

## Photon correlation spectroscopy: X rays versus visible light

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We have performed combined dynamic light scattering (DLS) and dynamic x-ray scattering (DXS) experiments on dense colloidal suspensions. The intermediate scattering functions obtained with these two techniques are compared directly. In the case of optically index matched samples, the comparison demonstrates that DXS yields accurate and reliable results. It is shown that the hydrodynamic interaction  $H(q)$  can be determined experimentally, without taking recourse to any theoretical model, by combining DXS and DLS. The combination of the two methods probes the dynamics over more than one decade in scattering vector. Experiments on optically opaque samples, where DLS fails, demonstrate the necessity to use x rays in these systems.

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### I. INTRODUCTION

Photon correlation spectroscopy is one of the most important techniques with which to study dynamical phenomena in soft condensed matter [1,2]. 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 [3]. 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 autocorrelation 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 [4]. By contrast, correlation spectroscopy with coherent x rays (DXS) has been developed only recently [5–9]. The most severe limitation of DLS, the occurrence of multiple scattering in dense systems, is absent for DXS. 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 [10]. Another limitation of DLS is the small range of accessible scattering vectors; DLS cannot probe the dynamics on a length scale smaller than about 200 nm. By contrast, DXS gives access to dynamic processes on an atomic length scale ( $0.01 \text{ nm}^{-1} \leq q \leq 10 \text{ nm}^{-1}$ ).

These exciting experimental developments have, in principle, expanded the potential of correlation spectroscopy enormously. However, the feasibility of DXS has been demonstrated mainly on systems displaying ultra slow dynamics (i.e., on the second time scale), such as colloidal particles suspended in glycerol [5,6,8] and polymer micelle liquids [7]. Faster dynamics has hitherto only been studied in the case of strongly scattering palladium aggregates [9] and in

the dilute limit [11]. For many interesting systems, such as concentrated colloidal suspensions, biological cells, or DNA molecules, however, the conditions are much less favorable for the application of DXS. These systems usually have aqueous environments and display fast dynamics, exhibit particle interactions, and scatter weakly. Interparticle interactions lead to a nonexponential time dependence of the intensity autocorrelation function measured by correlation spectroscopy. Resolving these interaction effects on an extended time scale requires the correlation functions to be measured with high statistical accuracy. Performing DXS 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. On the other hand, it is precisely in this kind of system that multiple scattering of visible light, which also affects the time dependence of the autocorrelation function, prevents an unambiguous interpretation of DLS results. If one is to benefit from the advantages of DXS as compared to DLS it is, therefore, of utmost importance to investigate whether quantitatively reliable and accurate results can be obtained by DXS in the case of dense, fast-moving systems.

In this paper, we report a direct comparison of DXS and DLS. The goal of this comparison is to establish the potential of DXS as a tool 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. For an optically index-matched sample, we demonstrate that the correlation functions obtained from DXS and DLS are in excellent agreement in the wave vector range accessible to both techniques. Combination of DLS and DXS allows us to study the dynamics over a wide range of scattering vectors. By comparison of DXS and DLS in the case of optically opaque samples we then show that the DLS results are severely affected by multiple scattering, making the use of x rays imperative. It is pointed out that, in contrast to advanced light scattering techniques, coherent x rays provide the unique possibility of directly measuring both dynamic and static properties of a colloidal suspension without the need to invoke any theoretical model. The simultaneous

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measurement of both statics and dynamics is of prime importance for systems where, unlike hard sphere suspensions, the structure is not known *a priori*.

## II. EXPERIMENT

DXS was performed at beamline ID10 (Troika) of the European Synchrotron Radiation Facility (ESRF) in Grenoble [12,13]. The sample was illuminated with 8.2 keV radiation from an undulator (wavelength  $\lambda = 1.51 \text{ \AA}$ ). The longitudinal coherence length  $\xi_l$  ( $\xi_l = \lambda^2/\Delta\lambda$ , with bandwidth  $\Delta\lambda/\lambda = 1.4 \times 10^{-4}$ ) was about  $1 \text{ \mu m}$ . A pinhole with a diameter of  $20 \text{ \mu m}$  was inserted  $130 \text{ mm}$  upstream from the sample to provide a collimated and partially coherent beam. The transverse coherence length at the position of the pinhole was about  $140 \text{ \mu m}$  in the vertical direction. A primary slit of  $200 \text{ \mu m}$  was used to obtain  $7.2 \text{ \mu m}$  transverse coherence length in the horizontal direction. An analyzing aperture of  $30 \text{ \mu m}$  size was used in front of a scintillation counter at a distance  $1.4 \text{ m}$  downstream from the sample. This configuration yielded an optimal trade-off between the degree of coherence and the count rate.

