
THEORETICAL AND MATHEMATICAL
PHYSICS

Measurement of Sizes of Colloid Particles Using Dynamic Light Scattering

K. G. Kulikov^{*a} and T. V. Koshlan^b

^a St. Petersburg State Polytechnical University, Politekhnikeskaya ul. 29, St. Petersburg, 195251 Russia

^b St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034 Russia

*e-mail: kulikov_kg@hotmail.ru

Received March 25, 2015

Abstract—Size distribution functions of colloid particles are obtained with the aid of dynamic light scattering for both polarized and depolarized components. Electron microscopy of the colloid particles is used to construct size distribution histograms. Numerical analysis yields good agreement of the experimental and theoretical size distributions. The size distribution function is derived from the solution to the corresponding integral equations using the Tikhonov regularization procedure.

DOI: 10.1134/S1063784215120099

INTRODUCTION

There has been considerable recent interest in the study of dispersed systems of the sizes of particles, which range from several to several thousands of nanometers. In most systems, the particles exhibit different electric charges, sizes, and electric parameters, so that the particles are distributed with respect to geometrical and electric parameters. The properties of systems substantially depend on such distributions, and, hence, the analysis of the distributions is a topical problem. A detailed study of the properties of dispersed systems, in particular, colloids is possible only with the aid of a combination of mathematical, physical, and chemical methods.

The purpose of this work is the development of a mathematical model for the determination of sizes of particles in suspension using the results of the dynamic light scattering (DLS) by colloid particles in solutions and the best results for model polydispersed solutions.

The work consists of several parts. The first part is devoted to the DLS method, which is widely employed in the study of polydispersed solutions. In the second (experimental) part, we consider the problems of study of depolarized and polarized components of scattered light and derive Fredholm integral equations of the first kind to determine size distribution function of colloid particles for both polarized and depolarized components of scattered light using the autocorrelation function that results from the DLS measurements. In the third part, we use the Tikhonov regularization procedure to solve the integral equations.

1. DYNAMIC LIGHT SCATTERING

The DLS method is widely used in the study of polydispersed solutions in physics, chemistry, biology, etc. The DLS method has several advantages: relatively short experimental time, low experimental costs, and possibility of the analysis of data that correspond to a wide range of distributions for particles with different molecular masses.

Note that the DLS theory must be used at relatively low concentrations of particles when the distances between particles are significantly greater than the particle sizes and the secondary light scattering can be disregarded.

The measurements of particle sizes are based on the analysis of intensity fluctuations of scattered light in the volume that contains colloid particles in solution at different time moments. The intensity fluctuations of scattered light result from the inhomogeneity of the medium. Random motion of particles that is caused by uncompensated impacts of molecules in solution leads to the intensity oscillations relative to a mean level. The frequency of such oscillations can be used to determine the diffusion coefficient of colloid particles, which depends on the particle sizes.

The autocorrelation function of light scattering determines the characteristic scales of time intervals over which the motion of scattering centers is correlated (i.e., depends on the positions at previous moments). To observe time correlations of the scattered radiation, we must use laser radiation, which is coherent and monochromatic. The size of the objects under study is comparable with the optical wavelength. For smaller particles, the incident radiation is uniformly scattered over all directions. In this case, the

autocorrelation function can be used to determine the correlations of intensity fluctuations. Note that the DLS method is the method for the study of structure and dynamics of liquid media based on the analysis of time autocorrelation function of the intensity fluctuations of scattered light. The further processing makes it possible to obtain the desired size distribution of particles.

Using the approach of [1], we consider normalized autocorrelation function of the light-scattering intensity:

$$g^{(2)}(q, \tau) = \frac{\langle I_s(q, 0)I_s(q, \tau) \rangle}{\langle I_s(q) \rangle^2}, \quad (1)$$

and the normalized autocorrelation function of the field of scattered radiation for the further calculation of the desired parameters (sizes and diameters of particles and coefficients of rotational and translational diffusion) [1, 2]

$$|g^{(1)}(q, \tau)| = \frac{\langle E_s(q, 0)E_s^*(q, \tau) \rangle}{\langle |E_s(q)|^2 \rangle}.$$

Here, brackets $\langle \rangle$ denote averaging over the ensemble of particles, and variable q is given by [3]

$$q = \frac{4\pi}{\lambda} \sin \left[\frac{\theta}{2} \right], \quad (2)$$

where λ is the wavelength and θ is the scattering angle.

