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ON MULTIPLE OPTICAL SCATTERING IN A SCANNING NEPHELOMETER.

by

David M. Barnett BEng.

A doctoral thesis submitted in partial fulfilment of the requirement for the award of doctor of philosophy of Loughborough University.

January 2000

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ABSTRACT

Optical nephelometry is the measurement of the angular distribution of light scattered from a particle suspension. Experimental nephelometers confirm the predictions of optical models and their readings are inverted to determine properties of unknown suspensions.

Single scattering models, which assume a single particle interaction prior to detection, are used to model tenuous suspensions in the nephelometer. Multiple scattering models can be used to obtain higher-order solutions, but lack generality. Any given method addresses some subset of possible problems, e.g. tenuous or dense suspensions, small or large particles. This thesis explores the feasibility of using empirical models to extrapolate the single scattering approach in a non-linear manner, improving the generality of a multiple-scattering description.

Initially, single scattering (Mie) theory for spherical particles is presented and extended to polydispersions of particles and to spectral scattering. The principle of integrating the single scattering result over a finite scattering volume is examined as a precursor to modelling the actual nephelometer.

A low-cost, PC controlled scanning nephelometer is developed with a 0.9° resolution and ±150° range and a small (~25ml) volume sample cell. The photodiode detector has a numerical aperture of 0.079, providing, for most angles, a scattering volume with length 10mm and cross-section determined by the HeNe laser source (~1mm²). The optics of the air/glass/water interfaces and of single and first-order multiple scattering over the scattering volume are modelled. These models are found to predict the scattering footprints observed in tenuous suspensions of spherical latex particles.

Experimental data are obtained from tenuous to relatively dense (5% by volume) suspensions of latex spheres over a size range of 54nm to 14μm. These data are compared with single and first-order multiple scattering and their form and dependencies are considered.

They are used to train an empirical neural (multi-layer perceptron) model of the multiple scattering based on particle characteristics and on the scattering footprint of the individual particles. This non-linear extrapolation of the single scattering model is applied to the nephelometer, improving the generality over a purely theoretical multiple scattering approach. The trained neural model is used, initially, to investigate some of the empirical characteristics of the multiple scattering process.
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On Multiple Optical Scattering in a Scanning Nephelometer.

28 January 2000

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Chapter 1. INTRODUCTION

'It should be possible to study...multiple scattering by carrying out experiments at high concentration for a system whose single scattering behaviour is well understood.' – Kerker\(^1\)
1.1. Overview

This chapter introduces the basics and rationale for the subject of single and multiple scattering and gives an overview of the remainder of the thesis.

1.2. Hypothesis

A simple nephelometric experimental methodology can be established with a fine angular resolution and wide angular range. The nephelometer can be modelled up to first-order multiple scattering. Empirical extensions to this basic scattering model can be made for multiple scattering effects based on experimental data, providing a more general solution than any one multiple scattering model.

1.3. Synopsis

When optical waves are incident on inhomogeneities in optical parameters, electromagnetic fields will be redistributed and 'scattered'. Measurement of the intensities of scattered radiation can provide information concerning the state of the inhomogeneities. Scattering inhomogeneities can take several forms, which can be loosely categorised into rough surfaces, random continua and random scatterers. Only random scatterers are considered in this thesis and more specifically, only the most straightforward to model (i.e. spherical) particles, are examined.

The scattering of light from single spherical particles is readily computed by Mie theory. This theory and its derivation are presented in Chapter 2, along with methods for visualising its predictions. The model of simple monochromatic light scattered in a single direction from a single particle, is extended in a number of ways. Firstly, by integrating over a finite scattering volume, the light scattered into a rectangular detector is computed. Secondly, the effects of a polydisperse suspension or a polychromatic source are considered.

In all but the most restricted of experimental arrangements, a single particle cannot be considered in isolation. The effects of light scattered from an ensemble of randomly positioned particles is the topic of much research, proving a variety of solutions for various degrees of particle interaction. It is the subject of this thesis, to model these effects empirically. The various theoretical models of multiple scattering are described in Chapter 3, with a first-order correction presented in some detail.

A nephelometer is a device for measuring light scattered from a particle suspension at one or more angles. Most nephelometers consist of a number of sensors at fixed angles, providing intensity information at those angles. The scanning nephelometer described in Chapter 4,
uses a single optical sensor mounted on a stepper motor driven rotation stage to obtain high angular resolution scattering measurements over a wide angular range.

In Chapter 5, the scanning nephelometer is examined. Methods for modelling singular and first-order multiple scattering, as described in chapters 2 & 3, are brought together with the optical geometry of the scanning nephelometer to provide initial predictions of intensities as measured by the scanning detector. These results are presented and compared with those actually obtained experimentally.

The predictions of single scattering theory for the scanning nephelometer match the experimental data adequately for low concentration samples. As the number of particles in the scattering volume increase, the single scattering assumption becomes insufficient. The first-order multiple scattering prediction gives a qualitatively similar prediction of increased concentration, but is best used for modelling scattering from highly absorbing particles and then only for relatively tenuous suspensions.

Chapter 6 describes a method of empirical modelling - artificial neural networks. Data from the experiments are used to train a neural network to predict multiple optical scattering as an extension of the single scattering prediction.

### 1.4. The Inverse Problem

The field of optical particle scattering is only useful if the scattering models can be inverted. Light intensities are measured and, if they are to be used, predictions of physical and optical properties of the scattering suspension (e.g. particle size and/or characterisation) must be made from them. The inversion of the scattering problem is a wide field of research, incorporating both analysis of the underlying physics and empirical models, such as neural networks. Before understanding of an inverse problem can be achieved, the forward problem, i.e. the prediction of scattered intensity from physical parameters, must be understood.

This thesis does not address the inverse problem, but attempts to further the ability to model the forward problem and to provide a tool for the investigation of particle scattering phenomena.

### 1.5. Practical Applications of Scattering Measurement

The qualitative study of scattering effects was used initially to explain a variety of optical effects such as the colour of the sky and changes in the colour of water. More recently it has been used quantitatively in many disciplines for the detection, measurement and identification of a wide variety of substances.
Optical particle scattering measurements are of particular use for the detection and monitoring of particles with size comparable to the wavelength of visible light\(^4\). Easily measurable parameters of light scattered from smaller particles are not determined uniquely by the particles' size, nor is particle size readily separated from them. Larger particles are more easily measured and detected by other techniques such as imaging microscopy.

In fields such as astronomy and meteorology, particles cannot be confined into an imaging region and so scattered radiation may be the only observable source of information available. In the absence of other data, the interpretation of scattering patterns provides the only method for analysis of phenomena of interest.

A third area of useful scattering measurements is for the routine monitoring of a continual process, for control or quality analysis. If the majority of parameters of a particle suspension are relatively consistent, or only a guideline measure is required, an efficient nephelometric system can be designed to monitor the remaining variables. For instance, a process may produce particles of consistent size and material, in which case a simple calibrated turbidity measurement\(^5\) can provide a surrogate for concentration. In the water industry, turbidity is measured as a surrogate for particle content; the single measure is dependent on the many variables of the particle content, but a rough guideline of the water quality is provided.

The following sections detail a variety of existing applications of scattering measurements, all of which fall into one or more of the three categories mentioned. The majority of these applications employ some analytical or empirical model of their readings to interpret the required information. Application of the analytical and neural modelling methods described in this thesis to data acquired from known conditions could provide further information or better compensation of experimental or multiple scattering effects.

### 1.5.1. Water Industry

Water legislation dictates various parameter limits which water entering community supplies should meet. Some of these parameters are based on optical measures i.e. colour and turbidity. The parameters are monitored for two main reasons - customer perception and health implications.

Measurements are made which are estimates of how the customer will perceive the colour\(^6\) and turbidity\(^15, 7, 8\) of supplied water. Limits set what the customer is likely to find acceptable. Colours above 15TCU (true colour units) can be detected in a glass of water\(^9\) and the appearance of turbidity less than 5NTU (nephelometric turbidity units) is considered acceptable.
The good treatment of water also has health implications. Treatment that has removed the vast majority of particles in a given size range is likely to have removed any microorganisms of a comparable size e.g. cysts of Giardia or Cryptosporidium\cite{10,11}. Unacceptable levels of particle content can also protect microorganisms from the effects of disinfection\cite{11}, which requires a turbidity of less than 5NTU. Ideally the median operating turbidity should be below 1NTU. Water treatment works aim for turbidity after filtration to be significantly lower than this limit.

Optical sensing of the particulate content of water also has implication in the treatment process itself \cite{12}. Turbidity and colour measurements, along with others, are made on raw water prior to treatment. These data provide information about how the water treatment process should be run e.g. what doses of chemical should be added. Additional relevant information could lead to greater efficiency in the treatment processes. Continual improvement of processes such as coagulation, have implications not only to the stage itself, but also to the running of further stages, e.g. reduced chemical cost for pH adjustment and disinfection, energy cost in back-washing and reduced waste\cite{13}.

The study of scattering processes could lead to the development of sensors capable of providing more detailed information about the particle content of water. This could, in turn, lead to improvement in the efficiency of the treatment process itself and/or the monitoring of treated water for potential hazards. Although the study of multiple scattering is of little use in potable water monitoring, it may be of relevance in particularly turbid raw waters.

Light scattering is also used as a measurement technique in experimental water treatment work\cite{14}. Accurate particle information is required in the chemical and physical study (e.g. coagulation and flocculation) of water treatment processes.

1.5.2. Transport Studies

Nephelometric and attenuation turbidity measurement, using standard commercially available turbidimeters, is frequently used to monitor suspended solids in stream transport studies\cite{15}. The effects of variations other than that of concentration (e.g. particle size and composition (mineral-organic ratio), water colour) must be assumed to be negligible for such results to be considered valid. Nephelometric study beyond basic turbidity can potentially provide a rich source of data, supplying a more accurate measure of particle content with additional information defining the particles' make-up\cite{16}.

1.5.3. Bio-optics

Optical scattering by inhomogeneities occurs in biological materials\cite{17}. Particle scattering occurs from anything from single red blood cells (a few μm in diameter) to muscle cells
millimetres in length\textsuperscript{[18, 19]}. Information from scattering (and absorption) studies provides valuable diagnostics, such as saturated oxygen levels from the photoplethysmographic signal\textsuperscript{[20]}

In tissues, cell and particle content is so high as to be considered a random continuum rather than a system of discrete scatterers. Even in whole blood, scatterer (erythrocyte) concentration ($5 \times 10^6\text{mm}^{-3}$, 40% by volume) is significantly higher than samples considered experimentally in this thesis. Continuation of this work could be considered by extending the theories into such a domain.

Studies\textsuperscript{[21]} have been made which use polarisation to determine variations in the concentration and morphology of red blood cells. A Stokes' polarimeter determines the full state of polarisation of scattered light, providing the required information about the sample.

Scattering measurement is also potentially useful in field of microbiology for identifying and distinguishing microorganisms\textsuperscript{[22]}.

1.5.4. Meteorology

The effects of scattering from aerosols (e.g. dust or smoke) and hydrometers (rain\textsuperscript{[23]}, fog, snow or hail) are usually referred to (along with echoes from trees, vegetation etc.) as clutter\textsuperscript{[24]} by conventional radar operators\textsuperscript{[25]}. To a weather radar, this clutter is essential for meteorological research and weather prediction. The analysis of the scattering, which in most cases, is well into the multiple scattering regime, is of interest to the study of precipitation patterns, thunderstorms, tornadoes and hurricanes.

1.5.5. Oceanography

The study of the optics of seawater can provide information about absorbing dissolved and colloidal humic organic matter, inorganic matter from land drainage and organic matter such as plankton and disintegrated cells\textsuperscript{[26]}. Concentrations of particulate in ocean water ranges from 0.04 to 18 mg/l with a size distribution in the 10nm to near millimetre range. Scattering from air bubbles also has a significant effect on observations of the ocean\textsuperscript{[27]}.

1.5.6. Research

Scattering studies employing commercial sizers or custom measurement equipment are used frequently in laboratory research to measure parameters of some chemical or physical process, e.g. droplet size in dense sprays\textsuperscript{[28, 29]}. In many of these situations, calibration data cannot be obtained since the experiments are purely individual phenomena. Modelling of the scattering processes is therefore essential, as empirical observations cannot be made for comparison.
1.6. **Nephelometry**

The study of light scattered from a sample and its angular dependence is generally referred to as nephelometry. The majority of the techniques described above are some form of nephelometry, whether it is a single turbidity measurement at 90° or a complex study of radar backscatter in meteorology. Nephelometry in its truest form takes scattering information from several carefully or arbitrarily chosen angles and interprets it accordingly. Inversion of this information into useful parameters defining the scattering sample can often be complex. Green⁴⁰ and other authors have used non-linear fitting techniques such as neural methods to model the inverse problem based on both theoretical and experimental forward models.

*Figure 1.1 – Green’s on-line nephelometer with removable source and detectors.*
Chapter 2. **SINGLE LIGHT SCATTERING FROM SPHERICAL PARTICLES**

'Red sky at night...'
2.1. **Aim**

This chapter gives an overview of accepted exact spherical particle scattering (Mie) theory, its derivation and its computation. The theory is extended in a number of ways useful in real world situations, while still maintaining the single scattering assumption.

2.2. **Introduction**

A single spherical particle isolated from all external influences within a detectable region is an unlikely occurrence. The modelling of light scattering in such a situation is analytically soluble and its result a good approximation to more likely circumstances. The computation of the intensity of light scattered from a single particle is presented in the early sections (§2.6) of this chapter and is considered a good approximation to a tenuous suspension of similar particles.

Light scattered at a single angle cannot be measured and any sensor, no matter how small, will always capture light falling into a finite solid angle. §2.7 and 2.8 integrate the basic theory over a realisable sensor for plane and narrow beam incident radiation respectively.

A tenuous suspension (i.e. a fluid containing few particles) will produce a scattered intensity equal to the sum of the light scattered from the individual particles in the scattering volume. In the case of a suspension of similar particles this sum will be a simple multiple of the single particle result. If the particles are dissimilar then the distribution of particles must be considered. §2.9 describes the integration of any known particle distribution to provide a mean intensity for a suspension of such particles. §2.11 provides the statistics of this scattering.

§2.10 and 2.12 consider the scattering of polychromatic light. The light scattering function is wavelength specific and so the scattering phenomena for different colours of light will be different. The total intensity of scattered polychromatic light is first considered and then the statistics and spectra of such light.

This chapter presents a number of methods for visualising scattering and spectral results. A three-dimensional presentation of scattered light (§2.6.4) allows visualisation of the entire azimuthal and scattering angle range. §2.12.1 allows the conversion of a spectrum of light into a VDU and printer compatible RGB triple approximation.

2.3. **Historical Overview**

The basic theory presented here is usually referred to as Mie theory, due to its presentation in Gustav Mie's\cite{Mie1908} 1908 paper\cite{Mie1908a, Mie1908b}. However, the solution to the problem was first submitted
in a memoir by A. Clebsch \cite{Clebsch}, 'Concerning the reflection on a spherical surface', some 47 years earlier. The history of this problem is the subject of a paper\cite{Clebsch} and is given some space in the main books on the subject of particle scattering\cite{Clebsch, Clebsch, Clebsch}.

Clebsch constructed solutions to the scalar wave equations. The elastic wave equations (this was some twenty years before the acceptance of Maxwell's theory of electromagnetic waves\cite{Maxwell}) had previously been reduced into these partial differential equations by G.G. Stokes\cite{Stokes}. He went on to develop the mathematical theory required to solve the boundary-value problem in which the wave propagating in an elastic medium impinges upon a spherical surface. The methodology presented in the paper used Cartesian co-ordinates, without the advantage of modern vector analysis or notation. The theory required the infinite series of products of spherical harmonics (associated Legendre functions) and Stokes' Bessel functions (named for their later presentation by Stokes\cite{Stokes}). These Bessel functions were defined by Clebsch and their recurrence formulae given.

In the following decades, Lord Rayleigh\cite{Rayleigh, Rayleigh, Rayleigh}, H. Lamb\cite{Lamb} and L. Lorenz\cite{Lorenz} continued and then repeated the work after accepting Maxwell's theories. Rayleigh\cite{Rayleigh, Rayleigh} failed to solve the problem exactly but solved for the approximation of a small sphere, using firstly dimensional analysis and then analytical consideration of the forces within the aether. Lamb, using methods similar to those of Clebsch, solved the vector-wave equation, forming the basis for several papers by other authors. In the year before his death, Lorenz simplified and refined Clebsch solution by excluding the generality of longitudinal waves (from elastic-solid theory) and by using spherical-polar co-ordinates.

This leads to Mie's 1908 paper, in which he explained the brilliant colours displayed by colloidal metal suspensions. His thorough and rigorous treatment of the problem of optical scattering and its application to a practical phenomenon provided a guide to future researchers in applied light scattering. There are others who apparently also solved the problem earlier, but failed to publish their results till years later.

2.4. Assumptions

The problem that this chapter attempts to solve is that of single scattering from an independent spherical particle. Beyond the obvious limitation that the particles be spherical, are the issues of single independent scattering. Particles in the field of view are considered independent; i.e. they are sufficiently far from each other that the fields within them do not interact with each other. This assumption allows the addition of intensities from individual particles. A small displacement in position changes phase entirely, which can thus be disregarded when effects are on average added. Estimates have shown that a mutual distance
of 3a (three times the particle radius, ~16\% by volume) is a sufficient condition for independence\(^4\).

The final assumption is that multiple scattering can be neglected. Light scattered by and incident upon each particle is considered to be unaffected by other particles. In reality each particle will have light incident upon it that has been scattered by every other illuminated particle. For sufficiently low particle concentrations, this intensity is completely negligible when compared with the intensity of the source.

2.5. **Approximations**

Various areas of parameter (refractive index/particle size/scattering angle) space have solutions that tend towards some simpler form. Van der Hulst\(^4\) details the regions of validity of these approximate solutions. Some of these solutions were obtained many years before the full rigorous solution that covers the entire refractive-index/particle size domain. They are, generally, less computationally expensive.

Rayleigh scattering is one of the most frequently encountered approximations, being valid for small \((x<1)\) particles, treating the electrically polarised particle as a simple dipole. Conversely, large \((x>>1)\) spheres have their own approximation, based on the asymptotic laws of electromagnetic waves which define geometrical optics\(^{44}\) and so treating the particle as a simple spherical lens. Rayleigh-Gans\(^{40}\) theory predicts scattering by particles whose refractive indices are similar to that of the surrounding media (i.e. \(m-1\))\(^1\). Conditions of total reflection (\(m\rightarrow\infty\)) also provide simple solutions as the electromagnetic waves fail to penetrate the particle. The corners of \(m-x\) space, provide problems for their respective approximations, but are covered by approximations\(^4\) of their own – anomalous diffraction (large particles with small refractive index differential) and optical resonance (small particle with large relative refractive indices).

This thesis does not consider any of these physical approximations nor approximations based on more empirical techniques (e.g. neural networks\(^{45}\)). The edges of the regimes of validity for each of the approximations are vague and it is tempting to stretch the realms of use. The number of calculations required by this thesis is well within the capabilities of modern computers. Even for integration over distributions of particles, spectra or angle range, calculation time is measured in, at most, hours. The coding and verification time involved in also implementing the various approximations can only be justified when vast numbers of calculations are required within a given region, on relatively limited computer resources.

\(^1\) \(x\) is particle size normalised to wavelength, \(m\) is refractive index relative to the background medium.
Also, as mentioned by Deirmenjian\textsuperscript{46}, 'since the modern computer has such an enormous capacity, there is no practical reason for further improving these approximations, which have already served their purpose.' Since that comment, there have been a further 30 years of rapid development in computing power.

2.6. Mie Theory

The subject of optical particle scattering is the core subject of several notable books\textsuperscript{1, 4, 36}, each of which presents Mie theory using different notation. The following sections derive the scattering of light from homogeneous spherical particles starting from Maxwell's equations and finishing with the solution of the scattering coefficients. This derivation, largely as presented by Bohren and Huffman\textsuperscript{36}, is given as a background to the sections that follow. In presenting the derivation, required functions, Bessel and associated Legendre, are graphed in two and three dimensions in order to help visualise their role in the Mie scattering solution.

The methods of computation of Mie scattering are discussed, together with some of the practicalities of performing such calculations.

2.6.1. Overview

Mie\textsuperscript{32, 33} applied Maxwellian electromagnetic field theory to the problem of the homogenous sphere illuminated by plane waves from one direction. The method consists of expressing incident, internal and scattered fields in terms of spherical waves centred on the particle, fitting the appropriate boundary conditions and solving the resulting differential equation at the sphere surface and in the far field.

2.6.2. Derivation

The Vector Wave Equations

Maxwell's equations are well known and accepted\textsuperscript{47, 48}. The electromagnetic field (E, H) satisfies the wave equation in a linear homogeneous medium,

\[
\nabla^2 E + k^2 E = 0
\]

\[
\nabla^2 H + k^2 H = 0
\]

where \( k^2 = \omega^2 \varepsilon \mu \). \( k \) is the wave-number, \( \omega \) is the circular frequency and \( \varepsilon, \mu \) are, respectively, the permittivity and permeability of the medium.
They are divergence free,
\[ \nabla \cdot \mathbf{E} = 0 \]
\[ \nabla \cdot \mathbf{H} = 0 \]
and are interdependent,
\[ \nabla \times \mathbf{E} = i\omega \mathbf{H} \quad (2.2) \]
\[ \nabla \times \mathbf{H} = -i\omega \mathbf{E} \quad (2.3) \]

**Scalar Wave Equation**

Finding solutions to the field equations,
\[ \nabla^2 \mathbf{M} + k^2 \mathbf{M} = 0 \]
can be reduced to the simpler problem of finding solutions to the scalar wave equation,
\[ \nabla^2 \psi + k^2 \psi = 0 \quad (2.4) \]

This involves defining the vector function, \( \mathbf{M} \), in terms of a constant ‘pilot’ vector, \( \mathbf{c} \), and a scalar ‘generating’ function, \( \psi \),
\[ \mathbf{M} = \nabla \times (\psi \mathbf{c}) \quad (2.5) \]

By taking the pilot vector, \( \mathbf{c} \), to be equal to a unit radial vector, \( \mathbf{r} \), we have a solution in spherical polar co-ordinates (Figure 2.1). The scalar wave equation 2.4 can be written in these spherical polar co-ordinates,
\[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} + k^2 \psi = 0 \]

**Separation of Variables**

A solution to this can be found by separation of variables, making the substitution,
\[ \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (2.6) \]
giving three soluble ordinary differential equations,
\[ \frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0 \quad (2.7) \]
\[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d \Theta}{d\theta} \right) + \left[ n(n+1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0 \quad (2.8) \]
The linearly independent solutions to equation 2.7 are

\[ \Phi_e = \cos m\phi \]
\[ \Phi_o = \sin m\phi \]

where \( e \) and \( o \) denote even and odd solutions respectively.

Figure 2.1 - Spherical polar co-ordinate system centred on a spherical particle.
\( \psi \) must be a single-valued function of \( \phi \) (the azimuthal angle) and as such

\[
\lim_{n \to \infty} \psi(\phi + \pi) = \psi(\phi)
\]

for all \( \psi \) where properties are continuous. All valid linearly independent solutions of equation 2.7 can be generated from \( m=1,2,3, \ldots \)

**Scattering Angle Term**

The finite solutions of equation 2.8 are the associated Legendre polynomials of the first kind\(^{[69]} \), \( P_n^m(\cos(\theta)) \), of degree \( n \) and order \( m \), with \( n=m,m+1, \ldots \) The associated Legendre polynomials are mutually orthogonal –

\[
\int_{-1}^{1} P_n^m(\mu)P_{n'}^{m'}(\mu)\,d\mu = \delta_{nn'} \frac{2(n+m)!}{2n+1(n-m)!}
\]

where \( \mu = \cos \theta \).

Functions of the Legendre polynomials as they appear in the final solution are plotted in figure 2.2.

**Radial Term**

Equation 2.9 can be simplified by substituting the dimensionless parameter \( \rho = kr \) and defining \( Z = R\sqrt{\rho} \)

\[
\rho \frac{d}{d\rho} \left( \rho \frac{dZ}{d\rho} \right) + \left[ \rho^2 - \left( n + \frac{1}{2} \right)^2 \right] Z = 0
\]

<table>
<thead>
<tr>
<th>( n )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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</thead>
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<tr>
<td>( \pi )</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>( \tau )</td>
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</tbody>
</table>

*Figure 2.2 - Scattering angle dependent functions - \( \pi_n = \frac{p_n^l}{\sin \theta} \) and \( \tau_n = \frac{dp_n^l}{d\theta} \).*

Blue circle indicates unit radius about origin. \( \theta = 0^\circ \) points to the right.
The linearly independent solutions of which are the Bessel functions\(^{50}\) of the first \(J_\nu\), and second, \(Y_\nu\) kind, where the order, \(\nu = n + \frac{1}{2}\), is half-integral. Linearly independent solutions of \(R\) in equation 2.9 are the spherical Bessel functions (Figures 2.3 & 2.4) –

\[
j_n(\rho) = \sqrt{\frac{\pi}{2\rho}} J_{n+\frac{1}{2}}(\rho)
\]

\[
y_n(\rho) = \sqrt{\frac{\pi}{2\rho}} Y_{n+\frac{1}{2}}(\rho)
\]

the factor \(\sqrt{\frac{\pi}{2}}\) being introduced for later convenience.

---

Figure 2.3 – Ricatti-Bessel functions of the first and second kinds.
Figure 2.4 - Spherical Bessel function of the first (a-d) and second (e-h) kinds calculated on a cross-section through the origin.
Solution to Scalar Wave Equation

Collecting the preceding solutions together into equation 2.6, the scalar wave equation 2.4 has the following solutions:

\[ \psi_{m\theta} = \cos m \phi P^m_n (\cos \theta) z_n(kr) \]
\[ \psi_{m\theta} = \sin m \phi P^m_n (\cos \theta) z_n(kr) \]

where \( z_n \) is either of the spherical Bessel functions, \( j_n \) or \( y_n \), or any linear combination of them. The other factors, \( \cos m \phi \), \( \sin m \phi \), \( P^m_n (\cos \theta) \) and \( z_n(kr) \), are also complete and so any function that satisfies the scalar wave equation 2.4 may be expanded as an infinite series in the above solutions.

