Dynamic Light Scattering at Low Concentration and in Turbulent Flow

Evelien Nijman
Stellingen

behorend bij het proefschrift
"Dynamic Light Scattering at Low Concentration and in Turbulent Flow"
van Evelien Nijman

1. In order to extend the applicable regimes of PCS to low concentrations and to
flowing conditions, an accurate and adjustable scattering volume is essential.

2. The use of an electronic filter with PCS measurements made at low concentra-
tion does not contribute significantly to the quality of the measurements.

3. Standard measuring equipment often falls between two stools: it offers many
options that you never use but not the specific option that you need.

4. In contrast to the writing of a thesis, bad time planning in the kitchen can yield
disastrous results.

5. An international department where only Dutch is spoken at the coffee table is
not really international.

6. You only really get to know your own culture when you live together with
someone from another one.

7. Even though the publication of research results which are "a little too opti-
mistic" can be a stimulus to the given scientific field, it is not a valid excuse for
doing it.

8. The anonymity obtained by the steel casing allows many car drivers to develop
their natural urge to jump the queue.

9. Combining a holiday with a congress in a foreign country may be financially
attractive but it does not increase the effectiveness of either.

10. You don’t need to like milk in order to work with pleasure in the milk industry.
Stellingen

behorend bij het proefschrift
"Dynamic Light Scattering at Low Concentration and in Turbulent Flow"
van Evelien Nijman

1. Het uitbreiden van de toepassingsmogelijkheden van standaard PCS apparatuur voor het meten bij lage concentratie en bij stroming, vereist een accuraat en regelbaar verstrooingsvolume.

2. Het gebruik van een electronisch filter bij PCS bij lage concentratie levert geen wezenlijke bijdrage aan de kwaliteit van de metingen.

3. Standaard meetapparatuur valt vaak tussen wal en schip: het bevat veel opties die je nooit gebruikt maar niet die specifieke optie die je nodig hebt.

4. In tegenstelling tot bij het schrijven van een proefschrift, kan een verkeerde tijdsplanning in de keuken desastreuze gevolgen voor het eindresultaat hebben.

5. Een internationale vakgroep waar aan de koffietafel alleen Nederlands wordt gesproken, is niet echt internationaal.

6. Je leert je eigen cultuur pas echt kennen wanneer je samenleeft met iemand uit een andere.

7. Alhoewel de publicatie van "wel erg optimistische" onderzoeksresultaten een stimulans kan zijn voor het wetenschapsgebied in kwestie, is dit geen geldig excuus ervoor.

8. Door de anonimiteit verkregen door zijn stalen omhulsel heeft menig automobilist zijn natuurlijke drang tot voordringen kunnen ontplooien.

9. Het combineren van vakantie met een buitenlands congresbezoek mag dan financieel aantrekkelijk zijn, het komt de effectiviteit van beide niet ten goede.

10. Je hoeft geen liefhebber van melk te zijn om graag in de melkindustrie te werken.
Dynamic Light Scattering at Low Concentration and in Turbulent Flow
Dynamic Light Scattering at Low Concentration and in Turbulent Flow

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus prof. dr. ir. J.T. Fokkema, voorzitter van het College voor Promoties, in het openbaar te verdedigen op 4 maart 2002 om 16:00 uur door

Evelien Johanna NIJMAN

scheikundig ingenieur

geboren te Eindhoven.
Dit proefschrift is goedgekeurd door de promotor:
Prof. B. Scarlett, M.Sc.

Samenstelling promotiecommissie:

Rector Magnificus,
Prof. B. Scarlett, M.Sc.,
Prof. dr. A. Schmidt-Ott,
Prof. dr. G. Frens,
Prof. dr. R. Finsy,
Prof. dr. S.E. Pratsinis,
Prof. B.M. Moudgil,
Drs. H.G. Merkus,

Technische Universiteit Delft, voorzitter
Technische Universiteit Delft, promotor
Technische Universiteit Delft
Technische Universiteit Delft
Vrije Universiteit Brussel
ETH Zürich
University of Florida
Technische Universiteit Delft

Drs. H.G. Merkus heeft als begeleider in belangrijke mate aan de totstandkoming van het proefschrift bijgedragen.

ISBN 90-901-5578-3

Copyright © 2002 by Evelien Nijman

The author encourages the use of the contents of this thesis, provided that the source is mentioned.
Summary

-Dynamic Light Scattering at Low Concentration and in Turbulent Flow-

Most particle and powder processes are studied using particle size and its change in time. The size range of interest can be anywhere from nanometers (the dispersion of pigments) to millimeters (crystals, granules). At the lower end of this range, the current development of nanotechnologies clearly asks for accurate, versatile and non-intrusive measurement methods.

A technique that is specifically suitable for measuring the size of sub-micrometer particles is dynamic light scattering. This technique is based on the random thermal motion that all small particles exhibit: the Brownian motion. The particle property that is obtained from a dynamic light scattering measurement is the diffusion coefficient, which is directly related to the particle size: the smaller the particles, the faster their motion. Since the invention of dynamic light scattering in the 60's, it has been developed into a standard measuring technique for dilute samples of sub-micrometer particles, and various commercial instruments are now available. In general, these instruments allow only off-line measurement of liquid dispersions in a small concentration range, and the errors introduced by sampling are usually not accounted for. However, for dynamic processes, in-line techniques are clearly required. For example, in aerosol particle production processes, sampling is often impossible because of the high speed at which the process takes place.

Dynamic light scattering is in principle well-suited for in-line applications, because it does not need to disturb the system. However, this potential for in-line measurement in various particle processes confronts the dynamic light scattering method with two new challenges, that are not accounted for in the standard technique: the particle concentration and the particle flow. These two challenges form the basis of this thesis work.

The first challenge is the size and concentration measurement at low particle concentration. When there are only a few particles present in the experimental measurement volume, a dynamic light scattering measurement can, under certain conditions be used to measure the particle concentration. Simulations and experiments have
shown that these conditions are twofold: the size and shape of the measurement volume must be well known, and the measurement time must be sufficiently long. For the size measurement at low particle concentration, it has been shown how the optical setup can be designed to obtain the highest quality measurement at each concentration.

The second challenge is the measurement in a turbulent flow. In that case, velocity fluctuations create an extra movement of the particles relative to each other, on top of their Brownian motion. The extent to which this influences the measured autocorrelation function, depends on the time and length scales characterizing the turbulence, compared to the time and length scale of diffusion. With aerosol measurements in a turbulent flow field, the influence of average velocity and turbulent intensity on the quality of a particle size measurement has been investigated.

The practical use of dynamic light scattering as an *in-line* measuring technique has been examined in two applications. The first is the size measurement of aerosol catalyst particles inside a reactor. The particle size of aerosol sampled from the reactor was found to be different from the particle size of the aerosol at the reactor conditions, which demonstrates the usefulness of *in-line* size measurement techniques. The second application is the measurement inside a spray of fine, highly charged droplets that are formed via electrohydrodynamic atomisation. In this case, the measured correlation functions did not yield the droplet size, but they did reveal information about the structure and the dynamics of the spray.

*Evelien Nijman*
Contents

Summary  i

List of symbols  vii

1 Introduction  1
   1.1 Measurement of sub-micrometer particles  1
   1.2 In-line measurement  2
   1.3 Overview of the thesis  3

2 Dynamic light scattering  5
   2.1 Introduction  5
   2.2 Brownian motion  6
      2.2.1 Diffusion coefficient  6
      2.2.2 Cunningham slip correction  7
   2.3 Light scattering  8
      2.3.1 Light: wave and particle  9
      2.3.2 Scattering by small particles  10
      2.3.3 Rayleigh theory  11
   2.4 Dynamic light scattering  12
      2.4.1 Photon correlation spectroscopy  15
      2.4.2 Coherence  16
   2.5 Conclusions  17

3 Dynamics of particle number fluctuations  19
   3.1 Introduction  19
   3.2 Scattering volume  20
   3.3 Particle number fluctuations  23
   3.4 Simulations  25
      3.4.1 Model  25
      3.4.2 Results  27
   3.5 Photon correlation experiments  30
3.5.1 Concentration variation ............................................. 30
3.5.2 Measurement duration ............................................. 32
3.5.3 Photon counting histogram ........................................ 33
3.6 Conclusions .............................................................. 34

4 Size measurement at low concentration 35
4.1 Introduction .............................................................. 35
4.2 Signal-to-noise ratio .................................................... 38
  4.2.1 Incomplete interference .......................................... 40
  4.2.2 Simulations ......................................................... 42
  4.2.3 Discussion ......................................................... 44
4.3 Number fluctuations ................................................... 46
4.4 Spatial coherence factor ............................................... 47
4.5 Finding the optimum scattering volume ............................. 48
4.6 Conclusions .............................................................. 50

5 Photon correlation spectroscopy in turbulent flow 51
5.1 Introduction .............................................................. 51
5.2 Uniform flow ............................................................ 52
  5.2.1 Non-dilute regime ................................................. 54
  5.2.2 Dilute regime ....................................................... 55
5.3 Velocity gradient in the scattering volume ......................... 56
5.4 Turbulent flow .......................................................... 57
  5.4.1 Turbulence and photon correlation spectroscopy ............... 59
  5.4.2 Characteristic time scales ....................................... 62
  5.4.3 Grid-generated turbulence ...................................... 62
5.5 Production of a monodisperse flowing aerosol .................... 63
5.6 Photon correlation experiments ...................................... 67
  5.6.1 Laboratory experiments ......................................... 68
  5.6.2 Windtunnel experiments ........................................ 73
5.7 Discussion and conclusions .......................................... 77

6 Applications ............................................................. 79
6.1 Aerosol catalysis ....................................................... 79
  6.1.1 Experimental setup .............................................. 80
  6.1.2 Experiments ...................................................... 84
6.2 ElectroHydroDynamic Atomisation .................................. 86
  6.2.1 Electrospray in the cone-jet mode ............................. 86
  6.2.2 Photon correlation spectroscopy experiments ................. 89
  6.2.3 Conclusions ...................................................... 96

7 General conclusions and perspectives ................................ 97
Bibliography 101
Summary in Dutch 107
Acknowledgement 109
Curriculum Vitae 111
# List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>radius of a circular detector surface</td>
<td>m</td>
</tr>
<tr>
<td>$C$</td>
<td>particle concentration</td>
<td>$\text{g/m}^3$</td>
</tr>
<tr>
<td>$C_C$</td>
<td>Cunningham slip correction factor</td>
<td>-</td>
</tr>
<tr>
<td>$d$</td>
<td>particle diameter</td>
<td>m</td>
</tr>
<tr>
<td>$d_m$</td>
<td>collision diameter</td>
<td>m</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
<td>$\text{m}^2/\text{s}$</td>
</tr>
<tr>
<td>$e$</td>
<td>amplitude of electric field</td>
<td>$\text{V/m}$</td>
</tr>
<tr>
<td>$E$</td>
<td>electric field</td>
<td>$\text{V/m}$</td>
</tr>
<tr>
<td>$E_p$</td>
<td>photon energy</td>
<td>J</td>
</tr>
<tr>
<td>$f$</td>
<td>focal length</td>
<td>m</td>
</tr>
<tr>
<td>$F$</td>
<td>force</td>
<td>$\text{kg m/s}^2$</td>
</tr>
<tr>
<td>$g^{(1)}$</td>
<td>normalised field autocorrelation function</td>
<td>-</td>
</tr>
<tr>
<td>$g^{(2)}$</td>
<td>normalised intensity autocorrelation function</td>
<td>-</td>
</tr>
<tr>
<td>$G^{(1)}$</td>
<td>field autocorrelation function</td>
<td>$\text{V}^2/\text{m}^2$</td>
</tr>
<tr>
<td>$G^{(2)}$</td>
<td>intensity autocorrelation function</td>
<td>$\text{W}^2/\text{m}^4$</td>
</tr>
<tr>
<td>$H$</td>
<td>magnetic field</td>
<td>$\text{A/m}$</td>
</tr>
<tr>
<td>$h$</td>
<td>number fraction of particle pairs</td>
<td>-</td>
</tr>
<tr>
<td>$i$</td>
<td>photon current</td>
<td>$\text{A/s}$</td>
</tr>
<tr>
<td>$i$</td>
<td>imaginary unit</td>
<td>-</td>
</tr>
<tr>
<td>$I$</td>
<td>intensity</td>
<td>$\text{W/m}^2$</td>
</tr>
<tr>
<td>$k$</td>
<td>wave number</td>
<td>$1/\text{m}$</td>
</tr>
<tr>
<td>$K$</td>
<td>conductivity</td>
<td>$\text{S/m}$</td>
</tr>
<tr>
<td>$K_1$</td>
<td>first cumulant</td>
<td>$1/\text{s}$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>second cumulant</td>
<td>$1/\text{s}^2$</td>
</tr>
<tr>
<td>$l$</td>
<td>length of scattering volume</td>
<td>m</td>
</tr>
<tr>
<td>$m$</td>
<td>particle mass</td>
<td>kg</td>
</tr>
<tr>
<td>$M$</td>
<td>grid mesh size</td>
<td>m</td>
</tr>
<tr>
<td>$n$</td>
<td>photon count rate</td>
<td>$\text{g/s}$</td>
</tr>
<tr>
<td>$n$</td>
<td>relative refractive index</td>
<td>-</td>
</tr>
<tr>
<td>$N$</td>
<td>number of particles in the scattering volume</td>
<td>-</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>$N_{tot}$</td>
<td>total number of particles</td>
<td>-</td>
</tr>
<tr>
<td>$p$</td>
<td>polarisability</td>
<td>$C^2 m^2/J$</td>
</tr>
<tr>
<td>$P$</td>
<td>probability after-effect factor</td>
<td>-</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$q$</td>
<td>scattering vector</td>
<td>1/m</td>
</tr>
<tr>
<td>$Q$</td>
<td>flow rate</td>
<td>$m^3/s$</td>
</tr>
<tr>
<td>$r$</td>
<td>particle position</td>
<td>m</td>
</tr>
<tr>
<td>$R$</td>
<td>distance</td>
<td>m</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$T$</td>
<td>sample time</td>
<td>s</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$U$</td>
<td>velocity</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$u'$</td>
<td>velocity fluctuation</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$v$</td>
<td>particle velocity</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$V$</td>
<td>velocity difference</td>
<td>$m/s$</td>
</tr>
<tr>
<td>$V$</td>
<td>volume element</td>
<td>$m^3$</td>
</tr>
<tr>
<td>$w$</td>
<td>beam radius</td>
<td>m</td>
</tr>
<tr>
<td>$W$</td>
<td>probability distribution function</td>
<td>-</td>
</tr>
<tr>
<td>$y_R$</td>
<td>Rayleigh range</td>
<td>m</td>
</tr>
<tr>
<td>$a$</td>
<td>dimensionless size parameter</td>
<td>-</td>
</tr>
<tr>
<td>$\beta$</td>
<td>dynamical friction factor</td>
<td>$s^{-1}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>coherence factor</td>
<td>-</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>energy dissipation rate</td>
<td>$m^2/s^3$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>relative permittivity</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>volume contrast factor</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>surface tension</td>
<td>N/m</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>velocity gradient</td>
<td>1/s</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>velocity gradient tensor</td>
<td>1/s</td>
</tr>
<tr>
<td>$\eta$</td>
<td>fluid viscosity</td>
<td>Pa s</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
<td>m</td>
</tr>
<tr>
<td>$\lambda_m$</td>
<td>mean free path</td>
<td>m</td>
</tr>
<tr>
<td>$\nu$</td>
<td>kinematic viscosity</td>
<td>$m^2/s$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>optical frequency</td>
<td>1/s</td>
</tr>
<tr>
<td>$\phi$</td>
<td>angle</td>
<td>°</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular frequency</td>
<td>1/s</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>radius of the scattering volume</td>
<td>m</td>
</tr>
<tr>
<td>$\tau$</td>
<td>delay time</td>
<td>s</td>
</tr>
<tr>
<td>$\theta$</td>
<td>scattering angle</td>
<td>°</td>
</tr>
</tbody>
</table>
### Constants

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>speed of light in vacuum</td>
<td>$3.00 \cdot 10^8$ m/s</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck's constant</td>
<td>$6.63 \cdot 10^{-34}$ J s</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>$1.38 \cdot 10^{-23}$ J/K</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>vacuum permittivity</td>
<td>$8.85 \cdot 10^{-12}$ C²/Jm</td>
</tr>
</tbody>
</table>
1.1 Measurement of sub-micrometer particles

Most particle and powder processes are studied using particle size and its change in time. This can be illustrated by examples as diverse as: the relation between colour and pigment size in paints, the deposition of inhaled drugs in the lungs, the nucleation and growth rate in crystallisers, or the granulation processes in fluid beds. In these processes, the size range stretches itself from nanometers (pigments) to millimeters (crystals, granules). At the lower end of this range, the current development of nanotechnologies clearly asks for accurate, versatile and non-intrusive measurement methods.

A technique that is specifically suitable for measuring the size of sub-micrometer particles is dynamic light scattering. This technique is based on the random thermal motion that all small particles exhibit: the Brownian motion. Due to their Brownian motion, the particles move around in random, and continuously changing, directions, as is shown in Figure 1.1. The particle property that is obtained from a dynamic light scattering measurement is the diffusion coefficient, which is directly related to the particle size: the smaller the particles, the faster their motion.

In a typical dynamic light scattering experiment, a laser beam shines into the sample, which can be a suspension of particles in a liquid, but also an aerosol. The particles in the sample will scatter the light in all directions. A detector that is
placed at a certain angle relative to the incident laser beam, collects only the light scattered at that specific angle, thereby defining the scattering volume as the cross section between the incident and the scattered beam, as is shown in Figure 1.2. The intensity of the scattered laser light that reaches the detector is not constant, but is fluctuating due to the continuous random movement of the particles. These intensity fluctuations form the basis of the dynamic light scattering technique: they contain the information about the particle movement. A high frequency of intensity fluctuations corresponds to a fast motion, and therefore to small particles.

1.2 \textit{In-line} measurement

Since the invention of dynamic light scattering in the 60's, it has been developed into a standard measuring technique for dilute samples of sub-micrometer particles, and various commercial instruments are now available. In general, these instruments allow only \textit{off-line} measurement of liquid dispersions in a small concentration range, and the errors introduced by sampling are usually not accounted for. However, for dynamic processes, \textit{in-line} techniques are clearly required. For example, in aerosol particle production processes, sampling is often impossible because of the high speed at which the process takes place.

Dynamic light scattering is in principle well-suited for \textit{in-line} applications, because it does not disturb the system. Moreover, since optical fibres can carry the scattered laser light over long distances, the processing of the data can take place far from the measurement location, so that even measurements in hazardous environments are possible. However, this potential for \textit{in-line} measurement in various particle processes confronts the dynamic light scattering method with two new challenges: the particle
concentration and the particle flow.

Problems with particle concentration occur both at too high and at too low concentrations. At high concentrations, multiple scattering, inter-particle interaction and the opacity of the sample complicate dynamic light scattering measurements, although the last problem has been successfully solved by making use of backscattering and optical fibres. At low concentrations measurements are complicated by fluctuations of the number of particles in the scattering volume. This effect starts down from about 100 particles in the scattering volume. For a typical setup, the size of the scattering volume is about $10^{-6}$ cm$^3$, which leads to a lower concentration limit of about $10^8$ particles/cm$^3$.

The problem with particle flow is, that it introduces an extra particle movement, on which the Brownian motion is superimposed. For the simple case of uniform flow, when all the particles have the same velocity, the influence on dynamic light scattering measurements has been thoroughly studied. However, when flow starts to be turbulent and the particle velocity becomes a fluctuating parameter, it is no longer obvious which part of the measured intensity fluctuations can be attributed to Brownian motion.

1.3 Overview of the thesis

The general aim of this research was to develop dynamic light scattering for in-line particle size measurement. For this, the two main difficulties connected to in-line measurement, low particle concentration and turbulent flow, have been investigated.

Chapter 2 contains the general theory of dynamic light scattering for particle size measurement. Specific theory connected to low particle concentration and to convection is given in later chapters covering these subjects.

In in-line aerosol applications, particle number fluctuations can play an important role. In the past, research has been done on number fluctuations, but in that research, the main point was usually the measurement of concentration. Therefore, moderately concentrated samples were used with very small scattering volumes, of the order of $10^{-10}$ cm$^3$. It will be shown in Chapter 3 how the insights in the dynamics of number fluctuations can be used for low concentrated samples using larger scattering volumes.

Whereas Chapter 3 is mainly concerned with the dynamics of the number fluctuations, Chapter 4 will focus on the effect of low concentration on the size measurement.

The influence of turbulent flow is treated in Chapter 5. It contains measurements in an aerosol flow with grid-generated turbulence. Both the effect of the overall flow component and of the turbulent velocity fluctuations are studied in this chapter.

Two in-line dynamic light scattering applications are presented in Chapter 6. The first is the size measurement of aerosol catalyst particles inside a reactor. The
size of these particles was believed to be of great influence for their catalytic activity. Since outside of the reactor, the aerosol easily agglomerated into a powder, it was essential to perform these measurements at the reactor conditions. The second application is measurement inside a spray that is formed via electrohydrodynamic atomisation. Such a spray consists of highly charged droplets that have a high velocity. At certain conditions, this method of atomisation can yield highly monodisperse particles. Characterisation of the spray process is therefore of great importance. The measurements presented in this chapter demonstrate what sort of information can be obtained in such complicated dynamic processes.
Dynamic light scattering

In this chapter, the theory of particle size measurement with dynamic light scattering is presented. It is explained how the random Brownian movement of particles can lead to intensity fluctuations of the scattered light and, subsequently, how the particle size can be obtained from these intensity fluctuations.

2.1 Introduction

The result of the interaction of light with small particles is regularly observed in everyday life. For example, dust or smoke particles ‘light up’ when they enter a beam of sunlight that shines through the window. The exact form of the interaction depends strongly on the size of the particle compared to the wavelength of the light. Particle sizing techniques based on the analysis of the pattern of scattered laser light make use of this size dependence. The scattering pattern is the angular intensity distribution of the scattered light. Besides information about the size of the particles, such a scattering pattern can also yield information about their shape [28].

The best results for particle sizing through analysis of the scattering pattern, are obtained for particles larger than 1 μm, since submicron particles of different sizes have only small differences in their scattering pattern. In the last 50 years, the technique has been constantly improved, by the development of suitable models that predict the scattering pattern for a wide range of particle sizes, and by computational power, which is necessary for the inverse problem of calculating the particle size distribution from a measured scattering pattern.

