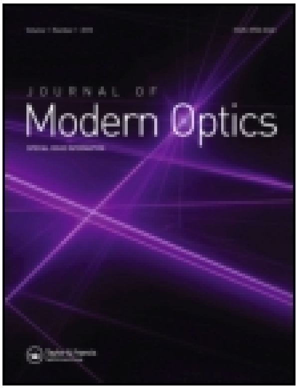

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Photon Correlation Measurements at Large Lag Times: Improving Statistical Accuracy

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Photon correlation measurements at large lag times: improving statistical accuracy

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Abstract. Dynamic light scattering and photon correlation spectroscopy are able to resolve large ranges of coherence times, and hence of scattering particle size or constant of diffusion, in a single measurement if a modern multiple-tau correlator is used. However, particular problems like bias and unsatisfactory statistical accuracy typically arise at very large lag-times. A novel normalization scheme is presented which cures the accuracy problem and provides reliable photon correlation data at large lag-times within significantly reduced total measurement times.

1. Introduction

Photon correlation studies of Brownian motion provide fast and accurate particle size or diffusion data on suspended particles in the submicron size range [1–4]. Numerous applications have been reported in many branches of physics, chemistry and biology. While the technique produces mean size accuracies of the order of 1%, its resolution capability for particle size distributions is known to be quite limited due to fundamental reasons, for example, bimodal distributions typically cannot be recognized unless the peaks are separated by more than a factor of two of their f.w.h.m. [4, 5]. However, some recent applications such as the study of the glass transitions [6] or, more generally, strongly interacting scattering particles [7, 8] require precisely the opposite capability, i.e. coverage of extremely wide distributions in the coefficients of diffusion, often several decades in a single measurement. In principle, such measurements are extremely well suited to photon correlation spectroscopy: the wider the distribution of diffusion coefficients, the easier it may be obtained from a measured correlogram via the inverse Laplace transformation.

Practical problems arise from two direction. The first is that of the availability of a correlator that provides a sufficiently large range of lag-times in one single experiment. Such an instrument is now commercially available and will be discussed in § 3. The second arises if excessively long averaging times must be employed, either because of economy or because of the limited stability of the colloidal system under investigation. If the total measurement duration does not exceed the largest lag-time by orders of magnitude, particular care is required to reduce statistical bias and estimator variance during the necessary normalization of the raw data. These statistical difficulties will be covered in § 2. The first successful applications of an improved normalization procedure will be presented in § 3.

2. Statistics of correlation data at large lag-times

Let n_j denote the number of photon detection events measured within a sampling interval of width t_s centred on a time jt_s. The obvious estimator for the temporal autocorrelation of n_j is

$$\hat{G}_k^{(2)} = \frac{1}{M} \sum_{j=1}^{M} n_j n_{j-k}, \tag{1}$$

where kt_s denotes the lag-time and M the total number of samples. Typical applications of photon correlation spectroscopy, such as velocimetry or particle sizing, do not require knowledge of the absolute magnitude of the measured correlogram. Normalization by dividing out the mean count rate,

$$\hat{S}_0 = \frac{1}{M} \sum_{j=1}^{M} n_j, \tag{2}$$

as it is measured in a separate 'monitor channel', yields the normalized correlogram,

$$\hat{g}_k^{(2)} = \hat{G}_k / \hat{S}_0^2, \tag{3}$$

which typically constitutes the basis of further evaluation [1–4]. For homodyne experiments [4, 9], the amplitude correlation $\hat{g}^{(1)}$ is obtained from (3) by subtraction of the baseline and taking the square root. As it is well known [10, 11], $\hat{g}_k^{(2)}$ is a biased estimator of the desired correlation,

$$g_k^{(2)} = \langle n_k n_0 \rangle / \langle n_0 \rangle^2, \tag{4}$$

where $\langle \ldots \rangle$ denotes ensemble averaging and the discrete random process n_j is assumed to be stationary. However, at small lag-times kt_s, M has almost always to be a very large number (some 10^6 or more) in order to obtain sufficient averaging over photon-counting noise. Being of order $1/M$, the bias in (3) is therefore neglected in most such applications of the photon correlation technique. A notable exception of this rule is the use of Oliver's technique of averaging over separately normalized correlograms obtained from processing short batches of data [11].