The DLS measurements were done with a light scattering instrument [14] set up at the ESRF. The DLS apparatus was designed such that it could house the same sample holders as used for x-ray scattering, enabling us to perform both DLS and DXS on exactly the same samples. The sample cells were suspended in an index matching bath, reducing scattering from the cell walls. A diode pumped frequency doubled Nd:YAG laser (wavelength  $532 \text{ nm}$ ) served as light source. A photomultiplier, mounted on a rotation stage, was used as detector. Correlation functions were computed with digital ALV5000/E correlators for both DXS and DLS.

Optically index-matched samples were produced by suspending silica particles (radius  $r = 56 \text{ nm}$ ) in a mixture of ethanol (refractive index  $n = 1.36$ ) and benzyl alcohol ( $n = 1.54$ ). The refractive index of the silica particles was determined by measuring the transmission at  $532 \text{ nm}$  in the forward direction as a function of the composition of the alcohol mixture. The maximum in transmission defined the point of index matching, which was found to be at  $n = 1.465$ . To induce multiple light scattering in a controlled way, the composition of the alcohol mixture was changed. The most strongly scattering sample was in pure ethanol. The colloid volume fractions were  $\phi = 16.4 \pm 0.3 \%$  for the index matched sample and  $7.8 \pm 0.1 \%$  for the opaque samples. The suspensions were sealed in thin walled glass capillaries with a diameter of  $2 \text{ mm}$ .

## III. RESULTS

### A. Optically index matched sample

Figure 1 shows an example of an intensity autocorrelation function  $g^{(2)}(t)$  obtained with x rays on the optically index-matched sample. 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. 1(a)]. At larger times ( $t > 0.03 \text{ ms}$ ), the correlation function of the sample scattering is seen. For comparison a reference correlation function taken with the incoming beam is shown,

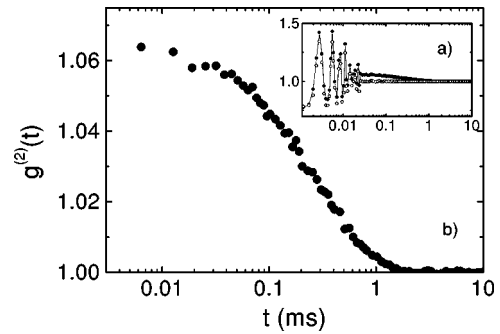


FIG. 1. X-ray intensity autocorrelation function, measured on a suspension of colloidal silica spheres ( $r = 56 \text{ nm}$ ) in alcohol. The inset shows the signal (●) and reference (○) functions before rebinning and division. The scattering vector  $q = 0.0461 \text{ nm}^{-1}$ .

which only exhibits the source fluctuation. The correlation times of the sample dynamics are of the order of  $100 \text{ \mu s}$  or longer, whereas the period of the source oscillations is about  $3 \text{ \mu s}$ . To average out the source fluctuations, the data were rebinned, i.e., the minimum sampling time was effectively increased from  $400 \text{ ns}$  to  $6.4 \text{ \mu s}$ . The correlation function was then divided by the reference signal to eliminate residual correlations in the source, yielding the function shown in Fig. 1(b).

From the measured intensity autocorrelation function the intermediate scattering function  $f(q, t)$  can be obtained according to  $g^{(2)} = 1 + \beta^2 |f(q, t)|^2$ . The amplitude of  $g^{(2)}$ , the coherence factor (or contrast)  $\beta^2$ , depends on the coherence properties of the source, the coherence preserving properties of all optical elements in the setup and the number of coherence areas observed at the detector. Optimizing the tradeoff between coherence and the available photon flux resulted in a contrast of  $5\text{--}10 \%$ . Figure 2 shows the intermediate scattering function corresponding to the intensity correlation function in Fig. 1(b). For a dilute suspension,  $f(q, t)$  would decay exponentially over the whole time range. Deviations from a single exponential decay can clearly be distinguished in Fig. 2, demonstrating the high statistical accuracy of the data. The deviations are due to interparticle interactions, which eventually lead to different time regimes for the dynamics [1,2]. The short time decay of the correlation function is indicated in Fig. 2 by a straight line.

