

# Multiple Light Scattering: Weak Localization and Dynamic Fluctuations

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## Abstract

Recent developments in multiple light scattering from disordered turbid media such as colloidal suspensions are outlined. Interferences between time reversed scattering paths give rise to a coherent enhancement of the backscattered intensity  $\alpha$ . Its dependence on angle and on absorption can be described, in the diffusion approximation, as a function of the length distribution of the scattering paths. Dynamic fluctuations of  $\alpha$  arising from Brownian motion of the scatterers are described similarly. Our experiments demonstrate the quantitative analogy between the time autocorrelation function and the dependence of  $\alpha$  on scattering angle and absorption. This makes possible to study single particles dynamics even under conditions of strong multiple scattering and to probe motion at small time and distance scales not accessible in single light scattering. The effects of interparticle interactions are briefly discussed.

Multiple scattering of waves by extended media containing randomly distributed scatterers is a very widespread phenomenon and thus of interest in many areas of physics and engineering. We focus on visible light propagating through essentially “white” colloidal suspensions such as submicron size polystyrene spheres at some 10% volume fraction in water. As the light experiences many successive scattering events inside the medium its propagation was early described [1] by a simple random walk of the intensity. This description assumes scalar waves and a scattering mean free path,  $l = 1/\sigma\Phi$  (given by the total scattering cross section  $\sigma$  and the density  $\Phi$  of scatterers) much larger than the optical wavelength  $\lambda$ . Note that since the particle’s diameter is comparable to  $\lambda$ , the single (Mie) scattering is anisotropic and hence the transport mean free path,  $l^*$  is larger than  $l$ . In addition interference effects over distances larger than  $l$  are assumed to average out because of the random spacial distributions of scatterers.

However, mostly electron transport studies [2] in impure metals have revealed that interferences between particular paths even much longer than  $l$  may remain after averaging over many random configurations of scatterers. For example the wave travelling through a given sequence of scatterers always constructively interferes with its time reversed counterpart, i.e. with the wave travelling through the same sequence in opposite direction. This mechanism enhances the backscattering probability and hence reduces the transport coefficient, such as the electric conductivity in the case of electrons. This is the origin of (weak) localisation. Obviously, this effect applies to any classical wave, such as light.

In this paper we consider optical backscattering from a thick planar sample much larger than the parallel incident light beam. We briefly resume the discussion of the angular dependence of the scattered intensity [3–5], its modification under addition of an absorbing dye [6, 7], and the dynamic

intensity fluctuations due to the Brownian motion of the scatterers [8–11]. These quantities are closely related and can be mapped into each other by simple exchange of variables [11].

In the process of diffusion through the sample most of the light will occasionally return into the vicinity of the interface and escape from the sample. The constructive interference between the time reversed pairs of paths gives rise to enhanced backscattering. Since almost all paths are open the total backscattering intensity should be two times greater than the incoherent wide angle intensity and the angular width of the backscattering cone of order  $\lambda/l^*$  [3]. This is because the mean square average distance, in the interface plane, between the ends of paths of length  $s$ ,  $\sqrt{sl^*}$ , is much larger than  $l^*$  for most paths and of order  $l^*$  for the shortest, and consequently, the coherence is lost at angles  $\theta \geq \lambda/l^*$  with respect to backscattering. The angular dependence of the coherent backscattering enhancement, also called the coherent albedo,  $\alpha(q)$ , can be written [3, 4] as a sum over contributions of all paths of average length  $s$

$$\alpha(q) = \int_0^\infty p(s) \exp(-q^2 sl^*/3) ds \quad (1)$$

with  $q \simeq \theta/\lambda$ . The weighting function  $p(s)$  is the fraction of the incident intensity scattered into paths of lengths  $s$ . Various expressions have been given for  $p(s)$  and, hence, for  $\alpha(q)$  [4]. They all yield  $p(s) \simeq s^{-3/2}$  in the limit of large  $s$ , a result easily obtained by solving the diffusion equation in a half space using the technique of mirror images. Therefore the small  $q$  behaviour of  $\alpha(q)$ , which is dominated by the paths with large  $s$ , is given by

$$\alpha(q) = 1 - \beta ql^* \quad (2)$$

$\beta$  is a constant of order unity. The backscattering cone has a triangular shape at small  $q$ .

