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Suppression of multiple scattering in photon correlation spectroscopy

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Abstract. While static and dynamic light scattering experiments have been a major source of information about the structure and dynamics of dilute colloidal systems or macromolecular solutions, their application to more concentrated samples is severely limited by multiple scattering. Our dual-colour photon correlation experiment achieves very efficient isolation of singly scattered light by cross-correlation over the full range of scattering angles between 20° and 140°. The dual-colour cross-correlation technique immediately yields dynamic structure factors, which are not affected by multiple scattering. A second use of dynamic dual-colour cross-correlation measurements is in estimating the ratio of singly and multiply scattered light. Finally the experiment allows very successful recovery of static information from dynamic light scattering data on concentrated samples with central two-body interaction forces.

1. Introduction

Applications of dynamic light scattering [1] typically rely on the assumption of single scattering, i.e. every detected photon is assumed to originate from one single scattering process on one scattering particle inside the illuminating beam. Single scattering does indeed dominate if the intensity of the scattered light is very weak as compared to the intensity of the illuminating beam. Low particle concentrations and small measurement volumes are commonly used to ensure validity of the single scattering assumption.

Typical applications in industrial environments as well as fundamental studies on strongly interacting colloidal systems, however, involve samples at high concentrations. Such samples generally produce strong scattered intensities, unless the measurement volume is kept inconveniently small. Hence many photons will be scattered more than once and multiple scattering must be included in a proper analysis of the experiment. Unfortunately, a full analysis of multiple scattering involves very lengthy calculations, which depend strongly on the geometrical details of the experiment (see e.g. [2]). Even worse, the additional randomness due to a varying number of scattering events with random intermediate scattering vectors tends to mask details in the desired correlation data.

Additional averaging due to multiple scattering occurs both in static as well as in dynamic light scattering. The static experiment shows a shift of scattered intensity towards larger scattering angles. The dynamic experiment shows additional spectral components at higher frequencies. Both experiments show a decreased resolution with

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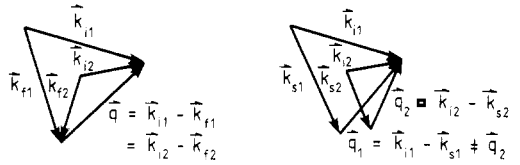

Figure 1. Wavevector arrangements for dual-colour cross-correlation, single scattering process (left) and first scattering process of a multiple scattering path (right).

increasing multiple scattering. However, the dynamic light scattering experiment may be modified to separate singly and multiply scattered light.

Such a modification was first suggested by Phillies [3, 4] and theoretically analysed by Dhont [5]. Phillies' experiment was, however, principally restricted to a scattering angle of 90° and required a rather cumbersome alignment procedure. We have recently overcome both these restrictions with a novel dual-colour set-up. The basic idea of this experiment as well as first applications to particle sizing and the study of strongly interacting colloidal systems are the central topics of this paper.

2. Dual-colour cross-correlation

Our dual-colour cross-correlation set-up [6] involves the use of colour coded beams to select only two of the possible four scattering paths in a dual-beam/dual-detector experiment. In order to obtain cross-correlation signals, we must use identical scattering volumes and identical scattering vectors $\boldsymbol{q}$ at both colours. The latter requirement implies different directions for the incident wavevectors $\boldsymbol{k}_{i1}$ and $\boldsymbol{k}_{i2}$ of the two illuminating beams as well as for the final wavevectors $\boldsymbol{k}_{f1}$ and $\boldsymbol{k}_{f2}$ selected by the two detection systems.

Figure 1 shows the desired arrangement of wavevectors, which leads to correlated singly scattered contributions in both colour channels. The 'decorrelation' of multiply scattered light is also demonstrated by a graph corresponding to the first scattering process in a multiple scattering path. Please note that the intermediate wavevectors $\boldsymbol{k}_{s1}$ and $\boldsymbol{k}_{s2}$ both have an identical direction, which is given by the relative position of the two scattering particles involved. With the exception of very few degenerate cases, the two scattering vectors $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ will not coincide and we cannot expect correlated contributions in the two colour channels. Theoretical estimates as well as experimental evidence support this result [7].

Figure 2 presents a schematic sketch of our experimental set-up. We use an argon ion laser operating at both the 488 nm and 514 nm wavelengths. Translation of the mirror M sets the angular difference between the two illuminating beams. The fibre coupled detectors 'look' at the same measurement volume and are adjusted to their proper locations in q-space through rotation of the goniometer (ALV SP-81) arm and the use of two small translation stages, which move the fibre tips.

