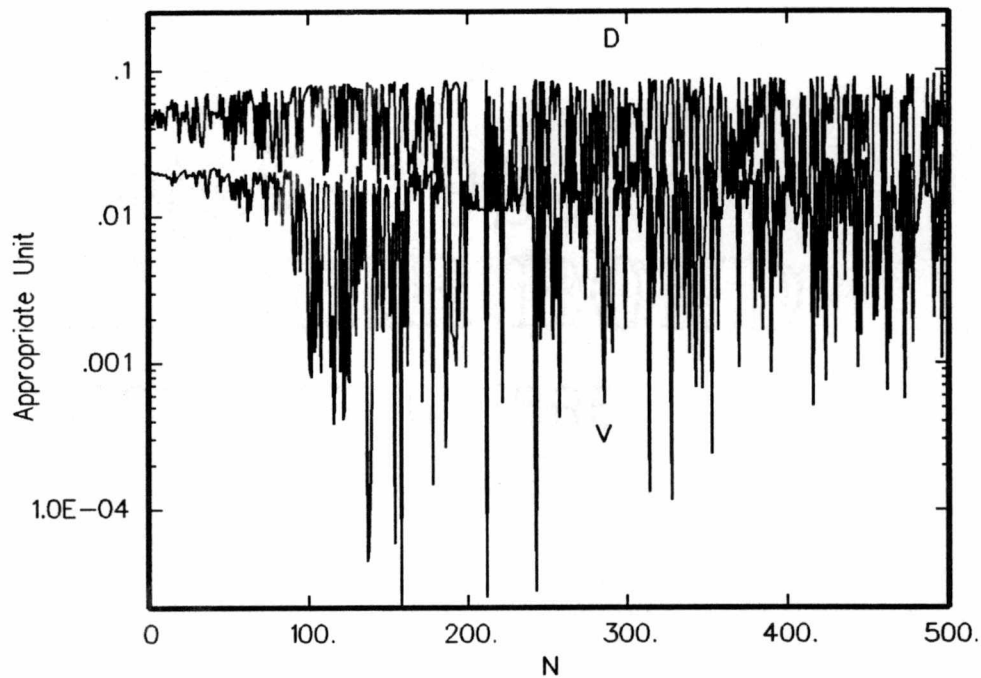


Figure 3.4.11A For D and V .

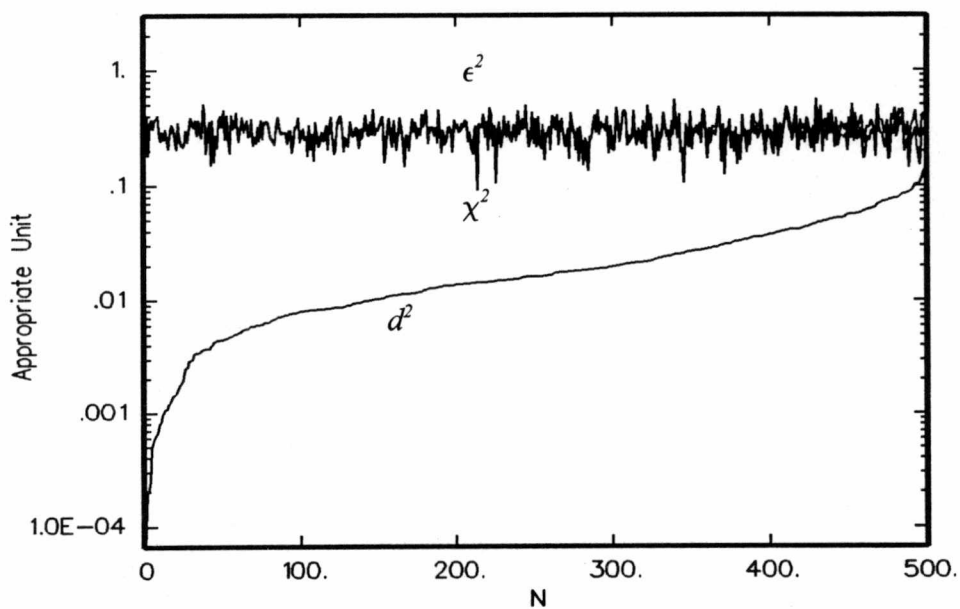


Figure 3.4.11B For d^2 , χ^2 , and ϵ^2 .

Figure 3.4.11 Deconvolution results for $\pm 25\%$ error (soot/extinction).

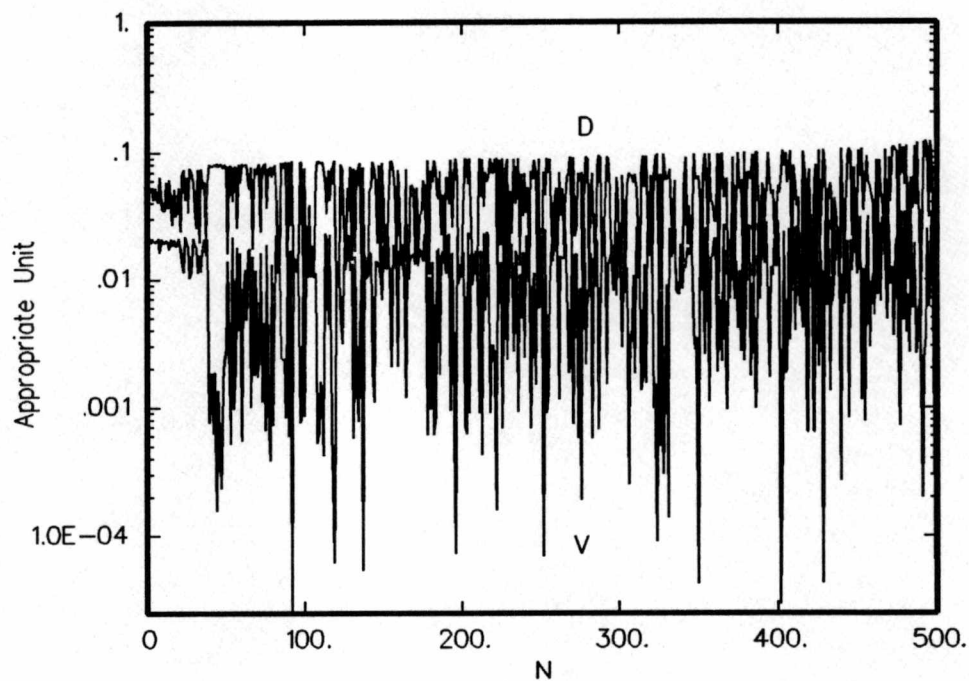


Figure 3.4.12A For D and V .

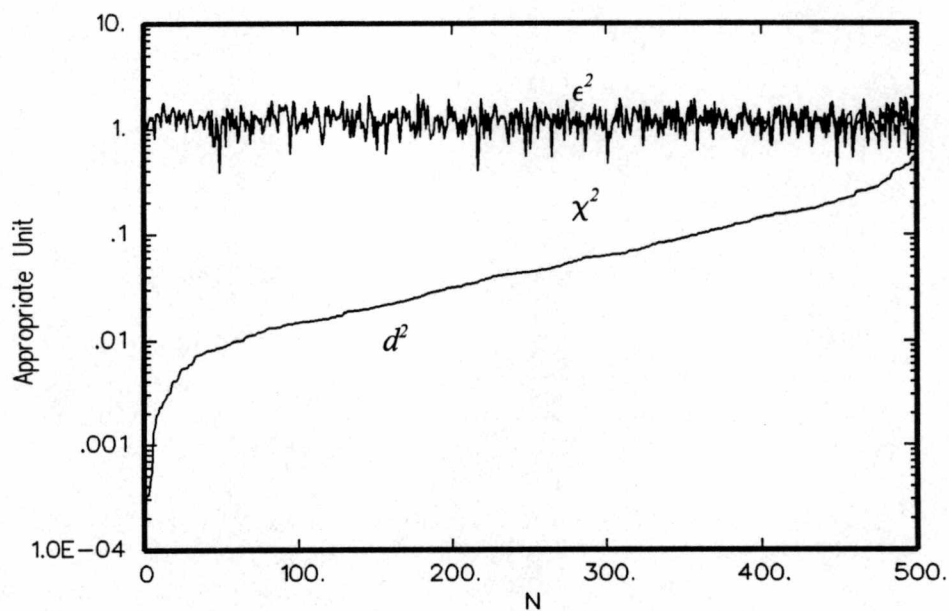


Figure 3.4.12B For d^2 , χ^2 , and ϵ^2 .

Figure 3.4.12 Deconvolution results for $\pm 50\%$ error (soot/extinction).

absorption or scattering, or both. It is also difficult to tell the differences in the extinction signals between two particulate systems which consist of the same material and occupy the same total extinction volume but have different size distributions, because the extinction signals are compensated by the difference in number densities (*i. e.* large distribution parameter with small number density and small distribution parameters with large number density).

The other fact is that for either scattering or extinction, the results for large water droplets are better than those for small soot particles. This is probably because the size parameter of the water droplets is about unity (< 10) which is the best situation for scattering or extinction signal to be meaningful, as pointed out by several authors.^[3] The wavelength range used for soot particles makes the size parameter x smaller than unity.

It is interesting that in Figures (3.4.7) through (3.4.9) the fluctuations in V are smaller than D , on the contrary to the water droplets system. It is easy to show that Eq(3.3.7) is violated in the soot system, *i.e.*, for $D = 0.05$, $V = 0.02$ ($\mu_0 = -2.996$, $\sigma_0 = 0.3853$)

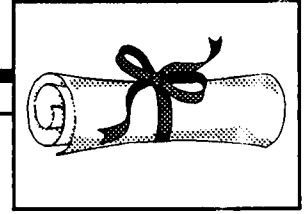
$$\frac{|\mu_0|}{\sigma_0} = 7.776 > 2.773 \quad (3.4.1)$$

The variation in the fluctuation behaviors of D and V for the two particle systems shows that the deconvolution results depends, in addition to measurement error and the kernel functions, on the profiles or the widths of the log-normal distributions. This topic will be discussed in detail in Chapter 4.

In summary, the Monte Carlo Simulation method and the results described in this chapter show that the DHS deconvolution method is valid for obtaining PSDF from

scattering and extinction measurements with random errors of up to $\pm 16\%$ for scattering and $\pm 10\%$ for extinction in the water droplet particle system with particle size about one micrometer. For the small soot particle system, the corresponding figures are $\pm 10\%$ for scattering and $\pm 6\%$ for extinction, respectively. In addition to above conclusions, one can also acquire the statistical information on the probability distribution for the resultant parameters (D , V). A complete discussion on this issue will be seen in next chapter.

Chapter 4



Reliability Analysis of Downhill Simplex Method

In section 1 of this chapter, the expressions for the appropriate variances of the four particle size distribution parameters ($\Delta\mu_0$, $\Delta\sigma_0$, ΔD_0 and ΔV_0) are derived and the validity of these expressions are compared to the simulated results. Section 2 discusses the restrictions imposed on the width of a log-normal distribution for a successful deconvolution. Section 3 investigates the uncertainties of χ^2 in the ΔD_0 and ΔV_0 domain. The MC simulation results are then utilized to obtain the mean and the variance for each PSDF parameter and are compared with those expressions derived in section 1.

§ 4.1 Variances in Distribution Parameters μ , σ , D and V

One scheme for showing the statistical characters of the PSDF parameters is to look at their distributions through multi-deconvolution results as was done in Chapter 3. It is obvious that, because the error for each data point is a random error, the distribution functions for the PSDF parameters will be normal distributed^[16] with μ_0 , σ_0 , D_0 and V_0 as the means within certain error margins, as discussed in Chapter 3. The goal is to find the expressions for the upper limit of the appropriate variances ($\Delta\mu_0$, $\Delta\sigma_0$, ΔD_0 and ΔV_0) with respect to the measurement errors and compare the results obtained from these relations with those obtained from the MC simulation results. Apparently, the relations of (3.3.7) and (3.3.8) can not be used for this purpose because they are just

the variance relations between the different sets of parameters based on the asymmetry properties of the log-normal distribution and have nothing to do with the error vector ϵ .

In order to examine the behaviors of μ and σ conveniently, Eqs.(2.1.10) and (2.1.11) are written as

$$p(\mu, \sigma, d) = \frac{1}{\sqrt{2\pi} \sigma d} \exp \left[-\frac{(\log d - \mu)^2}{2\sigma^2} \right], \quad (4.1.1)$$

$$\begin{aligned} \mu &= \ln D - \frac{\sigma^2}{2} \\ \sigma^2 &= \ln \left(1 + \frac{V^2}{D^2} \right). \end{aligned} \quad (4.1.2)$$

As derived in Chapter 2, the difference vector $\mathbf{d}$ of the fitted and original data vectors and the error vector ϵ satisfy

$$d^2 = [\mathbf{K}(\mathbf{f} - \mathbf{p})]^2 \leq \epsilon^2,$$

$$\text{or} \quad (\mathbf{K} \cdot \Delta \mathbf{f})^2 \leq \epsilon^2, \quad (4.1.3)$$

$$\text{where} \quad \Delta \mathbf{f} = \mathbf{f} - \mathbf{p}.$$

Because a tiny change in the trial PSDF $\mathbf{f}$ results from small changes in the parameters μ and σ , the differential form of $\Delta \mathbf{f}$ can be expressed as

$$\Delta \mathbf{f} = \frac{\partial \mathbf{f}}{\partial \mu} \Delta \mu + \frac{\partial \mathbf{f}}{\partial \sigma} \Delta \sigma.$$

In writing $\Delta \mathbf{f}$ as above, it has been assumed that $\Delta \mathbf{f}$ is so small that only the linear terms in $\Delta \mu$ and $\Delta \sigma$ are significant. Substituting $\Delta \mathbf{f}$ into (4.1.3) gives

$$\left[\mathbf{K} \cdot \left(\frac{\partial \mathbf{f}}{\partial \mu} \Delta \mu + \frac{\partial \mathbf{f}}{\partial \sigma} \Delta \sigma \right) \right]^2 \leq \epsilon^2 \quad (4.1.4a)$$

or

$$\sum_{i=1}^n \left[\Delta\mu^2 \left[\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial \mu} \right]^2 + \Delta\sigma^2 \left[\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial \sigma} \right]^2 + \Delta\mu\Delta\sigma \left[\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial \mu} \right] \cdot \left[\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial \sigma} \right] \right] \leq \epsilon^2. \quad (4.1.4b)$$

To single out the variance behavior of μ , assuming $\Delta\sigma = 0$ in (4.1.4a), one thus has

$$\left(\mathbf{K} \cdot \frac{\partial \mathbf{f}}{\partial \mu} \Delta\mu \right)_0^2 \leq \epsilon^2. \quad (4.1.5)$$

For a log-normal distribution, the partial derivative of $\mathbf{f}$ versus μ satisfies

$$\left. \frac{\partial \mathbf{f}}{\partial \mu} \right|_0 = \mathbf{f} \frac{\ln d - \mu_0}{\sigma_0^2}.$$

As discussed in Chapter 2, (4.1.3) is valid on a statistical basis. Equation (4.1.4) should be written as

$$\langle (\Delta\mu)^2 \rangle \leq \frac{\langle \epsilon^2 \rangle}{\left[\mathbf{K} \mathbf{f} \frac{\ln d - \mu_0}{\sigma_0^2} \right]^2} = \frac{\sigma_0^4 \langle \epsilon^2 \rangle}{\Gamma_\mu}, \quad (4.1.6)$$

where

$$\Gamma_\mu = [\mathbf{K} \cdot \mathbf{f}(\ln d - \mu_0)]^2 = \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) f(d) (\ln d - \mu_0) d(d) \right)^2. \quad (4.1.7)$$

The angle brackets in (4.1.6) indicate that the averages have been taken.

Applying the same procedures to σ , one can obtain

$$\langle (\Delta\sigma)^2 \rangle \leq \frac{\langle \epsilon^2 \rangle}{\left[\mathbf{K} \mathbf{f} \frac{(\ln d - \mu_0)^2 - \sigma_0^2}{\sigma_0^3} \right]^2} = \frac{\sigma_0^6 \langle \epsilon^2 \rangle}{\Gamma_\sigma}, \quad (4.1.8)$$

where

$$\Gamma_{\sigma} = [K \cdot f((\ln d - \mu_0)^2 - \sigma_0^2)]^2 = \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) f(d) ((\ln d - \mu_0)^2 - \sigma_0^2) d(d) \right)^2. \quad (4.1.9)$$

To simplify the notation, the angle brackets for averaging will be dropped hereafter, and all the variances of the distribution parameters should be understood as the averaged quantities.

One can see from Eq.(4.1.6) and (4.1.8) that both $\Delta\mu$ and $\Delta\sigma$ are linearly proportional to error ε . In addition, Eqs.(4.1.6) and (4.1.8) also reflect the dependence of the deconvolution results on the width of the log-normal distribution. Referring to Eq(4.1.2), it is obvious that of $\Delta\mu \sim \sigma_0^2$ and $\Delta\sigma \sim \sigma_0^3$ imply that a relatively broad distribution (with a large V/D ratio) would cause a large uncertainty in the parameters. The conclusion might explain the similar results reported by Taylor^[19] *et al* who performed the simulations for the experiment of photon correlation spectroscopy.

Following similar derivations for $\Delta\mu$ and $\Delta\sigma$, one can obtain the relations for ΔD and ΔV . The differential in vector $\mathbf{f}$ now is

$$\Delta \mathbf{f} = \frac{\partial \mathbf{f}}{\partial D} \Delta D + \frac{\partial \mathbf{f}}{\partial V} \Delta V.$$

Inserting the above expression into (4.1.3) yields

$$\left[K \cdot \left[\frac{\partial \mathbf{f}}{\partial D} \Delta D + \frac{\partial \mathbf{f}}{\partial V} \Delta V \right] \right]^2 \leq \varepsilon^2, \quad (4.1.10a)$$

or

$$\sum_{i=1}^n \left[\Delta D^2 \left[K_i \frac{\partial \mathbf{f}}{\partial D} \right]^2 + \Delta V^2 \left[K_i \frac{\partial \mathbf{f}}{\partial V} \right]^2 + \Delta D \Delta V \left[K_i \frac{\partial \mathbf{f}}{\partial D} \right] \left[K_i \frac{\partial \mathbf{f}}{\partial V} \right] \right] \leq \varepsilon^2. \quad (4.1.10b)$$

To single out the variance of D , one can set $\Delta V = 0$. Equation (4.1.10a) becomes

$$\left(K \cdot \frac{\partial f}{\partial D} \Delta D \right)_0^2 \leq \epsilon^2. \quad (4.1.11)$$

The partial derivative of f with respect to D can be expressed as

$$\frac{\partial f}{\partial D} = \frac{\partial f}{\partial \mu} \frac{\partial \mu}{\partial D} + \frac{\partial f}{\partial \sigma} \frac{\partial \sigma}{\partial D}.$$

Using (4.1.1) and (4.1.2), the above equation can be expressed as

$$\frac{\partial f}{\partial D} = \frac{1}{D(D^2 + V^2)} \left[f_1(d)(D^2 + 2V^2) - f_2(d) \frac{V^2}{\sigma} \right], \quad (4.1.12)$$

where $f(d)_1$ and $f(d)_2$ are defined as

$$\begin{cases} f_1(d) = \frac{\partial f(d)}{\partial \mu} = f(d) \frac{(\ln d - \mu)}{\sigma^2} \\ f_2(d) = \frac{\partial f(d)}{\partial \sigma} = f(d) \frac{(\ln d - \mu)^2 - \sigma^2}{\sigma^3} \end{cases} \quad (4.1.13)$$

The expression for the variance in D is then

$$(\Delta D)^2 \leq \frac{\sigma^6 D^2 (D^2 + V^2)^2 \epsilon^2}{\Gamma_D}, \quad (4.1.14)$$

where

$$\begin{aligned} \Gamma_D &= \left(\sigma^3 K \cdot \left[f_1(d)(D^2 + 2V^2) - f_2(d) \frac{V^2}{\sigma} \right] \right)^2 \\ &= \sum_{i=1}^n \left(\sigma^3 \int_0^{d_{\max}} K_i(d) \left[f_1(d)(D^2 + 2V^2) - f_2(d) \frac{V^2}{\sigma} \right] d(d) \right)^2 \\ &= \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) f(d) [(\ln d - \mu)(D^2 + 2V^2)\sigma - ((\ln d - \mu)^2 - \sigma^2)V^2] d(d) \right)^2. \end{aligned} \quad (4.1.15)$$

Following the same procedures as for D , one finds

$$\frac{\partial f}{\partial V} = \frac{V}{(D^2 + V^2)} \left[\frac{f_2(d)}{\sigma} - f_1(d) \right]. \quad (4.1.16)$$

The variance for V is then

$$(\Delta V)^2 \leq \frac{\sigma^6 (D^2 + V^2)^2 \varepsilon^2}{V^2 \Gamma_V}, \quad (4.1.17)$$

where

$$\begin{aligned} \Gamma_V &= \left(\sigma^4 K \cdot \left[\frac{f_2(d)}{\sigma} - f_1(d) \right] \right)^2 \\ &= \sum_{i=1}^n \left(\int_0^{d_{\max}} \sigma^4 K_i(d) \left[\frac{f_2(d)}{\sigma} - f_1(d) \right] d(d) \right)^2 \\ &= \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) f(d) [(\ln d - \mu)^2 - \sigma^2 - \sigma^2 (\ln d - \mu)] d(d) \right)^2. \end{aligned} \quad (4.1.18)$$

It is seen that both ΔD and ΔV are linearly proportional to the error level ε , just like $\Delta \mu$ and $\Delta \sigma$. It is convenient to write a common equation for all four parameters

$$\Delta \xi^2(\sigma_e) \leq \frac{\varepsilon^2(\sigma_e)}{P_\xi^2}, \quad (4.1.19a)$$

where P_ξ is defined as

$$P_\xi^2 = \left[K \cdot \frac{\partial f}{\partial \xi} \right]_0^2 = \sum_{i=1}^n \left[\int K_i(d) \left[\frac{\partial f(d)}{\partial \xi} \right]_0 d(d) \right]^2, \quad (4.1.19b)$$

where ξ can be either μ , σ , D or V and σ_e is the error level as introduced in Chapter 3. For any specific particulate system, the constant quantity P_ξ is easily computed. Table (4.1.1) gives the results of P_ξ for the water particle system introduced in Chapter 3.

The validity of all the expressions for $\Delta \mu_0$, $\Delta \sigma_0$, ΔD_0 and ΔV_0 have been proven by the Monte Carlo simulation results (as seen in the following), and the quantities $\Delta \xi$

and ϵ are all increasing with respect to σ_e . Taking the square root of (4.1.19), it can then be written as

$$\Delta\xi(\sigma_e) \leq \frac{\epsilon(\sigma_e)}{\left| \mathbf{K} \cdot \frac{\partial}{\partial \xi} \right|_0} = \frac{\epsilon(\sigma_e)}{P_\xi} . \quad (4.1.20)$$

Figures (4.1.1) and (4.1.2) plot the results for the simulation of water-drop scattering that was discussed in Chapter 3. Both sides of (4.1.20) are plotted *versus* σ_e which changes from $\pm 0\%$ to $\pm 50\%$ of the true data value. The figures show that (4.1.20) is well observed, especially for the sections of $\sigma_e < \pm 25\%$ where all the parameter's variances ($\Delta\mu_0$, $\Delta\sigma_0$, ΔD_0 and ΔV_0) and ϵ are approximately linearly related to σ_e , which is consistent with the relations indicated in (4.1.20).

Table (4.1.1) The calculated P_ξ 's for the water particle system.

<i>Systems</i>	P_μ	P_σ	P_D	P_V
<i>Water</i>	3.88	2.17	3.74	2.11

A significant implication of (4.1.20) or Fig.(4.1.1 - 2) is that for a certain error level σ_e in the experimental data, the probability distributions of the resultant PSDF parameters can be predicted which are Gaussian distributed around the mean value of ξ_0 with standard deviation of $\Delta\xi(\sigma_e)$ defined by (4.1.20).

Tables (4.1.2) - (4.1.5) list the means and variances of the PSDF parameters (D , V , σ_D and σ_V) calculated from the simulation results discussed in last chapter (water and soot particles of both scattering and extinction). The relative deviations (R_D , R_V as defined by (3.3.5)) are also listed to show the differences for the two distributions. Five hundred deconvolutions were performed for each error level ($\pm 2\%$, $\pm 6\%$, $\pm 10\%$, $\pm 16\%$,

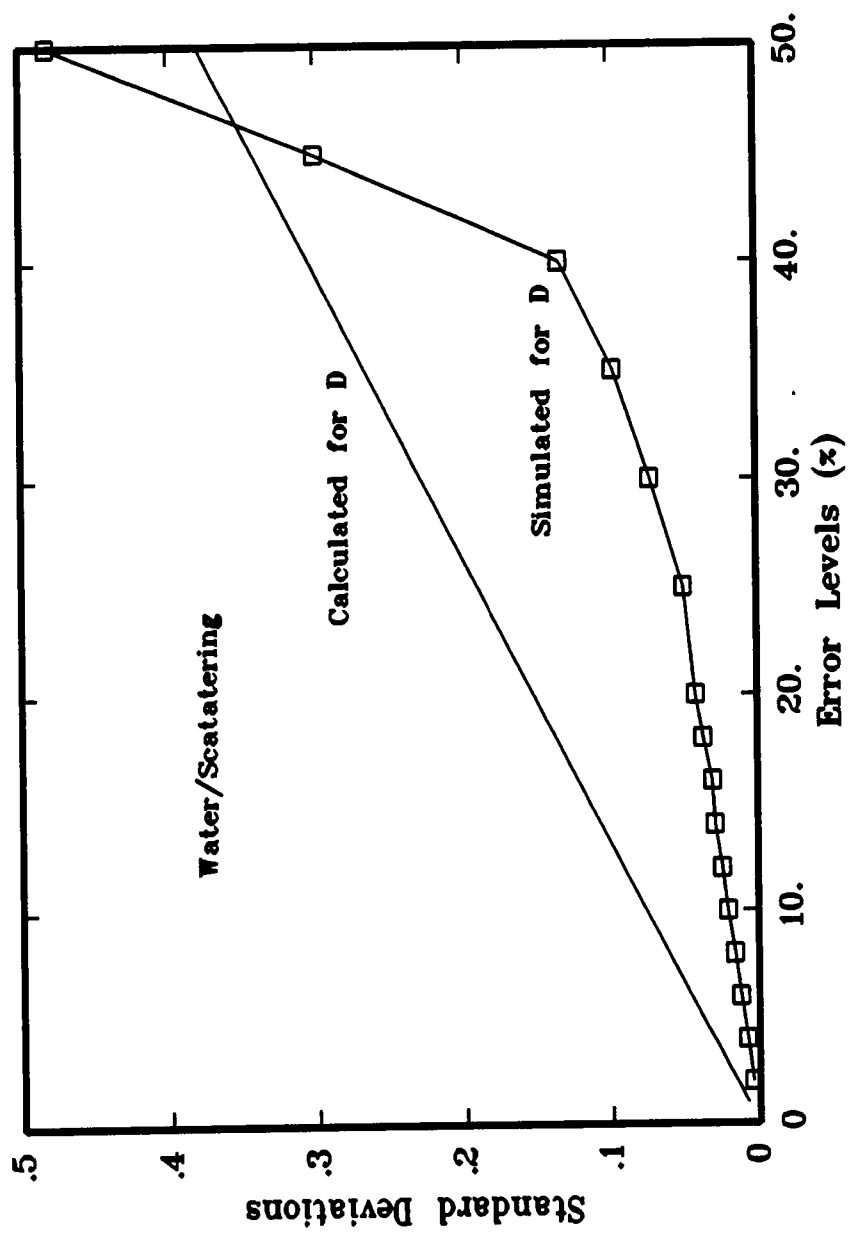


Figure 4.1.1 Simulated ΔD and calculated e/P_D from Eq.(4.1.20) for water/scattering case.

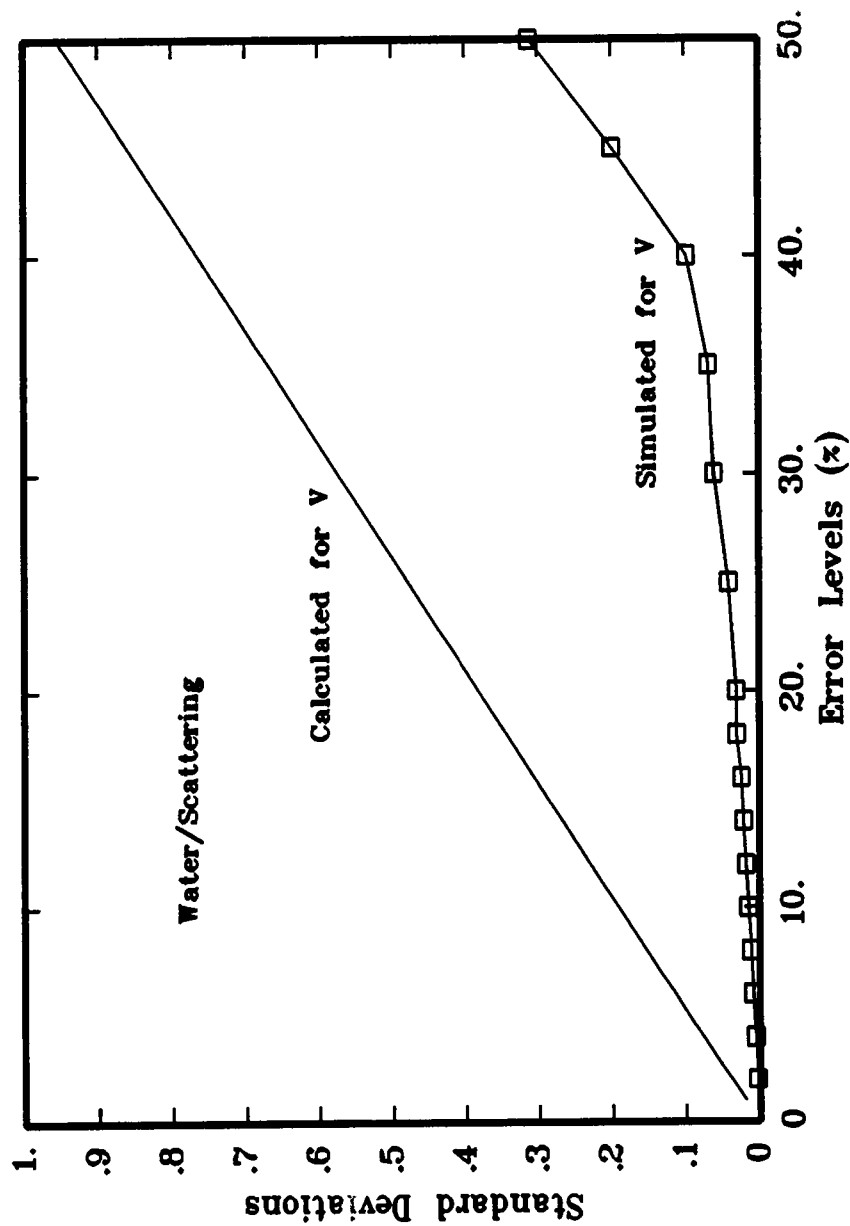


Figure 4.1.2 Simulated ΔV and calculated ϵ/P_V from Eq.(4.1.20) for water/scattering case.

Table 4.1.2 The simulation results of means and variances for D and V for water droplets scattering case in which $D_0 = 1.0$, $V_0 = 0.2$.

<i>error level</i>	$\langle D \rangle$	$\langle V \rangle$	σ_D	σ_V	R_D	R_V
$\pm 2\%$	1.000	0.200	3.568×10^{-3}	2.661×10^{-3}	3.57×10^{-3}	1.33×10^{-2}
$\pm 6\%$	1.000	0.199	1.717×10^{-2}	8.441×10^{-3}	1.72×10^{-2}	4.24×10^{-2}
$\pm 10\%$	0.999	0.197	1.952×10^{-2}	1.438×10^{-2}	1.95×10^{-2}	7.29×10^{-2}
$\pm 16\%$	0.996	0.197	3.205×10^{-2}	2.366×10^{-2}	3.22×10^{-2}	0.12
$\pm 25\%$	0.994	0.190	4.937×10^{-2}	4.175×10^{-2}	4.97×10^{-2}	0.22
$\pm 50\%$	1.019	0.256	0.383	0.268	0.38	1.05

Table 4.1.3 The means and variances of D and V (water/extinction).