Then, the relationship of the normalized autocorrelation function of the light-scattering intensity (measured quantity) and the field autocorrelation function is established by the Siegert equation [4]:

$$g^{(2)}(q, \tau) = A(1 + \beta |g^{(1)}(q, \tau)|^2), \quad (3)$$

where β is the coherence factor that depends on the laser beam and tuning of instrumental optics and A is the constant that is unity.

We may assume that the coefficient is $\beta = 0.7$ for the experiments on dynamic scattering.

When a laser beam passes through the liquid under study with suspended dispersed particles, the radiation is partially scattered by fluctuations of concentration of the number of particles that are involved in the Brownian motion.

In accordance with the Onsager hypothesis, the relaxation of microscopic fluctuations of concentration to the equilibrium level can be described using the first Fick law (diffusion equation). In this case, the autocorrelation function of the light-scattering intensity exponentially decays with time and the characteristic relaxation time is one-to-one related to the diffusion coefficient of particles.

In the simplest case (monodispersed solution that contains noninteracting spherical particles with identical sizes), the power spectrum of photocurrent represents a Lorentzian curve [5] with halfwidth Γ and the

intensity correlation function is the exponential function with relaxation time T_c .

In accordance with the results of [1, 4, 5], the normalized field autocorrelation function of scattered light is represented as

$$g^{(1)}(q, \tau) = \exp(-\Gamma\tau). \quad (4)$$

In this case, coefficient Γ is related to the physical parameters of the medium [6]:

$$\Gamma = \frac{1}{T_c} = Dq^2, \quad (5)$$

where D is the diffusion coefficient and quantity q is given by expression (2).

For polydispersed solutions with different sizes of particles, the spectrum of photocurrent represents a continuous set (integral) of Lorentzian curves with different halfwidths. Therefore, the distribution of particles with respect to sizes (diffusion coefficients) can be determined from the solution to the inverse spectral problem represented as the following integral equation [5, 6]:

$$g^{(1)}(q, \tau) = \int_0^{\infty} F(\Gamma) \exp(-\Gamma\tau) d\Gamma. \quad (6)$$

This integral equation provides the main principle of data processing in the DLS method.

In accordance with the Stokes–Einstein law, the motion of colloid particles in liquid can be described using the coefficients of translational and rotational diffusion. The latter coefficient is determined by the rotational action of the Brownian motion. Thus, we have [1, 5]:

$$D_t = \frac{kT}{6\pi\nu r}, \quad (7)$$

$$D_r = \frac{kT}{8\pi\nu r^3}, \quad (8)$$

where D_t is the coefficient of translational diffusion, D_r is the coefficient of rotational diffusion, k is the Boltzmann constant, T is the absolute temperature, ν is the viscosity of solution, and r is the hydrodynamic radius of particle.

2. EXPERIMENTAL

We study aqueous colloids of diamond particles. The particles are produced using an industrial synthetic method and exhibit polycrystalline structure and irregular shape.

For preparation of samples, diamond powder is weighted and mixed in water. The resulting polydispersed system is ultrasonically processed. Colloids with the needed concentration are obtained using dilution of the concentrated systems. The particles under study differ by geometrical characteristics.

Distilled water serves as the dispersion medium. We remove dust that disturbs the results of scattering using a reverse-osmosis membrane with a pore size of 200 nm. Multiple filtering through such a membrane makes it possible to obtain colloids that are virtually free of dust. Knowing the size distribution of particles and density of diamond, we use dilution to obtain the needed concentration of particles in the system under study. We study the colloid system with a concentration of particles of 0.0266 mg/mL. Prior to experiments, the colloids are ultrasonically processed at frequencies of 22 and 40 kHz, since the colloids are thermodynamically unstable and form aggregates.

A Photocor Complex spectrometer is used to study the light scattering by colloid particles. The working principle of the spectrometer is based on the DLS (photon correlation spectroscopy). In the experiments, the laser beam passes through the liquid that contains suspended dispersed particles and the radiation is partly scattered by the fluctuations of the concentration of particles. The particles are involved in the Brownian motion that can be described using the diffusion equation. The solution to such an equation yields a relationship of halfwidth Γ of the spectrum of scattered light (or characteristic time T_c of the relaxation of fluctuations) and diffusion coefficient D (expression (5)).

