Fluid dynamics in charge stabilized colloidal suspensions

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Experimental techniques

2.1 Dynamic structure factor

In this thesis, we will be concerned with measurements of the dynamic structure factor of colloidal suspensions by means of light- and x-ray scattering techniques. The dynamic structure factor in the time domain, \( S(q, t) \), describes the temporal decay of density fluctuations \( \delta n(q, t) \). It is defined by the autocorrelation function

\[
S(q, t) = \langle \delta n(-q, 0) \delta n(q, t) \rangle,
\]

(2.1)

where \( q \) is the wave vector of the fluctuation, \( t \) denotes time and the brackets indicate an equilibrium ensemble average. In the frequency domain, the dynamic structure factor is given by

\[
S(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \langle \delta n(-q, 0) \delta n(q, t) \rangle dt.
\]

(2.2)

Two kinds of density fluctuations are of interest here: fluctuations in the number density of the colloidal particles and density fluctuations in the suspending fluid. The latter remain as the volume fraction of colloids approaches zero. Both kinds of density fluctuations cause spatial inhomogeneities in the refractive index \( m(r, t) \). If light impinges on a colloidal suspension at a specific time \( t \), it is scattered by these spatial inhomogeneities in the refractive index. By investigating the time evolution or the frequency components
Figure 2.1: Schematic drawing of the dynamic structure factor in the case of colloidal suspensions. The width of the central peak is determined by the colloidal diffusion coefficient $D_0$. The Brillouin peaks are shifted by a frequency difference $\pm \omega$ with respect to the central peak and their width is $\Delta \omega$. $q_{in}$ and $q_{out}$ are the wave vector of the incoming and scattered light, respectively.

of the scattered light intensity it is, therefore, possible to obtain information on the relaxation of density fluctuations in the system.

In a colloidal fluid, fluctuations in the number density of colloids relax by diffusion, and light is therefore scattered quasi-elastically from these fluctuations. In chapters 3 and 4, we will employ two experimental techniques that are sensitive to this quasi-elastically scattered light: dynamic x-ray scattering (DXS) and dynamic light scattering (DLS). These scattering techniques measure the dynamic structure factor in the time domain. There is, however, also a small contribution of light that is inelastically scattered, i.e., whose frequency is shifted with respect to the incoming light. This frequency shift arises from the interaction of light with propagating density fluctuations, or
longitudinal sound modes [14]. Investigation of these sound modes by means of inelastic light scattering is called Brillouin spectroscopy, and we will apply this technique to suspensions of colloidal silica spheres in chapter 5. Brillouin spectroscopy yields the dynamic structure factor in the frequency domain.

Schematically, $S(q, \omega)$ will look as depicted in fig. 2.1. The central peak around $\omega = 0$ arises from the quasi-elastic scattering by the colloidal particles. In a dilute system, where the diffusion coefficient of the colloids does not depend on frequency, the width of the central peak is determined by the diffusion coefficient $D_0$ of the colloidal particles. This width is so small that it is hard to investigate in the frequency domain. Besides the (very strong) central peak, there are two peaks shifted with respect to the incoming frequency: the Brillouin doublet. The Brillouin scattering from sound modes is several orders of magnitude smaller than the quasi-elastic scattering from the colloids, even if the mean refractive index of the fluid approximately matches that of the colloidal particles. Because of the dominant role of the quasi-elastically scattered intensity, measuring the Brillouin doublet in a colloidal suspension is a challenging task, requiring an experimental technique that can separate the frequency components of the scattered light very sharply.

In a pure fluid, the dynamic structure factor looks qualitatively similar to fig. 2.1, but the central peak is then much smaller. The central peak in a pure fluid arises from temperature fluctuations (the density depends on temperature). The temperature fluctuations relax diffusively, and the width of the central peak is therefore given by the thermal diffusivity in this case.

In this chapter, we will give an overview of the experimental techniques used in this thesis to measure the dynamic structure factor.

### 2.2 Dynamic light- and x-ray scattering

#### 2.2.1 Theory

Electromagnetic radiation impinging on a sample with a spatially inhomogeneous refractive index or electron density, such as a random assembly of colloidal particles suspended in a fluid, is scattered by these inhomogeneities. The electric field amplitudes scattered by different regions in the sample interfere and thus create an intensity distribution of dark and bright regions in the far field, called a speckle pattern. The speckle pattern reflects the instantaneous configuration of the scatterers. If the scatterers move, for instance
as a result of Brownian motion, the speckle pattern will change in time such that initially dark regions become bright and vice versa. Thus, if one places a detector of the size of a typical speckle spot at a particular point in the far field, the intensity measured at this point will fluctuate in time according to the movement of the scatterers. At times short compared to the typical time scale of configurational changes of the assembly of scatterers, the intensity at a given point in space will be correlated with the initial intensity. By contrast, at large times the speckle pattern will bear no relation with the initial pattern and the intensity correlation will thus be lost. This property is quantified by the intensity autocorrelation function

\[
\overline{I(q, t)I(q, 0)} = \lim_{T \to \infty} \frac{1}{T} \int_0^T I(q, \tau)I(q, \tau + t)d\tau, \tag{2.3}
\]

where \(I(q, t)\) is the scattered intensity. For an ergodic system, the time average implied by the bar is equivalent to an ensemble average. In a photon correlation spectroscopy experiment, a fluctuating signal proportional to \(I(q, t)\) is fed into a computer that calculates the normalized intensity correlation function

\[
g(q, t) = \frac{\langle I(q, t)I(q, 0) \rangle}{\langle I(q) \rangle^2}. \tag{2.4}
\]

