Development of fiber optic based dynamic light scattering for a characterization of turbid suspension

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Development of Fiber Optic Based Dynamic Light Scattering for a Characterization of Turbid Suspensions

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1 Summary

Dynamic light scattering (DLS) is one of the most popular experimental techniques in the characterization of colloidal systems. However, its application to many systems of industrial relevance has often been considered to be too complicated due to the very strong multiple scattering in undiluted solutions. The interpretation of a DLS experiment becomes exceedingly difficult for systems with non-negligible contributions from multiple scattering. For larger particle sizes with high scattering contrast this immediately limits the technique to very low concentrations. Therefore investigations of many industrially relevant dispersions are not possible or require very high dilution, which results in a high probability for artefacts when working with emulsions and self-associating systems. A very elegant solution to this problem consists of suppressing multiply scattered light in dynamic light scattering experiments with a so-called cross correlation technique. With this technique highly turbid systems can be investigated in their natural state, which is an important improvement compared to other methods, such as dilution or contrast matching, where the sample composition need to be changed.

Based on these considerations we have constructed a so-called 3d cross-correlation instrument for the characterization of turbid samples. With this instrument two light scattering experiments are performed simultaneously having the same scattering volume and identical scattering vectors. Then the cross-correlation of the two obtained signals contains single scattering events only, and all contributions from multiple scattering are suppressed. However, the use of such an instrument for investigations of complex systems in an industrial environment represents a challenging task with respect to both the required precise matching of the two light scattering experiments and the necessary high stability. Therefore we used state of the art optical and opto-mechanical components. We were able to construct a laser light scattering instrument for measurements with highly turbid suspensions. Due to its compact design, the easy alignment and the high inherent stability it can be used for static and dynamic light scattering experiments in fundamental research as well as in industrial laboratories for routine measurements. This opens up a wide field of new applications ranging from particle sizing in industrially relevant systems such as emulsions to the determination of the dynamics of concentrated model suspensions that can not be optically matched.

Experiments with well defined model systems demonstrate clearly that highly turbid colloidal systems can successfully be characterized using the 3d instrument,
and that the particle size distribution, the particle form factors and static structure factors can be correctly determined. In a next step we show that the 3d cross-correlation technique is also applicable to complex 'realistic' systems of industrial relevance. Investigations of milk show that a dilution could lead to dramatic changes in the measured particle size distribution. Using the 3d instrument, however, it is often possible to investigate systems in their 'natural' state, or at least a dilution can be low. On further experiments with protein stabilized emulsions we then show how an access on particle interactions via measurements of the particle form factor and the static structure factor can be obtained, when investigating systems which are unstable against dilution. These experiments show that the 3d instrument represents a major improvement and allows for a quantitative characterization of undisturbed 'native' samples. We thus believe that this technique opens up new possibilities in the investigation of particle size distributions, equilibrium properties, the dynamic behaviour and stability of complex particle suspensions. This could be of considerable importance for a variety of industrial applications.
2 Zusammenfassung


Auf diesen Überlegungen basierend haben wir ein sogenanntes 3d Kreuzkorrelationsinstrument zur Charakterisierung von optisch trüben Proben gebaut. Mit diesem Instrument werden zwei Lichtstreuexperimente gleichzeitig durchgeführt, die das gleiche Streuvolumen und identische Streuvektoren besitzen. Eine Kreuzkorrelation der beiden Signale enthält dann nur Beiträge von Einfachstreuprozessen, alle

3 Introduction

Dynamic light scattering (DLS) is one of the most popular experimental techniques in the characterization of colloidal suspensions. DLS provides a measure of the time scale for fluctuations in the index of refraction of a complex fluid, and it probes these fluctuations on the length scale of the inverse of the scattering vector, $q^{-1}$. In the case of colloidal particles intensity fluctuations are predominantly caused by the diffusive motion of the particles. Based on the correlation between diffusion coefficient and particle size, DLS is now widely used as a very convenient and non-destructive method for particle sizing. The technique is suitable for the characterization of colloidal particles over a wide range of sizes from a few nanometers to several micrometers. Moreover, DLS is also frequently used for investigations of the dynamic behaviour of concentrated and/or strongly interacting colloidal suspensions and glasses, and it allows to follow processes such as aggregation and gelation. However, its application to many systems of industrial relevance has often been considered to be too complicated due to the very strong multiple scattering in undiluted solutions. The interpretation of a DLS experiment becomes exceedingly difficult for systems with non-negligible contributions from multiple scattering. Particularly for larger particles with high scattering contrast this limits the technique to very low concentrations, and a large variety of systems are therefore excluded from investigations with dynamic light scattering. One quite recent approach to this problem, which has already been implemented in commercial products, works in the limit of very strong multiple scattering, where a diffusion model can be used in order to describe the propagation of the light across the sample [1]. Unfortunately, this so-called 'diffusing wave spectroscopy' does generally not allow to determine important features such as polydispersity of the particles due to the inherent averaging over a large range of spatial length scales. A very interesting opposite approach aims at sufficiently suppressing contributions from multiple scattering from the measured photon correlation data. There exist a number of different theoretical and experimental approaches to this problem [2, 3, 4]. The general idea is to isolate singly scattered light and suppress undesired contributions from multiple scattering in a dynamic light scattering experiment (for details see [2]). This can be achieved by performing two scattering experiments simultaneously on the same scattering volume with identical scattering vectors but using different geometries. Then only singly scattered light will produce correlated fluctuations on both detectors. In contrast, multiply scattered light will result in uncorrelated fluctuations that contribute
to the background only due to the fact that it has been scattered in a succession of different q-vectors.

Several different proposals for an experimental realization of this task have been presented in the past. In his pioneering article Phillies outlined the possibility of suppressing multiple scattering by means of cross-correlation techniques and described a relatively simple experiment in which cross-correlation of counterpropagating laser beams in a turbid sample was used [3]. However, the use of this method for the characterization of colloidal suspensions is limited due to the fact that it is restricted to a scattering angle of 90° only. Several other experimental lay-outs not restricted to a single scattering angle were subsequently discussed by Schätzel [2], whose group in particular successfully implemented the two-colour method [5]. While this method has been demonstrated to work very well by several groups [6, 7], it is technically extremely demanding and requires very sophisticated alignment procedures. A particularly interesting scheme is the so-called 3d cross-correlation experiment, in which the two incident and the two detected light paths are placed at an angle $\delta/2$ above and below the plane of symmetry of the scattering experiment (see figure 1). The initial $(k_{i1}, k_{i2})$ and final $(k_{f1}, k_{f2})$ wave vector pairs are rotated by some angle about the common scattering vector $q = q_1 = q_2$ for the two scattering processes 1-1 and 2-2, whereas the two other scattering processes 1-2 and 2-1 detected in this experiment have different scattering vectors. These additional scattering processes will therefore contribute to the background only, which means that the maximum intercept for the 3d experiment is only one quarter of the value obtained for auto-correlation or other cross-correlation schemes such as the two-colour method, i.e. $\beta_{12,\text{ideal}} = 0.25$ [2]. Several research groups [8, 9, 10] have very recently demonstrated the feasibility of such an experiment and clearly shown that dynamic light scattering need not be restricted to dilute suspensions of small particles, but that it can be used to successfully characterize extremely turbid suspensions. This opens up a completely new field of suspension characterization using dynamic light scattering experiments combined with novel cross-correlation schemes in numerous areas of soft condensed matter research and technology.

The outline of this thesis is as follows: after an overview of the theoretical background of laser light scattering the experimental realization of the 3d cross-correlation instrument is described in detail. The feasibility of the instrument is demonstrated on dynamic and static light scattering experiments with well defined model systems. It is shown that optically turbid particle suspensions can be characterized with respect to size distribution, as well as the determination of the particle
form factor and static structure factor, where the latter provides an access to particle interactions. In a next step then the applicability of the 3d instrument to realistic systems of substantial industrial importance were investigated, and it is shown how the 3d instrument can help in the characterization of such systems in terms of size distribution, interaction potential and stability.
4 Light Scattering Theory

Scattering experiments continue to be used as a very powerful tool both in (soft) condensed matter research as well as in sample characterization. The basic principle of a scattering experiment [11, 12, 13] is an incident beam of particles or radiation, which impinges on a sample and is scattered by its microscopic structures $^1$ (see figure 2). With a detector the resulting scattering intensity is measured as a function of the scattering angle $\Theta$ between the incident and the scattered beam. Additional information about the sample properties can be obtained by analysing the scattered beam with respect to polarization, energy, wavelength, spin and so on, and the information obtained also depends on the nature of the interaction between the beam and the sample. Basically the structures that can be resolved with scattering experiments are of the same order of magnitude as the reciprocal of the scattering vector $q = 4\pi/\lambda \sin(\Theta/2)$. The energy $E$ of a particle is related to a wavelength $\lambda$ through the relation $E = h k$, where $h$ is Planck’s Wirkungsquantum and $k = 2\pi/\lambda$. This means that the smaller the wavelength $\lambda$ of the radiation or the higher the Energy $E$ of the particles, the smaller the structures that can be investigated with a scattering experiment. For example x-ray scattering and neutron scattering are commonly used to investigate crystal structures, small particles such as micelles or microemulsions, or local structural properties in polymers, while laser light scattering is often the method of choice in the characterization of colloidal systems [14, 15].

Interaction of light with matter depends on the electronic structure of the material as determined by its quantum mechanical properties. In most cases the results obtained with quantum field theory differ only little from the classical electrodynamic theory, which is used for the description of the theoretical background of laser light scattering in the following chapters. When an incident electromagnetic field in the form of a plane wave

$$E_i(r, t) = E_0 e^{i(k_ir - \omega t)}$$

impinges on matter, the response is a polarization of the charge distribution of the system. The deformation of the charge distribution by the electromagnetic field is described through the polarizability $\alpha(\omega)$ of the system, which in general is a tensor. In a microscopic picture the mechanisms of polarization of a non conducting

$^1$Dependent on the kind of beam these structures could be atoms, nuclei, electrons, particles, ...
Material are alignment of permanent dipoles, which try to follow the electromagnetic field; with increasing frequency this process relaxes and oscillations of ions and, at even higher frequencies, electrons come into resonance [16]. With the polarizability $\alpha(\omega)$ the complex dielectric constant $\varepsilon(\omega) = \varepsilon' + i\varepsilon''$ is determined $^2$, where the real part is the square of the index of refraction

$$n = \sqrt{\varepsilon'}$$  \hspace{1cm} (2)

and the imaginary part describes the absorption of light through the sample. The polarization mechanism can be viewed as caused by a force acting on the charges due to the electromagnetic field. As known from classical electrodynamics, these accelerated charges then radiate light [18]. If we now assume a perfectly homogenous medium which is illuminated by light, the illuminated region can then be divided into subregions which are small compared to the cube of the wavelength of the light $^3$. Then each of the atoms in a small subregion sees essentially the same incident field. In the far field picture the total scattered electric field is then a superposition of the scattered fields of each subregion. Due to the fact that the medium is homogeneous (and infinite in space), for each subregion another subregion can be found

$^2$According to Clausius-Mosotti [17] the polarizability $\alpha$ is related to the refractive index $n$ of an ideal gas through $\alpha = \varepsilon_0 V / N (n^2 - 1)$

$^3$These subregions are still homogeneous on the length scale of the wavelength of the light

---

**Figure 2**: Sketch of a scattering experiment. An incident beam of radiation or particles emitted by a source is scattered by a sample. The scattering intensity is measured as a function of the scattering angle $\Theta$. For details see text.
that cancels radiation due to destructive interference. Only the primary beam is visible in a homogeneous medium, and scattering occurs only at inhomogeneities in the medium or on surfaces. The reason that light nevertheless is scattered by a homogeneous medium is, according to Einstein, a result of local fluctuations of the dielectric constant $\varepsilon$ or the index of refraction $n$ in the medium [19]. Such local fluctuations take place, because in a liquid, for example, the atoms or molecules are constantly in motion. Therefore $\varepsilon$ or $n$ will fluctuate in a given subregion and total cancellation of the scattered light seen by the detector no longer takes place and a finite scattering intensity exists. If

$$\varepsilon(\mathbf{r}, t) = \varepsilon_0 \mathbf{I} + \delta \varepsilon(\mathbf{r}, t)$$  (3)

is the local dielectric constant of the medium where $\delta \varepsilon(\mathbf{r}, t)$ describes the fluctuations of the dielectric constant and $\mathbf{I}$ is the second rank unit tensor, the resulting scattered electric field is

$$\mathbf{E}_s(R, t) = \frac{E_0}{4\pi i k f R} \int_V d^3 r e^{i(q \cdot r - \omega t)} [\mathbf{n}_f \cdot [k_f \times (\delta \varepsilon(\mathbf{r}, t) \cdot \mathbf{n}_f)]]$$  (4)

The subscript $V$ describes that the integral is over the scattering volume, $R$ is the distance between the scattering volume and the detector, $\mathbf{q} = k_i - k_f$ is the scattering vector, $k_i$ and $k_f$ are the incident and final wave vectors of the light and $\mathbf{n}_i$ and $\mathbf{n}_f$ are unit vectors describing the polarization of the electromagnetic wave (see fig 3). For elastic or quasielastic scattering the change of the wavelength of the light is zero or small, so that $k_i \simeq k_f$. Working out the cross products in (4) the equation for the scattered electric field is simplified to

$$\mathbf{E}_s(R, t) = -\frac{k_f^2 E_0}{4\pi i k f R} e^{i k f R - \omega t} \delta \varepsilon_{ij}(\mathbf{q}, t)$$  (5)

where

$$\delta \varepsilon_{ij}(\mathbf{q}, t) = \mathbf{n}_f \cdot \delta \varepsilon(\mathbf{q}, t) \cdot \mathbf{n}_i$$  (6)

is the component of the dielectric constant fluctuation tensor in direction of the incident and final polarization of the light.

Equation (5) describes the scattering of electromagnetic waves through local fluctuations of the dielectric constant or the refractive index of the medium. Colloidal systems, however, often consist of particles dispersed in a solvent, or more generally, a two or more phase system where the different phases form structures with sizes in the range of nanometers or micrometers. Examples are suspensions of
solid particles, emulsions, aerosols or gels. Because the different phases normally have different refractive indices it is clear that in colloidal systems light is scattered by these structures. Assuming $N$ particles in the scattering volume and that the incoming wave is scattered only once before it reaches the detector, the scattered electric field is described by

$$E_S(q) = \sum_{i=1}^{N} b_i(q)e^{in_i}$$  \hspace{1cm} (7)$$

where $q$ is the scattering vector and $b_i(q)$ is the scattering amplitude of the $i$-th particle at the position $r_i$. For spherical particles $b_i(q)$ is given by

$$b_i(q) \sim a_i^3 j_1(qa_i/2) q a_i$$  \hspace{1cm} (8)$$

where $a_i$ is the particle diameter and $j_1(x)$ is the spherical Bessel function of index 1. The scattering amplitude is proportional to the particle volume and therefore larger particles scatter light more strongly than smaller ones. In a light scattering experiment the intensity $I_S(q)$ is measured rather than the electric field $E_S(q)$ with $I_S(q) = |E_S(q)|^2$. $I_S(q)$ is consequently proportional to the square of the particle volume or the particle diameter to the power of six. For the monodisperse case, where all particles are identical ($b_i(q) = b(q)$), it is given through

$$I_S(q) = N a^6 \sigma(q)$$  \hspace{1cm} (9)$$
Here \( N \) denotes the number of the particles with diameter \( a \) and \( \sigma(q) \) is the total scattering cross section. The total scattering cross section \( \sigma(q) \) or even more the differential scattering cross section \( d\sigma(q)/d\Omega \) is the important parameter, which determines the dependence of the scattered intensity on the scattering vector \( q \), respectively the scattering angle \( \Theta \). For a point scatterer and in the far field detection limit \( d\sigma(q)/d\Omega \) can be expressed through

\[
\frac{d\sigma}{d\Omega}(q) = \frac{I_S(q)}{I_0} R^2 = b^2(q) = \frac{16\pi^2}{\lambda^4} \alpha^2
\]

(10)

It is important to note that the differential cross section and therefore also the scattering intensity is proportional to \( \lambda^{-4} \) and to \( \alpha^2 \). This means that light with a shorter wavelength is scattered more strongly than light with a longer wavelength. The polarizability \( \alpha \), on the other hand, is directly related to the molar mass of the particle \( M \).