<i>error level</i>	$\langle D \rangle$	$\langle V \rangle$	σ_D	σ_V	R_D	R_V
$\pm 2\%$	1.001	0.200	1.107×10^{-2}	1.284×10^{-2}	1.11×10^{-2}	6.42×10^{-2}
$\pm 6\%$	1.007	0.193	3.225×10^{-2}	4.433×10^{-2}	3.12×10^{-2}	0.23
$\pm 10\%$	1.028	0.189	6.649×10^{-2}	7.215×10^{-2}	6.47×10^{-2}	0.38
$\pm 16\%$	1.042	0.168	9.645×10^{-2}	9.706×10^{-2}	9.26×10^{-2}	0.58
$\pm 25\%$	1.078	0.148	0.149	0.109	0.14	0.74
$\pm 50\%$	1.553	0.399	4.882	3.511	3.14	10.34

Table 4.1.4 The simulation results of means and variances for D and V for soot particle scattering case in which $D_0 = 0.05$, $V_0 = 0.02$.

<i>error level</i>	$\langle D \rangle$	$\langle V \rangle$	σ_D	σ_V	R_D	R_V
$\pm 2\%$	5.005×10^{-2}	1.998×10^{-2}	1.720×10^{-3}	1.490×10^{-4}	3.44×10^{-2}	7.46×10^{-3}
$\pm 6\%$	4.994×10^{-2}	1.981×10^{-2}	5.271×10^{-3}	6.035×10^{-4}	0.106	3.05×10^{-2}
$\pm 10\%$	5.191×10^{-2}	1.900×10^{-2}	1.062×10^{-2}	2.417×10^{-3}	0.205	0.127
$\pm 16\%$	5.203×10^{-2}	1.766×10^{-2}	1.565×10^{-2}	4.831×10^{-3}	0.301	0.274
$\pm 25\%$	5.355×10^{-2}	1.559×10^{-2}	2.022×10^{-2}	6.762×10^{-3}	0.379	0.434
$\pm 50\%$	5.467×10^{-2}	1.513×10^{-2}	2.323×10^{-2}	8.271×10^{-3}	0.425	0.547

Table 4.1.5 The means and variances of D and V (soot/extinction).

<i>error level</i>	$\langle D \rangle$	$\langle V \rangle$	σ_D	σ_V	R_D	R_V
$\pm 2\%$	4.986×10^{-2}	1.981×10^{-2}	4.792×10^{-3}	5.330×10^{-4}	9.61×10^{-2}	2.69×10^{-2}
$\pm 6\%$	4.909×10^{-2}	1.862×10^{-2}	1.146×10^{-2}	3.250×10^{-3}	0.23	0.17
$\pm 10\%$	4.964×10^{-2}	1.610×10^{-2}	1.920×10^{-2}	5.099×10^{-3}	0.39	0.32
$\pm 16\%$	4.869×10^{-2}	1.372×10^{-2}	2.424×10^{-2}	6.597×10^{-3}	0.50	0.48
$\pm 25\%$	4.723×10^{-2}	1.258×10^{-2}	2.688×10^{-2}	7.089×10^{-3}	0.57	0.56
$\pm 50\%$	5.254×10^{-2}	1.123×10^{-2}	3.008×10^{-2}	8.563×10^{-3}	0.57	0.76

$\pm 25\%$ and $\pm 50\%$ respectively) to achieve the desired statistical precision. As expected, the variances for D and V increase with the error level σ_e .

For the case of water scattering, Table (4.1.2) shows that the mean values of D are almost constant ($\sim 1.0 \mu m$, the true value) for all error levels, as are the mean values of V ($\sim 0.2 \mu m$, true value) except for the case of $\pm 50\%$ error for which $\langle V \rangle = 0.2561$. For the extinction case of the same water system, Table (4.1.3) shows that large deviations occur at error levels of $\pm 50\%$ for D ($\langle D \rangle = 1.553$) and $\pm 16\%$ for V ($\langle V \rangle = 0.1684$). This fact shows that the deconvolution results are more stable for scattering measurements than extinction measurements. The same trend can also be found in soot particle systems in Tables (4.1.4) and (4.1.5) except that the large deviations in D and V occur at smaller error levels. For example, for the soot scattering case, the large deviations appear at the error level of $\pm 25\%$ for D and $\pm 16\%$ for V ; for the soot extinction case, the corresponding error levels at which the large deviations occur are $\pm 25\%$ for D and $\pm 10\%$ for V . The different behaviors of R_D and R_V for small soot particles and water particles can be seen clearly from the tables; for large water particles, $R_D < R_V$ while for small soot particles, $R_D > R_V$.

Figures (4.1.3) - (4.1.10) plot the probability distributions of D and V , corresponding to Tables (4.1.2) - (4.1.5), for the water and soot particle systems for different error levels. The *Gaussian* distribution in each figure is calculated using the mean and variance values in the corresponding table entry, and all curves are normalized at the location of the mean to compare the simulated distribution and the corresponding *Gaussian* distribution. As the error level σ_e becomes higher, the gradual broadening of the profiles and shifting of the means of the distributions becomes apparent in these figures.

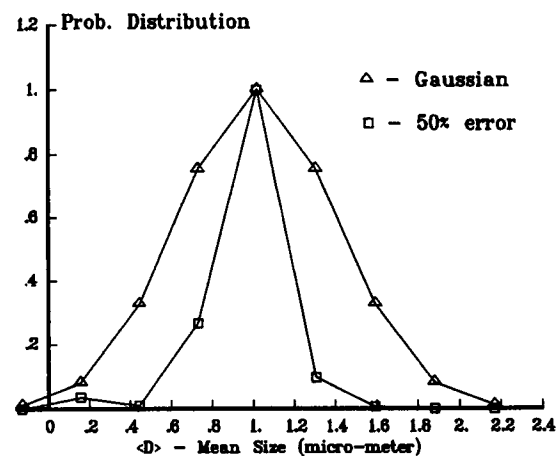
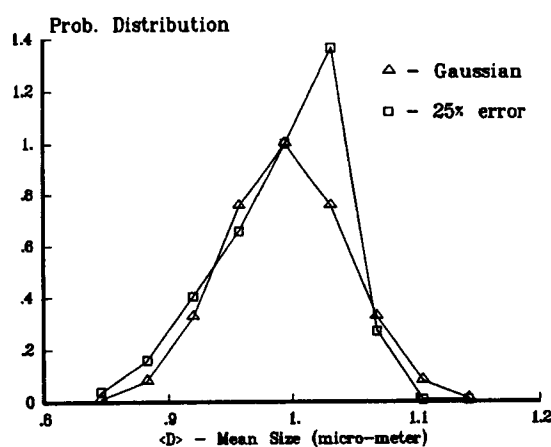
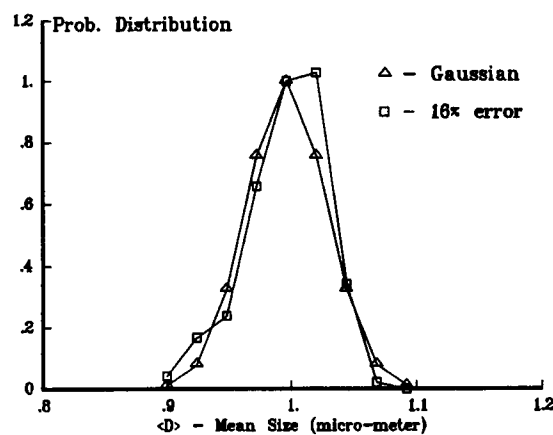
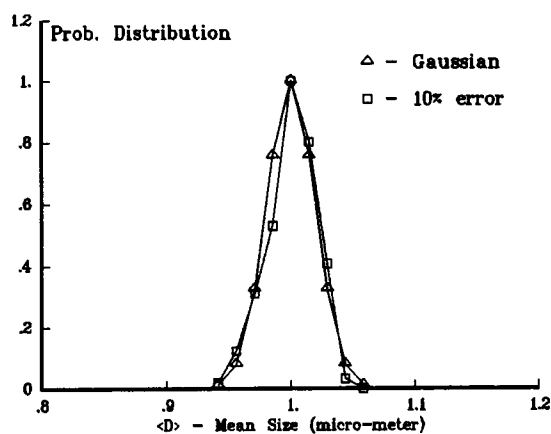
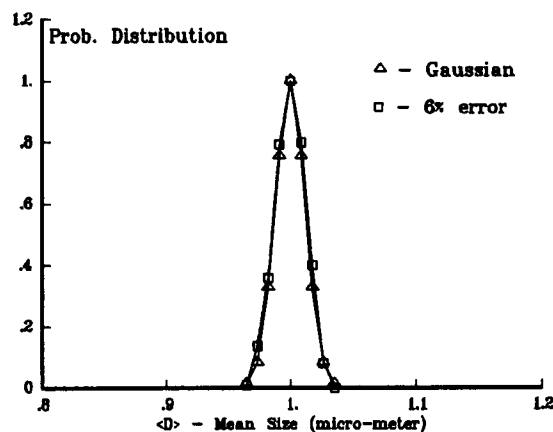
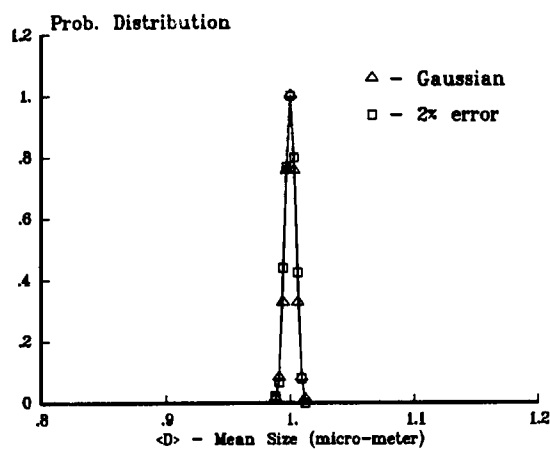


Figure 4.1.3 The probability distributions of $\langle D \rangle$ for various error levels, comparing with the true Gaussian distributions (data: water/scattering).

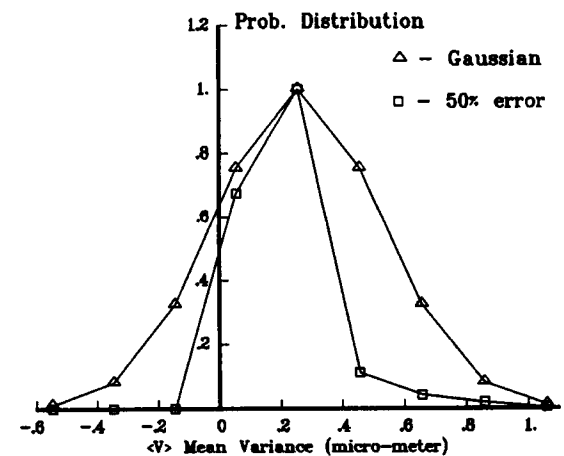
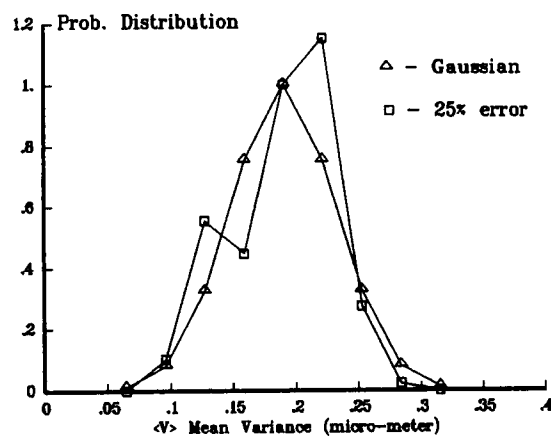
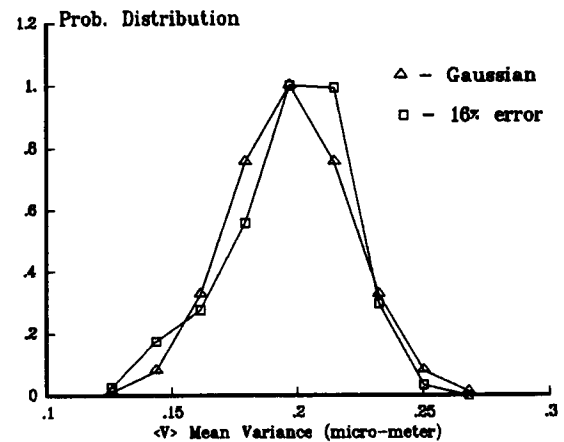
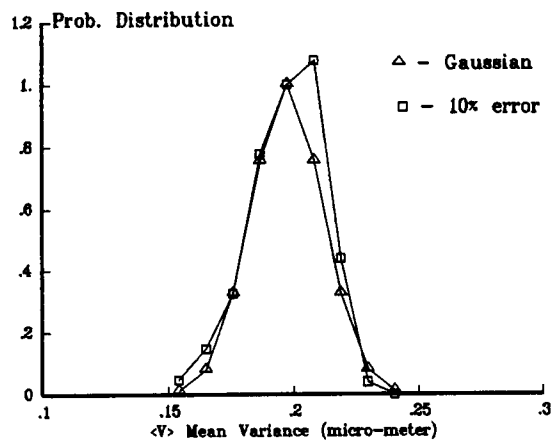
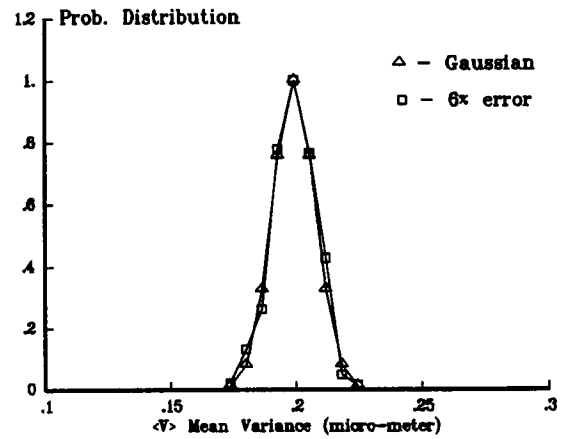
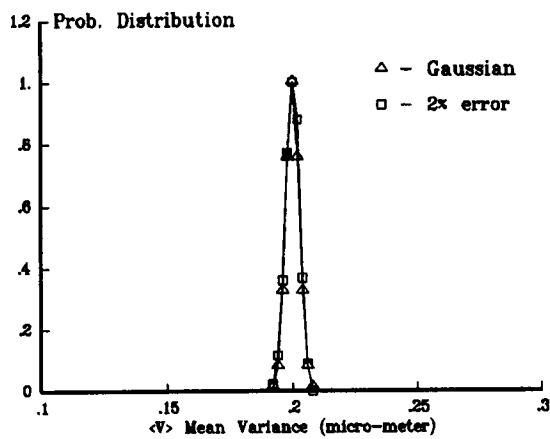


Figure 4.1.4 The probability distributions of $\langle V \rangle$ for various error levels, comparing with the true Gaussian distributions (data: water/scattering).

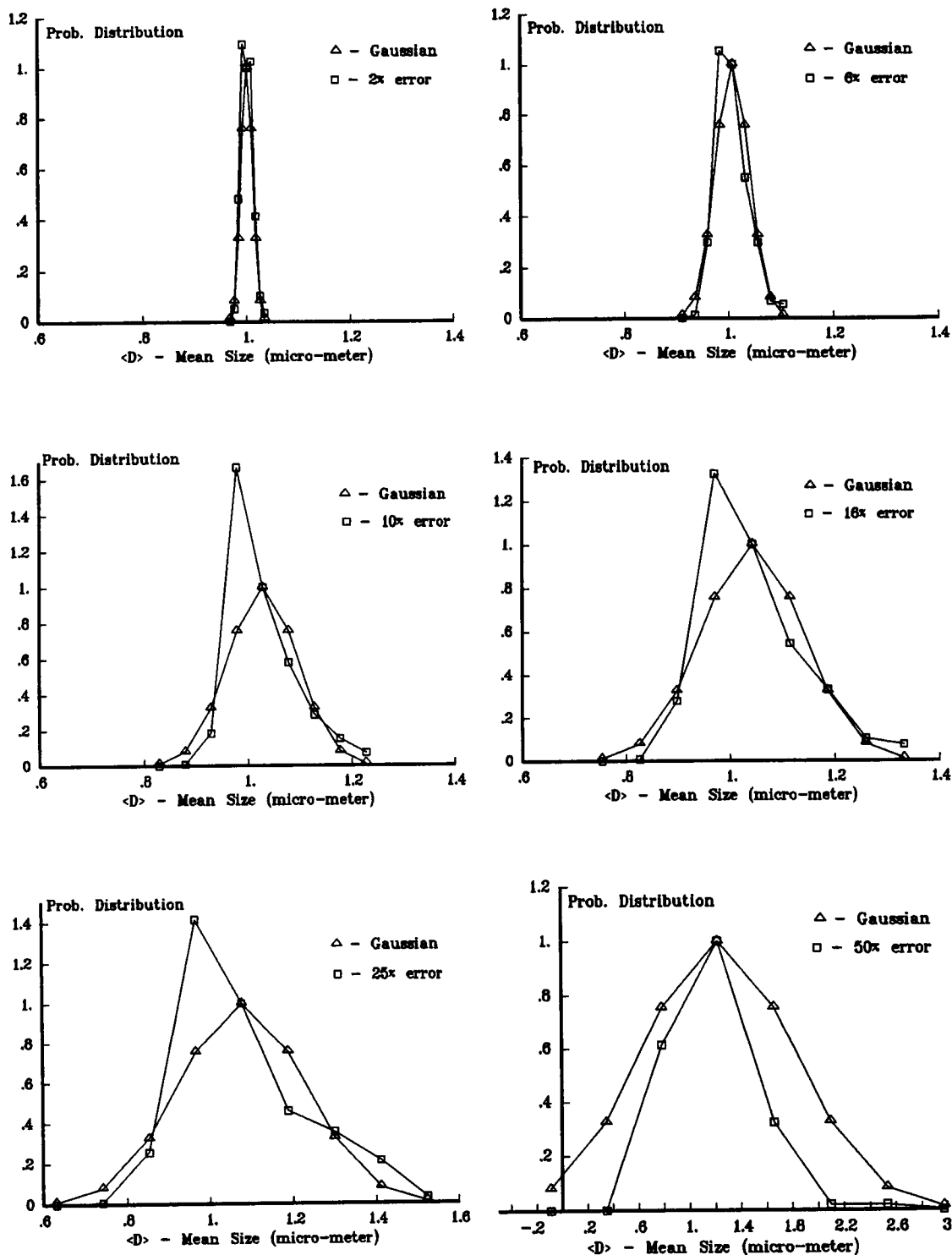


Figure 4.1.5 The probability distributions of $\langle D \rangle$ for various error levels, comparing with the true Gaussian distributions (data: water/extinction)

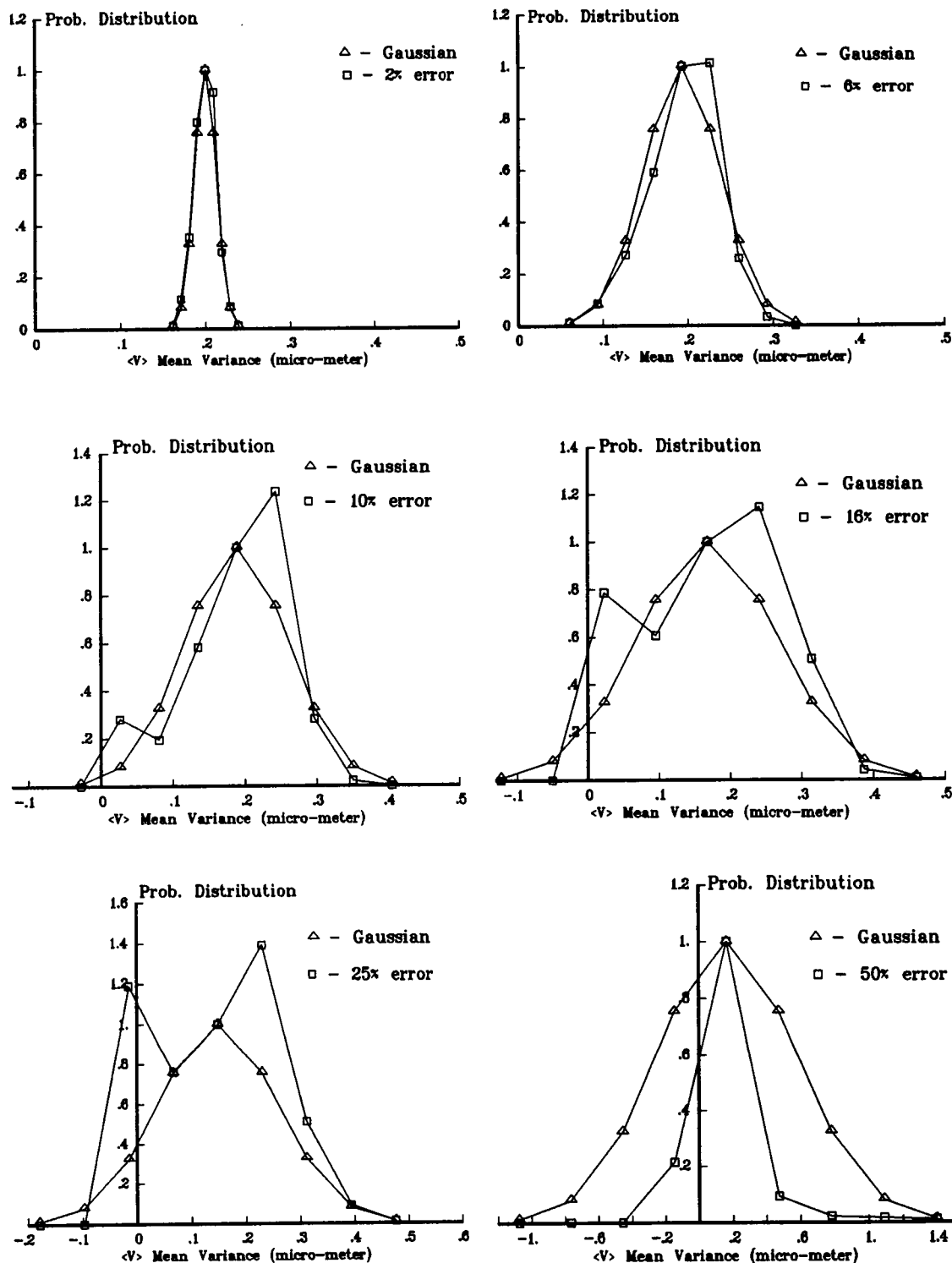


Figure 4.1.6 The probability distributions of $\langle V \rangle$ for various error levels, comparing with the true Gaussian distributions (data: water/extinction).

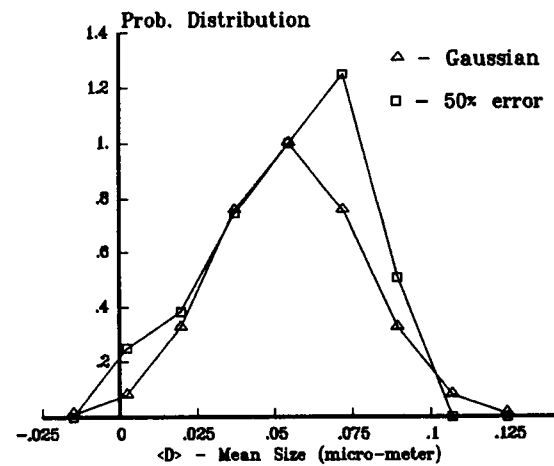
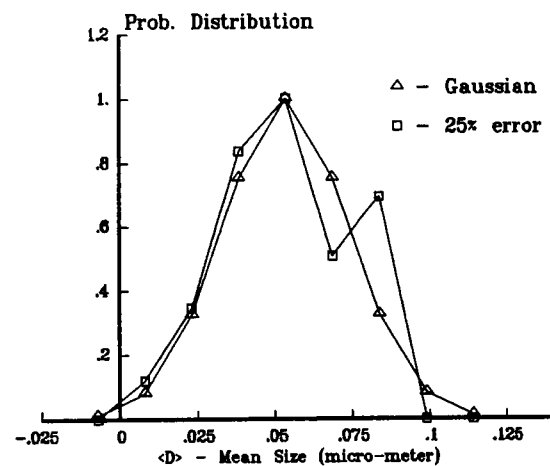
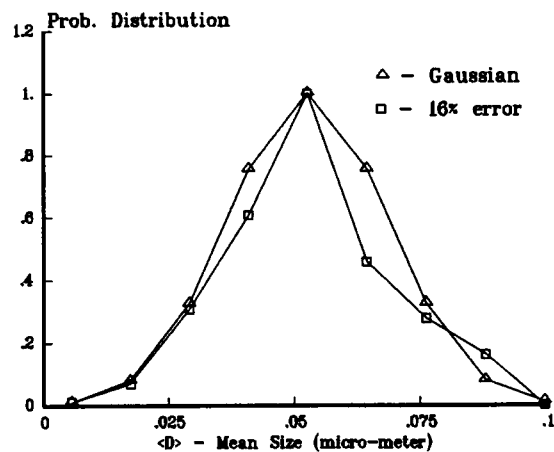
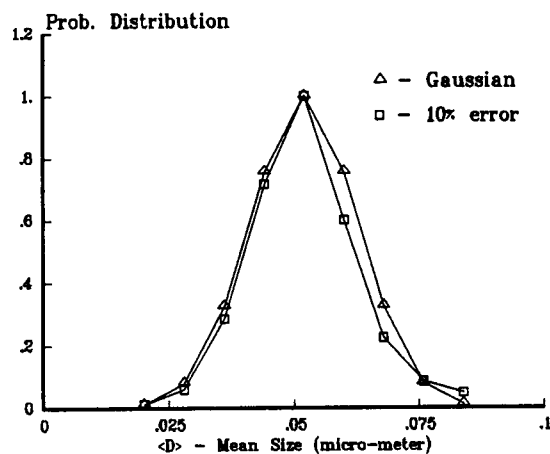
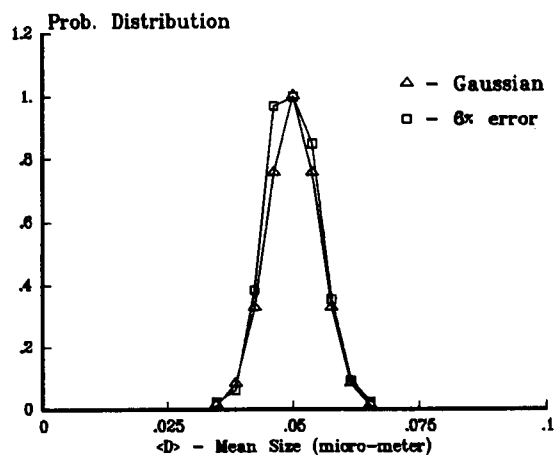
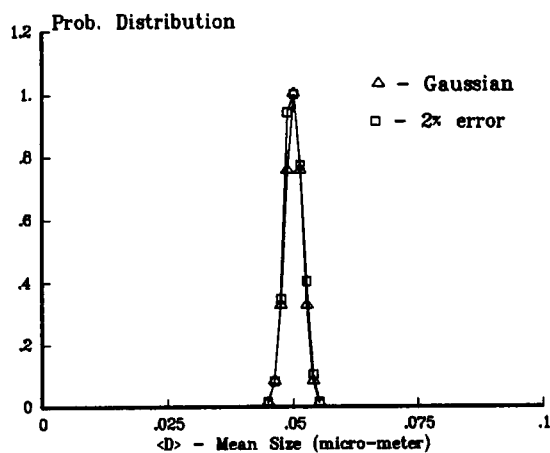


Figure 4.1.7 The probability distributions of $\langle D \rangle$ for various error levels, comparing with the true Gaussian distributions (data: soot/scattering).

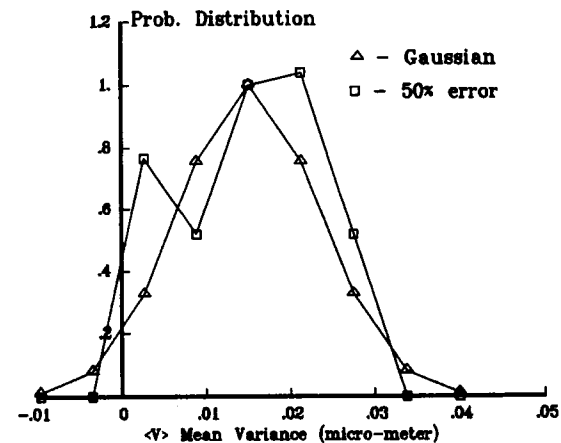
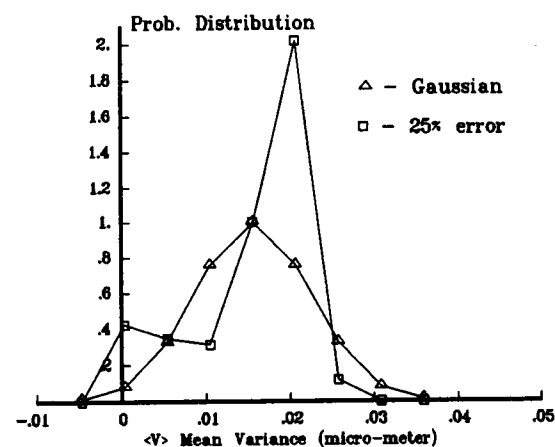
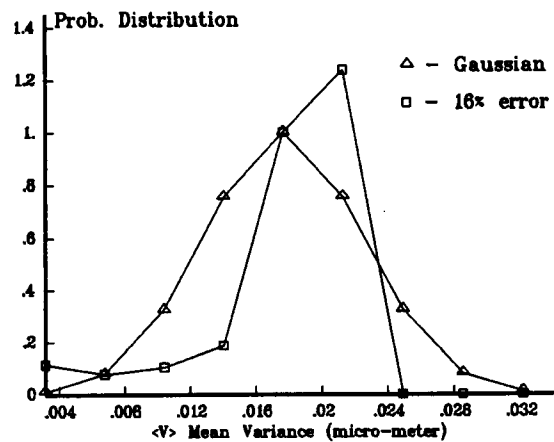
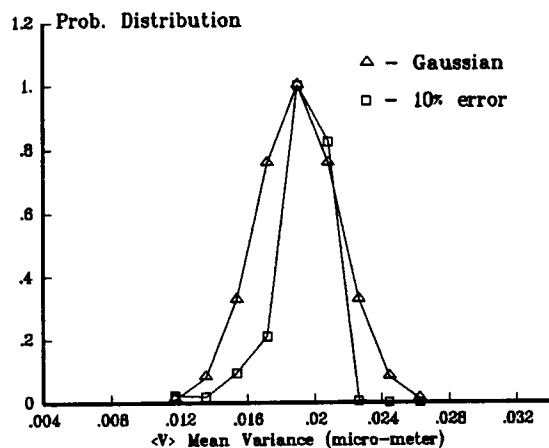
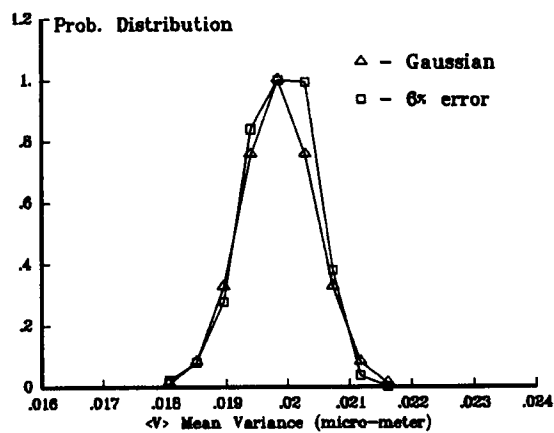
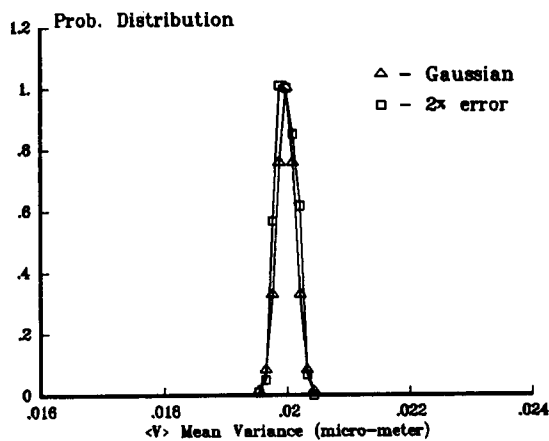


Figure 4.1.8 The probability distributions of $\langle V \rangle$ for various error levels, comparing with the true Gaussian distributions (data: soot/scattering).

