Fitting the correlation function

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The whole correlation function of the intensity of scattered light is usually determined from a single realization of the photocurrent. As a result, the values of the correlation function at different delay times are not statistically independent. A standard least-squares fitting procedure is not optimal for an analysis of such data. However, the benefits of mathematically rigorous but highly nonlinear and less stable methods are not known. We consider the test case of a Gaussian signal with a single-exponential correlation function without shot noise. In this case the fitting procedure, which is based on the maximum-likelihood principle for the observed signal, permits an analytical solution. We demonstrate that such a rigorous statistical analysis produces an approximately two times more-accurate result for the relaxation time than does the standard least-squares fit. This gain, however, is greatly reduced by the presence of shot noise, which introduces additional uncorrelated errors into the values of the correlation function.

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1. Introduction

In photon-correlation spectroscopy[1] (PCS) the quantity that is directly measured is the photocurrent as a function of time. The extraction of useful information from the time evolution of the photocurrent requires two additional data-processing steps. First, measurements of the photocurrent are used to calculate the correlation function (CF). The reason for the conversion is purely practical: A 15-min experiment with 1-μs resolution produces a gigabyte of information that is difficult to store and process. The CF represents all the essential information contained in the photocurrent in compact form. Indeed, a random signal with Gaussian statistics is completely characterized by its pair CF. The cases of non-Gaussian signals, when higher-order CFs contain meaningful additional information, are rare.[2] In the second step, the experimentally determined CF is compared with the theoretical prediction, and the parameters of the theory that produce the best fit are determined.

It is worthwhile to note that the basic concepts of signal processing in PCS were being developed when computational power was relatively limited. As a result, in a real-time experiment the CF could be determined only in a limited number of channels. To increase the number of channels, algorithms that skip some computations or use a clipped signal were introduced. Attention thus was focused on minimizing the loss of information in the measurement process and on the effects that a particular technical limitation or trade-off might have on the accuracy of final result.[3] Today, dramatic advances in computers allow us, in principle, to process a photosignal (a stream of times of arrival of photocounts) without any loss of information. The purpose of this paper is to discuss how good the current methods of analysis of the photosignal are and whether there is room for improvement.

One of the most common applications of PCS is the measurement of the diffusivity of particles in solutions and suspensions.[4] In this case the CF of the intensity fluctuations of the scattered light is a single exponential in an ideal, monodisperse system or a sum of exponential functions in a real system of neither identical nor spherical and interacting particles. In the following discussion we shall have in mind this particular application.

Fitting the experimental data to the theoretical curve inevitably involves certain *a priori* assumptions, both about the properties of the system under investigation and about the process of measurement. A direct fit to a particular model could be intolerant even to small deviations of this model from reality. Two other methods, less model dependent, are commonly used. The method of cumulants[5] is essen-

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tially a fit of the logarithm of the CF to a polynomial, usually a second-order polynomial. The regularization method[6,7] is essentially a fit of the CF to a sum of exponential functions with a smooth distribution of decay times. All these methods of data analysis have been used for a long time in practical application of PCS. However, they all ignore the fact that the values of the CF at different delay times are calculated from only one realization of the photocurrent and therefore are not statistically independent. In other words, the statistical errors in the experimentally measured CF are cross correlated.

The cross correlation in the values of the CF depends on how the CF is computed from the original photocurrent signal. Unfortunately, it also depends on the correlations in the signal, i.e., on the CF itself. That means that the cross-correlation matrix of errors can be determined only within the fitting procedure, simultaneously with the CF. As a result, the fitting procedure becomes highly nonlinear and might lose stability. We wish to evaluate when the benefits of a mathematically rigorous fitting procedure that takes into account the cross correlations in the CF outweigh the complications involved. The maximum benefit is expected when shot noise is negligible. Shot noise is a specific feature of PCS that arises from the probabilistic nature of photodetection process. As a result, uncorrelated statistical errors are introduced into the correlated signal. These signal errors translate into uncorrelated errors in the CF. Therefore when the shot noise is large the standard least-squares (SLS) fit becomes more appropriate. Here we report the case study of a Gaussian signal with a single-exponential CF in the absence of shot noise. In this case, full analytical analysis is possible. Examples of such a signal include the Nyquist noise of a capacitor–resistor circuit and the coordinate of the particle diffusing in the harmonic potential. In PCS experiments this is the case when the light is collected from many coherence areas and has high intensity.

We base our analysis on the maximum-likelihood principle (MLP). This principle provides the recipe for data fitting in complex cases. It requires consideration of the probability of observing the experimental data as a function of the parameters of the theory. The values of the parameters that maximize the probability produce the desired best fit. We apply the MLP to the realization of a random signal with Gaussian statistics and an exponential CF. We demonstrate that, for such a signal, analysis based on the MLP produces approximately twice as accurate a result for the relaxation time than does a SLS fit of the measured CF by an exponential.

