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SINGLE-BEAM MULTIPLE SCATTERING SUPPRESSION BY CROSS-CORRELATION IN VOLUME LIGHT SCATTERING (VLS) – (Section I)

VLS-1. Introduction

Beginning with the advent of the laser, dynamic light scattering has proved to be an invaluable technique for determining the dynamic properties of a variety of systems. It has been used to study order-parameter dynamics near the critical points of both pure fluids and binary mixtures. It provides the most accurate method known of determining the diffusion coefficient of macromolecules such as proteins and polymers, as well as that of colloidal particles. Because the radius of a spherical particle is determined very simply from knowledge of its diffusion coefficient, dynamic light scattering has become the method of choice for measuring the size of colloidal particles [8].

The method is not without problems however. In particular, for strongly scattering samples, not all of the scattered light originates as the result of single scattering. Under these conditions, it can be difficult to interpret data in any reliable way. One exception to this situation occurs in the limit of extremely strongly scattering samples, where the photons may be treated as diffusing throughout the sample [9-11]. In this case it has proved possible to deduce useful information regarding short time scale dynamics of the process giving rise to the scattering.

For dynamic light scattering in the intermediate regime where high order scattering is significant but the diffusing photon limit has not been reached, the most effective experimental method yet devised for dealing with multiple scattering is the cross-correlation technique invented by Phillips [12, 13], and extended by others [14-16]. Phillips’ method relies on the fact that in order for the incident light to be scattered in a particular direction, the wave vectors of the incident and scattered light must be coupled by that of the dielectric constant fluctuation responsible for the scattering, in a scattered momentum transfer \( q = k_i - k_s \) (see Ref. [8], p. 6). Here \( k_i \) is the wave vector of the incident light, \( k_s \) is that of the scattered light, and \( q \) is the wave vector of the fluctuation responsible for the scattering.

Because of the Bragg condition, two different beam-detector combinations can be aligned so as to simultaneously collect light which has been scattered by the same fluctuation. Of course, the two detectors also collect light which has been multiply scattered. This results in detector signals \( i_s(t) \) and \( i_s(t) \) which arise from both single and multiple scattering contributions. The single scattering contributions are strongly correlated with each other at all times, while the multiple scattering components are only weakly correlated. Measuring the temporal cross-correlation function of the two detector outputs \( \langle i_s(t) i_s(0) \rangle \), then provides the same information as would be obtained in the single scattering limit using a conventional single-beam, single-detector arrangement to measure \( \langle i(t) i(0) \rangle \).
Although feasible, the cross-correlation technique summarized above is expensive and difficult to align in practice. As a possible alternative, we [2, 17-24] and later others [25, 26] explored the possibility of using a single-beam, two-detector system. The basic idea hinges on the observation shown in Fig. I-1 that single scattering originates exclusively from the region of primary illumination, typically the small cross-section of a focused laser beam. Multiple scattering however arises from a broader ‘halo’ surrounding the incident beam, and thus appears to come from a significantly larger source.

Because scattered light arises from a spatially incoherent source, its spatial coherence properties are determined by the apparent dimensions of the source as viewed by the detector (van Cittert-Zernike theorem [27]). Consequently singly scattered light gives rise to correlated patches (time-dependent speckle) which are typically much larger in one dimension than they are in the other.

![Fig. I-1. Relative speckle size for single and multiple scattering.](image-url)
As shown in Figs. 1-1 – 1-3, they are large in the dimension in which the source appears small, namely transverse to the incident beam, and small in the dimension in which the source appears large, that is parallel to the incident beam. Multiply scattered light also gives rise to time-dependent speckle, but since the smallest source dimension for multiple scattering is larger than that for single scattering, the multiple scattering speckles are smaller than the single scattering speckles in the direction transverse to the incident beam.

