PARTICLE SIZE MEASUREMENT FOR
THE CONTROL OF INDUSTRIAL CRYSTALLIZERS
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THE CONTROL OF INDUSTRIAL CRYSTALLIZERS

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
on gezag van de Rector Magnificus,
prof.drs.P.A.Schenck,
in het openbaar te verdedigen
ten overstaan van een commissie
aangewezen door het College van Dekanen
op donderdag 3 september 1992 te 16.00 uur

door

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scheikundig ingenieur,

geboren te Rheden

Delft University Press / 1992
Dit proefschrift is goedgekeurd door de promotor

Prof. B. Scarlett M.Sc.

Cover Illustration:

Bocca della Verità ('The Mouth of Truth' in Rome, Italy)
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CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Boxman, Arthur

Particle size measurement for the control of industrial crystallizers / Arthur Boxman. - Delft : Delft University Press. - 111.
Thesis Delft University of Technology. - With ref. - With summary in Dutch
ISBN 90-6275-790-1
NUGI 841
Subject heading: crystals, measuring technique
A mia cara Chica
ACKNOWLEDGMENTS

The past years in Delft have been an exciting experience. This I believe was due to a good blend of the two essential ingredients: an interesting research topic and a fine group of co-workers. Here I would like to take the opportunity to thank some of those people particularly. First, Prof. Brian Scarlett, who convinced me to do a Ph.D. in particle technology. I will not forget his lessons in old-fashioned diplomacy which, so I was told, could make life so much simpler. The following members of the legendary UNIAK team: Johan Jager, Sjoerd de Wolf, Herman Kramer, Hans Gerla, Camiel Heffels, Ruari O’Meadhra, Folkert Bloembergen, Binnert Prins, Erik-Jan Bartels and Miriam Korstanje, but especially Rob Eek, for his friendship and time to teach me the basics of crystallizer control. Thanks! Henk Merkus for the discussions in which he was able to pinpoint the pitfalls of the results and theories. Loes Schouten for her enthusiastic support. Norman Mackay who started unraveling the Malvern black box and began the design of what later became the ROMA program. Arno (’Ciao!’) Hakem who demonstrated his talents by building ROMA (not in one day…) and giving it its final form. The project and I owe much of the very nice data to him. He and the PASTI group probably taught me most of what I know today about computers and programming. Particularly, I’m grateful to Michiel Spoer, for his time and patience. Thanks also to Reg Davies for allowing me the extra time to finish up the writing of this thesis. But most of all I’m indebted to Peter Verheijen. Without his insight, perseverance (WP thesaurus!) and help, this thesis would not have been here today. Peter, I will miss the late night pizzas, but also your stimulating questions and cooperation. Finally I would like to express my gratitude to the Dutch Foundation of Technology (STW), AKZO, DOW Chemicals, DSM, E.I. Dupont de Nemours, Eastman Chemical Company and ICI for their financial support of the UNIAK research program.

July 20 1992,
Newark, DE USA
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SUMMARY

The need for on-line sensors to monitor particulate processes is rapidly increasing. Such systems are a necessity to understand the complex phenomena of particle formation, growth and breakage. In this thesis some aspects of the design of an on-line sensor for particle size analysis are discussed. The technique used is based on forward light scattering, which covers a size range from about 1 to 2000 μm. The observations are used to develop a physical model and subsequently an effective control strategy for a 970 liter continuous crystallizer. The purpose of the controller is to manipulate the dynamics of the size distribution. Therefore a firm relation between process inputs and outputs (i.e., the crystal size distribution) must first be established. Secondly an intelligent interpretation of the recorded data, in this case a light scattering pattern is required. In the first chapter it is argued that validation of the sensor performance is an essential aspect of controller design.

Chapter 2 describes the theoretical basis of the forward light scattering technique. A stochastic approach for the validation of light scattering models is explained using size distributions with various degrees of polydispersity and refractive indices. Rather than considering the absolute errors introduced by using various approximate models, the ratio of the systematic error to the observed variability of the scattered intensities is taken as a measure for discrimination. The same criterion is followed to study the effect of discretization of the continuous size distribution. A theory is presented to explain the origin and magnitude of the intensity fluctuations which are encountered in light scattering experiments. In Chapter 3 the dynamics of the intensity signal are quantified and incorporated into a deconvolution algorithm. Added to this is a nonnegativity constraint which helps to avoid a highly oscillatory behavior of the model parameters. The suggested procedure not only yields a qualitative improvement of the solution, but also provides confidence intervals and an objective means for model discrimination.

The theories presented in Chapter 2 and 3 are integrated in a software
package, called ROMA, which serves as a diagnostic tool for actual measurements. One of its features entails testing the signals collected for their degree of auto- and cross-correlation which guides the researcher towards an improved design of the experiment. Chapter 4 describes how ROMA offers a flexible platform to find optimal solutions in off-line conditions, and how it functions as an autonomous entity in on-line applications. The measurement system was used to observe the dynamics of the crystal size distribution in a continuous crystallizer. Chapter 5 reports on the aspects of robustness, integration with the diluter and discusses the results. The median, or x50, and the logarithmic ratio of the x75 over the x25 are adequate descriptors for the location and spread of the crystal distribution. A statistical procedure to validate the quality of the individual measurements proved to be successful. The results are reproducible and show sufficiently strong correlation between process inputs and outputs. In a final experiment the measurement system was used to trace crystals in the first few minutes after the nucleation burst. It was shown that after this period a distribution is formed which originates from agglomeration of the primary nuclei.
SAMENVATTING

Er is een toenemende behoefte aan meetystemen voor het volgen van deeltjesprocessen. Deze systemen zijn onmisbaar voor het verkrijgen van informatie over hoe de deeltjes worden gevormd, uitgroeien en breken. Dit proefschrift behandelt een aantal ontwerpaspecten voor een on-line sensor voor deeltjesgrootte-analyse. De techniek is gebaseerd op voorwaardelijke lichtverstrooiing, en is in staat om deeltjes van 1 tot 2000 μm te meten. De observaties gedaan met dit systeem worden gebruikt om een fysisch model en vervolgens een effectieve regelstrategie te ontwerpen voor een 970 liter continue kristallisator. Het doel van de regelaar is om de dynamica van de kristalgrootteverdeling te manipuleren. Dit vereist ten eerste het vinden van een eenduidige relatie tussen procesingangen en uitgangen (hier de kristalgrootteverdeling). Ten tweede moeten de gemeten data, een lichtverstrooiingspatroon, intelligent worden verwerkt. In het eerste hoofdstuk wordt het belang van het toetsen van de meetresultaten onderstreept als een essentieel onderdeel voor het ontwerp van de regelaar.

Hoofdstuk 2 beschrijft de theorie van de voorwaardelijke lichtverstrooiing. Een stochastische benadering voor het toetsen van lichtverstrooiingsmodellen wordt uiteengezet en toegelicht aan de hand van deeltjesgrootteverdelingen met verschillende breedte en brekingsindex. In plaats van het beschouwen van de absolute fouten die worden geïntroduceerd door vereenvoudigde modellen wordt de verhouding tussen de systematische fout en de waargenomen variatie in de verstrooide intensiteiten genomen als een maat voor vergelijking. Op dezelfde manier wordt discretisatie van de continue deeltjesgrootteverdeling benaderd. Een theorie die zowel de oorsprong als de amplitude van de intensiteitsfluctuaties beschrijft wordt gepresenteerd in het laatste deel van dit hoofdstuk. Vervolgens worden in hoofdstuk 3 deze fluctuaties gekwantificeerd en geïncorporeerd in een deconvolutie algoritme. Het algoritme maakt gebruik van de randvoorwaarde die negatieve modelparameters uitsluit. Dit helpt om het sterk oscillatorende karakter van de modelparameters te onderdrukken. De
voorgestelde methode levert niet alleen een kwalitatief betere oplossing, maar bepaalt ook de betrouwbaarheidsintervallen en levert een objectieve manier voor modeldiscriminatie.

Een softwarepakket, ROMA, integreert de theorie van hoofdstuk 2 en 3 en wordt gebruikt om een diagnose op te maken van de metingen. Het helpt de onderzoeker het experiment beter op te zetten, door ondermeer de waargenomen signalen te testen op zelf- en kruiscorrelatie. In hoofdstuk 4 wordt beschreven hoe ROMA optimale oplossingen vindt in 'off-line' analyses, en hoe het functioneert als een autonome eenheid in 'on-line’ toepassingen. Het totale meet systeem is gebruikt om de dynamica van kristalgrootteverdelingen in een continue kristallisator te onderzoeken. Hoofdstuk 5 behandelt de robuustheid van het systeem, de integratie met de verdunningseenheid en bespreekt de resultaten. De mediaan, of $x_{50}$, en de logaritmische verhouding tussen de $x_{75}$ en de $x_{25}$ bleken adequate maten om de locatie en de breedte van de kristalgrootteverdeling mee te beschrijven. Een statistische maat geeft een indicatie voor de kwaliteit van de individuele metingen. De resultaten zijn reproduceerbaar en laten een duidelijke relatie zien tussen procesingangen en uitgangen. In een laatste experiment werd het systeem gebruikt om de eerste minuten na de kiemexplosie te volgen. Het blijkt dat na deze periode een verdeling is gevormd welke voortkomt uit agglomeratie van de primaire kiemen.
INTRODUCTION

Abstract. The development of adequate sensors is the key to the design of modern control systems. In particulate processes these sensors are essential to obtain a constant product with a well-defined size distribution coupled with a high degree of flexibility of operation. If the control of the process is based on a model, a proper definition of the relevant parameters that represent the size distribution is needed. Forward light scattering is introduced as a measuring technique which is capable of providing the controller with reliable on-line data on the distribution of a wide range of particle sizes.

Motivation

The development of effective sensors which provide information on the state of a process is needed for adequate monitoring and control of chemical processes. In particulate processes, such as crystallization and mineral processing (see eg, Herbst et al. 1992), where the birth, growth and breakage of particles are the dominant phenomena, the sensor collects on-line data which describes the size distribution of the particles at a specific location in the reactor. A complete characterization of the state of such a process requires additional information on the shape, composition and density of the particles in the reactor (Cooper 1992). The extent to which information is extracted from the acquired signal may vary. Typically three levels can be discriminated, which have an increasing degree of complexity:

- Monitoring;
- Control;
- FDI (Fault Detection and Isolation).

In the simplest case, monitoring, the data are used for inspection of the system.
This leads to an on-off situation, where either the system performs satisfactorily, or, if some threshold level is exceeded, the system is halted. This information is sometimes validated with statistical tools, such as cumulative sum techniques, but is usually restricted to limit checking. As an example, one might check for the presence of air bubbles or to ensure that all the particles in a flow have dissolved before the solvent is analyzed for composition. In the second case the data are used to manipulate the process by a controller system which then either keeps the process within the desired boundaries or steers it to new setpoint values. For this purpose a model of the process is necessary, which, due to the strong nonlinearity of the process, unknown hydrodynamics and other causes is quite often a tedious and laborious task. Finally, the most complex case is represented by FDI which needs, in addition to the controller, a means to discern faulty process conditions. Such conditions comprise, for example, a leak in the vessel or a plugged feed line. The time scale of the data acquisition, that is, the intensity at which the information is to be used, must also be considered. A global scheme is given in Figure 1.1.

![Diagram](image)

*Figure 1.1 The use of the data collected by the sensor depend on the time scale, ranging from minutes for detection of process faults to days for product planning and scheduling (Rowan 1992).*

One of the problems lies in the demand for more detailed information about the state of the process whilst the time permitted for the analysis is reduced.

This thesis describes a first step in the development of an intelligent sensor for on-line particle sizing for application in the control of continuous and batch crystallizers. A sensor in this respect refers to a complete measurement system: sample preparation, data collection, processing and transfer of the results to the controller. In a process, therefore, a sensor operates on two levels. On the process level is the hardware of the sensor. In the case of the forward light
scattering technique, as discussed in this thesis, this includes components such as the detector, laser, optical cell and diluter. The other level is designated the operator level. Here is located the software which is responsible for the data processing and validation of the result.

![Diagram showing process level and operator level with process, malvern, controller, filter, ROMA, and setpoint connected](image-url)

**Figure 1.2 Integration of the sensor in the information flow scheme. The Malvern, is located on the process level. The signal processing is carried out on the operator level. The results are transferred to the controller.**

An intelligent sensor should be able to diagnose not only its own state and performance, but also the results it produces. A complete diagnosis sequence consists of three layers:

- Detection of error sources;
- Isolation or discrimination of error sources;
- Assessment and reasoning.

In ordinary sensors these capabilities are absent, and an analogue signal is transferred to the controller (or operator), which is contaminated with errors originating from different sources, either from the process itself or from the detector. In this classical situation the signal is filtered before it reaches the
controller, which makes it more complicated to detect, let alone isolate, faulty behavior. This may cause the controller to respond to spurious process upsets, caused merely by problems associated with the detector. Such behavior will eventually frustrate the success of any control scheme, no matter how ingenious. Thus, starting from the raw signal that is collected, the sensor checks the quality of the signal, yields a result which is validated by a statistical test, allocates the remaining differences to specific error sources and, finally, transfers the result to the controller. Often more process information is required to complete the analysis than can be derived directly from the measurement itself. Examples are the temperature of the suspension, the specific shape of the particles, or the degree of agglomeration.

![Diagram](image)

*Figure 1.3 In an ordinary sensor an analogue signal is transferred to the controller, which may be corrupted by errors associated with the process or with the sensor performance itself (Henry and Wood 1992).*

In this thesis the first step in formulating such an intelligent system for the measurement of particle size distributions is discussed. This step comprises sensor validation at the operator level and is concerned with the understanding and quantification of all the measurement uncertainties. The approach uses the forward light scattering technique to estimate the size distribution, based on existing hardware (the Malvern 2600). The results of this research have been integrated into a software package (ROMA\(^1\)) which supervises the measurements. In the future this development will lead to improved hardware, for example a more sophisticated detector which is able to adapt automatically to

\(^1\) ROMA: Robust On-line Measurement and Analysis, or just a nice city in Italy.
the changing state of the process. Also, in order to relieve the demand on the computer time, it is possible to replace a number of software tools for analyzing the incoming raw signals by electronic equivalents. As a last step, which is indicated by the dashed box preceding the ROMA box in Figure 1.2, additional phenomenological knowledge may be supplied to the sensor. The latter is then referred to as a knowledge-based system (KBS), or expert system, which is usually based on 'if-then-else' structures. Another incentive, which could be included in this step, comes from the neural networks which currently receive great attention due to their ability to create structure in situations which are extremely difficult or impossible to describe with a model based on first principles.

The Forward Light Scattering Technique

The forward light scattering technique was selected to measure the size distributions on-line. The technique offers a few clear advantages which are particularly relevant in a process environment:

- Wide size range covered (2-3 decades);
- Fast measurement and analysis (usually less than 1 minute);
- The basic components, laser, detector, optical board and electronics are relatively simple and, therefore, inexpensive;
- A high degree of robustness with regard to temperature, vibration and other process conditions;
- Data can be physically interpreted, which allows error identification and validation of the results. This was extremely important for this research.

A serious disadvantage is the need to draw a sample from the reactor, either manually or automatically. Although this technique is already a major improvement over strictly off-line techniques such as sieving or sedimentation, an appropriate in-line technique, where a probe is directly dipped into the process, is certainly preferable. Ideally the particles should be measured without any interference from a measuring device, and an in-situ technique should be
used. A second drawback of the technique involves the sample concentration. This should be low enough to ensure single scattering and, in many cases therefore, a diluter is needed which adds to the complexity of the system. Also, the technique does not readily provide information on the number distribution and the shape of the particles. Other sizing techniques that are able to measure particles in the same size range are listed in Table 1.1. The last section of Chapter 5 covers some preliminary results obtained with these techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantage</th>
<th>Disadvantage</th>
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<td>Forward scattering</td>
<td>fast/reliable</td>
<td>dilution/sampling</td>
</tr>
<tr>
<td>Back scattering</td>
<td>in-line/cheap</td>
<td>interpretation</td>
</tr>
<tr>
<td>Acoustic attenuation</td>
<td>in-situ</td>
<td>high cost</td>
</tr>
<tr>
<td>Imaging</td>
<td>shape/numbers</td>
<td>slow/sampling</td>
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Table 1.1 Available measurement techniques for particle sizing in a process environment with particles in the range of 1-2000 μm.

Instruments based on forward light scattering are produced and sold by a large number of manufacturers. Interestingly enough, the size distributions obtained with these instruments all disagree, sometimes even for two instruments supplied by the same manufacturer. These differences arise due to a combination of error sources. The first category are experimental errors which can, generally, be avoided:

- Non-representative sampling;
- Dispersion difficulties;
- Damaging of particles (attrition, breakage);
- Agglomeration between particles;
- Misalignment of the optical system;
- Instability of the laser.

The second error source involves an inversion problem. The technique estimates the particle size distribution from the observed light intensities. Such a measure-
ment is said to be indirect since the particle size distribution is derived on the basis of a physical model. Even extended models are limited in some respect (e.g., by shape and concentration) and therefore introduce systematic errors. The central question is 'What constitutes the best estimate for the size distribution', knowing that the measurement is contaminated with various systematic and stochastic errors?

Scope of Thesis

The problem of finding the correct light scattering model was previously limited by the available computational power. Exact theoretical solutions, based on the Maxwell equations for spherical particles, were available as early as the beginning of this century. Approximate scattering theories were based on a whole range of models, all specifically tailored to fit certain regimes of particle size and refractive index. Amongst them we find the well known Fraunhofer diffraction theory the Rayleigh scattering theory, the anomalous diffraction theory, and several others. Their use was condoned by employing them only in those regimes where they approximated to the Mie solution. This resulted in contour plots for the errors, of which a typical example is shown in Figure 1.4. The plots are constructed for a range of refractive indices. With modern computing power Mie calculations have become common, stimulated further by the existence of effective algorithms. The severe disadvantage is that the complex calculations tend to obscure the inherent scattering mechanisms by representing the Mie

**Figure 1.4** Error contours indicate 5% deviation from the Mie solution, for different approximate theories for a range of particle sizes and refractive indices (Heller 1963).
solution in the form of an infinite series of terms. More importantly is the fact that all the comparisons were based on monosized particles rather than on particle size distributions. This tends to overestimate the errors. Since the number of measurement points is limited, and because experimental errors are always present in the measurement, the reconstructed size distribution has a limited resolution. Limited resolution is expressed by discretization of the solution to some degree, which also results in additional loss of information. Therefore, in Chapter 2, the various light scattering models are compared by considering the ratio of the systematic error to the stochastic variability of the observed intensities. In other words, the question to be answered is ‘To what extent are the above mentioned systematic errors detectable’, knowing that the signal collected is dynamic in nature? Specifically, the effect of replacing the Mie model by the simpler Fraunhofer diffraction model and the impact of discretizing the size distribution are discussed. The stochastic nature of the scattered intensity is modelled with Poisson statistics and is verified independently.

In Chapter 3 deconvolution of the recorded scattering pattern is discussed. Inverse problems generally suffer from a great sensitivity towards the measurement noise. Direct inversion typically causes severe oscillation of the solution, leading to unreliable data. Furthermore, the solution is very sensitive to small changes in the data collected and, in fact, a whole range of solutions can be generated. Several methods were devised to regularize the inverse problem. One of the methods was introduced by Phillips (1962). Basically the independent model parameters of the solution vector are linked by a second order scheme, thus enforcing a degree of smoothness of the solution.

Figure 1.5 Direct inversion of the scattering pattern leads to severe oscillations for the solution, which can be suppressed by adding smoothing instructions (Phillips 1962).
Although this circumvents the problem of the oscillations, the result may still contain some negative values which are physically meaningless. In the method outlined in Chapter 4, rather than smoothing a nonnegativity constraint is introduced. Secondly, the set of equations is weighted for all uncertainties included in the signal. These uncertainties are expressed by a covariance matrix, which incorporates both the variances of the signals and also the cross-correlation coefficients. After the deconvolution this enables model validation, using a chi-square test to assess the sum of residuals per degree of freedom. It also translates input uncertainties into confidence bands for the estimated parameters which represent the unknown size distribution. By changing the resolution and varying the position of the grid, the response on the parameters can be studied and optimal solutions can be isolated. This allows investigation of the relationship between the resolution of the parameters, on the one hand, and the degree of variability of these parameters on the other hand.

The light scattering theory presented in Chapter 2, combined with the approach for data processing offered in Chapter 3, form the basic ingredients for Chapter 4. Here the performance of the ROMA software package is demonstrated by integration of the data acquisition with the scattering model and the deconvolution module. The program serves as a diagnostic tool during the measurements. This leads to an improved design of the experiments by display-
ing the signals, checking the degree of auto- and cross-correlation and setting the proper time delay between successive detector readings.

The final goal for the development of this sensor was to observe crystal size distributions. Knowledge of the position and shape of these distributions is necessary for the design of control strategies for the 970 liter continuous evaporative crystallizer. In an earlier thesis by Jager (1990), the physical aspects, such as kinetics, scale up effects and size classification techniques were discussed. In another preceding thesis De Wolf (1990) addressed the modeling and system identification for such a crystallizer. Both the crystal size distributions in the fines and product flow were monitored for prolonged periods of time, whilst tracing also the response to changes in the input parameters. In another experiment the start-up behavior of the crystallizer was characterized requiring measurements at a very high rate. The results are reported in Chapter 5.

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VALIDATION OF LIGHT SCATTERING MODELS FOR POLYDISPERSE PARTICLE SYSTEMS

Abstract. A statistical method is outlined to validate a scattering model utilizing the complete Mie solution for lognormal size distributions in the range of 0.1 to 100 μm and a maximum scattering angle of 15°. The method outlined incorporates the concentration fluctuations and redistribution effects of the sample observed during a measurement. The theory presented to describe the resulting intensity fluctuations is fully confirmed by the "bootstrap" method and is used to find the scattering angles with most unstationary behavior. The consequences of using the approximate Fraunhofer diffraction theory and the discretization of the size distribution are discussed. The numerical aspects of accurate integration of the scattering functions with a size distribution are consigned to the appendix.

Introduction

In forward light scattering the particle size distribution (PSD) examined is reconstructed by comparison of the recorded scattering pattern and a scattering model which predicts how the incident light is distributed by particles of different size in space. The calculated PSD depends on the choice of a specific light scattering model and is also affected by the specific method of inverting the scattering data.

Inversion algorithms have been discussed extensively by many authors and are still a topic of considerable interest since this problem is common to all techniques based on indirect measurement. Attention is focused mainly on minimizing the effect of measurement errors, which otherwise result in physically impossible solutions, and secondly on calculating the information content of the measurement (eg, Groetsch 1977, Tikhonov and Arsenin 1977, Menke 1984). In Chapter 3 the development of an inversion algorithm is discussed.
Light scattering models describe the interaction between the incident light and the particle. The scattering functions implemented in the model take into account the relative refractive index, the size and shape of the particles and the wavelength of the light used. For various regimes of these parameters different functions have been derived, ranging from the uncomplicated diffraction theory to the complete but complex theory derived by Mie (1908) and others (Lorenz 1890 and Debye 1909)\(^1\). Several computer algorithms to calculate the latter solution have been developed (eg, Dave 1969, Lentz 1976, Grehan and Gouesbet 1979, Wiscombe 1980, Bohren and Huffman 1983, Fowler 1983, Wang and Van der Hulst 1991) and, with the increased power of the computers, the need for approximations seems superfluous. The major disadvantage of this approach is the difficulty of interpretation since the solution is merely represented as a series of many terms, up to several thousand for large particles. Secondly, the detailed structure of the scattering pattern, found after elaborate computations, may be true in theory for single scatterers but will be concealed in practice, when a field of scatterers of different size contributes simultaneously to the pattern. The assumption of spherical particles puts another restraint on the use of the Mie solution, since in practice such particle systems are rarely encountered. Corrections for nonsphericity, and other factors such as nonuniformity of the incident light intensity, are more easily implemented in approximate theories. Finally, the measuring technique itself, due to systematic errors introduced by intensity instabilities of the light source, fouling of the optical cell, incorrect background correction and electronic noise of the photo-detector, seriously limits the precision of the desired result (Bohren and Nevitt 1983).

In this chapter a statistical approach is outlined to compare an approximate model with the full Mie solution for lognormal size distributions rather than single particles in the size range of 0.1 to 100 μm and a maximum scattering angle of 15°. The method includes the effects of sample redistribution and fluctuations in particle concentrations during an observation. A theoretical

\(^1\) The complete solution for the scattering problem for spheres of arbitrary size is referred to as the Lorenz-Mie theory or simply the Mie theory. We will use the latter expression since it seems to be more familiar. The historic aspects are reviewed by Logan (1990), Kragh (1991) and Lilienfeld (1991).
description of the resultant intensity fluctuations is presented and the results are
given in the last section of this chapter. Earlier efforts to assess the legitimacy
of approximate theories in this regime were based on single particles (eg, Hodkinson 1966, Meehan and Gyberg 1973, Jones 1977, Boron and Waldie
1978, Ungut et al. 1981), or on a discrete number of sizes from a size
distribution (eg, Hodkinson and Greenleaves 1963, Roy and Tessier 1990). The
latter approach leads to inconsistent integration errors for different scattering
angles. This was avoided by implementation of an adaptive integration routine.
Results for several particle systems, with different refractive index, mean size
and degree of polydispersity are compared.

The proposed method was also applied to assess the effect of the systematic
error introduced by the discretization of the size distribution into a finite
number of size fractions.

The statistical approach is also promising for the study of ensembles of
nonspherical particles. Although exact solutions are available, after enormous
computational efforts, for some particular shapes (Asano and Sato 1980,
Muinonen 1989), their value is limited since, for sizing, only the average
scattering behavior of these particles is of interest (Bohren and Huffman 1983).
The same reasoning holds for the problem of multiple scattering or anisotropic
scattering, which again favors a statistical treatment rather than the tedious
derivation of an exact and rigorous theory.

Basic Light Scattering Theory

There are a number of textbooks on light scattering theory and its applications
in the field of aerosols and atmospheric sciences (eg, McCartney 1976,
Twomey 1977 or Hinds 1982). The following selection of books is suggested:
Van de Hulst (1957), Stone (1963), Kerker (1969), Born and Wolf (1980),
Bayvel and Jones (1981) or Bohren and Huffman (1983). Here the aim is solely
to introduce the important parameters encountered in the theory of light
scattering. This terminology is required for the treatment of the problems
discussed in this chapter and the subsequent chapters.

Scattering and absorption are interactions between matter, or inhomogeneities
of the medium, and light. In fact, scattering and absorption are responsible for most of the observations of objects in nature. As an example, black smoke appears black because all the visible light is absorbed. A dense rain cloud may also look black. However, in that case the water droplets, which are weakly absorbing particles, attenuate the incident light mainly by scattering. The deciding parameters involved in the interaction are discussed briefly below.

- The ratio of the particle size to the wavelength of the incident light, termed the size parameter $\alpha$, dictates the scattering behavior and is defined as

$$\alpha = \frac{\pi x}{\lambda}. \quad (2.1)$$

- The ratio of the complex relative refractive indices ($m$) of the particles and the medium in which they are suspended constitutes another important parameter:

$$m = \frac{m_{\text{part}}}{m_{\text{med}}} = (m_{\text{Re}} - m_{\text{Im}} i), \quad (2.2)$$

where a nonabsorbing medium is assumed. The refractive index is specific for each material and is a function of the wavelength of the radiation. It is also assumed that the particles are optically homogeneous, i.e., the refractive index is the same from the center to the surface of the particle in all directions. Otherwise, anisotropic scattering occurs.

