

# The Measurement of Very Small Particles by Cross Correlation or Avalanche Photodiode Detectors

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The measurement of particle size using dynamic light scattering, also known as photon correlation spectroscopy, is well known.<sup>1</sup> Scattered laser light is autocorrelated, fit either with cumulants to determine moments of the distribution, or with more sophisticated algorithms to determine the shape of the distribution. With appropriate laser power and scattering angles, sizes from 1 nm to a couple of microns have been determined.

In a typical case, the autocorrelation function is an exponential decay (monodisperse size), or a sum of decays (polydisperse size distribution). With rigid, globular particles, the autocorrelation function is given by:

$$C(\tau) = B \cdot \left[ 1 + A \cdot |g^1(\tau)|^2 \right]$$

, where B is the baseline, A is the so-called intercept-to-baseline ratio minus one (I/B - 1), and  $|g^1(\tau)|$  is the first-order, electric field autocorrelation function. For a monodisperse, rigid, globular sample it is a single exponential decay. For a polydisperse sample it is a sum of exponentials.

Theoretically, A = 1 if the detector sees exactly one coherence area as defined by the source and detector optics. This is the ideal case but depends greatly on compromises between laser power, scattering intensity per particle, and the detector optics. Often, to get a reasonable count rate from which the autocorrelation function is determined, one has to use a few coherence areas and live with the drop in A. Using a single-mode fiber optic produces nearly an ideal situation with A values above 0.9.<sup>2</sup> However, these fibers are designed for use with a particular wavelength. Using other wavelengths results in so-called “few-mode” detection and the value of A drops to 0.5 with two modes.

The decay time, or relaxation time, is by definition the inverse of the linewidth  $\Gamma$ . For a single exponential decay the relaxation time is given by:

$$1/\tau_r = D_T \cdot q^2$$

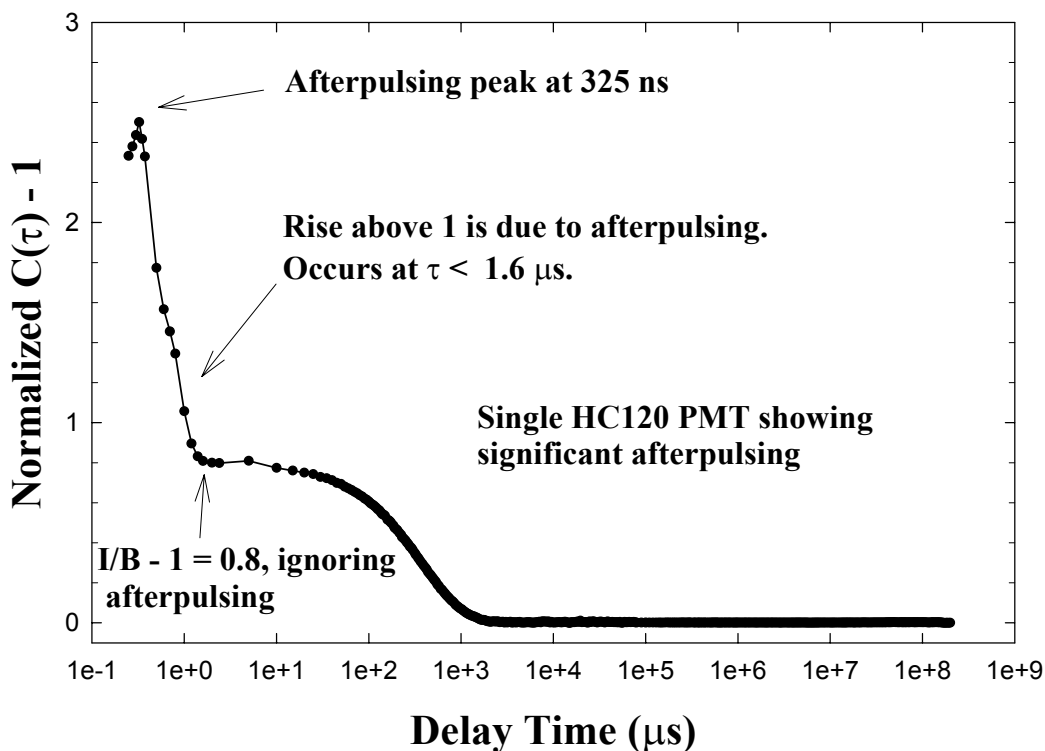
where  $D_T$  is the translational diffusion coefficient. It is inversely proportional to size and proportional to  $\tau_r$ .  $q$  is the absolute value of the scattering wave vector.  $q$  is proportional to  $\sin^2(\theta/2)$ , where  $\theta$  is the scattering angle. For very small particles, the decay will occur at a low delay time. Low delay times mean that not many photons per sampling time will be processed, resulting in noisy autocorrelation functions. Worse, afterpulsing, discussed below, becomes a significant distortion. While making measurements at low scattering angles will shift the decay times higher, reducing the afterpulsing problem, any aggregates or dust will scatter significantly more at low rather than higher angles.

