EFFECT OF MULTIPLE LIGHT SCATTERING ON DYNAMIC CHARACTERISTICS OF LIGHT SCATTERED FROM LATEX PARTICLES

Čestmír KOŇÁK[a], Jaromír JAKEŠ[a], František PETRÁŠ[b], Marie KÁRSKÁ[b] and Jan PEŘINA[b]

[a] *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6 and*
[b] *Joint Laboratory of Optics of the Czechoslovak Academy of Sciences and Palacký University, 772 46 Olomouc*

Received April 25, 1989
Accepted June 9, 1989

The effect of multiple light scattering on a homodyne intensity auto-correlation function and photocount distribution of scattered light has been studied. The analysis of quasielastic light scattering data has shown that even a small contribution (several percent) of multiple light scattering to the total scattered light intensity can be distinguished and identified by the Laplace transform inversion of the corresponding intensity auto-correlation function. The photocount distribution reflects the coherence time changes of the scattered light only.

Multiple light scattering (MLS) has not received much attention from the theoretical point of view because it is difficult to treat analytically. Nevertheless it is a very important problem in many fields, like light scattering from a dense dispersion of particles, scattering of electromagnetic waves from fluctuations in plasma etc. The problem of MLS in a dense dispersion of particles has been treated by some authors[1–10]. Recently, the intensity of light multiply scattered from concentrated suspensions of latex spheres has been found to be enhanced in the backscattering direction[6–10]. This enhancement is due to the so-called coherent back scattering effect which arises from the time reversal invariance properties of wave propagation (e.g. ref.[10]). From the point of view of quasielastic light scattering spectroscopy (QELSS), expressions for intensity auto-correlation functions including second order scattering contribution are important (e.g. refs[2–5]). These equations can be used to correct the experimental correlation functions for double scattering iteratively[4]. Recently, G. D. J. Phillies[11] proposed an alternative procedure for suppressing the multiple scattering effect in QELSS by a homodyne cross-correlation technique. His proposal for a two-beam, two-detector light-scattering spectrometer which is only sensitive to singly scattered photons was then successfully realized and tested[12].

Multiple-scattering artifacts represent a not uncommon difficulty in QELSS. To avoid it the problem of a sensitive indication of a significant MLS contribution to the total scattered light intensity is investigated in this study. For this purpose the effect of MLS on the homodyne intensity autocorrelation function, $G^{(2)}(\tau)$, and photocount distribution, $p(n, \Delta t)$ of the scattered light has been studied. The analysis of QELSS data has shown that even a small contribution (several percent) of MLS to the totally scattered light intensity can be distinguished and separated by the Laplace transform inversion of $G^{(2)}(\tau)$ using the constrained regularization calculation REPES similar to that of Provencher's CONTIN (refs[13,14]).

THEORETICAL

The scattering in rectangular optical cells of oblong form with width a and length b ($a < b$) is considered below. Let the scattering mean free path or extinction length L of a studied dense dispersion be comparable with the distance a and shorter than b. Thus, the incident laser beam entering the cell in parallel with the direction a is only slightly attenuated on propagation through the cell, while the light scattered at 90° from the laser beam may be multiply scattered on its way to the detector (see Fig. 1).

First, consider a single scattering due to the Brownian motion of small particles in a fluid. The electric field strength of scattered light, $\mathbf{E}(\mathbf{K}, t)$, is related to the position $\mathbf{r}_j(t)$ of the scattering particles (assumed to be identical). If the incident light of the wave vector, $\mathbf{k}_I$, is scattered into light of the wave vector, $\mathbf{k}_F$ (e.g. the scattering events at point A in Fig. 1), then

$$\mathbf{E}(\mathbf{K}, t) = \mathbf{E}_0\sigma \exp(-\alpha a/2) \times \exp(-i\omega_0 t) \times \sum_j^N \exp[i\mathbf{K} \cdot \mathbf{r}_j(t)] , \qquad (1)$$