- Another form of anisotropic scattering arises from the shape of the scatterers, sometimes referred to as 'form isotropy'. This includes surface roughness which becomes noticeable for particles much larger than the wavelength. For a nonspherical particle, its orientation in the incident beam constitutes another degree of freedom in controlling the scattered radiation. It is for this reason that analytical solutions, which are based on solutions of the Maxwell equations, have been derived for mathematically convenient shapes such as spheres, or other shapes which manifest some degree of
symmetry like fibers and oblate and prolate spheroids. In that case the boundary conditions can be conveniently expressed in an orthogonal system. Analytical solutions for nonspherical particles can be found in Barber and Massoudi (1982) where five methods are reviewed. An example of one of these methods, the separation of variables, is presented by Asano and Sato (1980) for spheroids. Another analytical method, based on the volume equation formulation, proposed by Hage et al. (1991), seems very promising for both inhomogeneous and arbitrarily shaped particles and was verified experimentally. The disadvantages of both these approaches are the lengthy calculations involved. An approximate solution has been derived for small values of $\alpha$. For such particles the scattering properties are almost independent of shape as long as the volume remains the same (eg, Van de Hulst 1957). For large values of $\alpha$ and small scattering angles, observed in the far field, the scattering pattern may be approximately described by Fraunhofer diffraction (see next section). Jones (1987) has shown that, even for completely arbitrarily shaped particles, the forward lobe of the scattering pattern remains almost unaffected in this regime. Outside this lobe, however, the pattern may deviate considerably due to specular and internal reflections. These results are in correspondence with earlier experimental findings by Zerull et al. (1977) who used the microwave analog technique. As an alternative for this regime a geometrical optics approach was pursued by Muinonen and coworkers (1989) to describe the scattering by crystals of various shapes. Mugnai and Wiscombe (1989) showed that, in a random particle field, shape has a much smaller effect on the scattered intensities than would be expected from computations done on a single particle with one preferential orientation. They conclude that a single average shape intensity curve is misleading and propose instead a lower and upper bound. A review of the problems introduced by nonspherical and inhomogeneous particles has been presented by Schuerman (1980). In this chapter the particles are assumed to be spherical.

- The measurement and description of the distribution of electromagnetic radiation following a scattering event is the prime objective of this chapter. The intensity (energy per unit time per unit area) of this radiation arriving
on a detector from an extended source is expressed in W/m². Intensity from a point source, a single scatterer, can be represented as W/sr, the total energy flux scattered per unit solid angle in the direction of the observation angle, θ.

• The phenomena caused by light cannot be explained by the magnitude of its intensity alone. Additional parameters which describe the state of polarization are required. The state of polarization of the incident light usually affects the scattering behavior and a scattering event invariably changes this state.

Figure 2.1 Polar diagrams for the degree of polarization of latex spheres in water, m=(1.20-0i) and λ₅=0.63 µm, α=1.0 (top left), 2.5 (top right), 10 (bottom left) and 100 (bottom right).
Commonly, two scattering functions of the intensity are introduced, $i_1$ and $i_2$, one for the perpendicular and the other for the parallel direction. The degree of polarization of the scattered light depends on the relative scattering in the two directions and may provide additional information about the size of the particles. It is defined as follows and obviously ranges between -1 and 1:

$$ P = \frac{i_1 - i_2}{i_1 + i_2}. $$  \hfill (2.3)

For small particles in particular, $P$ shows a slow variation which can be utilized to estimate their size. Kerker and La Mer (1950) used the polarization ratio, defined as $i_2$ divided by $i_1$, instead of $P$, for effective characterization of small particles. For larger sizes severe oscillations with both size and scattering angle may be expected in all directions, which makes the polarization pattern completely unpredictable. Examples are presented in Figure 2.1.

- The light used here is monochromatic, which means that it is limited to one frequency. The incident wavelength $\lambda$ given by

$$ \lambda = \frac{\lambda_o}{m_{med}}, $$  \hfill (2.4)

where $\lambda_o$ is the wavelength in vacuo. It is assumed that scattering is an elastic process where no frequency change occurs, i.e., the scattered light has the same wavelength as the incident light. This excludes Raman- and Brillouin scattering effects.

In a nonabsorbing medium an arbitrary particle modifies the light which falls upon it by the two basic mechanisms of scattering and absorption. The separate effects can be understood by tracing an imaginary ray of the incident light:
*Scattering*

A complex interaction occurs which consists of diffraction of the incident ray around the edges of the particle in the near-forward direction, reflection from the particle surface and refraction through the particle. In the latter case the ray possibly experiences several internal reflections before finally leaving the particle. The result is a distribution of scattered light in all directions.

*Absorption*

Some of the incident light which is refracted into the particle is absorbed and transformed into other forms of energy. The imaginary part of the refractive index, \( m \), is used to denote the fractional absorption within the particle. Many absorption mechanisms exist, depending on the wavelength used. A summary is presented in Bohren and Huffman (1983).

The sum of all the light removed by scattering and absorption is called extinction. This relation is commonly expressed in terms of the observed particle's cross-sections \( C_{\text{ext}} \), \( C_{\text{sca}} \) and \( C_{\text{abs}} \).

\[
C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}. \tag{2.5}
\]

When divided by the true geometrical cross-section \( G \) of the scatterer (e.g., \( \pi x^2/4 \) for a sphere with diameter \( x \)) they become the efficiency factors, \( Q_{\text{ext}} \), \( Q_{\text{sca}} \) and \( Q_{\text{abs}} \), for extinction, scattering and absorption respectively.

\[
Q_{\text{ext}} = Q_{\text{sca}} + Q_{\text{abs}}. \tag{2.6}
\]

The factor \( Q_{\text{ext}} \) is an oscillating function dependent on size and refractive index but eventually trending asymptotically to a value of 2 for large values of \( \alpha \). In Figure 2.2 examples of this behavior are given for both a nonabsorbing and an absorbing system. The calculations are based on (2.19). Clearly the ripple structure vanishes for the absorbing particles and the oscillations are dampened.

The total extinction of a cloud of particles is measured in the forward direction, where \( \theta = 0^\circ \). A detector collects light over a finite angular range, *e.g.*, by using a lens, undesirably including both the scattered- and the unperturbed
incident light. For large particles, the scattered light is subtended in an increasingly narrow forward cone and the problem of distinguishing the scattered from the incident light is aggravated. The parameter $Q_{ext}$ is a tool to calculate the particle concentration of the suspension examined. The effect of the angular aperture of the measuring device on the accuracy of the extinction efficiency are discussed in Gumprecht and Sliepcevich (1953a and 1953b). In the case of multiple scattering (see next section) the distinction between the true and the observed extinction coefficient becomes even more troublesome.

A beam traversing a nonabsorbing homogeneously mixed suspension in the $z$ direction, with $N$ identical particles per unit volume, each having an extinction cross-section $C_{ext}$, is attenuated in intensity, $I$, by each homogeneous slice as
\[-dI = NC_{\text{ext}}Idz.\] (2.7)

If the total path length is \(l\), then, after integration, Lambert-Beer's law is obtained for the transmission \(T\)

\[T = \frac{I}{I_o} = \exp(-NC_{\text{ext}}l),\] (2.8)

where \(I_o\) is the incident intensity. The obscuration of a beam is

\[Obs = 1 - T.\] (2.9)

The product \(NC_{\text{ext}}\) is referred to as the turbidity, \(\tau\). The product \(\tau l\) is the optical depth or optical thickness of the suspension. Usually the suspension contains particles of different size. Furthermore it is advantageous to use the extinction efficiency rather than the extinction cross section. Integrating (2.8) for a size distribution \(f(x)\) yields

\[1 - Obs = \exp\left(-Nl\int_0^\infty \frac{\pi x^2}{4} f(x) Q_{\text{ext}} dx\right),\] (2.10)

which is the total attenuation of the incident beam by a size distribution examined. Equation (2.10) is only valid when some supplementary conditions hold as will be discussed in the following section, but provides a means to estimate the particle concentration. The size distribution is obtained after deconvolution of the recorded angular distribution of scattered light.

Supplementary Limitations and Assumptions

In general the discussion of linear elastic light scattering by ensembles of arbitrary particles is restricted by imposing the following set of conditions to the problem:
• **Independent and incoherent scattering**
  It is essential that particles scatter as individual entities, that is no electrical interactions exists between them. Independent scattering is achieved when the particles are sufficiently distant from their neighbors. Van de Hulst (1957) suggests that the particle must be surrounded by an imaginary shell with a radius equal to three times the radius of the particle itself. This leads to a maximum permitted number concentration as a function of the particle diameter if we assume a monodisperse system (Table 2.1). In terms of volume concentration this corresponds to about 5%. The associated value for the obscuration calculated with (2.10) quickly approaches 100% with decreasing size, even for very short path lengths. The particles should also be randomly distributed. This eliminates the possibility of the existence of coherent phase relations between the scattering fields emanating from the individual particles. The total scattered intensity in the direction $\theta$ is then computed as the sum of all individual intensities in that direction. This is the principle of superposition. An exception must be made for scattering in the near forward direction where the phase differences typically remain, despite random particle separations and lead to coherent scattering (Bohren and Huffman 1983).

• **Single and multiple scattering**
  A final restriction is the assumption of single scattering. This involves the supposition that light scattered from a particle is not rescattered by another particle in the cloud. Although the scattered light is weak compared to the incident light, it is distributed in all directions and eventually, after many secondary scattering events, will destroy the characteristics of the original composite pattern. The limiting case is a isotropic intensity distribution which has lost all features. In that case the information content of the collected signal has been greatly reduced and so also the significance of the extracted parameters, in this case the resolution of the size distribution. In this regime multiple scattering dominates and computations to correct for this effect are elaborate. There is extensive literature available for study (eg, Hansen and Travis 1974, Van de Hulst 1980, Hirtleman 1988). The transition from the single to multiple scattering regimes is gradual and so a simple test
is to gradually increase the concentration. Then single scattering can be considered to prevail in those regions where a linear relationship with the scattered intensity is found. Another criterion is the optical depth which, according to Van de Hulst, should be less than 0.3. This translates to a maximum obscuration of about 26%. In practice a dilution system may be required to decrease the particle concentration of a sampled slurry which needs careful operation in order not to induce systematic errors greater than those caused by the effect of multiple scattering alone. An example of such a system is presented in Chapter 5.

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<tr>
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</tr>
</tbody>
</table>

### Various Scattering Functions and their Domains

The scattering functions discussed in this section define how the incident light intensity, coming from a remote source and collected at a great distance from the center of scattering, is distributed as a function of the scattering angle $\theta$. If monochromatic light from a laser source falls upon a scatterer, with intensity $I_o$ (W/m²), then the single scattered intensity $I(\theta)$ (W/m²) at angle $\theta$ is represented by

$$I(\theta) = I_o \frac{\lambda^2}{8\pi^2r^2}(i_1 + i_2)$$

or

(2.11)
\[ I(\theta) = \frac{I_o}{2k^2r^2}(i_1 + i_2), \quad (2.12) \]

with

\[ k = \frac{2\pi}{\lambda}. \quad (2.13) \]

Here \( r \) denotes the distance between the plane of observation and the particle, and \( k \) is the wave number or propagation constant.

![Graph](image_url)

**Figure 2.3 Scattered intensity at \( \theta = 15^\circ \) as function of \( \alpha \) indicating the various regimes, \( m=(1.20-0.6) \) and \( \lambda_s=0.63 \ \mu m. \)**

In order to evaluate the scattering properties of an ensemble of particles, it is enough to know the scattering functions for the individual particles. Various scattering functions may be discerned, depending primarily on the actual values of \( \alpha \) and \( m \) for the particle under study. This can be demonstrated by plotting...
\( \alpha \) against the sum of \( i_1 \) and \( i_2 \) for a fixed angle (Figure 2.3). For small values of the size parameter the curve is smooth and is proportional to the sixth power of the particle diameter. For larger particles the curve starts to oscillate until eventually the intensity increases consistently with the square of the diameter. The first regime can be described by the Rayleigh theory, the latter by diffraction theory. In the intermediate case, where the wavelength of the incident light becomes comparable with the particle diameter, the description can generally not be approximated but must be based on the complex solution of the Maxwell equations and is denoted as the Mie regime.

The influence of \( \alpha \) and \( m \) together is demonstrated in two polar scattering diagrams shown in Figure 2.4 and Figure 2.5, which show the angular distribution of the intensity, \( I(\theta) \), calculated from the Mie equations. The effect of the refractive index on the patterns for six particle sizes is portrayed for an absorbing and a nonabsorbing system. For small particles equal amounts are scattered in the forward and the backward direction. Increasing the particle size first causes peaks and troughs to develop and finally causes the intensity to concentrate to one primary peak in the forward direction. In this case the predominant scattering angle becomes very small and its intensity is, therefore, barely distinguishable from the undisturbed incident intensity. For the absorbing system we find a smoother pattern but it still exhibits the same characteristic behavior with increasing size. The fine structure is eliminated by the absorption of light inside the particle whilst the forward lobe remains intact. In effect this means that the pattern of the scattered light is still peaked in the forward direction.

The scattering regimes for nonabsorbing single particles can be located in a \( m-x \) plane as presented by Van de Hulst (1957). He also introduced a third parameter, which is a combination of the other two

\[
\rho = 2 \alpha (m-1). \tag{2.14}
\]

It is referred to as the phase shift parameter because it represents the total phase shift a ray experiences when it traverses a particle of diameter \( x \). These parameters can be supplemented with a fourth one, the scattering angle \( \theta \). Based heron approximate solutions for the scattering problem may be devised. First
Figure 2.4 Polar scattering diagrams for latex spheres in water, $m=(1.20-0)$ and $\lambda=0.63 \, \mu m$, $\alpha=0.1$ (top left), 2.5 (top right), 5 (middle left), 10 (middle right), 25 (bottom left) and 100 (bottom right).
Figure 2.5 Polar scattering diagrams for iron particles in air, $m=(1.27-1.37i)$ and $\lambda_p=0.44\ \mu m$, $\alpha=0.1$ (top left), 2.5 (top right), 5 (middle left), 10 (middle right), 25 (bottom left) and 100 (bottom right).
a few of the approximate solutions, ending with the Fraunhofer diffraction method, will be briefly discussed. Then the basic equations of the Mie solution, which encompasses all the approximate theories, are presented.

- **Rayleigh**
  When particles are very small compared to the wavelength inside the particle (\(\alpha < 1\) and \(\rho < 1\)), the scattered light is equally distributed in the forward and backward directions by the function \((1 + \cos^2 \theta)\), and its total intensity is proportional to \(\lambda^6\). Lord Rayleigh described the scattering in this regime in 1871. If \(m \to 1\) and \(\rho\) remains small, the Rayleigh-Gans or Rayleigh-Debye approximation is used. Kerker et al. (1978) examined the validity of the Rayleigh approximation.

- **Anomalous diffraction**
  Van de Hulst (1957) introduced the theory of anomalous diffraction. This regime is confined to values of \(\alpha > 1\) and \(m \to 1\). Although the relative refractive index is close to unity, rays will still suffer an appreciable phase shift because they have to travel a long path length inside the particle. A resulting forward field is formed after interference with the original field. Farone and Robinson (1968) extensively evaluated this approximation.

- **Geometrical optics**
  This is the tracking of the light rays through a particle. The particle must be large enough compared with the wavelength to represent the incoming wave as individual rays. The rays which fall upon the particle are refracted and reflected and the rays which pass near to the edges of the particle form a diffraction pattern in the far field. Each process accounts for half of the scattered radiation which is equal to the energy incident on the geometric cross-section. Fraunhofer diffraction theory describes the diffraction part (see next item). Generally the extent of this regime is spanned by \(\alpha > 1\), \(m > 1.1\) and scattering angles up to 30°. If these conditions hold, and at least some degree of polydispersity of the size distribution is present to eradicate phase effects, particle sizing may be successfully achieved whilst avoiding the complete Mie solution by simply adding the contributions from refraction and
reflection to the diffraction theory (Hodkinson and Greenleaves 1963, Kerker 1969 and Roy and Tessier 1990). Another interpretation of geometrical optics, leaving out the internally reflected rays, is presented by Ungut et al. (1981).

- **Fraunhofer**

For sufficiently large particles (α ≈ 1) the resulting scattering pattern in the near forward direction is accurately described by scalar diffraction theory alone (Born and Wolf 1980). If the pattern is collected in the far field, ideally at infinity, the pattern is predicted by the Fraunhofer diffraction theory, named after Josef Fraunhofer's description of dark lines in the solar spectrum made in 1817:

\[
    i_1(\theta) = i_2(\theta) = \alpha^4 \left[ \frac{J_1(\alpha \sin \theta)}{\alpha \sin \theta} \right]^2 (1 + \cos^2 \theta)/2 .
\]  

(2.15)

The bracket contains a Bessel function of the first kind and is known as the Airy function. The second part is known as the obliquity correction factor which extends its applicability to higher scattering angles, which become important for small particles (Hodkinson 1966).

The widespread use of this simple approximation stems from the fact that, in this regime, scattering is independent of the relative refractive index of the particles, which in many cases is difficult to determine, and also to the absence of multifarious calculations. The property exploited here is the stagnant shape and position of the primary scattering lobe for a wide range of values of \( m \). Only if the relative refractive index approaches unity should substantial deviations from the exact theory be expected and the anomalous diffraction approximation should be used instead. Otherwise, even for particles of various shapes, the characteristic lobe remains unchanged. Beyond the main lobe the theory starts to digress from the true scattering signature for transparent particles. Here geometrical optics could apply. Absorbing particles on the other hand extend the range of applicability. In practice therefore, the Fraunhofer theory is valid for a limited range of the scattering angle \( \theta \), relative refractive index \( m \) and size parameter \( \alpha \). If these conditions apply, the extinction efficiency is independent of size and

- **Mie**

For the Mie solution the scattering functions are developed by separation of variables in Maxwell's equations expressed in a spherical coordinate system. They consist of the square of the norm of complex amplitude components

$$i_1(\theta) = |S_1(\theta)|^2, \quad i_2(\theta) = |S_2(\theta)|^2.$$  \hspace{1cm} (2.16)

The complex amplitude components consist of a summation over an infinite number of terms. The terms include the scattering coefficients $a_n$ and $b_n$ which depend on both $\alpha$ and $m$, and the phase functions $\pi_n$ and $\tau_n$, which are a function of the scattering angle $\theta$:

$$S_1(\theta) = \sum_{n=1}^{\infty} \frac{(2n+1)}{n(n+1)} \{ a_n \pi_n(\mu) + b_n \tau_n(\mu) \},$$  \hspace{1cm} (2.17)

$$S_2(\theta) = \sum_{n=1}^{\infty} \frac{(2n+1)}{n(n+1)} \{ a_n \pi_n(\mu) + b_n \pi_n(\mu) \}.$$  \hspace{1cm} (2.18)

Here $\mu = \cos \theta$. The extinction efficiency factor, $Q_{ext}$, is expressed in the same manner but is dependent only on the scattering coefficients $a_n$ and $b_n$:

$$Q_{ext} = \frac{2}{a^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}\{a_n + b_n\}.$$  \hspace{1cm} (2.19)

The calculations of the scattering coefficients and the phase functions involve stable numerical schemes. Our calculations were based on the algorithm presented in the appendix of the book by Bohren and Huffman (1983) after it had been adopted and improved with respect to its stability, range and performance (see Appendix A).
A summarizing scheme of the regimes applicable for approximate theories of scattering by single particles is presented in Van de Hulst, 1957 p133 and p173. The next sections expand on the design of a discrimination criterion to validate the regimes of the approximate theories in measurements of polydisperse particle suspensions. Since the scattering pattern is then developed from a size distribution rather than one single particle, this obviously introduces an additional fifth parameter, the width of the distribution, which could alter the location of these regimes.

**Intensity Signatures of Polydisperse Particle Systems**

In practice, a sample contains particles of many sizes and the scattering characteristics are determined by the shape of the size distribution present. This was demonstrated extensively for some scattering properties by Hansen and Travis (1974). Obeying the limitations discussed in the previous sections, a composite scattering pattern is formed which is exactly equal to the sum of the patterns developed from all the individual particles. Shape effects are neglected here and the same refractive index for all the particles is assumed. It is thus enough to integrate (2.11) with a distribution function, \( f(\alpha) \), which represents the fraction of the total number of scattering particles in any size range.

\[
I(\theta) = K \int_0^\infty i(\theta, \alpha, m) f(\alpha) \, d\alpha .
\]  

(2.20)

In (2.20), \( i(\theta, \alpha, m) \) replaces the individual scattering functions for the parallel and the perpendicular direction and \( K \) is a constant which follows from (2.11) for a pattern observed at distance \( r \) and a constant sample illumination of the sample by a monochromatic light source. The frequency distribution function \( f(\alpha) \) may span several orders of magnitude of size for some particle systems. An adequate fit of the size distribution for many of these systems is constructed from two parameter frequency distribution functions. Related properties of the particle system for which the specific function was contrived are reflected in these associated parameters. Examples are the Rosin-Rammler distribution used for coarse materials, the Nukiyama-Tanasawa distribution for extremely broad
size ranges found in sprays, the power law distribution for aerosols and the exponential distribution, which can be applied to powdered materials (Hinds 1982). Another type of two parameter distribution is the normal distribution, which finds wide applicability because it is the predicted distribution for variables that are the result of an addition of independent stochastic terms. In the case that a variable is the product of stochastic factors, as in many particle processes, the logarithm of that variable will have a normal distribution, and hence the variable itself a lognormal distribution. Therefore the lognormal distribution has been used in this chapter as the model size distribution type, and is defined by

\[ f(\alpha) = \frac{1}{\ln\sigma \sqrt{2\pi}} \exp\left[-\frac{(\ln\alpha - E\{\ln\alpha\})^2}{2(\ln\sigma)^2}\right], \quad (2.21) \]

where \( E\{\ln\alpha\} \) is the expected value of \( \ln\alpha \), or the geometric mean, and \( \ln\sigma \) is the geometric standard deviation. Conversion to a mass based frequency distribution or to any other weighted distribution is performed by

\[ f_p(\alpha) = \frac{\alpha^p f(\alpha)}{\int_0^\alpha \alpha^p f(\alpha) d\alpha}, \quad (2.22) \]

where \( p \) is the power of the diameter of interest, for example 3 for a mass distribution. Examples of scattering patterns developed from the lognormal distributions are presented in Figure 2.6.

As shown in Figure 2.6, the detailed scattering structure of narrow size distributions fades as the distributions grow broader. This is expected because the 'neighbors' of each particle size fill the gap between two maxima with their own maxima. The most obvious distinction between the patterns is the change in the slope of the intensity decay with scattering angle.

The patterns depicted are idealized representations of an actual observation. In reality the pattern varies with time. If enough observations are made, the intensity of each scattering angle can be represented by an estimate of the mean value and spread. In the next section a discrimination criterion is proposed which accounts for these fluctuations, by estimating the variance of the
scattering pattern. It is assumed that the composition of the particle distribution itself remains unchanged while recording the patterns, that is no growth, agglomeration or breakage occurs. The magnitude of the variance is independently verified with the ‘bootstrap’ method in the final section of this chapter.

The discrimination criterion has been used to assess the applicability of the Fraunhofer scattering function as a function of the mean and standard deviation of the lognormal distribution for a set particle systems with different optical properties. Also the effect of discretization of the frequency distribution is examined. The continuous frequency distribution is approximated by a set of contiguous, logarithmically equidistant, size groups. The price of that approach is some distortion of the scattering pattern. The consequences of decreasing the resolution of these uniform distributions for the reconstruction of the original scattering pattern has been investigated. Discretization plays an important role in the problem of deconvolution, as will be demonstrated in the next chapter.
Design of a Discrimination Criterion for Scattering Models

First we shall define the variance of a scattering pattern in a homogeneously mixed suspension. Then, at any time $t$, the total scattered intensity is obtained by multiplication of (2.20) with the actual number of scatterers present in the illuminated section of the optical cell, $\nu$. The stochastic variable, $\nu$, follows a the Poisson distribution with a mean value equal to the average number of particles in that particular volume, $N$. The density of this distribution is given by

$$P(\nu) = \frac{N^\nu}{\nu!} \exp(-N). \quad (2.23)$$

The size parameter, $\alpha$, is the second stochastic variable in the scattering process. Its distribution is here described by the lognormal function of (2.21). The total scattered intensity at $\theta$ for a number of particles, $\nu$, is then

$$I(\theta) = \sum_{k=1}^{\nu} i(\theta, \alpha_k). \quad (2.24)$$

The expected equivalent scattering pattern, $E_\nu\{I(\theta)\}$, is then found from

$$E_\nu\{I(\theta)\} = K \sum_{k=1}^{\nu} E\{i(\theta, \alpha_k)\} \quad (2.25)$$

$$= K\nu L(\theta),$$

where the integrated intensity pattern is

$$L(\theta) = \int_{0}^{\infty} i(\theta, \alpha, m)f(\alpha)d\alpha. \quad (2.26)$$

Recognizing that the number of particles is also a stochastic variable, and $E\{\nu\} = N$, the expected pattern becomes
\[ E\{I(\theta)\} = KN L(\theta) . \] (2.27)

Similarly the square of the intensity pattern, with \( \nu \) fixed, yields
\[ I^2(\theta) = K^2 \left[ \sum_{k=1}^{\nu} \sum_{l=1}^{\nu} \delta(\theta, \alpha_k) \delta(\theta, \alpha_l) \right] , \] (2.28)
which leads to the following equation for the expected pattern:
\[ E_{\nu}\{I^2(\theta)\} = K^2 \left[ (\nu^2 - \nu) L^2(\theta) + \nu L_2(\theta) \right] . \] (2.29)

Here \( L_2 \) represents the square of the individual scattering functions for the terms where \( k = l \). Implementing again the Poisson distribution to describe the number of particles, the first term becomes \( E\{\nu^2 - \nu\} = N^2 \) and the second \( E\{\nu\} = N \). Substitution then reveals the result for the square of the expected pattern:
\[ E\{I^2(\theta)\} = K^2 \left[ N^2 L^2(\theta) + NL_2(\theta) \right] . \] (2.30)

The variance of the measured \( I(\theta) \) can be found from
\[ \text{Var}\{I(\theta)\} = E\{I^2(\theta)\} - (E\{I(\theta)\})^2 \]
\[ = K^2 NL_2(\theta) . \] (2.31)

After rearranging the terms it becomes:
\[ \text{Var}\{I(\theta)\} = K^2 \left[ NL^2(\theta) + N[L_2(\theta) - L^2(\theta)] \right] . \] (2.32)

The first term of (2.32) represents the change in intensity due to concentration fluctuations and the second term the effects of redistribution. Redistribution means that even when the number of particles is constant, the size distribution varies. Clearly, this effect does not occur in monodisperse systems, where only the first term remains. In the last section the dependence of these fluctuations on the width of the size distribution is examined. The contribution of the concentration fluctuations is compared with the added effect of redistribution.

