Fluid dynamics in charge stabilized colloidal suspensions
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Photon correlation spectroscopy: x rays versus visible light

We perform a direct comparison of cross-correlated dynamic light scattering (CCDLS) and dynamic x-ray scattering (DXS) for colloidal suspensions that are optically opaque due to multiple light scattering. Then, the dynamics cannot be probed by ordinary photon correlation spectroscopy with visible light. By contrast, multiple scattering is absent for x rays because of the small scattering cross section. Using DXS as a reference, we demonstrate that the detection of multiply scattered light can be suppressed by cross-correlating the signals from two closely spaced detectors. This comparison provides an independent, direct proof of the feasibility of CCDLS in the case of concentrated colloidal dispersions with interparticle interactions.

3.1 Introduction

Photon correlation spectroscopy is one of the most important techniques with which to study dynamical phenomena in soft condensed matter [3, 9]. If a random arrangement of scatterers is illuminated with coherent radiation, the scattered intensity shows a grainy interference pattern that reflects the instantaneous configuration of the scatterers [32]. Movement of the scatterers causes a corresponding movement of this so-called speckle pattern, which thus contains information about the dynamics of the system. Photon correlation spectroscopy measures the time dependent intensity (auto)correlation
function of the speckle pattern at a given spatial position. Correlation spectroscopy with visible light, known as dynamic light scattering (DLS), is a well established and widely used technique [33]. However, DLS suffers from one major drawback that severely restricts its applicability: multiple light scattering. This problem arises in particular for colloidal suspensions, which have been investigated quite extensively with DLS. Since the size of colloidal particles is of the order of the wavelength of visible light, they scatter light very efficiently. As a result, multiple scattering becomes important in dense colloidal systems as soon as the refractive index of the suspending fluid differs significantly from that of the particles. Multiple scattering of light renders the measurement of quantities depending on the scattering vector \( q \) difficult, since scattered light observed at a given point in space then originates from a wide range of possible light paths in the sample [5]. In recent years, two new experimental techniques have emerged that overcome the multiple-scattering problem: dynamic x-ray scattering (DXS) [34, 35, 36, 37, 38] and cross-correlated dynamic light scattering (CCDLS and TCDLS) [19, 20, 21, 22, 23, 39, 40, 41]. DXS has the additional advantage of enlarging the wave vector range substantially, giving access to dynamic processes on an atomic length scale. By contrast, DLS cannot probe the dynamics on a length scale smaller than about 200 nm.

These recent exciting experimental developments have, in principle, expanded the potential of correlation spectroscopy enormously. However, up to now only the feasibility of DXS has been demonstrated. These feasibility studies have been performed mainly on systems displaying ultra slow dynamics (i.e. on the second time scale), such as colloidal particles suspended in glycerol [34, 35, 37] and polymer micelle liquids [36]. Faster dynamics has hitherto only been studied in the case of strongly scattering palladium aggregates [38] and in the dilute limit [42]. Examples of optically opaque systems, where the use of DXS would be of great advantage, are abundant, e.g. concentrated colloidal suspensions in aqueous environments and protein solutions. However, the absence of multiple scattering for x rays is payed by the low scattering cross section. Performing photon correlation measurements under these conditions is a challenging task due to intensity limitations, the pulsed nature of synchrotron sources, and the imperfect coherence properties of the x-ray beam. It is essential to investigate, therefore, whether DXS gives accurate and reliable results, and can thus be employed as a substitute for DLS, in systems comparable to those conventionally studied with visible light.
Concerning cross-correlated dynamic light scattering, it is not clear to which extent and under which conditions this technique suppresses the detection of multiply scattered light sufficiently. The reason is that there has been no independent, multiple-scattering free technique with which to compare CCDLS. As a consequence, all indications that CCDLS is indeed capable of suppressing multiple scattering contributions are of an indirect nature and are only conclusive for dilute systems, where interparticle interactions are absent. Going to higher concentrations, one faces the problem that multiple scattering increases and at the same time, interaction effects become important; both have qualitatively similar effects on the correlation functions. It is therefore impossible to separate both effects without prior knowledge of the interparticle interactions, which is however exactly the information one hopes to obtain from DLS experiments.