In light scattering experiments often the so-called excess Rayleigh ratio \( \Delta R(q) \) is used [20].

\[
\Delta R(q) = \frac{1}{V_s} \frac{d\sigma}{d\Omega}(q)
= \frac{\Delta I_S(q)}{I_0} \frac{R^2}{V_s} \tag{11}
\]

Here \( \Delta I_S(q) \) denotes the difference between the intensity scattered by the suspension and the pure solvent, \( I_0 \) is the intensity of the incident beam and \( R \) is the distance between the scattering volume \( V_s \) and the detector. Normally the scattering volume is not known exactly. Nevertheless, to obtain absolute values of the scattering intensity and furthermore to exclude unwanted effects of misalignment of the instrument on the measured scattering intensity, \( \Delta I_S(q) \) is finally normalized with the scattered intensity \( I_{ref}(q) \) of a reference sample where the Rayleigh ratio \( \Delta R_{ref}(q) \) is known. Then \( \Delta R(q) \) is given by

\[
\Delta R(q) = \frac{\Delta I_S(q)}{I_{ref}(q)} R_{ref}(q) \left( \frac{n}{n_{ref}} \right)^2 \tag{12}
\]

For a suspension of monodisperse particles \( \Delta R(q) \) can be written as

\[
\Delta R(q) = K_c M P(q) S(q) \tag{13}
\]

\(^{4}\)This is the reason for the blue colour of the sky.
4.1 Static Light Scattering

with

\[ K = 4\pi^2 n^2 \frac{(dn/dc)^2}{N_A \lambda^4} \]
\[ n = \text{refractive index of the solvent} \]
\[ c = \text{particle concentration (mass/volume)} \]
\[ dn/dc = \text{refractive index increment} \]
\[ M = \text{molar mass of the particle} \]
\[ P(q) = \text{particle form factor} \]
\[ S(q) = \text{static structure factor} \]

4.1 Static Light Scattering: Particle Form Factor and Static Structure Factor

In a static light scattering (SLS) experiment the intensity of the scattered light is measured as a function of the scattering vector \( q \), which is experimentally available through a variation of the scattering angle \( \Theta \). \( I_S(q) \) is proportional to the scattering cross section \( \sigma(q) \) which in principle is a product of the particle form factor \( P(q) \), which essentially yields information about size and shape of the particles, and the static structure factor \( S(q) \), which reflects interactions between the particles.

\[ I_S(q) = N a^6 P(q) S(q) \]  \hspace{1cm} (14)

Therefore from a determination of \( P(q) \) we obtain the size and form of the particles. This is usually done with highly diluted samples to avoid influence of interaction effects through \( S(q) \) on the angular dependent scattering intensity. Under these condition \( S(q) = 1 \) for all \( q \), \( I_S(q) \) directly yields the particle form factor. In addition the static structure factor \( S(q) \) provides us with information of the interaction potential \( V(r) \) between the particles. \( S(q) \) can be obtained from the angular dependent scattering intensity if \( P(q) \) is known. It is also possible to get both, particle size or the radius of gyration \( R_g \) and interaction potential \( V(r) \) from the angular dependent scattering intensity.

The scattering intensity \( I_S(q) \) therefore is a product of a single particle property, the particle form factor \( P(q) \), and the static structure factor \( S(q) \) which describes the local structure based on the interactions between the individual particles. A illustration of the physical background of the particles form can be given with figure 4. Like the scattering by local fluctuations in a homogeneous medium, a particle
can be divided into volume elements with dimensions that are small compared to the wavelength \( \lambda \) of the light and consequently see the same incident electric field. The scattered intensity \( I_S(q) \) from the particle then is the superposition of the light scattered by all volume elements where interference effects due to the different optical path lengths from the volume elements to the detector have to be taken into account. The resulting particle form factor \( P(q) \), which is given by the scattering intensity \( I_S(q) \) divided by the scattering intensity without interference effects in forward direction \( I_S(q = 0) \), i.e. \( P(q) = I_S(q)/I_S(q = 0) \), decreases from unity at \( q = 0 \) and shows a angular dependence, which is characteristic for the size and also for the form of the particle. It should be mentioned that particles with dimensions small compared to the wavelength \( \lambda \) don't show these extrema in the particle form factor because the difference in the electric field seen by all subregions of the particle are negligible, and therefore also interference effects.

For a evaluation of particle sizes it is now necessary to find a relation between the variables wavelength \( \lambda \), particle radius \( r \), refractive index ratio \( m = n_p/n_s \) and the particle form factor \( P(q) \). If the particles are small compared to the wavelength of the light and/or for a small contrast between the particles and the solvent

\[
q r (m - 1) \ll 1
\]

(15)

\( P(q) \) can be calculated using the Rayleigh-Gans-Debye (RGD) approximation [21, 22, 23, 24, 25]. The theory assumes that each of the small volume elements, the particle is divided into, sees the same incident light wave. This implies that the
4.1 Static Light Scattering

phase of a wave transversing the particle is almost the same as it would be if the particle were not there. In the Rayleigh-Gans-Debye approximation generally $P(q)$ can be calculated from

$$P(q) = \left[ \frac{1}{V} \int e^{iqr} dV \right]^2$$

(16)

where $V$ is the particle volume. For the case of monodisperse spheres the integral in equation (16) can be calculated, and this leads to

$$P(q) = \frac{9}{(qr)^6} \left[ \sin(qr) - qr \cos(qr) \right]^2$$

(17)

In the limit of $qR_g \leq 1$ equation (16) is given through the 'Guinier-approximation' [26]

$$P(q) = e^{-\frac{q^2 R_g^2}{3}}$$

(18)

and with the expansion of the exponential function for $qR_g \ll 1$ this yields

$$P(q) = 1 - \frac{q^2 R_g^2}{3} + \cdots$$

(19)

With the equations (18) and (19) the value of $P(q)$ can be calculated in the limit of low scattering angles. Therefore, from an extrapolation of the measured Rayleigh ratio $\Delta R(q)$ to $q = 0$ the molar mass $M$ of the particles ($\lim_{q \to 0} \Delta R(q) \sim M$) and from the gradient of the curve the radius of gyration $R_g$ of the particles can be obtained.

For larger particles, but still in the range of the wavelength of the light, and/or large values of $m$ the RGD-approximation breaks down due to distortions of the incident electric field in the particle, caused by the difference in the index of refraction of the particle and that of the solvent. A complete solution to this problem, if the particles are spheres, exists with the Mie scattering theory [27], where the difference in the electric field inside and outside the particle is taken into account. The incident electric field outside and that inside the particle and the scattered electric field must satisfy specific boundary conditions at the surface of the particle. However, though Mie scattering is much more difficult to calculate than the Rayleigh-Gans-Debye solution, it describes the dependence of $P(q)$ on the particle size very well and it is also highly sensitive to the particle shape. A comparison of the particle form factors calculated with RGD and Mie theory with experimental data measured with spherical latex particles having a size in the range of Mie scattering is shown in

5 and in the limit of low concentrations where $S(0) = 1$
Figure 5: Comparison of the particle form factor $P(q)$ calculated with RGD and Mie theory with experimental data (suspension of latex spheres with $r = 274$ nm and $m = 1.2$. For details see text.

The Mie theory describes the experimental data very well, while the RGD approximation fails by calculating the depth and the position of the minima in $P(q)$. However, if the condition $qr(m - 1) \ll 1$ is satisfied, RGD works also very well. In a third regime of very large particles, $qr \gg 1$, Fraunhofer diffraction of the light occurs rather than scattering [28]. In large particles the electromagnetic wave hardly can penetrate and therefore the scattering process can be approximated by interaction of the wave with the cross section or aperture of the particle. Consequently no information about the internal structure and the overall shape of the particle can be obtained in the Fraunhofer regime. Similar to a grating the diffraction pattern is shifted to lower angles with increasing particle size, so that Fraunhofer diffraction is mainly used for calculating particle sizes in small angle light scattering instruments.

While $P(q)$ describes the intraparticle interference effects, the static structure factor $S(q)$ is a result of interference effects of the light scattered by different par-
4.1 Static Light Scattering

ticles. Each particle scatters light with an angular dependence given by \( P(q) \). But if there is a regular arrangement of the particles due to interactions between the particles, there exist fixed phase differences between the light scattered by different particles due to the different path lengths. A superposition of the light scattered by all particles, taking into account interference reveals the static structure factor \( S(q) \), a measure of the order in the system or the spatial correlations between particles. \( S(q) \) is given with

\[
S(q) = \frac{1}{N} \sum_{i,j=1}^{N} \langle e^{i q (r_i - r_j)} \rangle
\]

where the angular bracket denotes an ensemble average. For uncorrelated particles, i.e., an ideal gas of particles, \( S(q) = 1 \) for all \( q \). Correlation between particles means that they form a local structure similar to a lattice in a crystal. However, the interactions between the particles are less strong than in a crystal and consequently the order is in the range of some nearest neighbours. An expression for the local structure is the pair correlation function \( g(r) \) which is related to the static structure factor through

\[
S(q) = 1 + \rho \int d^3 r e^{i q r} [g(r) - 1]
\]

where \( \rho \) denotes the number density of the particles. \( g(r) \) directly describes the probability of finding a particle \( j \) at a distance \( r \) from the particle \( i \).

In figure 6 examples for different interaction potentials are shown. In a crystal the particles are arranged as in an almost perfect lattice (A). The static structure factor then shows the characteristic Bragg peaks and the pair correlation function reflects the fixed distances between the particles. The reason, while the peaks in \( S(q) \) and \( g(r) \) are not infinitesimally narrow is the finite temperature, which leads to oscillations of the particles. Because in colloidal systems particles do not form perfectly regular lattices due to the Brownian motion of the particles and the relatively weak interaction potentials compared to crystals formed by atoms, the static structure factor shows relatively broad peaks. Nevertheless, colloidal suspensions can also form crystals that show Bragg peaks depending on the concentration and interaction potential between the particles. An example for a hard sphere suspension is shown in (B). The order of the particles is only in the range of nearest neighbours, consequently \( S(q) \) shows mainly the peak for the nearest neighbours, the probability finding a particle at larger distances goes quickly to unity. Charge stabilized suspensions, however, show a more pronounced order at similar concentrations due to the long-range interaction potential (C). Dependent on the strength of the interaction
potential the particles can order similar to a lattice, with the consequence that $S(q)$ and $g(r)$ show more pronounced peaks than in a hard core suspension.

The static structure factor $S(q)$ can be calculated from 21. For monodisperse
4.2 Dynamic Light Scattering

particles and in the limit of low scattering angles \( q \to 0 \) it is related to the osmotic compressibility \( (\partial \Pi / \partial c)^{-1} \) of the suspension by

\[
S(0) = \frac{N_A k_B T}{M} (\partial \Pi / \partial c)^{-1}
\]

(22)

In a virial expansion of \( S(0) \) as

\[
S(0) = 1 - 2A_2 Mc + \cdots
\]

(23)

the second virial coefficient \( A_2 \) is related to the interaction pair potential \( V(r) \) through

\[
A_2 = \frac{2 \pi N_A}{M^2} \int \left[ 1 - e^{-\frac{V(r)}{k_B T}} \right] r^2 dr
\]

(24)

Combining equation 13 with the approximations of the particle formfactor (equation 19) and the static structure factor (equation 23) in the limit of \( q \to 0 \) yields to an expression from which the size and form of the particles and the interaction potential in terms of the second virial coefficient can be obtained, if the Rayleigh ratio \( \Delta R(q) \) and the concentration \( c \) is given through a measurement.

\[
\frac{Kc}{\Delta R(q)} = \frac{1}{M} \left( 1 + \frac{q^2 R_2^2}{3} \right) + 2A_2 c
\]

(25)

4.2 Dynamic Light Scattering

As described before in equation 5 scattering of light is due to local fluctuations in the dielectric constant or the index of refraction of the medium. Due to the fact, that in a suspension the particles usually have a different refractive index from the solvent, light is mainly scattered by the particles. Particles suspended in a liquid is not a static system, rather the particles are constantly in a so-called Brownian motion. As a result in a scattering experiment the phase relations of the light scattered by different particles change randomly and also the number of particles in the scattering volume fluctuates. Both effects lead to a fluctuation of the scattering intensity. Because the Brownian motion or diffusion of the particles in the suspension is the cause of the fluctuations, information about the diffusion process can be obtained from an analysis of the intensity fluctuations in terms of a time correlation function [14, 20]. Referring to figure 7 the time dependence of the scattered intensity looks like statistical noise. Nevertheless, if one looks at the intensity at two times separated by \( \tau \), the intensity values \( I(t) \) and \( I(t + \tau) \) do in general have different values. But if \( \tau \) is very small compared to the characteristic
time of the fluctuations, \( I(t) \) and \( I(t + \tau) \) will be very close, they are somehow correlated, while with increasing separation in time \( \tau \) the correlation will decrease. A measure of the correlation is the so-called intensity auto-correlation function.

\[
\langle I(t_0)I(t_0 + \tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{T} I(t)I(t + \tau) \, dt \quad (26)
\]

For ergodic systems the infinite time average is independent on the starting point \( t_0 \) so that it can be chosen as \( t_0 = 0 \) \([29]\). The intensity correlation function and its relation to the temporal fluctuations in intensity is shown in figure 7. The correlation starts with a maximum value of \( \langle I^2 \rangle \) and decays in the course of time to \( \langle I \rangle^2 \) with the characteristic decay time \( \tau_a \).

In a dynamic light scattering experiment (DLS) the fluctuations in the amplitude of the electric field are described by a normalized field correlation function

\[
g_1(q, \tau) = \frac{\langle E_S(q,t)E_S^*(q,t+\tau) \rangle}{\langle |E_S(q,t)|^2 \rangle} \quad (27)
\]

Due to the fact that in a DLS experiment intensities are measured rather than electric fields the experimentally available property is the intensity correlation function

\[
g_2(q, \tau) = \frac{\langle I_S(q,t)I_S(q,t+\tau) \rangle}{\langle |I_S(q,t)|^2 \rangle} \quad (28)
\]

\( g_2(q, \tau) \) is related to the field correlation function through the Siegert relation

\[
g_2(q, \tau) = 1 + |g_1(q, \tau)|^2 \quad (29)
\]

under the assumption of a Gaussian distribution of the intensity profile. In the case of monodisperse spherical particles the field auto-correlation function can be written
4.2 Dynamic Light Scattering

as

$$g_1(q, \tau) = S(q, \tau) \frac{H(q)}{S(q)}$$  \hspace{1cm} (30)

where

$$S(q, \tau) = \frac{1}{N\langle b^2 \rangle} \left( \sum_{i,j=1}^{N} b_i b_j e^{i q \cdot (\mathbf{r}_i - \mathbf{r}_j(\tau))} \right)$$  \hspace{1cm} (31)

denotes the dynamic structure factor, $H(q)$ describes the hydrodynamic interactions in the suspension and $S(q)$ is the static structure factor. In the limit of negligible interactions \textsuperscript{6} in the system the dynamic structure factor is a single exponential function with respect to the lag time $\tau$.

$$g_1(q, \tau) \sim e^{-D_C q^2 \tau}$$  \hspace{1cm} (32)

where $D_C$ is the collective diffusion coefficient of the particles in the suspension and $q$ is the scattering vector.