In order to justify the use of an approximate model instead of the Mie
solution, which is regarded as the reference model, a comparison of the systematic errors alone is dubious. More relevant is the ratio

\[
\frac{\text{systematic error}}{\text{stochastic variation}}.
\]

Generally, if the value of this ratio becomes too large the model is inadequate. Therefore (2.33) was used to express the average error between the two models if the angular resolution is perfect:

\[
\Delta = \frac{1}{(\cos \theta_1 - \cos \theta_2)} \int_{\theta_1}^{\theta_2} \frac{\left( E[I_{\text{appr}}(\theta)] - E[I_m(\theta)] \right)^2}{\text{Var}[I_m(\theta)]} \sin \theta d\theta. \quad (2.33)
\]

The purpose of this expression is to compare the weighted difference between both patterns and to average over a fixed angular range, \( \theta_2 - \theta_1 \). The \( \sin \theta \) term is added to distribute the number of imaginary detectors equally over a two dimensional area. Substitution of the appropriate terms in (2.33) shows that \( \Delta \) is a function of the number of particles contributing to the scattering pattern:

\[
\Delta = \frac{N}{(\cos \theta_1 - \cos \theta_2)} \int_{\theta_1}^{\theta_2} \frac{[I_{\text{appr}}(\theta) - I_m(\theta)]^2}{L_{2,m}(\theta)} \sin \theta d\theta. \quad (2.34)
\]

Qualitatively, a large \( \Delta \) indicates the existence of systematic deviations, significantly larger than predicted by the variance. When the variance of the intensity at any particular angle is relatively large, the need for an accurate description at that angle wanes. If the approximate model is of the same order, the result should be of the order of \( N \), since the sum of all the remaining differences in scattered intensity, weighted for the local variability, approaches unity.

Equation (2.34) supposes that absolute intensities are observed. Usually, only a relative pattern is recorded which is subsequently compared to the reference model. The best fit includes an arbitrary scaling of the recorded pattern:

\[
L_m(\theta) = \zeta L_f(\theta), \quad (2.35)
\]

where the scalar \( \zeta \) is found from a linear, least squares fit of (2.34):
\[
\zeta = \frac{\int_{\theta_i}^{\theta_2} \frac{L_{\text{appr}}(\theta) L_m(\theta)}{L_{2,m}(\theta)} \sin \theta d\theta}{\int_{\theta_1}^{\theta_2} \frac{L_{\text{appr}}(\theta)}{L_{2,m}(\theta)} \sin \theta d\theta}.
\]

(2.36)

The absence of an absolute measure obscures the differences in the patterns, and hence decreases \( \Delta \), which means that more observations are required to detect the disparity between the models.

To obtain a practical measure, (2.34) was divided by \( N \) to find the minimum number of particles, \( N_{\text{min}} \), necessary to discriminate between the approximate and the Mie theory:

\[
N_{\text{min}} = \frac{N}{\Delta}.
\]

The number of particles calculated was used to establish the regimes where the approximate theory holds. When the number of particles found is small the approximate theory is sufficient to describe the scattering behavior. Otherwise the Mie theory should be applied in order to avoid sizing errors. The consequences of this approach are evaluated for particle systems with different refractive index as a function of the mean and standard deviation of the size distribution. Only the near forward direction is evaluated, covering angles up to 15°, which is representative of the maximum reception angle of the instrument used here, the Malvern 2600 particle sizer².

**Mapping the Fraunhofer Regime**

The approximate theory examined here is the Fraunhofer diffraction theory because it is widely used for this angular range and is the more drastic

\(^2\) Manufactured by Malvern Instruments Ltd., Malvern, Worcestershire, England. Details of the instrument are presented in Chapter 3.
Figure 2.7 Scattering signatures for the same size distributions as presented in Figure 2.6 developed from the Fraunhofer diffraction theory.

Table 2.2 Concentration of particles at 10% obscuration according to (2.10) and the actual number of particles in the optical volume.

<table>
<thead>
<tr>
<th>x [μm]</th>
<th>[#/m³]</th>
<th>[#]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>10^{16}</td>
<td>10^9</td>
</tr>
<tr>
<td>1.0</td>
<td>10^{14}</td>
<td>10^7</td>
</tr>
<tr>
<td>10.0</td>
<td>10^{12}</td>
<td>10^5</td>
</tr>
<tr>
<td>100.0</td>
<td>10^{10}</td>
<td>10^3</td>
</tr>
<tr>
<td>1000.0</td>
<td>10^8</td>
<td>10^1</td>
</tr>
</tbody>
</table>

simplification of the scattering theory. The Fraunhofer patterns were constructed by implementation of (2.15) in (2.20). As an example, the Fraunhofer patterns for the distributions presented in Figure 2.6 are given in Figure 2.7. Smoothing of the scattering patterns is found as the size distribution becomes wider, but
the position of the minima and maxima is quite different. The two sets of patterns are investigated following the discrimination criterion given in (2.34). Here $I_{app}(\theta)$ is replaced by the intensity $I_f(\theta)$, predicted by the Fraunhofer theory. The results are presented as the minimum number of particles needed to detect the differences, as discussed in the previous section.

The consequences of the maximum angle of observation, $\theta_2$, was first investigated. The number of particles found was compared to the actual number of particles in the optical volume which is formed by the product of the beam width, $D$ (10 mm) and the path length, $l$ (3 mm). The estimated number concentration was calculated from (2.10) for 10% obscuration. Table 2.2 shows the data for a range of mean particle sizes, $E\{x\}$. In Figure 2.8 the theoretical minimum number of scatterers needed to detect the differences between the Fraunhofer and Mie scattering patterns is given as a function of $E\{x\}$ and $\ln \sigma$. This number apparently decays rapidly with increasing $\theta_{max}$. The monodisperse curves are

![Figure 2.8 Number of scatterers needed to discriminate between Mie and Fraunhofer with $E\{x\} = 0.1$ (top), $I$ (middle) and 10 $\mu$m (bottom) as function of $\ln \sigma$ and the maximum angle of observation.](image)
depicted bold face. A broader distribution lifts the curve indicating that more particles need to be observed before it is possible to discriminate between the models. Here a better agreement of the approximate Fraunhofer model is achieved. For $E\{x\}=10\ \mu m$ cross-overs appear for all values of $\theta_2$ and the smooth decay is replaced with an oscillating function. The 10% obscuration line intersects all the curves, albeit at different angles. As an example we take $E\{x\}=1\ \mu m$. Here 10% obscuration is equivalent to $10^7$ particles in the optical volume. To discriminate between Mie and Fraunhofer, $\theta_{max}$ should exceed $2^\circ$ for perfectly monodisperse distributions, and $4^\circ$ for $\ln\sigma=0.4$. The graphs show clearly that the position of this intersection is also a function of the mean size of the distribution. If $E\{x\}$ is raised, the maximum angle of observation decreases for constant obscuration, which implies that discrepancies are more readily detected for bigger particles. This can be understood if we take into account that the number of maxima and minima which fit into the angular range grows with particle size, as can be clearly seen from Figure 2.4 and Figure 2.5. Since the Mie and Fraunhofer patterns have been scaled for maximum overlap, differences are greatest at angles where the Fraunhofer function approaches 0. The remaining differences are caused by the tapered performance of the Fraunhofer function at larger angles. The result is in contradiction with the belief that the severest inconsistencies of the Fraunhofer model are caused by

![Figure 2.9 Validity of the Fraunhofer approximation represented by $N_{\text{min}}$ against $\ln\sigma$ for constant $E\{x\}$.](image)
small particles. This conclusion is confirmed by the increased maximum observation angle and the sharp increase in the number of particles needed for discrimination shown in Figure 2.8. A combination of a maximum observation angle of 15° and a moderate particle concentration guarantees that the approximating Fraunhofer scattering function can be distinguished from its equivalent Mie solution. Although the width of the size distribution generally adds to the number of scatterers required, its influence seems secondary. The effect of polydispersity is illustrated in the following two figures where $\theta_{\text{max}}$ is maintained at 15°. First Figure 2.9 shows the relation between $N_{\text{min}}$ and $\ln\sigma$ for a range of mean particle sizes. The number of particles increases rapidly with decreasing particle size. The essentially straight lines found for increasing $\ln\sigma$ are unexpectedly disrupted at $\ln\sigma=0.05$ and deflect, either upwards or downwards. For small particles the lines show a maximum which is displaced by two orders of magnitude when $\ln\sigma$ nears 0.2. In this region the Fraunhofer and Mie scattering patterns coincide much better. For even wider distributions, the deviations at the higher scattering angles due to the additional small particles again become more pronounced. In general many factors interact, which makes it difficult to postulate very precise rules. The number of scatterers needed for discrimination of the Fraunhofer model is largely dominated by the mean size of the distribution, its width seems less important. This is confirmed in
Figure 2.10, where \( N_{\text{min}} \) is depicted as a function of \( E\{x\} \). As could already be concluded from the previous figure, \( N_{\text{min}} \) shows a strong negative correlation with the mean size of the distribution. The slope found is approximately inversely proportional to \( x^4 \). For bigger particles this relation reaches a constant, asymptotic value.

\[
\begin{array}{l|cc}
\text{Description} & m_{\text{Re}} & m_{\text{Im}} \\
\hline
A: \text{Latex in water} & 1.16 & 0.0 \\
B: \text{Quartz in air} & 1.59 & 0.0 \\
C: \text{Crystals} & 1.05 & 0.0 \\
D: \text{Toner in water} & 1.50 & 0.8 \\
\end{array}
\]

In order to further validate the Fraunhofer and Mie scattering models, we investigated four particle systems with different refractive index. The four systems are listed in Table 2.3. Scattering patterns were calculated for all these systems and for a range of values at the mean size (0.1 to 50 \( \mu \text{m} \)) and the variance (0.001 to 0.4) of the lognormal size distribution. Figure 2.11 illustrates the scattering patterns for the four systems compared with the Fraunhofer solution for \( E\{x\} = 10 \ \mu\text{m} \) and \( \ln \sigma = 0.1 \). As expected, both the magnitude and characteristics of the pattern developed from the absorbing toner powder are well approximated by the Fraunhofer theory. The other systems deviate significantly, either in magnitude as for the crystal system, or by showing additional scattering at higher angles as

**Figure 2.11** Scattering signatures for the four particle systems of Table 2.3 derived from Mie compared with the approximating Fraunhofer solution, for \( E\{x\} = 10 \ \mu\text{m} \) and \( \ln \sigma = 0.1 \).
in the case of the latex beads. Since it has already been concluded that the width of the distribution can be neglected for discriminating between the Fraunhofer and Mie scattering functions, the influence of refractive index only is shown for $\ln \sigma = 0.1$ in Figure 2.12.

A negative slope is again found, proportional to $x^4$. The correlation is less smooth than was the case when the width of the distribution was changed. For particles larger than 10 $\mu$m the best correspondence with the Fraunhofer approximation is for the toner copier powder. Clearly the stochastic variation associated with the intensity patterns, makes it difficult to discriminate between the different particle systems, even for a wide range of refractive indices. In practice, the criterion used here, the theoretical number of particles, $N_{\text{min}}$, is affected by various other factors, which involve laser instabilities, detector response, deconvolution techniques, fouling of the optical system and alignment problems.

**Discretization Effects and Resolution Constraints**

In the previous discussion a continuous size distribution function was assumed. In many practical cases, a discrete description of the size distribution is determined. The continuous distribution is then approximated by a linear combination of discrete intervals which collectively span the total size range. This may have a dramatic effect on the appearance of the size distribution (Silverman 1986), and consequently on the ability to reconstruct the observed scattering pattern.
In this approach the fractions contained in each of the discrete intervals become the independent parameters, instead of the geometric mean and standard deviation which were used for the lognormal distribution. In this section the lognormal distribution is replaced by a set of loguniform distributions, that is, histograms with logarithmically equidistant boundaries. The scattering pattern computed is simply the sum of the individual discrete contributions and (2.20) is rewritten as:

\[ I_{\text{discr}}(\theta) = K \sum_{j=1}^{s} i(\theta, \alpha, m) f_j, \]  

(2.38)

where fraction \( f_j \) is calculated from

\[ f_j = \int_{a_{\text{low},j}}^{a_{\text{up},j}} f(\alpha) \, d\alpha. \]  

(2.39)

The effect on the resolution, \( R \), of the set of logarithmically equidistant intervals on \( N_{\text{min}} \) was investigated. \( R \) is defined as

\[ R = \ln \left( \frac{\alpha_{\text{up},j}}{\alpha_{\text{low},j}} \right). \]  

(2.40)

Obviously the limiting case is where \( R = 0\% \), which corresponds to the original continuous distribution. The other extreme is reached for large values of \( R \), when the continuous distribution is replaced by one loguniform distribution. If the positions of the lower and upper boundaries of the individual loguniform distributions are symmetrically distributed around \( E\{\alpha\} \), \( \alpha_{\text{low},j} \) and \( \alpha_{\text{up},j} \) are found from

\[ \alpha_{\text{low},j} = E\{\alpha\} \exp [(j_{\text{min}} + j - 0.5) R], \]  

(2.41)

\[ \alpha_{\text{up},j} = E\{\alpha\} \exp [(j_{\text{min}} + j + 0.5) R]. \]

Here \( j \) ranges between 0 and the number of intervals. The total range, \( \alpha_{\text{min}} \) to \( \alpha_{\text{max}} \), is taken as the 0.5 and 99.5% points of the cumulative distribution:
Figure 2.13 Discretization of a lognormal distribution as function of the ratio of $R$ over $ln\sigma$; $R/ln\sigma=0.5$ (top left), 1 (top right), 2 (bottom left) and 4 (bottom right), $ln\sigma=0.4$.

\[ j_{\text{min}} = \frac{I}{R} \ln \left( \frac{\alpha_{\text{min}}}{E\{\alpha\}} \right) - 1, \]

\[ j_{\text{max}} = \frac{I}{R} \ln \left( \frac{\alpha_{\text{max}}}{E\{\alpha\}} \right) + 1. \]

Equation (2.42) demarcates the actual number of intervals, $s$:

\[ s = j_{\text{max}} - j_{\text{min}}. \]

A convenient dimensionless measure for the degree of discretization is the ratio of the resolution over the width of the size distribution, expressed as the geometric standard deviation, $ln\sigma$:
\[
\frac{R}{\ln \sigma}
\] (2.44)

The number of intervals is approximately constant for a fixed ratio of \( R \) to \( \ln \sigma \) and is given in Table 2.4.

<table>
<thead>
<tr>
<th>( R/\ln \sigma )</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( s )</td>
<td>34</td>
<td>19</td>
<td>11</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

When \( R \) becomes of the order of \( 4 \ln \sigma \), the lognormal distribution is approximated by 7 loguniform distributions. This is shown in Figure 2.13. Deviations in the scattering pattern constructed from the discretized distribution are

Figure 2.14 The distortion of the intensity signature of the \( \ln \sigma = 0.02 \) distribution presented in Figure 2.6 (bold) plotted against two approximating loguniform distributions.
expected when $R$ becomes comparable to $\ln \sigma$. Examples of reconstructed scattering patterns are presented in Figure 2.14. It is obvious that discretization introduces smoothing proportional to the width of the intervals at the higher scattering angles but that the first lobe remains almost the same. This stems from the fact that the central part of the size distribution is much better approximated than the extremities. The question raised is whether the approximate pattern could be discerned from the true pattern, taking into account the variability of the pattern. Hereto the $\Delta$ criterion of (2.33) is applied, where $I_{\text{app}}(\theta)$ is replaced by the intensity $I_{\text{discr}}(\theta)$ resulting from the discretized model. To answer this question the effect of the width of the distribution, its mean size, and the ratio $R/\ln \sigma$ was investigated. The results are presented as the minimum number of particles required to observe differences and are summarized in Figure 2.15.

It is important to realize that the comparison made is of differences created in the light scattering patterns. Consequently, the result may appear contradictory to

*Figure 2.15 The effect of discretization expressed as the minimum number of scatterers needed to observe differences, for $\ln \sigma$=0.02 (top), 0.1 (middle) and 0.4 (bottom) as function of the ratio $R/\ln \sigma$. 
what would intuitively be expected. For example, the best fit is not obtained at small values of the ratio $R/ln\sigma$, in these simulations the lower limit was 0.1, but a maximum appears around $R=2ln\sigma$. This maximum shifts to $R=1.5ln\sigma$ for $ln\sigma=0.1$ and to $R=2.5ln\sigma$ for $ln\sigma=0.4$. The number of equidistant intervals needed to approximate the lognormal size distribution varies accordingly between 9 and 16. This result coincides remarkably well with the optimum number of size classes found in the experiments, as will be discussed in Chapter 4. Clearly, a penalty is to be paid when the resolution is ill-chosen, either too low or too high. In the first case the approximating scattering pattern simply becomes too coarse. Increasing the resolution, on the other hand, introduces a better match in the absolute sense but results in a large number of small differences. The fact that only relative patterns can be discerned, therefore explains the paradox. An optimum similarity on a relative basis is apparently reached around $R=2ln\sigma$. This feature is most pronounced for the narrowest distributions, due to a bad approximation of the steep slope involved. Secondly, when the mean diameter of the discretized size distributions is decreased, it becomes more difficult to discriminate from the continuous distributions. This again is due to the fact that only relative patterns are compared which become smoother for smaller particles. Thus, higher angles are required in order to observe differences between small particles. Alternatively, one could also increase the number of observations. Here the maximum scattering angle was kept at 15°. For mean sizes the dependence on the width of the distribution is almost negligible. Comparing the magnitude of the systematic errors introduced by approximation of Mie by Fraunhofer, it is seen, that, the error introduced is 100 to $10^4$ times bigger than can be caused by discretization.

Assessment of Intensity Fluctuations

A description of the nature of the intensity fluctuations as a function of scattering angle is required to assess the magnitude of the uncertainties introduced by the size distribution itself. These will further restrain the maximum resolution at which the size distribution can be recovered in an actual measurement. Because the individual scattering patterns of the contributing
particles are uncorrelated, an analytical expression for the distribution of the intensity fluctuations is unattainable. In order to evaluate the variance of this distribution for a particle system the ‘bootstrap’ method was applied. The bootstrap method has recently gained attention as a powerful tool to infer the distribution of an estimator which is a complicated function of its observations (Efron 1986). The method needs a series of observations that are generated by a Monte Carlo simulation of the scattered intensity for a range of angles. Here each observation is created by randomly selecting a particle from the size distribution, calculating its scattering pattern and by storing the result. If this operation is repeated many times, the size distribution composed of the selected particles should approach the true size distribution, assuming that the probability for the individual particles to be selected is in accordance with the density function of the size distribution. The estimated intensity, $E\{I(\theta)\}$ is then simply approximated by the average of all observations. For sufficient observations this value is analogous to the result obtained after integration of the size distribution as in (2.20). The second step is to construct a bootstrap sample by randomly making selections from the set of observations without removing the selected observation from the set, ie, allowing duplicate selections. The number of selections follows a Poisson distribution where the mean is equal to the number of observations. Next, the estimator of this sample is computed in the same manner as described before. This second step is repeated several times to create a large number of estimators for the successive bootstrap samples. The distribution of $E\{I(\theta)\}$ is examined by plotting a histogram of the bootstrap estimators or by computing the quan-tiles. The quantiles of a distribution are obtained by picking an element from the sorted series of estimators, for example, the 25% quartile or the 50% median. The major advantage of using quantiles to characterize the intensity distribution is that it is possible to identify skewed distributions and to improve the robustness, that is to minimize the risk of including outliers.

The bootstrap method was applied to study the intensity fluctuations of the three size distributions of Figure 2.6. One thousand particles were selected from each size distribution and the scattered intensity at 30 angles was calculated. For each angle a series of 1000 bootstrap estimators was created. The 25 and 75% quartile values of the scattered intensity were computed for the three size
Figure 2.16 Distribution of the 25 and 75% quantiles of the intensity fluctuations for the patterns of Figure 2.6, $ln\sigma = 0.02$ (+), 0.1 (□) and 0.4 (■), based on 1000 bootstrap estimators.

distributions. The magnitude of the fluctuations was expressed as the relative deviation from the $E\{I(\theta)\}$ value. The results are depicted in Figure 2.16. The areas enclosed by the quartile contours grow wider, up to 4% of $E\{I(\theta)\}$, as the width of the distribution increases. In other words, the location of the average pattern is less pronounced and it would take an increasing number of observations to establish its true location. Secondly the contours are definitely a function of the scattering angle. An striking example of fluctuating behavior is found around $1^\circ$ for the widest size distribution and around $5-6^\circ$ for the other two. These positions could be very useful as a means to examine the width of a size distribution, as they move to larger scattering angles when the size distribution becomes narrower.

The characteristics of the intensity fluctuations were investigated by plotting the complete series of bootstrap estimators as a frequency distribution. The results are shown in Figure 2.17 for three angles. The distributions of the es-
timators are symmetrical and follow nearly normal distributions. The fluctuating behavior for \( \ln \sigma = 0.4 \) at \( 1^\circ \) is reflected in a very broad, smeared out distribution, where the changes of all possible outcomes are virtually identical. Secondly, at \( 6^\circ \) the distributions of the fluctuations are interchangeable. At this scattering angle no identification of either one of the three size distributions is possible from examination of the relative fluctuations. The average width of the intensity distributions is clearly a function of \( \ln \sigma \), that is when \( \ln \sigma \) increases so does the width, but no direct relationship was found.

Equation (2.32) was used to calculate the standard deviation, \( \sigma \), as the square root of \( \text{Var}\{I(\theta)\} \). In order to compare the results with the bootstrap results of Figure 2.16, the \( \pm 0.67\sigma \) profiles of the relative intensity fluctuations were plotted in Figure 2.18, to coincide with the 25 and 75% quartiles for a normal distribution. \( N \) was taken to be 1000, the number of bootstrap estimators. A striking similarity with the results depicted in Figure 2.16 is found. The sharp increase in the fluctua-

\[ \text{Figure 2.17 Estimated distribution of scattered intensities at } 1 \text{ (top), } 6 \text{ (middle) and } 15^\circ \text{ (bottom), developed from the lognormal size distributions of Figure 2.6.} \]
Figure 2.18 Theoretical profiles of the ± 0.67σ limits of the intensity fluctuations derived from (2.32), assuming a normal distribution.

isations at 1° for lnσ=0.4, at 5° for lnσ=0.1 and at 6° for lnσ=0.02 are completely confirmed. This result means that the theoretical derivation of the intensity fluctuations is relevant and is a proper descriptor of the phenomenon. The contribution from concentration fluctuations alone is constant for all scattering angles and is inversely proportional to the square root of the number of particles. For Figure 2.18 this amount follows directly by substitution of (2.32):

$$\frac{\sqrt{\text{Var}\{I(\theta)\}}}{\text{E}\{I(\theta)\}} = \frac{0.67}{\sqrt{1000}} \times 100\% = 2.1\%.$$  

This line forms the lower limit of the fluctuations. The distinct characteristics in the fluctuation patterns are then due to the effect of redistribution. In Figure 2.19 the ratio of the redistribution effect to the total fluctuation is shown.
for size distributions with different degree of polydispersity:

\[
\frac{L_2(\theta) - L^2(\theta)}{L_2(\theta)}
\]

(2.45)

It illustrates that, in a scattering experiment, redistribution effects of the size distribution play an important role in the magnitude of the fluctuations. It further indicates that the locations of the maxima are dependent on the width of the distribution. Measurement of the angles of maximum fluctuation could serve as an additional tool to retrieve the width of the size distribution examined.

In Figure 2.20 the dependence of the total fluctuations is plotted as a function of \( E\{x\} \) while \( \ln \sigma \) is kept constant. The 0.1, 1 and 2 \( \mu m \) profiles are very smooth and slowly decrease with scattering angle. For the next three sizes, 5, 10 and 20 \( \mu m \), the profiles start to oscillate and minima and maxima appear. The primary maximum shifts to smaller scattering angles with increasing size.

![Image](image.png)

**Figure 2.19** The contribution to the total fluctuations from redistribution effects for lognormal size distributions with \( E\{x\} = 10 \mu m \).
Figure 2.20 Predicted fluctuations for lognormal size distributions with \( \ln \sigma = 0.1 \). The average number of particles is 1000. Statistical changes in the number concentration alone account for 2.1% of the fluctuations.

A closer look at the spectrum reveals that the distance between two successive maxima is inversely proportional to the mean size of the distribution. For example, for 20 \( \mu m \) we find 1.5° and for 5 \( \mu m \) the maxima span about 6°. This means that the number of fluctuation maxima detected contains information about the mean size of the particle size distribution. This spectrum is compared with the distribution of scattered intensity for the 20 \( \mu m \) size distribution in Figure 2.21. Incorporation of the complete spectrum of observed fluctuations in the inversion step, helps in restoring the size distribution and provides an estimate of its confidence intervals (Boxman et al. 1991), but could, therefore, also be useful as a direct means to assess the mean size and width of a particle distribution.
Validation of Light Scattering Models...

Figure 2.21 Distribution of scattered intensity and fluctuations developed from a lognormal size distribution with $E(x) = 20 \, \mu m$ and $\ln \sigma = 0.1$.

Conclusions

The proposed criterion $N_{min}$ gives an estimate for the theoretical number of particles needed to discriminate between approximations and the complete theory under ideal conditions. The criterion accounts for the fact that particles move in and out of the optical cell during the measurement which results in intensity fluctuations. It provides an objective measure to investigate trends and relationships. Noticeable is the prediction that the Fraunhofer approximation may give proper sizing results, even for sub micron sizes. This is inherently caused by the detection system where only relative scattering patterns are collected. It was also found that the Fraunhofer model is unable to differentiate accurately between particle systems with quite different refractive indices. Typically, $N_{min}$ decreases with $x^4$ until $x = 10 \, \mu m$, and then becomes constant.
A very weak function of the width of the distribution was noticed.

Discretization of the size distribution has been examined. It was shown that a best match is found in the range of $R=1.5\ln\sigma$ to $R=2.5\ln\sigma$. This translates to 9 to 16 size classes. Decreasing the mean size of the size distribution makes it more difficult to discriminate between the discretized and continuous distribution. This finding depends also on the maximum scattering angle observed. Increasing the width of the size distribution reduces the similarity of the approximation. The effect of discretization is less than replacing the Mie solution by a Fraunhofer model by a factor of 100 to $10^4$.

In the last section the nature of the intensity fluctuation was addressed. The theoretical derivation for the stochastic variation of the scattering pattern was verified with a bootstrap simulation. The analytical expression, based on discrete scattering events and modeled with Poisson statistics, was completely confirmed in this exercise. Secondly it was demonstrated that the fluctuations are a function of scattering angle due to so-called redistribution effects. Added to these fluctuations is the effect of concentration fluctuations, which are constant with scattering angle. The fluctuation patterns exhibit clear minima and maxima, which are very specific for the width of the distribution, and thus may form an attractive indicator for the polydispersity of the sample. Finally, the distance between two maxima in the fluctuation spectrum is directly related to the mean size of the distribution. The study of the variability of the scattering pattern may, therefore, not only be used as a weighting function to validate models, but also yields useful properties about the size distribution itself.