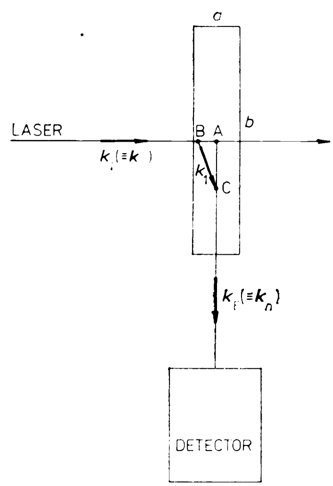

FIG. 1

A typical optical scheme of the scattering experiment, showing the incident beam ($\mathbf{k}_I$), scattering light ($\mathbf{k}_F$) going to the detector, a single scattering in volume A, and double scattering (with intermediate beam $\mathbf{k}_1$) in volumes B and C where $\boldsymbol{K} = \boldsymbol{k}_I - \boldsymbol{k}_F$ is the scattering vector ($|\boldsymbol{K}| = K = 4\pi n \,.\, \sin(\Theta/2)/\lambda$, where Θ is the scattering angle, λ is the wavelength of incident light in vacuo, and n is the refractive index of the medium, e.g. of the solvent in the case of dilute solutions), σ is the scattering cross section, E_0 is the amplitude of the electric field strength, α is the attenuation constant of the incident light intensity, N is the total number of particles in the scattering volume, and t is time.

Temporal fluctuations of scattered field may be advantageously described by the electric field auto-correlation function $G^{(1)}(K, \tau)$, defined as

$$G^{(1)}(K, \tau) = \langle E^*(K, t) \times E(K, t + \tau)\rangle\,, \tag{2}$$

where τ is time delay. For identical spherical particles undergoing free isotropic diffusion[15]

$$G^{(1)}(K, \tau) = |E_0|^2\, \sigma^2 \exp(-\alpha a) \times \exp(-DK^2\tau) \tag{3}$$

where D is the diffusion coefficient of free particles.

The second and higher order scattering contributions to the electric field strength of scattered light arise through successive single scattering processes in two or more separate sites of the cell (e.g. at points B and C in Fig. 1) containing a turbid suspension of particles. If the intermediate wave vector after the i-th collision is $\boldsymbol{k}_i$, one can introduce the successive transfer scattering vectors, $\boldsymbol{K}_i = \boldsymbol{k}_i - \boldsymbol{k}_{i-1}$. For a given sequence of n scatterers located at $\boldsymbol{r}_1 \ldots \boldsymbol{r}_n$ the phase factor, Φ, is $\prod_{j=1}^{n} \exp(\mathrm{i}\boldsymbol{K}_j\boldsymbol{r}_j)$. For identical spherical scatterers whose positions are uncorrelared we have

$$\langle(\Phi^*(0)\, \Phi(t)\rangle = \exp\left(-Dt \sum_{i=1}^{n} K_i^2\right). \tag{4}$$

If we assume that fields belonging to different sequences add incoherently on the average, and the successive $\boldsymbol{K}_i$ vectors are independent, the field correlation function for a given polarization is[5]

$$G^{(1)}(K, \tau) \approx \sum_n I_n \langle \exp(-DK^2\tau)\rangle^n\,, \tag{5}$$

where I_n is the total time-averaged intensity scattered by all sequences of the order n and the second factor is weighted by the form factor of a single sphere. Relation (5) is a good approximation for strongly scattering systems with small n sequences which do not contribute significantly.

The following conclusions follow from Eq. (5). Under the condition of a low contribution of MLS to the total scattering intensity, the single exponential correlation function (cf. relation (3)) for the first-order scattering should be distorted by the higher-order scattering contribution given by the right side of Eq. (5). For single scattering of identical particles the decay time distribution, $A(\tau_c)$, is a δ-function at $\tau_c = 1/DK_1^2$; it should be broadened by the second and higher order scattering. These higher-order contributions are expected mainly on the short time side of the δ-function because $1/D(\sum_{j=1}^{n} K_j^2) < 1/DK_1^2$, for most combinations of $\boldsymbol{K}_j$.