We were the first to point out [17, 21] and the first to demonstrate experimentally [18-20] that this idea, regarding the relative sizes of speckle arising from single versus multiple scattering, can be used to discriminate single from multiple scattering. This was accomplished by using two optical fibers leading to two separate detectors to collect scattered light at two closely spaced positions. We used optical fibers which were single-mode for 632.8 nm to collect scattered light at 514.5 nm. However single mode behavior is not necessary for the results reported below because each fiber only conveys light to a detector, with the fiber core acting as a small physical aperture stop. The fibers were not terminated with lenses, and thus served simply to collect light at two small regions. The two fibers were placed sufficiently close together to lie within one speckle of the singly scattered light, but not within one speckle of the multiply scattered light. Under these conditions we found that the cross-correlation function of the two detector outputs yielded useful data for the diameter of colloidal spheres, even when sample concentrations were

Fig. 1-2. The x and y axes represent the correlated intensity pattern from a cylindrical sample: $G_0 = \langle I_A(0) I_B(\Delta q) \rangle$ as a function of $\Delta q R_x$ and $\Delta q R_y$, where $R_x$ and $R_y$ are the dimensions of the scattering volume and $\Delta q$ is defined by the angle $q$ formed by the separation between the two fibers shown in Fig. 1-4.

Fig. 1-3. Horizontal cut through the speckle. The solid black lines designate the positions of the detectors. When the detectors are placed this far apart only single scattering will contribute to the time correlation function obtained by cross-correlating the signal from the two detectors. The measured correlation function is [1]:

$$\langle I_A(0) I_B(\Delta q, \tau) \rangle_q,$$

where $\Delta q$ is defined by the angle $q$ formed by the separation between the two fibers A and B.
so large as to render the 10 mm diameter samples visually opaque. The speckles shown in Figs. I-1 and I-2, and the placement of the detectors shown in Figs. I-3 and I-4 show how we select single scattering in the presence of multiple scattering. Later, in Fig. I-19 we will show how X-ray scattering, which has reduced contrast supports, our claims that we are able to detect single scattering in the presence of multiple scattering.

A supporting theoretical analysis has been provided elsewhere [1, 28] by our collaborator J. A. Lock.

VLS-2. Experimental Method

Our experimental arrangement is shown schematically in Fig. I-4. The cylindrical sample cells were 10.1 mm inner diameter glass test tubes of 11.6 mm outer diameter, held rigidly on the axis of a cylindrical glass vat containing either water or decalin as index matching fluid. The vat had an inner diameter of 80 mm and an outer diameter of 84.6 mm. Light from an argon-ion laser of vacuum wavelength $\lambda_0 = 514.5$ nm was brought to a focus near the axis, with a $1/e^2$ diameter of about 88 $\mu$m using a lens of focal length 100 mm. The beam entered the vat through a small polished flat area (not shown in Fig. I-4). Since the samples were suspensions of colloidal particles in water, some distortion of the focus occurred upon entering the sample cell when decalin (refractive index 1.48) was used as the matching fluid, but it had no observable effect on the results. Better optics for scattering from highly concentrated systems may be envisaged using square cuvette (which we discuss later), but this change does not affect the conclusions reported here. Our present geometry uses the sample cell and optional index matching vat as a cylindrical lens [29, 30], as shown in Fig. I-5, and thus collects light of a single scattering angle from along the entire beam path (when the illuminating beam has not been extinguished by turbidity). A ray-trace for this optical design is shown in Fig. I-5. Note that for a cylindrical lens
the focus, \( f \), for scattering from a single scattering angle is at \( f = R \frac{n}{n-1} \), where \( R \) is the radius of the cell (the index matching vat in this case) and \( n \) is the index of refraction of the liquid. For water, where \( n = 1.33 \) and a cell of radius 84.6 mm / 2 mm the focus is at approximately 170 mm. In actual practice, this positioning of the detection fibers is quite forgiving. From the ray-trace shown in Fig. 1-5, it is evident that the addition of an iris to stop the outermost rays from the edge of the sample cell provides highly collimated light at the detection fiber. For scattering from dilute single scattering samples the amount of light scattered does not change with angle. This has advantages that we will discuss in a later section when we address a technique for flare rejection that involves adding a sufficiently strong local oscillator.