Appendix A. Numerical Implications

Integration
Some of the calculations presented in this chapter were quite lengthy, and some effort was put into optimization. The basic problem was to get an accurate description of the scattered intensity as function of the size distribution and scattering angle. In the case that the detector itself covers an angular range, as is the case in practice, a double integral arises of the kind
\[ \overline{I}(\theta, \alpha) = K \int_{\theta}^{\theta+\Delta \theta} \int_{\alpha}^{\alpha+\Delta \alpha} i(\theta, \alpha, m) f(\alpha) \, d\alpha \, d\theta. \] (A.1)

Dividing the angular and size ranges into a fixed number of intervals may lead to very grave inaccuracies. In order to maintain the same relative accuracy over the whole size range and angular range simultaneously, a recursive integration scheme was implemented. In addition, Romberg’s method was implemented. This uses a higher order scheme for extrapolation of the successive refinements and is an excellent method for smooth integrands. Both integrals were split into a well defined number of sections to avoid aliasing, singularity points and premature convergence. The intensity function exhibits an oscillatory behavior for both \( \alpha \) as well as \( \Theta \). We found that a section with a size equal to a quarter of the wavelength of the oscillation was a suitable size. Another concern was
to decide at which section to start the integration, since the contributions from the particles at the 'tail' of the size distribution are considerably less than the accuracy required. A straightforward approach was to choose the second moment of the size distribution as the starting point for the computations, since for large enough particles the scattered intensity is proportional to their cross-section. Additionally, during the integration, the integration error was decreased as the contributions of the individual sections to the integral became less. The final code was based on object-oriented programming (Verheijen 1991). An example is presented in Figure A.1. The scattering pattern developed from a lognormal distribution with $E\{x\}=10 \, \mu m$ and $\ln \sigma=0.4$ is calculated. The size boundaries for this distribution, in which 99.5% of the particles are contained, are $4.2 \, \mu m$ and $240 \, \mu m$. From the graph it can be seen that the relative contributions decrease rapidly. Similarly the integration error is raised, although at a slower rate, in order to preserve overall accuracy. Since the intervals are based on the wavelength used, many more points are found at the larger end the distribution. Implementation of this procedure saved computation time and ensured the required accuracy.

**Mie routines**

Many researchers have worked on a practical numerical expression for the Mie solution (eg, Dave 1969, Lentz 1976, Wiscombe 1980, Ungut et al. 1981). Here the routine described by Bohren and Huffman (1983) was adopted. This method utilizes $n_{\text{max}}$ terms to achieve proper convergence for the Mie coefficients $a_n$ and $b_n$:

$$n_{\text{max}} = \alpha + 4 \alpha^3 + 2.$$  \hspace{1cm} (A.2)

Instability problems were found to occur for large values for the size parameter $\alpha$. The code was adapted for a PC, the recurrence relation for the phase functions was changed and some precautions were taken to prevent numerical inconsistencies. A vector structure was used to integrate size distributions over a finite angular range. Double precision was used in the algorithm. With this approach the intensity patterns and all the other related parameters were accurately calculated for $\alpha$ larger than 15000. For larger particles the PC has
**Table A.1** Comparison of parameters generated by Mie algorithms.

<table>
<thead>
<tr>
<th></th>
<th>Wang-Van der Hulst</th>
<th>Boxman-Verheijen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha=0.0001$</td>
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<td>$Q_{ext}$ 2.3068E-17</td>
</tr>
<tr>
<td>$m=(1.50-0.0i)$</td>
<td>$Q_{abs}$ 0.0</td>
<td>$Q_{abs}$ 0.0</td>
</tr>
<tr>
<td></td>
<td>$Q_{back}$ 3.4602E-17</td>
<td>$Q_{back}$ 3.4602E-17</td>
</tr>
<tr>
<td>$\alpha=100$</td>
<td>$Q_{ext}$ 2.0944</td>
<td>$Q_{ext}$ 2.0944</td>
</tr>
<tr>
<td>$m=(1.50-0.0i)$</td>
<td>$Q_{abs}$ 0.0</td>
<td>$Q_{abs}$ 0.0</td>
</tr>
<tr>
<td></td>
<td>$Q_{back}$ 1.7362</td>
<td>$Q_{back}$ 1.7368</td>
</tr>
<tr>
<td>$\alpha=1570.7963$</td>
<td>$Q_{ext}$ 2.01445</td>
<td>$Q_{ext}$ 2.01445</td>
</tr>
<tr>
<td>$m=(1.342-0.1i)$</td>
<td>$Q_{abs}$ 0.93354</td>
<td>$Q_{abs}$ 0.93354</td>
</tr>
<tr>
<td></td>
<td>$Q_{back}$ 0.023106</td>
<td>$Q_{back}$ 0.023106</td>
</tr>
<tr>
<td>$\alpha=18599^*$</td>
<td>$Q_{ext}$ -</td>
<td>$Q_{ext}$ 2.00254</td>
</tr>
<tr>
<td>$m=(1.5-0.0i)$</td>
<td>$Q_{abs}$ -</td>
<td>$Q_{abs}$ 0.0</td>
</tr>
<tr>
<td></td>
<td>$Q_{back}$ -</td>
<td>$Q_{back}$ 120.06226</td>
</tr>
</tbody>
</table>

* The largest value for $\alpha$ that could be handled by the PC.

**Table A.2** Comparison of CPU time (s) needed to evaluate Mie coefficients.

<table>
<thead>
<tr>
<th>$\alpha=\pi x/\lambda$</th>
<th>Bohren-Huffman</th>
<th>Boxman-Verheijen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m=(1.50-0.0i)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.212</td>
<td>6.4E-3*</td>
</tr>
<tr>
<td>5.2</td>
<td>0.535</td>
<td>20.0E-3</td>
</tr>
<tr>
<td>100</td>
<td>3.75</td>
<td>17.6E-2</td>
</tr>
<tr>
<td>250</td>
<td>8.55**</td>
<td>38.8E-2</td>
</tr>
<tr>
<td>500</td>
<td>16.5</td>
<td>7.6E-2</td>
</tr>
</tbody>
</table>

| $m=(1.50-0.1i)$         |                |                  |
| 0.1                     | 0.267          | 6.4E-3           |
| 5.2                     | 0.680          | 19.6E-3          |
| 100                     | 4.85           | 16.8E-2          |
| 250                     | 11.10          | 38.8E-2          |
| 500                     | 21.4           | 76.0E-2          |

* The values are all based on a PDP 11/23.
** The Bohren-Huffman routine showed instabilities for $g>250$. 
insufficient memory to run the program. The results were verified extensively and proved to be accurate. Wang and Van der Hulst (1991) presented data on a comparison between an Airy approximation and various Mie routines. They indicated that the original Bohren-Huffman routine suffered from numerical instabilities for $\alpha > 250$. Table A.1 shows how well the results are in agreement with the data generated by Wang, both for non-absorbing and absorbing particle systems.

In the same article, computing times of the original algorithm by Bohren and Huffman were presented, based on calculation on a PDP 11/23. These times are of the same order as is achieved with the other existing algorithms. In order to make an appropriate comparison of the effectiveness of this algorithm, the calculation time, based on a HP 486/25 was converted. Based on data provided by Digital Equipment a performance ratio of 40 between the HP 486/25 and PDP 11/23 was estimated. The results are summarized in Table A.2. It shows that the algorithm is 20 to 30 times faster for non-absorbing particles and 30 to 40 for the absorbing case. This makes it feasible to run Mie computations, even on a PC with modest capabilities.

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Symbols and Abbreviations

\[a,b\]  
Mie scattering coefficients.

\[C\]  
Observed cross section of particle.

\[D\]  
Beam width of illuminating laser source.

\[E(q)\]  
Expected value of stochastic variable \(q\).

\[f(\alpha)\]  
Size distribution function.

\[f_j\]  
Fraction of particles contained in class \(j\).

\[G\]  
Geometrical cross section.

\[I\]  
Scattered intensity.

\[i\]  
Scattering function.

\[K\]  
Constant.

\[k\]  
Wave number or propagation constant.

\[L\]  
Scattering function integrated with size distribution function \(f(\alpha)\).

\[L_2\]  
Square of scattering function integrated with \(f(\alpha)\), generally \(\neq L^2\).

\[l\]  
Path length of traversing beam.

\[m\]  
Relative refractive index.

\[N\]  
Average number of scatterers in optical volume.

\[Obs\]  
Obscuration.

\[P\]  
Degree of polarization.

\[P(\nu)\]  
Poisson distribution.

\[p\]  
Power of frequency distribution.

\[PSD\]  
Particle size distribution.

\[Q\]  
Efficiencies.

\[R\]  
Resolution.

\[r\]  
Distance between scatterer and observer.

\[S\]  
Amplitude function.

\[s\]  
Total number of discrete size intervals.

\[T\]  
Transmission.

\[t\]  
Time of scattering event.

\[\text{Var}\{q\}\]  
Variance of stochastic variable \(q\).
\( x \) Particle diameter.
\( z \) Direction of traversing beam.

**Greek**
\( \alpha \) (alpha) Size parameter.
\( \Delta \) (delta) Model discrimination criterion.
\( \lambda \) (lambda) Wavelength.
\( \mu \) (mu) Cosine of the scattering angle.
\( \nu \) (nu) Actual number of scatterers in optical volume at time \( t \).
\( \pi_n \) (pi) Phase function.
\( \rho \) (rho) Phase shift parameter.
\( \sigma \) (sigma) Standard deviation of size distribution.
\( \sigma^2 \) Variance of size distribution.
\( \tau \) (tau) Turbidity.
\( \tau_n \) (tau) Phase function.
\( \theta \) (theta) Scattering angle.
\( \varsigma \) (zeta) Scaling factor.

**Subscripts**
\( \text{abs} \) Absorption.
\( \text{appr} \) Approximated.
\( \text{discr} \) Discretized.
\( \text{ext} \) Extinction.
\( f \) Fraunhofer.
\( \text{Im} \) Imaginary part of complex number.
\( j \) Number of size interval.
\( k,l \) Counters that indicate the particles of \( f(\alpha) \).
\( \text{low} \) Lower.
\( m \) Mie.
\( \text{med} \) Medium.
\( \text{min} \) Minimum.
\( n \) Index of Mie term.
\( o \) Reference value.
\( \text{part} \) Particles.
\( \text{Re} \) Real part of complex number.
\( \text{sca} \) Scattering.
\( \text{upp} \) Upper.
\( 1 \) Perpendicular direction.
\( 2 \) Parallel direction.
DECONVOLUTION ALGORITHM FOR THE RECOVERY OF PARTICLE SIZE DISTRIBUTIONS

Abstract. A deconvolution algorithm is presented for the interpretation of light scattering patterns to determine a finite number of parameters of the particle size distribution. The proposed deconvolution procedure incorporates the stochastic nature of the observed intensities. This procedure constitutes an improvement of the solution since it provides error intervals and offers a better means of model discrimination.

Introduction

All of the strategies currently used to measure particle size distribution by deconvolution of forward light scattering experiments are based on the comparison of a light scattering model, which contains a set of calculated light intensity patterns, and the mean values of the recorded intensity pattern. In order to reconstruct the particle size distribution which causes this pattern an inversion algorithm is applied, based on either matrix inversion, integral transformation or a combination of both. The success of the deconvolution procedure depends upon the type of inversion technique employed and upon a proper choice of the parameters which describe the recorded light scattering pattern and which are contained in the model matrix.

In this chapter the development of a model-independent deconvolution procedure is discussed, that is no 'a priori' information about the size distribution is provided to the algorithm. This means that no assumptions are made about the shape of the particle size distribution. An alternative would be to assume that the particle size distribution follows a Normal, Log-Normal, Rosin-Rammler or some other type of distribution. The procedure incorporates the mean scattered intensity and its standard deviation. The use of the standard deviation provides a measure to assess the 'goodness-of-fit' of the deconvolution
step and is used to obtain confidence intervals for the resulting particle size distribution. Also a better understanding of the effects of measurement time, concentration and model matrix on the derived size distribution was pursued. Experimental verification of these goals is presented in Chapter 4.

Survey of Inverse Problems

Inverse problems are concerned with making estimates of the model parameters based on observed data and forms a natural opposite to the forward problem where the model parameters are already known and the data can be predicted (Menke 1984):

\[ \text{Forward problem:} \]
\[ \text{model parameters} \rightarrow \text{model} \rightarrow \text{prediction of data} \]

\[ \text{Inverse problem:} \]
\[ \text{data} \rightarrow \text{model} \rightarrow \text{estimates of model parameters} \]

The data usually reflect specific properties of the system studied, in this case the scattering pattern developed from a particle size distribution. A physical model to describe the problem must already be available beforehand. In general, however, it is possible to validate whether the model used is appropriate.

Inverse problems are found in many domains of applied science. Examples include x-ray diffraction to reveal molecular structures, tomography, seismology, microscopy, astronomy and light scattering (see for example Tikhonov and Arsenin 1977). Another example is 'system identification', \textit{ie}, finding the physical parameters from observations of the evolution of a dynamic system and characterizing the past states of that system. Typically in inverse problems the state of a system is interrogated by emitting a known amount of radiation of some sort from a well defined source. Next the interaction of this radiation with the system under study is examined by one or more detectors. The observations, an attenuation or scattering spectrum, which together form the data function, \( g \), are subsequently translated to reveal the set of unknown model parameters, the object function \( f \). If the problem is linear in nature, or can be approximately linearized, the following result is obtained:
Af = g \quad \quad (3.1)

A is a linear operator which represents the model. In many cases A is an integral operator, and a Fredholm equation of the first kind arises:

\[ \int K(x,y)f(y)dy = g(x), \quad (3.2) \]

where \( K(x,y) \) is called a kernel function. Several approaches exist to find the solution of this type of integral equation. This translation step itself is termed the deconvolution process but is also referred to in the literature as data inversion or unfolding (Groetsch 1977, Bertero 1986).

A direct algebraic approach to determine the model parameters may yield results which are physically unacceptable, for example negative temperatures, concentrations or size fractions. The latter occurs when application of the solution obtained produces an estimated data vector, \( \hat{g} \), quite similar to the measured one. Apparently, the information contained in the data can easily be distorted by contaminating finite measurement errors, leading to one or more of the following symptoms (Engl 1991):

- Amplification of high frequency errors;
- Restoration of stability by adding \textit{a priori} information;
- Intrinsic loss of information;
- Problem of finding optimum discretization parameter;
- Highly oscillatory solutions which are physically irrelevant.

Generally, such problems are said to be ill-posed or maybe better, improperly posed and violate one or more of Hadamard's postulates of 'well-posedness' (Hadamard 1923):

- For all data contained in \( g \), a solution exists;
- For all data, the solution is unique in \( f \);
- The solution depends continuously on the data.

The second condition constitutes one of the main problems, since usually a
whole range of solutions is feasible. Even if the data are measured with complete accuracy, they may not convey sufficient information on the desired parameters. Thus, proper detector location is crucial. Also premature truncation of a spectrum will dramatically reduce the information content. Finally, discretization will further decrease the uniqueness of the solution.

The main techniques encountered are integral transformation (eg, Shifrin and Kolmakov 1966, Perelman and Shifrin 1980, Koo 1987), expansion in eigenfunctions (eg, Bertero et al. 1985, Pike 1986), using Fourier series (Lanczos 1964), or numerical quadrature (Phillips 1962, Twomey 1963). These authors have all introduced specific features to circumvent the instability problems. Applying these features to improve the condition of the problem is called regularization. A version of the latter method to deconvolute scattering patterns is adopted in this chapter. This entails discretization of the integral in (3.2) into a sum of linear equations. The arguments which support such an approach include:

- The flexibility to implement different kernel functions. If more refined physical aspects are to be included into the physical model, an analytical solution for that particular kernel function may be arduous, or even impossible to find. An example of this can be found in the field of light scattering where analytical transforms of the Fraunhofer kernel function have been generated (Bertero and Pike 1983, Bertero et al. 1985). Expressions for the Mie solutions are still complicated although some results have been published (Arridge et al. 1989). In general, therefore, it is more straightforward to build the physical model, discretize it, and compute the coefficients of matrix $A$;

- Storage of the coefficients of the precalculated kernel function is simple and holds for all the subsequent measurements. This increases the speed of the deconvolution step;

- Once the coefficients are computed and stored, they provide a convenient means to change the resolution and grid of the object function. The latter is important if the requirement is to monitor a slowly changing process with the same overall accuracy. Secondly, the resolution required can be easily adjusted to comply with the quality of the measurement, that is the observed
signal to noise ratio;

- Kernel functions usually have smooth characteristics and therefore require only a few points to achieve sufficient approximation. In other words, increasing the number of points in the object function is ineffective since obtaining this accuracy from the integral transform is a very wearisome task and, in practice, not feasible, due for instance, to the poor resolution of the detector itself (Twomey 1977).

If an exact solution is absent a pseudo- or generalized solution is put forward. In this chapter a least-squares solution is proposed which minimizes the distance

$$|Af-g|,$$  \hspace{1cm} (3.3)

where $\| \|$ denotes the Euclidean length of the vector, by applying the so-called $L_2$-norm:

$$\|e\|_2 = \sqrt{\sum_i |e_i|^2}.$$  \hspace{1cm} (3.4)

In (3.4) $e_i$ is the prediction error, which measures the distance between the observed and computed data sets. The reason for adopting the $L_2$-norm is the assumption that the data follow Gaussian statistics. A relatively higher penalty is given, therefore, to those data which cause large prediction errors. Higher order norms put more and more emphasis on the larger prediction errors, whereas the $L_1$-norm treats all errors equally. Therefore, it is important to know the statistics of the observed data and, secondly, to devise effective filtering methods which eliminate outliers (Menke 1984). It can be proven that the least-squares solution exists and is unique and that the problem can be said to be well-posed.

In order to map the data vector onto the pseudo-solution some generalized inverse, $A^e$, is necessary. In this chapter, an overdetermined system is considered, that is, the number of linear equations exceeds the number of unknown model parameters, and the inverse takes the following form:
\[ A^{-g} = (A^T A)^{-1} A^T. \] (3.5)

Then the degree of instability of the problem, *ie*, the error transmission from the data into the solution, is typified by \( \text{cond}(A) \), the condition number of the model matrix \( A \):

\[
\text{cond}(A) = |A| |A^{-g}|. \] (3.6)

The factor \( \text{cond}(A) \) only expresses a qualitative measure for the 'well-posedness' of the problem but may be used to find the optimum scaling (Gentry and Calabrese 1986, Hirleman 1987, Bertero et al. 1988, Cooper and Wu 1990). In the next section, the method of numerical quadrature, is used to retrieve particle size distributions from observed light scattering patterns.

**Deconvolution of Light Scattering Patterns**


In a forward light scattering experiment, all particles present in the optical measuring volume contribute to the scattering pattern received by the photodiode array detector. The size of this volume is set by the width of the incident laser beam and the path length between the optical windows of the sample cell. The collecting transform lens, mounted behind the sample cell, focuses all individual scattering patterns onto the detector. The detector consists of 31 channels \( (n) \), which are in fact semi-circular rings. An additional detector

![Figure 3.1. Multi-element detector positioned in the backfocal plane of the collecting lens. A hole in the center is used to align the optical system and to measure the particle concentration.](image-url)
in the center is used to align the laser and measures the transmission by collecting the unscattered incident light (Figure 3.1). The detection angle covered by each ring is a function of its radial position and the focal length of the collecting lens used. A more detailed description of the instrument, including the dimensions of the detector rings, is given in Hirleman (1984). One read-out of all successive channels is henceforth referred to as a sweep. The final recording after a sweep contains an integrated intensity pattern, or energy pattern, which is then digitized by a 10 bit A-D converter and subsequently stored in the computer. A typical optical arrangement for forward light scattering experiments is depicted in Figure 3.2. The instrument used to record the scattering patterns was a Malvern 2600 Particle Sizer, equiped with a 5 mW He-Ne laser with a beam width of 9 mm.

In the method of numerical quadrature, the contributing particles are divided into $m$ discrete size classes and the scattering pattern recorded by $n$ detectors is written as a set of linear equations:
$$
\begin{pmatrix}
L_1 \\
L_2 \\
\vdots \\
L_n
\end{pmatrix}
= 
\begin{pmatrix}
a_{11} & a_{12} & \cdots & a_{1m} \\
a_{21} & a_{22} & \cdots & \cdots \\
\vdots & \vdots & \ddots & \vdots \\
a_{n1} & \cdots & a_{nj} & \cdots & a_{nm}
\end{pmatrix}
\begin{pmatrix}
q_1 \\
q_2 \\
\vdots \\
q_m
\end{pmatrix}
+ 
\begin{pmatrix}
\epsilon_{e1} \\
\epsilon_{e2} \\
\vdots \\
\epsilon_{en}
\end{pmatrix}
$$

(3.7)

In vector notation this reads

$$
L = Aq + \epsilon_e,
$$

(3.8)

where $L$ is the vector of the integrated light intensity, $A$ is the discretized kernel function or scattering matrix which contains the scattering coefficients $a_{ij}$ calculated according to the scattering function employed (e.g., Fraunhofer, anomalous diffraction or Mie theory), $q$ is the solution vector with the model parameters which contains the fraction of particles in each size class and $\epsilon_e$ represents the unknown experimental measurement error on $L$. Systematic errors in $L$ are propagated in the deconvolution step and are in some way consolidated into $q$. Various causes for the inclusion of experimental systematic errors may be identified:

- Misalignment of the optical system;
- Drifting laser intensity;
- Corrupted calibration factors for the multi-element detector;
- Inhomogeneous dispersion of the particles;
- Flaws in the collecting lens;
- Incorrect assessment of the background signals;
- Divergence of the incident beam.

The above list is far from complete and care should be taken in order to avoid these error sources since they directly affect the merit of the final solution. Systematic errors may also originate from the mathematics of the translation step and by assuming an incorrect scattering model.
The least squares solution of \( q \) is obtained by direct inversion of the set of linear equations. With \( n > m \) the system is overdetermined and the least squares estimators for \( \hat{q} \) are given by (eg, Lawson and Hanson, 1974):

\[
\hat{q} = (A^T A)^{-1} A^T L.
\]  

(3.9)

However, as discussed in the previous section, deconvolution by direct inversion often fails due to the measurement errors included in \( L \) and systematic errors contained in the scattering model matrix, \( A \). The set of equations for the solution is subject to severe oscillations and may yield negative equivalent fractions for some elements of \( \hat{q} \).

Several numerical methods have been developed to overcome the ill-conditioning of the inverse problem of (3.9): the Phillips-Twomey smoothing technique (Phillips 1962 and Twomey 1963), the Backus and Gilbert method (Backus and Gilbert 1967) and the Chahine iteration (Chahine 1968). Illustrative comparisons on the aspects of accuracy, stability and resolving power can be found in Fymat (1975) Wolfson et al. (1979a), Wolfson et al. (1979b) and Riley and Agarwal (1991).

The Phillips-Twomey (PT) inversion scheme is widely used, in particular in the field of forward light scattering, and therefore deserves some further attention. With this technique the oscillatory behavior of the solution vector is suppressed by adding an additional \( m \times m \)-matrix. This matrix, \( H \), serves as a smoothing matrix, as it effectively links the elements of \( \hat{q} \) by their second order differences. A smoothing scalar \( \gamma \) determines the extent of smoothing assimilated in the final solution,

\[
q = (A^T A + \gamma H)^{-1} A^T L.
\]  

(3.10)

The optimal choice of \( \gamma \) is left to the discretion of the user and is, in practice, determined by trial and error. The selected value is then used for a whole range of subsequent measurements, as for instance in the case of on-line process control. Furthermore, its absolute value depends on the coefficients included in the model matrix \( A \) which is often arbitrarily scaled. Inconsistent scaling makes a comparison with previous work irrelevant. The advantage of this modified model matrix inversion step is its speed compared to iterative procedures. The
main drawback is the inclusion of smoothing in \( \hat{q} \), particularly for narrow or irregular size distributions, since the solution was intrinsically designed to operate on smooth solutions only. Secondly, the absence of nonnegative size fractions is not guaranteed by the introduction of smoothing. Reviews of this method are presented by Chow and Tien (1976), Caroon and Borman (1979), King (1982) and Heuer and Leschonski (1985).

In order to eliminate the effects of smoothing and at the same time enhance both the speed and stability, another method of direct matrix inversion was designed. The following list of criteria were posed:

- Negative size fractions are unacceptable;
- Reliability, the same scattering pattern should result in the same size distribution. Thus the solution must be unique;
- Accuracy, the model parameters obtained should be representative of the actual size distribution;
- Speed, to allow measurements to be done for process control;
- Robustness. The solution should converge for all situations independently of starting-values;
- An objective measure for model discrimination;
- Error analysis on the retrieved size distribution, that is, confidence intervals should be assessed;
- Flexible, able to adapt to different resolutions dependent on the signal to noise ratio observed and allowing easy implementation into a software package (such as ROMA, see Chapter 4);
- Provide insight into experimental set-up, for example the optimum number of readings, the detector location and the stability of the collected signals;

Together with some additional features on signal processing which are presented in Chapter 4, these criteria lead to the development of an intelligent system which is able to diagnose itself. In a next step, a fully autonomous sensor should adapt to the changing circumstances in which the measurements are to be performed by selecting the best detector geometry, and thus improving further the results (Hirleman and Dellenback 1989). These particular features are of great importance for control systems which need a constant flow of
validated process outputs.

**Incorporation of Intensity Fluctuations**

When a measurement is performed a number of sweeps, \( s \), is recorded and stored in a computer. The successively recorded scattering patterns are all slightly different. The extent of the fluctuations observed between these patterns varies for each detector ring. This is caused by the following factors:

- Statistical variations of the particle size distribution contained in the optical measuring volume during successive recordings.
- Concentration effects due to local inhomogeneities of the dispersion.
- Non-sphericity of the particles examined, which leads to different scattering signatures for the same particle depending on its orientation in the optical measuring volume.
- Instability of the incident laser intensity.
- Noise introduced by the detector.

These fluctuations cause a sweep-to-sweep variability which can be quantified before entering the deconvolution step. This is achieved by comparing the light energy values for all individual sweeps on each ring. If the observed data are the sum of several independent random variables, the distribution of their sum will approach a Normal or Gaussian distribution which follows from the central limit theorem (Von Mises, 1964). This rather idealized representation predicts that, on average, measurements fall within \( \pm \sigma \) of the true value 68\% of the time and within \( \pm 2\sigma \) 95\% of the time. In practice such a perfect distribution is hardly achieved, and robust estimating techniques may be used, such as the bootstrap method presented at the end of Chapter 2. In addition, the data might be contaminated with outliers which can arise from various sources. These outliers deserve extra care since, otherwise, they lead to erroneous results. If possible they should be detected and subsequently removed by some filtering action. However, it will here be assumed that the intensity fluctuations collected by the detector follow a Gaussian distribution. Then the values on all channels
are characterized by an estimator of the expected value for their mean, \( \hat{\mu} \), and variance, \( \hat{\sigma}^2 \), as follows (see for example Milton, 1986):

\[
\hat{\mu}_i = \frac{\sum_{k=1}^{s} L_{i,k}}{s}
\]

(3.11)

and

\[
\hat{\sigma}_{ii}^2 = \frac{\sum_{k=1}^{s} (L_{i,k} - \hat{\mu}_i)^2}{s(s-1)}
\]

(3.12)

In an analogous manner, the degree of association which exists between the individual detector channels during the measurement can be characterized. The covariance matrix is constructed by comparing all sweeps on channel \( i \) with those on channel \( j \),

\[
\hat{\sigma}_{ij}^2 = \frac{\sum_{k=1}^{s} (L_{i,k} - \hat{\mu}_i)(L_{j,k} - \hat{\mu}_j)}{s(s-1)}
\]

(3.13)

A weighting matrix, \( W \), is now constructed which comprises all the computed variances and is in fact the inverse of the covariance matrix of the measured data:

\[
W = \text{cov}^{-1}(L) = \begin{pmatrix}
\sigma_{11}^2 & \sigma_{12}^2 & \ldots & \ldots & \sigma_{1n}^2 \\
\sigma_{21}^2 & \sigma_{22}^2 & \ldots & \ldots & \ldots \\
\ldots & \ldots & \ldots & \sigma_{ij}^2 & \ldots \\
\sigma_{n1}^2 & \ldots & \ldots & \sigma_{nn}^2
\end{pmatrix}^{-1}
\]

(3.14)

Alternatively, the covariance matrix of \( L \) can be transformed directly into its
corresponding cross-correlation matrix as follows:

$$\rho_{ij} = \frac{\hat{\sigma}_{ij}^2}{\sqrt{\hat{\sigma}_{ii}^2 \hat{\sigma}_{jj}^2}}.$$  \hspace{1cm} (3.15)

Next the equation for the least squares solution is weighted for the observed spread.