### Cross Correlation

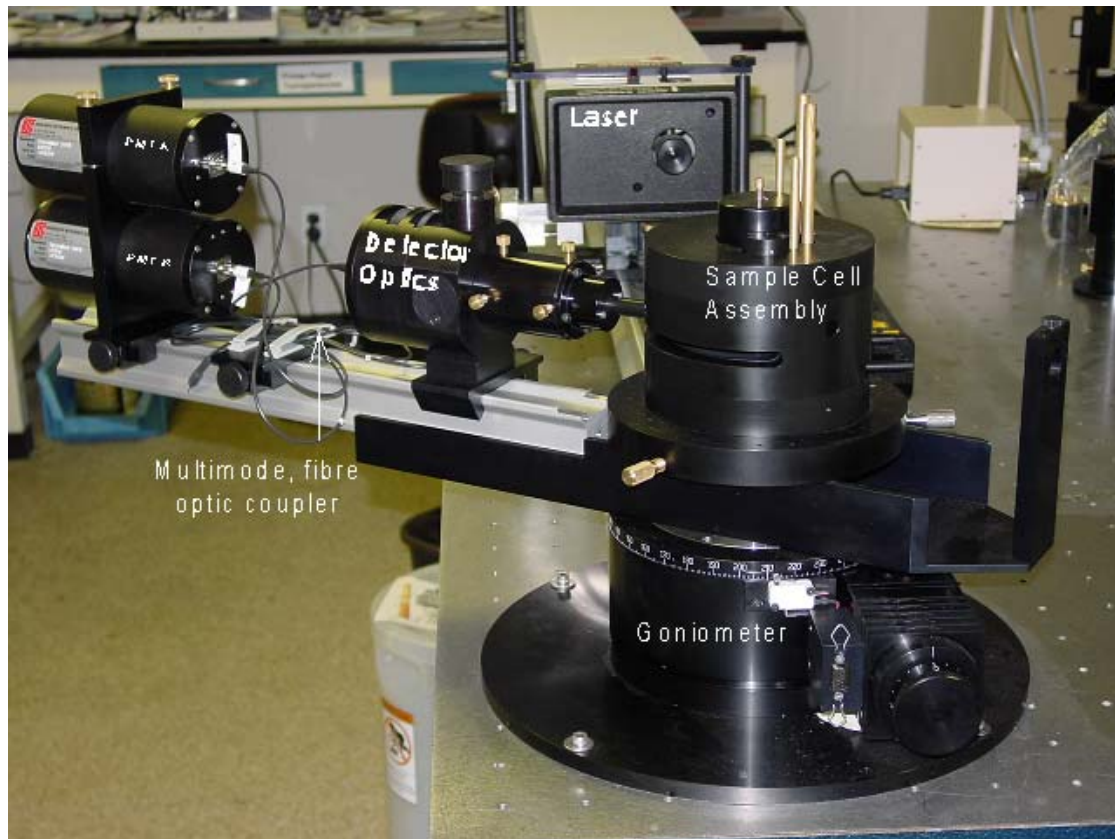
Afterpulsing is the result of processes in the detector, typically a photomultiplier tube, that result in correlated pulses, typically below a microsecond or two. The resulting afterpulse, if analyzed for particle size, will produce spurious results.