Under the condition that the electric field amplitude \(E(q, t)\) is a zero-mean complex Gaussian variable, \(g(q, t)\) is given by

\[
g(q, t) = 1 + \beta^2 \frac{(E^*(q, t)E(q, 0))^2}{\langle I(q) \rangle^2} = 1 + \beta^2 |f(q, t)|^2, \tag{2.5}
\]

where \(f(q, t)\) is the normalized intermediate scattering function. The contrast \(\beta^2 = g(q, 0) - 1\) depends on the coherence of the beam, the coherence preserving properties of the optical elements in the setup and the number of coherence areas observed at the detector. For incoherent radiation, \(\beta^2 = 0\) and \(g(q, t) = 1\). Similarly, if the detector area is much larger than the speckle size the measured intensity will always be identical to the average intensity and thus \(g(q, t) = 1\). In dynamic x-ray scattering experiments, optimizing the trade-off between the coherence and the available photon flux results in a contrast of typically 5 - 10 % [15, 16], whereas \(\beta^2\) is usually close to the ideal value of 1 in a DLS experiment.

In the case of single scattering by an arrangement of \(N\) identical particles, the scattered field amplitude in the far field is (apart from unimportant
Dynamic light- and x-ray scattering

factors that are omitted) given by

$$E(q, t) \propto b(q) \sum_{j=1}^{N} e^{iq \cdot r_j(t)}$$

(2.6)

where $r_j(t)$ is the position vector of particle $j$. The scattering amplitude $b(q)$ is basically the Fourier transform of the refractive index profile $m_1(r)$ of a scatterer,

$$b(q) \propto 4\pi \int_{0}^{\infty} [m_1(r) - m_0] \frac{\sin qr}{qr} r^2 dr,$$

(2.7)

where $m_0$ is the refractive index of the surrounding medium. The mean intensity is related to the static structure factor $S(q)$:

$$\langle I(q) \rangle \propto b(q)^2 \sum_{j=1}^{N} \sum_{k=1}^{N} \langle e^{iq \cdot [r_j(0) - r_k(0)]} \rangle \propto Nb(q)^2 S(q).$$

(2.8)

It follows from eqs. 2.5, 2.6 and 2.8 that for identical particles the normalized intermediate scattering function is given by

$$f(q, t) = \frac{1}{S(q)} \frac{1}{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \langle e^{iq \cdot [r_j(0) - r_k(0)]} \rangle = \frac{S(q, t)}{S(q)},$$

(2.9)

that is, $f(q, t)$ is directly related to the dynamic structure factor in the time domain. As is clear from eq. 2.9, the normalized intermediate scattering function contains correlations between the positions of different particles and thus depends on the interparticle interactions (see chapter 4).

For concentrated suspensions, where the decay of the dynamic structure factor is generally non-exponential, $f(q, t)$ is usually analyzed in terms of a cumulant expansion:

$$f(q, t) = e^{\Gamma_1(q)t + \Gamma_2(q)t^2 + \cdots}.$$  

(2.10)

Here, $\Gamma_1(q)$ is the first cumulant [3]. In a dynamic light scattering experiment, one is interested in the wave vector dependent decay of the normalized intermediate scattering function. In particular, the initial decay of $f(q, t)$ gives the collective short time diffusion coefficient $D(q)$ of the colloidal suspension [3], according to

$$\lim_{t \to 0} \frac{d \ln f(q, t)}{dt} = \Gamma_1(q) = -D(q)q^2.$$  

(2.11)
In a dilute system, the diffusion coefficient does not depend on $q$ and the normalized intermediate scattering function becomes single exponential,

$$f(q, t) = e^{-D_0 q^2 t},$$

(2.12)

where $D_0$ is the diffusion coefficient at infinite dilution.

In general, the mean intensity in eq. 2.8 may be written as

$$\langle I(q) \rangle \propto Nb(0)^2 P(q)S(q),$$

(2.13)

where $P(q) = b(q)^2/b(0)^2$ is the particle form factor. In the case of spherical particles, the form factor is given by [3]

$$P(q) = \frac{9}{(qa)^6}[\sin(qa) - qa \cos(qa)]^2.$$  

(2.14)

The relation 2.13 allows to obtain information on the static structure of the suspension from the time-averaged intensity. The form factor can be obtained from a dilute suspension, where $S(q) = 1$. In the case of x-rays, eq. 2.13 must be modified to [17]

$$\langle I(q) \rangle \propto NV^2 \Delta \rho_e^2 P(q)S(q),$$

(2.15)

where $V$ is the particle volume and $\Delta \rho_e$ the difference in electron density between the colloids and their surroundings.

### 2.2.2 Multiple light scattering

Expressions 2.9, 2.11 and 2.13 only hold for single scattering of light. This means that if one wants to measure the collective diffusion coefficient $D(q)$ or the static structure factor by light scattering, it has to be assured that the measurements are performed in the single scattering limit. The single scattering limit is characterized by the condition

$$l_s \gg L,$$

(2.16)

where $l_s$ is the mean distance between two scattering events (or scattering mean free path) and $L$ the sample size.