In this chapter, we report on a direct comparison of DLS, DXS and CCDLS. The goal of this comparison is to establish the potential of DXS and CCDLS as tools for investigating the dynamics of concentrated colloidal suspensions with fast dynamics. To this end, we study the diffusion of colloidal silica particles suspended in different liquids. We first demonstrate by a comparison of the correlation functions obtained with DLS and DXS on optically index matched samples that DXS gives accurate and reliable results. Then, having established the reliability of DXS, we use dynamic x-ray scattering to investigate the feasibility of CCDLS. By a direct comparison of the correlation functions obtained with these two techniques on optically opaque samples we show that the detection of multiply scattered light can effectively be suppressed by cross-correlating the signals from two closely spaced optical fibers. The results reported in this chapter open up the way to a new combination of experimental techniques that enables us to study the dynamics of dense, optically opaque colloidal suspensions over a wide range of scattering vectors: dynamic x-ray scattering, cross-correlated dynamic light scattering and small angle x-ray scattering. This combination overcomes the requirement to match the refractive indices of the colloidal particles and the suspending medium in order to avoid multiple scattering. As a consequence, we have complete freedom to tune the direct interaction between the colloids, allowing us to study the interplay between static and dynamic properties purely experimentally, without taking recourse to any theoretical model beforehand. We will report on these experiments in chapter 4.
### 3.2 Experimental

To induce multiple scattering of light in a controlled way, samples of varying refractive index contrast were produced by mixing different amounts of suspensions in ethanol (Aldrich, spectrophotometric grade, \( m = 1.359 \) [27]) and benzyl alcohol (Aldrich, 99.8 %, anhydrous, \( m = 1.538 \) [27]). The volume fraction of the samples was \( \phi = 0.078 \pm 0.002 \) and \( 0.164 \pm 0.003 \). The suspensions were sealed in cylindrical thin-walled glass capillaries (Müller Glas, diameter 2 mm, wall thickness 1/100 mm) that are suited for x-ray spectroscopy. Further details about the sample preparation and characterization are given in section 2.4.

The experimental setups used for cross-correlated dynamic light scattering and dynamic x-ray scattering are described in detail in sections 2.2.4 and 2.2.5.

### 3.3 Results

#### 3.3.1 Optically index matched sample

In this subsection, we investigate the performance and reliability of the new DXS technique in the case of fast moving colloidal suspensions. To this end, we compare DXS with the well-established DLS technique with a single laser beam and a single detector. To avoid multiple light scattering, we use an optically index matched sample (colloid volume fraction \( \phi = 0.164 \)).

Figure 3.1 shows an example of an intensity autocorrelation function, \( g(t) \), obtained with x rays. The pulsed nature of the synchrotron source causes oscillations with a period corresponding to the repeat time of the electron bunches in the storage ring. These oscillations dominate the correlation function at small times [Fig. 3.1(a)]. At larger times (\( t > 0.03 \) ms), the correlation function of the sample scattering is seen. For comparison a reference correlation function taken with the incoming beam is shown, which only exhibits the source fluctuation. The correlation times of the sample dynamics are of the order of 100 \( \mu \)s or longer, whereas the period of the source oscillations is about 3 \( \mu \)s. To average out the source fluctuations, the data were rebinned, i.e., the minimum sampling time was effectively increased from 400 ns to 6.4 \( \mu \)s. The correlation function was then divided by the reference signal to eliminate residual correlations in the source, yielding the function shown in
Figure 3.1: Intensity correlation functions obtained with coherent x rays on a sample of silica colloids in a mixture of ethanol and benzyl alcohol. (a) Raw data (bullets) and reference signal (open circles). (b) Correlation function after rebinning and division by the reference. The scattering vector $q = 0.0461 \, \text{nm}^{-1}$. 
Figure 3.2: Comparison of intermediate scattering functions obtained with both x rays (bullets) and visible light (diamonds). The comparison is done for an optically transparent sample at different scattering vectors: \( q = 0.0295(0.0297) \text{ nm}^{-1} \) (a), \( 0.0241(0.0238) \text{ nm}^{-1} \) (b) and \( 0.0144(0.0149) \text{ nm}^{-1} \) (c). The \( q \) values in parenthesis refer to x rays.
In Fig. 3.2, we show intermediate scattering functions obtained with both DLS and DXS at almost identical scattering vectors on the index matched sample. The $q$ vectors in this figure lie at the large $q$ end for light, but at the low $q$ side for x rays; the overlap allows a direct comparison of both techniques. As can be seen from Fig. 3.2, the intermediate scattering functions measured with x rays are in good agreement with those obtained by DLS (the small difference between DLS and DXS for the lowest $q$ is due to the fact that the functions were measured at slightly different scattering vectors). This comparison demonstrates that DXS yields accurate and reliable results for the dynamics of colloidal suspensions. By using a system comparable to those conventionally studied with light, we have shown that DXS can nowadays be used in the same time domain as DLS and should therefore be suitable as a substitute for DLS in cases where DLS fails due to multiple scattering.

