IMPROVEMENTS OF PHOTON CORRELATION TECHNIQUES

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Abstract—Quasi-elastic dynamic light scattering, better known as photon-correlation, is a preferred non-destructive technique to characterize colloidal suspensions and emulsions as to the size distribution of particles or droplets. We sketch the principle of measurement and indicate some of its limitations. These include the inability to work with highly concentrated suspensions where multiple scattering is significant, and the difficulty to deal simultaneously with relaxation times spanning several orders of magnitude such as they occur, e.g. in polymerizing solutions or in suspended biological matter. We describe system modifications which make it possible to eliminate these difficulties. A modified two-color optical setup together with cross-correlation permits the characterization of highly concentrated suspensions. A novel correlator layout permits the simultaneous evaluation of relaxation times over many orders of magnitude.

1. INTRODUCTION

Scattering of electromagnetic radiation is widely used to study the structure of matter. There the wavelength should be comparable to the size of interesting structural elements. Thus in the radar technique, scattering of centimeter waves is used to measure location and speed of flying objects or the topography of Earth and Venus surfaces. Similarly, scattering of X-ray is used to study the arrangement of atoms in solid or liquid matter. Scattering of optical wavelength is well suited for the study of colloidal suspensions and emulsions. There the size of the particles or droplets is usually smaller than the wavelength, but the distance between particles is larger. Indeed several light scattering techniques are available to measure various relevant parameters.

Colloidal suspensions are of considerable commercial interest since a sizeable fraction, around 1/3, of the product value of the chemical industry in Western countries comes in the form of suspensions or emulsions. Chemical and physical test procedures are applied for purposes of quality control of those products. Among them are light scattering techniques which are noninvasive and nondestructive and thus well suited for rapid routine measurements. Suspensions are also of scientific interest in several respects. We merely mention the fact that a colloidal suspension is a many particle system similar to ordinary liquids, but one where the interactive potential between particles can be changed at will (by chemical means). Research on the statics (the spatial arrangement of particles) and the dynamics (their Brownian motion modified by the interaction potential) of such colloidal systems hinges on the availability of suitable measuring techniques.

In the present paper, we deal with just one of these measuring techniques. It was named photon correlation by the research team around E. R. Pike, then at the Royal Signals and Radar Establishment in Malvern, England, who around 1970 started its development. The name alludes to the weak scattered light signal which is detected in terms of single photons, and which is processed to yield the temporal intensity auto-correlation function.

In the following section, we outline the photon correlation technique which has established itself as a standard measuring technique in many laboratories. This description is necessarily sketchy. For more details we refer to the literature. The purpose of this paper is to identify two shortcomings of technique which so far have limited its usefulness. One is the inability to deal with highly concentrated suspensions where multiple scattering is inevitable. The resulting distorted correlation functions do not permit a quantitative evaluation. The other is the inability of previously available correlators to cover a large range of relaxation times. Several widely differing relaxation times occur in composite systems, for example in polymerizing solutions or certain biological fluids as well as in the presence of strong particle interactions. In two further sections we describe modifications of the traditional photon correlation apparatus which eliminate these shortcomings.
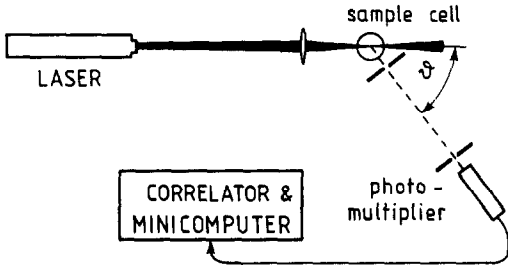
Fig. 1. Block diagram of photon correlation spectrometer.

2. PHOTON CORRELATION

Photon correlation spectroscopy is being practized in numerous laboratories and its theory and apparatus are described in several books.[1-4] It therefore suffices to outline the method briefly.