Solution to Vector Wave Equation

Substituting the solutions into the definition of \( M \) in terms of \( \psi \), equation 2.5, we have the vector spherical harmonics:

\[ M_{m\theta} = \nabla \times (r \psi_{m\theta}) \]
\[ M_{m\theta} = \nabla \times (r \psi_{m\theta}) \]
\[ N_{m\theta} = \frac{\nabla \times M_{m\theta}}{k} \]

These vector spherical harmonics can be expanded using the definition of curl expressed in spherical polar co-ordinates:\(^{[51]}\)

\[ M_{m\theta} = \frac{-m \sin \theta \sin \phi}{\sin \theta} P^m_n (\cos \theta) z_n(\rho) \hat{\varphi} - \cos m \phi \frac{dP^m_n (\cos \theta)}{d \theta} z_n(\rho) \hat{\theta} \]
\[ M_{m\theta} = \frac{m \cos \phi}{\sin \theta} P^m_n (\cos \theta) z_n(\rho) \hat{\phi} - \sin m \phi \frac{dP^m_n (\cos \theta)}{d \theta} z_n(\rho) \hat{\theta} \]
\[ N_{m\theta} = n(n+1) \cos \phi P^m_n (\cos \theta) \frac{z_n(\rho)}{\rho} \hat{\rho} + \cos m \phi \frac{dP^m_n (\cos \theta)}{d \theta} \frac{1}{\rho} \frac{d(p z_n(\rho))}{d \rho} \hat{\theta} \]
\[ - \frac{m \sin \phi}{\sin \theta} \frac{dP^m_n (\cos \theta)}{d \theta} \frac{1}{\rho} \frac{d(p z_n(\rho))}{d \rho} \hat{\varphi} \]
\[ N_{m\theta} = n(n+1) \sin \phi P^m_n (\cos \theta) \frac{z_n(\rho)}{\rho} \hat{\rho} + \sin m \phi \frac{dP^m_n (\cos \theta)}{d \theta} \frac{1}{\rho} \frac{d(p z_n(\rho))}{d \rho} \hat{\theta} + m \cos \phi \frac{dP^m_n (\cos \theta)}{d \theta} \frac{1}{\rho} \frac{d(p z_n(\rho))}{d \rho} \hat{\varphi} \]
Any solution to the field equations, 2.1-2.3, can be expressed in spherical co-ordinates, as an infinite sum of these vector harmonics.

**Orthogonality of Vector Spherical Harmonics**

It can be proved\(^{(36)}\) that the set of vector harmonics, 2.10-2.13, are mutually orthogonal in the sense that

\[
\int_0^{2\pi} \int_0^\pi \mathbf{M}_{emn} \cdot \mathbf{M}_{em'n'} \sin \theta d\theta d\phi = 0 \qquad \forall m, m', n, n'
\]

\((\mathbf{M}_{emn}, \mathbf{M}_{em'n'}), (\mathbf{N}_{emn}, \mathbf{N}_{em'n'}), (\mathbf{M}_{emn}, \mathbf{N}_{emn}), \) and \((\mathbf{M}_{emn}, \mathbf{N}_{emn})\) by virtue of the orthogonality of cosine and sine. \((\mathbf{M}_{emn}, \mathbf{N}_{emn})\) and \((\mathbf{N}_{emn}, \mathbf{M}_{emn})\) are shown to be orthogonal by showing that

\[
\int_0^n \left( p_n^m \frac{dP_n^m}{d\theta} + p_{n'}^m \frac{dP_{n'}^m}{d\theta} \right) d\theta = m p_n^m p_{n'}^m |_0
\]

vanishes for all \(n\) and \(n'\).

The associated Legendre function, \(P_n^m\), is related to the \(m\)th derivative of the corresponding Legendre polynomial, \(P_n\), by

\[
P_n^m(\mu) = \left( 1 - \mu^2 \right)^{\frac{m}{2}} \frac{d^m P_n(\mu)}{d\mu^m}
\]

where \(\mu = \cos \theta\). For \(\theta = 0\) and \(\theta = \pi\), \(\mu = 1\) and so \(P_n^m(\mu)\) vanishes, except when \(m = 0\).

For all \(m\) and \(n\), equation 2.14 vanishes.

The pairs, \((\mathbf{M}_{emn}, \mathbf{M}_{em'n'}), (\mathbf{N}_{emn}, \mathbf{N}_{em'n'}), (\mathbf{M}_{emn}, \mathbf{M}_{em'n'}),\) and \((\mathbf{N}_{emn}, \mathbf{N}_{em'n'})\), can be shown to be orthogonal by showing that

\[
\int_0^\pi \left( \frac{m^2}{\sin^2 \theta} p_n^m p_{n'}^m + \frac{dP_n^m}{d\theta} \frac{dP_{n'}^m}{d\theta} \right) \sin \theta d\theta = 0.
\]

\(P_n^m\) and \(P_{n'}^m\) satisfy 2.8, so

\[
2 \sin \theta \left( \frac{dP_n^m}{d\theta} \frac{dP_{n'}^m}{d\theta} + \frac{m^2}{\sin^2 \theta} p_n^m p_{n'}^m \right) = 2(n+1)p_n^m P_{n'}^m \sin \theta + \frac{d}{d\theta} \left( \sin \theta \frac{dP_n^m}{d\theta} P_{n'}^m + \sin \theta \frac{dP_{n'}^m}{d\theta} P_n^m \right)
\]

which integrates to zero given the orthogonality of \(P_n^m\).
Plane Wave Expressed in Vector Spherical Harmonics

In Cartesian co-ordinates the plane x-polarised wave is easily expressed –

$$E_i = E_0 e^{i k r \cos \theta} \hat{e}_x$$  \hspace{1cm} (2.16)

and the unit x-vector can be expressed in spherical polar basis vectors –

$$\hat{e}_x = \sin \theta \cos \phi \hat{e}_r + \cos \theta \cos \phi \hat{e}_\theta - \sin \phi \hat{e}_\phi$$ \hspace{1cm} (2.17)

The mutual orthogonality of the vector harmonics allows the plane wave, 2.16, to be expanded as an infinite sum of vector spherical harmonic terms –

$$E_i = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} B_{m,n} M_{m,n} + B_{m,n} M_{m,n} + A_{m,n} N_{m,n} + A_{m,n} N_{m,n}$$

where the coefficients are given by

$$B_{m,n} = \frac{\int_{0}^{2\pi} \int_{0}^{\pi} E_i \cdot M_{m,n} \sin \theta d\theta d\phi}{\int_{0}^{2\pi} \int_{0}^{\pi} |M_{m,n}|^2 \sin \theta d\theta d\phi}$$ \hspace{1cm} (2.18)

$$A_{m,n} = \frac{\int_{0}^{2\pi} \int_{0}^{\pi} E_i \cdot N_{m,n} \sin \theta d\theta d\phi}{\int_{0}^{2\pi} \int_{0}^{\pi} |N_{m,n}|^2 \sin \theta d\theta d\phi}$$ \hspace{1cm} (2.19)

The plane wave, when expressed in spherical polar co-ordinates, 2.17, contains only $\cos \theta$ in the $\hat{e}_x$ term and so given the orthogonality of sine and cosine, all $B_{m,n}$ and $A_{m,n}$ terms vanish and $B_{m,n}$ and $A_{m,n}$ terms vanish except for $m=1$.

At the origin the spherical Bessel function of the first kind is well behaved, while the spherical Bessel function of the second kind is not finite. This can be seen in figure 2.4. For this reason $z_s(\rho)$ must be taken to be of the first kind, $j_s(\rho)$.
The plane x-polarised wave can now be expanded as

$$E_i = \sum_{n=0}^{\infty} B_{o,ln} M_{o,ln}^{(0)} + A_{o,ln} N_{o,ln}^{(0)}$$

where \( (0) \) denotes \( \rho \)-dependency being spherical Bessel functions of the first kind.

The dot product in 2.18 can be expanded after substituting 2.11, 2.16 and 2.17 for \( M_{o,ln} \) and \( E_i \). This gives after integration and cancellation –

$$B_{o,ln} = \frac{E_0 (2n+1)}{2 j_n(p) n^2 (n+1)^2} \int_0^\pi d(\sin \theta P_n^1(\cos \theta)) e^{i\phi \cos \theta} d\theta$$

The associated Legendre function can be substituted for a Legendre polynomial using 2.15 –

$$P_n^1 = -\frac{dP_n}{d\theta}$$

Given that \( P_n \) satisfies 2.8, \( B_{o,ln} \) then contains Poisson’s integral\(^ {30} \) –

$$j_n(p) = \frac{i^{-n}}{2} \int_0^\pi e^{i\phi \cos \theta} P_n(\cos \theta) \sin \theta d\theta$$

The \( M_{o,ln}^{(0)} \) coefficient can now be written,

$$B_{o,ln} = E_0 \frac{2n+1}{n(n+1)} i^n$$

Similarly the \( N_{o,ln}^{(0)} \) coefficient can be extracted

$$A_{o,ln} = -iE_0 \frac{2n+1}{n(n+1)} i^n$$

The expansion of the plane x-polarised wave in spherical vector harmonics is

$$E_i = E_0 \sum_{n=0}^{\infty} i^n \frac{2n+1}{n(n+1)} (M_{o,ln}^{(0)} - iN_{o,ln}^{(0)})$$

\( 2.20 \)

Solution of Internal and Scattered Fields

The wave incident on the particle has been expressed in a set of co-ordinates in which the boundary conditions of the particle can easily be expressed. The solution of the resultant and scattered fields follows naturally.
Applying 2.20 to Maxwell’s equation, 2.2, we obtain the corresponding magnetic field –

$$H_1 = \frac{1}{i\omega \mu} \nabla \times E_1$$

$$= -\frac{k}{i\mu} \sum_{n=0}^{\infty} \frac{i^n}{n(n+1)} \left( M_{\text{e1}}^{(n)} + i N_{\text{e1}}^{(n)} \right)$$

(2.21)

Two other electromagnetic fields are of interest – the internal field ($E_1, H_1$) and the far-scattered field ($E_5, H_5$) – both of which can be similarly expanded as an infinite sum of spherical vector harmonics. The boundary conditions at the edge of the particle for these three field pairs can be expressed as a vanishing of fields normal to the surface –

$$(E_1 + E_5 - E_1) \times \hat{e}_r = 0$$

$$(H_1 + H_5 - H_1) \times \hat{e}_r = 0$$

(2.22)

The orthogonality of the vector harmonics, these boundary conditions and the form of the incident field, 2.20, imply the form of the internal field. Only harmonics in the incident field can be present in the resulting field.

$$E_1 = E_0 \sum_{n=0}^{\infty} \frac{i^n}{n(n+1)} \left( c_n M_{\text{e1}}^{(n)} - i d_n N_{\text{e1}}^{(n)} \right)$$

(2.23)

$$H_1 = -\frac{k_1}{\omega \mu_i} E_0 \sum_{n=0}^{\infty} \frac{i^n}{n(n+1)} \left( d_n M_{\text{e1}}^{(n)} + c_n N_{\text{e1}}^{(n)} \right)$$

(2.24)

where $k_1$ and $\mu_i$ are the wave number and the permeability inside the sphere.

For any particle radius, a, both the Bessel functions of the first, $j_n$, and second, $y_n$, kinds are well behaved for $\rho > ka$. The expansion of the scattered field, ($E_5, H_5$), can involve both kinds of Bessel function. Any linear combination of $j_n$ and $y_n$ is itself also a solution to 2.9. It is convenient then to use the spherical Hankel functions,

$$h_n^{(1)} = j_n + iy_n$$

$$h_n^{(2)} = j_n - iy_n$$

The Hankel functions of order $\nu$ can be expanded asymptotically for large $|\rho|$:

$$H_\nu^{(1)}(\rho) \sim \frac{2}{\pi \rho} e^{-i\frac{\pi \nu}{2}} \sum_{m=0}^{\infty} \frac{(-1)^m (\nu, m)}{(2i\rho)^m}$$

$$H_\nu^{(2)}(\rho) \sim \frac{2}{\pi \rho} e^{-i\frac{\pi \nu}{2}} \sum_{m=0}^{\infty} \frac{\nu, m}{(2i\rho)^m}$$
where \((v,m) = \left( v + m + \frac{1}{2} \right) \binom{v + m + 1/2}{m} \) and \(\Gamma\) is the gamma function.

The spherical Hankel functions can be given asymptotically for far field measurements \((\rho = kr > n^2 \text{ or } r > \frac{4a^2}{\lambda})\):

\[
h_n^{(0)}(\rho) \sim \frac{(-i)^n e^{i\rho}}{i\rho},
\]

\[
h_n^{(1)}(\rho) \sim \frac{i^n e^{-i\rho}}{i\rho}
\]

which correspond to outgoing and incoming spherical waves respectively. At significant distance from the particle the scattered wave will be outgoing and so we can neglect \(h_n^{(2)}\) terms.

The far-scattered field can be expanded in spherical vector harmonics:

\[
E_s = E_0 \sum_{n=0}^{\infty} \frac{2n + 1}{n(n+1)} \left( -b_n M_{(n)}^{(1)} + i a_n N_{(n)}^{(1)} \right)
\]

\[
H_s = \frac{k_l}{\alpha \mu_1} E_0 \sum_{n=0}^{\infty} \frac{2n + 1}{n(n+1)} \left( a_n M_{(n)}^{(1)} + b_n N_{(n)}^{(1)} \right)
\]

where \(^{(1)}\) denotes \(\rho\)-dependency being spherical Hankel functions of the first kind, \(h_n^{(1)}\).
Scattering Angle Dependency

The scattering angle, $\theta$, dependency has been incorporated in the form of the associated Legendre functions of the first order and their derivatives. Future equations and notation can be simplified by introducing two new functions of scattering angle –

$$\pi_n = \frac{p_n^l}{\sin \theta}$$

$$\tau_n = \frac{dP_n^l}{d\theta}$$

The spherical vector harmonics, 2.10-2.13, using this simpler notation are –

$$M_{el n} = -\sin \phi \pi_n (\cos \theta) z_n(\rho) \hat{e}_\theta - \cos \phi \tau_n (\cos \theta) z_n(\rho) \hat{e}_\phi$$  

$$M_{ol n} = \cos \phi \pi_n (\cos \theta) z_n(\rho) \hat{e}_\theta - \sin \phi \tau_n (\cos \theta) z_n(\rho) \hat{e}_\phi$$  

$$N_{el n} = n(n+1) \cos \phi \sin \theta \pi_n (\cos \theta) \frac{z_n(\rho)}{\rho} \hat{e}_t + \cos \phi \tau_n (\cos \theta) \frac{1}{\rho} \frac{dpz_n(\rho)}{d\rho} \hat{e}_\theta - \sin \phi \pi_n (\cos \theta) \frac{1}{\rho} \frac{dpz_n(\rho)}{d\rho} \hat{e}_\theta$$  

$$- \sin \phi \pi_n (\cos \theta) \frac{1}{\rho} \frac{dpz_n(\rho)}{d\rho} \hat{e}_\phi$$

$$N_{ol n} = n(n+1) \sin \phi \sin \theta \pi_n (\cos \theta) \frac{z_n(\rho)}{\rho} \hat{e}_t + \sin \phi \tau_n (\cos \theta) \frac{1}{\rho} \frac{dpz_n(\rho)}{d\rho} \hat{e}_\theta + \cos \phi \pi_n (\cos \theta) \frac{1}{\rho} \frac{dpz_n(\rho)}{d\rho} \hat{e}_\phi$$  

Figure 2.5 – Scattering angle dependent functions, $\pi_n$ and $\tau_n$ plotted for $n=1$-4. (Twin coloured mottling on some surfaces implies equal positive and negative components)
Boundary Conditions

The boundary conditions at the surface of the sphere, \( r = a \), (equations 2.22), can be expanded as

\[
E_{i0} + E_{i\phi} = E_{i\theta} \\
H_{i0} + H_{i\phi} = H_{i\theta} \\
E_{i\phi} + E_{i\theta} = E_{i\phi} \\
H_{i\phi} + H_{i\theta} = H_{i\phi}
\]

where \( M_{mn} \) refers to the \( \hat{e}_m \) component of \( M \).

Substituting the field equations, 2.20, 2.21, 2.23, 2.24, 2.26 and 2.27 using the spherical vector harmonics, 2.28-2.31, leads, after some manipulation, to

\[
\psi_n^{'}(mx) d_n + m \xi_n^{'}(x) a_n = m \psi_n^{'}(x) \\
\psi_n^{'}(mx) c_n + \xi_n^{'}(x) b_n = \psi_n(x) \\
\mu \psi_n^{'}(mx) c_n + \mu_1 \xi_n^{'}(x) b_n = \mu_1 \psi_n^{'}(x) \\
\mu \psi_n^{'}(mx) d_n + \mu_1 \xi_n^{'}(x) a_n = \mu_1 \psi_n(x)
\]

where

\[
x = \frac{2\pi a}{\lambda}, m = \frac{k_1}{k n_2} (n_1 \text{ and } n_2 \text{ being the refractive indices of the particle and medium respectively}) \text{ and the Ricatti-Bessel functions, } \psi_n(\rho) = \rho j_n(\rho) \text{ and } \xi_n(\rho) = \rho h_n^{(1)}(\rho) \text{ have been introduced to simplify these expressions and later computation.}
\]

The equations can be solved for the scattering coefficients \( a_n \) and \( b_n \). The internal field coefficients \( c_n \) and \( d_n \) are now neglected, not being required in the computation of the far scattered field.

\[
a_n = \frac{m \psi_n^{'}(x) \psi_n(mx) - m \psi_n^{'}(mx) \psi_n(x)}{m \xi_n^{'}(x) \psi_n(mx) - \psi_n^{'}(mx) \xi_n(x)} \\
b_n = \frac{\psi_n^{'}(x) \psi_n(mx) - m \psi_n^{'}(mx) \psi_n(x)}{\xi_n^{'}(x) \psi_n(mx) - m \psi_n^{'}(mx) \xi_n(x)}
\]

where the permeability of the particle and the surrounding medium have been assumed equal, i.e. \( \mu_1 = \mu \).
On Multiple Optical Scattering in a Scanning Nephelometer.

Overall Solution

The scattered electric field can be predicted using the expansion 2.26, the spherical vector harmonics 2.29 and 2.30 and the scattering coefficients, 2.32 and 2.33. The solutions to the Hankel function and associated Legendre functions are required to determine these.

2.6.3. Computation

The following sections detail the necessary recurrence relations and computations necessary to calculate Mie scattering intensities. Such calculations were performed originally tediously by hand\textsuperscript{52,53} but have now been implemented on a wide range of computer platforms\textsuperscript{54,55}. Calculations in this thesis are performed using Matlab, details of which can be found in Appendix A.

Bessel Functions

The spherical Bessel functions satisfy the recurrence relations\textsuperscript{50,56-58},

\[ z_{n-1}(p) + z_{n+1}(p) = \frac{2n+1}{\rho} z_n(p) \]

\[ (2n+1) \frac{dz_n(p)}{dp} = nz_{n-1}(p) - (n+1)z_{n+1}(p) \]

and so the Ricatti-Bessel functions satisfy,

\[ Z_{n-1}(p) + Z_{n+1}(p) = \frac{2n+1}{\rho} Z_n(p) \]

\[ \frac{dZ_n(p)}{dp} = Z_{n-1}(p) - \frac{n}{\rho} Z_n(p) \]

where \( Z_n = \rho z_n \) is any of the Ricatti-Bessel functions.

\( y_n \) is stable with respect to upwards recurrence and \( j_n \) is stable to downwards. The Ricatti-Bessel functions of the first and second kind \( \psi_n(p) = \rho j_n(p) \) and \( \zeta_n(p) = \rho y_n(p) \) are thus computed by downwards and upwards recurrence respectively.

\( \zeta_n \) is computed from initial conditions, \( \zeta_0(p) = -\cos p \) and \( \zeta_1(p) = -\frac{\cos p}{\rho} - \sin p \).

\( \psi_n \) assumes some small value for \( \psi_{n_{\text{min}}} = 10^{-10} \beta \) and that \( \psi_{n_{\text{min}}+1} = 0 \), where \( n_{\text{min}} \) is sufficiently higher than the highest required \( n \), \( n = n_e + \sqrt{101 + n_c} \). Downwards recurrence is used.
to determine $\psi_0$ as a multiple of $\beta$, which can then be equated with the known value $\psi_0(\rho) = \sin \rho$ to determine $\beta$.

The Ricatti-Bessel functions of the third kind, $\xi_n(\rho) = \rho h_n^{(1)}(\rho) = \psi_n(\rho) + i\zeta_n(\rho)$, are computed from the first two functions.

**Associated Legendre Functions**

There are recurrence relationships that satisfy the associated Legendre polynomials and so recurrence relationships satisfying the scattering angle functions used are easily derived—

\[
\pi_n = \frac{2n-1}{n-1} \mu \pi_{n-1} - \frac{n}{n-1} \pi_{n-2}
\]

\[
\tau_n = n\mu \pi_n - (n+1)\pi_{n-1}
\]

where $\mu = \cos \theta$. They can be computed by upwards recurrence from initial conditions, $\pi_0 = 0$ and $\pi_1 = 1$.

**Scattering Coefficients**

The scattering coefficients, $a_n$ and $b_n$, are calculated from the Ricatti-Bessel functions and the scattering angle functions described above, according to equations 2.32 and 2.33.

**Scattered Fields**

In the far field, the asymptotic solution of the Hankel function, 2.25, can be taken giving

\[
E_{1\theta} \sim E_0 e^{ikr} \cos \phi S_2(\cos \theta)
\]

\[
E_{2\theta} \sim -E_0 e^{ikr} \sin \phi S_2(\cos \theta)
\]

where

\[
S_1(\mu) = \sum_{n=1}^{n_{\mu}} \frac{2n+1}{n(n+1)}(a_n \pi_n(\mu) + b_n \tau_n(\mu))
\]

\[
S_2(\mu) = \sum_{n=1}^{n_{\mu}} \frac{2n+1}{n(n+1)}(a_n \tau_n(\mu) + b_n \pi_n(\mu))
\]

So far, only horizontally polarised incident light has been considered. The axes of our system are, however, arbitrary. Rotating the system by 90° through the azimuthal angle, $\phi$
would be equivalent to illumination with vertically polarised incident light. A relationship between incident and scattered fields in the form of Jones' vectors can be made –

\[
\begin{pmatrix}
E_{x*} \\
E_{ys}
\end{pmatrix} = e^{i(kr-\omega t)}
\begin{pmatrix}
S_1 & 0 \\
0 & S_2
\end{pmatrix}
\begin{pmatrix}
E_{x} \\
E_{ys}
\end{pmatrix}
\]  

(2.36)

and far field scattered electromagnetic waves can be predicted from particle and media parameters and incident wave characteristics.

**Stokes’ Vectors**

An arbitrary beam of light can be expressed as a vector of Stokes' parameters –

\[
S = \begin{pmatrix}
I \\
Q \\
U \\
V
\end{pmatrix} = I \begin{pmatrix}
1 \\
\cos 2\omega \cos 2\alpha \\
\cos 2\omega \sin 2\alpha \\
\sin 2\omega
\end{pmatrix} + (1 - P) \begin{pmatrix}
1 \\
0 \\
0 \\
0
\end{pmatrix}
\]

where I is the overall intensity, P is the degree of polarisation, \( \tan \phi = \frac{b}{a} \) is the ellipticity and \( \alpha \) is the polarisation azimuth.

**Mueller Scattering Matrix**

The Mueller matrix relating scattered intensities with incident intensities can be calculated from equation 2.36 –

\[
\begin{pmatrix}
I_s \\
Q_s \\
U_s \\
V_s
\end{pmatrix} = \frac{1}{k^2 r^2}
\begin{pmatrix}
S_{11} & S_{12} & 0 & 0 \\
S_{12} & S_{11} & 0 & 0 \\
0 & 0 & S_{33} & S_{34} \\
0 & 0 & -S_{34} & S_{33}
\end{pmatrix}
\begin{pmatrix}
I_i \\
Q_i \\
U_i \\
V_i
\end{pmatrix}
\]

where

\[
S_{11} = \frac{1}{2}(|S_2|^2 + |S_1|^2) = \frac{1}{2}(S_2^*S_2 + S_1^*S_1)
\]

(2.38)

\[
S_{12} = \frac{1}{2}(|S_2|^2 - |S_1|^2) = \frac{1}{2}(S_2^*S_2 - S_1^*S_1)
\]

\[
S_{33} = \frac{1}{2}(S_2^*S_1 + S_1^*S_2)
\]

\[
S_{34} = \frac{1}{2}(S_2^*S_1 - S_1^*S_2)
\]

(2.39)

---

Chapter 2 – Single Light Scattering from Spherical Particles
Having presented and derived Mie theory as presented by many authors, this work is extended in a number of ways in the following sections.

**Convergence of the Infinite Sum**

According to the literature \cite{4,36}, the scattered field series, 2.26 and 2.27, are uniformly convergent and so the infinite sum can be terminated after a finite number of terms, $n_c$. The resulting truncation error can be made arbitrarily small by taking sufficient terms. 'Sufficient' in this case is historically based more or less on guessing, although an extensive study was published by Wiscombe 601 which suggested:

$$n_c = x + 4.05 \sqrt{x} + 2 \quad (2.40)$$

Figure 2.7 shows the convergence of the calculated intensity for a given refractive index and scattering angle and a selection of particle sizes. It can be seen that in all these circumstances the Wiscombe criterion indicates the convergence point accurately. Figure 2.8 plots the convergence point for a selection of refractive indices and a range of particle sizes. This shows that the Wiscombe criterion is valid for a wider selection of instances.

![Figure 2.7 - Computed scattered intensity at 90° as multiple of final scattered intensity (as truncated at $n_c$) for a range of particle sizes. Vertical dashed lines indicate value of the required number of terms, $n_c$, as calculated by equation 2.40. In all instances $m=1.25.$](image-url)
The required limit can be explained in terms of the localisation principle\(^4, 61\) which states that terms in the Mie expansion of order \(n\) correspond to rays passing a distance \(k(n+\frac{3}{2})\) from the origin. Terms of order greater than \(x\) correspond to rays passing the sphere and are only affected by the induced field around the particle.

![Figure 2.8 - Number of terms required, \(n_{\text{required}}\), for convergence over a range of particle sizes, \(x\), refractive indices, \(m\) and vertically polarised incident light. Convergence is defined as a value being within 0.1\% of the intensity calculated with up to an additional two terms, for all integer degree angles. Predicted required terms, \(n_o\), as calculated by equation 2.40, are plotted for comparison](image-url)
2.6.4. Graphing Scattering Results

Scattering from any given particle or ensemble of particles is a function of scattering and azimuthal angles. The scattered intensity is traditionally plotted as a semi-logarithmic or linear Cartesian or a polar plot for each of two perpendicular polarisation states (sensibly 0 and 90°). This angle dependence of the scattering is the particles' scattering footprint. Alternatively, the intensity can be plotted in three dimensional polar co-ordinates, producing a surface whose distance from the origin is proportional to the intensity in that direction, or the logarithm of the intensity, so that features of scattering from larger particles can be observed despite the orders of magnitude difference between forward and backward scattering.

The resulting surface indicates the form of a scattering intensity profile for a left-to-right travelling incident ray through a medium containing the scatterers under consideration.