A background measurement is performed before the particles have entered the optical measuring volume which assesses the fluctuations caused by the laser, light from the surroundings and the detector itself. The variance of the measurement must be larger than the variance of the background which is thus added as a correction term. Since both variances are caused by random errors the total variance, which is then included in $W$, may be expressed as the sum of the variances observed for the background measurement ($bg$) and the sample measurement ($sm$),

$$\hat{\sigma}_{ii}^2 = \hat{\sigma}_{ii,sm}^2 + \hat{\sigma}_{ii,bg}^2.$$  \hspace{1cm} (3.16)

Finally, weighting with $W$, yields

$$\hat{q} = (A^TWA)^{-1}A^TWL.$$  \hspace{1cm} (3.17)

Weighting takes into account the differences in the measurement error on each channel and the correlation between the channels. If we assume the number of sweeps to be large, the statistical errors in the data vector will approach zero and, consequently, the remaining residuals after deconvolution can be said to be systematic and to stem from either the scattering model, the mathematics or the experiment itself. Added to the method is a nonnegativity constraint which helps to stabilize the solution, that is, to avoid any singularity in the $A^T A$-matrix. If negative elements appeared in $\hat{q}$ then the relevant row in model matrix $A$ was temporarily eliminated and the equation was applied again. This procedure was repeated until only positive elements were obtained and the conditions for the Kuhn-Tucker theorem were fulfilled (Menke 1984). The procedure converges to the same solution independent of the starting values (Verheijen 1991).
Statistical Evaluation of Size Distribution

After deconvolution the derived model parameters must be validated. An obvious first step is to inspect the fit of the model. The mean measured light scattering pattern is compared to the computed pattern which is found by direct substitution:

\[ L_c = A \hat{q} . \]  

(3.18)

The residuals for each detector channel are weighted with the observed total standard deviation of the collected signal, as given in (3.16):

\[ \frac{L_i - L_{c,i}}{\hat{\delta}_{ii}} . \]  

(3.19)

The sum of all the residuals together follows a chi-square distribution, which is also selected as the property to be minimized in the iteration step:

\[ \chi^2_{red} = \frac{\sum_{i=1}^{n} \left( \frac{\hat{\mu}_i - L_{c,i}}{\hat{\delta}_{ii}} \right)^2}{df} , \]  

(3.20)

where \( df = (n - m) \), is the number of degrees of freedom. The value of the reduced chi-square (\( \chi^2_{red} \)) is a measure of the goodness of fit and thus indicates whether the deconvolution has been successful. When \( df \) is large enough, \( \chi^2 \) is normally distributed with mean \( df \) and variance \( 2df \). Qualitatively, if \( \chi^2_{red} \) is unsatisfactorily large, then the profile of residuals will indicate the position of the detector channels with the most serious deviations. In that case the cause for the misfit should be analyzed. Generally, it can be said that a model is acceptable if \( \chi^2 \approx df \) or, alternatively, if \( \chi^2_{red} \) approaches unity. Otherwise, following the chi-square criterion, three causes may be identified for the remaining residuals (Press et al., 1988):

- The scattering model used is inadequate and should be rejected. Although the
underlying physics of the model is correct, e.g., the Fraunhofer diffraction approximation, the selected size range and resolution may be completely inappropriate;

- The random measurement errors are in reality larger than observed. Probably more readings are required to determine a proper estimate of the data distribution;
- The errors are not normally distributed. It is possible to be somewhat more lenient in this respect since, typically, inadequacy of the model dominates.

Secondly, the standard errors of the least squares estimators of the solution vector, \( \hat{q} \), can be studied. Gaussian statistics has been used to construct the covariance matrix of the light energy pattern. This means that the variance of \( \hat{q} \) can be directly derived from its weighted least squares solution as given in (3.17),

\[
\text{cov}(\hat{q}) = \text{cov}((A^TWA)^{-1}A^TWL) \chi_{\text{red}}^2 ,
\]

or

\[
\text{cov}(\hat{q}) = (A^TWA)^{-1}A^T W \text{cov}(L) WA(A^TWA)^{-1} \chi_{\text{red}}^2 ,
\]

\[
= (A^TWA)^{-1} \chi_{\text{red}}^2 .
\]

In the above equations the observed variability in the measurement data is linked to an estimate for the spread in the derived model parameters, in this case, the fractions of the size distribution. As will be shown, it is also possible to assess the actual confidence boundaries of the size distribution.

First, the arbitrarily scaled model parameters must be transformed into fractions, \( f \), in order to represent the particle size distribution. The normalization can be either number \((i=0)\), length \((i=1)\), surface \((i=2)\), or volume based \((i=3)\):
Figure 3.3 Schematic of the search procedure for the lower and upper confidence boundaries of each size fraction. The nonnegativity constraint explains the nod (see circle) in the parabola.

\[ f_{t,j} = \frac{\hat{q}_j x_j^t}{\sum_{j=1}^{m} \hat{q}_j x_j^t} \]  

(3.23)

\( x_j \) is the logarithmic mean of size class \( j \):

\[ x_j^t = \frac{x_{j,\text{max}}^t - x_{j,\text{min}}^t}{t \ln \frac{x_{j,\text{max}}}{x_{j,\text{min}}}} \]  

(3.24)

Then, after the solution with the \( \chi^2 \) that is closest to \( df \) is found, the individual size fractions are varied which will obviously raise the value of \( \chi^2_{\text{red}} \).
The amount of this increase depends on how susceptible the fraction is to small changes. It can be proven that for each fraction a parabolic represents the $\chi^2_{red}$. Due to the nonnegativity constraint, this parabola may consist of several 'sub-parabolas'. Knowing this relationship, pinpointing the confidence boundaries for the fractions involves moving along this parabola by varying one fraction whilst the others are fixed. This continues until the confidence limits for the $\chi^2_{red}$ are encountered. These limits follow directly from the F-distribution, in which two chi-square distributions are compared:

$$\chi^2_{red}(q)_{\text{limit}} = \left( \frac{F_{0.95}(1, df)}{df} + 1 \right) \cdot \chi^2_{red}(q).$$ \hspace{1cm} (3.25)

The shape of the parabola varies to a large degree for all fractions and may range from a deep gully to a rather flat one which represents the steady fractions. Transformation of the confidence boundaries from number based distributions to volume based distributions is not as straightforward as for the optimum size distribution itself. If desired it must therefore be computed separately.

Confidence intervals provide insight in the classical trade-off problem between a high resolution and a small variance of the model parameters on the other side. Increasing the resolution by making the discretization very fine supposedly allows examination of small features present in the size distribution. However, the variability of the model parameters is then large, expressed by a rather narrow version of the parabola depicted in Figure 3.3. This implies that the parameters are very sensitive to small changes. Averaging over a larger size range makes the remaining parameters less susceptible to changes in the observed data at the expense of less resolution (eg, Menke 1984).

**Demonstration**

In this section the concept of observing scattered intensity fluctuations and subsequently using them in the deconvolution step will be illustrated. Some of the features of the method are amplified. As an example, a sample of glass beads dispersed in water was measured with the Malvern 2600, using the ROMA software, which will be further discussed in the next chapter. Glass
Figure 3.4 Collecting light scattering data on channel 5, 10, 30, 15 and 25 (top to bottom) of the multi-element detector as function of the sweep number. The sample is glass beads, and the obscuration is 25%.

beads are essentially spherical particles and so disturbances of the scattering pattern due to different orientations of the particles are eliminated. The relative refractive index of glass beads in water is (1.55-0.0i)/1.33. The obscuration of the incident laser beam due to the light scattered by the particles in the optical volume was 25%. The focal length of the lens used in the experiment was 100 mm, covering an angular range from 0.1 to 8.1 degrees. During the experiment 1000 sweeps were recorded, each one separated by 157 ms. The 31st detector ring (outer-most) was not used.

Figure 3.4 shows the scattered light energy data collected by five detector channels, where a low channel number corresponds to a low scattering angle. Processing of the data from all the channels indicated that no auto-correlation exists between the successive sweeps and that the collected data are independently and randomly distributed around an average value. The width of scatter
Figure 3.5 Inspection of the distribution of the scattering data presented in Figure 3.4 reveals an approximate Gaussian behavior.

of the data around the average value depends on the channel number. This is illustrated in Figure 3.5 where the data for the five channels of Figure 3.4 have been sorted, showing that the distribution of light energy values is reasonably Gaussian. The average pattern recorded before and after the introduction of the sample show that the intensity of the scattered light collected by the detector is sufficient to be discerned from the background level.

Deconvolution of the recorded pattern was performed with a model matrix based on the Fraunhofer diffraction theory. This model matrix contains scattering patterns for a range of particle size classes. The width of these classes was chosen to be logarithmically equidistant with a total of 40 classes per decade, which accords with the ISO R20 standardization series:
Figure 3.6 Distribution of average light energy, before and after introduction of the glass beads, collected by the 30 channels of the detector.

\[ x_{\min} 10^{j/(z \times 20)}, \]  

where \( x_{\min} \) is the lower size limit contained in the matrix, \( j \) refers to the \( j^{th} \) size class and \( z \) divides the number of size classes per decade into multiples of 20. These classes form the finest grid possible. Changing the resolution of the discretization grid is achieved by clustering a finite number of these classes. The resolution, \( R \), is defined as the logarithm of the ratio between two successive size class boundaries of the resulting grid:

\[ \ln \frac{x_{j,\min}}{x_{j+1,\min}} \cdot 100\% . \]  

(3.27)

This sets the highest possible resolution at 5.8%. The solution for the quantity of particles contained in each size class is expressed as equivalent volume
fractions ($t=3$). The grid was set to 23% because this value seemed to be optimal in a wide variety of practical cases. This feature will be discussed further in Chapter 4. Next the number of size classes and the position of the lower and upper limit was investigated. Only the diagonal coefficients of the $W$-matrix were incorporated into the deconvolution step, thus assuming a negligible degree of cross-correlation between the channels. The recorded scattering pattern, was first corrected for the background and then translated into an intensity pattern before deconvolution. In Figure 3.7 the quality of the fit, expressed as the reduced chi-square, is plotted against the number of degrees of freedom derived. The best fit was obtained around 10 degrees of freedom, or 20 size classes, with an overall lower and upper size limit of 1.0 and 125.9 μm respectively. The effect of choosing fewer size classes leads rapidly to a dramatic increase of the $\chi^2_{\text{red}}$, caused by increasing truncation of the wings of the actual size distribution. On the other hand adding more classes does not reveal extra information and again raises the $\chi^2_{\text{red}}$.

Although the fit looks quite satisfactory (see top graph of Figure 3.8), the best value found for the $\chi^2_{\text{red}}$ was 224.6, which is far from the ideal value of 1. As will be shown in Chapter 4, 1000 sweeps is more than sufficient to eliminate the statistical errors and therefore only systematic errors remain. The Fraunhofer scattering model was replaced by the Mie model, based on the correct refractive index, in order to account for the transparency of the glass beads. This resulted in a $\chi^2_{\text{red}}$ of 203.2, which is only a slight improvement. Such an outcome was, nevertheless, expected from the considerations discussed in Chapter 2. It was decided, therefore, to retain the Fraunhofer model although both models can be considered inadequate due to the persistent inclusion of systematic errors of various kinds. Amongst others, these sources are the calibration factors of the detector channels, the rudimentary background correction and
the discretization scheme applied. The misfit was analyzed further by inspection of the residuals of all the channels individually according to (3.19). The residuals are quite evenly distributed over the channels, both in sign and amplitude, which in itself satisfactory, since a monotonic increase or decrease would indicate a serious inability of the scattering model to respond to the measurement. The residuals indicate that the remaining differences between the measured and calculated scattering pattern can be up to 10 times the standard deviation of the signal of a channel. This explains the substantial $\chi^2_{red}$ value of 224.6. The size distribution recovered was compared to its equivalent obtained with a modified Phillips-Twomey method. The ordinary PT-method applies direct inversion and may result in negative size fractions. These negative fractions are then rather arbitrarily set to zero, leading to enormous values for the $\chi^2_{red}$. Therefore a modified version was constructed which inherited all the features of the proposed method but is supplemented with additional smoothing capabilities:

**Figure 3.8** Results of deconvolution: fit of scattered intensity (top), recovered size distribution (middle) and plot of residuals (bottom). (+) indicates Phillips-Twomey equivalent, see text for details.
\[ \hat{q} = (A^T W A + \gamma H)^{-1} A^T W L. \] (3.28)

Clearly, if \( \gamma \) approaches zero, the original method is retained. By increasing the value of \( \gamma \) smoothing features will be more strongly incorporated in the distribution. This is demonstrated in the middle graph of Figure 3.8, for \( \gamma = 0.1 \). It shows that the PT-method, by linking the size classes by their second order differences, is unable to respond to rapid changes in the size distribution, and thus results in a smoother and more symmetrical solution. Including smoothing instructions always leads to a rapid increase of the \( \chi^2_{\text{red}} \) depending on the value of \( \gamma \). The effect is also underlined in the spectrum of the residuals where the differences are now significantly higher, that is, up to 40 times the observed standard deviation, yielding a \( \chi^2_{\text{red}} \) of 882.1.

The variability of the recovered size distribution was also investigated, following the theory outlined in the previous section. It is common to compute the 95% confidence intervals, although this is not a limitation of the method, and may be adapted in order to comply with specific needs. Obviously, the tighter the restrictions on the fractions of the size distribution, for example looking for the 99.5% intervals, the wider the estimated contours of the enveloping lower and upper limit will become. The power of estimating the confidence intervals is the insight provided in the resolution-variance trade-off. Simply increasing the resolution of the solution yields more model parameters, but also boosts the variability of these parameters. This is reflected in the increased \( \chi^2_{\text{red}} \). This logical conclusion derives from the fact that the information content of the collected pattern is a fixed quantity. Far too often, especially in

\[ ^1 \text{This value for } \gamma \text{ is related to a model matrix } A \text{ and a weighting matrix } W \text{ which are both scaled in such a way that their diagonals are unity.} \]
Figure 3.10 The 95% confidence intervals for the recovered size distribution presented in Figure 3.8. The largest variability is found at the extremities of the distribution.

commercially distributed software, the solution is given as a large number of size fractions which are quite often the result of absurd interpolation. This gives an unjustified sense of accuracy. A second aspect of confidence intervals, is that it makes the addition of 'cosmetic' routines superfluous. Here the size distribution is polished to meet certain ethical standards which are concerned with smoothness and with the elimination of undesired dents and bumps of the distribution. In the recovered size distribution for the glass beads we notice such a bump at the left tail of the distribution which, since the distribution is volume based, would represent a large number of particles. Estimating the 95% confidence intervals reveals that there is simply not enough information available to decide on the presence of these particles. Also, it means that more solutions can be constructed within the contours set by the lower and upper limit and that the interpretation should pay more attention to those limits than to the precise shape of the size distribution itself.
The method described here is sufficiently fast. On a 386SX PC, 16 MHz with a mathematical co-processor (80387), the analysis of the size distribution never takes more than 2 seconds, even for 1 degree of freedom. This eliminates the supposed advantage of the PT-method. For a complete analysis, including the confidence intervals for number, length, surface and volume based solutions, 10 degrees of freedom translates to about 6 seconds but this may vary by 20% depending on the problem. The routines have been written in Turbo Pascal 6.0 using object oriented programming, which allows a compact and flexible structure for the source code (Verheijen 1991). The flexibility of the code permitted implementation in the ROMA program (Haket 1992). Typical run times for the other cases are depicted in Figure 3.11. This shows that in practice, and even for control purposes, generation and analysis of the complete solution is feasible. Added to this is the philosophy that computation time should not be considered a barrier to further development, since that problem will be solved by the availability of even faster computers in the near future.

Conclusions

Inclusion of information on the intensity fluctuations offers an additional possibility to enhance the deconvolution step in forward light scattering. This is achieved by expressing the observed fluctuations as variances and using them to weight the equation of the least squares solution accordingly. Based on this concept a model independent inversion procedure has been presented. An increase in stability of the linear set of equations is achieved by the nonnegativity constraint rather than by adding smoothing. From the profile of residuals an indication is presented about the applicability of the model matrix applied to
describe the measurement. After deconvolution an estimate of the accuracy of the solution is obtained. Confidence intervals improve insight in the optimal location and resolution of the retrieved size distribution. The computing time involved is minimal, and forms no restriction. The ability to estimate error intervals is also very helpful for the design of control strategies for particulate processes where the manipulation of the particle size distribution is the primary objective, as in crystallization, polymerization and grinding operations.

Appendix A. Other Criteria for the Goodness of Fit

In order to select the appropriate model to fit the data, a number of criteria for the goodness of fit have been developed. The details of these tests are reviewed by Freeman (1985), but all need the variance of the residuals the number of data points and the number of free model parameters as the ingredients. The residuals are estimated as the reduced chi-square:

- Final Prediction Error (Akaike 1970):

\[
FPE = \chi^2_{\text{red}} \frac{(n+m+1)}{(n-m-1)} ;
\]  
(A.1)

- Akaike's Information Criterion (Akaike 1972):

\[
AIC = n \ln(\chi^2_{\text{red}}) + 2m ;
\]  
(A.2)

- Shortest Data Descriptor (Rissanen 1978):

\[
SDD = n \ln(\chi^2_{\text{red}}) + (n+1)\ln(m).
\]  
(A.3)

The above listed tools to decide on the goodness of fit are often employed in the field of parameter estimation and information theory (Söderström 1977). As a fourth criterion the condition of the model matrix was investigated. Rather than following the expression given in (3.6), the condition was computed as the ratio of the square root of the maximum to the minimum eigenvalue, which
follow from singular value decomposition (SVD) of the model matrix:

$$\text{cond}(A) = \frac{\sqrt{\lambda_{\text{max}}(A)}}{\sqrt{\lambda_{\text{min}}(A)}}.$$  \hspace{1cm} (A.4)

![Graphs showing relationship between four criteria and reduced chi-square.](image)

**Figure A.1** Relationship between four criteria for model selection and the \( \chi^2_{\text{red}} \). The resolution was kept constant at 23\%, the number of size classes was varied between 15 and 22, and the size range was shifted between 1 and 250 \( \mu \text{m} \).

The sample of glass beads was analyzed based on different grids for the size distribution. The resolution was kept at 23\% but the number of size classes was varied between 15 and 22, whilst the distribution could range anywhere from 1 to 250 \( \mu \text{m} \). The resulting values for the \( \chi^2_{\text{red}} \) were compared with the suggested other four fit criteria.

The restriction of looking at the condition of the matrix is that it intrinsically assumes white noise, which is then equally distributed over the angular range.
of the measurement (Hirleman 1987). Indeed, no obvious relationship to the \( \chi^2_{red} \) was found in contrast to the other criteria. These methods all weight the complexity of the model against the goodness of fit and, therefore, their measures match quite well with the \( \chi^2_{red} \). All identified the same 10 models as most appropriate, although the ranking differed slightly. This result confirms that the deconvolution algorithm described in this chapter not only provides a means to translate measurement uncertainties into an estimate of the degree of variability of the size distribution, but also renders a method for model discrimination which complies very nicely with existing methods.

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Private communication and programming of deconvolution routines.
Symbols and Abbreviations

\( a \)  
Element of scattering model matrix \( A \).

\( A \)  
(Scattering) model matrix (nxm).

\( \text{cond()} \)  
Condition number of model matrix (\( \cdot \)).

\( \text{cov()} \)  
Covariance matrix of \( \cdot \) (nxn or mxm).

\( df \)  
Degrees of freedom.

\( e \)  
Prediction error.

\( F(\cdot) \)  
F-distribution.

\( f \)  
Size fraction of PSD.

\( f \)  
General solution vector.

\( g \)  
General data vector.

\( H \)  
Smoothing matrix (mxm).

\( K(x,y) \)  
Kernel function.

\( L \)  
Integrated light intensity vector (n).

\( m \)  
Number of size classes.

\( n \)  
Number of detector channels.

\( PT \)  
Phillips-Twomey method.

\( q \)  
Estimated model parameters (m).

\( R \)  
Resolution of size grid.

\( s \)  
Total number of sweeps.

\( t \)  
Sets basis for size distribution.

\( W \)  
Weighting matrix (nxn).

\( x \)  
Particle diameter.

\( z \)  
Sets the number of size classes per decade.

Greek

\( \gamma \)  
(gamma) Smoothness scalar.

\( \epsilon \)  
(epsilon) Random measurement error (n).

\( \lambda(\cdot) \)  
(lambda) Eigenvalue spectrum of model matrix \( \cdot \) (m).

\( \mu \)  
(mu) Expected mean value of \( L \) (n).

\( \rho \)  
(rho) Coefficient of cross correlation.

\( \sigma \)  
(sigma) Expected standard deviation of \( L \) (n).

\( \sigma^2 \)  
Expected variance of \( L \) (n).

\( \chi \)  
(chi)

\( \chi^2_{\text{red}} \)  
Reduced sum of squares of the residuals.

Sub- and superscripts

\( bg \)  
Background.

\( c \)  
Calculated.

\( e \)  
Experimental.
\( g \) Generalized.
\( i \) Counter of \( n \).
\( j \) Counter of \( m \).
\( k \) Sweep number.
\( \text{limit} \) Limit value for \( x_{\text{red}}^2 \).
\( \text{min} \) Minimum.
\( \text{max} \) Maximum.
\( \text{red} \) Reduced.
\( \text{sm} \) Sample measurement.
\( T \) Transpose.
\( \wedge \) Unbiased estimator.
AUTOMATED MEASUREMENT AND INTERPRETATION OF SCATTERING PATTERNS

Abstract. A computer program has been developed to improve forward light scattering measurements. The program serves as a diagnostic tool and helps to reliably collect and interpret scattering patterns. This involves computation of the degree of auto- and cross-correlation of the pattern, correction of the observed background and takes into account the analog-to-digital conversion. The number of readings required to eliminate statistical errors is determined under off-line and on-line conditions. Finally a demonstration is presented to show the effects of discretization and its relation to the localization of the optimum resolution for the estimated model parameters.

ROMA

The method of forward light scattering has been extensively studied for its merits to measure size distributions both off-line and on-line. The technique measures the particle size distribution indirectly by collecting the light scattered by a particle field. In a successive step the pattern is translated into an estimate of the particle size distribution. In this step we have incorporated the variability of the signals in order to estimate the confidence intervals of the size distribution. The basic configuration of the technique and the details of the deconvolution of light scattering patterns are given in Chapter 3. The theoretical aspects of scattering and the available models are discussed in Chapter 2.

The wide use of the technique is due to several advantages which were listed in Chapter 1. The limited information offered by the commercially available software, and its ‘black box‘ character, stimulated the development of the ROMA program. Its purpose was to improve insight in the complex phenomena of forward light scattering and to function as the interface between the Malvern 2600 Particle Sizer and either the operator or the process computer of a
crystallization process. Hereto its design was based on three criteria:

- The program must be adaptable to perform measurements under various conditions, both off-line in a laboratory and on-line, working in a master slave relation with a process computer;
- It should offer an objective interpretation of the recorded light scattering patterns. This includes statistics of the signals collected and error analysis of the size distribution;
- The presentation of the result should be self explanatory and lead to an improved set-up of the experiment, indicate inadequacies of the scattering model and allow straightforward comparison with other methods.

The program, which runs on any IBM-compatible PC, was initially intended to replace the Malvern software, but is set up independently of the hardware configuration to allow connection to other forward light scattering instruments. The structure is geared towards easy implementation of new routines to meet any particular defined user task. The development of the ROMA program was started three years ago by Mackay (1989). Haket (1992) added several features to allow ROMA to act as a diagnostic tool in research applications and gave the program its present structure. The source code, written in Turbo Pascal (version 5.5 or 6.0), contains separate units which all support specific tasks. The hierarchy of the code is shown in Figure 4.1. The menu structure of the program is based on the Pastipas Libraries (Haket et al. 1990). The ROMALIB unit holds the general purpose routines, such as the keyboard handler, the user help, error messages and the status window. The other five units which constitute ROMA (ROMAEXP, ROMAEXP, ROMAMOD,
ROMASOL and ROMARES) represent the main menus and are transparent to the user:

- **Options.** This section primarily contains the parameters to control the communication between, on the one hand ROMA, the PC and host computer, and on the other hand ROMA and the Malvern instrument. The latter entails selecting the proper instrument file which contains the calibration factors of the detector;

- **Experiment.** The set-up of the experiment and the actual data collection is supervised in this section. It assigns a number of experimental parameters such as the focal length of the collecting lens, the number of sweeps which are to be accumulated for each measurement and the time delay between the individual sweeps. Moreover it is equipped to analyze the laser stability and check the sample concentration prior to the actual measurement. This ensures optimum experimental conditions;

- **Model.** Precalculated model matrices are stored on disk and can be selected in this section. Various models are available, based on different scattering theories, for example Fraunhofer or Mie. Secondly, the resolution of the matrix can be modified to satisfy the set of size classes best for the deconvolution of the scattering pattern;

- **Solve.** The solve section decides on how the statistical errors are to be included in the deconvolution algorithm. Other parameters encountered here involve the desired confidence limit for the size classes and the degree of smoothing if the Phillips-Twomey method is applied;

- **Results.** Here the various data are presented, obtained both before and after deconvolution. This can be either in tabular or graphical format. For further use, the data can be exported to be used by other programs such as spreadsheet software.
Recording and Analysis of Scattering Patterns

A measurement involves reading all channels of the detector several times. The result is a distribution of scattered light intensities integrated over the angles subtended by the channels of the detector, represented by $L$. One reading of all the channels is referred to as a sweep. While recording, a sweep to sweep variability is observed which can be characterized by a Gaussian distribution, as outlined in Chapter 3. In order to optimize the experimental set-up, detect faults in the alignment or electronic circuit and test the assumption of Gaussian statistics, the sweeps of each channel, including the central sensor, are first analyzed. The following aspects are explained in more detail:

- Plot of the distribution of the individual sweeps, together with a box plot (Chambers et al. 1983) which allows a quick review of the sweep-to-sweep variability of each channel;
- Detect the presence of signal periodicity in the collected data by computation of the auto-correlation spectrum;
- Verification of the proper time delay between successive recordings;
- Inspection of the degree of cross-correlation which exists between the channels. These values are later used to constitute the full weighting matrix used in the deconvolution step;
- Determination of the number of sweeps required to eliminate statistical measurement errors.

