Pulsed Diffusing-Wave Spectroscopy: Pathlength Specific Observation of Speckle Fluctuation Spectra from Dense Colloids

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Abstract. We introduce a probe of fluctuating dense random colloidal suspensions which uses phase fluctuations of optically gated photons to obtain pathlength specific speckle correlation functions.

1. Introduction

Nonlinear optical gating has enjoyed wide success over the years [1]. We describe a new class of gating experiment which we have developed and applied to study particle diffusion in colloids at high concentration. In contrast to previous work, the new scheme exploits the *phase fluctuations* of gated photons and enables the experimenter to access properties of dense colloidal suspensions that *multiply* scatter light.

Diffusing-wave spectroscopy (DWS) is a new method of light scattering [2,3] that exploits the diffusive nature of light transport in strongly scattering media to relate temporal intensity fluctuations of the scattered light to particle motion. Unlike traditional quasi-elastic light scattering methods, DWS probes particle motion in dense, *strongly scattering colloids* and over length scales much *shorter* than the wavelength of light.

In a typical DWS experiment a cw laser beam illuminates a colloidal suspension, and the temporal autocorrelation function of the multiply scattered output field is measured. Properties of the scatterers, such as their diffusion coefficient are extracted by analyzing this autocorrelation function. Microscopically one can envision each photon traveling ballistically between particles, and experiencing changes in propagation direction after each scattering event. Two length scales characterize photon transport in the media: (1) s, the total distance traveled by a photon, and (2) l*, the transport mean free path of the photon. Physically, l* (l*<<s) is the mean distance a photon travels before its propagation direction is randomized. Thus l* is the random walk step size for the "diffusing photons." If we consider only the electric field due to photons that travel a length s through the media, then the time-averaged autocorrelation function, $g_1(\tau,s)$, of the scattered field takes on a simple form when the particles move independently [2,3],

$$g_1(\tau,s) = \exp[-k_0^2\langle\Delta r^2(\tau)\rangle(s/l^*)/3] \quad . \tag{1}$$

Here $\langle\Delta r^2(\tau)\rangle$ is the mean square displacement of a particle in time τ and k_0 is the wavenumber of the light in the media.

The first DWS experiments used cw lasers [3] to measure the *total* electric field autocorrelation,$G_1(\tau)$, function. his can be computed by incoherently summing the contributions of each path-dependent $g_1(\tau,s)$, weighted by P(s), the probability a photon will travel a distance s through the media. For Brownian motion, $\langle\Delta r^2(\tau)\rangle = 6D\tau$, and $G_1(\tau)$ is the Laplace transform of P(s) with new scale factors.

In pulsed-DWS (PDWS) spectroscopy standard nonlinear optical gating methods [1] isolate the contributions of photons that travel paths of a single specified length through

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the media. The upconverted photons are then further processed. Using photon correlation techniques [3] we perform an intensity-intensity autocorrelation measurement on the upconverted photons. Effects such as sample absorption and experimental geometry are rendered unimportant. In addition to studying particle diffusion with greater precision, we can test fundamental elements of the original DWS theories.

2. Pulsed Diffusing-Wave Spectroscopy (PDWS)

The basic ideas of PDWS are illustrated in Fig. 1. A 100 MHz pulse train from a mode-locked Nd:YAG laser is divided between a sample and a reference line of variable length. Sample pulses impinge on a dense colloidal suspension of 0.46-μm-diam. polystyrene spheres in water. A portion of the output "speckle" is collected, and recombined with the reference pulse in a KTP crystal where it is upconverted. The sample pulse is temporally broadened due to multiple scattering in the suspension, and the reference pulse gates [1] out a small portion of the broad pulse. Importantly, the fluctuations of the gated speckle field are impressed upon the upconverted field! Thus, the standard autocorrelation measurement can be performed on the upconverted photons.

The autocorrelation function of the SH field is proportional to $g_1(\tau,s)$. By changing the relative delay between reference and sample arms we can vary s. Note that the temporal behavior of the *upconverted* autocorrelation function, $g_1(\tau,s,2\omega)$, no longer depends on the shape of P(s), and for fixed s, a plot of $\ln[g_1(\tau,s,2\omega)]$ vs τ directly yields the time dependence of $\langle \Delta r^2(\tau) \rangle$. In DWS any process that affected P(s), modified the temporal decay of the measured autocorrelation function. Thus even processes that *do not* effect particle diffusion must be properly accounted for in analyzing DWS data. PDWS eliminates these types of problems.