The field of particle scattering is a complex one and the figures that follow demonstrate some of the complexity present even in the relatively simple field of single spherical particle scattering. The similarity of first three figures, covering two orders of magnitude of particle size, show the difficulty of particle sizing for such small particles. As the particle size is increased additional features are added to the profile as higher-order modes affect the scattering. The sensitivity of such a measure to scattering angle can clearly be seen in the later figures.

Figure 2.10 shows how these figures can be used to demonstrate a physical principle. The area of the surface over which a finite sensor integrates is clearly seen on this figure. This figure also demonstrates the difficulty of the inverse problem, i.e. determining particle parameters from sensor readings. Relatively small changes in particle size and/or measurement angle can potentially have a great affect on sensor reading, as features pass the sensor. Inversions of the readings are thus liable to be unstable.
On Multiple Optical Scattering in a Scanning Nephelometer.

Chapter 2 – Single Light Scattering from Spherical Particles

On Multiple Optical Scattering in a Scanning Nephelometer.

22 February 2000

x=0.01

x=0.1

x=1

x=1.8

x=2
Figures 2.9 – Single scattering graphs for particles of increasing size and consistent refractive index (m=1.2). Graphs show horizontal (green) and vertical (blue) linear incident polarisation states. Surfaces plot log of intensity as distance from origin in scattering direction. Intensity scales are arbitrary, but consistent.
2.6.5. Cross-sections

A measure of the total extinction due to scattering and absorption can be of use in a number of studies (for example, first-order multiple scatter prediction, see §3.3). An imaginary sphere concentric to the particle is considered. The attenuation of the incident wave across this sphere is the extinction of the particle (assuming the medium is non-absorbing). This extinction will be due to absorption by the particle and by other waves leaving the sphere (due to scattering).

The extinction energy, \( W \), will be proportional to the energy of the incident wave. The constant of proportionality has units of area and so is referred to as the extinction cross-section, \( \sigma_t \). This area is made up of areas representing the two factors behind extinction; the absorption cross-section, \( \sigma_a \) and the scattering cross-section, \( \sigma_s \).

The scattering cross-section is the sum of scattered intensities leaving the imaginary sphere, \( \Lambda \), with unit incident intensity,

\[
\sigma_s = \frac{1}{I_0} \int_{\Lambda} I_s \, dA
\]

which can be solved analytically for a spherical particle \(^{136}\),

\[
\sigma_s = \frac{2\pi}{k^2} \sum_{n=1} \left( 2n + 1 \right) \left( |a_n|^2 + |b_n|^2 \right)
\]

The extinction cross-section for a spherical particle can also be similarly obtained \(^{136}\),

\[
\sigma_t = \frac{2\pi}{k^2} \sum_{n=1} \left( 2n + 1 \right) \Re(a_n + b_n)
\]

These two quantities, and thus the absorption cross-section, \( \sigma_a = \sigma_t - \sigma_s \), can easily be computed from the scattering coefficients computed previously (§2.6.3).

It is well documented \(^{62, 63}\) from observation of numerical results and attempted proofs \(^{64, 65}\) that these cross-sections tend to simple ratios in the large particle limit. For example, the extinction cross-section becomes double the geometric cross-section in the limit of \( x \) becoming infinite.
2.7. **Light Scattering Measured by a Finite Rectangular Sensor**

Analyses in the previous sections have predicted light scattering in a particular direction, defined by an azimuthal angle and an angle in the scattering plane. Any sensor will have a finite size and so, assuming a rectangular sensor, will collect all light scattered into some solid angle. Only when particle sensor separation tends towards infinity or sensor area tends to zero can single angle scattering be measured, at which point the measured energy will similarly tend to zero.

The measurement made by a finite rectangular sensor will be proportional to the sum of the light scattered into the relevant scattered angle –

\[
I_s(\theta, \delta\theta, \alpha, \delta\alpha, \ldots) = \int_{\theta-\delta\theta}^{\theta+\delta\theta} \int_{\alpha-\delta\alpha}^{\alpha+\delta\alpha} I_s(\theta, \alpha, \ldots) \mathrm{d}\alpha \mathrm{d}\theta
\]

(2.41)

where the sensor is centred on \((\theta, \alpha)\) and covers a solid angle of \((2\delta\theta, 2\delta\alpha)\). These angles are as measured in the medium, which can be different to external angles due to lensing between medium and the sensor (for example, see §5.4.1). Figure 2.10 shows the area of integration on a scattering function.

The following sections first consider strip sensors, a sensor with zero size in one of the two directions (either azimuth or scattering angle). The results are then combined to integrate over a truly finite sensor.

![Figure 2.10 – Scattered light intensity (from linearly polarised light) plotted as logarithmic distance from origin. Marked in red is an example area that would be measured by a realistic finite sensor (6mm square at 95mm from particle). Particle has size parameter \(x=6\) and refractive index \(n=1.25\).](image-url)
The integral is separable for the two angular dependencies and each are considered separately in the following sections. Integration in one direction (through azimuthal angles) is analytic while in the other (scattering angle) direction the integration must be computed numerically.

**Assumptions**

The distance factor, \( r \), in the calculation of intensity is a function of angle if the sensor face does not lie on a sphere concentric to the particle. In practical situations, any variation on distance is likely to be negligible when compared to the actual particle sensor separation and so can be neglected.

It is also assumed that there is no refraction between particle and sensor. A cylindrical vessel, for instance, will cause an increase in the effective scattering angle capture range of the sensor. This factor can be incorporated later by calculating the effective sensor area 'as seen by the particle', i.e. the numerical aperture of the sensor is calculated after all lensing is considered.

**2.7.1. Integrating with Respect to Polarisation Azimuth**

The Stokes' vector representation of arbitrarily polarised light is discussed on page 28. Multiplying by the Mueller scattering matrix, 2.37, provides the scattered Stokes' vector. From this we can predict the scattering of arbitrarily polarised light —

\[
S_1(\alpha) = \frac{I_1}{k^2 r^2} \begin{pmatrix}
S_{11} + S_{12} \cos 2\alpha \cos 2\alpha \\
S_{12} + S_{11} \cos 2\alpha \cos 2\alpha \\
S_{13} \sin 2\alpha + S_{14} \cos 2\alpha \sin 2\alpha \\
S_{14} \sin 2\alpha - S_{13} \cos 2\alpha \sin 2\alpha
\end{pmatrix} + (1 - P) \begin{pmatrix}
S_{11} \\
S_{12} \\
0 \\
0
\end{pmatrix}
\]

Placing a sensor at an azimuthal angle, \( \alpha \), from the measurement base plane is exactly equivalent to rotating the polarisation state of the incident light by an opposite angle. Assuming that the polarisation of the incident light is parallel to the measurement base plane allows polarisation azimuth to be substituted for sensor azimuth in the calculations.
The azimuthal integral in equation 2.41 can easily be calculated analytically –

\[
\int_{-\alpha}^{\alpha} S_{ij} d\alpha = \frac{I_1}{k^2 r^2} P \begin{pmatrix}
S_{11} \alpha + \frac{1}{2} S_{12} \cos 2\alpha \sin 2\delta \\
S_{12} \alpha + \frac{1}{2} S_{11} \cos 2\alpha \sin 2\delta \\
S_{13} \alpha \sin 2\alpha + \frac{1}{2} S_{14} \cos 2\alpha \cos 2\alpha \cos 2\delta \\
S_{13} \alpha \sin 2\alpha - \frac{1}{2} S_{14} \cos 2\alpha \cos 2\alpha \cos 2\delta \\
\end{pmatrix} + (1 - P) \delta \alpha \begin{pmatrix}
S_{11} \\
S_{12} \\
0 \\
0
\end{pmatrix}
\]

\[
= \frac{1}{k^2 r^2} \begin{pmatrix}
S_{11} & S_{12} & 0 & 0 \\
S_{12} & S_{11} & 0 & 0 \\
0 & 0 & S_{33} & S_{34} \\
0 & 0 & -S_{34} & S_{33}
\end{pmatrix}
\begin{pmatrix}
I_1 \sin 2\delta \\
Q_1 \sin 2\delta \\
U_1 \sin 2\delta \\
V_1 \sin 2\delta
\end{pmatrix}
\]

The overhead associated with this computation is negligible in comparison with other calculations.

**Effect of Finite Azimuthal Angle**

Figure 2.11 shows the scattering from two different particles into sensors of differing azimuthal range. The scattering intensity is symmetrical about both the horizontal and vertical polarisation axes, so integration over a half angle of 90° will give an azimuth and polarisation independent result.

It can be seen that for larger particles (e.g. (b) x = 4), the effect of azimuthal angle is negligible for all but the most expansive of sensors, i.e. sensors that collect almost all scattered light (2\(\delta \alpha > 60°\)) for a given scattering angle.

For smaller particles and in the extreme Rayleigh particles (e.g. (a) x = 0.1), where there are fewer but stronger features and a larger difference in scattering between horizontal and vertical incident polarisation, there is an averaging of the size of these features. For Rayleigh scatterers which have one feature for horizontal polarisation and none for vertical polarisation, the feature does not move, it simply becomes less (or more) pronounced.

The plots indicate the scattering of linearly polarised light. For unpolarised light there will be no effect of azimuthal integration (see equation 2.42). For partially polarised light there will be an effect proportional to the degree of polarisation.
Particle refractive index, \( m = 1.2 \). Particle size parameter is (a) \( x = 0.1 \) (b) \( x = 4 \). Incident light is horizontally polarised. Intensity scale is arbitrary but consistent.
2.7.2. Integrating with Respect to Scattering Angle

The scattering angle, $\theta$, dependency in the integral 2.41 can be separated completely from the azimuthal dependencies. The $\theta$-dependency lies in the scattering Mueller elements $S_{11}$, $S_{12}$, $S_{33}$ and $S_{34}$ and so these factors must be integrated with respect to scattering angle –

$$S_{11} = \int_{0}^{60} S_{11}(\theta) d\theta = \int_{0}^{60} \frac{1}{2} (S_{2}S_{2}^{*} + S_{3}S_{3}^{*}) d\theta$$

$$S_{12} = \int_{0}^{60} S_{12}(\theta) d\theta = \int_{0}^{60} \frac{1}{2} (S_{2}S_{2}^{*} - S_{1}S_{1}^{*}) d\theta$$

$$S_{33} = \int_{0}^{60} S_{33}(\theta) d\theta = \int_{0}^{60} \frac{1}{2} (S_{3}S_{3}^{*} + (S_{3}S_{3}^{*})^{*}) d\theta$$

$$S_{34} = \int_{0}^{60} S_{34}(\theta) d\theta = \int_{0}^{60} \frac{1}{2} (S_{3}S_{3}^{*} - (S_{3}S_{3}^{*})^{*}) d\theta$$

(2.43)

(2.44)

The elements of which can be calculated separately –

$$\int_{0}^{60} S_{i}S_{i}^{*} d\theta, \int_{0}^{60} S_{i}S_{j}^{*} d\theta \text{ and } \int_{0}^{60} S_{i}S_{i}^{*} d\theta$$

(2.45)

Integrals of Legendre functions

An alternative method would be to perform the numerical integration inside the infinite sums, 2.34 and 2.35. The integral would then be required only over the Legendre functions, $\pi_{n}$ and $\tau_{n}$. Such a calculation would have computation time of order $n_{c}^{2}n_{q}$ as opposed to $n_{c}n_{q}$ for integration of Jones' vector products, $S_{i}$ and $S_{j}$. $n_{b}$ being the number of abscissas used to estimate the integrals above.

Effect of Finite Scattering Angle

Figure 2.12 shows the scattering from two different particles into sensors of differing scattering angle range. The averaging of intensity over a range of angles obviously causes a reduction in the strength of any angle dependent features.

The effect of averaging on the scattering profile is to lessen the strength of any features present. In smaller particles with a single sharp feature, the size of the feature will be lost by a few orders of magnitude as the sensor reaches just a few degrees of capture. For larger particles, with shallower, subtler features the effect is negligible until very large capture
angles are considered. For (b) \( x = 4 \), the effect can be observed but is unlikely to be notable by experiment for a collection half angle of \( 10^\circ \). At \( 30^\circ \) the features are still just about recognisable and for larger sensors the general trends of the scattering function is all that can be determined.

### 2.7.3. Integrating over Sensor Area

The results of sections 2.7.1 and 2.7.2 can be combined to predict the intensity measured by a rectangular detector. The separability of the two angles make this a simple procedure, the scattering angle Mueller elements, 2.43-2.44, are inserted into the azimuth equation, 2.42 –

![Graph](image)

**Figure 2.12** - Light scattered into a sensor with finite scattering angle.

Particle refractive index, \( m = 1.2 \). Particle size parameter is (a) \( x = 0.1 \) (b) \( x = 4 \). Incident light is horizontally polarised. Intensity scale is arbitrary but consistent.
\[
\int_{\alpha-\delta\alpha}^{\alpha+\delta\alpha} S_y(\hat{\alpha}) d\hat{\alpha} = \frac{1}{k^2 r^2} \begin{pmatrix}
S_{11}^* & S_{12}^* & 0 & 0 & 1 \sin 2\delta\alpha \\
S_{12}^* & S_{11}^* & 0 & 0 & Q_1 \sin 2\delta\alpha \\
0 & 0 & S_{33}^* & S_{34}^* & U_1 \sin 2\delta\alpha \\
0 & 0 & -S_{34}^* & S_{33}^* & V_1 \sin 2\delta\alpha \\
\end{pmatrix}
\]

Some Example Results

Figure 2.13 shows the scattering profile for particles of relative refractive index \(m=1.2\) and size parameter \(x=0.1\) and \(x=4\) measured by a finite square sensor. It can be seen that the greater effect of finite scattering angle range dominates the change in profile shape and position although it is slightly modified for finite azimuth range.

As mentioned previously sensors up to 10° half angle (i.e. 20° solid angle) have little change from 'zero sized' sensors for larger particles. Sensors of 1-5° half angle (2-10° solid angle) would just be noticeable by experimental equipment.

Except in cases where large areas of light collection are used for detection of particularly low levels of scattering, a 10mm square sensor at 50mm would provide a conformable upper limit for detection angle in realistic set-ups. This is equivalent to 5.7° half angle.

A reasonable experimental or applied nephelometric set-up is thus unlikely to require integration of results, except for smaller particles or for exceptionally accurate results.
Figure 2.13 - Light scattered into a finite square (equal scattering and azimuthal angles) sensor. Particle refractive index, $m = 1.2$. Particle size parameter is (a) $x = 0.1$ (b) $x = 4$. Incident light is horizontally polarised. Intensity scale is arbitrary but consistent.
2.8. Narrow Beam Scattering Measured by a Finite Sensor

The previous sensor predicted the light scattered by an unbounded plane wave into a given solid angle. A realisable nephelometric system will be illuminated by some finite beam and in many cases by a narrow beam. If the numerical aperture of the sensor is independent of angle, as is the case with a scanning nephelometer, then the scattering volume will increase as sensor angle deviates from 90° (see figure 2.14). Similarly, the scatterer-sensor distance will be a function of the scatterer's position along the beam.

Scattering volume

The length of the scattering volume, \( L \), can be calculated by simple trigonometry,

\[
L = r \sin \theta \left( \cot(\theta - \delta \theta) - r \cot(\theta + \delta \theta) \right)
\]

\[
= \frac{2r \sin \theta \tan \delta \theta}{\sin^2 \theta - \cos^2 \theta \tan^2 \delta \theta}
\]

Assuming the beam is collimated, the cross-sectional area will be constant, and the scattering volume simply proportional to \( L \).

*Figure 2.14 - Scattering volume of narrow beam with finite sensor*
Scatterer-Sensor Distance

The distance between the centre of the beam along L and the sensor, can again be easily evaluated,

$$\hat{r} = r \frac{\sin \theta}{\sin \hat{\theta}}$$

The incident beam is considered narrow and so contribution to the scatterer-sensor distance from distance of the particles being off-axis is neglected.

Total Scattering

Consider a short length of the scattering volume, $d\hat{z}$, which lies at angle $\hat{\theta}$ (see figure 2.15). Scattering from a particle in this volume, according to equation 2.37, is given by

$$\begin{pmatrix} I_s \\ Q_s \\ U_s \\ V_s \end{pmatrix} = \frac{1}{k^2 \hat{z}^2} \begin{pmatrix} S_{11} & S_{12} & 0 & 0 \\ S_{12} & S_{11} & 0 & 0 \\ 0 & 0 & S_{33} & S_{34} \\ 0 & 0 & -S_{34} & S_{33} \end{pmatrix} \begin{pmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{pmatrix}$$

where $S_{ij}$ and $\hat{r}$ are functions of scattering angle $\hat{\theta}$. In general, the incident Stokes' vector intensities will also be a function of $\hat{\theta}$. However, the assumptions are that the medium is non-absorbing and that there are no particle interactions other than the measured scattering (i.e. the single scattering approximation). The incident field will, for now, be considered constant along the scattering volume.
If there is a particle density of \( N \) per unit volume and the beam has a cross-sectional area of \( C \) (i.e. for the narrow beam there are \( CN \) particles per unit length) then there will be \( CN d\tilde{z} \) particles in the short length.

Integrating the total scattered intensity over these elemental volumes for the entire scattering volume gives

\[
I_s = \frac{CN}{k^2} \int \frac{1}{r^2} \left( S_{11}(\tilde{\theta}) I_1 + S_{12}(\tilde{\theta}) Q_i \right) r \sin \theta \tan \theta \, d\tilde{z}
\]

(2.46)

where \( r = \frac{r \sin \theta}{\sin \tilde{\theta}} \) and \( \tilde{z} = \frac{r \sin \theta}{\tan \tilde{\theta}} \), so that

\[
I_s = \frac{CN}{k^2 r^2 \sin \theta} \int_{\theta-\beta_0}^{\theta+\beta_0} \frac{\sin^2 \tilde{\theta}}{r^2 \sin^2 \theta} \left( S_{11}(\tilde{\theta}) I_1 + S_{12}(\tilde{\theta}) Q_i \right) r \sin \theta \, d\tilde{\theta}
\]

(2.47)

This process can be repeated for the other Stokes' parameters giving

\[
\begin{bmatrix}
I_s \\
Q_s \\
U_s \\
V_s
\end{bmatrix} = -\frac{1}{k^2 r^2} \begin{bmatrix}
S_{11} & S_{12} & 0 & 0 \\
S_{12} & S_{11} & 0 & 0 \\
0 & 0 & S_{33} & S_{34} \\
0 & 0 & -S_{34} & S_{33}
\end{bmatrix}
\begin{bmatrix}
I_i \\
Q_i \\
U_i \\
V_i
\end{bmatrix}
\]

(2.48)

where

\[
S_{ij} = \frac{CN}{\sin \theta} \int_{\theta-\beta_0}^{\theta+\beta_0} S_{ij}(\tilde{\theta}) d\tilde{\theta} = \frac{CN r}{\sin \theta} S_{ij}^*.
\]

As with section 2.7.2, these parameters can be computed from the three integrals 2.45, by substituting the equations for the Mueller matrix elements, 2.38-2.39, into 2.48.

The elements of this Mueller matrix will tend towards infinity as the scattering angle tends towards \( 0^\circ \). With the assumptions made and the lack of bounds on the scattering volume, light scattered forwards from an infinitely long volume with no attenuation is measured. This effect can be seen in the figures 2.16.

Azimuthal Angle

The variation over azimuthal angle can be neglected, as the azimuthal range of the scattering volume is small due to the narrowness of the beam.
Figure 2.16 - Light scattered from a beam into a finite sensor. Particle refractive index, $m = 1.2$. Particle size parameter is (a) $x = 0.1$ (b) $x = 4$. Incident light is horizontally polarised. Intensity scale is arbitrary but consistent.
2.9. Mean Light Scattering from Distributions of Spherical Particles

Single Scattering Approximation

Previous sections have analysed light scattered from a single particle lying independently in space. As discussed briefly in section 2.4, the actual assumptions made are independence of particles, that multiple scattering can be neglected and that the spherical particles are similar. Under these assumptions, the light scattered from a collection of similar particles will be the sum of the light scattered from the individual particles:

\[ I_s(N, \theta, m, x) = N I_s(\theta, m, x) \]

where \( N \) is the mean number of particles in the scattering region.

For example, if there are a constant two independent particles in the scattering region then the intensity of scattered light measured at any angle will be double that scattered by one such particle.

Distributions of Particles\(^{24}\)

If there are two dissimilar particles in the scattering region the same principle applies – the intensity of the scattered light measured will be the sum of the light scattered from the two particles. The simple example can be generalised to an arbitrary collection of particles – the mean intensity of light scattered will be the sum of the light scattered from the individual particles.\(^{66}\)

\[ I_s(\theta, N(m, x)) = \int I_s(\theta, m, x) N(m, x) \, dm \, dx \]

where \( N(m, x) \) is the number distribution for particles of refractive index, \( m \) and particle size, \( x \), in the scattering region.

![Figure 2.17 - Light scattering from two (a) similar and (b) dissimilar spherical particles](image-url)
If the mean number of particles in the region is $N = \int N(m,x) dm dx$ then the probability distribution (PDF) of particles is $p(m,x) = \frac{N(m,x)}{N}$. For comparison with single scattering, the PDF should be considered, i.e. the scattering from a distribution of particles where the mean number of particles in the scattering region is one. The mean intensity of light scattered from a particle taken from a given distribution is

$$I_s(\theta, p(m,x)) = \int I_s(\theta, m,x)p(m,x) dm dx = I_s(\theta, m,x)$$  \hspace{1cm} (2.49)

2.9.1. Computation

Integration of Intensities

A brute force numerical method can be used to compute the mean scattering from particles chosen from a histogram of possible particles. The integral 2.49 becomes a sum over the possible particle species or bins in the histogram. A continuous PDF can be represented by an arbitrarily large number of particle species or an arbitrarily fine histogram.

$$I_s(\theta, N(m,x)) = \sum_p I_s(\theta, m_p,x_p)N_p$$

where $N_p$ is the fraction of particles with parameters $m_p$ and $x_p$.

This method computes all factors of particle scattering, including those which are particle independent, before the sum is performed. Some of these components can be taken outside of the sum, improving the efficiency of the computation by removing repetition of calculations.

Integration of Scattering Coefficients

Ideally only those factors dependent on the particle properties, i.e. the scattering coefficients, would be integrated. The solution of the scattered intensities is square in products of these coefficients. Integrating scattering coefficients would thus involve integrating coefficients of each order multiplied by the coefficients of every other order. The computation time for this is of order $n_\theta^n + n_p^n$, where $n_\theta$ is the number of elements in the histogram and $n_p$ is the number of angles for which scattering must be calculated.

In comparison, using the straight integration of intensities method described above has computation time of the order $n_\theta n_\theta n_p$ (as does computation of the scattering of the individual particle species).
Example Results

Figure 2.18 plots the effects of a (Normal\textsuperscript{[67]} polydispersion for a few relatively large particles, the effects being more pronounced for such particles. The general trends of the graphs are maintained with increasing particle diversity as the general form of scattering changes slowly with particle size. The detail of the angle and particle dependent effects are quickly lost for relatively low particle size ranges, especially in the back scatter direction where the angular features are more particle size dependent.

\textbf{Figure 2.18} - Mean scattered intensity from polydispersions of particle size. Particles have $m=1.25$. Blue lines represent monodispersion result. Distributions are Normal. Incident light is vertically polarised.
2.10. Mean Scattering of Polychromatic Light

So far solutions have been derived and computations described assuming a monochromatic light source, or detection of a single wavelength of light. Often scattering experiments will have a polychromatic source and so this assumption does not hold. The following sections first transform results from §2.9 to provide a means of computing overall scattered intensity. A more rigorous approach is discussed in §2.12 providing a scattered spectrum from a given experimental set-up.

2.10.1. Scattered Intensity

Equation 2.49 described the mean intensity scattered by a particle of size parameter and refractive index given by the probability distribution \( p(m, x) \). In general, both the relative refractive index and the particle size parameter are wavelength dependent -

\[
m = \frac{n_1(\lambda)}{n_2(\lambda)}
\]

\[
x = \frac{2\pi a}{\lambda}
\]

Firstly assuming a monodispersion of particle size and a single particle species (i.e. constant refractive index function), equation 2.49 can be rewritten in terms of the incident spectrum -

\[
I_s(\theta, m(\lambda), a, p(\lambda)) = \int I_s(\theta, m(\lambda), \frac{2\pi a}{\lambda}) p(\lambda) d\lambda
\]

(2.50)

This can again be generalised to allow for distributions of particles, by integrating over both PDFs -

\[
I_s(\theta, p(m(\lambda), a), p(\lambda)) = \int I_s(\theta, m(\lambda), \frac{2\pi a}{\lambda}) p(m(\lambda), a) p(\lambda) d\lambda da
\]

(2.51)

Sensor Responsivity

Equations 2.50 and 2.51 predict the light scattered in a given situation, this light must then be measured for the result to be of use. Any given sensor will respond to different wavelengths differently. Measurement in reaction to an incident spectrum will be \( V = \int I(\lambda) R(\lambda) d\lambda \), where \( R(\lambda) \) is the responsivity of the sensor, i.e. the measurement made due to unit intensity at wavelength \( \lambda \). Inserting the results of the above polychromatic scattering situation into this equation is exactly equivalent to replacing \( p(\lambda) \) with \( R(\lambda) p(\lambda) \) in the equations 2.50 and 2.51. In other words, the spectrum of wavelength used in the computation of scattered intensity should be the spectrum \textit{as would be measured by the sensor to be used.}
**Computation**

A system of particles, whether monodisperse or polydisperse, illuminated by a polychromatic source will have a distribution of particle size parameters. The particle size parameter is a function of wavelength and particle size, resulting in a distribution of parameters due to a distribution of wavelength. The computation of scattering from a distribution of $x$ is described adequately in section 2.9.1. In many situations an incident spectrum will not have a functional form but be represented by a histogram (e.g. as measured by a spectrometer), which is ideal for this computation.

**Results**

Figure 2.18 can equally be considered a graph of scattering from a single particle of a widening wavelength range source. The frequency of the source is normally distributed with a central wavelengths of $\frac{\lambda}{5}$, $\frac{\lambda}{7}$, and $\frac{\lambda}{10}$ particle radii. As discussed above, the particle size specific phenomenon such as some of the angular features will be lost when a non-spectroscopic measure is made of scattering of polychromatic light, even from monodisperse particles.
2.11. Statistics of Scattered Light

Whilst sections 2.9 and 2.10 provide a method for computing the mean intensity scattered by a given particle distribution and/or polychromatic source, this discards much relevant information. The statistics of the intensity of light scattered by particles can hold much information about the particles themselves. Second, third and sometimes higher moments about mean and/or origin could be of use. The following sections describe calculations of the full PDF of scattered intensity for a given PDF of particle parameters. So this can be implemented in Matlab (see Appendix A), a method of numerically describing an arbitrary PDF is required.