**Inspection of the individual sweeps**

The above mentioned box plot provides a simple means to inspect the individual data and thus yields a quick diagnosis of the correctness of the observed scattering pattern. A box plot is a robust indicator of the distribution of the channel data. In a first step the data are sorted and subsequently the box plot is con-

![Box plot diagram](image)

*Figure 4.2 Construction of box plots to characterize the observed scattering data on each channel.*
Figure 4.3 A box plot of 1024 sweeps collected from a toner powder measurement (top). After inspection of the box plot individual channels may be further scrutinized to validate the instrument's performance.

structured from the following five points: minimum, maximum, 25%, 50% (median) and 75%. In Chapter 5 it will be shown that a similar set of points is a robust measure to describe the location and the spread of the size distribution. Although a perfectly Gaussian distribution is symmetrical on a linear axis, quite often the box plots reveal some skewness of the observed scattered intensities: the 25% and 75%-point are located at different distances from the median
value. If the fluctuations are relatively small this may be due to discretization problems associated with the limited resolution offered by the analog to digital converter. In this situation incompatible estimates for the variance of the signal are obtained which requires more careful treatment. Nevertheless, the box plot gives an impression of the differences in variability between the individual channels. Secondly, outlying values which have nothing to do with the other data are readily spotted in box plots. Such values could, for example, indicate a spurious pulse of the electronic circuit or the presence of foreign material or air bubbles in the sample. An example is presented in Figure 4.3. The top graph contains the box plots for the 30 channels and the central sensor (channel '0'). In order to illustrate better the mutual differences, the means of the distribution have been set to zero. Ideally, all channels behave in a similar manner to channel 5 which displays a well balanced sequence of the individual data points, leading to a symmetrical distribution. The box plot also identifies the potentially faulty cases, represented by channel 23 and 24. Here an unusual distribution is found and the relative spread is rather small (1 to 2%). Channel 23 appears to be very stable and hardly any spread is observed whereas for channel 24 the distribution seems to be truncated on one side. No direct conclusions about the performance of the instrument can be drawn from this experiment alone but it is worthwhile to monitor the suspicious channels, which may prevent erroneous size distributions evolving from corrupted scattering patterns.

*Signal periodicity*

Before the actual measurement is started the laser stability should be verified. This is realized by recording the variability on the central sensor after alignment. The degree of auto-correlation for detector element \( i \) \((A_i)\) is calculated from the following expression:

\[
A_i(\tau) = \frac{\sum_{k=1}^{s-\tau} (L_{i,k} - \hat{\mu}_i)(L_{i,k+\tau} - \hat{\mu}_i)}{\hat{\delta}_{ii}^2 (s-\tau)},
\]

where \( \tau \) is the time lag, that is the number of sweeps between the recorded
sweeps, $s$ is the total number of sweeps of the experiment, and $\hat{\mu}$ and $\hat{\sigma}^2$ represent the mean and variance of the collected signal. If the successive recordings are independent and uncorrelated, the coefficients of the auto-correlation function should be close to zero even for small values of $\tau$. From equation (4.1) it can be seen that the accuracy of the coefficients decreases with increasing $\tau$, since fewer terms $(s-\tau)$ are averaged. By determining the auto-correlation function for the central sensor ($i=0$), intensity oscillations of the
laser can be recognized. Typically such instabilities are encountered directly after the laser has been switched on. The example presented in Figure 4.4 shows that it takes about one hour for the laser to stabilize. Although this may not be representative of all lasers, since this particular one was a few years old, the testing of other lasers revealed that at least half an hour is common. Obviously, as the variance of the signal is reduced, the auto-correlation function itself becomes wider. The band is extended further for high values of $\tau$, which is in agreement with the predicted behavior of the function.

The sample frequency
During a measurement recording of uncorrelated scattering data is essential for a proper analysis of the sample (see Chapter 3). In order to evaluate this requirement, the auto-correlation functions for all channels are computed for $\tau=1$, and tested for the hypothesis that $\eta=0$. According to Fisher's theorem the data are uncorrelated if $\eta$ lies outside the interval (see eg, Milton and Arnold 1986):

\[
\text{lower limit} = \frac{(1+\eta) - (1-\eta) \cdot e^{\frac{-2z_{\eta}}{\sqrt{s^2}}}}{\frac{2z_{\eta}}{\sqrt{s^2}}} \cdot \frac{(1+\eta) + (1-\eta) \cdot e^{\frac{2z_{\eta}}{\sqrt{s^2}}}}{e^{\frac{-2z_{\eta}}{\sqrt{s^2}}}},
\]

\[
\text{upper limit} = \frac{(1+\eta) - (1-\eta) \cdot e^{\frac{-2z_{\eta}}{\sqrt{s^2}}}}{\frac{2z_{\eta}}{\sqrt{s^2}}} \cdot \frac{(1+\eta) + (1-\eta) \cdot e^{\frac{2z_{\eta}}{\sqrt{s^2}}}}{e^{\frac{-2z_{\eta}}{\sqrt{s^2}}}}.
\]

(4.2)

In the limit of a large number of sweeps, the 95% confidence interval is given by $z_{0.05} = z_{0.025} = 1.96$. If the actual degree of correlation between successive sweeps of all the channels is located explicitly outside these limits, the sampling frequency is too high and needs to be reduced. In ROMA this is accomplished by setting the appropriate read-out delay between the sweeps. The example depicted in Figure 4.5 shows that the scattered intensities developed from the latex particles are still considered to be correlated at a sample frequency of 7.7/s, because more than 5% of the channels (ie, 1 or 2) have $A(\tau=1)$ values
which are beyond or just on the confidence limits. Decreasing the sample frequency to 2.6/s results in an acceptable degree of correlation. The maximum sampling frequency is significantly influenced by the experimental conditions. Replacing the small stirred cell by a flow-through cell allows sample frequencies to be increased by two orders of magnitude, as can be seen from Figure 4.5. Here, toner powder\(^1\) was circulated through the cell at 12 ml/s which resulted in a residence time of about 0.13 seconds. Whilst being

\(^1\) Kodak Ektaprint L Toner Cat 190 0752.
circulated the slurry was continuously mixed in a separate tank. This procedure lessens the chance for an identical sub-sample to be present in the incident beam in a successive sweep. Furthermore it causes a bigger sweeps-to-sweep variability, which also leads to a smaller value for \( A(\tau=1) \). On the other hand, if the sample is measured in a small cell where the optical volume forms a substantial part of the total volume of the cell, the sample frequency must be relatively low. The sizes associated with the latex and toner powder samples were of the same order (\( E\{x\} = 20 \mu m \) and \( 13 \mu m \) on a volume basis respectively), and in all cases 100 sweeps were analyzed.

**Degree of cross-correlation**

Rather than quantification of the measurement uncertainties of the individual channels individually, the degree of association between all participating channels was determined. Together these coefficients constitute the weighting matrix used in the deconvolution step. In Chapter 3 the cross-correlation coefficients were defined as

\[
\rho_{ij} = \frac{\delta_{ij}^2}{\sqrt{\delta_{ii}^2 \delta_{jj}^2}}. \tag{4.3}
\]

The confidence intervals are estimated in the same manner as in the case of auto-correlation, using (4.2), but \( \eta \) is now replaced by the computed value of \( \rho_{ij} \).

The degree of correlation between the channels can also be used to diagnose the stability of the laser. If the laser intensity is not constant some correlation will be expected which could not have been developed from the background itself, since this yields completely uncorrelated signals.

A closer look at the shape of the cross-correlation function, that is the series of coefficients for each particular channel, reveals a significant dependence on both the position of the channel in the scattering spectrum as well as on the sample concentration. The channels which are located around the maximum intensity of the scattering pattern show a high degree of correlation with the neighboring channels. The correlation function is smooth and near symmetrical. Moving towards the extremities of the scattering pattern, the channels become
Figure 4.6 Computing the cross-correlation function of channel 15 to identify a stable laser, just after switching on (top) and after 60 minutes. The bars inside the circles indicate the 95% confidence limits.

more independent of each other, their correlation functions are jagged and have a skewed profile. To understand this complex phenomenon is similar to understanding the intensity fluctuations as described in the last section of Chapter 2 and requires statistics to describe the interaction between the number of particles and the size distribution. A theoretical derivation has not been completed at the time of writing this thesis. The crux of the matter is that the outer parts of the scattering pattern are developed from particles which are themselves located at the extremities of the size distribution and therefore appear in the optical volume of the cell at a much smaller frequencies than particles close to the median of the distribution. The previous explanation assumes the selection of an appropriate lens which centers the principal part of the scattering pattern on the detector, since an improper choice would erase vital information and lead to a poor recovery of the size distribution. In the lower graph of Figure 4.7, the influence of the sample concentration, measured as the obscuration of the beam, on channel 15 is demonstrated. The data were again taken from experiments with toner powder. As the concentration increas-
es, the maximum in the cross-correlation function becomes sharper. For very high values of the obscuration, the channels are fully isolated and no correlation is found. Although, this has not been verified theoretically, a possible explanation would again involve a distinction between the number fluctuations and redistribution effects. Then, the number fluctuations dominate at low concentration, causing all the channels to go up or down at the same time, and leading to a high degree of correlation over the entire spectrum. If the concentration is high, the sample is much more homogeneously mixed, and the relative number fluctuation observed between successive sweeps is negligible. In this region the redistribution effects are dominant and the cross-correlation is a function of the width of the distribution.

This phenomenon has been proven to be very reproducible, not only for the toner powder but also for a wide variety of other particle systems.

**The number of sweeps**

The remaining dissimilarities between the measured and calculated scattering pattern are due to imperfections in both the measurement and the scattering model applied. The measurement error can be either systematic or statistical. Amongst the systematic errors are incorrect calibration factors for the detector channels, the discretization of the size distribution and an approximated
scattering model. Statistical errors encountered in forward light scattering involve variation of the total number of scattering particles and their size distribution, orientation effects of non-spherical particles, detector noise and laser instabilities. Although these might have different time scales, the sum of the effects will result in a sweep-to-sweep variability, as discussed in Chapter 3. However, the inclusion of random errors in the analysis can be reduced by increasing the total number of sweeps collected during a measurement. Since the total time needed for a measurement increases rapidly with the number of sweeps collected, it is important to estimate the number which still significantly improves the optimum fit, represented by the $\chi^2_{red}$. A minimum number of sweeps is required to accurately assess the variance of the observed fluctuations.

The relationship between the reduced chi-squared and the number of sweeps is derived from

$$
\chi^2_{red} = \frac{\sum_{i=1}^{n} \left( \frac{L_i - L_{c,i}}{\delta_{ii}} \right)^2}{n - m} = \frac{\sum_{i=1}^{n} \left( \frac{\Delta L_{model,i} + \epsilon_i}{\delta_{ii}^* / s} \right)^2}{n - m},
$$

where $\sigma^*$ is the standard deviation of the individual sweeps and $\Delta L_{model}$ is the error introduced by the scattering model. The above equation can be separated into three terms:

$$
\chi^2_{red} = \frac{1}{n - m} \left[ \sum_{i=1}^{n} \frac{(\Delta L_{model,i})^2}{\delta_{ii}^* / s} + 2 \sum_{i=1}^{n} \frac{\Delta L_{model,i} \cdot \epsilon_i}{\delta_{ii}^* / s} + \sum_{i=1}^{n} \frac{\epsilon_i^2}{\delta_{ii}^* / s} \right].
$$

The second term disappears for an adequate number of sweeps, since the random measurement error becomes zero. In the third term, $\epsilon$ is a standard normal random variable and its square has a chi-square distribution with one degree of freedom. The sum of variables which have a chi-square distribution, has itself a chi-square distribution with an expected value equal to the number of degrees of freedom, $n-m$. Consequently, substitution leads to a simplified expression for the $\chi^2_{red}$:
\[ \chi_{\text{red}}^2 = 1 + \frac{s}{n-m} \sum_{i=1}^{n} \frac{\Delta L_{\text{model},i}^2}{\hat{\sigma}_{ii}^2}. \]  

(4.6)

This relationship indicates that the reduced chi-square is proportional to the number of sweeps. The slope is a measure of the degree of model imperfection with respect to the intrinsic stochastic error of the measurement and is proportional to the number of particles.

The following two examples, taken from Haket (1992), illustrate the difference between the magnitude of the systematic and statistical errors involved. First Figure 4.8 shows the reduced chi-square and its associated standard error as function of the number of sweeps for the toner sample, measured at 22% obscuration. During the measurement 1024 sweeps were collected. From this set, 2 to 250 successive sweeps are selected by picking a
random offset in the range from 1 to 1024-s. Each set of sweeps was then treated as a separate measurement and subsequently deconvoluted with a Fraunhofer diffraction model. The procedure was repeated 25 times with the resolution of the size distribution constant. Evidently, the contribution from the systematic errors, represented by $\Delta L_{\text{model}}$, is large compared to the contribution of the random errors in the measurement, even for a few sweeps. The points in the figure constitute a straight line, as predicted by equation (4.6), although

![Figure 4.9](image)

*Figure 4.9 Identical to the previous figure, but the scattering pattern was developed from ammonium sulfate crystals (see Chapter 5).*

the intercept is larger than one. A possible explanation is that the measurement error, $\epsilon$, does not approach zero, independent of the number of sweeps per measurement, due to the limited resolution offered by the discrete detector output (see next section). In the second example given in Figure 4.9 a similar behavior is observed. In this case crystals were measured on-line (see Chapter 5). For this particular measurement the obscuration was 47%. The same procedure was followed to estimate $\chi^2_{\text{red}}$ and the standard errors. The Fraunhofer
diffraction model was used again and a similar result is obtained. The main difference is the much larger variance of the reduced chi-square values, which is caused by the wider size distribution of the crystals. This typically results in more severe statistical fluctuations. It also means that a larger number of sweeps is required. For this case it is noticed that a transition from a diffuse set of points, where the influence of the fluctuations is conspicuous, to a straight line at around 30 sweeps. It was concluded, therefore, that recording more than 100 sweeps is not relevant to the result and merely adds time to the measurement.

**Correction for A-D Conversion**

In the section on the box plots it was already pointed out that the analog-to-digital conversion has a limited resolution. The Malvern detector has a 10 bit converter which results in a maximum discretization of the measured value into 1024 levels. If the fluctuations on a particular channel are small then only the lower bit fluctuates and this can lead to highly inaccurate estimates for the true variance on that channel, \( \hat{\sigma}^2 \). Essentially, the normal procedure would tend to underestimate the variability and hence to put an unreasonable amount of weight on that particular channel in the deconvolution step. To counter this effect an additional limiting term is introduced, \( \sigma_{\text{limit},ii}^2 \), and incorporated in the formula which estimates the variance of the collected signal:

\[
\hat{\sigma}_{ii}^2 = \frac{\sum_{k=I}^{s} (L_{ik})^2 - (\sum_{k=I}^{s} L_{ik})^2 / s}{s(s-1)} + \sigma_{\text{limit},ii}^2 .
\] (4.7)

The minimum standard error of one sweep is approximated by 50% of the discretization interval. For the detector we assume that this interval has a uniform distribution, which makes the variance of that sweep equal to 1/12th of the square of the size of the interval. Rather than selecting this value for those cases where the observed variance was very low, a continuous expression was designed which exhibits the following characteristics. The function for the
variance of the signal, reduces to $1/12$ if no fluctuations are observed. This would have been zero without the correction for the discretization errors. The contribution of the additional term vanishes if the variance starts to exceed the lower limit and finally becomes negligible. This has been accomplished in ROMA by writing the $\sigma^2_{\text{limit,ii}}$ term as:

$$\sigma^2_{\text{limit,ii}} = \left( \frac{1}{12} \right) \left( \frac{\sum_{k=1}^{s} (L_k)^2 - (\sum_{k=1}^{s} L_k)^2/s}{1 + \frac{1}{12} (s-1)} \right).$$

(4.8)

An example of the effect of the correction term is demonstrated in Figure 4.10. Although the formula derived is a rather crude approach to the discretization problem, it has served to avoid absurd estimates for the variance which could arise particularly from background measurements where the fluctuations may be extremely small.

**Assessment of the Background**

A correct background measurement is essential to the method of forward light scattering. In order to obtain the true scattering pattern the estimated background is subtracted from the total pattern. Problems may arise from short term laser instability as was shown earlier in this section. That particular obstacle
may be eliminated quite simply by waiting for a certain amount of time but another phenomenon, the long term instability of the laser, remains. The latter seems to be hardly recognized but is a crucial factor in measurements which run for a prolonged period. Figure 4.11 exhibits the behavior of the laser intensity collected on the central sensor of the Malvern over 17 hours. Obviously, the background level varies and if no action is taken the measurements will be heavily biased or will be lost altogether. A straightforward remedy is to record the background regularly, ideally after every measurement but at least after a few measurements.

![Graph showing laser intensity variations](image)

*Figure 4.11 Variations of the laser intensity during 17 hours after start-up. The delay between the sweeps is one minute.*

The background itself arises mainly from laser light which is scattered by the sample cell and the collecting lens. The instrument is contained in a case so that no light from the surroundings can enter the system. If the incident beam is blocked directly behind the beam expander no significant signal is recorded. During the scattering experiment, the particles shield part of the incident light and therefore distort the original background. The result is a reduced observed background, which is, as a first order approximation, corrected by the transmission of the incident beam (Agrawal 1990):

\[
\hat{B}_i = \delta TB_{obs,i}. \tag{4.9}
\]

The suggested correction for the background level was verified by multiplying \( T \) with an additional background correction factor, \( \delta \). Clearly, if \( \delta \) equals \( 1/T \) the correction term returns unity, and the original background is retained. A toner sample was measured at 22% obscuration and the optimum solution was
Figure 4.12 The background correction factor $\delta$ as function of $\chi^2_{\text{red}}$ for a toner sample. The sample was measured at 22% obscuration and therefore the correction term vanishes for $\delta = 1.28$.

determined. The $\chi^2_{\text{red}}$ returned was considerably improved compared to the value found in the uncorrected situation. It was found that the optimum solution is always obtained for a background correction of 0.9 to 1.1 times the observed transmission. Figure 4.12 shows the $\chi^2_{\text{red}}$ for a whole range of values of the correction factor $\delta$.

The Optimum Size Grid

The ROMA program finds the optimum size grid for each problem. The optimum solution is defined as that solution which yields a minimum value for the $\chi^2_{\text{red}}$. Hereto a model matrix is constructed in a separate program which contains the coefficients computed according to some scattering model, for example Mie or Fraunhofer. Each matrix holds 128 classes with a high
resolution of 40 classes per decade. The width of the successive classes is logarithmically spaced, following the ISO R20 standard series. Rather than working with a fixed grid, as is common in the commercially available software, three independent variables can be set:

- The width of the size classes, defined by the resolution $R$, which was introduced in Chapter 2;
- The number of size classes $m$, where $m < n$;
- The position of the size distribution, determined by the offset from the first size class in the matrix.

Once these variables are set, a submatrix is taken from the full matrix and then used in the deconvolution step. The task of finding the optimum solution can be a tedious one, since well over 10,000 combinations are possible. Therefore it is necessary to rigorously restrict this amount using both common sense as well as all the $a$ priori information available. The effects which result from changing the grid of the solution are now illustrated. Again, toner powder measured at 22% obscuration is taken as an example. The scattering coefficients in the matrix were computed with a Fraunhofer diffraction model. The results are discussed in more detail in Haket (1992).

First the optimum position of the size distribution was determined. The total width of the size distribution was kept constant at about 1.9 decades by adding size classes to the extremities. The width of the size distribution can, therefore, be defined as

![Figure 4.13 In ROMA the optimum resolution for a solution can be found by changing three independent variables: the number, width and position of the size classes.](image)
Figure 4.14 The effect of $x_{\text{mean}}$ [μm] of the size distribution on the $\chi^2_{\text{red}}$. The width of the distribution was kept constant and $R$ is 17.3 (3), 23.0 (4), and 28.8% (5).

$$\text{width(}\text{decades)} = \frac{\text{number of classes}}{\text{width of class}} \cdot \frac{\text{number of classes per decade}}{40} \cdot \frac{\text{resolution}}{40}$$

(4.10)

where the number of classes per decade is 40 and the width of class is defined by its resolution. The position of the distribution is defined as the logarithmic center between the boundaries:

$$x_{\text{mean}} = \sqrt{x_{\text{high}} x_{\text{low}}}.$$  

(4.11)

The effect of changing the position was investigated for several values of the resolution $R$. The results are summarized in Figure 4.14. An uneven pattern is found over a fairly wide range for all resolutions. The oscillations are relatively large, dependent on the resolution and are very sensitive to minor shifts in the
position of the distribution. The optimum resolution, 23%, yields the most stable pattern over the widest range. Moving further out to either side results, as expected, in a tremendous increase in $\chi^2_{\text{red}}$, since here the constructed grid leaves out a significant part of the actual size distribution. In the second experiment the total width of the size distribution is varied, starting from the optimum position. The results are presented in Figure 4.15. Again a rather flat bottomed curve is found for 23%, yielding approximately equally optimal solutions over a wide range. A similar behavior was found for many other measurements of samples with a total width of 1.5 to 2.0 decades, indicating that 23% in such cases is an appropriate first guess. In this particular case, the optimum solution was located in the size range 1.59-70.8 \( \mu \text{m} \) for \( R=17.3\% \) and \( m=22 \) giving a $\chi^2_{\text{red}}$ value of 210. The optimum solutions for different resolutions are depicted in Figure 4.16. Going from a low to a high resolution the number of size classes is reduced, the size distribution becomes smoother.
and secondary peaks are removed. As the resolution decreases, the confidence intervals become narrower, for reasons discussed in the previous chapter.

Figure 4.16 Optimum solutions and 95% confidence intervals for a toner powder sample as a function of $R$. 
Both examples clearly show that some optimization is necessary in order to avoid serious discretization errors which result in large values for the $\chi^2_{red}$. On the other hand, if the optimum settings are located the remaining residuals in the fit are due to other sources, such as incorrect scattering coefficients, a corrupted background or other systematic errors. Therefore, there is no need to store the scattering matrix at higher resolutions than 5.8%. As a rule of thumb, resolutions ranging from 17.3 to 28.8% will perform well, unless the distribution becomes extremely narrow or extremely wide. From the previous discussion it is also apparent that some knowledge on the position of the distribution is required to avoid an extensive search. In on-line applications, such as discussed in Chapter 5, the distribution generally shifts slowly and then the optimum settings of the previous solution can serve as a starting point. A preliminary version of an automated search routine has been incorporated into ROMA.

Conclusions

The development of ROMA has improved the analysis of forward light scattering patterns. Analysis starts with the collected signals by checking the degree of auto- and cross correlation, and inspection of the distribution of the sweeps presented as box plots for each channel. As a consequence some measurement parameters may be adjusted. One of the aspects involves the choice of an appropriate time delay between the successive sweeps in order to ensure independent recordings. It is demonstrated in this chapter that the sample frequency hinges strongly on both the experimental conditions and the properties of the sample being analyzed. The number of sweeps reduces the random errors but in the examples tested, both off-line and on-line, collecting more than 100 sweeps seems superfluous and only adds to the measurement time.

In a second step the stochastic nature of the sweeps is quantified assuming a Gaussian distribution. A correction is introduced to reduce the effect of the limited resolution offered by the current 10 bit A-D converter. Otherwise, channels with fluctuations too small to be observed receive an enormous weight
in the subsequent deconvolution step. A second correction accounts for the modified background during the measurement. The part of the background which is shielded by the particles is approximated, to the first order, by the transmission of the incident laser beam. This approach offers a significantly better fit.

For the deconvolution step three independent variables are used to select the optimal size grid for the solution. This is an important advantage over a fixed grid since discretization errors can be quite substantial. Generally, the optimum resolution is close to 23% and the number of size classes lies in the range of 10 to 20. The remaining differences in the fit, expressed by the $\chi^2_{\text{red}}$, indicate the presence of systematic errors. Even after optimization of the measurement and the deconvolution large values for the $\chi^2_{\text{red}}$ persist and it may, therefore, be concluded that systematic errors still currently dominate the forward light scattering measuring method.

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Symbols and Abbreviations

\( A(\tau) \)  
**Auto-correlation function.**

\( B \)  
**Background vector (n).**

\( L \)  
**Integrated light intensity vector (n).**

\( m \)  
**Number of size classes.**

\( n \)  
**Number of detector channels.**

\( R \)  
**Resolution of size grid.**

\( s \)  
**Total number of sweeps.**

\( T \)  
**Transmission of incident beam.**

\( x \)  
**Particle size.**

\( z \)  
**Confidence interval limit.**

**Greek**

\( \alpha \) (alpha)  
**Degree of confidentiality.**

\( \delta \) (delta)  
**Background correction coefficient.**

\( \varepsilon \) (epsilon)  
**Random measurement error.**

\( \eta \) (eta)  
**Coefficient of correlation.**

\( \mu \) (mu)  
**Expected mean value of \( L(\eta) \).**

\( \rho \) (rho)  
**Coefficient of cross correlation.**

\( \sigma \) (sigma)  
**Expected standard deviation of \( L(\eta) \).**

\( \sigma^2 \)  
**Expected variance of \( L(\eta) \).**

\( \tau \) (tau)  
**Time lag.**

\( \chi \) (chi)  

\( \chi^2_{red} \)  
**Reduced sum of squares of the residuals.**

**Sub- and superscripts**

\( c \)  
**Calculated.**

\( \text{high} \)  
**Upper limit of size class.**

\( i,j \)  
**Channel number.**

\( k \)  
**Sweep number.**

\( \text{limit} \)  
**Lower limit of A-D conversion.**

\( \text{low} \)  
**Lower limit of size class.**

\( \text{mean} \)  
**Mean size of size distribution.**

\( \text{model} \)  
**Light scattering model.**

\( \text{obs} \)  
**Observed.**

\( \text{red} \)  
**Reduced.**

\( * \)  
**Indicates individual sweep.**

\( ^\wedge \)  
**Unbiased estimator.**
ON-LINE MEASUREMENT OF CRYSTAL SIZE DISTRIBUTION IN INDUSTRIAL CRYSTALLIZERS

Abstract. The observation of a continuous pilot scale crystallizer is discussed. The crystal size distribution (CSD), measured on-line with the forward light scattering technique, is used as the process input. A set of robust parameters is derived to describe the location and spread of the CSD. A statistical measure to validate the quality of the measurements is presented and was used to enhance the filtering capabilities. Experiments demonstrate the observation capabilities of the measurement system under various conditions. The results are reproducible and confirm a sufficiently strong correlation of process inputs and outputs. The system was also used, in combination with a CCD camera, to follow the fast process of agglomeration occurring in the first minutes after the initial nucleation burst.

The UNIAK Project

Crystallization is widely used as an industrial separation and purification technique, mainly because a product is obtained of high purity at low energy cost. The crystals which form the product can be characterized by the crystal size distribution (CSD). The CSD produced directly from the crystallizer is generally fairly wide and its shape and average size vary with time, caused by instability of the process itself and by undesired external disturbances. Both aspects severely impede successive unit operations such as filtration, drying and transportation. A typical scheme of a crystallizer in cascade with other unit operations is shown in Figure 5.1. The crystallizer should be able to conform to supply changes set by these operations. Secondly, product specifications must be satisfied. 'Off-spec' product is expensive in terms of capital investment and even more so if the need for storage is unavoidable. The trend for cost reduction and particularly the demand for high product quality in the chemical
industry forms the incentive for the design of **CSD** control systems. The fact that a wide variety of both bulk and fine chemicals is manufactured by, or is dependent on, batch or continuous crystallization processes makes the search for adequate **CSD** control systems a high priority.

