Diffusing-wave interferometry

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In this note we describe a qualitatively different approach to measure the temporal correlation functions of multiply scattered light from fluctuating dense random media. Our approach combines diffusing-wave spectroscopy with Michelson interferometry. Among other things, the new approach should enable experimenters to perform correlation measurements on very short time scales. The method is described, and then some new physical applications of the method are discussed.

1. Introduction

Diffusing-wave spectroscopy (DWS) [1–3] is a new class of dynamic light scattering measurement that is particularly well suited for the investigation of the dynamics of particles on very short time scales. The method differs qualitatively from traditional quasi-elastic light scattering (QELS) [4,5] in that it is only applicable in dense colloidal suspensions which multiply scatter light. Recently a quantitative DWS study of very early time particle diffusion has been carried out in a colloidal suspension of PMMA spheres in hexane [6]. This work experimentally demonstrated that it is essentially to incorporate a full hydrodynamic picture of the particle interactions when considering particle motion in the non-diffusive regime. Further work along these lines can be anticipated because these types of problems have not been studied quantitatively, and it appears highly desirable to push these measurements into shorter and shorter time regimes.

All DWS measurements performed thus far have been carried out in the time domain using standard photon correlation techniques. The temporal decay of the DWS intensity autocorrelation function provides a direct measure of the mean square particle displacement as a function of time. However, probing shorter and shorter time regimes becomes more difficult with photon correlation techniques since they are ultimately limited by the finite bandwidths of photomultiplier tubes and other detection electronics. On the other hand, no experiments have been reported which measure the fluctuation spectra in the frequency domain. This is probably because of the difficulties that arise in inverting the data and then extracting meaningful information from the wings of the spectral lines. Thus, although one of the most important new physical applications of DWS is connected with trying to understand very early time Brownian motion, to our knowledge all of the experimental efforts to push to shorter times have focussed on using faster photon correlators. Presently the smallest bin width in a commercially available photon correlator is 50 ns.

In this note we suggest a qualitative different approach for measuring these correlation functions, which can in principle enable the experimenter to study variation in the correlation function on the femtosecond time scale. Our approach combines diffusing-wave spectroscopy with Michelson interferometry. It is yet one more application of the Michelson interferometer, that appears to be quite

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practical in the context of DWS and early time particle dynamics. In essence the experimenter measures the coherence time of the sample output speckle with a Michelson interferometer. The measurement is in the time domain, where the connection to mean square particle displacement is clear, and, in addition, the measurement provides direct information on the more fundamental *electric field* correlation function, which is usually derived from *intensity* autocorrelation measurements using the Siegert relation [7]. In previous QELS experiments this type of approach was impractical because the sample coherence times were very long. With DWS, on the other hand, the correlation times are substantially shorter, and in fact can be made arbitrarily short by increasing the sample length. Thus the requirements on interferometer length and source coherence are modified considerably.

The plan of this note is as follows. We will briefly review the standard DWS results, drawing attention to the speckle correlation functions and the basic experimental set-up. Then we will discuss the interferometric version of the experiment. Finally we will touch on some interesting new applications of the method.

2. Review of diffusing-wave spectroscopy

In a standard DWS experiment a dense sample of Brownian particles is illuminated by a plane wave on the front face of the sample cell (see fig. 1), and a portion of the light that has propagated through the other face is collected through a small aperture at the output plane. The suspensions are usually housed in 2 mm thick quartz cells, and might typically be composed of ~ 0.5 μm diameter polystyrene spheres in water, at a volume fraction of between 1 and 30%. Microscopically one can envision each photon travelling ballistically between particles, and experiencing changes in propagation direction after each scattering event. All scattering events are elastic. Three length scales characterize photon transport in the media: (1) s, the total distance travelled by the photon, (2) l, the mean distance travelled by the photon between particle encounters, and (3) l^*, the transport mean free path of the photon. Physically l^* corresponds to the mean distance travelled by a photon

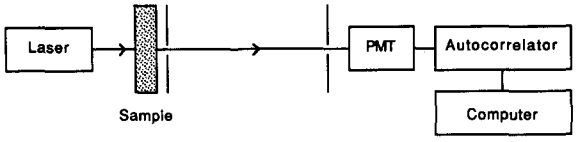

Fig. 1. Schematic of a typical DWS measurement. Light from a laser is directed onto a dense colloidal suspension. Each photon travels through the sample along a complicated path. At the output face a portion of the emerging speckle field is directed onto a photomultiplier tube (PMT), and the intensity autocorrelation function of the speckle is computed using standard photon correlation electronics.

before its propagation direction is completely randomized. Thus l^* is the random walk step size for the "diffusing" photons. In dense samples $s \gg l^*$ and the diffusion approximation for photon transport is usually quite good.