In the dilute limit, the scattering mean free path is given by

$$l_s = \frac{1}{n_{coll} \sigma},$$

(2.17)
where \( n_{\text{coll}} \) is the number density of colloids and \( \sigma \) the scattering cross section. Under the condition that the refractive index contrast is small, \(|m_1/m_0 - 1| \ll 1\), and the "phase shifts" are small, \(4\pi m_0 a|m_1/m_0 - 1|/\lambda \ll 1\), we have [18]

\[
\sigma \propto \pi a^2|m_1/m_0 - 1|^2. \tag{2.18}
\]

In these expressions, \( a \) is the radius of the scatterers, \( m_1 \) their refractive index and \( \lambda \) the wavelength of the scattered light in vacuo. The conditions for the validity of eq. 2.18, which is known as the Rayleigh-Gans approximation, are always fulfilled for the systems considered here. It is seen from eqs. 2.16, 2.17 and 2.18 that the single scattering limit can be achieved by letting either \( n_{\text{coll}} \to 0 \) or \( m_1/m_0 \to 1 \) (or both), i.e., the sample has to be dilute or the refractive index of the scatterers has to be nearly matched to that of the surrounding medium. These requirements put severe limitations on the applicability of the dynamic light scattering technique: in the interesting case of high particle concentrations, where interparticle interactions become important, the necessity to match the refractive indices of the particles and the suspending fluid restricts the possibility to vary the direct interaction between the particles. The direct interaction depends sensitively on the properties of the suspending fluid and one would therefore like to have complete freedom of choice.

The opposite to condition 2.16, i.e. \( l_s \ll L \), gives rise to multiple scattering, since then light is scattered many times on its path through the sample. In the case of strong multiple scattering, the transport of light intensity in the system can be modeled as a random walk between scatterers and is thus diffusive. The direction of light propagation will be randomized after only a few scattering events for diffusive light transport. The scattered intensity observed at any given point in space will then originate from a distribution of light paths in the sample. In other words, the light rays finally traveling in the direction of detection, \( q_{\text{out}} \), have originally been scattered in all possible directions and one therefore effectively observes an average over all possible scattering vectors \( q \). The essential wave-vector information is lost. The intensity correlation function decays much faster in the multiple scattering regime than in the single scattering limit, which is easily seen as follows. The phase difference between waves scattered by a particular scatterer at times \( t \) and \( t + \Delta t \) is proportional to the distance the scatterer moves in the time interval \( \Delta t \). If the light is multiply scattered by a large number of different scatterers, the phase differences accumulate and the time correlation will thus be lost quickly. In the limiting case of diffusive light transport, it is
nevertheless possible to extract useful information from intensity correlation functions, such as the size of the particles. Photon correlation spectroscopy in this limit is known as diffusing wave spectroscopy (DWS) [5].

### 2.2.3 Cross-correlated dynamic light scattering

The (strong) multiple scattering regime is characterized by the fact that the fraction of singly scattered light reaching the point of observation is small compared to the fraction of multiply scattered light. In this case, one cannot obtain $q$ dependent information from dynamic light scattering. However, there will always be a certain fraction of singly scattered light leaving the sample. In this section, we describe the technique of cross-correlated dynamic light scattering with a single laser beam (CCDLS), with which it is possible to selectively detect the singly scattered component of the total scattered intensity and thus obtain the $q$ dependent collective diffusion coefficient. The technique is applicable in cases where ordinary DLS has become unreliable due to multiple scattering, but the limit of diffusive light transport has not yet been reached. CCDLS has first been demonstrated experimentally by Meyer et al. [19]. Figure 2.2 shows the basic scattering geometry for CCDLS, as employed by these authors. A laser beam is focused into a sample cell, which is contained in a cylindrical index matching vat. The scattered light is coupled into two optical fibers that are separated vertically by a small distance $Y$. In terms of scattering vectors, the vertical distance between the fibers is $\Delta q = (4\pi m/\lambda) \sin(\Delta \varphi/2)$, where $m$ is the refractive index of the suspension and $\Delta \varphi$ the angular distance between the fibers. The signal from the two fibers is fed into two detectors whose outputs are cross-correlated.

A theoretical treatment of CCDLS has been given by Lock [20]. This author calculated approximately the contributions of single and double scattering to the time dependent intensity cross-correlation function for the geometry shown in fig. 2.2, assuming a cylindrical scattering volume. We will not repeat the rather cumbersome (but straightforward) calculations here, but give a graphical representation of the main outcome instead. Figure 2.3 shows Locks result for the field correlation functions at $t = 0$ as a function of the fiber separation $\Delta q$. Figure 2.3(a) shows field correlation functions for singly and doubly scattered light, fig. 2.3(b) the ratio of the double scattering contribution to the intensity correlation function to the single scattering contribution. The calculations have been done for $m_1 = 1.465$, $m_0 = 1.400$, $a = 55$ nm, $\lambda = 532$ nm, $L = 2$ mm, $R_{foc} = 100$ $\mu$m, $R_{ave} = 2$ mm and
$\phi = 0.1$. Here, $R_{ave}$ is the radius out to which each particle is surrounded by an isotropic environment of other particles (which is comparable to the radius of the sample cell [20]), $R_{foc}$ is the beam waist in the focus and $\phi$ is the volume fraction of particles. The correlation functions shown are

$$C_{1,2}(\Delta q) = \frac{\langle E_{1,2}^*(q - \Delta q/2, 0) E_{1,2}(q + \Delta q/2, 0) \rangle}{\langle E_1^*(q, 0) E_1(q, 0) \rangle},$$

