

Technology Update: Modulated 3D Cross-Correlation DLS

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Introduction

The purpose of this technology update is to provide an introduction to the modulated 3D cross-correlation technique for accurate light scattering measurements in turbid samples. While this technique is applicable both to dynamic light scattering (DLS) and static light scattering (SLS) methods, here we concentrate on the significant improvements afforded by the present technique to more standard and widely used DLS technologies. In the first part we give a brief introduction to DLS theory. In the second, we introduce and explain the modulated 3D cross-correlation technology. The final section of this update examines a dilute and then a turbid sample of 100 nm polystyrene particles measured in autocorrelation, 3D cross-correlation, and modulated 3D cross-correlation modes. By comparing measurement procedures and results for the three techniques we demonstrate the improved accuracy and the advantages of the 3D systems over conventional DLS instrumentation.

1. DLS Theory

Dynamic light scattering (DLS) refers to the method of observing temporal fluctuations of coherent light scattered by a population of spatial refractive index fluctuations. The source of the refractive index fluctuations are most typically colloidal particles undergoing random motion in a liquid medium under the driving force of stochastic thermal forces, ie Brownian motion. The temporal fluctuations of the scattered light arise due to the time-varying constructive and destructive interference of light waves radiated from the particles randomly moving closer to and further away from each other. The motion of the colloidal particles is dictated by the system temperature, the solution viscosity, and their size or more accurately their hydrodynamic radius (R_h). Robust physical relations exist to directly link these parameters to the measured temporal light fluctuations.

The typical quantity calculated from the intensity fluctuations in a DLS experiment is the intensity autocorrelation function given by

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2}$$

where $I(t)$ is the time-varying measured scattered intensity, τ is a variable lag time, the angle brackets denote an ensemble average (equivalent to a time average for ergodic samples), and the dependence on the scattering vector q has been suppressed [1]. The field autocorrelation function is the more physically relevant quantity and is given by

$$g^{(1)}(\tau) = \frac{\langle E(t)E^*(t+\tau) \rangle}{\langle E(t)E^*(t) \rangle^2}$$

and is related to the intensity autocorrelation function by the Siegert relation

$$g^{(2)}(\tau) = B + \beta [g^{(1)}(\tau)]^2$$

where B is the baseline and β accounts for non-idealities in the instrumentation setup.

The field autocorrelation function or dynamic structure function describes the temporal decay of a particular orientation of the sample within the scattering volume. At short times the system is nearly stationary and so the value of the correlation function is approximately equal to unity. Due to the random nature of the forces applied to the system by Brownian motion, the correlation of the system state at time τ with the initial state approaches zero at longer times.

The decay rate of the field correlation function can be approximated as a single exponential for a monodisperse particle solution

$$g^{(1)}(\tau) = e^{-\Gamma\tau}$$

The exponential decay constant is given by

$$\Gamma = Dq^2$$

where D is the diffusion coefficient and q is the scattering vector which is defined as

$$q = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right)$$

where n is the solution refractive index, λ_0 is the laser wavelength, and θ is the scattering angle. The diffusion coefficient for non-interacting colloidal particles in a Newtonian (purely viscous) fluid is given by the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\eta R_h}$$

where k_B is the Boltzmann constant, T is the sample temperature, η is the solution viscosity, R_h is the hydrodynamic radius. Using this simple model of particle motion in solution, the exponential decay can be related directly to the hydrodynamic radii of the scattering particles. It should be noted that the hydrodynamic radius can differ from the radius measured by other means such as TEM since surfactants or double-layers that form around the particle in the test solution will influence the diffusive motion of the particle.

