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Laser correlation spectroscopy of nanodispersed solutions in the region of transition to multiple light scattering

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ABSTRACT The work considers the application of laser correlation spectroscopy to the investigation of dispersed systems for such a case, which can be regarded as a transitional to the multiple scattering regime. It is shown that even a slight violation of the condition of single scattering by the increasing of concentration of scattering centers can affect the result of particle size measurements. It should be taken into account when studying colloids.

KEYWORDS aser correlation spectroscopy, multiple light scattering, nanoparticles

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1. Introduction

The laser correlation spectroscopy method (LCS), which is used in the study of various types of dispersed systems, had been developed primarily for the case of single-scattering of probing radiation [1,2]. However, the task of investigation of a structure with multiple scattering is also relevant, and LCS can be used here in one form or another, although artifacts are observed that significantly affect the determination of sample characteristics. Despite the existence of a number of works in the field, the theoretical understanding of such processes is still in progress.

This article discusses an important variant of LCS application: testing of the solutions at such particle concentrations for which the single light scattering transforms into multiple one. The theoretical results are compared with the experimental data obtained on polystyrene latex colloids, which serve as a model system for comprehension of the effects in this boundary region.

2. Theoretical analysis of the autocorrelation function of multiple scattered light

When finding the particles size by the LCS method, the autocorrelation function $G^{(2)}(\tau) = \langle I(t+\tau)I(t)\rangle$ of the scattered light intensity I is measured. Subtracting the base line $G^2(\infty)$ from it gives one the expression $G(\tau) = G^{(2)}(\tau) - G^{(2)}(\infty)$. Further we will refer to it simply as the autocorrelation function (ACF) of the scattered light.

It has been shown that if light is scattered by a colloidal solution with particles of radius r, the ACF depends on τ exponentially [1–3]:

$$G(\tau) = A\exp(-\Gamma\tau), \tag{1}$$

where

$$\Gamma = \frac{kTq^2}{3\pi\eta r}. \tag{2}$$

Here, k is the Boltzmann constant, T is the temperature, η is the viscosity of the carrier medium, and q is the length of the wave vector of the scattered radiation; $q = (4\pi n_0/\lambda)\sin(\theta/2)$, where n_0 is the refractive index of the medium, λ is the wavelength of the incident radiation, and θ is the scattering angle.

By determining Γ from the exponential approximation (1) of the experimental data and using expression (2), one can easily obtain the particle size in a monodisperse colloidal solution.

The ACF analysis can be performed in a more general form. Let us define the value of Γ as

$$\Gamma = -\frac{\partial \ln G(\tau)}{\partial \tau}\Big|_{\tau=0}. \tag{3}$$

For an exponential ACF, formula (3) provides the same value for Γ as earlier. It can be shown that in the case of a polydisperse system, when the ACF is nonexponential, determination Γ by expressions (3) and (2) gives the average value of the particle size [3,4].

Let Γ_1 be the value defined by the expression (3) for the ACF of light scattered at an angle of 90° in a dilute solution, when the scattering can be considered as single one. As the concentration of particles c increases, the mean free path of the photon l will decrease, and the scattering becomes multiple. For this case, we denote the value of Γ defined by (3) as Γ_m and represent it as $\Gamma_m = N\Gamma_1$, where N is the multiplicity of scattering.

It has been demonstrated previously [5,6] that when a spherical cuvette of diameter d is used to place the sample, and under the condition $l \ll d$, the value of N can be calculated by the following formula:

$$N = \frac{d^2}{l^2}(1-\bar{\mu})F(\theta), \tag{4}$$

where $\bar{\mu}$ is the average cosine of the angle of single scattering, and for $F(\theta)$, the expression was obtained:

$$F(\theta) = \frac{3}{2}\cos^2\frac{\theta}{2}\Big(1 - 4\cos\frac{\theta}{2}\int\limits_0^1 \frac{y^2dy}{\sqrt{1+2y^2\cos\theta+y^4}}\Big). \tag{5}$$

We would like to note that the integral in equation (5) can be expressed in terms of complete elliptic integrals of the first and the second kind $K(x)$ and $E(x)$:

$$\int\limits_0^1 \frac{y^2dy}{\sqrt{1+2y^2\cos\theta+y^4}} = \frac{1}{3\sin^2\frac{\theta}{2}}\Big[(1+\cos\theta)K(\sin\frac{\theta}{2}) - (3+\cos\theta)E(\sin\frac{\theta}{2})\Big].$$

Note that

$$l = \frac{1}{\sigma n} = \frac{m}{\sigma c}, \tag{6}$$

where σ is the cross-section of light scattering on a particle, n is the particle number concentration, m is the mass of the particle, c is the mass concentration of particles.