Figure 1 shows a block diagram of the apparatus. Laser light penetrates the sample of a colloidal suspension and some of it is scattered. A narrow beam of scattered light under angle ϑ is limited by pin holes. These assure coherent detection, i.e. a plane optical phase front over the photosensitive surface of the photomultiplier. At the same time, the received intensity is low so that single photon detection recommends itself. The voltage pulses at the photomultiplier output are changed to standard pulses by means of a threshold circuit and a triggered pulse generator. In view of the statistical nature of the photodetection process, the resulting pulse sequence is the Poisson transform of the scattered light intensity. A sample time clock provides time increments Δt. Let $n(t)$ be the number of photodetection pulses between t and $t + \Delta t$. The digital correlator calculates the so-called photon correlation function

$$G^{(2)}(\tau) = \langle n(t + \tau)\, n(t) \rangle. \tag{1}$$

Here τ is the delay time which is given in multiples of Δt, the brackets indicate ensemble or equivalently time averaging.

Figure 2 is a block diagram of the Malvern correlator, which with some modifications and improvements, is still standard in many laboratories. This device forms an approximate photon correlation function where in equation (1) the delayed photon count $n(t + \tau)$ is reduced to a one-bit signal. The true number $n(t + \tau)$ is counted and replaced by 1 if it exceeds a given threshold, and by 0 otherwise. This procedure, known as clipping, may degrade the precision of the measured $G^{(2)}(\tau)$. But it permits a rather simple electronic implementation of the required multiplication through a logical AND function.

We mention two disadvantages of this correlator design for later reference. In order to avoid dead time distortions,[5] all the logic in Fig. 2 must be designed for very short pulse separations, 50 ns typically. But due to the random nature of photon counting, the average pulse separation will be one or more orders of magnitude larger, leaving the expensive fast electronic circuitry idle most of the time. The correlation function is calculated for a linear sequence of delays $\tau = m\Delta t$ where $1 < m < m_{max}$. The index m is also known as the channel number. For economical reasons it is not practical to have the number of channels m_{max} larger than perhaps several hundred. Hence, the time range on which physical processes can be studied is limited to two orders of magnitude.
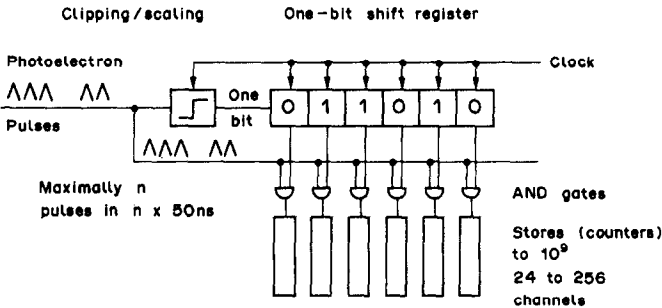

Fig. 2. Block diagram of the Malvern real-time digital correlator.

Efforts have been made to increase this range by "staggering" several correlators, but the price is increased complexity and reduced accuracy. Our alternative correlator design is outlined in Section 4 of this paper.

If the light scattering medium is a monodisperse, non-interacting colloidal suspension, i.e. one with uniform particle size, then theory says that

$$G^{(2)}(\tau) = c_1 + c_2 \exp(-q^2 D\tau). \tag{2}$$

Here c_1 and c_2 are constants, D is the diffusion constant which according to the Stokes–Einstein relation for spherical particles is

$$D = \frac{kT}{6\pi\eta R}. \tag{3}$$

k is Boltzmann's constant, T is temperature, η is the solvent viscosity, and R is the particle radius. The scattering wave vector is

$$\vec{q} = \vec{k}_f - \vec{k}_i \tag{4}$$

where $\vec{k}_i$ is the wave vector of the incident laser beam and $\vec{k}_f$ that of the final scattered radiation, and its magnitude is given by the Bragg formula

$$q = 4\pi n \sin \frac{\vartheta}{2} \Big/ \lambda, \tag{5}$$

where n is the solvent index of refraction and λ the laser vacuum wavelength.