2. Theory

Let us assume that a Gaussian random signal $x(t)$ with a zero average is measured at N equidistant moments of time: $0, \Delta t, 2\Delta t, \ldots, (N-1)\Delta t$ and that the set of results $x_0, x_1, x_2, \ldots, x_{N-1} \equiv \{x\}$ has no error of measurement. The probability density of measuring this sequence of data is

$$P(\{x\}) = (2\pi)^{-N/2}(\det \mathbf{G})^{-1/2} \exp\left(-\frac{1}{2} x_k \mathbf{G}_{kl}^{-1} x_l\right). \tag{1}$$

Here $\mathbf{G}$ is the digitalized CF of the signal, $\mathbf{G}_{kl} = G(|k-l|)$. The symbols in bold type represent matrices, and summation over repeated indices is assumed. According to the MLP, we should find $\mathbf{G}$ that maximizes $P(\{x\})$ for the experimentally observed set $x_0, x_1, x_2, \ldots, x_{N-1}$. If the CF is a known function of its parameters the parameters that yield a maximum of $P(\{x\})$ have to be determined.

It is worthwhile to note that the experimental values of the signal $\{x\}$ enter the distribution in Eq. (1) only in the combination $x_k \mathbf{G}_{kl}^{-1} x_l$. As $\mathbf{G}$ and therefore $\mathbf{G}^{-1}$ depends only on the difference of their indices, this combination can be rewritten as a trace of a matrix product:

$$x_k \mathbf{G}_{kl}^{-1} x_l = \mathrm{Tr}(\mathbf{G}^{-1} \cdot \mathbf{g}), \tag{2}$$

where the nonnormalized experimental CF $g(|k-l|)$ is given by

$$\mathbf{g}_{kl} \equiv g(|k-l|) = \sum_{j=0}^{N-|k-l|} x_j x_{j+|k-l|}. \tag{3}$$

First, we see that $P(\{x\})$ depends exclusively on the complete, i.e., calculated by use of all possible pairs of data points, experimental CF. Thus for a signal with Gaussian statistics the complete experimental CF contains the same information as the original set of data $\{x\}$. Second, not all points of the measured CF are equally important, as is assumed for the SLS fit. What actually matters is the combination $\mathrm{Tr}(\mathbf{G}^{-1} \cdot \mathbf{g})$. The difference is especially dramatic in the case of a single-exponential CF.

Let us assume that

$$\mathbf{G}_{kl} = A \exp(-\Gamma \Delta t |k-l|) \equiv A a^{|k-l|}, \tag{4}$$

where $a = \exp(-\Gamma \Delta t)$. The inverse of matrix Eq. (4) turns out to be of tridiagonal form

$$\mathbf{G}_{kl}^{-1} = \frac{1}{A(1-a^2)} \begin{bmatrix} 1 & -a & 0 & 0 & \cdots & & & & \\ -a & 1+a^2 & -a & 0 & \cdots & & & & \\ 0 & -a & 1+a^2 & -a & \cdots & & & & \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ & & & & \cdots & -a & 1+a^2 & -a & 0 \\ & & & & \cdots & 0 & -a & 1+a^2 & -a \\ & & & & \cdots & 0 & 0 & -a & 1 \end{bmatrix}, \tag{5}$$

as can easily be verified by direct multiplication.

Using Eq. (5) for the inverse correlation matrix, we immediately find that the combination in Eq. (2) can be written as

$$\mathrm{Tr}(\mathbf{G}^{-1}\cdot\mathbf{g}) = \frac{(1+a^2)g_0 - 2ag_1}{A(1-a^2)}. \tag{6}$$

Here we have neglected small, of the order of $1/N$, edge effects [the first and the last diagonal members of matrix equation (5) are 1 instead of $1 + a^2$]. We see that the probability of observing a particular realization of the random signal with Gaussian statistics and a single-exponential CF depends on only the zeroth, $g_0 \equiv g(0)$, and the first, $g_1 \equiv g(1)$, channels of the full CF calculated according to Eq. (3). In other words, the MLP leads to a stunning recipe for fitting a single-exponential CF: use only the first two channels of the CF. This counterintuitive suggestion is, of course, valid only for a truly single-exponential function and only in the absence of shot noise. Neither of these assumptions holds for the actual PCS experiment. However, when the random fluctuations are measured directly and not by means of photon counting this is exactly how the data analysis is carried out. We consider this issue in more detail in Section 4 below.