In general the system will not be monodisperse and therefore must be modeled as an integral of exponential decays

$$g^{(1)}(\tau) = \int G(\Gamma) e^{-\Gamma\tau} d\Gamma$$

where the integral of $G(\Gamma)$ is normalized to one. For monomodal particle size distributions, the most robust and straightforward fitting strategy is to apply the method of cumulants. The method of cumulants provides a scheme for extracting the distribution of decay constants and hence particle sizes. The method uses a moment-generating function that models the mean (1st moment), variance (2nd moment), skew (3rd moment) etc of a distribution by expressing the function as a Taylor series expansion. A cumulant is simply the logarithm of a moment generating function, and so a cumulant fit entails a Taylor series expansion of the logarithm of a moment-generating function. This enables the determination of the mean exponential decay (1st cumulant), the variance (2nd cumulant, equal to the 2nd moment), the skew (3rd cumulant, equal to the 3rd moment), as given by

$$\ln[g^{(2)}(\tau) - 1] = \ln\left(\frac{\beta}{2}\right) - \bar{\Gamma}\tau + \frac{\kappa_2}{2!}\tau^2 - \frac{\kappa_3}{3!}\tau^3$$

where $\bar{\Gamma}$ represents the mean decay, κ_2 is the second cumulant, and κ_3 is the third cumulant.

More complex size distributions are most accurately modeled with the CONTIN algorithm. This method solves for an arbitrary particle size distribution having certain constraints including non-negativity, continuity, etc [2]. However, greater care is required in the application of this method due to its use of an ill-defined numerical Laplace transform and assumptions regarding the physical and optical properties of the particle population. Nonetheless, multimodal size distributions can be accurately determined with this method whereas this is not possible using a cumulant analysis.

2. Modulated 3D Cross-Correlation DLS

Accurate analysis of DLS data relies on the measurement of single scattering events, meaning that each detected photon has been scattered only once in the sample. Therefore, dilution is typically a necessity for highly scattering and concentrated samples. However, the dilution process and especially the verification of adequate dilution can be extremely time-consuming. Furthermore, for samples wherein a concentration-dependent behavior is of interest, dilution is not an option. Index matching of the solvent can be accomplished in some cases, but this in general has limited applicability to a few model systems. Rather than avoiding multiple scattering by careful sample requirements, one can instead seek to suppress the effects of multiple scattering on the measured data.

One particularly powerful technique for suppressing multiple scattering is 3D cross-correlation. This technique relies on the cross-correlation of two measurements to extract single-scattering information from the same scattering volume and the same nominal scattering vector. In this scheme the single-scattering information is common to both measurements while multiple scattering information is uncorrelated, thereby leading to its effective suppression [3]. However, one important drawback of the 3D technique is that one photon detector measures the scattered light intensity at the desired scattering vector, but also receives a contribution at

a second undesired scattering vector given by the relative geometry to the second illumination beam operating at the same wavelength. A four-fold reduction in the cross-correlation intercept arises from cross-talk between the two simultaneous scattering experiments executed in this way. The intercept refers to β , the adjusted y -intercept of the intensity cross-correlation function given by

$$g_2(q, t) = \frac{\langle I(q, 0)I(q, \tau) \rangle_T}{\langle I(0) \rangle_T^2} = 1 + \beta |g_1(q, \tau)|^2$$

where I is the measured intensity at a given scattering vector q and lag time τ , brackets indicate an ensemble average taken over time T , and g_1 is the normalized field correlation function. The value of β strongly influences measurement accuracy and precision due to its pivotal role in accurately fitting models to the measured data. For strongly scattering samples where only a small component of the detected light is singly-scattered, the signal-to-noise ratio of the measurement becomes unacceptably low as the magnitude of the cross-correlation intercept falls into the noise of the baseline fluctuations.

A significant improvement to this method is obtained by modulating the two incident laser beams temporally and gating the detector outputs at frequencies exceeding the timescale of the system dynamics. This robust modulation scheme eliminates cross-talk between the two beam-detector pairs and leads to a four-fold improvement in the 3D cross-correlation intercept [4]. The illumination beams are alternately activated with high speed intensity modulators and the detection electronics are gated in unison. A schematic of the hardware and methodology are shown in Fig. 1, while Fig. 2 illustrates the modulated 3D hardware components.

