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STATIC AND DYNAMIC MULTIPLE SCATTERING OF LIGHT

G. MARET[a] and P.E. WOLF[b]

[a]*Hochfeld Magnetlabor, Max Planck Institut für Festkörperforschung, Fed. Rep. Germany*
[b]*Centre de Recherches sur les Très Basses Températures, CNRS, F-38042 Grenoble Cedex, France*

Invited paper

An overview over recent progress in static and dynamic multiple light scattering is given. Interferences between time reversed multiple scattering paths result in a coherent enhancement of the static backscattering intensity, illustrated by various experiments. The angular shape, $I(\theta)$, of the backscattering cone is discussed in terms of the path length distribution. The time auto-correlation function $C(t)$ of the fluctuating light intensity multiply scattered from liquid colloidal suspensions can be interpreted similarly. Our data corroborate the analogy between $I(\theta)$ and $C(t)$. From this it appears possible to extract information on the single particle dynamics even under conditions of strong multiple scattering.

1. Introduction

This article is an attempt to briefly review recent progress in the understanding of static and dynamic light scattering from disordered strongly turbid substances where the light experiences many successive scattering events. Despite of the important theoretical development in this area (see e.g. ref. [1] for overview), which was largely stimulated by the work on electron transport in disordered systems describing the weak and strong localization phenomena, we put emphasis on experimental results and on the outline of the underlying physics.

Multiple scattering of waves by extended disordered media is a very widespread phenomenon and thus of interest in many areas of physics and engineering. Examples include electrons and phonons in impure solids, neutrons in nuclear reactors, radar and optical photons in the turbulent atmosphere, clouds and interstellar dust. We focus on visible light propagating through essentially "white" colloidal suspensions such as submicron size polystyrene spheres at some 10% volume fraction in water, and powders of microcrystals such as $BaSO_4$, TiO_2 or diamond. Schuster [2] in 1905 first described light propagation through the atmosphere by a simple random walk of the intensity over large distances. This description implies several assump-

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tions: (i) The wave is scalar, i.e. polarization effects are ignored. (ii) The scattering mean free path, $l = 1/\sigma\Phi$, given by the total scattering cross section σ and the density Φ of scatterers, is much larger than the optical wavelength λ, but much smaller than the dimensions of the medium. If the size of scatterers (R) is much smaller than λ the scattering is isotropic (Rayleigh scattering) and the random walk step length or transport mean free path l^* equals l. For larger R the single scattered intensity becomes peaked around the forward scattering direction (Mie scattering) and therefore l^* is greater than l. (iii) All interference effects over distances larger than l^* are averaged out because of the random spacial distributions of scatterers. Hence, for example, a short pulse of photons would spread out by diffusion with diffusion constant $D = cl^*/3$.

2. Coherent backscattering

During the past two decades it was realized, mostly in the field of multiple electron scattering [3], that interferences between particular scattering paths even much longer than l^* may remain after averaging over many random configurations of scatterers. 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, i.e. the electric conductivity in the case of electrons. This is the origin of (weak) localization. Obviously, this effect is by no means restricted to electrons, but applies to any (classical) wave including light.

Let us consider optical backscattering in the particular geometry of a planar wave, such as an expanded laser beam, incident normally on an infinite halfspace containing scatterers. The sample may be a cell much thicker and much wider than l^*, containing a dense colloidal suspension. Most of the incident light will start diffusive paths roughly within a distance l^* from the interface. If absorption can be neglected, all paths will occasionally return into the vicinity of the interface and the light ultimately escape into the empty half space. The constructive interference between the time reversed pairs of paths then give rise to enhanced backscattering. For each pair the coherent enhancement equals the incoherent intensity propagating through these paths and hence the integrated backscattering enhancement should be 2. Most paths will be open; if the distance between the starting and end point of each path is r, the phase shift between time reversed path is $2\pi\theta r/\lambda$. Hence constructive interference will be lost at angles θ larger than $\simeq\lambda/r$ with respect to backscattering. Of course the distribution of r is wide. For long paths where the diffusion approximation applies the average distance $\sqrt{\langle r^2\rangle}$ can be related to

the path length s and l^* by $\langle r^2 \rangle \simeq l^* s$. Therefore paths of length s will on average give rise to an enhanced backscattering cone of angular width $\lambda / \sqrt{l^* s}$. The shape of the total backscattering cone will depend on how the intensity is distributed as a function of s. We shall come back to this later. But since $s \geq l^*$, the total width of the cone will be at most of order λ / l^*. Estimation of l^* from Mie-scattering for a typical case of 0.5 μm diameter non-interacting polystyrene spheres at 10% volume fraction in water gives $l^* \simeq 20$ μm corresponding to $\lambda / l^* \simeq 1°$. Similar order of magnitudes can be estimated for other typical "white" substances. The narrowness of the cone has perhaps prevented its early observation. It is worth noting at this point that various observations of enhanced optical backscattering have been made since a long time [4]; they are interpreted in terms of geometric shadowing or intraparticle interference effects and none of them seems to be clearly related to the transport mean free path.