Analysis of the scattering pattern is a static measuring technique. This means that the intensities at different points on the scattering pattern are obtained by averaging over the measurement time. Dynamic light scattering techniques, on the contrary, measure fluctuations of the scattered light, usually at a single angle. These fluctuations are the result of varying interparticle distance, due to displacement of the particles. For such measurements, it is necessary to have a monochromatic coherent light source. Monochromatic light is light of only one wavelength or colour. In a coherent light beam, all the light is in the same phase. A laser beam has both these
properties.

The particle displacement that causes the scattered intensity to fluctuate, can consist of several factors: Brownian motion, convection, electrophoresis, etc. Particle size measurement makes use of the displacement resulting from the Brownian motion, because this motion is related to the particle diameter, as will be explained in the next section.

2.2 Brownian motion

Because of the thermal motion of molecules, a particle suspended in a fluid will continuously experience collisions from the fluid molecules. In a gas, the frequency of such collisions is about $10^{14}$ times per second [20] and in a liquid even as high as about $10^{21}$ per second [6]. These collisions will cause the motion of the particle to be continuously altered. The result is a random motion of the particle, which is called the Brownian motion after the botanist Robert Brown, who was the first to witness it in 1827 on pollen grains in water. The Brownian motion of a particle is quantified via its diffusion coefficient.

2.2.1 Diffusion coefficient

A mathematical description of Brownian motion starts with the Langevin equation, which describes the change of the particle's velocity $v$ with time [6]:

$$\frac{dv}{dt} = -\beta v + \frac{F(t)}{m}. \quad (2.1)$$

In this equation, the term $-\beta v$ represents the dynamical friction (drag), which is governed by Stokes' law:

$$\beta = \frac{3\pi \eta d}{m}. \quad (2.2)$$

Here $m$ and $d$ are the mass and the diameter of the particle and $\eta$ is the viscosity of the fluid. The fluctuating part of equation 2.1, $F(t)$, is assumed to be independent of $v$ and to vary extremely rapidly compared to the variations of $v$.

Because of the stochastic character of the Langevin equation, it is not possible to solve it. Therefore, it has to be treated in terms of probability distributions. One of the boundary conditions that is used is that the particle velocities follow the Maxwell distribution:

$$W(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp \left[ -\frac{m|v|^2}{2k_B T} \right], \quad (2.3)$$

where $k_B$ is the Boltzmann constant and $T$ is the temperature. It is then found that for time intervals much longer than $1/\beta$, the probability distribution of a particle
displacement from position \( r(0) \) to position \( r(t) \) can be written as:

\[
W(r(t); r(0)) = \frac{1}{(4\pi Dt)^{3/2}} \exp \left[ -\frac{|r(t) - r(0)|^2}{4Dt} \right],
\]

where the diffusion coefficient \( D \) is given by the Stokes-Einstein relation:

\[
D = \frac{k_B T}{3\pi \eta d}.
\]

The general equation for the mean square displacement of the particles is:

\[
\langle |r(t) - r(0)|^2 \rangle = 6 \frac{k_B T}{m\beta} \left( t - \frac{1}{\beta} (1 - \exp[-\beta t]) \right).
\]

Here the square brackets denote a time average. This equation can be simplified for two extreme cases. For \( t \to \infty \):

\[
\langle |r(t) - r(0)|^2 \rangle = 6Dt,
\]

and for \( t \to 0 \)

\[
\langle |r(t) - r(0)|^2 \rangle = \frac{3k_B T}{m} t^2.
\]

For particle size measurements with dynamic light scattering, the time scale of the experiment is usually \( \gg 1/\beta \), justifying the use of equation 2.7.

### 2.2.2 Cunningham slip correction

Stokes' law, regarding the drag force on a particle, is based on the assumption that the relative velocity of the fluid at the surface of the particle is zero. For aerosol particles, this assumption is not always met. The reason is that a gas can not be treated as a continuous fluid, but must be seen as separate molecules that are moving around in free space and that collide with each other and with the particles.

For comparison: the rate of molecular collisions with a surface is \( 3 \cdot 10^{27} \) per m\(^2\) per second for air at 1 atm and 20°C. This means that a particle with a diameter of 100 nm will experience \( 10^{14} \) collisions per second. This is a factor \( 10^7 \) less than in liquids!

The particle size relative to the spacing between the gas molecules determines whether or not the gas can still be treated as a continuous fluid. Because the motion of the particles is influenced by the collisions with the gas molecules, the spacing between the gas molecules is characterised by the mean free path, rather than by the average distance between the gas molecules. The mean free path is defined as the average distance traveled by a molecule between successive collisions [20] and is given by:

\[
\lambda_m = \frac{k_B T}{\sqrt{2\pi d_m^2} P},
\]
where $P$ is the pressure and $d_m$ is the collision diameter of the molecules. The latter is the distance between the centres of two molecules at the instant of collision. For air at 1 atm and 20°C, the mean free path is 0.066 μm. The relative size and spacing for a 0.1 μm particle is visualised in Figure 2.1.

![Figure 2.1: The relative size of a particle, a gas molecule and the mean free path at 1 atm and 20°C. From [20].](image)

When an aerosol particle is of the order of the mean free path, or smaller, it experiences a reduced drag force due to 'slip' at its surface. The factor by which the drag is reduced was first derived by Cunningham in 1910 and is called the Cunningham slip correction factor, given by:

$$C_C = 1 + \frac{\lambda_m}{d} \left( 2.34 + 1.05 \exp \left[ -0.39 \frac{d}{\lambda_m} \right] \right). \quad (2.10)$$

As a result of the reduced drag, the diffusion coefficient becomes:

$$D = \frac{k_BT C_C}{3\pi \eta d}. \quad (2.11)$$

### 2.3 Light scattering

The principle of dynamic light scattering is based on the fact that the scattered interference pattern is not constant due to the Brownian movement of the scatterers relative to each other. For a description of both the scattering process and the detection process, the wave-theory as well as the particle- (or photon-)theory of light are necessary.
2.3.1 Light: wave and particle

Light is an electromagnetic wave, and is made up of an electric field and a magnetic field that oscillate in directions perpendicular to each other and to the direction of propagation, as is shown in Figure 2.2.

![Wave-representation of light](image)

**Figure 2.2:** Wave-representation of light. The electric field component $E$ and the magnetic field component $H$ oscillate perpendicular to each other and to the direction of propagation.

The mathematical description of the electric field component $E$, travelling in the $y$-direction is:

$$E = E_0 \cos (ky - \omega t),$$  

(2.12)

where $k = 2\pi n_m / \lambda_0$ is the wave number, $\lambda_0$ is the wavelength in vacuum, $n_m$ is the refractive index of the medium, $\omega = 2\pi n_m c / \lambda_0$ is the angular frequency of the light and $c$ is the speed of light in vacuum. $E_0$ is the maximum amplitude of the oscillating field. In calculations, it is often convenient to use complex variables:

$$E = E_0 \exp [i (ky - \omega t)].$$  

(2.13)

Unpolarised light has electric field components in all directions of the $xz$-plane. A polarisation filter can remove one of these components, leaving so-called plane-polarised light.

An electromagnetic wave carries energy, which is measured as an intensity in Watts per square meter. The instantaneous intensity is given by:

$$I_{\text{inst}} = c \varepsilon_0 E^2,$$  

(2.14)

where $\varepsilon_0 = 8.85 \cdot 10^{-12} \text{ C}^2/\text{Jm}$ is the permittivity of vacuum. A detector is not capable of measuring the electric field, but can only measure the intensity. The response time
of a detector is so long \((> 10^{-9} \text{ s})\), that it integrates over many cycles of the optical frequency \((\approx 6 \cdot 10^{14} \text{ Hz})\). Therefore, a measured intensity is the cycle average over the instantaneous intensity of equation 2.14, which is:

\[
I = \frac{c\varepsilon_0}{2} E_0^2.
\]  

(2.15)

It can be represented as the square of the envelope of the electric field, as is shown in Figure 2.3 for a fluctuating intensity.

![Figure 2.3: Envelope of the electric field component. Solid line: electric field component; dashed line: envelope.](image)

Although the theory of dynamic light scattering will be best understood using the wave theory of light, the detection process is based on the photon or 'particle' theory of light. In this theory, the energy that is transported by the light is divided over photons, each one carrying an amount of energy given by:

\[
E_p = h\nu,
\]  

(2.16)

where \(h = 6.63 \cdot 10^{-34} \text{ Js}\) is Planck's constant, and \(\nu = c/\lambda_0\) is the optical frequency. Even though the energy of a photon is only about \(10^{-19} \text{ J}\), it is possible with modern detectors to detect single photons with an efficiency up to about 50%.

### 2.3.2 Scattering by small particles

When a light beam strikes a particle, several phenomena take place, as is illustrated in Figure 2.4. Firstly, some light is reflected. This can happen both on the outside of the particle, or on the inside via internal reflection. Secondly, the light is refracted during the passage from the surrounding fluid to the particle and later from the particle back to the surrounding fluid. Thirdly, some light is diffracted. That is, it slightly changes direction due to the presence of the particle. This is the main scattering mechanism for particles that are much larger than the wavelength of the light. And finally, depending on the material of the particle, it may be absorbed. The reflected, refracted and diffracted rays of light will have a phase difference, leading to interference. This
2.3. Light scattering

interference results in a scattering pattern. For spherical, homogeneous particles, this scattering pattern is a function of the following variables:

- the size of the particle compared to the wavelength of the light, $\lambda$, which is usually represented as the dimensionless size parameter $\alpha$:

$$\alpha = \frac{\pi d}{\lambda}, \quad (2.17)$$

- the refractive index of the particle, $n_p$, compared to the refractive index of the surrounding medium, $n_m$:

$$n = \frac{n_p}{n_m}. \quad (2.18)$$

Actually, the refractive index consists of a real and an imaginary part, where the imaginary part accounts for absorption.

The general and rigorous theory for describing scattering for all particle sizes and all refractive indices, is the Mie theory. However, especially for large particles, this may take long calculation times. Therefore, some approximating theories have been developed. In the next section, the Rayleigh theory, which is the approximation for small particles, will be described. The insights obtained from this theory will be sufficient for most dynamic light scattering applications.

2.3.3 Rayleigh theory

This theory is valid for particles that are small compared to the wavelength of light. When a beam of light strikes such a particle, the particle is assumed to react as a single oscillating dipole. The intensity $I_p$ scattered by a single particle, as a function of the scattering angle $\theta$ is given by:

$$\frac{I_p}{I_{0,u}} = \frac{8\pi^4}{\lambda^4 R^2} \left( \frac{p}{4\pi \varepsilon_0} \right)^2 (1 + \cos^2 \theta), \quad (2.19)$$
where $I_{0,u}$ is the intensity of the unpolarised incident light and $R$ is the distance from the particle to the detector. The polarisability of the particle, $p$, is a measure of the ease with which the electrons in the particle can be displaced, and is therefore a measure of the magnitude of the dipole that is created when a light wave interacts with the particle. It is proportional to the volume of the particle:

$$p = \frac{\pi \varepsilon_0 d^3}{2} \frac{n^2 - 1}{n^2 + 2}. \quad (2.20)$$

Some important findings from equations 2.19 and 2.20 are, that the scattering intensity increases with the 6th power of the particle diameter, and with the inverse 4th power of the wavelength of the light. This wavelength-dependence is the reason why the sky is blue: of the whole spectrum of light coming from the sun, the molecules in the atmosphere scatter the blue light stronger than the light with longer wavelengths.

The effect of polarisation of the incident light beam on the angular scattering intensity is shown in Figure 2.5. To obtain a maximum scattered intensity at all angles, dynamic light scattering measurements are usually done using a laser source that is polarised perpendicular to the scattering plane.

![Figure 2.5: Polar diagram of Rayleigh scattering. 1: polarised with electric vector \( \perp \) plane of drawing, 2: polarised with electric vector in plane of drawing, 1+2: total. From [22].](image)

2.4 Dynamic light scattering

In static light scattering experiments, the wavelength of the incident and the of scattered light are assumed to be the same. Therefore, it is also called elastic light scattering. For moving particles however, the wavelength of the scattered light has undergone a small frequency shift due to the Doppler effect. This effect is the result of a relative motion between the source and the receiver of light. A well known comparable effect takes place for sound: the tone of an ambulance that is moving towards an observer, is higher than the tone of the same ambulance that is moving away from this observer.

Because dynamic light scattering makes use of the small Doppler frequency shift, it is also referred to as quasi-elastic light scattering (QUELS). The frequency shifted
light can be analysed both in the frequency domain by spectral analysis, or in the
time domain by photon correlation spectroscopy or photon counting statistics. In this
thesis, photon correlation spectroscopy is used.

For dynamic light scattering experiments, an ensemble of particles is needed to
create the changing interference pattern. The scattering geometry is shown in Figure 2.6.

![Figure 2.6: Geometry for dynamic light scattering experiments. The light scattered at an angle $\theta$ is detected by a photomultiplier. The scattering vector $\mathbf{q}$ is the difference between the incident and the scattered wave vector.](image)

The incident light beam is coherent: at each cross-section of the beam, the phase
is constant. However, scattered light that reaches the detector has travelled a total
distance from the source, via a particle, to the detector. The exact distance that a
ray of light travels depends on the location of the scattering particle. Light scattered
from an ensemble of particles has a distribution of traveled path lengths, and therefore a distribution of phases. Depending on the phase differences between the rays,
constructive or destructive interference takes place at the detector surface. When the
relative particle positions change due to movement of the particles, the distribution
of phases and thereby the interference pattern changes.

At a certain time $t$, the amplitude of the scattered field as it reaches the detector,
is the sum of the complex amplitudes of the fields scattered by all the $N_{tot}$ individual
particles in the system:

$$E(t) = \sum_{j=1}^{N_{tot}} e(\mathbf{r}_j(t)) \exp[\mathbf{i} \mathbf{q} \cdot \mathbf{r}_j(t)].$$

(2.21)

The amplitude factor $e(\mathbf{r}_j)$ depends on the position $\mathbf{r}_j$ of the particle in the laser
beam. The scattering vector \( \mathbf{q} \) is defined in Figure 2.6 and has a magnitude:

\[
q = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2}.
\]  

(2.22)

The ray scattered by a particle at position \( \mathbf{r}_j \) will have a phase difference relative to a ray path that passes through the origin, of \( \mathbf{k}_j \cdot \mathbf{r}_j - \mathbf{k}_0 \cdot \mathbf{r}_j = \mathbf{q} \cdot \mathbf{r}_j \).

A different representation of the amplitude of the total scattered field from equation 2.21, is that of a random walk in the complex plane, as is shown in Figure 2.7. For uniform illumination, this is a random walk with constant step length [37]. For

\[\text{Figure 2.7: Coherent multi-particle scattering, represented as a two-dimensional random walk in the complex plane. In this case, the total field scattered from 6 particles is the net displacement after 6 random steps.}\]

an illumination profile that is Gaussian in three dimensions, the step length has a Gaussian distribution. The angles between steps are random, because the position of the particles is random and therefore \( \mathbf{q} \cdot \mathbf{r}_j \) is a random variable.

The total intensity scattered by the ensemble of particles is found from the square of the sum of the electric fields:

\[
I_s (t) = \frac{\varepsilon_0}{2} \sum_{l,m=1}^{N_{\text{tot}}} e (\mathbf{r}_l (t)) e (\mathbf{r}_m (t)) \exp \{ i \mathbf{q} \cdot (\mathbf{r}_l (t) - \mathbf{r}_m (t)) \}
\]

(2.23)

\[= \frac{\varepsilon_0}{2} \sum_{j=1}^{N_{\text{tot}}} \left[ e (\mathbf{r}_j (t)) \right]^2 \]
2.4. Dynamic light scattering

\[ + \frac{c\varepsilon_0}{2} \sum_{l \neq m=1}^{N_{\text{tot}}} e(r_l(t))e(r_m(t)) \exp[iq \cdot (r_l(t) - r_m(t))], \]

where the first term represents the time average of the scattered intensity, \( \langle I_s \rangle \), and the second term is the fluctuating part. This fluctuating part can be anywhere in the range between \(-\langle I_s \rangle\) and about \( \langle I_s \rangle \). The time between the occurrence of the two extremes of \( I_s \) can be roughly estimated as the time required for two particles to move with respect to each other far enough to change the phase of their scattered light with \( \pi \) radians.

### 2.4.1 Photon correlation spectroscopy

For a quantification of the frequency of the intensity fluctuations, autocorrelation is used. The field autocorrelation function \( G^{(1)}(\tau) \) is defined as:

\[ G^{(1)}(\tau) = \langle E^*(t) E(t + \tau) \rangle = \langle E^*(0) E(\tau) \rangle, \quad (2.24) \]

where the superscript * denotes the complex conjugate, and the brackets denote a time average. Filling in the total scattered field from equation 2.21 gives:

\[ G^{(1)}(\tau) = \sum_{l,m=1}^{N_{\text{tot}}} \langle e(r_l(0))e(r_m(\tau))\exp[iq \cdot (r_m(\tau) - r_l(0))] \rangle \]

\[ = \sum_{l,m=1}^{N_{\text{tot}}} \langle e(r_l(0))e(r_m(\tau)) \rangle \langle \exp[iq \cdot (r_m(\tau) - r_l(0))] \rangle. \quad (2.25) \]

This factorisation of the sum is allowed when the motions of the different particles are uncorrelated. The field autocorrelation function is normalised by dividing by the average of the squared field:

\[ g^{(1)}(\tau) = \frac{\langle E^*(0) E(\tau) \rangle}{\langle (E(0))^2 \rangle} \quad (2.26) \]

\[ = \frac{\sum_{l,m=1}^{N_{\text{tot}}} \langle e(r_l(0))e(r_m(\tau)) \rangle \langle \exp[iq \cdot (r_m(\tau) - r_l(0))] \rangle}{\sum_{j=1}^{N_{\text{tot}}} \langle e(r_j(0))e(r_j(0)) \rangle} \]

\[ = \langle \exp[iq \cdot (r(\tau) - r(0))] \rangle_p. \]

Here \( \langle \rangle_p \) denotes an ensemble average over all the particles. For Brownian motion, the probability distribution \( W(r(t);r(0)) \) of a displacement \( r(t) - r(0) \) was given in
equation 2.4. Combining these equations gives:

\[
g^{(1)}(\tau) = \int W(r(\tau); r(0)) \exp[iq \cdot (r(\tau) - r(0))] d^3r
\]

\[
= \frac{1}{(4\pi D\tau)^{3/2}} \int_{-\infty}^{\infty} \exp \left[ -\frac{(r(\tau) - r(0))^2}{4D\tau} \right] \exp[iq \cdot (r(\tau) - r(0))] d^3r
\]

\[
= \exp[-Dq^2\tau]. \quad (2.27)
\]

In the optical configuration used in this thesis and shown in Figure 2.6, photon correlation spectroscopy is performed in the self-beat mode, which means that besides the light that is scattered by the Brownian particles, no other light reaches the detector. In that case, it is not possible to determine \(g^{(1)}\) in a direct way, since it is not possible to measure the field directly. The only accessible parameter is the scattered intensity, which can be measured with a photomultiplier or photodiode. The intensity fluctuations are then measured as a fluctuating photocurrent \(i(t)\), or as fluctuations in the photon count rate \(n_{\Delta T}(t)\), which is the number of photons detected during a time interval \(\Delta T\). Therefore, what is directly measured is the intensity autocorrelation function:

\[
G^{(2)}(\tau) = \langle I_s(0) I_s(\tau) \rangle, \quad (2.28)
\]

which is normalised to give:

\[
g^{(2)}(\tau) = \frac{\langle I_s(0) I_s(\tau) \rangle}{\langle I_s \rangle^2}. \quad (2.29)
\]

The relationship between \(g^{(1)}\) and the measured \(g^{(2)}\) is not always simple. In the special case where the distribution of \(E(t)\) is Gaussian, which is true for a large number of independently moving particles in Brownian motion, the Siegert-relation is obtained:

\[
g^{(2)}(\tau) = 1 + \beta_{coh} g^{(1)}(\tau)^2. \quad (2.30)
\]

Here \(\beta_{coh}\) is the spatial coherence factor, which is the result of the spatial integration of the scattered intensity over the surface area of the detector, and of the temporal integration of the scattered intensity over the sample time of the correlator. The effect of the temporal integration can usually be neglected, but the spatial coherence is an important parameter in the design of an experimental setup and will be discussed in the next paragraph.

### 2.4.2 Coherence

The instantaneous interference pattern of light that is scattered by an ensemble of small particles, is a pattern of dark and light areas, so-called 'speckles'. The fluctuating interference pattern can be seen as the displacement of these speckles. A detector
that measures the instantaneous intensity that is collected on its surface, will measure the strongest fluctuations when its surface area is small compared to the size of one speckle.

The normalised variance of the intensity comes back in the intensity correlation function $g^{(2)}$ as the spatial coherence factor $\beta_{coh}$ [26]. This coherence factor has a value of 1 for point sources and point detectors, and decreases when the size of the scattering volume or the surface area of the detector increases. For a circular detector surface with radius $B$, the coherence factor has been derived by Jakeman et al. [24]:

$$\beta_{coh} = \sum_{s=0}^{\infty} \left( \frac{(2s + 2)!}{((s + 1)!)^2 (s + 2)!} \right)^2 (-1)^s \left( \frac{1}{2} \kappa B \right)^{2s},$$  (2.31)

where $\kappa = k_0 \sigma / 2R$, $\sigma$ is the radius of the scattering volume and $R$ is the mean distance from the scattering volume to the detector.

2.5 Conclusions

The theory presented in this chapter describes how the intensity fluctuations of light scattered by an ensemble of submicron particles are related to, and can be used to measure, the particle size. The assumptions on which this theory is based, set the limits for its application. When any of these assumptions is not justified, care must be taken in the interpretation of measurement results. The most important assumptions are the following:

*The particle size distribution is monodisperse.*

For a polydisperse particle size distribution, the field autocorrelation function of equation 2.27 changes to contain the weighted sum of the diffusion coefficients of each size fraction [13]:

$$g^{(1)}(\tau) = \sum_{i=1}^{n} c_i \exp \left[ -D_i q^2 \tau \right],$$  (2.32)

where $c_i$ is the normalised intensity weight of the particles with diffusion coefficient $D_i$.

