

Multiple Light Scattering from Disordered Media. The Effect of Brownian Motion of Scatterers*

G. Maret

Hochfeld-Magnetlabor des Max Planck Instituts für Festkörperforschung, Grenoble, France

P.E. Wolf

Centre de Recherches sur les Très Basses Températures, CNRS, Grenoble, France

Received July 31, 1986

We have measured the time autocorrelation function of the light intensity multiply scattered from turbid aqueous suspensions of submicron size polystyrene spheres in directions near backscattering. It is found strongly non-exponential at short times revealing the very fast decay of coherence in extended scattering loops due to the thermal motion of the many spheres involved; the longest living decay time is found remarkably close to the single particle backscattering relaxation time even under conditions of interparticle interactions. These features are only weakly affected by the particular interference effect between time-reversed pairs of loops giving rise to the coherent backscattering enhancement. A simple argument is presented which accounts for these observations.

1. Introduction

Recently the light scattering from turbid colloidal suspensions of submicron size polystyrene spheres has been found enhanced inside a narrow cone around the backscattering direction [1–3]. Like the principle mechanism responsible for weak localization of electrons in impure metals, this effect can be understood [4, 5] in terms of classical interference between a particular wave multiply scattered along a certain scattering path and the wave travelling along the time reversed counterpath. The theoretical angular and polarization dependence of the scattered intensity [6] are in good agreement with the experiments.

In the former work the scatterers have been considered stationary though such spheres in water undergo Brownian motion essentially characterized by their Stokes-Einstein translational diffusion constant *D*. This approximation is justified for the coherent backscattering effect as the time it takes the light to travel even through the largest scattering paths $(\approx 10^{-11} \text{ s [3]})$ is much smaller than the diffusion time of a single sphere over an optical wavelength $\lambda = 2\pi/k_0(1/Dk_0^2 \approx 10^{-3} \text{ s})$; thus the spatial coherence between each pair of paths is not affected by the motion of the spheres. However, the motion plays an important role: The angular dependence of the intensity scattered by an identical sample but with spheres being "frozen in" in position would reveal large fluctuations due to interferences known as "speckle"; in a fluid sample these interferences are averaged out, on a time scale of seconds, by the thermal motion of the spheres.

In this paper we discuss in detail the dynamic effects of the simultaneous motion of all scatterers within a multiple scattering path. To this end we have performed quasi-elastic light scattering experiments on aqueous suspensions of latex spheres with different diameters in the single scattering and very multiple scattering concentration ranges both in the vicinity of the backscattering direction and at wider angles. In multiple scattering, inside and outside the backscattering cone, we observe a rapid loss of coherence at short times followed by a gradual slowing down, the longest relaxation time being found surprisingly close to the single particle diffusive backscattering relaxation time for all samples studied. We present simple arguments which qualitatively explain these observations.

^{*} Dedicated to Prof. Klaus Dransfeld on the occasion of his 60th birthday

2. Experimental

The static light scattering set up used has been described earlier [3]. Using 0.5 mm diameter pinholes at typically 1 and 2 m distance from the sample the angular resolution was ≈ 1 mrad. For some measurements the sample cell was inserted into a 10 cm index matching cell to prevent heterodyne mixing [7] of scattered light with light reflected from the sample cell surfaces. The spectral broadening of the scattered light was determined at fixed angle by directly measuring the normalized homodyne time autocorrelation function $G^{(2)}(t)$ of the fluctuating light intensity I(t) [7] (i.e. of the output pulse rate of the photomultiplier tube) by means of a 64 channel digital multibit correlator MALVERN K7025.