### 3.3.2 Variation of the optical contrast

In the following, we will employ DXS to establish the feasibility of cross-correlated dynamic light scattering. Since multiple scattering is absent for x rays, this is probably the only independent, direct way of assessing the potential of CCDLS. To elucidate the significance of this point, we show a number of calculated intermediate scattering functions, together with a measured correlation function on a dense, index matched sample ($\phi = 0.3$), in fig. 3.3. The calculations have been done for a scattering angle of 90°; the time axis has been normalized by $\tau_0 = 1/D_0 q^2$. In a dilute system, the correlation function exhibits a single exponential decay (dashed line). Contributions from double scattering (dotted line, ratio double scattering to single scattering 1/1) lead to a non-exponential decay [20]. Double scattering not only influences the initial decay, which becomes more rapid than in the dilute limit, but also the long-time behavior. The dash-dotted and the dash-double-dotted line represent the differing wave limits in the backward- and forward scattering geometries, respectively [5]. The correlation functions in the diffusing limit are strongly non-exponential and deviate enormously from the single-scattering correlation function, indicating that multiple scattering strongly distorts the correlation functions. In fact, multiple scattering spoils the relation between the correlation function and the $q$ dependent diffusion coefficient, $D(q)$, and non-exponentiality factor, $\Delta(q)$ [43] (see chapter 4, eq.
Results

Figure 3.3: Intermediate scattering functions for: a dilute system in the single scattering limit (dashed line), single scattering and contributions from double scattering (dotted line), the diffuse limit in forward scattering geometry (dash-double-dotted line), the diffuse limit in backward scattering geometry (dash-dotted line), single scattering in the case of heterodyne detection (solid line), and single scattering in a dense system (circles). The time axis is reduced with $\tau_0 = 1/D_0 q^2$. The scattering angle $\theta = 90^\circ$.

4.5). In the diffuse limit, however, there is at least a model to interpret the correlation functions in terms of an average diffusion coefficient [5]. By contrast, in the region between single scattering and diffuse limit, an interpretation of the correlation function in terms of quantities related to colloidal dynamics is hardly possible. The solid line in fig. 3.3 shows a single scattering correlation function in the case of heterodyne detection [24], i.e., in the presence of a constant intensity $I_c$ in addition to the fluctuating intensity $(I_c/\langle I \rangle = 0.5)$. Heterodyning also leads to a non-exponential correlation function, the initial decay being less rapid than in the homodyne case. The circles show a measured correlation function on a dense system. The correlation function on the dense sample is strongly non-exponential as a result of interparticle interactions. Another effect that leads to non-exponential cor-
relation functions is size polydispersity [9]. We see from this discussion that a number of very different effects have a qualitatively similar influence on the form of the correlation functions, complicating the interpretation of their time dependence. Up to now, the feasibility of cross-correlation dynamic light scattering techniques has been demonstrated on dilute systems indirectly by showing that the correlation functions obtained with these techniques were single exponential [19, 21]. It is clear from fig. 3.3 that in a dense system, where the correlation function is *intrinsically non-exponential*, this kind of indirect proof breaks down. Without prior knowledge of the contributions of heterodyne detection, polydispersity and, above all, interparticle interactions it is impossible to draw conclusions about the importance of multiple scattering from the form of the correlation function in the case of dense systems. Similar arguments hold for schemes for correcting the light scattering data for double scattering, as given for example by Dhont [44]. This author developed an iterative correction scheme and applied it to suspensions of colloidal silica and latex particles. In all cases, a $q$ dependence of the diffusion coefficient remained after the correction for double scattering and was attributed to polydispersity and interparticle interaction effects, which requires *a priori* knowledge of these effects. However, the non-exponentiality and the $q$ dependent relaxation rate associated with the interparticle interactions is exactly the information one wants to obtain from the dynamic light scattering experiments. To resolve this dilemma, comparison with an independent, multiple scattering-free technique is essential.