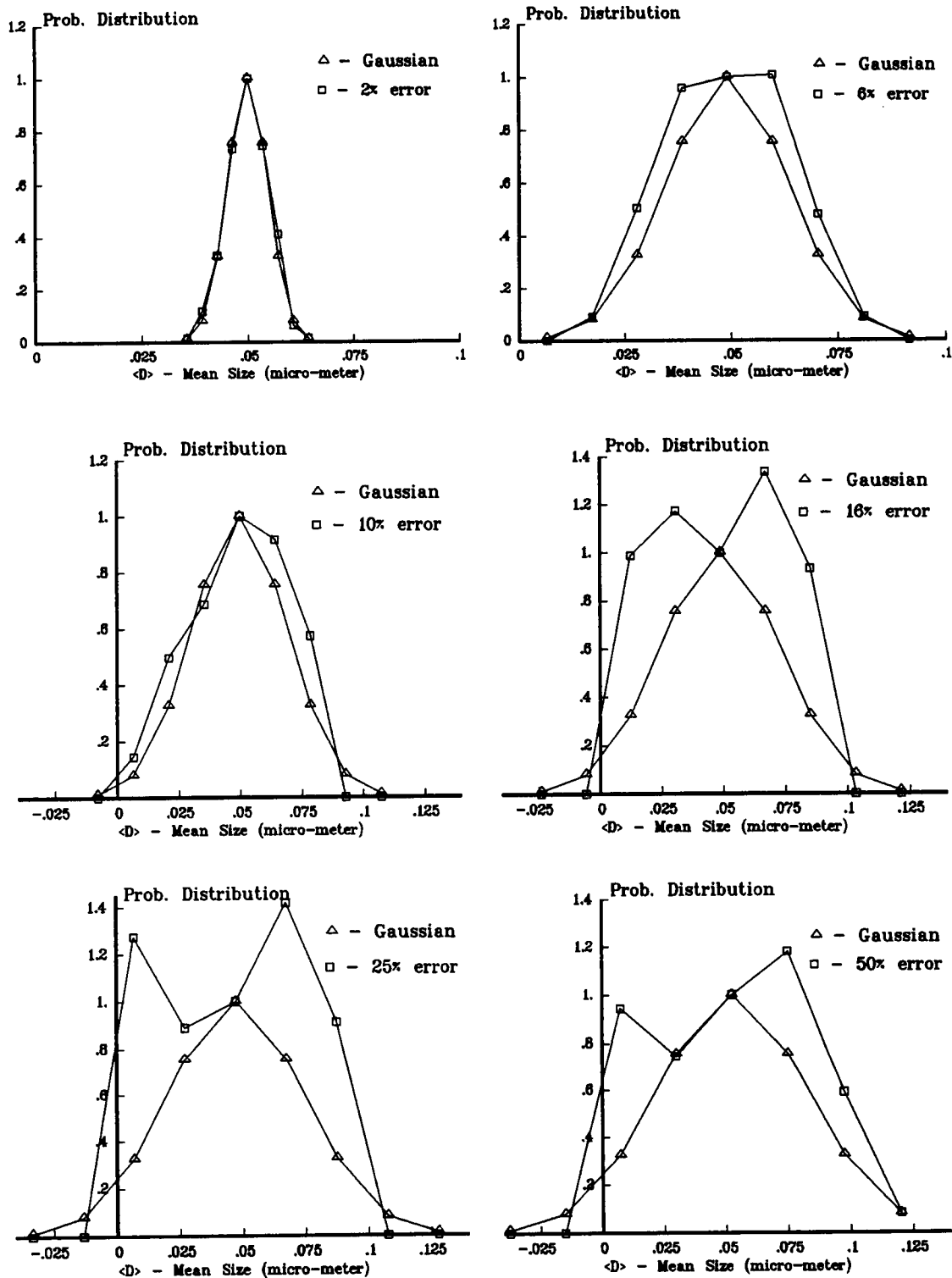


Figure 4.1.9 The probability distributions of $\langle D \rangle$ for various error levels, comparing with the true Gaussian distributions (data: soot/extinction).

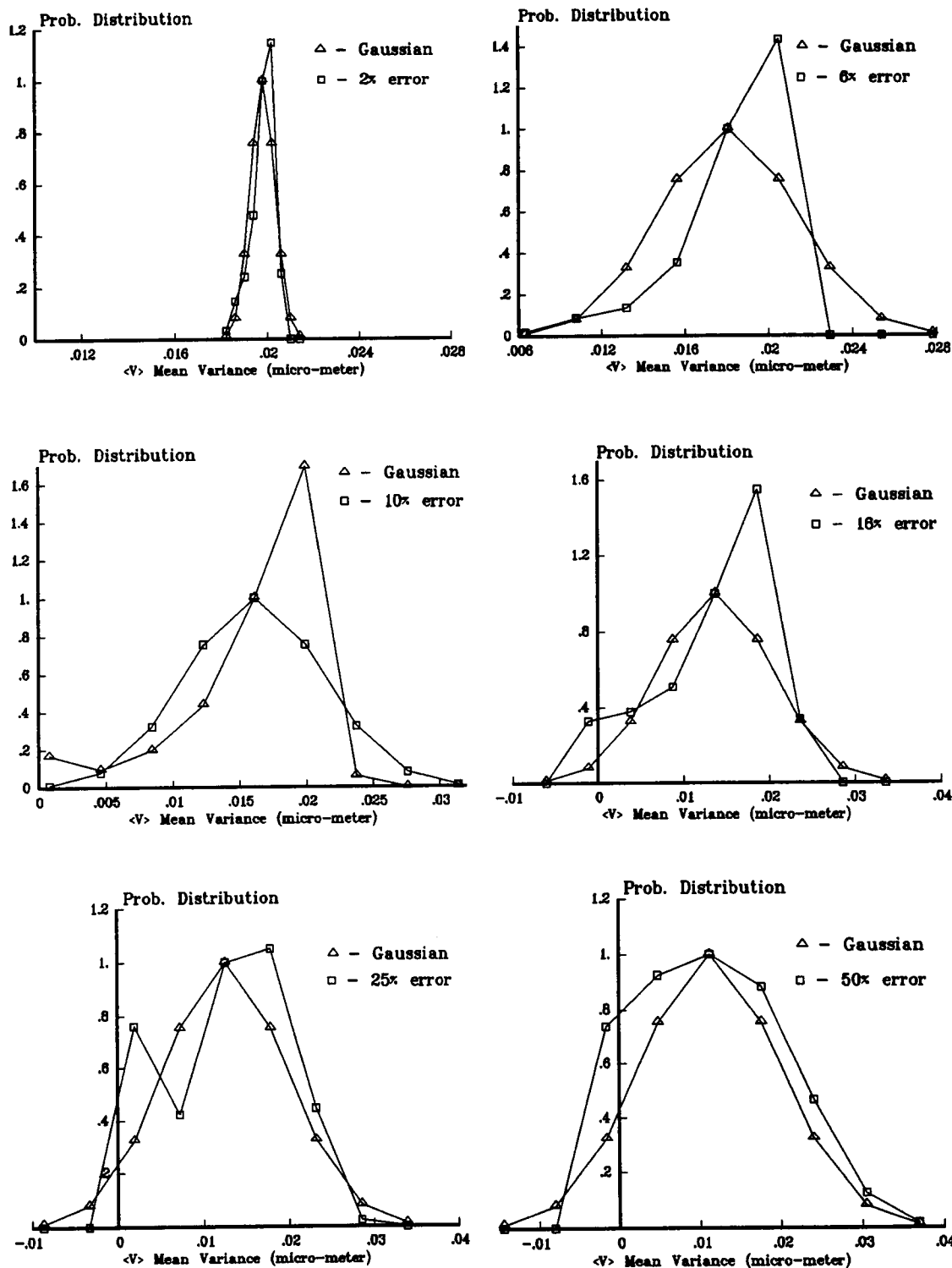


Figure 4.1.10 The probability distributions of $\langle V \rangle$ for various error levels, comparing with the true Gaussian distributions (data: soot/extinction).

§ 4.2 Restrictions on Particle Size Distribution Functions

Now let us examine what the restrictions are to be imposed on the distribution functions for a successful deconvolution. Although the discussion is concentrated on the log-normal distribution, the same method can be applied to any other distribution function.

The profile of a log-normal distribution function can be characterized by the ratio of the variance and mean, V/D . To see the effect of that ratio V/D on the variances of the distribution parameters μ , σ , D and V , It is convenient to begin with $\Delta\mu$ and $\Delta\sigma$ in (4.1.5) and (4.1.7) because the PSDF is defined explicitly with μ and σ in (4.1.1). Equations (4.1.5) - (4.1.8) can be simplified as

$$(\Delta\mu)^2 \leq = \frac{\sigma_0^4 \varepsilon^2}{\Gamma_\mu} \quad (4.2.1)$$

$$(\Delta\sigma)^2 \leq = \frac{\sigma_0^6 \varepsilon^2}{\Gamma_\sigma}, \quad (4.2.2)$$

where

$$\Gamma_\mu = \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) f(d) (\ln d - \mu_0) d(d) \right)^2 \quad (4.2.3)$$

$$\Gamma_\sigma = \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) f(d) ((\ln d - \mu_0)^2 - \sigma_0^2) d(d) \right)^2. \quad (4.2.4)$$

It is clear from Eqs.(4.2.1) and (4.2.2) that both $\Delta\mu$ and $\Delta\sigma$ are proportional to the square power and the cubic power of σ_0^2 , respectively. For a rough estimate of the width, it is natural to require that the value of σ_0 less than unit so that it will not enlarge the error ε in (4.2.1) and (4.2.2), *i. e.*,

$$\sigma_0 = \ln \left(1 + \frac{V_0^2}{D_0^2} \right) \leq 1,$$

or

$$\frac{V_0}{D_0} \leq \sqrt{e-1} \approx 1.31. \quad (4.2.5)$$

Equation (4.2.5) sets a restriction for the ratio V/D for a log-normal distribution, which is expected to be satisfied for most applications to real particulate systems. In the deconvolutions, it has been shown clearly that a narrow PSDF is recovered more easily, quickly, and accurately than a broad one. In this sense, a narrower PSDF is preferred. Moreover, the disadvantage of using a broad log-normal PSDF to simulate a real particulate system is that it takes much longer time to calculate the Mie functions for the large size particles at the long tail section of the broad log-normal PSDF where the probability of particle is almost negligible.

The other extreme case that needs to be considered is when the width of the distribution is much smaller than the mean. In this situation, the only factor that might cause $\Delta\mu$ and $\Delta\sigma$ to diverge is the zero points of the integrand in the denominators of (4.1.5) and (4.1.7). Because the kernel functions $K_i(d)$ are well-behaved and increase as the particle diameter d increases, the only nodes for $\Delta\mu$ are located at

$$d_\mu = e^{\mu_0}, \quad (4.2.6)$$

and the only nodes for $\Delta\sigma$ are located at

$$d_{\sigma\pm} = e^{\mu_0 \pm \sigma_0}. \quad (4.2.7)$$

These zero points in the integrand will not cause divergence for (4.1.1) and (4.1.2) as long as the PSDF $f(d)$ has a finite width. The influences they might have are some cancellations in the integrations of (4.2.3) and (4.2.4) because of the existence of

negative values in the integrands, and $\Delta\mu$ and $\Delta\sigma$ can be increased to some degree.

The only possibility for Γ_μ or Γ_σ to become zero is that the distribution function $f(d)$ is so narrow that it can be approximated by a δ function in which the pole point for $\Delta\mu$ is located at d_μ or $d_{\sigma\pm}$:

$$f_\mu(d) \approx \delta(\ln d - \mu_0), \text{ or } \delta(d - e^{\mu_0}) \quad (4.2.8)$$

and for $\Delta\sigma$, the pole point is located at

$$f_\sigma(d) = \delta((\ln d - \mu_0) \pm \sigma_0), \text{ or } \delta(d - e^{\mu_0 \pm \sigma_0}) \quad (4.2.9)$$

According to the definition of the δ function, the relation

$$F(x_0) = \int_{x_1}^{x_2} F(x) \delta(x - x_0) dx, \quad x_1 < x_0 < x_2$$

is true for any function $F(x)$. Apparently the mean of x is just x_0 .

For an extremely narrow distribution, it is easy to show that the square of the width of the distribution function uniformly approaches zero; *i. e.*,

$$V_\mu^2 = \int_0^\infty d^2 f_\mu(d) d(d) - D_\mu^2 \approx d_\mu^2 - d_\mu^2 = 2d_\mu(d_\mu - d_\mu) = 0,$$

and

$$V_{\sigma\pm}^2 = \int_0^\infty d^2 f_{\sigma\pm}(d) d(d) - D_{\sigma\pm}^2 \approx d_{\sigma\pm}^2 - d_{\sigma\pm}^2 = 2d_{\sigma\pm}(d_{\sigma\pm} - d_{\sigma\pm}) = 0$$

where o means a first-order infinitesimal.

Using the power series expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots, \quad -1 < x \leq 1$$

it is easy to show that σ^2 approaches zero as fast as V^2 :

$$\sigma^2|_{V^2 \rightarrow 0} = \lim_{V^2 \rightarrow 0} \ln(1 + \frac{V^2}{D^2}) \simeq \frac{V^2}{D^2} - \frac{1}{2}(\frac{V^2}{D^2})^2 + \dots \sim o. \quad (4.2.12)$$

Therefore, the two δ functions above would give the means of d_μ and $d_{\sigma\pm}$ which make the functions Γ_μ and Γ_σ become zero at these points; i. e.,

$$\begin{aligned} \Gamma_\mu &= \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) \delta(\ln d - \mu_0)(\ln d - \mu_0) d(d) \right)^2 \\ &= \sum_{i=1}^n \left(K_i(e^{\mu_0}) \lim_{(\ln d - \mu_0)} (\ln d - \mu_0) \right)^2 = \frac{K_s}{4} \sigma_0^4 \Big|_{\sigma_0^2 \rightarrow 0} \sim o^2, \end{aligned} \quad (4.2.10)$$

and

$$\begin{aligned} \Gamma_\sigma &= \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) \delta(\ln d - \mu_0) [(\ln d - \mu_0)^2 - \sigma_0^2] d(d) \right)^2 \\ &= \sum_{i=1}^n \left(K_i(e^{\mu_0}) \lim_{(\sigma_0 \rightarrow 0)} \left(\frac{\sigma_0^4}{4} - \sigma_0^2 \right) \right)^2 \sim K_s \sigma_0^4 \Big|_{\sigma_0 \rightarrow 0} \sim o^2, \end{aligned} \quad (4.2.11)$$

where K_s is defined as

$$K_s = \sum_{i=1}^n K_i^2(d_\mu). \quad (4.2.12)$$

This is very easy to calculate even with a personal computer.

In deriving Γ_μ in (4.2.10) and Γ_σ in (4.2.11), the pole points d_μ and $d_{\sigma\pm}$ are replaced by D because the two points overlap in the limit of $\sigma_0 \rightarrow 0$ and are equal to the mean D (see Eq(4.1.2)). The first relation in (4.1.2) or

$$\frac{\sigma_0^2}{2} = \ln D - \mu_0$$

has been used to simplify the expressions.

The fact that both the pole points of $d_{\sigma\pm}$ and d_μ approach the mean D_0 when σ_0 is close to zero can be illustrated by an example. In the simulations, $\mu_0 = -0.02$ ($D_0 =$

1.0 μm , $V_0 = 0.2 \mu\text{m}$) one can calculate that

$$d_{\sigma \pm}|_{\sigma_0 \rightarrow 0} = d_{\mu} = e^{\mu_0} = \approx 0.98 \mu\text{m} \approx D_0$$

which is almost the same as the mean.

One can see that even in this situation, the variances for μ and σ will not diverge. Substitute Γ_{μ} and Γ_{σ} into (4.2.1) and (4.2.2) respectively, one has

$$\langle (\Delta\mu)^2 \rangle \sim \frac{\sigma_0^4 \langle \varepsilon^2 \rangle}{\Gamma_{\mu}} \Bigg|_{V^2 \rightarrow 0} = \frac{4 \langle \varepsilon^2 \rangle}{K_s} \quad (4.2.13)$$

$$\langle (\Delta\sigma)^2 \rangle \sim \frac{\sigma_0^6 \langle \varepsilon^2 \rangle}{\Gamma_{\sigma}} \Bigg|_{V \rightarrow 0} = \frac{\sigma^2 \langle \varepsilon^2 \rangle}{K_s} \sim 0 \rightarrow 0. \quad (4.2.14)$$

Equations (4.2.13) and (4.2.14) are reasonable; because for a δ function distribution, the width σ has a specific value — zero, throughout the whole deconvolution procedure. The problem becomes a one-dimensional curve fitting, and therefore, the variance for σ approaches zero while the variance in μ remains finite.

It is easy to show that d_{μ} is also the zero point of Γ_D and Γ_V if the PSDF $f(d)$ is a δ function. Keeping in mind that σ and V go to zero at the same speed, (4.2.5) can now be written as

$$\begin{aligned} \Gamma_D &= \sum_{i=1}^n \left(\sigma^3 \int_0^{d_{\max}} K_i(d) \left[f_1(d)(D^2 + 2V^2) - f_2(d) \frac{V^2}{\sigma} \right] d(d) \right)^2 \\ &\approx \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) \delta(d - d_{\mu}) \{ (\ln d - \mu)(D^2 + 2V^2)\sigma + V^2[\sigma^2 - (\ln d - \mu)^2] \} d(d) \right)^2. \end{aligned}$$

Using (4.2.10) and ignoring the higher order terms of σ^2 , Γ_D can be simplified as

$$\Gamma_D = \sum_{i=1}^n \left(K_i(d_\mu) \left\{ \frac{\sigma^3}{2} (D^2 + 2V^2) + V^2 \sigma^2 \left(1 - \frac{\sigma^2}{4} \right) \right\} \right)^2$$

$$\approx \frac{\sigma^6 D^4}{4} \left(1 + 2 \frac{V^2}{D^2 \sigma} \right)^2 K_s \sim o^3 \rightarrow 0.$$

From (4.1.14), the variance for D takes the value of

$$(\Delta D)^2 = \frac{\sigma^6 D^2 (D^2 + V^2)^2 \epsilon^2}{\Gamma_D} = \frac{4 D^2 (1 + V^2/D^2)^2 \epsilon^2}{(1 + 2V^2/D^2 \sigma)^2 K_s} \Bigg|_{(V \rightarrow 0)} \approx \frac{4 D^2 \epsilon^2}{K_s}. \quad (4.2.15)$$

The relation for V can be obtained in a similar manner. From (4.1.8), Γ_V has the following form

$$\Gamma_V = \sum_{i=1}^n \left(\int_0^{d_{\max}} K_i(d) \delta(d - d_\mu) [(\ln d - \mu)^2 - \sigma^2 - \sigma^2 (\ln d - \mu)] d(d) \right)^2$$

$$= \sum_{i=1}^n [K_i(d_\mu) \sigma^2 (1 + \sigma^2/4)]^2 = \sigma^4 (1 + \sigma^2/4)^2 K_s \sim o^4$$

The variance for V then approaches to zero like

$$(\Delta V)^2 = \frac{\sigma^8 (D^2 + V^2)^2 \epsilon^2}{V^2 \Gamma_V} = \frac{\sigma^4 (D^2 + V^2)^2 \epsilon^2}{V^2 (1 + \sigma^2/4)^2 K_s} \Bigg|_{(V \rightarrow 0)} \sim \frac{V^2 (1 + V^2/D^2) \epsilon^2}{K_s} \rightarrow 0 \quad (4.2.16)$$

where (4.2.8) has been used.

It is not surprising that the pair $(\Delta D, \Delta V)$ have very similar limiting forms as the pair $(\Delta \mu, \Delta \sigma)$ since they play the similar roles in log-normal distribution functions as defined in (4.1.1).

From the discussion above, it is clear that the DHS method for the deconvolution of the PSDF for a particulate system with a narrow distribution function is more efficient than for a particulate system with a broad distribution function. This is similar the results of reference [19]. The physical meaning of this fact is that the summation of the contribution to the signal from different sized particles of a broad distribution

tend to "smear" or "blur" the information content of the signals.

Another advantage of deconvolving a very narrowly distributed particulate system is the lessening of the computational load. The complicated integration in the Γ 's defined by (4.1.6), (4.1.8), (4.2.5) and (4.2.7)) can be simplified by just calculating a K_s defined by (4.2.12) to obtain a rather good approximation. Furthermore, one can estimate the ratios of the variances for the distribution parameters which depend only on the distribution parameters without performing any Mie function calculations.

Denoting σ_r as the value of σ_0 for very narrow distributions, Eq.(4.2.12) becomes

$$\sigma_r = \frac{V}{D}. \quad (4.2.17)$$

Using (4.2.13) and (4.2.14) before taking the limit, the ratio of the variances in μ and σ for a distribution with narrow (but not zero) width is

$$\left. \frac{\Delta\sigma}{\Delta\mu} \right|_{V \ll D} = \frac{\sigma_0}{4 - \sigma_0^2}. \quad (4.2.18)$$

The variances in D can be expressed as

$$(\Delta D)^2 = \frac{4D^2(1 + V^2/D^2)^2 \epsilon^2}{(1 + 2V/D)K_s}$$

and the variance for V has the form of

$$(\Delta V)^2 = \frac{16V^2(1 + V^2/D^2)^2 \epsilon^2}{(4 + V^2/D^2)^2 K_s}.$$

The ratio of variance in V and D for a narrow distribution with non-zero width is then

$$\left. \frac{(\Delta V)}{(\Delta D)} \right|_{V \ll D} = \frac{2\sigma_r(1 + \sigma_r)}{(4 + \sigma_r^2)}. \quad (4.2.19)$$

It is clear from (4.2.5), (4.2.18) and (4.2.19) that for a log-normal distribution that it is the ratio of V/D (not individual D or V) that affects the deconvolution results. Another feature is that, unlike (3.3.6) which is for the synthetic particle system, the relative variance in V is about half of that in D for a very narrow distribution; *i. e.*,

$$\left. \frac{(R_V)}{(R_D)} \right|_{V \ll D} = \frac{2(1 + \sigma_r)}{(4 + \sigma_r^2)}. \quad (4.2.20)$$

because at this time the ratio of $\Delta\sigma/\Delta\mu$ in (4.2.18) is so small that it violates (3.3.8).

§ 4.3 Valley Zones for d^2 and the Distribution of PSDF Parameters

In order to understand fully the mechanism of the deconvolution procedure, it is necessary to examine the behavior of the control quantity χ^2 during the deconvolution. Because the DHS deconvolution minimizes χ^2 as defined in (2.3.1), by adjusting the distribution parameter D and V , it is proper to look at the behavior of χ^2 within the D and V domains by considering χ^2 as a function of D and V

$$\chi^2(D, V) = [\bar{r}(D, V) - \bar{g} - \bar{e}]^2.$$

The small quantity $\chi^2(D, V)$ can be expanded in the vicinity of (D_0, V_0)

$$\begin{aligned} \chi^2(D, V) = \chi^2|_0 &+ \left[\frac{\partial \chi^2}{\partial D} \Delta D + \frac{\partial \chi^2}{\partial V} \Delta V \right]_0 \\ &+ \frac{1}{2} \left[\frac{\partial^2 \chi^2}{\partial D^2} \Delta D^2 + \frac{\partial^2 \chi^2}{\partial V^2} \Delta V^2 + 2 \frac{\partial^2 \chi^2}{\partial D \partial V} \Delta D \Delta V \right]_0 + \dots \end{aligned} \quad (4.3.1)$$

The left hand side of (4.3.1) can be evaluated at some point ($D \neq D_0$, $V \neq V_0$)

$$left = \chi^2(D, V) = \sum_{i=1}^n \left[(t_i - g_i)^2 + \epsilon_i^2 - 2(t_i - g_i)\epsilon_i \right] \leq 2 \sum_{i=1}^n \epsilon_i^2 - 2 \sum_{i=1}^n \Delta t_i \epsilon_i \quad (4.3.2)$$

where equation (2.3.11)

$$\sum_{i=1}^n (t_i - g_i)^2 \leq \sum_{i=1}^n \epsilon_i^2$$

has been used. To compare with the right hand side of (4.3.1), the quantity Δt_i in (4.3.2) must also be expanded to the second order

$$\Delta t_i = \left[\frac{\partial t_i}{\partial D} \Delta D + \frac{\partial t_i}{\partial V} \Delta V \right]_0 + \frac{1}{2} \left[\frac{\partial^2 t_i}{\partial^2 D} \Delta D^2 + \frac{\partial^2 t_i}{\partial^2 V} \Delta V^2 + 2 \frac{\partial^2 t_i}{\partial D \partial V} \Delta D \Delta V \right]_0 + \dots \quad (4.3.3)$$

Care must be taken in deriving the right hand side of (4.3.1) because the vector $\mathbf{t}$ is exactly equal to the vector $\mathbf{g}$ at (D_0, V_0) , or

$$\vec{t}|_0 - \vec{g} = K(\vec{f}|_0 - \vec{p}) = 0, \quad (4.3.4)$$

and hence $\chi^2(D, V)$ does not reach its minimum at (D_0, V_0) . Actually, $\chi^2(D_0, V_0)$ has the form of

$$\chi^2(D_0, V_0) = \sum_{i=1}^n (t_i|_0 - g_i - \epsilon_i)^2 = \sum_{i=1}^n \epsilon_i^2 \quad (4.3.5)$$

As the result, the first derivatives of χ^2 with respect to D and V do not vanish as is commonly expected in a least square algorithm. Using (4.3.4), the various derivatives in χ^2 can be calculated as

$$\left. \frac{\partial \chi^2}{\partial D} \right|_0 = 2 \sum_{i=1}^n [t_i|_0 - g_i - \epsilon_i] \frac{\partial t_i}{\partial D} = -2 \sum_{i=1}^n \epsilon_i \frac{\partial t_i}{\partial D}, \quad (4.3.6a)$$

$$\left. \frac{\partial \chi^2}{\partial V} \right|_0 = 2 \sum_{i=1}^n [t_i|_0 - g_i - \epsilon_i] \frac{\partial t_i}{\partial V} = -2 \sum_{i=1}^n \epsilon_i \frac{\partial t_i}{\partial V}, \quad (4.3.6b)$$

$$\left. \frac{\partial^2 \chi^2}{\partial D^2} \right|_0 = \frac{\partial}{\partial D} 2 \sum_{i=1}^n [t_{i|_0} - g_i - \epsilon_i] \frac{\partial t_i}{\partial D} = 2 \sum_{i=1}^n \left(\frac{\partial t_i}{\partial D} \right)^2 - 2 \sum_{i=1}^n \epsilon_i \frac{\partial^2 t_i}{\partial D^2}, \quad (4.3.6c)$$

$$\left. \frac{\partial^2 \chi^2}{\partial V^2} \right|_0 = \frac{\partial}{\partial V} 2 \sum_{i=1}^n [t_{i|_0} - g_i - \epsilon_i] \frac{\partial t_i}{\partial V} = 2 \sum_{i=1}^n \left(\frac{\partial t_i}{\partial V} \right)^2 - 2 \sum_{i=1}^n \epsilon_i \frac{\partial^2 t_i}{\partial V^2}, \quad (4.3.6d)$$

$$\left. \frac{\partial^2 \chi^2}{\partial D \partial V} \right|_0 = \frac{\partial}{\partial D} 2 \sum_{i=1}^n [t_{i|_0} - g_i - \epsilon_i] \frac{\partial t_i}{\partial V} = 2 \sum_{i=1}^n \left(\frac{\partial t_i}{\partial D} \frac{\partial t_i}{\partial V} \right) - 2 \sum_{i=1}^n \epsilon_i \frac{\partial^2 t_i}{\partial D \partial V}. \quad (4.3.6e)$$

Substituting Eqs.(4.3.2) and (4.3.3) on the left side of (4.3.1) and Eqs.(4.3.4)-(4.3.6a-e) on the right side of (4.3.1), Eq.(4.3.1) becomes

$$\sum_i \epsilon_i^2 \geq \sum_i \left(\frac{\partial t_i}{\partial D} \right)^2 (\Delta D)^2 + \sum_i \left(\frac{\partial t_i}{\partial V} \right)^2 (\Delta V)^2 + 2 \sum_i \left(\frac{\partial t_i}{\partial D} \frac{\partial t_i}{\partial V} \right) \Delta D \Delta V \quad (4.3.7)$$

For a specific error ϵ , Eq.(4.3.7) clearly defines an elliptical zone S in the ΔD and ΔV domains, with the center at the origin and tilted at some angle. In the deconvolutions discussed in Chapter 3, it is within this area that the calculation program contracts the simplex and reaches the bottom of the valley.

Equation (4.3.7) can be written as

$$t_D^2 (\Delta D)^2 + t_V^2 (\Delta V)^2 + 2 \vec{t}_D \cdot \vec{t}_V \Delta D \Delta V \leq \epsilon^2, \quad (4.3.8)$$

where the vectors $\mathbf{t}_D$ and $\mathbf{t}_V$ and their inner product are defined by

$$t_D^2 = \mathbf{t}_D \cdot \mathbf{t}_D = \sum_{i=1}^n \left(\frac{\partial t_i}{\partial D} \right)_0^2 = \sum_{i=1}^n \left(\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial D} \right)_0^2 \quad (4.3.9a)$$

$$t_V^2 = \mathbf{t}_V \cdot \mathbf{t}_V = \sum_{i=1}^n \left(\frac{\partial t_i}{\partial V} \right)_0^2 = \sum_{i=1}^n \left(\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial V} \right)_0^2 \quad (4.3.9b)$$

$$\mathbf{t}_D \cdot \mathbf{t}_V = \sum_{i=1}^n \left[\frac{\partial t_i}{\partial D} \right]_0 \left[\frac{\partial t_i}{\partial V} \right]_0 = \sum_{i=1}^n \left[\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial D} \right]_0 \left[\mathbf{K}_i \cdot \frac{\partial \mathbf{f}}{\partial V} \right]_0. \quad (4.3.9c)$$

It is obvious from (4.3.9a) and (4.3.9b) that the vectors $\mathbf{t}_D$ and $\mathbf{t}_V$ are just the gradients of the deconvolution along the directions of D and V respectively. The cross terms in (4.3.7) or (4.3.8) are formed by the inner product of $\mathbf{t}_D$ and $\mathbf{t}_V$ as indicated by (4.3.9c). From a geometric point of view, this represents the spatial directional correlation between the two vectors. From the point of view of deconvolution, it represents the degree of interdependence of the deconvolution between the two dimensions. A perfect situation is a zero-cross term which means that $\mathbf{t}_D$ is perpendicular to $\mathbf{t}_V$ and that the deconvolution along the two dimensions are independent. Equation (4.3.8) then becomes an right elliptical zone. A disastrous situation would be that $\mathbf{t}_D$ is parallel to $\mathbf{t}_V$ which means there is only one independent deconvolution, Eq.(4.3.8) would be a straight line, and no valley zone would exist.

Because the DHS deconvolution is to minimize χ^2 to get the distribution parameters D and V , the zone S should also be the region within which D and V are Gaussian distributed as was discussed in Section 4.1. Keeping in mind that $\Delta \mathbf{t} = \mathbf{K} \cdot \Delta \mathbf{f}$, it is easy to see that (4.2.8) is the same as (4.1.10b) and that $\mathbf{t}_D$ or $\mathbf{t}_V$ is just P_D or P_V , as defined by (4.1.19b) and listed in Table (4.1.1). This fact is a good indication that the zone S is indeed the final solution region for the distribution parameters D and V . Equations (4.1.14) and (4.1.17) therefore define the intersections of the ellipse on the two axis.

The angle ϕ between $\mathbf{t}_D$ and $\mathbf{t}_V$ can be obtained from

$$\cos \phi = \frac{\mathbf{t}_D \cdot \mathbf{t}_V}{t_D t_V}. \quad (4.3.9d)$$

Table (4.3.1) gives the values of t_D , t_V , $t_D t_V$ and ϕ for the water/scattering system. One can see that the kernel functions are relatively ill-conditioned or inter-dependent because t_D^2 is more than 3 times larger than t_V^2 resulting in a large tilt angle $\phi=47.8^\circ$.

The cross-term can be eliminated by rotating the coordinate system. The resultant equation is then

$$\frac{\Delta D^{*2}}{L_D^{*2}} + \frac{\Delta V^{*2}}{L_V^{*2}} \leq 1 \quad (4.3.10)$$

where the "*" denotes the quantities in the rotated coordinate system. The rotation angle θ_D , which is independent of error, can be obtained from

$$\tan(2\theta_D) = \frac{2t_D t_V}{t_D^2 - t_V^2} \quad (4.3.11)$$

The semi-major and -minor axes of the ellipse have the form

$$L_D^{*2} = 2\varepsilon^2(\sigma) \left[t_D^2 + t_V^2 - \sqrt{(P_D^2 - P_V^2)^2 + 4 t_D t_V^2} \right]^{-1} \quad (4.3.12a)$$

$$L_V^{*2} = 2\varepsilon^2(\sigma) \left[t_D^2 + t_V^2 + \sqrt{(P_D^2 - P_V^2)^2 + 4 t_D t_V^2} \right]^{-1} \quad (4.3.12b)$$

where the error ε has been written as a function of the error level σ_e .

It can be seen that as the error ε increases, the two axes of the ellipse increase linearly, and a family of ellipses with the same origin is generated. The values of P_ξ ($\xi = \mu, \sigma, D$ and V) for the water/scattering case have been listed in Table (4.1.1).