For the case of polydisperse suspensions of particles $g_1(q, \tau)$ is not anymore a single exponential function of the time, it is rather a sum of exponentials for each species of particles in the suspension. The evaluation of the particle size from the correlation function then is more complicated. In principle it can be done by performing an inverse Laplace transformation on $g_1(q, \tau)$ in order to obtain the size distribution $G(\Gamma)$ of the particle suspension \textsuperscript{30, 31, 32}. Unfortunately the inverse Laplace transformation is an ill-conditioned problem, i.e. any statistical noise, which is ever present in a measured correlation function, will lead to different possible results for the size distribution. Therefore it is important to measure correlation functions with high statistical accuracy when using the inverse Laplace transformation for the evaluation of particle size distributions. Replacing the discrete sum in equation 31 and equation 30 by an integral over the size distribution $g_1(q, \tau)$ can be expressed through

$$g_1(q, \tau) = \frac{\int_0^\infty N(r)r^6 P(qr)e^{-D_0(r)q^2 \tau} dr}{\int_0^\infty N(r)r^6 P(qr) dr}$$  \hspace{1cm} (33)

This equation can be written as

$$g_1(q, \tau) = \int_0^\infty G(\Gamma)e^{-\Gamma \tau} d\Gamma$$  \hspace{1cm} (34)

with

$$G(\Gamma) = \frac{N(r)r^6 P(qr)}{\int_0^\infty N(r)r^6 P(qr) dr}$$  \hspace{1cm} (35)

\textsuperscript{6}Then $H(q) = 1$ and also $S(q) = 1$. 

and $\Gamma = D_0 q^2$ is the decay rate. For narrow size distributions $g_1(q,\tau)$ can be expanded around the average decay rate $\langle \Gamma \rangle$

$$g_1(q,\tau) = e^{-\langle \Gamma \rangle \tau} \left[ 1 + \frac{\sigma}{2} (\langle \Gamma \rangle)^2 \tau^2 + \cdots \right]$$  \hspace{1cm} (36)

From a so-called cumulant analysis [33] of $g_1(q,\tau)$ the average decay rate $\langle \Gamma \rangle$ and the coefficient of variation $\sigma$ can be obtained.

### 4.3 Cross-Correlation

The evaluation of data from a static or dynamic light scattering experiment, as described above, is based on the assumption that the laser light is only singly scattered before it reaches the detector. If multiple scattering of the light occurs, an interpretation of the data is difficult if not impossible due to the fact that multiply scattered light has lost its close relation to the scattering vector $q$. However, while the calculation of the dynamic structure factor $S(q,\tau)$ is extremely difficult if multiply scattered light contributes to the scattering intensity, there exist a technique to suppress multiple scattering contributions with a so-called cross-correlation experiment. The general idea is to isolate singly scattered light and suppress undesired contributions from multiple scattering in a dynamic light scattering experiment (for details see [2]). This can be achieved by performing two scattering experiments simultaneously on the same scattering volume (with two laser beams, initial wave vectors $k_1$ and $k_2$, and two detectors positioned at final wave vectors $k_f$ and $k_f'$) and cross-correlating the signals seen by the two detectors.

$$G_{12}(\tau) = \langle I_1(t) I_2(t + \tau) \rangle$$  \hspace{1cm} (37)

If both experiments then have the same scattering vector $q$, but use different scattering geometries, and in the absence of multiple scattering, the corresponding relations between the dynamic structure factor $S(q,\tau)$ and the measured auto-correlation ($G_{11}^{(1)}(\tau)$) and cross-correlation ($G_{12}^{(1)}(\tau)$) function, where (1) indicates singly scattered photons, can then be written as

$$G_{11}^{(1)}(\tau) = I_1^{(1)} I_2^{(1)} (1 + \beta |S(q,\tau)|^2)$$  \hspace{1cm} (38)

$$G_{12}^{(1)}(\tau) = I_1^{(1)} I_2^{(1)} (1 + \beta_{12} |S(q,\tau)|^2)$$

where $I_1$ and $I_2$ are the average scattered intensities seen by detectors 1 and 2, respectively, and the intercept of the cross-correlation function $G_{12}^{(1)}(\tau)$ is given by

$$\beta_{12} = \beta e^{-\frac{k_f^2 R^2}{4}} e^{-\frac{k_f^2}{R^2}}.$$  \hspace{1cm} (39)
4.3 Cross-Correlation

The intercept $\beta$ detected in the auto-correlation experiment primarily depends on the detection optics, and the additional terms describe the reduction of the intercept due to phase mismatch ($\delta q = |\delta q|$ describes the match of the scattering vectors $q_1$ and $q_2$) and misalignment ($\delta x = |\delta x|$ is the spatial match of the scattering volumes). For single scattering, both auto- and cross-correlation therefore yield the same information. However, in the case of multiple scattering, the situation changes. In the auto-correlation experiment the multiply scattered photons contribute to $G_{11}(\tau)$ as well and make an interpretation of the data and a deduction of $S(q, \tau)$ very difficult if not impossible. However, in the cross-correlation experiment outlined above only singly scattered light will produce correlated intensity fluctuations on both detectors. In contrast, multiply scattered light will result in uncorrelated fluctuations that contribute to the background only due to the fact that it has been scattered in a succession of different q-vectors, and the contributions from multiple scattering to the signal are suppressed by a factor of order $(R\delta k_j)^{-1}$, where $\delta k_j$ denotes the magnitude of the smallest of the two wavevector combinations $k_{i2} - k_{i1}$ and $k_{i2} + k_{f1}$ [2]. This leads to the following expression for $G_{12}(\tau)$

$$G_{12}(\tau) \approx I_1 I_2 + \beta_{12} I_1^{(1)} I_2^{(1)} |S(q, \tau)|^2$$

(40)

where $I_j$ is the average intensity summed over all contributions (singly and multiply scattered photons) measured at detector $j$, and $I_j^{(1)}$ contains the singly scattered light only. Such a cross-correlation experiment should thus provide us with the dynamic structure factor $S(q, \tau)$ even for turbid suspensions, and multiple scattering will be visible in the decreasing intercept only.

Cross-correlation experiments can be realized using different geometries for the two scattering experiments. In the Phillips set-up [3] scattered light from both experiments is measured with both detectors. Therefore it is limited to a single scattering angle of $\Theta = 90^\circ$ (figure 8 A). For experiments with a variable scattering angle either light from the wrong experiment must be prevented to enter the detectors, as it is done in the two colour set-up [5]. Here the two experiments use different wavelengths and interference filters block the light from the wrong experiments in front of the detectors (figure 8 B). The signals from the wrong experiments can also be decorrelated using a geometry where they produce different scattering vectors [2]. This is realized in the 3d set-up (figure 8 C).
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counterpropagating beams
fixed scattering angle $\theta = 90^\circ$
$q_1 = -q_2$

two different wavelengths $\lambda_1 \neq \lambda_2$
variable scattering angle, but
difference angle $\delta q$ depends on $\theta$

variable scattering angle $\theta$
3-dimensional scattering geometry

Figure 8: An outline of the wave vector arrangement for different cross-correlation schemes. A: Phillies, B: Two colour, C: 3D coding

4.4 3d Cross-Correlation Scheme

4.4.1 Intercept of the Cross-Correlation Function

The intercept $\beta$ of the correlation function can be viewed as the signal-to-noise ratio of the dynamic light scattering experiment, i. e. the difference in the correlation function in the limit of $\tau \to 0$ and $\tau \to \infty$, $g_{ij}(0) - g_{ij}(\infty) = \beta$ ($i = j = 1$ for auto-correlation, $i = 1$, $j = 2$ for cross-correlation experiments, respectively). The theoretical maximum of $\beta$ is $\beta_M = 1$ for an auto-correlation experiment, while
4.4 3d Cross-Correlation Scheme

in a cross-correlation experiment $\beta$ depends on the geometry of the beam paths \cite{2, 14}. The reason for this is, that in a cross-correlation experiment each of the two detectors 'sees' the light from both incident beams and therefore also from the wrong experiment. Thus the cross-correlation function can be written as

$$G_{12}(\tau) = \langle I_1^1(0)I_2^1(\tau) \rangle + \langle I_1^1(0)I_2^2(\tau) \rangle + \langle I_1^2(0)I_2^1(\tau) \rangle + \langle I_1^2(0)I_2^2(\tau) \rangle$$

(41)

where Arabic numbers denote the detector and Roman numbers denote the incident beam.

In the 3d cross-correlation experiment the undesired contributions from the 'wrong' incident beams are still detected by the photomultipliers, but they produce different scattering vectors $q_1 \neq q_2$ and are therefore decorrelated. In eq. 41 only the second term gives correlated contributions to $G_{12}(\tau)$

$$g_{12}(\tau) = \frac{3\langle I_1^1 \rangle \langle I_2^1 \rangle + \langle I_1^1(0)I_2^2(\tau) \rangle}{\langle I_1^1 + I_2^1 \rangle \langle I_1^2 + I_2^2 \rangle}$$

(42)

The intercept for the 3d cross-correlation experiment is $\beta_{12} = 0.257$.

A reduction of the theoretically obtainable intercept can take place due to detector non-linearities \cite{34}, misalignment of the instrument, and due to restrictions in the overlap volume. While detector non-linearities mainly take effect at high count rates, the latter two points need to be considered. Any misalignment, either in the spatial match of the scattering volumes or in the scattering vectors will lead to a lower intercept described by

$$\beta = \beta_0 e^{-\frac{4\delta q}{R}} e^{-\frac{4\delta q R^2}{2}}$$

(44)

To give an example of the precision in alignment required for an intercept of $\beta = 0.9\beta_0$, for a frequently used value for the beam radius of $R = 100 \mu$m the two scattering volumes should be closer than 5 $\mu$m and the two scattering vectors should not differ more than $\delta q = 0.005 \mu$m$^{-1}$.

\footnote{In the two colour experiment described above two laser beams different in wavelength ($\lambda_1 = 488$ nm and $\lambda_2 = 514$ nm from an Ar+-laser) are used. Narrow bandwidth interference filters in front of the detectors block the undesired contributions from the 'wrong' incident laser beam and therefore for the cross-correlation function we get (see eq. 41)

$$g_{12}(\tau) = \frac{\langle I_1^1(0)I_2^1(\tau) \rangle}{\langle I_1^1 \rangle \langle I_2^1 \rangle}$$

(43)

with the maximum intercept of $\beta = 1$.}
4.4.2 Overlap Volume

Because in a cross-correlation experiment the intensity originating from incident beam 1 is correlated with the intensity originating from incident beam 2, the scattering volume seen by the detectors must be illuminated by both incident beams. If there exist regions where only one incident beam can be seen by the detectors, $\beta_{12}$ will decrease consequently. Figure 9 shows the geometrical arrangement of the two incident laser beams. The volume where the two beams overlap is marked. Due to the difference angle $\delta_{3d}$ of the two beams it is getting smaller with increasing distance to the center. The scattering volume, however, is the common volume of the incident beams and the detector beams. The dark shaded region in figure 9 reflects the projection of the scattering volume at a scattering angle of $\Theta = 90^\circ$. If the diameters of the detection beams are larger than the diameters of the incident beams, there exist regions detected from the photomultipliers that are outside the overlap volume of the two beams. The brighter shaded region indicates the projection of the scattering volume at a scattering angle of $\Theta = 10^\circ$. It is to first approximation a factor $1/\sin \Theta$ larger than the scattering volume at $\Theta = 90^\circ$, but a larger part of the volume is illuminated only by one incident beam. The intercept of the cross-correlation function can be written as

$$\beta_{12} = \frac{\langle I_{1}^{ov} \rangle \langle I_{2}^{ov} \rangle}{\langle I_{1} \rangle \langle I_{2} \rangle} = \frac{V_{ov}^2}{V_1 V_2} \quad (45)$$

where $I_{i}^{ov}$ are the scattering intensities originating from the overlap volume of the two incident beams and $I_{i}$ are the scattering intensities originating from the total scattering volume (including those regions which are illuminated by one beam only). Because of equation 45 and the fact that the ratio of the overlap volume and the scattering volume $V_{ov}/V_{sv}$ depends on the scattering angle, as discussed above, the intercept is a function of the scattering angle, i.e. $\beta_{12} = \beta_{12}(\Theta)$. Therefore $\beta_{12}$ decreases for large and for small scattering angles and has its maximum value at $\Theta = 90^\circ$, and this effect is stronger for larger values of the difference angle $\delta_{3d}$. Experimentally $\beta_{12}(\Theta)$ can be determined by measuring a highly diluted sample.

4.4.3 Goniometer Angle and Scattering Angle

In the 3d cross-correlation experiment the plane of symmetry, which is defined by the plane of the goniometer, and the two scattering planes of the individual experiments are not identical. Therefore the scattering angle $\Theta$ and the angle of the goniometer, denoted with $\Theta_{Goni}$, are not identical. The difference depends on the difference angle
Figure 9: Overlap volume (fat lines) and scattering volume (shaded areas) for scattering angles of $\Theta = 90^\circ$ (dark grey) and $\Theta = 10^\circ$ (slightly grey). For details see text.

$\delta_{3d}$ of the experiment and is also a function of the goniometer angle. Figure 10 shows a sketch of the wavevector arrangement of one scattering experiment. Goniometer-, scattering- and difference angle are given through the trigonometric functions

$$\sin \frac{\Theta_{Gon}}{2} = \frac{AB}{OA}$$

$$\sin \frac{\Theta}{2} = \frac{CD}{OC}$$

$$\cos \frac{\delta}{2} = \frac{OA}{OC}$$

(46)

Because the triangle OAB is the projection of the triangle OCD on the plane of symmetry, the distances AB and CD are identical. Combining the equations in 47 results in the expression for the scattering angle

$$\sin \frac{\Theta}{2} = \cos \frac{\delta}{2} \sin \frac{\Theta_{Gon}}{2}$$

(47)

In the limit of low goniometer angle $\Theta_{Gon} \to 0$, $\Theta_{Gon}$ and $\Theta$ are identical, while at $\Theta_{Gon} = 180^\circ$ the scattering angle is $\Theta = \Theta_{Gon} - \delta$. The relation of $\Theta$ to the goniometer angle is shown in figure 11. In the actual angular range of the instrument from $\Theta_{Gon} = 5^\circ$ to $\Theta_{Gon} = 125^\circ$ the maximum difference between goniometer- and scattering angle, located at $\Theta_{Gon} = 125^\circ$ results in a deviation of the scattering vector of $\Delta q/q \leq 2\%$. 
Figure 10: Sketch of the wave vector arrangement of one scattering experiment to explain the relation of the scattering angle $\Theta$ to the goniometer angle $\Theta_{Gon}$ and the difference angle $\delta$. The shaded plane is the plane of symmetry or the goniometer plane of the experiment.

Figure 11: Relation between the scattering angle $\Theta$ and the goniometer angle $\Theta_{Gon}$ for a difference angle of $\delta = 14^\circ$.

4.4.4 Correction for Static Light Scattering Experiments

With the 3d cross-correlation instrument also static light scattering measurements in turbid samples can be done. The undesired contributions from multiply scattered
4.4 3D Cross-Correlation Scheme

Light to the measured scattered intensity $I_S$ can be excluded by performing a combined static and dynamic cross-correlation experiment. In the static measurement $I_S$ is determined as a function of $q$, while the dynamic measurement gives the part of $I_S$ which is only singly scattered via the intercept $\beta_{12}$ of the cross-correlation function (see equation 40). In the measurement the reduced intercept $\beta_{12}/\beta_{12}^{(1)}$ is used, where $\beta_{12}^{(1)}$ is the intercept measured with a diluted sample without multiple scattering contributions. This automatically corrects for the effects caused by the overlap volume and misalignment of the instrument, which lead to an angular dependence of the intercept. The single scattering intensity as a function of the scattering vector can then be calculated from

$$I_1^{(1)}(q) = \sqrt{I_1^{(1)}(q)I_2^{(1)}(q)} = \sqrt{\frac{\beta_{12}}{\beta_{12}^{(1)}}I_1(q)I_2(q)}$$  \hspace{1cm} (48)

If rectangular cells together with the $\Theta - 2\Theta$ set-up, described in chapter 5, are used in the experiment in order to measure with short light paths $s(\Theta)$ inside the sample cell, the measured intensity has to be corrected for two effects, namely for Fresnel refraction for non-incident beams on the scattering cell and for the turbidity of the sample, because the length of the light paths $s(\Theta)$ vary with the scattering angle. As a result, both the single scattered light and the total scattering intensity decrease at angles different from 90°.