*There is only single scattering.*

At high particle concentration, there can be double or even multiple scattering, which means that a ray of light is scattered by more than one particle before it reaches the detector. The result is that the measured particle size is too small.

At very high particle concentration, multiple scattering can be used to the advantage. In that case, the technique of diffusing wave spectroscopy [33] is used, which even requires the number of scattering events to be 100 or more. The technique is based on the assumption that photons from the incident beam diffuse by means of
repeated scattering as they propagate through the sample.

*The particles move independently.*
This means that there is no interaction between the particles, and requires the particle concentration to be not too high. The limiting concentration depends on the type of interaction and on the particle size. For smaller particles, the limit is reached at a lower volume fraction.

*The amplitude distribution of the scattered field is Gaussian.*
At low particle concentration, when there are less than about 100 particles in the scattering volume, the amplitude distribution of the scattered field is no longer Gaussian and the Siegert relation given by equation 2.30 no longer holds. The effects of a low particle concentration are discussed in Chapter 3 and Chapter 4 of this thesis.

*The only particle movement is the Brownian motion.*
When there is an additional source of particle motion, the probability distribution of a particle displacement \( r(t) - r(0) \) will deviate from the one that is used in equation 2.27. Chapter 5 deals with the influence of overall flow, and specifically turbulent flow.
Dynamics of particle number fluctuations

In photon correlation spectroscopy measurements at low particle concentration, fluctuations in the number of particles in the scattering volume result in an extra decay in the autocorrelation function. This chapter deals with this so called "number fluctuation decay" which, under certain conditions, can be used to measure the particle concentration. Simulations and experiments showed that these conditions are twofold: the size and shape of the scattering volume must be well known, and the measurement time must be sufficiently long.

3.1 Introduction

The theory presented in Chapter 2 about photon correlation spectroscopy is based on the assumption that the number of particles in the scattering volume is large (> 100). At lower concentrations, fluctuations in the number of particles in the scattering volume lead to fluctuations in the average scattered intensity, which will result in an extra decay in the autocorrelation function. Because the intensity fluctuations due to a changing number of particles in the scattering volume, are much slower than the intensity fluctuations due to the Brownian motion, the autocorrelation function will decay on two widely separated time scales. In the literature on number fluctuations, several terms are in use to describe these two decays. They are given Table 3.1.

<table>
<thead>
<tr>
<th>first decay</th>
<th>second decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>coherent decay</td>
<td>incoherent decay</td>
</tr>
<tr>
<td>fast decay</td>
<td>slow decay</td>
</tr>
<tr>
<td>Brownian motion decay</td>
<td>number fluctuation decay</td>
</tr>
</tbody>
</table>
Figure 3.1: Measured autocorrelation functions at different concentrations of 204 nm latex spheres in water. The scattering angle was 90°.

The effect of the number fluctuations becomes visible in the measurements shown in Figure 3.1. At a particle concentration of $8.7 \cdot 10^8$ particles per cm$^3$, the autocorrelation function shows a single exponential decay, as was predicted by the Siegert relation of equation 2.30. The autocorrelation function at a concentration about 100 times lower, clearly shows an extra decay, at a timescale of about 1 second.

The particle concentration at which number fluctuations start to play a role, depends on the size of the scattering volume. In a typical experimental setup, this size is of the order of $10^{-6}$ cm$^3$. This means that number fluctuations appear when the particle concentration is below about $10^8$ particles/cm$^3$.

In this chapter, the dynamics of the particle number fluctuations that are responsible for the slow decay will be described. It will be shown that, in this decay, information about the particle concentration is contained. However, for this information to be obtained from a real measurement, it will turn out that the duration of a measurement is an important factor. Besides that, the scattering volume must be precisely defined. With the insights obtained in this chapter, the influence of the low concentration on size measurement will be discussed in Chapter 4.

3.2 Scattering volume

When the movement of particles in and out of the scattering volume is studied, it is of course essential to have a clear definition of this scattering volume. The difficulty is that the scattering volume does not have definite boundaries, but is in fact determined by the intensity profile of the laser beam and by the profile as it passes through the detection optics.

The description of the scattering volume will be done on the basis of the optical configuration that has been used for the experiments in this chapter. This is the
3.2. Scattering volume

![Diagram of scattering setup]

**Figure 3.2:** The Brookhaven Instruments Model BI-200-SM goniometer setup. P₁, P₂ and P₃ are 3 mm apertures, L₁ and L₂ are lenses, S is a 200 µm slit, BS is a beam stop and P₄ is a variable pinhole. The quartz vat is filled with decaline as index-matching liquid.

Commercially available Brookhaven Instruments BI-200-SM goniometer setup. This standard setup is chosen because it is robust and accurate. A schematic drawing is given in Figure 3.2. First, the laser beam is focused by lens L₁ into the centre of the sample vessel. This vessel is placed in a quartz vat which is filled with decaline. Decaline has the same refractive index as glass, and this way refraction of the incoming and scattered light is minimised. At the end of the vat, a beam stop minimises back reflection of the incident beam.

The laser beam operates in the TEM₀₀ mode. In this mode, the beam has a Gaussian intensity profile. Since the incident beam is travelling in the y-direction, the intensity variations are in the xz-plane. This is described here as variations in the amplitude factor:

\[ e(r) = E_{\text{max}} \exp \left[ -\frac{x^2 + z^2}{w^2} \right], \quad (3.1) \]

where \( E_{\text{max}} \) is the field at the centre of the laser beam and \( w \) is the radius of the beam where the intensity has dropped to \( 1/e^2 \) of its maximum value. The lens focuses the beam into a *beam waist* of \( w_0 \):

\[ w_0 = \frac{\lambda f}{\pi w}, \quad (3.2) \]

where \( f \) is the focal length of the lens. The beam waist at the focal point is thus inversely proportional to the radius of the unfocused beam. Outside of the focal point, the beam diverges. The axial distance from the focal point where the beam radius
Figure 3.3: Schematic drawing of the scattering volume. The beam is focused into a waist of radius $w_0$. The detection optics project a length $2l$ of the beam on the photomultiplier.

has increased by a factor $e$ is given by the Rayleigh range:

$$y_R = \frac{\pi w_0^2}{\lambda},$$  \hspace{1cm} (3.3)

so the smaller the beam waist, the stronger it diverges. For the lenses used in the experiments of this thesis, the Rayleigh range was long enough for the beam radius to stay constant throughout the scattering volume. The shape of the scattering volume is shown in Figure 3.3. The intensity profile of the detected beam depends on the configuration of the detection optics. It is usually assumed that the 'smearing out' of the intensity due to diffraction at the slit can also be described by a Gaussian profile. In our optical system, the laser beam propagates in the positive $y$-direction, and the detector is placed in the $xy$-plane at an angle $\theta$. The detected amplitude of the electric field scattered by a particle at position $r_j$ is given by the product of the laser beam profile and the detection optics profile:

$$e(r_j) = E_{max} \exp \left[-\frac{x_j^2 + z_j^2}{w_0^2}\right] \exp \left[-\frac{(x_j \cos \theta - y_j \sin \theta)^2}{l^2}\right],$$  \hspace{1cm} (3.4)

where $2l$ is the length of the beam that is projected onto the photomultiplier. Because $e(r_j)$ is a continuous function, the scattering region does not have a well-defined volume. Therefore, the effective scattering volume $V$ is defined as the intensity function $(e(r)/E_0)^2$ integrated over all space:

$$V = \frac{\pi}{2} \frac{w_0^2 l}{\sin \theta}.$$  \hspace{1cm} (3.5)

In our experimental setup, the beam waist is 55.2 $\mu$m and the radius of the detected beam is 40.2 $\mu$m. This results in an effective scattering volume of $2.4 \times 10^{-7}/(\sin \theta)$ cm$^3$.
If, however the profile of the detection optics is not Gaussian, but is assumed to be homogeneous across the slit width, the electric field amplitude factor becomes:

\[
e(r_j) = \begin{cases} 
E_{max} \exp \left[ -\frac{x_j^2 + z_j^2}{w_0^2} \right] & \text{if } (x_j \cos \theta - y_j \sin \theta) \leq l \\
0 & \text{if } (x_j \cos \theta - y_j \sin \theta) > l.
\end{cases}
\] (3.6)

This leads to the following **hard-ended** effective scattering volume:

\[
V_h = \pi \frac{w_0^2 l}{\sin \theta}.
\] (3.7)

Since the optical configuration of the Brookhaven BI-200-SM is such that the effect of slit diffraction is reduced to a minimum [9], equation 3.7 may be more appropriate than equation 3.5. The size of the effective scattering volume is then \(3.8 \cdot 10^{-7} / (\sin \theta)\) cm³. Because the actual profile is probably in-between those two, both the Gaussian/Gaussian scattering volume and the hard-ended/Gaussian scattering volume are used in the calculations in this chapter.

### 3.3 Particle number fluctuations

The first studies of particle number fluctuations were made using microscopic observations of small volumes of a colloid system. Svedberg [43] followed the number of microscopically visible colloid particles in time, and was able to derive the diffusion coefficient from these number fluctuations.

The first measurements of number fluctuations using photon correlation spectroscopy were made by Schaefer [38, 36]. He derived the intensity autocorrelation function that includes the so-called non-Gaussian concentration fluctuations. The term non-Gaussian refers to the fact that when the number of particles in the scattering volume is small, the amplitude distribution of the scattered field is no longer Gaussian. In that case, the Siegert relation (equation 2.30) no longer applies, and the intensity autocorrelation function now also contains a term describing the particle number fluctuations:

\[
g^{(2)}(\tau) = 1 + \beta_{coh} \exp \left[ -2Dq^2\tau \right] + \frac{\langle \delta N(0) \delta N(\tau) \rangle}{\langle N \rangle^2}
\] (3.8)

Here, \(\langle N \rangle\) is the average number of particles in the scattering volume and \(\delta N(\tau) = N(\tau) - \langle N \rangle\) is the fluctuation of the total number of particles in the scattering volume. The correlation of these number fluctuations is:

\[
\langle \delta N(0) \delta N(\tau) \rangle = \frac{\langle N \rangle}{V} \iint \left( \frac{e(r_1)}{E_0} \right)^2 \left( \frac{e(r_2)}{E_0} \right)^2 W(r_2(\tau) ; r_1(0)) \, dr_1 \, dr_2,
\] (3.9)
where \( W(\mathbf{r}_2(\tau) \mid \mathbf{r}_1(0)) \) is the probability already mentioned in equation 2.4, that a particle will be at position \( \mathbf{r}_2 \) at time \( \tau \) if it was at position \( \mathbf{r}_1 \) at time 0. When these equations are worked out, the following autocorrelation function is obtained:

\[
g^{(2)}(\tau) = 1 + \beta_{\text{coh}} \exp \left[-2Dq^2\tau\right] + \gamma \frac{1}{\langle N \rangle} \left(1 + \frac{4D\tau}{w_0^2}\right)^{-1} \left(1 + \frac{4D\tau}{l^2}\right)^{-1/2}.
\] (3.10)

The volume contrast factor \( \gamma \) is a result of the fact that the effective volume decreases when it is squared [7]. The value depends on the shape of the scattering volume. In fact, it can be calculated for any shape, using:

\[
\gamma = \frac{\int \left(\frac{\epsilon(\mathbf{r})}{E_0}\right)^4 d\mathbf{r}}{\int \left(\frac{\epsilon(\mathbf{r})}{E_0}\right)^2 d\mathbf{r}}.
\] (3.11)

Table 3.2 summarises the results for effective scattering volume and for the volume contrast factor.

**Table 3.2:** Effective scattering volume and volume contrast factor \( \gamma \) for different intensity profiles.

<table>
<thead>
<tr>
<th>intensity profile</th>
<th>( V_0 )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>spherical Gaussian</td>
<td>( \left(\frac{\pi}{2}\right)^{3/2} \frac{w_0^2l}{\sin \theta} )</td>
<td>( \left(\frac{1}{2}\right)^{3/2} )</td>
</tr>
<tr>
<td>hard-ended Gaussian</td>
<td>( \pi \frac{w_0^2l}{\sin \theta} )</td>
<td>( \frac{1}{2} )</td>
</tr>
</tbody>
</table>

The correlation function of equation 3.10 decays on two time scales. The fast decay reflects the changes in phase difference of the scattered fields due to the Brownian motion. This is why it is also called the coherent part of the correlation function. The slow decay reflects the diffusion of particles through the scattering volume. Because the average number of particles in the scattering volume, \( \langle N \rangle \), is proportional to the reciprocal height of the number fluctuation decay, measurements at low particle concentrations can, in principle, be used for the determination of the concentration.

A problem with this concentration measurement however, was already reported by Schaefer [38]. He found that, especially at small \( \langle N \rangle \), a large variation in the measured number fluctuation decay is found, due to the long time constant associated with the number fluctuations. This was also observed in our experiments. The magnitude of these variations is shown in Figure 3.4 and clearly increases at decreasing concentration. In our measurements, we also observed that the variation in the number fluctuation decay decreased when the duration of the measurement was increased.
3.4 Simulations

In order to obtain a better understanding of the dynamics of the number fluctuations, we studied the influence of the measurement time, using both simulations and experiments. In the next section, the simulations will be described and analysed, and after that, experimental verification of the simulation results will be presented.

3.4 Simulations

The characteristic time for the number fluctuation decay is $\tau_N = \sigma^2/4D$, where $\sigma$ is the radius of the scattering volume. For the geometry of the Brookhaven BI-200-SM, where $\sigma \approx 50 \, \mu m$, and for a liquid suspension of particles of $\pm 200 \, nm$, $\tau_N$ is $\pm 5$ minutes. However, for the number fluctuation decay to be developed completely, a measurement should last longer than $\tau_N$. We made simulations of photon correlation spectroscopy measurements to study what the effect is of the duration of a measurement, on the development of the number of particles in the scattering volume and on the autocorrelation function.

3.4.1 Model

The simulation geometry is a spherical scattering volume, placed in the centre of the much larger, cubic simulation volume containing $M$ particles. At first, the particle system is generated by placing the $M$ particles regularly into the simulation volume. Next, the particles are given Brownian displacements, taken randomly from the probability distribution of equation 2.4:

$$W(\Delta x) = \frac{1}{\sqrt{4\pi Dt}} \exp \left[ -\frac{\Delta x^2}{4Dt} \right].$$ (3.12)
The same is done for the $y$ and $z$-directions. This approach is permitted when the time step $t$ is much longer than the particle relaxation time $\tau_r = m/(3\pi d \eta)$, where $m$ and $d$ are the mass and the diameter of the particle, and $\eta$ is the viscosity of the liquid. For liquid dispersions, the experimentally accessible delay times of a photon correlation experiment are always much longer than the particle relaxation time. Therefore, the Brownian motion in such dispersions can be safely approximated by these random, independent displacements.

The size of the cubic simulation volume is chosen large enough, that the probability is effectively zero that a particle located initially within the scattering volume leaves the cubic simulation volume in one time step. Particles, located close to the cubic volume boundary, that would leave the volume during a Brownian motion step, do not bounce at the boundary planes, but re-enter the volume on the opposite side. The initially regularly placed particles are given enough Brownian displacements, so that at the beginning of a simulation they are randomly distributed throughout the cubic simulation volume.

A simulation consists of a number of equal time steps. For each time step, the new particle configuration is determined from the random Brownian displacements. For this particle configuration, the intensity at the detector surface is calculated from the amplitude and phase of the fields scattered by all the particles. At high particle concentration, the autocorrelation function of these intensities is in agreement with the calculated autocorrelation function, as is shown in Figure 3.5.

Both the situations of the Gaussian/Gaussian scattering volume and of the hard-ended/Gaussian scattering volume are considered.

Also, for each particle configuration, the effective number of particles in the scat-

![Figure 3.5](image)

**Figure 3.5:** Simulated autocorrelation function for a high concentration of 501 nm spheres in water, with a scattering angle of 45°.
3.4. Simulations

Scattering volume is calculated for the Gaussian/Gaussian case via:

$$ N = \sum_{j=1}^{M} \left( \left( \exp \left[ -\frac{x_j^2 + z_j^2}{w_0^2} - \frac{(x_j \cos \theta - y_j \sin \theta)^2}{l^2} \right] \right)^2 \right), \quad (3.13) $$

and for the hard-ended/Gaussian case via:

$$ N = \sum_{j=1}^{M} \left\{ \left( \exp \left[ -\frac{x_j^2 + z_j^2}{w_0^2} \right] \right) \right\}^2, \quad (3.14) $$

where $M_j$ is the number of particles for which $(x \cos \theta - y \sin \theta) \leq l$.

3.4.2 Results

The simulations presented here were made with 204 nm particles at a concentration of $2.0 \cdot 10^6$ particles/cm$^3$ and a scattering angle of 60°. This corresponds to the measurements of the dispersions in liquid that are shown as dotted lines in Figure 3.4. The size of the scattering volume was chosen the same as in the Brookhaven goniometer setup: $w_0 = 55.2$ μm and $l = 40.2$ μm. The average effective number of particles in the scattering volume is then 0.5575 for the Gaussian/Gaussian case, and 0.8896 for the hard-ended/Gaussian case. For both cases, the autocorrelation function of the detected intensities was calculated. Although the intensity is used for calculating the autocorrelation function, it are the fluctuations in the particle number that are responsible for the number fluctuation decay. Therefore, the interesting parameter to follow is the effective particle occupation number in the course of the simulation. An example of this is shown in Figure 3.6. This figure makes clear how the intensity

![Figure 3.6: Fluctuations of the particle occupation number and of the scattered intensity.](image)
fluctuations follow the number fluctuations. The extra fluctuations observed for the intensity are the result of interference. Their time scale is clearly much shorter than that of the number fluctuations.

When a large number of independent samples is taken, the occupation number of a scattering volume with hard-ended boundaries in all 3 dimensions can be described by Poisson statistics:

\[ P(N) = \frac{(N)^N}{N!} \exp[-\langle N \rangle]. \tag{3.15} \]

Here \( P(N) \) is the probability of finding \( N \) particles in the scattering volume. One of the characteristics of the Poisson distribution is that the variance is equal to the average: \( \text{Var}(N) = \langle N \rangle \). However, this is not what we find from the occupation number statistics of the simulation results (Figure 3.7). These results show that for large simulation times, the relative variance of \( N \) approaches a constant value, but not \( \langle N \rangle \). For the Gaussian/Gaussian case, \( \text{Var}(N)/\langle N \rangle \) approaches \( 2^{-3/2} \), and for the hard-ended/Gaussian case it approaches \( 2^{-1} \). Similar to the factor \( \gamma \) in the correlation function of equation 3.10, this value of the variance is a result of the fact that the effective (Gaussian) volume decreases when it is squared.

For these simulations, the characteristic number fluctuation decay time \( \tau_N \) is \( \pm 300 \) s. However, from Figure 3.7 it can be concluded that a measurement should last at least \( 100 \cdot \tau_N \) for the variance of \( N \) to become constant. It is interesting to know what autocorrelation function will be obtained when the measurement time is shorter than \( 100 \cdot \tau_N \). For a simulation with time steps of 10 s, autocorrelation functions were calculated after different measurement durations. For each simulation time, the

\[ \begin{align*}
\text{(a) Gaussian/Gaussian scattering} & \quad \text{(b) hard-ended/Gaussian scattering} \\
\text{volume.} & \quad \text{volume.}
\end{align*} \]

**Figure 3.7:** The relative variance of the number of particles in the scattering volume is not constant for short simulation times.
3.4. Simulations

Table 3.3: Simulation results for the average and the variance of the number of particles in the scattering volume, and for the height of the number fluctuation decay of the autocorrelation function.

<table>
<thead>
<tr>
<th>duration [s]</th>
<th>Gaussian/Gaussian</th>
<th>hard-ended/Gaussian</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average $N$</td>
<td>Var($N$)</td>
</tr>
<tr>
<td>100</td>
<td>0.148</td>
<td>0.003</td>
</tr>
<tr>
<td>700</td>
<td>0.165</td>
<td>0.009</td>
</tr>
<tr>
<td>1000</td>
<td>0.441</td>
<td>0.233</td>
</tr>
<tr>
<td>10000</td>
<td>0.640</td>
<td>0.271</td>
</tr>
<tr>
<td>26000</td>
<td>0.608</td>
<td>0.179</td>
</tr>
<tr>
<td>100000</td>
<td>0.510</td>
<td>0.171</td>
</tr>
</tbody>
</table>

average and the variance of the number of particles in the scattering volume, and the height of the number fluctuation decay are listed in Table 3.3. The number of particles, averaged over the total simulation time will be written as $\langle N \rangle_m$, to distinguish it from the calculated, expected average number, $\langle N \rangle$, that would be obtained for an infinitely long simulation or measurement time.

The simulated height of the number fluctuation decay and that calculated using $\gamma/\langle N \rangle_m$ are plotted in Figure 3.8-a. Only at simulation times of 10000 s and

![Figure 3.8a and 3.8b](image)

(a) The solid line is the value that should be obtained for long simulation times.

(b) The height of the measured number fluctuation decay depends on the average number in the scattering volume, but also on its variance.

Figure 3.8: Simulation results for the height of the number fluctuation decay for the Gaussian/Gaussian scattering volume.
longer is the correct height found. Also, it is clear that for shorter simulation times, the height can not be predicted by $\gamma/\langle N \rangle_m$. A more appropriate value would be $(\text{Var}(N)/\langle N \rangle_m)/\langle N \rangle_m$, because the relative variance is a measure of how much the occupation number fluctuates. As shown in Figure 3.8-b, this fits indeed the measured values very well.

From these simulations, it can be concluded that a correct concentration measurement can only be made when the occupation number, averaged over the duration of a measurement, $\langle N \rangle_m$ approaches the expected average occupation number. Besides that, the measurement should last long enough for $(\text{Var}(N)/\langle N \rangle_m)$ to approach $\gamma$. When the duration of a measurement is $< 100 \cdot \tau_N$, the value of $(\text{Var}(N)/\langle N \rangle_m)$ is much lower than $\gamma$, and the height of the number fluctuation decay is too low, resulting in a concentration measurement that is too high. When the duration of a measurement is longer, but still $< 100 \cdot \tau_N$, the value of $(\text{Var}(N)/\langle N \rangle_m)$ fluctuates around $\gamma$, and approximately the correct concentration is found, but still with a large standard deviation.

