Multispeckle 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 (multispeckle) 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 scheme provides access to a large range of correlation times thus opening an experimental window for the study of slowly relaxing and arrested systems, such as viscoelastic complex fluids, colloidal glasses, and gels.

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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 than 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 systems in (quasi)equilibrium. Only the advent of multispeckle detection schemes made it possible to conveniently monitor very slow relaxation processes. Dynamic light scattering using a digital charge coupled device or complementary metal-oxide semiconductor camera as a detector offers the possibility to perform simultaneously a large number of independent experiments thus achieving ensemble averages in real time [10]. But unfortunately 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 [11–13]. However, due to the strong multiple scattering DWS offers more flexibility in the experimental design, which we have exploited in our approach. In this paper we report on a two-cell detection scheme for diffusing wave-spectroscopy that provides an effective multispeckle 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 papers [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]. 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. If combined with the well established two-cell DWS technique (TCDWS) [19] correlation times from 10 ns or less up to duration of measurement can be accessed. Such improved experimental performance is mandatory if progress is to 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 neodymium-doped yttrium vanadate $Nd:YV_{04}$ laser ("Verdi" from Coherent Inc.) operating at $\lambda_0=532$ nm is used to illuminate a circular ground glass mounted on a five-phase stepper motor (RK-564 AC from Vexta). Through scattering and dephasing the ground glass creates a speckle with a nearly Gaussian optical field [20]. 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 monomode fiber and analyzed by a photomultiplier and a digital photon counter (Correlator.com, New Jersey). The photon counting device

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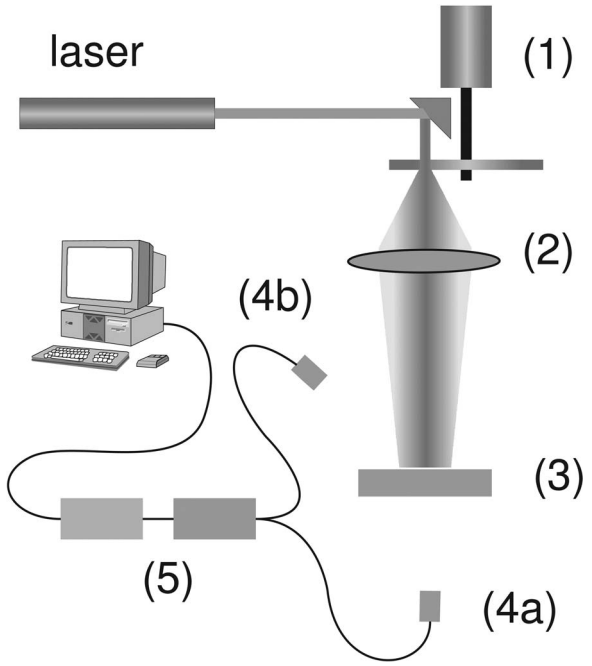

FIG. 1. Experimental setup. Laser light is scattered from a ground glass rotated by a fast stepper motor (1) and the transmitted light is collected by a lens (2) to illuminate the sample (3). Single-mode fibers collect the scattered light in either transmission (4a) or reflection (4b). The collected light is subsequently analyzed by a single-photon detector and digital photon counter (5).

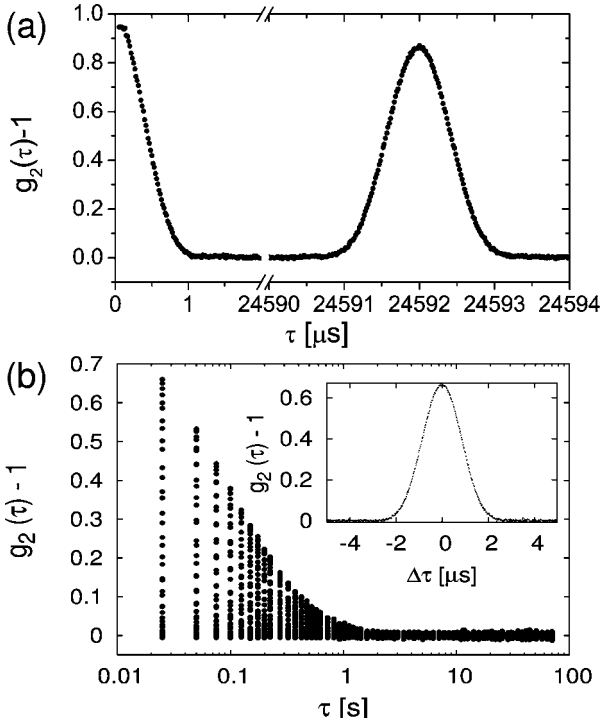

FIG. 2. (a) Zeroth- and first-order correlation echo in backscattering from a rigid Teflon slab for a rotation frequency of $f_r \approx 40$ Hz. The echo width at $1/e$ points is $2\tau_r \approx 1.15$ μs. (b) DWS echoes in backscattering for a sample of TiO_2 in glycerol. Inset shows the echo shape for this sample.

