Development of the method of laser Doppler spectroscopy of nanoparticles in liquids and implementation of the method in the LAD-079 spectrometer

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Abstract. In this work, a method for physicochemical and biological optical studies of the nanoparticles size distribution is developed. Its implementation in the LAD-079 spectrometer is described. The distinctive features of the LAD-079 spectrometer include the following. Multi-angle parallel measurements of static and dynamic light scattering, scattering angle from 0–180 degrees. Probing at three wavelengths with the ability to analyze the polarization activity of the sample (488 nm, 532 nm, 650 nm). Programmable precision thermostat with an error less than 0.1°C in the range 0 ± +80°C with the possibility of building and software implementation of the experiment plan. Robust monobloc design of the spectrometer that does not require adjustments and a special optical table. The ability to measure the size of dispersed nanoparticles in low-transparent liquids.

1. Introduction
The possibilities of studying and diagnosing complex structures in nanofluids are of great interest for mechanics, thermal physics, chemistry, and biology [1–4]. The obtained diagnostic information is especially promising for controlling such physical parameters of nanofluids as thermal conductivity, phase transitions, vortex formation, etc. The aim of this series of works was to create a method and systems for physicochemical and biological optical studies of nanoparticle size distributions and molecular weights of polymers and nanosized objects under conditions of a precision programmable thermostat.

The beginning of work on laser granulometry (determination of the size distribution of nanoparticles) of nanofluids was initiated by a comprehensive program of fundamental and applied research “Transport processes in nanofluids and flows in micro- and nanochannels” under the direction of Corresponding Member RAS Alekseenko S.V. In 2008, at the request of colleagues and with the support of Academician Grachev M.A., the program of import substitution of the Siberian Branch of the Russian Academy of Sciences and investments of Institute of optoelectrical information technologies, the corresponding methods were developed, implemented on a modern element base in laser Doppler spectrometers for the diagnosis of nanoparticles in solutions.

The operation of the semiconductor laser Doppler spectrometers-anemometers is based on a parallel multi-angle spectral analysis of the results of multibeam interference of laser radiation scattered by nanoparticles displaced due to Brownian motion in a thermostated liquid (the closest analogue is multichannel photon correlation spectroscopy). Measurement of the correlation functions of fluctuations of the scattered light intensity and integral scattering intensities in the given angular
spectra makes it possible to determine the diffusion coefficients of dispersed particles in a liquid, and, finding a solution to the inverse ill-posed problem, to calculate the spectrum of hydrodynamic sizes of nanoparticles in liquids and the molecular weight of polymer molecules. The size distribution of nanoparticles is calculated based on the analysis of diffusion coefficients in the framework of the Stokes-Einstein model. The range of measured sizes is in the range from nanometer to ten microns [5].

2. Method
The laser Doppler spectroscopy method based on the analysis of the autocorrelation function of laser radiation scattered at a certain angle.

Nanoparticles suspended in solution constantly participate in the Brownian motion of the medium, which causes microscopic fluctuations in their local concentration. These fluctuations lead to local inhomogeneities of the refractive index of the medium. When a laser beam passes through such a medium, some of the light will be scattered by these inhomogeneities. The fluctuations in the scattered light intensity will correspond to fluctuations in the local concentration of dispersed particles.

Information on the particle diffusion coefficient is contained in the time-dependent correlation function of intensity fluctuations. The time autocorrelation function, according to the definition, has the following form:

$$G(\tau) = \langle I(0) \cdot I(t-\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T I(t) I(t-\tau) dt$$

(1)

where $T$ is the integration time (the time of accumulation of the correlation function), $I(t)$ is the intensity of the scattered radiation. At $\tau = 0$, the autocorrelation function is equal to the root mean square intensity $<I^2>$, for long times there is no correlation, and the autocorrelation function is equal to the square of the average scattering intensity:

$$G(\tau) = \langle I(0) \cdot I(t-\tau) \rangle = \langle I(0) \rangle \cdot \langle I(t-\tau) \rangle = <I>^2$$

(2)

The relaxation of microscopic concentration fluctuations to an equilibrium state can be described by the diffusion equation:

$$\frac{\partial c(\vec{r}, t)}{\partial t} = -D \frac{\partial^2 c(\vec{r}, t)}{\partial \vec{r}^2}$$