Due to the $\Theta - 2\Theta$ set-up of the instrument the incident laser beams hit the surface of the sample cell under half of the difference of the goniometer angle $\Theta_{Gon}$ to 90°, i.e. $\theta = (90° - \Theta_{Gon})/2$. Neglecting the effect caused by the difference angle $\delta_{sd}$, the polarization of the incoming light is parallel to the sample cells surface. From the Fresnel equations [28] for this case the transmission $T$ through the sample cell is given by $T = I/I_0$, where $I$ is the transmitted light intensity for an incident intensity $I_0$. The surfaces water-glass and glass-water with their corresponding refractive indexes for water $n_w$ and glass $n_G$ result in transmission coefficients of

$$T_{WG} = \frac{n_G \cos \theta_G}{n_W \cos \theta_W} \left( \frac{2 \sin \theta_G \cos \theta_W}{\sin(\theta_W + \theta_G)} \right)^2$$  \hspace{1cm} (49)

$$T_{GW} = \frac{n_W \cos \theta_W}{n_G \cos \theta_G} \left( \frac{2 \sin \theta_W \cos \theta_G}{\sin(\theta_G + \theta_W)} \right)^2$$

A scheme of the angles used for this calculation is shown in figure 12. Combining these equations with the Snellius law $\sin \theta_G/\sin \theta_W = n_W/n_G$ the transmission
through a sample cell filled with water caused by Fresnel refraction is
\[
T = \frac{256 \sin^4 \theta_G \cos^4 \theta_W \sin^4 \theta_W \cos^4 \theta_G}{\sin^8(\theta_G + \theta_W)}
\] (50)
where \(n_G = 1.54\) for quartz and \(n_W = 1.33\) for water.

If \(s(\theta)\) denotes the optical path length inside the sample cell and \(\tau\) is the turbidity of the sample, which can be calculated from a transmission measurement using \(\tau = s^{-1} \ln(I_0/I)\), the angular dependent correction for the sample turbidity is given by
\[
T^\tau(\theta) = e^{-\tau s(\theta)}
\] (51)
The transmission corrections for non-incident beams on the sample cell (Fresnel correction) and for the sample turbidity are shown in figure 13 for a sample with the turbidity \(\tau = 1\) mm\(^{-1}\) and a path length of \(s_0 = 1\) mm.
Figure 13: Correction for the transmitted intensity through a rectangular sample cell placed in a $\Theta - 2\Theta$-goniometer. Shown are the Fresnel correction and the correction for sample turbidity.
5 Experimental Realization

A schematic layout of the experimental set-up is shown in figure 14. The experiments with turbid colloidal model suspensions described in chapter 6 were obtained with an argon-ion laser (Coherent Innova 300-8) operating at a wavelength of $\lambda_0 = 488$ nm as the light source. To extend the measurable range of sample turbidity to even higher values (eq. 10) a HeNe laser (Spectra Physics, model 127) operating at $\lambda_0 = 633$ nm then was implemented as the light source for the experiments described in chapters 7, 8 and 9. A polarization preserving single mode fiber (Dantec DAN 60x30) is used in order to bring the illuminating beam to the instrument. The laser beam is split into two parallel beams, which are then focused onto the scattering cell by the lens $L_1$ (planar convex, focal length 90 mm, diameter 63 mm, Spindler & Hoyer). This lens has been chosen in order to allow for a sufficiently large $\delta$ required for an efficient suppression of contributions from multiple scattering. In our current set-up we have chosen values of $R \leq 50 \mu$m for the beam waist at the scattering volume and $\delta = 14^\circ$, which results in a suppression of double scattering by approximately a factor of $7 \cdot 10^{-3}$ for $\lambda_0 = 632.8$ nm (The efficiency for suppressing higher order contributions is much higher, for details see [2]). The scattering cell is immersed in an index match

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$^6$This is valid for the experiments described in chapters 7, 8 and 9. For the experiments described in chapter 6 beam waist and difference angle were $R = 50$ nm and $\delta_{ad} = 18^\circ$ which results in a suppression factor of $4 \cdot 10^{-3}$. 

Figure 14: An outline of the experimental set-up for 3d cross-correlation.
vat (ALV 88/ALV, without flat entrance and exit windows, outer diameter 85 mm). Water is used as the index matching fluid. The vat temperature is controlled via a heat exchanger coil, which is connected to a thermostat. An identical lens \( L_2 \) is used for the detection side, and the scattered light with wave vectors \( k_{f1} \) and \( k_{f2} \) is collected and guided by a combination of a GRIN lens and a single mode fiber \( (F_1, F_2, OZ\ Optics) \) [35, 36]. The end of each fiber is connected via standard SMA fiber connectors to a home-built housing for a photomultiplier tube (PM; H5783P-01, Hamamatsu), and the PM signal is processed by two amplifier/discriminators (C3866 photon counting unit, Hamamatsu) and fed into a digital correlator (ALV 5000/E, ALV). For turbid colloidal suspensions, due to the strong attenuation of the singly scattered intensity which essentially decays like \( I^{(i)} \sim \exp(-s/L) \), where \( s \) is the optical path across the cell for singly scattered light and \( L \) is a characteristic length scale (photon transport mean free path length), which may easily be less than 1 mm for dense colloidal suspensions, the size of the scattering cell becomes important. In order to avoid a strong reduction of the singly scattered light and the subsequent reduction in signal, the light path should be of the order of \( L \). In principle this could be achieved best by using flat cells. However, since these cells will then be used in general with beams at non-normal incidence angles, this will lead to considerable beam deflection and displacement. We therefore implemented a different approach outlined in figure 15. We use square cells with 10 mm path length that are of superior optical quality for experiments at low scattering angles, and position them such that the scattering volume is located in a corner of the cell to have short optical path lengths. For experiments at scattering angles different from 90° we turn the cell in a so-called \( \Theta - 2\Theta \) geometry, where the sample is rotated by half the rotation angle \( (90° - \Theta) \) in order to recover a symmetrical situation in which the displacement of the incident and scattered beam almost cancel. This \( \Theta - 2\Theta \) geometry is implemented by using a combination of a \( x - y \) translation stage and a motorized rotational stage above the sample position, which can be controlled from within the ALV correlator software and allows for automated measurements of the angular dependence of the static and dynamic structure factor.
5.1 Detailed Description of the Opto-Mechanical Components

5.1.1 Producing Parallel Beams

Using a single mode optical fiber for the incident laser light has significant advantages compared to a 'direct' laser beam. The single mode fiber not only guides the light or, more precisely, the TEM$_{00}$-mode from the laser to the instrument, it also works as a high quality spatial filter. Out of the fiber always comes a beam with the desired Gaussian intensity profile. Furthermore an exchange of the laser is easy to perform as only the laser beam must be coupled into the fiber without re-alignment of the whole light scattering instrument. As long as single mode operation is fulfilled, even lasers working at different wavelengths can be used. In the used DANTEC fiber a collimator is included which allows a variation of the focal point from negative
values to approximately 200 mm. A collimated \((f \rightarrow \infty)\) laser beam is adjusted, the beam propagation then is described by

\[ w(z) = w_0 \sqrt{1 + \left( \frac{\Theta_{\text{div}} z}{w_0} \right)^2} \]

where \(w(z)\) denotes the beam radius at a distance \(z\) from the beam waist where the radius is \(w_0\). The divergence \(\Theta_{\text{div}}\) of the laser beam with the wavelength \(\lambda\) is given through \(\Theta_{\text{div}} = \lambda/(\pi w_0)\). In the actual set-up a HeNe-laser with \(\lambda = 632.8\) nm and a beam waist at the exit of the fiber \(w_0 = 1\) mm is used. This results in a divergence angle of \(\Theta_{\text{div}} = 2 \cdot 10^{-4}\). Although due to the beam splitting the two resulting parallel beams have a difference in path length of 3 cm, the divergence angle is small enough that the beam radii are nearly identical at equal distances from the scattering volume. The beam splitter and the mirror for the generation of the two parallel beams are mounted on prism tables, which allow rotation and tilt.

### 5.1.2 Lenses

The transmission and detection lenses \(L_1\) and \(L_2\) are used to generate the difference angle \(\delta_{3d}\) between the incident and the detection beams and to focus the beams at the scattering volume. Therefore they are arranged with common focal points on the optical axis. This system projects an object located in infinity to an image also in infinity. The lens of best form for this task is a planoconvex lens. In the 3d instrument two planoconvex singlets made of BK7 with a clear aperture of 60 mm and a focal length of \(f = 90\) mm are used. They are mounted with a two axis lens holder, which allows to tilt the optical axis, on a x-y-z translation stage. The main optical error of the lens system for beams parallel to the optical axis is spherical aberration. But, because the position of the two beams is fixed with respect to the optical axis, even spherical aberration is not an issue in the 3d set-up.

For the 3d instrument a set-up is chosen, where the two parallel beams have a distance of 1.5 cm from the optical axis. Taking into account the index matching vat, filled with water with a refractive index of \(n = 1.33\) the difference angle can be calculated to \(\delta_{3d} = 14^\circ\). From Gaussian beam propagation the place of the beam waist is given trough

\[ z' = \frac{zf^2}{z^2 + \left( \frac{\pi w_0^2}{\lambda} \right)^2} \]

where \(z'\) is the distance of the beam waist from the focal point of the lens at the image side and \(z\) accordingly for the object side, \(f\) is the focal length and \(w_0\) the
beam waist before focussing. For a well collimated laser beam focussed by a lens with a short focal length, as in the 3d set-up, $z' = 0$, i.e. the waist of the focussed beam is at the focal point of the lens. The radius at the beam waist $w_f$ can be calculated using

$$w_f^2 = w_0^2 \frac{f^2}{z^2 + \left(\frac{\pi w_0^2}{\lambda}\right)^2}$$

In the present set-up $f = 90$ mm, $w_0 = 1$ mm and $z = 26$ cm. The beam diameter then is calculated to be $w_f = 36$ μm. Experimentally we obtain a rough estimate if $w_f < 100$ μm using a pinhole, where both beams have to pass through.

5.1.3 Detection Unit

With the detection unit a symmetric arrangement of the incoming laser beams and the beam paths formed by the detection optics has to be fulfilled. It consists of a lens $L_2$ identical to $L_1$ and two single mode optical fibers equipped with grin lenses. The lens and optical fibers mount allow tilt and translation in x-y-z direction for the lens and in y-z direction for the fiber mounts. To allow measurements at different scattering angle the whole detection unit is mounted on the arm of the main goniometer.

5.1.4 Alignment of the Instrument

Due to the fundamental principle of the cross-correlation technique the alignment of a light scattering instrument where this technique is implemented is an important and often also difficult issue. It should guarantee identical scattering vectors for the two individual scattering experiments with an identical scattering volume placed on the rotational axis of the instrument. As the signal-to-noise ratio of the cross-correlation function strongly depends on the quality of the alignment any misalignment leads immediately to a limitation of the maximum turbidity of the sample to be investigated and of the statistics of the experiment, i.e. on a partially misaligned instrument the duration of the measurement has to be prolonged to obtain the same statistical accuracy compared to a (nearly) perfect aligned one.

In this particular realization of the 3d instrument described above, a lens is used to focus the two laser beams with the focal points at the scattering volume, and to direct the two beams symmetrically to the plane of the goniometer so that they cross each other at the scattering volume placed on the rotational axis of the instrument. For the detection of the scattered light an identical lens is used together
5.1 Detailed Description of the Opto-Mechanical Components

with two single mode optical fibers that pick up the beam paths symmetrically to the illuminating laser beams. This guarantees identical scattering vectors and of course a common scattering volume. The goal of the alignment procedure is thus to focus with the first lens the two incoming laser beams, which define a plane perpendicular to the plane of the goniometer, on one point on the rotational axis of the instrument such, that the bisector of the angle between the two beams lays in the plane of the goniometer. Furthermore, at a scattering angle of zero degree the detection beam paths must completely overlay the paths of the two illuminating laser beams.

The alignment procedure can be divided into a mechanical and an optical adjustment part, a flow chart describing the alignment procedure is shown in figure 16. The main steps of the mechanical part are the alignment of the housing, the index matching vat, and the second goniometer with respect to the main goniometer in order to ensure that they have identical rotation axis. The main steps of the optical part are to generate two parallel laser beams which cross the rotational axias of the instrument perpendicular, and placing the two lenses in such a way that the two incident and detection beams, respectively, are crossing in that point on the rotational axis which lays in the middle of the two points where the beam paths hit the axis without the lenses.
Experiment 5: Experimental Realization

- Centering of the housing
- Centering of the index match vat
- Centering of the second goniometer unit (separately)
- Mounting the Dantec fiber and adjustment of a collimated laser beam passing the rotational axis of the goniometer
- Splitting the laser beam into two parallel beams
- Mounting of the detection fibers and adjusting maximum transmitted intensity
- Mounting and centering of the second goniometer unit
- Mounting and adjusting the lenses
- Fine tuning with a measurement with a highly diluted sample to achieve maximum intercept

Figure 16: Survey of the alignment procedure.
6 Characterization of Turbid Colloidal Suspensions Using Light Scattering Techniques Combined with Cross-Correlation Methods

6.1 Materials and methods

Measurements were performed at different scattering angles \( \Theta \), and 10 intensity auto- (ACF) or cross- (CCF) correlation functions were taken. Measurement durations were 60 seconds for ACF and 120 seconds for CCF determination. The correlation functions were individually analysed using a second order cumulant analysis [33] and an inverse Laplace transform algorithm (CONTIN) [31, 32]. The resulting intensity weighted size distributions were then averaged for each scattering angle [20]. For static light scattering (SLS) experiments the intensity measured in the course of the CCF determination was used (i.e., 10 measurements of 120 s each), and the value of the intercept \( \beta_{12} \) was obtained from the cumulant fit.

The suspensions were also investigate at very low concentrations by means of SLS using a commercial goniometer system (ALV/DLS/SLS-5000F single mode fiber compact goniometer system with ALV-5000 fast correlator). Measurements were made for scattering angles \( 15^\circ \leq \Theta \leq 150^\circ \) at an increment of 1°, and 10 measurements for 10 seconds were averaged for each angle. The suspensions were inserted into cylindrical quartz cells with 8 mm inner diameter (Hellma, 540.110-QS). Measurements were performed at a temperature of \( T = 25.0 \pm 0.01^\circ C \).

Materials: The polystyrene latex particles used in these measurements (specifications: Polybead polystyrene microspheres) were obtained from Polyscience.