To collect scattered light from two nearby points in the far field, we arranged the polished ends of two optical fibers, which are single-mode for 633 nm, to touch at the cladding diameter so that the cores were 0.25 mm apart. We placed the end of this fiber pair 170 mm from the system axis just above the horizontal plane containing the incident beam, with the fibers one above the other; that is, separated in the direction transverse to the beam, the direction in which the single scattering speckle is large. Being slightly above the plane reduced the flare effects of multiple internal reflections for this geometrical configuration. Flare effects need to be avoided since they can act as a local oscillator which can deleteriously move the measured decay times away from the self-beat regime toward the homodyne regime [2, 5, 31]. Given a beam diameter of 88 \( \mu \)m, the vertical extent of the single scattering speckle should be of order \( (\lambda / d)R \approx 1.0 \) mm at a distance of 170 mm. Consequently the two fibers, separated by only 0.25 mm, should collect light which is well correlated provided it originates only within the incident focused beam. For our geometry, the scattered light consists of small speckles which are much taller than they are wide, and which fade in and out of existence continually at any one place as the particles diffuse. Since the two fibers often lie within a single speckle the optical powers they each collect tend to be correlated. Careful visual observation of samples which exhibit multiple scattering reveals an apparent bright line (scattered light emerging directly from the beam itself) lying within a much larger and more diffuse region. This diffuse source is light which has been scattered out of the illuminating beam and has subsequently been rescattered one or more times, with the final scattering event directing it into the eye. Since this source appears larger than the beam, we expect it to produce speckle which is much shorter vertically than the 0.25 mm separation of the fibers, and thus to contribute little to the cross-correlation of optical powers collected by the two fibers. Because both the single and multiple scattering sources have about the same dimension parallel to the incident beam, we would not expect to discriminate single scattering were the fibers separated horizontally rather than vertically.

We have not yet attempted to optimize the fiber spacing chosen using the rough criteria described above. This is partly because no single optimum angular separation may exist. The optimum depends not only on the optical geometry, but also on the scattering cross section, because its magnitude and angular dependence clearly affect the apparent source dimension for multiple scattering. Thus from a practical point of view optimization will also probably depend on the nature and concentration of the sample. See however the paper by Nobbmann et al. [25] which reports results obtained using our method but with variable fiber spacing.
The light collected by each fiber was delivered to an actively-quenched silicon avalanche photodiode (EG&G Optoelectronics Canada, model SPCM-AQ-141-FL) capable of single photon counting. These detectors produce ~10 ns TTL level pulses at rates proportional to the instantaneous optical power reaching each detector. The resulting pulse streams \( n_a(t) \) and \( n_b(t) \) were fed to a Brookhaven Instruments model BI-9000AT digital correlator which can compute either the temporal auto-correlation function

\[
G(\tau) = \langle n(t + \tau) n(t) \rangle
\]

(1.1)

for either pulse stream, or the temporal cross-correlation function

\[
G_{\lambda\beta}(\tau) = \langle n_{\lambda}(t + \tau) n_{\beta}(t) \rangle = \langle n_{\beta}(t + \tau) n_{\lambda}(t) \rangle
\]

(1.2)

for both.

The correlator determines the number of counts received during each interval \( (t, t + T) \), which we have denoted by \( n(t) \) in Eqs. (1.1) and (1.2). By simultaneously forming the products of the current \( n(t) \) value and the \( n \) values corresponding to 256 different delay times \( \tau \), and accumulating these products for a sufficient time, an acceptably accurate measurement of either \( G(\tau) \) or \( G_{\lambda\beta}(\tau) \) can be formed. Note that the correlator actually computes an approximate correlation function since the time series is of bounded length and averaged over a finite number of time series.

