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# Light scattering from independent particles—nongaussian correction to the clipped intensity correlation function

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**Abstract.** We consider Rayleigh scattering of laser light from an assembly of independent particles. We allow the particle number $M$ within the scattering volume to fluctuate around a certain mean value $\langle M \rangle$. We derive a general formula for the intensity moments and find the nongaussian correction to the single-clipped-at-zero photocount correlation function to order $1/\langle M \rangle^2$.

## 1. Introduction

We consider a light-scattering experiment where there are $N$ independent (non-interacting) particles contained in a container with volume $V$. A laser beam is focused into a small region of the medium resulting in a well-defined scattering volume $v$. For a homogeneous system, such as $N$ brownian particles dispersed in a liquid medium, the average number of particles in the scattering volume is then

$$\langle M \rangle = N\frac{v}{V}. \tag{1}$$

In the following calculation we shall eventually take the thermodynamic limit in which $N \to \infty$, $v/V \to 0$ in such a way that $\langle M \rangle$ is a finite number. This limiting process is necessary for us to be able to neglect the unknown wall effect of the container and is also rather plausible in the practical experimental set-up where $v/V$ can easily be made as small as $10^{-7}$. Depending on the concentration of the brownian particles, $\langle M \rangle$ can then be made to range from less than unity to many hundreds. There is a class of experiments involving macromolecules in solution (Benedek 1968, Cummins and Swinney 1969) or motile micro-organisms in suspension (Nossal *et al* 1971, Nossal and Chen 1972) in which $\langle M \rangle$ is fairly large and the assumption of independent movements is still valid. We shall consider the Rayleigh scattering of laser light from these independently-moving particles.

## 2. Calculation of nongaussian correction

A powerful technique which can be used to study slowly-varying time-dependent phenomena in liquids is intensity correlation spectroscopy (Jakeman and Pike 1969,

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Chen and Polonsky-Ostrowsky 1969). In this method of spectroscopy one essentially measures time-dependent statistical properties of fluctuations in the scattered-light intensity. One can write the scattered field amplitude generally as

$$E_s(t) = \lambda \sum_{i=1}^{M} \exp(i\boldsymbol{q} \cdot \boldsymbol{r}_i(t)) \tag{2}$$

where $\lambda$ is the scattering amplitude of each particle in the scattering volume and $\boldsymbol{q}$ is the wavevector transfer of the scattering. (We have assumed the scattering volume to be uniformly illuminated by the laser beam.) Equation (2) can also be written (see Schaefer and Berne 1972),

$$E_s(t) = \lambda \sum_{i=1}^{N} b_i(t) \exp(i\boldsymbol{q} \cdot \boldsymbol{r}_i(t)) \tag{3}$$

with the random variable $b_i(t)$ defined as

$$b_i(t) = \begin{cases} 1 & \text{if particle } i \text{ is in } v \\ 0 & \text{if particle } i \text{ is not in } v. \end{cases}$$

Inclusion of $b_i(t)$ in (3) conveniently allows us to sum over all particles $N$. We can also write the instantaneous number of particles in $v$ as

$$M(t) = \sum_{i=1}^{N} b_i(t) \tag{4}$$

from which it follows

$$\langle M \rangle = \sum_{i=1}^{N} \langle b_i(t) \rangle = N\langle b \rangle. \tag{5}$$

By comparing (5) with (1) we identify $\langle b \rangle = v/V$ so that in the thermodynamic limit $\langle b \rangle \to 0$. In a previous paper (Chen and Tartaglia 1972) we treated a special case of a fixed number of particles in the scattering volume. This limiting case can be obtained from the present treatment by letting $\langle b \rangle \to 1$ and $N = \langle M \rangle$ so that the fluctuation of the number of particles in the scattering volume can be neglected.