This study is not the classic study of statistical optics\textsuperscript{[68]}, which uses measures of fluctuations within coherent light sources and their interactions with inhomogeneities to analyse phenomena. However, the use of the scattering from incoherent structured light has been shown to provide information about the scattering media\textsuperscript{[69, 70]}. A model of scattered intensity from polydispersions will be required to study size fluctuations in a similar way.

Gregory\textsuperscript{[71, 72]} has proposed use of fluctuations in incoherent transmitted turbidity to obtain particle and particle concentration information. The main fluctuations in the turbidity signal are due to fluctuations in the number of particles, however to rigorously model the turbidity of a polydispersion the statistics of the individual scattering will be required.

Similarly, the spectrum of light scattered when particles are illuminated by a polychromatic source is often of interest; possibly containing information about the scattering particles. The procedure for converting from incident spectrum (described as a ‘PDF’ – a normalised spectral power distribution) to a scattered spectrum is investigated in the next section.

2.11.1. Distributions of Particles

Histograms of PDFs

So that a PDF can be described numerically it must be ‘binned’ into a histogram. The histogram is described by the edges of these bins and the probability of lying in each of these bins. The size and range of these bins can be sized arbitrarily, so as to satisfy the necessary accuracy of the application, or to represent the information known about the sample. A test sample will often have been sized, giving a percentage of the particles lying in any given size range; exactly how the PDF will be represented.

In all situations the contents across any given bin is assumed uniform and any function applied to the PDF is assumed linear across any given bin. These assumptions can always be
valid by making the bin size arbitrarily small. Even if the PDF is uniform across a given range, use of multiple bins will provide greater accuracy when non-linear functions are applied to the distribution, as the function becomes represented by more linear sections.

**Applying a Function to a Variate**

A second variate can be defined as a function of a variate with a known PDF. If the function is monotonic, this can be done by applying the function to the edges of the bins. The probability density in each range will be changed accordingly, as the actual probability of being in each range remains unchanged.

**Resampling the PDF**

Once a function has been applied to a PDF, it may be necessary to resample the PDF to ‘realign’ the bins. A histogram may be mapped onto a new set of bins by transferring an appropriate proportion of each probability into each new bin as necessary – see figure 2.21. The assumption used is that the distribution is uniform across each of the bins, which, if the remap is performed after application of a function to a variate, follows from the assumptions of previous uniformity and local linearity of the function.
Non-Monotonic Functions

If a function is applied to the variate which is not monotonic a change of order of the bin edges may occur. This can be resolved by reordering the bin edges and redistributing the probabilities between the bins proportionally, as in remapping. Errors can occur where changes in slope occur within a bin (another requirement for locally linear functions) as demonstrated by the error in Figure 2.20(b).

2.11.2. Scattered Intensity PDF from Size Distributions

The intensity of light scattered by a given distribution of particles is a variate that is a function of those particles. The methods described above can be applied, considering the transposition from particle size to intensity to be, in general, a non-monotonic function.

![Figure 2.20 - Application of non-monotonic function to a histogram.](image)

![Figure 2.21 - Remapping of histogram onto a new set of bins.](image)
Example Results

Figure 2.22 - 90° scattering from particle size distributions centred on x=10 - Normally distributed with standard deviation $\sigma$. $m=1.25$, vertically polarised incident light.
Figure 2.22 shows the probability distributions of 90° scattered intensities for a series of increasing spread normally distributed particle size distributions. A narrow distribution of particle sizes ($\sigma=0.1-0.2$) produces a narrow roughly normal distribution of scattered intensities. Over the particle size range (~10±0.5), the scattering function is roughly linear (see figure 2.23) and gives a simple mapping from particle size to scattered intensity.

As the range increases to encompass minima, maxima or saddle points ($\sigma>1$), peaks appear around those stationary points. A stationary point implies a region of low and zero intensity-size gradients. Particles of all sizes in this region will exhibit similar intensities of scattering and so a probability peak will appear around these points. This can be seen clearly for $\sigma=0.5-1$ in figure 2.22.

For large ranges ($\sigma>5$) there are many saddle points and so the form of the single particle scattering function is echoed in the intensity PDF.

With the exception of the most tenuous of particle suspensions measured by extremely sensitive equipment, acquisitions of such complex PDFs are very unlikely. In principle, a photo-multiplier tube could be used to measure scattering in a similar geometry to current obscuration sizers and could, in theory, perform such single particle measurements. In a more conventional system, however, the sum of the light scattered from at least a few particles is likely to be measured at any given time. Assuming single scattering, the recorded PDF will thus be the sum of a number of variates taken from this distribution.
2.11.3. Multi-dimensional PDFs

In the same way that one-dimensional PDFs can be binned into a histogram, a multidimensional PDF can be binned in a similar way. A grid or matrix of probabilities represents the PDF, the edges of which are labelled.

A two-dimensional PDF is required, in general, to represent a spherical particle distribution, as particles vary in both size and refractive index.

2.11.4. Scattered Intensity PDF from Size and Refractive Index Distributions

As with a one-parameter distribution a function of the two variates can be applied to produce a dependent one-dimensional variate. By applying the scattering function to a refractive index/size distribution scattering intensity PDFs can be produced for real-world samples.

In the absence of appropriate data some assumption concerning the inter-relationship between refractive index and particle size is necessary, however studies\textsuperscript{[73]} have shown that real samples have significant correlation between material (and so refractive index) and particle size.

Applying a Function to Two-Dimensional Histograms

Each bin in the histogram is now a rectangular area in two-dimensional space. Applying a function to the corners one bin will provide four results. If there is any deviation in the linearity assumption in either direction then a single plane will not fit through these four points. Fitting a best plane to these points would be a first approximation. A second option is to take an assumed value (the mean) for one of the two parameters (as discussed below in section 2.12.1). This option leads to a simpler solution by producing just two edge values whilst losing little in accuracy provided that the grid is sufficiently fine.

Applying the Scattering Function

The Mie scattering function can be applied to the two-dimensional PDF as discussed, producing a PDF of scattered intensity at each angle.

Example Result

Figure 2.24 shows a distribution of particles varying in both size and refractive index. The distribution is made up of two distinct species of particle, each with its own Gaussian peak. Realistic samples are likely to have distinct refractive index values each with their own particle size distribution; the sample being made up of particles of different substances. Only where mutual refractive index and particle size information is combined in this way is a
Figure 2.24 – Example size/refractive index distribution.

single integration of intensities more efficient than individual analysis of each particle type followed by appropriate weighting by relative particle count and summation.

Figure 2.25 shows the resulting 90° scatter distribution for single particles taken from the distribution shown. Arguments describing the distributions in §2.11.2 are valid for the two-dimensional distributions also, with the effects smoothed out over a wider variation of particle parameters.

2.12. Spectra of Scattered Light

The size of a particle scattering light used in the calculations is relative to the wavelength of illuminating light. Calculations have predicted the monochromatic light of a given wavelength scattered by a given particle. A particle illuminated by polychromatic light will scatter the different frequencies of light at different efficiencies, producing, in general, a change in perceived colour as the system is viewed from different angles. By applying scattering theory to each wavelength in a spectrum, the modified scattered spectra can be produced across the full angular range.
2.12.1. Histograms of Spectra

An electromagnetic spectrum can, in general, be considered as a PDF of wavelength (or frequency) multiplied by the total intensity. A spectrum can be represented in the same way as the PDFs described above, the power will be gathered into bins in the same way that probabilities are gathered in the histogram representation of a PDF. The output of a spectrometer will likely provide intensity values in each of many equally sized wavelength bins. The data will often be in this histogram form by default.

**Functional Transformations of Power Spectra**

A transformation of a power spectrum can take one of two forms.

Some phenomena transform the wavelength of light and so cause a shift and/or spreading of a power spectrum. Doppler shifting is an example of this. In such an instance, the wavelengths of edges of the histograms will be shifted to redistribute the power over the wavelength range. The issues of applying such a transformation and complexes of non-monotonic functions are discussed above in section 2.11.1.

Alternatively, the intensity/power of light can be transformed in some wavelength dependent way. In such a case the individual bins are considered individually. Each bin is approximated by a discrete point lying at the centre of that histogram and all calculations are made as though all power in that bin was carried at the chosen central wavelength. This representation is shown graphically in Figure 2.26.

![Histogram of Spectra](image)

*Figure 2.25 – 90° scattered intensity from particles with mutual size and refractive index pdf given in figure 2.24.*
Visualising Spectral Histograms

A given spectrum can be transformed into a RGB triple \(^{74}\) representing the colour that would be perceived. This RGB value can then be output to a computer monitor to give a representation of the spectrum. The colour perceived on the monitor or on a printout should then be similar to that perceived by looking at light of the original spectrum. Many scattering effects produce observable colour effects - e.g. the blueness of the sky, the redness of an evening sky - being able to visualise spectra, aids in the interpretation of such phenomenon.

The RGB 'colour' of the whole spectrum will be an integral of the spectrum multiplied by the individual spectra of the relevant approximations to red, green and blue (See Figure 2.27).

\[
R(\text{spectrum}) = \int R(\lambda)I_{\text{spectrum}}(\lambda)\,d\lambda
\]

and likewise for G and B, where \(R(\lambda)\) is the red spectral value at wavelength \(\lambda\) and \(I_{\text{spectrum}}\) is the intensity of the required spectrum at wavelength \(\lambda\).

If the RGB is represented as a \(N\times3\) and the spectrum by a \(N\times1\) matrix then the RGB triple integral can be calculated by a simple matrix multiplication\(^{74}\) -

\[
\text{RGB}_s = I_s^T \times \text{RGB}_\lambda
\]

The RGB values as a function of wavelength can be represented as\(^{75}\) -

\[
R = \begin{cases} 
440 - \lambda, & \text{if } \lambda < 440 \\
60, & \text{if } 440 \leq \lambda < 510 \\
\lambda - 510, & \text{if } 510 \leq \lambda < 580 \\
70, & \text{if } \lambda \geq 580 
\end{cases}
\]
\[ \begin{align*}
\hat{G} &= \begin{cases}
0 & \lambda < 440 \\
\frac{\lambda - 440}{50} & 440 \leq \lambda < 490 \\
1 & 490 \leq \lambda < 580 \\
\frac{645 - \lambda}{65} & 580 \leq \lambda < 645 \\
0 & \lambda \geq 645
\end{cases} \\
\hat{B} &= \begin{cases}
0 & \lambda < 490 \\
\frac{510 - \lambda}{20} & 490 \leq \lambda < 510 \\
0 & \lambda \geq 510
\end{cases}
\end{align*} \]

These functions can be seen in figure 2.27.

This gives a basic functional form which must fall off at the vision limits and be gamma corrected (i.e. modelled for the non-linearity of the human eye) –

\[ \begin{align*}
\hat{V} &= \begin{cases}
0 & \lambda < 362\frac{7}{3} \\
0.3 + 0.7 \frac{\lambda - 380}{40} & 362\frac{7}{3} \leq \lambda < 420 \\
1 & 420 \leq \lambda < 700 \\
0.3 + 0.7 \frac{780 - \lambda}{80} & 814\frac{2}{3} \leq \lambda < 700 \\
0 & \lambda \geq 814\frac{2}{3}
\end{cases}
\end{align*} \]

where \( \hat{V} \) is any of R, G or B and \( \gamma \) is the gamma correction value, typically 0.8. All units are in nm. This is the value to actually use, with negative values taken as zero.

A spectrum can now be visualised both as a power spectrum histogram over wavelength and an estimate of perceived colour. Figure 2.28 gives an example.

---

**Figure 2.27** – Transformation Spectra of Red, Green and Blue. Top bar shows spectral colours as produced using this scheme.
2.12.2. Scattered Spectra

The scattering of light by particles is a function of wavelength, but does not alter the wavelength – assuming Raman (fluorescence/electron state change) and Brillouin (Doppler shift due to particle motion) effects are excluded. As discussed above, in such a situation each individual wavelength can be considered separately. $x = \frac{2\pi a}{\lambda}$ is computed for each element in the histogram ($\lambda$ taken as the mean wavelength for that element). From this $x$ and the wavelength dependent refractive index, a scattered intensity factor is computed. This result can then be used to modulate the wavelength dependent incident intensity, $I_i(\lambda)$. So, assuming polarisation state is wavelength independent –

$$I_s(\theta, \lambda) = I_s(\theta, m(\lambda), x(\lambda))I_i(\lambda)$$

Figure 2.29 shows an example of the angular and wavelength dependence of this calculation. A distinct blue shift can be observed in the forward scattering direction, a phenomenon observable by eye in the atmosphere and in fluid suspensions (e.g. milk).
Example Scattered Spectra

Figure 2.29 – Power spectra of light scattered at 30° intervals from a particle of radius 300nm and refractive index relative to the medium of 1.25 (independent of wavelength). The incident radiation is uniform ‘white’ light as shown on the left. Radius of the central figure is proportional to the logarithm of the total scattered intensity.

Figure 2.29 shows the spectra and colour of light scattered by a spherical particle illuminated by a uniform ‘white’ light source. The predicted effects are similar to the effects that are observable by illuminating a particle suspension such as milk. Forward scattered light has a blue tinge, while backward scattered light is redder.
2.13. Discussion

2.13.1. Single Particle Scattering

The introductory sections of this chapter (up to section 2.6) present a rigorous method for the determination of light scattered by a single spherical particle. Although there are very slightly more efficient methods of computation (e.g. logarithmic derivatives\(^{1,36}\)), the one given is the most fundamental and is most readily expanded.

Unlike much of the common literature\(^{1,4,24,36}\) the functions used in the calculations and the geometry of the scattering have been clearly represented. The demonstration of this information allows a good understanding of the source of various fluctuations and thus provides grounds on which to develop a system of required basis functions for future approximations of the single scattering function (as by Naimimohasses\(^{45}\)).

2.13.2. Finite Sensors

The rigorous single particle scattering solution makes a good match to more useful measurable parameters for sufficiently tenuous solutions. The low concentration single scattering approximation has been integrated over finite systems, specifically finite rectangular sensors measuring light scattering from particles illuminated by an unbounded plane source and by a narrow uniform beam.

The effects of finite size in the azimuthal direction is small but easily computed - the solution being analytical (the integration is over a simple trigonometric dependency). The integration over scattering angle must be performed numerically, but has a more dramatic effect. Increasing sensor size in either direction has the effect of smoothing out angular features from the function, however, increasing scattering angle has the greater effect on the angular dependency.

The basic methods described in this chapter for integrating over a realistic system form a basis for the modelling of a realised nephelometer in chapter 5. The basic narrow beam, finite sensor model is expanded upon by incorporating lensing effects of a cylindrical cuvette.

2.13.3. Distributions of Particles and Wavelength

In this chapter it has been discussed how light scattered from a polydispersion of particles can be modelled by numerically integrating the basic single scattering function with respect to the variate over a given PDF. As would be expected, over a polydispersion of particle size any specifically size dependent features will be lost, while the general trends of the particles
in the given size range will be maintained, for example large particles maintain a strong forward scattering characteristic but lose all but the largest of angular minima and maxima.

Measuring light scattered from monodisperse particles illuminated by a polychromatic light source is exactly equivalent to measuring light from a polydispersion sample in a monochromatic light source. The size parameter important to light scattering is normalised to illuminating wavelength and so modulating incident wavelength will inversely modulate the size parameter. Any work carried out for particle size fluctuations is equally valid for polychromatic sources, with the simple consideration of refractive index wavelength dependency.

Use of a white light source in scattering measurements can ensure that local minima and maxima will not cause results to fluctuate when sizing with normalised nephelometric measurement. A sufficiently wide spectrum will mean that a suitable normalised scattering measurement can, in principle, be made to be monotonic for particle size, although detailed size measurement may be lost.

Figure 2.29 shows example theoretical results for spectroscopic nephelometry. The wavelength and particle size dependency of light scattering can be used to obtain information about a given sample. By taking spectroscopic measurements at a number of angles, or by successively illuminating a sample by a number of sources with different wavelengths, information can be gathered concerning the particulate (and absorbing nature) of the sample and medium.

2.13.4. Scattering from Polydispersions

Number Fluctuations

Twersky\textsuperscript{771} considered the propagation of light through a medium of discrete scatterers. He discussed the scattering solution from a number of particles with a general undetermined vector defining their 'significant properties', including their position in the scattering space. For his illustrations, he limited the analysis to similar particles, i.e. position being the only parameter.

Analyses in this chapter provide firstly a mean intensity (§2.9) and then statistical information (§2.11) for scattering from a spherical particle taken from a particle distribution. Further work could take the analyses of Twersky and the number fluctuation work of other authors\textsuperscript{781} and combine them with these analyses to provide a useful statistical prediction of incoherent scattering from particle ensembles.
The current statistical solution for scattering from a single particle is only of use in very limited application, such as flow-cytometry\cite{79, 80} where single particles are passed through the scattering volume successively.

**Approximations**

The analysis of single scattering from a particle taken from a distribution as presented in this chapter is rigorous, and for the histograms as defined, exact. Studies have been made\cite{81} which attempt to model scatter from various distributions of particle size and generalise the result. It was found that a single size parameter, namely the ratio of the third to second moment of the diameter (i.e. the ratio of mean volume to mean surface area), was of much greater importance than any difference in shape of the distribution.
Chapter 3. MULTIPLE OPTICAL PARTICLE SCATTERING

'Even the very simplest law of scattering for the individual particles (isotropic scattering) leads to complex mathematics in the multiple-scattering problem' — van de Hulst
3.1. **Aim**

This chapter presents accepted multiple scattering theories and accepted approaches to modelling multiple scattering. A simple first-order model is implemented.

3.2. **Introduction**

The theories presented in Chapter 2 predict the light scattered from a single particle. The majority of the fundamental texts which present spherical particle scattering\textsuperscript{1, 4, 36} go little further than this, presenting only this single scattering theory. This approximation is useful in tenuous media, where the number of multi-particle interactions is small and the extinction due to scattering is negligible.

The single scatter approximation is put to good effect in areas such as weather radar\textsuperscript{25}. Concentrations in particle suspensions are sometimes low enough to be in, or it is possible to dilute a sample into, the single scattering regime, to provide information concerning, for example, particle size. Dilution is often not possible however, due to process constraints, or is not desirable, due to phase transitions caused by the dilution process\textsuperscript{82}.

Multiple scattering theories can be categorised into one of two regimes; those for relatively tenuous suspensions and those for dense suspensions. The former takes basic single particle scattering and corrects for varying number of particle interactions, starting with first-order multiple scatter which corrects for scattering extinction and through Foldy-Twersky theory\textsuperscript{83} which takes into account multiple particle interactions.

Dense suspensions are modelled by a diffusion approximation, where the flux passing through infinitely small scattering volumes are integrated and individual scattering events are not considered.

This chapter presents first-order multiple scatter correction in some detail and gives a brief overview of other multiple scatter corrections. The first-order correction is a relatively trivial extension of the single particle scattering presented in the previous chapter, whereas other scattering theories rely on completely different methodologies.

It is claimed\textsuperscript{82} that single scatter approximations can be used up to 100ppm (~5% extinction) and first-order for samples with up to 70% extinction.

3.3. **First-Order Multiple Scattering**

The single scattering approximation makes the assumptions that the field incident on each particle in the volume of interest is equal to field incident on the system and that the wave
received by the receiver will be equal to the sum of those scattered by the individual particles in the scattering volume, see figure 3.1(a).

First-order multiple scattering keeps the fundamental single-scattering assumption that all light measured by the receiver has been scattered once and only once, but drops the other assumptions above. This results in a lower limit for the intensity measured. The intensity reducing effects of multiple scattering are modelled but the additional optical power scattered into the sensor is neglected.

Schnablegger and Glatter offer Hartel’s theories, which derive very similar first-order results derived from the equation of radiative transfer. This forward model is then inverted to provide colloidal sizing from scattering for samples with extinctions up to 70%.

3.3.1. Extinction

As light travels through the medium its intensity will be attenuated by extinction, both absorption and scattering (see figure 3.1(b)). For this chapter, absorption by the medium will be neglected as the experiments considered in other chapters use de-ionised water as a medium, which has relatively low absorption at the wavelength used (0.3% extinction over a
Following the work presented in this thesis, a study of the interaction of colour (wavelength dependent absorption of the medium) and turbidity (scattering of the sample) was carried using a modified version of the scanning nephelometer using a white light source and fibre optic coupled spectrometer. Absorption was simply incorporated in the absorbance equation, 3.1, below by adding the absorption, \( \alpha = 2k\Im(n_2) \) to the scattering extinction in the absorbance, \( A \).

The Beer-Lambert absorption and scattering law states that the intensity of light will decrease exponentially with distance travelled through the absorbing and scattering medium,

\[
I = I_0 e^{-Ad}
\]

where \( d \) is the path length through the medium, \( I_0 \) is the intensity on entering the medium and \( A \) is the absorbance per unit length.

Extinction caused by a single particle is defined by its extinction cross-section, \( \sigma_e \), see §2.6.5. It is the area through which light is removed from the incident wave. The total absorbance through a given volume will be given by \([24, 63, 84]\),

\[
A = N\sigma_t
\]

where there are \( N \) particles per unit volume and \( \sigma_t \) is the extinction cross section of a single particle. \( A \) is thus the extinction per unit distance through the volume.

### 3.3.2. Small Scattering Volume

In a system where the source is a narrow beam and the receiver has a small numerical aperture, resulting in a small observed scattering volume, the path length will be consistent and independent of scattering angle. Figure 3.2 shows a simple system based around a cylindrical cuvette, with the scattering volume at its centre. The path length through the

![Figure 3.2 - Extinction of light before and after scattering.](image-url)
medium in this geometry is \(2r\), the diameter of the vessel. Nephelometric calibration (normalisation of angular scattering to a measure at a single angle, usually \(0^\circ\)), first-order effects can be completely removed,

\[
\frac{I_\theta}{I_0} = \frac{I_0 e^{-2Ar}}{I_0 e^{-2Ar}} = S(\theta)
\]

simply leaving the scattering amplitude function.

### 3.3.3. Significant Path Length

In a geometry with a narrow beam and significant receiver numerical aperture (as described in §2.8), the path length will be dependent on the angle integrated. The form of the scattering will change with angle.

The path length along which attenuation may take place consists of two parts, that before scattering, \(\hat{z}\), and that after, \(\hat{r}\) (see figure 3.3). These two quantities can be evaluated,

\[
\hat{z} = r \left( \cos \theta - \sin \theta \cot \hat{\theta} \right)
\]

\[
\hat{r} = \frac{r \sin \theta}{\sin \hat{\theta}}
\]

where \(\hat{z}\) is taken as the distance, at \(\hat{\theta}\), along the beam from point \(O\) on the nominal scattering angle, \(\theta\) and \(r\) is the distance from the receiver to the beam along the nominal scattering angle.

---

Figure 3.3 - Optical path length along and from narrow beam.
Assuming, in the first instance, that the entire path length is in the scattering medium, then the quantity measured by the receiver can be estimated (from equation 2.46). The incident intensity at any point will be attenuated by $e^{-Nz}$ and the scattered intensity will be further attenuated before reaching the sensor by $e^{-Nz}$.

$$I_s = \frac{CN}{k^2 \sin \theta} \int_{0}^{\theta} \left( S_{11} (\theta) I_1 e^{-Nz} + S_{12} (\theta) Q_1 e^{-Nz} \right) e^{-Nz} d\theta$$

$$= \frac{CN}{k^2 \sin \theta} \int_{0}^{\theta} \left( S_{11} (\theta) I_1 + S_{12} (\theta) Q_1 \right) e^{-Nz} \frac{\cos \theta \sin \theta}{\sin \theta} d\theta$$

where $z$ is the distance through the medium to $O$.

This analysis can be repeated for the other Stokes' parameters giving

$$\begin{pmatrix}
I_s \\
Q_s \\
U_s \\
V_s
\end{pmatrix} = \frac{1}{k^2 \sin \theta} \begin{pmatrix}
S_{11}^n & S_{12}^n \\
S_{12}^n & S_{11}^n \\
0 & 0 \\
0 & -S_{34}^n
\end{pmatrix} \begin{pmatrix}
I_1 \\
Q_1 \\
S_{34} \\
V_1
\end{pmatrix}$$

where $S_{ij}^n = \frac{CN}{\sin \theta} e^{-Nz} \int_{0}^{\theta} \left( S_{ij} (\theta) \right) e^{-Nz} \frac{\cos \theta \sin \theta}{\sin \theta} d\theta$.

### 3.3.4. Effect of First-order Multiple Scatter

Figure 3.4 shows the intensity scattered at 90°. For low concentrations of scatterer the effects of multiple scattering are small and there is a linear increase in intensity with concentration, i.e. the single scattering approximation applies. In general, there will be a linear increase of intensity with concentration due to single scattering but an exponential decrease due to extinction. At a certain cut off concentration (determined by particle parameters and scattering angle) the measurable intensity begins to vanish.
It is expected that first-order multiple scattering theory is valid for a small region beyond the single scattering regime for particles which are at least moderately absorbing, i.e. where total particle extinction is significantly greater than scattering effects. Soon after the optical power lost to scattering becoming significant then so will the rescattering of light into the sensor (i.e. second and higher order scattering).

Angular Effect

Figure 3.5 shows the angular form of an increasing concentration of particles. It would be expected that the intensity of forward scattered light would decrease with increased concentration due to growing extinction. The intensity of back scatter would be expected to increase, however, as the smaller path length of some of the scattering experiences less extinction. Both of these effects are demonstrated in the figure.
3.4. Radiative Transfer

Light entering a dense suspension of particles will, in general, undergo many interactions with particles before leaving the medium to be measured, see figure 3.1(d). The angular dependent flux and energy densities passing in to and out of any small elemental volume in the medium can be considered. By reducing these volumes indefinitely, a series of integro-differential equations can be established which define the transport of flux through the medium based on the mean parameters of individual particles\cite{24,85}. The particle dependencies are incorporated into the equations in the form of a probability that light entering a small volume from a given direction will leave in any other given direction - a function of the form of the light scattering.
The light scattered by a dense suspension of particles is at best described by this transport of radiative flux, i.e. radiative transfer, diffusion approximation or transport theory. The theory works on a macroscopic level and loses much of the information acquired from rigorous study of diffraction effects. It's study will not be continued in this thesis as the concentrations for which it is most relevant are beyond those considered here.

3.5. Other Multiple Scattering Theories

Other multiple scattering theories tend to either extend the order of scattering or concentrate scattering information/approximation into the transport equations.

An example of an extended transport equation is the approximation for particles large compared to the wavelength, since the vast majority of light is scattered forwards, only forward travel of flux need be considered. Such small angle approximations are used to model propagation in particulate media[86-88] and to correct for extinction theories[89].