The scattered radiation is detected by a photodetector the output signal of which is processed using a digital correlator. The resulting autocorrelation function can be used to calculate the mean size or size distribution of particles (expressions (11) and (12)).

The measurements are performed at scattering angles ranging from 20° to 150° (the accuracy is 0.01°), the refractive index of water is 1.3310, the refractive index of diamond is 2.408, and the wavelength of the incident radiation is 654 nm.

2.1. Study of the Depolarized and Polarized Components of Scattered Light

In the DLS method, the incident radiation is normally polarized but the presence of depolarized component is also possible.

Thus, the intensity of the autocorrelation function of polarized scattered light can be represented as a discrete exponential decay that can be related to the coefficient of translational diffusion. The relaxation rate of such a regime can be represented in terms of the decay time of the autocorrelation function for the polarized component of scattered light [4]:

$$\Gamma_{vv} = D_t q^2. \quad (9)$$

The analysis of the polarized component of the scattered radiation can be used to study the translation diffusion of particles. A detailed analysis of the rotational dynamics necessitates the study of the depolarized component. The measurements of the depolar-

ized component of scattered radiation are often used for the study of parameters of relatively small colloid particles. In this work, the horizontally polarized scattered radiation (depolarized component) is measured using polarizer (*vh*).

The intensity of the autocorrelation function of the depolarized scattered radiation can be represented as a sum of two discrete exponential decays depending on the coefficients of translational and rotational diffusion, respectively [4]:

$$\Gamma_{vh} = D_t q^2 + 6D_r. \quad (10)$$

It was mentioned in [7, 8] that the polarized radiation can be used to characterize the translational diffusion coefficient. The rotational diffusion coefficient was disregarded. However, in this work, we numerically choose functions that determine translational (7) and rotational (8) diffusion for the kernel of integral equation (6) (Fig. 1). The results show that both translational and rotational diffusion must be taken into account for the vertically polarized radiation.

Based on expressions (4), (9), and (10) and numerical approximation, we represent the normalized field function for the polarized scattered radiation for monodisperse systems:

$$g^{(1)}(q, \tau)_{vv} = \exp(-q^2 D_t \tau) (1 + \gamma \exp(-6D_r \tau)),$$

$$g^{(1)}(q, \tau)_{vh} = \exp(-q^2 D_t \tau) \exp(-6D_r \tau).$$

Here, quantities D_t and D_r are given by expressions (7) and (8), respectively; *vv* is the polarized component; and *vh* is the depolarized component.

We consider the normalized field function for the polarized scattered radiation. Using expressions (6)

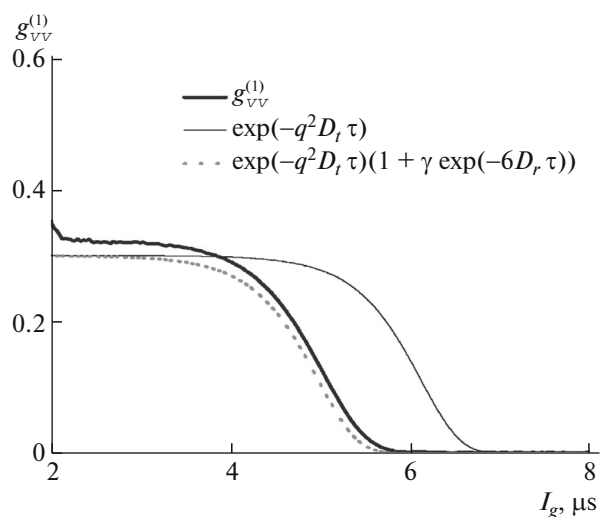


Fig. 1. Selection of functions that determine the translational and rotational diffusion for the kernel of the integral equation.