At large lag-times, i.e. for sampling times t_s very large compared with the average separation of two successive photon detection pulses, as well as being very much in excess of the fastest coherence times present in the signal, it becomes unpractical to use very large numbers M of samples and hence large total measurement times Mt_s. More importantly, it is not really necessary to average over very many samples, because on the time-scales considered, photon-counting noise is almost negligible; even most fluctuations of the underlying signal are reasonably well averaged within a single sample n_j (all those that occur on shorter time-scales). A typical photon-counting signal at large lag-times may be written as

$$n_j = \bar{n}(1 + \delta_j) \tag{5}$$

with

$$\langle \delta_j \rangle = 0 \tag{6}$$

and

$$\langle \delta_j^2 \rangle = \sigma^2 \ll 1. \tag{7}$$

The normalized autocorrelation of such a signal is

$$\langle n_k n_0\rangle = \bar{n}^2(1+\langle\delta_k\delta_0\rangle). \tag{8}$$

Using for brevity the correlation coefficient of δ_j,

$$\rho_k = \langle\delta_k\delta_0\rangle/\sigma^2, \tag{9}$$

we may rewrite (8) as

$$\langle n_k n_0\rangle = \bar{n}^2(1+\sigma^2\rho_k), \tag{10}$$

and (4) as

$$g_k^{(2)} = 1+\sigma^2\rho_k. \tag{11}$$

Inserting these definitions in (3) and expanding the denominator into a Taylor series about $\delta_j=0$, we obtain an approximation of our estimator for the normalized correlogram,

$$\begin{aligned}
\hat{g}_k^{(2)} = \hat{G}_k/\hat{S}_0^2 &= \left(1+\frac{1}{M}\sum_{j=1}^{M}\delta_j+\frac{1}{M}\sum_{j=1}^{M}\delta_{j-k}+\frac{1}{M}\sum_{j=1}^{M}\delta_j\delta_{j-k}\right)\left(1+\frac{1}{M}\sum_{j=1}^{M}\delta_j\right)^{-2}\\
&= \left(1+\frac{1}{M}\sum_{j=1}^{M}\delta_j+\frac{1}{M}\sum_{j=1-k}^{M-k}\delta_j+\frac{1}{M}\sum_{j=1}^{M}\delta_j\delta_{j-k}\right)\\
&\quad\times\left(1-\frac{2}{M}\sum_{j=1}^{M}\delta_j+\frac{3}{M^2}\sum_{j,l=1}^{M}\delta_j\delta_l-\dots\right)\\
&= 1+\frac{1}{M}\sum_{j=1-k}^{0}\delta_j-\frac{1}{M}\sum_{j=M-k+1}^{M}\delta_j+\frac{1}{M}\sum_{j=1}^{M}\delta_j\delta_{j-k}-\frac{1}{M^2}\sum_{j=1}^{M}\sum_{l=1-k}^{M-k}\delta_j\delta_l\\
&\quad-\frac{1}{M^2}\sum_{j=1}^{M}\sum_{l=1-k}^{0}\delta_j\delta_l+\frac{1}{M^2}\sum_{j=1}^{M}\sum_{l=M-k+1}^{M}\delta_j\delta_l+O(\delta^3).
\end{aligned} \tag{12}$$

From (12) we immediately obtain the estimator expectation

$$\langle\hat{g}_k^{(2)}\rangle = 1+\sigma^2\rho_k-\frac{1}{M^2}\sum_{j,l=1}^{M}\langle\delta_j\delta_{l-k}\rangle, \tag{13}$$

where the last term is the bias and terms of order higher than δ_j^2 have been neglected. The bias may be further evaluated as

$$\langle g_k^{(2)}\rangle - g_k^{(2)} = -\frac{\sigma^2}{M^2}\sum_{j,l=1}^{M}\rho_{j-l+k} = -\frac{\sigma^2}{M^2}\sum_{p=1-M}^{M-1}(M-|p|)\rho_{p+k}, \tag{14}$$

or a triangularly weighted average over the correlation coefficients. If M greatly exceeds the range of lag indices k for which ρ_k is non-zero, (14) may be further approximated as

$$\langle\hat{g}_k^{(2)}\rangle - g_k^{(2)} \approx -\frac{\sigma^2}{M}\sum_{k=-\infty}^{\infty}\rho_k. \tag{15}$$