To determine the actual parameters A and a that maximize the probability $P(\{x\})$, we need an expression for the determinant of correlation matrix $\mathbf{G}$. Using the explicit expression in Eq. (5) for the inverse-matrix, we can show straightforwardly by induction that

$$\det \mathbf{G} = A^N(1-a^2)^{N-1}. \tag{7}$$

Substituting Eqs. (6) and (7) into Eq. (1) and taking the logarithm, we find that, in the limit $N \gg 1$,

$$-2\ln(P) = \frac{(1+a^2)g_0 - 2ag_1}{A(1-a^2)} + N\ln(A) + N\ln(1-a^2) + \text{const}. \tag{8}$$

One can easily verify that the right-hand side of Eq. (8) has a minimum when

$$A = g_0/N, \qquad a \equiv \exp(-\Gamma\Delta t) = g_1/g_0, \tag{9}$$

which is exactly how one would determine the amplitude and the relaxation time of the correlation function, given only the first two channels of the CF. The nontrivial fact here is that this is actually the best way to determine A and a for the single exponential CF without shot noise.

It is interesting to compare the above analysis with the more intuitive approach that is based on the statistical properties of the CF itself.[8] If the measurements of the CF are carried out for many correlation times, as is usually the case, the CF can be viewed as the sum of many independent measurements. It is therefore fair to assume that the experimental values of the CF are distributed according to a Gaussian distribution:

$$P(\{g\}) = (2\pi)^{-M/2}(\det \mathbf{V})^{-1/2} \times \exp -\frac{1}{2}\sum_{\tau,\tau'}^{M} \delta g(\tau)\mathbf{V}^{-1}(\tau,\tau')\delta g(\tau'). \tag{10}$$

Here M is the number of points at which the CF is computed, and $\delta g(\tau) \equiv g(\tau) - G(\tau)$. Matrix $\mathbf{V}(\tau,\tau')$ is a correlation matrix of the deviations of the measured CF from the real one:

$$\mathbf{V}(\tau,\tau') = \langle \delta g(\tau)\delta g(\tau')\rangle = \langle g(\tau)g(\tau')\rangle - G(\tau)G(\tau'). \tag{11}$$

The angle brackets denote averaging over time. The best fit should maximize the probability $P\{g\}$ or, equivalently, minimize the functional

$$\tilde{\Omega} = \frac{1}{2}\sum_{\tau,\tau'=0}^{M} \delta g(\tau)\mathbf{V}^{-1}(\tau,\tau')\delta g(\tau'). \tag{12}$$

This approach, the generalized least-squares (GLS) fit, takes into account the correlations in the data to be fitted. The obvious advantage of the GLS fit is that one can calculate $\mathbf{V}(\tau,\tau')$ for the real photocounting process[9] without assuming Gaussian statistics for the photocurrent and for any algorithm used to compute the CF. For a Gaussian signal and for the CF given by Eq. (3), we readily find [by substituting Eq. (3) into Eq. (11) and neglecting edge terms] that

$$\mathbf{V}(\tau,\tau') = N\sum_{t}[G(t+\tau)G(t-\tau') + G(t-\tau)G(t-\tau')]. \tag{13}$$

We now show that, when the measurements are carried out for many correlation times and the difference between the measured and the actual CFs becomes small, the original probability distribution [Eq. (1)] for the signal converts into Gaussian distribution equation (10) for the CF. In other words, the MLP reduces to a GLS fit in the limit $N \to \infty$.

Let us rewrite Eq. (1) as

$$P(\{x\}) = (2\pi)^{-N/2}\exp\left(-\frac{\Omega}{2}\right), \tag{14}$$

where

$$\Omega = \mathrm{Tr}(\mathbf{G}^{-1}\cdot\mathbf{g}) + \ln(\det \mathbf{G}). \tag{15}$$

The functional Ω is proportional to N. When N is large the probability $P(\{x\})$ has a sharp maximum at the minimum of Ω. The minimum occurs when $\mathbf{G}$ is close to the experimentally calculated CF, $\mathbf{g}$. With this in mind, we denote

$$\mathbf{G} \equiv \mathbf{g}\cdot(\mathbf{1} - \mathbf{u}) \tag{16}$$

and expand the functional Ω in a power series of $\mathbf{u}$. Taking the determinant of both sides of Eq. (16), we find that

$$\det \mathbf{G} = \det \mathbf{g}\,[1 - \mathrm{Tr}(\mathbf{u}) + (\mathrm{Tr}\,\mathbf{u})^2/2 - \mathrm{Tr}(\mathbf{u}\cdot\mathbf{u})/2 + \ldots]. \quad (17)$$

It is also easy to verify by direct multiplication that

$$\mathbf{G}^{-1}\cdot\mathbf{g} = (\mathbf{1} + \mathbf{u} + \mathbf{u}\cdot\mathbf{u} + \ldots). \quad (18)$$

Substituting Eqs. (17) and (18) into Eq. (15), we see that the terms of the first order in $\mathbf{u}$ disappear, as expected, and that

$$\Omega = N + \ln(\det \mathbf{g}) + \frac{\mathrm{Tr}(\mathbf{u}\cdot\mathbf{u})}{2} + O(\mathbf{u}^3). \quad (19)$$