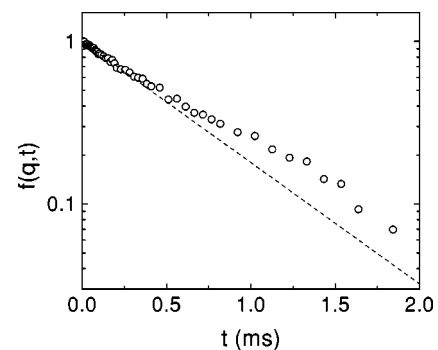


FIG. 2. Intermediate scattering function for a suspension of silica colloids ( $16.4 \text{ vol } \%$ ) in a mixture of ethanol and benzyl alcohol. The scattering vector  $q = 0.0461 \text{ nm}^{-1}$ . The straight line is an exponential fit to the initial decay of the intermediate scattering function.

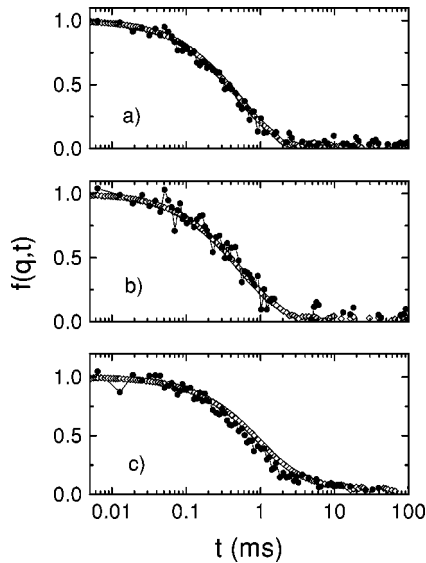


FIG. 3. Comparison of intermediate scattering functions obtained with both x rays ( $\bullet$ ) and visible light ( $\diamond$ ). The comparison is done for an optically transparent sample at different scattering vectors:  $q = 0.0295(0.0297) \text{ nm}^{-1}$  (a),  $0.0241(0.0238) \text{ nm}^{-1}$  (b), and  $0.0144(0.0149) \text{ nm}^{-1}$  (c). The  $q$  values in parenthesis refer to x rays.

In Fig. 3, 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, the intermediate scattering functions measured with x rays are in very good agreement with those obtained by DLS over the whole time range (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 reliable results can be extracted from DXS even in fast relaxing systems.

At times short compared to the structural relaxation time of the system the decay of  $f(q,t)$  can be approximated by an exponential, with a characteristic time  $\tau(q) = -1/\Gamma(q)$ . Here,  $\Gamma(q)$  is the first cumulant, defined by  $\Gamma(q) = \lim_{t \rightarrow 0} [d \ln f(q,t)/dt]$ . This exponential decay corresponds to a diffusive motion of the colloids. The short-time diffusion coefficient,  $D_s(q)$ , is related to the first cumulant by  $D_s(q) = -\Gamma(q)/q^2$  [1]. In Fig. 4 the inverse of the short-time diffusion coefficient is shown.  $D_s(q)$  was determined by fitting the initial decay of the intermediate scattering functions in a range where no deviations from an exponential behavior could be observed. The diffusion coefficient for a dilute suspension  $D_0$  was measured with DLS. It is seen in the  $q$  region accessible to both DLS and DXS that the results are in very good agreement. The figure demonstrates that by combining DLS and DXS on an index-matched sample, where multiple scattering of light is unimportant, the dynamics can be probed over more than one decade in  $q$  ( $4.4 \times 10^{-3} \leq q \leq 5.4 \times 10^{-2} \text{ nm}^{-1}$ ).