EXPERIMENTAL

Samples

The samples were prepared by diluting a suspension of monodisperse polystyrene latex particles 94 nm in diameter. The mean particle diameter was determined by photon correlation spectroscopy. The high monodispersity of the latex particles was confirmed by electron microscopy.

Apparatus

The experimental setup of the optical system used for measuring the homodyne intensity correlation function, $G^{(2)}(K, \tau)$, and photocount distribution $p(n, \Delta t)$ of light scattered from dense dispersions of latex particles is shown in Fig. 2.

The light source used was a *He–Ne* laser (Spectra Physics 125 A) or an Ar-ion laser (Zeiss Jena), illuminating a sample cell through a lens L of local length, *f*, 130 mm. The beam diameter at the focal region, calculated by neglecting the laser beam divergence, was about 50 μm. All measurements were performed at a scattering angle, Θ, of 90°. The scattered light was detected through the diaphragm DP (1·0 mm in diameter) and the pin-hole PH (0·035 mm in diameter) located 350 mm from the diaphragm DP. Thus, the viewing angle of the photomultiplier $\simeq$0·16° and the coherence area $\approx$0·15 mm².

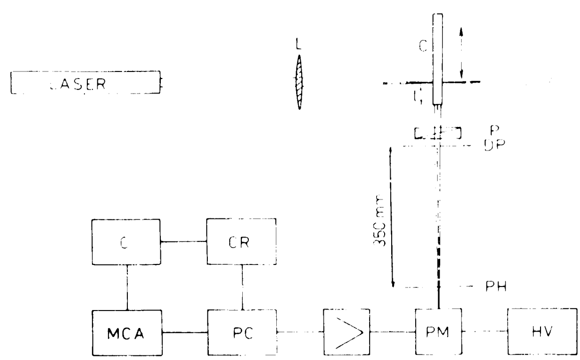

FIG. 2

A block diagram of the instrument used: L lens, C cell movable perpendicularly to the laser beam, P polarizer, DP diaphragm, PH pinhole, PM photomultiplier C31034 (RCA), PC photo counting system, CR correlator, MCA multichannel analyser, C computer, HV high voltage source

The rectangular sample cell (2 × 10 mm) could be displaced perpendicularly to the laser beam in order to change the optical path of the scattered light in the sample, l. The accuracy of position setting was 0·02 mm. Such an arrangement enabled us to change the contribution of MLS without changing the concentration of latex particles in the suspension.

A cooled photomultiplier and a photometric read-out system, operating in the photon counting mode, were used to detect the scattered light. The photopulse signal from the read-out system was converted by a frequency-to-voltage converter and analysed by a multichannel analyzer. Simultaneously, the multi-time auto-correlation function (MTCF) covering 3·5 decades of delay time was recorded by a multi-tau, single-bit, 96-channel digital correlator. The correlator measured with three different sampling times simultaneously.

Data Treatment

The Laplace transform of normalized correlation function of the scattered light intensity, $g^{(2)}(\tau)$, was inverted using a constrained regularization calculation REPES similar to that of Provencher's CONTIN (refs[13,14]) to obtain $A(\tau_c)$.

RESULTS AND DISCUSSION

The results presented and discussed here were obtained on the dispersion of latex particles having a concentration of 1·7 . 10^{-2} g ml^{-1}. The scattering mean free path (the extinction length), L, evaluated from transmission measurements was 1·2 and 1 mm at λ 514·5 and 632·8 nm, respectively.