The first two terms in Eq. (19) are independent of $\mathbf{G}$ and can be omitted. Note that, according to its definition [Eq. (16)] $\mathbf{u} = \mathbf{1} - \mathbf{g}^{-1}\cdot\mathbf{G}$. Thus, the functional Ω to be minimized for finding $\mathbf{G}$ is

$$\Omega = \frac{1}{2}\mathrm{Tr}[\mathbf{g}^{-1}\cdot(\mathbf{g} - \mathbf{G})\cdot\mathbf{g}^{-1}\cdot(\mathbf{g} - \mathbf{G})]. \quad (20)$$

Using the fact that matrices $\mathbf{g}$ and $\mathbf{G}$ depend on only $\tau = |k - l|$ and neglecting edge effects in the summations, we can rewrite Eq. (20) as

$$\Omega = \sum_{\tau,\tau'=-N}^{N} \delta g(\tau)\mathbf{W}(\tau, \tau')\delta g(\tau'), \quad (21)$$

where

$$\mathbf{W}(\tau, \tau') = \frac{1}{2}\sum_t \mathbf{G}^{-1}(t + \tau)\mathbf{G}^{-1}(t + \tau'). \quad (22)$$

Of course, $\mathbf{G}$ in Eq. (22) is interchangeable with $\mathbf{g}$, as we should keep only terms of the order $\mathbf{u}^2$ in Eq. (15).

At first glance $\mathbf{W}$ cannot be the inverse of $\mathbf{V}$ as given by Eq. (11). However, these two matrices are of different rank even if $M = N$. Indeed, the summation in Eq. (21) is carried out over both positive and negative τ and τ', whereas the summation in Eq. (12) is over only nonnegative τ and τ'. If we use the symmetry of the CF to change Eq. (21) to the form of Eq. (12), we obtain a covariance matrix of the form

$$\tilde{\mathbf{W}}(\tau, \tau') = \frac{1}{2}\sum_t [\mathbf{G}^{-1}(t + \tau) + \mathbf{G}^{-1}(t - \tau) - \mathbf{G}^{-1}(t)\delta(\tau)] \times [\mathbf{G}^{-1}(t + \tau') + \mathbf{G}^{-1}(t - \tau') - \mathbf{G}^{-1}(t)\delta(\tau')]. \quad (23)$$

One can verify by multiplication that, indeed, $\tilde{\mathbf{W}} = \mathbf{V}^{-1}$. The fact that the actual number of channels in the CF, $M \ll N$, is of no consequence, provided that $G(\tau)$ is negligibly small when $\tau > M$.

The above analysis can be reproduced in a simple form in the spectral domain. Indeed, because $\mathbf{G}_{ik}$ depends on only $k - l$, in the limit $N \to \infty$ a Fourier transform diagonalizes this matrix. Probability equation (1) can then be rewritten as

$$P(\{x_\omega\}) = \pi^{-N/2}\prod_{k=0}^{N/2}\left(\frac{1}{I_{\omega_k}}\exp -\frac{{x_{\omega_k}}^2}{I_{\omega_k}}\right), \quad (24)$$

where

$${x_{\omega_k}}^2 \equiv \left|\sum_{m=0}^{N} x_m \exp -i\omega_k m\Delta t\right|^2 \quad (25)$$

is a harmonic of the power spectrum of the measured signal,

$$I_{\omega_k} \equiv \sum_{m,n=0}^{N} \mathbf{G}_{mn} \exp -i\omega_k(m - n)\Delta t \quad (26)$$

is the actual (discrete) power spectrum of the signal, and

$$\omega_k = \frac{2\pi k}{N\Delta t}, \qquad k = 0, \quad 1, \ldots, N/2. \quad (27)$$

Omitting a nonessential normalization constant, we can rewrite Eq. (24) as

$$-\ln(P) = \sum_{k=0}^{N/2}\left[\frac{{x_{\omega_k}}^2}{I_{\omega_k}} + \ln(I_{\omega_k})\right]. \quad (28)$$

When $N \to \infty$, obviously ${x_{\omega_k}}^2 \to I_{\omega_k}$. Expanding Eq. (28) to second order in small differences between the experimental ${x_{\omega_k}}^2$ and the actual I_{ω_k}, we immediately find that

$$-\ln(P) = \sum_{k=0}^{N/2}\left(\frac{{x_{\omega_k}}^2 - I_{\omega_k}}{I_{\omega_k}}\right)^2. \quad (29)$$

Equation (29) is equivalent to Eq. (20) and represents a well-known fact: Spectral harmonics of the random signal are statistically independent, and all have the same relative error.