The discovery of the coherent backscattering effect outlined above was made by Kuga and Ishimaru [5] in 1984, who described a small (≃15%) enhancement from a 10% colloidal latex suspension which rapidly disappeared on dilution. Tsang and Ishimaru explained this observation by the interference between time reversed double scattering paths [6] and later by full multiple scattering [7]. Independent experiments at substantially improved angular resolution by van Albada and Lagendijk [8] and Wolf and Maret [9] 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 ($\Phi \propto 1/l^*$), a triangular shape of the cone near backscattering and the effects of polarization and particle size. The analogy of this effect and the weak localization phenomena was thereby made explicit. As pointed out by Akkermans, Wolf and Maynard [10] the particular triangular singularity is a consequence of the particular length distribution of scattering paths in the half space geometry: Since the behaviour of the cone at angles θ near backscattering ($\theta = 0$) is dominated by the long loops, the diffusion approximation can be used; then the distribution of the end-points of paths of length s entering at $r = 0$ is a Gaussian with width $\sqrt{sl^*}$. The θ-dependence of the coherent intensity, which originates from interference between time reversed paths with coherent end points at $r = 0$ and $r = r$, is simply given by the Fourier transform of the above Gaussian distribution. The coherent cone from all paths of length s is thus a Gaussian of width $\lambda / \sqrt{sl^*}$. The full coherent backscattering cone, sometimes called coherent albedo $\alpha(\theta)$, is obtained by integration over s,

$$\alpha(\theta) = \int_{l^*}^{\infty} p(s)\, \mathrm{e}^{-q^2 s l^*}\, \mathrm{d}s\,, \tag{1}$$

with $q \simeq \theta/\lambda$. The problem reduces to finding the weighting function $p(s)$, which is the fraction of the incident intensity scattered into paths of length s, or, equivalently, the probability of leaving the medium after a journey of length s. Various approaches can be used to find $p(s)$. For small s, $p(s)$ is of course sensitive to the choice of the boundary conditions or the details of how the incident intensity is converted into diffusing intensity and back to emerging intensity. The behaviour of $\alpha(\theta)$ at small θ, however, is dominated by large s and hence less sensitive to the boundary conditions. Using a starting ($r = 0$) and end point (r) located at a distance l^* from the interface inside the medium, the method of images (i.e. substracting from the probability to reach r in full space on a path s the probability to reach the mirror image point of r respective to the interface) one easily finds $p(s) \simeq s^{-3/2}$. The integral (1) then becomes $\alpha(\theta) = 1 - \beta q l^*$ with a constant β of order unity. The triangular singularity of $\alpha(\theta)$ originates from the slow power law decay of the weighting functions of the Gaussians in eq. (1).

This concept has been verified experimentally by measurements of the width and shape of the coherent backscattering cone on samples of finite thickness [11, 12] or containing absorbing dye [12, 13]. In the first case paths of length $s \geq L^2/l^*$ essentially conduct their light into transmission and the backscattering cone was found to round off at corresponding small angles. An extended comparison of transmission and reflection data with a rigorous scalar wave theory was recently made by van der Mark et al. [14]. In the second experiments the intensity experimentally decays along the paths with an absorption length l_a adjustable by the dye concentration. The observed rounding of the cone occured at angles below $\lambda/\sqrt{l^* l_a}$ as expected when multiplying $p(s)$ in eq. (1) by a factor e^{-s/l_a}. In addition the absorbing dye also decreases the incoherent (wide angle) intensity α_i according to

$$\alpha_i(l_a) = \int_{l^*}^{\infty} p(s)\, e^{-s/l_a}\, ds\,. \tag{2}$$

Eqs. (1) and (2) have the same form, with $q^2 l^*$ corresponding to $1/l_a$. The triangular q-dependence of $\alpha(\theta)$ therefore maps into $\alpha_i(l_a) = 1 - \beta\sqrt{l^*/l_a}$. This mapping has been quantitatively verified experimentally [13]. A combined measurement of $\alpha_i(l_a)$ and $\alpha(\theta)$ thus allows an experimental determination of β and l^*. Another direct demonstration of the relation between cone width and path length has been recently provided by Vreeker et al. [15] who observed the shrinkage of the cone width as a function of time in the echo from a femtosecond light pulse.