### 3.5 Photon correlation experiments

To check how this theory applies, experiments were carried out with samples of low concentration. In the first series, the measurement time was constant and the particle concentration was varied. In the second series, the particle concentration was constant and the measurement time was varied. The particles used were 204 nm polystyrene nanospheres supplied by Duke Scientific (lot# 20613) and diluted with filtered water. The light source was a vertically polarised Lexel 95 Argon laser, operating at a wavelength of 514.5 nm. The samples were placed in a Brookhaven BI-200-SM goniometer, on which the angle could be set with 0.1° accuracy. The alignment at all angles was confirmed before and after the measurements to make sure that the scattering volume was indeed located at the focal point of the lens. The scattered light was detected through the Brookhaven BI-200-SM detection optics into an ALV-SO/SIPD photomultiplier, and the signal was then sent to an ALV-5000/E correlator board.

#### 3.5.1 Concentration variation

At a scattering angle of 60°, measurements of two minutes were made for particle concentrations between $2.0 \cdot 10^6$ and $2.3 \cdot 10^9$ particles/cm$^3$. This measurement duration is much smaller than $100 \cdot \tau_N$. Pinhole diameters of 100 and 200 μm were used. Some of the measured autocorrelation functions are shown in Figure 3.9. The correlation function measured at $4.5 \cdot 10^6$ particles/cm$^3$ shows a horizontal plateau before the number fluctuation decay, whereas the correlation function measured at $2.0 \cdot 10^6$ particles/cm$^3$ shows a continuous decay connecting the coherent and the number fluctuation decay. For each measurement, the height of the number fluctuation...
3.5. Photon correlation experiments

**Figure 3.9:** Measured correlation functions at different particle volume fractions at a scattering angle of 60° and with a pinhole diameter of 200 μm.

decay is obtained from a least-squares fit of the correlation function of equation 3.10. In Figure 3.10, the resulting values of the height of the number fluctuation decay and the calculated expected values are shown. From this figure, it is concluded that all of the heights measured at these short measurement durations are too low, which means that the variance of the occupation number is too low for measurement times ≪ τ_N. Furthermore, this figure makes clear that the exact intensity profile of the scattering volume has only a small effect on the final expected height of the decay. Precisely, the concentration that would be found using the assumption of a Gaussian/Gaussian scattering volume is a factor 2/\sqrt{\pi} higher than the concentration that would be found using the assumption of a hard-ended/Gaussian scattering volume.

**Figure 3.10:** The height of the number fluctuation decay of the 2-minute measurements is lower than the calculated height for long measurement times.
Figure 3.11: The measured height of the number fluctuation decay increases with measurement time, but the measurements are still too short to draw conclusions about the shape of the scattering volume (Gaussian in three or in only two dimensions).

3.5.2 Measurement duration

The development of the number fluctuation decay with time is determined from experiments with measurement durations ranging from 30 seconds to 1 hour. The concentration was $2.0 \cdot 10^6$ particles/cm$^3$. In Figure 3.11, the measured height of the number fluctuation decay is shown to increase with measurement time. This confirms the simulation results. However, for the calculated, expected height to be obtained, a measurement time of 10 hours would be needed, which is too long for practical photon correlation spectroscopy measurements.

Of course, the required measurement time can be decreased by choosing a smaller

Figure 3.12: The time to reach a constant value for the relative variance of the number of particles in the scattering volume increases when the particle concentration decreases. The number beside each curve represents the $\langle N \rangle$ that was used in the simulation. A scattering volume with radius $\sigma = 5 \, \mu m$ was used.
scattering volume. A factor 10 decrease in the dimension of the scattering volume, would lead to a factor 100 decrease in $\tau_N$. However, this would also lead to a factor 1000 decrease in $\langle N \rangle$. At low concentration, this would lead to a drastic decrease of the probability of finding a particle near the centre of the scattering volume. This results in an increase in the time that is necessary to reach a constant value for $\text{Var}(N)/\langle N \rangle_m$. Simulations show that this increase in measurement time starts at particle occupation numbers below $\langle N \rangle = 0.2$. Some typical simulation results are plotted in Figure 3.12.

### 3.5.3 Photon counting histogram

From the simulations, it became clear that the relative variance of the occupation number during an experiment is an important parameter. Unfortunately however, in an experiment it is not possible to follow the relative variance of the occupation number in time. The only accessible parameter is the photon count rate. Some measured photon counting histograms are shown in Figure 3.13-a.

In Figure 3.13-b, the relative variance of the photon counts is plotted against the height of the measured number fluctuation decay. The relative variance of the intensity depends on the particle concentration and on the intensity of the incident laser beam, but is also found to be proportional to the height of the number fluctuation decay. This implies that following $(\text{Var}(I)/\langle I \rangle)$ during a measurement can be used to show when it has reached a constant value (but not $\gamma!$). That can be used to indicate that the measurement time has been sufficiently long.

![Photon counting histograms](image1)

| 4.5 $10^9$ particles/cm$^3$, 50 mW laser power |
| 2.0 $10^9$ particles/cm$^3$, 50 mW laser power |
| 2.0 $10^9$ particles/cm$^3$, 250 mW laser power |

![Variance of the measured intensity](image2)

| 4.5 $10^9$ particles/cm$^3$, 50 mW laser power |
| 2.0 $10^9$ particles/cm$^3$, 50 mW laser power |
| 2.0 $10^9$ particles/cm$^3$, 250 mW laser power |

(a) Photon counting histograms.  
(b) Variance of the measured intensity.

**Figure 3.13:** Photon statistics at low particle concentrations.
3.6 Conclusions

In this chapter, the dynamics of the particle number fluctuations that occur at low concentrations have been studied. It was found that for particles dispersed in a liquid, the long time constant associated with the number fluctuation decay of the intensity autocorrelation function leads to excessively long measurement times that are necessary to obtain reliable values for the particle concentration from this decay (10 hours for 200 nm particles!).

More precisely, it was concluded from simulations of particle number fluctuations, that a correct concentration measurement can only be made when the particle occupation number averaged over the duration of a measurement, \( \langle N \rangle_m \), approaches the expected average occupation number. This requires a measurement time which is about 100 times longer than the characteristic time scale of the number fluctuation decay, \( \tau_N \). When the measurement time is \( \ll 100 \cdot \tau_N \), the concentration measurement yields a concentration that is too high. When the measurement time is longer, but still \( < 100 \cdot \tau_N \), approximately the correct concentration is obtained found, but with a large standard deviation.

The analysis of the measurement time in this chapter was made on the basis of behaviour of 200 nm particles in water. For smaller particles however, the diffusion coefficient is higher, resulting in a shorter number fluctuation decay time. The diffusion coefficient of 20 nm particles in water is 10 times higher than that of the 200 nm particles, so that in the same setup, the measurement time is reduced by a factor 10 (to 1 hour).

However, the best opportunities for concentration measurement on the basis of the intensity autocorrelation function, are in aerosols. Here, the diffusion coefficient of particles compared with their size equivalents in water, is 60 up to 1000 times higher!
Size measurement at low concentration

This chapter deals with the coherent decay of the autocorrelation function. The quality of a size measurement is influenced by the signal-to-noise ratio, which is the height of this coherent decay. It will be shown how this signal-to-noise ratio is related to the particle concentration and to the size of the scattering volume. When designing an optical setup for photon correlation spectroscopy measurements at low particle concentrations, this relation can be used to determine the optimum size of the scattering volume for each concentration.

4.1 Introduction

In Chapter 3, the particle number fluctuations at low particle concentration have been described. The focus was on the development of the incoherent decay of the intensity autocorrelation function. It was found that when the measurement time is shorter than 100 times the characteristic number fluctuation decay time, the height of the incoherent decay is, in general, too low. This is the result of the fact that the variation in the occupation number after a short measurement time is, on average, less than the variation that would be observed after infinite measurement time. It was concluded that concentration measurement from the height of the incoherent decay therefore requires either a small scattering volume or a long measurement time.

In view of these results, the question arises what the effect is of the low concentration on the possibility of a size measurement, and in particular, how the experiment can be designed for optimally measuring the size. For that, the factors determining the shape of the coherent part of the autocorrelation function will be discussed.

At the low concentrations it has been found [55] that size measurement via analysis of the coherent decay of the autocorrelation function yields particle sizes that are less reproducible and too high. In the ideal case where a measurement lasts long enough for the number fluctuations to be completely developed, the coherent and incoherent decay are usually far enough separated in time to be able to make a good size analysis.
In practical cases however, this is often not the case. The autocorrelation function then has, instead of a horizontal plateau after the coherent decay, a continuously decreasing shape.

For the separation of the coherent and the incoherent part of the autocorrelation function, an electronic filter has been proposed by Willemse et. al. [55], that filters out fluctuations below a certain frequency. However, the problem that leads to the size overestimation at low particle concentrations, is not the low frequency fluctuations, but incidental high frequency number fluctuations that are found back in autocorrelation functions for too short measuring times. Therefore, for a given optical setup, the only solution is to increase the measuring time. It becomes clear now, that for size measurement at low concentrations it is important to use an optimal optical configuration. In the design of such a configuration, the necessary measurement time should be considered, but it must be realised that also the quality of the coherent decay should be taken into account. One way to address this quality is via the height of the coherent decay, also called the signal-to-noise ratio, or the % merit. It will be shown in this chapter that this signal-to-noise ratio depends, besides on the size of the scattering volume via the spatial coherence factor $\beta_{coh}$, also on the number of particles in the scattering volume.

A schematic overview of the effects of the size of the scattering volume and of the particle concentration is shown in Figure 4.1. At high concentrations, multiple

<table>
<thead>
<tr>
<th>Concentration measurement possible</th>
<th>'normal' size measurement</th>
<th>multiple scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>low signal-to-noise ratio (section 4.2)</td>
<td>not completely developed number fluctuations (section 4.3)</td>
<td>low spatial coherence factor (section 4.4)</td>
</tr>
</tbody>
</table>

**Figure 4.1:** Effect of the size of the scattering volume and of the particle concentration on photon correlation spectroscopy measurements.
scattering takes place. This means that the light that reaches the detector is the result of more than one scattering event, and as a result, the correlation function decays on a faster time scale than it would with only single scattering. This can be understood by considering the case where only double scattering occurs. The autocorrelation function is then given by:

\[ g^{(2)}(\tau) = 1 + \beta \exp \left[ -2D \left( q_1^2 + q_2^2 \right) \tau \right], \tag{4.1} \]

where \( q_1 \) and \( q_2 \) are the scattering vectors of the first and second scattering event, respectively, integrated over all the combination of angles for which \( \theta_1 + \theta_2 = \theta \). The result is a correlation function which is the same as would be measured at a scattering angle of 180°, with its corresponding fast decay time.

The concentration range at which 'normal' size measurement is possible shifts downwards with increasing size of the scattering volume. However, when the scattering volume becomes too large, the spatial coherence factor decreases, and reduces the height of the coherent decay.

As was discussed in Chapter 3, concentration measurement from the particle number fluctuation decay, in reasonable measurement times, is only possible for aerosols or for small scattering volumes. Small scattering volumes are used in the field of fluorescence correlation spectroscopy. There, particles in the scattering volume emit fluorescent light after being exited in a highly focused laser beam. Because the delay time between excitation and emission is random, the emitted light is incoherent, and therefore exclusively the number fluctuation decay is measured.

At low particle concentration and moderate size of the scattering volume, concentration measurement is complicated by the excessively long measurement times that are required. The possibility of size measurement in this regime will be evaluated in this chapter.

At low particle concentration, reducing the scattering volume brings the number fluctuation decay time back to reasonable values. Nevertheless, the required measurement time remains long due to the low possibility of a particle coming near the centre of the scattering volume. Furthermore, as the average number of particles in the scattering volume reduces to values less than 1, the signal-to-noise ratio, which is the height of the coherent decay, drastically decreases because of incomplete interference of the scattered light. This effect will also be discussed in this chapter.

From this overview, it can be concluded that size measurement at low concentration usually means choosing the lesser of three evils: a low signal-to-noise ratio, an incomplete number fluctuation decay or a low spatial coherence factor. In this chapter, each of them will be discussed, with the aim of finding general guidelines for the design of the optimum scattering volume.
4.2 Signal-to-noise ratio

In Chapter 2, the height of the coherent decay was explained to be determined by the spatial coherence factor $\beta_{coh}$. This spatial coherence factor is completely determined by the optical geometry of the experimental setup. The height of the coherent decay is also called the signal-to-noise ratio, because it is a measure of how much of the detected intensity contains useful information. In this chapter, this signal-to-noise ratio will be written as $\beta$.

Figure 4.2 shows intensity autocorrelation functions that are measured at a constant scattering angle and scattering volume, but at different concentrations of 204 nm latex particles in water. These measurements clearly show that the signal-to-noise ratio is not only determined by the optical geometry, but also by the particle concentration. Besides the decrease in the signal-to-noise ratio, at particle occupation numbers below 10 the coherent decay also starts to be noisy. The number fluctuation decay is only visible for the lowest concentration in this figure.

The signal-to-noise ratio for 4 different scattering angles and two pinhole diameters

![Graphs showing autocorrelation functions](image)

**Figure 4.2:** Autocorrelation functions measured at various concentrations of 204 nm latex particles in water. The scattering angle was 90° and the pinhole diameter 100 μm. A three-dimensional Gaussian scattering volume is assumed, with an effective size of $2.4 \cdot 10^{-7}$ cm$^3$. 
Figure 4.3: Measured signal-to-noise ratio at different concentrations and scattering angles. Filled circles: 100 µm pinhole; open circles: 200 µm pinhole.

are shown in Figure 4.3. These figures clearly show that the signal-to-noise ratio $\beta$ decreases both towards high and towards low particle concentrations. The decrease of $\beta$ with increasing pinhole diameter is the result of a decrease of spatial coherence.

The decrease in $\beta$ towards high particle concentrations can be explained by the increase in the amount of multiple scattering. The coherence area for multiple scattered light is smaller than that for single scattered light [30]. This means that for a constant size of the detector area, the interference speckles will be more averaged out. At the same time, the correlation function moves towards smaller decay times, as predicted by equation 4.1. This leads to an underestimation of the particle size at high concentrations.
For the explanation of the decrease in $\beta$ towards low particle concentrations, it is necessary to realize that the signal-to-noise ratio is a combination of different effects [31]:

$$\beta = \beta_{coh}\beta_{non}\beta_{int}. \quad (4.2)$$

The first effect is the spatial coherence factor $\beta_{coh}$. For a pinhole detection system, a typical value is $\beta_{coh} \approx 0.9$, and for a single-mode optical fiber receiver, the optimal value of $\beta_{coh} = 1$ is always achieved. The second effect is that of detector nonlinearities. They make the intensity fluctuations less pronounced, resulting in $\beta_{non} \approx 0.9$ for moderate count rates. For a given optical geometry and at moderate count rates, $\beta_{coh}$ and $\beta_{non}$ are independent of the particle concentration. The last effect, $\beta_{int}$, takes into account the fact that only a part of the measured scattered intensity is a result of constructive or destructive interference. The rest of the measured intensity can be considered as noise. This effect will be examined in the following sections.

### 4.2.1 Incomplete interference

In the description of the scattering volume in Chapter 3, the amplitude of the electric field scattered by a particle at position $r_j$ in a three-dimensional Gaussian scattering volume was given by:

$$e(r_j) = E_0 \exp \left[ - \frac{x_j^2 + z_j^2}{w_0^2} \right] \exp \left[ - \frac{(x_j \cos \theta - y_j \sin \theta)^2}{l^2} \right]. \quad (3.4)$$

From this equation it was concluded that, because the scattering volume has no hard-ended boundaries, a certain particle is not either in or out of the measuring volume, but the amount with which it contributes to the total occupation of the scattering volume depends on its position. A particle exactly in the centre of the scattering volume counts for 1; a particle anywhere else counts for $(e(r_j)/E_0)^2$. This way, the effective particle occupation number could be calculated via:

$$N = \sum_{j=1}^{M} \left( \left( \exp \left[ - \frac{x_j^2 + z_j^2}{w_0^2} - \frac{(x_j \cos \theta - y_j \sin \theta)^2}{l^2} \right] \right)^2 \right). \quad (3.13)$$

When in equation 3.4, we take $E_0 = 1$, the value of the measured intensity will fluctuate due to interference between light scattered from the different particles, around the value of $N$. For an average particle occupation number $\langle N \rangle = 1$, simulation results of such number fluctuations and intensity fluctuations are shown in Figure 4.4-a. For lower $\langle N \rangle$ however, the probability of the presence of more than 1 particle near the centre of the scattering volume becomes very low. The result of this low probability on the scattered intensity can be seen in Figure 4.4-b. Here, the intensity follows the occupation number almost completely, instead of fluctuating around it. The absence of interference fluctuations, indicates that most of the time, the total intensity is the
4.2. Signal-to-noise ratio

Figure 4.4: Simulation results for the occupation number and corresponding scattered intensity for two particle concentrations.

Result of scattering by the particle that is the closest to the centre of the scattering volume, and by particles that are much further away from the centre. The result is then that the interference is not complete. This idea is visualised in Figure 4.5. In the next section, simulation results will be used to quantify this incomplete interference.

(a) The amplitudes of the two waves are equal, leading to complete interference.
(b) The ratio of the amplitudes of the two waves is 1/10, leading to incomplete interference.

Figure 4.5: The two waves have a small frequency difference, so that when they are added up ('interfere'), a beating signal is obtained. The intensity of such a beat signal is the square of the envelope of the (positive) electric field wave.
4.2.2 Simulations

The simulation model is the same as the one used in Chapter 3. This time, a very small spherical scattering volume of radius 5 μm was used. The configuration of particles throughout the total simulation volume was calculated for 1000 time steps for the highest particle concentration, up to 200000 time steps for the lowest concentration where it took more steps to obtain a stable average. The time steps were chosen much longer than the characteristic number fluctuation decay time, so that each particle configuration after a Brownian movement step is completely independent from the former. After each time step, the particle configuration will result in an effective number of particles in the scattering volume and in a total scattered intensity.

The simulations were performed for average particle occupation numbers ranging from ⟨N⟩ = 100 down to ⟨N⟩ = 0.001. The relative intensity, I/N, is a measure of the extent to which the value of the intensity fluctuates around the particle occupation number. Each time step of the simulation yields an effective occupation number and a relative intensity. For concentrations between ⟨N⟩ = 20 and ⟨N⟩ = 0.1, these are plotted in Figure 4.6. Down to ⟨N⟩ = 10, the shape of these figures remains the same. However, as the concentration decreases, more and more particle configurations occur where there is incomplete interference, which is expressed in an increased density of points around I/N = 1.

For the calculation of the β_int-part of the signal-to-noise ratio from these simulation results, β_int is written as a function the amount of intensity resulting from interfering scattering events (indicated by the subscript int) compared the total measured intensity [31]:

$$\beta_{\text{int}} = \frac{\langle I_{\text{int}} \rangle^2}{\langle I_{\text{tot}} \rangle^2}. \quad (4.3)$$

In this equation, the intensities are squared, because the intensity autocorrelation function is also built up of squared intensities. For each particle configuration, the part of the intensity that is a result of interference, I_{int}, is calculated. For that, the first step is to determine for that configuration whether interference is complete or not. This depends on the amplitude of the field scattered by the strongest scatterer, e_{max} = \sqrt{N_{max}}, relative to the sum of the amplitudes of all the scattered fields. There are two possible situations, which are also drawn in Figure 4.7:

1. The amplitude of the field scattered by the strongest particle is higher than the sum of the fields scattered by the rest of the particles. In that case there is incomplete interference. The interfering part, I_{int}, of the total amount of scattered light can be written as:

$$I_{\text{int}} = I_{\text{tot}} - (2e_{\text{max}} - e_{\text{tot}})^2. \quad (4.4)$$

2. The amplitude of the field scattered by the strongest scatterer is lower than the sum of the fields scattered by the rest of the particles. The interference is then complete, and I_{int} = I_{tot}.
4.2. Signal-to-noise ratio

Figure 4.6: Distribution of relative intensities.
Figure 4.7: The bar represents the sum of the amplitudes of all the scattered fields. In the upper drawings, the black part represents the strongest scattering particle, and the white part represents all the particles except the strongest scatterer. In the case of incomplete interference, the light scattered from the particles in the white part, interferes with only a fraction (the grey part) of the light scattered from the strongest scatterer.

4.2.3 Discussion

The resulting simulated values of $\beta_{\text{int}}$ are plotted in Figure 4.8. When this figure is compared with the measured values of $\beta$, as were shown in Figure 4.3, it is found that in the experiments, the signal-to-noise ratio already starts to decrease when $\langle N \rangle$ becomes lower than 100. This means that in our experiments, there is an additional effect that is responsible for this decrease in signal-to-noise ratio. This effect comes from the noise, which is all the detected light that is not the result of particle scattering. For the experiments at 90°, the detected intensities at the different concentrations are shown in Figure 4.9-a. These are shown as relative intensities, because the laser output power was increased as the particle concentration decreased. The noise was determined as the intensity measured for a clean water sample, at the same values of the laser output power. The signal-to-noise ratio was then calculated as:

$$\beta = \beta_{\text{coh}}\beta_{\text{non}} \frac{\langle I_{\text{tot}} - I_{\text{noise}} - I_{\text{incomplete}} \rangle^2}{\langle I_{\text{tot}} \rangle^2},$$

(4.5)

where $\beta_{\text{coh}}\beta_{\text{non}}$ is taken as a constant. As is shown in Figure 4.9-b, this explains the measured signal-to-noise ratio at the low concentrations satisfactorily. This means that, at the experimental conditions used, the noise predominates the effect of incomplete interference.
4.2. Signal-to-noise ratio

Figure 4.8: Calculated $\beta_{int}$ from simulations at low concentrations.

The results of this paragraph imply that the lower limit of the average particle occupation number is about 0.01. Below this value, practically no interfering light reaches the detector, no matter how large or small the size of the scattering volume is.

Figure 4.9: Intensity and signal-to-noise ratio at a scattering angle of 90°.
Chapter 4. Size measurement at low concentration

4.3 Number fluctuations

In this paragraph, the second possibility for measurement at low concentration is presented: moderate size scattering volumes, for which the number fluctuation decay time is too long for correct concentration measurement, as was discussed in Chapter 3. The question for such measurements is, whether it is possible to obtain the correct particle size from the correlation function.