(3)

where $c(\vec{r}, t)$ is the concentration and $D$ is the diffusion coefficient of particles. It can be shown that the autocorrelation function of the intensity decays exponentially with time and the characteristic relaxation time is uniquely related to the diffusion coefficient of particles $D$. The correlation function of the scattered light intensity is described by the following expression:

$$G(\tau) = a \cdot \exp\left(\frac{-2\tau}{t_c}\right) + b$$

(4)

where, in accordance with the solution of the diffusion equation, the inverse to the characteristic decay time of the autocorrelation function is

$$\frac{1}{t_c} = Dq^2$$

(5)

The wave vector of fluctuations of concentration $q$ is described by the expression:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

(6)

In expressions (4), coefficients $a$ and $b$ are experimentally determined constants, $n$ is the refractive index of the medium in which dispersed nanoparticles are weighed, $\lambda$ is the laser radiation wavelength, $\theta$ is the scattering angle.

The constants $a$, $b$, and $t_c$ are determined experimentally by approximating the obtained correlation function by the theoretical exponential function (4). Figure 2 shows an example of an autocorrelation function (in blue) and its approximation (in red). The x-axis is the time in seconds, the y-axis is the value of the functions.
Based on the experimental data obtained, the diffusion coefficient of particles in the solution is calculated. Further, using the Stokes-Einstein formula, the hydrodynamic radius of particles $R_\Gamma$ is calculated:

$$R_\Gamma = \frac{kT}{6\pi \eta D}$$

(7)

where $D$ is the diffusion coefficient of particles in a liquid, $\eta$ is the viscosity of the liquid, $T$ is the temperature, and $k$ is the Boltzmann constant.

Thus, a comprehensive analysis of formulas (1) – (7) reduces the calculation of the hydrodynamic radius of particles to solving the integral equation:

$$\int_{a}^{b} f(R) \exp\left(-\frac{kT}{R}\right) dR = g(t)$$

(8)

where the sought function $f \in \mathbb{R}$ specifies the particle size distribution on the interval $[a, b]$, $t$ is the correlation time $(0 < t < T)$,

$$k_e = \frac{(4n\pi / \lambda)^2 kT}{6\pi \eta} \sin^2\left(\frac{\theta}{2}\right)$$

$k_e$ is a constant depending on the parameters of the experiment, $g(t)$ is the value of the autocorrelation function obtained experimentally. From the physical properties of the experiment, it follows that the solution $f$ should be sought in the space of positive, smooth, convex functions.

It should be noted that the critical parameters in the dynamic light scattering method are the accuracy of determining the temperature, scattering angle $\theta$, and viscosity $\eta$. The error in determining the hydrodynamic radius of particles is related to the error in determining the temperature $\Delta T$ by the following formula:

$$\Delta R_\Gamma = \frac{k}{6\pi D} \left| \frac{\Delta T}{\eta} - \frac{\partial \eta}{\partial T} \cdot \frac{T \Delta T}{\eta^2} \right|$$

(9)

The main contribution to the error in determining the hydrodynamic radius is made by the term $\Delta T / T$, other terms can be omitted. It is convenient to write the error in determining the hydrodynamic radius in relative form:
\[ \delta R_t = \frac{\Delta R_t}{R_t} = \frac{\Delta T}{T} \] 

(10)

With a temperature measurement error of 0.1 °C, the relative error in determining the hydrodynamic radius of particles will not exceed 0.04%. To calculate the particle size distribution according to the autocorrelation function data in the presented spectrometers, the freely distributed CONTIN algorithm [6], implemented in the 70th by S. Provincher, is most often used. Various researchers have noted the shortcomings of this program. For example, particle size distributions obtained from polymodal solutions with particles of close sizes (in a ratio of 1:1.5–1:3), as well as wide distributions have a high error and do not correspond to the true nature of the sample under study. Together with the CONTIN program, developers often propose alternative versions of algorithms, the accuracy of which is no better than the CONTIN program. As a rule, such algorithms are designed for a narrow range of subproblems, such as the analysis of unimodal distributions.

3. Device realization

The semiconductor laser Doppler spectrometer-anemometer for diagnostics of nanoparticles in solutions LAD-079 was created in 2008. The spectrometer includes both hardware support for most of the known optical methods of information diagnostics and the implementation of new methods for laser diagnostics of nanoobjects in liquids.

