Dynamic light scattering in subdiffusive regimes

Gabriel Popescu and Aristide Dogariu

For describing the fluctuating signal scattered from a multiple-scattering system, diffusive-wave spectroscopy makes use of a diffusion model that provides the path-length distribution of scattered waves for a specific geometry. Using the recently introduced optical path-length spectroscopy, we show that the diffusion model fails to describe wave propagation in the low-order multiple-scattering regime. We propose a new methodology with which to obtain information about the dynamic properties of nondiffusive scattering systems. We use optical path-length spectroscopy to obtain experimentally the path-length distribution of optical waves scattered from dynamic colloids, which are multiply scattering but not in the diffusion limit. The experimental results show that, with this new technique, the accuracy of dynamic measurements is significantly improved in subdiffusive scattering regimes.

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1. Introduction

The technique of dynamic light scattering (DLS) has been established as a powerful method for investigating dynamic processes. By measuring the temporal fluctuations of the scattered light, one can extract detailed information about the dynamics of the scattering medium.[1] Originally, DLS applications were limited to weakly scattering media for which the light propagation could be described by a single-scattering model. An important breakthrough in the field of dynamic light scattering is the extension of DLS to strongly scattering media.[2–4] The technique is referred to as diffusing-wave spectroscopy (DWS). In DWS, the intensity of the scattered light is a summation over all possible scattering trajectories in the medium, and phase correlations are neglected. Therefore the coherence length of the radiation used must exceed the longest scattering path detected. If λ is the wavelength of light and N is the typical number of scattering events that light undergoes in the medium the characteristic decay time of the temporal autocorrelation function is given by the time that it takes for a scatterer to move over a distance $\lambda/\sqrt{N}$. This characteristic time is much longer in typical DLS experiments, as it is set by the time required by the scatterers to move over a distance q^{-1}, where q is the wave vector. Thus, DWS is suitable for investigations of much slower dynamic processes, such as those developed in glassy systems, and this property of DWS opens a new field of applications.

The description of the DWS signal relies on a photon-diffusion model to produce the optical path-length distribution $P(s)$ of waves propagating in the medium. One usually obtains this distribution by assuming a diffusive propagation of optical waves and solving the associated diffusion equation. This technique has been used for the study of particle motion in concentrated fluids such as colloids and microemulsions and in other systems that are characterized by strong multiple scattering. More recently, important results have been obtained with measurements of viscoelastic fluids,[5] magnetorheological suspensions,[6] periodically strained suspensions,[7] proteins,[8] etc. The technique has also been successfully applied to the study of nonergodic systems, such as particles in a gel matrix.[9]

However, many of the dynamic systems of practical interest, although they are multiply scattering, are not optically diffusive and therefore cannot be characterized by the DWS treatment presented above. The region of transition from single scattering to the diffusive scattering regime, in the context of dynamic light-scattering experiments, has been studied and the experimental data have been described by use of a combination of cummulants weighted by empirical

The authors are with the School of Optics, Center for Research and Education in Optics and Lasers, University of Central Florida, Orlando, Florida 32816. A. Dogariu's e-mail address is acd@creol.edu.

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constants.[10] The light transport was modeled with a telegrapher equation, and a discontinuous-source model was used; the technique was applied to optically thin samples in a transmission geometry.[11] Unfortunately, that model was exact only for the one-dimensional case. Thus, so far, DLS has found little application for characterizing media that are neither single scattering nor diffusive. Accordingly, to assess the dynamic structure accurately, it is highly desirable to provide a simultaneous and independent measurement of the photon path-length distribution. In this paper, we show how $P(s)$ can be experimentally obtained by optical path-length spectroscopy (OPS) and further be used to describe dynamic scattering signals. This procedure extends the applicability of dynamic light scattering to systems that are not optically diffusive.

The paper is organized as follows: In Section 2 we review the principle of OPS, which allows the characteristic $P(s)$ to be measured for any multiple-scattering medium. In Section 3 the methodology of integrating the OPS with the DLS technique is presented. The new technique allows accurate information on the dynamic properties of optically subdiffusive colloidal systems to be obtained. A discussion and conclusions of the study are presented in Section 4.