While this bias problem has been known since the early days of photon correlation [10], a second problem originating from (12) at small values of M seems to have been overlooked until now, except for some of our own work on recurrence-rate correlation [12]. Even though the boundary terms in (12), associated with sums over just the first or the last k samples considered, cancel each other in the ensemble average, they still contribute to the variance of our estimator. This contribution may become very significant, because it is of an order in δ_j lower than the desired correlation term. A quantitative estimate may be obtained by noting that the typical estimator variance of the correlation estimator is of the order of σ^4/M [13],

$$\mathrm{Var}\left(\frac{1}{M}\sum_{j=1}^{M}\delta_j\delta_{j-k}\right)=O(\sigma^4/M), \tag{16}$$

while the dominating boundary terms have a variance of order $k\sigma^2/M^2$,

$$\mathrm{Var}\left(\frac{1}{M}\sum_{j=1-k}^{0}\delta_j+\frac{1}{M}\sum_{j=M-k+1}^{M}\delta_j\right)=O(k\sigma^2/M^2). \tag{17}$$

The latter equation may be obtained without further specification of the δ_j-statistics as a lower bound estimate, if we neglect the correlation between δ_j and δ_l for $j\neq l$. In this case we obtain

$$\mathrm{Var}\left(\frac{1}{M}\sum_{j=1-k}^{0}\delta_j\right)=\frac{1}{M^2}\sum_{j=1-k}^{0}\sum_{l=1-k}^{0}\langle\delta_j\delta_l\rangle>\frac{1}{M^2}\sum_{j=1-k}^{0}\langle\delta_j^2\rangle=\frac{k\sigma^2}{M^2},$$

and hence (17).

If σ^2 falls below $1/M$, as it may well do far in the tail of a photon correlation function, our estimator noise is determined by fluctuations of the boundary terms in (12) rather than by the uncertainty of the desired correlation term.

Fortunately, this problem may be overcome completely by removing the asymmetry in the normalization procedure (3). Using a new monitor channel,

$$\hat{S}_k=\frac{1}{M}\sum_{j=1-k}^{M-k}n_j, \tag{18}$$

for the delayed data samples, we may replace the conventional estimator (3) or the normalized correlogram by the symmetrized estimator:

$$\hat{g}_k^{(s)}=\hat{G}_k^{(2)}/(\hat{S}_0\cdot\hat{S}_k). \tag{19}$$

A quick calculation proves, that the boundary terms drop out of the expression for the normalized correlogram's estimator and we obtain

$$\begin{aligned}g_k^{(s)}=G_k/(S_0S_k)&=\left(1+\frac{1}{M}\sum_{j=1}^{M}\delta_j+\frac{1}{M}\sum_{j=1}^{M}\delta_{j-k}+\frac{1}{M}\sum_{j=1}^{M}\delta_j\delta_{j-k}\right)\\&\quad\times\left(1+\frac{1}{M}\sum_{j=1}^{M}\delta_j\right)^{-1}\left(1+\frac{1}{M}\sum_{j=1}^{M}\delta_{j-k}\right)^{-1}\\&=\left(1+\frac{1}{M}\sum_{j=1}^{M}\delta_j+\frac{1}{M}\sum_{j=1}^{M}\delta_{j-k}+\frac{1}{M}\sum_{j=1}^{M}\delta_j\delta_{j-k}\right)\\&\quad\times\left(1-\frac{1}{M}\sum_{j=1}^{M}\delta_j-\frac{1}{M}\sum_{j=1}^{M}\delta_{j-k}+\frac{1}{M^2}\sum_{j,l=1}^{M}\delta_j\delta_l\right.\\&\quad\left.+\frac{1}{M^2}\sum_{j,l=1}^{M}\delta_j\delta_{l-k}+\frac{1}{M}\sum_{j,l=1}^{M}\delta_{j-k}\delta_{l-k}+\dots\right)\\&=1+\frac{1}{M}\sum_{j=1}^{M}\delta_j\delta_{j-k}-\frac{1}{M^2}\sum_{j,l=1}^{M}\delta_j\delta_l+O(\delta^3).\end{aligned} \tag{20}$$

in place of (12). The bias problem is identical for both estimators, but additional variance due to boundary effects may be avoided altogether by symmetrical normalization.

