Multi-speckle diffusing wave spectroscopy with a single mode detection scheme

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We present a detection scheme for diffusing wave spectroscopy (DWS) based on a two cell geometry that allows efficient ensemble averaging. This is achieved by putting a fast rotating diffuser in the optical path between laser and sample. We show that the recorded (multi-speckle) correlation echoes provide an ensemble averaged signal that does not require additional time averaging. Furthermore, combined with traditional two-cell DWS, the full intensity autocorrelation function can be measured with a single experimental setup. The new scheme provides access to a large range of correlation times thus opening a new experimental window for the study of slowly relaxing and arrested systems, such as viscoelastic complex fluids, colloidal glasses and gels.

The surging interest in slowly relaxing and arrested colloidal systems such as gels or glasses (1-3) has created a need to monitor dynamic properties on time scales of seconds and minutes. Light scattering is certainly one of the best methods for this purpose since it offers convenient access to such key dynamic properties as the intermediate scattering function or the particle mean square displacement. Traditionally a single speckle mode of scattered light is detected and fluctuations are recorded over a time much longer that the relaxation time. However, this time averaging scheme is not applicable to rigid, nonergodic systems. For these systems the ensemble average can be obtained by summing a collection of consecutive experiments conducted on different sample realizations. Usually the sample is translated or rotated and a scan over a large number of independent speckles is performed (4-7). A major drawback of this approach is the extensive duration of measurements. It is not unusual today to investigate relaxation process on time scales of seconds and minutes with a corresponding measurement time of hours and days. As a matter of fact several authors have reported data collection time more than a day for a single intensity correlation function (e.g. (8, 9)). Besides being tedious and time consuming this approach is restricted to the systems in quasi-equilibrium. Only the advent of multi-speckle detection schemes made it possible to conveniently monitor very slow relaxation processes. Dynamic light scattering using a digital (CCD/CMOS) camera as a detector offers the possibility to perform simultaneously a large number of independent experiments thus achieving ensemble averages in real time (10). Compared to single photon counting the limited dynamic range of digital cameras and the typically high dark counts result in a somewhat lower accuracy. But fortunately with a time resolution of typically 1-10 ms digital camera based detection is restricted to rather long correlation times. Thus, traditional photon correlation spectroscopy has to be made as well in a separate experiment if access to the full range of correlation times is required.

All considerations above apply equally to both dynamic light scattering (DLS) in the single scattering regime and diffusing wave spectroscopy (DWS) in the multiple scattering regime (11, 12, 13). However, due to the strong multiple scattering regime DWS offers more flexibility in the experimental design, which we have exploited in our approach. In this paper we report on a new two-cell detection scheme for diffusing wave spectroscopy (DWS) that provides an effective multi-speckle averaging using single mode detection. To obtain an ensemble averaged signal we illuminate our sample with the laser light scattered from a rotating diffuser and we analyze reflected or transmitted light. We show that echoes in the recorded correlation function appear at any revolution while the correlation function of the sample remains finite. Each echo signal is generated by a large number of independent speckles thus efficient ensemble averaging is performed. Moreover, we demonstrate that the intensity correlation function of the sample can be extracted from the two-cell echoes.

The detection of single and multiple scattering correlation echoes was discussed in previous articles (14-18). Echo DWS was initially introduced in the analysis of nonlinear shear deformation (14, 15). In the single scattering regime Pham et al. recently demonstrated the use of echo DLS for efficient ensemble averaging (17). Our DWS scheme implements a new physical optical principle to record the ensemble averaged intensity correlation function. In contrast to previous echo experiments in our case the sample is at rest. Thus high rotation or oscillation frequencies can be realized without any mechanical disturbance of the system under study. The possibility to perform multi-speckle experiments with a traditional DWS light scattering scheme thus opens the pathway for a new type of fast and precise experiments. If combined with the well established two-cell DWS technique (TCDWS) (20) correlation times from 10 ns or less up to duration of measurement can be accessed. Such improved experimental performance is mandatory if progress shall be made in the expanding field of slowly relaxing and arrested systems, such as viscoelastic complex fluids, colloidal glasses and gels (1-3).