2. Optical Path-Length Spectroscopy

A multiple-scattering regime is usually associated with wave propagation through optically dense random systems and is commonly described in terms of a diffusion equation. This is an approximation for energy transport for which isotropic elastic scattering and wave propagation at a constant group velocity are considered and the polarization and the interference effects are neglected.[12] We relate the transport mean free path l_t to the photon-diffusion coefficient by considering a constant energy transport velocity. This scattering parameter depends on both the number density of scatterers and size and shape of each individual scatterer. For media of finite thickness L, the condition under which the diffusion theory is generally valid is $l_t/L \ll 1$. Moreover, it is required that the absorption length l_{abs} be much larger than both l_t and L. It is worth mentioning that the reliability of the diffusion approximation has been questioned, and experiments of time-resolved diffuse transmission have shown that the approximation becomes increasingly less reliable when the thickness of the sample decreases and the anisotropy factor increases. It has also been shown that, when internal reflections at the boundary and scattering anisotropy are properly taken into account, the range of validity of the diffusion approximation can be extended.[13]

Diffusive-wave propagation depends on the specific scattering geometry and is characterized by the probability density $P(s)$ of optical path lengths through the medium. This comprehensive quantity, which describes the statistics of the light through many scattering events in a random medium, can be estimated for different experimental configurations, but, so far, direct experimental studies of the distribution of optical path lengths have been limited to investigations of the temporal broadening of short light pulses that propagate diffusely.[14]

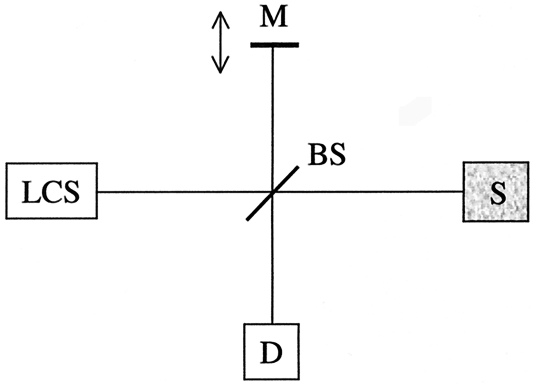

Fig. 1. Michelson geometry for OPS measurements: LCS, low-coherence source; BS, beam splitter; M, mirror; D, detector; S, sample under investigation.

Recently, we proposed a novel approach to investigating the properties of multiple-scattering systems. Based on the principle of low-coherence interferometry, the new technique, called OPS, directly infers the path-length distribution $P(s)$ of waves backscattered in a specific geometry.[15] A typical OPS signal consists of backscattered intensity contributions that correspond to waves scattered along closed loops that have the same optical path lengths and, in addition, have the total momentum transfer $4\pi/\lambda$ (backscattering).

Light from a broad-bandwidth source is first split into a probe and a reference beam, which are retroreflected from a targeted scattering medium and from a reference mirror, respectively, and are subsequently recombined to generate an interference signal, as described in Fig. 1. The low-coherence source has a central wavelength and a coherence length that are much smaller than the characteristic scattering length l_t.

If one assumes quasi-monochromatic optical fields ($\Delta\lambda/\lambda \ll 1$) the detected intensity has the simple form

$$I_d(\Delta s) = I_s(\Delta s) + I_{\mathrm{ref}} + 2[I_s(\Delta s) I_{\mathrm{ref}}]^{1/2} |\gamma(\Delta s)| \cos(2\pi \Delta s/\lambda), \quad (1)$$

where I_d, I_s, and I_{ref} are the detected, scattered, and reference intensities, respectively. The optical path difference between the scattered and the reference fields is denoted Δs, and λ is the central wavelength. The complex degree of coherence γ is essentially the normalized field cross-correlation function: $\gamma(\Delta s) = \langle E_s(0) E_{\mathrm{ref}}^*(\Delta s)\rangle / \langle E_s(0) E_{\mathrm{ref}}^*(0)\rangle$, with the angle brackets denoting ensemble averaging. The function γ is proportional to the Fourier transform of the optical spectrum of the radiation used, and its width defines that coherence length l_c. To obtain the maxima of interference requires that Δs be a multiple of a wavelength and the condition $\Delta s < l_c$ has to be met. In