 $G^{(2)}(t) = \langle I(0) * I(t) \rangle / \langle I(0) \rangle^2.$

For the ideal case of single scattering from an ensemble of non-interacting Brownian spheres $G^{(2)}(t)$ equals 2 at correlation time t=0 (full coherence) and decays exponentially to the average value 1 (no coherence) with a rate $1/\tau = 2Dq^2$, q being the scattering vector. In a real experiment $G^{(2)}(0)$ is somewhat smaller than 2 as full coherence cannot be reached due to the nonzero size of scattering volume and of illuminated detector surface, residual stray light etc. which is included in the experimentally determined long time $(t \to \infty)$ baseline $\langle I(0) \rangle^2$. D is obtained from a two parameter (τ , $G^{(2)}(0)$) single exponential fit at q fixed by the scattering angle Θ ($q = 4\pi n/\lambda \sin \Theta/2$), n being the sample's refractive index taken to be 1.33 for H_2O in our case and λ the optical wavelength = 0.5145 μ m). Spheres with four different radii R (0.054 + / -0.0014), 0.23 + / - 0.00240.153 + / -0.00420.398 + / -0.002 µm according to the manufacturer's specifications) were investigated. The R-values were checked by $G^{(2)}(t)$ measurements at $\Theta = 90^{\circ}$ in dilute samples and found $(D = k T_0/6\pi \eta R)$ to agree within the experimental error of $\approx 1\%$. All data taken at temperature T_0 between 19 and 25 °C were referred to 20 °C by correcting, as usual, the *t*-scale for T_0 and the temperature dependence of the viscosity η of water.

3. Results and Discussion

Figure 1, curve (a) shows the typical result of a $G^{(2)}(t)$ measurement in the single scattering regime at low concentrations. The data were taken at a scattering angle slightly off backscattering ($\Theta = 165^{\circ}$) in order to reduce heterodyne mixing. The decay found is single-exponential – as expected-, except for long correlation times where residual heterodyne mixing (we



Fig. 1. Normalized autocorrelation function $G^{(2)}(t)-1$ of the light intensity scattered from aqueous suspensions of 0.46 µm diameter polystyrene spheres. $T_0 = 23$ °C, $\Theta = 165^{\circ}$. (a) + : solid fraction $\phi \approx 2 \cdot 10^{-5}$, single scattering (b) 0: $\phi \approx 0.1$, multiple scattering, analyzer parallel to the incident vertical polarization (VV). (c)*: same as (b) but analyzer perpendicular to the incident polarization (VH). The inset shows the fast short time decay for cases (b) and (c). The slope of the dashed line is the theoretical single scattering relaxation rate

could not eliminate) caused some deviation. For the same reason the slope at short times appears slightly smaller than what it should be from the *R*-value (0.23 µm) measured at $\Theta = 90^{\circ}$. Note that the corresponding relaxation time $\tau_0 \approx 0.5$ ms is essentially [8] the *shortest single* particle relaxation time which can occur in such a light scattering experiment.

However, as demonstrated by curves (b) and (c) of Fig. 1, the correlation function in the multiple scattering regime at the same scattering angle and for the same spheres (at a solid fraction ϕ of 10%) decays much *faster* than this at small t, is strongly non-exponential and, at t larger than τ_0 , dies out fairly single-exponentially with a rate $1/\tau_{\infty}$ very similar to the single particle relaxation rate $1/\tau_0$. Fitting the long time data [9] (for curve (b) and $t > 2\tau_0$) we find $\tau_{\infty}/\tau_0 = 1.20 + /-3\%$ in this case. As summarized in Table 1 the same long time behavior was observed near backscattering ($\Theta = 178^{\circ}$) for all bead diameters studied at $\phi = 10\%$ (Fig. 2) in the commercial samples and at $\phi = 1\%$ (dilution in deionized water).

These observations clearly demonstrate the general existence of a whole set of relaxation times with an upper bound remarkably close to τ_0 , apparently independent of interparticle distance within the covered concentration range. This is at first a surprisingly general result.