The reason for introducing CCDLS in addition to DXS here is twofold. First, since DXS operates at the limit of what is possible with modern synchrotron technology, it is certainly not a technique to be used for routine work, such as for example particle sizing. By contrast, a CCDLS setup is compact and easy to use in the laboratory. Secondly, CCDLS can be employed to extend photon correlation measurements to small wave vectors that are not accessible to DXS. In fact, in the following chapter it will become clear that only a combination of CCDLS, DXS and SAXS is powerful enough for the experiments on colloidal dynamics we have in mind.

### 3.3.2.1 CCDLS correlation functions

Figure 3.4 shows intensity correlation functions obtained with CCDLS at a scattering angle of 30°; since the single-scattering relaxation rate goes to zero as $q^2$ (see eq. 2.11), whereas the multiple-scattering relaxation rate is in first
Figure 3.4: (a) Dynamic light scattering intensity autocorrelation function (squares) and cross-correlation functions (circles, triangles, diamonds and crosses) for silica colloids in a mixture of ethanol and benzyl alcohol. The refractive index contrast is 1.063. The volume fraction of colloids is 0.078. The scattering angle $\Theta = 30^\circ$. For the cross-correlation functions, the fiber separation increases from top to bottom. (b) Correlation functions shown in (a) normalized with their zero-time intercept $\beta^2$. The time axis in (b) is reduced with the initial decay time of the correlation functions.
approximation independent of $q$, we expect the largest influence of multiple scattering at small scattering angles. The volume fraction is $\phi = 0.078$ and the refractive index contrast is $m_1/m_0 = 1.063$; this refractive index contrast is the second largest investigated in this study and is substantially larger than for the measurements to be reported in the following chapter. Figure 3.4(a) shows unnormalized correlation functions, fig. 3.4(b) normalized correlation functions. The squares are the autocorrelation function, the other symbols show cross-correlation functions with varying fiber distance as indicated in the figure. Several features are apparent from fig. 3.4(a). First, the amplitude of the autocorrelation function, $\beta^2 = 0.94$, is close to the ideal value of 1 [24], indicating a good performance of the setup. Secondly, the amplitude for cross-correlation is substantially smaller than for autocorrelation and drops strongly with increasing fiber distance; at the largest fiber distance of $Y = 4.8$ mm, $\beta^2 = 0.026$. This behavior is expected on the basis of the theory by Lock (see fig. 2.3). Thirdly, the correlation functions are non-exponential, the non-exponentiality being largest for the autocorrelation function. In cross-correlation, the non-exponentiality first decreases as the fiber distance is increased, but seems to remain almost constant for $Y \geq 3.2$ mm. In particular, the correlation function remains non-exponential even for the largest fiber distance. The non-exponentiality indicates that a distribution of relaxation rates rather than a single relaxation rate is present in the system. As discussed above, it is impossible to decide on the basis of the CCDLS measurements alone whether the remaining non-exponentiality at large fiber distances is due to interparticle interactions, which one is interested in, or due to residual contributions from multiple scattering. Fourthly, the initial decay of the correlation functions is less rapid for cross-correlation than for autocorrelation and the decay rate decreases with increasing fiber distance.

In fig. 3.4(b) we display normalized correlation functions, i.e., the correlation functions shown in fig. 3.4(a) divided by the amplitude. The time axis in fig. 3.4(b) is scaled by the initial decay time $\tau$ of the correlation functions, as obtained from the first cumulant [see fig 3.9(a)]. The scaling of the time axis eliminates the differences in the initial decay of the correlation functions, such that differences in the long-time behavior become more apparent. It is evident that multiple scattering contributions affect the long-time behavior as well as the initial decay.