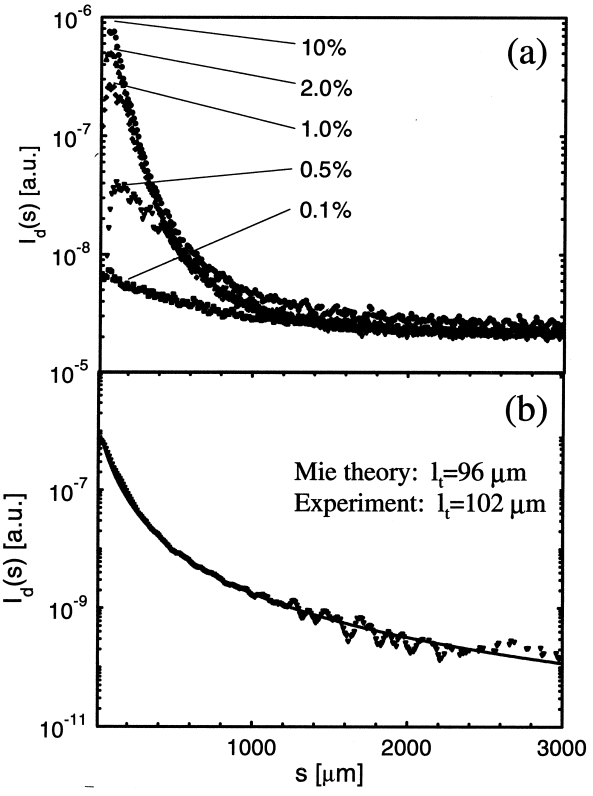

Fig. 2. (a) OPS signals for 0.356-μm polystyrene microspheres suspended in water at different volume fractions, as indicated. (b) OPS data for 0.51-μm polystyrene particles with a volume fraction of 10%; also shown is the fit with the diffusion model.

practice, in using heterodyne detection, one measures only the envelope of the interference term and neglects the oscillating factor (carrier). In the OPS configuration, I_s corresponds to the reflectance of a multiple-scattering medium, and the coherence properties of the light act as a bandpass filter in the optical path-length domain with a width given by the coherence length. By tuning the optical length of the reference arm and detecting the interference term, one obtains the optical path-length distribution of light backscattered from the sample. In our experiments, as a result of heterodyning, the dynamic range achieved is greater than 90 dB. The same single-mode optical fiber is used to send the light to and collect it from the random medium. The dimensions of the samples of interest here are larger than 1 cm × 1 cm × 1 cm. Whereas low-order scattering components are detected as a result of the backscattering geometry, the longest optical paths recorded are limited to a finite value because of limitations on the sensitivity of the detector. Thus for the media studied the influence of the boundaries on the scattering process is negligible.

Typical experimental results are presented in the logarithmic plot of Fig. 2(a) for 0.356-μm-diameter polystyrene microspheres suspended in water at different particle concentrations, as indicated. As can be seen, the OPS technique is highly sensitive to changes in the scattering regime that are induced by variations of particle concentrations. For the lowest concentrations shown the single-scattering regime is reached, as is suggested by the exponential decay of the corresponding signal. For all the other samples presented in Fig. 2 a more complex behavior can be observed, which is an indicator of a multiple-scattering regime. After detection the path-length-resolved signals can be normalized with the area under the curve to yield the probability density of backscattered waves $P(s)$.

It is worth mentioning that, in the particular configuration of OPS, the source and the detector physically overlap and the incident beam is narrow, collimated, and normal to the surface of the medium. This is a purely experimental situation that can easily be described mathematically as a point-source–point-detector configuration at the boundary of a semi-infinite medium. Therefore, one can use OPS to study subtle properties of scattering media and answer questions regarding the applicability of various approaches.[16]

In media with negligible absorption the diffuse energy density $\Psi(\mathbf{r}, t)$ satisfies the diffusion equation $(\partial/\partial t - D\nabla^2)\Psi(\mathbf{r}, t) = \delta(\mathbf{r})\delta(t)$, where $\delta(\mathbf{r})\delta(t)$ is the impulse source at time $t = 0$, $r = 0$, and D is a diffusion coefficient given by $D = (vl_t)/3$. Setting a mixed boundary condition such that Ψ vanishes linearly on the plane $z = -z_e$ permits the diffusion equation to be solved, and the photon flux is obtained from Fick's law.[17] Assuming an average energy transport velocity v, the path-length dependence of the energy flux detected in the particular OPS geometry ($r = 0$) can be evaluated as