Kuga and Ishimaru [12] first observed a small ( $\simeq 15\%$ ) and narrow ( $< 1^\circ$ ) backscattering enhancement from a 10% colloidal latex suspension which rapidly disappeared on dilution. Tsang and Ishimaru interpreted this observation by the interference between time reversed double scattering paths [13] and later by full multiple scattering [14]. Experiments at substantially improved angular resolution [15, 16] on similar colloidal latex revealed an enhancement factor much closer to two, a linear dependence of the width of the cone on the particle’s concentration ( $\Phi \propto 1/l^*$ ), and a triangular shape of the cone near backscattering in fair quantitative agreement with theory [3, 5, 7]. The analogy of this effect and the weak localisation phenomena was thereby made explicit.

The quantity  $p(s)$  depends on the sample geometry. Addition of absorbing dye to the colloidal suspension essentially cuts the intensity of the long paths. On average, the intensity then exponentially decays along the paths with an absorption length  $l_a$  adjustable by the dye concentration. This rounds off the cone at angles below  $\lambda\sqrt{3/l^*l_a}$  as easily seen when multiplying  $p(s)$  in eq. (1) by a factor  $\exp(-s/l_a)$ . This has also been verified experimentally [6, 7]. In addition the absorbing dye decreases the incoherent wide angle intensity  $\alpha_i$  according to

$$\alpha_i(l_a) = \int_0^\infty p(s) \exp(-s/l_a) ds. \quad (3)$$

Equations (1) and (3) have the same form with  $(ql^*)^2/3$  corresponding to  $l^*/l_a$ . The triangular  $q$ -dependence of  $\alpha(q)$  therefore maps into [7]

$$\alpha_i(l_a) = 1 - \beta \sqrt{3l^*/l_a}. \quad (4)$$

again in agreement with experiments [7].

Coherent backscattering requires averaging over different configurations of scatterers. In aqueous suspensions of submicron size spheres the spacial distribution of the scatterers fluctuates due to Brownian motion. The scattered light intensity then fluctuates typically on a msec to  $\mu$ sec time scale [8, 10, 17, 18]. This is still slow compared to the time of flight of a photon even through very long loops and therefore the interference between time reversed paths is not affected by Brownian motion. Measuring  $\alpha(q)$  integrated over times longer than msec provides a convenient way of configurational averaging.

But studying the temporal fluctuations in multiple scattering is of more general interest in its own: Quasielastic light scattering (QELS) is widely used for measuring dynamic properties such as diffusion constants and hence particle sizes in colloidal suspensions. In its standard form [19] this technique is restricted to dilute suspensions where only *single* scattering occurs. In this case the scattering vector  $Q$  is set experimentally and for noninteracting Brownian particles the time autocorrelation function of the total scattered field  $E_s$  is  $C(t) = \langle E_s(t)E_s^*(0) \rangle = \exp(-D_0Q^2t)$ ;  $D_0$  is the diffusion constant of the scatterers. Even a small amount of double or triple scattering makes the interpretation of data quite intricate since the information about the scattering vector  $Q$  is partially lost. This technique thus appeared inappropriate for studying optically dense suspensions. However, it has been realized recently [8, 9, 17, 18] that in the regime of very multiple scattering, where the transport theory of light applies, useful information may be obtained from the decay of  $C(t)$ . We have shown [7] that  $C(t)$  can be expressed in terms of the Green's function describing the diffusive transport of the intensity, like  $\alpha(q)$  and  $\alpha_i(l_a)$ . Since this is extensively discussed in Refs. [10, 11] we simply resume the result:

For independently moving scatterers and under the current assumptions made for static multiple scattering, the correlation function  $C(t, s)$  along a path with  $n$  scattering events can be written as the product of the average single scattering correlation functions  $\Pi \langle \exp(-D_0Q_i^2t) \rangle$  where  $Q_i$  denotes the scattering vector associated with the  $i$ th scattering. For long paths the  $Q_i$  are independent and hence  $C(t, s) \simeq \langle \exp(-D_0Q^2t) \rangle^n$ , which becomes at short times, i.e., in the first cumulant approximation,  $\exp(-D_0 \langle Q^2 \rangle nt)$ . From the relation between the scattering mean free path  $l$  and

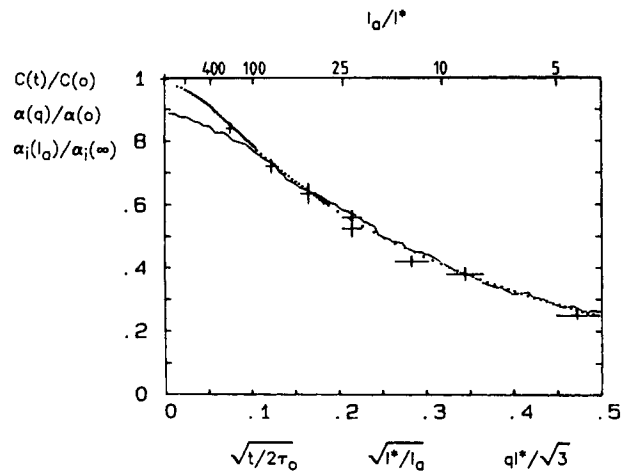


Fig. 1. Angular dependence of the static coherent backscattering enhancement  $\alpha(q)$ , (continuous line), absorption dependence of the static incoherent intensity  $\alpha_i(l_a)$ , (crosses), and dynamic correlation function  $C(t)$ , (dotted line), measured for 0.46  $\mu$ m diameter polystyrene latex at 10% volume fraction in water.  $l^* = 22 \mu$ m [7] and  $\tau_0 = 1.0$  ms [8] are experimentally known nonadjustable parameters.

the transport mean free path  $l^*$ , one obtains  $\langle Q^2 \rangle = 2k_0^2 l/l^*$ . Therefore

$$C(t, s) = \exp(-s/l^*t/2\tau_0). \quad (5)$$

$\tau_0$  denotes the single backscattering relaxation time  $1/D_0(2k_0)^2$ . This simple argument shows that the coherence of long paths relaxes with much greater rate than the single backscattering rate  $1/\tau_0$ . The total correlation function is given by weighted integration over  $s$

$$C(t) = \int_0^\infty p(s) \exp(-ts/2\tau_0 l^*) ds \quad (6)$$

which has the same form than eq. (1) and eq. (2). Therefore the limiting behaviour of  $C(t)$  at small times is

$$C(t) = 1 - \beta \sqrt{3t/2\tau_0}. \quad (7)$$

Comparison of eqs. (1), (3) and (6) shows that  $\alpha(q)$ ,  $\alpha_i(l_a)$  and  $C(t)$  are identical expressions when the scaled variables  $(ql^*)^2/3$ ,  $l^*/l_a$  and  $t/2\tau_0$  are used, whatever  $p(s)$ . In particular the triangular singularity of  $\alpha(q)$  near backscattering maps into a square root singularity of  $\alpha_i(l_a)$  at small dye concentration and into a square root singularity of  $C(t)$  at short correlation times. In Fig. 1 we compare data of  $\alpha(q)$ ,  $\alpha_i(l_a)$  and  $C(t)$  for 0.46  $\mu$ m diameter polystyrene spheres at  $\Phi = 10\%$  in water. Both axes are appropriately scaled as required by eqs. (1), (3) and (6). With the exception of  $\alpha(q)$  at small  $q$ , which is somewhat rounded due to the finite experimental angular resolution, the agreement between the three data sets appears fair, even well beyond the linear regime. This may suggest that the above scaling could extend outside the validity of the diffusion approximation. The data also suggest that a combined measurement of  $\alpha(q)$ ,  $\alpha_i(l_a)$  and  $C(t)$  yields directly values for  $\beta$ ,  $l^*$  and  $\tau_0$  for an unknown sample. Experiments with spheres of different known sizes [10, 11] also show that the above  $\sqrt{t/\tau_0}$  scaling is correct and provides a measurement of the particle's diffusion constant (and radius) from QELS even under conditions of strong multiple scattering. This promises new potential applications of QELS, for example particle sizing in dispersion paints, milk etc.