Our experimental setup is shown in Fig. 1. A frequency-doubled Nd:YVO₄ laser ("Verdi" from Coherent) operating at λ₀ = 532 nm is used to illuminate a circular ground glass mounted on a 5-phases stepper motor (RK-564 AC from VEXTA). Through scattering and dephasing the ground glass creates a speckle with a nearly gaussian optical field (19). We collect the transmitted light coming from the ground glass and focus it onto the sample with a spot size diameter of roughly 5 mm. The scattered light is then collected with a mono mode fiber and analyzed by a photomultiplier and a digital photon counter (correlator.com, New Jersey, USA). The photon counting device records the time intervals between photons arrivals in a data file with a resolution of 1/60 MHz = 12.5 ns. The high temporal resolution, comparable to the dead time of...
FIG. 1: Experimental setup: Laser light is scattered from a ground glass rotated by a fast stepper motor (1) and the transmitted light is collected by a lens (2) to illuminate the sample (3). Single mode fibers collect the scattered light either in transmission (4a) or reflection (4b). The collected light is subsequently analyzed by a single photon detector and digital photon counter (5)

the detector, assures that there is no more than one photon arriving at a time step for a typical experimental count rate of 10-500 kHz. The stepper motor is operated at frequencies up to 75 Hz. The measured intensity correlation function (ICF) \( g_1^{(2)}(\tau) - 1 \) contains information from both the sample and the rotating diffuser. To distinguish the dynamics due to the sample internal motion \( g_1^{(2)}(\tau) - 1 \) and due to the rotating diffuser \( g_1^{(2)}(\tau) - 1 \) in a quantitative way we take advantage of previous studies of similar two-cell geometries. Scheffold et al. have shown that the ICF \( g_1^{(2)}(\tau) - 1 \) from a sandwich of two optically independent cells can simply be expressed by a product of the correlation functions of the two individual cells [20]:

\[
g_1^{(2)}(\tau) - 1 = [g_1^{(1)}(\tau) - 1] \cdot [g_1^{(2)}(\tau) - 1],
\]

The two cell geometry can be also realized using a very slowly rotating diffuser as suggested by Viasnoff et al. [21]. In this version the two cells are separated by a distance of several centimeters which ensures complete decoupling of light propagation in both cells. This realization of Two-Cell DWS is similar to our experimental setup. However, in previous studies the diffuser was rotated slowly in order to average a large number of arrested speckles over time whereas in our case the diffuser motion is fast and periodical. To illustrate the different contributions we first consider the scattering signal from a rigid sample without internal motion. Any fluctuation of the detected laser light is produced in this case by the motion of the random diffuser. Fig. 2(a) shows the typical intensity correlation function of light scattered by a teflon slab of 2 mm thickness with a motor rotation frequency \( f_r \) close to 40 Hz. At short times the rotation gives rise to a complete decay of the ICF on a characteristic time \( \tau_r \) set by \( f_r \) and a corresponding echo width of \( 2\tau_r \). Each of the speckles reappear identical in the next revolutions resulting in echoes in \( [g_1^{(2)}(\tau) - 1] \). At \( T_r = 1/f_r \) and any multiple integer values \( n = 2, 3, 4, \ldots \) a correlation peak is observed. Echoes are found indistinguishable for backscattering and transmission (data not shown). A detailed discussion of the echo shape is beyond the scope of this letter but we expect many similarities to the formalism developed for single scattering echoes [17]. However, the number of speckles sweeping over the detector can be readily estimated from our experiments to be \( N \approx T/f_r > 2 \cdot 10^4 \). This means already after \( n + 1 \) revolutions the correlation function of the \( n \)th echo is known with an accuracy better than 1/\( \sqrt{N} \approx 1\% \).