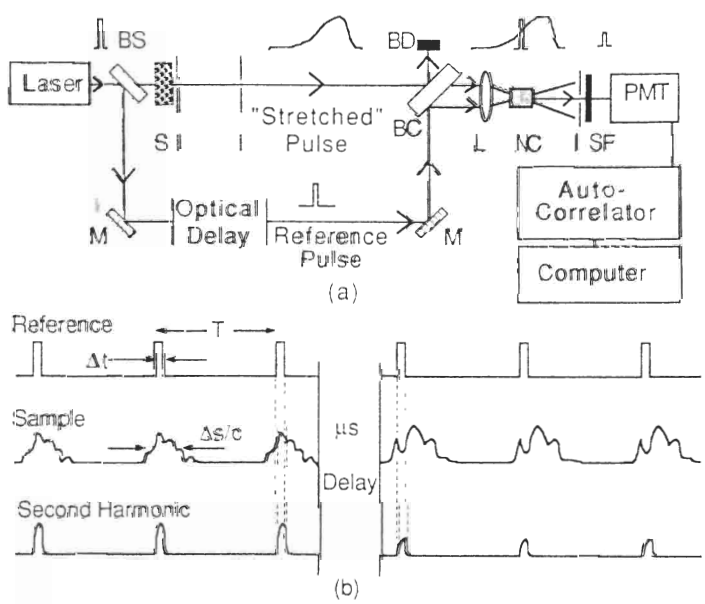

Fig. 1: (a) Schematic of experimental set-up: BC, beam combiner; BD, beam dump; BS, beam splitter; I, iris; L, lens; M, mirror; NC, nonlinear crystal (KTP); PMT, photomultiplier tube; S, sample; SF, second-harmonic spectral filter. (b) Sketch of reference, sample, and upconverted pulse intensities during two time intervals separated by several microseconds.

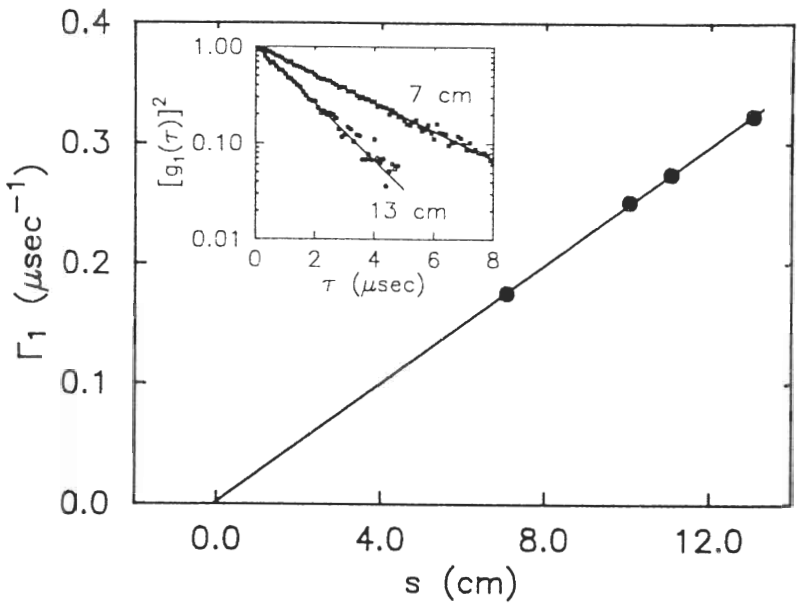

Fig. 2: Inset: Plot of the upconverted intensity autocorrelation function $[g_1(\tau,s,2\omega)]^2$ *vs* τ. Main: Plot of the temporal decay rate, Γ_1, of the upconverted field autocorrelation function vs reference arm delay *s*.

To illustrate the basic features of PDWS we have carried out measurements on the Brownian dynamics of dense colloidal suspensions. Typical photon count rates were between 80 and 600KHz, allowing normalized intensity autocorrelation functions to be obtained with 100nsec time resolution in ~15 minutes. The intensity and field correlation functions are related through the Siegert relation [3]. In the inset of Fig. 2 we plot typical SH intensity autocorrelation functions $[g_1(\tau,s,2\omega)]^2$ vs τ. The volume fraction of spheres was 0.3, the sample thickness was 2 mm, and the reference arm delays were s=7.0 cm and s=13.0 cm. In contrast to DWS measurements the curves decay exponentially. Using this sample we performed measurements at different optical delays s. In the main part of Fig. 2 we plot the temporal decay rate, Γ_1, of the upconverted field autocorrelation function vs. reference arm delay *s*. These measurements corroborate the primary result of DWS. That is, the path-dependent electric field autocorrelation function decays exponentially at a rate proportional to s.

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3. References

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