A measurement of the photon correlation function allows the evaluation of the particle radius using equations (2) and (3). In practice this works well with monodisperse systems. With suitable apparatus the measurement and evaluation take a few minutes and the achieved accuracy is in the percent range. The result is often termed the hydrodynamic radius because it is based on the Stokes drag formula for the sphere. Results of reduced accuracy are obtained with polydisperse samples, i.e. where there is a spread of particle radii. In that case equation (2) contains a convolution of exponential functions with the distribution function of diffusion constants. This in essence is a Laplace transform. Hence the distribution of diffusion constants or of radii is obtained by an inverse Laplace transform. For principal reasons and because of measurement noise this can be done much less accurately. Still, results on size distribution so obtained are adequate in many applications.

Examination of the theory leading to equation (2) shows that it is derived under the assumption of single scattering only. Multiple scattering inevitably occurs in samples with higher particle concentration which also lead to sizeable attenuation of the incident laser radiation. Multiple scattering leads to a distortion of the photon correlation function. There is no easy-to-handle theory of multiple scattering which would allow the analysis of measured photon correlation functions for particle radii and distribution functions of radii. As a consequence experimentalists restrict their work to dilute suspensions where single scattering occurs exclusively. This is too bad because concentrated samples are more interesting. As a rule commercial suspensions are highly concentrated. The inability of photon correlation techniques to characterize them adequately thus is a handicap to industry. The study of interacting Brownian particles is of interest to science. Because of the short range of interacting potentials, their effect in dilute samples is minimal. Significant interactions occur in concentrated samples only. These interactions can be studied only if a way is found to cope with multiple scattering.

3. DECORRELATION OF MULTIPLE SCATTERING

According to equations (2) and (4), the photon correlation function does not depend on the laser wavelength or wave vector as such, but only on the scattering wave vector $\vec{q}$. It should be pointed out, however, that this is true only if there are no contributions of multiple scattering to the detected signal. Thus, if the directions of two incident laser beams with wavevectors $\vec{k}_{i1}$ and $\vec{k}_{i2}$ and the
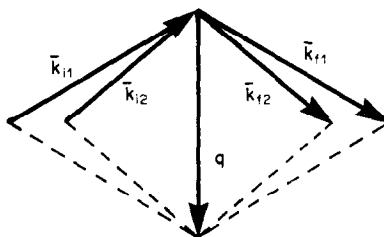
Fig. 3. Wave vectors for equivalent single scattering by two wavelengths.

corresponding detected beams are arranged as in Fig. 3, the single scattering parts of the respective photon correlation functions are the same,

$$G^{(2)}(\tau) = \langle n_1(t + \tau)n_1(t) \rangle = \langle n_2(t + \tau)n_2(t) \rangle. \tag{6}$$

In this equation unessential factors of proportionality are omitted. A little reflexion shows that the single scattering photon correlation function can likewise be obtained by cross correlating both detected signals:

$$G^{(2)}(\tau) = \langle n_1(t + \tau)n_2(t) \rangle. \tag{7}$$

The implementations of the photon correlation function by autocorrelation, equation (6) or by cross correlation equation (7) differ, however, with respect to multiple scattering. Consider a double scattering event as sketched in Fig. 4. The rigorous treatment by Drewel[6] has shown that detected double scattered photons influence the shape of the autocorrelation functions, but not of the cross correlation function. Briefly the argument is as follows. In a single wavelength setup, doubly scattered light from any two particles has a fixed phase relation with respect to single scattered light. Depending on the relative phase, the doubly scattered contribution may increase or decrease the optical amplitude at the detector. In the average it leads to a small increase of amplitude and hence of photon rate. Thus double (and more generally multiple) scattering leads to enhanced autocorrelation functions at shorter delay times. In the two-wavelength setup, the distance between two scattering particles amounts to a different number of wavelengths, that is to different phase delays. Thus the double scattering contributions to the optical amplitudes at both detectors have a random phase difference, i.e. they are decorrelated. The photon numbers $n_1(t)$ and $n_2(t)$ for a given time slot thus may be enhanced or decreased due to multiple scattering in an uncorrelated way. Thus the cross correlation function (7) represents the single scattering photon correlation function. The only effect of multiple scattering is an increase of the constant background, i.e. the constant c_1 in equation (2).