Auto-correlation Functions

The relative integral scattering intensity, I, is plotted in Fig. 3 as a function of l, the optical path length of scattered light in the latex suspension (see Fig. 2). The

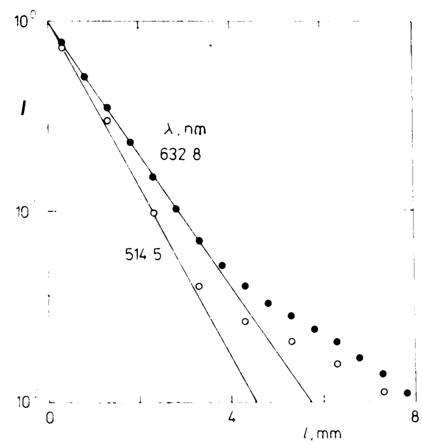

FIG. 3

The relative integral scattering intensity, I, as a function of l; I in arb. units scattering data were recorded by photomultiplier with a viewing angle of 0·16°. The intensity I in Fig. 3 follows the Lambert–Beer law up to l 3 and 3·5 mm (the linear parts in Fig. 3) with the corresponding values of the attenuation constant, α, 10·2 and 8·22 cm^{-1} for the light with λ 514·5 nm and 632·8 nm, respectively. Therefore, the approximation used in the theoretical part for description of the primary laser propagation is applicable to this particular suspension. The deviations from the linear dependences at higher values of l are due to an appreciable contribution of MLS.

The distribution functions of decay times, $A(\tau_c)$, obtained by the Laplace transform inversion of $G^{(2)}(K, \tau)$ measured with light of 632·8 and 514·5 nm are shown for various distances l in Figs 4 and 5, respectively. The distribution $A(\tau_c)$ may be reduced to two main separated bands picked up at a short time, τ_{cs}, and long time, τ_{cs}, at small values of l (0·3 or 3·3 mm in Fig. 4 and 0·3 or 1·3 mm in Fig. 5). With increasing l these originally narrow bands get broader and simultaneously the short time process becomes more pronounced. A single broad band can be found at higher values of l. The contribution of the long time process becomes practically negligible at l 9·3 mm for λ 514·5 nm (cf. Fig. 5*b*), which manifests itself by a narrowing of the corresponding band. The values of τ_{cs} and τ_{cl} obtained from the maxima of $A(\tau_c)$ are given for λ 632·8 and 514·5 nm in Table I. It can be seen in Table I that the short mode generally decreases, provided it is well separated, with increasing l, while τ_{cl} is essentially independent of l. The difference observed between the distribution $A(\tau_c)$ at the corresponding values of l in Figs 4 and 5 is mostly due to different scattering cross-sections of particles, σ, and the scattering vectors in the experiment, thus, both $\delta(\sim 1/\lambda^4)$ and $K(\sim 1/\lambda)$ should be greater for λ 514·5 nm than for λ 632·8 nm.

TABLE I

Characteristic decay times (τ_{cs}, τ_{cl}) at various path length (l) of scattered light

λ = 632·8 nm			λ = 514·5 nm		
l mm	$\tau_{cs} \cdot 10^{-1}$ μs	$\tau_{cl} \cdot 10^{-2}$ μs	l mm	$\tau_{cs} \cdot 10^{-1}$ μs	$\tau_{cl} \cdot 10^{-2}$ μs
0·3	7·2	4·1	0·3	3·2	2·5
3·3	6·2	3·6	1·3	3·8	2·5
6·3	1·5	—	2·3	3·4	—
—	—	—	4·3	2·9	—
—	—	—	6·3	2·9	—
—	—	—	9·3	1·8	—

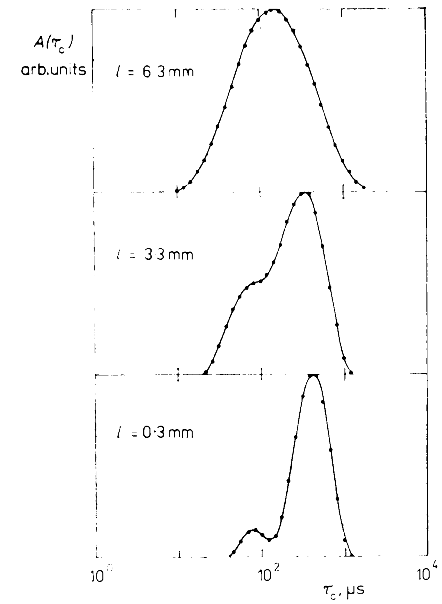

FIG. 4

Distribution of decay times ($A(\tau_c)$) as obtained from correlation functions measured with incident light 632·8 nm at various distance l