The distinctive features of the laser Doppler spectrometer-anemometer for diagnostics of nanoparticles in LAD-079 solutions include the following:

1. Multi-angle parallel measurements of static and dynamic light scattering at angle from 0–180°.
2. Probing at three wavelengths with the possibility of analyzing the polarization activity of the sample.
3. Typical measurement time is from several seconds to several minutes.
4. Work with domestic and imported test tubes and cuvettes, small sample volume 0.5–1 ml, when using special micro cuvettes – up to 10 μl, compatibility with Malvern cuvettes.
5. Programmable precision thermostat with an error less than 0.1°C in the range 0 °C–+80°C with the possibility of building and software implementation of the experiment plan.
6. Precision silicon stable multichannel photodetector, operation under photon confinement conditions with a noise level close to the theoretical limit, providing the maximum measurement accuracy of nanoparticles.
7. Robust monobloc construction of the spectrometer, which does not require adjustments and a special optical table.
8. Possibility of measuring the size of dispersed nanoparticles in low-transparent liquids.
9. Original software for automated experiments with the possibility of developing and implementing new diagnostic methods.

4. Results

Below are the experimental results of granulometric measurements of some samples. Duke certified polystyrene particles (Dukescientific.com, ref. 3100A) with a size of 102 ± 3 nm were examined to test and calibrate the laser Doppler spectrometer. The solution has a concentration of 0.05%. The particles refract light well, the signal is strong in all channels, up to backscattering (162 degrees). The measurement method is dynamic light scattering. The data accumulation time for a single measurement is 1–5 seconds. The experiment time (accumulation of the results of single measurements) is 20–600 seconds. Measurement angle 90 degrees. The experiments were carried out at a sample temperature of 20°C.
**Figure 3.** Laser spectrometer of nanoparticles in liquid LAD-079 range 1 nm – 10 µm. 4 lasers at 3 wavelengths – 488 nm, 532 nm, 650 nm. 10 photodetectors, thermostat +5 ÷ +80°C, accuracy is better than 0.1°C

In figure 4 the result of processing the experimental data by the algorithm proposed by the author is presented. The resulting distribution corresponds to the expected 102 nm.

**Figure 4.** Results of experimental measurements of 100 nm standard Duke monodisperse polystyrene nanoparticles.

The paints of SUN Innovations were studied in order to introduce a laser Doppler spectrometer of nanoparticles in liquid LAD-079. Particles obtained by grinding the pigment in a bead mill were investigated to diagnose the quality of grinding of a pigment of a dye of solvent paints. Butyl glycol acetate (C8H16O3) at a concentration of 1:100 – 1:1000 was used as a solvent until a transparent colored solution was obtained. The viscosity of the solvent at 20°C was taken equal to 1.79 mPa·s, the refractive index – 1.414.

The measurement method is dynamic light scattering. The data accumulation time for a single measurement is 1–5 seconds. The experiment time (accumulation of the results of single measurements) is 20–600 seconds. The dimensions were measured at a scattering angle of 90 degrees. The sample temperature was maintained at 20°C. The measurement results were processed by the algorithm developed by the author and the CONTIN program[6].
Figure 5 shows the measurement results of GK-5 inks and conductive inks with silver salts, respectively. The results of the algorithm developed by the author are presented first (on the left) in the form of histograms. The CONTIN [6] subroutine results on the right as a smooth graph. X-axis - nanometers, Y-axis - the relative number of particles with a given size in arbitrary units.

![Figure 5. Particle distribution of SUN Innovations GK-5 paint in C8H16O3 solution. On the left are the results of the developed algorithm, on the right are the results of CONTIN[6]. The distribution shown in Figure 5 is bimodal. The main peak is wide – 250–500 nm, an additional peak is 50–150 nm. The research results obtained correspond to the expected ones and meet the requirements of SUN Innovations.](image)

Conclusions
A method of laser Doppler spectroscopy of nanoparticles in liquids for diagnostics and granulometry of nanofluids has been developed and implemented. The efficiency of the proposed method is experimentally confirmed by the successful performance of test measurements of reference nanofluids. Experiments on laser granulometry of many nanofluids, including polymers, inorganics, etc., have been performed in cooperation with specialists from a number of institutes of the SB RAS. The results of the device operation on calibration particles, organic and inorganic substances with polymodal and bimodal distribution, and the possibility of measuring the sizes viruses and other biological objects.

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