It is easy to show (Chandrasekhar 1943, Appendix 3) that the random variable $M$ is Poisson-distributed in the limit $N \to \infty$. If, for simplicity, one takes the fluctuation of $M(t)$ to decay exponentially with a decay constant $\beta$, then one can also derive the result

$$\frac{\langle b(t_1)b(t_2) \rangle}{\langle b \rangle} \equiv h(e^{-\beta\tau}, \langle b \rangle) = e^{-\beta\tau} - \langle b \rangle e^{-\beta\tau} + \langle b \rangle \tag{6}$$

where $\tau = |t_2 - t_1|$. (In fact the decay will not, in general, be a simple exponential.) The intensity of scattered light is related to the scattered amplitude by $I(t) = E_s^*(t)E_s(t)$ and therefore we can use expression (3) to calculate the first-order intensity correlation function

$$\begin{aligned} \langle I_1 I_2 \rangle &= \lambda^4 \sum_{ijkl}^{N} \langle b_i(t_1)b_j(t_1)b_k(t_2)b_l(t_2) \exp(-i\boldsymbol{q} \cdot \boldsymbol{r}_i(t_1)) \exp(i\boldsymbol{q} \cdot \boldsymbol{r}_j(t_1)) \exp(-i\boldsymbol{q} \cdot \boldsymbol{r}_k(t_2)) \\ &\quad \times \exp(i\boldsymbol{q} \cdot \boldsymbol{r}_l(t_2)) \rangle \\ &= \lambda^4 \sum_{ijkl}^{N} \langle b_{i1}b_{j1}b_{k2}b_{l2} \rangle \langle A_{i1}^* A_{j1} A_{k2}^* A_{l2} \rangle \end{aligned} \tag{7}$$

where the abbreviations $I(t_1) \equiv I_1$, $b_i(t_1) \equiv b_{i1}$, $\exp(i\mathbf{q} \cdot \mathbf{r}_i(t_1)) \equiv A_{i1}$ etc have been used. The factorization of averages in (7) follows from the fact that, under normal experimental conditions, the time scale of fluctuations of the $b$'s is three to four orders of magnitude slower than that of the $A$'s. Thus it is a very good approximation to treat the two types of variables as statistically independent. We can then evaluate the averages in (7) by noting that the only non-vanishing terms in the bracket containing $A$'s are those with $i = j$, $k = l$ (including $i = j = k = l$) and $i = l \neq j = k$. Thus denoting $g_{12} = |\langle A_{i1}^* A_{i2} \rangle| = |\langle A_{j1} A_{j2}^* \rangle|$ and using the relation $\langle I \rangle = \lambda^2 N \langle b \rangle = \lambda^2 \langle M \rangle$, we have

$$\begin{aligned}\frac{\langle I_1 I_2 \rangle}{\langle I \rangle^2} &= \frac{1}{\langle M \rangle^2}\left(\sum_{i,k}^{N} \langle b_{i1} b_{k2} \rangle + \sum_{i \neq j}^{N} \langle b_{i1} b_{i2} \rangle \langle b_{j1} b_{j2} \rangle g_{12}^2\right) \\ &= \frac{1}{\langle M \rangle^2}\left(\sum_{i \neq k}^{N} \langle b \rangle^2 + \sum_{i}^{N} \langle b_1 b_2 \rangle + \sum_{i \neq j}^{N} \langle b_1 b_2 \rangle^2 g_{12}^2\right) \\ &= \frac{1}{\langle M \rangle^2}\{N(N-1)\langle b \rangle^2 + Nh(\mathrm{e}^{-\beta\tau}, \langle b \rangle) + N(N-1)\langle b \rangle^2 g_{12}^2\} \qquad (8)\end{aligned}$$

where we have used the fact that $\langle b_1 b_2 \rangle^2$ is essentially $\langle b \rangle^2$ in the time range where $g_{12}^2$ has appreciable value. Expression (8) agrees with Schaefer and Berne's result if we take the thermodynamic limit discussed in the Introduction. On the other hand, if we take $\langle b \rangle = 1$ and $N = \langle M \rangle$, we obtain the result for a fixed number of particles (Chen and Tartaglia 1972, equation (5)). It is worth noting that the short time limit ($\beta\tau \ll 1$) of the former result can be obtained simply by averaging the latter result over a Poisson distribution for the number of particles in the scattering volume.

