Pulsed diffusing-wave spectroscopy: High resolution through nonlinear optical gating

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We introduce a diffusing-wave spectroscopic probe which utilizes light pulses and exploits the phase fluctuations of optically gated photons to eliminate the usual average over photon pathways. The principles are discussed and experimentally demonstrated. In addition to testing several critical elements of the original multiple-light-scattering theories, we have studied diffusion of polystyrene spheres in the high-volume-fraction limit where hydrodynamic interactions are important.

Recently, a spectroscopy has been developed and applied to study the properties of colloidal suspensions that multiply scatter light.[1-3] The technique, called diffusing-wave spectroscopy (DWS), exploits the diffusive nature of light transport in strongly scattering media to relate temporal intensity fluctuations of the scattered light to average particle motion. In contrast to traditional dynamic-light-scattering methods,[4,5] DWS probes particle motion over length scales much shorter than the wavelength of light, and offers the possibility of studying the strongly correlated particle motions present in dense colloidal liquids.

In a typical DWS experiment a continuous beam of light illuminates a colloidal suspension of particles that scatter photons quasielastically. The experimenter fixes the light input and output geometry, and measures the temporal autocorrelation function of the multiply scattered output intensity. Properties of the scatterers, such as their average diffusion coefficient, can be extracted by analyzing this autocorrelation function. In order to obtain quantitative information, one must know the distribution of photon paths through the medium, and must be able to determine parameters such as the photon transport mean free path l^* and the photon absorption length l_a in the medium. In the original DWS experiments the distribution of photon paths was calculated for each geometry within the photon diffusion approximation and l^* was calculated from Mie theory.

However, various difficulties often arise in applying these procedures. In certain important geometries, such as backscattering, the diffusion approximation breaks down and interpretation of the autocorrelation function is complicated.[6] Moreover, l^* cannot always be calculated and an independent measurement is required. Finally, all DWS measurements are sensitive to a *distribution of photon path lengths,* and the extracted diffusion constant is, therefore, an average value weighted over a range of *different time scales.*

In this paper we discuss and experimentally demonstrate a pulsed-DWS (PDWS) technique which overcomes these difficulties. Our scheme does not depend on the *distribution* of photon path lengths through the medium and, therefore, eliminates most geometric considerations from the analysis. It provides a direct measure of l^*, is insensitive to absorption, and offers a much simpler data set from which to interpret the temporal decay of the autocorrelation function. These features are particularly valuable in regimes where diffusion is time dependent. In addition to providing support for our basic ideas, the experiments offer a fairly stringent test of some important and unverified assumptions in the original DWS theory. Finally, in the course of carrying out these measurements we have studied the effects of particle concentration on particle diffusion in the high-volume-fraction limit. We briefly discuss these findings.

We begin by recalling the main results of the DWS theories. For simplicity, consider scattering from a colloidal suspension consisting of many noninteracting, spherical scatterers. Transport of light through the medium is governed by the diffusion equation $\partial U/\partial t = D_l \nabla^2 U$, where U represents the space- and time-dependent energy density of the light field, $D_l = cl^*/3$ is the light diffusion coefficient, and c is the speed of light in the medium. A central assumption in DWS theories is that the temporal autocorrelation function of the scattered electric field $E(t)$ can be written as a sum over scattered photon pathways through the sample. The *path-dependent* scattered electric field, $E_S(t,s)$, derived from photons that travel a distance s through the medium, is used to calculate a *path-dependent* autocorrelation function

$$G_1(\tau,s) = \langle E_S^*(t,s) E_S(t+\tau,s)\rangle / \langle |E_S|^2 \rangle .$$

The total scattered electric-field autocorrelation function $g_1(\tau)$ is then obtained by incoherently summing the contributions over all s,[3]

$$g_1(\tau) = \frac{\langle E^*(t)E(t+\tau)\rangle}{\langle |E|^2\rangle} = \int_0^\infty P(s) G_1(\tau,s)\, ds$$
$$= \int_0^\infty P(s) \exp[-(s/l^*) k_0^2 \langle \Delta r^2(\tau)\rangle/3]\, ds . \quad (1)$$

Here, τ is the delay time, $P(s)$ represents the probability that an incident photon travels a distance s before emerging from the medium, k_0 is the wave vector of the light in the medium, and $\langle \Delta r^2(\tau)\rangle$ is the time-dependent mean-square displacement experienced by a particle in the sam-

ple during the time interval τ. For a particle undergoing simple Brownian motion with diffusion constant D, we can replace $\langle \Delta r^2(\tau) \rangle$ by $6D\tau$, and, $g_1(\tau)$ is essentially the Laplace transform of $P(s)$. From Eq. (1), it is clear that the resolution with which a DWS measurement can probe particle motion is limited by the width of $P(s)$. This is a significant limitation when one is studying a system for which $\langle \Delta r^2(\tau) \rangle$ is not a linear function of τ, since the integration process will smear out subtle features of the motion. Such a situation arises, for example, on time scales when particle motion is changing from ballistic to diffusive.