(2.19)

where the subscripts 1 and 2 refer to single and double scattering, respectively. It is seen from fig. 2.3(a) that for $\Delta q = 0$, i.e. autocorrelation, $C_2$ is by almost a factor 4 larger than $C_1$ for this particular example, meaning that double scattering contributes much more to the total field autocorrelation function than single scattering. However, as the fiber separation $\Delta q$ is increased, $C_2$ decays much faster than $C_1$, such that the single scattering contribution becomes dominant at large fiber separation. From fig. 2.3(b) it is seen that the ratio of the double scattering contribution to the intensity
Figure 2.3: (a) Electric field cross-correlation function for single scattering $(C_1)$ and double scattering $(C_2)$ at time $t = 0$ as a function of fiber distance. The correlation functions are normalized to $C_1$ at zero fiber distance. The system parameters are given in the text. (b) Ratio of the square of the correlation functions shown in (a), $\frac{C_2^2}{C_1^2}$, as a function of fiber separation.
correlation function to the single scattering contribution, $C_2^2/C_1^2$, decreases as $\Delta q^{-2}$ at larger fiber separations. For $\Delta q = 600 \text{ cm}^{-1}$, the double scattering contribution is less than 1% of the single scattering contribution in this particular case. The fiber separation at which this suppression of doubly scattered light is achieved is much smaller than the wave vectors $q$ typically probed by dynamic light scattering, $\Delta q/q \approx 10^{-2}$; this ensures that the uncertainty in $q$ introduced by CCDLS is negligible.

The theoretical analysis given by Lock demonstrates that CCDLS is in principle capable of separating singly from multiply scattered light. However, an experimental verification of the method as well as an investigation of its range of applicability in terms of $l_s/L$ is highly desirable, if this technique is to be used for studying the dynamics of dense colloidal suspensions. Meyer et al. [19] measured the diffusion coefficient of polystyrene latex spheres suspended in water in a range of concentrations. The diffusion coefficient measured in cross-correlation was almost independent of concentration, whereas the one extracted from autocorrelation functions changed dramatically as the concentration of particles was increased. Furthermore, the cross-correlation functions were single exponential. From these observations they inferred that the cross-correlation functions were unaffected by multiple scattering. However, this is an indirect proof that relies on the assumption that the true diffusion coefficient is independent of concentration and the single-scattering correlation function is single exponential, which is only valid in the dilute limit. An independent test of the reliability of CCDLS has so far not been presented. In chapter 3, we will give the first direct and independent proof of the feasibility and reliability of CCDLS by directly comparing this new technique with dynamic x-ray scattering, where multiple scattering does not play a role.

Another cross-correlation dynamic light scattering technique is the so-called two-color dynamic light scattering method (TCDLS) [21, 22, 23]. In this technique, two laser beams with different colors are incident on the sample and the scattered light is detected by two spatially separated detectors. Each detector is sensitive to only one of the two colors. The relative positions of the detectors and the incoming beams are aligned such that both detectors probe the same scattering vector $q$ for single scattering. For higher order scattering, light arriving at the detectors has initially been scattered in random directions and thus originates from different scattering vectors. As a result, the intensity cross-correlation of the detector outputs is much smaller for multiply scattered light than for singly scattered light and multi-
ple scattering detection is thus greatly suppressed, in a similar fashion as for the two-fiber CCDLS setup considered in this chapter. The main drawback of the TCDLS method is the tedious alignment procedure resulting from the fact that basically two complete DLS setups are used simultaneously, under the condition that both of these setups probe the same scattering volume and wave vector. Probably due to this difficult alignment, TCDLS has not been used extensively in practice. By contrast, the two-fiber CCDLS technique presented here is as easily to align and use as ordinary DLS and should therefore be suited for routine work. This simplification of the experimental setup is achieved by relaxing the requirement that both detectors probe exactly the same $q$ for single scattering; instead, one allows a small separation in $q$ space also for single scattering. The feasibility of TCDLS has been investigated by measuring concentration dependent correlation functions and diffusion coefficients on dilute systems similar to the experiments by Meyer et al. [19]. From the fact that for cross-correlation the diffusion coefficient remained independent of concentration and the intensity correlation functions were single exponential, it was concluded that TCDLS effectively suppresses the detection of multiply scattered light [21]. We emphasize again that such an indirect way of demonstrating the potential of cross-correlation techniques fails for interacting particles, where the diffusion coefficient is intrinsically concentration dependent and the correlation functions non-exponential. Also for TCDLS, there is no independent, direct experimental verification. Therefore, since all cross-correlation dynamic light scattering techniques basically rely on the same physical principles, we believe that the results presented in this thesis are of general importance.