If one considers only photon paths of length s through the media, then it is relatively straightforward to derive an expression for the time-averaged autocorrelation function,

$$g_1(\tau, s) = \langle \boldsymbol{E}^*(t+\tau)\boldsymbol{E}(t)\rangle / \langle |\boldsymbol{E}(t)|^2\rangle ,$$

of the scattered field $\boldsymbol{E}(t)$. For example, assuming that the particles move independently, that the particle displacement is a random Gaussian variable, and that the photon momentum transfer in each scattering event is independent of particle displacement, one can show that [3,8]

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

where $\langle \Delta r^2(\tau)\rangle$ is the mean square particle displacement of a particle in time τ, and $k_0 = 2\pi/\lambda$ is the wavevector of the incident light field. Eq. (1) is the primary result of the simplest DWS treatment. Notice that, in contrast to QELS, the path-dependent field correlation function $g_1(\tau, s)$ is sensitive to particle motion on length scales $\lambda/(s/l^*)^{1/2}$, which, since $s \gg l^*$, is generally much less than λ. Thus the DWS correlation functions decay much more quickly in time than their single scattering counterparts.

The first experiments demonstrating these ideas were carried out with cw lasers [2,3]. In this case one actually measures a more complicated total correlation function, $G_1(\tau)$, that is computed by incoherently summing the contributions of each path-dependent correlation function, weighted by the

probability that a photon will travel a distance s through the medium. More recently the form of the path-dependent function in eq. (1) has been directly verified [9]. For the purpose of this paper, the reader need only note that the more complicated result is reasonably well approximated by eq. (1), provided we insert an appropriate *most probable value*, s_{max}, for s in eq. (1).

3. Diffusing-wave interferometry and applications

We will now describe diffusing-wave interferometry (DWI). A schematic of the basic experimental set-up is shown in fig. 2. The experimenter illuminates a dense sample of Brownian particles with a laser beam just as in the conventional DWS experiments. In the present scheme, however, the output speckle field, $E(t)$, is collected, collimated, and directed into a Michelson interferometer. If the length of arm one (two) is L_1 (L_2), then after recombination the beams are delayed by $\tau=2(L_1-L_2)/c$ with respect to one another. Here c is the speed of light. The intensity measured at the photomultiplier tube is given by

$$I(\tau)=\tfrac{1}{8}\langle |E(t)+E(t+\tau)|^2\rangle , \qquad (2)$$

where $\langle\ \rangle$ denotes a time average. For a nearly monochromatic input beam this reduces to

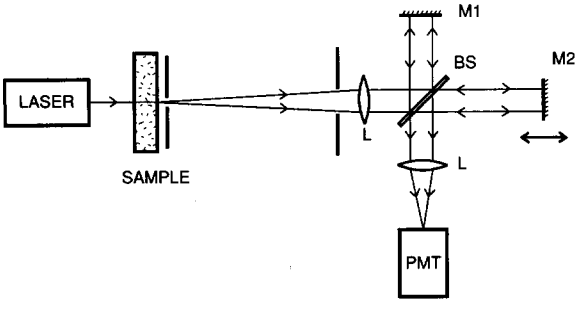

Fig. 2. Schematic of a DWI measurement. M1, M2 denote mirrors; BS denotes beam splitter-combiner; L denotes lenses. Output speckle from the sample is collimated and then directed into a Michelson interferometer. A relative temporal delay is introduced between the two split-off fields, and the beams are recombined on a photomultiplier tube (PMT). The visibility of the fringes is measured, thus enabling the experimenter to measure the speckle field correlation function (see text).

$$I(\tau)=\tfrac{1}{4}\langle |E(t)|^2\rangle \times\{1+[\langle E^*(t+\tau)E(t)\rangle/\langle |E(t)|^2\rangle]\cos\omega\tau\} , \qquad (3)$$

where $\omega=ck_0$ is the angular frequency of the input beam. The envelope multiplying the oscillating term above is often referred to as the *visibility* of the source field [10]. The reader will notice that it is also the temporal autocorrelation function of the scattered speckle field. In our case this visibility will decay on a time scale that depends on the coherence of the laser, and on the spectral broadening induced by the dense sample of moving particles. If the laser coherence time is reasonably large, it is possible to prepare the sample so that the decay of the field visibility is due almost entirely to the correlation function of the speckle field.

Therein lies the utility of the new approach. By measuring the fringe visibility as a function of τ, we directly measure the speckle *field* temporal autocorrelation function. Importantly this measurement is in the time domain so that contact with the multiple light scattering theory is straightforward. Furthermore the temporal resolution of the method is a *single optical cycle.* Although in principle the method will work with all elastic scattering experiments, it is not suited in practice for conventional QELS (single-scattering) experiments because the speckle correlation times in these experiments are typically milliseconds. In this case one would need very long interferometers and very stable laser sources. Perhaps this explains why this correlation method has not been previously contemplated in these contexts.