A sketch of the optical system is shown in Fig. 5. The argon laser provides a green and a blue wavelength. Shifting the mirror M in the direction indicated changes the separation of the two beams leaving the Koesters prism and hence their angular difference in the scattering volume. The detector equipment is mounted on a movable arm of the goniometer. Both scattered signals are
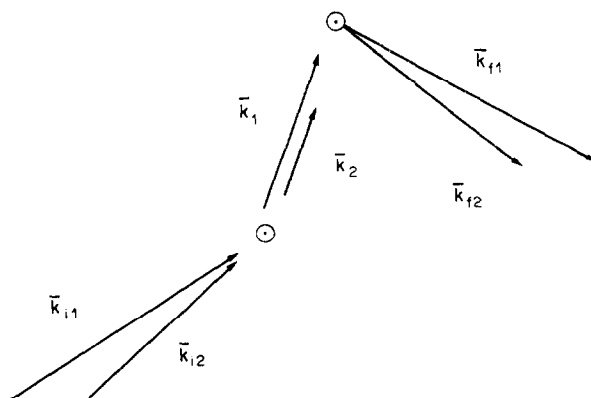
Fig. 4. Double scattering leads to decorrelated phase delays at both wavelengths.
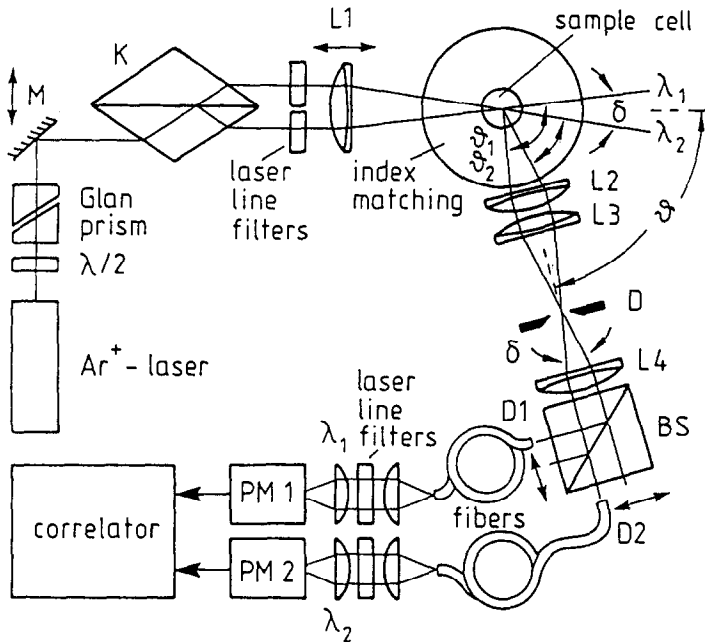
Fig. 5. Block diagram of Drewel's two-color photon correlation spectrometer.

to be detected at rather closely spaced points in the far field. To make this possible, a beam splitter BS is used and the light is transmitted through glass fibers to both photomultipliers. The position of the mirror M, of the goniometer arm and the position of the fiber apertures D1 and D2 can be moved by programmed step motors. This allows for a rapid change of the scattering angles.

Figure 6 shows an example of measurement of a fairly concentrated colloidal suspension. The plot shows the logarithm of $G^{(2)} - c_1$ vs time on a linear scale. The top curve refers to autocorrelation of the blue signal, the middle one to that of the green one. Both curves show some curvature arising from multiple scattering. The bottom curve refers to cross-correlation of both signals. The resulting straight line proves the suppression of multiple scattering effects. Obviously such measurements allow for rather reliable evaluation of the particle radius.

Decorrelation of multiple scattering is desirable not only in the analysis of concentrated colloidal suspensions and emulsions. It is also of interest in studies of critical opalescence. As is well known, in pure liquids the degree of scattering increases as the critical point is approached. Close to the critical point multiple scattering becomes significant. The decorrelation technique described here still permits a valid measurement of the relaxation time of the fluctuations.

Fig. 6. Plots of $\ln(G^{(2)} - c_1)$ vs delay time τ. Top: green wavelength, autocorrelation; middle: blue wavelength, autocorrelation; bottom: both wavelengths, cross correlation.