The  $q$  dependence of the short-time diffusion coefficient in dense suspensions stems from direct and hydrodynamic interactions between the colloidal particles [1,2]. The direct

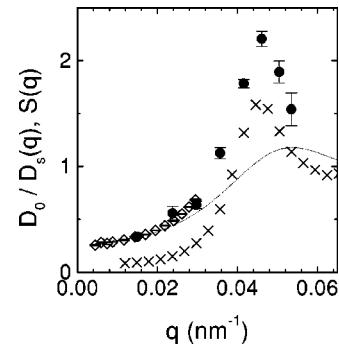


FIG. 4. Inverse of the short-time diffusion coefficient ( $\diamond$ ,  $\bullet$ ) and static structure factor ( $\times$ ) of silica spheres, suspended in an alcohol mixture ( $\phi = 0.164$ ). Diamonds are DLS results, filled circles DXS. The diffusion coefficient is scaled by that for a dilute suspension,  $D_0$ . The dotted line represents the static structure factor of a hard sphere system at  $\phi = 0.164$ .

interactions are caused, for example, by a screened repulsive Coulomb potential in charge stabilized systems. The hydrodynamic interaction is mediated by the suspending fluid. Taking these interactions into account, the short time diffusion coefficient is given by  $D_s(q) = D_0 H(q)/S(q)$ , where  $S(q)$  is the static structure factor and  $H(q)$  a function representing the hydrodynamic interaction. As can be seen from Fig. 4, the inverse of the diffusion coefficient has a  $q$  dependence similar to the structure factor, as expected. At the peak position of the structure factor, diffusion is strongly slowed down as compared to a dilute system, which is known as the cage effect [15]. By contrast, the repulsive interactions between the particles lead to an enhancement of diffusion at small  $q$  [16].

The structure factor in Fig. 4 was obtained by dividing the static scattered x-ray intensity  $I(q)$  by the form factor  $P(q)$ , obtained from static small angle x-ray scattering. Both  $I(q)$  and  $P(q)$  were measured in the same experimental setup as used for DXS. For comparison, we show a calculation of the Percus-Yevick hard sphere structure factor at the same volume fraction. It is evident that structural correlations in the system considered here are much more pronounced than in a hard sphere system. The strong structural correlations result from the electrostatic repulsion between the particles.

### B. Optically opaque sample

Figure 5 shows relaxation rates of a colloidal suspension (silica in ethanol) with an appreciable refractive index contrast of  $1.465/1.360 = 1.077$ . It is seen that the relaxation rates obtained with dynamic x-ray scattering, plotted against  $q^2$ , lie on a straight line through the origin. The straight line in Fig. 5 represents the relation  $\tau^{-1} = D_0 q^2$ , where  $D_0$  has been calculated from the Stokes-Einstein formula. The DXS results are compatible with this relation.

The absolute values as well as the  $q$  dependence of the relaxation times obtained with DLS differ strongly from the DXS results. It is evident that even for a moderate refractive index contrast and particle volume fraction, multiple scattering effects are dominant for light. The dominant role of multiple scattering for this sample makes it clear that any attempt to correct the DLS results for multiple scattering effects would be unreliable. To elucidate this point, the inset

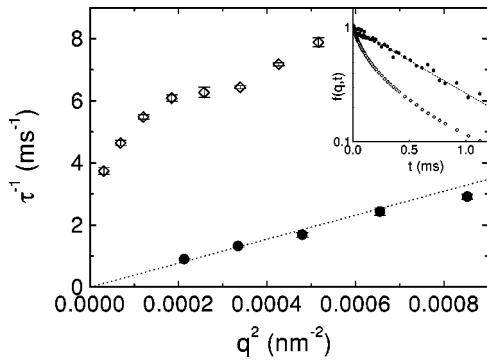


FIG. 5. Correlation rates measured with DLS ( $\diamond$ ) and DXS ( $\bullet$ ) on a suspension of silica colloids in ethanol ( $\phi=0.078$ ). The dotted line represents the low density limit as obtained from the Stokes-Einstein relation. The inset shows intermediate scattering functions at  $q=0.0183 \text{ nm}^{-1}$ . The dashed line in the inset represents an exponential decay.

in Fig. 5 shows a direct comparison of intermediate scattering functions for DLS and DXS. Whereas the correlation function obtained with x rays decays exponentially, the one measured with light is strongly nonexponential. In principle, the nonexponential decay can have several causes: multiple scattering [10], heterodyne detection [14], polydispersity, or sample effects as a consequence of particle interactions [1,2]. Some of these possible causes, such as heterodyne detection, are purely instrumental. These effects also change the  $q$  dependence of the first cumulant, since they all depend on the scattering angle. In order to correct the light scattering results for multiple scattering, information about the relative importance of all these effects as well as a reliable model for multiple scattering is needed. It is clear that under these conditions, it will be difficult to reliably extract the relevant information from the light scattering data.