$$I_d(s) = a l_t^{-3/2} z_e s^{-5/2} \exp\left(-\frac{3 z_e^2 l_t}{4s}\right), \qquad (2)$$

where a is a constant and z_e is the extrapolation length ratio that defines the boundary condition and quantifies the reflection at the boundaries.[18] Up to a normalization operation, $I_d(s)$ can be regarded as the probability distribution of optical path lengths that correspond to waves that have traveled through the medium along closed loops and have also accumulated a total momentum transfer equal to $4\pi/\lambda$. The path-length-resolved backscattered intensities that correspond to a suspension of polystyrene microspheres with a 0.1 volume fraction and a particle diameter of 0.51 μm are shown in Fig. 2(b). By applying the conventional Mie scattering theory, we found for this medium that the value of the transport mean free path is 96 μm. When experimental data are fitted with the functional form predicted in Eq. (2), the value of $l_t = 102$ μm is inferred. The procedure was applied to various diffusive systems, and the excellent agreement with conventional estimations proves the capability of the OPS procedure to retrieve optical path-length distribution $P(s)$ of waves propagating in diffusive random media. Taking advantage of its particular features, such as its dynamic range, path-length resolution, and purely experimental geometry, we applied OPS to investigate the dif-

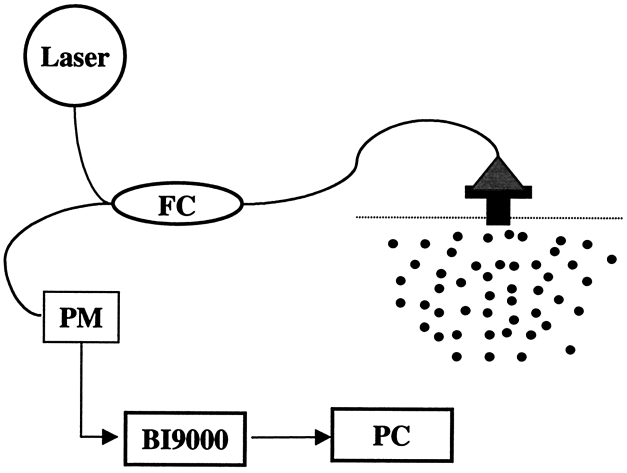

Fig. 3. Experimental setup for dynamic scattering measurements: FC, fiber coupler; PM, photomultiplier; BI9000, digital correlator; PC, computer.

fusion process in bounded media. Evidence was found that the extrapolation length ratio z_e depends not only on the reflectivity at the boundary but also on the anisotropy of the single-scattering process.[16]

In what follows, we show how OPS can be integrated with DLS measurements in multiple-scattering media that are not well described by the diffusion equation. The purpose of these studies is to enlarge the domain of applicability of DLS, bridging the gap between the traditional DLS and DWS.

3. Dynamic Light Scattering in Subdiffusive Regimes

In quantifying the temporal fluctuations of the light scattered from a dynamic suspension, one has to evaluate the associated field autocorrelation function. For a fluctuating electromagnetic field that is scattered multiple times the normalized autocorrelation function has the form of an average over all possible paths weighted by the optical path-length probability density[4]:

$$g^{(1)}(\tau) = \int_0^\infty P(s)\exp\left(-\frac{2\tau}{\tau_0}\frac{s}{l_t}\right). \tag{3}$$

In Eq. (3), $\tau_0 = (Dk_0)^{-1}$, where D is the diffusion coefficient of the scatterers in the suspending fluid and k_0 is the wave vector associated with the optical field. For Brownian particles of diameter d, the diffusion coefficient relates to the temperature T and the viscosity η of the medium through the well-known Stokes–Einstein expression $D = k_B T/(3\pi\eta d)$, where k_B is Boltzmann's constant. In practice, the intensity rather than the field autocorrelation function is measured, and therefore a relation between the two autocorrelation functions is always needed.