In the following sections we will discuss the application of the two cell echo and compare the different data analysis schemes. We have prepared a colloidal dispersion of titanium dioxide powder (Ref: 0041255 from Warner Jenkinson Europe Ltd.), particle diameter roughly 200-300 nm, in glycerol at a volume fraction of \( \approx 0.5\% \). To further increase the viscosity the sample is kept at 5.7 ± 0.5°C. In this viscous opaque medium the correlation function decays over a range of lag times accessible both to the echo technique and traditional time averaging. Fig. 2 shows the result of the echo measurement in backscattering geometry for a frequency of 40 Hz.

In the viscous glycerol solution the scatters undergo diffusive motion expressed by the mean square particle displacement \( \langle r^2(\tau) \rangle = 6D_0\tau \), where \( D_0 = k_BT/6\eta a \) is the Einstein diffusion coefficient. For the backscattering geometry the ex-
perimental ICF is described by the expression 1,2:

\[ g_s^{(2)}(\tau) - 1 = \beta \cdot \exp [-2\gamma \sqrt{6\tau / \tau_0}] \]  

(2)

with a relaxation time \( \tau_0 = 1/Dk^2 \) and a factor \( \beta \) that describes the intercept of the correlation function. \( \gamma \) is a constant of order \( \gamma \approx 2.1 - 2.3 \) (VH detection) 13.

It follows from Eq. 2 that \( g_s^{(2)}(\tau) - 1 \) can be extracted from the echo-peak value since at lag times \( \tau = n/f, \) one expects \( g_s^{(2)}(n/f) - 1 = 1. \) However, the echo peak height might be affected by slight imperfections in the rotation. Furthermore a detailed resolution of the peak maximum can be costly in computation time in particular for higher rotation frequencies. A more practical way of dealing with this problem is to analyze the peak area rather than the peak height. Pham et al. have shown for the case of single scattering echoes that the peak area is directly proportional to ideal peak height, suffering very little from slight imperfections in rotation 17. The peak area can be obtained by numerical integration or simply by increasing the sampling time \( \tau_r. \) The latter approach is equivalent to triangular-weighted integration 23 and moreover significantly reduces the computation time of \( g_s^{(2)}(\tau) - 1. \)

The relevant information is contained in the sample correlation function \( g_2^{(2)}(\tau) - 1. \) To study the influence of the integration time window and the sampling time \( \tau_r \) we have varied both parameters over large range. Instead of numerical integration we simply sum the points of the correlation function \( g_M^{(2)}(\tau) - 1. \) No significant dependence is found (within reason) as long as the time window covers well the correlation peak. As a matter of fact a single correlation channel of sampling time \( \tau_s = 12 \mu s \) centered at the echo position provides nearly the same level of accuracy as integration over 960 channel at 12.5 ns resolution. In Fig. 3 we compare the echo-data collected during 12 seconds to a time averaged measurement over 20 minutes. Dividing by the normalization factor \( \beta \) we obtain basically identical results from both methods 26. Despite a dramatically shorter measurement time, the noise level is lower for the Echo-measurements.

In order to record these narrow correlation echoes special emphasis has been given to the data analysis. In a traditional linear correlator the ICF is obtained by averaging products of photon counts in a certain sampling time interval \( \tau_s \) separated by lag time \( \tau \) (channel) 11. Over several decades of lag times the linear channel layout however becomes impractical and the computation time increases rapidly. The usual solution to this problem in hardware correlators is to use a multi-tau scheme as introduced by Schätzl 23: to decrease amount of data the sampling time is doubled after a fixed number of steps. The correlation function is well resolved for the shortest lag times while the resolution is decreased for longer lag times. This loss in resolution is however not acceptable for our signal since all echoes have the same width, even at large lag times. On the other hand only a small number of correlation channels is needed to resolve the ICF in the vicinity of the correlation echoes. Furthermore not all echoes need to be resolved to cover a given range of lag times. Thus, if the parameters are optimized, as shown later in the text, simple multiplication can still be the most efficient method.