The basic ideas of PDWS are illustrated in Fig. 1. We employ a laser that emits a train of identical light pulses. Each pulse has a temporal duration Δt and a carrier frequency ω_0. Adjacent pulses within the train are separated by a time T. A beam splitter divides the pulse train into reference and sample pulse trains. The reference train is optically delayed, and the sample train is directed into the suspension which is contained in a rectangular glass cell. Light pulses emerging from the opposite side of the cell are "stretched" due to the distribution of photon path lengths. In order for PDWS to be most effective, the pulse broadening due to multiple scattering must be large compared to the input pulse width and small compared to the train repetition rate, i.e., $\Delta t \ll \Delta s/c \ll T$, where Δs represents the characteristic width of $P(s)$. The scattered pulse train is then recombined with the reference pulse train in a frequency doubling crystal, and a second-harmonic (SH) pulse train is produced when the two input fields

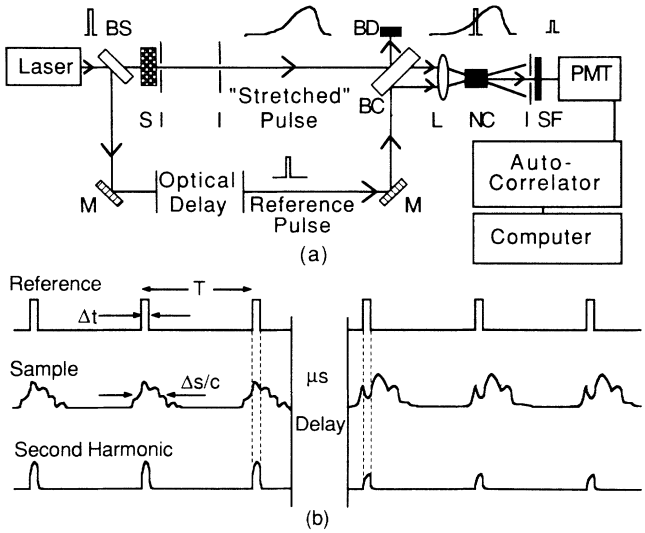

FIG. 1. (a) Schematic of the experimental setup: BC, beam combiner; BD, beam dump; BS, beam splitter; *I*, iris; *L*, lens; *M*, mirror; NC, nonlinear crystal; PMT, photomultiplier tube; *S*, sample; SF, second-harmonic spectral filter. (b) Sketch of the reference, sample, and second-harmonic pulse intensities during two intervals of time separated by several microseconds (see text for definition of Δs). Temporal fluctuations in the sample pulse intensity on the microsecond time scale arise from particle motion. Notice that the second-harmonic pulse intensity follows the fluctuations in the sample pulse and arises from only a narrow range of photon path lengths.

nonlinearly mix.[7,8] If s' is the *difference* in path length between the reference and sample arms when the sample is *removed,* then each pulse within the SH train will have a field $E_O(2\omega_0,t)$ proportional to the product of the reference field, $E_R(t)$, and the *path-dependent scattered field* $E_S(t,s')$. When fluctuations in the reference field are negligible, $E_R(t) = E_R$ and we have

$$E_O(2\omega_0,t) \propto E_R E_S(t,s') . \tag{2}$$

In most cases of interest, the time scale of the fluctuations in the phase of $E_S(t,s')$ is much longer than T and the autocorrelation function of the SH photons is given by

$$\begin{aligned} g_1(2\omega_0,\tau) &\propto |E_R(\omega_0,t,s')|^2 \langle E_S^*(t,s') E_S(t+\tau,s') \rangle \\ &\propto P(s') G_1(\tau,s') . \end{aligned} \tag{3}$$