The experimental setup for our dynamic scattering measurements is presented in Fig. 3. An Ar^+ laser with a central wavelength of 467 nm is coupled into a single-mode fiber, which represents one arm of a 1×2 fiber coupler. The output of the coupler is immersed in the colloidal suspension under investigation, and the backscattered light is collected through the same fiber. Without additional optical components the signal is detected by a photomultiplier that is connected to a digital correlator (Brookhaven Instruments, Model BI9000). Because of the refractive-index contrast between the fiber core and the suspension solvent, the detected signal has two components: the light backscattered from the dynamic system, E_s, and the light that is due to the Fresnel reflection at the fiber–medium interface, E_F. The total intensity detected can be written as

$$I(t) = I_s(t) + I_F(t) + 2\ \mathrm{Re}\{E_s(t)E_F^*(t)\exp[i\Phi(t)]\}, \tag{4}$$

where I_s and I_F are the intensities associated with the scattered and the specular components, respectively, and Φ is the phase of the Fresnel reflected field. In our geometry the specular field is static in both phase and amplitude; thus if the rapidly varying terms are neglected the intensity autocorrelation function becomes

$$\begin{aligned} G^{(2)}(\tau) &= \langle I(t)I(t+\tau)^*\rangle \\ &= I_F{}^2 + 2I_F\langle I_s\rangle + \langle I_s(t)I_s(t+\tau)^*\rangle \\ &\quad + I_F[G^{(1)}(\tau) + G^{(1)}(\tau)^*]. \end{aligned} \tag{5}$$

In Eq. (5), $G^{(1)}$ is the autocorrelation function of the scattered field, and the brackets indicate time averaging. In the case of scattering from common colloidal systems the Fresnel component is always much stronger than the scattered field; therefore the relation between the normalized intensity and the amplitude autocorrelation functions takes a simple form

$$g^{(2)}(\tau) = 1 + 2\beta\ \mathrm{Re}[g^{(1)}(\tau)], \tag{6}$$

where $\beta = \langle I_s\rangle/I_F \ll 1$. Thus, by measuring the intensity autocorrelation function, one can determine the amplitude autocorrelation and obtain information about the dynamic properties of the colloidal suspension through Eq. (3). The main goal of the present study is to use the distribution $P(s)$ measured with OPS, rather than to calculate it from a diffusion model. When Eqs. (6) and (3) are combined, both $P(s)$ and $g^{(2)}(\tau)$ are experimentally measured, and therefore the dynamic properties of the colloid, i.e., τ_0, can be inferred without assuming a diffusive transport of light.

Systematic experiments to test the validity of the proposed approach have been conducted. Polystyrene microspheres with a 0.121-μm diameter were suspended in water, and their concentration was adjusted by controlled mixing with deionized water. The dimensions of the samples were the same as in the OPS experiments. However, inasmuch as here the particle concentration is decreasing, the diffusion model of Eq. (2) is expected to yield a less reliable description of the light propagation in these media.

To check the validity of the diffusion approach, we performed OPS and dynamic scattering measure-

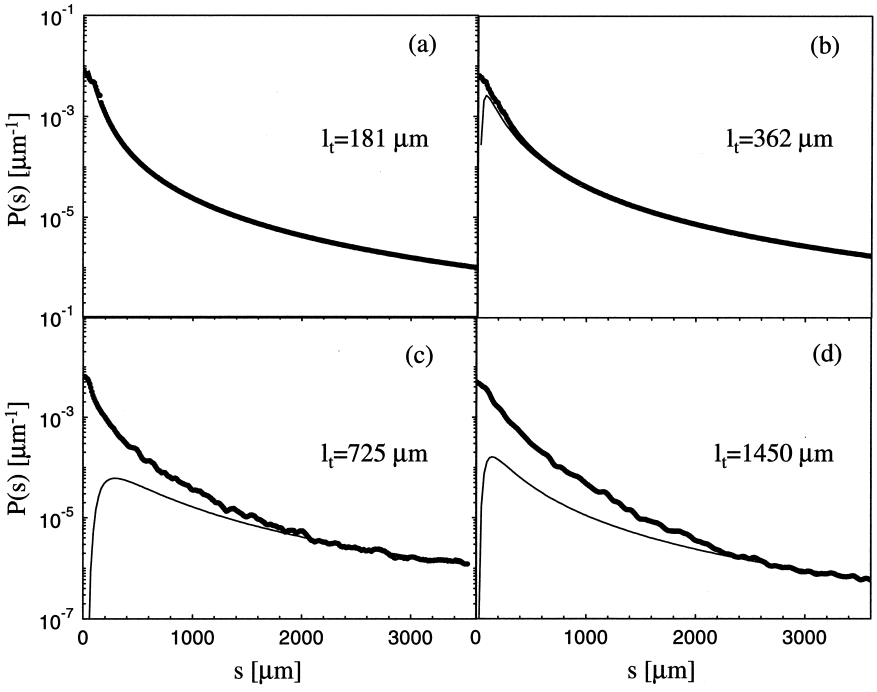

Fig. 4. $P(s)$ measured for suspensions with four values of l_t, as indicated. The thin continuous curves were obtained from the diffusion model of Eq. (2).