Finally we briefly elaborate on the feasibility of experiments probing the early time, pre-diffusive dynamics of Brownian particles, and on the new information one may be able to obtain with DWI. The time scale for the transition from ballistic to diffusive particle motion is set by the viscous damping time, $T=m/6\pi\eta a$, where m is the mass of the Brownian particle, a is its radius, and η is the viscosity of the surrounding fluid [11]. For aqueous suspensions of polystyrene microspheres with diameters between 0.1 and 1.0 μm; T ranges between approximately 1 and 30 ns, and particles typically move a few angstroms in this time. This early time behavior of the particle can be characterized by the

temporal velocity correlation function $W(\tau) = \langle v(0)v(\tau)\rangle$. At $\tau=0$ the equipartition theorem gives $W(0)=3k_bT/m$, where k_b is the Boltzmann constant and T is the sample temperature. For $\tau \sim T$ the motion of the particle is complicated, being governed by the solution hydrodynamics. For $\tau \gg T$, the particle executes a random walk, and the motion is fully diffusive; in this limit $W(\tau)$ approaches zero.

Early Langevin theories predicted a simple exponential decay of $W(\tau)$ due to viscous damping [11]. However, more recent theories predict a much more complicated decay, with several time scales [12,13]. The earliest time scale is set by molecular collision times. The finite compressibility of the fluid sets another time scale, about 1 ns [12], which is given by the ratio of the particle size to the speed of sound in the medium. The velocity autocorrelation function is estimated to decay by 30% or more over this time interval. The long-time decay of $W(\tau)$ is much slower, and is predicted to vary as $\sim\tau^{3/2}$. This slow decay reflects the subtle interplay between fluid induced motion of the particle, and particle induced motion of the fluid.

With DWI, the entire range of *time* scales relevant to the transition from ballistic to diffusive motion is experimentally accessible for the first time. However, to explore the early time Brownian dynamics, one must also be able to measure particle motion over *length* scales comparable to an angstrom. Here the multiple scattering plays a crucial role in extending the range of accessible length scales to less than an angstrom. As an example, a sample of 0.2 μm diameter polystyrene spheres in water at a volume fraction of 30% has a transport mean free path of $l^* \sim 10$ μm for 527 nm wavelength light [14]. For a sample of thickness $L=1$ *cm*, $g_1(\tau)$ will decay by 10–20% in ~ 5 ns; for a 5 cm thick sample, $g_1(\tau)$ will decay by 2 decades in ~ 5 ns. In this time the particle moves about an angstrom. The energy losses due to photon diffusion, backscattering and collection, are estimated to be less than 10^{-13} (10^{-16}) of the incident light beam energy for a 1 cm (5 cm) thick sample cell. Thus photon counting is easily feasible with commercially available 1 W cw laser sources. In addition the coherence length of the light must be comparable to the typical photon length s through the cell [15]. This distance is approximately $s \sim 0.4L^2/l^*$, for $L=5$ cm and $l^*=$'10 μm, $s \sim 100$ m. This is just within the range of commercially available dye lasers. Experiments of this nature are underway in our laboratories.

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References

[1] M.J. Stephen, Phys. Rev. B 37 (1988) 1.
[2] G. Maret and P.E. Wolf, Z. Phys. B 65 (1987) 409.
[3] D.J. Pine, D.A. Weitz, P.M. Chainkin and E. Herbolzheimer, Phys. Rev. Lett. 60 (1988) 1134.
[4] B.J. Berne and R. Pecora, Dynamic light scattering (Wiley, New York, 1976).
[5] N.A. Clarke, J.H. Lunacek and G.B. Benedek, Am. J. Phys. 38 (1970) 575.
[6] D.A. Weitz, D.J. Pine and R.J.A. Tough, Phys. Rev. Lett. 63 (1989) 1747.
[7] E.O. Schulz-Duboid, in: Photon correlation techniques in fluid mechanics, ed. E.O. Schulz-Dubois (Springer, Berlin, 1983) p. 6.
[8] F.C. MacKintosh and S. John, Phys. Rev. B 40 (1989) 2383.
[9] A.G. Yodh, P.D. Kaplan and D.J. Pine, Phys. Rev. B 42 (1990) 4744.
[10] M. Born and W. Wolf, Principles of optics (Pergamon, New York, 1980).
[11] S. Chandrasekhar, Rev. Mod. Phys. 15 (1943) 1.
[12] R. Zwanzig and M. Bixon, Phys. Rev. A 2 (1970) 2005.
[13] E.J. Hinch, J. Fluid Mech. 72 (1975) 499.
[14] D.J. Pine, D.A. Weitz, J.X. Zhu and E. Herbolzheimer, J. Phys. (France) 51 (1990) 2101.
[15] P.E. Wolf and G. Maret, in: Scattering in volumes and surfaces, eds. J. Nieto-Vesperinas and J.C. Dainty (North-Holland, Amsterdam, 1990).