For the experiments with 204 nm latex particles at different concentrations, measured in the Brookhaven goniometer setup described in Chapter 3, the autocorrelation functions are fitted using equation 3.10. The duration of the measurements was 2 minutes, and the characteristic time of the number fluctuation decay was calculated to be about 5 minutes. Nevertheless, equation 3.10 fits the shape of the autocorrelation function quite well. Two examples are shown in Figure 4.10. The large difference in signal-to-noise ratio and in the noise in the coherent decay between the correlation functions measured at the 30° and 90°, is the result of the higher scattering intensity at low angles. The particle sizes that were obtained from these fits are shown in Figure 4.11. These results show that, except for the scattering angle of 90°, down from about 100 particles in the scattering volume the measured particle size is too large. Increasing the amount of detected light via an increase in the pinhole diameter, does not make a difference for the measured size.

From these measurements, it can be concluded that the presence of the number fluctuation decay leads to a 50% overestimation for concentrations down to $\langle N \rangle \approx 1$ and at lower concentrations to a higher and less reproducible measured size. This is

![Figure 4.10](image-url)

(a) $\theta = 30^\circ$.  
(b) $\theta = 90^\circ$.

Figure 4.10: Measured and fitted autocorrelation function of 204 nm particles. The concentration is $4.5 \cdot 10^6$ particles/cm$^3$, and the scattering angles are $30^\circ$ and $90^\circ$. 
Figure 4.11: Measured particle size at different scattering angles and concentrations, relative to the nominal particle size, $d_0$. Filled circles: 100 μm pinhole; open circles: 200 μm pinhole.

especially the case for the measurements at 30°, because at this low scattering angle, the measurements are more sensitive to the presence of large dust particles.

4.4 Spatial coherence factor

The third possibility for measuring at low particle concentrations, is to increase the size of the scattering volume, and thereby increase $\langle N \rangle$. As already explained in Chapter 2, the consequence of increasing the size of the scattering volume is that the
Chapter 4. Size measurement at low concentration

The spatial coherence factor $\beta_{coh}$ will decrease according to:

$$\beta_{coh} = \sum_{s=0}^{\infty} \left[ \frac{(2s + 2)!}{(s + 1!)^2 (s + 2)!} \right]^2 (-1)^s \left( \frac{1}{2} \kappa B \right)^{2s},$$

(2.31)

where $\kappa = k_0 \sigma / 2R$, $\sigma$ is the radius of the scattering volume and $R$ is the mean distance from the scattering volume to the detector. In Figure 4.12, the relationship between the spatial coherence factor and the radius of the scattering volume is shown.

![Graph showing spatial coherence factor vs. radius of the scattering volume](image)

**Figure 4.12:** Spatial coherence factor for as a function of the size of the scattering volume. The following parameters were used: $B = 100 \mu m$, $R = 20$ cm.

### 4.5 Finding the optimum scattering volume

Having established the relations between the signal-to-noise ratio, the concentration and the dimensions of the scattering volume, the next step is to use this knowledge for determining an optimum for the size of the scattering volume. This is the scattering volume where the highest signal-to-noise ratio can be achieved for a given concentration. It is a compromise between a low spatial coherence factor $\beta_{coh}$ for a large scattering volume and a low $\beta_{int}$ for a small scattering volume that contains a small number of particles.

For each value of the size of the scattering volume, the corresponding spatial coherence factor can be calculated from equation 2.31. For a certain concentration, the average number of the particles in the scattering volume, $\langle N \rangle$, depends on the size of the scattering volume. This number is combined with the relationship between $\beta_{int}$ and $\langle N \rangle$ that was found from the simulations and experiments (Figure 4.9-b).

The results of these calculations are shown in Figure 4.13. From these figures it
4.5. Finding the optimum scattering volume

(a) At low $\langle N \rangle$, only the effect of incomplete interference is taken into account. (b) At low $\langle N \rangle$, both the effect of incomplete interference and noise are taken into account.

Figure 4.13: Signal-to-noise ratio as a function of the particle concentration and the size of the scattering volume. Each line represents a constant value of the signal-to-noise ratio. The calculations were made for a particle size of 204 nm and a detector with a radius of 100 μm placed at a distance of 20 cm from the scattering volume.

It can be seen that, for a certain particle concentration, increasing size of the scattering volume will lead to an increase in the signal-to-noise ratio, up to the volume where the maximum achievable value for this concentration is reached. Further increasing the scattering volume will then lead to a decrease in the signal-to-noise ratio. It is clear from this figure, that the optimum concentration is not the same for all particle concentrations!

It must be noted here, that the signal-to-noise ratio is not the only parameter that determines the quality of a particle size measurement at low concentration. Koppel [26] stated that for the statistical accuracy of dynamic light scattering measurements, the critical parameter is the photocounts/coherence area/correlation time, which is independent of the number of coherence areas. This means that increasing the size of the scattering volume and thereby decreasing the spatial coherence, has no effect of the statistical accuracy of a size measurement. However, since a larger volume will contain more particles, the particle sizing capability will be increased due to the smaller effect of the particle number fluctuations.
4.6 Conclusions

At low particle concentration, the quality of a size measurement with photon correlation spectroscopy can be improved by choosing a suitable size of the scattering volume. It was demonstrated in this chapter, that a low average number of particles in the scattering volume leads to a decrease in the signal-to-noise ratio due to the effects of noise and incomplete interference of the scattered light. This decrease becomes considerable for values of \( \langle N \rangle \) below 1.

Increasing the size of the scattering volume to increase \( \langle N \rangle \) leads to a decrease in the signal-to-noise ratio via a decrease in the spatial coherence factor. It has been shown how, for each concentration, it can be calculated for which size of the scattering volume the maximum signal-to-noise ratio is obtained.

The presence of an incomplete number fluctuation decay at low values of \( \langle N \rangle \) leads to an overestimation of the particle size up to 50% for concentrations down to \( \langle N \rangle \approx 1 \). At lower concentration an even higher and less reproducible sizes are found. Measurements at such low values of \( \langle N \rangle \) are advised against, also since the signal-to-noise ratio is very low for such measurements.
Photon correlation spectroscopy in turbulent flow

In a turbulent flow, velocity fluctuations create an extra movement of the particles relative to each other. The extent to which this influences the measured autocorrelation function, depends on the time and length scales characterizing the turbulence, compared to the time and length scale of diffusion. In this chapter, first, a theoretical overview of photon correlation spectroscopy in different flow fields is given. After that, aerosol measurements in a turbulent flow field are presented. The influence of average velocity and turbulent intensity on the quality of a particle size measurement is investigated.

5.1 Introduction

In most in-line dynamic light scattering applications, the system is not static, but there is some overall velocity. Such is the case for many particle production processes, were in-line size measurement is a valuable tool for monitoring or control of the process. The velocities encountered in such processes can be as high as 30 m/s, and it will probably not be a surprise that the collective flow of the particles through the laser beam has an influence on the measured autocorrelation function. For the case of simple laminar flow, this influence has been thoroughly studied [7, 29], but when the flow starts to be turbulent and the particle velocity becomes a fluctuating parameter, it is no longer obvious which part of the autocorrelation function can be attributed to diffusion. Several optical configurations have been worked out for measuring the turbulent velocity fluctuations in situations where the diffusional motion could be neglected. However, in particle size measurement the diffusion is the only interesting parameter, and the turbulence is a disturbing factor. The development such a particle size measurement in a turbulent flow using dynamic light scattering still has a long way to go.
In this chapter, particle size measurement in a turbulent aerosol flow is investigated. Firstly, the theoretical derivation of the autocorrelation function in different flow fields is presented. This presentation follows an order of increasing complexity of the flow field. It begins with uniform flow (section 5.2), continuing with some comments about the situation where there is a constant velocity gradient within the scattering volume (section 5.3) and finishing with turbulent flow (section 5.4). Secondly, measurements in aerosol flows are presented. These measurements were all conducted with aerosol particles generated with an evaporation-condensation aerosol generator. This apparatus and its features are described in section 5.5. Two sets of experiments were realised. The first experiments were carried out in the laboratory and the situation is such that the very beginning of the appearance of turbulence in the measurements is seen. Parametric influence of velocity, particle size and scattering volume are discussed. The second experiments were conducted in a wind tunnel. There, the effect of flow velocity and turbulence are clearly seen. Finally, in section 5.7, the influence of the flow field on practical size measurements is discussed.

5.2 Uniform flow

The simplest flow geometry is a system of particles in uniform flow. For a dynamic light scattering experiment, this means that all the particles in the scattering volume are subjected to the same overall flow velocity. The position vector of a particle can then be decomposed into two parts:

\[ \mathbf{r}_j(t) = \mathbf{v}t + \mathbf{r}_j^D(t), \]  

(5.1)

where \( \mathbf{v} \) is the velocity and \( \mathbf{r}_j^D \) is the part due solely to diffusion. The collective particle motion introduces no changes in the relative particle position; the result is that when the scattered field is visualised as was done in Figure 2.7, the collective motion only means a rotation of the random walk graph in the complex plane [39]. The optical geometry in the case of uniform flow is often chosen as in Figure 5.1. The direction of flow is then perpendicular to the scattering plane. The influence of the velocity on the measured intensity fluctuations is that caused by the particles travelling through the intensity profile of the scattering volume. The field autocorrelation function of equation 2.25 becomes:

\[ G^{(1)}(\tau) = \sum_{i,m=1}^{N_{tot}} \langle e(\mathbf{r}_i^D(0)) \, e(\mathbf{v} \tau + \mathbf{r}_m^D(\tau)) \exp[i \mathbf{q} \cdot (\mathbf{v} \tau + \mathbf{r}_m^D(\tau) - \mathbf{r}_i^D(0))\rangle. \]  

(5.2)

This autocorrelation function involves two averages: one over the diffusional motion of the particle, and the other over the translatational motion of particles traversing the scattering volume. When the diffusive displacement for times comparable with the experimental diffusion time \( \tau_D = 1/2Dq^2 \), is much less than the characteristic size
5.2. Uniform flow

Figure 5.1: Here, the laser beam propagates in the z-direction, and the detector is placed in the xz-plane. The scattering vector \( \mathbf{q} \) therefore also lies in the xz-plane.

of the scattering volume, these two averages may be taken as independent and thus separable, leading to:

\[
G^{(1)}(\tau) = \exp[i\mathbf{q} \cdot \mathbf{v}\tau] \sum_{l,m=1}^{N_{\text{tot}}} \langle e^{(0)}(0) e^{(0) + \mathbf{r}_m^D(\tau)} \rangle \\
\times \langle \exp[i\mathbf{q} \cdot (\mathbf{r}_m^D(\tau) - \mathbf{r}_l^D(0))] \rangle. \tag{5.3}
\]

The derivation of the intensity autocorrelation function \( g^{(2)}(\tau) \) has been performed by Chowdhury et al. [7] and by Weber [52], and results in:

\[
g^{(2)}(\tau) = 1 + \beta \exp[-2Dq^2\tau] \exp \left[ -\frac{\gamma}{w_0^2} \tau^2 \right] + \frac{\gamma}{\langle N \rangle} \exp \left[ -\frac{\gamma}{w_0^2} \tau^2 \right], \tag{5.4}
\]

where \( w_0 \) is the focused beam waist. The last term in this equation is the non-Gaussian term, and accounts for the intensity fluctuations that are observed at low particle concentrations. Similar to the static number fluctuation case, the volume contrast factor \( \gamma \) corrects the height of this decay for the intensity profile of the scattering volume. For non-dilute systems, the non-Gaussian term can be neglected. The middle term is the coherent term. It contains the coherence factor, the exponential decay due to particle diffusion, and the decay due to the particles traversing the laser beam, which is Gaussian in time. The analysis of a correlation function measured in uniform flow is different for the non-dilute and for the dilute case. Both cases are described in the next sections.
5.2.1 Non-dilute regime

For the non-dilute regime, two methods are available, which both come down to fitting the argument of the exponent with a second-order polynomial.

Cumulant analysis

For non-flowing polydisperse systems, the size distribution is often obtained from a cumulant analysis of the correlation function [25]:

\[ g^{(2)}(\tau) = 1 + \beta \exp \left[ -2K_1 \tau + K_2 \tau^2 \right], \tag{5.5} \]

where \( K_1 = \langle Dq^2 \rangle \) is the first cumulant, and contains the intensity weighted average particle size. The second cumulant, \( K_2 = \langle \Delta(Dq^2) \rangle \), contains the width of the distribution. The cumulant fit is a standard utility in any commercial photon correlation spectroscopy software. When a flowing polydisperse system is analysed with the cumulant method, the beam transit term enters the correlation function also with a \( \tau^2 \) dependence. This means that the measured second cumulant \( K'_2 \) is then given by

\[ K'_2 = K_2 - \frac{v^2}{w^2}, \tag{5.6} \]

where \( K_2 \) is due solely to polydispersity [40].

Y-function

Chowdhury et al. introduced the Y-function to separate particle size information and beam transit information:

\[ Y(\tau) = -\frac{1}{\tau} \ln \left[ \frac{g^{(2)}(\tau) - 1}{g^{(2)}(0) - 1} \right] = 2Dq^2 + \frac{v^2}{w^2} \tau = \frac{1}{\tau_D} + \frac{\tau}{\tau_t}, \tag{5.7} \]

where \( \tau_D \) is the diffusion decay time and \( \tau_t \) is the beam transit time. When \( Y(\tau) \) is plotted against \( \tau \), a straight line is obtained, of which the intercept yields the diffusion coefficient and the slope yields the velocity. This method has also been used by Van Druenen et al. [11] for particle size measurement in a silicon nitride flame. One of the advantages of such a graphical representation is that disturbing effects such as afterpulsing and multiple scattering can be detected.

The results of Chowdhury et al. from their simplified experimental system, a flowing liquid dispersion, show that size information can be extracted, even when the beam transit time due to uniform flow was considerably faster than the diffusion decay time. However, at the highest flow rate that they used, when \( \tau_t \sim \frac{1}{5} \tau_D \), they found that \( \tau_D \) appeared too small by as much as 30%, which indicates the error one should expect for such a measurement.
Polydispersity of course has the same influence on the results of the $Y$-function analysis as is has on the results of the cumulant analysis. Which method is preferred depends on the application: analysis of the $Y$-function is somewhat more labour-intensive, but thereby quickly shows the presence of any disturbing effects.

5.2.2 Dilute regime

Chowdhury et al. [7] already derived the non-Gaussian term in the correlation function for uniform flow, but only mention it's possible use for dilute aerosol systems. They are the first to find the factor $\gamma = 2^{-3/2}$ in the non-Gaussian term, which is the result of the decrease of the effective scattering volume when the Gaussian intensity profile is squared.

Further investigation on dilute flowing aerosols was done by Weber et al. [53]. They used the number fluctuation-term in equation 5.4 to measure the concentration, and observed that the most accurate simultaneous size and concentration results could be obtained when the height of the coherent and the incoherent decay of equation 5.4 were about equal. Therefore, they increased the aperture size of the detector and thereby decreased the spatial coherence factor $\beta$, to lower the coherent decay when the concentration became too high.

A complete theoretical and experimental analysis for flowing, low-concentrated aerosols was given by Weber [52] and by Weber and Schweiger [54]. They have measured autocorrelation functions for which the coherent decay is only little influenced by the particle transit time, which means that $\tau_D \ll \tau_l$. When the aerosol velocity increases and the particle transit time decreases, the coherent decay and the number fluctuation decay become less separated in time and besides that, the coherent decay will become dominated by the particle transit term. From their measurements, they could determine the laminar flow profiles in aerosol, and were able to measure concentration at a broad range of concentrations. A problem with their concentration measurements was however, that their concentrations were a factor 40 too high compared to those obtained with a condensation particle counter. Besides losses due to the sampling from the tube, they attributed the difference to the fact that the scattering volume might not have been located at the beam waist. This explanation was based on the analysis of Taylor and Sorensen [46], in which the effect of the spherical wavefront of the laser beam was taken into account. That analysis showed that the coherent beam-transit term is independent of the position of the scattering volume relative to the focal point of the incident beam, and only depends on the focused beam waist. However, the incoherent beam-transit time and also the effective occupation number depend on the local beam waist, which implies that as the scattering volume moves away from the focal point, the incoherent term decays slower, and has a lower amplitude. It must be realised however, that when such measurements are used for measurement of the velocity, the coherent and the incoherent term yield different beam transit times.
5.3 Velocity gradient in the scattering volume

The second flowing system to be discussed is shear flow. This becomes relevant when there is a considerable velocity gradient within the scattering volume. Experimental analysis of shear systems are usually performed in a Couette cell, where a constant shear rate $\gamma$ is obtained. Fuller et al. [14] derived the intensity autocorrelation function that allowed measurement of the local velocity gradient.

Here, we discuss one of their results, which is that for the case of simple shear where the main flow is in the $x$-direction and velocity gradient tensor is given by:

$$\Gamma = \gamma \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$  \hfill (5.8)

When the beam transit time due to the main velocity component is large, the intensity autocorrelation function becomes:

$$g^{(2)}(\tau) = 1 + \exp \left[ -2D \left( q_x^2 \left( 1 + \frac{1}{3} (\gamma \tau)^2 \right) + \gamma \tau q_x q_y + q_y^2 + q_z^2 \right) \right]$$

$$\times \left| \int \int \int e^2(x) \exp[-i\gamma q_x y \tau] \, d^3x \right|^2.$$  \hfill (5.9)

This function decays on three time scales: $\tau_f = 1/\gamma$, $\tau_D = 1/2Dq^2$, and $\tau_s$, which is the characteristic time scale of particle displacement over a length scale $q^{-1}$:

$$\tau_s = \frac{1}{q\gamma |w| \cos \phi}.$$  \hfill (5.10)

Here $\phi$ is the angle between the scattering vector $q$ and the local mean velocity vector $v$. For measurement of velocity gradients, this angle is normally set to zero in order to minimise $\tau_s$, as in Figure 5.2. Fuller et al. state as conditions for measurement of the velocity gradient that $\tau_s \ll (\tau_f, \tau_D)$. They have found that this condition is almost always satisfied. In that case, the correlation function is made up of the contributions of all components of the gradient of the projected velocity $v \cdot q$.

Now when the aim is to measure the diffusional motion instead of the velocity gradient, the time scales must be chosen so that $\tau_D$ will dominate the correlation function. In particle size measurement in a flowing system it is most usual and also most convenient to use the configuration of Figure 5.1. There, the main direction of flow is perpendicular to the scattering plane. In that case, the angle $\phi$ is 90°, and
consequently \( \tau_s \) becomes very large. The remaining two constraints are then:

\[
\frac{\tau_D}{\tau_f} \ll 1, \tag{5.11}
\]

and

\[
\frac{\tau_D}{\tau_f} = \frac{\gamma}{2Dq^2} \ll 1. \tag{5.12}
\]

The effect when restriction 5.11 is not fulfilled, has already been discussed by Chowdhury et al. [7], as mentioned in section 5.2.1. That leaves only restriction 5.12. With an aerosol diffusion coefficient of the order \(10^{-9}\), and a scattering vector of the order of \(10^7\), this means that the velocity gradient must be \(\ll 10^5 \text{ s}^{-1}\).

### 5.4 Turbulent flow

The last step in complexity is that towards turbulent flow. Although this chaotic and unpredictable behaviour of fluid flow has been studied for many decades, still no good definition of it has been established. Usually, the degree of turbulence is characterised by the dimensionless Reynolds number (Re), which is the ratio between inertia forces and viscous forces:

\[
Re = \frac{\rho v d}{\eta}, \tag{5.13}
\]

where the length scale \(d\) is that of the system that is studied: in tube flow, it is the tube diameter, but for the settling behaviour of particles in a tube, it is the particle diameter. At low Re, the flow is laminar, and the variations in the flow are predictable in time and in space. When Re increases, the flow becomes unstable, and above some critical Re, it is fully turbulent. The flow in a tube is laminar for Re \(< 2000\) and turbulent for Re \(> 4000\). The flow around a particle, however, is only laminar for Re \(< 0.2\). These differences in upper limits are the result of the enhanced importance
of inertial forces for a fluid flowing around a particle compared to the straight-line flow along a pipe.

Many models describing turbulence are based on the idea that was first put forward by Richardson [35] and further developed by Kolmogorov, that there is a hierarchy of turbulent disturbances on different scales. At the largest scale of turbulence, there is energy input into large eddies. These large eddies break down into smaller eddies and thereby turbulent energy is transported from the large to the small eddies. This cascade process continues until at the smallest scale, the kinetic energy is dissipated to heat. This smallest scale of turbulence is called the Kolmogorov length scale, and the corresponding time scale the Kolmogorov time scale $\tau_K$.

Typical of all turbulent flows is that the velocity at a certain point in space or in time is not constant but fluctuates. The higher the degree of turbulence, the more intense are the velocity fluctuations. Because particles immersed in a turbulent fluid move randomly due to these velocity fluctuations, turbulence is likely to disturb dynamic light scattering measurements of Brownian motion. In the following analysis, we make some assumptions to simplify:

1. **The particles follow the flow.**
   The particle relaxation time $\tau_p = m/3\pi \eta d$ is a measure of how well a particle follows fluctuations in the flow pattern. Particles with a long relaxation time have a strong inertia, and are not able to move along the streamlines of small turbulent eddies. This is the case for larger particles, and for particles that have a high relative density. Unlike in liquid systems, an unavoidable problem in aerosols is that there is always a large relative density.