6.2 Results and discussion

We have performed measurements with a bimodal dispersion of polystyrene spheres in order to demonstrate the capability of the technique to suppress contributions from multiple scattering in turbid colloidal suspensions. We have prepared two suspensions of highly monodisperse latex particles with radii of \( R_1 = 23 \) nm and \( R_2 = 274 \) nm, respectively, which we both carefully and individually characterized by static and dynamic light scattering experiments. The corresponding q-dependence of the scattering intensity obtained with these dispersions is shown in 17. The two suspensions were then mixed and the relative concentrations were adjusted such (weight ratio \( c_1/c_2 = 8.77 \)) that the two particle components equally contribute to
Figure 17: Results from sample characterization of two different polystyrene spheres with radii of $R_1 = 23$ nm and $R_2 = 274$ nm. Results from static light scattering experiments with the individual and almost monodisperse particle suspensions (E: $R = 23$ nm; G: $R = 274$ nm). Shown are the time average intensities $I(q)$ as a function of the magnitude of the scattering vector $q = (4\pi n/\lambda_0) \sin(\theta/2)$. The stock solutions were diluted and the relative concentrations were adjusted to the same weight ratio as used in the experiments with mixtures.

the total scattering intensity $I(q)$ of the mixture at a scattering angle of 48°. Due to the very pronounced particle form factor of the larger spheres in the accessible q-range, their relative contribution to $I(q)$ varies considerably with scattering angle, which in principle should be measurable in a classical particle sizing experiment with dynamic light scattering. Measurements were done at four scattering angles where the two particle components of the suspension have different contributions to the intensity weighted size distribution. For this particular concentration ratio of the mixture the theoretical dynamic structure factor can be calculated from the known concentrations and form factors of the particles. Direct and hydrodynamic interactions which can also influence the dynamic structure factor depend on the size and concentration of the particles and on the salt content of the sample. In our measurements the sample with the highest concentration had a salt content of 0.1 mmol/l. The resulting Debye length of $\kappa^{-1} = 28$ nm together with the chosen
6.2 Results and discussion

Particle radii and volume fractions ensure that effects of direct and hydrodynamic interactions on $S(q, \tau)$ can be neglected, and $S(q, \tau)$ can thus be described by

$$S(q, \tau) = \frac{\int_0^\infty N(r)A^2(q, r)e^{-D_0(r)\eta^2 \tau} dr}{\int_0^\infty N(r)A^2(q, r)dr}$$

(55)

where $A^2(q, r) \sim r^6 P(q, r)$ and $D_0(r) = kT/6\pi \eta r$ represent the scattering intensity and diffusion coefficient of a particle with radius $r$, respectively, and $\eta$ is the viscosity of the solvent.

At $\Theta = 34^\circ$ almost only the large spheres are visible in the intensity weighted size distribution and their contribution to the total intensity corresponds to approximately 90%, at $\Theta = 48^\circ$ both components have the same contribution, while at $\Theta = 61^\circ$, the large spheres contribute approximately 70% and the small ones approximately 30%, and at $\Theta = 86^\circ$ the small particles dominate the intensity weighted size distribution with 85%. The corresponding two distinct populations are clearly visible in a dynamic light scattering experiment for each scattering angle when performing auto-correlation measurements on dilute suspensions (transmission $T = 0.95$) and using Contin [31, 32] in order to perform the inverse Laplace transformation required to obtain the size distribution. We are in fact able to quantitatively recover the appropriate relative amplitudes in the intensity weighted size distribution from Contin as shown in figure 18.

However, the situation completely changes for higher particle concentrations. This is demonstrated with auto-correlation measurements for an undiluted mixture at a total latex concentration of 0.21% by weight. Although the colloid concentration is still relatively low and the collective diffusion coefficient measured by dynamic light scattering is only slightly influenced by contributions from interparticle interactions, the mixture is now completely turbid with a transmission of $T = 0.05$. This has a very pronounced effect on the results obtained from auto-correlation measurements. As shown in 20, the intercept of the auto-correlation function has decreased considerably, we observe strong distortions at short lag times $\tau$, and the characteristic decay times are much smaller now. While the decrease in intercept is mainly caused by the fact that the coherence length of the laser is shorter than the average photon path length in the sample, the shift of the characteristic correlation times measured in an auto-correlation experiment is a genuine effect of multiple scattering.

This has been verified using an Ar$^+$ laser with an etalon installed, which leads to an increase of the coherence length from 2-3 cm to approximately 10 m. The intercept measured for the concentrated sample is then the same as for the diluted sample shown in figure 20.
Figure 18: A comparison of the theoretically calculated intensity-weighted distribution of hydrodynamic radii (dashed line, based on the measurement of the individual dilute monodisperse suspensions) with the results obtained from an application of Contin to the auto-correlation functions measured with dilute (solid line) and concentrated (dotted line) bimodal mixtures for different scattering angles $\Theta$. (A): $\Theta = 34^\circ$; (B): $\Theta = 48^\circ$; (C): $\Theta = 61^\circ$; (D): $\Theta = 86^\circ$.

This for example severely limits the ability to recover the correct distribution of diffusion coefficients or particle hydrodynamic radii in particle sizing experiments with large particles such as emulsion droplets to low concentrations only. This is also evident from figure 18 A-D, which show the result from Contin when applied to the auto-correlation function measured with the turbid suspension. The resulting distribution of decay times is completely distorted due to the effects of multiple scattering, and any attempt to recover a correct particle size distribution from such a measurement would utterly fail.

In contrast to the results obtained from auto-correlation experiments, the use
6.2 Results and discussion

Figure 19: A comparison of the theoretically calculated intensity-weighted distribution of hydrodynamic radii (dashed line) with the results obtained from an application of Contin to the cross-correlation functions measured with the 3d instrument and concentrated bimodal mixtures (solid line) for different scattering angles \( \Theta \). (A): \( \Theta = 34^\circ \); (B): \( \Theta = 48^\circ \); (C): \( \Theta = 61^\circ \); (D): \( \Theta = 86^\circ \)

of a 3d cross-correlation set-up allows us to very efficiently suppress any effects from multiple scattering. This is shown in figures 20 and 19 A-D, where the cross-correlation function and the corresponding distribution of hydrodynamic radii from Contin have been plotted. The intercept is much lower due to the combined effect of the intrinsically lower value for the ideally aligned instrument \( \beta_{12,\text{ideal}} = 0.25 \) and the actual phase mismatch and misalignment, which results in an intercept of \( \beta_{12} \approx 0.17 \) for our instrument, and the effect of multiple scattering. However, the actual distribution of decay times remains unchanged as is already clearly visible from a comparison of the auto-correlation function from the dilute sample and the cross-correlation function obtained from the turbid sample (see figure 20). Figures
Figure 20: Results from auto- and cross-correlation experiments with dilute and concentrated mixtures of two different polystyrene spheres with radii of $R_1 = 23 \text{ nm}$ and $R_2 = 274 \text{ nm}$. A comparison of the measured auto-correlation function with a dilute (dashed line) and concentrated (dotted line) mixture and the cross-correlation function obtained with the 3d instrument from a concentrated mixture (solid line).

19 A-D demonstrate that the use of a 3d cross-correlation scheme allows us to determine the correct distribution of decay times (or hydrodynamic radii) even for highly turbid suspensions.

While the measurements above show clearly that the suppression of multiply scattered light allows us to isolate the single scattering dynamic structure factor and therefore to determine correct size distributions even for highly turbid suspensions, we also can go one step further: combined static and dynamic light scattering experiments using the 3d spectrometer can provide us with the $q$-dependence of the differential scattering cross section $d\sigma(q)/d\Omega$, which can be used to determine the single scattering particle form factor or the static structure factor of colloidal suspensions. The basis for this is the fact that the intercept of the cross-correlation function depends on the ratio between the singly scattered light $I^{(1)}(q)$ and the total scattered intensity $I(q)$ (eqn. 40). The mean intensity measured in a static light scattering experiment contains contributions from singly scattered and from different orders of multiply scattered light. To extract the single scattering contribution...
6.2 Results and discussion

$I^{(1)}(q)$, $I(q)$ has to be corrected with the reduced intercept $\beta_{12}/\beta_{12}^{(1)}$ of the cross-correlation function where $\beta_{12}^{(1)}$ denotes the intercept measured in the limit of single scattering only, which can be measured independently in a dynamic light scattering experiment with a highly diluted sample. The single scattering contribution to the total intensity observed at detectors 1 and 2 can thus be obtained from

$$I^{(1)}(q) = \sqrt{I_1^{(1)}(q)I_2^{(1)}(q)} = \sqrt{I_1(q)I_2(q)\frac{\beta_{12}}{\beta_{12}^{(1)}}}$$

The $q$-dependence of the scattering intensity measured on a classical goniometer system for a dilute suspension of highly monodisperse latex particles with radius $R = 274$ nm is shown in figure 21 A. In the accessible $q$-range the normalized particle form factor $P(q) = I(q)/I(0)$ shows distinct minima and maxima that are typical for relatively monodisperse spherical particles. A calculation using Mie-theory for these latex particles with a given polydispersity of $\sigma = 2.9\%$ results in very good agreement with the experimental data. However, the scattering data has a very different appearance when measured at higher concentrations, where multiple scattering becomes important. This is illustrated with static light scattering data obtained on the 3d instrument for two different particle concentrations, where significant multiple scattering leads to low transmission values of $T = 12\%$ and $T = 1.5\%$, respectively (see fig. 21 A). For these turbid suspensions, the minima and maxima of the form factor are smeared out due to multiple scattering effects. The contribution from multiple scattering becomes dominant close the minima in $P(q)$, where the intensity is several orders of magnitude lower than in forward direction.

It is obvious from figure 21 A that even the presence of small amounts of multiple scattering already leads to completely wrong numbers for the polydispersity and the average particle size in any attempt to fit a (Mie) scattering function for polydisperse suspensions to the experimental data. The important role of multiple scattering becomes even more obvious when looking at the reduced intercept $\beta_{12}/\beta_{12}^{(1)}$ as a function of $q$ for both suspensions shown in figure 21 B, which we obtained from simultaneous cross-correlation experiments. This quantity directly yields the ratio of singly to multiply scattered light, whereby a value of 1 means that there is no multiple scattering, and a decrease in the intercept corresponds to an increasing contribution from multiply scattered light in $I(q)$. The fact that we obtain $\beta_{12}/\beta_{12}^{(1)} > 1$ for the first two data points of the sample with 12 % transmission is due to an artefact mainly caused by dust effects at very low scattering angles, which can influence the intercept of the cross-correlation function. This is also evident when
looking at the standard deviations for the different values also given in Figure 21 B, which are largest at very low scattering angles and in the minima of the form factor, and which are in general larger for the sample with the lower concentration, where contributions from dust are not completely dominated by the contribution from the latex particles.

A combination of the total scattered intensity $I(q)$ and the reduced intercept $\beta_1/\beta_1^{(1)}$ together with equation 48 directly allows for a calculation of the single scattered intensity $I^{(1)}(q)$, which is plotted for both concentrations in figure 21 C. The thus obtained corrected intensities agree very well with the calculated $P(q)$ for singly scattered light. These results demonstrate, that we can evaluate the single particle form factor even under circumstances, where close to the minimum in $P(q)$ the contribution from single scattering is less than 10% of the total intensity. It is of course clear that such a procedure is not restricted to applications in particle sizing, but allows for the correction of multiple scattering contributions to the static structure factor in strongly interacting colloidal suspensions, where $S(q)$ shows a strong $q$-dependence and the scattered intensity can be suppressed significantly [37].

The ability to suppress multiple scattering and determine the $q$-dependence of singly scattered light has some important consequences for static light scattering measurements. In particular for systems with very pronounced $q$-dependence of the scattered intensity such as for large particles or suspensions of strongly interacting colloids, one generally aims for conditions where the system is only weakly scattering. By this one tries to ensure that multiple scattering does not cover the regions with low intensity. This makes these measurements highly susceptible to contributions from background (solvent, reflexes, stray light from cuvettes and vat, dust etc.), and consequently measurements at low values of $q$ become exceedingly difficult. However, if one can successfully correct for multiple scattering, these aspects lose their importance, and we can choose experimental conditions where the scattering from the particles completely dominates any background contamination. We have in fact been able to benefit from this and perform SLS measurements at angles as low as $\Theta = 5^\circ$, which would be impossible for a conventional approach using normal scattering cells and a goniometer system.

Our measurements show that the use of the 3d cross-correlation technique in dynamic light scattering experiments allows to effectively suppress contributions of multiple light scattering. The current value of $\beta_1 \approx 0.2$ for the intercept in the cross-correlation function achieved with our instrument is high enough that we obtain correlation functions of sufficient accuracy in order to successfully apply inverse
6.2 Results and discussion

Figure 21: Results from static light scattering experiments with dilute and concentrated turbid monomodal particle suspensions ($R = 274 \text{ nm}$, $\sigma = 2.9\%$).

(A): Normalized scattering intensity $P(q) = I(q)/I(0)$ as a function of $q$ for dilute suspension measured on a commercial goniometer system ($E: T = 0.95$), and concentrated suspensions measured on the 3d instrument ($\bullet$: concentration 0.01\%, $T = 12\%$; $\square$: concentration 0.05\%, $T = 1.5\%$). Also shown is a theoretical calculation for polydisperse spheres following a Schulz distribution with average radius 274 nm and polydispersity $\sigma = 2.9\%$ using Mie theory. (B): The reduced intercept $\beta_{12}/\beta_{12}^{(1)}$ obtained from cross-correlation function measurements using the 3d instrument with dilute and concentrated suspensions as a function of $q$. ($\bullet$: concentration 0.01\%, $T = 12\%$; $\square$: concentration 0.05\%, $T = 1.5\%$) The error bars given are standard deviations obtained from 10 individual measurements. (C): Single scattered normalized intensity $P(q) = I(q)/I(0)$ as a function of $q$, where multiple scattering contributions have been corrected for by using figure 21 B and equation 48, for concentrated suspensions measured on the 3d instrument ($\bullet$: concentration 0.01\%, $T = 12\%$; $\square$: concentration 0.05\%, $T = 1.5\%$). Also shown is a theoretical calculation for polydisperse spheres following a Schulz distribution with average radius 274 nm and polydispersity $\sigma = 2.9\%$ using Mie theory.
Laplace transformation programs such as Contin after measurements of typically 60-300 seconds. This opens up a wide field of new applications ranging from particle sizing in industrially relevant systems such as emulsions to the determination of the dynamics of concentrated model suspensions that cannot be optically matched. Moreover, we can directly use the relation between the experimentally determined intercept of the cross-correlation function and the amount of multiple scattering and correct the measured values of the scattered intensity $I(q)$ for contributions from multiple scattering. Therefore, our 3d spectrometer can not only be used for DLS, but also for systematic SLS studies of turbid suspensions.
7 Static Structure Factor of Strongly Interacting Colloidal Suspensions

7.1 Introduction

Structural properties of colloidal systems are of considerable interest in colloid science. Understanding the interactions, which cause these structures, can help to find a relationship between microscopic characteristics and macroscopic properties of colloidal systems which is also of industrial relevance [38, 39]. Liquid state theory and light scattering experiments are often the theoretical and experimental tools used to describe suspensions of interacting particles. A considerable progress in the understanding of the structural properties of colloidal suspensions has been achieved by making an analogy to simple liquids, i.e. by treating the suspension as a 'macrofluid'. The colloidal particles then play the role of the fluid molecules, and the solvent only enters as a continuum characterized by the corresponding continuum parameters such as dielectric constant, index of refraction, or ionic strength (or Debye length) [40, 41].