### 2.2.4 CCDLS setup

In the CCDLS setup (fig. 2.4), a diode pumped, frequency-doubled Nd:YAG laser (Coherent DPSS 532, $\lambda = 532$ nm) served as the light source. The beam was focused in the sample to a beam waist of about $R_{\text{foc}} = 100 \ \mu m$. The scattered light was collected by a lens with focal length 20 mm at a distance of $R_1 = 145 \ \text{mm}$ from the sample and focused on a pinhole with a diameter of 100 $\mu m$. The pinhole served to eliminate stray light. The optical fibers were located at a distance of 395 mm from the sample. A slit in front of the fibers served to further reduce background light and to define the effective detector size in the horizontal direction. The fibers were mounted on a vertical slit whose size could be varied by means of a micrometer screw;
Figure 2.4: Basic configuration of the cross-correlation dynamic light scattering setup.

This allowed to vary the core-core fiber distance between 2.4 and 6.0 mm. The vertical extent of the single-scattering speckle at the position of the collecting lens should be of the order of \((\lambda/R_{foc})R_1 \approx 0.8\) mm. The collection optics leads to a magnification of the vertical speckle size by about a factor 10, i.e., the vertical extent of the speckle is about 8 mm at the position of the fibers. Therefore, singly scattered light is expected to be correlated within the range of fiber distances available. The apparatus was designed such that it could house the same sample cells as used for dynamic x-ray scattering, enabling us to perform both CCDLS and DXS on exactly the same samples. The sample cells were suspended in a bath of Toluene (Acros, 99 %, refractive index \(m = 1.4965\)) to reduce stray-light scattering from the cell walls. The temperature of the toluene bath was actively stabilized at 30 °C, using a feed-back mechanism (Malvern instruments temperature controller
Figure 2.5: Schematic diagram of the configuration of beamline ID10A at the European Synchrotron Radiation Facility.

RR 56), to avoid a temperature difference between the CCDLS and the DXS measurements. Two multimode optical fibers (ALV, core diameter 300 μm) were used to couple the scattered light into two photomultipliers (ALV single photon detectors) whose outputs were cross-correlated. Correlation functions were calculated with a digital ALV5000/E correlator. A linear polarizer in the incoming beam and an analyzer in front of the collecting lens ensured that only the VV component of the scattered light was detected. The detectors were mounted on a rotation stage to vary the scattering angle.

In order to compare dynamic x-ray scattering with dynamic light scattering in the case of optically index matched samples, we employed a slightly different DLS setup with a single photomultiplier (Malvern instruments). This setup had been used extensively in previous experiments and has been described in detail in [24].

2.2.5 DXS setup

Dynamic x-ray scattering was performed at beamline ID10A of the European Synchrotron Radiation Facility in Grenoble [16]. Figure 2.5 shows a schematic drawing of the setup. The sample was illuminated with radiation of 8.2 keV energy (wavelength $\lambda = 1.51 \, \text{Å}$), supplied by a single bounce Si(111) monochromator. A vertically focusing Rh-coated Si mirror was set to a critical energy just above 8.2 keV for harmonics rejection. Photon correlation spectroscopy requires the sample to be illuminated with coherent radiation. More specifically, the maximum path length difference in the sample has to be comparable to the longitudinal coherence length $\xi_l$ and the lateral size of the scattering volume has to be comparable to the transverse coherence length $\xi_t$. The coherence length is the distance over which the phases of the beam re-
main correlated, either along the propagation direction (\(\xi_t\)) or perpendicular to it (\(\xi_t\)). Along the propagation direction, the phases become uncorrelated if the beam is not perfectly monochromatic\(^1\). Accordingly, the longitudinal coherence length is determined by the bandwidth \(\Delta \lambda/\lambda\) of the x-ray source, \(\xi_t \approx \lambda(\lambda/\Delta \lambda) = 1 \mu m\). The transverse coherence length is determined by the source size\(^2\) \(S\) and the distance from the source \(R_s\), \(\xi_t \approx \lambda R_s/2S\). The maximum path length difference is \(PLD = L[1 - \cos(\Theta)] + h \sin(\Theta)\), where \(L\) is the sample thickness, \(h\) the diameter of the scattering volume and \(\Theta\) the scattering angle. The condition \(PLD < \xi_t\) was fulfilled for \(q < 0.96 \text{ nm}^{-1}\), which was sufficient for the present experiments. The transverse coherence length was set by primary slits to 144 \(\mu m\) vertically and 14 \(\mu m\) horizontally at a distance \(R_s = 44 \text{ m}\) from the source. A collimating pinhole aperture with a diameter of 20 \(\mu m\) was inserted 0.13 m upstream from the sample to select a partially coherent beam. We chose this configuration to optimize the trade-off between the degree of coherence on one hand and intensity- and stability requirements on the other. A guard slit was positioned right in front of the sample capillaries to eliminate parasitic scattering from the collimating aperture. In order to detect intensity fluctuations the detector aperture has to be comparable to the angular size \(\lambda/h\) of the intensity speckles. Therefore, an analyzing aperture of 30 \(\mu m\) size was placed in front of a scintillation counter at a distance of \(R_2 = 2.3 \text{ m}\) from the sample. The speckle size at this position is approximately \(R_2 \lambda/h = 17 \mu m\). The sample cells were placed in an evacuated chamber which was heated to 30 \(^\circ\text{C}\) with a Peltier element. Intensity correlation functions were recorded with digital ALV5000/E correlators. A reference correlation function was obtained from the air scattering just in front of the sample to record intensity fluctuations in the incoming beam. The time averaged signal from the scintillation counter was used for small-angle x-ray scattering measurements, keeping the experimental conditions unchanged with respect to the dynamic measurements.