records the time intervals between photon 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 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 normalized intensity correlation function $[g_M^{(2)}(\tau)-1]$ is calculated either at full 12.5 ns resolution using the time-of-arrival approach of Chopra and Mandel [24] or at lower resolution with a traditional linear correlator approach [11]. We note that the time needed for an optimized data processing is negligible compared to the total measurement time. Alternatively a hardware linear correlator can be used to record the correlation function in real time. The stepper motor is operated at frequencies up to 75 Hz. The measured intensity correlation function (ICF) $[g_M^{(2)}(\tau)-1]$ contains information from both the sample and the rotating diffuser. To distinguish the dynamics due to the sample internal motion $[g_S^{(2)}(\tau)-1]$ and due to the rotating diffuser $[g_E^{(2)}(\tau)-1]$ in a quantitative way we take advantage of previous studies of similar two-cell geometries. Scheffold *et al.* have shown that the ICF $g_M^{(2)}(\tau)-1$ from a sandwich of two optically independent cells can simply be expressed by a product of the correlation functions of the two individual cells [19]:

$$g_M^{(2)}(\tau) - 1 = [g_E^{(2)}(\tau) - 1][g_S^{(2)}(\tau) - 1]. \quad (1)$$

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 TCDWS 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. Figure 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 τ_r set by f_r and a corresponding echo width of $2\tau_r$. Each of the speckles reappears identically in the next revolutions resulting in echoes in $[g_E^{(2)}(\tau)-1]$. 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 paper 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 $N \approx T_r/2\tau_r > 2\times 10^4$. This means already after $n+1$ revolutions the correlation function of the nth echo is known with an accuracy better than $1/\sqrt{N} \approx 1\%$.

It is now worthwhile to comment on the accessible time range at a given rotation frequency. The echo period cannot

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 period 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 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 to both the echo technique and traditional time averaging. Figure 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 $D_0 = k_B T/6\pi\eta a$ is the Einstein diffusion coefficient. For the backscattering geometry the experimental ICF is described by the expression (neglecting absorption) [12]

$$g_S^{(2)}(\tau) - 1 = \beta \exp(-2\gamma\sqrt{6\tau/\tau_0}) \tag{2}$$

with a relaxation time $\tau_0 = 1/Dk_0^2$ and a factor β that describes the intercept of the correlation function. γ is a constant of order $\gamma \approx 1.5$–2.5 depending on the detected polarization state [22].

It follows from Eq. (2) that $g_S^{(2)}(\tau) - 1$ can be extracted from the echo-peak value since at lag times $\tau = n/f_r$ one expects $g_E^{(2)}(n/f_r) - 1 = 1$. 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 τ_s. The latter approach is equivalent to triangular-weighted integration [23] and moreover significantly reduces the computation time of $g_M^{(2)}(\tau) - 1$.

The relevant information is contained in the sample correlation function $g_S^{(2)}(\tau) - 1$. To study the influence of the integration time window and the sampling time τ_s 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 as long as the time window covers well the correlation peak. As a matter of fact a single correlation channel of sampling time $\tau_s = 12$ μs centered at the echo position provides nearly the same level of accuracy as integration over 960 channels at 12.5 ns resolution. In Fig. 3 we compare the echo data collected during 12 s to a time averaged measurement over 20 min. Dividing by the normalization factor β we obtain basically identical results from both methods.[1] Despite a dramatically shorter measurement time, the noise level is lower for the echo measurements.

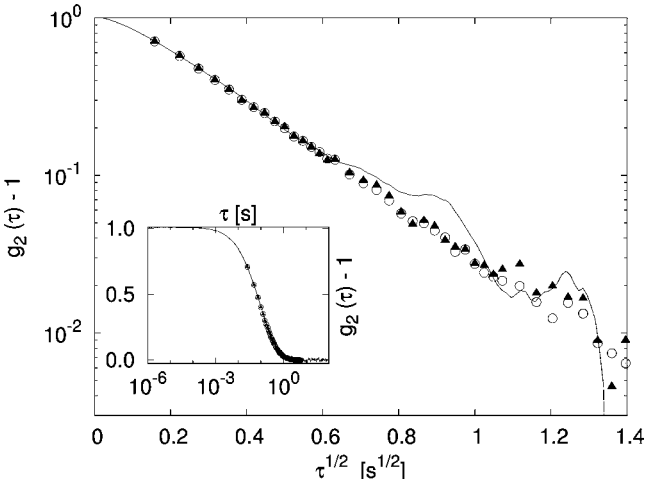

FIG. 3. Normalized ICF in backscattering from TiO_2 suspended in glycerol (VH geometry; perpendicular polarization). Solid line, ICF from time averaging over 20 min., Symbols, echo analysis of a 12 s measurement ○; data at 12 ns resolution from time-of-arrival data processing (▲); linear correlator with sampling time 12 μs. Inset: Linear-log plot of the same data.