The signal-to-noise ratio clearly becomes worse as the fiber distance is increased, which is a consequence of the dropping amplitude.
Figure 3.5: Normalized dynamic light scattering intensity autocorrelation function (squares) and cross-correlation function (crosses) for silica colloids in an alcohol mixture (refractive index contrast 1.063, volume fraction 0.078, scattering angle 30°, fiber separation 4.8 mm for cross correlation). The dashed line represents the initial decay of the cross-correlation function. The dotted line represents the double-scattering intensity correlation function in the dilute limit. The solid line represents a mixture of double- and single scattering functions with a ratio of 1.3:1 at t = 0.

In fig. 3.5 we compare some of the DLS correlation functions to calculations with the (dilute) theory given by Lock [20]. The purpose of this comparison is to estimate the importance of multiple scattering contributions. The squares show the autocorrelation function, the crosses the cross-correlation function at Y = 4.8 mm. The dashed line represents an exponential corresponding to the initial decay of the cross-correlation function. The dotted line shows the intensity correlation function for pure double scattering; it decays by a factor of about 7 faster than the cross-correlation function, indicating that multiple scattering has an enormous effect on the decay rate. In order to fit the initial decay of the measured autocorrelation function, we
have mixed double- and single scattering field correlation functions with a ratio of 1.3/1, taking the initial decay of the cross-correlation function as the single scattering limit. The solid line represents the square of the mixed field correlation function. Again it is seen that the correlation function becomes strongly non-exponential as a result of double scattering contributions. The reason is the fact that the decay rate of the double scattering correlation function is composed of contributions from different wave vectors \( q \), leading to a distribution of decay rates in the mixed correlation function. The initial decay of the mixed correlation function is by about a factor of 4 faster than that of the cross-correlation function. It should be noted, however, that a comparison to the calculations by Lock can only give a rough idea about the role of multiple scattering for our systems, since it is a theory for the dilute limit.

3.3.2.2 Comparison with DXS

Figure 3.6 shows a direct comparison of normalized dynamic light scattering and dynamic x-ray scattering intensity correlation functions at identical scattering vectors. The sample is the same as that discussed above. The DXS results are compared to the DLS autocorrelation function and the DLS cross-correlation function at a fiber distance of 3.2 mm. The data are represented by lines instead of points in this figure for clarity. It is evident that the DLS autocorrelation function deviates substantially from the DXS result; the initial decay of the DLS autocorrelation function is more rapid than in the case of DXS. By contrast, the DLS cross-correlation function is practically identical to the correlation function obtained with x rays. This direct comparison demonstrates that the detection of multiply scattered light is indeed suppressed by the CCDLS technique. Note that the DLS cross-correlation function as well as the DXS correlation function are non-exponential. This observation shows that the non-exponentiality remaining as the fiber distance is increased, as discussed above, is not due to residual contributions from multiple scattering or to heterodyne detection, but results from inter-particle interactions.

Figure 3.7 shows a direct comparison of normalized dynamic light scattering and dynamic x-ray scattering correlation functions for two other samples, one with a lower refractive index contrast than hitherto discussed \( [m_1/m_0 = 1.036, \text{fig. 3.7(a)}] \) and one with a larger contrast \( [m_1/m_0 = 1.077, \text{fig. 3.7(b)}] \); the volume fraction is 0.078 as before. For the lower contrast, the
Figure 3.6: Normalized intensity autocorrelation functions (solid line dynamic x-ray scattering, dotted line dynamic light scattering) and dynamic light scattering intensity cross-correlation function (dashed line) for silica colloids in an alcohol mixture (refractive index contrast 1.063, volume fraction 0.078). The scattering vector $q = 0.0187 \text{ nm}^{-1}$.