The structure of colloidal suspensions arising from the interactions between the particles can be quantitatively described with the pair correlation function $g(r)$, which is the probability of finding a pair of particles separated by the distance $r$. It is directly related to the static structure factor $S(q)$ via

$$S(q) = 1 + n \int [g(r) - 1] e^{-iqr} \, d^3r$$

which can be measured in a static light scattering experiment. The scattering intensity $I_s(q)$ measured as a function of the scattering angle $\Theta$ or the scattering vector $q$ is given by equation 14. The particle form factor $P(q)$ contains information about size, shape and the internal structure of the particles, and the static structure factor $S(q)$ reflects the order in the suspension based on the interactions between the particles. $S(q)$ can also be written as

$$S(q) = \frac{1}{N} \sum_{i,j=1}^{N} \langle e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle$$

where the angular brackets denote an ensemble average. Equation 58 is a measure of the correlations between the particles $i$ and $j$ located at positions $\mathbf{r}_i$ and $\mathbf{r}_j$, and for uncorrelated particles $S(q) = 1$ for all $q$. Suspensions of charged monodisperse particles exhibit a characteristic form for the static structure factor, which closely...
resembles $S(q)$ found for simple liquids. In the limit of $q \to 0$ it starts from a small value $S(0)$, which is directly related to the isothermal compressibility $\chi$ of the suspension through

$$S(q = 0) = n k_B T \chi$$  \hfill (59)$$

$S(q)$ then increases with increasing $q$ and has its main maximum where the correlations are strongest, which is at the reciprocal of the mean interparticle distance $d$. Since the interparticle distance can be calculated from the volume fraction $\Phi$ of the suspension and the particle volume $V_p = 4\pi/3a^3$ through $d = \sqrt[3]{V_p/\Phi}$, the position of the main peak scales with $\Phi^{1/3}$. At higher values of $q$ the higher order minima and maxima in $S(q)$ become less pronounced and approach a value of one which corresponds to the value of an ideal particle gas\textsuperscript{10}. The peak positions in $S(q)$ in reciprocal space correspond to an increased probability of finding two particles separated by a position $r$, i.e. to a peak in $g(r)$. In order to find a relation between the experimentally determined static structure factor, the pair correlation function and the interaction potential, analogies to the theory of simple liquids are often made, i.e. the particle suspension is treated as a 'macrofluid'. In simple liquids the Ornstein-Zernike equation

$$h(r) = c(r) + n \int h(|r - s|) c(s) \, d^3s$$  \hfill (60)$$
is used to provide this link \cite{42}. It consists of the total correlation function $h(r) = g(r) - 1$, which is split into a part describing the direct correlations between two particles through $c(r)$, and the sum of indirect correlations mediated by the other particles. Since equation 60 contains no information about the interaction potential an additional closure relation is needed to link the interaction potential to the pair correlation function. A simple closure relation is for example the mean spherical approximation (MSA) \cite{41} which has often been used to describe relative weakly interacting particles. The relation between the direct correlation function $c(r)$ and the interaction potential $U(r)$ is given through

$$c(r) = -\beta U(r)$$  \hfill (61)$$

where \(\beta = 1/(k_B T)\) is the reciprocal thermal energy. On a more sophisticated level, the Percus-Yevick (PY) and the hypernatted chain (HNC) \cite{41} closure relations are

\textsuperscript{10}For particles that interact with a short range hard sphere potential, the main peak of $S(q)$ is related to the nearest neighbour shell of particles around a primary particle, i.e. at $d = 2a$, which leads to $q_{\text{max}} \sim 2\pi/d$. 
often applied to describe the structural properties of particle suspensions. Because it is known that the PY closure relation leads to good results for short ranged hard sphere potentials and the HNC closure relation for long ranged Yukawa potentials, the Rogers-Young closure \[43\]

\[ h(r) = -1 + e^{-\beta U(r)} \times \left( 1 + \frac{\exp\{f(r)[h(r) - c(r)]\}}{f(r)} - 1 \right) \] (62)

aims at taking advantage from both closures by combining PY and HNC with a mixing function

\[ f(r) = 1 - e^{-\alpha r} \] (63)

where \( \alpha \) is the mixing parameter. In the limit \( \alpha \to 0 \) the Rogers-Young closure reduces to the PY and for \( \alpha \to \infty \) to the HNC closure. The mixing parameter \( \alpha \) can be obtained by calculating the isothermal compressibilities \( \chi_f^T \) and \( \chi_v^T \) via the fluctuation and the virial route. While the fluctuation compressibility is directly given by the static structure factor in the limit of \( q \to 0 \)

\[ \chi_f^T = \frac{\beta}{n} S(0) \] (64)

the virial compressibility can be calculated from the equation of state

\[ \chi_v^T = \left( \frac{\delta(\beta P)}{\delta n} \right)^{-1}_T \] (65)

where the pressure \( P \) is given through

\[ \frac{\beta P}{n} = 1 - \frac{2}{3} \pi \beta n \int_0^\infty r^3 g(r) \frac{dU}{dr} \, dr \] (66)

Because these closure relations are approximations the compressibilities calculated via both routes are generally not identical. In the Rogers-Young closure the mixing parameter \( \alpha \) is chosen in such way, that \( \chi_f^T = \chi_v^T \). In this way the RY closure guarantees thermodynamic consistency, at least for the compressibility, and it provides very accurate results for the pair correlation function \( g(r) \) when compared to 'exact' Monte Carlo simulations.

Light scattering experiments with 'real' particle suspensions often have to deal with polydispersity in size, charge or refractive index of the particles. An interpretation of the light scattering data consequently has to take this polydispersity into account \[44\]. In the theoretical calculation the continuous distribution of particles generally is replaced by a histogram which then results in a mixture of particles.
consisting of \( p \) components. Sizes \( a_\mu \) and number densities \( n_\mu \) of the components are chosen such that the first two moments of the histogram and the continuous distribution have the same values. The Ornstein-Zernike equation now is given by a coupled set of integral equations

\[
h_{\mu\nu}(r) = c_{\mu\nu}(r) + n \sum_{\lambda=1}^{p} \left( \frac{n_\lambda}{n} \right) \int h_{\mu\lambda}(r) c_{\lambda\nu}(|r - r_1|) \, d^3r_1
\]

which have to be solved with the generalized Rogers-Young closure relations.

With a polydisperse sample the scattering intensity is the weighted sum of the particle components, and equation 14 can be written in a modified form as

\[
I_S(q) = n\overline{a^6} \overline{P(q)} \overline{S(q)}
\]

where \( \overline{a^6} \) and \( \overline{P(q)} \) represents intensity-weighted average particle volume and particle form factor, respectively,

\[
\overline{a^6} = \frac{\sum_{\mu=1}^{p} N_\mu(a)(a_\mu^6)^2}{\sum_{\mu=1}^{p} N_\mu(a)a_\mu^6}
\]

\[
\overline{P(q)} = \frac{\sum_{\mu=1}^{p} N_\mu(a)(a_\mu^6)^2 P_\mu(q)}{\sum_{\mu=1}^{p} N_\mu(a)(a_\mu^6)^2}
\]

and \( \overline{S(q)} \) the effective structure factor taking into account the size distribution. \( I_S(q) \) no longer simply factors into single particle quantities \( P(q) \) and a part describing the interparticle correlations \( S(q) \) only. The effective static structure factor

\[
\overline{S(q)} = \frac{1}{\overline{P(q)}} \sum_{\mu,\nu=1}^{p} B_\mu(q) B_\nu(q) S_{\mu\nu}(q)
\]

where \( B_\mu \) denotes the scattering amplitudes and \( S_{\mu\nu} \) the partial static structure factors, depends now also on single particle properties. The partial static structure factors are defined as

\[
S_{\mu\nu}(q) = \frac{1}{n} \sum_{j=1}^{n_\mu} \sum_{k=1}^{n_\nu} \langle e^{i\mathbf{q} \cdot (\mathbf{R}_j^{(\mu)} - \mathbf{R}_k^{(\nu)})} \rangle
\]

Because of the different size, charge or refractive index of the particles the partial static structure factors have their maximum at different values of \( q \). As a consequence the peak in \( S(q) \) is shifted and reduced and higher order oscillations are washed out. Furthermore the value of \( S(0) \) increases with increasing polydispersity \([45]\), thus \( S(0) \neq nk_BT\chi \).

In this chapter we demonstrate that with the 3d cross-correlation instrument the static structure factor \( S(q) \) can be measured in particle suspensions that exhibit a
7.1 Introduction

high turbidity. This provides a direct access to the interaction potential for systems which were previously excluded from these investigations due to multiple scattering contributions to the measured $I_S(q)$. For example aqueous suspensions of charged polystyrene spheres, which are widely used as model systems, cannot be optically matched, which limits the concentration where multiple scattering effects can safely be neglected to volume fractions of $10^{-3}$ or lower, depending on the particle size, when using standard light scattering instruments.

A survey of the existing data on structure factors in deionized suspensions reveals a characteristic discrepancy between theoretical predictions and experimental data [46, 37]. While integral equations are capable of reproducing the peak position and the height of the minima and maxima in $S(q)$ quite accurately if polydispersity is properly taken into account, the theoretical values for $S(q)$ are generally too low at low values of $q$. A typical example is given in figure 22. There are several possible reasons for their finding. A particularly exciting possibility would be the recently proposed attractive interactions of electrostatic origin between charged particles [47, 48], that although relatively weak, would contribute measurably to $S(q)$ at low values of $q$. However, several other possible explanations exist for this discrepancy between theory and experimental data. First of all, polydispersity is known to result in an increased forward scattering intensity [44]. Nevertheless we believe that this is an unlikely explanation, as some of the published results have been performed with very well characterized model particle suspensions where the size distribution was known precisely. Another reason could be the presence of a small number of aggregates. To first approximation they would correspond to something like an uncorrelated gas of big particles in a highly correlated liquid of small ones. Their contribution to the intensity could then lead to a significant increase in $I_S(q)$ at low values of $q$, where $S(q)$ for the small 'monomeric' particles would be small and their contribution to $I_S(q)$ considerably suppressed. Finally, as for deionized suspensions $S(q)$ can be very low at low $q$ values, the presence of small amounts of multiple scattering, which would not be measurable for non interacting (i.e. highly screened) particles at these low volume fractions, could contribute significantly and thus lead to apparently too high values for $S(q)$.

Therefore we have performed a systematic study of the static structure factor as a function of particle volume fraction with our 3d-instrument, which allows us to determine the amount of multiple scattering and subsequently correct for it. Particular care was given to the precise determination of the sample polydispersity and a careful preparation in which all possible precautions have been made to prevent
aggregation and remove all existing large particles.

7.2 Materials and Methods

7.2.1 Experimental Set-Up

The experiments were performed using the 3d cross-correlation instrument described in chapter 5.

7.2.2 Methods

Measurements were done with suspensions of latex spheres (diameter: (110±10) nm) with volume fractions in the range from 0.05% to 1% by volume. As it was found that the suspensions crystallize when fully deionized due to the long-range electrostatic interactions of the highly charged particles, a mixture of ethanol and water was used.
as the solvent. A volume ratio of 70% ethanol and 30% water prevents crystallization in the investigated concentration range, because the alcohol changes the association-dissociation equilibrium of the surface charge groups, the number of charges per particle decreases and the strength of electrostatic interactions between the particles is thus lower. The suspensions were filtered using a 0.8 μm filter membrane (Versapor acrodisc, Gelman) into the quartz sample cells (rectangular cells, 10 mm × 10 mm, and cylindrical cells with an inner diameter of 8 mm, Hellma). In order to achieve fully deionization the samples were kept at least 10 days in contact with equal volumes of mixed bed ion exchanger resin (Dowex) prior to a measurement.

Combined static and dynamic light scattering experiments were performed in order to suppress multiple scattering and to obtain the single scattering cross section $\sigma(q)$. Scattering intensities and the corresponding correlation functions were measured at intervals of 1° in the angular range from $\Theta = 10^\circ$ to $\Theta = 125^\circ$ at a temperature of 25°C. Ten measurements were done at each scattering angle, each having a duration between 20 s and 120 s, depending on the scattering angle and the sample concentration. The correlation functions were analysed using a second order cumulant analysis in order to obtain the intercept $\beta_{12}$ of the cross-correlation function needed for the correction of the scattering intensity for multiple scattering contributions. Additionally the diffusion coefficient is calculated from the cumulant fit. The ten runs then were averaged.

Highly diluted aqueous suspensions of the latex particles were also characterized by means of dynamic and static light scattering with a commercial goniometer system (ALV/DLS/SLS-5000F single mode fiber compact goniometer system). To avoid an influence of electrostatic interactions a 5 mM/l NaCl was added to the solvent. The particle size distribution was calculated with the inverse Laplace transformation routine Contin. Furthermore the particle size distribution was measured with transmission electron microscopy. The micrographs were calibrated using a Pt-grid with 2160 lines/mm.

7.2.3 Materials

The suspension of sulfate latex particles with the diameter of 110±10 nm used for the experiments was obtained from UDC. It is stabilized with 2500 sulfate groups on the surface which are fully protonated at pH 7. The stock solution has a concentration of 8.3 % by volume.
7.3 Results and Discussion

The latex particles were characterized by static and dynamic light scattering and transmission electron microscopy. In figure 23 experimental data measured with a highly dilute suspension (0.001 % by volume) in an ethanol/water mixture (volume ratio 70/30) as the solvent are compared with the particle form factor calculated with Mie-theory. A fit to the experimental data reveals a particle radius of 59 nm, which was also found from DLS experiments. However, from transmission electron microscopy considerably too small values with $r = (87.2 \pm 7.3)$ nm were obtained. This behaviour could be due to a combination of the effect of the drying process in the sample preparation and to a shrinking of the particles in the presence of the electron beam and is also described in the literature.

Static structure factors were measured for particle concentrations ranging from 0.04 % to 1 % by volume. As solvent a mixture of 70 parts ethanol to 30 parts water was used and the suspension was fully deionized using an ion exchanger. Deionized suspensions with water as the solvent show the formation of a colloidal crystal at low volume fractions of approximately 0.1 % for these particles. These crystallized
7.3 Results and Discussion

samples, however, show Bragg-peaks with a high intensity in the $I(q)$ which are superimposed on the liquid structure peak. While the crystal can be shear melted by simply shaking the suspensions and the Bragg peaks disappear, re-crystallization takes place after about 10 s, which is a too short time for the measurement. Using an ethanol/water mixture as the solvent, the alcohol prevents the suspensions from cristallization up to volume fractions higher than 1%. Scattering intensities were measured as a function of the scattering angle with combined static and dynamic light scattering experiments and subsequently corrected for turbidity\textsuperscript{11} and multiple scattering. A normalization of $I_S(q)$ and division by the measured particle form factor then provides the static structure factor $S(q)$. Theoretical calculations were performed solving the Ornstein-Zernike equation with the Rogers-Young closure taking into account the polydispersity of the latex particles ($r = 59$ nm, $\sigma = 8.6\%$). Results are shown in figure 24 for different volume fractions. The results demonstrate clearly that the static structure factor $S(q)$ can be measured in particle suspensions up to high volume concentrations that exhibit a high turbidity. This allows now to obtain important information about interaction effects in colloidal suspensions which were previously not accessible. The experimental data are quantitatively in good agreement with theoretical results obtained from solving the Ornstein-Zernike equation with the Rogers-Young closure relation.

For higher concentrations the position of the main peak in $S(q)$ is shifted towards larger values in $q$. The values of the effective charge used in the Rogers-Young calculation vary between 160-250 charges per particle. However, our ability to analyse the data at higher concentrations is limited due to problems in the normalization of the scattering data. Since our data are not on absolute scale and we lack a very precise knowledge of the particle concentration, we would need at least the second peak in $S(q)$ in the accessible $q$ range in order to unambiguously normalize the experimentally determined $S(q)$. This is particularly important as the height of the main peak determines the effective charge, i. e. is an adjustable parameter. We therefore plan to investigate the highest concentrations also with small-angle neutron scattering (SANS), where we have both overlap with light scattering data at low $q$ and can extend the $q$ range to much higher values, where $S(q)$ has reached its asymptotic limit of one, and where the oscillations in the particle form factor become clearly visible. Nevertheless the light scattering data for these high concentrations (0.5\% and 1\%) are shown in figure 25. The symbols represent the measured scattering

\textsuperscript{11} when using rectangular cells
intensities while the line represents the particle form factor (on an arbitrary scale)\textsuperscript{12}.