Table (4.3.1) Quantities of t_D , t_V , $t_D t_V$

t_D^2	t_V^2	$t_D t_V$	ϕ
13.96	4.44	5.29	47.80°

Using those numbers, the ellipse's semi-axis L_ξ ($\xi = \mu, \sigma, D$ and V) and the rotation angles of the valley zones for different errors ε were calculated and listed in Table (4.3.2).

Table (4.3.2) L_ξ 's, θ_D , and θ_μ for different error levels

$\sigma_\varepsilon\%$	L_D	L_V	L_μ	L_σ	θ_D	θ_μ
2	4.14×10^{-3}	1.48×10^{-3}	4.37×10^{-3}	1.41×10^{-3}	24.0°	24.9°
10	2.10×10^{-2}	7.49×10^{-3}	2.21×10^{-2}	7.15×10^{-2}	24.0°	24.9°
16	.335	.120	.354	.114	24.0°	24.9°
30	.687	.246	.726	.234	24.0°	24.9°

To compare the predictions of the valley zone in (4.3.7), Figures(4.3.1) - (4.3.4) plot 3-dimensional meshes for $d^2(D, V, \sigma_\varepsilon)$ in the DHS simulation results (for water) for three different error levels. The upper figure in each pair shows the appropriate Gaussian distribution function in which the function $f(D, V)$ is defined by

$$f(D, V) = \frac{1}{\varepsilon^2} (t_D^2 D^2 + t_V^2 V^2 + 2 \overline{t_D} \cdot \overline{t_V} D V); \quad (4.3.13)$$

the quantities of t_D , t_V and $t_D t_V$ are defined by Eq.(4.3.9). The lower figure of each pair shows the variation of the logarithm of d_{min}^2 , which is almost the same as χ_{min}^2 and which is found from the 500 deconvolution simulations that were discussed in Chapter 3. The means and the variances of the d_{min}^2 have been listed in Table (4.1.4). From these figures one can see that the valley regions of χ^2 coincide with the regions predicted by (4.3.7).

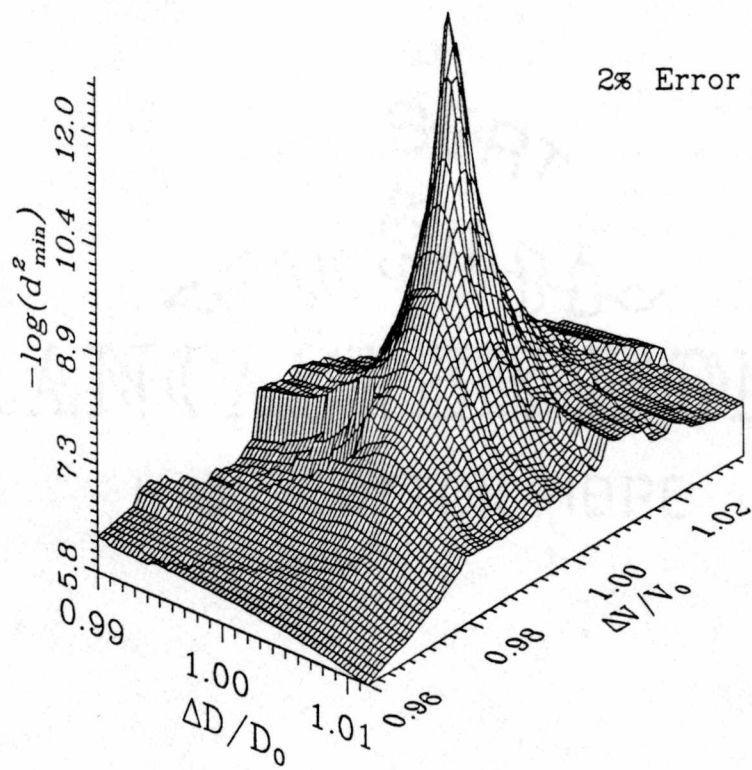
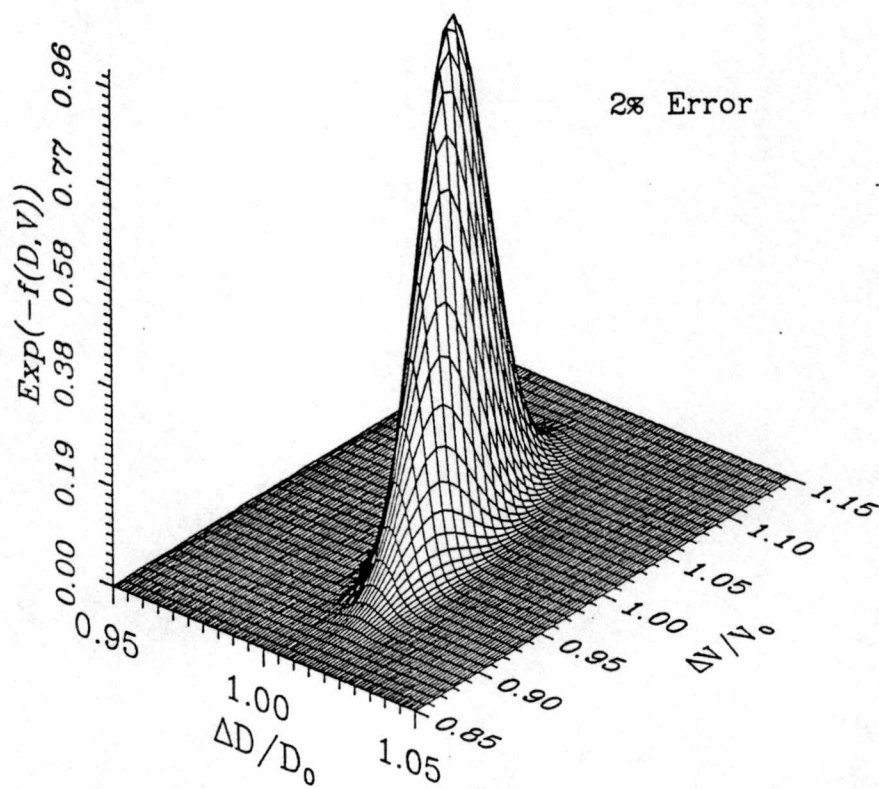


Figure 4.3.1 The valley zone of d^2 for water/scattering simulations (2% random error).

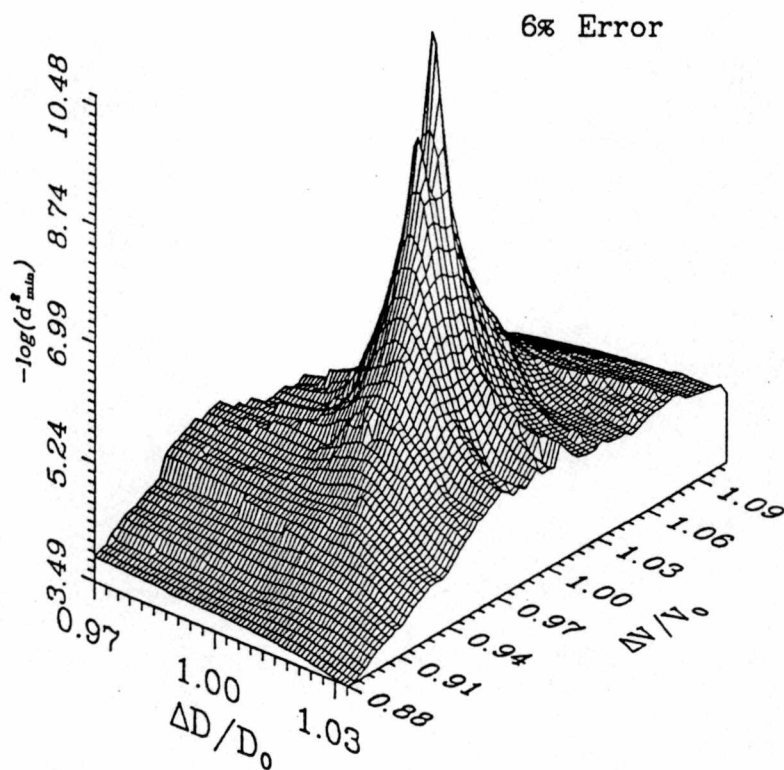
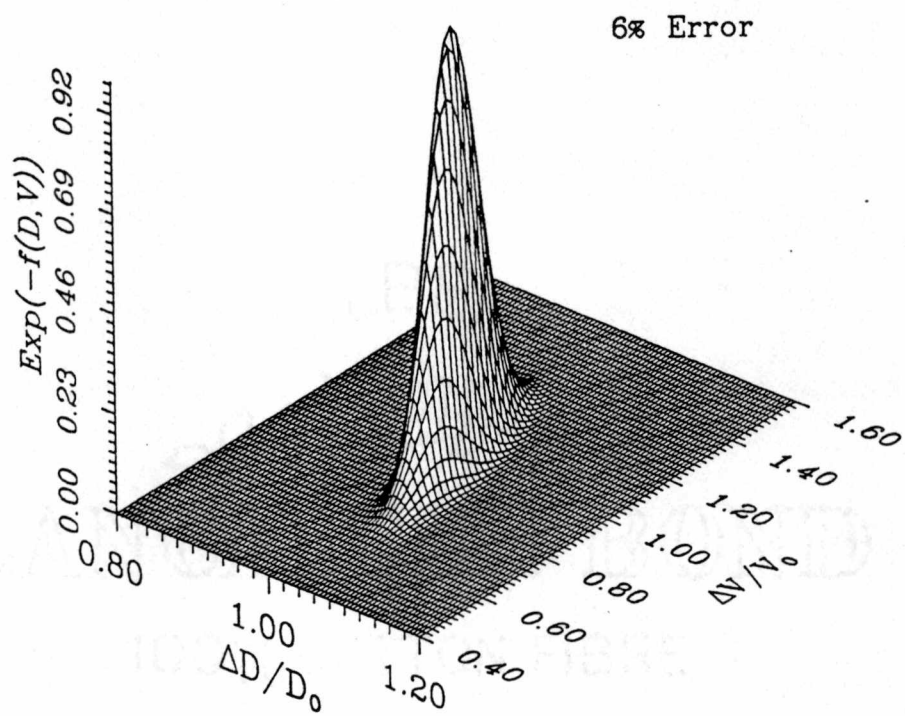


Figure 4.3.2 The valley zone of d^2 for water/scattering simulations (6% random error).

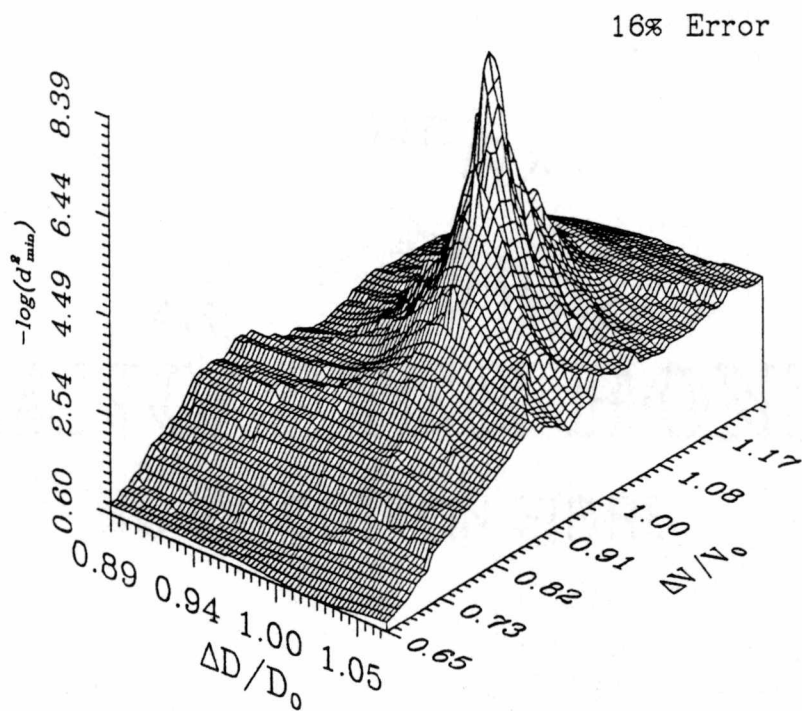
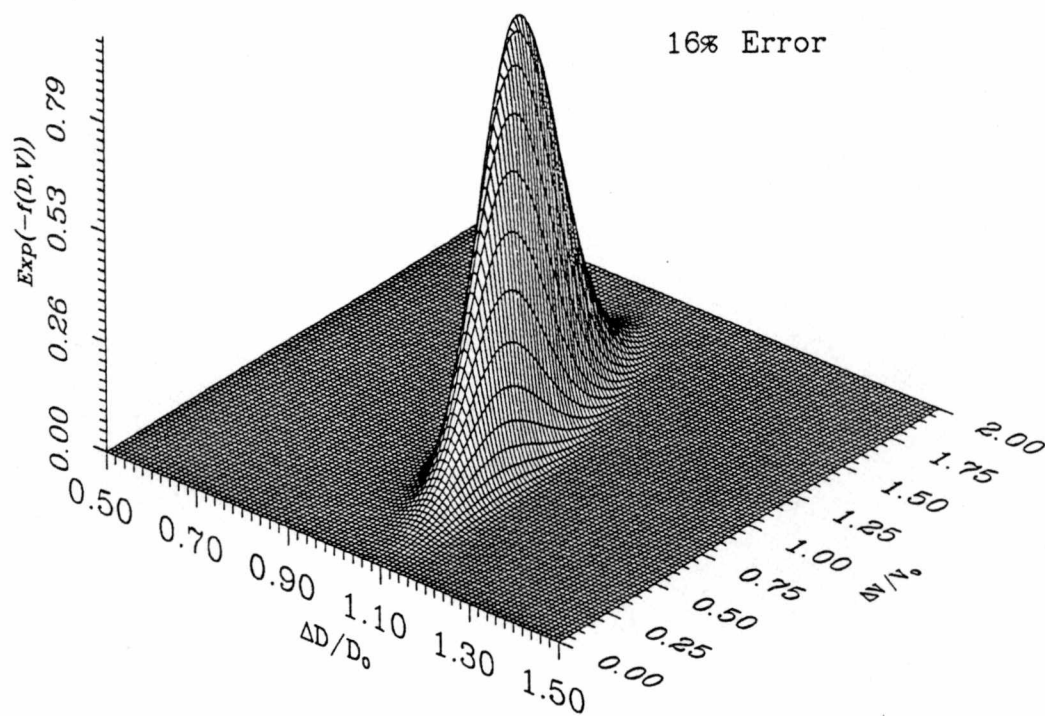
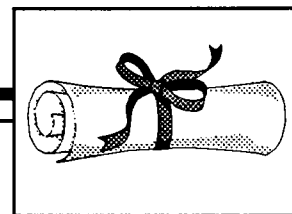


Figure 4.3.3 The valley zone of d^2 for water/scattering simulations (16% random error).

Chapter 5



Information Content of Optical Measurements

It is always the first and the most important consideration for any attempt of obtaining knowledge from nature through measurements: how should one plan or design an experiment? That is, what kind of experiment should be performed and how should it be performed? This question can be divided into two sub-issues:

- (1) among all available experiments, how to choose a suitable one and
- (2) for an experiment chosen, how to decide which measurements should be made to obtain the needed information.

These two seemingly simple questions are critically important for an experimentalist. It is neither possible nor necessary, due to various restrictions, to perform all experiments or make all possible measurements. For example, one can only measure the scattering signals for a limited number of scattering angles (from tens to more than a hundred). Actually, as will be seen in section 5.2, making excessive measurements would introduce extra errors and therefore reduce the accuracy of the results. Therefore, one must make sure, before doing an experiment, that there is enough information content in the measurements. Failure to do so may result in either waste of time and resources or faulty data.

The question is quite straightforward for the concerns of this dissertation. Based on the information content, two issues must be considered:

- (1) between the scattering and extinction, which experiment should be chosen, and
- (2) among the possible scattering angles or optical wavelengths, which ones should be preferred.

This chapter is to perform an information content analysis to the work in previous chapters and to answer the above questions. In general, there are two kinds of information content analysis applicable to optical experiments: one is to extract the useful information directly from the measurements themselves based on the behaviors of the fluctuations of the data; and the other one is to analyze the interdependence of the kernel functions throughout a certain domain and to gain knowledge about the information content of the data, based on linear functional space theory.^[10] The second one has been chosen in this dissertation because it will lead to the answers of the above questions.

§ 5.1 Linear Functional Space Theory for Optical Measurements

By introducing the linear function space theory into the discussion of the inversion of indirect measurements, Twomey^[10] *et al* developed a measure for the information content for sets of experimental, and particularly optical, data.

In analogy to the geometrical vector analysis definition, a function of a single argument $p(r)$ can be considered as a function vector with finite or infinite dimensions ($r = r_1, r_2, \dots, r_n$ or $r = [0, \infty]$). In a general computation program, $p(r)$ usually has finite dimensions because for a specific precision requirement, only a limited number of points of $p(r)$ will actually be evaluated. The inner product of two such function vectors $p(r)$ and $q(r)$ is defined as

$$I = (p, q) = p \cdot q = \int_a^b p(r)q(r)dr. \quad (5.1.1)$$

Similar to the scalar product of two geometrical vectors, the quantity I is a scalar. If $I = 0$, the two function vectors are orthogonal on the interval (a, b) .

Similarly, the (length)² or the norm of $p(r)$ is given by

$$|p(r)|^2 = \int_a^b p^2(r)dr. \quad (5.1.2)$$

The other properties of linear space, such as Schwartz inequality

$$(p \cdot q)^2 \leq |p|^2 |q|^2, \quad (5.1.3)$$

and Gram-Schmit orthogonalization, *etc.*, can also be derived, see [10] for details.

By analogy, a function of two independent variables can be treated as a second-order tensor. A useful example of such a tensor is the optical kernel function $K(\alpha, r)$, as introduced in Chapter 2. In this kernel function, α could be a scattering angle or a wavelength of light, and r could be the particle size. The expressions $K^+ K$ and $K K^+$ are also tensors which form the co-variance matrix C and its dual matrix B as introduced in Chapter 2.

A function vector might be expressed by different representations. For example, the expression for an optical measurement (Eq.(2.2.1))

$$g(\alpha_i) = \int_0^\infty K(\alpha_i, r)p(r)dr \quad (5.1.4)$$

can be considered as a transformation of the particle size distribution function $p(r)$ from coordinate space r into the other space α , through the transformation matrix $K(\alpha, r)$.

Actually, the action of such a mathematical transformation corresponds to nothing but the optical measurement, and the resultant $g(\alpha)$ constitutes the measurement vector.

An ideal situation is that the space spanned by $K(\alpha, r)$ is complete and orthogonal. One can therefore represent any PSDF $p(r)$ by a linear combination of the base functions. Actually, there do exist such experiments such as interferometer or interferometer-spectrometers, where the kernel function is $e^{j\alpha x}$ which has an infinite number of zero points along the domain. The measurements in such experiments are the Fourier transformations of the desired spectral function $f(x)$:

$$g(y_j) = \int_{-\infty}^{\infty} e^{-iy_j x} f(x) dx. \quad (5.1.5)$$

The recovery of $f(x)$ in (5.1.5) is just a simple inverse Fourier transformation and is not normally considered an "inversion" problem. The transformation of $g \rightarrow f$ is a unitary one, $\mathbf{f} = \mathbf{W}\mathbf{g}$ in vector notation. With $\mathbf{W}^*\mathbf{W} = \mathbf{I}$, the error in $\mathbf{f}$ is related to the error ϵ in $\mathbf{g}$ by $|\Delta \mathbf{f}|^2 = \epsilon^* \mathbf{W}^* \mathbf{W} \epsilon = |\epsilon|^2$.

The kernels in optical scattering or extinction or other indirect sensing experiments are inherently exponential in character, and the transformation of an unknown function $f(x)$ is closer to a Laplace transformation than a Fourier transformation; that is

$$g(y_j) = \int_0^{\infty} e^{-y_j x} f(x) dx. \quad (5.1.6)$$

Because there are no roots for such a kernel e^{-yx} along the path of integration no matter what the value of y is (both y and x are real), the kernels are not orthogonal and they necessarily provide a skewed non-orthogonal system of base functions in function

space. Although one can always use the Schmit orthogonalization method to form an orthogonal space in which any PSDF $p(\alpha, r)$ can be expanded as

$$p(r) = \sum_i a_i \hat{\phi}_i(r) \quad (5.1.7)$$

provided $p(r)$ lies inside in the space, the coefficients for such an expansion will usually exhibit large positive and negative fluctuations. The inversion of such a system will result in an enlargement in the experiment errors.^[10] Using the Linear Inversion method for PSDF, Henning^[9b] *et. al* have performed such procedures as (5.1.7), and some ten significant base functions which are used to recover part of the PSDF have been plotted. The remaining part of the PSDF is lost because it lies out of the space spanned by the kernels.

Because the space formed by most optical scattering or extinction kernels $K(\alpha, r)$ is, in general, neither complete nor orthogonal, only part of the PSDF could be directly recovered. The recovery of the remainder of the PSDF requires more physical information on the system, such as constraints.

In Eqs.(5.1.1) through (5.1.4), the weight function $w(r)$ has been omitted to simplify the notation. Actually these weight functions can not be absent from computations because the orthogonality and completeness of some functions are defined with weight (such as some polynomials). In a practical computation with a computer, a weight is always needed in calculating the integration. From hereafter, the weight function is omitted and a summation is used in place of an integration for simplicity.

§ 5.2 Information Content in Optical Measurements

The information content of a set of similar measurements for some properties of the system sometimes is quite limited. In other words, not all the measurements are independent. Since all physical measurements contain errors, the inter-dependent data points contribute nothing to the results but noise. For example, if the first three data points of an experiment exhibit exceptional linearity with respect to some variable (wavelength, scattering angle, etc.), then the fourth measurement within that variable range adds little to the result and can be excluded.

In general, if the n data points roughly satisfy

$$\sum_{j=1}^n a_j g_j = 0, \quad (5.2.1)$$

the data are not independent and one of them g_l can be approximately expressed by the linear combination of other others; *i.e.*,

$$g_l = a_l^{-1} \sum_{j \neq l}^n a_j g_j; \quad a_l \neq 0, \quad (5.2.2)$$

where

$$\sum_{j=1}^n a_j^2 = 1. \quad (5.2.3)$$

to eliminate a trivial case with all null a_j 's. Therefore, the l th measurement is redundant or useless and should be avoided. In other words, the measurements g_j 's are not independent.

A relevant question is how to tell if there is any dependent data point in the measurements? A good starting point is to look at the overlap behavior of the kernel functions $K(\alpha, r)$ within the interested range of particle size (a, b)

$$C_{ij} = \int_a^b k(\alpha_i, r)k(\alpha_j, r)dr \approx \sum_{k=1}^m K(\alpha_i, r_k)K(\alpha_j, r_k). \quad (5.2.4)$$

This is just the element of covariance matrix as introduced in Chapter 2. For an ideal situation in which all the kernels are independent or orthogonal, $\mathbf{C}$ is a diagonal matrix with uniformly distributed eigenvalues which are the diagonal elements of $\mathbf{C}$. For a practical situation, $\mathbf{C}$ usually has relatively large off-diagonal elements which result in a wide range of eigenvalues ($\lambda_{max} / \lambda_{min} \sim 10^{6-9}$). The important role that $\mathbf{C}$ takes in a deconvolution can be seen through the difference between the resultant PSDF $f(r)$ and the true PSDF $p(r)$. For the Linear Inversion method Eq(2.2.6) the difference is

$$|\delta p(r)|^2 = \sum_{i=1}^n \frac{\epsilon_i^2}{\lambda_i}, \quad (5.2.5a)$$

and for the DHS deconvolution method the difference is, from Eq.(2.4.8),

$$|\delta p(r)|^2 \leq \frac{m \langle \epsilon^2 \rangle}{\sum_{j=1}^m \lambda_j}. \quad (5.2.5b)$$

Apparently the existence of the small eigenvalues results in an unstable inversion in Linear Inversion method (5.2.5a). Although the DHS method is stable, the existence of the redundant measurements will still increase overall error ϵ^2 and hence increase the total error in the results.

According to Twomey,^[9] the information content can be indicated by the fraction of the eigenvalues of $\mathbf{C}$. In performing an information content analysis, the eigenvalues are usually sorted in a decreasing order. For n data points, the first k data contain the fraction of the information content of

$$\sum_{j=1}^{k \leq n} \lambda_j / \sum_{i=1}^n \lambda_i. \quad (5.2.6)$$

The next question is how to determine, among the n data points, which group of k data points contains enough (say 99%) information and how to select these points. Because the distribution of the eigenvalues of C represents the inter-dependence of the kernels, it is natural to search for an acceptable minimum eigenvalue. Obviously, the criteria of the minimum acceptable eigenvalue λ_{min} of C or of the number k depends on the measurement precision. For a higher precision experiment, more data can be included because the details can be "seen" and hence each of the data can be distinguished. For the same experiment with a lower precision, some of the data have to be excluded because the details have been lost. Obviously, it is desirable to have a qualitative criteria for such a justification. In the following, two similar criteria are introduced which were derived separately by Twomey^[9] which is clear in the physics of the problem, and Ben-David^[12] et. al., which is more convenient to calculate. The two derivations are then combined to adopt the merits.

In Twomey's derivation, the measured vector g with error vector ϵ can be expressed as

$$g_j + \epsilon_j = \int K_j(r)p(r)dr, \quad j=1,2,\dots \quad (5.2.7a)$$

It is convenient to scale the above equation by two factors α and β through

$$\alpha g_j + \alpha \epsilon_j = \int (\alpha/\beta) K_j(r) \beta p(r) dr \quad (5.2.7b)$$

so that the g_j and the length of $p(r)$ are almost unity; i.e.,

$$g_j \approx 1, \quad \int p^2(r)dr = |p^2| \approx 1. \quad (5.2.7c)$$

Assuming that g_l can also be predicted using (5.2.2) and denoting the calculated one as g'_l , one may reasonably include an error $\delta(r)$ in the corresponding kernel $k_l(r)$:

$$k_l(r) + \delta(r) = -a_l^{-1} \sum_{j \neq l} a_j k_j(r). \quad (5.2.8)$$

Substitute (5.2.8) into (5.2.7a) to find

$$g_l + \epsilon_l = \sum_{j \neq l} \left(-\frac{a_j}{a_l} \right) \int K_j(r) p(r) dr + \int \delta(r) p(r) dr. \quad (5.2.9)$$

Substituting (5.2.7a) into equation above with subscript l replaced by j , the difference between the measured and predicted g_l is

$$g_l - g'_l = \int \delta(r) p(r) dr - [\epsilon_l + \sum_{j \neq l} \left(-\frac{a_j}{a_l} \right) \epsilon_j]. \quad (5.2.10)$$

It is easy to see that the first term on the right hand side of (5.2.10) is an unpredictable error resulted from the approximation in the kernels, and the second term is from the experiment error. For a set of measurements to be reasonably independent, the effect of the error from any single measurement must be smaller than the error of the other kernels' linear combination; *i.e.*,

$$\left[\sum_{j \neq l} \frac{a_j}{a_l} \epsilon_j \right]^2 \leq (\delta(r) \cdot p(r))^2 \quad (5.2.11)$$

Applying the Schwartz inequality (5.1.3), the upper bond of the right-hand side of (5.2.11) is obtained

$$(\delta(r) \cdot p(r))^2 \leq \int \delta^2(r) dr \times \int p^2(r) dr = |\delta(r)|^2 |p(r)|^2. \quad (5.2.12)$$

Another approach is to use the mean value theorem to obtain

$$\left| \int \delta(r) p(r) dr \right|^2 = p_m^2 \left| \int \delta(r) dr \right|^2 \leq p_m^2 \int \delta^2(r) dr. \quad (5.2.12)$$

Using an unitary transformation like (2.3.7), the integration can be written as

$$\int \delta^2(r) dr = a_i^{-2} \sum_{ij} a_i a_j \int K_i(r) K_j(r) dr = a_i^{-2} \mathbf{a}^* C \mathbf{a} = a_i^{-2} \mathbf{a}'^* \Lambda \mathbf{a}', \quad (5.2.13)$$

where C is just the covariance matrix and, after transformation, Λ is its eigenvalue matrix, and $\mathbf{a}'$ is the transformed vector.

The value of (5.2.13) may vary from between the maximum $\lambda_{max}/a_i'^2$ (with $a'_i = 1$ and all others = 0) and the minimum $\lambda_{min}/a_i'^2$ (with $a'_i = 1$ and others = 0). thus, recalling that $a_i \leq 1$,

$$\text{left side of (5.2.10)} \leq \begin{cases} |p|^2 \lambda_{min} & \text{(Schwartz's inequality)} \\ |p_m|^2 \lambda_{min} & \text{(using mean value).} \end{cases} \quad (5.2.14)$$

$$(5.2.15)$$

If there is no correlation between the experiment error vector ϵ and the unit vector $\mathbf{a}$, the expected norm of $\sum a_j \epsilon_j$ of the right hand side of (5.2.10), which is the length of the projection of the random vector ϵ on the unit vector $\mathbf{a}$, is evidently $n^{-1} |\epsilon|^2$ which is the mean square relative error e^2 . The value of a_i must lie between $n^{-1/2}$ and 1, and except for very large n , is not too different from unity. Thus the error component $a_i^{-1} \sum a_j \epsilon_j$ has a magnitude not too different from the error magnitude $|\epsilon|$. Now condition (5.2.11) can be written as

$$\lambda_{min} > \frac{|\epsilon|^2}{n}, \quad (5.2.16)$$

provided the system has been properly scaled.

The result derived by Ben-David^[12] *et. al.*, is similar to (5.2.16). Instead of dealing with the experimental data $\mathbf{g}$, Reference [12] considers a linear combination of kernels $K_j(r)$ and the related errors $\delta_j(r)$ as a small but non-zero quantity q

$$\sum_{j=1}^n a_j [K(\alpha_j, r) + \delta(\alpha_j, r)] = q(r), \quad (5.2.17)$$

where the coefficient a_j satisfies (5.2.8).

Taking the square average on both sides of (5.2.17) and assuming δ_j is a Gaussian distributed additive error

$$\delta_j(r) = N[0, P_j^2 K_j^2(r)], \quad (5.2.18)$$

where N represents a normal statistic about zero and a variance $P_j^2 K_j^2(r)$ and $P_j \leq 1$, one finds the following expression

$$\langle q^2 \rangle = \sum_{i,j} a_i a_j \int_a^b K_i(r) K_j(r) dr + \sum_j a_j^2 P_j^2 \int_a^b K_j^2(r) dr, \quad (5.2.19)$$

where $\langle \delta_j \rangle = 0$ and $\langle \delta_j^2 \rangle = P_j^2 K_j^2(r)$ have been used. The integration over particle size r includes the contributions from all particles in the averaging procedure.

The integrations in the first and second terms of (5.2.19) are just the elements of covariance matrix C_{ij} and C_{ii} , respectively. Assuming that the kernels are normalized so that

$$\int_a^b K_i^2(r) dr = 1 \quad (5.2.20)$$

and using the transformation like (5.2.13), Eq(5.2.19) can then be written as

$$\langle q^2 \rangle = \sum_j a_j^2 \lambda_j + \sum_j a_j^2 P_j^2. \quad (5.2.21)$$

The minimum value of the first term is apparently $\lambda_{\min}$, the minimum eigenvalue of C. Using the Schwartz inequality (5.1.3) for the second term of (5.2.21), one has

$$\langle q^2 \rangle = \lambda_{\min} + \left[\sum_{j=1}^n a_j^2 P_j^2 \leq \sum_{j=1}^n a_j^2 \sum_{j=1}^n P_j^2 = nP^2 \right],$$

where Eq(5.2.3) has been used and constant $P_j = P$ has been assumed. To ensure a signal-to-noise ratio of 10, the condition for n kernels to be independent requires $\lambda_{\min}$ larger than the quantity in the bracket in above equation, or

$$\lambda_{\min} \geq 10nP^2. \quad (5.2.22)$$

Result (5.2.22) is similar to (5.2.16) but for a factor of n which is significant when n , the number of total measurements, is large. Actually, using the Schwartz inequality in (5.2.21) is too strict to the kernels of scattering and extinction measurements which form a highly dependent set. This will be seen in performing the information content analysis on the experimental system in Chapter 7. In order to obtain a more tolerant condition, the maximum value of P

$$\sum_{j=1}^n a_j^2 P_j^2 \leq P_{\max}^2 \sum_{j=1}^n a_j^2 = P_{\max}^2,$$

is used to obtain the result of

$$\lambda_{\min} \geq 10P_{\max}^2 \quad (5.2.23a)$$

which is about the same as (5.2.16). The mean value of P can be used to find

$$\lambda_{\min} \geq 10 \bar{P}^2. \quad (5.2.23b)$$

In any actual calculation in the information content analysis, the covariance matrix C has to be scaled or normalized using a convenient method. Equation (5.2.20) is one of the normalization method which implicitly depends on the PSDF (through the integration limit) and Eq.(5.2.7c) is another one which explicitly depends on the PSDF. Although there are some differences in the eigenvalues of C , these two normalization methods basically give the same results in determining the information content for a set of optical data. Like many researchers,^[12,9b] Equation (5.2.20) is adopted here because:

- (1) it is convenient, *e. g.*, one can normalize C by

$$C_{ij} = \frac{\int_a^b K_i(r) K_j(r) dr}{\left[\int_a^b K_i^2(r) dr \int_a^b K_j^2(r) dr \right]^{1/2}} \quad (5.2.24)$$

- (2) it does not depend on individual PSDF as long as the interested range of particle size has been included and
- (3) it allows us to compare different the distribution of eigenvalues of kinds of kernels, *e.g.* scattering *versus* extinction.