DLS cross-correlation function agrees well with the DXS correlation function, whereas the autocorrelation function decays more rapidly. This behavior is expected on the basis of the previous discussion. For the larger refractive index contrast of 1.077, however, neither the DLS autocorrelation function nor the cross-correlation function agree with the DXS result, indicating that the limit of the present setup has been exceeded. The amplitude of the DLS intensity cross-correlation function corresponding to fig. 3.7(b) is only 0.014 at $Y = 4.8 \text{ mm}$; it might have been possible to further reduce the contribution of multiple scattering to the correlation function by operating at an even larger fiber distance, but only at the cost of a forbiddingly small amplitude. In our setup, the field of view of the two detectors was limited by
Figure 3.7: Normalized intensity autocorrelation functions (squares dynamic x-ray scattering, triangles dynamic light scattering) and dynamic light scattering intensity cross-correlation function (circles) for silica colloids in an alcohol mixture (volume fraction 0.078). The refractive index contrasts are 1.036 (a) and 1.077 (b). The scattering vector $q = 0.0114 \text{ nm}^{-1}$ (a) and $0.0184 \text{ nm}^{-1}$ (b). The dashed line in (b) is a guide to the eye.
the collection optics, in contrast to the setup of Meyer et al. [19], in order to avoid heterodyne detection; this is essential due to the small sample capillaries used. As the fiber distance increases, the overlap between the field of views of the two detectors will reduce; this effect will lead to a further reduction of the amplitude. It may be possible to reduce this problem by further optimizing the setup. However, for the present setup multiple scattering-free cross-correlation measurements within a reasonable averaging time cannot be performed anymore for this strongly scattering sample, showing the practical limits of the CCDLS technique. A simple calculation according to eq. 2.18 shows that $l_s/L \approx 0.05$ for the sample corresponding to fig. 3.7(b); at this point, it is seems to be necessary to resort to DXS alone to obtain $q$ dependent experimental information with reasonable accuracy.

3.3.2.3 The initial decay

We now discuss the effect of multiple scattering on the initial decay rate of the intermediate scattering function, which we are eventually interested in to obtain the $q$ dependent collective diffusion coefficient. Figures 3.8 and 3.9 display the initial relaxation rates, obtained from an exponential fit to the correlation functions at small times, for DLS autocorrelation, DLS cross-correlation and DXS. The refractive index contrasts corresponding to the data shown in figs. 3.8(a), 3.8(b), 3.9(a) and 3.9(b) are 1.017, 1.036, 1.063 and 1.077, respectively. The volume fraction is 0.078 for all samples. The data are plotted against $q^2$, since in a dilute sample the diffusion coefficient is independent of scattering vector and thus $\tau^{-1} \propto q^2$ for single scattering. It is seen from fig. 3.8(a) that for the lowest refractive index contrast, the DLS relaxation rates are practically independent of fiber distance and are the same for auto- and cross-correlation. Reasonable agreement with the DXS results is found for all DLS measurements, indicating that multiple scattering does not play an important role for this sample. A calculation shows that $l_s/L = 1$ for this sample, i.e., multiple scattering is indeed expected to be of minor importance. The data do not follow a straight line through the origin, which again indicates that interparticle interactions play a role. Without direct comparison with DXS it would be impossible to unambiguously attribute the apparent deviation of the relaxation rates from a pure $q^2$ dependence to interparticle interactions; there is thus no intrinsic way of assessing the reliability of the cross-correlation technique.

Figure 3.8(b) shows relaxation rates for a sample with a refractive index
Figure 3.8: Initial decay rates of intermediate scattering functions for silica colloids in mixtures of ethanol and benzyl alcohol (volume fraction 0.078). The refractive index contrasts are 1.017 (a) and 1.036 (b). The relaxation rates have been obtained from DLS autocorrelation (squares), DXS (bullets) and DLS cross-correlation (circles fiber distance 2.4 mm, triangles 3.2 mm, diamonds 3.9 mm and crosses 4.8 mm).
Figure 3.9: Initial decay rates of intermediate scattering functions for silica colloids in mixtures of ethanol and benzyl alcohol (volume fraction 0.078). The refractive index contrasts are 1.063 (a) and 1.077 (b). The relaxation rates have been obtained from DLS autocorrelation (squares), DXS (bullets) and DLS cross-correlation (circles fiber distance 2.4 mm, triangles 3.2 mm, diamonds 3.9 mm and crosses 4.8 mm). The dashed line in (b) represents the dilute limit, $1/\tau = D_0 q^2$. 
contrast of $m_1/m_0 = 1.036$. The DLS autocorrelation data now deviate appreciably from the DXS results as far as the absolute value is concerned. The curvature of the plot remains similar, i.e., multiple scattering basically leads to an additional offset in the data. This is expected, since the multiple scattering relaxation rate is approximately independent of the scattering angle [45]. We note, however, that because of the appreciable deviation of the data from a pure $q^2$ dependence, it would be difficult to extrapolate the DLS data to $q = 0$, to obtain the offset, and thus correct the results for multiple scattering. Cross-correlation greatly reduces the discrepancy with the DXS data. At a fiber distance of 4.8 mm, the cross-correlation data agree to within 5% with the DXS results, demonstrating that the detection of multiply scattered light is suppressed efficiently.