\(^1\)The phase difference in time \(t\) is \(\Delta \omega t\), where \(\Delta \omega\) is the frequency spread. We define the coherence time \(t_c\) by \(\Delta \omega t_c = 2\pi\). The longitudinal coherence length then follows from \(\xi_t = c_0 t_c\) and \(\Delta \omega = 2\pi c_0 \Delta \lambda/\lambda^2\), where \(c_0\) is the speed of light.

\(^2\)Rays that are emitted at different points in an extended source have a phase difference if observed at a point transverse to the beam. This phase difference affects the visibility of interference fringes. One can define the transverse coherence length as the distance beyond which the visibility has reduced to less than 50 \% [6].
2.3 Brillouin spectroscopy

2.3.1 Theory

In this section, we briefly summarize the theory underlying the Brillouin doublet shown schematically in fig 2.1. For a detailed description, we refer to [14].

The intensity of light scattered from a pure fluid is, to a good approximation, proportional to the dynamic structure factor, as given by eq. 2.2. Thus

\[ I(q, \omega) = (e_{in} \cdot e_{out})^2 \left( \frac{\partial \varepsilon}{\partial n} \right)_T^2 S(q, \omega), \]  

(2.20)

where \( e_{in} \) and \( e_{out} \) are the polarization vectors of the incoming and scattered light, respectively, \( \varepsilon \) the dielectric function and \( T \) the temperature\(^3\). This relation between the scattered intensity and the dynamic structure factor allows to measure \( S(q, \omega) \) by Rayleigh-Brillouin scattering.

The dynamics of fluctuations in a pure fluid is governed by the continuity equation, the equation of motion, and the energy conservation equation. If the fluctuations are small, these equations may be linearized and then read [14, 25]

\[
\begin{align*}
\frac{\partial \delta n}{\partial t} + n_0 \nabla \cdot \mathbf{u} &= 0 \\
Mn_0 \frac{\partial \mathbf{u}}{\partial t} &= -\nabla \delta p + \eta \nabla^2 \mathbf{u} + \left( \eta_b + \frac{1}{3} \eta \right) \nabla (\nabla \cdot \mathbf{u}) \\
\frac{\partial \delta \varepsilon}{\partial t} + (e_0 + p_0) \nabla \cdot \mathbf{u} &= \Lambda \nabla^2 \delta T.
\end{align*}
\]

(2.21)

Here, \( \mathbf{u} \) is the fluid velocity field, \( M \) the molecular mass, \( p \) the pressure field, \( \eta \) the shear viscosity, \( \eta_b \) the bulk viscosity, \( \varepsilon \) the density of internal energy and \( \Lambda \) the thermal conductivity. The space- and time dependence of all quantities appearing under the derivatives has been omitted for clarity. The subscript 0 denotes equilibrium values. The fluctuations in eqs. 2.21 are not all independent, but are related by the local equilibrium thermodynamic equations of state; this allows to eliminate two of the fluctuations and thus close the set of equations. The equations may then be solved by Laplace

\(^3\)Equation 2.20 is only approximately correct since it neglects the dependence of the dielectric function on temperature (at constant density), which for most liquids is however small.
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transform, which is a lengthy but straightforward procedure. We only give the final result for the dynamic structure factor here, which we are interested in:

\[ S(q, \omega) = \frac{1}{\pi} S(0) \left\{ (1 - \frac{1}{\gamma}) \frac{D_T q^2}{\omega^2 + [D_T q^2]^2} \right. \]

\[ + \frac{1}{\gamma} \left( \frac{\Gamma_B q^2}{[\omega - \omega(q)]^2 + [\Gamma_B q^2]^2} + \frac{\Gamma_B q^2}{[\omega + \omega(q)]^2 + [\Gamma_B q^2]^2} \right) \]

\[ + \frac{1}{\gamma} \frac{3\Gamma_B - D_v}{\omega + \omega(q)} \left( \frac{\omega - \omega(q)}{[\omega + \omega(q)]^2 + [\Gamma_B q^2]^2} - \frac{\omega - \omega(q)}{[\omega - \omega(q)]^2 + [\Gamma_B q^2]^2} \right) \]. \tag{2.22}

Here, \( S(0) \) is the static structure factor at \( q = 0 \), \( \gamma = C_p / C_v \) is the specific heat ratio, \( c \) the adiabatic sound velocity, \( D_T = \Lambda / M n_0 \) the thermal diffusivity, \( D_v = \frac{m}{M n_0} \) the longitudinal kinematic viscosity and \( \Gamma_B \) the sound damping coefficient. The first term on the right hand side of eq. 2.22 represents the central peak (Rayleigh peak) of a pure fluid, whose width is given by the thermal diffusivity. The next two terms represent the Brillouin doublet. The Brillouin peaks have a Lorentzian line shape and are shifted by a frequency

\[ \pm \omega(q) = \pm cq \] \tag{2.23}

with respect to the central peak. The full width at half maximum of the Brillouin peaks is given by

\[ \Delta \omega = \Gamma_B q^2 = \left( D_v + D_T (\gamma - 1) \right) q^2. \] \tag{2.24}

The last two terms in eq. 2.22 are usually negligible.