ments in identical geometries on suspensions with the same values for the transport mean free path. Figure 4 shows the path-length distribution experimentally obtained from OPS for suspensions with various values of the transport mean free path, as indicated. The solid curves represent the analytic function of Eq. (2) and correspond to values of these transport mean free paths. As can be seen, the agreement of the experimental data with the diffusion model diminishes considerably as the value of l_t increases. We conclude that, for these samples as well as for others of lower concentrations, the diffusion equation does not furnish a satisfactory description of the optical path-length distribution. However, the fact that the experimental curves in Fig. 4 do not have a simple negative exponential behavior means that they contain significant multiple-scattering features. These scattering media can be characterized as multiply scattering but not diffusive, and the light scattered by such systems can be considered as propagating in a subdiffusive regime. If, to describe the intensity autocorrelation function in this situation, one uses Eq. (3) with $P(s)$ estimated from the diffusion equation, erroneous results are to be expected. So far, DLS techniques have not been able to characterize accurately this type of colloidal suspension.

To overcome this difficulty, we use the $P(s)$ functions experimentally obtained with OPS, as described above. In Eq. (3), we evaluate numerically the Laplace transform for an interval of values for the characteristic time τ_0. The Laplace transforms are then compared with the data, and the best fit is retained. The results obtained for samples with the same values of l_t as those presented in Fig. 4 are summarized in Fig. 5. The continuous curves were obtained with our procedure, and the dashed curves were generated from path-length distributions obtained from the diffusion equation that describes the point-source–point-detection geometry, i.e., the conventional DWS treatment. As can be seen, the data are accurately described by our approach for all the samples. Thus the procedure proposed here can be regarded as a new methodology for obtaining the values of τ_0 for any multiple-scattering medium, with no need to rely on a diffusion model.

In our systematic investigation the same approach was applied to systems at various levels of dilution. The errors introduced by use of path-length distributions that were given by the diffusion equation become more significant as the transport mean free path increases. The results obtained in terms of the characteristic time associated with colloidal suspensions of same particles over a broader range of concentrations are summarized in Fig. 6. For comparison the results of the best fit obtained with the diffusion model used to infer $P(s)$ are also shown in the figure. The value of $\tau_0 = (Dk_0)^{-1}$ was calculated for a water viscosity of $\eta = 0.9548$ cP, corresponding to our working temperature of 22 °C. The figure shows the relative error of the measured τ_0^{exp} with respect to the expected value τ_0. The abscissa represents the maximum optical path length s_m detected with OPS and normalized to the transport mean free path. In practice, the maximum-detectable path length is limited by the sensitivity of the detection system, and it usually differs from one sample to another. However, to compare media