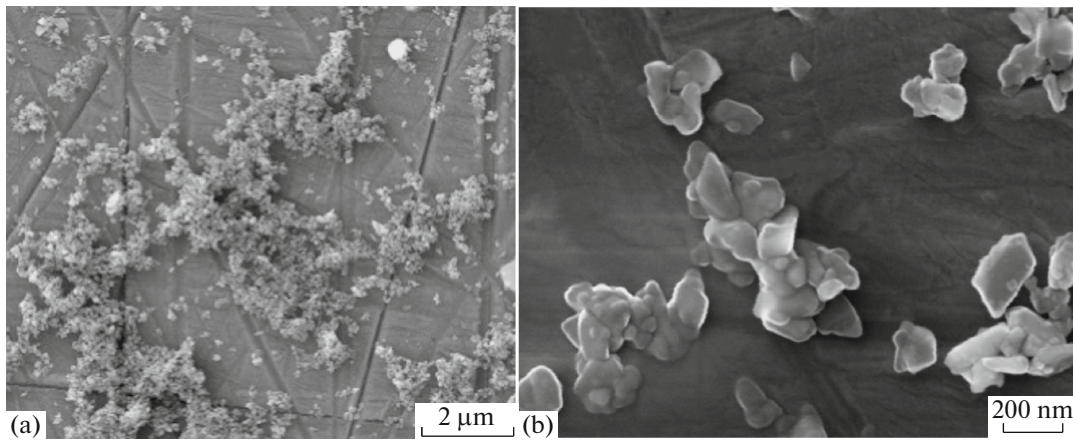


Fig. 2. Electron microphotographs of diamond particles that are obtained using transmission electron microscope at different resolutions.

and (7), we obtain the following formulas for polydisperse systems:

$$g^{(1)}(q, \tau)_{vv} = \int_{r_{\min}}^{r_{\max}} \exp(-q^2 D_r \tau) (1 + \gamma \exp(-6D_r \tau)) f(r) dr, \quad (11)$$

$$g^{(1)}(q, \tau)_{vh} = \int_{r_{\min}}^{r_{\max}} \exp(-q^2 D_r \tau) \exp(-6D_r \tau) f(r) dr, \quad (12)$$

where r_{\min} is the minimum size of particles, r_{\max} is the maximum size of particles, and γ is the coefficient related to the anisotropy of particles ($\gamma \approx 1.2$).

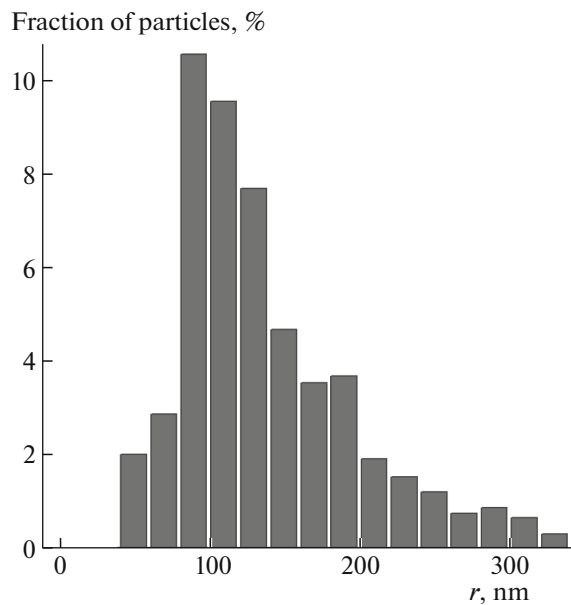


Fig. 3. Histogram that characterizes the size distribution of particles.

Note that Eq. (11) and (12) are the Fredholm integral equations of the first kind with respect to size distribution function of colloid particles $f(r)$.

For the dispersed system with a relatively low concentration of particles in the absence of interaction between particles when the secondary scattering by particles is relatively low, the experimental effect caused by external action on the system is normally determined by the sum of contributions of single particles and can be represented using expressions (11) and (12). We choose the wavelengths of the incident radiation in such a way that the oscillation character of the diffraction by particles is absent.

3. DETERMINATION OF THE SIZE DISTRIBUTION OF COLLOID PARTICLES

In this part, we consider the solution to integral equations (11) and (12) that makes it possible to determine size distribution function $f(r)$ for colloid particles using DLS for polarized and depolarized components. In such formulation, integral equations (11) and (12) are mathematically classified as ill-posed problems. Several methods can be used to numerically determine function $f(r)$ using Eqs. (11) and (12) but strict rules for the selection of solutions are missing. In our opinion, the Tikhonov regularization procedure [9, 10] must be preferred.

To determine the size distribution function of diamond particles, we preliminarily perform electron microscopy. Figure 2 presents the electron microphotographs of the samples at different resolutions and scales. Figure 3 shows the histogram that characterizes the size distribution for the dispersed phases under study. It is seen that the size of particles ranges from 50 to 300 nm.