Figure I shows a normalized autocorrelation function. Below  $1.6 \mu\text{s}$ , the afterpulsing in this Hamamatsu HC120 PMT is particularly striking. The rise above a value of 2, indicating that  $A$  is larger than the theoretical value of 1, is obvious. The peak at 325 ns is characteristic of this particular PMT. The EMI 9863 tube, for example, while having peaks in this same range, often does not rise above the expected plateau until just below  $1 \mu\text{s}$ . In the case depicted in Figure I, as long as the data are fit from delay times above  $1.6 \mu\text{s}$ , the results are normally acceptable. The novice is often unaware of afterpulsing, having been taught to fit from correlator channel 2 on, regardless of the chosen sample time.

**Figure I: Autocorrelation, 250 ns to 200 s.**

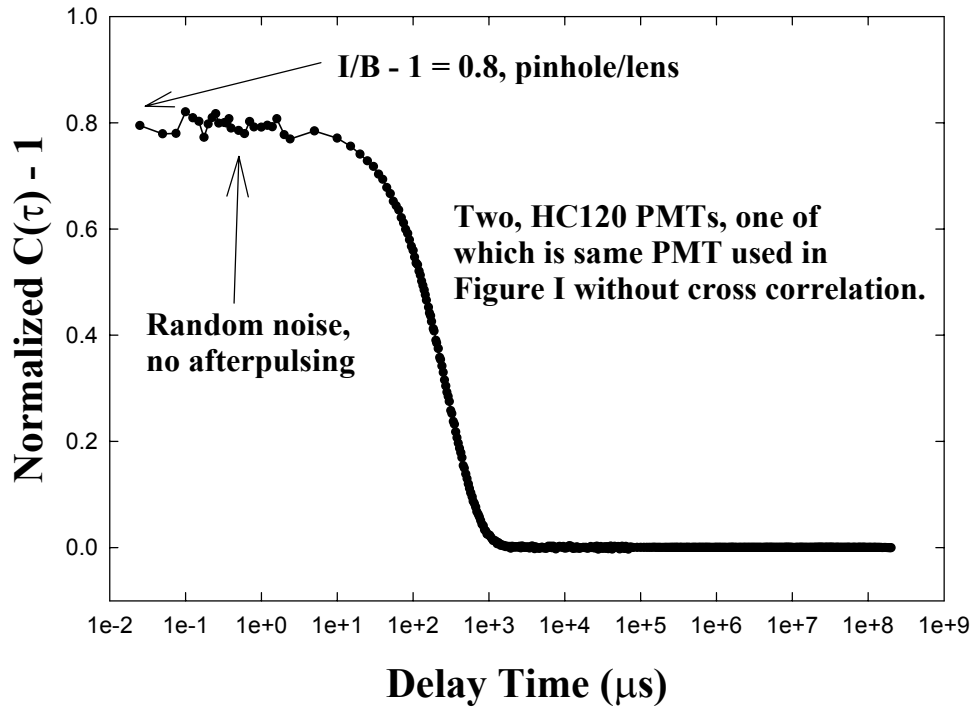


Note that the  $I/B-1$  value for A, ignoring the rise above the plateau, is 0.8. This is a very good value considering the data were collected with a classic pinhole/lens detection scheme and not single-mode fiber optics. The configuration for this and the other cross correlation functions shown is depicted in the photograph. This is a BI-200SM goniometer from Brookhaven Instruments. Normally, either an avalanche photodiode (APD) or a single PMT housing is attached to the detector optics. The output of the detector is processed by a Brookhaven Instruments BI-9000AT digital autocorrelator that is not visible in the photograph.