![Diagram](image)

**Figure 5.1** Schematic diagram of an industrial crystallizer in cascade with other unit operations (Jones 1985).

Development of control strategies and improvement of the crystallizer design constitute the main goals of research in the UNIAK (Universal Instrumentation and Automation of Crystallizers) project. The research focuses specifically around the following items:

- Physical modeling and system identification;
- Classification techniques for fine and product crystals;
- Formulation of nucleation and growth kinetics;
- Development of on-line **CSD** measurement techniques;
- Design and implementation of **CSD** control algorithms.
In this chapter experiments with the UNIAK 970 liter pilot scale crystallizer are reviewed. The next section addresses the requirements for a control system, and in particular its link with the CSD observation system herein. The experimental section concentrates on the performance of the forward light scattering technique as an on-line CSD observation system. Its ability to adequately characterize the CSD was demonstrated by prolonged continuous experiments. Secondly, during the start-up of batch runs, fast measurements of the CSD were made which verified the agglomeration that occurs in the very first stages of nucleation. First a few aspects of the experimental facilities are highlighted.
Crystallizer

The project owns a 22 and a 970 liter draft tube baffled (DTB) crystallizer equipped with fines removal which are used for both batch and continuous crystallization. Supersaturation drives the crystallization process which is maintained by evaporation of water from the saturated liquor at 50°C. The temperature is controlled with the pressure which can vary between 70 and 250 mbar. In continuous operation, a crystal free, saturated feed stream enters the reactor at the bottom whilst simultaneously product and fines are removed. The slurry of the crystallizer is internally circulated by an impeller. Heat is supplied by the internal heat exchanger and by the returned fines flow, where enough heat is added to dissolve all the fine crystals. During a continuous experiment the average concentration of crystals ranges from 10 to 15 vol%, whereas in a batch experiment the final concentration could easily exceed 30 vol%. A schematic diagram of the 970 liter crystallizer is presented in Figure 5.2.

![Diagram showing control hierarchy and structure of data acquisition of the UNIAK plant.](image)

**Figure 5.3** Control hierarchy and structure of data acquisition of the UNIAK plant.

The process is fully automated and includes a frequency control for the
pumps and stirrer. A programmable logic controller (PLC) is used to control the background- and dilution unit, alarms and temperature of the supply vessels. A Process Monitoring and Control (PMC) program controls all the relevant process parameters. The PMC program resides in the HP1000 process computer and is also responsible for the communication with the ROMA program (see Chapter 4) located in the Olivetti M24 computers which control the two Malvern 2600 particle sizers. Data are collected, transferred and stored at a maximum rate of one measurement in 2 minutes. The HP1000 is connected with the VAX3100 system which allows direct data manipulation. The data acquisition and control scheme is shown in Figure 5.3.

Hydrocyclone product classification
The number of process inputs which can effect the CSD is limited (Jager et al. 1992). Effective methods must act directly on the size distribution by means of internal or external classification techniques. One such method is the separation of the largest crystals from the crystallizer contents. A scalping type of operation is preferred where the CSD is truncated at some specific diameter. A flat bottom hydrocyclone was installed to separate the slurry drawn from the crystallizer into an overflow which is returned to the reactor, and an underflow, the classified product, which contains the largest crystals. The classification is, in general, not well defined but a function of crystal size. The shape of this grade efficiency curve is affected by the flow and concentration of the unclassified product which enters the cyclone, as well as the design parameters. Precise knowledge of the position of this curve is fundamental for implementation of the controller and currently receives, therefore, great attention in the project.
Fines Removal

The classic process input for control of the CSD is fines removal. In continuous crystallization processes its influence is found in the suppression of disturbances in the effective nucleation rate and in an increase of the average crystal size. For batch-wise crystallization it helps to shape the initial size distribution and removes the unwanted crystals which originate from primary and secondary nucleation in the subsequent growth phase. An effective fines removal system was designed and integrated into the process. Its principle is based on the existence of a size dependent drag force on the crystals in an annular zone of the crystallizer. The force is created by an adjustable suction flow from six individual discharge pipes at the top of the annular zone. This leads to the removal of the crystals smaller than some classification size from the reactor. The withdrawn crystals are then dissolved in a separate vessel by addition of extra heat. An accurate theoretical description of the classification function is required for constructive use of this process input in a control system (Prins 1991).

The fines background unit

Regular recording of the background level of the Malvern particle size analyzers is indispensable for an effective correction of spurious signals which arise from sources other than the light scattered by the particles. An additional problem, which has escaped general attention, is long term intensity fluctuations of the laser. This could lead to misleading interpretations for the obscuration and the CSD. An example of the drifting laser intensity is presented in the experimental section.

The most suitable medium for background corrections of CSD measurements is saturated, crystal free liquor with the same temperature as the sample. Other media result in an incorrect assessment of the background level. Mother liquor is also used during alignment of the laser and the detector.

Incorrect backgrounds particularly handicap the measurement of the CSD of the fines since the low concentration, together with the small size of the crystals, yield a weak scattering pattern. Therefore, a fully automated background unit (Figure 5.5) was constructed for the second Malvern in which two, pneumatically actuated, three-way valves select either the fines flow
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(situation B) or the external mother liquor (A) while the other is bypassed. Circulation of the mother liquor at a high velocity avoids encrustation. The two-way valve in the fines bypass channel maintains a sufficient linear velocity of the fines flow through the optical cell (Prins 1991).

![Diagram of flow process]

**Figure 5.5** Background unit for the measurement of fines 1. Filter 2. Pneumatically actuated three-way valve 3. Diameter reduction 4. Optical cell of Malvern 5. Pneumatically actuated two-way valve.

*Dilution of the product flow*

Dense particle slurries, such as the product flow, are unacceptable in forward light scattering as discussed in Chapter 2. Multiple scattering effects can be avoided by diluting the sample before measurement to an appropriate concentration. This is accomplished when the obscuration values of the diluted sample range from 10 to 30%. The first dilution unit was designed by Kruijer (1985) and Jager (1990) and was upgraded and extensively tested by Bartels (1991) and Gerla (1991). They considered the following design criteria:

- The diluted sample should be representative of the actual CSD at the sampling location. This excludes growth and dissolution, attrition and
classification of the crystals in the dilution step. Introduction of air bubbles by leaking seals poses a serious additional problem which needs to be eliminated. In the present unit the time needed for dilution is kept short, a constant temperature is maintained, piping is restricted to an absolute minimum and a Watson/Marlow 604 U/R pump was selected for its superior non-abrasion characteristics. The same external saturated crystal free dilution liquor as for the background unit was used.

![Flow scheme of the present dilution unit. The samples taken from either the product flow or hydrocyclone overflow are first isolated and then diluted by direct injection dilution liquor.](image)

- After dilution the sample should be homogeneously distributed over the measuring loop and contain enough crystals to be statistically accurate. This number ranges from $10^4$ to $10^5$, based on a maximum deviation from the mean crystal size of 1%. In practice the current sample size, 400 ml, easily exceeds this requirement, because it is based on a worst case scenario defined by the lowest crystal concentration and the largest crystal size in the reactor. The sample size should be small enough not to influence the crystallization kinetics. Dilution is achieved by filling the measuring loop by isokinetic withdrawal from the product flow with a smooth discharge pipe
and subsequent injection of the crystal free saturated liquor (Figure 5.6).

- Flexibility and robustness of the dilution unit are a prerequisite for process control. During operation, a wide range of slurry concentrations, 2 to 30 vol%, is offered to the unit for dilution. Trouble free operation is essential. The smooth surface and insulation properties of PFA tubing avoids encrustation which would eventually completely hinder the flow. A sufficient velocity of the flow in the unit is maintained to avert settling of the crystals.

- The unit needs to be fully automated and capable of a high sampling rate. The following functions are implemented: a) dilution, b) measurement of the CSD from the unclassified product flow and cyclone overflow and c) background measurement. The time needed to perform any of these functions is 14, 75 and 20 seconds. Finally, rinsing with water cleans the entire unit. The PMC activates the PLC of the dilution unit to perform one of the above functions and to trigger the ROMA program.

Control Aspects of Crystallization

One of the decisive aspects of the control problem is the existence of a robust control system which stabilizes the CSD and corrects for transients by applying a reduced set of physically attainable process inputs. The three basic components of a control system for an industrial crystallizer are summarized below (De Wolf 1990).

An on-line CSD measurement system

A CSD measurement system should be able to observe the CSD dynamics, transients and oscillations. Although secondary parameters, such as concentration, may also be observed, full control of the product quality requires the complete size distribution of the crystals from various locations of the crystallizer. The system should be able to supply the controller with a sufficient number of observations, in comparison to the residence time, to prevent process excursions. This requirement makes off-line techniques, such as sieving, obsolete. Jager (1990) found that the results obtained with the forward light scattering technique correlate well with the data gathered by off-line sieve
analysis (Figure 5.7). Furthermore, each observation must involve a sufficient number of particles in order to be statistically relevant.

![Figure 5.7 A comparison between the forward light scattering technique, using the original Malvern software, and sieve analysis. The left graph is based on area, and the right is based on mass (Jager 1990).](image)

A good understanding of the reliability of the data collected is essential. This particularly concerns reproducibility and accuracy. Reproducibility is important from a control point of view, since it is a measure of the internal consistency of the instrument. Accuracy reflects how close the result is to the true outcome and can be compared with other sizing methods. Accuracy may be improved by calibration or by a more appropriate interpretation method of the collected signals. Although it is preferable that the outcome has a clear relationship with the actual diameter of the particles, especially for physical modeling of the process, it may be sufficient to utilize an empirical response for a wide range of input signals.

It is advantageous if the system is able to validate its measurements in order to protect the control system from unnecessary upsets. This is ensured in two ways. Firstly, by adding to the result a measure which describes how satisfactorily the data were interpreted by the instrument software. Incorrect observations may result from malfunctioning hardware, invalid background measurements, fouling or blockage of the lines, or crystals which have grown beyond the proper detection limits of the current settings. The additional
measure transferred to the controller is used to weight the result or, in extreme situations, to ignore the result completely. Secondly the result should be accompanied by confidentiality limits. This gives insight into the degree of variability of the result. It is also a measure of the information content of the collected data. Since this amount is fixed, ludicrous interpolation of the result into many size classes only fabricates more data with no additional information offered to the controller. Identification of the position of the confidence limits helps the controller to discriminate true upsets of the process from local fluctuations which are merely created by an incorrect interpretation of the recorded signals.

**Process inputs**

Control of the CSD is established by the availability of process inputs. These inputs should be attainable in industrial practice. Inputs such as crystallization temperature, mean residence time of the crystals in the system and rate of evaporation affect the entire CSD which reduces their practical value. Size classification is a means to manipulate specific sizes of the CSD. In a fines removal system the very small crystals are separated from the mixed suspension in the reactor and subsequently dissolved. The withdrawal of the large product crystals by sedimentation or hydrocyclones may be employed as another input. Clearly, both methods hereby affect the mean residence time for those crystals.

**Controller**

A controller should preserve process stability and performance taking into account model uncertainties and constraints on the controller outputs. Previous work in the field of CSD control was mainly focused on proportional single input-single output (SISO) control schemes (Randolph *et al.* 1987 and Rohani and Lee 1987). The performance of these schemes was investigated with limited models. The nucleation rate or closely related variables, were used as process outputs. As a process input the fines removal rate was used. The main drawbacks of this approach for CSD control are the lack of a reliable, on-line CSD measurement system, the small scale of operation, the use of limited SISO control structures and the absence of controller input variables which are directly related to the CSD characteristics to be controlled.
Multivariable controllers, which require more effective process inputs and outputs, must be implemented to prevent transients and offsets of the CSD. The design of such controllers needs a dynamic model to describe the process dynamics. The required model can be derived by physical modeling where the birth, growth and removal of crystals is related to population dynamics. The method is complicated and elaborate. A crude alternative to physical modeling, is the derivation of a black box model. Here the crystallization process is deliberately disturbed by test signals and analyzed by subsequently tracing its response. In system identification both methods are interconnected by an estimation technique to assess the relevant process parameters (Ljung 1987, Söderström and Stoica 1989).

Summary of Experimental Conditions

Experiments were performed with the continuous, evaporative pilot scale (970 liter) draft tube baffled crystallizer operated in accordance with the above stated process model hypotheses. The crystallizer was fed with saturated crystal free liquor. Vapor was extracted at the top of the crystallizer with two condensers. Heat was supplied with an internal heat exchanger positioned in the draft tube.

Classification of fines was established in the annular zone and is based on differences in settling velocities of crystals in the mother liquor. Product classification was performed with a flat bottom hydrocyclone. The overflow of the hydrocyclone was returned to the crystallizer and the underflow was taken as the product flow.

The system was fully automated by a HP1000 process computer. Local PID controllers were used to control the temperature in the crystallizer, the total heat input, the crystallizer level, the level in the hydrocyclone overflow vessel, the fines flow, the hydrocyclone feed flow and the temperature of the dissolved fines.

An Endress & Hauser M-point density meter was used to monitor the total solids concentration in the reactor.

CSD measurements were taken at three different locations: the unclassified product flow, which was isokinetically withdrawn from the crystallizer, the
overflow of the hydrocyclone system and the fines flow (SL1, SL2 and SL3 respectively). The range of the crystal sizes in the process, typically evolves over three decades by length (or $10^9$ by mass!). This exceeds by far the capabilities of any single instrument configuration. Therefore the fine and product crystals were measured separately by two different particle analyzers. The scattered light was recorded by two Malvern 2600 particle sizers using different collimating lenses. A 300 mm lens was mounted to observe the fine crystals at SL3 and a 1000 mm lens to observe the classifier product and overflow crystals at SL1 and SL2 respectively. The optical path length in both cells was 3 mm. In the deconvolution step 20 size classes were determined, based on a logarithmically equidistant grid with 23% resolution, i.e., the width of successive size classes is increased by a factor of 1.26. The lower size limit was set to 13 μm and the upper limit to 1335 μm. The sampling frequency was kept at a rate of one sample in 2 minutes for all sample locations. Backgrounds were recorded after 8 measurements to correct for laser instability, as shown in Figure 5.9.
Figure 5.9 Example of observed instabilities of the 5 mW He-Ne laser of the Malvern 2600. Every 8 measurements a new background pattern is recorded to prevent misinterpretation of the measurements.

An ammonium sulphate-water system was used as the model material. The crystallizer was operated at a constant level and at a constant temperature of 50°C. The total heat input was 120 KW, and the fines were dissolved by increasing the temperature of the fines flow by 10°C. The feed flow to the crystallizer was just saturated at 50°C and its temperature was slightly raised before entering the vessel to ensure a crystal free feed. In the case of no product classification the mean residence time of the slurry in the crystallizer was kept constant at a value of 75 minutes. For product classification the hydrocyclone feed flow was 1.0 liters/s which resulted in a product flow of 0.13 liters/s. Slurry circulation in the crystallizer was forced with a marine type impeller which rotated at a speed of 320 rpm.
Observation of CSD Dynamics in a Continuous Crystallizer

In this section the observability aspects are discussed. The proposed inputs of the control system are on-line CSD data, collected at three different sample locations by means of forward light scattering. Table 5.1 reviews the continuous experiments which were performed to identify the relationship between the controller inputs and outputs. Product classification was absent in all the experiments, except for Exp5. The data were obtained by the UNIAK team and were used to study several aspects of industrial crystallization.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Flow rate (liters/s)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp1</td>
<td>1.0</td>
<td>Dilution unit tested</td>
</tr>
<tr>
<td>Exp2</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Exp3</td>
<td>2.0</td>
<td>Step change in fines flow</td>
</tr>
<tr>
<td>Exp4</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>Exp5</td>
<td>1.0</td>
<td>Hydrocyclone added</td>
</tr>
<tr>
<td>Exp6</td>
<td>3.4</td>
<td>Maximum fines flow</td>
</tr>
</tbody>
</table>

A prerequisite for control is the existence of relevant process output parameters. In terms of the CSD the parameters should be robust estimators of the properties of the distribution considered. The number of measurement variables which can be obtained is limited. This requires a careful consideration of the size parameters that are used to control particulate processes. If the control of the process is based on a reduced physical model, as derived in the previous section, the sizing data should contain sufficient information in order to enable, after combination with other available data, an adequate reconstruction of the state of the process. Also a strong relationship between the controller inputs and outputs should be present. Robustness indicates that outliers are irrelevant in the reduced set of parameters, but the observability of the process dynamics is preserved. Good observability means that process
transients are detected in a clear response in at least one of the selected output parameters. Parameters which are often used are the central location of the size distribution and the spread around that size. Robust parameters fulfilling the above requirements are derived from the quartiles of the size distribution, defined by:

$$\int_{x=0}^{x_k} f_v(x) \, dx \triangleq \frac{k}{100}, \quad (5.1)$$

with $k=25, 50$ and $75$. The median ($x_{50}$), is a descriptor of the CSD which is relatively insensitive to uncertainties in the extremities of the distribution, since it defines the location where 50% of the observed distribution has a smaller size. The robust estimator for spread is the interquartile range, denoted as $qr$. It was found that the level of inaccuracy over the whole size range is relatively uniform so the interquartile range was taken on a logarithmic scale, defined as:

$$qr \triangleq \ln \frac{x_{75}}{x_{25}}. \quad (5.2)$$

This parameter is a measure of the spread, which has the added advantage of being dimensionless (Figure 5.10).

Other choices of the output parameters to characterize the local CSD may be computed. For instance, the CSD can also be reconstructed from its moments. In ROMA the moments are defined relative to the distribution type selected,
\[ \hat{M}_i = \frac{\sum_{j=1}^{m} \hat{q}_j x_j^i}{\sum_{j=1}^{m} \hat{q}_j x_j^i} = \sum_{j=1}^{m} \hat{q}_j x_j^{i-1}, \quad (5.3) \]

where \( i \) is used to indicate the basis of the distribution (see equation 3.24). By definition \( \Sigma q_j = 1 \), and thus \( M_i = 1 \). Based on the moments a set of mean diameters can be defined,

\[ x(a,b) = \sqrt{\frac{a-b}{M_a}} \cdot M_b. \quad (5.4) \]

Frequently used size parameters are the volume mean diameter \( x(4,3) \) and the Sauter mean diameter \( x(3,2) \). The mean of a distribution is equal to \( M_{i+1} \), and its standard deviation results from

\[ \sigma_i = \sqrt{M_i \cdot M_{i+2} - M_{i+1}^2}. \quad (5.5) \]

Error analysis shows that particularly the higher moments are rather sensitive for inaccuracies at the extremities of the distribution. A demonstration showing the difference in behavior between the mean and median is presented in Figure 5.16.

A third method uses an analytical expression for the size distribution. Examples of often used expressions are the lognormal distribution presented in Chapter 2, or the Rosin-Rammler distribution. The parameters are estimated with a nonlinear procedure.

Alternatively, sometimes the fraction of particles smaller or larger than some particular, critical crystal size length needs to be controlled rather than the position of the CSD. Another choice to be made is whether the critical diameter monitored should be based either on a number, length, surface or volume based distribution. The presence of a small number of fine particles is completely overshadowed by the large ones in a wide size distribution, such as the unclassified product from the crystallizer, if the distribution is expressed as volume fraction. The impact of these small crystals could be tremendous for
successive product handling operations, such as filtration. Similarly, for production, the total volume or mass of the particles larger than some size may be the important factor.

The proposed controller outputs, the location and spread of the CSD, are used here to demonstrate the possibilities and limitations of the current CSD observation system, based on forward light scattering. Some results were previously reported by Eek et al. (1992). System identification should reveal whether the suggested outputs are adequate to estimate the state of the process. In the following sections various results obtained with the measurement system are discussed.

**Growth behavior**

Information on the open-loop behavior of the process was obtained by two different outgrowth responses of the CSD on the initially unseeded crystallizer (Exp3 and Exp4). In the first experiment (Exp3), a fines flow of 1.0 liters/s and in the second experiment (Exp4) a fines flow of 2.2 liters/s was applied. During these experiments unclassified product was removed.

Figure 5.11 and Figure 5.12 show the dynamic behavior for 4 different relative volume fractions of the unclassified product measured at sampling point SL1 over a period of 40 hours during Exp3 and Exp4 respectively. The fractions demonstrate a damped, oscillatory behavior, often found in evaporative crystallizers. This situation is very unfavorable since it produces a lot of 'off-spec' product. The period of the oscillation is about six hours for both fines withdrawal rates. In Figure 5.14 an overall view is given of the behavior of successive volume fractions, showing the crystal growth and its oscillatory character. In this special case a limit cycle of the process occurred, which means that dampening of the oscillations is absent. This case is discussed in more detail in the next section, and is of great importance for controller design (Eek 1992). The larger fines withdrawal rate in Exp4 resulted in a slower dampening of the oscillations. Several hypotheses were postulated to explain this instability (Randolph and Larson 1962 and Jager 1990). Most theories are founded on changes in the level of supersaturation in the reactor, which cause periodic bursts of new nuclei. We found that also severe fracture of the large crystals occurred, due to collisions with other crystals as well as with the
impeller and possibly also with the wall. The word fracture is used here rather than attrition since the latter would imply a slow rounding process of the crystals. Another term used is macro attrition, as opposed to micro-attrition which describes the formation of crystals up to 1 μm. Probably both mechanisms are present. The very fine fragments, which are formed by micro attrition, are hardly detected within the volume based size distribution. The resulting fragments, with an unknown size distribution, remained unnoticed in the subsequent distributions until they had reached about 100 μm, due to the poor resolution offered by the mounted 1000 mm lens. These small crystals, together with the crystals which were formed by the other nucleation mechanisms, both primary and secondary, are then included in the next generation of the CSD (Dauday 1987). Adding to the complexity is the chance that these new, small crystals may be dissolved before they can grow. This is dependent on some critical minimum length and the level of supersaturation. Although new crystals are formed by all of the above described mechanisms, the chances for the next generation to persist are particularly favorable at relatively high levels of supersaturation. This condition arises when the ratio of total surface area to total crystal volume of the previous size distribution has been reduced beyond some critical limit. Examples and discussion of this phenomenon are given below.

The upper and middle graph of Figure 5.13 show what happens to the size distributions with time. The distribution shifts to the right until it reaches its maximum size. Then a bimodal distribution appears which eventually is reduced to a monomodal distribution since no large crystals could be detected. This assumption was confirmed by pictures taken during the experiment (Heffels 1992). The 'first generation' crystals had nearly immaculate structures with sharp edges, but in the subsequent cycles many crystals were found to be damaged, scraped, showed twinning or had notches. Probably this extreme form of secondary nucleation could be avoided if the large crystals are removed by an effective classifier before they are damaged. Thus, one of the primary objectives in controller design is to find an optimum path to the desired steady state values whilst all excursions are suppressed.

From these figures the growth behavior is easily discernable. The subsequent volume fractions shift to the right with increasing size. The spikes superimposed on the trend are larger for fraction 9 and 18 than for the other two. This
Figure 5.11 Start-up response of four CSD volume fractions with a fines flow of 1.0 liters/s (Exp3): \(f_{50}:84-106 \, \mu m, f_{112}:168-212 \, \mu m, f_{157}:353-422 \, \mu m, f_{418}:669-843 \, \mu m\).
Figure 5.12 Start-up response of four CSD volume fractions with a fines flow of 2.2 liters/s (Exp4): 
$f_{0.06}$: 84-106 μm, $f_{0.12}$: 168-212 μm, $f_{0.15}$: 353-422 μm, $f_{0.18}$: 669-843 μm.
suggests that the variability in these fractions is larger, which is in accordance with previous findings that the extremities of the size distribution are measured less accurately. The information available for these particular size classes is limited due to truncation of the recorded scattering pattern. For this reason it is important to have an estimate of the variability within the fractions. The 95% confidence intervals for fractions 12, 15 and 18 were calculated using the theory of Chapter 3. It demonstrates the differences in information content between the three fractions. Fraction 15, which is in the middle of the size distribution shows a narrower band than fractions 12 and 18 which represent the crystals at the extremities of the distribution (Figure 5.15). The relative widths of the confidence intervals at time=30 hrs are approximately 30, 15 and 40% respectively. This allows discriminating between local disturbances which are less than the accuracy of the measuring system, and which ought to be ignored, and true disturbances of the process which require an appropriate action.

The lower graph of Figure 5.13 shows the fines distribution averaged over 50 samples measured at SL3. The shape and position of the fines distribution
remains unaffected during the experiment. The number of small crystals measured by the analyzer shows the same oscillation as seen in the individual fractions of the unclassified product and which is reflected by the obscuration of the incident beam. As expected, a higher fines withdrawal rate enables larger crystals to be removed from the annular zone. This was successfully detected by the instrument, which was mainly due to regular background corrections.
Figure 5.15 The estimated 95% confidence intervals for the volume fractions 12, 15 and 18 of Exp3.

using the separate unit. In this way the effects of long term laser instability and fouling of the cell were minimized. On average the obscuration was of the order of 3%, with peaks sometimes up to 20% occurring directly after a new burst of fines. Therefore most of the time the magnitude of the light scattered by the
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finest was comparable with the background signal. Although the total number of fines is in itself an important parameter, the control of the crystallization process needs an accurate description of the complete size distribution as a function of the fines withdrawal rate in order to estimate the classification efficiency curve.

**Median vs mean size to describe the location of the CSD**
The location of the size distribution, expressed as the median or \(x_{50}\) is compared with the mean. The latter was used by Jager (1990) en De Wolf (1990) to describe the dynamic behavior of the 970 crystallizer.

![Diagram](image)

*Figure 5.16 The median vs the mean as a descriptor for the location of the CSD. Data are taken from Exp4.*

In the example shown in Figure 5.16 a representative part from Exp4 was taken and the parameters were computed. Both mean and median preserve the period of the oscillation observed with the individual size fractions. The amplitude of the median is estimated at 27% of the average value for the time frame shown.
For the mean size we only find 17%, and therefore the signal provides less
detailed information on the state of the process. A second advantage of the
median size is that the successive values are clearly less noisy, that is, the
signal is more robust towards small disturbances.

Reproducibility of the experiments
The number of process inputs is limited and consequently only a limited number
of significant process outputs can be utilized. These outputs should be
representative and should contain sufficient information to reconstruct the CSD
of the process. With this in mind the set of 20 fractions derived from each
measurement was reduced to a set of two: the x50 as a measure of the location
and the qr as a measure of the spread of the CSD.

For identification of the evaporative crystallization process it is important to
verify that the process behaves in a reproducible manner. In Figure 5.17 the
outgrowth response of 3 experiments (Exp2, Exp3 and Exp5) under identical
conditions, with 1.0 liters/s fines removal, is compared in terms of the x50 and
qr.

It may be concluded that the results are reproducible apart from small
differences associated with each experiment. In all cases the maximum value for
the x50 is almost 600 μm, the minimum value is around 250 μm and the period
of the oscillation is roughly 6 hours. Noticeable is the change in the shape of
the oscillation for the x50 compared with that of the individual size class
fractions. The skewed behavior indicates a gradual growth of the median crystal
size followed by a very sudden collapse. The growth trajectory is essentially
straight. This conclusion can also be deducted from the positions of the shifting
minima and maxima of the individual fractions in Figure 5.11.

The 4 hrs and 7 hrs curves, depicted in the top graph of Figure 5.13, show
the typical shape of the size distributions before and after the collapse. Then the
size distributions that follow contains the 'second generation' crystals, of which
many have originated from secondary nucleation, using the attrition fragments
of the 'first generation' crystals as seeds. This is represented by the 10 hrs
curve.

