Low-coherence heterodyne photon correlation spectroscopy

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ABSTRACT

Photon Correlation Spectroscopy (PCS) is routinely used to investigate the dynamics of colloidal particles undergoing Brownian motion. This technique is applicable to low-density colloidal suspensions where the effects of multiple light scattering are minimal. We introduce a new low-coherence heterodyne PCS technique that allows direct investigation of colloidal suspensions of higher concentration than previously accessible using standard PCS. In this technique, low-coherence optical heterodyne interferometry is used to suppress multiple light scattering, allowing preferential detection of single scattering events.

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1. INTRODUCTION

Photon correlation spectroscopy (PCS) is a time-domain dynamic light scattering technique that seeks to extract information about the dynamics of colloidal particles in suspension. The modern roots of this technique date from the early 1960’s\textsuperscript{1,2}. Since that time PCS has been used to investigate a wide variety of colloidal suspensions in the fields of biology, chemistry, and physics\textsuperscript{3,4}. Despite its practical success, PCS is limited to very dilute (single scattering) samples. This makes it impossible to apply this technique to study the particle dynamics of a wide range of naturally occurring colloidal suspensions without dilution.

More recently diffusing wave spectroscopy\textsuperscript{5,6,7,8} (DWS) has been introduced as a technique to study dynamics of colloidal particles in dense random media where multiple scattering dominates. DWS allows useful information about particle dynamics to be extracted from samples where the photon behavior is diffusive, \( L/\ell^* > 1 \), where \( L \) is the sample cell thickness and \( \ell^* \) is the photon transport mean-free-path length or random walk step size.

In this paper, we describe a low-coherence heterodyne photon correlation spectroscopic transmission technique which extends the scatterer concentration range that can be successfully investigated in a photon correlation experiment. This technique enables the study of colloidal suspensions that possess a threefold increase in concentration beyond what can be probed by traditional PCS. This new technique partially fills a concentration niche between traditional PCS and DWS. We find that the scattering coefficient, i.e. the number of scattering events per unit sample length, is the critical parameter that determines the range of applicability of low-coherence photon correlation spectroscopy.

2. DESCRIPTION OF THE EXPERIMENT

We have used a low-coherence heterodyne detection scheme\textsuperscript{9,30} to suppress multiply scattered light and preferentially detect single scattering events. Figure 1 illustrates the modified Mach-Zehnder experimental arrangement. Two laser sources were used, in turn, to investigate the effect of source coherence length. The “long” coherence length source was a HeNe laser (633 nm) possessing a coherence length of 0.4 m, while the “short” coherence length source was a diode laser (800 nm) with a 400 \( \mu \text{m} \) coherence length. The aperture in front of the photo-diode detector PD was a 200 \( \mu \text{m} \) pinhole and the sample to detector distance was \( \approx 46 \text{ cm} \).
Figure 1: The modified Mach-Zehnder interferometer used to conduct a heterodyne photon correlation spectroscopic experiment. A diode laser (800 nm) and a HeNe laser (633 nm) were used along with other major components; SF, spatial filter; BS1, BS2, beamsplitters; AOM1, AOM2, acousto-optic modulators; BE, beam expander; TS, translation stage; PH1 (1 mm), PH2 (200 μm), PH3 (1 mm), pinholes; and PD, a photodiode detector. The lock-in reference was obtained by electronically mixing the 80.1 MHz and 80 MHz signals.

The light in the reference arm of the interferometer (lower arm of Fig. 1) was Doppler shifted by using two acousto-optic modulators (AOMs). The first modulator upshifted the frequency by 80.1 MHz while the second modulator downshifted it by 80 MHz. This provides the net 100 kHz frequency shift necessary for our lock-in detection scheme. It should be noted that the diode laser possessed sufficient coherence to allow normal AOM operation. A right angle prism mounted on a motorized translation stage provided the variable delay required to match the optical path lengths of the two interferometer arms.

The key experimental idea is that the path length of the two interferometer arms are matched for light that has scattered once in the sample cell. Such single scattered light will add coherently with light from the reference arm while light that has multiply
scattered a distance greater than the source coherence length will add incoherently. The coherent component of the detected signal may only be a small fraction of the optical radiation impinging on the detector. This coherent component, however, will be seen to beat at 100 kHz, owing to the Doppler shifted reference arm. Thus, the lock-in amplifier will detect a 100 kHz signal whose magnitude is fluctuating due to scatterer motion while ignoring the larger incoherent intensity.