The nominally 107 nm or 204 nm diameter particle samples obtained from Bangs Laboratories were suspensions of polystyrene latex spheres in distilled water. (The particle sizes we quote are based on hydrodynamic radii. When electron microscopy is used to verify dynamic light scattering standards, the polystyrene latex spheres are dried before being measured, thus giving a reduced value for the measured diameter.) We show data with concentrations that range from 0.0017 weight % to as high as 5 weight % in some cases. We initially measured particle diameters for dilute suspensions that were essentially free from multiple scattering by using conventional optics at a 90° scattering angle. The extremely dilute samples scattered so little light compared with residual flare that more consistent measurements were obtained from 0.01 weight % samples which were still essentially transparent. Samples of different concentrations were prepared by diluting a suspension of polystyrene latex spheres, supplied at a nominal concentration of 10 weight %, determined by the manufacturers by evaporation to dryness and stated to vary by as much as ±10%. The diluent was distilled water filtered with a pore size of 0.22 microns, to remove dust. It was not found necessary to further filter the samples after dilution. The specimen tubes were rinsed with similarly filtered water before charging and sealing with ‘parafilm’.
VLS-3. Results

To quantify the way multiple scattering affects the auto-correlation function, we measured $G(\tau)$ for a number of suspensions of the nominally 107 nm diameter spheres with concentrations ranging from 0.0017 weight % initially up to 1 weight %. The measurements were made at a 90° scattering angle using one of the two optical fibers to collect the scattered light. Results for the normalized auto-correlation functions $G(\tau)/B - 1$ versus delay time $\tau$, are shown on a semilog plot in Fig. 1-6 for six different concentrations. Fig. 1-6 was prepared using baseline values determined by fitting a single exponential where intercept, baseline and exponential coefficient were all allowed to float. Typically the fitted baseline and the baseline calculated within the correlator from the sample time and actual number of pulses received agreed to within a few tenths of a percent or better. As we shall see later, this difference should not be ignored for the later cross-correlation functions from which it is possible to extract good size measurements even when the zero delay time intercept becomes extremely small.

For monodisperse samples of sufficiently low concentration that they are free from multiple scattering, plots such as those shown in Fig. 1-6 should be linear, and indeed those corresponding to the two lowest concentrations appear very nearly so. Examining the auto-correlation functions of the higher concentration samples reveals that $G(\tau)$ becomes increasingly non-exponential. The rapid initial decay evident for the 0.5 and 1.0 weight % samples is characteristic of strong multiple scattering [9-11], supported by the obvious visual opacity of the samples.

![Normalized autocorrelation functions for increasing concentrations of nominally 107 nm diameter polystyrene latex spheres in aqueous suspension.](image)

Fig. 1-6. Normalized autocorrelation functions for increasing concentrations of nominally 107 nm diameter polystyrene latex spheres in aqueous suspension.
Cross-correlation functions $G_{AB}(\tau)$ for the same samples were measured using each of the fibers to collect the scattered light at nearby points. Some of these measurements are presented in Fig. I-7, which shows $G_{AB}(\tau)/B - 1$ versus $\tau$ on a semilog plot. Because the decaying portion of $G_{AB}(\tau)$ is only a small fraction of the baseline $B$ for the cross-correlation data, especially for the higher concentration samples, we determined $B$ for each data set by fitting to a single exponential decay plus a baseline. That the curves of $G_{AB}(\tau)/B - 1$ presented in Fig. I-7 are linear to within experimental accuracy shows that the cross-correlation data for all the concentrations studied are consistent with single exponential decay. This is in marked contrast with the results for the auto-correlation measurements shown in Fig. I-6, which clearly contain a broad spectrum of decay rates for the higher concentration samples.

Quantitative analysis of the data was performed on the measured cross- and auto-correlation functions by the two-cumulant expansion given by

$$G_{AB}(\tau) = A \exp \left[ -2 \left( K_1 \tau - \frac{K_2}{2} \tau^2 \right) \right] + B$$