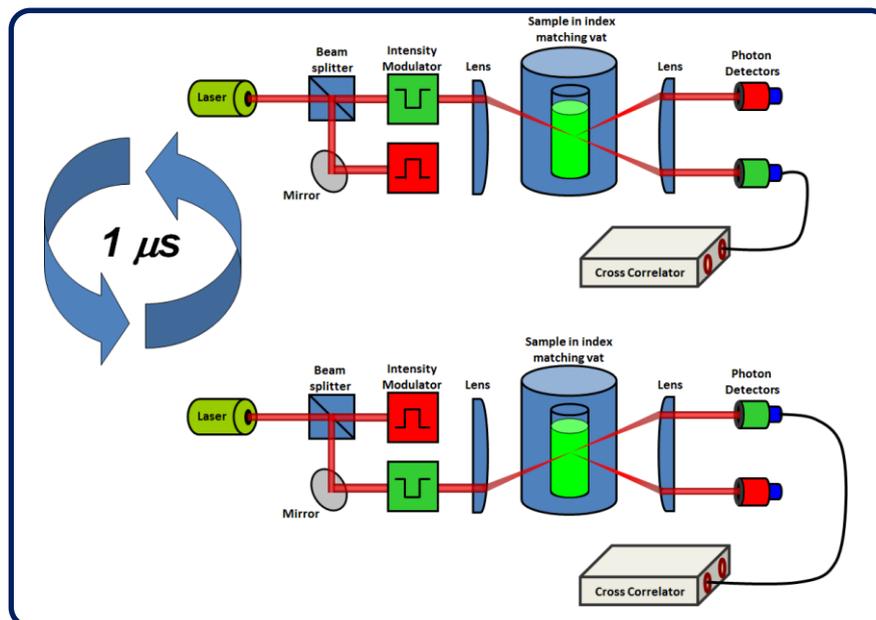


FIG. 1. Schematic of modulated 3D cross-correlation light scattering instrument showing the two states wherein one of the modulators is activated and one detector is gated.

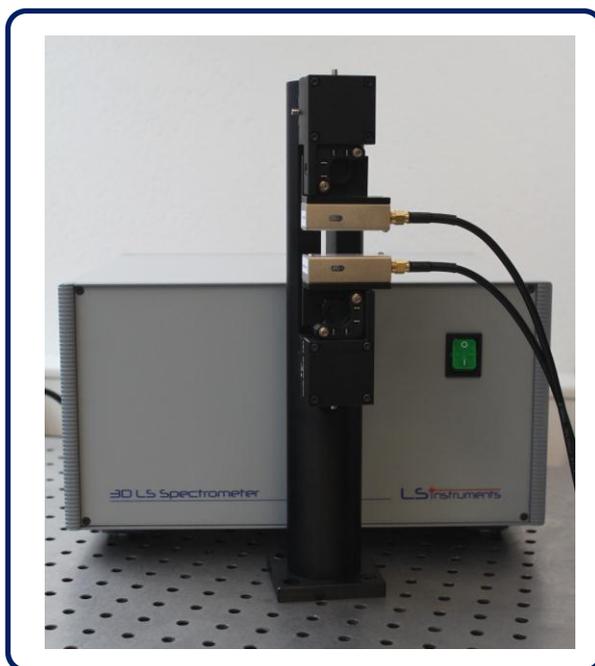


FIG. 2. Modulated 3D cross-correlation light scattering hardware upgrade including mechanics, acousto-optics, and electronics.

3. Sample Measurements

We demonstrate the utility of the four-fold improvement in the cross-correlation intercept measured relative to a standard 3D arrangement, and furthermore compare the results to regular DLS auto-correlation measurements taken for a dilute sample. In these experiments we used standard Latex particles with 100 nm diameter at a range of volume fractions up to 1.5% in water with a polydispersity of 15%. Fig. 3 illustrates the intensity correlation functions measured in auto-, cross- and modulated cross-correlation modes for the most dilute sample.

The quality of a DLS measurement of a particular sample is determined by the intercept of the correlation function (height of the function at the lag time $\tau=0$) as well as by the photon statistics (the product of measurement time and scattered intensity). For a given sample, scattering angle, measurement duration and scattered light intensity, a higher intercept leads to a better signal to noise ratio (SNR). Using the 3D modulated cross-correlation technology we obtain an intercept close to 0.8 (red circles) for measurement of a dilute sample. The intercept obtained with the normal auto-correlation DLS is marginally better with an intercept of approx. 0.95 (blue triangles). However, the autocorrelation measurement does not account for multiple scattering. Thus despite having a slight advantage over modulated 3D cross-correlation in terms of SNR, the obtained particle size is wrong in the presence of multiple scattering (see Fig. 4). This effect is worse for higher concentrations when singly-scattered light is overwhelmed by multiply-scattered contributions.