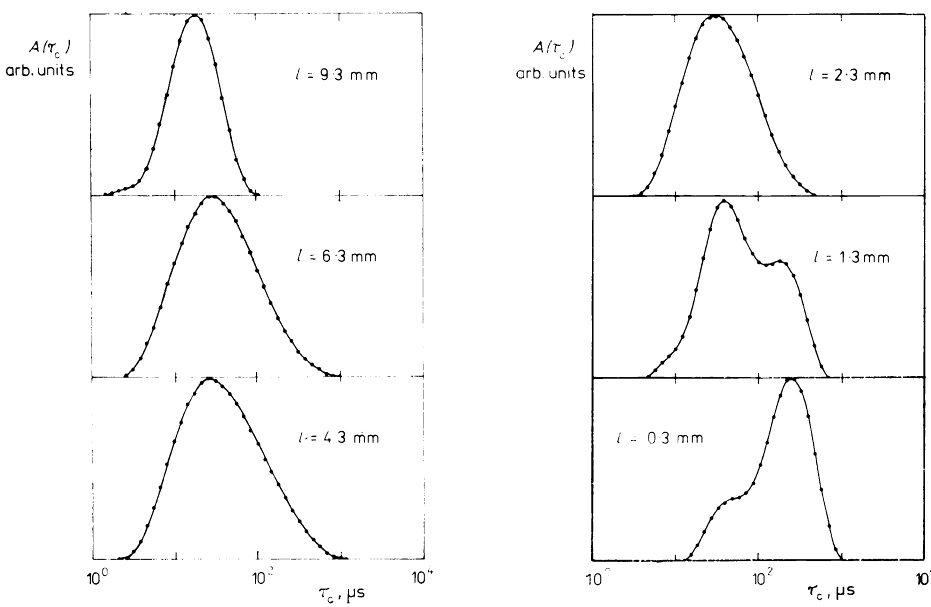

FIG. 5

Distribution of decay times as obtained from correlation functions measured with light 514·5 nm at various distances l

Long Time Mode

The band in the distribution $A(\tau_c)$ picked up at τ_{cl} (for small values of l) can mostly be attributed to the single scattering process in the suspension. This interpretation is based on the experimental observation that the values of τ_{cl} (cf. Table I) are very close to the characteristic relaxation time in dilute latex suspensions, τ_{cd}, where MLS is known to be negligible; $\tau_{cd} \approx 354$ and 536 μs for λ 514·5 and 632·8 nm, respectively. Moreover, the long time modes have a diffusive character because τ_{cl} are proportional to K^{-2}. In other words, the shift of the long time band towards the region of shorter times for λ 514·5 nm in comparison with that for λ 632·8 nm results from the $K^{-2}(\lambda^2)$ dependence of τ_{cl}. The small difference ($\sim$25%) between τ_{cd} in dilute suspensions and τ_{cl} values could result from interactions between particles, which cannot be neglected in undilute systems under study[15]. The above interpretation is in full agreement with results of Maret and Wolf[5] who found in their back-scattering QELS experiments that the longest living decay time is remarkably close to the single particle back scattering relaxation time.