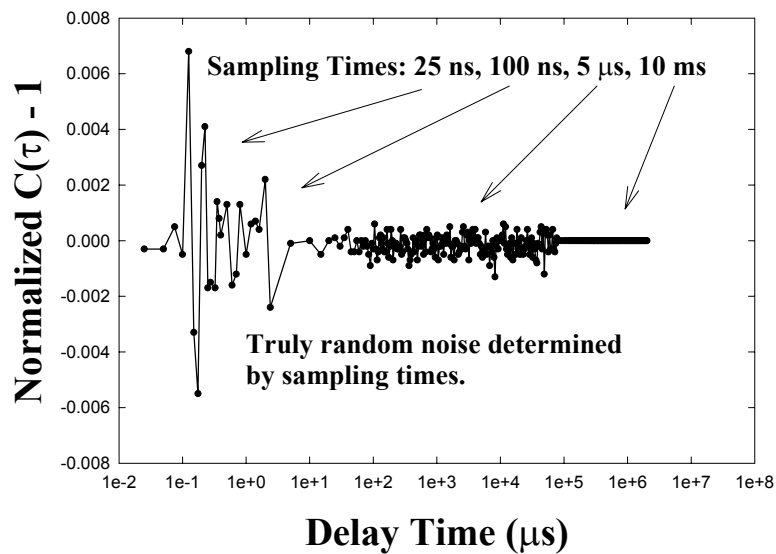
Since the afterpulsing in one PMT is not affected by afterpulsing in another PMT, using cross correlation as shown in Figure II essentially eliminates this distortion. Note that the same Hamamatsu HC120 PMT was used along with another one as shown in the photograph. The light selected by the BI-200SM standard detector optics was viewed by a multimode, fiber optic coupler and split into two, nominally equal parts before being fed into PMTs A and B. The cross correlation function in Figure II is remarkably free from distortion, with only the random noise determined by the scattered intensity and the various sampling times. Thus, when fitting such a function, the data all the way down to 25 ns may be used. Note that the  $I/B-1$  is again 0.8, but the  $C(\tau)-1$  does not rise above the theoretical limit of 1.

**Figure II: Cross Correlation, 25 ns to 200 s.**



To explore the random errors and to check that the afterpulsing was eliminated, a white light source was substituted for the scattered light from a real sample. Figure III shows the results. Here the data are normalized to points between 1 and 2 seconds. As predicted, a flat correlation function is observed. The random noise is evident and predictable from the four sampling time regions of the BI-9000AT digital autocorrelator: 25 ns, 100 ns, 5  $\mu\text{s}$ , and 10 ms.