In fact, it is easy to show that even using normalization (5.2.20), Eq.(5.2.23) can also be obtained following Twomey's treatment.

Similar to the Monte Carlo simulations discussed in Chapter 3, assume that the error ϵ_j is Gaussian distributed with zero mean and variance $P_j^2 g_j^2$, one has

$$\langle \epsilon_j^2 \rangle = P_j^2 g_j^2 = P_j^2 \left[\int K_j(r) p(r) dr \right]^2 \leq P_j^2. \quad (5.2.25)$$

By squaring and taking averages on both sides of (5.2.10), one obtains

$$\langle (g_l - g_l')^2 \rangle = (\delta(r) \cdot p(r))^2 + \sum_{j=1}^n \left(\frac{a_j}{a_l} \right)^2 \langle \epsilon_j^2 \rangle.$$

The condition (5.2.11) should then be written as

$$(\delta(r) p(r))^2 \geq \sum_{j=1}^n \left(\frac{a_j}{a_l} \right)^2 \langle \epsilon_j^2 \rangle. \quad (5.2.26)$$

Substituting (5.2.25) into (5.2.26) and using Schwartz inequality on both sides of (5.2.26), one finds

$$|p|^2 \int \delta(r)^2 dr \geq |p|^2 \sum_{j=1}^n \left(\frac{a_j}{a_l} \right)^2 P_j^2 \int K_j^2(r) dr. \quad (5.2.27)$$

Next use (5.2.13) and normalization (5.2.20) in the above equation to get

$$a'^* \Lambda a' \geq \sum_{j=1}^n a_j^2 P_j^2. \quad (5.2.28)$$

Replacing the left hand side of (5.2.28) with its minimum value $\lambda_{\min}$ and apply the mean value theorem to the right hand side, one finds

$$\lambda_{\min} \geq \bar{P}^2 \sum_{j=1}^n a_j^2 = \bar{P}^2. \quad (5.2.29)$$

By requiring a signal to noise ratio of 10, the condition for n measurements to be independent is found to be

$$\lambda_{\min} \geq 10 \bar{P}^2. \quad (5.2.30)$$

Condition (5.2.30) is very important in determining how many data should be included in inversion or deconvolution. Too few or too many data points would, depending on the measurement precision, either lose information or add extra noise to the result. If the signal to noise ratio S/N is very high which means small $P_{\max}$, one can

include more data in the deconvolution. If the S/N is relatively low, one has to delete some data points because they contribute more noise than information.

A more practical question is: suppose it is known, through eigen-analysis (5.2.30), that among the n data points there is one redundant data which results in the violation of (5.2.16); now, how does one determine which measurement is to be deleted.

According to Twomey's^[9] scheme, first of all, find the eigenvector $\mathbf{u}_n = (u_{n1}, u_{n2}, \dots, u_{nn})$ of the covariance matrix $\mathbf{C}$ corresponding to the minimum eigen value λ_n ; then select within the n elements the one with the maximum absolute value, say u_{ni} ; and the measurement corresponding to that value g_i is the one needs to be deleted. The reason is simple: the smallest eigenvalue λ_n can be expressed as

$$0 \approx \phi(r)\sqrt{\lambda_n} = u_{n1}K_1(r) + \dots + u_{ni}K_i(r) + \dots + u_{nn}K_n(r), \quad (5.2.31)$$

where $\phi(r)$ is the orthogonal base function, or conveniently,

$$K_i(r) \approx \frac{u_{n1}}{u_{ni}}K_1(r) + \frac{u_{n2}}{u_{ni}}K_2(r) + \dots + \frac{u_{nn}}{u_{ni}}K_n(r). \quad (5.2.32)$$

Using the relation $\mathbf{g} = \mathbf{K} \cdot \mathbf{p}$ and ignoring the small quantity $\lambda_n^{1/2}$, one finds

$$g_i(r) \approx \frac{u_{n1}}{u_{ni}}g_1(r) + \frac{u_{n2}}{u_{ni}}g_2(r) + \dots + \frac{u_{nn}}{u_{ni}}g_n(r). \quad (5.2.33)$$

Equation (5.3.20) means that the measurement g_i can be formed by the minimum contributions from other measurements through a simple linear combination and the resultant error, which is the same magnitude as $\lambda_n^{1/2}$, is less than the relative experimental error (referring to Eq(5.2.30)). From a mathematical point of view, the elements of the eigen vectors corresponding to the bigger eigenvalues are uniformly distributed (roughly equal), while on the contrary, the elements of the eigen vectors

corresponding to the smaller eigenvalues are alternating in signs and oscillately distributed, and therefore contribute cancellations in (5.2.20). By deleting g_i and therefore u_{ni} , one actually eliminates the most oscillatory term and hence stabilizes the data system.

§ 5.3 Physical Significance of Covariance Matrices C and B.

To look at the physical meaning of the two covariance matrices, it is helpful to write their elements as

$$\begin{cases} C_{ij} = \sum_{k=1}^m K(\alpha_i, r_k) K(\alpha_j, r_k) \\ B_{ij} = \sum_{k=1}^n K(\alpha_k, r_i) K(\alpha_k, r_j). \end{cases} \quad (5.3.1)$$

The physical meaning of C_{ij} is that it represents the correlations between the kernels of the i th and the j th wavelengths for extinction measurements (or scattering angles for scattering measurement) throughout the whole range of particle diameters; while B_{ij} indicates the correlations between the signals from a particle with radius r_i and another one with r_j over the whole range of measurements points. If one considers the particle size r as a coordinate space, and the photon's frequency (wavelength), or the scattering angle which reflects momentum change of photons, as a momentum space, then C_{ij} could be understood as a measure of the correlation for the two kernels of two different momentum points over the whole coordinate range while, in contrast, B_{ij} would be thought as an indication of the correlations for the two kernels at two different coordinate locations over the whole momentum space. The matrix $\mathbf{K}$ transforms vectors between the two spaces such as (2.2.3) and (2.2.4) provided that the

vectors are within the spaces spanned by $\mathbf{K}$. A direct relation between $\mathbf{C}$ and $\mathbf{B}$ is give by (2.4.7ab).

The covariance matrix $\mathbf{C}$ plays an important role in the theory of linear inversion and is widely used in stability evaluation, information content analysis, *etc.*^[9,10] From the experimental point of view, C_{ij} reflects the dependence between the i th measurement (e.g. at the i th angle or wavelength) and the j th measurement over all possible sizes of the particles in the system. It therefore provides the basis for justifying which group of wavelengths (scattering angles) can yield more information than others.

On the contrary, the matrix $\mathbf{B}$ drew little attention and has not yet been singled out for discussion. Basically, B_{ij} ($i \neq j$) describes the correlations over all signals measured between one category particles with radius r_i and another category with radius r_j . If their signals overlap each other on the range of the measurements, which results in a relatively large B_{ij} , one can not detect the size information using that experiment no matter how many measurements are made. B_{ij} thus, in principle, tells if an experiment is suitable for a specific system. Ben-David *et al*^[12] obtained the same result with that of Twomey's which uses the matrix $\mathbf{C}$ for the stability analysis for linear inversion. Although it is not mentioned, the eigenvalues λ 's in Reference [12] are, in fact, that of dual covariance matrix $\mathbf{B}$'s instead of $\mathbf{C}$'s.

From the discussion above, one can see that all of the characteristic information about the measurement system is contained in the kernels of $\mathbf{K}(\alpha, r_j)$ which relate the two coordinate systems (α and r). One of the combinations of $\mathbf{K}(\alpha, r_j)$ gives correlation the matrix $\mathbf{C} = \mathbf{K}\mathbf{K}^+$ in α space and the distribution of the eigenvalues of $\mathbf{C}$ reflects the size of the space. For example, if there are, among n eigenvalues, only m eigenvalues which satisfy (5.2.23), the space spanned by the kernels is m dimensional. That means

there are only m independent measurements in that data set. Another combination of $\mathbf{K}(\alpha_i, r_j)$ yields the matrix $\mathbf{B} = \mathbf{K}^+ \mathbf{K}$ which reflects the size of the space of $\mathbf{r}$ through its eigenvalue distribution. If a PSDF $p(r)$ lies basically inside the space spanned by $\mathbf{K}(\alpha_i, r_j)$, then the corresponding experimental data contains all of the information of $p(r)$. If part of $p(r)$ is out side of the space spanned by $\mathbf{K}(\alpha_i, r_j)$, then that part of information would be lost unless some other information, *e.g.*, some restrictions, is imposed on the $p(r)$. Therefore, matrix $\mathbf{C}$ and $\mathbf{B}$ reflects the characteristics or information content of $\mathbf{K}(\alpha_i, r_j)$ through different points of view. One can use $\mathbf{C}$ to perform information content analysis as was done in the last section or, in principle, use $\mathbf{B}$ to do the same thing. To see this clearly, one begins with a equation similar to (5.2.17) with the roles of α and $\mathbf{r}$ exchanged

$$\sum_{j=1}^m a_j [K(\alpha_k r_j) + \delta(\alpha_k r_j)] = q(\alpha_k), \quad (5.3.2)$$

in which the coefficient a_j satisfies (5.2.8). The physical meaning of (5.3.2) is clear; it is just the linear combination of kernels of $K(\alpha_j)$ and the related error $\delta(\alpha_j)$ for a specific particle size parameter r_k . Taking the square average on both sides of (5.3.1) and assuming a Gaussian additive noise for δ ,

$$\delta(\alpha_k r_j) = N[0, P_k^2 K^2(\alpha_k r_j)], \quad (5.3.3)$$

One obtains the following expression by sum over all possible α_k ,

$$\begin{aligned}
\sum_{k=1}^n \langle q^2(\alpha_k) \rangle &= \sum_{ij} a_i a_j \sum_{k=1}^m K(\alpha_k r_i) K(\alpha_k r_j) + \sum_j a_j^2 P_j^2 \sum_{k=1}^n K^2(\alpha_k r_j) \\
&= \sum_{ij} a_i a_j B_{ij} + \sum_j a_j^2 P_j^2 = a'^* B a' + \bar{P}^2,
\end{aligned} \tag{5.3.4}$$

where the matrix transformation formulas (2.4.2) have been used. If γ_l is the l th eigenvalue of **B**, the condition that l independent functions exist is thus

$$\gamma_l \geq \bar{P}^2. \tag{5.3.5}$$

Result (5.3.5) is very similar to that of (5.2.23) if a factor of 10 (signal to noise ratio) is multiplied on the right-hand side of (5.3.5). This is reasonable because the traces of **C** and **B** are equal as derived in (2.4.8).

Although the equivalence of using **C** and **B** in doing information content analysis has been shown through the derivations of Eqs.(5.3.2) - (5.3.5), it is natural and easy to use **C** instead of **B** because the measurement data points are always discrete and therefore finite in number, while the particle size r is always continuous and is treated more conveniently in integration form in (5.2.19) than (5.3.4). One of the direct uses of **B** is introduced in the stability analysis in section 2.4. The results obtained in this chapter will be used in analyzing the information content of the multi-angle scattering measurement.

The last topic of this chapter is given to the discussion of the information content of the particle systems introduced in Chapter 3. The normalization method (5.2.24) is used. The eigenvalues for all four situations: water scattering, water extinction, soot scattering and soot extinction are calculated and plotted in Fig.(5.3.1). Assuming the experiment accuracy is about 1% for all situations, according to (5.2.20), the cut-off is then $10 \times (.01)^2 = 10^{-3}$. From the figure one can see that for water/scattering

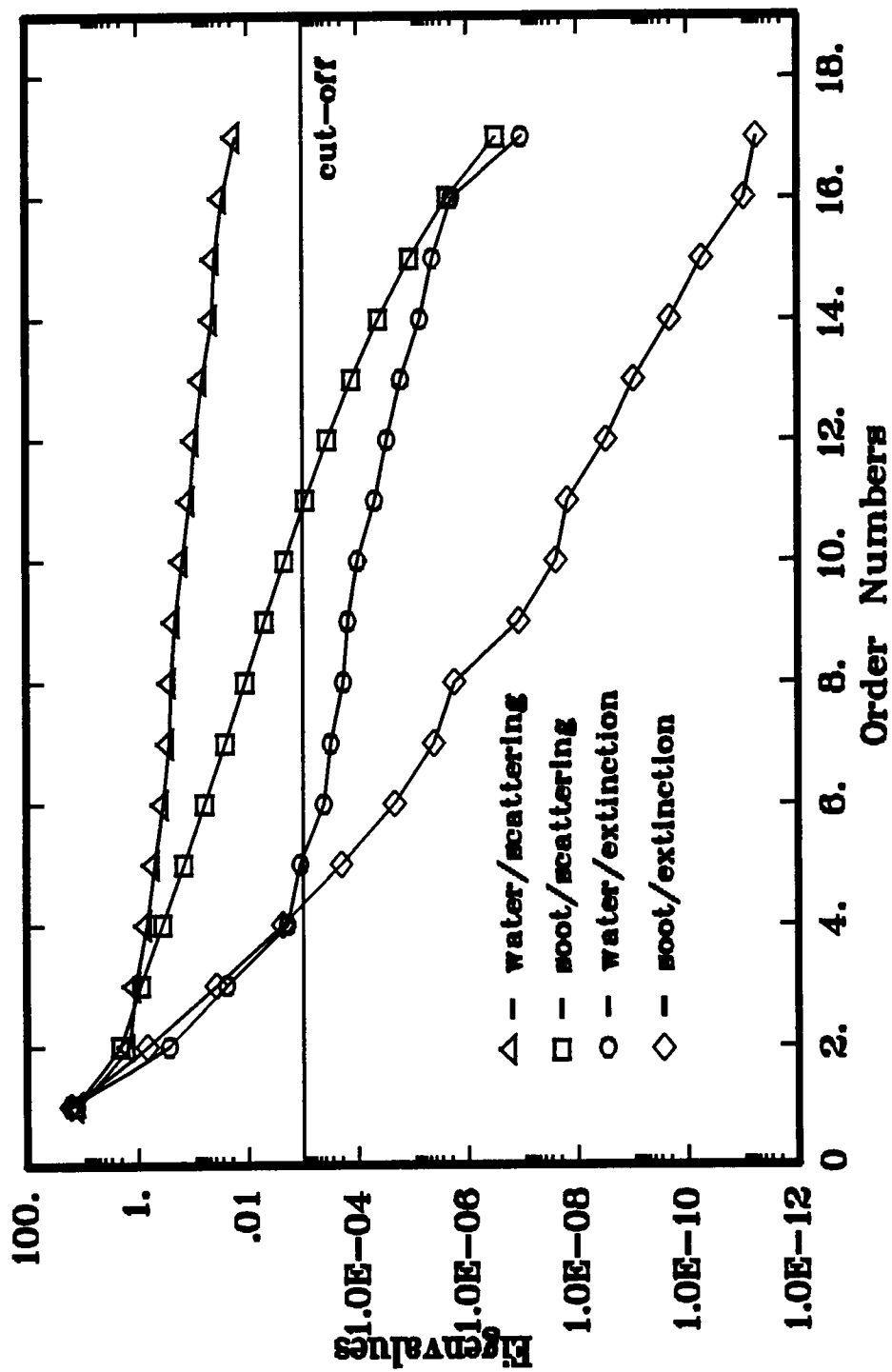
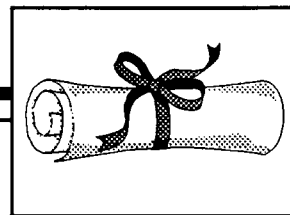


Figure 5.3.1 The eigenvalues of the simulated water and soot particle systems. The cut-off is 10^{-3} for the accuracy of 1%.

case, all the 17 eigenvalues are above the cut-off which means all the measurements are usable. The next one is the soot/scattering case which has about 10 good measurements. The water/extinction and soot/extinction both have about 4 eigenvalues above the cut-off, but the water/extinction case is a little bit of better because the slope of the decrease of the eigenvalues is smaller. The information content analysis method discussed in this chapter will be applied to the an experimental system in Chapter 7.

Chapter 6



Scattering Experiments for Pure Water Droplets

Although the Monte Carlo simulations in Chapter 3 provide a good measure in verifying the predictions in previous chapters, applying the DHS deconvolution method to experimental results is an indispensable final justification and cannot be replaced by simulations.

In this chapter, the experiment, angular scattering of a laser beam by water droplets, is described. The DHS deconvolution technique is then applied to the experimental data to calculate the PSDF parameters and the results are compared with the theoretical predictions given in the previous chapters. The desired parameters are: particle size parameters (D, V), number density N and the complex index of refraction (n, k).

The reason an angular scattering experiment was chosen, rather than a multi-wavelength extinction experiment, is simply because the scattering contains more information than the extinction for the spectral range of conventional available light sources, as pointed out in the information content analysis in Chapter 5. Further, the spherical shape of water droplets allows the application of the simple and strict Mie theory and therefore the calculation errors in the deconvolutions are negligible.

§ 6.1 Experiment Setup

Shown in Fig.(6.1.1) is the configuration of the scattering experiment. To obtain spherical particles, a TSI-9306 atomizer was used to generate a water droplet spray, as seen in Fig.(6.1.2). The distilled water in the reservoir was sprayed through 1 to 6 jets with pressurized air. The cylindrical particle field has a diameter of 27 mm at the interception position with the laser beam. By adjusting the number of jets, the air pressure, and the air flow rate, one can obtain particles with different size distributions and different number densities. To avoid multiple-scattering while maintaining adequate signal intensities, the flow rate was controlled at about 48 liters/minute (l/min) and was monitored by a flow meter (MKS, 0258B-50000SV). The light source was a He-Ne laser ($\lambda = 632.8$ nm) with 25 mW output power (Aerotech, LSR-25P). The incident beam diameter of the laser was controlled at 2mm which is much smaller than the diameter of the particle field L_0 (27 mm). Because Mie scattering theory is polarization sensitive, a high quality polarizer (Optics Research PHU-10) was utilized to ensure that the incident beam was vertically polarized (within $\pm 1^\circ$) with respect to the scattering plane (*i.e.*, the table plane). The detector was a photodiode package (Thor Labs-PDA50) with a responsivity in the range of 3×10^4 V/W - 3×10^7 V/W of the spectral range of interest. A high gain ($\sim 10^6$) amplifier used in the photodiode package sends the output to a lock-in amplifier (EG&G-5104) synchronized by beam chopper (EG&G-196) synchronization at the chopping frequency of 3000/min. There is no special requirement on the two flat mirrors (any brand). Other components in Fig.(6.1.1) such as the beam splitter and the reference beam detector were used in the experiments for absorbent water droplets, as will be seen in Chapter 7. The beam splitter was a piece of BK-7 glass with reflection of 4% - 8% and the reference beam detector was the photodiode

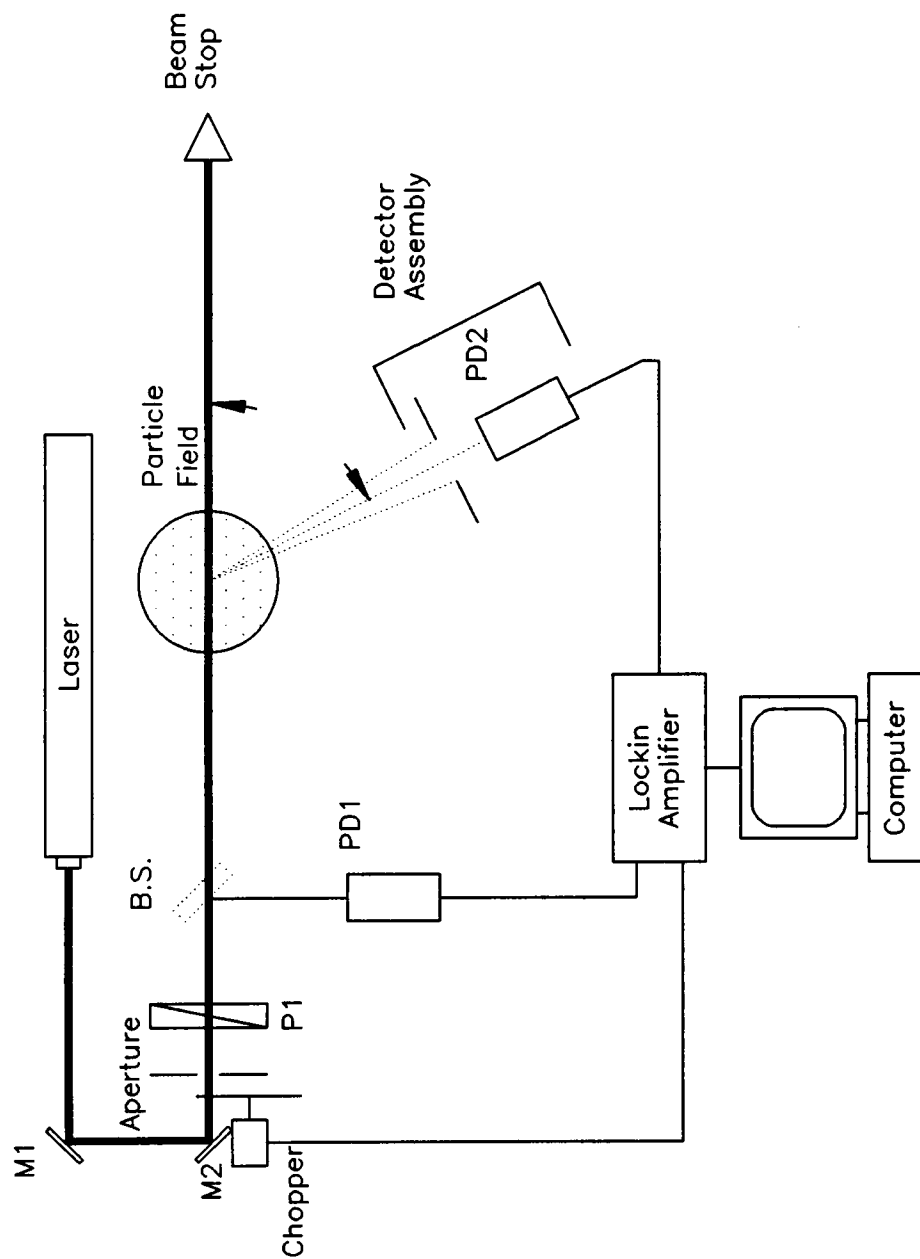


Figure 6.1.1 Schematic graph of scattering experiment set-up viewed from top. M_1 , M_2 mirrors, P_1 polarizer, B.S., beam splitter, $PD1$, $PD2$, photo-diodes.

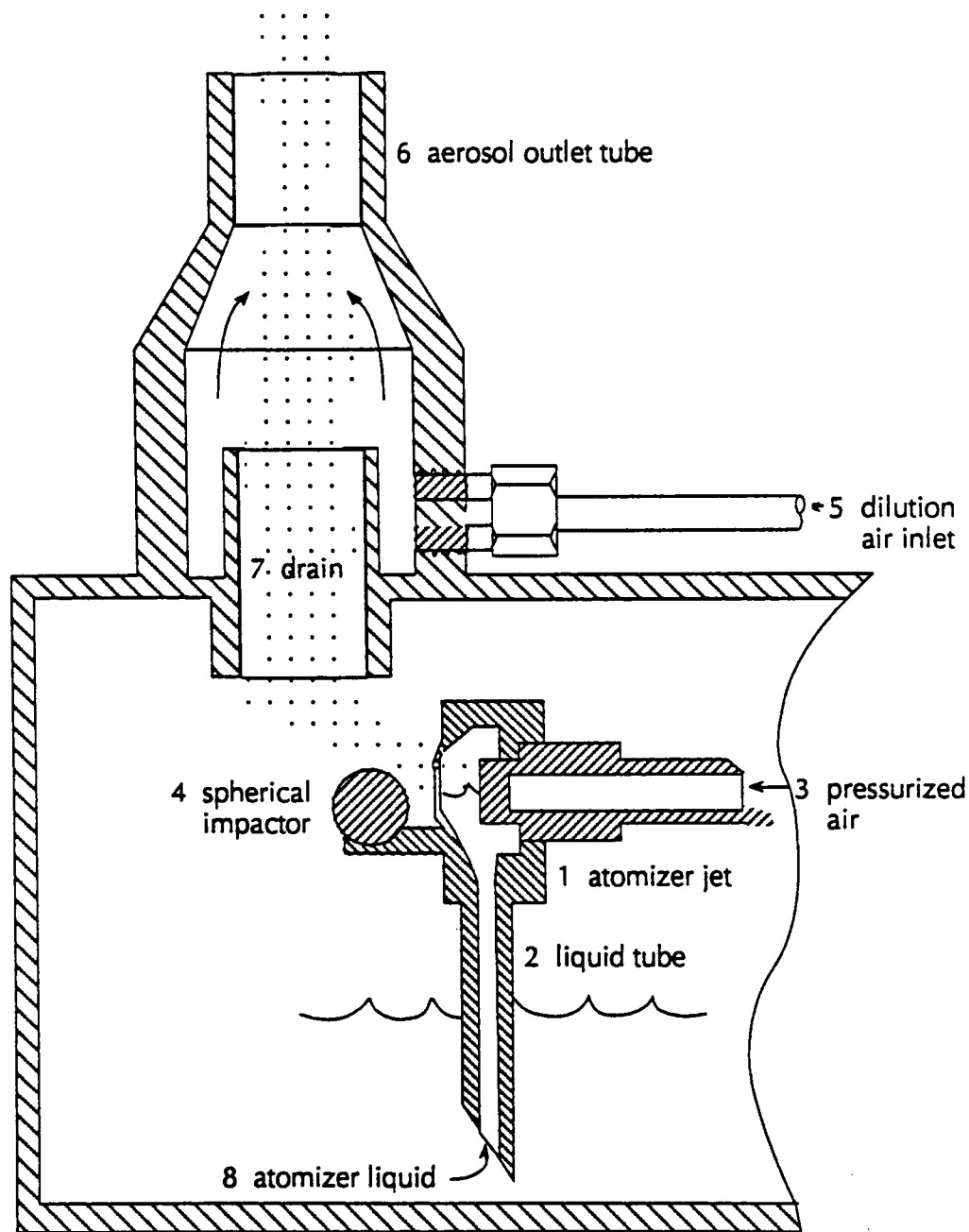


Figure 6.1.2 Schematic drawing of the particle generator, a atomizer made by TSI Inc.
Source, Instruction manual for Model 9306 6-Jet Atomizer, TSI Inc.

made by Thor Labs (PDA150). The system was carefully aligned and shielded to avoid stray light coming into the detector. The use of the lock-in amplifier effectively eliminates the background signals. The experimental data were registered using a PC-computer through a GPIB-488 interface (National Instrument).

The detector assembly, with an optical spatial filter, was mounted on a rotation arm. The arm can be rotated (with $\pm 0.5^\circ$ precision) in the scattering plane to collect scattered signals for the scattering angles of $20^\circ - 160^\circ$ with an increment of 5° . At each scattering angle, 50, 100, or 500 data points were acquired by the computer. The mean and standard deviation were determined and recorded as the experiment value and error bar (in volts), respectively. Because of the finite solid angle subtended by the detector at the scattering center, the Mie kernels must be integrated over that solid angle according to Eq.(3.2.12b-d). Since Mie theory has the wonderful feature of requiring only the ratios of scattered light and the incident intensity, no absolute light intensity was required for the deconvolution.

Because the magnitude of the scattering signals varies by more than two order of magnitude and the requirement of the experimental data of being free of system errors, to avoid systematic errors, the linearity of the photodiode detector was calibrated using a polarizer. The deviation of the linearity of the measured signals S_m with respect to the calculated signals S_c using Malus law was small and can be expressed as

$$\log S_m = \log(1.07 \pm 0.03) + (1.01 \pm 0.01) \log S_c. \quad (6.1.1)$$

Figure (6.1.3) shows the relation of (6.1.1) and all the data were normalized by the signal from the reference beam detector (8.3×10^{-4} Volts). The average relative deviations of S_m with respect to S_c is less than 4% which is below the fluctuations of

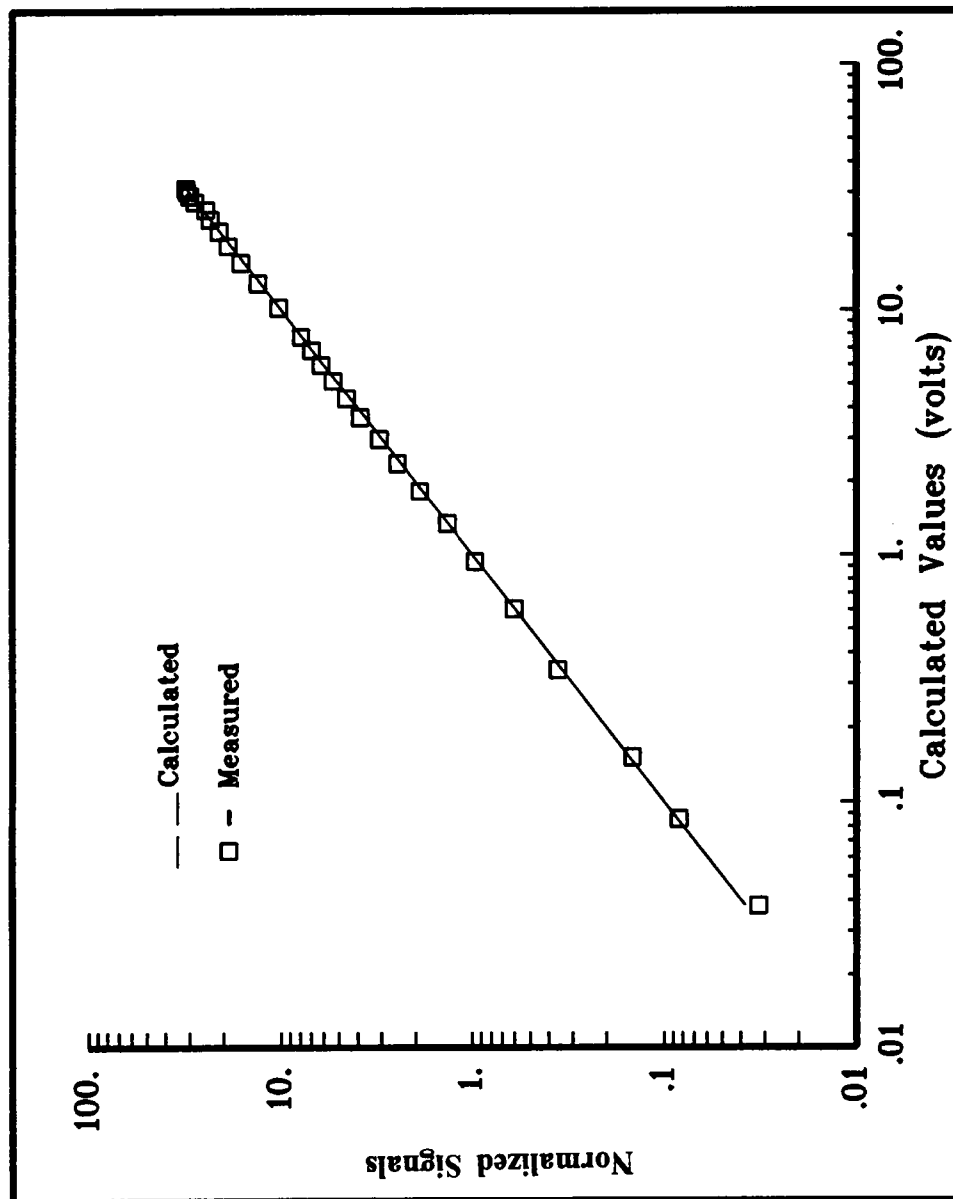


Figure 6.1.3 The linearity calibration profile for the Photo-diode.

the scattering signals. It may have been noticed that the relatively large deviation of S_m from S_c occurs only at the lowest signal end. The cause of this deviation is that this signal level ($< 2 \times 10^{-6} V$) is below the lock-in amplifier operating range ($3 \times 10^{-6} \sim 3 V$).