Short Time Mode

According to the theoretical analysis, the MLS manifests itself by a contribution to $A(\tau_c)$ mostly at $\tau_c < \tau_{cl}$. Therefore, the band found at shorter τ_c should be due to the MLS processes. The experimental fact that this contribution provides a band with the clearly defined maximum at τ_{cs} is somewhat surprising and does not follow from the simple considerations in the theoretical part. Moreover, τ_{cs} values at small l are 5·7 and 7·8 times smaller than τ_{cl} for λ 632·8 and 514·5 nm, respectively, so that the band maxima could not be due to contributions of the double scattering events as the maximum value of $K_1^2 + K_2^2$ ($\Theta_1 = 135°$, $\Theta_2 = 135°$) is at most 3·4 times smaller than K for Θ 90°. However, we have to keep in mind that at the actual noise level the resolving power of the Laplace transform inversion is about one half decade only and that the REPES method, similarly to CONTIN, has a pronounced tendency to generate artifact shoulders or side peaks (see e.g. Fig. 2*c* of ref.[14]). Thus, the side peak may be interpreted as a collective manifestation of MLS of the second and higher orders. The shift of the short time band to shorter τ_c with increasing l indicates that scattering processes of increasingly higher order are enforced with increasing l (cf. Figs 4 and 5). Because the differences between the positions of the short time bands measured at the same values of l for λ 632·8 and 514·5 nm are greater than the corresponding changes of K, it follows that the higher order scattering processes are more efficient at shorter λ due to the wavelength dependence of the scattering cross-section.

TABLE II

An analysis of experimental $p(n, \Delta t)$

	$\Delta t = 1$ ms ($\Delta t/\tau_{c1} = 2{\cdot}4$)			$\Delta t = 4$ ms ($\Delta t/\tau_{c1} = 9{\cdot}6$)			
l mm	$\langle n \rangle$	M	τ_{co} μs	$\langle n \rangle$	M	τ_{co} μs	τ_c μs
0·3	4·2	2·4	420	9·4	9·0	440	410
6·3	4·4	4·6	220	9·0	22·8	175	150
9·3	4·4	8·3	120	9·4	39·1	102	—

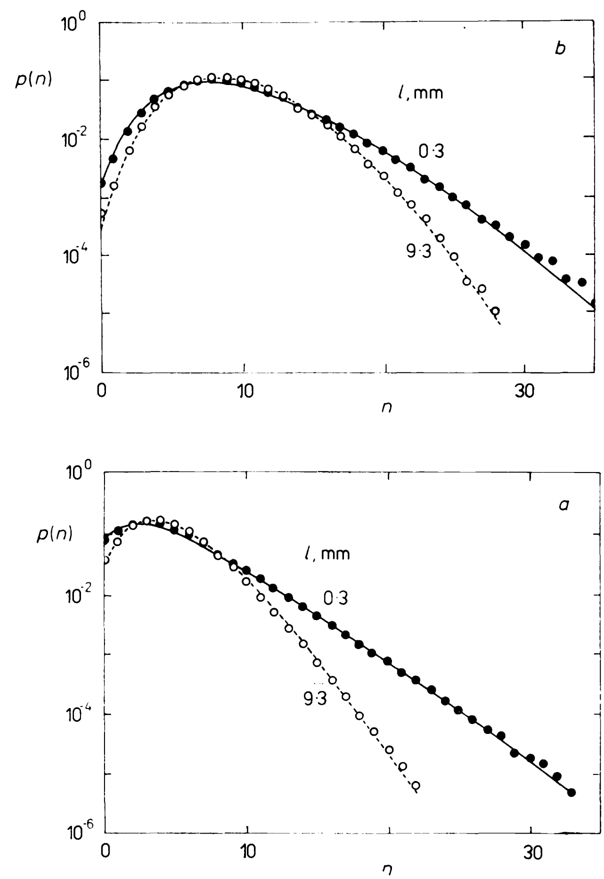

FIG. 6

Comparison of the experimental (points) and theoretical (full lines) photocount distributions for Δt 1 ms (*a*) or 4 ms (*b*)