2. **The particles do not influence the flow pattern.**
   Validation of this last assumption can be done using Figure 5.3, which is the regime map of the interactions between particles and turbulence [12]. The main parameter describing these interactions is the volume fraction of particles, $\phi_p$. For very low volume fractions, the particle motion depends on the state of turbulence, but due to the small amount of momentum transfer from the particles to the fluid, their effect on the flow is negligible. The interaction is called **one-way coupling**. At volume fractions between $10^{-6}$ and $10^{-3}$, there is **two-way coupling**. In this regime, the momentum transfer from the particles is large enough to alter the turbulence. This can be either production or dissipation, depending on the ratio of the particle relaxation time, $\tau_p$, to the Kolmogorov time scale, $\tau_K$. For small particles, i.e. small relaxation time, the large surface area of the particles leads to a high dissipation rate of turbulent energy. On the other hand, large particles will have a high particle Reynolds number $Re_p$, whereby turbulent energy is produced via the formation of a turbulent wake behind the particle. In the last regime, where the particle concentration is high, collisions between particles take place, resulting in **four-way coupling** of the interactions.
5.4. Turbulent flow

![Figure 5.3: Regime map of the interactions between particles and turbulence. From [12].](image)

5.4.1 Turbulence and photon correlation spectroscopy

Besides the measurement of diffusion coefficients, one of the first applications of dynamic light scattering has been the measurement of turbulence. First via line-width measurements of the spectrum [4], and later via photon correlation spectroscopy. Photon correlation spectroscopy in turbulent flow has been developed mainly to measure the turbulence characteristics. This means that the optical configuration and the particle size were chosen such that the Brownian motion decay in the autocorrelation function was dominated by the turbulence effects and could therefore be neglected. The first to publish the application of self-beat correlation spectroscopy to measure
turbulence are Ikegami et al. [23], soon followed by Tong et al. [49]. Both derive the autocorrelation function for measuring the velocity difference \( \mathbf{V}(\mathbf{R}, t) \) of a pair of particles separated by a distance \( \mathbf{R} \):

\[
\mathbf{V}(\mathbf{R}, t) = \mathbf{v}(\mathbf{r}(t)) - \mathbf{v}(\mathbf{r}(t) + \mathbf{R}),
\]

where \( \mathbf{v}(\mathbf{r}(t)) \) is the local velocity of the fluid. From the total field scattered by \( N \) particles:

\[
E(t) = E_0 \sum_{j=1}^{N} \exp[-i\mathbf{q} \cdot \mathbf{r}_j(t)],
\]

the intensity correlation function becomes:

\[
g^{(2)}(\tau) = \frac{1}{N^2} \left\langle \sum_{k,j,m,n} \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_k(t) + \mathbf{r}_m(t + \tau) - \mathbf{r}_n(t + \tau))] \right\rangle.
\]

(5.16)

The particles are assumed to follow the motion of the fluid:

\[
\mathbf{r}_j(t + \tau) = \mathbf{r}_j(t) + \int_0^{t+\tau} \mathbf{v}(\mathbf{r}(t'))dt'.
\]

(5.17)

so that equation 5.16 becomes:

\[
g^{(2)}(\tau) = 1 + \frac{1}{N^2} \sum_{m \neq n} \langle \exp[i\mathbf{q} \cdot \mathbf{V}(\mathbf{R}(m,n), t) \tau] \rangle
\]

\[
= 1 + \frac{2}{N^2} \sum_{m \geq n} \langle \cos (\mathbf{q} \cdot \mathbf{V}(\mathbf{R}(m,n), t) \tau) \rangle.
\]

(5.18)

Because the turbulent eddy turnover time \( t_R \) is much longer than the time of interest in the experiment, the integral in equation 5.17 is replaced by \( \mathbf{V}(\mathbf{R}(m,n), t) \tau \). When \( N \gg 1 \), the summation in equation 5.18 can be converted into an integration over the scattering volume:

\[
g^{(2)}(\tau) = 1 + \int_0^{L} h(R) \langle \cos (\mathbf{q} \cdot \mathbf{V}(\mathbf{R}, t) \tau) \rangle dR.
\]

(5.19)

where the scattering volume is assumed to be quasi-one-dimensional with length \( L \), and \( h(R) \) is the number fraction of particle pairs in the scattering volume that are separated by distance \( R \). The weighted average over all particle separations can be
rewritten using the probability density $P(V(R))$ that two particles, separated by a distance $R$, have a velocity difference $V(R)$:

$$g^{(2)}(\tau) = 1 + \int_{-\infty}^{\infty} P(V(R)) \times \cos(qV(R)\tau)dV(R)dR.$$  \hspace{1cm} (5.20)

Here, the inner integral is the Fourier cosine transform of $P(V(R))$. This equation is in fact quite general for most photon correlation spectroscopy experiments. In the case of a stationary system, where the only particle motion is the Brownian motion, $V(R)$ is independent of $R$, and $P(V(R))$ is a Gaussian function [18]. For a turbulent system, various functions of the probability density $P(V(R))$ have been applied.

**Functional form of $P(V(R))$ in turbulent flow**

The measurements by Tong et al. [49] show that for relatively small values of $V(R)$, $P(V(R))$ is well represented by a Lorentzian function:

$$P(V(R)) \propto \frac{1}{1 + \left(\frac{V(R)}{u(R)}\right)^2}.$$  \hspace{1cm} (5.21)

Here, the scaling velocity $u(R) \sim R^\zeta$, where $\zeta$ is a function of $Re$. These results were found for measurements that were conducted at very modest values of $Re$. The scaling behaviour is observed above a Reynolds number of 500, which corresponds to much lower turbulence than normally associated with scaling behaviour. The functional form of the autocorrelation function $g^{(2)}-1$ for the velocity difference distribution of equation 5.21 becomes an incomplete gamma function with $qu(L)\tau$ as its argument [49].

Further studies have resulted in a more general description of $P(V(R))$, by approximating it by the product of a Lorentzian and a Gaussian function [32]:

$$P(V(R)) \propto \exp \left[ -\frac{1}{2} \left( \frac{V(R)}{u_G(R)} \right)^2 \right] \frac{1}{1 + \left( \frac{V(R)}{u_L(R)} \right)^2}.$$  \hspace{1cm} (5.22)

This description is based on the fact that turbulence is often found to be not completely space-filling. The ratio of the widths of these two distributions, $u_G(R)/u_L(R)$ is found to be approximately 3, and independent of $Re$. The Gaussian distribution represents the large turbulent velocity fluctuations which take part in the turbulent cascade. These are called the active regions of the flow. The Lorentzian distribution represents the small velocity fluctuations which do not participate in the turbulent cascade and which are called inactive [10].
Chapter 5. Photon correlation spectroscopy in turbulent flow

Autocorrelation function for turbulence and Brownian motion

When the number of particles in the scattering volume is large and the beam transit time can be neglected, the autocorrelation function can be written as [32]:

$$g^{(2)}(\tau) = 1 + \beta \exp \left[ -2Dq^2 \tau \right] \times \int_0^L h(R) \int_{-\infty}^{\infty} P(V(R)) \times \cos(qV(R)\tau) dV(R) dR.$$ (5.23)

Here, $P(V(R))$ is the distribution of the turbulent velocity differences only. This equation shows that the measurement of the diffusion coefficient requires $\tau_D$ to be smaller than the time scale that is associated with the turbulence. A discussion of the different time scales that are involved in a photon correlation spectroscopy measurement in a turbulent flow is given in the next section.

5.4.2 Characteristic time scales

For the case of laminar flow, presented in section 5.2, the two time scales of interest are the diffusion time $\tau_D = 1/2Dq^2$ and the beam transit time $\tau_t = w/v$. Chowdhury et al. [7] observed that size measurement starts to become problematic when $\tau_D > 5\tau_t$. When the correlation function is also influenced by turbulence, there are two extra time scales involved. The first is the time scale that characterises the velocity fluctuations. For a scattering volume of length $L$, this time scale is of the order of $\tau_T = 1/qu(L)$, where $u(L)$ is the scaling velocity for the eddies of size $L$, because the fastest turbulent decay rate is associated with the largest eddies that are observed by the detector [18]. The second turbulent time scale is the turbulent turnover time. For eddies of size $R$, this turnover time is $\tau_R = R/u(R)$. When this time scale is larger than the decay time of the correlation function, it may be assumed that each pair of particles separated by a distance $R$, is moving at constant velocity $V(R)$.

Because the smallest time scale dominates the autocorrelation function, it is the safest to choose $\tau_D \ll (\tau_t, \tau_T, \tau_R)$ for measurement of the diffusion coefficient. However, in practical circumstances this is not always possible. The result that this has on the measured correlation function will be discussed later in this chapter.

5.4.3 Grid-generated turbulence

A method of generating nearly isotropic and homogeneous turbulence, is placing a grid in a uniform stream. Such a grid creates turbulent eddies which contain an amount of kinetic energy. As the fluid moves away from the grid, this energy is transformed into heat by viscous dissipation.
5.5 Production of a monodisperse flowing aerosol

For a grid composed of rods that are placed regularly at a distance $M$ apart in a square array, the decay of turbulence behind the grid has been experimentally studied by various researchers, and is described by Batchelor [2]. It is found, that the flow can be assumed isotropic and homogeneous for distances from the grid between $10M$ and $120$ to $200M$. The velocity fluctuations can then be described by:

$$
\left( \frac{U}{w} \right)^2 = a \left( \frac{x}{M} - \frac{x_0}{M} \right)
$$

(5.24)

where, for square-mesh grids, $a \approx 134$ and $x_0/M \approx 10$. The length scale of the smallest eddies, the Kolmogorov length scale, for the flow behind the grid can be estimated by:

$$
l_K = \left( \frac{\nu^3}{\epsilon} \right)^{1/4} \approx 3.1M \left( \frac{x}{M} \right)^{1/2} \left( \frac{UM}{\nu} \right)^{-3/4}.
$$

(5.25)

where $\nu$ is the kinematic viscosity of the fluid and $\epsilon$ is the viscous energy dissipation rate. When this is combined with the definition of the Kolmogorov time scale:

$$
\tau_K = \left( \frac{\nu}{\epsilon} \right)^{1/2},
$$

(5.26)

the following expression is found:

$$
\tau_K = \frac{l_K^2}{\nu} \approx 9.61 \frac{M^2}{\nu} \left( \frac{x}{M} \right) \left( \frac{UM}{\nu} \right)^{-3/2}.
$$

(5.27)

The Reynolds number for the grid flow is defined as:

$$
\text{Re} = \frac{\rho u M}{\eta}.
$$

(5.28)

5.5 Production of a monodisperse flowing aerosol

The experiments described in this chapter were performed with aerosol particles with a narrow size distribution, in order to have only one diffusion coefficient. An effective method of producing monodisperse aerosol particles is via the condensation of a vapour onto small nuclei. This condensation is a diffusion controlled process, which means that the surface area of a growing particle increases at a constant rate:

$$
d^2 = d_0^2 + bt
$$

(5.29)

Here, $b$ is a constant and $d_0$ is the diameter of the nucleus. Because all particles grow at the same rate, variations in the size of the nuclei have little effect on the final particle diameter. The first experiments with such a generator were reported by Sinclair and LaMer in 1949 [41], who lead a gas flow containing small nuclei through a chamber of boiling low vapour pressure liquid. The saturated gas stream was then cooled in order
to let the liquid condensate onto the nuclei. A modified generator is that of Rapaport and Weinstock [34], whereby the vapour is supplied by evaporation of a spray of polydisperse droplets. The advantage of this method is that continuous heating of the liquid is not necessary, and decomposition can be avoided. The setup used in our experiments is of the type of Rapaport and Weinstock, and is shown in figure 5.4. As the low vapour pressure liquid, di-ethylsebacate (DES) of 98% purity was used. It has a boiling point of 312°C and a density of 963 kg/m³. Although in several studies di-octylphthalate was also found to give good monodispersity [8, 48], this liquid is possibly carcinogenic [21], and the use of DES is preferred. The condensation nuclei are made up of the non-volatile impurities present in the DES.

Figure 5.5: Velocity of a unit-density particle as it is accelerated through the nozzle. The nozzle exit is at 0 mm. From [1].
The produced droplets were measured with an API aerosizer (Amherst Process Instruments). The aerosizer measures the aerodynamic diameter of single particles. This is done by acceleration of the aerosol through a nozzle to near-sonic velocity, and subsequent measurement the time-of-flight of a particle between two laser beams. As can be seen in Figure 5.5, small particles are accelerated more by the accelerating air stream than large particles, and therefore have a smaller time-of-flight. The time-of-flight is related to the aerodynamic diameter, which is the equivalent diameter of a particle of unit density that would settle at the same velocity in air at standard conditions. It is the product of the physical (geometric) diameter and the square root of the density. The lower detection limit of the aerosizer is around 0.2 μm; it is mainly determined by the detection limit of the scattered light intensity.

Measured distributions of the geometric particle size as a function of the evaporation temperature are shown in Figure 5.6. The air flowrate through the nebuliser was 4.2 l/min, and the cooling temperature was 15°C. Above 100°C, at most tem-

![Figure 5.6: Distribution of the geometric size of DES droplets as a function of the evaporation temperature.](image-url)
temperatures a narrow monomodal distribution is obtained which changes around 200°C, within a small temperature interval, from 1.4 μm to about 0.7 μm. This decrease in the particle diameter can be caused either by an increase in the number of nuclei, or by a decrease in the amount of vapor available for condensation. Loss of vapor due to condensation onto the walls of the cooling tube would however lead to a gradual decrease in size. The jump in size, with a bimodal distribution in between, indicates a change to a homogeneous nucleation regime, whereby suddenly the number of nuclei increases by a factor of almost 10. This explanation would mean a strong increase in the number of particles counted by the aerosizer. However, this is not observed, since the particle counting efficiency of the aerosizer strongly decreases with decreasing particle size [47, 50].

The change of average diameter and the corresponding relative standard deviations over the whole temperature range are shown in Figure 5.7. Above 100°C, the relative standard deviation is well below 0.05, except around 200°C, where the production of bimodal distributions leads to higher standard deviations.

Photon correlation spectroscopy measurements of some of these aerosols in non-

![Figure 5.7: Mean diameter and relative standard deviation of DES droplets, produced at different evaporation temperatures.](image)
5.6 Photon correlation experiments

Figure 5.8: PCS measurements of DES droplets, produced at different evaporation temperatures. (a) Autocorrelation functions. (b) Comparison with aerosizer measurements.

flowing condition were done to compare them with the aerosizer measurements. The wavelength was 514.5 nm, and the scattering angle was 90° C. The results are shown in Figure 5.8. Two things can be concluded from these measurements. Firstly, a number fluctuation decay is measured for the aerosol produced at 145° C, but not for the higher temperatures. This confirms the hypothesis that the decrease in size around 200° C is the result of homogeneous nucleation of the DES vapour. Secondly, although the size measured with photon correlation spectroscopy follows the same trend with temperature as that measured by the aerosizer, there is a factor 2 to 3 difference. This is probably due to a small misplacement of the aerosizer nozzle into the vacuum chamber, which would lead to a structural overestimation of the size. For small particles, this overestimation will be the largest due to their steep acceleration curve (Figure 5.5).

5.6 Photon correlation experiments

For the photon correlation spectroscopy measurements, the two different configurations shown in Figure 5.9 were used. The first configuration corresponds to experiments in a laboratory setup, and the second configuration to experiments carried out in a windtunnel. In the first configuration, the aerosol flows through a tube, at the entrance of which a grid is placed to create the turbulence. The incident laser beam is parallel, but in opposite direction to the main aerosol flow. Because the scattering volume in this setup is determined by the length of the laser beam that is projected
onto the detector, this configuration allows variation of the beam transit time. In this setup, the maximum mean aerosol velocity is 13 cm/s, and therefore only small mesh Reynolds numbers are achieved. However, as is shown in this section, it is still possible to see minute influences of the flow field on the autocorrelation function. Namely, the autocorrelation function is found to decay on three separate time scales.

In the second configuration, the experiments are performed in a windtunnel, where mean aerosol velocities up to 4.5 m/s can be reached. This configuration is chosen because it approaches the most what we could expect from a real-life situation. Moreover, the aerosol flow is chosen perpendicular to the scattering plane, since this is the easiest configuration for most in-line measurement applications. It requires only two windows at the measurement location in the walls of the tube or reactor.

5.6.1 Laboratory experiments

The experiments were performed in the setup shown in Figure 5.10. The aerosol from the evaporation-condensation generator was led through a glass tube of 60 cm long and 73 mm diameter. The aerosol velocity was adjusted by addition of filtered air. This means that an increased velocity is always accompanied by dilution. The flow through the nebuliser was kept at a constant value of 4.2 l/min and the flow rate of the clean air was varied between 0 and 28.6 l/min. In this way, the mean velocity in the tube could be varied between 1.7 and 13 cm/s. The light source was a vertically polarised Lexel 95 Argon laser operating at 514.5 nm wavelength. The beam was focused by a 500 mm focal length lens, and reflections at the aerosol entrance were minimised using a beam stop. The beam waist is 126 μm and the Rayleigh ratio is 97 mm, so the beam radius remains constant along the scattering volume. The scattered light from the focal point is detected at a scattering angle of 90°C. It is
5.6. Photon correlation experiments

![Diagram of setup for measurement of droplets in a turbulent flow](image)

**Figure 5.10**: Setup for the measurement of droplets in a turbulent flow. \( L_1 \) and \( L_2 \) are lenses, \( M \) is a mirror, \( S \) is an adjustable slit and \( P \) is a pinhole.

Projected by a 160 mm focal length lens onto a slit, and spatially filtered by a 150 \( \mu \)m pinhole placed 85 cm from the slit. The size of the scattering volume can be adjusted by the slit opening, which can be set between 0 and 4000 \( \mu \)m, with steps of 10 \( \mu \)m. The ALV-SO/SIPD photomultiplier was used in the dual mode, so that the signal was quasi cross-correlated.

The grid used in these experiments has a mesh size \( M \) of 1.55 mm. Combined with the aerosol velocities that were used, this leads to a maximum grid Reynolds number of about 20. At such values of \( Re \), only small deviations from laminar flow are expected to be observed. The different parameters that were studied are the aerosol flow rate, the size of the scattering volume, and the amount of turbulence (which decreases with increasing distance from the grid).

**Variation of the particle size and of the aerosol flow rate**

For aerosol sizes of 0.91 \( \mu \)m and 0.26 \( \mu \)m, correlation functions at two different aerosol flow rates are shown in Figure 5.11. The measurement location behind the grid was 10 cm, resulting in a value of \( x/M \) of 64. The slit opening was 500 \( \mu \)m, and because the lens focuses the scattering volume 1:1 onto the slit; the length of the scattering volume was also 500 \( \mu \)m. The beam transit times for the flow rates of 1.7 cm/s and 9.3 cm/s, are \( 1.5 \times 10^{-2} \) s and \( 2.7 \times 10^{-3} \) s respectively.

The three graphics shown, correspond to three different scales of the \( y \)-axis. This allows us to see the three different decays which are present in the autocorrelation functions. The first two decays are consistent with what is expected from equation 5.4 for the uniform flow situation. Namely, the first decay does not vary with the flow velocity, which is in agreement with the fact that \( \tau_D \ll \tau_L \). Also the second decay, which is the number fluctuation decay, shows agreement with the uniform flow sit-
Figure 5.11: Autocorrelation functions measured at $x/M = 64$, for two different particle sizes and two aerosol flow rates.
uation. With increasing flow rate, the characteristic time decreases, and the height increases due to the dilution of the aerosol. However, the decay is faster than would be expected from the beam transit time calculated above. This indicates that there is also a velocity component in the direction perpendicular to the laser beam. The beam transit time in this direction is related to the beam waist, which is only 126 μm. The number fluctuation decays further show that the concentration of the 0.91 μm aerosol particles is lower than that of the 0.26 μm aerosol particles. This is in agreement with the result found for the stationary aerosols that were shown in Figure 5.8-a.

Besides the two decays corresponding to diffusion and particle transit, a small extra decay is observed, which is not found for stationary or laminar flowing aerosols. Because the deviation from laminar flow is low in these experiments, the height of this decay is very low. It seems however, that this height is independent of the velocity. The time scale of this decay is of the order of seconds.

Variation of the distance from the grid and of the size of the scattering volume

In this series of experiments, the size of the scattering volume was varied in order to adjust the beam transit time, and the distance from the grid at which the measurements were made was varied in order to change the amount of turbulence. In Figure 5.12, two sets of measurements are shown, both measured at an overall aerosol velocity of 9.3 cm/s and with particles of 0.26 μm. In the first set, the scattering volume is located at 5 cm downstream of the grid, and in the second set at 10 cm. In both sets, three different sizes of the scattering volume are shown. They correspond to three slit openings: 4000, 2000 and 800 μm. Similar to the measurements in the previous paragraph, three decays are observed. The first decay (coherent decay) exhibits different heights for the different scattering volumes. The height decreases for increasing size of the scattering volume. This is expected from the change in spatial coherence, as was discussed in Chapter 4. The second decay (number fluctuation decay) also exhibits different heights. This is explained by a decrease in the number of particles in the scattering volume as this volume decreases. Moreover, it must be noted that at both measurement locations, the first and second decays are nearly similar.

For the third decay, a difference is observed between the two measurement locations. The measurements at 5 cm from the grid show an influence of the size of the scattering volume on the decay. On the contrary, in the measurements at 10 cm from the grid the shape of the third decay is independent of the size of the scattering volume.

The outcome of these measurements can be summarised as follows:

- first decay
  This decay is not disturbed by the presence of the grid. In all the measurements described here, the correct particle size was obtained.
Chapter 5. Photon correlation spectroscopy in turbulent flow

(a) Scattering volume located 5 cm from the grid.

(b) Scattering volume located 10 cm from the grid.

Figure 5.12: Autocorrelation functions measured at a flow rate of 9.3 cm/s at two distances from the grid and with three different sizes of the scattering volume.
5.6. Photon correlation experiments

- second decay
  As expected, the height of this decay reflects the number fluctuations. It increases when the particle concentration decreases or when the size of the scattering volume decreases. The characteristic time scale of this decay is faster than would be expected for a laminar flow, indicating that there is also a flow component perpendicular to the main direction of the flow.

- third decay
  This decay only observed for the flow through the grid and not for laminar flows. With a particle size of 0.26 \( \mu \)m, the height of the decay is independent of the overall flow rate and of the overall particle concentration. However, there is a difference observed between the two measurement locations. At 10 cm from the grid, the height of the decay is independent of the size of the scattering volume, while at 5 cm from the grid, the height is found to increase with decreasing size of the scattering volume. The hypothesis that follows from these results is that this third decay represents an extra concentration fluctuation, caused by the distortion of the aerosol flow as it passes through the grid.

5.6.2 Windtunnel experiments

A windtunnel, designed and built by Boender [3], was used to create higher turbulence levels than in the laboratory setup. A photograph of the windtunnel is shown in Figure 5.13, and in Figure 5.14, a schematic drawing is given. With 4 fans, gas velocities

![Photograph of the windtunnel at DelftChemTech](image)

**Figure 5.13**: Photograph of the windtunnel at DelftChemTech
between 3 and 4.7 m/s could be obtained. The measurement section is 4 m long, 1 m high and 0.5 m wide. The aerosol generator described in section 5.5 was used to produce monodisperse DES droplets of 0.26 and 0.91 μm. Because of the necessity of a relatively large number concentration of aerosol particles, the particles were introduced at the beginning of a tube of 7.3 cm diameter and 60 cm length that was placed along the streamlines in the centre of the windtunnel. At the end of this tube, a grid with mesh size \( M = 6.2 \text{ mm} \) was placed. Measurement locations behind the grid of \( x/M = 10 \) and \( x/M = 20 \) were used. The flow characteristics, as calculated with the equations presented in section 5.4.3, are given in table 5.1.