§ 6.2 Scattering Volume Correction and Spatial Filter

An important factor for any experiment concerning finite scattering volume (dimension) is the change of the scattering volume as the scattering angle (θ_i) changes. Several authors have pointed out this problem,^[3,4,7] but there is no general rule to correct for this effect since it depends on the individual situation. Figure (6.2.1) shows, along with the design of a spatial filter, how the scattering dimension changes at different scattering angles for a detector of a finite viewing angle η .

The experimental system in Fig.(6.1.1) is basically a one-dimensional scattering system because the laser beam diameter is much smaller than the scattering dimension at any angle. Therefore, only the changes in the scattering length need to be considered and the related quantities are denoted as:

L_0 : the length of laser beam that intercepts the particle field.

$L(\theta_i)$: the length which the detector views along the laser beam direction, as determined by the scattering angle θ_i .

Depending on the optical configurations, there are three situations between L_0 and $L(\theta_i)$ that need to be considered, as shown in Fig.(6.2.2):

- (1) Near field: $L_0 \geq L(\theta_i)$ for all angles — the detector is close to the scattering center.
- (2) Medium field: $L_0 \leq L(\theta_i)$ for some angles and $L_0 \geq L(\theta_i)$ for the other angles — the detector is at moderate distance from the scattering center.

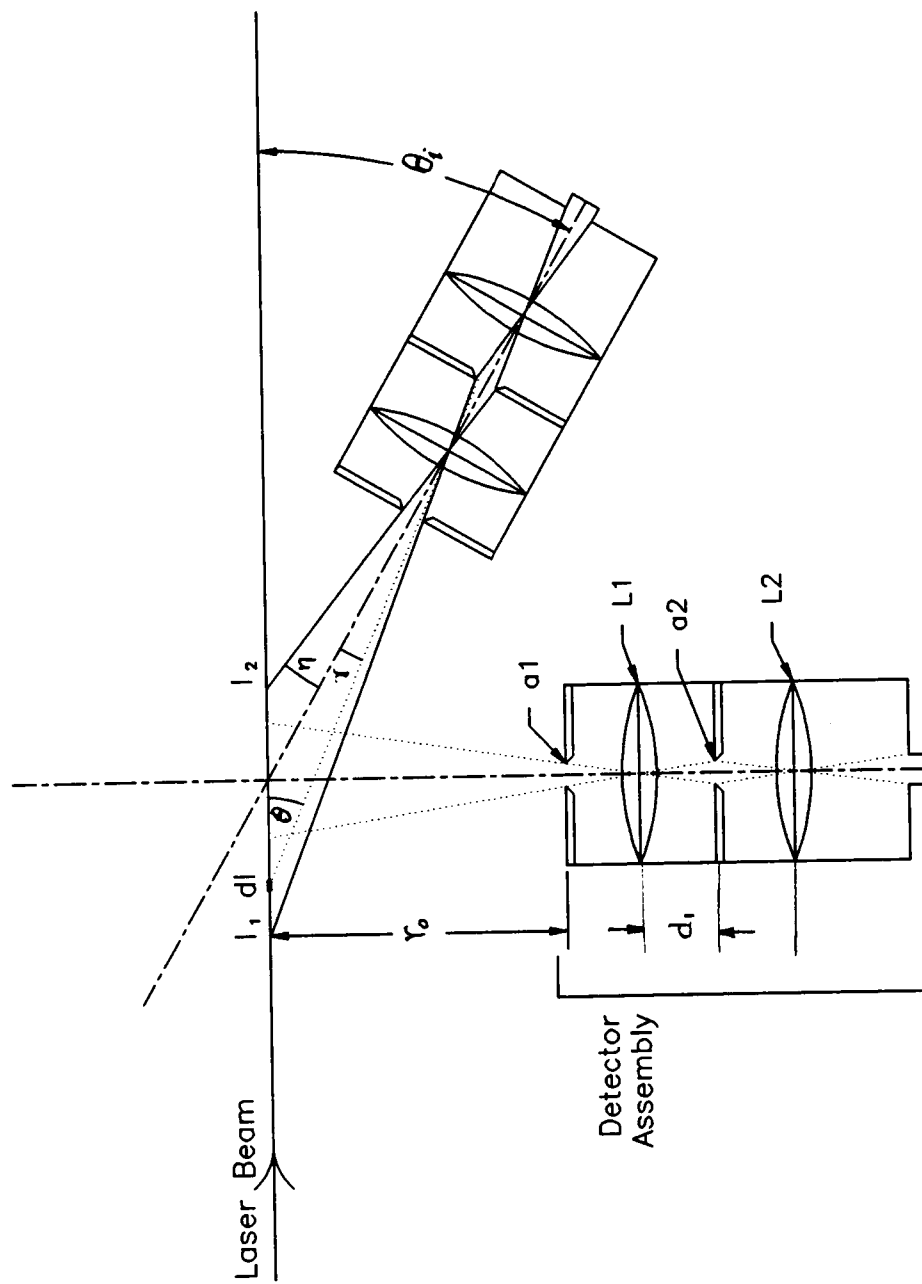


Figure 6.2.1 The geometrical configuration of the scattering length change and the design of spatial filter.

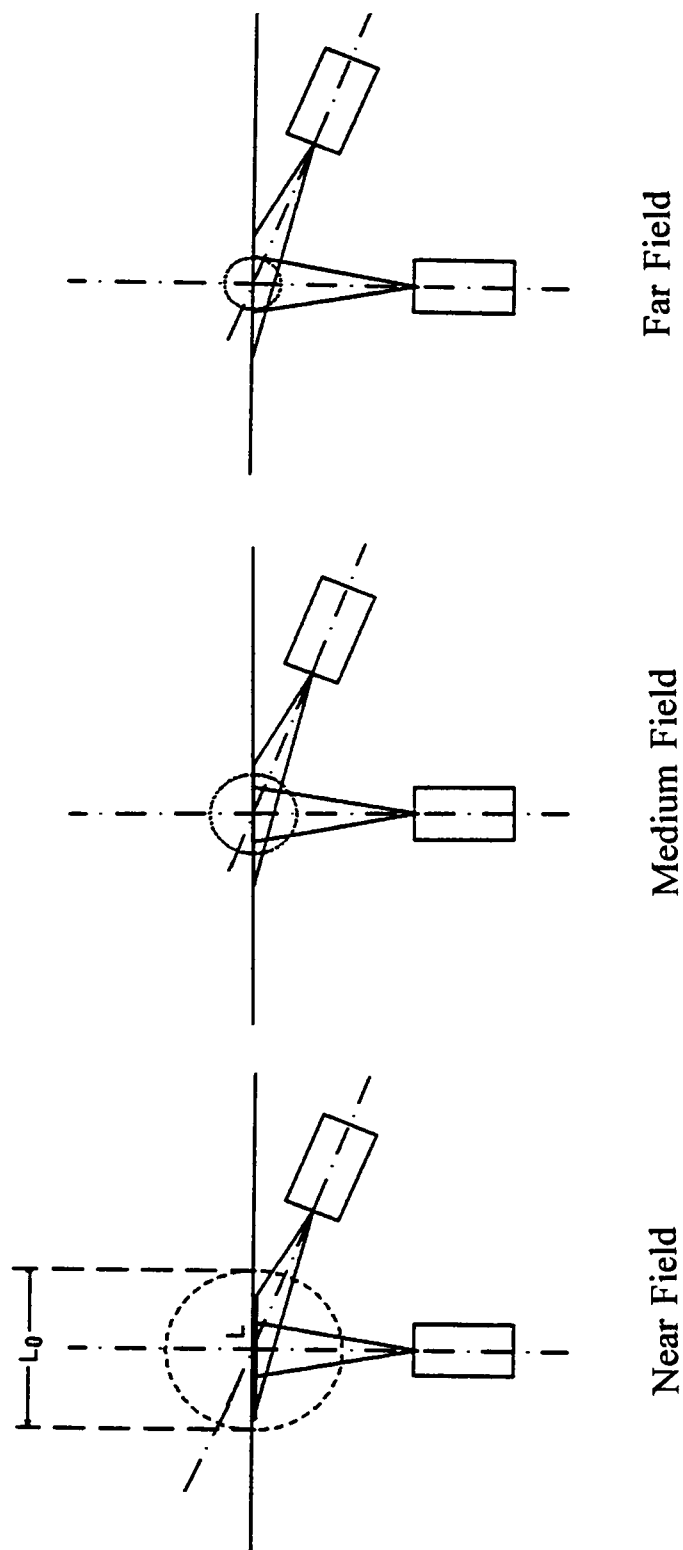


Figure 6.2.2 Three experimental configurations. From left to right, near, medium and far field.

(3) Far field: $L_0 \leq L(\theta_i)$ — the detector is far from scattering center.

The most straightforward way of dealing with the scattering length change is referred to here as the geometrical correction method (GCM). By attributing all scattering signals as being from the center of the scattering length, this method simply multiplies a factor of $\sin(\theta_i)$ to the experiment data, or equivalently, divides the fitted data by $\sin(\theta_i)$. It will be seen from the experimental data analysis in next section that this method is good only for such a situation in which at any angle, only part of the illuminated scattering dimension is viewed by the detector, which is the Near Field situation as listed above. Examining the geometrical configuration of Fig(6.2.1), it can be shown that the ratio of the scattering length "seen" by the detector at any scattering angle $L(\theta)$ and the same quantity at scattering angle of 90° is

$$\frac{L(\theta_i)}{L(90^\circ)} = \frac{1}{2} \cos(\eta) [(\sin(\theta_i - \eta))^{-1} + (\sin(\theta_i + \eta))^{-1}], \quad (6.2.1)$$

where the angle η is the half view-angle of the detector. Eq.(6.2.1) is valid, of course, only when $\eta < \theta_i$. When η is sufficiently small relative to θ_i , that it can be neglected, Eq.(6.3.1) yields the $\sin(\theta_i)$ correction method. Table (6.2.1) shows the differences between the two results when $\eta = 1^\circ$, which is close to the configurations of the experiments performed in this dissertation. It is obvious from this table that the differences are very small when scattering angles are between $30^\circ - 150^\circ$.

To correct the deficiency of the GCM, a method is introduced which is denoted as the dimension integration method (DIM) to treat the observed scattering-length problem. Instead of attributing all signals as being from the scattering center, the DIM considers the scattering signals as the integration of contributions from all points along

the scattering dimension from l_1 to l_2 , as is shown by Fig.(6.2.1). Referring Eq.(2.1.5), the scattering signal can be expressed as

$$\tau_s = N \int_{l_1}^{l_2} \cos \gamma dl \int_0^{\infty} C_s(\theta_i, l, r) p(r) dr, \quad (6.2.2)$$

where the inclusion of the factor $\cos(\gamma)$ is because the element dl is not at the center of field of view of the detector assembly.

Table 6.2.1 Comparison of the two correction formula at some angles.

Formula	$\theta=10^\circ$	20°	30°	40°	50°	60°	70°	80°	90°
$\sin^{-1}(\theta_i)$	5.7588	2.9238	2.0000	1.5557	1.3054	1.1547	1.0642	1.0154	1.0000
Eq(6.3.1)	5.8167	2.9310	2.0021	1.5567	1.3059	1.1550	1.0644	1.0156	1.0000

It is convenient to change the integration variable from dl to $d\theta$ via

$$l = r_0 \frac{\sin(\theta - \theta_i)}{\sin \theta}. \quad (6.2.3)$$

Equation (6.2.2) can then be written as

$$\tau_s(\theta_i) = N r_0 \sin \theta_i \int_{\theta_i - \gamma_{i+}}^{\theta_i + \gamma_{i-}} C_s(\theta, \theta_i) \frac{\cos(\theta - \theta_i)}{\sin^2 \theta} d\theta. \quad (6.2.4)$$

Assuming the view angle of the detector is η , the $\gamma_{i\pm}$ in the integration limits are determined by

$$\gamma_{i\pm} = \begin{cases} \eta & \text{for Near Field,} \\ \eta, \text{ or } \tan^{-1} \zeta & \text{for Medium Field,} \\ \tan^{-1} \zeta & \text{for Far Field,} \end{cases} \quad (6.2.5a)$$

where

$$\zeta = \tan^{-1} \left(\frac{\sin \theta_i}{\frac{2r_0}{L_0} + \cos \theta_i} \right). \quad (6.2.5b)$$

In order to control $\gamma_{i\pm}$, a spatial filter was designed as shown in Fig.(6.2.1). The first aperture a_1 controls the solid angle subtended by the detector assembly at the center of the scattering length. It was adjusted so that a maximum scattering signal is obtained with a good image of the scattering length passing through the first lens. The second aperture a_2 is located exactly at the image plane of the first lens L_1 . By changing a_2 and the distance d_1 , one is actually adjusting the section of the scattering length which can be seen by the detector. The view angle η in (6.2.5a) is determined by

$$\eta = \tan^{-1} \left(\frac{a_2}{2d_1} \right). \quad (6.2.6)$$

The position of the second lens L_2 is determined to make sure all signals passing through a_2 are collected into the photo-diode assembly.

The photographs of the spatial filter and the scattering experiment set-up are shown in Fig.(6.2.3). The spatial filter is shown on the top part of Fig.(6.2.3) with the scattering volume indicated by a small arrow above the black particle spray pipe. The scattering volume of the water droplet field was lit by the incident laser beam and thus appeared on the photograph as a bright short line. The components of the spatial filter can be recognized easily by referring to Fig.(6.2.1). The bottom part of Fig.(6.2.3) shows the experiment set-up, the laser beam came from the left side and the detector was collecting scattering data at 40 degree with respect to the incident laser beam.

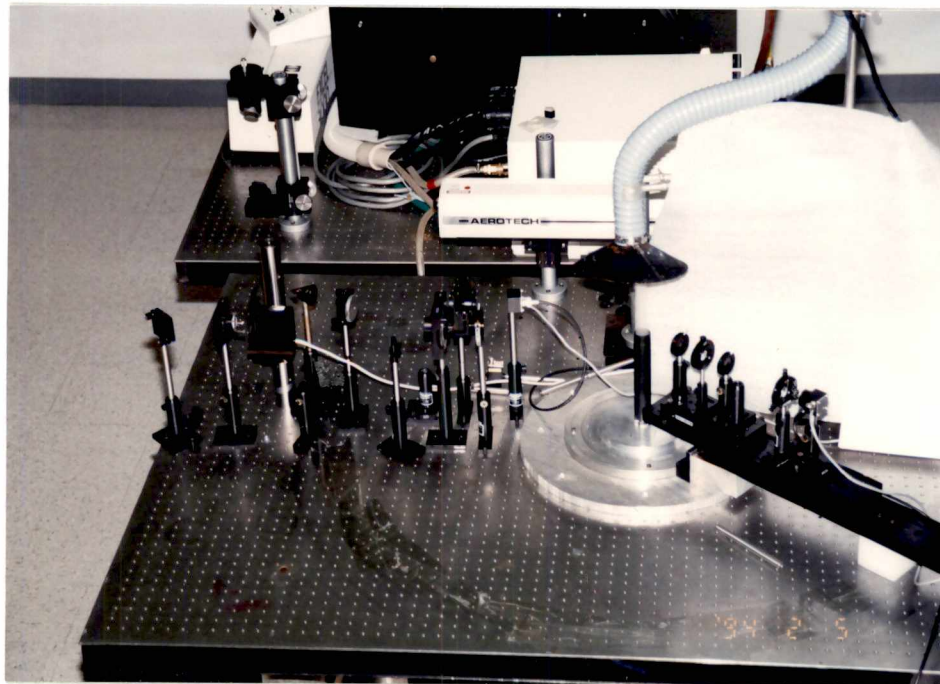
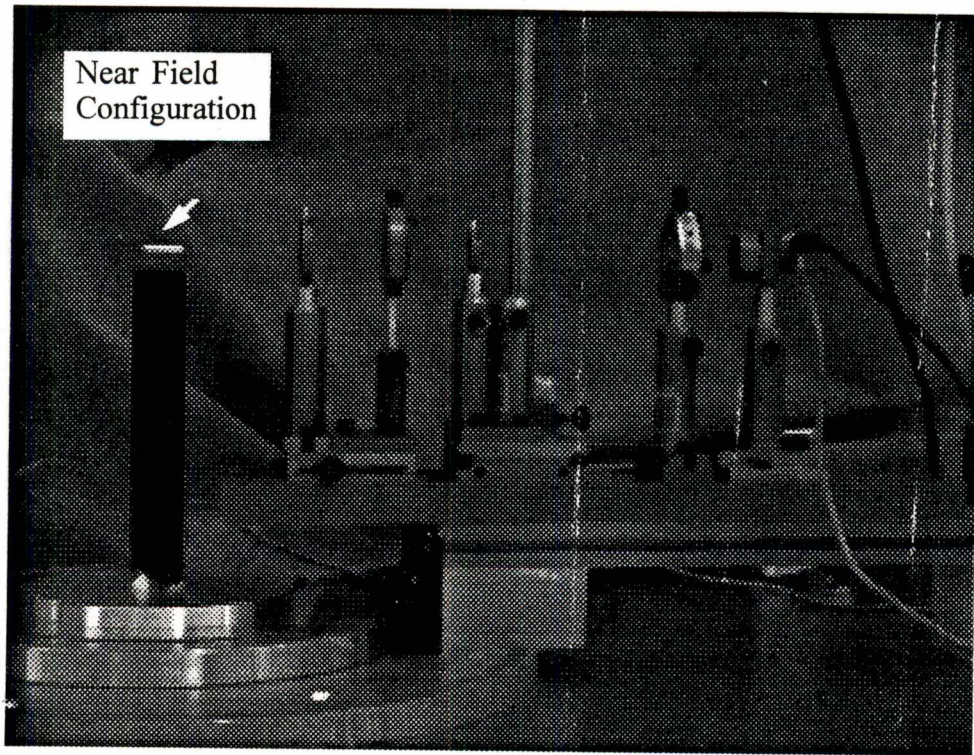


Figure 6.2.3 Photographs of the spatial filter and experiment set-up.

§ 6.3 Experimental Results and Discussions

To compare all three methods of scattering length corrections, the experiments are performed with different geometrical configurations as listed in Table (6.3.1), and the results will be detailed in the subsequent material.

In the deconvolutions of the experimental data, all three length-correction methods were utilized for each geometrical configuration and the experimental data were normalized by a data value at a specific scattering angle (80 degrees). There are three advantages of data normalization. First, one does not have to measure simultaneously the incident laser power and the scattered powers, which can differ by four- to six-orders of magnitude, and therefore the total measurement error is reduced. Second, the unknown number density N in (6.2.2) can be eliminated by the normalization procedure. In fact, once the PSDF is obtained from the deconvolution, one can calculate the number density N by using the signal at a specific angle θ_i (90° for example) by the following equation, referring to Eq(2.1.4) and (2.1.5)

$$N = \frac{I_s}{I_0 L_{(90^\circ)} \tau_p}, \quad \text{where} \quad \tau_p = \int_0^\infty C_s(r) p(r) dr. \quad (6.3.1)$$

Third, the results of the three length correction methods can be directly compared because the big differences in signals among the three experimental configurations have been canceled by the normalization. Fourth, some kinds of the systematic errors might be eliminated. For example, if the experimental data are somehow changed by a factor of ν , due either to the optical detector or the electrical amplifier, the normalization

method can eliminate this factor by using the ratios of the data in the deconvolution calculations.

Tables (6.3.2) - (6.3.4) list the deconvolution results for the PSDF parameters D and V for the three geometrical configurations and the three correction methods. The quality χ_{min} in those tables is defined by

$$\chi^2_{min} = \sum_{i=1}^n \frac{(t_i - g_{\epsilon_i})^2}{g^2_{\epsilon_i}}, \quad (6.3.2)$$

where t_i and g_{ϵ_i} are fitted data and experimental signals, respectively. The quantity ϵ in these tables is the relative error of the experiment. For any successful deconvolution, the following relation must be satisfied, according to the discussion in Chapter 2 (see, e.g., Eq(2.3.14)):

$$\chi^2_{min} \leq \epsilon^2. \quad (6.3.3)$$

Using Eq(6.3.2), the large numerical values of the small scattering-angles are eliminated which would otherwise have had too much weight during the deconvolution procedure. The errors for the particle size distribution parameters of D and V are calculated using Eq(4.1.14) and (4.1.17), respectively.

Table 6.3.1 Three geometrical configurations parameters for experiments. All lengths are in mm and all angles are in degree. The length L_0 is 27mm for all configurations.

<i>Cases</i>	r_0	a_1	a_2	d_1	d_2	α	η
<i>Near Field</i>	137.5	4.45	1.37	53	60	2.9	0.74
<i>Med. Field</i>	269.9	7.21	3.54	46	55	1.88	2.20
<i>Far Field</i>	522.3	9.11	3.20	39	54	1.11	2.35

Table 6.3.2 Results for **Near Field** configuration with $\bar{\epsilon} = 4.04 \times 10^{-2}$

Correction methods	$D(\mu m)$	$V(\mu m)$	$\bar{\chi}$	Validity
Integration	2.902 ± 0.10	1.609 ± 0.12	$2.32 \times 10^{-2} < \bar{\epsilon}$	yes
Sin θ	2.915 ± 0.12	1.605 ± 0.10	$2.32 \times 10^{-2} < \bar{\epsilon}$	yes
None	9.333	5.176	$0.285 > \bar{\epsilon}$	—

Table 6.3.3 Results for **Medium Field** configuration with $\bar{\epsilon} = 5.34 \times 10^{-2}$

Correction methods	$D(\mu m)$	$V(\mu m)$	$\bar{\chi}$	Validity
Integration	2.850 ± 0.15	1.711 ± 0.14	$5.23 \times 10^{-2} < \bar{\epsilon}$	yes
Sin θ	2.517	0.282	$0.274 > \bar{\epsilon}$	—
None	4.200	2.695	$0.127 > \bar{\epsilon}$	—

Table 6.3.4 Results for **Far Field** configuration with $\bar{\epsilon} = 1.15 \times 10^{-1}$

Correction methods	$D(\mu m)$	$V(\mu m)$	$\bar{\chi}$	Validity
Integration	2.739 ± 0.19	1.519 ± 0.21	$3.85 \times 10^{-2} < \bar{\epsilon}$	yes
Sin θ	0.608	0.663	$0.609 > \bar{\epsilon}$	—
None	2.617 ± 0.20	1.536 ± 0.24	$3.68 \times 10^{-2} < \bar{\epsilon}$	yes

From Table (6.3.2), one can see that for the Near-Field configuration, both the integration and $\sin\theta$ length correction methods (in which Eq.(6.3.3) is satisfied) give correct results that are in good agreement. The None-correction method fails because Eq(6.3.3) is violated. This result is reasonable because, in this configuration, the scattering length $L(\theta)$ viewed by the detector changes dramatically as the scattering angle θ changes; *e.g.*, $L(20^\circ) \approx 2.9 \times L(90^\circ)$. Therefore, the length correction must be considered for the Near-Field configuration. Because only part of L_0 (the total length of laser beam intercepts with the particle field) is seen by the detector, the *Sin* θ method gives the same good results as the Integration method because the smaller contribution from the far end of the scattering length l_1 is compensated by the larger contribution from the near end of l_2 ; see Fig.(6.2.1). Figure (6.3.1) plots the experimental curves with error bars and also the three fitted curves; Fig.(6.3.2) is a logarithmic version of Fig.(6.3.1) to show the details. The *sin*(θ) correction method is suggested in this configuration simply because it saves computational time. For these experimental conditions, the particle size distribution can be described by a log-normal distribution function with the mean diameter $D \approx 2.9\mu m$ and width $V \approx 1.6\mu m$, as plotted in Fig(6.3.3).

In Table (6.3.3), one can easily tell that for the Medium-Field configuration only the Integration method gives correct answers which are in approximate agreement with those of the Near-Field situation. The other two methods fail because in this configuration L is smaller than L_0 at some angles which are close to 90° (*Sin* θ method is valid) and is larger than L_0 at other angles which are far from 90° (No-correction method is valid). Therefore, only the Integration method is recommended for this configuration. By carefully measuring the angle η , one might combine the $\sin\theta$ and No-

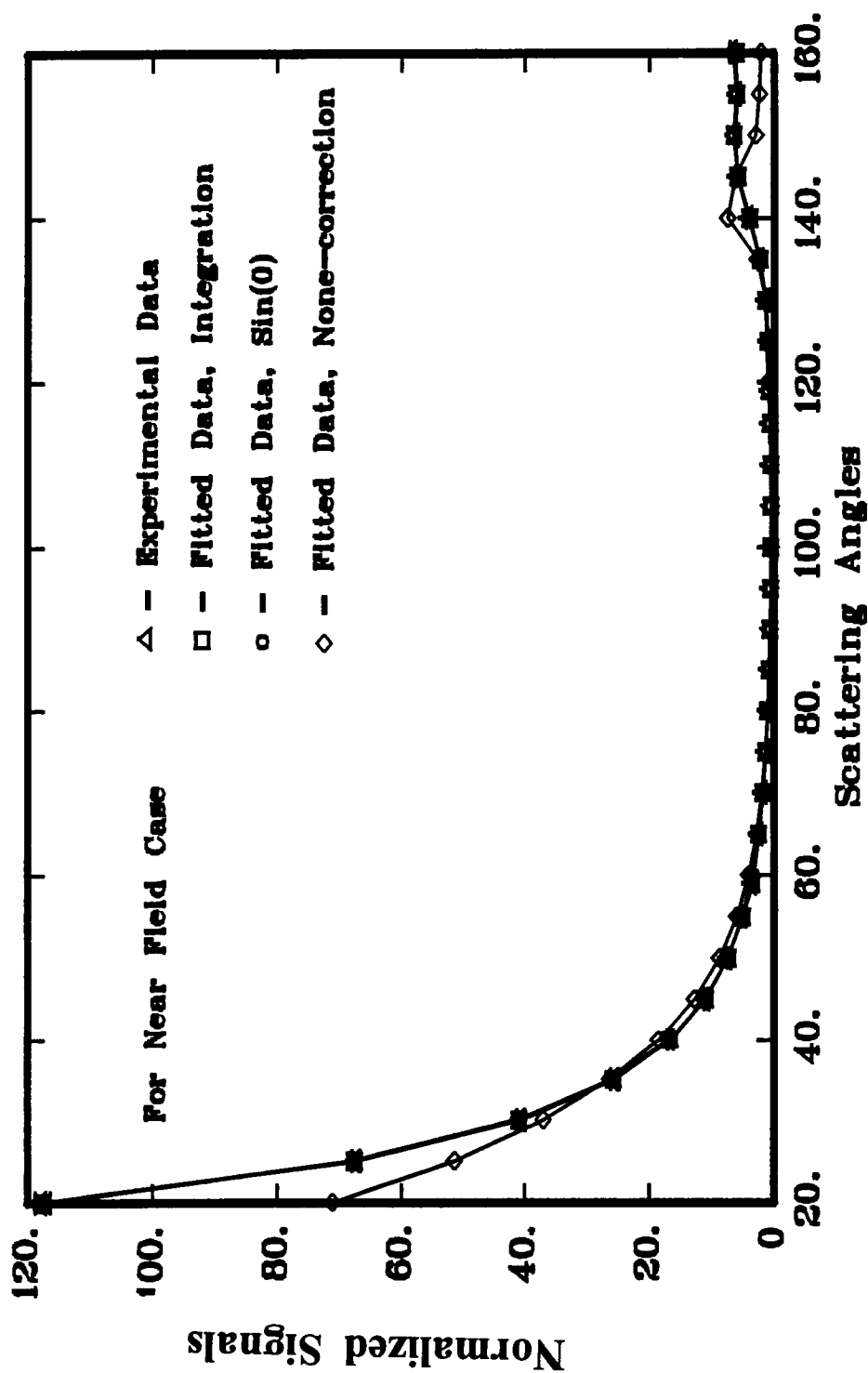


Figure 6.3.1 The Near-Field experiment data with error bars and the fitted data of three scattering length correction methods. The error bars are so small that they are hard to be seen.

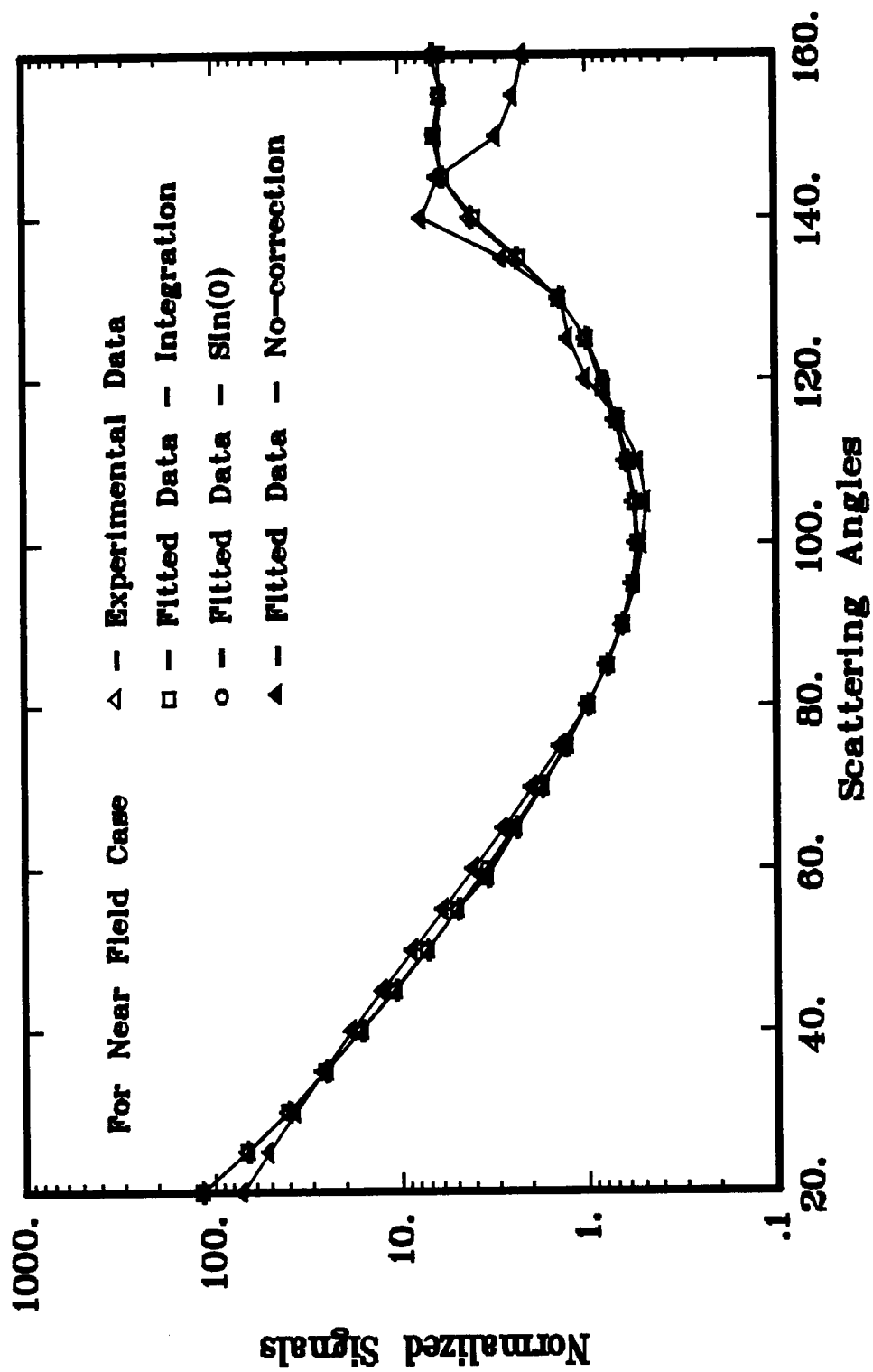


Figure 6.3.2 A log-version of Fig.(6.3.1).