In the dense media where multiple scattering usually cannot be avoided the scatterers are eventually spatially correlated. We sketch the corresponding modifications to eq. (7) for the case of short range interparticle correlations, as outlined in more detail in Refs. [10, 11]. The static effect of correlations between scatterers is accounted for by the structure factor  $S(Q)$  of the suspension. For short range correlations a current approach to the problem of time correlations is then to divide the suspension in small uncorrelated regions with locally defined  $S(Q)$ , which act as new elementary scatterers. This appears reasonable as long as the correlation length is much smaller than  $l$ . The time autocorrelation function of the field single-scattered from such a region [or the dynamic structure factor  $S(Q, t)$ ] is, for  $t \ll \tau_0$  [20]

$$S(Q, t) = S(Q) - DQ^2 t \simeq s(Q) \exp[-DQ^2 t/S(Q)]. \quad (8)$$

The physical meaning [20] of eq. (8) is that for small times the absolute decay of correlations is the same than for noninteracting particles because the scatterers do essentially not yet feel each other. Only the static value at  $t = 0$ , i.e.,  $S(Q)$  is affected by interparticle interference resulting in a faster decay in the normalized autocorrelation function. Since the angular dependence of the field,  $S(Q)$ , scattered from the new elementary scatterers differs from the case of noninteracting particles, the transport mean free path is modified. One has  $l^*/l = 2k_0^2 \langle S(Q) \rangle / \langle Q^2 S(Q) \rangle$ . The field autocorrelation function becomes  $\simeq (\langle S(Q, t) \rangle / \langle S(Q) \rangle)^n$ , which is for small times  $C(t, s) \simeq \exp[-n(1 - \langle S(Q, t) \rangle / \langle S(Q) \rangle)]$ . Comparison with eq. (5) shows that substitution of  $\tau/2\tau_0$  by  $l^*/l [1 - \langle S(Q, t) \rangle / \langle S(Q) \rangle]$  accounts for interparticle correlations in  $C(t)$ . With  $S(Q, t)$  from eq. (7) we find that  $C(t)$  has the same form than eq. (6) with a new characteristic time  $\tau'_0$  which is related to  $\tau_0$  by  $\tau'_0/\tau_0 = \langle Q^2 S(Q) \rangle / \langle Q^2 \rangle$ . Thus short range interactions are not expected to modify the functional form of  $C(t)$  at short times and, in particular, the square root singularity is preserved. There is just a rescaling of the time scale. We can evaluate this scaling factor for hard core interactions, which are probably dominant for the polystyrene latex suspensions discussed above, where Coulomb interactions are effectively screened. In this case the static structure factor is known [21]: For a suspension with  $\Phi = 0.1$ ,  $S(Q)$  increases from 0.45 at  $Q = 0$  to 1 at  $Q \simeq \pi/R$ , where  $R$  is the particle radius. The average  $\langle Q^2 S(Q) \rangle$  emphasizes only the high  $Q$  region of  $S(Q)$ , where  $S(Q) \simeq 1$ , because the particle

diameter is comparable to the wavelength. Thus, the effect of the spatial correlations, which are reflected by the behaviour of  $S(Q)$  at low  $Q$ , will tend to average out. Then, the time scale of the decay is only slightly modified with respect to the noninteracting case. This probably explains why the data of Fig. 1, although obtained with  $\Phi = 0.1$ , coincide with  $\alpha(q)$  and  $\alpha_i(l_a)$  when the time scale is scaled by the free particle diffusion time  $\tau_0$ .

Work is in progress to study suspension under conditions of stronger correlations controlled by varying the ionic screening of the charged latex spheres.  $S(Q)$  is independently determined by small angle neutron scattering in order to check the scaling with  $\tau'_0$ .

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