4. THE ALTERNATIVE CORRELATOR CONCEPT

In Section 2 it was pointed out that, in the Malvern correlator and correlator designs derived from it, the electronic processing takes place in a small fraction, typically 0.01 of the time. This inefficient use of the electronics is necessitated by the real-time operation: the electronics must be ready to process an incoming photon pulse whenever it arrives.

A more efficient use of the electronics is possible if the time scales of photon pulse arrivals and of electronic processing 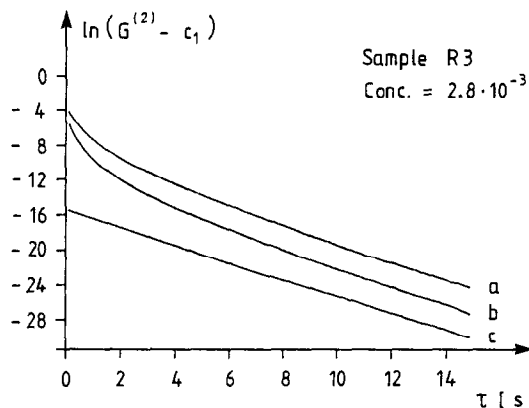are decoupled. To be specific, assume the photon correlation experiment runs with delay time increments Δt of 50 μs, a typical value. By comparison, a single multiplication and subsequent addition takes 50 ns, i.e. one thousands of Δt. As shown in the input section of the block diagram Fig. 7, photon pulses arriving in the time increment Δt are counted, for example in a 4-bit format. At the end of Δt the number $n(t)$ is transferred to a section of a random access memory (RAM). Concurrently numbers that were stored previously in another section of the RAM are read out and processed in the correlator circuit proper, but now at a much faster rate. The processing for a few correlator channels—eight in a particular design—takes a very small fraction, roughly 1/1000 in our example, of the time in which these data were taken originally. Thereafter the correlator electronics can be used for other tasks.

Every correlator channel is laid out to permit the multiplication of two 4-bit numbers and the addition of the result to the contents of a store within 50 ns. This aim is effected by table look-up. The entire 4-bit by 4-bit multiplication table contains 256 entries of 8-bit numbers and may be stored in a read-only memory (ROM). Besides the possible values of products $n(t + \tau) n(t)$. The ROM also contains values of $[n(t + \tau) - n(t)]^2$. Whereas averaging the products yields the correlation function, averaging the squared differences yields the so called structure function, which also serves to characterize statistical sequences.[7,8] The ROM is addressed by a 9-bit number, 1 bit for the choice of correlation or structure function, and two 4-bit numbers $n(t + \tau)$ and $n(t)$. Its output is the desired 8-bit number which then is added to the contents of the appropriate channel store.

The correlation (or structure) function for further channels may be obtained by recirculating the same data through the correlator electronics over and over, but with increasing delay times τ. By this kind of multiplex operation, the apparent number of correlator channels may be made very high, up to several hundred in our example.

Even more interesting is another mode of operation. After passing the correlator shift register, two consecutive 4-bit data are added. In this way a data string is generated with half the original number of entries but now they refer to time increments $2\Delta t$. Again the correlation (or structure) function is formed for the following but coarser spaced delay times. The processing time for this portion is only half that of the first portion since the length of the string is halved.

This procedure is iterated many times. Provisions are made that the sums do not exceed the 4-bit format for the first few iterations. For later iterations, more bits are accepted because then the

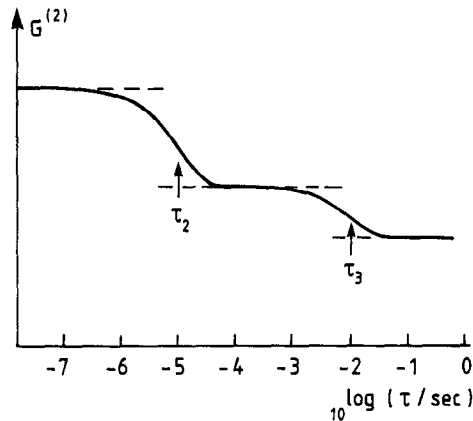Fig. 7. Block diagram of the ALV digital, quasi-real-time, logarithmic structurator/correlator.