(1.3)

with $A$, $B$, $K_1$, and $K_2$, adjustable. This method of analysis is commonly used for polydisperse samples that exhibit a range of decay rates, as do our auto-correlation functions. For the many sets of cross-correlation data, fits including the second cumulant, show a consistent value of about 0.028 for the reduced second cumulant. This low value, conventionally associated with polydispersity justifies the validity of a single exponential fit as a method of estimating
relaxation time and hence particle diameter. We related the first cumulant to an effective diffusion coefficient \( D \) [32], by

\[
K_1 = D \, q^2
\]  \hspace{1cm} (1.4)

where \( q \) is the scattering wave vector given by

\[
q = \frac{4 \pi n}{\lambda_0} \sin \left( \frac{\theta}{2} \right)
\]  \hspace{1cm} (1.5)

Here \( n \) is the refractive index of the suspension, and \( \theta \) is the scattering angle. We obtained an apparent particle diameter from

\[
D = \frac{k_B \, T}{6 \pi \eta a}
\]  \hspace{1cm} (1.6)

Here \( k_B \) is Boltzmann’s constant, \( T \) the absolute temperature, \( \eta \) the viscosity, and \( a \) the apparent particle radius. The results of this analysis are summarized in Fig. I-8, which presents the apparent particle diameter versus sample concentration derived from both the auto- and cross-correlation functions. The results from auto- and cross-correlation agree reasonably well at the lowest concentrations, but disagree seriously for the higher concentration samples. Two main conclusions can be drawn from Fig. I-8. Firstly, multiple scattering can so severely distort auto-correlation function data as to result in apparent particle diameters more than an order of magnitude smaller than the true diameter. Secondly, the simple artifice of cross-correlating the scattered intensity at two nearby points virtually eliminates this effect.

Further results from the data analysis are shown in Fig. I-9, which displays...
the zero delay time intercept for each correlation function analyzed to produce the results already shown in Fig. I-8. Here we see that while the auto-correlation intercept changes little for the more concentrated samples, the intercept for cross-correlation falls steeply. This occurs because a smaller fraction of the detected light is correlated for the more turbid samples as the ratio of multiply scattered light to singly scattered light increases. We find that excellent estimates of particle diameter are obtainable from cross-correlation functions acquired in times not significantly longer than those conventionally used for auto-correlation and dilute suspensions. This is the case even for the cross-correlated signal for the more concentrated samples, which have an extremely small signal amplitude. Both theory and our experience with samples having an even higher concentration than those shown in Fig. I-8 have shown that for the case of even higher concentrations either a longer run time or a smaller diameter sample cell may be required. Note that because of the rapid initial decay of the auto-correlation functions for the more concentrated samples, the near constancy of the zero delay time intercept is not apparent when the data are displayed as they are in Fig. I-6.

There appears a small, but noticeable drop in the particle sizes derived from cross-correlated data at the higher concentrations. Results of modeling for hard-sphere interactions are shown in Fig. I-10. For volume fractions below 5% the difference between the piece-wise continuous model used by Pusey and Tough [33] and the Percus-Yevick model differ only in the third decimal place, and these models are nearly identical for our concentration range. However, neither of the models represented in Fig. I-10 accounts for ionic potential, which increases with volume fraction. Please note that FORTRAN software for the Beenakker-Mazur model, which works at higher concentrations than those shown in Fig. I-10, is provided in Appendix I-A. The hard-sphere interaction model shows the right trend to explain the droop, but this appears quantitatively insufficient to account for the changes seen in the effective particle size. Since all multiple scattering suppression schemes have some ‘leakage’ we have addressed this concern [34] by optical masking to remove some of the excess multiple scattering. For this we

![Fig. I-10](image_url)

*Fig. I-10. Computed effects of interactions for different particle diameters vs. concentration (piecewise continuous and Percus-Yevick are essentially identical in this concentration range). Ionic interactions are not accounted for in this model.*
have also added a vertical slit, instead of the circular iris that was used for obtaining the data in Fig. I-8. With this approach, a significant additional improvement is realizable by examining the sample confined near the corner of a square cuvette. These two additions, shown in Fig. I-11, result in much enhanced intercept values, that is, we can now use shorter data acquisition times to acquire for data of a similar quality. Alternatively, data of higher quality should now be obtainable from highly concentrated systems using the measurement times previously required.