In the experiments performed in the windtunnel, the overall aerosol flow was perpendicular to the scattering plane, which corresponds with the optical configuration as shown in Figure 5.9-b. The top-view of the setup is schematically shown in Figure 5.15. The laser source in these experiments was a polarised 35 mW HeNe laser (Melles Griot 05-LHP-927). The unfocused beam diameter is 1.25 mm and the wave-

<table>
<thead>
<tr>
<th>( v ) [m/s]</th>
<th>Re</th>
<th>( l_K ) [mm]</th>
<th>( \tau_K ) [ms]</th>
<th>( l_K ) [mm]</th>
<th>( \tau_K ) [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1020</td>
<td>0.34</td>
<td>6.3</td>
<td>0.48</td>
<td>12.4</td>
</tr>
<tr>
<td>3.7</td>
<td>1260</td>
<td>0.29</td>
<td>4.6</td>
<td>0.41</td>
<td>9.1</td>
</tr>
<tr>
<td>4.7</td>
<td>1600</td>
<td>0.24</td>
<td>3.2</td>
<td>0.34</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Table 5.1: Turbulence characteristics
5.6. Photon correlation experiments

Figure 5.15: Top-view of the setup inside the windtunnel. \( v_1 \) is the velocity from the aerosol inlet flow and \( v_0 \) is the velocity generated by the windtunnel.

length is 632.8 nm. This beam is focused with a 500 mm focal length lens at the measurement location, which was located behind the centre of the tube exit. The focused beam waist was 161 \( \mu \)m. The collection optics are shown in the front-view of the setup in Figure 5.16.

Figure 5.16: Front-view of the setup inside the windtunnel. M is a mirror, \( L_2 \) is a 300 mm lens, S is a 2000 \( \mu \)m slit and P is a pinhole.

Measurements at a low aerosol velocity

The first set of measurements described here were made without the fans of the windtunnel turned on. The production aerosol flow leads to a velocity of 1.7 cm/s through the grid. The measured autocorrelation functions for the two different particle sizes and two different measurement locations are shown in figure 5.17. For comparison, the calculated autocorrelation function for the uniform flow case, as calculated with equation 5.4 for the known values of flow rate, particle size and beam diameter, is also
shown in this figure. The values of $\beta$ and of $\gamma/\langle N \rangle$ are chosen to fit the measurements of $x/M = 10$.

Compared to the calculated autocorrelation function, an extra decay is observed, at a timescale of the order of 0.1 s. For the measurements with the particles of 0.26 $\mu$m, no number fluctuation decay is present, and the extra decay is the same for each of the two measurement locations. On the contrary, for the measurements with the particles of 0.91 $\mu$m, where the concentration is lower, there is a number fluctuation decay. Here, the height of the extra decay is higher for the measurement that is made closer to the grid. This is in agreement with the observations made from the measurements in the laboratory-setup.

**Measurements at a high aerosol velocity**

A high velocity in the windtunnel was obtained by turning on one or more of the fans. Measurements of 0.26 $\mu$m aerosol particles at a mean velocity of 3.7 m/s are shown in Figure 5.18. Again, for one of the measurements, the calculated correlation function obtained using the expression for uniform flow of equation 5.4, is plotted in this figure. Contrary to the measurements made at a low overall velocity, due to the high overall velocity used in these experiments, the coherent and the non-coherent term overlap. However, the theoretical expression of equation 5.4 still fits the first decay of the measured autocorrelation function well. The same is found for the measurements with 0.91 $\mu$m particles and the measurements at a mean velocity of 4.7 m/s. This means that, at the combinations of velocity and turbulence level used in these measurements, the contribution of turbulent velocity differences, although
predicted by equation 5.23 does not influence the autocorrelation function.

Similar to the measurements at a low aerosol velocity, both autocorrelation functions show and extra decay. The shape of this decay depends on the measurement location, indicating that it depends on the degree of turbulence. A closer look at the measurement at \( x/M = 10 \) reveals a feature found in all high velocity measurements at this location: a small oscillation at the end of this decay. It is found that the frequency of this oscillation increases with increasing mean aerosol velocity. In the measurements at \( x/M = 20 \), this oscillation is no longer present. Instead, the decay becomes slower and the height increases. When we look at the Kolmogorov time scales at the two locations behind the grid, they do agree with the time scale of the slow decay. However, the oscillations found at \( x/M = 10 \) suggest a regular fluctuation, which is more likely to be associated with the turbulent turnover time. The closer to the grid, the more regular this fluctuation is.

### 5.7 Discussion and conclusions

In the theoretical overview in this chapter, the autocorrelation functions for different types of flow were presented. The main points that came out of this overview are:

- For the case of laminar (uniform) flow, the autocorrelation function consists of two decays. The first decay contains the diffusion time and the beam transit time of particles flowing through the scattering volume. The second decay, which appears only at low particle concentration, contains the beam transit time.

- For the case of turbulent flow, velocity fluctuations lead to an extra movement of the particles relative to each other. The autocorrelation function for a high
particle concentration contains a single decay. This decay is the product of the Brownian motion term, the team transit term and a term describing the velocity differences between the particles in the scattering volume.

• When the characteristic beam transit time is more than 5 times faster than the characteristic diffusion time, the beam transit term will dominate the autocorrelation function, and the Brownian motion can not be measured anymore.

The measurements in various turbulent flows presented in this chapter, show an extra decay in the autocorrelation function which is not present in measurements made in a laminar flow. This extra decay is found both at the very small Re ($\approx 10$) in the laboratory experiments and at the higher values of Re ($\approx 1500$) obtained in the windtunnel. However, contrary to what is predicted in equation 5.23, the turbulent velocity differences and the diffusion do not appear in the autocorrelation function as two terms multiplied by each other, but the turbulence leads to the addition of an extra term in the correlation function.

The theory presented in section 5.4.1 on turbulence and photon correlation spectroscopy applies to non-dilute systems, while in most of our experiments there were number fluctuations due to low concentrations. However, this does not completely explain the deviation of our results from this theory. For example, the measurements shown in Figure 5.17 have no number fluctuation decay, but do have the extra "turbulence" decay. The explanation for this is that this third decay represents an extra concentration fluctuation, caused by the distortion of the aerosol flow as it passes through the grid. This also clarifies why the extra decay in the measurements at high velocity in the windtunnel is so much higher at larger distance from the grid. Due to the distortion of the flow, the aerosol particles quickly diffuse out of the centerline of the windtunnel, leading to more intense concentration fluctuations at the measurement location.

A practical result that comes out of these measurements, is that for the range of Reynolds number studied, the effect turbulence on a particle size measurement is small. At the high flow rates used in the windtunnel, size measurement becomes nearly impossible, but this is due to the dominance of the beam transit term. This means that the main limitation in many practical size measurement applications, such as the measurement inside an aerosol flame reactor, is not the possible existence of turbulence, but simply the high flow rate. As was shown theoretically by Taylor and Sorensen [46], in dilute systems, measuring away from the focal point of the laser beam might help such cases. In that case, the coherent decay depends on the beam transit time based on the focused beam waist, whereas the number fluctuation decay depends on the transit time based on the local beam waist. This way, it may be possible to separate the two decays, and analyse the coherent decay by itself.
Applications

In this chapter, two in-line applications of dynamic light scattering are presented. The first is the size measurement of aerosol catalyst particles inside a reactor. The particle size of aerosol sampled from the reactor was found to be different from the particle size of the aerosol at the reactor conditions, which demonstrates the usefulness of in-line size measurement techniques. The second application is the measurement inside a spray of fine, highly charged droplets that are formed via electrohydrodynamic atomisation. In this case, the measured correlation functions did not yield the droplet size, but they did reveal information about the structure and the dynamics of the spray.

6.1 Aerosol catalysis

An entirely new field of heterogeneous catalysis has recently been introduced by Glikin et al. [16, 17]. For gas-phase reactions, his catalyst system consists of nano-size particles that, contrary to the commonly used systems, are not placed on a carrier but are in the form of an aerosol. Such an aerosol catalyst has many advantages compared to those that are placed on a carrier. Since the active material does not have to be reached via small pores, aerosol catalysis does not suffer from diffusion limitations at the carrier pores. Moreover, pore plugging by reaction products or by contaminants in the reactants is avoided. Furthermore, a catalyst in the aerosol form has a higher strength and thermal stability, allows easy regeneration by mechanical treatment, and is simpler and less expensive to produce.

Yet, the most striking advantage of this catalytic system, is that it has an activity that is far superior to that of its carrier-based analogues. Reaction rates were found to be 4 to 5 orders of magnitude higher. Such an enormous increase in reaction rate of course offers great opportunities to many industries. However, the question as to what exactly causes this high activity is still open.

In the experiments of Glikin et al., the catalyst is introduced into the reactor as a finely milled powder. A fluid bed of inert particles disperses the catalyst powder, which then flows along with the reactants and is removed from the product stream
by a cyclone. Because the catalyst is highly dispersed in the reactor, there is no diffusion limitation. However, calculations have shown that the high dispersion alone can not lead to an activity increase of 5 orders of magnitude. Another parameter that may be responsible for the high activity is the high surface area due the breaking up of the initial powder particles into finer (agglomerates of) primary particles. BET measurements on the aerosol sampled from the reaction zone did not show a significant increase in active surface area compared to measurements on the initial powder. However, it is not unlikely that the real surface area in the dispersed aerosol state is different from that of the sampled powder.

It is clear that the questions described above cannot be solved without the help of in-line measuring techniques. Weber et al. [51] have shown that the correlation between catalytic and photoelectric activity can be used to study the catalytic activity of aerosol particles. This may help to determine whether the increased catalytic activity of nanoparticles is mainly the result of the dispersed aerosol state, or the result of changed material properties for the nanoparticles compared to the bulk material. In this section, we describe in-line size measurements with photon correlation spectroscopy that were performed in the laboratory of Glikin in Severodonetsk, Ukraine.

6.1.1 Experimental setup

Reaction and catalyst

The model reaction used in these experiments is the deep oxidation of acetic acid:

\[
\text{CH}_3\text{COOH} + 2\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}.
\]

For this reaction, oxidation efficiencies between 99.95% and 99.99% are obtained, and the conditions are chosen such that the concentration of CO in the off-gases never exceeds 20 mg/m³. The reaction takes place at a temperature of 600°C, and the catalyst is iron oxide. X-ray diffraction has shown that this is α-Fe₂O₃ with a polycrystalline structure with crystallite sizes of 11 to 16 nm for the initial powder, and 21 to 32 nm for the samples from the reaction zone.

Reactor

A drawing of the reactor is shown in Figure 6.1. The diameter of the reactor is 50 mm and the height is 1 m. The iron oxide powder is introduced at the bottom, is dispersed by the mechanical action in the fluid bed of inert particles, and is transported through the reactor with the gas flow. At two heights, 65 cm and 90 cm, glass windows are placed in the reactor walls that allowes entrance of the laser beam and exit of the scattered light.
Photon correlation spectroscopy

A photograph of the setup that was used for the in-line photon correlation spectroscopy measurements is shown in Figure 6.2. In Figure 6.3, the same setup is schematically drawn to show the placement of the optical components. The light source is a 16 mW HeNe laser (Melles Griot 05-LHR-981). The beam is focused with a 500 mm focal length lens through the glass window into the centre of the reactor. The exit window is situated at 120° from the entrance window, resulting in a scattering angle of 60°. The scattered light is collected with a GRIN lens connected to a single mode optical fibre (OZ-optics LPC-03-488-3.5/125-1.4-6.6-3.0-4), and transported through the fibre to an ALV/SIPD photomultiplier. The signal was processed with an ALV-5000/E correlator.

In this setup, the main advantage of the use of an optical fibre for the detection is the ease of alignment. The experiments were done on several measurement locations inside and outside the reactor, and for every location the optical system had to be aligned. Compared to a classical slit-lens-pinhole system, the alignment of the lens-ended fibre was considerably faster.
Figure 6.2: Setup for in-line measurement of aerosol catalyst particles with photon correlation spectroscopy.
Figure 6.3: Schematic drawing of the reactor showing the setup for photon correlation spectroscopy.
6.1.2 Experiments

Measurements were made at different conditions in the reactor: at room temperature without reaction, and at 600°C with and without reaction. Two autocorrelation functions that were measured at 600°C in the upper part of the reactor are shown in Figure 6.4. Three decays can be distinguished in these functions. The third decay is actually an oscillation, which is due to the periodically changing catalyst concentration. This will be described later in this section. The first two decays are attributed to the particle diffusion, the velocity and the number fluctuations. Even though the measurement durations were between 5 and 15 minutes, the coherent decay remained noisy. This made it difficult to obtain accurate values for the particle size. The range of particle sizes that were found in the upper part of the reactor are shown in Table 6.1. In the lower part of the reactor, the occasional passage of inert fluid bed particles through the scattering volume disturbed most of the measurements.

As a comparison, the powder was also measured after it was dispersed in water. There, diameters of 0.7-1.3 μm were found. Besides that, the powder was measured as an aerosol sampled from the top of the reactor, and sampled just before the cyclone.

Table 6.1: Measured particle size at different conditions inside the reactor.

<table>
<thead>
<tr>
<th>temperature [°C]</th>
<th>reaction</th>
<th>particle diameter [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>-</td>
<td>0.2-0.25</td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>600</td>
<td>+</td>
<td>0.2-0.25</td>
</tr>
</tbody>
</table>
These measurements in non-flowing dilute aerosol yielded particle sizes from 0.6 to 0.8 μm.

The particle size measured outside the reactor is about twice the size that is measured inside the reactor. This indicates that the dispersed state of the powder inside the reactor, resulting from the mechanical action of the fluid bed, changes as the aerosol is sampled from the reactor. Furthermore, the size measured inside the reactor is still about 10 times larger than that of the crystallites. However, this does not exclude the presence of individual crystals inside the reactor. This is because due to the noise in the autocorrelation function, and due to the presence of the clustered crystallites of about 0.2 μm, it was not possible to measure such nanoparticles.

**Pulsating catalyst feed**

In all the measurements that were made inside the reactor, an oscillation in the correlation function was found. Further investigation revealed the connection between this oscillation and the catalyst feeding mechanism. The catalyst powder was introduced in the reactor using a rotary valve feeder. This resulted in a pulsating catalyst feed, whereby the frequency of the pulses depended on the number of holes in the feeder. This pulsating feed resulted in a regularly fluctuating concentration of aerosol, which appears as oscillations in the measured correlation functions, as shown in Figure 6.5. The frequency of the oscillations for the 8-hole feeder is exactly twice the frequency of the 4-hole feeder.

![Graph](image)

**Figure 6.5:** Oscillating correlation functions resulting from the regular pulses of catalyst feed.
6.2 ElectroHydroDynamic Atomisation

An interesting phenomenon, both scientifically and in practice, is the electrohydrodynamic atomisation of liquids. When a conducting liquid is pumped through a nozzle at a low flow rate and an electric field is applied over the nozzle and some counter electrode, a spray of highly charged droplets, also called an electrospray, is formed. At certain conditions, electrospraying can yield highly monodisperse particles. Characterisation of the spray process is therefore of great importance.

6.2.1 Electrospray in the cone-jet mode

When no electric field is applied, a droplet will form at the end of the nozzle, will grow and fall down. When an electric field is applied, a surface charge is induced in the growing droplet. This surface charge, together with the electric field, creates an electric stress at the liquid surface. When the electric field and the liquid flow rate are in the appropriate range, the electric stress will overcome the surface tension stress and the droplet will transform into a conical shape. The charge carriers in the liquid (ions) are accelerated towards the cone apex, which will result in the emergence of a liquid jet from the tip of the cone. This jet will break up into highly charged droplets.

This mode of spraying is called the cone-jet mode. In this mode, it is possible to produce highly monodisperse droplets. This is determined by the mechanism of the jet break-up. In Figure 6.6, jet break-up at increasing liquid flow rate is shown. At a low flow rate, the jet breaks up due to radial instabilities, and only one droplet size is formed. As the flow rate increases, one or more secondary droplets will be formed.

![Figure 6.6: Break-up mechanisms of the jet. (a) radial instabilities; (b) one secondary droplet per primary droplet; (c) secondary droplet and satellite; (d) azimuthal instabilities. From [5].](image-url)
6.2. ElectroHydroDynamic Atomisation

Figure 6.7: Domain of a stable cone-jet spray for a solution of heptane + 0.3% Stadis 450. From [45].

per primary droplet. The small secondary droplets will move to the outside of the spray, due to their high electrical mobility. At high flow rate, azimuthal instabilities appear, which lead to whipping of the jet.

The domain of flow rate and applied voltage at which a stable cone-jet exists, has been determined by Tang and Gomez [45]. With a nano-flash shadowgraph system, they monitored the stability of the electrospray. For a solution of heptane + 0.3% Stadis 450, the resulting stable domain is shown in Figure 6.7. Below the lower voltage limit, a pulsating spray was found, with irregular emissions of liquid. Above the higher voltage limit, various types of instabilities were observed, depending on the liquid flow rate. The azimuthal instability occurs at high voltage and high flow rate. Tang and Gomez found that in a small sub domain at lower flow rate and intermediate voltage, 'gentle' whipping occurred. Although the jet is not stable in this regime, the pattern of droplet break-up is still the same as that of the stable cone-jet spray, and therefore, still monodisperse droplets are obtained.

Models for the jet break-up: scaling laws

Models of the break-up of the jet have led to scaling laws that can be used to calculate the droplet size as a function of liquid properties and flow rate $Q$. The liquid properties of interest are the surface tension $\gamma$, the viscosity $\mu$, the relative permittivity $\varepsilon_r$, the density $\rho$ and the conductivity $K$. It has been found that the applied voltage has negligible influence on the droplet size. The model presented here is that of Gañán-
Calvo [15]. It assumes that the size of the jet and of the droplet are comparable, which is allowed when the viscosity of the liquid does not significantly affect the breaking process. Depending on the value of the dimensionless parameter $a$:

$$a = \left( \frac{\gamma^3 \varepsilon_0^2}{\mu^3 K^2 Q} \right)^{1/3},$$

(6.1)

two different scaling laws are found:

$$\frac{d}{d_0} = \begin{cases} 
1.6 \left( \varepsilon_r - 1 \right)^{1/6} \left( \frac{Q}{Q_0} \right)^{1/3} - \left( \varepsilon_r - 1 \right)^{1/3} & \text{for } a \leq O(1) \\
1.2 \left( \frac{Q}{Q_0} \right)^{1/2} - 0.3 & \text{for } a \gg 1,
\end{cases}$$

(6.2)

where

$$d_0 = \left( \frac{\varepsilon_0^2 \gamma}{\rho K^2} \right)^{1/3}, \quad Q_0 = \frac{\varepsilon_0 \gamma}{\rho K},$$

(6.3)

and $\varepsilon_0$ is the vacuum permittivity. This difference in scaling behaviour between the high viscous and high conducting liquids ($d \propto Q^{1/6}$) and the less viscous and less conducting liquids ($d \propto Q^{1/2}$) is caused by a difference in acceleration mechanism of the liquid jet. At high viscosity, the velocity profile in the jet is flat, whereas at low viscosity, the charged outside layers of the jet are accelerated faster than the centre part.

### Spray investigation methods

Several techniques have been used to characterise electrosprays. Phase Doppler Anemometry (PDA) has been used to measure the droplet size and the velocity. Gañán-Calvo et al. [15] made PDA measurements at the centre of the spray to collect data for the development of their scaling laws. Tang and Gomez [44] used PDA to measure droplet size, droplet concentration and velocity as a function of the location in the spray. Some of their results are shown in Figure 6.8. The graphs show that within a spray, the velocity decreases both with increasing axial distance from the nozzle, and with increasing radial distance from the centre of the spray. The concentration profiles show that the maximum number density is located away from the centre of the spray. This is due to the repulsion of the equally charged droplets.

Hartman et al. [19] used a high speed camera to study the jet break-up and to measure the droplet size. For droplet sizes in the submicron range, size measurement becomes difficult. The accuracy of PDA is low because the particle size is comparable to the wavelength of the laser. Furthermore, the fast evaporation of these small droplets prevents measurement of their original size in off-line measurements. A solution has been proposed by Ku et al. [27]. They collect the sprayed droplets near the counter electrode, freeze them directly and subsequently measure them with
transmission electron microscopy. These experiments require the evaporation time to be much larger than the flight-time to the counter electrode, and the also much larger than the freezing time. Both these requirements were met in their experiments.

For measurements with photon correlation spectroscopy, it is expected that the high velocity of the droplets will dominate the coherent decay of the autocorrelation function. Furthermore, the droplet formation mechanism and the electrostatic repulsion of the particles will influence the particle motion. In this section, we will investigate whether it is possible to extract useful information from measurements in such a complex system.

### 6.2.2 Photon correlation spectroscopy experiments

Three different sets of experiments were done. In the first set, ethylene glycol was sprayed at different flow rates. The droplet size is expected to increase with flow rate, according to the scaling laws. The velocity of the droplets is also expected to change. In the second set of experiments, ethanol was sprayed at a constant flow rate, and the applied voltage was varied. This is expected to yield a constant droplet size but a varying velocity. In the last set of experiments, measurements are made at different locations in a spray of ethanol. The setup of the experiments is shown in Figure 6.9. The lens and the laser source are different for the different sets of experiments. The detection of the scattered light is the same as was used in the experiments in the aerosol reactor described in the previous section. The physical properties of the two spray liquids are given in Table 6.2.
**Figure 6.9:** Setup for photon correlation spectroscopy measurements of an electrospRAY.