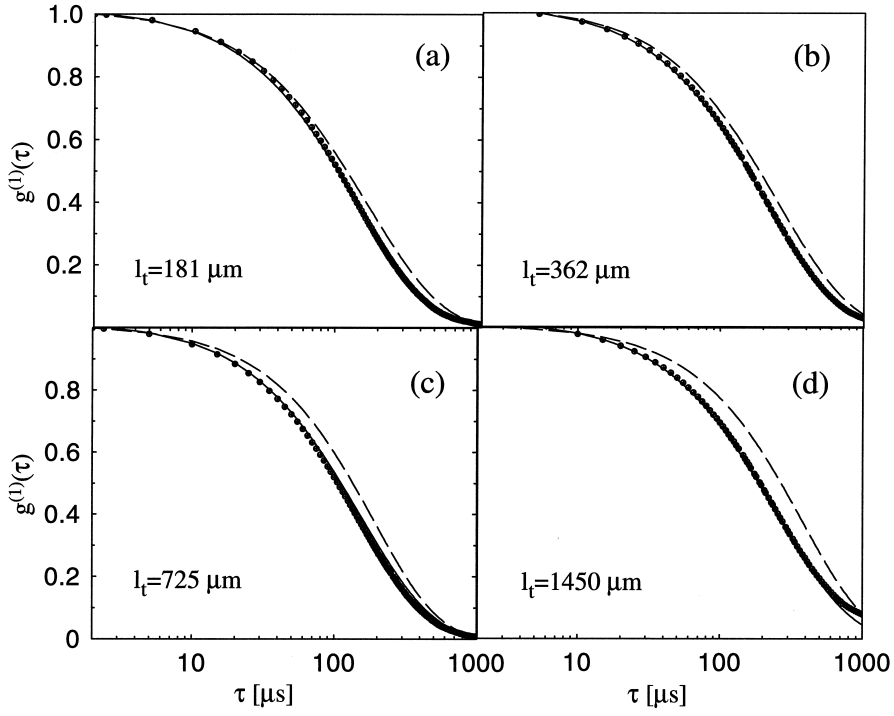

Fig. 5. Normalized field autocorrelation functions for colloidal suspensions of various values of l_t, as indicated. The continuous curves are the best fits to the data obtained by numerical evaluation of the Laplace transform of Eq. (3) with the measured $P(s)$ distributions. The dashed curves correspond to DWS, as described in the text.

with different particle densities, we set the limit of the measurement for all the samples at the maximum value that was not affected by the noise in the case of the most dilute of the series of samples. We point out that, in transmission measurements, the ratio between the thickness of the sample and the transport mean free path is the parameter that we used to measure the scattering strength of a medium. This ratio is usually referred to as the optical density of the medium. In a backscattering geometry, however, such a geometrical constraint is usually missing; thus the ratio $N = s_m/l_t$ seems to be the appropriate parameter that can be used instead. From the results summarized in Fig. 6 it can be seen that our approach is a significant improvement compared with the conventional treatment based on the diffusion model. As the single-scattering regime is approached (lower values of N in Fig. 6), the error of our technique increases also, approaching a value of 20%.

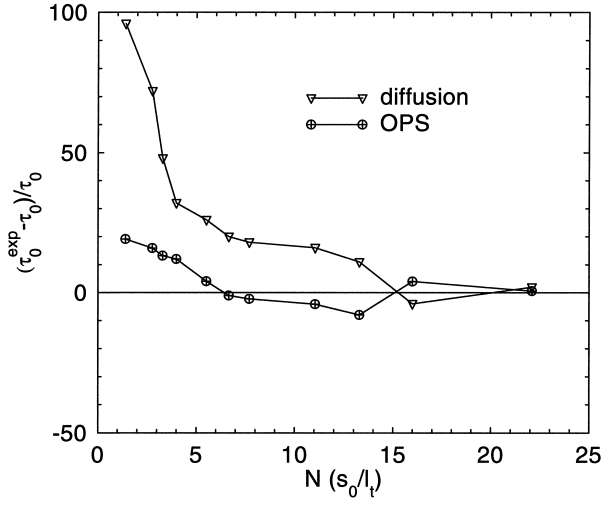

Fig. 6. Relative error of the experimental value τ_0^{exp} with respect to the theoretical value τ_0 for a series of colloidal suspensions characterized by different parameters s_m/l_t.

4. Discussion and Conclusions

The new methodology presented here has been proved to expand successfully the use of DLS techniques into the intermediate domain of optical densities, which is not covered by either DLS or DWS. In practice, there are many dynamic systems that multiply scatter light and yet are not optically diffusive. For this class of media using the technique of DWS, which is based on a diffusion model, inherently gives erroneous results. One can understand that this is so by recognizing that the path-length distribution $P(s)$ provided by the diffusion equation fails to describe the light transport in the low-order multiple-scattering regime.

We proposed using OPS as an alternative method of obtaining $P(s)$ experimentally for such scattering regimes. The capability of OPS for giving accurate $P(s)$ distributions has been proved for scattering media over a broad range of optical densities. OPS works in a backscattering geometry, which, from a theoretical point of view, can be described as a simple point-source–point-detector configuration. Operat-

ing in such a simple geometry helps in investigating refined effects on light transport in random media. By evaluating the temporal correlation function with the measured $P(s)$ as the main ingredient, we obtained information about the dynamic properties of colloidal suspensions over a broad range of optical densities that are otherwise inaccessible to DWS.

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