There are alternative techniques that allow a fast computation of the correlation function. One of the most efficient methods is based on the fast Fourier transform (FFT). According to the Wiener-Khinchin theorem the auto-correlation function of the signal can be determined as an inverse Fourier transform of its power spectrum which is the square of the Fourier amplitudes (for details see 24). For a given sampling time \( \tau_r \) FFT provides the correlation function for all available channels much faster than any other technique. However, in order to resolve the echoes shape the sampling time has to be decreased which requires large data arrays and long processing time.

Quite a different approach to calculate the ICF was put forward by Chopra and Mandel 25 in their photon time-of-arrival correlator. It estimates the distribution of time intervals between photons arrivals which is shown to be proportional to the ICF. In contrast to the methods mentioned above computation can not be accelerated by increasing the sampling time since photons arrivals have to be recorded as separate events. This approach is much faster only if high resolution data is required and if the data is provided in a suitable format as it is the case for our photon recorder. We have used this method to calculate the ICFs in Fig. 2 at the highest available resolution of 12.5 ns.

To optimize the data analysis we compare different methods: the linear correlator, FFT and the time-of-arrival correlator. The data of a 12 seconds measurement at an average count rate of 210 kHz is analyzed under identical conditions. Correlation echoes are calculated up to echo number 240, corresponding to \( \tau = 6 \) seconds and the time delay between echoes is doubled after each linear block of 16 and a total number of 60 echoes is calculated. The time resolution of time-of-arrival correlator is determined by the 12.5 ns hardware time step. For the time of arrival-correlator the computation time is ca. 14 seconds for an echo integration window of 6 µs based on a 1.7 GHz Intel Xeon processor system. By calculating correlation coefficients only at the echo peak position the processing time decreases to 10 seconds. The FFT correlation function contains all available lag times and computation time is inversely proportional to the sampling time \( \tau_r. \) For the same data it takes 1.7 seconds with 12 µs sampling time and less than one second for 24 µs. Processing the data with the linear correlator can be even faster. The whole analysis takes approximately 1.5 seconds if a single channel for each calculated echo with a sampling time of 12 µs is chosen. Most of this time is needed to convert the raw data to the format photon-counts per sampling time, which could be easily done on-the-fly during data recording. In conclusion we find that the time needed for an optimized data processing scheme is negligible compared to the total measurement time.

Finally we would like to comment on the accessible time range at a given rotation frequency. The echo period can not be known with absolute accuracy and at very high orders the sampling time and echo period will not match any more and the signal is lost. We commonly perform measurements up to echo number 1000 covering three orders of magnitude in lag-time. Since the echo width is only of the order of 1 µs the pe-
FIG. 3: Normalized ICF in backscattering (VH- geometry: perpendicular polarization). Solid line - ICF from time averaging over 20 minutes, Symbols - echo analysis of a 12 second measurement ($\tau$) - data from time-of-arrival data processing, (▲) - linear correlator with sampling time 12 $\mu$s. Inset: Lin-log plot of the same data.

dior has to be known with nanosecond accuracy. To overcome this difficulty for even higher order echos one might think of monitoring the echo period continuously during processing. In this case, however, the echo shape has to be resolved in detail which goes at the expense of computation speed. A more practical way to increase the time window is by performing several measurements at different rotation speed. For such a scheme the integral time of measurement will still be set approximately by the longest measurement.

In the summary we have shown that our Two-Cell Echo approach allows to measure the ensemble averaged DWS correlation function nearly in real time. Existing DWS experiments can be easily upgraded if the laser power is sufficient to drive the two-cell echo experiment. Besides a simple device for precise mechanical oscillation or rotation and a suitable photon counter or correlator no other hardware is needed. Furthermore, combined with traditional two-cell DWS at very low rotation speeds, the full intensity autocorrelation function can be measured with a single experimental setup covering more than 10 decades in correlation time.