Assuming $\theta = 90°$ (herewith $F \approx 0.15$), from (4)–(6), it is easy to obtain the following formula

$$\Gamma_m \cong 0.15\, d^2\sigma^2\frac{c^2}{m^2}(1-\bar{\mu})\Gamma. \tag{7}$$

From this expression, it is clear that if the particle concentration increases, the value of Γ_m increases. Accordingly, this will lead to a decrease in the average particle radius, determined by formula (2).

At relatively small particle concentrations c, when the photon mean free path is comparable with the size of the scattering volume, expression (7) cannot be applied quantitatively. However, we assume that even in this case (i.e., in the transition regime between single- and multiple-scattering), an apparent decrease in the average particle size will also be observed for increasing c, since the probability of photon collisions with particles increases even with a slight increase in concentration. This leads to a broadening of the scattering spectrum, a more rapid decay of the ACF near zero, a growth of the value of Γ found by formula (3), and ultimately to the specified effect.

3. Effect of scattering centers concentration on LCS results

To verify experimentally the above statements, the standard LCS method was used [1]. The source of optical radiation was a He-Ne laser ($\lambda = 632.8$ nm), which was focused onto a center of a cuvette containing the solution under study. The cuvette had a rectangular cross-section with the size 10 × 10 mm (the results obtained with it, being qualitative, certainly can be compared with the conclusions of the theory developed for a spherical cuvette). The light scattered by the sample was transmitted to an optical fiber and, after passing through it, was recorded by a photodetector. The scattering angle was 90°. The signal was fed to an analog-to-digital converter and then to a computer, where it was processed, resulting in the ACF. A more detailed description of this setup can be found in articles [7,8], which describe experiments performed using the same approach as in this work.

Aqueous solutions containing polystyrene latex particles with a nominal radius of approximately 30 nm (this material is commercially available) were taken as test substances. The measurements were performed at the following solid phase concentrations: 0.1, 0.3, 1.0, 2.9, 8.2, and 41 mg/ml.

The calculations of Γ corresponding to the expression (3) were performed as follows. The logarithm of the ACF was approximated by a quadratic polynomial $f(\tau) = A + B\tau + C\tau^2$ using sixty initial points of the ACF, and Γ was taken to be $-B$. This value is more stable to ACF measurement errors than that found by the derivative of its logarithm over several points in the initial section of the linear approximation.

The concentration dependence of Γ is shown in Fig. 1. It can be seen that, as it follows from expression (7), Γ increases monotonically with increasing of c.

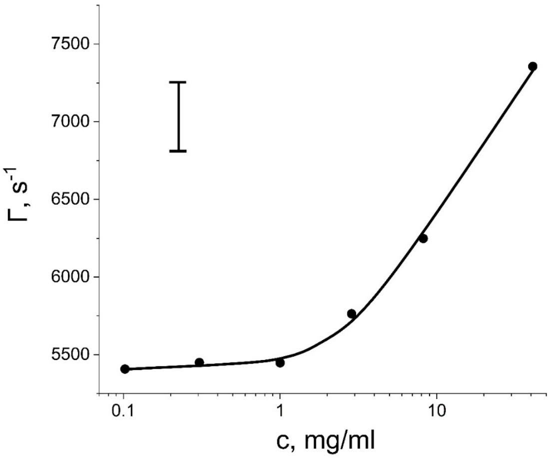

FIG. 1. Dependence of $\Gamma = -B$ on the concentration of particles

To estimate the photon mean free path l and the scattering multiplicity, an experiment on the attenuation of light was carried out, and the Bouguer–Lambert–Beer extinction law $I_d = I_0 \exp(-d/l)$ was used (I_0 and I_d are the intensities of the incident and transmitted light through the cuvette, respectively).

For the concentration of 41 mg/ml, $l \approx 4$ mm was obtained. In this case, at $d = 10$ mm, the value of N calculated by formula (4) is close to 1 (here the average cosine was taken $\bar{\mu} = 0.026$, that was found by Mie scattering theory). The calculated value of N means that for this and lower concentrations, the experiment was performed for the regime where the transition to multiple scattering is just beginning, and expressions (4)–(7) can only be applied qualitatively.