Thus, we see that the SH electric field will experience the same *fluctuations* due to particle motion as the scattered electric field for a single path length. By varying the path length difference s' between the sample and reference arms, the reference pulse "gates" the electric field $E(t)$ so that only a very narrow range of photon path lengths centered about $s' = s$ contribute to the fluctuations of the unconverted electric field. The autocorrelation function of the SH field is simply the integrand of Eq. (1) evaluated at the appropriate s,

$$g_1(2\omega_0,\tau) \propto \exp[-(s/l^*) k_0^2 \langle \Delta r^2(\tau) \rangle / 3] . \tag{4}$$

Note that the temporal behavior of the autocorrelation function no longer depends on the shape of $P(s)$, and for a fixed s, a plot of $\ln[g_1(2\omega_0,\tau)]$ vs τ directly yields the time dependence of $\langle \Delta r^2(\tau) \rangle$.

An important additional feature of this scheme is that the dependence of the average SH intensity, $\langle |E_0(2\omega_0,t)|^2 \rangle$, on the reference delay s, is proportional to $P(s)$. Thus, we can directly measure $P(s)$ for any geometry. By fitting the results to the predictions of photon diffusion theory, we can experimentally determine l^* and l_a.

Optical gating has been used with considerable success in time-resolved luminescence studies of semiconductors,[8] and more recently in coherent backscattering measurements.[9] The present application is qualitatively different from the cases above in that it exploits the *phase fluctuations* of the gated electric field. By eliminating the average over photon pathways, our technique is essentially a very-high-resolution version of DWS. We expect that just as a number of high-resolution laser spectroscopic techniques have revealed microscopic perturbations in the frequency domain, the precision of PDWS will yield new information on problems concerning particle motion on different time scales.

To illustrate the basic features of PDWS we have carried out a number of measurements on the Brownian dynamics of dense colloidal suspensions. The light source we used was a mode-locked Nd-YAG laser ($\lambda = 1.06$ μm) that produced a 100-MHz train of 90-ps pulses. The average output power of 5 W was split evenly between the reference and sample beams (see Fig. 1). Transmitted light collected from a small area directly opposite the input beam was imaged, along with the reference beam, into

a KTP (potassium titanyl phosphate) doubling crystal ($5\times5\times5$ mm^3, type II). The second-harmonic photons were spatially and spectrally filtered from the fundamental photons and collected. Typical photon count rates were between 80 and 600 kHz, allowing normalized intensity autocorrelation functions, $g_2(\tau)=\langle I(t)I(t+\tau)\rangle/\langle I\rangle^2$, to be obtained with 100-ns time resolution in 2–20 min. The normalized field autocorrelation functions are related to $g_2(\tau)$ through the Siegert relation $g_2(\tau)=1+\beta|g_1(\tau)|^2$, where β is a constant determined primarily by the size of the detection aperture.[4]

In the inset of Fig. 2(a) we plot typical SH intensity autocorrelation functions $|g_1(2\omega_0,\tau)|^2$ vs τ. The sample used in this measurement was a suspension of 0.460-μm-diam polystyrene spheres in water. The volume fraction was $\phi=0.30$, the sample thickness was 2.0 mm, and the reference arm delays were $s=7.0$ and 13.0 cm. We emphasize that, in contrast to DWS measurements,[3] the curves decay exponentially. Some of our runs exhibited a slight upward curvature at longer times. This effect is due to our relatively long pulse durations and will be eliminated in the future by using shorter laser pulses.

Using this sample, we have performed measurements at different optical delays s. In Fig. 2(a) we plot the slope Γ_1 of the $\ln|g_1(2\omega_0,\tau)|$ vs τ curve as a function of s. Below this plot, in Fig. 2(b), we show our measurement of $P(s)$ obtained by measuring the time-averaged SH photon yield as a function of reference delay. We also calculated $P(s)$ by solving the diffusion equation[10] subject to boundary conditions which ensure that there is no flux of diffusing photons into the medium[11] [see dashed curve in Fig. 2(b)]. The solid line through the data represents the best fit of theory to experiment after we account for the finite laser pulse duration and the small absorption of light by water. Aside from an overall normalization, the only adjustable parameter is l^*. From the $P(s)$ data we deduce that $l^*=31.6$ μm.[12] This value of l^*, coupled with the measured slope of the Γ_1 vs s curve, yields a particle diffusion coefficient of $D=6.20\times10^{-9}$ cm^2/s for this sample.