For the single-exponential CF, on substituting Eq. (4) into Eq. (26), we find (for $N \to \infty$) that

$$I_{\omega_k} = \frac{AN(1 - a^2)}{1 + a^2 - 2a\cos\omega_k\Delta t}. \quad (30)$$

This is a discrete form of the Lorentz curve. As we can see from Eq. (24), the probability of observing a realization of the signal with the power spectrum ${x_{\omega_k}}^2$ depends only on the combination $\Sigma{x_{\omega_k}}^2/I_{\omega_k}$. In the case of a single-exponential CF, that is, with I_{ω_k} given by Eq. (30), this combination is expressed exclusively through the zeroth and the first Fourier harmonics of the measured power spectrum, which, of course, are the zeroth and the first channels of the CF. Note that fitting the whole spectrum with a pure Lorentzian [using the exact minimization functional Eq. (28)] is mathematically equivalent to using the first two channels of the CF.

It seems that the zeroth and the first channels of the CF are too close to each other to provide for a

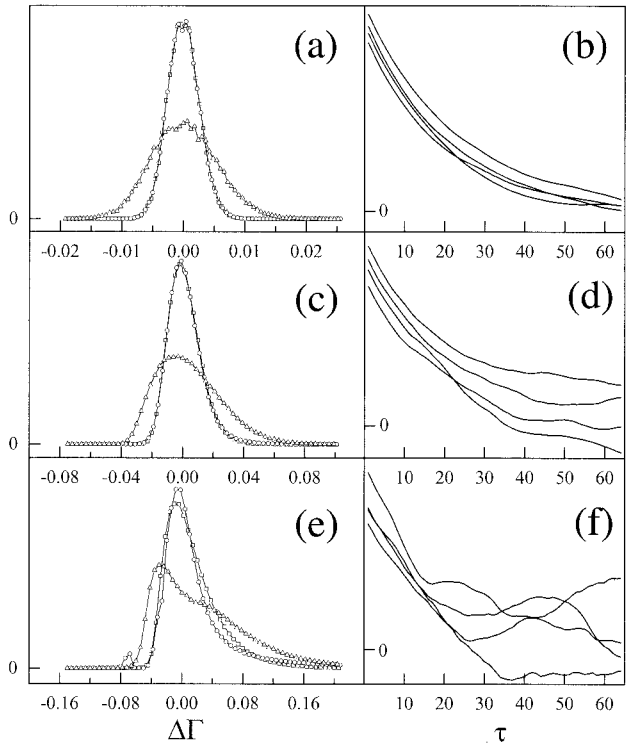

Fig. 1. (a), (c), (e) Distributions of the inverse relaxation time Γ_{fit} as calculated from the simulated single-exponential CF without shot noise. Triangles, SLS fit; squares, GLS fit; circles, the MLP fit. The CFs were calculated in $M = 64$ channels from (a), (b) $256M$ points; (c), (d) $16M$ points; (e), (f) $2M$ points. The x axis shows $\Delta\Gamma = \Gamma_{\text{fit}} - \Gamma$, where $\Gamma = 0.05$ was used to simulate the CFs. The y axis shows the probability of a particular error $\Delta\Gamma$ for each method. (b), (d), (f) Representative simulated correlation functions.

reliable determination of the relaxation time because even small errors will be dramatically magnified. However, the errors in these channels are nearly completely correlated (in the absence of shot noise), and the slope is maintained much more accurately than it might seem. The simulated CFs presented in Figs. 1(b), 1(d), and 1(f) illustrate this fact well. To trace explicitly how this happens, let us calculate the variance of parameters determined by the MLP. The variance can be calculated from the likelihood probability given by Eq. (8) by means of the Cramer–Rao estimate.[10] However, for our special case there are simple analytical expressions (9) for A and Γ. It is more economical and more illuminating to calculate the variance of these parameters directly. For example, the variance of $\Gamma_{\text{fit}} = 1/\Delta t \ln(g_1/g_0)$ can be calculated as follows:

$$\langle \delta\Gamma^2 \rangle = \frac{1}{\Delta t^2}\left[\frac{\langle \delta {g_0}^2 \rangle}{G(0)^2} - 2\,\frac{\langle \delta g_0 \delta g_1 \rangle}{G(0)G(1)} + \frac{\langle \delta {g_1}^2 \rangle}{G(1)^2}\right]. \quad (31)$$

When Δt is small, g_0 and g_1 are close to each other, and the middle term in Eq. (31) nearly cancels the first and the last terms. Indeed, substituting Eqs. (11) and (13) and the explicit form for G [Eq. (4)], we find that

$$\langle \delta\Gamma^2 \rangle = \frac{a^{-2} - 1}{N\Delta t^2} \equiv \frac{\exp(2\Gamma\Delta t) - 1}{N\Delta t^2}. \quad (32)$$

It is the factor $\exp(2\Gamma\Delta t) - 1 \approx 2\Gamma\Delta t$ that reflects the cancellation of the correlated errors. This factor dramatically decreases the error in Γ_{fit}, which, in the limit $\Gamma\Delta t \ll 1$, becomes

$$\frac{\langle \delta\Gamma^2 \rangle}{\Gamma^2} \approx \frac{2}{\Gamma T}. \quad (33)$$

Here $T \equiv N\Delta t$ is the total time of measurement. The relative error in A_{fit} is exactly the same:

$$\frac{\langle \delta {g_0}^2 \rangle}{A^2} = \frac{4}{N(1 - a^2)} \approx \frac{2}{\Gamma T}. \quad (34)$$

The errors in Γ_{fit} and A_{fit} are independent of Δt as long as $\Gamma\Delta t \ll 1$.