With industrial applications in mind, we pursued using our multiple scattering suppression technique with these two additions changes when for rapidly sizing particles over a large range of concentrations. We were able to get reasonable diffusion coefficient measurements in two minutes, as shown in Fig. I-13, because the vertical slit blocked a significant amount of multiple scattering that would have been in the field of view on either side of the detection fibers and because there is less multiple scattering near the entrance of the sample cell. The improved intercepts obtained are shown in Fig. I-12. While the data that we acquired using measurement
times longer than two minutes was of higher quality, a careful reacquisition of those same data sets could achieve data of similar quality in much less time by using the approach just outlined. Without belaboring this point, we will refer to our higher quality data to as we continue our discussion.

To give some impression of the quality of the fits in Figs. 1-6 and 1-7, Fig. 1-14 and Fig. 1-15 shows deviation plots of the difference between fit and data, normalized by the amplitude $A_i$ of
the decaying portion of the correlation function. Fig. I-14 is for the cross-correlation data of Fig. I-7 corresponding to sample concentrations of 0.2, 0.5, and 1.0 weight %. Eq. (I.3) provides a good, but perhaps not perfect, description of the cross-correlation function when the detection of multiple scattering is suppressed. For comparison, Fig. I-15 displays similar plot for the three auto-correlation functions of Fig. I-6 for the same high concentration samples. As expected, these data are clearly and systematically non-exponential. A quantitative measure of the overall scattering power of the various samples may be obtained from the fraction of the incident beam power transmitted through the 10.1 mm diameter samples. Results of our attempts to make such measurements for various concentration samples of the nominally 107 nm diameter particles are shown in Fig. I-16. The points show the results of two separate measurements of transmission for the same samples taken some weeks apart and with different optics. The measurement of the ratio of scattered intensity, $I_s$, (or power) to incident intensity, $I_i$, (or power) is referred to as
the Beer-Lambert law when high concentrations are not involved. When high concentrations are not involved this ratio is related to turbidity, $\tau^*$, for the pathlength $R$, by $\frac{I_S}{I_i} = \text{Exp}[-R \tau^*]$.

This is related to the Rayleigh ratio, $\mathcal{R} = \frac{I_S}{I_i} \frac{R^2}{V}$ (where $V$ is the scattering volume), by the integration of $\mathcal{R}$ over the whole solid angle: $\tau^* = \int_0^\Omega \mathcal{R} \, d\Omega(\theta, \phi)$ [35]. The solid curve in Fig. I-16 is calculated from the theoretical Mie scattering cross-section. The calculated and measured results agree reasonably for concentrations below about 0.5 weight %, but above that concentration the measurements lie increasingly above the theory. We believe that the increasing excess of measured power over the Mie model is the result of the detector observing a small amount of scattered light, which becomes increasingly more significant as the transmittance reduces.

The main conclusion from these results is that even for samples transmitting less than one part per million of the incident power, spatial cross-correlation allows accurate determination of particle size. Note however, that under such strong scattering conditions most of the single scattered light detected must have originated within a millimeter or so of the point where the beam enters the samples.

We now extend the measurements to angles other than 90°. We measured both auto- and cross-correlation functions for the same set of various concentration samples of the nominally 107 nm spheres at scattering angles of 60°, 90°, 120°, and 135°. These data were analyzed by fitting the correlation function using Eq. (1.3) as before, with $A$, $B$, $K_1$, and $K_2$ adjustable. The apparent
Particle diameters are presented in Fig. I-17. The values of diameter inferred from the auto-correlation functions are severely influenced by multiple scattering for the higher concentration samples. They are also dependant on scattering angle, yielding a systematic underestimate of the particle size which gets worse as the angle is moved more to the forward direction. In contrast, values of diameter inferred from the cross-correlation functions show no systematic dependence on scattering angle even at the highest concentrations. However the values of diameter estimated from the cross-correlation functions do show a progressive decrease at concentrations of 1 weight % and above. This effect could arise from repulsive interactions among the particles, or it might be an artifact of our optical geometry.