3. Correlator for large lag-times

Even though the symmetrical normalization scheme (19) looks like a straightforward and fairly obvious idea, it cannot be implemented for almost all the correlators used in photon correlation experiments today, because these machines simply do not provide the additional monitor channels S_k. Of course there are good reasons for this. Besides the considerable cost of a separate monitor channel for each lag-time channel in the correlator, the main reason is that these correlators are simply not well suited to process low-variance data. The requirements to process high count rates and to provide small lag-time channels as well, calls for fast special-purpose hardware. Typically, such hardware is built to process data with limited resolution (say, 4 bits) in order to remain economically feasible. At such a low resolution, scaling has to be used if t_s becomes large [14] and this typically introduces quantization noise far in excess of both sources of noise considered in § 2 at very large lag-times. As a consequence, even with additional monitor channels, such an instrument will be of little use, if long tails of correlograms must be determined very accurately.

A novel correlator architecture is needed if correlograms are to be measured over extremely large ranges of lag-times. Our structurator/correlator [7, 15] with separate sampling and processing sections connected through fast data buffers offers a multiple sample-time mode, where t_s and the lag-times are both doubled every 8 channels. The 4×4 bit hardware processor typically covers the lag-time range between 1 μs and 8 ms using 10 sample-time values from 1 to 512 μs, respectively. For larger lag-times and sample times, the 4×4 bit accuracy would lead to significant quantization noise. Hence, a separate processor built around a 68000 microprocessor was designed to compute the correlogram at lag-times between 8 ms and more than 60 s. Full 16-bit accuracy of the processor is used to avoid any further scaling. This 68000 correlator was recently modified to include additional monitor channels, a separate one for each lag-time value.

As a result, the instrument is able to measure simultaneously a photon correlation function at lag-times between 1 μs and more than 1 min. Full real-time performance is achieved and processing precision increases from the initial 4 bits to the final 16 bits. Additional monitor channels are provided at those large lag-times (>8 ms) where they may be useful to reduce the estimator variance of the normalized correlation by symmetric normalization. (The structurator/correlator is commercially available through ALV, Langen, F.R. Germany as the ALV-3000 with option ALV-3030.)

4. Measurements at large lag-times

In order to demonstrate the importance of symmetrical normalization at large lag-times, measurements were performed on aqueous suspensions of polystyrene spheres. The latex was prepared by standard emulsion polymerization. Extensive cumulant analysis of correlation data obtained from dilute samples yielded a mean diameter of 83 nm and a polydispersity of about 9%.

The data presented here were obtained from a sample of volume concentration $2{\cdot}2 \times 10^{-4}$ (after filtering through a Millipore filter of pore size 100 nm). The measurements were performed using an Ar^+ laser operated in the light-regulated mode at a wavelength of 514·5 nm. The laser output of 0·5 W was attenuated by a $\lambda/2$-wave plate–glan prism combination to produce a count rate of about 300 kHz under 30° scattering angle. The optomechanical system was an ALV SP-81 goniometer, the correlator an ALV 3000 with multiple-tau extension ALV-3030.

The correlator data were processed on a Sirius 1 microcomputer such that one set of data was normalized both conventionally and with our new symmetric normalization scheme. Figures 1 and 2 show the results of both normalization procedures applied to a single set of measured correlation data. In order to enhance the visibility of noise at large lag-times, first-order correlation functions are plotted, which were obtained by baseline subtraction from the second-order correlation function and a square-root operation. Data points, which fell below the baseline (due to noise) were plotted as the negative square root of the absolute value. This procedure is commonly used for the analysis of photon correlation functions, and is acceptable for Gaussian, i.e. many-particle, signals (Siegert relation, [1–4, 9].