The experimental data shown in figure 24 are in good agreement with the calculations using the Rogers-Young closure relation. At low concentrations, the main peak occurs at too low values of \( q \) in order to unambiguously determine the asymptotic value \( S(0) \) and test for the previously existing discrepancies between theoretical calculations and experimental data. Under these conditions we are limited by the enormous influence of dust particles, which cause enormous fluctuations of the intensity at values of \( \Theta \leq 16^\circ \). It is clear that a systematic comparison of theory and experiment will require an additional effort both in sample preparation as well as an improved measurement protocol with the use of improved software dust filter. However, it is important to point out that even under these conditions multiple scattering cannot be completely neglected at low values of \( q \), and the use of a classical light scattering set-up would result in a measurably too high intensity at low \( q \). At higher concentration, the main peak has moved to sufficiently high values of \( q \) in order to provide us with a first comparison between experimental data and theoretical results for \( S(q) \) in the limit of small \( q \) values. While the data at \( c = 0.11\% \) is in reasonable agreement with the theory, we still observe a characteristic deviation for \( c = 0.23\% \). However, it is clear that we need additional experiments and a considerable experimental effort in order to reach any conclusions about the possible reasons for this deviation. Nevertheless, our data shown in figure 24 clearly demonstrate our improved capability to study structural and dynamic properties of strongly interacting colloidal dispersions, and to investigate and test the applicability of modern theories to improve our understanding of colloid stability, interactions and structure evaluation.

\textsuperscript{12}We also plan to change the present set-up for the 3d instrument to allow measurements on absolute scale and therefore a normalization of scattering data.
Figure 24: Static structure factors measured with latex suspensions ($r = 59$ nm) at different concentrations. The experimental data are compared with Rogers-Young calculations.
Figure 25: Scattering intensity and particle form factor (on an arbitrary scale for latex suspensions ($r = 59$ nm) with 0.5% and 1% concentrations.)
8 Influence of Dilution on the Particle Sizes in Milk

8.1 Introduction

Dynamic light scattering is a powerful tool for a characterization of colloidal systems. It is a non-destructive, convenient and fast method for investigations of the particle size distribution in colloidal suspensions, and it is also frequently used for investigations of interaction potentials (see chapter 7), colloidal dynamics and stability. However, as the method is known to fail for samples with non-negligible turbidity, many systems, often of industrial relevance, could not be investigated with dynamic light scattering in the past. We therefore developed a so-called 3d cross-correlation experiment, where the disturbing contributions from multiple scattered light are suppressed, and the measurable range of samples can be extended to high turbidity or concentration. The construction of the instrument was described before in detail and its performance was tested using measurements with well defined model systems (see chapter 6).

Here we now make a next step and demonstrate the applicability of the technique to complex suspensions of practical and technological relevance. In industrial processes, 'real world' systems often need to be characterized with respect to their particle size distribution. If the size of the particles is in the colloidal range, light scattering methods can in principle be used. Frequently undesired multiple scattering effects due to the mostly high sample turbidity are avoided with a dilution of the sample. While this often is not a problem for systems such as suspensions of inorganic particles, many other systems, like for example emulsions or self associating systems, react with a significant change of the sample properties upon changes of the concentration or the composition of the sample. It is clear that the 3d cross-correlation instrument could help to overcome this problem and enable us to use light scattering techniques for a much larger range of samples than previously considered.

As a 'real world' system we choose milk, which is a subject of great interest in the food industry because many products are based on it. The composition of cow milk is given in table 1. Milk can be characterized as a colloidal suspension with a trimodal distribution of whey proteins, casein micelles and milk fat in water, where the components are also polydisperse in size [49]. In this article the behaviour of the particle size distribution of milk under dilution is described. A characterization of
such a complex system under conditions where the signal content in the measured correlation function will be significantly reduced due to contributions from multiple scattering also represents a considerable task with respect to the data analysis. Laplace inversions require in order to recover size distributions from DLS experiments are difficult to handle even under ideal conditions of high signal-to-noise ratio. Therefore we also developed a new data analysis procedure which is described in this chapter as well.

8.2 Materials and Methods

8.2.1 Experimental Set-Up

The experiments were performed using the 3d cross-correlation instrument described in chapter 5.

8.2.2 Methods

8.2.3 Multi Angle Inverse Laplace Transformation

A dynamic light scattering experiment probes the fluctuations in the intensity of the scattered light which are mainly caused by the diffusive motion of the particles. For the calculation of the particle size distribution an inverse Laplace transformation is performed on the measured correlation function. The inversion of $g(\tau)$, however, is an ill-conditioned problem, this means that any noise $\epsilon(\tau, \Gamma)$ on the measured correlation function, which is ever present in a dynamic light scattering experiment, leads to a typically infinite set of possible results for the calculated size distribution $G(\Gamma)$ that fit

$$
g^{(1)}(\tau) = \int_{\Gamma_{\min}}^{\Gamma_{\max}} e^{-\Gamma \tau} G(\Gamma) \, d\Gamma + \epsilon(\tau, \Gamma) \tag{72}
$$
8.2 Materials and Methods

within the noise level. In general a higher noise level restricts the resolution of $G(\Gamma)$, because any variation in $g(\tau)$ smaller than the noise contribution cannot taken into account for the calculation of $G(\Gamma)$. While the position of the (main) peaks in $G(\Gamma)$ of a polydisperse sample can often be recovered quite precisely using inversion methods like exponential sampling or Contin [30, 32] even with decreasing resolution, the amplitude of these peaks can normally not be obtained better than a factor of two even under close to ideal conditions. Because the noise on the correlation function depends on the height of the intercept $\beta$, where a smaller intercept means a relatively higher noise level, and in a cross-correlation experiment $\beta_{12}$ decreases with increasing sample turbidity, the resolution in $G(\Gamma)$ that can be obtained in a cross-correlation experiment is not as good as in an auto-correlation experiment performed with a sample having negligible turbidity and with comparable duration of the measurement. Of course, a prolonged measurement decreases the noise level and therefore increases the resolution, but there are often practical limits for the duration of an experiment.

A method which improves the accuracy of the calculated size distribution consists in a simultaneous fit of a set of correlation functions measured at different scattering angles $\Theta$ with the additional constraint that the scattering intensities calculated from each size distribution, taking into account the corresponding particle form factors, are reproduced. This is based on the fact that in a polydisperse sample the intensity weighted size distribution, as it is usually calculated with an inverse Laplace transformation, varies with the scattering angle due to the fact that the particle form factors of each particle species are different (see figure 18). Consequently the contribution of a particle species to the scattered intensity varies with the scattering angle, and the amplitude in the size distribution for this species can be recovered best at its maximum contribution to $I_S$. The angular dependence of the size distribution $G^I(q, r)$ can be taken into account by performing a Mie calculation [27, 50] to obtain the appropriate particle form factors $P(q, r)$ and

$$ G^N(r) = \frac{1}{r^6 P(r, q)} G^I(r, q) $$

(73)

where $G^N(r)$ then is the number distribution of particles, which no longer depends on $q$. Therefore the refractive index ratio $m = n_P/n_S$ of the particles ($n_P$) to the solvent ($n_S$) is needed as an additional input parameter for the Mie calculation. A simultaneous fit of a set of correlation functions measured at different scattering angles improves the result by taking advantage of the different contributions of the particle species at different angles. The constraint of the same angular dependence of
the intensity calculated from each individual size distribution increases the resolution of the size distribution, and particularly the peak heights, to about the maximum resolution obtainable for every single particle species at their maximum contribution to the scattering intensity. Because the particle form factor possesses a pronounced angular dependence for particles larger than a radius of approximately $\lambda/2$, best results of this method can be expected for experiments with suspensions of particles with dimensions comparable or larger than the wavelength $\lambda$ of the light. (Details of the algorithm and its performance will be given elsewhere [51].)

8.2.4 Methods

For the dilution series the different types of milk used for the experiments were diluted prior to a measurement with deionized water to volume ratios milk to sample of 1:1 (or undiluted), 1:10, 1:100 and 1:1000. The samples then were inserted either in a round quartz cell with a inner diameter of 8 mm (for dilutions 1:100 and 1:1000) or in a rectangular cell (10 mm $\times$ 10 mm) for the other, more turbid samples. For the rectangular cells the path length inside the cell was adjusted to $s \geq 400 \mu$m, depending on the turbidity of the sample, to obtain a high signal-to-noise ratio $\beta_{12}$. Measurements were done within a time of 5 hours after dilution. Three cross-correlation functions, each measured for a duration between 60 s and 300 s, were taken in an angular range $30^\circ \leq \Theta \leq 120^\circ$ at intervals of $5^\circ$. Ten measurements, covering the whole angular range and equally spaced in $\Theta$ were used for the multi angle inverse Laplace transformation in order to recover the size distribution of the particles. The individual results then were averaged for each dilution step. A refractive index $n_p = 1.5$ of the particles was used for the calculation of the particle form factors $P(q,r)$. All measurements were performed at a temperature of $25^\circ$C.

8.2.5 Materials

Measurements were performed using three kinds of milk different in composition. Customary, homogenized full-cream cow milk with a milk fat content of 3.8% by volume and skimmed cow milk with a milk fat content of 0.3% by volume were used. In addition a protein-stabilized emulsion based on vegetable oil was characterized. The emulsion was obtained from Dr. M. Leser, Nestec, Switzerland.
8.3 Results and Discussion

We have performed measurements of milk at different stages of dilution. Multiple scattering effects are only negligible at the highest dilution of 1:1000 for the kinds of milk investigated, the higher concentrated samples show clear signs of multiple scattering. Especially with the undiluted samples the paths of the incident laser beams hardly can be seen in the background of multiply scattered light. While an auto-correlation experiment performed with these samples would fail badly and yield a completely wrong particle size distribution, the 3d cross-correlation experiment successfully allows to suppress the multiply scattered light. This results in a correct measurement of the size distributions even in undiluted milk. Because milk is known to have a relatively high salt content of about 0.1 M/l [49], long range electrostatic interactions can be neglected, which otherwise are known to influence the diffusion coefficients of the particles from which a size distribution is calculated (see eq. 30).

8.3.1 Full-Cream Cow Milk

The particle size distributions of full-cream cow milk measured with a dilution of 1:1000 and with undiluted milk is shown in figure 26. A bimodal size distribution is visible for both cases. The undiluted milk shows a peak located at a radius of 80 nm with a shoulder up to radii of 1000 nm, while radii of 65 nm and 200 nm for the milk diluted 1:1000 are measured, i.e. we observe a shift to smaller values in size upon dilution. From a comparison with the sizes of the different particle components given in table 1, it seems reasonable that the first peak in the size distribution represents the casein micelles and the second peak the milk fat droplets. However, a clear classification is not possible, because the peak positions are too close and we know from the literature that these two populations both have a broad size distribution [49]. Nevertheless, based on a conversion of the intensity weighted size distribution to volume fractions using Mie theory, the resulting volume ratios of 1.6:1 for the small to the large particle fraction are in reasonable agreement with the predictions given in table 1 given for casein micelles and fat globules. In the diluted sample (1:1000) the ratio is only 1.1:1.

The whey proteins whose radius of 5 nm is very small compared to the other particle components in milk, cannot be recovered even with the improved multi angle fit method, because their contribution to the scattering intensity is too small when compared to the large casein micelles and emulsion droplets. While the more concentrated samples cannot be measured with conventional DLS due to the multiple
scattering of the light, the sample with a dilution 1:1000 was also measured with a conventional dynamic light scattering instrument (ALV/DLS/SLS-5000F). The measured particle size distribution is exactly the same as measured with the 3d cross-correlation instrument, which supports the performance of the 3d cross-correlation instrument.

Undiluted milk with a total particle volume fraction of about 16 % and the presence of large fat droplets with radii up to 1 μm represent a sample which is at the limit of the capability of our 3d instrument in its present design\textsuperscript{13}. While it is still measurable, the intercept of the cross-correlation function of about 0.02 clearly limits the obtainable resolution of the size distribution due to the low signal-to-noise ratio when compared with a dilute sample. Nevertheless we believe it is

\textsuperscript{13}This limit can be pushed to even higher turbidity using a laser wavelength in the near infrared regime.
quite remarkable that such a polydisperse sample with a volume fraction of more than 15 % and containing a significant amount of large particles can be correctly characterized with dynamic light scattering, and that the resulting quality of the obtained size distribution is of comparable quality as usually obtained with highly diluted samples.

An explanation of the behaviour of the full-cream milk upon dilution can be found with results of previous measurements with casein micelles. Casein micelles are known to consist of sub-micelles with radii between 5 nm and 20 nm. The size reported for the compact micelle is between 50 nm and 140 nm in radius. If calcium is removed for example due to dilution with pure water or dialysis, the casein micelles disintegrate and form small submicelles [52, 53, 54, 55, 56]. For this reason the size distribution measured with the dilution 1:1000 is shifted to smaller values. Because the submicelles are small in size, it is difficult to see them in the presence of the large fat droplets. Therefore the volume concentration of the casein peak in the size distribution appears to be reduced upon dilution. A better characterization of the behaviour of casein micelles upon dilution can in fact be obtained from experiments with skimmed cow milk.

8.3.2 Skimmed Cow Milk

In the skimmed milk almost all of the milkfat is removed and only a small amount of 0.3 % by volume remains. Skim milk is mainly whey proteins and casein micelles suspended in water. Measurements of a dilution series with skimmed cow milk are shown in figure 27. In the undiluted case the particle size distribution shows a main peak at a radius of 140 nm and a smaller one located at a radius of about 500 nm. While the latter one represents the residual fat, the main peak describes the size distribution of the casein micelles, which are the main particle component in skimmed milk. Calculated from the peak area and assuming a casein micelle concentration of 11 % by volume we obtain a volume content of the milkfat of 0.5 %. Again, the contribution of the whey proteins to the scattering intensity is too small to be seen in a scattering experiment. Dilution of the skimmed milk, however, shows an interesting effect on the measured particle size distribution. The amplitude of the main peak located at 140 nm radius decreases considerably and a second peak appears at a radius of 22 nm. This can be explained with a disintegration of the casein micelles into small submicelles upon dilution.

Since the size distribution is normalized to a total area of 1, the peak areas
Figure 27: Particle size distribution of skimmed cow milk consisting mainly of casein micelles with a residual milkfat content of 0.3 % at different steps of dilution. For details see text.
Figure 28: Behaviour of the casein micelles peak in the size distribution upon dilution. Rescaled from figure 27. For details see text.
directly correspond to the volume concentrations of the different particle classes. More than half of the volume fraction of the casein micelles shows disintegration into the smaller submicelles upon dilution. The volume ratios are 1.2:1 for the dilutions of 1:10 and 1:100 and 1.3:1 for the sample with the dilution of 1:1000. Furthermore the form of the peak of the remaining particle class at 140 nm radius is continuously shifted to smaller values in size, which again supports the disintegration of the casein micelles upon dilution (see figure 28). This is in good agreement with previous reports found in the literature, where a disintegration of casein micelles has been found upon a removal of calcium from the solvent either due to dialysis or dilution [56]. As dilution has been a prerequisite to successfully use light scattering for these systems [57, 58], a considerable effort has been made in the past to find a suitable diluent which does not affect the particle size distribution of the casein micelles. Although good results were obtained with dialysed ultracentrifugate of skimmed milk and dialysed whey, the reasonable long time and the temperature stability of undiluted milk is not guaranteed at high dilution [56].