Substituting of Γ, determined as above, into (2) yields the dependence of the nominal values of the particle radius on the concentration, demonstrated in Fig. 2. It shows that the apparent value of R, measured by the LCS method, decreases with an increase in c. Since there is no actual change in the particle size, this phenomenon can only be attributed to a decrease in the photon mean free path and an increase in the scattering multiplicity of light in the colloidal solution. Note that knowledge of this fact especially can be useful in synthesizing and studying media such as magnetic fluids [9], where even a small deviation in particle size can lead to significant changes in macroscopic properties [10].

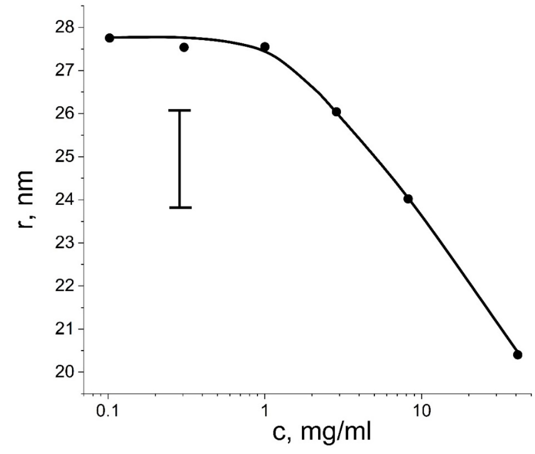

FIG. 2. Dependence of the calculated average radius of particles on their concentration

4. Conclusion

It has been established that when investigating dispersed systems using laser correlation spectroscopy, it is necessary to take into account the effect that, as the region of the multiple scattering of probing radiation approaches, the seeming size of the particles begins to depend on their concentration. It has been experimentally shown that this feature can already be observed even in regions where the scattering multiplicity only slightly differs from unity. This fact is important for examination the characteristics of colloids with relatively high solid phase content.

References

[1] Stetefeld J., McKenna S.A., Patel T.R. Dynamic light scattering: a practical guide and applications in biomedical sciences. *Biophys. Rev.*, 2016, **8** (4), P. 409–427.

[2] Nepomniashchaia E.K., Aksenov E.T., Bogomaz T.A., Velichko E.N. Use of laser correlation spectroscopy to investigate the parameters of biological suspensions. *J. Opt. Technol.*, 2015, **82** (3), P. 162–165.

[3] Cummins H.Z., Pike E.R. (Eds.) Photon Correlation and Light Beating Spectroscopy. Springer, Great-Malvern, 1974, 584 p.

[4] Dietz R. (Ed.) Industrial Polymers: Characterization by Molecular Weight. Transcripta Books, Teddington, 1975, 136 p.

[5] Ivanov D.Yu., Soloviev A.V. The effect of laser radiation on the temperature of highly scattering media, *Deposited scientific work*, Dep. in VINITI 22.04.1992, N 1357-B92, 19 p.

[6] Kostko A.F., Pavlov V.A. Location of the effective diffusing-photon source in a strongly scattering medium. *Appl. Opt.*, 1997, **36** (30), P. 7577–7582.

[7] Pleshakov I.V., Ryzhov V.A., Marchenko Ya.Yu., Alekseev A.A., Karseeva E.K., Nevedomskiy V.N., Prokof'ev A.V. Agglomeration of magnetite nanoparticles with citrate shell in an aqueous magnetic fluid. *Nanosystems: Phys. Chem. Math.*, 2023, **14** (3), P. 334–341.

[8] Pleshakov I.V., Alekseev A.A., Fofanov Ya.A. Observation of the processes of formation and growth of aggregates in a magnetic fluid by laser correlation spectroscopy. *Tech. Phys. Lett.*, 2025, **51** (8), P. 72–76.

[9] Pleshakov I.V., Alekseev A.A., Bibik E.E., Ilichev I.V., Prokof'ev A.V. Effect of laser radiation on magnetite nanoparticles in deposited ferrofluid. *Nanosystems: Phys. Chem. Math.*, 2024, **15** (3), P. 346–351.

[10] Punit T., Sarvendra K., Jitendra K., Singh S.P., Pant R.P. Finite size effect on structural, morphological, magnetic, and magneto-optical properties of Fe_3O_4 based nanofluids. *J. of Materials Science: Materials in Electronics*, 2025, **36** (36), 2310.

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