**Figure III: Cross Correlation, White Light, 25 ns to 2 s.**

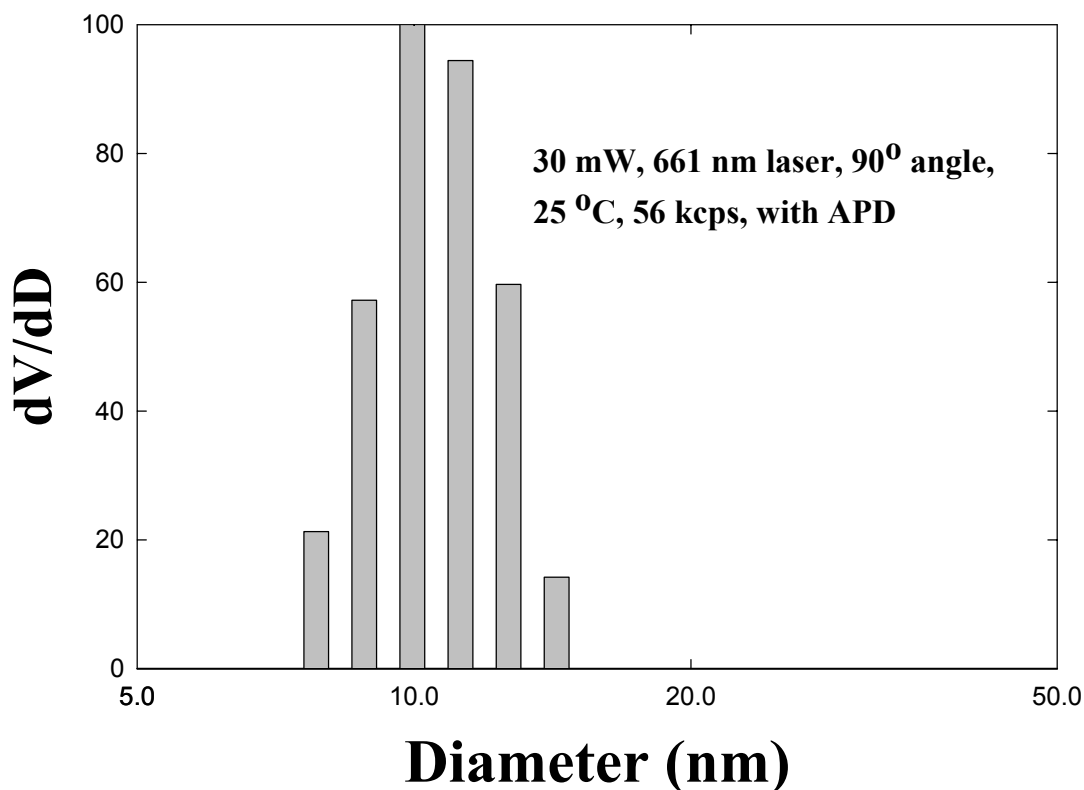


## Avalanche Photodiodes

While cross correlation is useful when sizing very small particles at all but low scattering angles, and for complex fluid characterization and diffusing wave spectroscopy, many situations do not require the extra expense. A common problem is the cost of lasers with sufficient power and a small size to allow convenient measurements of, for example, globular proteins in the 1 nm to 10 nm size range. Here avalanche photodiodes are useful since they have a 10-fold increase in quantum efficiency in the red wavelengths compared to a typical PMT.<sup>3</sup>

Figure IV shows the size distribution for Vitamin E, a nominal 10 nm micelle in water. The results were obtained with the Brookhaven 90Plus using a single-mode fiber optic pickup and an APD. Without the APD the count rate is very low and the resulting correlation function is noisy. With the APD, the results are repeatable. Due to dead-time effects, APDs are not useful below about 200 ns in delay time. Cross correlation will not lift this fundamental limitation.

**Figure IV: Size Distribution for Vitamin E Micelles  
Using APD Detector in 90Plus**



## Summary

For measurements without distortion down to a few nanoseconds in delay time, cross correlation is preferred. Even relatively inexpensive PMTs, such as the Hamamatsu HC120, can be used for this purpose.

When scattering intensity is weak, such as it is for small particle sizes, and powerful lasers are either too large, inexpensive, or, in the case of solid state lasers, have limited lifetimes, the APD is preferred.

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<sup>1</sup> R. Finsy, "Particle Sizing by Quasi-elastic Light Scattering", *Adv. Coll. Interf. Sci.*, **52**, 79-143, (1994).

<sup>2</sup> J. Ricka, "Brownian Dynamics in Strongly Scattering Porous Media—Dynamic Light Scattering with Single-mode Matching", *Macromolecules*, **79**, 45-55 (1994).

<sup>3</sup> R.G.W. Brown, J.G. Burnett, J. Mansbridge, C.I. Moir, "Miniature Laser Light Scattering Instrumentation for Particle Size Analysis", *Appl. Opt.*, **29**, 4159-4169, (1990).