We can now extend the computational technique used above to obtain the higher order two-time intensity correlation functions. By actually writing it out in terms of $b$'s and $A$'s we find that we can generally write

$$\frac{\langle I_1 I_2^k \rangle}{\langle I \rangle^{k+1}} = \frac{1}{\langle M \rangle^{k+1}} \sum_{l=1}^{k} C_l(k)(N^{[l+1]}\langle b \rangle^{l+1} + lN^{[l]}\langle b \rangle^l h(\mathrm{e}^{-\beta\tau}, \langle b \rangle)) + f(k, N, \langle b \rangle) g_{12}^2 \qquad (9)$$

where $N^{[l]} \equiv N(N-1)\ldots(N-l+1)$ and $C_l(k)$ is a coefficient defined as

$$C_l(k) = \sum_{\{a\}} (k; a_1, a_2, \ldots, a_k)' \frac{k!}{(1!)^{a_1}(2!)^{a_2}\ldots(k!)^{a_k}} \qquad (10)$$

and the summation is over a set of $\{a\}$ satisfying two conditions:

$$\begin{aligned} &a_1 + 2a_2 + \ldots k a_k = k \\ &a_1 + a_2 + \ldots a_k = l. \end{aligned} \qquad (11)$$

The coefficient $(k; a_1, a_2, \ldots, a_k)'$ is the number of ways of partitioning a set of $k$ different objects into $a_j$ subsets containing $j$ objects for $j = 1, 2, \ldots, l$, and is tabulated up to $k = 10$ in Abramowitz and Stegun (1965). $f(k, N, \langle b \rangle)$ is an unknown coefficient to be determined shortly. We have, as before, used the fact that we can neglect the slow time dependence of the $b$'s whenever they multiply $g_{12}^2$.

In the limit $|t_2 - t_1| \to \infty$, $g_{12} \to 0$, $h \to \langle b \rangle$ we get

$$\frac{\langle I \rangle \langle I^k \rangle}{\langle I \rangle^{k+1}} = \frac{1}{\langle M \rangle^{k+1}} \sum_{l=1}^{k} C_l(k)(N^{[l+1]}\langle b \rangle^{l+1} + lN^{[l]}\langle b \rangle^{l+1}). \qquad (12)$$

In this expression, if we further set $\langle b\rangle = 1$, $\langle M\rangle = N$ we get the intensity moments

$$\frac{\langle I^k\rangle}{\langle I\rangle^k} = \frac{1}{N^{k+1}}\sum_{l=1}^{k} C_l(k)(N^{[l+1]} + lN^{[l]})$$

$$= \frac{1}{N^k}\sum_{l=1}^{k} C_l(k)N^{[l]} \tag{13}$$

which agrees with results obtained previously (Chen and Tartaglia 1972) for a fixed number of particles. To get the intensity moments for the case when $\langle M\rangle$ is variable we let $N \to \infty$ and $\langle b\rangle \to 0$ in (12) to obtain

$$\frac{\langle I^k\rangle}{\langle I\rangle^k} = \sum_{l=1}^{k} C_l(k)\frac{\langle M\rangle^l}{\langle M\rangle^k}. \tag{14}$$

From the intensity moments (14) we then determine the unknown factor $f(k, N, \langle b\rangle)$ by setting $t_1 = t_2$ in (9). In this case we have $h = 1$ so that

$$\frac{\langle I^{k+1}\rangle}{\langle I\rangle^{k+1}} = \frac{1}{\langle M\rangle^{k+1}}\sum_{l=1}^{k} C_l(k)(N^{[l+1]}\langle b\rangle^{l+1} + lN^{[l]}\langle b\rangle^l) + f(k, N, \langle b\rangle). \tag{15}$$

Again we recover the result for a fixed number of particles $f(k, N, 1)$ (Chen and Tartaglia 1972) by setting $\langle b\rangle = 1$, $\langle M\rangle = N$. However, for the present discussion we set $\langle b\rangle = 0$ and $N \to \infty$ which then gives

$$f(k, N, 0) = \frac{\langle I^{k+1}\rangle}{\langle I\rangle^{k+1}} - \sum_{l=1}^{k} C_l(k)\left(\frac{\langle M\rangle^l}{\langle M\rangle^k} + l\frac{\langle M\rangle^l}{\langle M\rangle^{k+1}}\right)$$

$$= \sum_{l=1}^{k+1} D_l(k+1)\frac{\langle M\rangle^l}{\langle M\rangle^{k+1}} \tag{16}$$

where

$$\begin{aligned} &D_{k+1}(k+1) = C_{k+1}(k+1) - C_k(k) = k!k \\ &D_l(k+1) = C_l(k+1) - C_{l-1}(k) - lC_l(k), \qquad l = 2, 3, \ldots k \\ &D_1(k+1) = 0. \end{aligned} \tag{17}$$