For the smallest beads $(2R=0.109 \ \mu\text{m})$ it can be understood as due to the important contributions of single and double scattering which both give the same relaxation time (τ_0) in the backscattering direction; here we neglect interactions between spheres which

Table 1. Experimental long time relaxation rate in the multiple scattering regime normalized to the single scattering rate at $\Theta = 180^{\circ}$ for different bead diameters and solid fractions. The errors indicate the dispersion of results as obtained from different samples, which is larger than the error for a given sample. See text for the other quantities

2R (μm)	φ (%)	τ_{∞}/τ_0	Q (µm ⁻¹)	S(Q)	$S(2k_0)$
0.109	1	0.98+/-0.05	21.9	0.94	
	10	1.07 + / - 0.05	22.9	0.62	0.80
0.305	1	1.00 + / -0.05	12.8	0.98	
	10	1.06 + / -0.05	13.9	0.93	0.98
0.46	1	1.05 + / -0.05	9.5	1.0	
	10	1.20 + / -0.05	10.4	1.02	0.99
0.80	1	0.97 + / - 0.1	6.1	1.05	
	10	1.15 + / - 0.1	6.6	1.08	1.00



Fig. 2. $G^{(2)}(t)-1$ as a function of the reduced correlation time (t/R) for different radii R of polystyrene spheres: $\phi = 0.1$. The dashed line has the same meaning as in Fig. 1. (•) $R = 0.054 \mu m$, (+) $R = 0.15 \mu m$, (0) $R = 0.23 \mu m$, (*) $R = 0.4 \mu m$

will be discussed below. For the larger beads having an anisotropic (q-dependent) form factor the contribution of single and double scattering to $G^{(2)}(t)$ is estimated smaller than about 1%, while extrapolation of the experimental single exponential long time decay to t=0 gives values of about 10% of $G^{(2)}(0)$. This and the weak polarization dependence of the latter signal [10] (see Fig. 1) clearly indicates that the long time regime is not controlled by single or double scattering. Hence for the larger beads the occurrence of τ_0 as the longest relaxation time has a different physical origin. It can be understood, we believe, from the following argument.

Let us consider the wave multiply scattered by a given sequence of *n* scatterers located at $\mathbf{r}_1, \ldots, \mathbf{r}_n$. The phase factor Ψ is $\exp[i\mathbf{q}_1\mathbf{r}_1] \ldots \exp[i\mathbf{q}_n\mathbf{r}_n]$, where the \mathbf{q}_i 's are the successive transfer wavevectors \mathbf{q}_i $=\mathbf{k}_i - \mathbf{k}_{i-1}$, \mathbf{k}_i the wavevector after the *i*th collision, \mathbf{k}_0 the incident wavevector and \mathbf{k}_n the emergent (detected) wavevector. Since the *n* scatterers – being assumed non-interacting - move independently we have

$$\langle \Psi(0) \Psi^*(t) \rangle = \exp\left[-Dt \sum_i q_i^2\right].$$

Now we assume, like for the transport theory of light [11], that the fields belonging to different sequences add incoherently on the average; this again relies on the assumption of no interactions. Furthermore, since for sufficiently large beads the sequences with small n do not significantly contribute, we neglect the condition $\sum_{i} \mathbf{q}_i = \mathbf{k}_n - \mathbf{k}_0$ and assume independence of the

successive \mathbf{q}_i 's. The field correlation function for a given polarization then becomes

$$\langle E(0) E^*(t) \rangle \approx \sum I_n \langle \exp[-Dt q^2] \rangle^n$$

where I_n is the total time-averaged intensity scattered by all sequences of order n and the second factor $\langle \rangle$ is weighted by the form factor of a single sphere. A further simplification is to retain only the first cumulant $\exp[-Dt\langle q^2 \rangle]$, where $\langle q^2 \rangle$ can easily be written as $(2k_0)^2 l/2l^*$; $2k_0$ is the backscattering wavevector, l the scattering mean free path and l^* the effective transport mean free path, i.e. the average distance over which the k_i 's become uncorrelated. This shows that the correlation function of a n scattering sequence depends on L/l^* , its length in units of l^* rather than on n = L/l. More precisely we write

$$\langle E(0) E^*(t) \rangle \approx \int I(L) \exp\left[-Lt/(4l^*\tau_0)\right] dL$$
 (1)

where I(L) is the contribution of paths of length L to the scattered intensity and $2\tau_0 = 1/D(2k_0)^2$ the heterodyne single scattering relaxation time. As the direction of propagation of the incoming light is lost over a distance of order l^* the minimum length L significantly contributing to (1) is $2l^*$. We thus find, indeed, that the time decay of $|\langle E(0) E^*(t) \rangle|^2$ and hence of $G^{(2)}(t)$ occurs with a relaxation time of order τ_0 – as observed. Furthermore, according to (1), $G^{(2)}(t/\tau_0)$ should be a function independent of the bead size (R) as long as R is large enough to ensure $l^* \ge l$. As shown in Fig. 2 this again appears in rough agreement with the experiment, the differences from one size to another being likely due to the approximate nature of the transport theory.