After a relatively gentle period of growth, the breakdown of the size
distribution occurs in less than 30 minutes, lowering the maximum x50 by
Figure 5.17 Comparison of $x_{50}$ [$\mu$m] and $qr$ [-] observed during three runs under identical experimental conditions. The bar represents the resolution of the grid (0.23), which is equal to the width of one size class.

almost 400 microns. The lower graph of Figure 5.17 summarizes what happens to the width of the distribution at that particular time. The $qr$ rises from about 0.2 to 1.2 for all three experiments, which reflects a shift of 4 to 5 size classes between the small and large crystals present in the reactor. During the growth period, $ie$, between two disruptions of the CSD, the width of the size distribution decreases at first to reach an average low, value of about 0.2 and then remains fairly constant. This indicates that in the beginning the small crystals grow faster than the larger ones, effectively reducing the width of the CSD.

The period of the oscillation and also the absolute values of the three experiments under identical experimental conditions are reproducible in both $x_{50}$ and $qr$. The $qr$ traces the monomodal-bimodal-monomodal transition perfectly, and thus seems, together with the $x_{50}$, are well suited to characterize
the dynamics of the size distribution.

**Effect of fines withdrawal rate**

In Figure 5.18 and Figure 5.19 the effect of different fines flows on the $x_{50}$ and $qr$, for samples taken from the annular zone of the crystallizer, is presented.

*Figure 5.18* The influence of fines removal on the $x_{50} \, \mu m$: 1.0 (top, Exp.3), 2.2 (middle, Exp.4) and 3.4 (bottom, Exp.6) liters/s.
Three flows were investigated: 1.0 (Exp3), 2.2 (Exp4) and 3.4 liters/s (Exp6). All the fines contained in the flow were dissolved in the external heat exchanger by raising the temperature of the flow by 10°C. This is different to the original system where only part of the fines flow was dissolved and the other part was bypassed (De Wolf 1987). To eliminate the added complexity created by

![Graphs showing the influence of fines removal on the qr]
possible crystal breakage, growth and agglomeration of the bypassed crystals, and to increase robustness, it was decided that only the withdrawal rate itself would be used as the process input. The saturated clear liquor was returned to the crystallizer. The total heat input into the system, supplied by a combination of the internal and the external heat exchanger, was kept constant at 120 KW. An attempt was made to verify the usefulness of the fines withdrawal rate as an effective process input.

The results indicate that a larger fines removal rate stimulates the oscillatory behavior of the size distribution with time. The amplitude of the oscillation increased proportionally with an increased rate. For the first maximum in the x50 the variation was almost 200 μm per 1.2 liter/s increase. This means that the crystals can grow to a larger size as more small crystals are removed. Consequently it takes longer for the next generation of crystals to survive. Also, at higher flow rates, larger crystals are entrained in the annular zone, as was seen from Figure 5.13. This could have an additional effect on the size of the largest crystals in the system. The period of the oscillation is only slightly influenced, but also seems to increase with the removal rate. Dampening of the oscillation is diminished as the removal rate increases, whereas at the highest rate no dampening occurred at all. A similar behavior as for the x50 is found for the qr. The magnitude of the peaks also increases with the removal rate. This increase in the maximum width of the distribution can be understood if the fragments appear at the same crystal length whilst the maximum crystal size is enlarged. In the intermediate growth periods, the removal rate seems to have no effect on the width of the distribution, and an average qr of 0.2 is recovered.

Another example of an effective process input is the residence time of the crystal slurry in the reactor. The average residence time was changed by varying the flow of the unclassified product. The results, not reproduced here, show that in this case the amplitude of the oscillations in the x50 remains unaffected, but that the period is proportionally manipulated with the product flow (Eek 1992).
Step response in fines flow

It is of paramount importance that not only true process disturbances but also changes instigated by the controller are detected by the on-line sensors. The next stage involves a correct translation of the recorded signals in order to obtain reliable estimates for the output parameters which are then entered into the control system. The response of the measurement system was tested by a step change in one of the input variables of the process. The fines removal rate was instantaneously changed from 1.0 to 2.2 liters/s exactly 40 hours after start-up. The process was assumed to be in steady state since no oscillations were found for the CSD in both the x50 and qr. The output parameters selected to monitor the consequences for the CSD due to this step change were the fines obscuration (obsf) and x50 (Figure 5.20).

Before the step change the fines obscuration averaged around 2%. Its pattern

![Graphs of x50 and obsf over time]

**Figure 5.20** The relationship between the x50 [μm] and the obsf [%] after a step change in the fines flow from 1.0 to 2.2 liters/s at Time = 40 [hrs] of Exp3.
was rather noisy which is due to the inaccuracy of the signal involved at these low levels. This was one of the main reasons which thwarted a successful measurement of the fines size distribution. Directly after the step change the signal elevated and started to rise. Although wildly fluctuating, the trend is obvious and shows a significant increase in the number of fine crystals. Throughout the first hours after the step change no recognizable modification in the $x_{50}$ signal is seen. Only after about 2 hours (almost 2 times the residence time) does the $x_{50}$ start to respond whereas by that time the fines obscuration signal has already increased fourfold, indicating a severe process disturbance. This is understandable since the $x_{50}$, based on volume, is not very sensitive for an increased fines population. Therefore, it may be concluded that a combination of both output parameters is sufficiently effective to recognize a process change. This experiment demonstrates that it is essential to be able to accurately monitor the fine crystals in the reactor, for it is here process disturbances are readily reflected. Tracing the fines indirectly by following the obscuration, may give a lead of up to several residence times before any modifications are noted in the product crystals.

**Product classification**

The effect of product classification on the process was studied by removing product with the classifier during 10 hours after the start-up of Exp5. The ROMA program was adapted to measure the three relevant flows: fines, unclassified product and hydrocyclone overflow. The fines removal flow was 1.0 liters per second.

In Figure 5.21 the $x_{50}$ of both the feed (upper) and classifier return flow (lower) are shown. Steady state of the CSD was achieved much sooner than in Exp3 and Exp4, approximately 10 hours after start-up no significant changes are observed in the CSD. The location of the $x_{50}$ remained the same as that in to those experiments without product classification (eg, Exp3). From the lower graph, it is apparent that the hydrocyclone was able to separate the size distribution: the returned flow contained significantly smaller crystals (almost 150 µm) than the unclassified product flow. By following the obscuration values for both flows in combination with the observed size distributions, it was possible to calculate the relative mass flows. The zero values present in the
Figure 5.21 The $x_{50} \, [\mu m]$ of the unclassified product going to the hydrocyclone ($Q_{pf}$) and the overflow after classification which is returned to the crystallizer ($Q_{pr}$).

signal for $x_{50}$ of the classifier return flow are caused by severe blockage of one of the dilution unit tubes.

**Validation of measurements**

Improved insight into the reliability of the CSD measurement system was achieved by using the $\chi^2_{red}$-value of the fit. The $\chi^2_{red}$ is obtained after solving the linear model outlined in Chapter 3. An example of how the $\chi^2_{red}$-value reports on the quality of unfiltered measurements during the first 5 hours after start-up of Exp4 is depicted in Figure 5.22.

Firstly, the $\chi^2_{red}$ serves as an effective outlier detector. This is demonstrated at 0.9, 1.9, 2.8 and 3.2 hours, which indicate times at which there were communication problems between the PC and the host. For such cases the $\chi^2_{red}$-values automatically assumed zero, warning the host about the corrupted data.
These points are reflected in the $x50$ as individual peaks. The $\chi^2_{red}$-signal can also be used in a more refined method of weighting the relative contributions of successive measurements. A closer look at the $x50$ trend between 2.2 and 2.6 hours reveals that those data are out of line with the neighboring points. For the controller it is important to verify whether these points truly reflect the process conditions. Without an additional measure this would have been impossible. Therefore the filtering capabilities of the $\chi^2_{red}$-signal were investigated. Clearly, the correlation between the quality of the fit and the values of the $x50$ obtained is excellent. This information was used to filter the output parameters. For the above mentioned hump in the $x50$ a substantial rise in the $\chi^2_{red}$-signal was found, which tells the controller (or operator in general) that the increase in $x50$ is induced by the instrument rather than by the process.

The above described method of outlier detection was used to filter the raw signals presented in the previous figures. Gaps originating from one or more

![Graphs showing $x50$ and Reduced $\chi^2$ over time](image)

*Figure 5.22 The $\chi^2_{red}$-signal as a measure for the quality of the CSD compared to the $x50$ [\(\mu m\)] during the start-up of Exp4.*
outliers were filled by linear interpolation. An example of this procedure is shown in Figure 5.23 where the raw data from Exp3 were first tested for outliers by removing all data points with a $\chi^2_{\text{red}}$-value outside the 0.2-100 band. The choice for this band is arbitrary, but seemed reasonable. A perhaps better

![Graphs showing data analysis process]

Figure 5.23 Filtering the raw signal (top) with the $\chi^2_{\text{red}}$. The remaining outliers (middle) resulted from experimental errors and were removed manually, to give the final result (bottom).
approach would have been to take the 95% confidence intervals of the fit, which themselves follow a $\chi^2$-distribution. Typically the current procedure eliminated less than 2% of all the data points. The resulting gaps could easily be restored by simple linear interpolation. The procedure is illustrated in the top two graphs of Figure 5.23. The very few remaining outliers needed a more sophisticated approach. Although, according to the $\chi^2_{\text{red}}$-criterion the data were valid, they clearly conflicted with the other points. Usually this is due to severe experimental errors. In this example they resulted from unsaturated dilution liquor which dissolved part of the sample while it was diluted. An additional signal is therefore needed as a safeguard to monitor such events. For example, the phenomenon of the unsaturated liquor was detected perfectly by a sudden sharp drop in the obscuration signal, indicating a lower concentration of crystals in the optical cell.

![Graph](image)

**Figure 5.24** A scatter plot of $\chi^2_{\text{red}}$ as a function of the obscuration during one of the test experiments. The present dilution unit operates at 10 to 20% obscuration.

In the first experiment, Exp1, the performance of the dilution unit was
studied and the time for dilution was varied to find the optimum. Figure 5.24 displays a scatter plot of the obscuration values for the unclassified product flow versus the $\chi_{\text{red}}^2$ obtained after deconvolution for 500 points of Exp1. The scatter plot illustrates that the 10 to 30% obscuration region results in low values for the $\chi_{\text{red}}^2$, leading to more reliable estimates of the size distributions. At higher obscuration values, an exponential increase in the $\chi_{\text{red}}^2$ is found. This is due to multiple scattering which distorts the desired single scattering pattern. The consequence is that the size distributions found are systematically different from the actual one in the process. It is, therefore, recommended to operate the dilution unit at a narrow range of the obscuration, preferably between 15 and 25%. A more effective filtering scheme than described above could be devised if the obscuration is included. Thus, rather than simply discarding points above an arbitrary $\chi_{\text{red}}^2$-level, valid measurements should be located in a fixed region of the obscuration-$\chi_{\text{red}}^2$ plane. In practice, instead of having a fixed dilution time, the obscuration value should be used to control the dilution unit. After the appropriate concentration has been reached the program must activate the actual measurement of the scattering pattern. Also, dependent on the $\chi_{\text{red}}^2$-value, a second measurement could be performed. During the experiments the dilution unit performed well, yielding slurries with fairly constant obscuration values in the desired range.

Finally, it can be concluded that the deconvolution procedure using the Fraunhofer diffraction model is satisfactory since the values of the $\chi_{\text{red}}^2$-signal are typically close to the ideal value of 1 (see also Chapter 4). This means that, although no information on the shape and refractive index was included in the model, it is sufficient to translate the scattering data into a reliable size distribution. In other words, due to the uncertainties of the signal, the systematic errors remain unobserved, even if more sophisticated models, for example Mie, were used. This in accordance with the theory outlined in Chapter 2.

The examples shown in this section stress the relevance of an additional signal which constantly monitors the quality of the measurements.

Resolution
The resolution of the measurement system for the product measurements was estimated from a selected part of Exp4 (32 to 40 hours after start-up). The
actual values for $x_{50}$ were compared to an averaged signal obtained by a moving average over 15 points (Figure 5.25). This approach is justified by the assumption that, over a limited time frame the measurements can be considered as duplicates.

![Graph](image)

**Figure 5.25** Unprocessed and filtered trend of the $x_{50}$ [$\mu$m] for a selected part of Exp4 (upper) and the corresponding residuals (lower).

The upper graph shows the averaged line with the actual data for the $x_{50}$. In the lower graph the differences are plotted as residuals. A standard deviation of 8 microns was found. This means that process excursions which result in changes in the $x_{50}$ smaller than about 10 $\mu$m will be overlooked.

An alternative way to estimate the variability of the output parameters, $x_{50}$ and $qr$, is to find the confidence intervals, similar to the procedure for the individual fractions (see Figure 5.15).
Tracking Nucleation and Agglomeration in Batch Crystallization

Knowledge about the shape, position and spread of the distribution of crystal sizes directly after start-up is needed for correct modeling of the process dynamics. This distribution is then implemented in the growth model. The distribution is formed within a few minutes after the nucleation burst. In this short time frame it is common for some crystallization processes that agglomerates\(^1\) are formed which significantly contribute to the overall growth process. The mechanism of formation is described by the collision of two individual crystals. If the contact time is sufficient, the adhesion is transformed into a permanent state of contact by cementation. After consolidation voidage remains between the two crystals which can eventually cause fluffy structures. The result is the appearance of a bimodal size distribution which consists of large crystals, side by side, with small crystals formed exclusively from primary growth. The theoretical description of the secondary crystal formation for dilute systems comprises factors such as crystal size, agglomerate size, mechanical stresses introduced by agitation and local supersaturation levels of the solute. This finally leads to an expression of the agglomeration efficiency, that is, the probability that a collision results in a stable agglomerate. A closely related process is that of rupture which may occur simultaneously. Breakage is studied extensively in the field of size-reduction processes. Analytical and empirical expressions for both growth and breakage are available for incorporation in the population balance, but the difficulty is to assess the magnitude of all the parameters involved (Beckman and Farmer 1987, Hogg 1992). Experimental verification of the nucleation-growth-breakage processes is therefore needed. Current observation systems lack either the speed or the ability to characterize the size distribution in terms of position, spread and shape. The forward light scattering technique used in these experiments for the observation of process inputs was adapted slightly to record the rapid changes in size distribution at the early stages after nucleation. Additional routines were implemented in the

\(^1\) The word agglomeration is used here to indicate the formation of clumps of moderately or strongly bonded crystals. Sometimes this phenomenon is referred to as aggregation (Nelson 1988).
ROMA program. An undiluted flow of 0.2 liters/s was drawn directly from the reactor. The analyzer was equipped with a 300 mm lens. To validate the distributions, the results were compared with images taken with a CCD camera. Experimental conditions were the same as for the continuous experiments but the experiment was interrupted after 10 minutes and all the crystals were dissolved. This start-up procedure was repeated many times to assess its reproducibility. The method to appraise the start distribution is presented and discussed. A more complete overview of the work on modeling of the start-up size distribution is presented in Korstanje (1992).

**Fast CSD Measurements**

The experiments were divided into two stages. The first covered the first few minutes directly after the nucleation burst and aimed at finding the initial shape of the distribution. The second was concerned with modeling the open-loop growth phase which followed. For the second stage a normal sampling frequency of 1 sample in every 2 minutes was sufficient. This stage was observed with a second analyzer, which was equipped with a 1000 mm lens. In order to accurately monitor the start-up, the ROMA software was changed. The maximum sampling rate was increased to almost one thousand measurements per minute by manipulating the individual sweeps. The preliminary experiments were performed at a rate of 12 measurements per second. Later it was found that 1 measurement per 6 seconds was enough to adequately track the start-up of the crystallization process. One measurement consisted of 100 sweeps. The size class boundaries for deconvolution were set to 6 and 600 μm for the lower and upper limits. The resolution was decreased to 16 classes, corresponding to 28.8%.

In Figure 5.26 successive volume distributions are presented. There is a clear transition of distributions in a very short time frame. The bottom graph shows the final distribution which is used to model the outgrowth behavior. The 95% confidence intervals indicate a relatively large uncertainty in the size classes that contain the large particles. In order to be able to understand the transients, the same output parameters, x50 and qr, were used to track the start-up phenomena. In Figure 5.27 a representative result of the experiment is depicted. The results were extremely reproducible. During start-up three regions
can be discriminated:

- Small crystals, with x50 of about 50 \( \mu \text{m} \) are formed instantaneously. Before the burst a few large crystals always seemed to be present, which accounted for a relatively large fraction of the volume based size distribution. At this stage no apparent growth occurs, and a fairly straight line is found for all quantiles of the distribution. The spread, expressed as the \( qr \), remains fairly constant. From the obscuration signal it is deduced that the number of crystals rapidly increases. This period lasts about 1.5 minutes.

- As the obscuration reaches 30\%, a bimodal distribution is suddenly formed. The two maxima are located at 50 and 250 \( \mu \text{m} \). In this intermediate stage all the small crystals disappear and the number of large crystals grows. The transition is completed in about 1 minute. The increase in crystal size is too quick to be explained by crystal growth mechanisms, and severe agglomeration of the 50 \( \mu \text{m} \) crystals is suspected. The \( qr \) develops a maximum which is related to the width between the two distributions. The obscuration decreases slightly since the agglomeration reduces the crystal surface. Reduction of the crystal

*Figure 5.26 Volume distributions of the nucleation and successive agglomeration. The bottom graph gives the final CSD and its 95\% confidence intervals.*
Figure 5.27 The start-up behavior, followed by the x50 [µm], qr [-], obscuration [%] and reduced chi-square. It demonstrates three regions: before (1), during (2) and after (3) agglomeration.
surface due to dissolution of the 50 μm crystals is very unlikely since this would require heavily unsaturated liquor to be present in the reactor.
• In the final stage again a monomodal distribution is found. The x50 starts at about 250 μm and then monotonically grows to larger sizes. The width of the start-up distribution remains constant and the obscuration slowly increases again.

The lower graph of Figure 5.27 demonstrates the response of the $\chi^2_{red}$ during the initial start-up. At first it shows that adequate solution are obtained. Then the obscuration becomes too high, and multiple scattering occurs. Since the model is unable to describe this phenomena, this effect results in a much higher residual for the fit. Secondly, the transition from a monomodal to bimodal distribution leads to problems with the fixed grid. The bimodal is simply to wide to be accurately represented. After the transition stage is completed, and a monomodal size distribution is retrieved, the model again is adequate. This clearly demonstrates the need for a adaptive grid.

Verification with Camera
The undiluted sample drawn from the crystallizer was passed simultaneously through the optical cell of the analyzer and also through an identical cell which was used to take online images of the same crystals with a Videk CCD (Charged Coupled Device) camera manufactured by Kodak. The resolution of this camera is 1024 by 1024 pixels and a maximum of 256 grey levels can be discerned. The pixels are 6.8 by 6.8 μm. Images were recorded every 10 seconds during a period of 6 minutes after nucleation. Homogeneous light was obtained from an electronic flash (10 μs), which was used to freeze the

Figure 5.28 Schematic view of on-line CCD camera 1. Electronic flash with parabolic reflector 2. Diffusor 3. Crystal slurry 4. Optical cell 5. Macro lens (30mm) 6. CCD camera.
Table 5.2 Number of crystals counted with the on-line CCD camera
(Cusell and Elsinghorst, 1992).

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images, in combination with a parabolic reflector and diffusor. Although the resolution is decreased by the limited focal depth, the resolution of the macro lens, the resolution of the detector itself and the thickness of the cell windows, it was estimated that crystals larger than 40 μm can still be adequately distinguished. The crystals were flowing through the cell with a linear velocity of 1 m/s. A schematic view of the camera is depicted in Figure 5.28 (Heffels 1992).
Figure 5.29 Start-up behavior followed with the CCD camera. The successive frames represent 20, 40, 80, 150 and 240 seconds after nucleation (top left, top right, middle left, middle right and bottom left, respectively). Classification into four size ranges was done manually, and the corresponding results are summarized in Table 5.2.
The results obtained with the camera completely confirm the assumption of agglomeration in the few minutes directly after the nucleation burst. In the first frames (after 40 and 80 seconds; Figure 5.29) the number of crystals increases dramatically. Also, before the burst some large crystals can be discerned, as was detected by the ROMA program. Then the 50 μm crystals stick together to clusters which range in size between 150 and 500 μm. This causes the number of crystals to reduce (see eg, 150 seconds). Finally all the small crystals have disappeared, and the agglomerates start to grow (see eg, 240 seconds). The crystals were classified into four size groups by manual counting. Although the statistics are poor, due to the limited number of crystals contained in a single frame and the blurry transitions between the edge of the crystal and the liquor, the results are in excellent agreement with the sizing data obtained with the forward light scattering technique. The results are summarized in Table 5.2.

The agglomeration mechanism which was postulated from the scattering results was supported by the camera. The time of the transitions and the sizes of the single crystals as well as those of the agglomerates given by both techniques coincide well. The advantage of the camera is that it camera also reveals shape information about the crystals, which is not provided by the forward light scattering. Shape information is valuable since it provides a window on the actual process conditions in the crystallizer. Specific shapes are expected to arise from extremely high supersaturation, a high degree of attrition, or, for instance, the presence of foreign material.

Other Developments

In the UNIAK project two additional sizing techniques were tested for their ability to correctly characterize the ammonium sulfate crystals. The Partec 200, which is manufactured by Lasentec, uses backscattering. The light from a photodiode is focused to a very small spot behind the optical window. This spot scans at a fixed rate, and reflections from the particles are picked up and subsequently digitized at high speed into eight channels, depending on the duration of the reflection. The scanning rate is sufficiently fast to eliminate the influence of the flow velocity. The length of the pulses detected is therefore directly pro-
portional to the size of the particle. Since the beam may scan across the particle near its center as well as closer to its edges, a chordlength distribution is obtained. This distribution is then deconvoluted into a size distribution, based on direct inversion of a set of linear equations (Hobbel et al., 1991). The advantage of backscattering is that it eliminates the problems associated with high concentrations. Therefore sampling can be avoided, and the probe can dipped into the slurry directly. A major disadvantage is that the result may depend on the reflection properties of the material. Secondly, significant changes in the chordlength distribution are created by varying the threshold level of the A-D converter. Software was written to replace the manufacturer's program, in order to gain more flexibility and insight (Haket 1991). The instrument was tested at various locations in the crystallization process. A special ball valve was designed to study the optimal angle of the probe to the flow. The crystals in the fines flow could not be detected by the Partec, due to low reflectivity of the ammonium sulfate crystals. Some preliminary results were gathered for the unclassified product flow. In general the trending data were significantly more noisy than collected by the forward light scattering technique. Moreover the resolution with respect to size was poor. The total reflectance was found to be an excellent indicator for the time of the nucleation burst. The experiences with the Partec in the UNIAK crystallizer have been summarized by Ferro (1991).

Finally some ultrasonic spectrometry experiments were performed. This technique is also referred to as acoustic scattering. The attenuation of an ultrasonic wave in a particle suspension is recorded for a range of frequencies, typically from 1 to 100 MHz. The spectrum,
equivalent to an intensity distribution as observed in forward light scattering, is then translated into a size distribution. The prominent advantage of this technique is the ability to measure in undiluted slurries, with concentrations up to 25% by volume (Riebel and Löffler, 1989). A commercially available system, OPUS, manufactured by Sympatec was tested for its ability to measure ammonium sulfate crystal slurries representative for the UNIAK process. The results were promising, but some deviations with the expected distribution were found. This might have been due to systematic errors in the extinction matrix used, which was based on quartz sand. Furthermore, slurry concentrations had to be over 1 vol% and particles should not be smaller than 5 μm (Bloembergen 1992).

Conclusions

Experimental
The dynamic behavior of the crystallizer is observed well with the proposed measurement system. Oscillations originate from the small crystal size region which appear at an approximate size of \( x < 100 \) μm. Differences in the CSD of the fine crystals for various fines flows are also adequately observed. Since, in the case of fines, the scattering pattern is very weak as compared to measurements in the product flow, adequate background corrections are essential. The reduced set of output parameters proposed to describe the CSD consists of a robust estimator for the location, the median (\( x_{50} \)), and the logarithmic quartile ratio (\( qr \)). The measurements were demonstrated to be highly reproducible in terms of these two variables. Step changes of the fines removal rate were promptly observed by the measuring system. The same observability was noticed when the crystallizer was operated permanently at three different rates of fines flow. The measurement system also outputs an indirect measure of the CSD dynamic behavior in the obscuration signal. The product classification is monitored by comparing the median values of the distributions of the unclassified feed flow and the return flow to the crystallizer. The \( \chi^2_{red} \) is used as an effective filtering method to weight the measurements. The reliability of the measurements is good. A \( \chi^2_{red} \) close to 1 was observed implying a legitimate
choice of the deconvolution model. The estimated variability was estimated to be 8 microns. Preliminary results on modeling look very promising. Simulation revealed that stability of the CSD can be accomplished by proportional feedback of the fraction of crystals smaller than 100 μm to the fines withdrawal rate.

Intelligent sensors
Although it was demonstrated that the forward light scattering technique was able to find the representative size distributions at all times, even if the characteristics of the size distribution changed very rapidly, a combination of this technique with an imaging technique is suggested (Boxman and Scarlett 1988). A field scanning technique, commonly based on an indirect measurement technique, is able to observe thousands of particles in a very short time frame. In combination with the appropriate deconvolution routines a statistically accurate size distribution is returned. Model uncertainties included in the deconvolution step, such as minimum and maximum size, shape, defects, structure, the presence of foreign material, agglomeration and concentration information, could be provided by the camera.

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Symbols and Abbreviations

\[ f_{v,j} \] \hspace{1cm} \textit{Volume fraction}
\[ \text{CSD} \] \hspace{1cm} \textit{Crystal Size Distribution.}
\[ f(x) \] \hspace{1cm} \textit{Size distribution function of crystals.}
\( M_i \) \hspace{1cm} i^{th} \text{ moment of distribution.}

\( m \) \hspace{1cm} \text{Number of size classes.}

\( \text{obs} \) \hspace{1cm} \text{Obscuration.}

\( \text{PLC} \) \hspace{1cm} \text{Programmable Logic Controller.}

\( \text{PMC} \) \hspace{1cm} \text{Process Monitoring and Control.}

\( q \) \hspace{1cm} \text{Vector of estimated size fractions (m).}

\( qr \) \hspace{1cm} \text{Quartile ratio, a measure of the width of the CSD.}

\( \text{SL1, SL2, SL3} \) \hspace{1cm} \text{Sample location points.}

\( x \) \hspace{1cm} \text{Crystal size (diameter of equivalent sphere).}

\( x_{50} \) \hspace{1cm} \text{Median of CSD.}

\( \text{UNIAK} \) \hspace{1cm} \text{Universal Instrumentation and Automation of Crystallizers.}

**Greek**

\( \chi \) \hspace{1cm} \text{(chi)}

\( \chi^2_{red} \) \hspace{1cm} \text{Reduced sum of squares of the residuals.}

**Sub- and superscripts**

\( f \) \hspace{1cm} \text{Fines.}

\( i \) \hspace{1cm} \text{Indicates weight of moment.}

\( j \) \hspace{1cm} \text{Size class number.}

\( t \) \hspace{1cm} \text{Sets basis for size distribution.}

\( v_j \) \hspace{1cm} \text{Volume fraction of size class } j.

\( ^\wedge \) \hspace{1cm} \text{Unbiased estimator.}