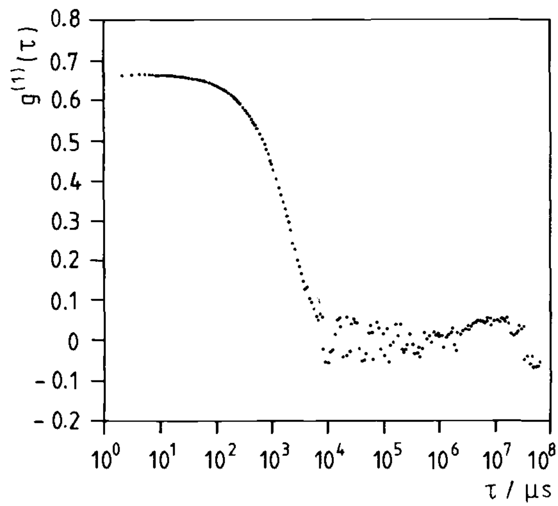

Figure 1. Measured photon correlation function: standard asymmetrical normalization.

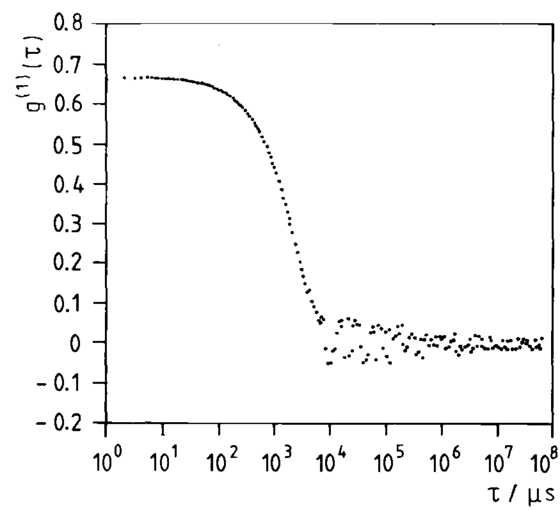

Figure 2. Measured photon correlation function: new symmetrical normalization.

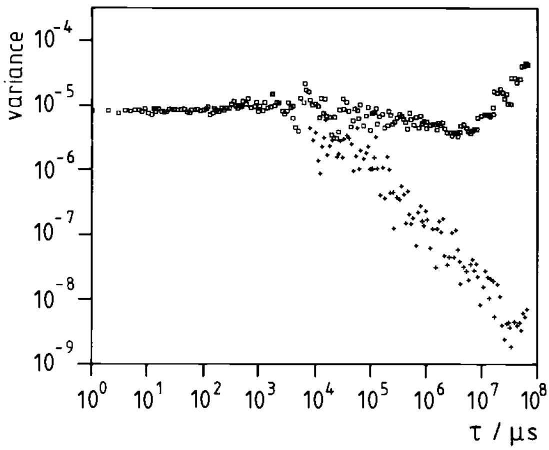

Figure 3. Experimental estimator variance obtained from 10 second-order correlation functions for symmetrical (+) and asymmetrical (□) normalization.

For a quantitative comparison of noise in a single correlator channel, however, the second-order correlation function seems to be more appropriate. Firstly, because it is the raw data produced by the correlator, and secondly, because the square-root operation used to compute the first-order correlation function strongly distorts the noise dependence on lag-time.

Several sets of 10 measurements each were performed to obtain experimental values of the estimator variance of all the 191 channels of a multiple-tau correlogram. Variance results of one such set are plotted in figure 3. The total measurement time of each of the 10 runs used to produce figure 3 was 150 s. The data displayed in figures 1 and 2 are a single run taken from this same set of measurements.

Figure 3 clearly demonstrates the effectiveness of symmetrical normalization in the far tail of photon correlation functions. At lag-times of some 10 s, the symmetrically normalized correlogram shows a decrease in variance of about three orders of magnitude as compared to short lag-time values, while the conventional normalization scheme even leads to a slight growth of estimator variance.

Similar results were obtained on measurements under different scattering angles and with other samples. Generally we find a similarly dramatic deviation in estimator noise as in figure 3. However the onset of the decrease in noise due to symmetrical normalization is shifted to larger lag-times for signals with increasing coherence times.

5. Conclusions

Theoretical considerations as well as experimental evidence indicate the importance of a symmetrical normalization scheme for photon correlation functions at large lag-times, where relative signal fluctuations become small and the total number of samples is no longer a very large number. Significant decreases in total measurement time are feasible for all photon correlation experiments where long tails of the correlogram must be determined accurately, for example, measurements on strongly interacting particles, glass transitions, and so on. A first hardware and software realization of the symmetrical normalization procedure was implemented in the ALV-3000 structurator/correlator and the accompanying evaluation program ODIL.

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