### C. Hydrodynamic interaction

Since  $S(q)$  has been measured, it is possible to obtain the hydrodynamic interaction  $H(q)$  experimentally, independent of any theoretical model. The fact that no calculation of the structure factor on the basis of theoretical models for the direct interaction is required to extract the hydrodynamic function from the data, allows for a rigorous experimental test of theories for  $H(q)$ . Figure 6 shows the hydrodynamic

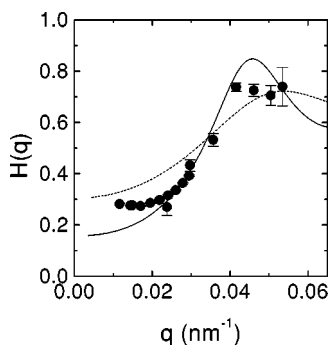


FIG. 6. Hydrodynamic function for a suspension of charge-stabilized colloidal silica spheres in a mixture of ethanol and benzyl alcohol ( $\phi=0.164$ ). The dashed and full lines represent calculations for hard spheres and charged spheres, respectively.

function obtained from the data shown in Fig. 4. The data are compared to the theory of Beenakker and Mazur [17] for hard spheres (dashed line) and charged particles (full line). In the latter case, we have taken a hard-sphere fit to the measured structure factor with an effective volume fraction  $\phi_{\text{eff}}=0.32$  and an effective hard sphere radius  $r_{\text{eff}}=70 \text{ nm}$ , as an input for the theory. This corresponds to the treatment of Genz and Klein [18], except that they use a more elaborate method for fitting the structure factor. The theory of Beenakker and Mazur is based on an expansion of the collective diffusion coefficient in correlations of density fluctuations and takes into account many-body hydrodynamic interactions.

Surprisingly, the experimental results seem to follow the hard sphere calculation more closely than the one for charged spheres at small and large wave vectors. Whereas the structure factor strongly deviates from that of hard spheres and has a pronounced peak (see Fig. 4), the hydrodynamic interaction shows much less structure. We find  $H(q)<1$  at all wave vectors for this slightly charged system, corresponding to a hydrodynamic hindrance of diffusion. This behavior is similar to that of hard spheres [16], but it is in contrast to earlier DLS measurements on slightly charged silica at moderate volume fractions  $\phi\leq 0.1$  [19,20]. These experiments report  $H(q)>1$  at the peak position of the static structure factor  $q_m$  corresponding to an enhancement of diffusion by hydrodynamic interactions. Recent experiments on highly charged silica particles at very low volume fractions ( $\phi<0.01$ ) also show that diffusion can be enhanced at the structure factor peak [21]. It has been suggested that this enhancement effect is due to the backflow of the displaced fluid, which supports the motion of particles in opposite directions. By contrast, the retardation of diffusion at  $q_m$ , that is characteristic of hard sphere systems, is due to near field hydrodynamic effects [22]. Our result indicates, in view of the earlier work mentioned above, that the qualitative behavior of the hydrodynamic interaction is very sensitive to small changes in the direct interaction. However, experimental data on  $H(q)$  as a function of volume fraction and ionic strength, that should show a transition from enhanced to retarded diffusion *within the same system*, are lacking so far. This paucity of experiments is in part due to the problems encountered with DLS, in particular multiple light scattering. In order to avoid multiple scattering at high volume fractions it is necessary to match the refractive indices of the colloidal particles and the suspending medium. This, however, strongly restricts the freedom to change the direct interaction. Even at very low volume fractions, multiple light scattering constitutes a problem. Härtl *et al.*, for instance, find a strong disagreement between experimentally determined hydrodynamic functions and theory at small wave vectors [21], but cannot exclude that this is due to multiple scattering. Detailed measurements of  $H(q)$  in dense systems, using DXS, are currently in progress in our group [23].

## IV. SUMMARY

In summary, we have shown by a direct comparison of dynamic x-ray scattering and dynamic light scattering that DXS yields accurate and reliable results for the dynamics of colloidal suspensions. By using systems comparable to those conventionally studied with light, we have demonstrated that



DXS is capable of overcoming the limitations of light scattering that severely restrict experiments on colloidal dynamics. We have shown that by a combination of DLS and DXS the hydrodynamic function can be measured over a wide  $q$  range, without taking recourse to any theoretical model. The hydrodynamic interaction was found to slow down diffusion at all wave vectors. This result differs from earlier experiments on charge stabilized suspensions, demonstrating the need for further investigations.

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