We can now compute the two-time intensity correlation function for the case when $\langle M\rangle$ is variable by substituting (16) into (9) and letting $\langle b\rangle \to 0$, $N \to \infty$ to obtain

$$\frac{\langle I_1 I_2^k\rangle}{\langle I\rangle^{k+1}} = \sum_{l=1}^{k} C_l(k)\left(\frac{\langle M\rangle^l}{\langle M\rangle^k} + l\frac{\langle M\rangle^l}{\langle M\rangle^{k+1}}\mathrm{e}^{-\beta\tau}\right) + g_{12}^2\sum_{l=1}^{k+1} D_l(k+1)\frac{\langle M\rangle^l}{\langle M\rangle^{k+1}}. \tag{18}$$

We can write out the expansion in (18) explicitly up to order $1/\langle M\rangle^2$,

$$\frac{\langle I_1 I_2^k\rangle}{\langle I\rangle^{k+1}} = k!\left(1 + \frac{k\,\mathrm{e}^{-\beta\tau} + \frac{1}{2}\binom{k}{2}}{\langle M\rangle} + \frac{\frac{1}{2}\binom{k}{2}(k-1)\,\mathrm{e}^{-\beta\tau} + (1/3!)\binom{k}{3} + \frac{3}{4}\binom{k}{4}}{\langle M\rangle^2}\right)$$

$$+ g_{12}^2 k!\left(k + \frac{\frac{3}{2}\binom{k}{3} + 2\binom{k}{2}}{\langle M\rangle} + \frac{\frac{15}{4}\binom{k}{5} + \frac{20}{3}\binom{k}{4} + \frac{5}{2}\binom{k}{3}}{\langle M\rangle^2}\right). \tag{19}$$

Equations (14) and (18) are the basic results of the present paper. For their applications we shall consider the photocount factorial moment and the clipped photocount

correlation function. The $k$th normalized factorial moment of the photocount is equal to the $k$th intensity moment (Mehta 1969) given by (14), that is,

$$\frac{\langle n(n-1)\dots(n-k+1)\rangle}{\langle n\rangle^k} = \frac{\langle I^k\rangle}{\langle I\rangle^k} = \sum_{l=1}^{k} C_l(k)\frac{\langle M\rangle^l}{\langle M\rangle^k}$$
$$= k!\left[1+\frac{1}{2!}\binom{k}{2}\frac{1}{\langle M\rangle}+\left\{\frac{1}{3!}\binom{k}{3}+\frac{3}{4}\binom{k}{4}\right\}\frac{1}{\langle M\rangle^2}+\dots+\frac{1}{\langle M\rangle^{k-1}}\right]. \tag{20}$$

The single-clipped-at-zero photocount correlation function and the average clipped photocount are given respectively by (Chen and Tartaglia 1972)

$$\langle n_1 n_2^{(0)}\rangle = \langle n\rangle - \langle n\rangle \sum_{j=0}^{\infty}\frac{(-\langle n\rangle)^j}{j!}\frac{\langle I_1 I_2^j\rangle}{\langle I\rangle^{j+1}} \tag{21}$$

$$\langle n^{(0)}\rangle = 1-\sum_{j=0}^{\infty}\frac{(-\langle n\rangle)^j}{j!}\frac{\langle I^j\rangle}{\langle I\rangle^j} \tag{22}$$

which can be calculated explicitly up to order $1/\langle M\rangle^2$ for the present case by using (19) and (20),