Photocount Distribution

The selected experimental photocount distributions $p(n, \Delta t)$ at λ 632·8 nm are shown as the data points in Fig. 6 for the respective sampling times Δt 1 and 4 ms. The experimental conditions were selected so that Δt was 2·4 times (Fig. 6*a*) and 9·6 times (Fig. 6*b*) longer than τ_{cl} for l 0·3 mm and the detection area $\approx 1 \,.\, 10^{-3}$ mm^2 was much smaller than the coherence area $\approx 0{\cdot}15$ mm^2. The intensity of incident laser light was controlled in such a way that the mean number of photopulses per Δt, $\langle n \rangle$, was kept close to 4 and 9 for Δt 1 and 4 ms, respectively. A typical result of this experiment is a successive narrowing of $p(n, \Delta t)$ with an increasing value of l (cf. Fig. 6). Because the experimental distributions are similar to those for a superposition of coherent and chaotic optical fields[16], they were fitted to the corresponding theoretical distribution (Mandel–Riece formula)[16]

$$p(n, \Delta t) = \frac{\Gamma(n + M)}{n!\, \Gamma(M)} \left(1 + \frac{M}{\langle n \rangle}\right)^{-n} \left(1 + \frac{\langle n \rangle}{M}\right)^{-M}, \qquad (6)$$

where $M = \Delta t / \tau_{co}$ is the number of the degrees of freedom, $\langle n \rangle$ is the mean number of photocounts, Γ is the gamma function, and τ_{co} is the mean coherence time. Physical arguments for applying formula (*6*) are given in ref.[9]. By minimizing the sum of squared deviations from $p(n, \Delta t)$ (modified Powell–Fletcher method) we calculated the three parameters – $\langle n \rangle$, M, τ_{co} – in Eq. (*6*). The very good agreement between experiment and theory validates the applied procedure. The parameters $\langle n \rangle$, M, τ_{co} of the fitting procedure are collected in Table II. The values of τ_{co} evaluated from $p(n, \Delta t)$ are close to the mean correlation times, τ_c, found from the auto-correlation functions (cf. Table II.). These results indicate that the photocount distribution $p(n, \Delta t)$ merely reflects the coherence time changes of scattered light in agreement with the conclusions of ref.[9].

CONCLUSIONS

The Laplace transform inversion of homodyne auto-correlation functions can distinguish and identify contributions of MLS to the totally scattered light in those cases where they are comparable with that of single particle scattering.

The authors thank Dr J. Křepelka for his kind help with fitting Eq. (6) to experimental data.

REFERENCES

1. Crosignani B., DiPorto P., Bertolotti M.: *Statistical Propertices of Scattered Light*, Chap. 4. Academic Press, New York 1975.
2. Bertolotti M.: *Photon Correlation Spectroscopy and Velocimetry*, NATO Adv. Study Inst. Ser, Ser. B *23* (H. Z. Cumming and E. R. Pike, Eds), p. 22 (1977).

3. Van Rijswijk F. C., Smith U. L.: Physica, A *83*, 121 (1976).
4. Dhonj J. K. G.: Physica, A *129*, 374 (1985).
5. Maret G., Wolf P. E.: Z. Phys., B *65*, 409 (1987).
6. Kuga Y., Ishimaru A.: J. Opt. Soc. Am., A *1*, 831 (1984); A *2*, 616 (1985).
7. Van Albada M. P., Lagendijk A.: Phys. Rev. Lett. *55*, 2692 (1985).
8. Wolf P. E., Maret G.: Phys. Rev. Lett. *55*, 2696 (1985).
9. Wolf P. E., Maret G., Akkermans E., Maynard R.: J. Phys. Fr. *49*, 63 (1988).
10. Akkermans E., Wolf P. E., Maynard R., Maret G.: J. Phys. Fr. *49*, 77 (1988).
11. Phillies G. D. J.: J. Chem. Phys. *74*, 260 (1981).
12. Phillies G. D. J.: Phys. Rev., A *24*, 1939 (1981).
13. Provencher J. W.: Makromol. Chem. *180*, 201 (1979).
14. Jakeš J.: Czech. J. Phys., B *38*, 1305 (1988).
15. Berne B. J., Pecora R.: *Dynamic Light Scattering*. Wiley, New York 1976.
16. Peřina J.: *Coherence of Light*, Chaps 10, 17. Reidel, Dordrecht 1985.

Translated by L. Kopecká.