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[1] K.A. Dawson, Curr. Opin. Colloid Interface Sci. 7, 218 (2002), L. Cipelletti and L. Ramos, ibid., 7, 228 (2002), J.L. Harden and V. Viasno, ibid. 6, 438 (2001).
[2] K.N. Pham, A.M. Puertas, J. Bergenholtz, S.U. Egelhaaf, A. Moussad, P.N. Pusey, A.B. Schofield, M.E. Cates, M. Fuchs, and W.C.K. Poon, Science 296 (2002).
[3] T. Eckert and E. Bartsch, Phys. Rev. E 89, 125701 (2002).
[4] P. Pusey and W. Megen, Physica A 57, 705 (1989).
[5] F. Scheffold and P. Schurtenberger, Soft Materials 1, 139 (2003).
[6] J.-Z. Xue, D. Pine, S. Milner, X. Wu, and P. Chaikin, Phys. Rev. A 46, 6550 (1992).
[7] K. Schätzl, Applied Optics 32, 3880 (1993).
[8] C. Beck, W. Hartl, and R. Hempelmann, The Journal of Chemical Physics 111, 8209 (1999).
[9] W. van Megen and S.M. Underwood, Phys. Rev. E 49, 4206 (1994).
[10] E. Bartsch, V. Frenz, J. Baschnagel, S. Schürrl, and H. Sillerscu, J. Chem. Phys. 106, 3743 (1997), L. Cipelletti and D. Weitz, Rev. Sci. Instrum. 70, 3214 (1999), A. Knaebel, M. Bellour, J.-P. Munch, V. Viasno, F. Lequeux and J.L. Harden, Europhys. Lett. 52, 73 (2000), V. Viasno, F. Lequeux and D. Pine, Rev. Sci. Instrum. 73, 2336 (2002).
[11] B. Berne and R. Pecora, Dynamic Light Scattering. With Applications to Chemistry, Biology, and Physics (Dover Publications, Inc., New York, 2000).
[12] G. Maret and P.-E. Wolf, Z. Phys. B 65, 409 (1987).
[13] D. Pine, D. Weitz, P. Chaikin, and E. Herbolzheimer, Phys. Rev. Lett. 60, 1134 (1988).
[14] P. Hébraud, F. Lequeux, and J.P. Munch, Phys. Rev. Lett. 78, 4657 (1997).
[15] R. Höhler, S. Cohen-Addad, and H. Hoballah, Phys. Rev. Lett. 79, 1154 (1997).
[16] W. van Megen, T.C. Mortensen, S.R. Williams, and J. Müller, Phys. Rev. E 58, 6073 (1998).
[17] K. Pham, S. Egelhaaf, A. Moussaid, and P. Pusey, Rev. Sci. Instrum. 75, 2419 (2004).
[18] G. Petekidis, A. Moussaid, and P.N. Pusey, Phys. Rev. E 66, 051402 (pages 13) (2002).
[19] L. Basano and P. Ottonello, J. Phys. E: Sci. Instrum. 14, 1257 (1981).
[20] F. Scheffold, S. Skipetrov, S. Romer, and P. Schurtenberger, Phys. Rev. E 63, 061404 (2001).
[21] V. Viasno, S. Jurine, and F. Lequeux, Faraday Discussions 123, 253 (2003).
[22] L. Rochas.Ochoa, S. Romer, S. Skipetrov, F. Scheffold and P. Schurtenberger, Phys. Rev. E 65, 051403 (2002).
[23] K. Schätzl, M. Drewel, and S. Stimac, J. Mod. Opt. 35, 711 (1988).
[24] W. Press, S. Teukolsky, W. Vetterling, and B. Flannery, Numerical Recipes in C: The Art of Scientific Computing (Cambridge University Press, Cambridge, 1992).
[25] S. Chopra and L. Mandel, Rev. Sci. Instrum. 43, 1489 (1972).
[26] With a glycerol (99%) viscosity of $\eta \approx 5\,\text{Pas}$ at $T=5.7\,\text{°C}$ we expect a relaxation time $\tau_0 = 1/D_{ll}^2 \approx 7.5 - 11.5$ seconds. From a fit of equation (2) to the data we obtain $\tau_0 = 8.1$ seconds ($\gamma=2.2$)