Fig. 8. Correlation function with two different time constants plotted vs logarithm of delay time τ.

processing of the correlation function is no longer done by the correlator electronics, but by a built-in minicomputer. After 21 such doubling steps the time increment Δt has gone from 50 ns to 0.1 s. The resulting photon correlation function is plotted best with $G^{(2)}$ on the ordinate on a linear scale, but the delay time τ as abscissa on a logarithmic scale.

Is such a spread of the time scale of about 7 orders of magnitude useful in practice? Consider a typical photon correlation function

$$G^{(2)}(\tau) = c_1 + c_2 \exp(-t/\tau_2) + c_3 \exp(-t/\tau_3). \tag{8}$$

In the plot (Fig. 8) it is assumed that τ_2 and τ_3 differ by about 3 orders of magnitude. Are such situations observed in the laboratory? We mention a few examples.

Monodisperse colloidal suspensions can be made according to certain recipes. But it is extremely difficult to transfer samples into a sample cell for photon correlation measurement without collecting a little bit of dust. Dust particles typically are several orders of magnitude larger than the colloid particles and hence give rise to a slow term in the correlation function. In fact much of early photon correlation work deals with this difficulty. When using a traditional correlator with linear delay time spacing, the presence of dust merely leads to a minute tilt of the base line. Being able to survey all relevant time scales at once allows detailed statements on the presence of dust and also allows a less uncertain characterization of the colloidal system.

Colloidal suspensions of interacting particles are a subject of current research interest. The Brownian motion is modified if the range of interactive potentials approaches the average distance between particles. Brownian motion or diffusion then involves two different processes. Self-diffusion is the Brownian motion of single particles essentially as it would occur in a highly dilute suspension. It is restricted to small displacements and it leads to a shorter relaxation time in the photon correlation function. Collective diffusion describes the relative motion of ensembles of particles and thus leads to a larger relaxation time.

In macromolecular chemistry, the process of polymerization in solution is of interest. Soon after the start, some monomers are firmly tied together to form a loose polymer network of long chains. Other monomers remain single and move about in Brownian motion through the gaps of the network. One expects a fast relaxation time associated with diffusing monomers and a slow relaxation process associated with the overdamped motion of the network links. Through photon correlation measurements one can identify both processes. Usually small distributions of relaxation times are observed rather than two sharp time constants. With photon correlation measurements the entire course of polymerization may be followed *in vitro*.

A similar situation often prevails within living cells. Fibers of macromolecules form a loose elastic network which is tied to the cell walls. Its damped fluctuating motions give rise to a slow contribution in the photon correlation function. Macromolecules like proteins and DNA often diffuse about within the cell, although sometimes their motion is directed. This leads to a faster part of the correlation function.

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5. SUMMARY

Photon correlation spectroscopy is an established measuring technique in the colloid science and related fields. In this paper we have shown how two of its traditional limitations can be overcome. The first refers to concentration. Previously reliable photon correlation data were obtainable only in rather dilute samples. The decorrelation scheme, described in Section 3, makes it possible to analyze any concentration. Reliable data can always be obtained as long as some light is scattered from the sample. The other previous limitation concerns the available time scales. Whereas traditional correlator designs lead to restrictions in the usable delay time scale, the novel correlator design overcomes these restrictions. This makes possible the study of composite systems where fluctuations of the constituents may be associated with drastically different time constants.

Acknowledgements—We feel that the concepts presented in this paper should be useful not only in the colloid science but also in work dealing more generally with the scattering of electromagnetic radiation or particle beams. We are indebted to our co-workers who did much of the laboratory work on which this paper is based. This applies in particular to Dr M. Drewel who designed the two-color photon correlation spectrometer. Two versions of the logarithmic structurator/correlator Fig. 7 are manufactured and marketed by ALV, D-6070 Langen. For a number of years, our work has been supported by grants of Deutsche Forschungsgemeinschaft. One of us (K. Sch.) appreciates receiving a Heisenberg stipend.

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