In the presence of multiple scattering the modulated cross-correlation measurement (red) gives the correct result, as does the cross-correlation measurement (black), but with a four-fold better SNR. The cross-correlation intercept drops in the presence of multiple scattering

wherein its magnitude is related to the amount of singly-scattered light remaining. The weak residual singly-scattered light in cases of high sample turbidity is more precisely measured by the modulated than the standard 3D cross-correlation hardware due to its 4-fold larger correlation function magnitude.

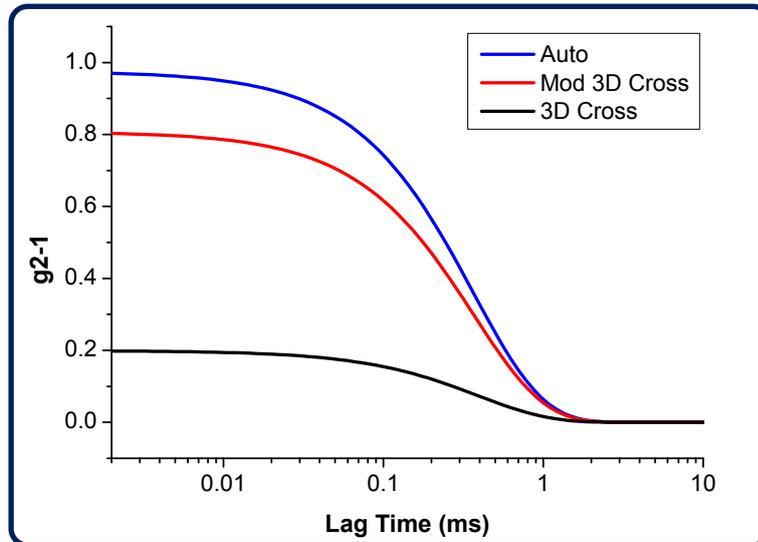


FIG. 3. Comparison of correlation functions measured using Auto, Cross- and Modulated Cross-Correlation modes.

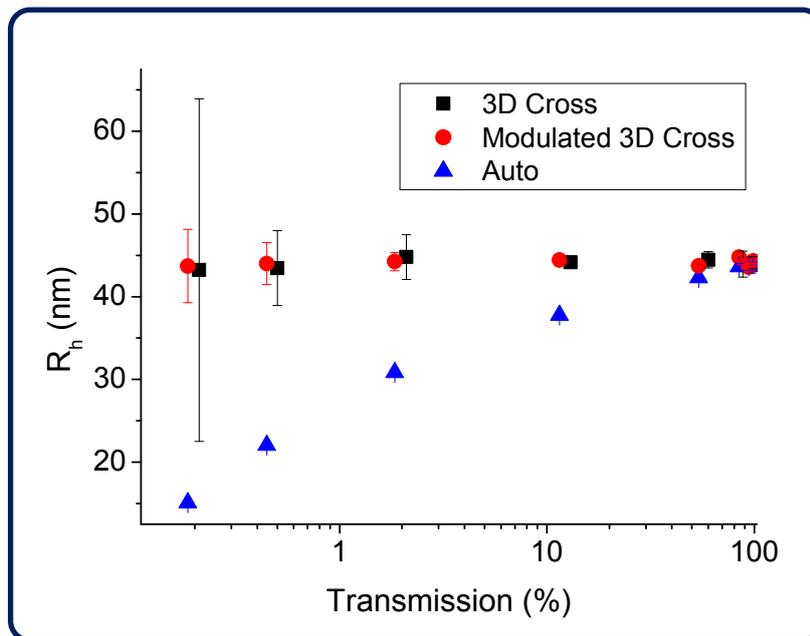


FIG. 4. Comparison of obtained particle hydrodynamic radius using 3D cross-correlation mode (box, black), auto-correlation mode (triangle, blue) and modulated 3D cross-correlation mode (circle, red) for 100nm nominal radius particles.

References

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