Without violating generality and correctness of the formulation of the problem, we approximately con-

sider diamond particles as spheres in the first approximation.

Based on such an assumption, we calculate the scattering indicatrix of spherical particles (Mie problem) for the vertically polarized component of radiation with allowance for the multimodal distribution of the samples with respect to sizes and compare the result with the experimental curve that is obtained using the DLS method (Fig. 4).

The comparison of the curves shows good agreement of the theoretical and experimental results and, hence, proves the above hypothesis.

We consider the Fredholm integral equation of the first kind with smooth kernel $K(x, s)$:

$$Au \equiv \int_a^b K(x, s)u(s)ds = f(x), \quad x \in [c, d], \quad (13)$$

where $K(x, s) \equiv \exp(-q^2 D_r \tau)(1 + \gamma \exp(-6 D_r \tau))$ and $f(x) \equiv g^{(1)}(q, \tau)_{vv}$ or $K(x, s) \equiv \exp(-q^2 D_r \tau) \exp(-6 D_r \tau)$ and $f(x) \equiv g^{(1)}(q, \tau)_{vh}$, $u(s) \equiv f(r)$, $a \equiv r_{\min}$, and $b \equiv r_{\max}$.

We assume that $K(x, s)$ is a real function that is continuous in the rectangle $G = ([c, d] \times [a, b])$ and $f(x) \in L_2[c, d]$.

We also employ approximation $f_\delta(x)$ of function $f(x)$, such that $\|f(x) - f_\delta(x)\|_{L_2} \leq \delta$.

Based on the a priori assumptions, we suppose that $u(s)$ is a piecewise smooth function and choose $U = W_p^1[a, b]$. Let function $K(x, s)$ be changed by function $K_h(x, s)$, such that $\|K(x, s) - K_h(x, s)\|_{L_2(G)} \leq h$. Then, we have $\|A - A_h\|_{W_2^1 \rightarrow L_2} \leq h$, where A_h is an integral operator that corresponds to kernel $K_h(x, s)$.

Using the Tikhonov procedure for the construction of the regularization algorithm [9, 10], we proceed from expression (13) to the minimization of the smoothing functional

$$M^\alpha[u] = \|A_h u - f_\delta\|_{L_2}^2 + \alpha \|u\|_{W_2^1}^2 \rightarrow \min, \quad (14)$$

where

$$\|u\|^2 = \int_a^b u^2(s)ds, \quad \|u'\|^2 = \int_a^b (u'(s))^2 ds,$$

$$\|A_h u - f_\delta\|^2 = \int_c^d \left[\int_a^b K(x, s)u(s)ds - f(x) \right]^2 dx.$$

Then, expression (14) is represented as

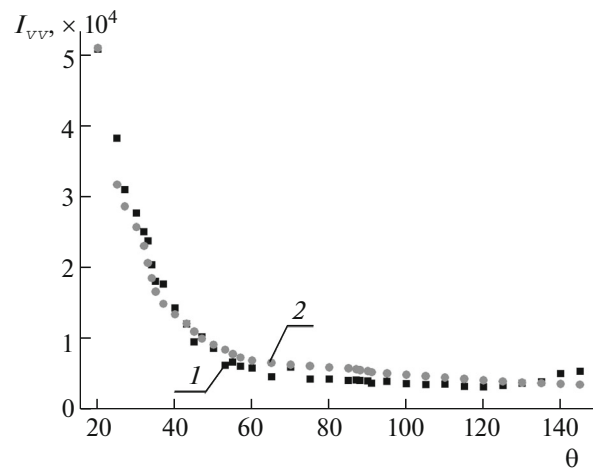


Fig. 4. Angular dependences of scattering for a spherical colloid diamond particle: (1) experimental curve that is obtained with the aid of DLS and (2) theoretical curve that is calculated using the solution to the Mie problem.