For most experiments described here, all translation stages were controlled manually and a change of q typically took about 1 min. Full computer control by stepping motors has recently been completed and the accessible q-range has now been extended to 5–30 μm^{-1}, corresponding to angles between 20° and 140°.

3. Particle sizing

As a typical example for possible improvements in particle sizing we show results obtained on a monodisperse sample of 49.2 nm radius polystyrene latex spheres at a

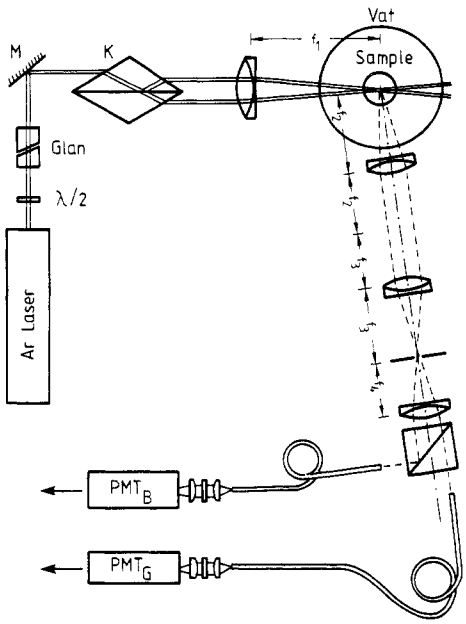

Figure 2. Optical set-up of the dual-colour cross-correlation experiment. M, mirror; K, dichroitic double Köster's prism.

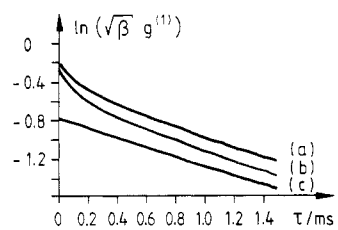

Figure 3. Measured auto-correlations at 514 nm (a) and 488 nm (b) and dual-colour cross-correlation (c) for $q = 10\,\mu m^{-1}$. Sample of free latex spheres.

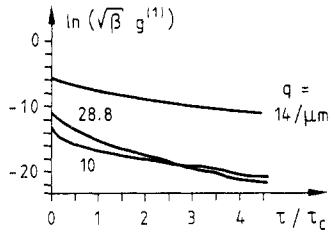

Figure 4. Dual-colour cross-correlation data obtained for interacting charged latex spheres at three different values of the scattering vector, below, at and above the peak position in the structure factor.

volume fraction of 0.0028 particles in a KCl solution (5 mmol l^{-1}). The salt concentration was chosen in order to shield electrostatic interactions efficiently. The particle concentration was small enough for us to ignore hard-core and hydrodynamic interactions as well.

Due to the high index of refraction of polystyrene as compared to water, the sample was highly turbid with a mean free path for photon scattering of the order of 1.3 mm. The incident beams were attenuated by scattering from the sample to as little as 0.002 of their initial intensity after the pass through the cuvette (inner diameter 8.4 mm).

The high degree of multiple scattering clearly shows up in the measured auto-correlation functions in figure 3. Instead of being straight lines, the displayed logarithms of $g^{(1)}(\tau)$ show a strong curvature, particularly at small lag times. Distortions are worse at the shorter wavelength, as is to be expected. A cumulant analysis [8] of these data

yields mean particle sizes 20% below the real value and completely exaggerated polydispersities.

In contrast, the dual-colour cross-correlation is almost a perfect single exponential and does, indeed, produce correct mean size (to 2% accuracy) and polydispersity, as checked by measurements at lower volume concentrations. Measurements at other values of the scattering vector and at even higher volume concentrations (up to 0.01) showed similar results and clearly demonstrated the usefulness of dual-colour cross-correlation for particle sizing in turbid samples.

The plot in figure 3 includes an intercept factor $\sqrt{\beta}$ [9]. β is significantly reduced by the ratio of single to multiple scattering in the cross-correlation experiment. This reduction may well be used for quantitative investigations of multiple scattering. Another possible application is the correction of static light scattering data, which are distorted by multiple scattering. However, our experience indicates unsatisfactory repeatability of β-measurements due to extreme alignment sensitivity.