Light polarization affects in a twofold manner the coherent backscattering [1, 16]. First, because of the dipolar directional characteristics (of Rayleigh scattering) the spacial distribution of the short paths is not isotropic with respect to the incident beam. There are more paths in the plane perpendicular to the incident polarization vector, as demonstrated by van Albada et al. [11] by the anisotropic shape of the cone from short paths, measured using the finite slab technique. Second, it is easy to show [1, 10, 16, 17] that for parallel orientation of incident and detected polarisation, the coherence between time reversed paths is fully preserved. Under crossed polarization the situation is more complex and coherence rapidly decays with s. Both statements agree with experiments [9, 11, 13]. MacKintosh and John [17] have pointed out that for point-like scatterers the use of circularly polarized light of the same helicity in the incident and detected beams would represent the closest approach to the scalar case. In addition it eliminates [12] the contribution from single scattering not subject to the coherent backscattering enhancement. Magneto-optical rotation (Faraday-effect) is expected [17] to destroy the coherent backscattering, but an experimental observation has not been reported so far presumably because of the need of very high magnetic fields for otherwise suitable background media.

Coherent backscattering requires averaging over different configurations of scatterers. In the colloidal liquids discussed above the spacial distribution of the scatterers fluctuates due to Brownian motion. As outlined below the scattered light intensity then fluctuates typically on a ms to μs time scale. 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 $\alpha(\theta)$ integrated over times longer than ms provides a convenient way of configurational averaging. This is not so for solid samples (like $BaSO_4$ powder, TiO_2 particles, paper, etc.) where the well-known speckle pattern – rapid angular variations of the scattered intensity with angular correlations of order λ/d_0, d_0 being the diameter of the incident beam – obscures the coherent backscattering. Naturally, averaging over the speckles by displacing [18], rotating [19] or tilting the sample between successive angular scans recovers the backscattering cone. Kaveh et al. [19] have analyzed the statistics of the speckle pattern inside the backscattering cone from dried $BaSO_4$ microparticles by exploring the intensity distribution in 15 angular scans. They reported large deviations from the Gaussian statistics known in single scattering speckle. Similar solid samples and colloidal suspensions were investigated by Wolf et al. [13] taking a substantially higher number of samplings using a fast electronic correlator; they clearly reveal no deviations from Gaussian statistics other than the small unavoidable and well-known effect due to the use of a non-zero observation aperture.

3. Dynamic multiple scattering

We now return to the effects of Brownian motion in the case of colloidal liquids. In *single* backscattering of non-interacting particles the speckle spots fluctuate at a rate $1/\tau_0 = 4D_0k_0^2$, $2k_0$ being the backscattering wave vector and D_0 the diffusion constant of the particles. For 0.5 μm diameter polystyrene spheres in water at room temperature and $\lambda = 514$ nm, τ_0 equals about 1.0 ms. For smaller scattering vectors (Q) this time becomes correspondingly larger ($1/D_0Q^2$). In the so-called quasielastic light scattering technique (QELS), one measures, at fixed Q, electronically the time autocorrelation function of the fluctuating light intensity which in the above case decays single-exponentially with rate $2/\tau_0$. This important technique is widely used for particle sizing and dynamical studies of interacting complex fluids, but was essentially restricted to single scattering. In *multiple* scattering the knowledge of the individual scattering vectors is lost, but one can easily show that, for isotropic scattering the mean square average $\langle Q^2 \rangle$ equals $2k_0^2$ corresponding to 90°-scattering, and for anisotropic scattering $\langle Q^2 \rangle = 2k_0^2 l/l^*$. For independently moving scatterers and under the current assumptions made for static multiple scattering, the field correlation function $C(t, s)$ along a path of length s is given by the product of the average single scattering correlation functions ($e^{-2D_0\langle Q^2\rangle t}$) and hence $C(t, s) = e^{-st/l^*\tau_0}$. This simple argument shows that the coherence of long paths should relax with much greater rate than the single backscattering rate $1/\tau_0$. Our experiments [20] confirmed this. The form of the total correlation function is given by weighted integration over s,

$$C(t) = \int_{l^*}^{\infty} p(s)\, e^{-ts/\tau_0 l^*}\, ds \tag{3}$$

which has again the form of eq. (1) and eq. (2). Therefore the limiting behaviour of $C(t)$ at small times is $C(t) = 1 - \beta\sqrt{t/\tau_0}$. This square root singularity which has also been derived by more sophisticated techniques [21] has been observed by us [22] and by Pine et al. [23]. Small rounding effects found at very short times are attributed to finite size effects cutting very long paths. There is no indication for a universal limiting initial relaxation rate, the observation of which had been claimed by Rosenbluh et al. [24] based on data from a comparatively slow video-movie speckle analysis. The experiments with spheres of different known sizes [22, 23] 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. Measurements on colloidal glasses by Pine et al. [23] have suggested the possibility of directly determining mean square displacements or Debye–Waller factors in such systems. In transmission the correlation function is expected [21] to be much closer to a single exponential than in reflection because of the predominance of paths of lengths in the vicinity of L^2/l^*. The initial relaxation rate should be $\simeq L^2/\tau_0 l^{*2}$. The agreement between theory and experiments appears very satisfactory for different geometries of illumination and the dominant relaxation rate was found proportional to L^2 [23].