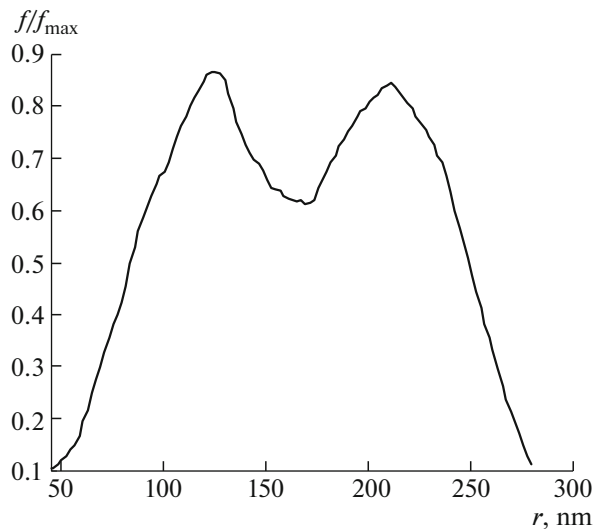


Fig. 5. Size distribution function of particles for the polarized field component.

$$M^\alpha[u] = \int_c^d \left[\int_a^b K(x, s)u(s)ds - f(x) \right]^2 dx + \alpha \left[\int_a^b u^2(s)ds + \int_a^b (u'(s))^2 ds \right] \rightarrow \min. \quad (15)$$

The Tikhonov condition [9, 10] follows from condition (15):

$$(A_h^* A_h + \alpha C)u^\alpha = A_h^* f.$$

Here, A_h is the operator from $W_2^1[a, b]$ to $L_2[c, d]$, A_h^* is the conjugate operator with respect to A_h , A_h^* is

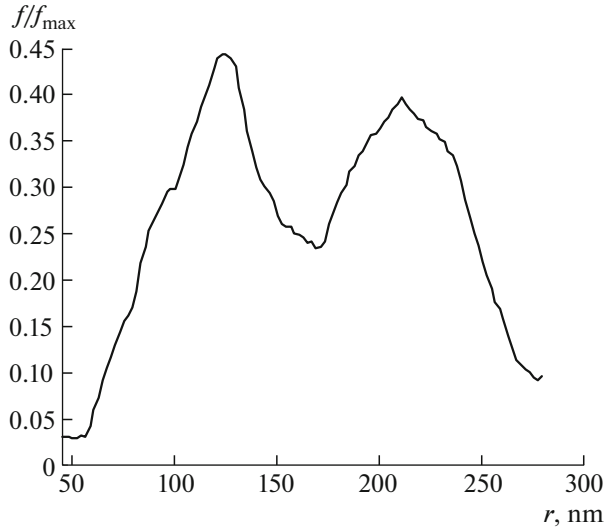


Fig. 6. Size distribution function of particles for the depolarized field component.

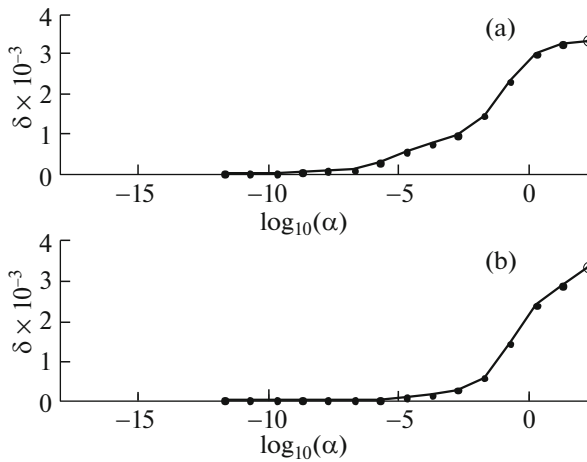


Fig. 7. Determination of the regularization parameter using the method of relative residual in the solution of the integral equation for (a) polarized component (the regularization parameter is 0.018557 and the residual is 0.0033444) and (b) depolarized component (the regularization parameter is 0.057204 and the residual is 0.0032044) at $h = 0.01$ and $\delta = 0.01$.

the operator from $L_2[c, d]$ to $W_2^1[a, b]$, and C is the operator the matrix of which is determined in [10].

In the above formulation, we consider operator A_h of the original integral equation that acts from $L_2[a, b]$ to $L_2[c, d]$ (i.e., the information regarding the smoothness of the exact solution is missing). Then, the smoothing functional is written as

$$M^\alpha[u] = \|A_h u - f_\delta\|_{L_2}^2 + \alpha \|u\|_{L_2}^2 \rightarrow \min$$

and the Tikhonov equation is represented as

$$(A_h^* A_h + \alpha E) u^\alpha = A_h^* f,$$

where E is the unity operator.