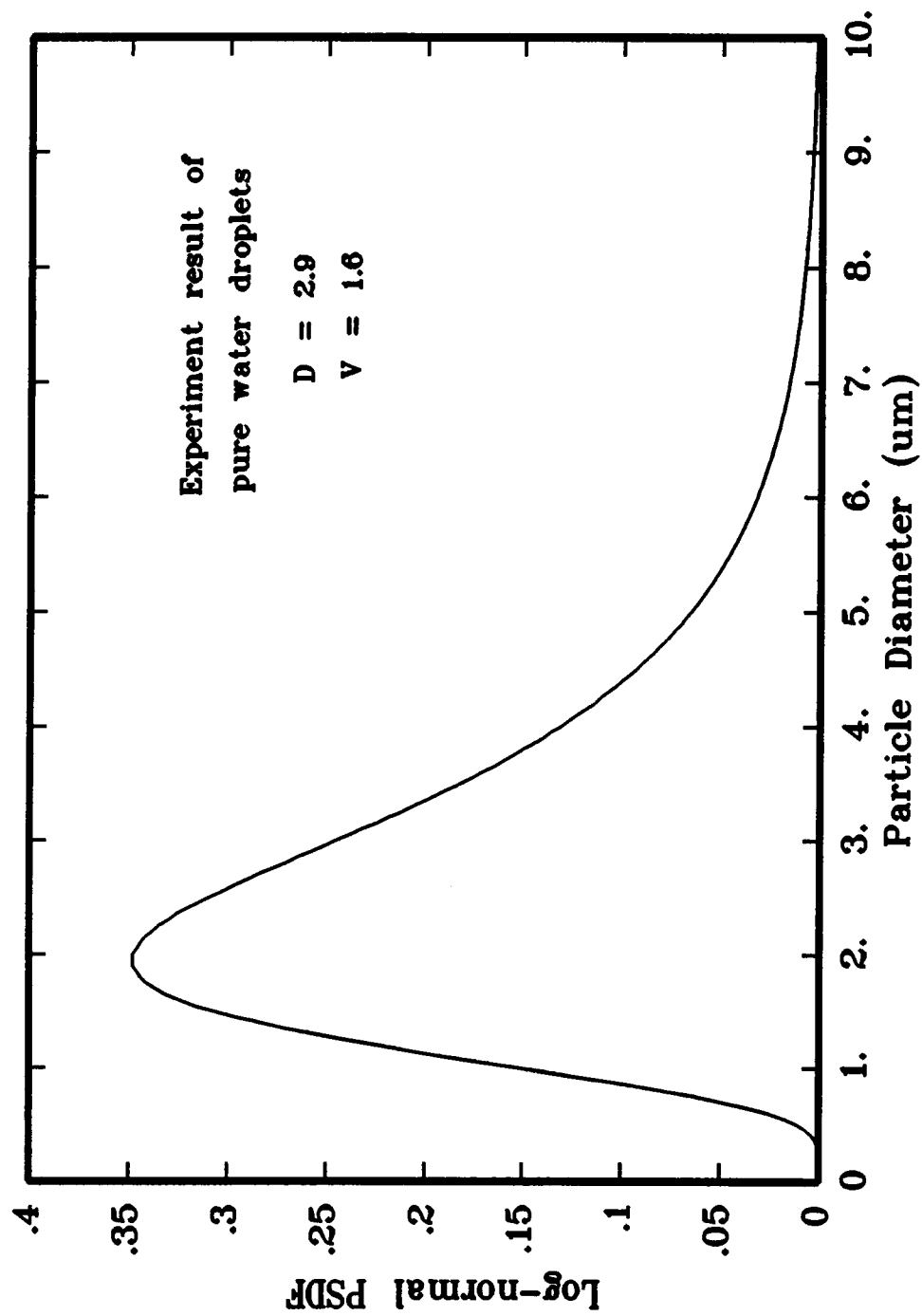


Figure 6.3.3 Particle size distribution function from pure water droplets scattering experiment ($D = 2.9\mu m$, $V = 1.6\mu m$).

correction methods in the deconvolution procedure to obtain reasonable results if the computing resources are limited. Figures (6.3.4) and (6.3.5) show the relative scattering curves.

Table (6.3.4) shows that the Integration and the None methods give good results and that the $\sin\theta$ correction fails in Far-Field configuration. In the Far-Field configuration the view angle is so big that the total length of L_0 is seen by the detector and again, the weaker signal by the far end of L_0 is more or less compensated for by the stronger signal from the near end of L_0 . Therefore, the total scattering length is the same at all angles, and the length correction has little effect. Although the Integration method is, in principle, a comparatively strict method and is valid for all configurations, it has some drawbacks. One of these drawbacks for the Integration method is that it takes much longer to do the numerical computations (about a factor of 6 to 8). The other drawback is that it relies much more on the precision of measurements of the configuration parameters as listed in Table (6.3.1). Therefore; some additional measurement errors can be introduced into the deconvolution. Perhaps this is why the χ^2_{min} of the Integration method is slightly larger than that of the $\sin\theta$ method in the Near-Field case, and that of the No-correction method in the Far-Field case. The increase in the experimental error bar $\bar{\epsilon}$ as the detector assembly is moved away from the scattering length might be caused by the increasing in fluctuations of the signals as they became weaker and weaker. Figures (6.3.6) and (6.3.7) show the corresponding results.

From the discussion above, it can be concluded that the change in scattering length must be considered in the deconvolution calculations. If possible, one should use a Near-Field configuration and use the $\sin(\theta)$ correction method, since it requires less

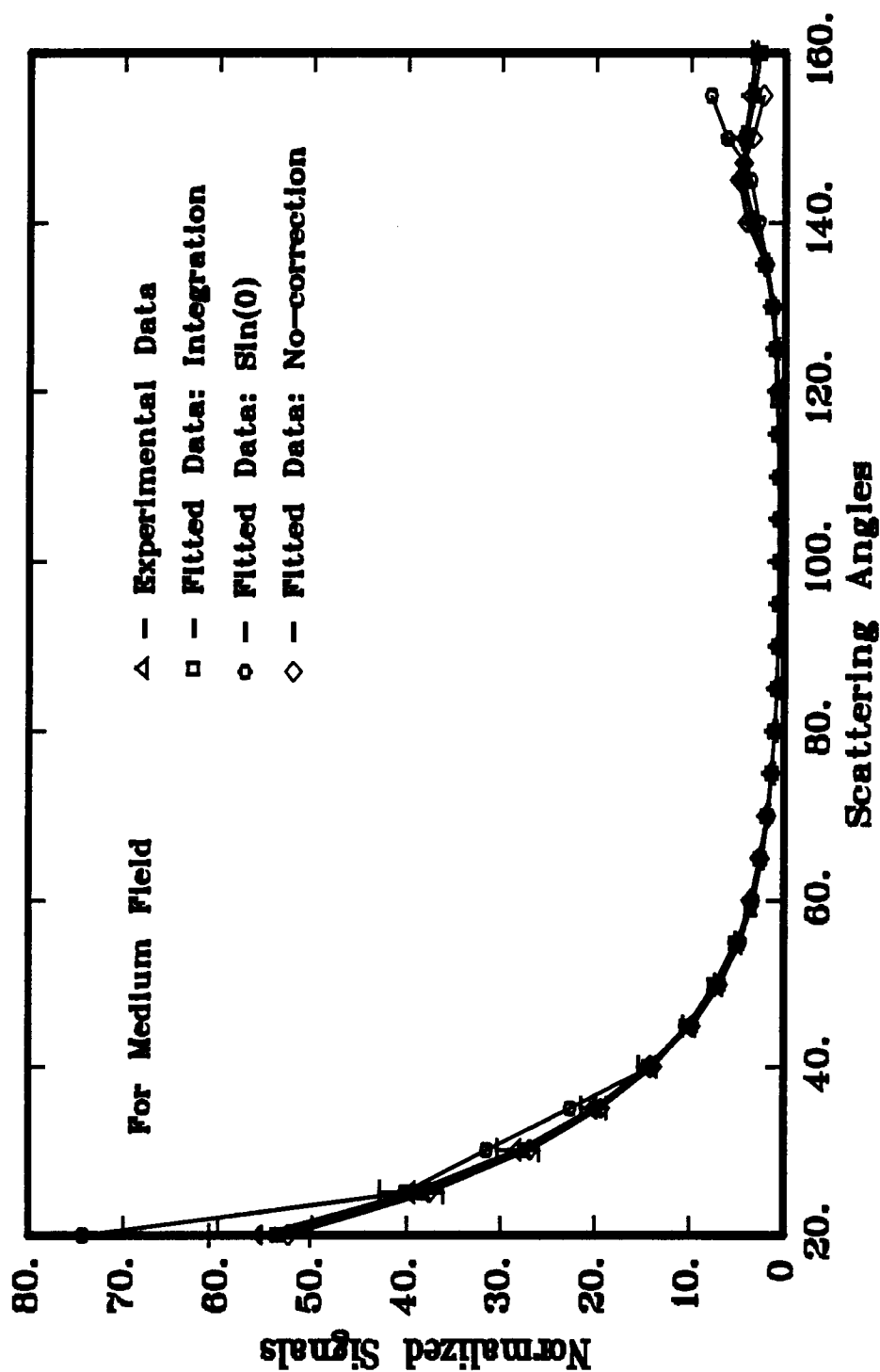


Figure 6.3.4 The Medium-Field experiment data with error bars and the fitted data of three scattering length correction methods.

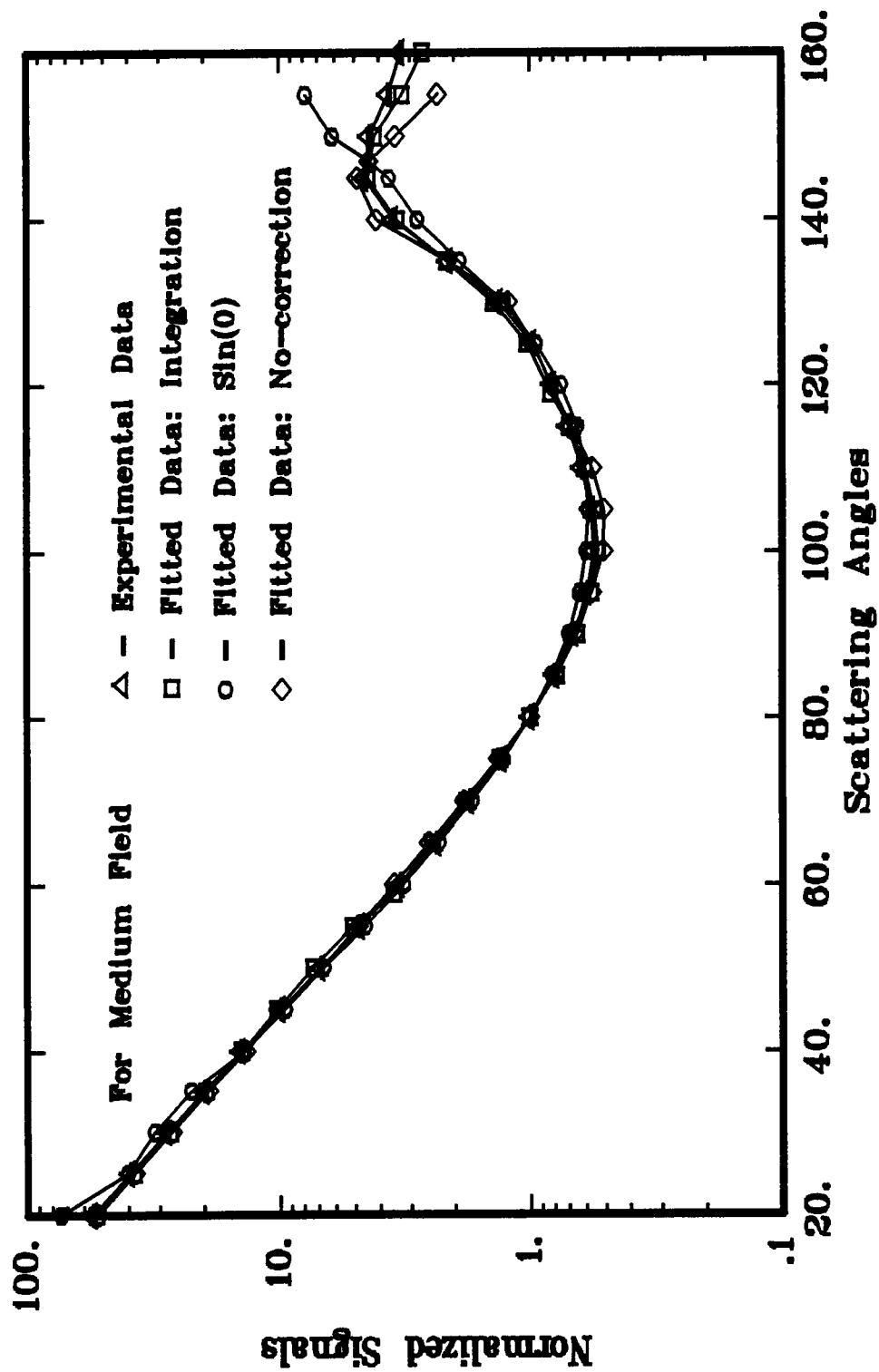


Figure 6.3.5 A log-version of Fig.(6.3.4).

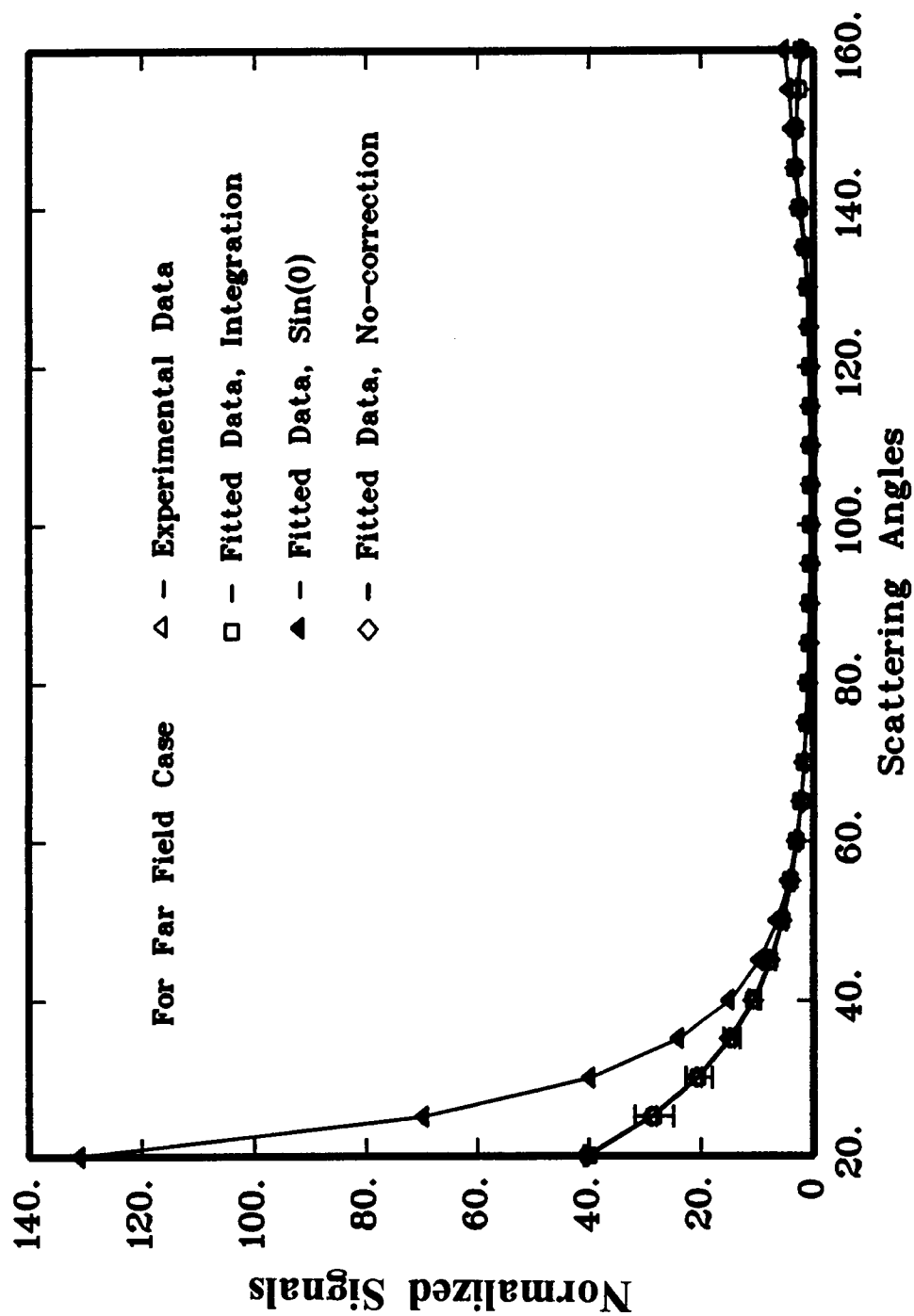


Figure 6.3.6 The Far-Field experiment data with error bars and the fitted data of three scattering-length correction methods.

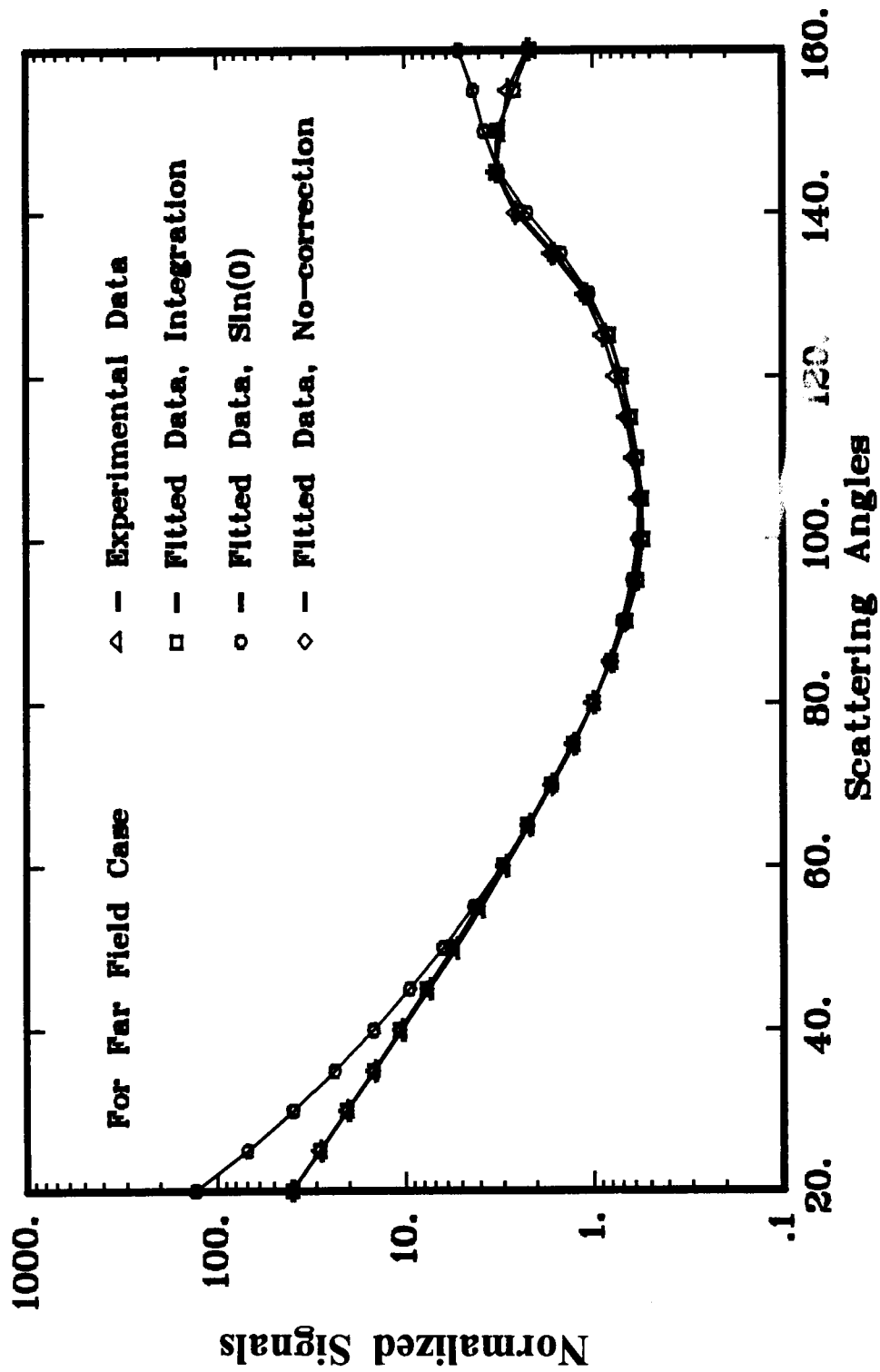
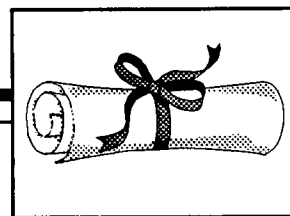


Figure 6.3.7 The log-version of Fig.(6.3.6).

computer time and is less dependent upon the configuration parameters. When the scattering signals are relative weak, the Near-Field configuration can provide a higher signal-to-noise ratio and therefore can reduce the relative measurement error.

Chapter 7



Scattering Experiments for Absorbent Droplets

In any inversion or deconvolution calculation, the real and imaginary parts of the index of refraction ($n(\lambda), k(\lambda)$) input into the program are the only parameters (or the only information) identifying the material that constitutes the scattering particles. To see the influence of the index of refraction and the types of various spherical particles on the deconvolution results and the validity of the DHS method, the index of refraction of the previously studied water particles will be systematically varied and the deconvolution will be repeated.

§ 7.1 Determination of Index of Refraction for Laser-dye Solutions

A convenient method of changing the index of refraction of water is to add laser-dye (say, rhodamine 6G) to form an absorbent solution. Because the index of refraction is wavelength dependent, it will be necessary to have the ability to predict the wavelength variation distribution of the index of refraction for any specific laser-dye concentration C which is not readily obtainable from literature.

The solvated dye molecules can form monomers, dimers or polymers in a solvent, depending on the dye concentration (moles/liter, or M), whereas for a dilute solution, monomers dominate with few dimers ($C_m < 10^{-5}$ M). For an intermediate

concentration, dimers dominate ($C_d \sim 10^{-3}$ M). Because very high concentration solutions will not be used, only monomers and dimers need to be considered.

For clarity, it is convenient to denote the real part of the complex index of refraction as the index of refraction n and the imaginary part k as the optical constant, and on occasion the wavelength dependant notation will be omitted.

The optical constant k for a unit concentration solution can be written as^[21]

$$k(\lambda) = k_m(\lambda)X + k_d(\lambda)(1 - X), \quad (7.1.1)$$

where k_m and k_d are optical constants for monomers and dimers respectively. X is the fraction of monomers in the solution which relates to the concentration C through^[22]

$$\frac{X^2}{1 - X} = \frac{D_e}{C} \quad (7.1.2)$$

where D_e is the equilibrium constant (not be confused with the mean particle diameter D in a log-normal distribution). For a known D_e , One can write X explicitly as

$$X = \frac{D_e}{2C} \left[\left(1 + \frac{4C}{D_e} \right)^{1/2} - 1 \right] \quad (7.1.3)$$

The spectra of k_m and k_d for rhodamine 6G in water can be obtained from Reference [22] and X can be calculated through (7.1.3), provided that the parameter D_e is known. Combining (7.1.1) and (7.1.2), one finds

$$D_e = \frac{(k - k_d)^2}{(k_m - k)(k_m - k_d)} C. \quad (7.1.4)$$

Equation (7.1.4) can be employed to calculate the wavelength-independent parameter D_e if a single quantity k is known at any wavelength for a specific concentration C ($C_m < C < C_d$). For a dimerized solution, $C = C_d$ and $k = k_d$, and one

has $D_e = 0$ and $X = 0$ from Eqs.(7.1.4) and (7.1.2), respectively. This means that dimers dominate. If $C = C_m$ and $k = k_m$, one finds $D_e = \infty$ and $X = 1$ which is the case of a diluted solution for which only monomers dominate. For any other concentration, Eqs.(7.1.4) and (7.1.2) can be used to obtain D_e and X , and the total spectrum of $k(\lambda)$ can be obtained through (7.1.1).

With the $k(\lambda)$ at hand, one can calculate the index of refraction $n(\lambda)$ through the *Kramers-Kronig* relations

$$\begin{cases} n(\lambda_0) = 1 + \frac{2\lambda_0^2}{\pi} P \int_0^{\infty} \frac{k(\lambda)d\lambda}{\lambda(\lambda_0^2 - \lambda^2)} \\ k(\lambda_0) = -\frac{2\lambda_0}{\pi} P \int_0^{\infty} \frac{n(\lambda) - 1}{\lambda_0^2 - \lambda^2} d\lambda, \end{cases} \quad (7.1.5)$$

where P indicates a *Cauchy* principle integration.

Actually, the *Kramers-Kronig* relations are suitable for any pair of a complex physical quantities. Equation (7.1.5) is exact provided that the whole spectrum of $k(\lambda)$ (or $n(\lambda)$) is known. Using the calculated $k(\lambda)$, one can compute $n(\lambda)$ using (7.1.5) and *visa versa*. The correctness of using (7.1.5) to calculate n from known k or *visa versa* has been verified in this work and by many authors.^[21, 23]

The spectra for k_m and k_d were taken from the curves of Reference [22] for Rhodamine 6G(Rh6G)/water solution and the accuracy is unknown because the curves were not accurately scaled. The optical constant k of pure water in visible spectral range is very small (10^{-8} - 10^{-10}). Adding Rh6G in water changes k dramatically, especially in 400 to 550 nm wavelength region, even for a very low concentration. The typical concentration for a monomer-dominated solution is $C_m = 4 \times 10^{-5} M$ and for a dimer-dominated solution is $C_d = 2.9 \times 10^{-3} M$ as described in [21]. A photograph for pure

water and laser-dye solutions of different concentrations is shown in Fig.(7.1.1). The color changes dramatically between pure water and a dimerized solution. In contrast, for such concentrations the changes in n are on the order of 10^{-3} or less and are not considered significant.

To verify the calculation method for $k(\lambda)$ using Eqs.(7.1.1) - (7.1.4), a solution of Rh6G/water with a concentration of $C = 2.9 \times 10^{-4} M$, that is, ten times dilution of the dimer concentration, was prepared. A scattering experiment using this solution was then performed using an incident laser with wavelength of $\lambda_0 = 496.5 \text{ nm}$. The corresponding optical constant $k_0 = 2.00 \times 10^{-4}$ at this wavelength was obtained by deconvolving the experimental data. The equilibrium constant $D_e = 8.93 \times 10^{-7}$ was calculated by substituting k_0 in Eq.(7.1.4) and $X = 5.40 \times 10^{-2}$ using (7.1.2). The spectrum of $k(\lambda)$ at $C = 2.9 \times 10^{-4} M$ was then calculated using (7.1.1) and plotted in a figure which will be seen in next section, together with the experimental results of five other laser wavelengths. The agreement of the calculated curve and experimental results is excellent (as will be seen), considering the unknown accuracy of the read-out spectra for $k_m(\lambda)$ and $k_d(\lambda)$ from the published curves.^[22] The details for the experiment, the data reduction, and the tabulated results are discussed in next section.

§ 7.2 Experiment Results for Absorbent Droplets

Theoretically, the DHS deconvolution method can provide the optical properties and the number density of the particulate system, in addition to the particle size distribution function parameters. To test this ability of the DHS method using the experimental data, the experiments on the absorbent water droplets were performed. The solution is the Rhodamine 6G in water as mentioned in last section, which has a peak



Figure 7.1.1 The picture of the liquids used in the experiments. From the left to right, pure water, Rh6G/water solution of $C = 2.9 \times 10^{-4} M$, and Rh6G/water solution of $C = 2.9 \times 10^{-3} M$.

profile of $k(\lambda)$ within the wavelength region of the six Argon laser wavelengths, 457.9, 476.5, 488.0, 496.5, 501.7 and 514.5 nm. The exact location of the peak of $k(\lambda)$ depends on the concentration of the solution.

The goal of this experiment is to obtain all five parameters (D , V , N , n , and k) of the particulate system by deconvolving the scattering data. Deconvolution results were desired from the scattering data for each of the six wavelengths and for different laser-dye concentrations under the same experimental conditions, and the resultant PSDF parameters (D , V) are then compared with those for pure water. Therefore, stable experimental conditions are necessary. Because many experiments need to be performed this time (for different wavelength and different dye-concentrations), the experimental conditions must be more stable than those for pure water. To solve the problem of laser power fluctuation, the laser beam was split using a beam splitter into a reference beam and an incident beam to the particle field, as shown in Fig.(6.1.1). The ratio of the incident beam intensity I_0 and the reference beam I_r basically remains unchanged with respect to the laser out put power and thus the influence of the fluctuations of laser power has almost been eliminated. For these experiments, the Near-Field configuration was used for the detector system, and the dilution air flow rate was reduced to 45 l/min.

The system was calibrated as follows. Before taking scattering data, the ratio of the intensities of the transmitted (scattering angle $\theta_i = 0$) and the reflected beams on the beam split, $R_0 = I_0/I_r$, was measured using the attenuated incident laser beam. After the particle generator (atomizer) was turned on, the experiments were performed by simultaneously measuring the scattered signal $I_s(\theta)$ and the reference beam's signal I_r' , and the ratio $R(\theta) = I_s(\theta)/I_r'$ was calculated. The final scattering data was the ratio of the $R(\theta)$ and R_0 , or

$$S(\theta) = \frac{R(\theta)}{R_0} = \frac{I_s(\theta)/I'_r}{I_0/I_r} \quad (7.2.1)$$

Using this method can basically eliminate all the effects of reflection and transmission of the optics. The scattering angle ranges from 40° to 140° degree with 5° increment. The angular ranges of 20° - 35° and 145° - 160° were excluded to reduce the errors introduced by the change of the scattering length.

The deconvolution results are listed in Tables (7.2.1) to (7.2.2) for the solutions with concentrations of $C = C_d = 2.9 \times 10^{-3} M$ and $C = C_d/10$, respectively. The deconvolution procedures are the same for the pure water case as discussed in section 6.3, except that now four parameters (D , V , n and k) are deconvolved simultaneously. With Eq(6.3.1), the number density is obtained using the scattering data acquired at the scattering angle of 90° . The quantities of $\bar{\chi}$ and $\bar{\epsilon}$ in Table (7.2.1) and (7.2.2) are the mean square roots of the deconvolution data and experiment data respectively, as defined as follows

$$\bar{\chi} = \left(\frac{\chi^2_{\min}}{n} \right)^{1/2} = \left(\frac{1}{n} \sum_{i=1}^n \frac{(t_i - g_{e_i})^2}{g_{e_i}^2} \right)^{1/2}, \quad \bar{\epsilon} = \left(\frac{1}{n} \epsilon^2 \right)^{1/2} \quad (7.2.2)$$

The errors in the size distribution parameters are calculated using Eq(4.1.14) and (4.1.17), the same way as for the non-absorbent particle system.

It can be seen from Table (7.2.1) and Table (7.2.2) that, for each concentration, the size parameters D and V are basically the same for different wavelengths, which is of being expected because the experimental condition were the same. The index of refraction of the dye solution n is almost unchanged from the pure water situation which agrees with others' results.^[21] Another result was that as the laser-dye

Table 7.2.1 Results for dimmerized Rh6G/water solution with $C = 2.9 \times 10^{-3} \text{M}$.

$\lambda(\text{nm})$	$D(\mu\text{m})$	$V(\mu\text{m})$	$N(\text{cm}^{-3})$	n	k	$\bar{\chi}$	$\bar{\epsilon}$
457.9	1.83 ± 0.04	1.25 ± 0.08	$5.86 \times 10^5 \pm 2\%$	1.340	9.93×10^{-5}	9.01×10^{-3}	1.53×10^{-2}
476.5	1.81 ± 0.09	1.25 ± 0.20	$6.84 \times 10^5 \pm 4\%$	1.338	7.34×10^{-4}	8.92×10^{-3}	3.37×10^{-2}
488.0	1.71 ± 0.02	1.14 ± 0.05	$8.34 \times 10^5 \pm 2\%$	1.336	1.68×10^{-3}	1.01×10^{-2}	9.34×10^{-3}
488.0(5D)	1.82 ± 0.02	1.09 ± 0.6	$7.61 \times 10^5 \pm 2\%$	1.337	1.59×10^{-3}	1.15×10^{-2}	9.34×10^{-3}
496.5	1.77 ± 0.04	1.09 ± 0.14	$9.08 \times 10^5 \pm 3\%$	1.339	2.09×10^{-3}	1.25×10^{-2}	2.10×10^{-2}
501.7	1.99 ± 0.07	1.12 ± 0.19	$5.74 \times 10^5 \pm 3\%$	1.344	1.25×10^{-3}	1.20×10^{-2}	2.36×10^{-2}
514.5	1.89 ± 0.03	1.06 ± 0.07	$7.08 \times 10^5 \pm 2\%$	1.341	7.73×10^{-4}	1.32×10^{-2}	9.93×10^{-3}

Table 7.2.2 Results for diluted Rh6G/water solution with $C = 2.9 \times 10^{-4} \text{M}$.