Within a numerical constant of order unity the same result can be obtained (more easily) by introducing an average momentum transfer $Q = \langle q^2 \rangle^{1/2}$ involved in each single scattering event, and estimating the smallest mean number N of scattering events needed to return to backscattering. This can be done by considering a random walk on the surface of a sphere of radius $k_0 = 2\pi n/\lambda$ in **q**-space, from \mathbf{k}_0 to $-\mathbf{k}_0$ with step length Q.

$$\pi k_0 = Q \, V N.$$

The corresponding total relaxation rate $1/\tau_{\infty} = NDQ^2$, which is the smallest mean relaxation rate, therefore equals $\pi^2/4\tau_0$.

The above argument was derived in the absence of interparticle interaction. Let us now estimate their role: it is well known [12, 13] that for single scattering from Brownian spheres the apparent short time relaxation rate determined in a light scattering experiment is $1/\tau = D_s q^2/S(q)$, D_s being the self diffusion coefficient of the interacting spheres and S(q) the static structure factor. There is extensive literature [14] on the q-dependence of S(q) for highly charged polystyrene spheres at low ionic strength. As the ionic strength of our commercial non deionized samples was not known, we carried out some measurements at $\phi = 10\%$ and $\phi = 1\%$ after dialysis to 10 mM NaCl (corresponding to a Debye screening length of 3 nm). The results [15] were identical to those obtained with commercial samples demonstrating that the ionic strength of the latter is large enough for the coulombic interactions to be considered unimportant. The dominant interaction between spheres appears therefore hard-core repulsion. In this case S(q) can be estimated using the analytical result of Wertheim [16]. S(q=0)is found 0.45 and 0.92 for $\phi = 10\%$ and 1%, respectively, reflecting the change in the osmotic colloidal compressibility due to the excluded volume of the spheres, S(q) has a weak maximum (≈ 1.1 for $\phi = 10\%$, ≈ 1.02 for $\phi = 1\%$) near $q = \pi/R$ and rapidly tends towards 1 at higher q-values.

A crude estimate of the correction of the relaxation time due to hard core repulsive interactions is then $\tau \approx \tau_0 S(Q)$. (Note that in our multiple scattering experiment the structure factor remains a relevant quantity because the phase coherence length, l, is much larger than R.) In order to obtain Q we have to take into account the anisotropy, or q-dependence, of the single scattering intensity in our system of interacting finite size spheres. In the evaluation of $\langle q^2 \rangle$ this is done by weighting q^2 with S(q) P(q), P(q) being the form factor of the spheres:

$$Q^{2} = \langle q^{2} \rangle = \int_{0}^{2k_{0}} q^{2} S(q) P(q) q \, \mathrm{d}q \Big/ \int_{0}^{2k_{0}} S(q) P(q) q \, \mathrm{d}q.$$

The calculated values of S(Q) turn out (Table 1) to be very close to 1 – except for the 0.109 µm diameter spheres – essentially because the Q-values are located in the vicinity of the first maximum in S(q). From this very simple averaging procedure it therefore appears conceivable to expect the multiple scattering relaxation rate little affected by excluded volume type interactions for all our samples (except for the 0.109 µm spheres, where $1/\tau$ should be some 20%– 30% higher at $\phi = 10\%$ than at $\phi = 1\%$, depending on the relative weight of single and double scattering). This is in general agreement with our experiment.