$$\frac{\langle n_1 n_2^{(0)}\rangle}{\langle n\rangle\langle n^{(0)}\rangle} = 1+\frac{1}{1+\langle n\rangle}\frac{e^{-\beta\tau}}{\langle M\rangle}+\frac{\langle n\rangle^2}{(1+\langle n\rangle)^3}\frac{e^{-\beta\tau}}{\langle M\rangle^2}$$
$$+\frac{g_{12}^2}{1+\langle n\rangle}\left(1-\frac{\langle n\rangle^2+3\langle n\rangle}{2(1+\langle n\rangle)^2}\frac{1}{\langle M\rangle}-\frac{5\langle n\rangle^4+25\langle n\rangle^3-19\langle n\rangle^2}{12(1+\langle n\rangle)^4}\frac{1}{\langle M\rangle^2}\right) \tag{23}$$

$$\langle n^{(0)}\rangle = \frac{\langle n\rangle}{1+\langle n\rangle}\left(1-\frac{\langle n\rangle}{2(1+\langle n\rangle)^2}\frac{1}{\langle M\rangle}+\frac{2\langle n\rangle^2-7\langle n\rangle^3}{12(1+\langle n\rangle)^4}\frac{1}{\langle M\rangle^2}\right). \tag{24}$$

We notice that in the expression for the photocount factorial moment (20), the first term gives the well known gaussian result (Mehta 1969) and therefore the nongaussian correction appears as powers in $\langle M\rangle^{-1}$. As for the clipped photocount correlation function (23), we observe the following three limiting cases:

$$\lim_{\tau\to\infty}\frac{\langle n_1 n_2^{(0)}\rangle}{\langle n\rangle\langle n^{(0)}\rangle} = 1 \tag{25}$$

$$\lim_{\langle n\rangle\to 0}\frac{\langle n_1 n_2^{(0)}\rangle}{\langle n\rangle\langle n^{(0)}\rangle} = \frac{\langle n_1 n_2\rangle}{\langle n\rangle\langle n\rangle} = \frac{\langle I_1 I_2\rangle}{\langle I\rangle^2} = 1+\frac{1}{\langle M\rangle}e^{-\beta\tau}+g_{12}^2 \tag{26}$$

$$\lim_{\langle M\rangle\to\infty}\frac{\langle n_1 n_2^{(0)}\rangle}{\langle n\rangle\langle n^{(0)}\rangle} = 1+\frac{1}{1+\langle n\rangle}g_{12}^2. \tag{27}$$

Equation (25) is an exact limit to be obeyed by any two-time correlation function. Equation (26) gives the same result as obtained by Schaefer and Berne (1972). Furthermore (27) gives, as it must, the same result as obtained by Jakeman and Pike (1969) assuming from the start that the scattered field is a gaussian random process. It is possible to check experimentally expression (23) by first measuring $\langle n^{(0)}\rangle$ to obtain $\langle M\rangle$ and then using this value to check the nongaussian terms in (23) by varying $\langle n\rangle$.

## 3. Conclusions

We have calculated correction terms to the single-clipped-at-zero photocount correlation function (for gaussian light), which arise due to the nongaussian nature of the scattered light when the mean number of particles in the scattering volume is not 'essentially infinite'. When studying large scatterers ($\gtrsim 1$ μm) with a focussed laser beam, these nongaussian terms can become appreciable. Thus, in view of the wide use of clipped correlation in intensity fluctuation spectroscopy, the calculation of their magnitude provided in this paper is of obvious interest. Two final points should be made. Firstly, throughout this paper we have assumed uniform illumination of the scattering volume and total spatial coherence of the scattered electric field over the photo-sensitive area of the detector. The effects of more realistic beam profiles and incomplete spatial coherence on equations (23) and (24) are extremely difficult to estimate, though such calculations have been performed for the first few photocount factorial moments (Schaefer and Pusey 1972). Secondly, it should be mentioned that, by using the method of scaled photocount correlation (Schaefer and Berne 1972, Jakeman *et al* 1972), which, like clipping, has the experimental advantages of being a 'one-bit' technique, one can measure the true intensity correlation function (equation (8)), directly, thus avoiding the difficulties introduced by clipping. Scaling has the disadvantage, when compared to clipping, of requiring, in some instances, somewhat longer experimental run-times to achieve a given accuracy.

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