$\lambda(\text{nm})$	$D(\mu\text{m})$	$V(\mu\text{m})$	$N(\text{cm}^{-3})$	n	k	$\bar{\chi}$	$\bar{\epsilon}$
457.9	2.31 ± 0.04	1.61 ± 0.07	$2.84 \times 10^5 \pm 3\%$	1.340	2.82×10^{-5}	1.01×10^{-2}	1.65×10^{-2}
476.5	2.57 ± 0.04	1.62 ± 0.07	$2.48 \times 10^5 \pm 2\%$	1.330	4.75×10^{-5}	1.10×10^{-2}	1.43×10^{-2}
488.0	2.40 ± 0.02	1.54 ± 0.04	$2.55 \times 10^5 \pm 2\%$	1.336	1.37×10^{-4}	1.40×10^{-2}	1.09×10^{-2}
488.0(5D)	2.43 ± 0.02	1.41 ± 0.05	$2.59 \times 10^5 \pm 2\%$	1.336	1.25×10^{-4}	1.94×10^{-2}	1.09×10^{-2}
496.5	2.51 ± 0.03	1.64 ± 0.06	$2.50 \times 10^5 \pm 3\%$	1.336	2.00×10^{-4}	1.03×10^{-2}	1.60×10^{-2}
501.7	2.34 ± 0.06	1.62 ± 0.10	$3.05 \times 10^5 \pm 4\%$	1.338	1.61×10^{-4}	1.59×10^{-2}	2.16×10^{-2}
514.5	2.22 ± 0.03	1.50 ± 0.05	$3.76 \times 10^5 \pm 2\%$	1.336	8.71×10^{-5}	1.15×10^{-2}	1.16×10^{-2}

concentration increases, the mean size of the droplets decreases. This is because the surface tension of the solution has been reduced as the concentration increases resulting an decrease in the particle size, and a detailed discussion and investigation will be presented subsequently.

The fact that the k values decrease for all wavelengths as the laser-dye concentration decreases can also been seen from the tables and is to be expected according to Eq.(7.1.1). The differences in particle size parameters for different wavelengths for each concentration probably resulted from time-dependent drift of the flow field. The results exhibited good repeatability.

In the center of each table, denoted as (5D), are listed the results for a 5-dimensional deconvolution (of the parameters of D , V , N , n and k) at the wavelength of 488.0 nm . The similar results of 4- and 5-dimensional deconvolutions lead credibility to the ratio method for eliminating the number density N .

Shown in Fig.(7.2.1) is the dimer optical constant $k_d(\lambda_i)$, $i = 1, 2, \dots, 6$, of the deconvolution results which is to be compared with the curve taken from Ref.[21]. The agreement is excellent considering potential inaccuracies in reading the published curve.

For the absorbent droplet data obtained with a dye concentration of $2.9 \times 10^{-4}M$, the optical constant obtained from the deconvolution is shown in Fig.(7.2.2) as a function of the wavelength. Also shown in Fig.(7.2.2) is the optical constant calculated using the method described in Section 7.1. The agreement of the two methods is good, except for the point at the wavelength 514.5 nm , since the deconvolution result is approximately one-tenth of that for the solution of concentration $C = 2.9 \times 10^{-3}M$, as it is expected to be.

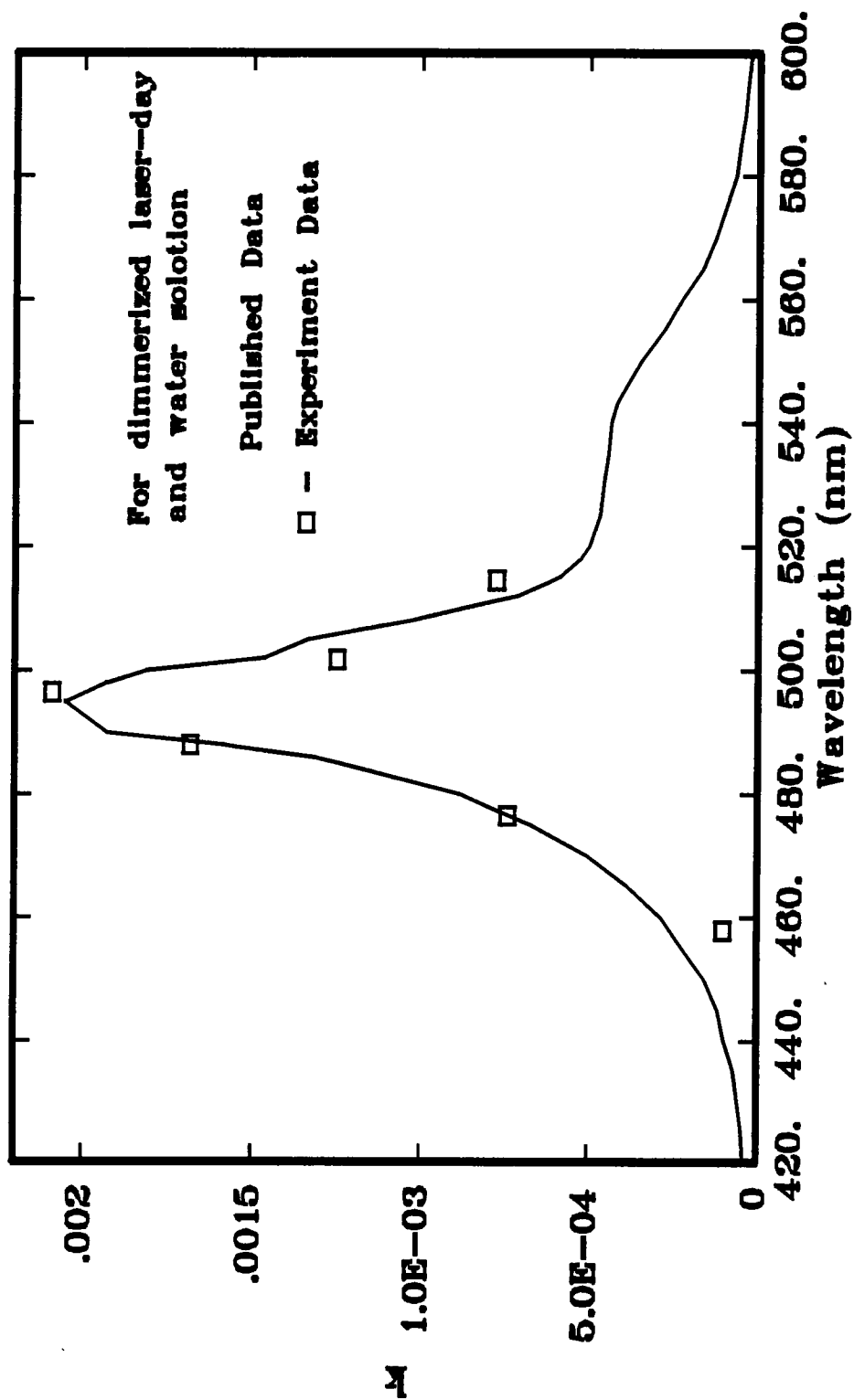


Figure 7.2.1 The comparison of $k(\lambda)$ for the published curve and experiment data. The particles are laser-dye/water droplets of concentration $C_d = 2.9 \times 10^{-3}$ mole/liter.

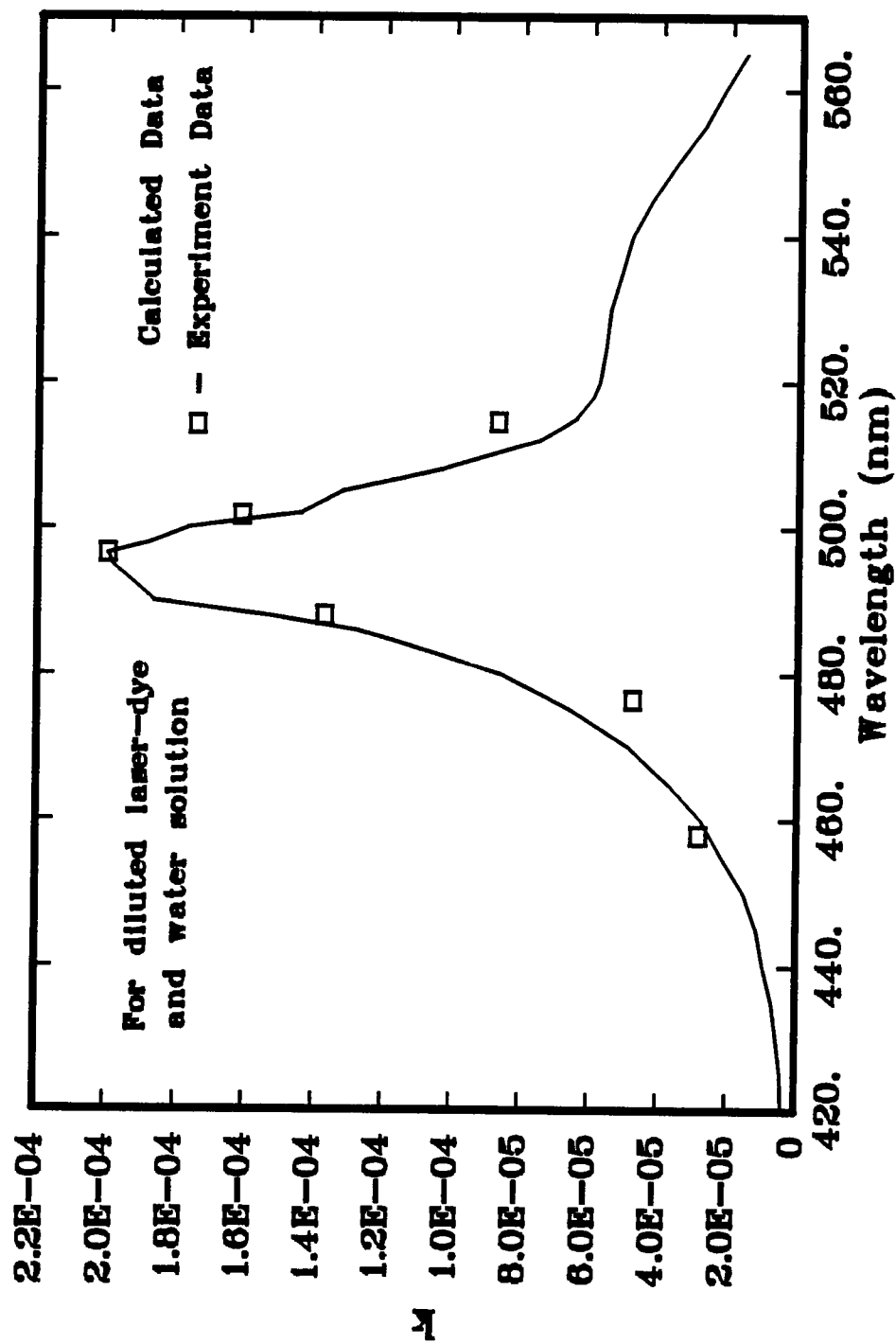


Figure 7.2.2 The comparison of $k(\lambda)$ of calculated curve and experiment data. The Particles are laser-dye/water droplets with concentration $C = 2.9 \times 10^{-4}$ mole/liter.

§ 7.3 Particle Size versus Laser-dye Concentration

The deconvolution results for the mean particle diameter, as shown in Table (7.2.1 - 2), indicate a systematic variation with the dye concentration. Since the addition of dye to the water droplet can be expected to alter certain physical properties of the droplet, such as surface tension, the behavior of the atomizer was investigated. Little, if any, information was provided by the atomizer vendor. As a result, use was made of the results of Ref. [24] who reported that the mean particles diameter produced by atomizers of the type employed for this work satisfy

$$D(\mu m) = \frac{585}{v} \left(\frac{\sigma}{\rho} \right)^{1/2} + 597 \left(\frac{\mu}{(\sigma \rho)^{1/2}} \right)^{0.45} \left(1000 \times \frac{Q_d}{Q_L} \right)^{1.5} \quad (7.3.1)$$

where σ (dyne/cm) is the surface tension, v (m/s) is the air speed, μ (dyne/cm²) is the viscosity, ρ (g/cm³) is the liquid density, and Q_d/Q_L is the ratio of the air flow rate with respect to liquid flow rate.

For $Q_d/Q_L \geq 5000$, the first term dominates and Eq.(7.3.1) becomes

$$D(\mu m) = \frac{585}{v} \left(\frac{\sigma}{\rho} \right)^{1/2}, \quad (7.3.2)$$

Since, for this work, $Q_d/Q_L > 6 \times 10^5$ and the density change of the liquid resulting from the mixture is insignificant, it is seen that the ratio of the mean diameter of dye-mixture particles and the mean diameter pure-water particles is

$$\frac{D_d}{D_w} = \left(\frac{\sigma_d}{\sigma_w} \right)^{1/2} \quad (7.3.3)$$

where σ_d and σ_w are the surface tensions of the dye-mixture and water, respectively. Because all the experiments were performed at the room temperature (about 300°K),

the effect of the fluctuation in temperature on the surface tension of the liquid can be neglected.^[25]

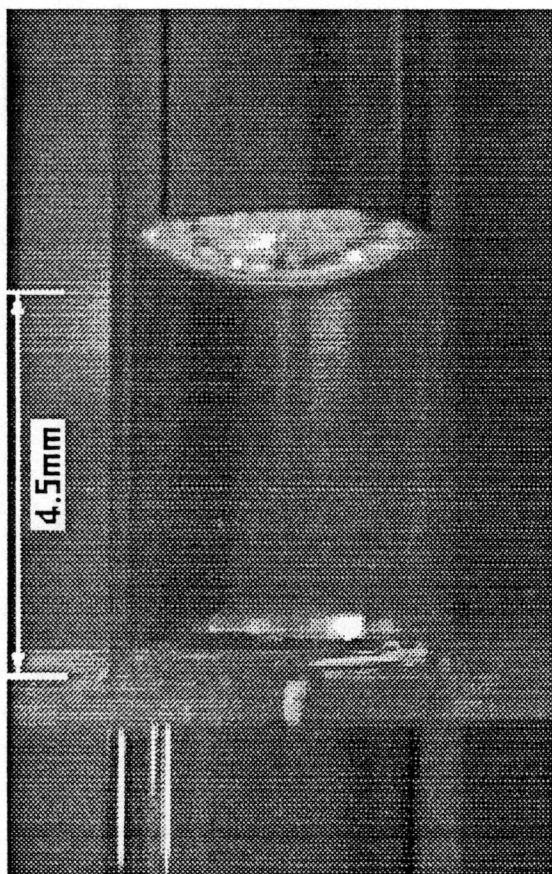
No data were found that provided σ for arbitrary dye-water mixtures, so the surface tensions σ of the dye-mixture was measured. To accomplish this, use was made of the relation between σ and the height h of the meniscus of the liquid in a capillary tube^[25]

$$\sigma = \frac{gb(D_1 - D_2)}{2\cos\theta} h, \quad (7.3.4)$$

where g is the acceleration of gravity, b is the interior radius of the capillary tube, D_1 is the density of the liquid, D_2 is the density of air, and θ is the contact angle of the liquid surface with respect to the wall of the capillary tube. The contact angle will be taken as zero, since it is only with a zero contact angle that accurate results can be obtained by the capillary tube method of measuring surface tension.^[25]

Further, only the systematic variation with dye concentrations of the DHS experimental results for the mean droplet diameter was of interest. Therefore, it was decided that the ratio of σ_d and σ_w would be determined to compare with the D_d/D_w ratio. To accomplish this, the heights were measured of water and the water-dye mixture inside a capillary tube of known uniform diameter. This was done using a CCD camera and an enlarged image on the computer terminal's screen, as shown in Fig.(7.3.1). A calibration was performed to relate the height of the liquid surface to the CCD pixel number. It was found that only for the dye mixture of $C = 2.9 \times 10^{-3} M$ was the difference in height sufficiently large relative to water to yield sufficiently precise data for the desired computation. Using these results and Eq.(7.3.2), the ratio D_d/D_w was determined and are shown in Table (7.3.1). Scattering measurements and DHS

Water



Rhodamine 6G

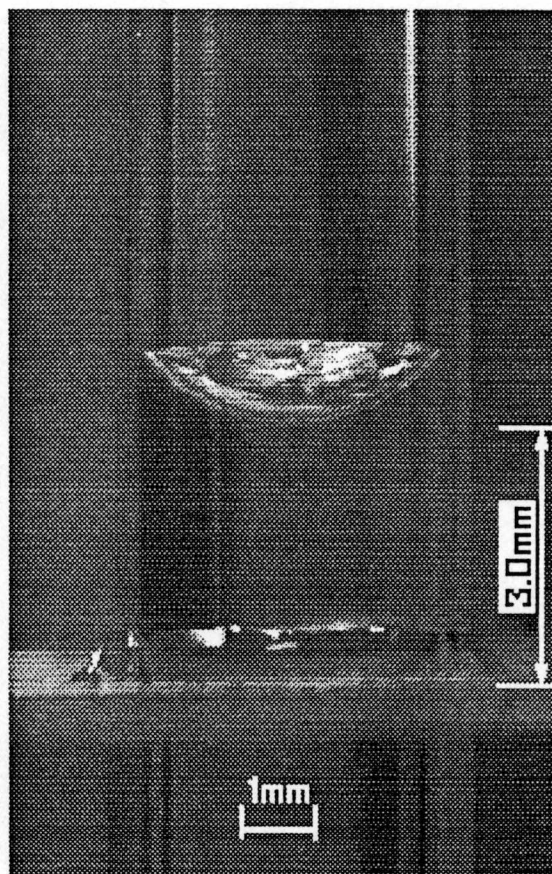


Figure 7.3.1 The picture for the liquid level heights in the capillary tubes for the surface tension measurement.

deconvolution were performed for this case (using the same dye-mixture and water as capillary height measurement) and the results are also shown in Table (7.3.1). The agreement is excellent. It is concluded that the systematic variation in D with dye concentration is due to the variation of surface tension σ of the liquids.

Table (7.3.1) The mean size ratio from the two experiments.

From scattering measurements.	From surface tension measurements
0.80 ± 0.04	0.79 ± 0.06

The last topic to be discussed is the information content of the experimental data. Because of the similarity of the experimental measurements for different wavelengths, only one case was examined, viz., the data of $\lambda = 476.5nm$ and $C = 2.4 \times 10^{-3} M$.

Using the method introduced in Section 5.2, the eigenvalues of the normalized covariance matrix C were calculated and listed in Table (7.3.2) in decreasing order. According to Eq.(5.2.22) or (5.2.30), the cut-off for the eigenvalue is equal to $10\bar{\epsilon}^2 = 1.14 \times 10^{-2}$ with the quantity $\bar{\epsilon} = 3.37 \times 10^{-2}$ found from Table (7.2.1). This cut-off has included a factor of 10 to ensure the condition is sufficiently strict for a general case. Even for this cut-off, one can see from Table (7.3.2) that among the 21 eigenvalues, only two are below the cut-off indicated approximately by a small arrow. This means the measurement basically contains no redundant data. Therefore all the data in this measurement can be used for deconvolution and the results should be stable. Carefully examining the distribution of the eigenvalues, three features are noted:

- (1) the first eigenvalue is more than ten times larger than the second and,

- (2) from the second eigenvalue, the values are almost uniformly decreasing, and
 (3) a relatively big decrease in value appears between the 19th 20th eigenvalues,
 which is just the cut-off location.

Table 7.3.2 The 21 eigenvalues of the normalized covariance matrix for the scattering case of wavelength $476.5nm$ and $C = 2.9 \times 10^{-3} M$. The cut-off eigenvalue is 1.14×10^{-2} .

15.75	1.475	1.005	.7367	.4683	.3538	.2702
.2034	.1903	.1417	9.581×10^{-2}	7.2793×10^{-2}	5.9230×10^{-2}	4.2372×10^{-2}
3.1987×10^{-2}	2.6060×10^{-2}	2.2091×10^{-2}	1.4382×10^{-2}	1.3427×10^{-2}	$\uparrow 9.6236 \times 10^{-3}$	2.8944×10^{-3}

According to the information analysis knowledge described in Chapter 5, feature (1) is due to the inter-dependence of the scattering kernels, as discussed in Chapter 5 and by others.^[10,12] Using Twomey's estimation method Eq.(5.2.6), the first measurement contains 75% information of the whole experiment! The rest of the measurements contribute uniformly no more than 25% information. Feature (2) reflects the suitability of the cut-off calculation of Eq.(5.2.20), which really measures the inter-dependency of the measurement. Should one use Eq.(5.2.22) for the cut-off, one would get $10n\bar{\epsilon}^2 = .239$ (n is the number of scattering angle) and only 6 measurements are independent according to Table (7.3.2). This is the reason that the condition for cut-off Eq.(5.2.22) is considered to be too strict. Feature (3) implies the suitability of the information-content analysis method adopted in this work.

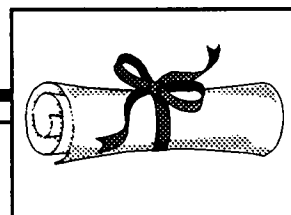
If one is not satisfied with the existence of the two eigenvalues which are below the cut-off, one can delete two scattering angles, using the deleting method suggested by Twomey. These angles are, according to the order of deletion, 100° and 105° . The

new normalized covariance matrix after the deletion has the eigenvalues listed in Table (7.3.3), with the minimum value above the prescribed cut-off.

Table 7.3.3 The 19 eigenvalues of the normalized covariance matrix after the deletion for the scattering case of wavelength $476.5nm$ and $C = 2.9 \times 10^{-3} M$. The last one is larger than the cut-off eigenvalue 1.14×10^{-2} .

14.24	1.399	.9215	.6705	.4025	.3064	.2188
.1968	.1694	.1228	8.0280×10^{-2}	7.2006×10^{-2}	5.0917×10^{-2}	4.2007×10^{-2}
3.1069×10^{-2}	2.4902×10^{-2}	2.0923×10^{-2}	1.3870×10^{-2}	1.2271×10^{-2}	↑	

Chapter 8



Summary and Conclusions

In the final part of this dissertation, the major achievements are summarized, the conclusions and important relations are provided and the possible future studies for the retrieval of the PSDF from optical measurements are noted.

Summary:

The use of downhill simplex (DHS) curve-fitting technique for the deconvolutions of the particle size distribution function of optical scattering and extinction data is introduced and discussed in this dissertation. As expected, this technique does perform a vector-optimized least-square search. The results for the simulated data have been tested according to Eq.(2.3.14a) and other parameters (such as β , β' , R_D , and R_V), and the agreements of the theoretical predictions and the simulation calculations are excellent. The solution for experimental data for which the exact data is not available may be justified according to (2.3.14b). The equations and relations for assessing the deconvolution results and the particle-size parameters have been derived and tested. The *dual covariance matrix* $\mathbf{B}$ has been revealed for the first time and is used to estimate the stability of the DHS deconvolution method. The stability of this method has been compared with the Linear Inversion method. The availability of this method and, further, the predictions of the DHS method were verified using Monte Carlo simulation.

The reliability analysis yields the relations of the widths of the size parameters and the measurement errors which are also confirmed valid by simulation results. The restrictions on the log-normal PSDF for a successful deconvolution have been discussed and the same method can be applied to other functional forms for PSDF. The two opposite extreme limits on the width of log-normal PSDF have been examined and the simplified equations in calculating the widths of parameters are given. The predictions on the valley zone of $\chi^2(D, V)$ have been verified by the deconvolution of the simulated data.

The information analysis of linear functional space theory provides an important method in designing the experiment approach and deconvolution strategies. Combining the works by Twomey and Ben-David, *et. al*, the relation which can be used in deciding the information content of an experiment plan has been re-derived and the related quantities have been explicitly defined. The validity of the information-content relation and the definitions were verified by the simulated and experiment results. The physical significance of the covariance matrices **B** and **C** is discussed at the end of the information analysis.

To verify the predictions of the previous chapters, experiments were performed on pure and laser dye-doped water droplets. The problem of the variation with observation angle of the scattering length (volume) was carefully discussed and the Dimension Integration method was introduced which is applicable to any one-dimensional scattering system. Each of the scattering-length correction methods was tested against three experimental configurations (near, medium and far field). The results showed that the Dimension Integration method is suitable for all the configurations but has a drawback of requiring large computational times. The

conditions for other two methods have also been discussed. The design of a space filter used in the experiments was proved to be effective.

In preparing for the experiments for absorbent particle system, a method of calculating the spectrum of the optical constant $k(\lambda)$ was revealed in this dissertation for a dye-doped solution with any concentration provided the concentration is not too high. This method is tested to be valid with the subsequent experiment results. To test the ability of the DHS deconvolution method for providing, in addition to the size parameters, the droplet number density N , the index of refraction n and the optical constant k , experiments were performed using absorbing water droplets. The results showed good agreement both for the particle size parameters for the experiments of different wavelengths and the optical constant values with respect to the published and predicted curves. This robust, multi-parameter capability makes the DHS deconvolution method useful for a broad range of applications.

The experimental results also revealed that the existence of laser-dye in water can reduce the size of particles, depending the laser-dye concentration. Further, this work demonstrated the interdependency of the scattering kernels and the predicted relations of the information content analysis.

Conclusions:

The major achievements for the DHS deconvolution method introduced in this dissertation are:

- (1) The method is good for retrieving the PSDF from optical measurements and the quality of the results can be assessed by the relations of $\chi^2 < \epsilon^2$ and $|\Delta f|^2 < \epsilon^2$.

- (2) The method is reliable, and the uncertainties in PSDF parameters D and V can be estimated by $(\Delta D)^2 \leq \epsilon^2/P_D^2$ and $(\Delta V)^2 \leq \epsilon^2/P_V^2$.
- (3) By requiring $\Delta D/D$ (or $\Delta V/V$) smaller than 20%, the method can tolerate random error level up to $\pm 25\%$ and $\pm 6\%$ for water droplets with a mean diameter of $1.0\mu m$ for scattering and extinction situations, respectively. The values for the smaller soot particles with mean diameter of $0.05\mu m$ are $\pm 10\%$ and $\pm 6\%$, respectively.
- (4) The information content of the scattering measurements can be expressed by $\lambda_{min} \geq 10\bar{\epsilon}^2$, which was verified by the deconvolution results of the experiment data.
- (5) The angular variation of the effective scattering volume must be considered, and the dimension-integration correction method developed in this work was satisfactory for all three configurations of one-dimensional optical scattering problems.
- (6) The optical constant $k(\lambda)$ of laser-dye/water solution calculated using Eqs.(7.1.1) - (7.1.4) and were in agreement with the experiment and the index of refraction $n(\lambda)$ can be obtained using the *Kramers-Kronig* relations.
- (7) The experimental results demonstrated the consistency and validity of the DHS deconvolutions for 2-, 4- and 5-parameters. The PSDF parameters depend on the experimental conditions, e.g., flow rate of the dilution air.
 - (a) $D \approx 2.9\mu m$ and $V \approx 1.6\mu m$, for pure water droplets (flow rate 48 lit/min).
 - (b) $D \approx 1.8\mu m$, $V \approx 1.1\mu m$, for dye solution of concentration $C = 2.9 \times 10^{-4}$ lit/min, dilution air flow rate 45 lit/min.
 - (c) $D \approx 2.4\mu m$ and $V \approx 1.5\mu m$, for dye/water solution of concentration $C = 2.9 \times 10^{-3}$ M, dilution air flow rate 45 lit/min.

- (8) The decrease in the mean diameter of the particles as the increase of the laser-dye concentration is caused by the decrease in the surface tension of the solutions.
- (9) The DHS method developed in this work can be applied to other similar data reduction problems.

Future Studies Recommended:

- (1) The calculations for the Mie kernels needs to be further modified for specific needs. The computing speed of the kernels should be improved to enable the practical use of personal computers to perform in situ, real-time analysis of the results.
- (2) The information content analysis should be further investigated to maximize the usefulness of the experimental data. The calculations of this work show that merely deleting some of the data, which are deemed redundant, does not improve the results significantly. In other words, it is necessary to develop a numerical scheme not only to specify which measurements are redundant but also to form these data by linearly combining those "significant" data to get a better data set for the deconvolution calculation.
- (3) Because most solid particles are not spherical, this method should be generalized to include non-spherical particles!^[26]

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Appendix
Test of Gaussian Integration Algorithm

Test of Gaussian Integration Algorithm

The test of the Gaussian quadrature integration method was performed using the test function $F(x)$ introduced in Chapter 3, with the parameters of $\alpha = 0.1$, $\beta = 50$ and $\gamma = 0.5$. The PSDF $p(x)$ is a log-normal distribution with $D = 3.0$, $V = 1.5$. The integration being tested is

$$I = \int F(x)p(x)dx = \sum_{i=1}^{k_{max}} F(x_i)p(x_i)w(x_i) \quad (A.1)$$

where the PSDF $p(x)$ is defined in Eq.(2.1.10), k_{max} is the number summation terms and w is the weight. The analytical result I_0 for the integration was obtained through Eq.(3.2.10) and has been included in Table (A.1). Figure (A.1) plots the profile of the integrand of Eq.(A.1).

Table (A.1) listed the test results for different number of summation terms in which the errors are the absolute value of the relative errors between I_0 and I .

Table A.1 The test results for Gaussian integration method comparing to $D_0=3.0$, $V_0=1.5$ and $I_0 = 1.10497$.

k_{max}	D	V	I	error
30	2.99879	1.49484	1.26519	0.45
50	2.99851	1.49392	1.14105	3.26×10^{-2}
100	2.99823	1.49304	1.10482	1.40×10^{-4}

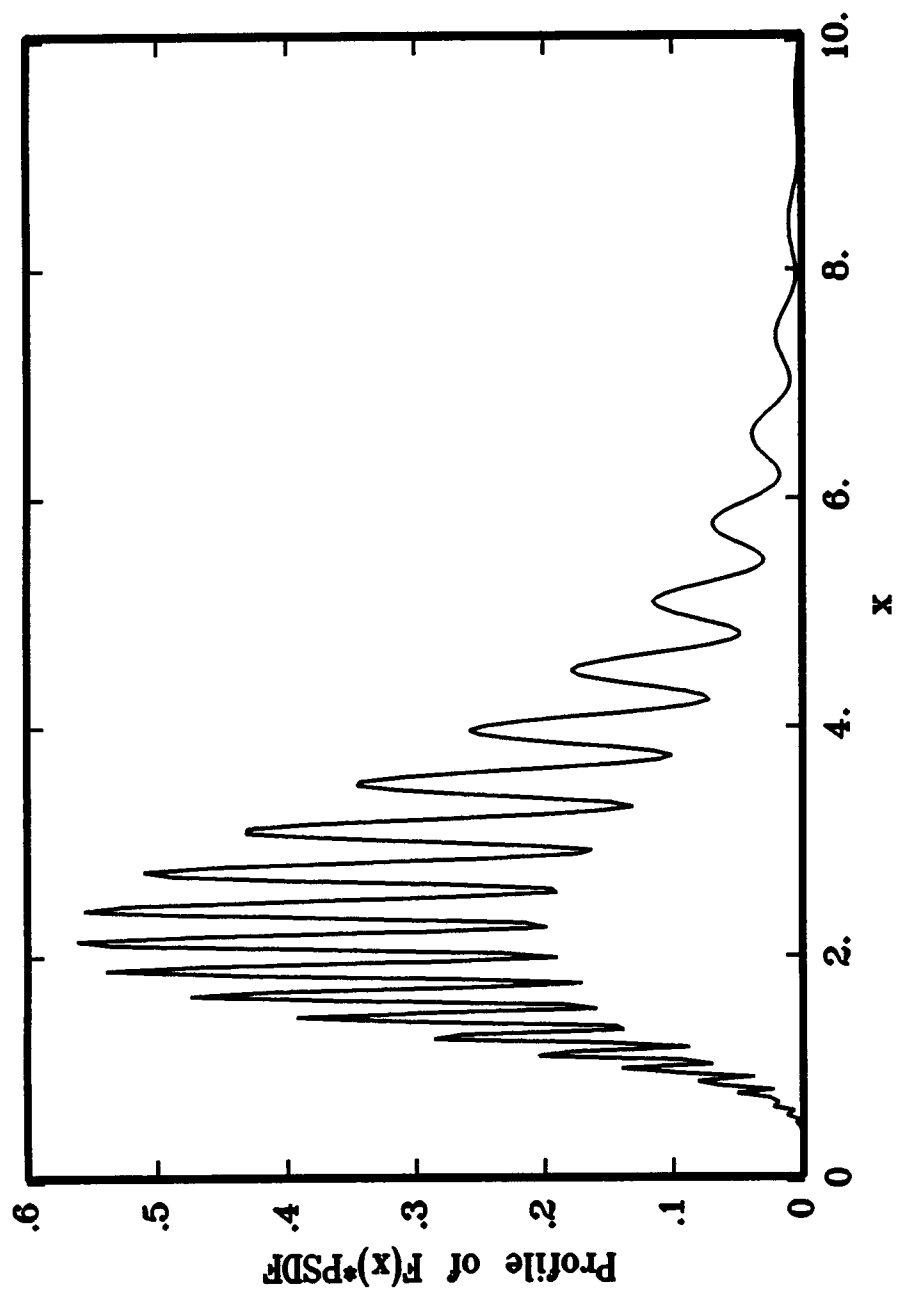


Figure A.1 The profile of the function $F(x) \times PSDF$, with $\alpha = 0.1$, $\beta = 50$ and $\gamma = 0.5$.

VITA

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