To verify the applicability of the method to particles of a different diameter we present results in Fig. I-18 for 90 ° scattering from particles of a similar material but a nominal diameter of 204 nm. The stability of the first cumulant from the cross-correlation function, and hence the inferred particle diameter, as the suspension concentration increases to opacity, is encouraging. The rapid increase in value of the first cumulant from the auto-correlation functions shows the usual particle size underestimate from the auto-correlation function.
when multiple scattering is significant. The cross-correlation results correspond to a diameter of 214 nm in very reasonable agreement with the nominal value.

VLS-4. Discussion

Our experimental results demonstrate the promise of the new method of spatial cross-correlation originally proposed [17] and described by Meyer et al. [18-20]. The ability to make reliable easily interpretable dynamic light scattering measurements on strongly scattering samples is valuable in both basic research and in industrial applications. Examples of research areas where multiple scattering is significant, and measurements currently difficult, include the study of particle dynamics in strongly interacting systems, critical point phenomena, and in vivo biological and medical studies. Examples of the many industrial applications include characterization of various slurries used for grinding and polishing, paint particle studies, sizing of particles in concentrated suspensions, and quality control of products which may involve colloidal intermediate stages.

In this text, we have emphasized and demonstrated the feasibility and reliability of the method as applied to colloidal suspensions. We have used simple collection optics consisting of adjacent bare fibers without collimation lenses. Each fiber collects light from along the entire sample, which is not the most effective way to selectively discriminate against multiply scattered light. A better method might be to use collimating lenses to restrict the accepted light to that originating in a localized portion of the sample or, as we showed, placing a vertical slit in front of the detection fibers. Using bare fibers has the advantage, however, of being extremely easy. We calculated and confirmed experimentally that the distance of the fibers from the focus formed by the sample cell or the sample cell and its accompanying index matching vat is rather forgiving. The only critical alignment is the vertical alignment of the fibers so that the line joining the centers of their exposed faces is perpendicular to the beam. In practice we achieved this by rotating the fiber pair about an axis parallel to the fiber axes to maximize the amplitude of the cross-correlation function measured for a single scattering sample. No other alignment was necessary, and the fibers remained aligned for many months.

For isotropic particles, single scattering is highly polarized; multiple scattering is not. An analyzer allowing the fibers to accept only $I_{\|}$ restricts the sensitivity of the cross-correlation function to multiple scattering only. This rather simple test was used to confirm that the chosen fiber spacing was adequate to suppress the multiple scattering contribution to the cross-correlation function. For our fiber spacing, corresponding to an angular separation of 1.5 mrad, the multiple scattering contribution was immeasurably small. By making such measurements as a function of the fiber spacing, or equivalently the angular separation of the two fibers, one can quantify exactly how the multiple scattering contribution to the cross-correlation function reduces with increasing fiber separation. Such measurements have been made both for $I_{\|}$ and $I_{\perp}$ by Nobbmann et al. [25], using an arrangement nearly identical with ours, but with each fiber terminated by a collimating lens. Their results clearly demonstrate the correctness of the physical ideas which guided our invention of this technique, specifically the relatively much greater extent of single scattering speckle as opposed to multiple scattering speckle, in the direction transverse to the beam.

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As our results show, the amplitude of the cross-correlation function relative to the baseline falls dramatically as multiple scattering increases (see Fig. 1-9). This is because the baseline is proportional to the square of the detected total intensity, while the amplitude of the decaying portion is proportional to the square of the detected intensity from single scattering alone. This observation leads to the possibility of using the measured zero delay time intercept for cross-correlation to deduce the fraction of the total scattered intensity arising from single scattering. Specifically, the ratio of the measured intercept to its value for single scattering dilute from samples, is equal to the square of the ratio of the detected single scattered intensity to the total intensity.

Applying this reasoning to the data for the 1 weight % sample, for example, suggests that only about 4 % of the light reaching the detectors was singly scattered. If this sort of analysis proves robust in practice, spatial cross-correlation may make static light scattering measurements usefully quantitative even for very strongly scattering samples.