In conclusion, it is not too surprising that the actual theoretical predictions and experiments coincide well (even quantitatively) under conditions where the long scattering paths dominate, i.e. in the *small* angle behaviour of the backscattering cone, its modification under *weak* absorption, the *short* time variation of the dynamic correlation function and the transmission at slabs much *thicker* than l^*. In these cases the diffusion approximation appears valid and the details of the description near the interface are qualitatively unimportant. This is not true for the short paths (wide angles in $\alpha(\theta)$, long times in $C(t)$), where, in addition, the random walk model for the path's statistics breaks down. One of the interesting open questions is how the static and dynamic multiple scattering may be affected by and properly described in the case of substantial interparticle interaction.

What happens when the mean free path l^* becomes comparable to the wavelength, when one might expect a transition into the strong (Anderson-) localization regime? Watson et al. [25] have designed a pulsed picosecond experiment which allowed to detect contributions from paths of up to several meters; but they did not observe any deviation, due to localization, from the absorption limited decay of the echo. Genack [26] has used titania microparticle samples with l^*-values around 1 μm, but his transmission data at large L were also controlled by absorption. Owing to the limited refractive index of non-absorbing materials in the visible range it seems very difficult to obtain sufficiently small l^*-values for visible light localization.

References

[1] E. Akkermans, P.E. Wolf, R. Maynard and G. Maret, J. Phys. France 49 (1988) 77.
[2] A. Schuster, Astrophys. J. 21 (1905) 1.
[3] See e.g.: G. Bergmann, Phys. Rep. 107 (1984) 1.
[4] W.E. Egan and E. Hilgeman, Appl. Optics 15 (1976) 1845; H.C. Bryant and N. Jarmie, Scientific American, July (1974).
[5] Y. Kuga and A. Ishimaru, J. Opt. Soc. Am. A1 (1984) 831; Y. Kuga, L. Tsang and A. Ishimaru, J. Opt. Soc. Am. A2 (1985) 616.

[6] L. Tsang and A. Ishimaru, J. Opt. Soc. Am. A1 (1984) 836.
[7] L. Tsang and A. Ishimaru, J. Opt. Soc. Am. A2 (1985) 1331.
[8] M. van Albada and A. Lagendijk, Phys. Rev. Lett. 55 (1985) 2692.
[9] P.E. Wolf and G. Maret, Phys. Rev. Lett. 55 (1985) 2696.
[10] E. Akkermans, P.E. Wolf and R. Maynard, Phys. Rev. Lett. 56 (1986) 1471.
[11] M. van Albada, M.B. van der Mark and A. Lagendijk, Phys. Rev. Lett. 58 (1987) 361.
[12] S. Etemad, R. Thompson, M.J. Andrejco, S. John and F.C. MacKintosh, Phys. Rev. Lett. 59 (1987) 1420.
[13] P.E. Wolf, G. Maret, E. Akkermans and R. Maynard, J. Phys. France 49 (1988) 63.
[14] M.B. van der Mark, M.P. van Albada and A. Lagendijk, Phys. Rev. B 37 (1988) 3575.
[15] R. Vreeker, M.P. van Albada, R. Sprik and A. Lagendijk, preprint.
[16] M.J. Stephen and G. Cwilich, Phys. Rev. B 34 (1986) 7564.
[17] F.C. MacKintosh and S. John, Phys. Rev. B 37 (1988) 1884.
[18] S. Etemad, R. Thompson and M.J. Andrejco, Phys. Rev. Lett. 57 (1986) 575.
[19] M. Kaveh, M. Rosenbluh, I. Edrei and I. Freund, Phys. Rev. Lett. 57 (1986) 2049.
[20] G. Maret and P.E. Wolf, Z. Phys. B 65 (1987) 409.
[21] M. Stephen, Phys. Rev. B 37 (1988) 1.
[22] P.E. Wolf and G. Maret, submitted.
[23] D.J. Pine, D.A. Weitz, P.M. Chaikin and E. Herbolzheimer, Phys. Rev. Lett. 60 (1988) 1134.
[24] M. Rosenbluh, M. Hoshen, I. Freund and M. Kaveh, Phys. Rev. Lett. 58 (1987) 2754; M. Kaveh, M. Rosenbluh and I. Freund, Nature 326 (1987) 778.
[25] G.H. Watson, P.A. Fleury and S.L. McCall, Phys. Rev. Lett. 58 (1987) 945.
[26] A.Z. Genack, Phys. Rev. Lett. 58 (1987) 2043.