**Table 6.2:** Physical properties of ethanol and ethylene glycol at T=20°C.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_r$ [-]</th>
<th>$\gamma$ [N/m]</th>
<th>$\rho$ [kg/m$^3$]</th>
<th>$\eta$ [mPa s]</th>
<th>$K$ [$\mu$S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>25.1</td>
<td>0.02275</td>
<td>789.3</td>
<td>1.2</td>
<td>60</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>38</td>
<td>0.048</td>
<td>1109</td>
<td>20</td>
<td>119</td>
</tr>
</tbody>
</table>

**Flow rate**

Measurements at 4 different liquid flow rates were made in a spray of ethylene glycol. The light source was a vertically polarised 35 mW HeNe laser (Melles Griot 05-LHP-927). The beam was focused by a lens of 8 cm focal length into the centre of the spray, 1 cm below the nozzle outlet. The distance between the nozzle and the counter electrode was 5 cm, and the applied voltage was 9.50 kV. According to the scaling laws, the size of the produced droplets increases with flow rate. The calculated droplet sizes are given in Table 6.3. Three autocorrelation functions are shown in Figure 6.10. The decay clearly becomes faster when the flowrate is increased. This indicates an increase in the velocity of the droplets. An interesting feature of these autocorrelation functions is that they drop below zero and then gradually climb back to the baseline, as can be seen from Figure 6.10-b. Such an exponentially damped cosine is typical of underdamped surface light scattering, i.e. a scattering sample when a local oscillator
6.2. ElectroHydroDynamic Atomisation

Figure 6.10: Correlation functions measured at different liquid flow rates.

is present [42]. However, in our optical configuration, no local oscillator was present.

In the measurements in the aerosol reactor, the oscillation in the correlation function was caused by a regularly fluctuating concentration. In an electrospray in the cone-jet mode, the break-up of the jet and the production of droplets is also a very regular process. Therefore, it seems plausible that the oscillation is a result of the regular droplet formation. The time scale of the damped oscillation in the correlation functions decreases with increasing flow rate. However, the calculated time between the formation of two droplets, which is given in Table 6.3, increases with increasing flow rate. So far, no satisfactory explanation for this damped oscillation has been found.

Table 6.3: Initial primary droplet size and primary droplet production rate for different liquid flow rates of ethylene glycol.

<table>
<thead>
<tr>
<th>$Q$ [ml/hr]</th>
<th>$d$ [µm]</th>
<th>time between two droplets [µs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.7</td>
<td>$8.5 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>0.5</td>
<td>4.3</td>
<td>$3.0 \cdot 10^{-7}$</td>
</tr>
<tr>
<td>1</td>
<td>5.9</td>
<td>$4.0 \cdot 10^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>9.5</td>
<td>$5.4 \cdot 10^{-7}$</td>
</tr>
</tbody>
</table>
Applied voltage

These measurements were made with the same setup as described above, but with ethanol as spray liquid. The liquid flow rate was 1 ml/hr, and the applied voltage was varied for the different measurements. The spray remained in a stable cone-jet mode, and therefore the droplet size does not change with the applied voltage variation.

Tang and Gomez concluded from their experiments and calculations, that the droplet radial motion and, consequently, the jet lateral spreading are driven primarily by the space charge field. However, the droplet axial motion is driven primarily by the external field. This means that for a measurement of the axial velocity in the centre of the spray, the space charge force can be neglected. As a result, the velocity of the particles is expected to increase with an increase in the applied voltage.

![Figure 6.11: Correlation functions measured at different applied voltages.](image)

Three correlation functions are shown in Figure 6.11. As expected, the decay becomes faster for increasing voltage difference. These correlation functions also drop below zero, but a different pattern is found compared to the correlation functions for varying liquid flow rate. Here, all correlation functions come back to the same line. Since for these measurements the droplet size, and therefore the rate of droplet formation is constant, these measurements are in favour of the theory that this damped oscillation is a result of the regular process of jet break-up.

Azimuthal instabilities

The transition of the stable cone-jet regime towards a break-up mechanism with azimuthal instabilities can be clearly seen from photon correlation spectroscopy measurements. As soon as the jet starts to show a whirling motion, the concentration of
droplets in the measuring volume starts to fluctuate strongly.

Figure 6.12 shows two correlations functions that were measured in a spray of ethylene glycol with a flow rate of 0.5 ml/hr. The distance between the nozzle outlet and the counter electrode was 24 mm, and the measurements were made 4 mm below the nozzle. The frequency of the whirling motion is 34 Hz for the measurement at 9.5 kV, and 62 Hz for the measurement at 10 kV. This means that the instability increases with an increase in the electric field strength.

This instability shows up in the correlation function at voltages and flow rates for which the spray still seems to be stable from an inspection by eye. Therefore, for assuring operation of a spray in the stable cone-jet mode, dynamic light scattering is an excellent and simple technique.

**Location in the spray**

The last set of measurements consists of a vertical and horizontal scan through a spray of ethanol. The liquid flow rate was 1 ml/hr, and the applied voltage was 8.4 kV. The distance between the nozzle outlet and the counter electrode was 126 mm.

For these measurements, the 514.5 nm beam of a vertically polarised Lexel 95 Argon laser was focused with a lens of 300 mm focal length at the measurement location in the spray. The detection system was identical to that of the previously described measurements.

The first thing that is seen when the laser beam shines through the spray is the segregation of the primary and secondary droplets, resulting in a scattered laser beam consisting of three segments. The segregation is a result of the high electrical mobility of the small secondary droplets, which drive them towards the outside of the spray,
leading to a spray as in Figure 6.13. The presence of the smaller droplets at the outside of the spray is not only observed as a laser beam that is 'cut' into three, but also by a difference in the measured autocorrelation function, as is shown in Figure 6.14. This figure shows three correlation functions that are measured 46 mm below the nozzle. Two of the measurements were made at the inner part of the spray, at 5 and 15 mm from the centre, and one measurement was made in the outer part, at 25 mm from the centre. The correlation function measured at the outside of the spray, where the small secondary droplets are, shows a much slower decay than the correlation functions measured near the centre of the spray. This transition in decay times is quite abrupt, and it can be concluded that the velocity of the secondary droplets is much smaller than that of the primary droplets.

At every distance below the nozzle, such a transition can be found, and therefore a scan through the spray leads to the shape of the spray, as is shown in Figure 6.15.

When the measurements are analysed using equation 5.4 for uniform flow at low
Figure 6.15: Overview of the correlation functions measured at different distance $z$ below the nozzle and distance $r$ from the centre of the spray. (+) fast decay corresponding to the large primary particles; (0) slow decay corresponding to the satellites; (-) no correlation function.

Concentration, a velocity profile of the spray is obtained, as shown in Figure 6.16. The velocity is found to decrease with distance from the nozzle and with distance from the centre, similar to the results found by Tang and Gomez. Therefore, the uniform flow models seems to be appropriate for the motion of the droplets in an electrospray that is operating in a stable cone-jet mode.

Figure 6.16: Velocity of the droplets at different radial ($r$) and axial ($z$) positions in the spray.
6.2.3 Conclusions

The applications of in-line measurements of dynamic light scattering that were presented in this chapter, show how this technique can be used to obtain more insight into a system for which the experimental access is limited.

In the measurements in the reactor with aerosol catalysis, a mean particle size of the aerosol inside the reactor of 0.2-0.3 μm was obtained. When these particles were measured outside of the reactor, either sampled as an aerosol or dispersed in a liquid, particle sizes 2-5 times larger were found. This difference shows the importance of in-line measurements.

Because of the extremely high catalytic activity of the aerosol particles, particle sizes of the order of the crystallite size (10-30 nm) were expected to be found. This was not the case however. The noise in the autocorrelation function and the presence of the clustered crystallites that are about 10 times larger than the single crystallites, make it impossible to measure such nanoparticles, even if they are present.

The second in-line application, the characterisation of the electrospray, yields mainly information about the structure of the spray. From a horizontal and vertical scan through the spray, the position of the primary and the secondary particles in the spray and also the velocity profile of the droplets was obtained. Furthermore, analysis of the autocorrelation function was found to allow an easy inspection of the stability of the cone-jet mode. An instable spray results in oscillations in the autocorrelation function at a time scale of 0.01-0.1 s. A damped oscillation at a time scale of about $10^{-5}$ s is observed in many of the correlation functions, but the origin of this oscillation is still unclear.
General conclusions and perspectives

The dynamic light scattering technique is able to measure diffusion coefficients of submicrometer particles without the need for assumptions on their refractive index or density. Combined with the fact that the technique is non-intrusive, it is an attractive method for in-line particle size measurement.

However, the conditions in the environment in which the in-line measurements are to be performed, are usually far from the ideal conditions for dynamic light scattering. These ideal conditions include that the sample is non-flowing and dilute, but not so dilute that there are less than about 100 particles in the scattering volume. Whenever the real measurement conditions deviate from these ideal ones, care needs to be taken during the optical design of the experiment, and with the analysis of the measurements. In this thesis, two causes of non-idealness that are often encountered, especially for the analysis of aerosols, have been studied. The first is low particle concentration and the second is turbulent flow.

At low concentration, both the measurement of particle concentration and particle size were studied. When the average number of particles in the scattering volume is low, number fluctuations lead to a slow decay in the autocorrelation function, in addition to the fast decay caused by the diffusion of the particles. Theoretically, the height of this slow decay is inversely proportional to the average number of particles in the scattering volume, and therefore allows measurement of the concentration. It was found however, that in practice this concentration measurement is complicated by the length of the measurement time that is required for the height of the slow decay to reach a constant value. This time depends on the variation in the particle occupation number during the measurement, and this variation is driven by diffusion of particles through the scattering volume. In standard photon correlation spectroscopy equipment, the size of the scattering volume is such (about $5 \cdot 10^{-7} \text{ cm}^3$), that the necessary measurement time is about 10 hours for 200 nm particles dispersed in a liquid. Therefore, an accurate measurement of the concentration in such equipment is not realistic. However, in a research setup, the size of the scattering volume can be lowered, yielding more reasonable measurement times. The best opportunities for
concentration measurement on the basis of the intensity autocorrelation function, are in aerosols. Here, the diffusion coefficient of the particles is a factor 60 to 1000 times higher than in liquids, so that the necessary measurement time is reduced by a factor 60 to 1000!

The quality of a size measurement at low concentration, is investigated by studying the signal-to-noise ratio, which is the height of the coherent decay. Measurements have shown that this signal-to-noise ratio decreases towards high and towards low concentrations. Simulations of photon correlation experiments at low concentrations show that the decrease of the signal-to-noise ratio towards low concentrations is the result of two factors. They are incomplete interference and a decrease of the scattered light intensity. Incomplete interference occurs when the larger part of the scattered light that reaches the detector, comes from a single particle. These two effects result in a lower concentration limit of about 1 particle in the scattering volume. At low concentration, it may be useful to increase the size of the scattering volume to increase the number of particles in this scattering volume. However, this leads to a decrease in the spatial coherence factor, which results in a decrease in the signal-to-noise ratio. It is shown in this thesis how the competition between these two effects (incomplete interference and decreased scattered light intensity vs decreased spatial coherence) leads to an optimum size of the scattering volume for each particle concentration.

The second case of non-idealness treated in this thesis is that of turbulence. In a turbulent flow, the displacement of the particle relative to each other is the result of both Brownian motion and of turbulent velocity fluctuations. Theoretically, this results in the diffusion decay in the autocorrelation function being multiplied by a decay describing the velocity difference between the particles within the scattering volume. However, experimentally, the main effect of the turbulence on the autocorrelation function was found to be caused by concentration fluctuations. These fluctuations are independent of the low concentration number fluctuations described before. Therefore, they lead to a separate decay in the autocorrelation function.

Our measurements showed that a low amount of turbulence has no influence on the size measurement. In the highly turbulent regime, only measurement of the velocity was possible. This is because the time scale of the velocity has become much shorter than the time scale of diffusion. Thus, the limit met in turbulent flow measurement is primarily related to the collective particle velocity and not to the amount of turbulence.

Also in the in-line applications of photon correlation spectroscopy, structural concentration fluctuations are often observed and are sometimes even dominating the measurements. Such fluctuations have usually nothing to do with the particles that are to be measured, but are a result of the dynamics of the measuring system, for example a regular dosing of aerosol material into a reactor. Despite these concentration fluctuations, in-line measurement with photon correlation spectroscopy has been
shown to be a valuable tool in the analysis of systems for which other experimental access is limited.

The investigations made in this thesis work have set the limits for measurement at low concentration and turbulent flow in the current state of technology and knowledge. Nevertheless, I believe that by applying the following recommendations these limits can be shifted further.

From our study of measurement at low concentration it clearly appears that the possibility of changing the scattering volume would be a powerful tool. It would allow accurate measurements of concentration and size at concentrations a thousand times lower than the current limit. In standard equipment, this could be achieved by incorporating a variable slit in the detection optics.

We have seen that the evolution of the variance of the number of particles in the scattering volume during a measurement, is related to the evolution of the height of the number fluctuation decay. When the variance has become constant, the correlation function has reached a stable shape and allows for concentration measurement. Calculating the photon counting statistics during a measurement will allow for a significant reduction in the measurement time. With this system, the operator will know when the measurement is completed. This can be achieved by including these calculations in the autocorrelator board.

The current use of optical fibres limits the possibility to vary the size of the scattering volume. However, they offer high spatial coherence and easy alignment and are therefore very practical for in-line measurements. Thus, it would be a definite improvement be able to combine these two advantages. The most robust option is the development of a laser source and receiving optics in one probe, so that alignment difficulties in harsh environments can be avoided.

In the last decade, much particle research has shifted to the field of nano-particles. Because of the low amount of scattering from nano-particles, detection systems must be very sensitive. The fast diffusion should not be a problem: correlators with delay times as short as 5 ns are already on the market. However, a new problem arises for such small particles, resulting from the fact that the relaxation time of nano-particles becomes of the order of their diffusion time. This requires theoretical work on the analysis of the autocorrelation functions. This work consists of developing an adequate inversion method.
Bibliography


Samenvatting

- Dynamische lichtversstrooiing by lage concentratie en in turbulente stroming -

De meeste deeltjes- en poederprocessen worden bestudeerd aan de hand van de deeltjesgrootte en zijn verandering in de tijd. Het deeltjesgroottebereik dat daarbij van belang is kan variëren van enkele nanometers (bij het dispergeren van pigmenten) tot enkele milimeters (kristallen, granules). Gezien de huidige ontwikkelingen in de nanotechnologie, wordt het steeds belangrijker om aan de onderkant van dit deeltjesgroottebereik nauwkeurige, veelzijdige en niet-storende meettechnieken ter beschikking te hebben.

Een techniek die specifiek geschikt is voor het meten van de grootte van submicrometer deeltjes, is dynamische lichtversstrooiing. Deze techniek is gebaseerd op de willekeurige thermische beweging die alle kleine deeltjes vertonen: de Brownse beweging. De deeltjes eigenschap die wordt verkregen uit een dynamische lichtversstrooiingsmeting is de diffusiecoëfficiënt, welke direct gerelateerd is aan de deeltjesgrootte: hoe kleiner de deeltjes, hoe sneller ze bewegen. Sinds de uitvinding van dynamische lichtversstrooiing in de jaren 60, is het onwrikkeld tot een standaard meettechniek voor verdunne monsters van sub-micrometer deeltjes, en er zijn momenteel verscheidene commerciële apparaten beschikbaar. Over het algemeen kunnen er met deze apparaten alleen off-line metingen van vloeistof-suspensies worden gedaan, en worden de fouten die ontstaan bij het nemen van een monster niet meegenomen. Voor dynamische processen echter, zijn in-line technieken duidelijk een vereiste. In een aerosol produktieproces bijvoorbeeld, is het nemen van een monster vaak onmogelijk vanwege de hoge snelheid waarmee het proces zich voltrekt.

Dynamische lichtversstrooiing is in principe zeer geschikt voor in-line toepassingen, omdat het het systeem niet hoeft te verstoren. Deze mogelijkheid voor in-line metingen in diverse deeltjesprocessen confronteert de meetmethode echter met twee nieuwe uitdagingen, welke in de huidige standaard meettechniek nog niet zijn verwerkt: de deeltjesconcentratie en de deeltjesstroming. Deze twee uitdagingen vormen de basis van dit promotiewerk.
Samenvatting

De eerste uitdaging is de meting van deeltjesgrootte en -concentratie bij lage deeltjesconcentratie. Wanneer er zich maar weinig deeltjes in het experimentele meetvolume bevinden, kan een dynamische lichtverstrooiingsmeting onder bepaalde omstandigheden worden gebruikt voor het meten van de deeltjesconcentratie. Simulaties en experimenten hebben aangetoond dat deze omstandigheden tweevoordig zijn: de vorm en de grootte van het meetvolume moeten nauwkeurig bekend zijn, en de duur van de meting moet lang genoeg zijn. Voor meting van de deeltjesgrootte bij lage concentratie, is er aangetoond hoe de optische opstelling ontworpen kan worden om bij iedere concentratie de beste kwaliteit meting te verkrijgen.

De tweede uitdaging is de meting in een turbulente stroming. In dat geval veroorzaken snelheidsfluctuaties een extra beweging van de deeltjes ten opzichte van elkaar, bovenop hun Brownse beweging. De mate waarin dit de meetresultaten beïnvloedt, hangt af van de tijd- en lengteschalen die de turbulentie karakteriseren, vergeleken met de tijd- en lengteschalen van diffusie. Met metingen aan een aerosol in een turbulente stroming is de invloed onderzocht die de gemiddelde stroomsnelheid en de mate van turbulentie hebben op een deeltjesgroottemeting.

Het praktische gebruik van dynamische lichtverstrooiing als een in-line meettechniek is bestudeerd aan de hand van twee toepassingen. De eerste is de deeltjesgroottemeting binnenin een reactor, in een aerosol van katalysedeeltjes. De deeltjesgrootte van de aerosol die als monster uit de reaktor was genomen, bleek verschillend van de deeltjesgrootte die onder reaktoromstandigheden was gemeten. Dit toont aan hoe nuttig een in-line meettechniek kan zijn. De tweede toepassing is de meting in een spray van zeer kleine, hoog geladen druppeltjes. In dat geval was het niet mogelijk de deeltjesgrootte te meten, maar werd er wel informatie verkregen over de structuur en de dynamica van de spray.

Evelien Nijman
Dankwoord

Het leuke van een dankwoord schrijven van een proefschrift, is dat de rest van het boek dan klaar is. Daarnaast geeft het de mogelijkheid nog eens terug te denken aan de mooie kanten van de promotie. Die promotie begon nadat prof. Scarlett mij na mijn afstuderen had overtuigd dat onderzoek zeer geschikt voor mij was, of ook, ik zeer geschikt voor onderzoek. De afgelopen vier jaar heb ik daar nog wel eens aan getwijfeld, maar uiteindelijk ben ik erg blij dat ik toen die keuze heb gemaakt, en ik wil prof. Scarlett dan ook bedanken voor zijn vertrouwen dat hij in mij heeft getoond.

Voor het kiezen van een project waren er diverse mogelijkheden. Jan en Alexander hadden juist allerlei spannende ontdekkingen gedaan op het gebied van het meten met PCS bij lage concentraties, en dankzij hun enthousiasme ben ik aan dit project begonnen. Uiteindelijk is het resultaat heel anders geworden dan dat we bij aanvang verwacht hadden, maar dat toont aan welke vrijheid ik heb gekregen in het uitstippelen van mijn weg.

Henk, drie, nee twee dingen. Ten eerste ben ik erg blij dat je diverse keren mijn hoofdstukken hebt gelezen, zonder te klagen dat ik jouw aanmerkingen van de vorige keer nog steeds niet verwerkt had. Daarnaast vond ik het erg gezellig dat je vaak bij de koffiepauze aanwezig was, met interesse voor de mensen die verder ging dan ISO-normen en zeven.

Ik deed eigenlijk het liefste "gedachtenexperimenten", maar de echte experimenten moesten ook gebeuren. Een aantal studenten hebben erg nuttige metingen gedaan, en daar ben ik Michiel, Donny, Chris en Jan zeer dankbaar voor. Merlin wist waarschijnlijk niet waar hij aan begon toen hij ervoor koos om een scripje over PCS in stromende media te schrijven. Ik denk dat hij trots kan zijn op het resultaat. De "gedachtenexperimenten" kregen meer vorm toen Bjorn me op weg hielp met de simulaties. Ik had nooit gedacht dat ik dat zo leuk zou gaan vinden dat ik niet meer weg te slaan was bij de computer!

De opa’s van onze oude deeltjesgroep, Alexander en Wim, hebben gezorgd voor de aanvangsgezelligheid in de groep. Later hebben waarde collega’s dat weten voort te zetten en ervoor gezorgd dat er altijd wel weer een gezellige discussie over auto’s of hoofdsteden was, waar ik naadloos bij aan kon sluiten. Renske en Annemoon, gelukkig waren jullie er af en toe bij om het onderwerp te veranderen.
Sjaak, Ma, John, Arief, Ramanan and Arjan were always helpful in discussing scattering problems, lending equipment, or helping me with the \LaTeX\ problems.

Kees, het was een spannende reis naar de Oekraïne. De wilde avonturen op de vliegvelden, de gevaarlijke reis met de trein en iedere dag weer een verrassingsmenu, ongeacht wat we bestelden. Daarnaast ben je ook erg goed in het inbouwen van autoradio’s. Daan, je was altijd goed in het winnen van weddenschappen, wat mij diverse keren bioscoop heeft gekost. A natural winner, zal ik maar zeggen. Flip, ondanks dat je een groot gedeelte van mijn promotie ofwel bij Gist, ofwel in Australië zat, hebben we veel lol gehad in de tijd dat je wel hier was. Lekker port drinken in Coimbra, en met een scheef hoofd naar een slechte film kijken. Richard, ik ben erg blij dat we elkaar als kamergenoot hebben uitgekozen en gehouden. Ik had mezelf geen grotere steun kunnen toewensen in de zware tijden van het schrijven.

Mijn ouders ben ik erg dankbaar dat ze altijd voor me klaar stonden en staan, en vooral dat ze veel begrip hadden voor alle drukte het afgelopen jaar.

En Damien, al ben je dan geen "waarde collega", je bent voor mij wel een zeer waardevolle liefde en vriendschap. Stiekum ben jij wel het mooiste wat er uit mijn promotie is voortgekomen!

Evelien
Curriculum Vitae

Name: Evelien Johanna Nijman
Date of birth: 27 April 1971
Place of birth: Eindhoven
1984-1990: VWO, Griftland College, Soest
1990-1996: Chemical Engineering, TU Delft, cum laude
1997-2001: PhD, Particle Technology Group, TU Delft
2001-: DMV International, Veghel