It is seen from the above equations that the sound velocity \( c \) can be obtained from the position of the Brillouin peaks and the sound damping from their width. In a colloidal suspension, the sound waves propagating in the fluid will be scattered by the colloidal particles. The scattering will add to the sound attenuation 2.24, which is the subject of chapter 5.

2.3.2 Brillouin setup

The setup used for Brillouin spectroscopy is shown schematically in fig. 2.6. Green light from an argon-ion laser (Coherent Innova 100) at a wavelength of 514.5 nm issplit by a beam splitter cube. 99% of the incoming light intensity is focused, via a movable arm, into the sample cell; the remaining 1
Figure 2.6: Schematic drawing of the Brillouin setup. The meaning of the abbreviations is as follows: beam splitter (B), mirror (M), lens (L), pinhole (P), filter (F) and photomultiplier tube (PMT).

% are used as a reference beam for alignment and stabilization. The sample cell is located in an index matching bath of glycerol ($m = 1.474$) to reduce stray light scattering from the cell walls. The scattered light is collected by a lens and focused onto a pinhole, defining the outgoing wave vector. The magnitude of the scattering vector $q$ is related to the scattering angle $\Theta$ by\footnote{Equation 2.25, which is strictly valid only for elastic scattering, holds to a very good approximation since the Brillouin shift is very small.} [14]

$$q = \frac{4\pi m}{\lambda} \sin(\Theta/2),$$

(2.25)

where $m$ is the index of refraction of the suspension. The scattered light is then collimated into a triple-pass Fabry-Perot (FP) interferometer (Burleigh instruments) and detected at the exit of the interferometer by a photomulti-
Figure 2.7: Transmission of the triple-pass Fabry-Perot interferometer as a function of averager channel. The distance between two consecutive orders defines the free spectral range (FSR). The solid line in (b) represents a fit to the transmission peak with the third power of a Lorentzian curve.
plier tube (PMT, Products for Research inc.). The interferometer is operated in triple-pass configuration to achieve a high contrast; this is necessitated by the fact that the intensity of the central Rayleigh peak for colloidal suspensions is several orders of magnitude larger than that of the Brillouin peaks, even if the average refractive indices of the colloids and the suspending fluid closely match. An additional interference filter for 514.5 nm in front of the PMT serves to further reduce background light. The distance between the mirrors of the FP is scanned piezoelectrically, using a programmable ramp generator (Burleigh RC 43). The signal from the PMT is fed into a multi-channel averager (EG & G 4202), triggered by the ramp generator. The FP is placed in a temperature stabilized container to minimize thermal drift. The remaining thermal drift is actively compensated by applying a compensation voltage to the piezoelectric crystals on the FP mirrors. The compensation voltage is controlled by a feedback mechanism that keeps a reference signal, either the reference beam or the strong central Rayleigh peak, within a given time window for each scan (Burleigh DAS-10 FP stabilization system). The PMT is cooled to 0 °C to reduce dark counts.

Figure 2.7 shows the transmission of the Fabry-Perot interferometer as a function of the averager channel, which is proportional to the mirror distance. The measurement was obtained with the reference beam. Figure 2.7(a) shows a scan over one free spectral range (FSR), fig. 2.7 focuses on one of the transmission peaks. Light is transmitted through the FP whenever the mirror distance is a multiple of half the light wavelength, since then light waves, that are multiply reflected between the mirrors, interfere constructively at the exit of the FP. The transmission peaks are broadened mainly as a result of the finite mirror reflectivity and deviations from perfect parallelism of the mirrors. Figure 2.7(b) shows the line shape of a transmission peak. For a triple-pass FP, the instrumental line shape \( T(\omega) \) may be approximated by a triple Lorentzian [26]:

\[
T(\omega) \approx \frac{A}{1 + k^2(\omega - \omega_0)^2}^3,
\]

where \( A \) is the amplitude, \( \omega_0 \) the central frequency, and the full width at half maximum is given by \( 1.02/k \). The line in fig. 2.7(b) represents a fit to the transmission peak with eq. 2.26. It is seen that the line shape is represented reasonably well by a triple Lorentzian, although deviations are apparent in the wings. From the ratio of the amplitude to the background,
which is hardly visible on this scale, we obtain a contrast of $10^5$. The finesse (the ratio of the FSR to the peak width) is 52.

**Calibration of the setup** To calibrate the FSR of the interferometer, we measured a series of Brillouin spectra in pure ethanol. Figure 2.8 depicts a Brillouin spectrum of pure ethanol at a scattering angle of $\Theta = 90^\circ$, obtained from an average over about $10^3$ sweeps. The two Brillouin peaks are clearly visible on this scale. To stabilize the FP, part of the reference beam has been admitted, which gives the strong peaks at $\omega/\omega_{FSR} = 0, 1$. From a Lorentzian fit to the Brillouin peaks we find that the Brillouin shifts of the two orders agree to within 1 % and the widths to within 4 %; this indicates a good linearity of the scan and reasonable stability of the setup.