However, a detailed analysis of Table 1 shows that the experimental long time relaxation rates at $\phi = 10\%$ seem somewhat smaller than the corresponding rates at $\phi = 1\%$ and that the difference appears larger for $2R = 0.8 \,\mu\text{m}$ and $0.46 \,\mu\text{m}$ than for $2R = 0.305 \,\mu\text{m}$ and 0.109 μm . This observation is not consistent with the excluded volume effect as discussed above. It may be due to hydrodynamic effects which are expected to correct D by a quantity of relative order -2ϕ [14, 17, 18]. Thus at large ϕ the hydrodynamic effect would partially compensate the structure factor effect, or even overcompensate it at large R, in reasonable agreement with our data. Our main conclusion, notwithstanding, remains that the longest living relaxation time in such a multiple scattering experiment is a good measure – in all cases investigated - for the hydrodynamic radius of the spheres.

The above discussion might suggest that the presence of relaxation times smaller than τ_0 in Fig. 1 could be due to the q-dependence of S(q) since S(q) < 1 at small q. However relaxation curves for 0.46 µm spheres at $\phi = 3\%$, for which S(q) is always very close to 1 while l^* is still small enough to make sure that all scattering paths are seen by the detector, show the same short time behavior than those at $\phi = 10\%$. Hence the largest part of the non-exponential decay of $G^{(2)}(t)$ is due to multiple scattering. This is also demonstrated by the following study of the angular dependence of the relaxation curves.

What happens inside the backscattering cone? As outlined above for scattering paths with n > N each path has its own relaxation time which is inversely proportional to its length. The overall shape of $G^{(2)}(t)$ then depends on the relative weight of the different paths. Inside the backscattering cone I(L) must be corrected to account for the interferences between pairs of paths. Since even the shortest relaxation times are very long compared to the time of travel of light through the largest loops the phase coherence between pairs of paths is fully preserved in the backscattering direction ($\varphi = 0$) and hence I(L) must be replaced by 2 I(L) in Eq. (1). This obviously does not change the normalized quantity $G^{(2)}(t)$. At $\varphi > 0$ but still inside the cone only paths of extension smaller than λ/ϕ i.e. of length $L < (\lambda/\phi)^2/l^*$ contribute significantly to the intensity enhancement [6]. This means the relative weight of long paths is less than at $\varphi = 0$ and therefore $G^{(2)}(t)$ should decay, in the short time regime, more slowly than at $\varphi = 0$ or outside the cone. As illustrated by measurements of $G^{(2)}(t)$ at various φ inside and outside the cone (shown in Fig. 3) we indeed observe both of these features [19]. In fact



Fig. 3. The normalised autocorrelation function $G^{(2)}(t) - 1$ measured at an angle φ from backscattering referred to the data at $\varphi = 40$ mrad. (•) $\varphi = 0$, (+) $\varphi = 1$ mrad, (*) $\varphi = 3$ mrad, (0) $\varphi = 6$ mrad. The dashed line corresponds to the single scattering relaxation at $\varphi = 0$ ($\Theta = 180^{\circ}$). The inset shows the corresponding theoretical estimates

putting I(L), as estimated earlier theoretically in the so-called diffusion approximation [20], into Eq. (1)

$$I(L) \approx 1/\sqrt{L' \{ \exp[-3l^*/4L'] - \exp[-3(2.4)^2 l^*/4L'] \}}, \quad L' = L - l'$$

we calculate for $G^{(2)}(t)$ the curves shown in the inset. They are very similar to the experimental data in both time dependence and angular dependence.

In conclusion our quasielastic multiple light scattering data on turbid colloidal suspensions reveal that Brownian motion of the scatterers results in a rapid strongly non-exponential short time decay of coherence which is only weakly affected by the particular interference responsible for coherent backscattering. In the fairly single exponential long time regime the decay rate appears remarkably close to that for single particle single backscattering, in good agreement with our crude estimate.

Finally, it has been suggested [2] that the multiple scattering intensity could have large fluctuations related to the universal fluctuations [21] of the conductance in disordered metals. The relation, if any, between the *bulk* conductance and the intensity I(t) scattered *from* our sample in a given direction is not clear to us; our results show, whatever, that for a given polarization [22] $G^{(2)}(0) \approx 2$, or $\langle I^2 \rangle - \langle I \rangle^2 \approx \langle I \rangle^2$, in agreement with the usual hypothesis of gaussianlike distributed scattered fields [7].