The expanded representation by Twersky[77] extends the order of the scattering by summing the field due to successive scatterers, but neglecting fields scattered from the same particle more than once. Although this representation highlights the processes involved, it is not practical to obtain useful results from this theory. The theory integrates over the scattering volume for all possible spatial distributions of particles, making it very computationally expensive for all but the greatest of simplifications.

The Foldy-Twersky equation integrates over the scatterers to predict the total coherent and incoherent fields within the scattering volume, it extends Foldy's earlier work[90] which solved the field equations for scalar waves passing through a volume of isotropic scatterers, which has been generalised by Lax[91] for anisotropic scatterers. Similarly, this theory is not practical for prediction of measurable quantities in a realisable nephelometer.

Ishimaru[83] compares the Foldy-Twersky equations with transport theory and shows, as would be expected, that under certain assumptions the two theories coincide.

The assumption that any given particle does not scatter any given photon more than once can be extended to consider planes of particles (usually tens or hundreds) and assuming that there is not intra-plane multiple scattering. Once approximations, e.g. Rayleigh[92, 93] or Fraunhofer diffraction (circular disk assumption)[94], have been made rays can be traced from plane to plane and multiple scattering between planes approximated.

3.6. Discussion

Research into the field has established a wide variety of solutions to the forward problem of multiple scattering, not to mention the many, many more corrections and extensions for
multiple scattering to the inverse problem. A general, exact solution to the problem of
scattering from more than a single particle must be considered as a new boundary value
problem; anything less relies on assumptions and approximations.

The methods discussed in this chapter attempt, in one way or another, to model the effects of
the interaction of electromagnetic waves with multiple particles. It is the aim of this thesis to
develop an empirical model of multiple scattering as an extension of the single scattering
approximation. The application of multiple scattering theories to the cell of the scanning
nephelometer has not and will not, therefore, be considered.

The first-order multiple scattering correction presented here is a computationally trivial
extension of single scattering, requiring little more work to implement. This model of
scattering will be implemented for the scanning nephelometer cell and its results compared
with those of pure single scattering and with experimental data.

The basic models of first-order multiple scatter presented in this chapter make no boundaries
on scattering volume. At very large (~180°) and very small angles (~0°) the length of the
scattering volume is very large, the effects of extinction are thus exaggerated. The angular
effects of this model are not expected to be as great in realistic scattering cells.
Chapter 4. The Scanning Nephotometer
4.1. **Aim**

This chapter presents the optical, mechanical, electronic and software aspects of the experimental set-up used for obtaining nephelometric intensity readings at many angles.

4.2. **Introduction**

4.2.1. **Requirements**

To perform an analysis of the effects of multiple scattering on the scattering footprint, a system is required capable of measuring the footprint of a given sample. In the single scattering regime the footprint should be in some way comparable with that predicted by known theories and their extensions (Chapter 2). The angular range should be as complete as possible, to provide both forward and back scattering readings. The angular resolution should be in the order of a single degree, so that some of the finer features may be resolved. Most nephelometers have only sufficient angles for a particular application or cover a small angular range (e.g. 0-50° or 0-80°).

To investigate the scattering of spherical particles the use of latex spheres is required. To produce a suspension of high concentration of more than a few millilitres is prohibitively expensive. The experiment must use a sample chamber with a sample volume in this order of magnitude.

4.2.2. **Overview**

The scanning nephelometer can be considered as four systems, the optical (§4.3), the mechanical (§4.4), the electrical (§4.5) and the data acquisition software and it's interface (§4.6).

The optical source used was an HeNe laser, chosen for its collimated beam, it's high degree of linear polarisation and its relatively high power - providing measurable results in relatively weak scattering regimes. The sensor was a photodiode with a pinhole aperture providing a simple intensity to voltage conversion amplifiable and measurable electronically. The source is chopped mechanically to provide ambient signals for subtraction from the scattering signal.

Building a static nephelometer with a sufficiently high angular resolution and range would require some form of photodiode array with at least 200 directional pixels. The array would be need to curve around the sample tube. It was decided to use a single moveable
photodiode to facilitate greater versatility and for the simplicity of the associated acquisition electronics. The sensor is rotated around the sample tube by a computer controlled stepper motor driven assembly providing a 0.9° step resolution.

The photodiode signal is amplified by a simple inverting amplifier circuit before being passed to a PC I/O card for conversion to a digital value. A signal from the chopper is also passed to the card and ambient subtraction is performed digitally in post-processing. The stepper motor is controlled by two lines from an I/O card connected to a standard stepper motor driver chip; two microswitches mark the end positions of the nephelometer’s angular range.

The software receives set-up parameters from the user, i.e. the number of readings to average over and the number of runs to perform on each sample. The stepper motor is controlled and readings taken via the I/O card before being displayed on screen and written to file for later analysis. Ambient and signal first to third moments are written to the text file in addition to the statistics of the resulting ambient-subtracted scattering intensities.

4.2.3. History

An earlier version of this scanning nephelometer consisted of the current tube assembly and scanning arm mounted on a manual rotation stage. Accurately performing an experiment with a 5° resolution for a single sample could be done on only about two samples per day. Lights would need to be switched on, the rotation stage moved, readings initiated etc. for each and every angle.

The addition of the computer controlled stepper motor to the system has reduced the experiment from several hours of laborious measurement to ~20 minutes of unsupervised readings and has increased the angular resolution by a factor of $5^{1/2}$.

With the automation of the stepper motor control, the PC reading of sensor output was also implemented. Rather than a single reading being taken at each angle, thousands are taken, providing statistical intensity information, in addition to the mean optical reading; information that is not used in this project but may have uses is statistical analysis of the scattering.

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† It has been used in later studies to pick out a relatively small subset of the possible angles for study.$^{[99]}$
4.3. **Optics**

4.3.1. **Source**

The source used was a Carl Zeiss LGK 7634 class IIIa Helium Neon Laser, with a wavelength of 633nm and power of 5mW.

4.3.2. **Chopper**

An optical chopper\(^{[100]}\) with 2 apertures on an 80mm wheel was placed in the source beam. Equal arm and aperture sizes chopped the source between on and off with a 50:50 duty cycle.

A slotted opto-switch mounted on the perimeter of the chopper wheel monitors the cycle of the chopper. The chopper was aligned such that the signal from this switch coincided with the signal measured by the sensor in the 0° position, producing zero phase difference on an oscilloscope.

See §4.5.2 for more information about the chopper electronics.

4.3.3. **Sensor**

The sensor is based around a Burr-Brown OPT202\(^{[101]}\) opto-electronic integrated circuit containing a photodiode and a transimpedance amplifier. The photodiode area is 0.09x0.09" (2.29x2.29mm) on one face of a 5-pin SIP package. It has a specified current responsivity of 0.45A/W at 650nm (~0.43A/W at 633nm) and a corresponding voltage output of 0.45V/μW with the internal 1MΩ feedback resistor used. The non-linearity is specified at 0.01% full scale (FS = 10V) and the voltage noise 1mV in bandwidth 0.1Hz - 100kHz.

The sensor has a response that varies with the angle of incidence of the illuminating radiation. The response characteristic from the data sheet\(^{[101]}\) is reproduced in figure 1.1. The sensor was placed such that the angle \(\theta_s\) lies in the azimuthal plane and the angle \(\theta_r\) lies in the scattering plane. As will be seen later the azimuthal range is very small (and as can be

![Figure 4.1 - Angular response of OPT202. (reproduced from Burr-Brown data sheet).](image-url)
seen has a flatter response function). The scattering angle response function is fitted closely by the polynomial,

$$V(\theta_\gamma) = -0.1032\theta_\gamma^3 - 0.2514\theta_\gamma^2 - 0.0310\theta_\gamma + 0.9965$$  \hspace{1cm} (4.1)

where $\theta_\gamma$ is measured in radians.

This leads to a 0.4% variation over $4.5^\circ$ (see §4.3.4). Any effect of the angular response of the sensor can be safely neglected. If this effect had been found to be significant, the angular dependency, 4.1, could be incorporated into the angular integral 2.47 or into the definition of the Mueller elements for 2.48.

### 4.3.4. Sensor assembly

The sensor is fixed to the back face of a Darvic (hard plastic) tube with a pinhole aperture at the front. This cylinder is mounted on a post, which is in turn mounted onto the scanning arm of the nephelometer. The sensor post is the point from which any future position measurements of the sensor are made.

Figure 4.2 shows the dimensions of this sensor head. The half angular range of the sensor is $\delta \theta = 4.51^\circ$, giving a numerical aperture, $NA = 0.079$. The focal position of the sensor is a distance behind the pinhole, $r^* = 9.5\text{mm}$, which makes the focal point $r = 0.5\text{mm}$ before the post.

The post was positioned 57mm from the centre of the tube mounting, making the distance from the sensor to the vessel centre 56.5mm.

---

**Figure 4.2 – Numerical aperture of sensor assembly.**

*All dimensions in millimetres.*
4.3.5. Sample Tube

The sample tubes used were disposable Samco soda glass specimen tubes (nominal 12mm OD, code G050/20). The relative refractive index of the glass is 1.5. The tubes were measured as internal diameter of 10.9mm (nominally 10) and an external diameter of 12.8mm (nominally 12).

4.3.6. Tube holder

The tube holder has a bored hole 1-2mm greater diameter than the sample tubes. 1mm thick high density Plaztezote lines this hole. The tube was inserted into the foam-lined cylinder. Its position and orientation can be adjusted subtly and quickly; it then remains rigid for the duration of a scan.

4.4. Mechanical Set-up

The scanning nephelometer consists of an optical sensor which is scanned around an arc concentric to a cylindrical sample tube. Intensity measurements are made at regular intervals around that arc.

Figure 4.3 - Scanning nephelometer.
The scanning stage is driven by a computer controlled stepper motor. This motor drives, via a 2:1 belt gear, a rotation stage, onto which the sensor assembly is attached. The rotation stage turns through 0.9° per step of the motor, at each of which an intensity measurement can be made.

Sensor position can be changed along the rotation arm, increasing or decreasing the sensor-sample distance.

The scanning nephelometer can be seen in figures 4.3 and 4.4.

4.4.1. Stepper Motor and Gears

The stepper motor used to drive the sensor arm is a 4 phase hybrid stepper motor\[^{102}\] (12V, 0.6A with detent torque 30mHm, holding torque 0.5Nm). The motor has a step angle of 1.8° (accuracy 5%).

This stepper motor drives a 24 tooth gear which in turn drives a 48 tooth gear with a toothed connecting belt. The nephelometer stage and the sensor are rotated at 0.9° per step of the motor.

4.4.2. Micro-switch End Stops

Two long-lever V4 microswitches (not shown on figure) are attached to a board mounted onto the nephelometer body. The rotation arm impinges on the lever and closes the switch when the sensor would otherwise pass in front of the light source. Signals from these switches are used by the stepper motor control software to ensure that the sensor stays in a useful range.

A modified use of the nephelometer has used these end-stops to stop the motor from driving into detection optics.
Figure 4.4 — Front and top elevations of scanning nephelometer.
4.5. **Electronics**

The electronics for the experiment were consolidated onto a single board, so that signals could be passed through a single ribbon cable connector to the PC. The electronics can be considered as a number of independent sensing and control systems.

The optical sensor (a photodiode) signal is amplified on the board by a simple adjustable operational amplifier circuit. The chopper supplies a digital signal which is passed directly to the PC. The stepper motor system consists of a standard stepper motor drive chip circuit and connections to end stop microswitches.
4.5.1. Sensor and Amplifier

The sensor is a Burr-Brown OPT202\textsuperscript{[101]} photodiode. The feedback and output pins are connected to use the 1MΩ feedback resistor, giving the nominal gain of 1V/μA and voltage responsivity of ~0.45V/μW at 633nm. Other characteristics of the OPT202 can be found in §4.3.3.

The sensor output is amplified on board using a standard inverting amplifier circuit\textsuperscript{[103]} using a 701 operational amplifier. A variable resistor in the feedback path allows the circuit to be trimmed to provide a saturating voltage for the forward direction and to maximise the use of available resolution on the Lab-PC's ADC.

4.5.2. Chopper

The optical chopper and its control are part of a self-contained unit designed and built by P.J. Greenhill as an undergraduate project\textsuperscript{[100]}. An opto-switch detects chopper position, which is aligned to coincide with source chopping. The output of this opto-switch is used to provide a rate count that is displayed on an LCD display. The chopper's rate is dependent on motor supply voltage that is set by two potentiometers on the unit's front panel. For the experiments, a chopping frequency in the order of 25Hz (20-40Hz) was used.

The logic square wave output of the opto-switch is also fed to a BNC socket mounted on the front of the control console. This signal is passed to the experiment's control board and in turn to the PC, where it is used to select data into ambient and scattering data - see §4.6.3.

4.5.3. Stepper motor driver

The stepper motor driver uses a standard SAA1027 stepper motor drive chip\textsuperscript{[104]} controlled by three lines from the PC's I/O card. See figure 4.5.

4.5.4. PC interface

The PC controls the stepper motor and reads information from the microswitches, chopper and sensor through a National Instruments Lab-PC+ I/O board\textsuperscript{[105]}.

Two of the eight single-ended analogue inputs were used, one for each of the chopper and the sensor. Each of these lines has 12 bit resolution with a typical relative accuracy (non-linearity) of ±0.5 LSB and a range of ±5V (with a software selectable signal gain of 1-100). System noise is specified at 0.3 LSB for unity gain up to 0.6 LSB for gain of 100. The inputs have a specified impedance of 0.1GΩ in parallel with 45pF.

The Lab-PC+ board has two single-ended, 12 bit analogue output channels which are not used for this experiment.
Of the boards three TTL-compatible 8-bit digital I/O ports using 8255A PPI, one is used for each input and output, for the end-stop microswitches and stepper-motor control respectively.

Connection from the Lab-PC+ to the experiment board uses a 50-pin keyed ribbon cable, connecting to male connectors on both boards.

4.6. Software

The software to control the experiment and to retrieve and record the resultant data was written for MS Windows 3.1 using Visual C++ 2.0 based on a standard AppWizard application. Classes to represent the two main experiment elements, namely the sensor system and the stepper motor were created.

The software described here was used for the experimental procedure described in this chapter to obtain the results detailed in Chapter 5 and analysed in Chapter 6. This code has now been superseded by Matlab code and associated interfaces, controlling and monitoring the stepper motor and sensors from within the Matlab environment. The Matlab environment provides a simpler development space for new experiments and methods and provides quicker and more versatile access to experiment data.

4.6.1. Hardware interface

The interface with the National Instruments Lab-PC+ board was implemented using a number of low level functions supplied in the National Instruments NI-DAQ C library. These functions were coded into two C++ classes, one for each of the experiments primary elements.

Each of these two classes store the data acquisition board's parameters, i.e. the board identifier and port and channel numbers for various purposes. These parameters are later passed to the NI-DAQ functions to indicate appropriate channels.

A single instance of each of these classes is instigated as a member of the MFC document class, within which procedural functions are implemented.

The first of the two classes, StepperMotor, is described here. The other, Sensor, is described below in §4.6.3.

StepperMotor

The StepperMotor class acts as a level of abstraction between the experimental procedure and the Lab-PC+ channels controlling and monitoring the stepper motor.
The class stores a number of member variables. Seven variables store the Lab-PC+ parameters - the board ID, the stepper motor control output port, the channels on that port for direction and step lines, the microswitch input port and the channels on that port for each of the two end-stops. The remaining variables store information about the stepper motor itself. The current position is stored, along with the positions of each of the end-stops (minimum and maximum). The number of steps per revolution and the maximum step frequency are also set as member variables.

The positional variables are left public, so that other objects in the program can access their values without need of dedicated functions. For greater robustness, access functions should be written for these parameters in any further, more widely accessible versions of the code.

A constructor sets these parameters to states set by variables passed to the function. Current position is set initially to zero, maximum frequency to 20 (Hz) and minimum and maximum positions are set as unknown (-1).

The end-stop positions each have an access function which returns their positions in degrees rather than their stored form of steps.

A function is available which sets the current position as zero, changing the values of the end-stop positions appropriately (if they have been set).

The remaining functions deal with the movement of the stepper motor.

`Step` is the class' main function, stepping the stepper motor a single step in a specified direction. First, the appropriate end-stop position and microswitch are checked to ensure that the stepper motor can safely step in that direction. If a microswitch is found the current position is set as the end-stop position. If the direction of movement required is different to the previously moved direction then the direction line is changed to the new value, and the system waits for a quarter of a second before continuing. After waiting for half the minimum step period since the previous step, the step line is taken high, there is another wait of a half step period before taking the line low again. This pulse causes the motor to undertake a single step. The value of the current position is appropriately updated.

Other functions call `Step` a varying number of times. Two functions, `FindMin` and `FindMax`, step until the appropriate end-stop is found. A `Goto` function has two forms, each to step until a given position is reached, either in steps or degrees. The `Goto` function works best if the end-stops have been found, so that it is known which direction must be moved to reach a given position without passing through the end-stops.
4.6.2. Graphic User Interface

The graphical user interface supplied standard AppWizard coded features, i.e. a menu, status and toolbar and printing of the view. Once data has been collected for the first time the view displays the last acquired data (averaged over any repetitions) as a polar plot, on a menu-selectable logarithmic or linear scale.

Menu options allow configuration of the filename, the number of samples used to generate each average and the number of times the experiment should be repeated for each execution.

4.6.3. Data recording

Sensor

The Sensor class acts as an interface between the experimental procedure and the Lab-PC+ channels monitoring the sensor and chopper.

The class stores an number of member variables. Three variables store the Lab-PC+ parameters - the board ID and the analogue channels for the chopper and sensor signals. Parameters defining the data collection i.e. the number of samples to average over for each reading, the number of data to reject around the chopper edges (see below) and the files for data recording.

As data are collected, they are stored in public member variables that can be accessed externally to the object. Data are stored as means and second and third moments about the origin for each of the ambient, the signal and the ambient-subtracted scattering data. The number of data collected for each of the ambient and signal are also made public.

The class constructor sets the data collection, the I/O board parameters and whether or not to save all raw data to file. Data files are opened - a '.out' file to store raw data, if required, and a '.mom' file to store the moments of the acquired data. These files are closed in the class destructor.

A NewFiles function allows the files to be closed and new files to be opened - useful between experiments.

GetData is the class' main working function. The required number of data are synchronously acquired from the data and chopper channels. If necessary, these data are written to the raw data file.
Sensor data are then either rejected or separated into either scattering signal or ambient signal depending on the state of the chopper signal. The first and last acquired data are rejected for a single rejection length. Either side of a change in chopper signal, rejection length data are also rejected. For example, if the rejection length is 2, then 2 data are rejected at the start, 2 at the end and 5 around each change in chopper state. The chopper signal comes from an opto-coupler (see §4.3.2) through which the lower portion of the chopper blade passes, the source passes through the upper portion of the blade's path. Any misalignment of the chopper will result in an error between the opto-coupler signal and the chopping of the source, hence the need to reject data. See figure 4.6 for an example of the signals.

Once data are separated into ambient and scattered, powered sums (i.e. sum, sum squared and sum cubed) for each are calculated. These sums are then divided by the number of data in each category to produce the first, second and third moments about the origin. First and third moments are inverted to allow for the inverting amplifier in the circuit. From these quantities the ambient-subtracted statistics of the scattered intensity can be calculated (assuming independence of the signals).

The calculated moments are subject to the amplification of quantisation noise due to the digitisation of the analogue signal. The effect of quantisation error in the reproduction of scattering distributions has been shown analytically to be insignificant for a reasonable (12+ bit) acquisition system.

![Figure 4.6 - Separation of ambient and scattering data.](image)
4.6.4. Procedure

The actual experimental procedure is implemented as a menu handler in the document class. The document has as members both the sensor and the stepper-motor objects.

When the user selects the menu option to execute the experiment (or presses F12), data are acquired at the current position (§4.6.3), the motor steps backwards (§4.6.1) taking data at each step until the minimum end-stop is reached. The motor is returned to the starting position and data are similarly acquired in the forwards direction from the start. After returning to the start, the process is repeated the number of times specified by the user.

While data are being acquired an average ambient-subtracted intensity is calculated for each step position for later graphing.

4.7. Samples

Aqueous samples of polystyrene latex spheres of a range of sizes were made up at various concentrations.

4.7.1. Particles

The particles used were Polymer Laboratories polystyrene plain white Microspheres (polymerised homo- and co-polymers of styrene)\(^{[107]}\). They are purchased in 25ml aqueous suspensions at 10\% by volume in 0.02\% sodium azide preservative solution.

Relative refractive index of the polystyrene latex is 1.54 and density of 1.05 gcm\(^{-3}\).

The particle size range is relatively small (<5%) in all but one case and so for later modelling purposes they will be considered monodisperse.

4.7.2. Water

The water used throughout the experiments was deionised Reagent Grade Water.

4.7.3. Samples

Samples were prepared by successive dilution of the particle suspensions with pure (see §4.7.2 above) water. Initial samples were prepared with equal quantities of a 10\% suspension and water, producing a 5\% suspension. From this, each suspension was diluted 3:1 producing samples of 5\%, 1.25\%, 3.125ppt, 781ppm, ... 2.98ppb, 0.7ppb, 1.86ppb. Later experiments used a 2.5\% initial suspension, to provide samples between these results.
On Multiple Optical Scattering in a Scanning Nephelometer.

28 January 2000

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Table 5.1 - Particle Parameters

4.8. Procedure

A single set of samples are prepared as described in §4.7.3, i.e. a range of concentrations for a single particle size. Experiments are performed on these samples within a couple of days. If the samples are left for any significant period of time, the integrity of the particle shape and size is affected. Old samples have been observed to have distinctively different scattering footprints and coagulations of particles can occasionally be seen by eye.

The sample tube is shaken and placed in the holder. Position is adjusted so that the observed beam at the first glass/air interface coincides with that of the beam reflected from the second water/glass/air interface. The vertical orientation is adjusted so that this is true after rotation of the holder by any angle.

The stepper motor is placed roughly in the 0° (straight through) position, and the sensor height is adjusted to coincide with the horizontal beam plane. This can be achieved by aligning the beam with the pin hole in the sensor body.

The software is set to 5000 readings to make up each average and 3 passes. The whole experiment is performed in a dark room to minimise ambient light.
4.9. Discussion

The scanning nephelometer described in this chapter retrieves scattering results as required. Examples of a comparison between theory and experiment follow.

There are a number of issues that arose during the performance of the experiments, the modelling of the experimental set-up and the analysis of results which suggested some improvements in any future scanning nephelometer and its use.

4.9.1. Example Result

Figure 4.7 shows the average results from a single set of experiments compared with a model of the nephelometric conditions. The closeness of the curves begin to demonstrate the use of the scanning nephelometer. Further results and analysis are presented in the next chapter.

4.9.2. Settling

Polystyrene latex has a density of 1.05 g cm$^{-3}$ as compared to 1 g cm$^{-3}$ for pure water. The particles thus have a slight tendency to sink. Small particles (a few micron radius or smaller) are held in suspension by Brownian motion. Larger particles will settle over time. Particles in the order of 2 μm settle measurably over the course of an experiment (~20 minutes), although useful results can still be obtained. Particles that are 10 μm or larger sink quickly, the exponential decrease in signal due to decreasing suspended content dominates the measurement, making them all but useless for analyses of scattering.

There are two possible solutions that solve the problem of settling in the scanning nephelometer by maintaining the suspension. Firstly, the relative density of the medium could be increased. This could be accomplished by the addition of a solute. Issues of required solute concentration and of changes to refractive index would need to be addressed.

Secondly, an agitation procedure could be implemented. Possible methods of agitation would include the addition of a magnetic ‘flea’ to the sample tube, rotated or vibrated by an external magnetic field, stirring by a rotary stirrer (the tubes are currently sealed with a plastic plug, which would need to be removed) or by the implementation of a sonic bath i.e. vibrating of the tube at sonic frequencies. Any reliable and robust implementation of these would require significant further research.

A third solution is to reduce the experiment time and so reduce the amount of settling over the course of an experiment. Nephelometers have been built previously\cite{29} that use many sensors around the scattering volume, taking a momentary measurement of the scattering footprint. The angular resolution over a large angular range of a viable set-up is significantly lower than that of the scanning device.
The experimental results are the gradient of scattering intensity with respect to concentration over an assumed single scattering regime and should thus be a mean measure of the single scattering properties of the particle for each of two experiment runs. The theoretical curve plots the modelled nephelometry results as presented in Chapter 6. The single scattering curve plots the scattering from a single sphere.

Particle size is 7.31 μm. Incident light is vertically polarised.

Alternatively, the settling could be modelled. If the physical parameters of the particles (size, density etc.) and the medium (viscosity, density etc.) are known then Stokes' sedimentation equation\(^6^7,10^8\) can be used to model the settling process. A time stamp placed on each measurement would provide a factor by which the recorded intensity should be scaled to provide an effective 'snap-shot' scattering footprint at a single instant. For the initial study presented in this thesis, which uses particles with known properties, this solution would be sufficient, however for future studies using this equipment, where less well understood particles are investigated then the solution would not be possible.

4.9.3. Sensor Distance

As will be seen in the next chapter, the numerical aperture of the sensor and the sensor-sample distance are such that light scattered from the entire sample tube is collected by the
sensor. To make the sensor more angle specific, the sensor could be moved closer to the tube. The sensor post is already mounted so that it has adjustable position.

Similarly, the angular sensitivity could be increased by increasing the length of the sensor and thus increasing the photodiode-pinhole distance and so reducing the numerical aperture of the sensor.

Both of these measures would result in a reduction in the intensity of measured light. A corresponding increase in the signal amplification would be required to re-optimise the sensor range.

4.9.4. Glass Interfaces

The sample tube optics are briefly mentioned in §4.3.5 and are modelled in Chapter 5. Diffraction and reflection at the glass/medium and glass/air interfaces result in deviations in the light measured by the sensor. In theory, these deviations can be modelled, however, the sample tubes are, by necessity of many consecutive experiments, cheap and disposable. They are not of optical grade and modelling the medium/glass/air interfaces as concentric cylinders is at best an approximation. Higher grade optics would be prohibitively expensive and would require thorough cleaning between experiments, massively slowing the procedure.

Removal of the cylindrical interfaces would result in a greater potential for accurate reproduction of particles' scattering footprints. This could be achieved by inserting some form of rotating flat window into the sample chamber. This would require custom building of the sample chamber which would as mentioned above require thorough cleaning, made difficult by moving parts in the chamber.