Our approach is not limited to liquid (ergodic) systems but can also be applied to solid (nonergodic) soft materials. The possibility to perform a true multispeckle analysis with a classical DWS light scattering scheme allows fast and precise experiments. Combined with the well established two-cell DWS technique [19] correlation times from 12.5 ns up to the duration of measurement can be accessed. In the following we will discuss such an application to a gelling biopolymer solution. We have studied the dynamics of 4 wt % commercial (food grade) gelatin solution in water where a small amount of polystyrene tracer particles (diameter 720 nm) has been added during preparation to a final concentration of 1 wt % (transport mean free path $l^* \simeq 270$ μm). At this point it worthwhile to point out that the gelation of biopolymer solutions is of wide interest in food science but also represents an interesting polymer model system in soft matter physics. It has been demonstrated in previous studies that DWS is an ideal tool to follow dynamic changes in the elastic properties of (bio)polymer solutions [19,25]. In our experiment the gelatin solution is filled into a

[1]With a glycerol (99%) viscosity of $\eta \approx 5$ Pa·s at $T = 5.7$ °C we expect a relaxation time $\tau_0 = 1/Dk_0^2 \approx 7.5$–$11.5$ s. From a fit of Eq. (2) to the data we obtain $\tau_0 = 8.1$ s ($\gamma = 2.2$)

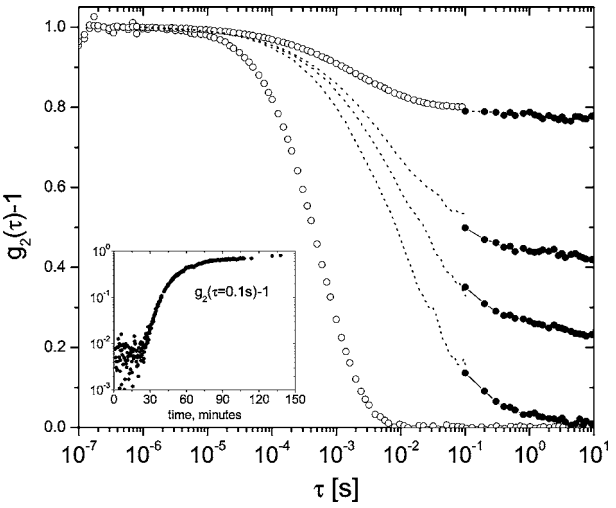

FIG. 4. Time evolution of the ICF for a gelling mixture of 4 wt % gelatine and 1 wt % polystyrene tracer spheres (diameter 720 nm) in water kept at 22 °C. Data taken at 1, 41, 57, 68, and 138 min. Symbols, two-cell DWS based on a hardware multi-τ analysis ○; echo analysis of 15 s measurements (●). Dotted line, ICF determined according to Ref. [4] with motor at rest. Inset: Time evolution of the echo correlation function at $\tau=0.1$ s.

2-mm-path-length cuvette (Hellma, Germany). Before the measurement the sample is heated to approx. 60 °C, well above the melting point and subsequently kept at 22±0.1 °C during the experiment. Rapid quenching is ensured by immersing the sample for 60 s in a temperature controlled water bath before transferring it to the sample cell holder (kept in air). Figure 4 shows the time evolution of the ICF in backscattering geometry. The first data set was recorded with the motor at rest using a standard multiple-tau hardware correlator. The motor speed is then set to $f_r=10$ Hz ($T_r=0.1$ s) and the photon stream is recorded in 15 s intervals during the whole gelation process. The echo correlation function is calculated as described above in the range $\tau=0.1-10$ s. We obtain absolute values of the correlation function by dividing the peak area with the values obtained from a solid block of Teflon [where $g_S^{(2)}(\tau)-1=\beta=\text{const}$]. The data obtained by this simple procedure are shown as full symbols in Fig. 4. The onset of a nonzero echo signal after approximately 20 min is directly related to the transition from a fluid to a solid gel. As shown in the inset the gel elastic modulus increases rapidly in a first stage and then grows more slowly. After more than two hours an additional TCDWS measurement has been carried out for 600 s at a dramatically reduced motor speed. Equation (1) then provides access to to the ICF at short times $\tau<T_r=0.1$ s. If combined with the last recorded echo measurement the full correlation function spanning from 10^{-8} to 10 s is recovered as shown in Fig. 4. An alternative way to monitor the short time dynamics is the nonergodicity correction of Pusey and van Megen (for details see Ref. [4]). It is possible to reconstruct the ensemble average correlation function from a time averaged measurement if the ratio of time $\langle I\rangle_T$ and ensemble averaged scattered intensity $\langle I\rangle_E$ is known. The latter is not accessible by a simple time averaged experiment. Our echo measurement, however, directly provides this information. We have thus stopped the motor a few times during the experimental run and recorded the photon stream again for 15 s. The resulting ICF's at short correlation times (dotted lines in Fig. 4) show an excellent match with the echo measurements at longer correlation times.

In summary we have shown that our two-cell echo approach allows us 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.

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