Note Added in Proof

References

- 1. Kuga, Y., Ishimaru, A.: J. Opt. Soc. Am. A8, 831 (1984)
- 2. Van Albada, M.P., Lagendijk, A.: Phys. Rev. Lett. 55, 2692, (1985)
- 3. Wolf, P.E., Maret, G.: Phys. Rev. Lett. 55, 2696 (1985)
- 4. Kmelnitskii, D.E.: Physica **126** B + C, 235 (1984) Bergmann, G.: Phys. Rev. B**28**, 2914 (1983)
- 5. Akkermans, E., Maynard, R.: J. Phys. (Paris) Lett. 46, L1045 (1985)
- Akkermans, E., Wolf, P.E., Maynard, R.: Phys. Rev. Lett. 56, 1471 (1986)
- 7. Berne, B.J., Pecora, R.: Dynamic light scattering. New York: John Wiley 1976
- 8. The relative difference of q^2 between $\Theta = 165^{\circ}$ and $\Theta = 180^{\circ}$ is less than 2%
- Errors in each point were estimated using the procedure given by Jakeman, E., Pike, E.R., Swain, S.: J. Phys. A Gen. Phys. 4, 517 (1971)
- 10. The comparison between the normalized curves (b) and (c) is significant because the scattered intensity is nearly fully depolarized
- See e.g. Ishimaru, A.: Wave propagation and scattering in random media. Vol. 1. New York: Academic Press, 1978
- 12. Pusey, P.N.: J. Phys. A: Math. Gen. 8, 1433 (1975)
- 13. Ackerson, B.J.: J. Phys. Chem. 69, 684 (1978)
- 14. See e.g. Hess, W., Klein, R.: Adv. Phys. 32, 173 (1983)
- 15. We did not systematically use these dialysed samples since they tend to precipitate after some time
- 16. Wertheim, M.S.: Phys. Rev. Lett. 10, 321 (1965)
- 17. Felderhoff, B.: J. Phys. A 11, 929 (1978)
- 18. Hanna, S., Hess, W., Klein, R.: Physica 111 A, 181 (1982)
- 19. At small φ values the correlation function had to be corrected for the contribution of the beamsplitter (Ref. 3) which was measured separately
- 20. See Ref. 6: the expression given here is slightly different from Eq. (6) of Ref. 6 and corresponds to a random walk starting at a distance l^* from the interface and terminating at the interface. This seems appropriate to the case considered here where $l^* \approx 20 \text{ } \mu\text{m} \gg l \approx 3 \text{ } \mu\text{m}$
- 21. Altschuler, B.L., Khmelnitskii, D.E.: Pis'ma Zh. Eksp. Teor. Fiz. 42, 291 (1985) (JETP Lett. 42, 359 (1985))
 - Lee, P.A., Stone, A.D.: Phys. Rev. Lett. 55, 1622, 1985
- 22. Without analyser, the detected intensity variance is about two times smaller than in the VV or VH configurations, showing that the two polarizations are nearly uncorrelated
- Kaveh, H., Rosenbluh, M., Edrei, I., Freund, I.: Phys. Rev. Lett. 57, 2049 (1986)

G. MaretP.E. WolfHochfeld-MagnetlaborCentre de Recherches sur lesdes Max-Planck-InstitutTrès Basses Températures – CNRSfür Festkörperforschung166x166xF-38042 Grenoble CedexF-38042 Grenoble CedexFranceFranceFrance

Recently the intensity scattered by a nonabsorbing solid sample in the very multiple scattering regime $(l^* \approx 5 \,\mu\text{m})$ was reported [23] to have a nonexponential probability distribution, with $G^{(2)}(0) \approx 1.3$. This was attributed to the large value of $\lambda/l^* (\approx 0.1)$. In contrast, we found $G^{(2)}(0) \approx 1.8$ in our experiment independent of λ/l^* which was varied between 10^{-4} (dilute) and 0.04 ($\Phi \approx 0.2$, $l^* \approx 10 \,\mu\text{m}$).