The obvious remaining solution is to submerse sensors into a bath of the medium containing the particulate. Such an experimental set-up has been implemented by IROE\textsuperscript{[169]} for study of colour and turbidity. A scanning nephelometer was built which scans a GRIN fibre around a central scattering area within a bath of the sample medium. This configuration presumably requires some extensive cleaning protocol between experiments to achieve reasonable accuracy, although a procedure of continual increase of concentration (by successive addition of particles) could be used for a study of concentration effect. Another failing of this nephelometer is the required size of the vessel, which (from diagrams of the experiment) is in the order of 0.5 litres. To produce more than a few millilitres of a high concentration suspension latex spheres is not feasible with the budget available.
4.9.5. Concentration Range

The upper limit range of concentrations used in the study was defined by the availability of affordable particle suspensions. The lower limit was defined by practicable dilution.

Results in chapter 5 show that the noise floor of the equipment has easily been reached by the lower dilution limit. Measurement at lower concentrations would require more accurate titration protocols, more sensitive measurement equipment and much more optically perfect cuvettes. The linear range of the single scattering regime is sufficient to imply any required observations and data for lower concentrations are not necessary.

The measurement of scattering beyond 5% particle content could provide interesting data. Chapter 5 shows interesting multiple scattering effects in the back scatter regime for concentrations greater than 0.5%. Similar effects may be observable in side scatter directions at higher concentration and so study of such phenomenon could provide interesting further experimentation.

Latex spheres are available in concentrations up to 50% by volume, although at this concentration they are prohibitively expensive. Other, cheaper, particles are available in solid form and study of these particles up to their suspension limit would be possible. These other particles tend to be neither spherical nor monodisperse and so comparison between theory and experiment becomes difficult.

4.9.6. Polarisation

The nephelometer described measures the intensity of scattered light at a variety of angles. The study of the effect on polarisation state of singly and multiply scattered light is of interest, but beyond the scope of this thesis. A relatively simple extension to the nephelometer could be made to provide the necessary results. Mie theory can be used to predict the entire Stokes' vector of scattered light and measurement of such parameters would provide a good basis for comparison. The Stokes' parameters are chosen as measurable intensities, i.e. the sums/differences of intensities after being passed through an arrangement of polarising elements. A Stokes' polarimeter in the form of a fibre optic based division of wavefront polarimeter (DOWP) has been developed at Loughborough University for the study of biological samples. Such a DOWP or other Stokes' polarimeter could be implemented as a sensor head on a scanning nephelometer, either stationary with a scanning source or rotating as with the nephelometer described here.

The use of polarisation in 'turbidity' (60°, 90° and 120°) measurement using an ellipsometer and a diode laser is discussed by Miran Baygi et al.
Chapter 5. THEORETICAL AND EXPERIMENTAL SCATTERING DATA
5.1. Aim

This chapter brings together models and the experimental conditions to make predictions of the intensities measured by the scanning nephelometer. These results are compared with the experimental data.

5.2. Introduction

Chapters 2 and 3 presented a number of scattering theories. These theories are used to model the scanning nephelometer described in chapter 4.

§5.3 lists the relevant parameters of the experimental apparatus used. §5.4 incorporates the lensing and reflections of a finite cylindrical sample tube into single and first-order multiple scattering (FOMS) predictions. The results of both the experiments and the models are a set of scattered intensities that vary with particle concentration, angle, particle size and polarisation of the incident light.

The remaining sections of this chapter present the experimental data alongside the theoretical predictions as a function of each of these parameters in turn. Concentration dependency is the main subject of this thesis and is presented first in §5.5 where a good agreement of form between theory and practice is demonstrated. A method of deriving an averaged single scattering result from these experimental data is described, which is used in the following sections to compare theoretical and practical single scattering results, before consideration of higher concentration effects.

5.3. Experimental Parameters

The following sections present the relevant physical and optical parameters of the components used in the experiment.

5.3.1. Refractive Indices

The refractive index of the particle (latex) is quoted by the manufacturer as $n_p = 1.59$ around 633nm.

The refractive index of the background medium (water) is well known as $n_w = 1.33$ at 633nm.

The refractive index of the particle relative to the background is $m = \frac{n_p}{n_w} = 1.128$.

The refractive index of the tube (silica glass) is 1.50.
5.3.2. Particle Size

The particles used were spheres of radii, \( a = 54\,\text{nm}, 488\,\text{nm}, 1\,\mu\text{m}, 1.99\,\mu\text{m}, 4.23\,\mu\text{m}, 7.31\,\mu\text{m}, \) and \( 14.94\,\mu\text{m}. \)

The laser has wavelength \( \lambda = 633\,\text{nm}. \) The wave-number is \( k = \frac{2\pi}{\lambda} = 9.926\,\mu\text{m}^{-1}. \)

The dimensionless size parameters are \( x = ka = 0.536, 4.84, 9.93, 19.8, 42.0, 72.6, 148. \)

5.3.3. Concentrations

In addition to zero concentration samples, samples of concentrations, \( C, \) ranging from 1.86 ppb to 5% by volume were prepared. A 5% base stock was used and successively diluted by a factor of 4. A second set of experiments using a 50% diluted (2.5% by volume) base stock was performed. The two sets of experiments create a set of results with each concentration 50% of the next higher concentration.

The data from the two sets of experiments have been kept separate and are plotted in different colours on many of the graphs. The experiments were carried out months apart and it is possible that some degradation of the particles could have occurred in this time. Also, the experiment apparatus was dismantled and reassembled in between experiments and repeatability of some positioning cannot be guaranteed and so the second set of data have been rescaled to match the mean of the primary data set.

For modelling purposes the number density, \( N, \) is required. The volume of a single spherical particle is well known and so the number density can be evaluated -

\[
N = \frac{C}{V} = \frac{3C}{4\pi a^3}
\]

5.3.4. Centre-Sensor Distance

The sensor distance, as calculated in §4.3.4 is 56.5 mm. The numerical aperture is 0.079 corresponding to a half angular range of 4.51°.

5.3.5. Tube

The sample tubes used have a measured internal diameter of 10.9 mm (nominally 10) and an external diameter of 12.8 mm (nominally 12).
5.4. **Modelling the Experiment**

5.4.1. **Lensing of Cylindrical Sample Tube**

Before reaching the sensor the scattered light must pass two cylindrical refractive index discontinuities at the water/glass and the glass/air interfaces. These discontinuities will cause refraction. The numerical aperture of the sensor and the section of the incident beam from which scattered light is collected will not directly correspond. Light scattered from a small elemental volume a distance, \( z \), from the centre of the vessel in a direction, \( \theta \), will be perceived by the sensor as having been scattered in a different direction, \( \Theta \), from another point, \( Z \), from the centre (see figure 5.1).

A similar modelling of the geometry of a light-scattering cell has been performed previously\(^{[82]}\), but with the added simplification of a narrow cylinder detection, thus neglecting the actual lensing of the chamber. Study of path length and of reflection from water/glass interfaces are treated in a similar way.
Forward Calculation

For use in the integrals, 2.47, the values of \( Z \) and \( \Theta \) are required as functions of \( z \) and \( \Theta \). This transformation is required only if some external angle dependent effect, such as sensor angular response, is being considered. The final parameters are best expressed in terms a series of intermediate variables, each being physical lengths or angles. Some of these parameters are required for other calculations, e.g. the path lengths within the medium if extinction effects are being considered. Implementation of the integration can be simplified by separation of the variable calculations.

\[
l_1 = \text{the inner tube radius}
\]
\[
l_2 = \text{the outer tube radius}
\]
\[
\hat{\Theta} = \text{the scattering angle from the particle}
\]
\[
z = \text{the scatterer-centre distance}
\]
\[
n_0 = \text{the refractive index of air}
\]
\[
n_g = \text{the refractive index of glass}
\]
\[
n_w = \text{the refractive index of water}
\]
\[
l_w = \sqrt{l_1^2 - z^2 \sin^2 \hat{\Theta} - z \cos \hat{\Theta}}
\]
\[
\cos \beta = \frac{l_w \cos \hat{\Theta} + z}{l_1}
\]
\[
\alpha_4 = \hat{\Theta} - \beta
\]
\[
\sin \alpha_3 = \frac{n_w \sin \alpha_4}{n_g}
\]
\[
\varepsilon = \beta + \alpha_3
\]
\[
\sin \alpha_2 = \frac{l_1}{l_2} \sin \alpha_3
\]

\( l_1 \) is the distance travelled through water after scattering.

\( \beta \) is the angle made at the centre between the beam and the line passing through the inner edge of the tube where the scattered beam passes (not shown)

\( \alpha_4 \) is the scattered beam incident angle with the glass/water interface - water side

\( \alpha_3 \) is the scattered beam incident angle with the glass/water interface - glass side

\( \varepsilon \) is the angle made by the scattered beam in the glass and the original beam

\( \alpha_2 \) is the scattered beam incident angle with the glass/air interface - glass side
\( l_s = l_2 \cos \alpha_2 - \sqrt{l_1^2 - l_2^2 \sin^2 \alpha_2} \)

\( x_2 = z + l_\omega \cos \hat{\theta} + l_s \cos \varepsilon \)

\( \sin \phi = \frac{l_\omega \sin \hat{\theta} + l_s \sin \varepsilon}{l_2} \)

\( \sin \alpha_1 = \frac{n_2}{n_0} \sin \alpha_2 \)

\( \Theta = \varepsilon - \alpha_2 + \alpha_1 \)

\( Z = R \cos \phi - (a \sin \theta + b \sin \varepsilon) \cot \Theta \)

\( l_s \) is the distance travelled in the glass

\( x_2 \) is the length from the centre to the point where the beam passes the outer edge of the tube is projected onto the beam. \( x_2 < 0 \) implies \( \phi > 90^\circ \)

\( \phi \) is the angle made at the centre between the beam and the line passing through the outer edge of the tube where the scattered beam passes (not shown)

\( \alpha_1 \) is the scattered beam incident angle with the glass/air interface - air side

\( \hat{\Theta} \) is the angle made by the scattered beam in the air and the original beam

\( Z \) is the scatterer-centre distance as perceived from air
**Backwards Calculation**

To determine the limits on the integral, the numerical aperture, given by $\Theta$, must be transformed in terms of scattering angle, $\theta$. This also requires $Z$ which can be computed from the centre-sensor distance and the angle $\Theta$.

$$Z = r(\cos \theta - \sin \theta \cot \Theta)$$

$\sin \alpha_1 = \frac{Z \sin \Theta}{l_2}$

$\phi = \Theta - \alpha_1$

$\sin \alpha_2 = \frac{n_0}{n_6} \sin \alpha_1$

$l_6 = l_2 \cos \alpha_2 - \sqrt{l_1^2 - l_2^2 \sin^2 \alpha_2}$

$\sin \gamma = \frac{l_6}{l_1} \sin \alpha_2$

$\beta = \phi - \gamma$

$\alpha_3 = \gamma + \alpha_2$

$\sin \alpha_4 = \frac{n_6}{n_w} \sin \alpha_3$

$\Theta = \beta + \alpha_4$

$z = l_1 \frac{\sin \alpha_4}{\sin \Theta}$

$r$ is the distance from the tube centre to the sensor focal point.

$\theta = \Theta$ is the angle at the centre between the beam and the sensor i.e. the nominal scattering angle.
Total Internal Reflection

Total internal reflection occurs for scattering angles of 64-115° for light scattered from particles in the incident beam within ~0.5mm (varies with scattering angle - maximum at ~90°) of the vessel walls. The relative scattering volume affected by this total internal reflection is small (<5%) in comparison with the total possible scattering volume and the reflected scattered power will be a fraction of the total scattered power for particles in that volume.

Reflections of scattered light from the glass surfaces is of the same degree of significance as second or higher order multiple scattering, which is not considered theoretically in this thesis. No reflections of scattered light will be modelled.

Limits

The above formulae provide the length and angular limits as defined by the numerical aperture of the sensor. At low forward and backward angles the observed scattering region, according to this calculation, goes beyond the edges of the sample tube. Since the above system of equations is not readily solvable for $z$, the value of $\hat{\Theta}$ which is coincident on the tube edge ($z=l_1$) must be found using a linear search. The resulting measurement angle can be seen in figure 5.2.

![Figure 5.2](image)

**Figure 5.2 - Measurement angle as limited by numerical aperture (5°) and extent of sample tube (5mm radius). Refractive indices are taken as 1.33/1.5/1. Centre-sensor distance is 56.5mm. External tube radius is 6mm.**
5.4.2. Single Scattering

The single scattering of light from a narrow beam into a finite sensor was derived in §2.9. The lensing effects of the cylindrical tube are derived above. To model the intensity measured from the scanning nephelometer from single particle scattering, integral 2.46 must be calculated with consideration of the lensing.

\[
I_s = \frac{CN}{k^2r^2} \int_{z_1}^{z_2} \left( S_{11}(\theta)I_i + S_{12}(\theta)Q_i \right) dz
\]  

(5.1)

The distance between each elemental scattering volume and the sensor, as perceived by the sensor is given by

\[ r = \frac{r \sin \theta}{\sin \hat{\theta}} \]

which can be substituted into 5. to give

\[
I_s = \frac{CN}{k^2r^2 \sin^2 \theta} \int_{z_1}^{z_2} (S_{11}(\hat{\theta})I_i + S_{12}(\hat{\theta})Q_i) \sin^2 \hat{\theta} d\hat{\theta}
\]

The transformation from volume position, z, into scattering angle, i.e. the angle at which light from a given position is scattered into the sensor, is not readily calculable. The integral must be calculated with respect to the one independent variable from which all other variables can be uniquely determined - \( \hat{\theta} \). The abscissa will be evenly spaced in \( \hat{\theta} \) rather than in the integrand, z. The extended trapezium rule\[^{[56]}\] cannot be used. Rigorous multiple application of the trapezium rule has to be used over the unequal trapeziums. The values of both z and the integral must be stored for each point as the integration is refined. Figure 5.3 shows the abscissa, even in \( \hat{\theta} \) uneven in z.
Figure 5.3 - Integration of scattering elements. Abscissa equally spaced in external angle (left). Integration with respect to distance through path (right).

As previously, the entire Stokes' vector for the scattered light can be computed -

\[
\begin{pmatrix}
I_s \\
Q_s \\
U_s \\
V_s
\end{pmatrix} = \frac{1}{k^2r^2} \begin{pmatrix}
S_{11}^x & S_{12}^x & 0 & 0 \\
S_{12}^x & S_{11}^x & 0 & 0 \\
0 & 0 & S_{33}^x & S_{34}^x \\
0 & 0 & -S_{34}^x & S_{33}^x
\end{pmatrix} \begin{pmatrix}
I_i \\
Q_i \\
U_i \\
V_i
\end{pmatrix}
\]  

(5.2)

where \(S_{ij}^x = \frac{CN}{\sin^2 \theta} \int_{z_i}^{z} S_{11} \sin^2 \theta dz\)

5.4.3. First-Order Multiple Scattering

As derived in §3.3.3 first-order multiple scatter can be incorporated into the Mueller matrix integrals. Equation 5.2 is still valid with the simple introduction of an exponential decay term into the calculation of the Mueller matrix elements -

\[
S_{0}^x = \frac{CN}{\sin^2 \theta} \int_{z_i}^{z} S_{11} \sin^2 \theta e^{(L+\mu L-\eta L)}dz
\]

5.4.4. Reflection of incident beam

The incident beam will meet four refractive index interfaces in its passage through the system - air/glass, glass/water, water/glass and glass/air. The summed relevant effect of reflections from these surfaces is a reflected, backwards travelling beam in the medium, with intensity proportional to that of the forward travelling beam, which will cause scattering. In the absence of extinction, this backwards travelling beam, \(I'\) will have an intensity given by
\[ I^- = \frac{R_1 - 2R_1R_2 + R_2}{1 - R_1R_2} I^+ \]

where \( I^- \) is the total forwards travelling beam entering the medium (consisting of direct illumination and light reflected from multiple surfaces), \( R_1 = \left( \frac{n_0 - n_g}{n_0 + n_g} \right)^2 \) is the reflectivity of the air/glass interface and \( R_2 = \left( \frac{n_w - n_g}{n_w + n_g} \right)^2 \) is the reflectivity of the glass/water interface.

For the refractive indices quoted in §5.3.1 this results in \( I^- = 0.0431 I^+ \).

A single reflection at a surface can be considered as the same degree of significance as a particle interaction. This treatment corresponds in importance to first-order multiple scatter correction.

Extinction due to the particles (and similarly absorption in the medium, if present) can be incorporated; reducing the intensity of the incident beam at the second glass passing through the medium. The backwards travelling beam is given by \( I^- e^{-2N\sigma_l} \).

The backwards travelling beam will scatter from particles and be measured by the sensor. Light measured from this reverse beam by a sensor at position \( \Theta \) will be equal to light measured for an equal intensity forward beam by a sensor at \( 180^\circ - \Theta \). Total measurement will be

\[ S = I^+ S(\Theta) + I^- S(180^\circ - \Theta) \]

In the calculations performed later, scattering at angles in the range of 0 to \( 180^\circ \) at a 0.9° interval are modelled. Both \( S(\Theta) \) and \( S(180^\circ - \Theta) \) are readily available.

Figures 5.4-5 show the concentration dependency of scattering at 90°. Other scattering angles have similar profiles (e.g. figure 5.6).
5.5. Concentration Dependency

Figure 5.4 - 90° scattered intensity as a function of particle concentration. Plotted are the results from the two sets of experiments and a single fit to their linear region (above noise floor, before significant multiple scattering ~10-1000ppm). The red line is the theoretical first order multiple scattering result.

Incident light is horizontally polarised. Intensity is plotted on a logarithmic scale, the 1:1 gradient implies linear relationship.
On Multiple Optical Scattering in a Scanning Nephelometer.

Chapter 5—Theoretical and Experimental Scattering Data

Figure 5.5 - 90° scattered intensity as a function of particle concentration. Plotted are the results from the two sets of experiments and a single fit to their linear region (above noise floor, before significant multiple scattering ∼10-1000ppm). The red line is the theoretical first order multiple scattering result.

Incident light is vertically polarised. Intensity is plotted on a logarithmic scale, the 1:1 gradient implies linear relationship.
Theoretical First-Order Multiple Scatter

The theoretical (red) curves clearly show the initial linear relationship between scattered intensity and concentration. At some particle size and angle dependent point the extinction due to particle content begins to become significant. In this FOMS model the measured intensity decays exponentially with concentration from the underlying linear relationship.

As light passes through the particle-containing medium the intensity is reduced exponentially. An effective scattering volume can be estimated based on the sum of the intensity along this volume. For zero extinction the effective length of this scattering volume will be the geometric diameter of the vessel. This effective length will decay with extinction cross-section of the individual particles and with the number density of those particles. The graph in figure 5.7 shows the effective scattering volume over a range of concentration.
Figure 5.7 - Demonstration and graph (for 4.23μm particles) of effective scattering volume based on the intensity of light incident on particles in the scattering volume.

The diagram in figure 5.7 shows the position of the scattering volume for a vessel illuminated from the left. For forward scattering the total distance travelled through the medium will, in general, be of the order of the vessel diameter and so measurable scattered intensity will decay continually with increasing concentration. For back scatter some scattered light will have a very small path length through the medium, leaving little chance for light to be absorbed or scattered out of plane before or after the measured scattering event. At higher concentrations, the main effect of the extinction is the reduction of effective near scattering volume with increasing concentration rather than the exponential reduction of incident radiation on particles further into the medium. Figure 5.6 clearly shows this rise in measured intensity in the back scatter direction, as additional scattering from increased particle content becomes a greater effect than the loss of scattering volume.

Experimental Data

Data from the single scattering regime of the experiment have been averaged. The rate of change of scattered intensity with concentration where the single scattering assumption holds is directly proportional to the scattered intensity. By fitting this gradient to the available data
in an assumed single scattering regime, an average scattering value can be estimated for further study. This single-scattering parameter can be used in investigations of angular and particle dependencies. Below 10 ppm, noise dominates the signal and mean intensities are roughly constant. Above 800 ppm multiple scattering effects begin significantly and the linearity of single scattering is lost. The range for the single scatter average is taken as 10-800 ppm. This measure of scattering is a generalisation of specific turbidity[^13], which is turbidity (90° scatter normalised to 0° intensity) divided by concentration, used in some particle studies.

A single scattering prediction acts as an approximate upper limit of scattering in general. Although in extreme back-scattering directions it may be possible that several lower angle scattering incidents could result in a higher measurement, it is unlikely that the positive effect of any multiple scattering will be greater than the extinction due to scattering out of the measurement plane.

The FOMS prediction acts as a lower limit of scattering. In FOMS, negative (i.e. intensity reducing) effects of multiple scattering are modelled while all positive effects are neglected. The general form of the experimental profiles is to follow the shape of the FOMS prediction, but to cut-off at a higher concentration. The non-linearity with increasing concentration due to multiple scattering only measurable at concentrations higher than predicted. This is presumably due to the unmodelled positive scattering effects.

At very high concentration, when scattering becomes isotropic, scattered intensity becomes independent of additional concentration. In principle, if radiation from a given scattering volume is isotropic then addition of more non-absorbing scatterers will have no effect on the scattering function for that volume.
5.6. **Angular Dependency**

5.6.1. **Single Scattering**

Figure 5.8 - Scattered intensity as a function of angle (°). Plotted are the concentration gradient fits to the single scattering regime of two sets of experiments. The red line is the theoretical single scattering result for the Nephelometer. For comparison, the theoretical (pure Mie) single particle prediction has been plotted in purple. Intensity units are arbitrary. Incident light is horizontally polarised. Concentration is constant by volume.
Figure 5.9 - Scattered intensity as a function of angle (°). Plotted are the concentration gradient fits to the single scattering regime of two sets of experiments. The red line is the theoretical single scattering result. For comparison, the theoretical (pure Mie) single particle prediction has been plotted in purple. Intensity units are arbitrary. Incident light is vertically polarised. Concentration is constant by volume.
Figures 5.8-9 compare the angular form of the theoretical and experimental scattering. The mean of the intensities in the central (40-150°) region have been equated to align the data.

For larger particles the general trends of the experimental data match those of the theory with some of the larger features also being matched in angular position if not in magnitude (e.g. fluctuations in 0-90° range for 1μm particles vertically and horizontally polarised and 120° feature in vertically polarised 7.31μm particle graph).

Also shown on these figures is the single particle prediction. This is the light scattered from a single particle, devoid of issues of integration along a path length or lensing of a cuvette. In comparison to this, the corrections made for path length and lensing can be seen to be significant especially in the backwards scattering directions.

5.6.2. Increasing Concentration

Theoretical Results

![Theoretical Results Diagram](image)

*Figure 5.10 - Scattered intensity as a function of angle. Plotted are theoretical first order multiple scattering results.*

*Incident light is vertically polarised.*
Figure 5.10 shows the effect of increasing concentration on the angular scattering profile as predicted by FOMS. The traces show the effect with vertically polarised incident light; the effects with horizontally polarised light differ only in detail. The linearity in the single scattering regime can be clearly seen in the sub-6250 ppm traces, with no change in the angular form of the scattering.

Once multiple scattering effects become significant the traces can be separated into three distinct regions. In the forward scattering region (<40°), the effects of FOMS reduce the overall scattering (exponentially as indicated by figure 5.6) and then introduce enhancement of angular dependent features as scattering angle range is reduced by increasing extinction from across the angular range. Similarly in the back scatter direction (>140°), decreasing effective scattering volume limits the angular range measured and increases the form of the angle dependent functions. In the remaining side scatter direction, path length is more consistent across the angular range and so decrease in light reaching the sensor decreases consistently and exponentially with increasing concentration.
Experimental Results

Figure 5.11 - Scattered intensity as a function of angle. Plotted are scattering results from experiment 2.

Incident light is horizontally polarised.
Figure 5.11 plots the experimental equivalent of figure 5.10, the angular dependent scattering profile across a range of concentrations. As with the theoretical data, the effects of vertically and horizontally polarised incident light differ only in detail.

The linear increase of scattering intensity in the single scattering regime can be seen in these data. Noise dominates the signal for very low concentrations and the signal saturates in the forward scattering direction, however the otherwise consistent increase can still be seen.

Regions of the various scattering effects are less clearly defined in practice than the FOMS predicts. However, the first-order model predicts some observed effects. In all cases an initial increase in forward scattering is soon dominated by a consistent decrease after some cut-off concentration. In the back-scatter direction the decrease in the effective scattering volume with increasing concentration causes the measured and predicted scattered intensities to become concentration independent. These effects can be seen in figures 5.10 and 5.11.

An effect not predicted well by FOMS is the loss of angular features as true (greater than first-order) multiple scattering becomes dominant and the average number of particle interactions prior to measurement increases and the measurement of local minima and maxima in the underlying scattering profile becomes impossible.

The overall aggregate of these phenomena is to tend towards isotropic scattering. Forward scattered light is reduced and back scattered light is increased due to multiple particle interactions; both angle and particle dependency of the scattering are lost.
5.7. **Particle Size Dependency**

5.7.1. **Single Scattering**

![Graphs showing scattered intensity as a function of particle size.](image)

*Figure 5.12 - Scattered intensity as a function of particle size. Plotted are the concentration gradient fits to the single scattering regime of two sets of experiments. The red line is the theoretical single scattering prediction.*

*Concentration is constant by volume.*

Figure 5.12 plots the theoretical and experimental single scattering data against particle size. The data have been scaled to equate means at points where data are available for all plots.
Rayleigh predicted, as a limit of Mie theory, that as particle gets small, scattering (intensity, cross-section etc.) become proportional to a power of the particle size. The linearity of the intensity with respect to the particle size in the sub-0.1μm region implies that this phenomenon has not been lost by integration over the vessel. These data are normalised to constant volume concentration, reducing this power by three and the integration will also affect this factor. This theoretical result can only be backed up by a single pair of data points for particles of a single size, providing no information about the experimental linearity in this range, but being roughly consistent with the drop in scattered intensity at this size.

As particles leave the Rayleigh scattering regime, particle size features are introduced and a size of maximum scattering is reached at about 1μm. Intensity decay from this maximum is consistent between theory and experiment, especially at 90°.

As with the small particle approximation, large particles follow a power law, i.e. scattering is proportional to a power (less than that for Rayleigh scatterers) of particle size. Once data are normalised to constant volume, this manifests as a linear downwards trend on the log-log plot as particle size increases.

### 5.7.2. Increasing Concentration

**Theoretical Results**

Increased scattering efficiency around 1μm becomes more relevant in the FOMS predictions. Large extinction cross sections, cause a large extinction of incident and scattered light causing measured intensities to rapidly decay for particles of these sizes. Relatively low (~1ppt) concentrations cause several orders of magnitude loss of measured intensity. This effect can be seen clearly in figure 5.13.

For very small (<0.05μm) and very large (>10μm) particles the effect of FOMS cannot be observed until higher concentrations (>0.6% for large particles, higher for small particles) have been reached.

Even single small particles produce roughly isotropic scattering and thus the combined effects of multiple scattering cannot readily be observed, since the tendency of multiple scatter is towards this form of scattering.