As the refractive index contrast is increased further, the discrepancy between the DLS autocorrelation results and the DXS data becomes larger, as can be seen from fig. 3.9(a) [$m_1/m_0 = 1.063$]. At the smallest scattering angle of 30°, the DLS relaxation rate is larger than the DXS relaxation rate by about a factor 4. Cross-correlation again greatly reduces this discrepancy. For a fiber distance of $Y = 4.8$ mm, the CCDLS data agree reasonably well with the x-ray data in the whole $q$ range. However, the cross-correlation amplitude is typically only 2% for this sample at the largest fiber distance, requiring averaging times of about 0.5 h to obtain a reasonable signal-to-noise ratio. For this sample, we find $l_s/L \approx 0.08$, which seems to be close to the practical limit of the current setup considering the small cross-correlation amplitudes.

Figure 3.9(b) shows relaxation rates at a refractive index contrast of 1.077. In this case, the silica particles were suspended in pure ethanol (volume fraction 0.078 as before). Since the viscosity of ethanol is well known, we can estimate the diffusion coefficient $D_0$ in the dilute limit from the Stokes-Einstein relation; the dashed line in fig. 3.9(b) represents the relation $\tau^{-1} = D_0 q^2$. The DXS data are close to the dilute limit for this sample. The DLS autocorrelation relaxation rates, on the other hand, are about one order of magnitude larger than the DXS relaxation rates, indicating that multiple scattering has now become dominant. Although cross-correlation again greatly reduces the discrepancy between DLS and DXS, there remains a large difference even for the largest fiber distance; obviously, the limits of the present CCDLS setup have been exceeded with this sample. To elucidate this point, we show the DLS autocorrelation function at 30° at short times in fig. 3.10. The dashed line represents the dilute single scattering limit. It is evident that
Figure 3.10: Normalized dynamic light scattering intensity autocorrelation function (squares) for silica colloids in ethanol (refractive index contrast 1.077, volume fraction 0.078, scattering angle 30°). The dashed line represents the single scattering, dilute limit. The dotted line represents the double-scattering intensity correlation function in the dilute limit.

The autocorrelation function decays much faster than this limit. The dotted line shows the intensity correlation function for pure double scattering in the dilute limit, as calculated according to Lock's theoretical expressions. At very short times, the measured autocorrelation function decays even faster than expected for pure double scattering; this could be due to either particle correlations, which are not included in the theory of Lock, or it may be an indication that higher order scattering has become important. An indication that higher order scattering plays a role also comes from the $q$ dependence of the autocorrelation relaxation rates [fig. 3.9(b)], that differs significantly from the behavior of the samples with smaller refractive index contrasts. It is clear that multiple scattering strongly dominates over single scattering for this sample and, therefore, CCDLS is not capable anymore of sufficiently
supressing the multiple scattering contributions.

3.4 Conclusions and outlook

In this chapter, we have demonstrated by a direct comparison of cross-correlated dynamic light scattering with DXS that CCDLS suppresses the detection of multiply scattered light. We found our present CCDLS setup to be effective up to a nominal ratio of the scattering mean free path to the sample size of $l_s/L \approx 0.08$. An analysis in terms of the theoretical treatment by Lock [20] shows that at small angles, the ratio of the contribution of doubly scattered light to the electric field correlation function to the contribution of singly scattered light should be about 1/1 in this case. For samples that are even more strongly scattering, CCDLS fails and one has to resort to DXS alone. By using DXS as an independent reference, we have overcome the intrinsic dilemma of previous attempts to suppress multiple scattering detection or to correct correlation functions for multiple scattering: in order to assess the quality of these methods, one needs to have information on interparticle interactions beforehand, which is however precisely the kind of information one would like to obtain from DLS experiments. With the experiments presented in this chapter we have established the potential of a new combination of experimental techniques that is free from multiple scattering effects: CCDLS, DXS and SAXS. In the following chapter, we will apply this combination to investigate the dynamics of charge stabilized colloidal suspensions.