8.3.3 Emulsion Based on Vegetable Oil

Particle size distributions of protein stabilized emulsions based on vegetable oil are given in figure 29. For the undiluted case the distribution shows a maximum at a radius of 190 nm with shoulders up to 1000 nm and down to about 20 nm in radius. If the emulsion is diluted the maximum of the size distribution is shifted to smaller values. The mechanism of this is not yet clearly understood, but it looks like the larger particles are dissolved upon dilution. Previous measurements done with a small angle light scattering instrument (Mastersizer, Malvern) with a diluted sample show a bimodal distribution of particle sizes with its main peaks at radii of 150 nm and 6 μm. In figure 30 the measurement with the Mastersizer is compared with auto-correlation measurements with a diluted sample and cross-correlation measurements with the undiluted sample. The size distributions in figure 30 are intensity weighted, this means that they are strongly weighted by the larger particles. From a comparison of the cross-correlation measurement and the auto-correlation measurement with the data obtained from the Mastersizer it is clearly visible that a dilution of the emulsion reduces the size of the particles.

However, these measurements clearly demonstrate again that a dilution of samples made in order to avoid multiple scattering in a light scattering experiment can change the particle size distribution drastically.
8.3 Results and Discussion

Figure 29: Particle size distribution of a protein stabilized emulsion based on vegetable oil. For details see text.

It is obvious that the 3d cross-correlation instrument represents a major improvement and allows for a quantitative characterization of the undisturbed 'native' particle size distribution in natural milk as well as in artificial emulsions. We thus believe that this technique opens up new possibilities in the investigation of the equilibrium properties, dynamic behaviour and stability of complex particle suspensions that could be of considerable importance for a variety of industrial applications.
Figure 30: Intensity weighted particle size distribution of a protein stabilized emulsion based on vegetable oil. For details see text.
9 Protein Stabilized Emulsions

9.1 Introduction

In chapters 6 and 7 we have shown that we are able to characterize model systems of high turbidity by means of particle size distribution and interaction potential with a 3d cross-correlation instrument. Chapter 8 then demonstrates that this technique is also applicable to complex real world systems such as undiluted milk. It has been shown that changes in the composition of such complex systems, for example due to dilution, leads to artificial results in the measured particle size distribution. We now go even one step further and investigate the possibilities in characterizing complex systems with respect to size distribution, stability and interaction potential by means of light scattering. As model systems we choose whey protein stabilized emulsions, which are of great importance in industry as well as in general research [59, 60].

Emulsions occur widely in nature, and they are the basis of many products in various industrial fields, for example paints, pharmaceuticals and in food industry, to name only a few. In this chapter we focus on whey protein stabilized emulsions which are of particular importance as food model systems [61]. From liquid dispersions to gels a wide range of microstructures can be studied. Basically two immiscible liquids are mixed where one phase builds small droplets dispersed in the continuous phase. Since the emulsification process requires a lot of energy for the formation of the new surfaces, emulsions are thermodynamically unstable. The two phases separate with time due to coalescence driven by van der Waals interaction between the droplets. To avoid phase separation, stabilizing agents such as for example detergents or proteins are added. During the emulsification process proteins lower the surface tension and therefore reduce the amount of energy needed for the formation of the droplets. Furthermore a layer of proteins is adsorbed on the droplet surface which increases the stability of the emulsion due to steric and electrostatic stabilization.

9.2 Materials and Methods

9.2.1 Experimental Set-Up

The light scattering experiments were performed using the 3d cross-correlation instrument described in 5.
9.2.2 Materials

For the preparation of the emulsions a commercial whey protein BIPRO (Le Sueur
Isolates, Le Sueur, MN, USA) was used as the stabilizing protein. The total protein
content was 89 % consisting of the three components β-lactoglobulin (79 %), α-
lactalbumin (15 %) and serum albumin (5 %). Less than 10 % of the protein is
denatured. As the oil we used soya oil (Morgia) with a density of 915 kg/m³ at
20°C.

9.2.3 Methods

Preparation of the Protein Solution Light scattering studies had shown that
without further modification an aqueous solution of the Bipro protein also contains
large particles, which probably are aggregates of denatured protein. To avoid an
influence from these particles on the measured size distribution of the emulsion, the
BIPRO protein was purified prior to the preparation of the emulsion. An aqueous
solution of 10% BIPRO by weight was prepared, and the pH of the solution was
shifted with 0.1 N HCl near the isoelectric points of the three protein components.
Because the pH of the solution did not exactly match the isoelectric points of the
individual proteins, only a small amount of the native protein but most of the denat-
urated protein aggregates. The solution then was centrifuged in an ultracentrifuge
at 5000 g in order to remove the larger aggregates. Then the pH of the remaining
solution, which was now almost clear, was adjusted to pH 7 with 0.1 N NaOH. The
salt was removed with a dialysis against an excess of deionized water and the so-
lution was lyophilized. For the preparation of the protein solution 3 % by weight
of the purified protein mixture was dissolved in deionized water under moderate
magnetic agitation for 1-2 hours. Small deviations from pH 7 of the solution were
adjusted using 0.1 N HCl.

Emulsion Preparation Emulsions were prepared by mixing soya oil (20 % by
weight) with the protein solution. The mixture then was prehomogenized with
a commercial mixer and immediately afterwards homogenized using a laboratory
homogenizer (Modell H5000) with a head pressure of 80 bar. Two passages were
done for the homogenization process.

Light Scattering Experiments Particle size distributions were determined by
means of dynamic light scattering at a temperature of 25°C. Multiple scattering
effects due to the high turbidity of the emulsions were suppressed using the 3d cross-correlation technique. Measurements were done with protein stabilized emulsions of different concentrations from 0.01 % to 10 % oil content by weight. As solvent for the dilution deionized water was used. Three cross-correlation functions of 120 s to 300 s duration each were taken, where the duration of the measurements increases with the concentration, at different scattering angles $\Theta$. In order to obtain a reasonable intercept of the cross-correlation function even with the highly concentrated samples the light paths inside the rectangular sample cell (Hellma) were adjusted to values of $s \geq 200 \mu m$. Each set of correlation functions, covering the whole range of measured scattering angles, were analysed using a multi angle inverse Laplace transformation. The routine is described in chapter 8.2.3 and [51]. The resulting size distributions were then averaged.

Investigations of the emulsions in terms of interaction potential were performed with combined static and dynamic light scattering measurements. The measured average scattering intensity $I_s$, which contains contributions of different orders of multiply scattered light, is corrected with the reduced intercept of the cross-correlation function, which directly gives the part of $I_s$ which is singly scattered. After correction the single scattering differential cross section $d\sigma(q)/d\Omega$ is obtained which is a product of the particle form factor and the static structure factor, i.e. $d\sigma(q)/d\Omega \sim P(q) S(q)$. While the particle form factor depends on the size, shape and the internal structure of the emulsion droplets, the static structure factor describes the interactions between the particles. Basically $P(q)$ can be measured in the absence of particle interactions, which in general is fulfilled with highly diluted samples. But, as emulsions are known to possibly react upon dilution with a change of their size distribution, particle form factors need to be determined also at the same concentrations as the measurement of the structure factor. Particle interactions hereby, at least electrostatic, are reduced subsequently by increasing the ionic strength of the emulsion to 50 mM by adding NaCl. Three measurements, each lasting 30 s were done in the angular range from $\Theta = 20^\circ$ to $\Theta = 120^\circ$ every $2^\circ$. The total scattering intensity and the intercept of the cross-correlation function were analysed as a function of the scattering angle to obtain the differential scattering cross section. Another possibility consists in a calculation of $P(q)$ from the size distribution measured with the dynamic light scattering experiment and using Mie theory with the according polydispersity. In this step we profit from the fact that the DLS results are much less affected by interaction effects due to a partial cancellation of direct and hydrodynamic interactions.
9.3 Results and Discussion

9.3.1 Size Distribution

Size distributions of the emulsion droplets were measured for different concentrations diluted from an emulsion prepared with 20 % oil and 3 % protein content by weight. The results are shown in figure 31. A maximum concentration of 10 % oil and 1.5 % protein content could be measured with the 3d cross-correlation instrument in the present set-up. Further diluted samples to an oil content of 5 %, 1 %, 0.1 % and 0.01 % by mass were measured. The dilution series first shows only small changes in the size distribution for the two highest concentrations (10 % and 5 % oil) with the peak maximum located at a radius of r = 180 nm. A broad distribution of oil droplets from 90 nm up to 700 nm in radius is visible. Further dilution of the emulsion then shifts the size distribution to smaller radii, where the position of the main peak is now located at radii lower than 100 nm, and a shoulder to large particle sizes remains. These experiments show clearly that whey protein stabilized emulsions are not stable upon dilution with respect to their size distribution. Although the undiluted emulsion with 20 % oil content is too turbid to measure the dilution series shows significant changes, as expected, at high dilutions. As for 'normal' auto-correlation experiments even the highest diluted sample with 0.01 % oil is still too turbid to be measured, a dilution required for such experiments would lead to completely wrong results for the size distribution. However, with cross-correlation experiments, even if the 'natural' concentration cannot be measured, the concentration can be orders of magnitude higher than for auto-correlation measurements, and we therefore expect the measured size distribution to be close to the 'real' size distribution of the undiluted sample. This assumption is clearly supported by the dilution series, which indicate that the droplet size distribution remains constant first before it starts to change at higher dilution.

Without aiming to describe the reason of this effect of the dilution on the size distribution which needs further investigations, the modification of the oil droplets upon dilution has serious consequences on quantities such as the droplet surface area, which in principle can be calculated from DLS results. The surface area is needed as an important value for example in the study of protein coverage and stability of emulsions. In previous studies the surface area was typically calculated from an average droplet size obtained from a cumulant fit of dynamic light scattering data measured with highly diluted samples. In view of our findings, it is worth pointing out that size distributions, as obtained from a light scattering measurement, are intensity
Figure 31: *Particle size distributions of an emulsion consisting of 20% soya oil stabilized with 3% whey protein in water for different steps of dilution. For details see text.*
weighted. This means that the size distribution reflects the scattered intensity $I_s$ as a function of the particle size. Because $I_s(q) \sim r^6 P(q)$, larger particles strongly dominate the size distribution, which due to the particle form factor depends also on the scattering vector. An average size, as for example obtained from the cumulant fit, is therefore weighted by the large particles. For polydisperse samples, such as the emulsion investigated, a calculation of the surface area would therefore strongly underestimate the total surface area. Better results can be obtained by calculating the number density distribution $G_n(r) = 1 / (r^6 P(q,r)) G_I(q,r)$ where $P(q,r)$ can be calculated with Mie theory. The multi angle inverse Laplace transformation used in these experiments represents a clearly improved approach. This yields the volume distribution, from which also the surface area of polydisperse samples can be obtained. However, while such an analysis can be used in combination with traditional auto-correlation measurements on a classical goniometer system, the second important point to consider is the change in the size distribution upon dilution of the emulsion. From a histogram distribution we see that the specific surface area increases with dilution. This is caused due to the larger surface to volume ratio of the smaller particles. It is thus only from a measurement with undiluted or slightly diluted samples where one can hope to obtain a reasonable estimate of the total surface area. Such experiments are only possible with cross-correlation schemes that allow effectively suppressing multiple scattering and performing measurements of the droplet size distribution at different scattering angles.

9.3.2 Interactions

The effect of dilution on the size distribution of the protein stabilized emulsion has serious consequences for the determination of particle interactions. Because the average particle form factor changes with dilution, $P(q)$ can’t be measured with a highly diluted sample, as it is normally done. Because $P(q)$ then has to be measured at the same concentration as $S(q)$ and $I_s(q) \sim P(q)S(q)$, particle interactions have to be suppressed. Two routes for the measurement of the particle form factor at higher concentrations are investigated.

First electrostatic interactions can be screened with an increased ionic strength of the sample by adding salt. The emulsion is then expected to be hard-sphere like, although care has to be taken as the size distribution may change in response to the weaker electrostatic stabilization at higher salt content. Emulsions were measured at three different concentrations (0.01%, 0.1% and 1% oil) with deionized water and
with a 50 mM/l solution as solvent. The static structure factor \( S(q) \), calculated as the ratio of the scattering intensities measured without and with salt, where both intensities were corrected for multiple scattering and turbidity, is shown in figure 32. In the accessible q-range we find \( S(q) \approx 1 \), that means that there is no regular structure in the sample due to electrostatic interactions. In addition to this experimental approach, we have also tried to estimate \( S(q) \) theoretically for the sample with 1 % oil content. \( S(q) \) was calculated using the Rogers-Young closure of the Ornstein Zernike equation from the measured size distribution \( r = 60 \) nm, \( \sigma = 0.4 \) from fitting a Schultz distribution to the experimental data, typical values of 250 nm² for the surface charge area, and 0.5 mM salt content. In agreement with the measured static structure factor, \( S(q) \) shows only small deviations from unity.

The second route to determine the particle form factor at higher concentrations consists in a calculation of \( P(q) \) from the size distribution measured in a DLS experiment. Due to a partial cancellation of direct and hydrodynamic interactions, measured size distributions with a DLS experiment are much less affected by interaction effects. Assuming a hard-sphere like behaviour the measured collective diffusion coefficient \( D_C \) behaves like \( D_C = D_0(1 + 1.4\Phi) \), where \( D_0 \) is the diffusion coefficient of the particles without interactions and \( \Phi \) is the volume fraction of the particles. For the calculation of the particle form factor either the measured size distribution can be described for example by a Schultz distribution, or the continuous distribution can be replaced by a histogram. Using Mie-theory the average particle form factor can then be calculated.

In figure 33 \( P(q) \) calculated from the size distribution is shown compared to the measured normalized scattering intensity. Calculated and measured data are in excellent agreement. This is quite remarkable since \( I_S(q) \) is very sensitive to the size of the particles and, for polydisperse systems, also on the relative volume fractions of the individual particle size classes. Therefore a precise method for the determination of the size distribution is clearly required in any attempt to quantitatively calculate \( I_S(q) \) from DLS data. In general relative scattering amplitudes can be obtained not better than a factor of two from Laplace inversion methods, even under ideal conditions for the signal-to-noise ratio. However, the multi angle inverse Laplace transformation provides improved results for the particle size distribution which are the basis for these calculations.

This now allows us for the first time to obtain a consistent picture of particle size distributions, interaction effects and stability of highly concentrated complex colloidal suspensions such as emulsions and thus perform for example an in-situ
Figure 32: Static structure factor determination via screening of electrostatic interactions. △: 0.01 %, ○: 0.1 %, □: 1 % oil

investigation of stability and aggregation under realistic conditions relevant for a wide variety of commercially important systems.
Figure 33: Normalized scattering intensity (solid line: calculated from the size distribution, symbols: measured) for different oil concentrations: △: 0.01 %, ○: 0.1 %, □: 1 %.
10 Outlook

This work demonstrates clearly that using cross-correlation techniques colloidal systems of high turbidity can quantitatively be investigated. A maximum of information can be recovered with such experiments due to the strong suppression of multiple scattered light. Although the cross-correlation technique is implemented in a DLS experiment also SLS measurements can be done using the direct dependence of the intercept of the cross-correlation function on the ratio of single scattered to total scattered intensity. It is particularly shown that the 3d cross-correlation instrument constructed in this work possesses a high stability and is relatively easy to align when compared to commercially available normal light scattering instruments. Therefore it can be used also in an industrial environment.

Another important result of this thesis is the clear demonstration of the importance of multiple scattering when working with quite dilute systems. Significant amounts of multiply scattered light also can be present under these conditions, for example at scattering angles where the particle form factor or the static structure factor have a minimum, and strongly influence a quantitative analysis of the light scattering data. With the 3d instrument, on the other hand, such influences of multiple scattering can be avoided easily. Finally, it is clear that the instrument is not restricted to 3d cross-correlation experiments but can also be used in normal auto-correlation mode.

Based on the experience with this work a new generation of 3d cross-correlation instruments has now emerged, which will have an even more compact and robust design. As a new feature modern diode lasers with the wavelength in the near infrared regime will be used as the light source, thus considerably extending the range of measurable samples to even higher turbidity or concentration. We believe that these spectrometers will open new and exciting possibilities for an investigation of the static and dynamic properties of colloidal systems, and extend the range of systems that can be studied with optical techniques significantly.
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References


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