Figure 2.9 shows the position of the Brillouin peaks as a function of the
scattering vector $q$. Data are shown for pure ethanol and a mixture of ethanol and 58 vol% benzyl alcohol. This alcohol mixture is used later as index matching solvent for the colloids. It is seen that the peak position depends linearly on the wave vector, as expected for a pure fluid. The straight lines in fig. 2.9 are linear fits to the data. The slope of the lines should be given by the sound velocity (see eq. 2.23), which allows to determine the free spectral range; we find $\nu_{FSR} = 18.19 \pm 0.06$ GHz. Having obtained the FSR from the ethanol measurements, we can determine the sound velocity of the ethanol/ benzyl alcohol mixture to be $c = 1462 \pm 7$ m/s. This result is in good agreement with $\bar{c} = 1400$ m/s, where $\bar{c} = \phi_1 c_1 + \phi_2 c_2$ is the volume average of the sound velocities of the two fluids (with $c_{ethanol} = 1207$ m/s [27] and $c_{benz.al.} = 1540$ m/s [28]).
2.4 Sample preparation and characterization

In all experiments we used colloidal silica spheres (mean radius $a = 54.9 \pm 0.1$ nm, polydispersity $\Delta a/a = 0.042 \pm 0.005$, density $\rho = 1.93 \pm 0.03$ g/cm$^3$, refractive index $m = 1.465 \pm 0.004$), synthesized following the micro emulsion technique [4]. The particles were suspended in varying fluids (ethanol, benzyl alcohol, ethanol/benzyl alcohol mixtures, or water/glycerol mixtures, depending on the purpose) by centrifuging the initial stock suspension, removing the supernatant, and adding the desired solvent; this procedure was repeated several times for rinsing. The fluids were filtered several times (Millipore filters, pore size 0.45 or 0.2 μm) to remove dust particles. The particle density was determined by drying a concentrated suspension of known volume and weight in a solvent of known density and weighing the residue. The volume fraction of the samples was determined by drying a known volume at 90 °C and weighing the residue; weight concentrations were converted to volume fractions using the measured particle density. The refractive index of the silica particles was determined by measuring the light transmission (at a wavelength of 532 nm) in the forward direction for suspensions in different mixtures of ethanol ($m = 1.359$) and benzyl alcohol ($m = 1.538$), at a constant temperature of 25 °C. The maximum in transmission defined the point of index matching. The refractive indices of the alcohol mixtures were measured with an Abbe refractometer, thermostated at 25 °C [29].

For the Brillouin experiments, the silica particles were suspended in an optically index matching mixture of ethanol and benzyl alcohol, in order to reduce the intensity of the central Rayleigh peak and to avoid multiple light scattering. A sample with a maximum volume fraction of colloids was produced by centrifuging a concentrated suspension at 3000 rpm in the sample cell and removing all of the remaining fluid. The resulting suspension was a highly viscous, transparent sediment. Samples of lower volume fraction were produced by adding known amounts of fluid to the initial suspension. The colloids were resuspended by stirring and with aid of an ultrasonic bath. The sample cell was a cylindrical quartz cuvette with an inner diameter of 8 mm. At each step in the dilution series, the height of the suspension in the cuvette, and thus the total volume, was measured. The volume fraction was determined by drying a known amount of the last suspension in the series, i.e., the most dilute one, and weighing the residue. The volume fractions of the more concentrated samples were then determined relative to the most dilute one, according to the known volumes of these suspensions as measured...
Figure 2.10: Small angle x-ray scattering intensity for a dilute sample of silica colloids in a mixture of ethanol and benzyl alcohol. The solid line represents a fit to the data with the form factor for spherical particles.

before. In this way, the range of volume fractions was determined to have been $0.077 \leq \phi \leq 0.63$, i.e., the initial sediment consisted of an almost randomly close packed structure. This finding is in accordance with the results of Ballato et al. [30], who investigated the influence of forced sedimentation (centrifugation) on the microstructure of the resulting colloidal sediment. They found, by field emission scanning electron microscopy, that centrifuged silica colloids formed a disordered sediment, whereas an ordered structure was obtained for undisturbed sedimentation.

The size and polydispersity of the particles was determined by measuring the particle form factor with small-angle x-ray scattering (SAXS) at the ESRF (for a drawing of the setup see fig. 2.5). SAXS is an ideal tool for the characterization of colloidal particles due to the fact that multiple scattering is absent for x-rays and, more importantly, it covers a much wider $q$ range.
than static light scattering [31]. Figure 2.10 shows the static scattered x-ray intensity for a dilute ($\phi < 0.005$) sample in an index matching mixture of ethanol and benzyl alcohol. The data are fitted to the form factor expression for spherical particles (eq. 2.14), with an additional prefactor to adjust the absolute value. Expression 2.14 was convoluted with a Schulz distribution for the particle radius to account for polydispersity [9]. As can be seen from fig. 2.10, an almost perfect fit is obtained with $a = 54.9 \pm 0.1$ nm and $\Delta a/a = 0.042 \pm 0.005$. 