4. Interacting samples

On placing the same latex particles as used above into very pure water, their effective surface potential of about 65 mV (measured by AWPS [10, 11]) creates sufficiently long-range electrostatic repulsion to produce strong interactions. Static light scattering data show a pronounced peak (>2.5) in the static structure factor. At a volume concentration of 0.0026 we obtained the dual-colour cross-correlation functions displayed in figure 4. The three correlation functions were measured at q-values below, at and above the first peak in the structure factor. In order to eliminate the q^2-dependence, lag times were plotted in units of $1/(q^2D)$, the decay time observed for free particles at the same value of the scattering vector q.

Both a more complicated q-dependence as well as a spread of time constants are clearly visible. In particular, the latter effect was completely masked by multiple scattering in ordinary auto-correlation measurements. The large variations in intercept are due to the pronounced static structure factor.

For colloids like our latex system, where central two-body interaction forces dominate, short-time expansions of the dynamic structure factor are well known to yield the static structure factor $S(q)$ as the initial slope [12],

$$\lim_{\tau \to 0} g^{(1)}(\tau) = 1 - q^2 D\tau / S(q). \tag{1}$$

This relation is extremely useful if turbidity of the sample strongly distorts measured static light scattering data, in particular at large scattering angles. Figure 5 provides an example. Again we used rather monodisperse 49.2 nm radius polystyrene latex in pure water. Even without form factor correction, we still observed a strong increase in intensity for large q at high sample concentration, as is typical for multiple scattering.

Figure 6 contrasts these static data with $S(q)$ as determined from dynamic dual-colour cross-correlation measurements through use of equation (1). The structure factors show the expected shift of the first peak towards larger q-values with increasing concentration as well as the rather small change in peak height, which has been noted by other experimenters on systems with 'soft' interaction potentials [13]. The large error bars on the highest concentration data are a consequence of the very small intercept and signal-to-noise ratio due to extreme turbidity of the sample.

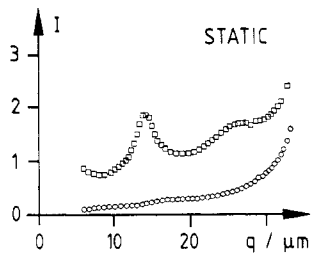

Figure 5. Static light scattering data obtained at the sample concentrations 0.0029 (squares) and 0.0044 (circles), showing severe multiple scattering distortions.

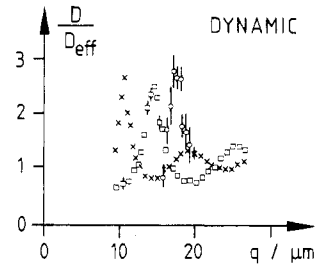

Figure 6. Static structure factor obtained from first cumulants of dual-colour cross-correlation experiments; sample concentrations as in figure 5 and 0.0013 (crosses).

Please note that short-time expansions of photon correlation functions are most strongly affected by multiple scattering distortions. Hence our ability to suppress multiple scattering proved to be absolutely essential in order to obtain reliable static structure factor data from dynamic light scattering experiments.

5. Conclusions

Light scattering in turbid colloidal suspensions generally suffers from multiple scattering. Measurement errors or at least a loss in resolution are typical consequences.

For dynamic light scattering experiments, dual-beam and dual-detector set-ups may be used to eliminate multiple scattering contributions by cross-correlation. We designed a dual-colour cross-correlation experiment that allows the isolation of light fluctuations due to single scattering over a large range of scattering angles. A well defined alignment procedure and a stable mechanical design allow reproducible adjustment and reliable operation of the device over long periods of time. Changes of the scattering angles are possible within less than one minute under full computer control.

In particle sizing applications, artificial polydispersity and shifts in measured particle radii due to multiple scattering are completely eliminated, even for samples with a transmission as small as 0.001. The only penalty involved is the increase in the total duration of the experiment required to achieve sufficient statistical accuracy, which results from the rapid decrease in intercept with increasing levels of multiple scattering..

The study of interacting systems may be extended to a much larger range of systems than previously accessible, since multiple scattering may be suppressed over a substantial range of scattering angles, again up to severe turbidities. The isolation of singly scattered light proved to be particularly important for short-time expansions of photon correlation data and the extraction of static structure data.

A first commercial version of our dual-colour cross-correlation experiment has recently (1989) been installed at an industrial laboratory (ALV Laser Vertriebsgesellschaft mbH, D-6700 Langen, Federal Republic of Germany).

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