VLS-5. Future Applications in Volume Light Scattering

Considering future applications of our work on multiple scattering suppression, the obvious application of significantly extending the concentration range of dynamic light scattering has been augmented by the insights inspired by the recent availability of high brilliance X-ray sources from a synchrotron. A partially coherent beam of X-rays can now be formed to perform dynamic X-ray scattering (DXS) [24, 36-38] on length scales, until recently the sole domain of light scattering [8, 39]. The combination by Riese et al. [7, 24, 40-42] at UvA of the cross-correlated dynamic light scattering [19] introduced above with DXS and Small Angle X-ray Scattering (SAXS) allows optically opaque colloidal suspensions to be probed in a way that reveals novel physics: the phenomenon of hydrodynamic screening [40]. See Fig. 1-19 on the next page for proof that dynamic cross-correlation and dynamic X-ray scattering obtain the same results in a multiple scattering solution, where dynamic autocorrelation breaks down.

We have also looked at combining cross-correlation with a local oscillator to address the ill-conditioning problems introduced by flare light [2, 3, 5, 31]. Essentially the local oscillator pushes the scattered light signal to an asymptotic limit and cross-correlation provides the added benefit of mitigating the affects of multiple scattering. The advantages of adding a local oscillator include an increased signal-to-noise, reduction of stray light effects, a larger allowed angular range and the ability to use smaller specimens due to the reduction of stray light effects, improved resolution of multiple particle sizes because only the cross-terms of the beating process are then significant, the signal no longer has to be Gaussian, and weak signals benefit from the gain supplied by the local oscillator [2] (see Fig. 1-20). While the gain of adding a local oscillator is significant, combining our cross-correlation technique described above to a local oscillator using monomode fibers and couplers for wavefront matching deserves future studies, as outlined by Meyer et al. [2, 3] and Smart et al. [5] in their papers and patent (pending).
Fig. 1-19. A comparison of Dynamic Light Scattering (DLS) using autocorrelation and cross-correlation with Dynamic X-ray Scattering (DXS). This shows that autocorrelation breaks down due to multiple scattering, which results from the difference in index of refraction of the particles ($m_1$) and solvent ($m_2$) and sample thickness traversed before exiting at a particular scattering angle in Fig. (a) being greater for much of the scattered light than in Fig. (b). Figs. 1-19 (a) and (b) indicate results obtained for scattering angles of 30° and 110°, respectively. DXS is not susceptible to multiple scattering and provides the same results as our cross-correlation technique, i.e., a straight line on a semi-log plot. Because of multiple scattering, the decaying exponential (whose semi-log plot is a straight line) is not the signature of the autocorrelated signal.
Fig. I-20. As noted above, in Meyer et al. [2, 3], and in Smart et al. [5], the addition of a local oscillator allows one to move out of the equation fitting region where small amounts of flare light corrupt the data analysis. Additional benefits of this approach are described in section VLS-5, which is entitled “Future Applications in Volume Light Scattering”. To aid in identifying the symbols in the figure above, only every 20th data point is shown for the hollow symbols and every 5th data point for the solid symbols.

VLS-6. Appendix I-A: Hard Sphere Diameter Compensations

Existing models for hard sphere interactions from Pusey and Tough, and from Percus and Yevick have been examined, in certain specific cases and up to a volume concentration of 0.075, and shown to be similar, but not identical. Circumstantial evidence was available from the original Applied Optics data and its reprocessed versions to suggest the importance of correction of measured diameter, using some external knowledge. To become useful, this work must be extended. The cross-correlation technique has now been sufficiently improved by using square cuvettes and optical masking slits to make better measurements in volume concentrations comparable with the limits of the above calculations, offering the possibility of empirical closure where none was previously available. Also it would be useful to study the Beenakker model,
which purports to handle higher concentrations, with a view to its correspondence with both the Pusey-Tough and Percus-Yevick predictions, in the regions were they have common territory. The Percus-Yevick source code used in Fig. 1-10 is included as an Appendix on the CD ROM that accompanies this text.