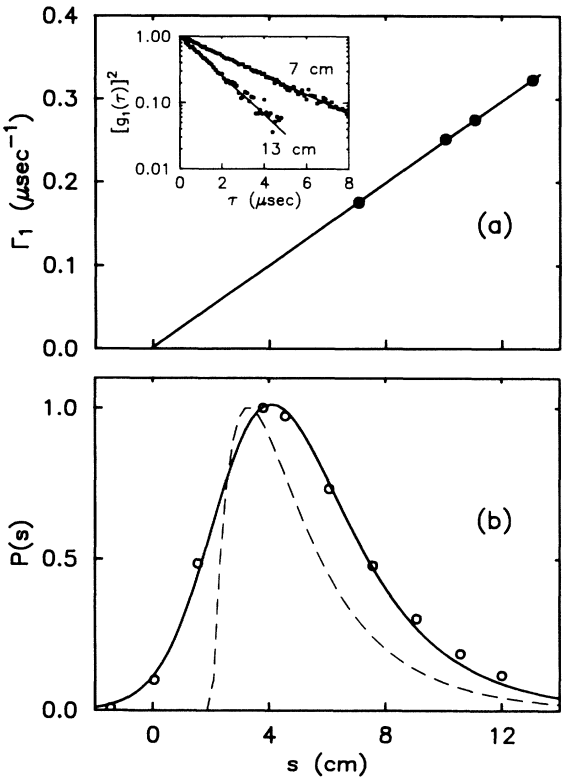

FIG. 2. (a) Plot of the decay rate Γ_1 of the SH temporal field autocorrelation function as a function of reference arm delay s [same scale as (b)]. The solid line is a least-squares fit to the data. Inset: Plot of SH intensity autocorrelation function $\ln|g_1(2\omega_0,\tau)|^2$ vs τ for $s=7.0$ cm and $s=13.0$ cm. Both curves exhibit the expected single-exponential decay. (b) $P(s)$: measured (open circles) and calculated (solid line). The dashed line represents $P(s)$ for δ-function input pulses.

Within the limitations of the current apparatus, these measurements corroborate the primary result of DWS. That is, the electric-field autocorrelation of photons which have diffused s/l^* steps, decays by $\exp(-2k_0^2D\tau)$ per step. This is explicitly demonstrated over path lengths between 2200 and 4100 steps. Experiments are currently underway to test this hypothesis in the more complicated backscattering geometry where it is expected to break down.

In addition to the measurements described above, we report preliminary results of a concentration-dependent study undertaken with this technique in the high-volume-fraction limit. In Table I we tabulate our measured values of l^* and D for various particle volume fractions ϕ. We also indicate a theoretical estimate of the self-diffusion coefficient based on corrections due to hydrodynamic interactions.[13] While we obtain good agreement at the lowest concentration, there clearly exists a substantial deviation between theory and experiment at higher concentrations, particularly at $\phi=0.10$. These deviations may arise, in part, from the effects of collective particle motion. At present, however, the origin of the deviations are unclear and further studies are underway to understand them.

In conclusion, we have introduced a pulsed-DWS technique which enables us to isolate the contributions of particular photon paths to the autocorrelation function. This substantially improves the interpretation and spatial resolution of conventional DWS experiments. Shorter light

TABLE I. Summary of diffusion and l^* data for various volume fractions of polystyrene. Also shown are theoretical estimates for the self-diffusion coefficient $D=D_0(1-1.83\phi)$ (Ref. 13), where $D_0=k_BT/6\pi\eta a$ is the Stokes-Einstein diffusion coefficient and ϕ is the volume fraction of spheres.

Concentration (vol. fraction)	l^* (μm) (Expt.)	D (cm^2/s) (Expt.)	D (cm^2/s) (Theory)
0.05	148 ± 16	$(1.06\pm0.10)\times10^{-8}$	1.14×10^{-8}
0.10	61.8 ± 4.0	$(7.34\pm0.80)\times10^{-9}$	1.03×10^{-8}
0.20	41.7 ± 3.4	$(7.85\pm0.78)\times10^{-9}$	7.97×10^{-9}
0.30	31.6 ± 2.2	$(6.20\pm0.47)\times10^{-9}$	5.67×10^{-9}

pulses will permit the observation of ballistic particle motions and more complicated systems in greater detail. The technique has enabled us to explicitly test various assumptions of DWS theory, and it can be applied in the important backscattering geometry where some of the assumptions of the photon diffusion approximation are known to break down. Several projects along these lines are currently underway in our laboratories.

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