Note that, if the total number of data points N is fixed, Eq. (32) provides a recipe for the optimal spacing of these points. One can easily verify that the error in Γ_{fit} has a minimum at $\Gamma\Delta t \approx 0.79$, i.e., the measurements has to be taken every 0.79 times the correlation time. Too-sparse measurements give little information about the correlations, whereas too-dense measurements are not independent. In contrast, the error in A [Eq. (34)] does not have a minimum. If N is fixed the best estimate of A is obtained when measurements are spread as far away from one another as possible so that they are the least correlated.

In a real experiment, however, what is fixed is not N but the total time of measurement, $T = N\Delta t$. In this case, clearly the smaller Δt is, the better. However, when Δt becomes small compared with the correlation time the adjacent measurements are strongly correlated and do not provide independent information. As a result, even when $N \to \infty$ as $\Delta t \to 0$ the errors in the fitting parameters converge to their finite limiting values given by relation (33) and Eq. (34).

The variations in A_{fit} and Γ_{fit} are not independent. It can readily be shown that

$$\frac{\langle \delta A \delta\Gamma \rangle}{A\Gamma} \approx -\frac{2}{\Gamma T}. \quad (35)$$

Comparing relation (35) with relation (33) and Eq. (34), we discover that, within the leading $\Gamma\Delta t$ terms, relative errors in Γ_{fit} and A_{fit} are not only equal but also completely anticorrelated. This result means that the relative error in the product $\Gamma_{\text{fit}}A_{\text{fit}}$ is less than the relative error in each of these quantities separately. In the limit $\Gamma\Delta t \ll 1$, $\Gamma_{\text{fit}}A_{\text{fit}} \approx (g_0 - g_1)/\Delta t$. The error in this quantity turns out to be

$$\frac{\langle \delta A\Gamma \rangle}{A\Gamma} \approx -\frac{2}{N}. \quad (36)$$

Thus the accuracy of the product ΓA is determined not solely by the total time of measurement but also by how often the data are taken. The relative error in this product decreases with Δt and is less by a factor of $\Gamma \Delta t$ than the errors in A and Γ separately. This fact is explained in Section 4 below.

3. Simulations

We performed computer simulations to compare the effectiveness of three fitting procedures, i.e., a SLS fit that assigns the same absolute error to every channel and ignores correlations between CF channels, a GLS fit based on minimization functional equation (12) that takes into account the cross correlation of the statistical errors in CF but assumes that these errors have Gaussian statistics, and a MLP fit based on minimization functional equation (15) that is derived from the MLP for the observed signal. Here we study the test case of a single-exponential CF without shot noise. In this case the most rigorous MLP approach reduces simply to Eqs. (9), which use only the first two channels of the CF. This is the most dramatic difference from the SLS fit, and we therefore expect to obtain the upper bound on the benefit that can be achieved by refined statistical analysis of the CF.

The sequence of random numbers with Gaussian statistics and the single-exponential CF was generated in the following way: First, 8192 random numbers with Gaussian statistics and mean squares equal to 1 were generated. Then the sequence $\{r_i\}$ of uncorrelated random numbers with Gaussian statistics was produced by the random selection of one of these 8192 numbers. The sequence $\{x_i\}$ of random numbers with Gaussian statistics and a single-exponential CF was produced from the sequence $\{r_i\}$ according to the following rule: $x_i = a x_{i-1} + r_i$. We chose a value of $a = \exp(-0.05)$, with a correlation time of $1/\Gamma = 20$. The first 1024 points were discarded. For large i, regardless of the initial value, $x_i \approx \sum_{k=0}^{\infty} r_{i-k} a^k$, and $g(k) \equiv \langle x_i x_{i-k} \rangle = a^k/(1 - a^2)$. To produce the CF of the desired amplitude A one should simply multiply the sequence $\{x_i\}$ by $[A(1 - a^2)]^{1/2}$.