The autocorrelation function of this fluctuating coherent signal is computed and fit to the single exponential decay model appropriate for a monodisperse colloidal suspension,

\[ G(\tau) = 1 + Ae^{-2Dq^2\tau} \]

where \( A \) is a parameter related to the number of coherence areas seen by the detector, \( D \) is the translational diffusion constant of the colloidal particles, \( q \) is the scattering vector, and \( \tau \) the temporal variable. The translational diffusion constant for spherical particles is given by the Stokes-Einstein relation as

\[ D = \frac{k_BT}{6\pi\eta r} \]

where \( k_B \) is Boltzmann's constant, \( T \) the absolute temperature, \( \eta \) the viscosity of the suspending fluid, and \( r \) the colloidal particle radius. The scattering vector is related to the scattering angle \( \theta \) by \( q = (4\pi/\lambda) \sin(\theta/2) \), where \( \lambda \) is the wavelength of light in the suspending fluid. Thus, the characteristic decay time of the intensity autocorrelation function \( (1/2Dq^2) \) for a suspension of monodisperse colloidal particles can be varied significantly by changing the scattering angle. A scattering angle of approximately 10° was used so that the detected intensity fluctuations would be slow enough to permit lock-in detection.

The path lengths of the two interferometer arms were initially matched by replacing the sample cell in Fig. 1 with a deflection mirror, adjusted for 10° deflection, and a compensating cell. This compensating cell was our standard sample cell filled with filtered water. The translation stage (TS) was then adjusted until the maximum beat signal was observed on the lock-in (i.e. the interferometer arms were of equal optical path length). This initial alignment procedure yielded an interferometer that was close to the final matched condition. The interferometer was converted to its final experimental configuration, shown in Fig. 1, by removal of the deflection mirror with the compensating cell now playing the role of sample cell. Final optical path length matching was accomplished by filling the sample cell with the colloidal suspension to be studied.
The motorized translation stage (TS) was then moved under computer control and the laser source interferogram recorded, essentially the beat signal amplitude versus optical path length difference. During this matching procedure the lock-in time constant was greatly increased to “average out” the intensity fluctuations caused by scatterer motion. It is, of course, just such intensity fluctuations that will be analyzed in this study. The position of zero path length difference is clearly seen on the resulting interferograms as it corresponds to the location of maximum fringe visibility (or equivalently maximum beat amplitude), $V = \frac{f_{\text{max}} - f_{\text{min}}}{f_{\text{max}} + f_{\text{min}}}$ (see Fig. 2). Finally, the translation stage was adjusted to this zero path length difference location and the lock-in time constant was reduced to allow the desired intensity fluctuations to be recorded.

![Figure 2](image)

**Figure 2:** Diode laser (800 nm) interferogram. Zero interferometer optical path length difference is indicated as the location of maximum fringe visibility. Regions of enhanced visibility, “coherent side modes”, are also clearly indicated outside of the central coherent peak.
3. DISCUSSION OF RESULTS

The aqueous colloidal suspensions used in this study were of monodisperse polystyrene spheres of 0.997 μm mean diameter with a dispersion of less than 2%. This mean diameter was determined by the manufacturer using electron microscopy. Care was taken to avoid particle settling by addition of deuterium-oxide (D₂O) to the suspending fluid, making the polystyrene spheres neutrally buoyant. The volume fractions utilized ranged from 0.001% to 0.01% yielding from one-third to three scattering mean-free-path lengths across our 1 cm sample cell. We find that the number of scattering path lengths across the sample cell (L/ℓ, where ℓ is the calculated photon scattering mean-free-path length) is the relevant experimental parameter, rather than the volume fraction. For example, a 0.01% aqueous suspension of 1 μm polystyrene spheres yields the same number of scattering lengths across a 1 cm cell as a 0.1% suspension across a 1 mm cell or a 7.0% suspension of 0.1 μm spheres across the same 1 mm cell. The dramatic difference in volume fraction necessary to achieve the same scattering coefficient for various scatterer diameters is due to dramatic discrepancies in the corresponding Mie cross-sections for the respective particle sizes.