Large particles have large volumes, a given volume concentration of large particles obviously has a smaller particle count than an equivalent concentration of smaller particles. The number of particle interactions that light measured will have undergone will be much lower than for smaller particles, producing a less notable multiple scattering effect.
Figure 5.13 - Scattered intensity as a function of particle size. Plotted are the theoretical first order multiple scattering predictions.
Figure 5.14 - Scattered intensity as a function of particle size from experiment 1.
Experimental Results

The general trends observed above from the theoretical graphs can be seen, even if much more subtly, in the experimental data plotted in figure 5.14. Intensities for small (54nm) particles increase monotonically with concentration. The effect of increased concentration can be seen to be most pronounced on particles in the central particle size region, with particles of 7.31μm only being effected at the highest concentrations. These particle size effects are perhaps best observed in the figures in §5.5 where plots are against the many concentrations for the seven particle sizes under consideration.

5.8. Discussion

5.8.1. Experiment: Theory and Practice

A model has been developed which considers the optics of the scanning nephelometer scan. Comparison of the single scattering experimental data with those of the nephelometer model and single particle scattering (figures 5.8-9), show that the model goes someway to correcting for the optics of the chamber.

This model having been established leaves a pathway for future research into a variety of particles. The scanning nephelometer apparatus can be used to obtain scattering results quickly and cheaply. The results of any such study can be compared with theoretical results for spheres of a comparable size using the models presented here. With the cuvette model established, investigations into other phenomenon, such as multiple scattering, can be made.

5.8.2. Infinite Dilution and First-order Multiple Scattering

It is commonplace to extrapolate low concentration scattering data back to infinite dilution to obtain a measure of single scattering. This has been executed on the experimental data in the 10-800ppm region to obtain a 'single particle' scattering result, i.e. the scattering intensity from a single particle averaged over all possible positions in the scattering region. This reading is then compared with angle and particle size dependent theoretical single scattering.

The upper limit of single scattering differs between practice and the FOMS prediction. This 'cut off' concentration, i.e. the concentration at which a non-linear increase can first be observed, differs by up to an order of magnitude. This approximation is stated as being most applicable to highly absorbing particles in a narrow beam. Although the latter is true of the scanning nephelometer, the latex particles used are only very weakly absorbing (absorption being neglected in the model) and so the discrepancy between this theory and experiment is to be expected.
The FOMS approximation does offer some insights into observable phenomenon. The general form of the intensity/concentration dependency is still valid for early multiple scattering. The simplified scattering model has, for instance, been used to explain features of the dependency in back scatter direction. In conclusion, although the approximation does not provide quantitative predictions at post single scattering concentrations, it does provide a qualitative model of some interesting effects.

5.8.3. Angular Dependent Scattering

Figures 5.8-9 show the angle dependency of single scattering in the scanning nephelometer. For the larger particles, there is a good match between theory and experiment, with many of the major features predicted by the single scattering model being observable in the experimental data, comparable with those achieved by other systems with smaller angular range.

The correspondence for smaller particles is less. The general form of the scattering profile is lost for the smallest particles (54nm). Experimental procedural error in sample handling or a coagulation of the particles are possible explanations of this result.

FOMS predicts three distinct angular regions for multiple scattering effects. In the forward and backward scattering directions, scattering becomes limited to a decreasing effective scattering volume and so the dramatic loss in the scattering measurement due to extinction is not observed. For side scatter, the scattering region is more consistent and so the predicted scattering is effected consistently by extinction. The experimental results go some way to supporting this phenomenon. Although the regions are softer than the naïve theory predicts, the general principle of measured intensity being reduced most around 90° can be observed.

5.8.4. Particle Size Dependency

As discussed in chapter 4, financial constraints limit the number of particle samples available for these scattering experiments. Most angular scattering experiments (e.g. Smart et al.) using spherical latex standards have considered only a single particle size. The form and trends of the particle size dependency can be seen to roughly follow that predicted by single scattering theory for the seven data points available.

FOMS predicts a region around 1μm, which is particularly susceptible to multiple scattering effects, this is backed up in a smoother form by the experimental results. This phenomenon is best explained by considering the two extremes. Very small particles exhibit isotropic scattering, spreading flux evenly across the angular range, a second particle interaction will redistribute the light isotropically. The effect of any second interaction will be small. As particle size becomes large, scattering tends towards the forward direction. In the limit, all
scattered flux will travel forwards and so the effect of any particle interaction will be small. Between these limits, scattering footprints demonstrate many features, multiple particle interactions will alter these features and so the effects of multiple scattering will be more pronounced.
Chapter 6. Neural Models of Multiple Scattering

'I never make predictions and I never will'
- Paul Gascoine
6.1. **Aim**

This chapter introduces neural networks and uses them to model the non-linear scattering function of increasing concentration.

6.2. **Introduction**

Neural networks are a means of modelling an arbitrary mapping to arbitrary accuracy based on presentation of example data. Historically, the basis of neural computing has been inspired by the studies of biological networks \[^{114}\]. Research continues along this vein, but much of the recent development has been carried out by rigorous application of mathematical and statistical formulation to the basic concepts.

Within this chapter, neural networks are considered as universal function approximators, i.e. they provide the mapping from one set of parameters to another set of parameters. §6.3 presents some established applications of neural networks to the field of optical scattering. §6.4 presents the basic functional form of the multi-layer perceptron and describes in broad terms the training methods used. Finally, §6.5 first describes the functional form required of a mapping for multiple scattering modelling and then presents the results of such a neural model.

6.3. **Application of Neural Networks in Optical Scattering**

Neural networks have been used in many applications to interpret scattering data (e.g. Green\[^{30}\]) and invert the scattering problem. Fewer implementations have been made to model any form of the forward problem.

6.3.1. **MieNet**

This is one of the few applications of neural modelling of the forward scattering problem.

Each of the approximations to Mie theory discussed in chapter 2 predicts scattering for some subset of particle space to reasonable accuracy. In many cases the ranges of validity are overstated and the methods sometimes used out of context. It is also accepted that rigorous Mie theory, as used in this thesis, is too computationally expensive for many applications.

In his thesis\[^{45}\], Naimimohasses introduces MieNet, a neural network architecture that models the single scattering function for a variety of regions of the particle domain. A neural network was trained to predict the logarithm of scattered intensity, which it achieved to an accuracy at least comparable with theoretically based approximations, except in the
domains of very low scattered intensity. The computational time in making this prediction is in excess of three orders of magnitude less than that of Mie theory.

6.3.2. Inverse Problem

The problem of predicting parameters describing the conditions causing a measured scattering profile based purely on those data is often a difficult and ill-posed one. This kind of mapping (scattering data to the physical state of the system) is, however, a typical problem for neural computing solution.

A neural network can be trained taking scattered intensities (theoretical or experimental) as inputs and the parameter(s) required as output(s). Once the network is trained it will act as a mapping between the scattering data and those parameters under investigation. This technique has been put to good effect in the prediction of the concentration of and the classification of various types of oil pollutants. Scattered intensity at five angles is used to discriminate between three types of oil and to predict their concentration. It can also be used in the more direct application of the inverse problem to determine particle size and to classify particle shape.

6.3.3. Sensor Optimisation

Neural networks consist of many interconnections between neurons. Algorithms exist which 'prune' these connections to improve the efficiency and generalisation of the trained network, based on the data presented. These techniques usually crop individual connections between neurons or remove neurons from the networks internal structure.

This process can be applied to a system for sensor optimisation. A network can be trained as described in the previous section, predicting required parameters, based on a massively redundant input space. Sensitivity to given inputs can be determined across the data set, in the same way that sensitivity to internal connection is calculated in pruning algorithms. The least sensitive inputs are those that contain the least relevant information and should thus be pruned from the system. After retraining, the pruning process can be repeated. Once there is significant degradation in the network's ability to predict the characteristics due to the pruning of an input, then the previous input set is theoretically the minimum and optimum set required.

This technique has been used to design optimal nephelometers. Massively redundant theoretical nephelometers are initially considered with sensors at many angles. After pruning an optimal angular arrangement of sensors remains.
6.4. **Neural Networks**

6.4.1. Scope

This thesis does not present any new theories of neural modelling. The application of established neural techniques to mapping a function is presented. This section describes the basic methods used, further details can be found in the few cited references, and references therein. Neither details of Bayesian analysis nor the derivation of the methods used will be presented.

The methods presented in this section are taken from Bishop's book[^121^]. Details and further references for these algorithms can be found there.

6.4.2. Neural Function Approximation

Although there are a variety of architectures for neural network function approximation, only one is considered in this thesis - the multi-layer perceptron (MLP).

The MLP consists of, in general, one or more processing layers and an output layer. Each processing (hidden) layer contains a vector of processing elements (neurons), each of which has a weighted connection from the previous and to the following layers. It is the refinement of the weights of these connections that causes the network to fit to a given data set. It can be shown[^122^] that a two-layer MLP with sufficient neurons can approximate any function to arbitrary accuracy and so only two-layer MLPs need be considered.

Outputs of the hidden processing elements are a sigmoidal function of the weighted sum of the input elements -

\[
z = g(Wx + b) \tag{6.1}
\]

![Two-layer multi-layer perceptron](Figure 6.1 - Two-layer multi-layer perceptron)
where \( \mathbf{z} \) is the vector of neuron outputs, \( \mathbf{g} \) is the hyperbolic tangent, \( \mathbf{W} \) is the input weight matrix, \( \mathbf{x} \) is the input vector and \( \mathbf{b} \) is the positioning bias vector.

The output of the network is then the weighted sum of these neural outputs -

\[
f(\mathbf{x}) = \mathbf{v} \mathbf{z}(\mathbf{x}) + canumber{6.2}
\]

where \( \mathbf{v} \) is the output weight row vector and \( c \) is the output bias.

Appropriate evaluation of the weights, \( \mathbf{W} \) and \( \mathbf{v} \), and the biases, \( \mathbf{b} \) and \( c \), allow the MLP to fit to any function given sufficient neurons.

### 6.4.3. Network Training

Any function fitting optimisation will consist of the minimisation of some measure of error between the approximator and the function. The usual error function for fitting a mapping to sample data is the sum of squares error -

\[
E = \sum_n (f(x_n) - y_n)^2
\]

where \( \{x_n, y_n\} \) are the input/output pair for a single sample.

One of the simplest forms of training for the MLP is gradient descent. The error gradient, \( \frac{dE}{dW} \) (the derivative of the mean square error with respect to each weight and bias), for a given sample is readily computable by application of the chain rule\(^\text{[114]}\). Errors can be 'back propagated' through the network as the chain rule is applied to calculate derivatives in each layer. Weights can be adjusted by an amount proportional to this gradient (summed over all samples), taking the functionality of the MLP closer to that of the function represented by the samples.

The more efficient method of MLP training used for the work in this thesis is the scaled conjugate gradient algorithm. In the gradient descent algorithm, at each iteration the weight is moved by an amount proportional to the gradient, in the direction of maximum gradient. It is sensible to select the step size to minimise the error in a given direction at each step. If such one-dimensional minimisation is carried out then it is further useful to ensure that the direction of minimisation is perpendicular in weight space to previous search directions, preserving previous training. Such a search describes the conjugate gradient algorithm. The computational efficiency can be improved by allowing a scalable step size inaccuracy at each step. The scaled conjugate gradient algorithm follows a method of successively perpendicular steps through weight space with step sizes approximated by a positive definite Hessian. Further details are presented by Bishop\(^\text{[121]}\).
6.4.4. Regularisation

Occam's razor is the principle that we should prefer simpler models over more complex ones. Models with a minimum of variance are favoured, i.e. models which are less sensitive to the data set; a factor which must be weighed against bias - the accuracy of the model in fitting the data set.

The most obvious way to reduce the variance in an MLP is to reduce the number of neurons. More generally, solutions with less variance functions are favoured. This can be achieved by adding to the cost function (6.3) a term which represents the complexity of the mapping -

\[ \tilde{E} = E + \nu \Omega \]  \hspace{1cm} (6.4)

where \( \nu \) is the regularisation parameter and \( \Omega \) is the regulariser. \( \Omega \) is chosen such that a low value corresponds to a reduction in function variance.

A simple form of regulariser implements weight decay, with \( \Omega \) being a sum of squares of the weights -

\[ \Omega = \sum_i w_i^2 \]  \hspace{1cm} (6.5)

where \( w_i \) is any element of \( W \) or \( v \) in equations 6.1 and 6.2. A minimisation of this regulariser increases the smoothness of the mapping by favouring smaller weights in the network.

6.4.5. Bayesian Methods

The choice of \( \nu \) in 6.4 defines the form of the MLP solution and must be chosen accordingly. Too large a value of \( \nu \) will lead to a large bias as the network fails to fit to the required contours of the solution. Too small a value of \( \nu \) will allow the network to overfit and map to any noise within the data.

Application of Bayes' theorem to the selection of \( \nu \), allows the data to provide evidence for an appropriate value. In this context, \( \nu \) becomes a hyperparameter in the training process and is optimised alongside the weights to provide a best solution to the mapping problem. The hyperparameter(s) of the training process are re-evaluated between successive periods of training - a network will be trained with arbitrary initial values, evidence for the hyperparameter value(s) will be estimated, the network will be retrained and the process repeated for as many iterations as necessary.
Bayesian methods can be used to provide a full family of solutions, with corresponding probability distributions. This provides distributions of MLP output which is beyond the requirements of this application.

The application of Bayes' theorem to the selection of $\psi$ is described by Bishop\textsuperscript{[121]} and the reader is referred there for further details.

6.4.6. Automatic Relevance Determination (ARD)

The regularisation scheme 6.4 with regulariser 6.5 has an internal inconsistency of dimensions. If the input and internal parameters do not have exactly the same scale (and units) then the single regularisation parameter is insufficient. The cost function 6.4 can be generalised to a regularisation vector -

$$\tilde{E} = E + \psi \Omega$$

where $\psi$ and $\Omega$ are row and column vectors respectively. Weight decay can then be represented by $\psi$ having $\Omega$ as a vector of squares of weights.

By symmetry of the MLP, the internal weights, $\nu$, are all of the same scale and can be regularised by a single parameter. This leads to a regularisation scheme with an individual parameter for each of the MLP inputs and a single parameter for the internal weights\textsuperscript{†}.

With successive application of Bayesian evidence to the selection of these parameters, reliance on those inputs which are most relevant to the determination of the output will grow and the dependence on less pertinent variables will diminish. The resulting vector $\psi$ becomes a measure of the relevance of individual inputs, with a large value corresponding to an irrelevant input.

6.4.7. Netlab

Many of the algorithms presented in Bishop's book\textsuperscript{[121]} have been implemented in Matlab, forming a toolbox of functions - Netlab\textsuperscript{[123]}. Amongst these functions are implementations for neural network training (including MLP training using scaled conjugate gradient), Bayesian evidence, regularisation and automatic relevance determination. This toolbox was used for all the work described in this chapter.

\footnote{† In the implementation used there were also parameters for each input bias and output bias.}
6.5. **Neural Models of Multiple Scattering**

In chapter 5, two theoretical fits were made to the general scattering problem. The single scattering approximation made a prediction linear with respect to concentration and the FOMS predicted the effect of particle extinction on measured intensity. These theories formed bounds on the actual intensities, but neither gave a good approximation to all of the results. Other theories would provide models of multiple scattering over various subsets of concentration and particle parameter space.

Based on data from the experiments described in chapter 4, the results of which are presented in chapter 5, an empirical model is possible. The experimental data can be used to train a network which will learn to model the multiple scattering process.

6.5.1. **The Functional Mapping**

Intensity measured in the scanning nephelometer is dependent on particle size and concentration, on the polarisation state of the incident illumination and on the observation angle. These are the parameters by which the experimental data are categorised, other parameters, e.g. source wavelength and particle refractive index, were constant across the entirety of the experiments and should be included as input to a more general model, but would serve no purpose here. A network could be trained which predicted scattered intensity based on these four parameters (or simple functions thereof) alone. However, in doing so the MLP is not only modelling the effects of multiple scattering, but also representing the underlying single scattering result. The neural modelling of single scattering is the basis of an entire PhD thesis[^451] (see §6.3.1) and the associated issues of MLP size and input functionality is not a trivial one.

So that the MLP is modelling only the effects of multiple scattering as an extension of the single scattering result, the single scattering intensity, in the form of the gradient as described in §6.5 is presented as an additional input.

Multiple scattering will depend greatly on the scattering footprint of the individual particles. For example, large particles with large forward scattering intensities give multiple scattering results which can be modelled with a modified radiative transfer technique. Information describing the general form of the scattering footprint can be passed to the neural model to assist in the modelling process. Three values were passed to help define the form of the particle scattering - a rough measure of forward scatter (~60°), side scatter (90°) and backwards scatter (~120°). While these values are not necessarily true representations of forward and backward scatter, they give some indication of them and are readily available from the experimental data.

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6.5.2. Scaling and Transformation

Many of the parameters involved in the scattering process cover a range spanning several orders of magnitude and the data are spread logarithmically across that range. Passing the logarithm of these parameters requires the MLP to make a linear rather than a logarithmic internal mapping, an easier task for the network. A scaled and centred logarithm of concentration, radius and the various single scattering values were used as inputs. The MLP output was trained to the logarithm of the measured intensity.

Naimimohasses\textsuperscript{45} showed the value of passing trigonometric transformations of scattering angle rather than (or as well as) the angle itself to an MLP in the prediction of single scattering. The mapping between single and multiple scattering is expected to be a simpler one than that prediction and so a single parameter is sufficient. The cosine of the scattering angle is a one to one function over the range 0-180\degree, which is a sufficient range of interest due to the experiment's symmetry. The cosine of scattering angle is passed as a neural input.

The linear polarisation state of the illuminating radiation can be best represented by the second element of a normalised (to $1=1$) Stokes' vector. In general, this would provide a value in the range -1 to 1. For the data available a value of 1 (vertical) or -1 (horizontal) was passed.

6.5.3. Training

An 8 input, 1 output MLP with 25 hidden neurons was trained using the scaled conjugate gradient algorithm under Netlab. Data from the second of the two sets of experiments was pre-processed as described above and presented to the network. Every 10 training cycles the regularisation parameters were re-estimated using the Bayesian evidence framework. The bulk of the time for the training process was taken with the estimation of these regularisation hyperparameters.

![Figure 6.2 - Options for inputs to neural model.](image)

(a) Basic parametric input.
(b) Additional single scattering information.
6.5.4. Validation

The methods used in the network training and regularisation are well defined and well tested. It is usual to set aside a subset of the available data to validate the generalisation ability of the trained model. In this application, to provide a rigorous validation procedure, the entire data from at least a single particle size should be set aside. However, with such a small number of particles available for training it was decided not to set aside such valuable data. The purpose of this procedure is to determine the basic feasibility of the networks fitting to the multiple scattering data and to observe the resulting function dependency. Visual validation of the trained network is carried out by observing the general form with respect to various parameters, rather than the rigorous numerical validation against a valuable data subset.

Only data from the second of the two sets of experiments were presented for training and as such the first set of data acts as a validation set. However, where the two sets of data differ (see figure 5.4), the MLP cannot expect to fit to the unseen set. The inability of the model to fit to the other experiment is an indicator that there is some systematic error in the experimental procedure.

The first set contains data for particles of 1μm radius, which can act as a genuine validation set, although a single point in the particle size regime is insufficient to adequately check the generalisation, it does give a possible indication of successful fitting.

Errors

Network prediction errors can be calculated for each of the two data sets, providing a relative measure of the quality of the prediction for those data. The table below gives the root-mean-square errors of the training and validation sets. Errors have been averaged over data for the range 15.3° to 162°, all particles except 54nm, both polarisation states and all finite concentrations. In addition to the errors for experimental input, errors have been calculated for presentation of theoretical (as per Chapter 5) single scattering to the inputs.
It can be seen that the errors for the training and validation sets are similar where experimental data is input to the MLP. Inasmuch as the validation procedure is adequate, this demonstrates the generalisation of the neural model.

Error for theoretical input is, on average, approximately double that of experimental input. The following sections demonstrate that the general trends of the multiple scattering are followed despite a relatively large r.m.s. error. The lower error of the validation set is most likely due to the inclusion of \( \mu m \) particles, for which the single scattering predictions are relatively accurate.
6.5.5. MLP Predictions

Concentration Extrapolation

Figure 6.3 – 90° scattered intensity as a function of particle concentration (by volume).

Plotted are the experimental data (X) and neural predictions (-).

Incident light is horizontally polarised.
Figure 6.4 – 90° scattered intensity as a function of particle concentration (by volume).

Plotted are the experimental data (X) and neural predictions (-).

Incident light is vertically polarised.
Figure 6.5 – Scattered intensity as a function of particle concentration (by volume). Plotted are the experimental data (X) and neural predictions (-).

Incident light is vertically polarised. Particles are 4.23 μm.

Training Data

The figures 6.3-5 above plot experimental data against MLP predictions. The blue and green lines indicate MLP predictions made with experimental single scattering data presented as input. The red line gives a purely theoretical result, with an MLP prediction made with scaled theoretical (Mie) single scattering values as input.

It can be seen from these plots that the MLP has fitted to the training data, i.e. the green line fits the green crosses in all cases. The general trend of the multiple scattering has been well modelled, i.e. the linear increase with concentration in the single scattering regime and the decay from this at higher concentrations.

Also modelled is the levelling off at the noise floor of the experiment, the logarithmic transformation of the intensities prior to training has caused the network to exaggerate the effect. For very low concentrations (<1 ppm), the predicted intensity actually rises, due to the logarithmic transformation and the lack of low concentration data for several of the particle sizes. Below the MLP's range of linear prediction (<10 ppm), the estimated value should be considered unreliable.

Similarly, the smaller effect of multiple scattering in backward scatter directions, is not as well modelled as other features. Figure 6.5 shows a maximum in the intensity at ~1% concentration for 149.4° scatter, whereas experimentally no maximum was reached below the upper concentration limit of 2.5%.
Validation Data

As was expected, where the two data sets differ slightly (e.g. 7.31μm particles), the neural model fails to predict this difference. Otherwise the network predicts well across the data set. Predictions made for 1μm particles, for which no training was given, are comparable to predictions made on the training set - the multiple scattering 'cut-off concentration' is slightly over estimated. This indicates that the MLP has generalised well.

Theoretical Input

The neural network requires four single scattering measurements as input. The results discussed so far have used experimental data to supply these inputs. Theoretical predictions of nephelometric scattering as discussed and demonstrated in chapter 5 can equally supply these inputs. The red curves of figures 6.3-5 demonstrate such predictions.

For all but the smallest of particles (for which the predictions were worst in chapter 5), these completely theoretical predictions are satisfactory. The general trends of the data are still followed even where details of 'cut-off' concentrations and of intensity levels are slightly inaccurate.

With a general empirical predictor of multiple optical scattering established, further as yet unavailable graphs can be now be investigated.
Angle Dependency

Figure 6.6 – MLP prediction (Mie theory input) of angle dependent scatter over a range of concentrations. Predictions have been divided by concentration to observe effects of multiple scattering.

Incident light is vertically polarised.

With the general multiple scattering predictor established, predictions can be made of the effects of multiple scattering from arbitrary particles. The details of these predictions may not be accurate, however the general trends demonstrated warrant investigation.

Figure 6.6 plots the scattering footprint of four different theoretical particles over a wide concentration range. The blue lines (10ppm) match closely the single scattering result predicted by the nephelometer model. As concentration increases and the effect of multiple scattering is introduced, the intensity falls below the single scattering prediction. As would be expected the intensity becomes more isotropic, back scattered light being increased with respect to forward scatter and angular features being lost. As concentration increases further (>1%), the extinction of the sample is great, with the intensity of light passing through the medium being small compared to that which leaves the medium towards the source, presumably after several particle interactions.
Particle Size Dependency

![Graph showing particle size dependency](image)

**Figure 6.7** — MLP prediction (Mie theory input) of particle size dependent 90° scatter over a range of concentrations. Predictions have been divided by concentration to observe effects of multiple scattering.

_Incident light is vertically polarised._

Figure 6.7 plots 90° scattered intensity as predicted by the MLP as a function of particle size in the same way that figure 5.12 plots the results as predicted by first order multiple scatter. The general form of the two predictions are similar, with a central area particularly sensitive to multiple scattering and regions less than 0.1μm and greater than about 10 microns being less sensitive. The explanation of this phenomenon is given in §5.7.2.

Two faults in the MLP prediction that can be clearly seen from figure 6.7. Firstly, for small (Rayleigh) particles, the trends of the scattering are wrong. Theory clearly shows that scattering increases with particle size, and not reach a minimum as seen in the figure. The data on which the network is trained contains only a single particle size in the sub-400nm range on which to base its experience. Experimental error in these data have been exaggerated by the network being trained and generalised through the sub-500nm range, predicting increased scattering with decreasing particle size.

Secondly, for larger particles which exhibit fine angle and particle size dependent features, these features are not lost with increasing concentration. The network obviously bases its initial approximation on that supplied in the inputs, which will contain many of the fine
features of single particle scattering. As concentration increases and so the number of particle interactions also increases, the fine features which are both angle and size dependent will be lost. The model has predicted the general trends of multiple scattering across the particle size range, but the fine size dependent features have not been lost at high concentration. For the neural model to make this prediction data would be required for many more particle sizes.

6.5.6. Parametric Dependency

![Graph showing the relative relevance of the eight inputs.](image)

Implementation of ARD increases the ability of a network to generalise and reduced reliance on noisy and irrelevant inputs. As a side effect of this process a measure of the relevance of each input is provided in the form of its individual regularisation coefficient. Figure 6.8 graphs the relative relevance of the eight inputs. Although the inputs have not been perfectly normalised and so the input regularisers have different units, they have been roughly normalised to give a 0 to 1 range, and so the parameters can be compared.

As could be predicted, the reliance on concentration is greatest. The scattering in the nephelometer will vary strongly with concentration, information which is not represented by any of the other inputs.

The other three primary inputs, i.e. angle, size and polarisation, are input to the model in two ways, directly and by the dependence of the single scattering results on their value. The values of the regularisation parameters show that the information contained in the single scattering footprint is of most relevance, with almost equal importance being given to side, forward and scattering angle values. A reasonably strong reliance on particle size, in addition to the scattering data, demonstrates that the form of multiple scattering is strongly dependent on the particles' relative size.
6.6. Discussion

This chapter has shown the feasibility of training a neural model with experimental data to extend basic scattering. The empirical model extends the theory into a regime which is difficult or impossible to model analytically.

A method of data preparation has been used which presents the scattering data to a multi-layer perceptron, scaled and transformed to assist the training process. This has resulted in a model that extends the single scattering data into the multiple scattering regime by use of the scattering footprint.