A simulation consisted of generating a sequence $\{x_i\}$ of a particular length N, calculating the full CF in 64 channels, and determining the parameters A and a by the three methods described above. Simulations were repeated 10^6 times so that a reliable distribution of the parameters obtained from the fitting procedures about their true values was accumulated. The results for the CF that were accumulated for $\approx$800 correlation times ($N = 2^{14}$), $\approx$50 correlation times ($N = 2^{10}$), and $\approx$6.5 correlation times ($N = 128$) are summarized in Fig. 1. In Figs. 1(b), 1(d), and 1(f), we can see four representative CFs that were obtained for each of these accumulation times. Figure 1(b) corresponds to the longest accumulation that produces the most accurate CF with a statistical accuracy of approximately 3.5%. Figure 1(d) shows the CF at an intermediate accumulation that corresponds to an accuracy of $\approx$14%. Figure 1(f) shows the CF that was accumulated over only 6.5 correlation times and corresponds to a statistical accuracy of 40%. Note that all these CFs are smooth because no shot noise is present. Figures 1(a), 1(c), and 1(e) show the probability distribution for the inverse correlation time obtained from the simulated data. In each case, the abscissa is the deviation of the Γ_{fit} from the actual value $\Gamma = 0.05$, and the ordinate is an arbitrarily normalized number of simulations that produce a particular Γ_{fit}.

Table 1. Statistical Errors in the Parameters of the Single-Exponential CF Obtained by Use of the SLS Fits and the GLS and the MLP[a]

Fitting Type	Accumulation N		
	16,384	1024	128
SLS			
σ_{AA}	0.0550	0.2179	0.5992
$\sigma_{\Gamma\Gamma}$	0.1058	0.4304	1.4509
$\sigma_{\Gamma A}$	0.1161	0.4484	1.2632
GLS[b]			
σ_{AA}	0.0496	0.2030	0.5392
$\sigma_{\Gamma\Gamma}$	0.0511	0.2415	2.2023
$\sigma_{\Gamma A}$	0.0116	0.0542	0.4789
MLP			
σ_{AA}	0.0494	0.1966	0.5364
$\sigma_{\Gamma\Gamma}$	0.0509	0.2210	0.8845
$\sigma_{\Gamma A}$	0.0116	0.0540	0.4949
Theory			
σ_{AA}	0.0494	0.1976	0.5590
$\sigma_{\Gamma\Gamma}$	0.0494	0.1976	0.5590
$\sigma_{\Gamma A}$	0.0110	0.0442	0.1250

[a]For each method $\sigma_{AA} \equiv \langle \delta A^2 \rangle^{1/2}/A$, $\sigma_{\Gamma\Gamma} \equiv \langle \delta \Gamma^2 \rangle^{1/2}/\Gamma$, and $\sigma_{\Gamma A} \equiv \langle \delta(\Gamma A)^2 \rangle^{1/2}/(\Gamma A)$ are shown as well as the theoretical values expected for the MLP fit. The CF was calculated in $M = 64$ channels. Each value was obtained from 10^6 simulations.

[b]The GLS fit used the covariance matrix equation (13).

The results of the simulations are summarized in Table 1. This table lists the relative mean-squared deviations of parameters A, Γ, and $A\Gamma$ from their expected values as obtained with all three methods. In addition, the theoretical expectations for the MLP fit given by relations (33) and (36) and Eq. (34) are presented. Regardless of the accuracy of the measurements, the SLS fit produces an approximately 2 times broader distribution in Γ_{fit} than do the GLS and the MLP fits, which both take into account the cross correlation in the statistical errors of the CF. Furthermore, the SLS fit completely fails to reveal the anticorrelation in the A and the Γ errors and produces a relative error in $A\Gamma$ as if A and Γ were independently measured quantities. The GLS fit for which it is assumed that the CF itself has Gaussian statistics turns out to be nearly equivalent to the MLP fit. In fact, in the longest accumulations $N = 2^{14}$; the difference in the parameters obtained by these two methods was less then 1% of the parameter variation from one simulation to another. Even when the CF is measured with very low accuracy, $N = 128$, the GLS approach produces a sharp, although somewhat displaced, distribution with only a slightly worse

mean-squared spread than does the rigorous MLP method. However, at such a low accuracy the GLS approach occasionally loses stability and produces parameters that are far from the true value.

4. Discussion

We investigate in this paper the role of channel-to-channel cross correlations in the CF in the analysis of the PCS data. Inasmuch as shot noise masks this cross correlation, we considered the limiting case in which shot noise is absent. We discovered that, in the absence of shot noise, the optimal way to fit the single exponential CF reduces to Eqs. (9), so that only the first two channels of the CF are utilized. This proposition does not make sense to anyone who has ever carried out a PCS experiment. The reason is that shot noise is an inherent part of such an experiment. To elucidate the physical meaning of these results, let us forget for a moment about light scattering. The classic example of a Gaussian signal with a single-exponential CF comprises equilibrium fluctuations of a single thermodynamic variable, for instance, the position $x(t)$ of a particle diffusing in a one-dimensional quadratic potential. The equation of motion of such a particle is