Figures 5 and 6 present the size distribution functions for polarized and depolarized components, respectively. In this case, the experimental autocorrelation function is approximated using a cubic polynomial for the vv polarization and the fifth degree polynomial for the vh polarization. Unknown coefficients a_i ($i = \overline{1,5}$) are determined using the least squares procedure.

The plots of the size distribution functions of the colloid particles show a possibility of aggregation of particles in the interval 150–250 nm. Such a possibility follows from the analysis of the histogram in Fig. 3, which was obtained using electron microscopy. The main peak of the histogram corresponds to the distribution maximum at a size of 100 nm. The TEM image (Fig. 2) also shows the formation of the low-density fractal-type nonlinear structures upon drying. Thus, we may assume that the second peak of the size distribution function corresponds to the aggregation of relatively small particles to large agglomerates.

Note that function u^α that minimizes functional (14) or (15) depends on regularization parameter α . The regularization parameter corresponds to coefficients h and δ , which characterize the accuracy of determination of the kernel of integral equation and experimental data. In practice, an increase in the noise in the experimental profile necessitates stronger smoothing to satisfy the a priori data regarding the smoothness. Therefore, it is important to determine the accuracy level of the experimental data and unambiguously determine the corresponding regularization parameter and, hence, solution u^α . To determine the regularization parameter that provides the optimal relation of the experimental results and a priori data, we employ the method of relative residual [10]

$$\|Au^\alpha - f\|/\|f\| = \delta. \quad (16)$$

Thus, expression (16) makes it possible to automatically determine the regularization parameter using the accuracy of the kernel of integral equation and experimental data (Fig. 7).

CONCLUSIONS

Size distribution functions of colloid particles are found using the DLS data. The experimental results are obtained with the aid of a Photocor Complex spectrometer for polarized and depolarized components of the scattered field. The numerical analysis yields good agreement of the experimental results and theoretical size distribution of particles in solution. The proposed approach can be efficient in the study of the DLS by colloids.

The systems under study and the method for the calculation of the sizes of particles can be extended to

the solutions of nanotubes, rigid-chain polymers, and suspensions of structures consisting of nanotubes and macromolecules. The experimental dependences will be represented as integral equations with different kernels and results of alternative physical experiments.

ACKNOWLEDGMENTS

We are grateful to the Department of Molecular Biophysics and Polymer Physics, Faculty of Physics, St. Petersburg State University (in particular, Prof. V.V. Voitylov, V.I. Rolich) for providing experimental facilities.

The authors gratefully acknowledge the assistance of the Interdisciplinary Resource Center for Nanotechnology of St. Petersburg State University.

REFERENCES

1. P. Zakharov and F. Scheffold, *Light Scattering Reviews 4* (Springer Praxis Books, Chichester, 2009), pp. 433–467.
2. Redouane Borsali and Robert Pecora, *Soft Matter Characterization* (Springer, Berlin, 2008).
3. D. A. Ivanov, Th. Grossmann, and J. Winkelmann, *Fluid Phase Equilibria* **228–229**, 283 (2005).
4. H. Matsuoka, *Colloids Surf., A* **109**, 137 (1996).
5. K. A. Anenkova, G. P. Petrova, V. V. Gibizova, L. A. Osminkina, and K. P. Tamarov, *Opt. Spectrosc.* **115**, 166 (2013).
6. W. Tscharnuter, in *Encyclopedia of Analytical Chemistry* (Wiley, Chichester–New York, 2000), pp. 5469–5485.
7. M. Hoffmann, S. W. Claudia, H. Ludger, and A. Wittemann, *ACS Nano* **3**, 3326 (2009).
8. D. Brogioli, D. Salerno, V. Cassina, S. Sacanna, A. P. Philipse, F. Croccolo, and F. Mantegazza, *Opt. Express* **17**, 1223 (2009).
9. A. N. Tikhonov and V. Ya. Arsenin, *Solutions of Ill-Posed Problems* (Halsted, New York, 1977).
10. A. N. Tikhonov, A. V. Goncharskii, V. V. Stepanov, and A. G. Yagola, *Numerical Methods for Solution of Ill-Posed Problems* (Kluwer Academic, Dordrecht, 1995).

Translated by A. Chikishev