The fit to the training and validation data is good for data which are self consistent, i.e. where there is no observable experimental error. Use of a theoretical scattering footprint rather than the experimental single scattering extrapolation has established the trained network as a data-free, purely analytical multiple scattering predictor. The fit of this predictor to the experimental data is good, where the fit of the predicted footprint matches the experimental data (i.e. for all but the smallest particles considered). This implies a functional reliance on the scattering data passed to the network as input. For small (<<1μm) particles, where the scattering footprint is not consistent between theory and practice, the neural model cannot be relied on.

The ability of the network to predict the effects of multiple scattering can be compared with the first-order multiple scattering model by considering figures 5.4 and 6.3. The modelling of the multiple scattering is clearly closer to the experimental results with the neural model than the FOMS prediction. By considering 1μm samples in particular, which were not used for the MLP training, a genuine comparison of the two techniques can be made. For theoretical input, the neural model misplaces the single scattering result, but the closeness of fit of the multiple scattering effect is orders of magnitude closer than for the FOMS prediction.

The ability of the MLP to generalise between the data points and extrapolate beyond them can be at best assumed, since there is insufficient data to fully validate the network. With the current data set training the model, the resulting network provides a tool for qualitative consideration of multiple scattering phenomena.

This qualitative tool has been applied to perform a few simple studies of multiple optical scattering in the scanning nephelometer. A study of the effect on the scattering footprint of multiple scattering has been carried out by predicting the footprint over 5 orders of magnitude of concentration for a number of theoretical particles (figure 6.6). These studies
have confirmed a tendency towards isotropic scattering with increasing concentration. Angular features are lost as the effects of multiple scattering become significant.

The application of the model to particle size dependency has exhibited some anomalies. The trends of the low concentration prediction of the network are inconsistent with the single scattering results. The unreliability of the small size data combined with the generalisation of these errors has resulted in an obviously incorrect prediction for small particles.

It is expected that in the multiple scattering regime, fine particle size (and angle) dependent phenomena will be lost due to an averaging over multiple particle interactions. The neural network, provided with the single scattering prediction, acts as an extrapolator, extending the single scattering prediction into the high concentration regime. The general trends of the multiple scattering are predicted as would be expected, however, there is insufficient data passed to the network for it to remove the finer features from the input data.

With these two anomalies discussed, the qualitative effects of the multiple scattering can be considered. The predictions of the network match, in general form, the predictions of FOMS. Particles in the order of a micron are most affected by the single scattering phenomenon, while larger particles (greater than a few microns) are less affected. The physical reasons for this have been discussed in chapter 5.

One final consideration of the neural model is its parametric dependency. ARD, as well as improving the efficiency of network training, proves a measure of input dependency. The main task of the neural model is to extrapolate single scattering data into a higher concentration regime and obviously the concentration is by far the greatest influence on the mapping function (almost four times more relevant than the next most significant parameter). Further dependency of the model is based mainly on the scattering footprint, predominately on the scattering at the angle under consideration and at 60° and 90°. The scattering profiles of the individual particles are represented by the single scattering intensities and so any reliance on the particle parameters themselves is, in theory, secondary.

6.6.1. Expansion of this Study

The ability of a neural network to learn the multiple scattering effects has been demonstrated and the dependence of this is based on the individual scattering profiles. By making the input of the scattering profile to the MLP more complete and/or more efficient, a more expansive model of multiple scattering could be carried out. Particles of any form (not just spheres), size and optical properties could be examined. Their single scattering profiles would be input to the network and their multiple scattering intensities output. After such an expanded study, a general single scatter to multiple scatter converter would be available.
Chapter 7. DISCUSSION
7.1. Hypothesis

At the beginning of this research, the following hypothesis was suggested -

*A simple nephelometric experimental methodology can be established with a fine angular resolution and wide angular range. The nephelometer can be modelled up to first-order multiple scattering. Empirical extensions to this basic scattering model can be made for multiple scattering effects based on experimental data, providing a more general solution than any one multiple scattering model.*

7.2. Experimental Conclusions

A scanning nephelometer has been developed and tested. Scattering measurements can be made on small volumes of particle suspensions, allowing affordable studies to be made on expensive test materials. The nephelometer has an angular range of ±150° with a resolution of 0.9°, a range and resolution which surpasses most reported nephelometric systems.

Models of single scattering and first-order multiple scattering have been established and implemented in Matlab. Modifications for the geometry of the nephelometer have been formulated and implemented. This model predicts the relative intensity of light scattered from the spherical test samples to acceptable accuracy. The general form and several of the angular features have been successfully predicted.

The system has a few limitations. Due to the scanning nature of the system, experiments are relatively slow (15+ minutes per triple pass scan). Larger (e.g. >10μm latex) and/or heavier particles tested in the system will settle considerably over the scanning, giving inconsistent and unreliable results. Modelling of the settling process, combined with a relative timestamp on data reading could be used to compensate for this. Alternatively, some method of agitation or relative density matching could be incorporated into the system or sample preparation procedure to help maintain the suspension of particles.

Scattering results for small (54nm) particles seem to contradict theory and therefore be unreliable. There are a number of explanations for this, e.g. coagulation of the particles or contamination of the sample.

7.2.1. Modification

The modular nature of this set-up allows modifications to be made to its components. A further experimental study has already been carried out using the basic configuration. A white light source replaced the laser and a fibre-coupled spectrometer replaced the detector.
The development time for the experiment was short, allowing a spectroscopic scattering study to be carried out quickly and effectively.

7.3. Theoretical Conclusions

Rigorous single scattering theory for spherical particles is well established, having been in existence for nearly a century. The extension of Mie theory to a particle taken from a distribution of particle parameters offers a tool for investigating realistic scattering patterns from non-ideal samples. Likewise, the extension to polychromatic light potentially provides information valuable to spectroscopic studies. Such theory is required for the modelling of the modified system described above.

Many multiple scattering theories have been developed which cover various regimes of concentration, particle size and/or other particle parameters. Each of these approximations is only valid for a limited region of possible parameter space, e.g. small/large particles, tenuous/dense suspensions, absorbing/non-absorbing particles, high/low relative refractive index. Any theoretical method that does not consider the interaction of fields in neighbouring particles will be invalid at concentration higher than 16% by volume\[^6\]. Single scattering is valid only up to 100ppm (5% extinction) and FOMS, at best, up to 70% extinction\[^82\]. FOMS is also invalid for systems with low absorption, as the extinction is mainly due scattering and so the assumptions become invalid at concentrations where the single scattering assumption first breaks down. Radiative transfer provides a macroscopic solution to the problem of a scattering media and works best for higher concentration suspensions, lacking the rigour to model to the single scattering effects. Various diffusion models rely on any of a number of approximations which are valid for only a subset of parameter space, e.g. large particles\[^86-88\] or isotropic scattering.

The most rigorous solutions (Twersky\[^77\] and Foldy-Twersky\[^90\]) rely are extensive and as such much more computationally expensive than other methods.

This thesis has provided a computationally light methodology for empirically extrapolating the single scattering (infinite dilution) prediction of Mie theory well into the multiple scattering regime, as far as experimental data are available. The model is empirical and so any effects of field interaction, particle or medium absorption or other particle dependent phenomenon can be modelled by the network.

The methodology has been executed on a relatively wide particle size range (3 orders of magnitude), but with a relatively small number of different particle samples. While the exact predictions generalised by this empirical neural model cannot be expected to be numerically accurate, the trends observable offer valuable insight into the multiple scattering
phenomenon. Some observable consequences of multiple scattering observed from the model were the greater effect of multiple scattering on particles in the order of a few wavelengths and the greater effect in the side scatter direction.

7.4. **Suggested Modifications and Extensions**

7.4.1. **Experimental**

As mentioned above, the experimental equipment is modular and easily modified to change source and/or detector configurations. This leads to a few obvious refinements to the system.

Angular resolution of the single particle scattering footprint could be improved by use of a sensor with a smaller numerical aperture. The current configuration was chosen so as to provide a reasonable dynamic range of intensity, whilst maintaining a relatively short integration period. Use of a smaller numerical aperture sensor configuration would require a more sensitive sensor or longer integration time but would result in a shorter scattering volume and a scattering footprint with clearer angular features.

The value of the information present in the polarisation is clear from the relative scattering footprints of vertically and horizontally polarised light. A particle illuminated by polarised light will scatter light which is only partially polarised. The degree of depolarisation and more specifically the degree of linear/vertical/circular polarisation are as dependent on angle and particle parameters as the mean scattered intensity itself. Measurement of the scattered light with a Stokes’ polarimeter and modulation of a light source polarisation state, could provide the elements of the scattering Mueller matrix and so a complete description of the scattering process. Methods described and used in Chapter 6, to predict the scattered intensity with a neural network, could equally be applied to the prediction of all the Mueller matrix elements over a range of concentrations, particle size and angle.

A study of colour and turbidity has already been made using a modified version of the scanning nephelometer. Such a modified system, with a white light source and a spectrometer, provides information concerning the wavelength dependence of the scattering (and absorption) process. By completing a study equivalent to that described in this thesis, on a spectroscopic detector, an extra dimension could in principle be added to the empirical scattering model, adding greater worth to the knowledge to be gained from that model.

7.4.2. **Neural Model**

Chapter 6 implements a simple data preparation scheme to train a elementary neural model. It was not the purpose of this thesis to investigate the most efficient representation of data to
the empirical model nor to develop new neural models. If a more expansive data set (i.e. a finer particle size resolution) were to be used to train a neural model it would be worthwhile to consider and investigate alternate representations of the scattering footprint.

The study demonstrated the reliance of the neural model on the nominal scattering footprint information. Alternate representations of the scattering efficiency of the particles could provide a more accurate model with better generalisation. The basic information required is the overall scattering efficiency and the general shape of the scattering footprint. The former would be well represented by the scattering cross-section (and/or extinction cross-section, if absorbing particles are to be considered) and the later by the degree of forward scatter, e.g. \(\langle \cos \theta \rangle\). These parameters are inspired by physical multiple scattering theories, e.g. extinction cross-section is used in the FOMS. Other representations could equally take accepted multiple scattering parameters as a basis.

7.4.3. Particle shape

Mie theory is often used as a predictor for non-spherical particles in the absence of more accurate models in a similar way to the use of single scattering approximation is used as a 'best guess' for particle suspensions. Neural models could be applied to correct for non-sphericity of particles, in general or over a sub-set of possible particles. Experiments with spherical and non-spherical particles would provide a data set. An empirical model could be trained with inputs which describe the size of the particle and some representation of its shape along with the Mie prediction for an equivalent spherical particle. The network could then, in principle, correct for the shape of the particle as necessary.

7.5. Use of this Research

The methodology established by this research has a number of direct uses. Firstly, it acts as a tool for the understanding of a multiple scattering process, based on experience but extrapolated across parameter space. By completing experiments across the parameter range of real world samples and over an appropriate concentration range, studies of multiple scattering for specific applications can be made.

Multiple scattering within any nephelometric system required can be modelled using a similar neural model, provided some form of single scattering model can be evaluated. The extrapolation of the empirical data can provide information about the multiple scattering process. The data provided by the model can be used to establish limits on the validity of any assumptions made. The neural model itself can act as a look-up table with which to invert the scattering problem - by trial and error the suspension parameters can be found which match an observed scattering footprint.
The field of optimal sensor design can make use of the fully trained neural model and the scanning nephelometer. The massively redundant nephelometer can be optimised to provide a static nephelometer with an ideal sensor configuration. The process uses an neural model to invert the scattering problem and relies on a virtual nephelometer to provide data. The multiple-scattering neural model easily provides these data. It is arguable that it would be more efficient to provide the experimental data directly to the inverting network. However, by modelling the forward scattering process, the optimisation procedure can be better understood and issues of data separability and uniqueness of solutions can be investigated by considering the trends across parameter space.


102. RS, *Hybrid Stepper Motors*. RS Components, Corby, Northants 232-5749


107. Quality Control Department, PL-Latex and PL-Microspheres Certificates of Analysis. Polymer Laboratories, 4 Jan - 19 July 1996. QCFL202/1


Appendix A. MATLAB CODE
A.1. Introduction

This chapter details the Matlab scattering code developed for this thesis. §A.2 details the single scattering (Mie) model and its required functions. The majority of this code has been made available on the internet since it was first written in 1996. Its efficiency and validity has been improved by suggestions from its international users and it has been used by a number of researchers (e.g. Zhang et al.\textsuperscript{27}) to provide single scattering predictions for their research. §A.3 details the extensions for finite sensors as described in §2.7 and 2.8. §A.4 describes the simple implementation of scattering from particle distributions and incident polychromatic light. §A.6 provides modified scattering functions to model first-order multiple scattering effects. §A.7 details the code used to model the scanning nephelometer with single and first-order multiple scatter.

At the time of submission of this thesis these functions will be available at the author's website, http://staff1.lboro.ac.uk/~eldb3. Contact with the Optical Engineering Group, Department of Electronic Engineering, Loughborough University should provide a link to the current location of the code.

A.2. Single Scattering

These functions provide scattering data for, in general, multiple values of refractive index and/or particle size. Values passed to these functions may be scalar or vector. If both refractive index and particle size (and in the case of the cross-section functions, wavelength) are vectors then they should be of the same dimension, the values being treated as pairs. Results can be obtained for a set of refractive index values over a set of particle sizes by columnising(;) a meshgrid of the vectors and subsequently reshaping the results.

A.2.1. Single Sphere Scattering

The \texttt{SphereSc} function implements Mie theory to predict the scattering from a single spherical particle, i.e. the equations 2.34-2.39. \texttt{SphereSc(m, x, I, ang)} returns a matrix containing the prediction for a particle of refractive index relative to the medium of \texttt{m}, size parameter \texttt{x} with incident light having Stokes' vector \texttt{I}, predictions are made for scattering angle \texttt{ang} in radians. The first dimension of the return matrix spans the four elements of the Stokes' vector of the scattered light. If \texttt{m} and/or \texttt{x} are vectors then the second dimension spans their values. The final dimension (second for scalar \texttt{m} and \texttt{x}, third otherwise) spans the angles passed to the vector.
Example use of code:

\[
S = \text{SphereSc}(1.3, 1:5, [1:1:0:0], (0:180)*\text{pi}/180);
\text{semilogy}(0:180, \text{squeeze}(S(1,:,:)))
\]

plots the scattered intensity footprint of particles of relative refractive index 1.3 and size parameters 1, 2, 3, 4 and 5.

### A.2.2. Scattering and Extinction Cross-sections

The functions `ScatteringCS` and `ExtinctionCS` return the scattering and extinction cross-sections respectively, as described in §2.6.5. `crosssection` returns both of these parameters. All three functions receive \((m,a,wv)\) as parameters, the relative refractive index, particle radius and the wavelength of the incident light (radius and wavelength in the same units). Any of the parameters may be vectors, resulting in a corresponding vector return.

### A.2.3. Scattering Coefficients

\([a,b]=\text{ScatCoef}(m,x,nmax)\) returns the scattering coefficients \(a_n\) and \(b_n\) for the refractive index and particle size supplied for all \(n\) from 1 to \(nmax\). Return is a matrix, the first dimension of which spans the values of \(n\). The second dimension spans refractive index and/or size if either are passed as vectors. Computation follows equations 2.32 and 2.33.

Both the single scattering function and the cross-section functions use this function.

### A.2.4. Bessel Functions

Two functions, \(\text{RB1}\) and \(\text{RB2}\), return the Ricatti-Bessel functions of the first (\(\psi_a\)) and second (\(\zeta_a\)) kinds respectively for the parameter(s) passed, for all \(n\) from 1 to \(nmax\). Details of their recursive computation can be found in §2.6.3.

These functions are required in the calculation of the scattering coefficients. Their values are plotted in the figures 2.3 and 2.4.

### A.2.5. Legendre Functions

The scattering angle dependency of the Legendre functions are incorporated in the functions \(\pi_n\) and \(\tau_n\). \([p,t]=\text{ALegendr}(\text{ang}, \text{nmax})\) returns these values for angles passed (in radians) for all \(n\) from 1 to \(nmax\).

These functions are required in the calculation of single scattering. Their values are plotted in the figure 2.2.
A.3. Finite Sensor Code

AzSphereSc, ScSphereSc, FSphereSc and BSphereSc are modified versions of Spheresc. The first two functions model the effects of finite azimuth and scattering angle, as described in §2.7.1 and 2.7.2 respectively. These effects are combined as per §2.7.3 in Fspheresc, to predict for a finite rectangular sensor. BSphereSc models scattering from a narrow beam of finite length (§2.8).

These functions integrate the results of the functions used in the single particle scattering function, using the function scintegrals to compute $S_{xy}$ from equations 2.43-2.44. Each are passed parameters describing the region of integration, as appropriate.

A.4. PDF and Polychromatic Scattering

PSphSc is a simple implementation of mean scattering from a particle distribution. A particle parameter vector(s) is passed to the function along with a vector of associated probabilities. sssphSc consists of a single call to that function after a transformation from a wavelength distribution vector pair to a particle size parameter distribution.

A whole series of functions have been developed for the handling of PDFs in histogram form and the various methods for their use as described in §2.11 and 2.12. These methods implement one and two dimensional PDF objects which can be resampled using the functions that have been written. Functions are also available for plotting these PDFs as two and three dimensional histograms and coloured spectra and for transforming spectra objects into RGB triples.

Three functions implement scattering statistics. ScatterPDFx and ScatterPDFmx predict the single scattered intensity from a one and two dimensional PDF of particles, respectively. ScatterSpectrum predicts the spectrum of light scattered from a single particle given an incident spectrum.

A.5. Visualisation

A single function, Scatter3d, provides visualisation of the scattering function as described in §2.6.4. The function receives refractive index and particle size parameter and plots the three-dimensional scattering 'footprint'.

A.6. First-Order Multiple Scattering

FOMS predictions are made for the narrow beam geometry with an extension to the BSphereSc code, FirstOrderSc. The integration over the scattering volume with
extinction, $S_{xy}$, is computed in `FirstIntegrals`, which requires another custom function `stretch` to stretch parameters over the abscissas.

### A.7. Nephelometer Model

The models of the scanning nephelometer described in chapter 5 are implemented in a series of functions. `Nephelometer` and `Nephelometer1` predict the single and first-order multiple scattering respectively. Parameters of the tube and sensor positions are passed in addition to particle parameters to provide a prediction of scattering as measured by the scanning nephelometer.

These functions use integration functions, `NephIntegrals` and `NephIntegrals1`, to perform the integration across the vessel. Functions `TubeParam` and `FindTube` transform the integrand into the other measurement parameters in the scattering vessel, as detailed in §5.4.1.
B.1. Terms

azimuth angle made with incident ray in plane perpendicular to scattering plane.

scattering plane plane containing incident ray and scattered ray of interest.

horizontal polarisation a wave having electric field in the scattering plane

0° scattering forward scattering, i.e. scattering in the direction of the incident radiation.

B.2. Notation, parameters and functions

Internal parameters in the computation of scattering from the scanning nephelometer in Chapter 5 are listed in that chapter and have not been included here.

(1) solution with \( \rho \)-dependency being spherical Bessel functions of the first kind.

(3) solution with \( \rho \)-dependency being spherical Hankel functions of the first kind.

\( \hat{r} \) signifies with respect to integrand position in scattering volume integrations, e.g. \( \hat{r}, \hat{z}, \hat{\theta} \).

\( \hat{r} \) signifies first order multiple scattering solution

\( \times \) signifies scanning nephelometer solution

\( \overline{N}, \langle N \rangle \) mean or expected value

\( \Im/\Re \) imaginary/real part

\( c \) pilot vector for \( H \) and \( E \)

\( \hat{e}_{x/r/\theta/q} \) unit \( x/\text{radial/scattering} \) angle/azimuthal vector

\( r \) unit radial vector

\( E \) electric field vector

\( E_{\text{in/s}}/ \) incident/scattered/ internal electric field vector

\( H \) magnetic field vector

\( H_{\text{in/s}}/ \) incident/scattered/ internal magnetic field vector

\( M \) either of \( H \) or \( E \) in vector field equation

\( M_{\text{sph}} \) vector spherical harmonic (solution of \( M \))

\( N \) other of \( H \) or \( E \) in vector field equation

\( N_{\text{sph}} \) vector spherical harmonic (solution of \( N \))
On Multiple Optical Scattering in a Scanning Nephelometer. 28 January 2000

\( a \)  particle radius

\( a_n \)  coefficients for \( M_{o}^{(i)} \) in \( E_s \)

\( b_n \)  coefficients for \( N_{e}^{(3)} \) in \( E_s \)

\( c_n \)  coefficients for \( M_{i}^{(i)} \) in \( E_i \)

\( d \)  path length through medium

\( d_n \)  coefficients for \( N_{e}^{(i)} \) in \( E_i \)

\( h_n^{(s)} \)  spherical Hankel function of the \( s^{th} \) kind of order \( n \)

\( i \)  the complex identity, \( \sqrt{-1} \)

\( j_n \)  spherical Bessel function of the first kind of order \( n \)

\( k \)  wave number in medium

\( k_i \)  wave number in particle

\( l_{1/2} \)  inner/outer radius of cuvette

\( l_w \)  path length through water after scattering

\( m \)  refractive index relative to background medium

or separation constant in separation of \( \psi \)

\( n \)  separation constant in separation of \( \psi \)

\( n_{1/2} \)  relative refractive index of particle/medium

\( n_{p/w/g} \)  relative refractive index of particle/water/glass

\( n_e \)  termination index for 'infinite' sum in Mie calculation

\( n_p \)  number of abscissas in particle distribution

\( n_0 \)  number of angles for which scattering calculations are to be calculated

\( p(m,x) \)  normalised particle number distribution

\( p(\lambda) \)  spectral distribution

\( r \)  radial particle-sensor (focal point) separation

\( r^{1.5} \)  sensor focal position relative to pinhole/sensor post

\( x \)  dimensionless particle size parameter

\( y_n \)  spherical Bessel function of the second kind of order \( n \)

\( z \)  length along scattering volume (from nominal scattering centre)

\( z_n \)  either of \( j_n \) or \( y_n \), or linear combination of them

Appendix B - Notation 169
A absorbance per unit length = total extinction cross section
A_{mn} coefficients for \textbf{M}_{mn} in \textbf{E}_i
B_{mn} coefficients for \textbf{N}_{mn} in \textbf{E}_i
B(\lambda) blue transformation spectrum
C cross-sectional area of scattering volume
E_0 modulus of incident electric field
G(\lambda) green transformation spectrum
I^+\mp forward/backward travelling incident intensity
I_s incident/scattered intensity
L length of scattering volume along narrow beam
N particle number density
N(m,x) particle number distribution
NA numerical aperture, cos(\theta)
P degree of polarisation
P_n Legendre polynomial of the first kind, degree n
P^m_n associated Legendre polynomial of the first kind, degree n, order m
Q_{is} incident/scattered degree of horizontal polarisation
R radial component of \psi
R_{1/2} reflectivity of air-glass/ water-glass interface
R(\lambda) red transformation spectrum
S_{1/2} parallel/perpendicular efficiency factors for scattering electric fields. The elements of the Jones' scattering matrix.
S_{xy} Mueller scattering matrix elements.
S_{xy}^\ast ...integrated over scattering angle range of sensor.
S_{xy}^\ast ...for narrow beam source.
U_{is} incident/scattered degree of 45° polarisation
V volume of single particle
V(\lambda/\theta) sensor or eye responsivity to wavelength/angle
V_{is} incident/scattered degree of circular polarisation
Z radial term in derivation of Mie theory, R \sqrt{\rho}

or length along scattering volume as perceived outside vessel
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>polarisation azimuth</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Dirac delta function</td>
</tr>
<tr>
<td>$\delta \theta$</td>
<td>receiver half-angle</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>permittivity of background medium</td>
</tr>
<tr>
<td>$\phi$</td>
<td>azimuthal angle between scattered and incident rays</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>gamma correction value</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength of light in the medium</td>
</tr>
<tr>
<td>$\mu$</td>
<td>permeability of background medium</td>
</tr>
<tr>
<td>$\mu_i$</td>
<td>permeability of particle</td>
</tr>
<tr>
<td>$\pi_n$</td>
<td>scattering angle dependent function, $\frac{P_n'}{\sin \theta}$</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>scattering angle component of $\psi$ in derivation of Mie theory</td>
</tr>
<tr>
<td>$\rho$</td>
<td>normalised radial distance, kr</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>standard deviation (of normal particle size distribution)</td>
</tr>
<tr>
<td>$\sigma_{sv}$</td>
<td>scattering/absorption/extinction cross section</td>
</tr>
<tr>
<td>$\tau_n$</td>
<td>scattering angle dependent function, $\frac{dP_n'}{d\theta}$</td>
</tr>
<tr>
<td>$\xi_n$</td>
<td>Ricatti-Bessel function of the third kind, order $n$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>circular frequency</td>
</tr>
<tr>
<td>$\psi$</td>
<td>scalar generating function for scalar wave equation</td>
</tr>
<tr>
<td>$\psi_n$</td>
<td>Ricatti-Bessel function of the third kind, order $n$</td>
</tr>
<tr>
<td>$\zeta_n$</td>
<td>Ricatti-Bessel function of the second kind, order $n$</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>azimuthal component of $\psi$</td>
</tr>
</tbody>
</table>

**Appendix B - Notation**
C.1. Sample Preparation

Samples were prepared from reagent grade deionised water and Polymer Laboratories polystyrene latex Microspheres.

An initial sample was prepared in a test cuvette by pipetting a single quantity of 10% suspension and three quantities of water to produce a 2.5% suspension (or two quantities to two quantities for a 5% initial sample). After agitation, a single quantity of this suspension was transferred to a second cuvette and diluted with three quantities of water. This process was repeated to produce samples of successive dilution. A single particle size sample at a range of concentrations constituted a single sample set.

In addition to these samples, a pure water sample was prepared alongside each sample set.

Each sample was labelled with a letter code and the sample’s particle size and concentration logged.

C.2. Experimental Procedure

The sample cuvette was inserted into the tube holder. The cuvette was adjusted such that the source beam observed at the first air glass interface was coincident with that of the beam reflected from the second air glass interface.

For each set of experiments, the laser was adjusted such that the polarisation was either vertical or horizontal.

The software was set to take 5000 readings to produce each intensity mean and to undertake three scans of the experiment.

Once the experiment was set up, the software was initiated, which allowed a short period of time for the dark room to be left.

C.3. Data Preparation

Data were recorded into ASCII files containing the angular position of the sensor and the intensity averages. Filenames were recorded alongside sample codes. These files were read into Matlab and stored in a single five-dimensional matrix (representing the mean intensity values at a given concentration, particle size, angle and polarisation) for each experiment.

Data were initially corrected for zero concentration offset, by subtracting the average of the pure water sample values associated with that sample set and angle.
An infinite dilution approximation was made by taking the gradient of a best (minimum least squares) linear fit to the samples in the single scattering region (i.e. those samples with concentrations of 10-1000ppm). These gradients can be seen plotted on figures 5.4-6.