$$\gamma \frac{\mathrm{d}x}{\mathrm{d}t} = -kx + f, \tag{37}$$

where γ is the friction coefficient, k is the elastic constant of the potential, and f is a random force. We know that the position of this particle is a random variable with Gaussian statistics and that its correlation function is[11]

$$\langle x(0)x(t)\rangle = \frac{k_B T}{k} \exp\left(-\frac{k}{\gamma} t\right), \tag{38}$$

where $k_B T$ is the Boltzmann constant times the absolute temperature. Let us now imagine that we have measured the positions of the particle x_0, x_1, $x_2, \ldots, x_N$ at times $0, \Delta t, 2\Delta t, \ldots, N\Delta t$ and that we wish to determine the amplitude $A = (k_B T)/k$ and the decay constant $\Gamma = k/\gamma$ of the single-exponential correlation function [Eq. (38)]. Note that the product $A\Gamma = (k_B T)/\gamma$ is actually a diffusion coefficient D of the particle, which is independent of the elastic constant of the potential.

Obviously, if we wish to determine the amplitude of the particle fluctuations, we just calculate $A = \langle x^2\rangle$, which is exactly what Eqs. (9) recommend. The correlation time Γ^{-1} is the time needed for diffusion over a distance $A^{1/2}$. During this time, $x(t)$ remembers its initial value. That is why the number of truly independent measurements of A (or of Γ) is ΓT, where T is the total time of the experiment and the errors in these parameters are given by relation (33) and Eq. (34). However, the product $A\Gamma$, which is a diffusion coefficient, can be determined much more accurately. Indeed, every pair of consecutive measurements x_n and x_{n+1} provides an estimate of the diffusion coefficient. The accuracy of this estimate does not decrease as $\Delta t \to 0$, provided that values of x are measured exactly. In fact, the mean-squared displacement of the particle over a period of time that is short compared with Γ^{-1} is completely determined by the diffusion, $D = \langle (x_{n+1} - x_n)^2\rangle/2\Delta t$, and is independent of the position of the particle. Furthermore, the error in the diffusion coefficient that is calculated from a pair of consecutive measurements is statistically independent of the error in the diffusion coefficient that is calculated from a different pair. The sequence $x_0, x_1, x_2, \ldots, x_N$ provides N independent measurements of the diffusion coefficient. That is why the accuracy of the product ΓA is given by relation (36) and is much better than the accuracy of A or Γ separately. Note that $\langle (x_{n+1} - x_n)^2\rangle \equiv 2(g_0 - g_1)$, and therefore the value of ΓA, is indeed extracted from the first two channels of the CF.

The above example of the diffusing particles allows us to elucidate the role that shot noise plays in fitting the correlation function. Imagine that the position of the particle is determined not exactly but with an error. If this error exceeds the typical $|x_{n+1} - x_n|$, the determination of the diffusion coefficient from the individual pairs becomes impossible, and the whole CF has to be analyzed. In photodetection the original signal x is replaced with a Poisson distribution of integer numbers with average value x. Only when the shot noise is very low, that is, when $x \gg 1$, does this Poisson distribution provide a sufficiently accurate estimate of x, and the analysis of the CF can therefore be limited to the analysis of only consecutive data points.

A single correlation time in the random process results from the absence of memory in the process. The conditional probability of observing signal x_2 at moment t_2, provided that the value x_1 was observed at the preceding moment t_1, is independent of the history before t_1. Thus in the case of a single-exponential CF the correlation between adjacent points contains all the information about the statistical properties of the signal, provided that the measurement of the signal has no error.

The fact that the first channels of the CF contain practically all the information explains the efficiency of the cumulant method for the analysis of a CF with a narrow distribution of relaxation times. However, using just the first two channels of the CF to fit the CF with a single-exponential function is clearly ill advised. The reason is that fine tuning of the fitting procedure based on *a priori* assumptions of the statistical properties of the CF makes the fitting procedure less stable to errors in these *a priori* assumptions. Because an actual CF always has some shot noise and never is exactly a single exponential, it is hard to imagine a real situation when using just the first two channels of the CF, as both the GLS fit and the MLP do, would be better than a SLS fit. Taking into account the cross correlation of the errors in the CF guarantees improvement in the accuracy of the results only if the assumptions that we used to calculate these cross correlations are indeed valid.

Our analysis demonstrates that a refined statistical analysis of the CF approximately doubles the accuracy of the estimation of the correlation time for the single-exponential CF without shot noise compared with the SLS fit. That increase corresponds to an approximately 4 times gain in the accumulation time. However, for a more complex CF and in the presence of shot noise this advantage quickly evaporates. We can also see from Table 1 that, even in a relatively short experiment, the errors in the CF can be treated as Gaussian random variables and that a GLS fit successfully extracts all the information in the CF. However, one has to be careful to ensure that the covariance matrix used in the GLS fit adequately represents reality. For a short measurement a rigorous MLP treatment that is based on Eq. (15) is clearly beneficial.

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