Data were collected for both the “long” and “short” coherence length sources over the entire range of volume fractions probed. Figure 3 illustrates the “long” coherence length data. The vertical axis represents the experimentally determined scatterer diameter divided by the manufacturer’s stated diameter. Thus, a value of one represents agreement with the stated scatterer size. The horizontal axis represents scatterer concentration (increasing from left to right) as the number of photon scattering mean-free-path lengths across the sample cell. Figure 3 clearly shows that the experimentally extracted scatterer size is accurate until the single scattering limit is exceeded. Once the single scattering limit is exceeded (L/ℓ > 1) there is a dramatic decrease in the apparent scatterer size corresponding to a dramatic increase in the intensity autocorrelation decay rate. One expects the intensity fluctuations to be more rapid when multiple scattering is involved and Fig. 3 dramatically illustrates this fact. The inset shows a typical intensity autocorrelation function and fit (to eqn. 1) obtained with the “long” coherence length source for L/ℓ ≈ 0.75.
Figure 3: Experimentally determined scatterer diameter \( (d_{\text{exp}}) \) expressed as a fraction of the manufacturer's reported diameter \( (d_{\text{manf}}) \) versus optical thickness \( L/\ell \), where \( L = 1 \) cm is the sample cell thickness and \( \ell \) is the photon scattering mean-free-path length. Data was obtained using 0.997 \( \mu \)m polystyrene spheres in water with a HeNe laser source possessing a coherence length of 0.4 m. Inset shows a typical normalized correlation function and corresponding fit for \( L/\ell \approx 0.75 \).

Figure 4 summarizes the “short” coherence length data. The scatterer concentration, reported as \( L/\ell \), that can be successfully probed has increased by a factor of three while the actual volume fraction has increased somewhat more, due to the wavelength difference of the two laser sources. The regime probed by this low-coherence technique is beyond the single scattering limit and yet has not entered the diffusive regime as \( L/\ell^* \ll 1 \). Again, the inset shows a typical intensity autocorrelation function and fit obtained, this time with the “short” coherence length source, for \( L/\ell \approx 0.75 \).
Figure 4: Experimentally determined scatterer diameter \( (d_{\text{exp}}) \) expressed as a fraction of the manufacturer's reported diameter \( (d_{\text{manf}}) \) versus optical thickness \( L/\ell \), where \( L = 1 \) cm is the sample cell thickness and \( \ell \) is the photon scattering mean-free-path length. Data was obtained using 0.997 \( \mu \)m polystyrene spheres in water with a diode laser source possessing a coherence length of 400 \( \mu \)m. Inset shows a typical normalized correlation function and corresponding fit for \( L/\ell \approx 0.75 \). The difference in time-scale probed for the two laser sources is a result of differing wavelength and a small change in scattering angle.

Both the “short” and “long” coherence length data indicate an increase in intensity autocorrelation decay rate as the single scattering regime is exceeded. Contributions from higher order scattering cause the characteristic intensity fluctuations to be more rapid and thus increase the intensity autocorrelation decay rate. This increased decay rate leads to an underestimate of the scatterer diameter, \( d_{\text{exp}}/d_{\text{manf}} < 1 \). It is noted that this underestimate occurs more gradually for the “short” coherence length data (Fig. 4) than for the “long” coherence length data (Fig. 3) as their respective maximum \( L/\ell \) are exceeded. This agrees with expectations as all scattering \( (< 0.4 \text{ m}) \) that takes place within the sample cell will be coherent with the reference arm when the “long” coherence length source is used while only those multiple scattering paths that are within the small coherence length \( (< 400 \mu \text{m}) \) of the “short” source will be detected during its use. Thus,
the rapidity with which multiple scattering negatively impacts the data collected using the “long” coherence length source is greater than that collected using the “short” coherence length source, as observed.

The question that naturally arises is, what limits the concentration that can be successfully probed? The answer may lie in the interferogram of Fig. 2. This figure shows that outside the central region of high fringe visibility lie “coherent side modes.” That is, for example, if a photon in the sample arm multiply scatters a path length that exceeds the length of the reference arm by ≈1.3 mm it will again experience partial coherence with the reference arm and contribute to the detected signal rather than being rejected. A short coherence length light source without or with reduced “coherent side modes” may further extend the applicability of this technique. A super-luminescent diode (SLD) might be considered as a light source but it introduces the additional limitation of greatly reduced optical power, making even lock-in detection of the single scattered component difficult.

4. CONCLUSIONS

In summary, we have shown that a low-coherence heterodyne photon correlation spectroscopic experiment extends the concentration of samples that can be successfully investigated into the multiple scattering regime. This technique partially fills a niche in that samples outside the regime of applicability of either traditional PCS or the newer DWS may be probed.

5. ACKNOWLEDGMENTS

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