Features of coherent optical method for studies of nanoscale objects in liquid media

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Abstract

The possibility of measuring average size and mean-square movement value of nanoscale objects in liquid media by using optical correlation method with spatial averaging of the data on intensity distribution of scattered radiation was investigated and shown. The average size of TiO₂ nanoparticles in distilled water and vacuum oil solutions was determined by using the above-mentioned method.

Keywords: Optical correlation method, nanoscale objects, scattered radiation

1. Introduction

At present, dynamic light scattering (also known as photon correlation spectroscopy) is a popular technology for studying statistical and dynamical characteristics of the nanoscale objects in liquid media [1]. The technology is based upon time dependence of autocorrelation function of the scattered light intensity on characteristics of the scattering centers in the liquid media [2-3]. Despite the popularity of this method it has several disadvantages. For example, experimental studies can be carried out in a single point only and it takes a lot of time for full data acquisition, which is needed for time averaging; there are measurement errors in case of deficient laser beam calibration. In addition, this technology requires complex and expensive equipment and software [2-3].

By now speckle correlation method which uses spatial averaging of the data on intensity distribution of scattered radiation has been developed, and it is successfully used for processing of the signals of single fiber multimode interferometers [4].

It seems prospect to use this method for processing of the pattern of intensity distribution of the radiation scattered by nanoscale objects in the liquid media for the purposes of measuring of characteristics of nanoscale objects.

This method is distinguished by simplicity of signal processing required; moreover, standard CCD matrix and software only are needed.

Thus, the purpose of the work is to develop optical correlation method based upon spatial averaging of the data on distribution of the intensity of radiation scattered by nanoscale objects in liquid media and CCD usage for the studies of characteristics of the objects.

2. Approach description

Let us suppose that suspension contains nanoscale objects which are in Brownian motion. Laser (Fig. 1, 1) radiation with wavelength 630 nm is scattered by liquid media (2) with TiO₂ nanoparticles and at the output of a collecting lens (3) is registered by CCD matrix (5) with a PC (6). Let us assume that every particle which scatters incident radiation is a source of secondary spherical waves. Electric field will be the sum of electric fields of scattered (E_i) and non scattered (E_0) waves. In the focal plane of the lens (Fig. 1, 3) electric field of the scattered wave can be described as
\[ E_1 = \frac{\exp(-ikf_0 - ik \frac{x^2}{2f_0})}{f_0} \sum_{m} A_m \exp(ik \frac{\chi_{m} + \delta \xi_{m}(t)}{f_0} - i\varphi_m), \]  

where \( A_m \) - amplitude and \( \varphi_m \) - initial phase of the scattered wave, \( f_0 \) - focal length of the lens, \( \xi_{m} \) - initial coordinate of a nanoparticle, \( \delta \xi_{m}(t) \) - time dependence of the lateral movement of the nanoparticle, \( x \) - coordinate in the CCD matrix plane, \( k = \frac{2\pi}{\lambda} \) - wave vector, \( \lambda \) - radiation wavelength. Radiation intensity in the focal plane of the lens is also combined of intensities of scattered and non scattered waves.

We consider correlation properties of intensity of the scattered wave \( I_2(x) \). Let us suppose that every scattering particle moves to a random distance \( \delta \xi_n \), and amplitude \( A_m \) and initial phase \( \varphi_m \) of the scattered wave don’t change. Then intensity of the new scattered wave is

\[ \bar{I}_2(x) = \frac{1}{f_0^4} \sum_{n} \sum_{m} \sum_{s} \sum_{r} A_n A_m A_s A_r \exp \left( ik \frac{x(\xi_n + \delta \xi_n - \xi_m - \delta \xi_m) - i(\varphi_n - \varphi_m)}{f_0} \right), \]  

Correlation of intensities \( I_2(x) \) and \( \bar{I}_2(x) \) will be

\[ \overline{I_2 \bar{I}_2} = \frac{1}{f_0^4} \left( \sum_{n} \sum_{m} A_n A_m \right)^2 \]  

where \( \overline{\cdot} \) means spatial averaging. Considering speckle field as ergodic [5], one can find that only summands which have \( n = m, r = s \) and \( n = s, m = r \), give contribution to the sum (3) so

\[ G(t) = \overline{I_2 \bar{I}_2} = \frac{1}{f_0^4} \left( \sum_{n} \sum_{m} A_n^2 A_m^2 + \sum_{n} \sum_{m} A_n \delta \xi_n \right) \]  

where \( N \) – scattering centers amount. Considering shifts as being equally spaced within range from \(-\zeta\) to \(\zeta\) and going from summation to integration, we obtain

\[ \overline{I_2 \bar{I}_2} = \frac{I_0^2}{f_0^4} N^2 \left( 1 + \sin^2 \left( k \frac{x\zeta(t)}{f_0} \right) \right) = a + b \rho, \]  

where \( a,b \) - coefficients, \( \rho \) - correlation coefficient value [6] between \( I_2(x) \) and \( \bar{I}_2(x) \). It is easy to show that

\[ \overline{I_2^2} = \overline{\bar{I}_2^2} = 2 \frac{I_0^2}{f_0^4} N^2 \quad \text{and} \quad \overline{I_2} = \overline{\bar{I}_2} = \frac{I_0}{f_0} N \]  

Correlation coefficient value is

\[ \rho = \sin^2 \left( k \frac{x\zeta}{f_0} \right) \]
Value of the $\zeta$ in case of uniform law within range from $-\zeta$ to $\zeta$ is $\sqrt{3}$ times higher than value of mean-square shift of particles [6]. Symbolizing $\zeta$ as $\sigma$ and after substitution into equation (7) we obtain

$$\rho = \sin^2 \left( k \frac{\sqrt{3} x \sigma}{f_0} \right)$$  

(8)

For high values of the correlation coefficient dependence (8) virtually coincides with exponential one. Thus, by measuring correlation coefficient for different angle $\frac{x}{f_0}$ values on can obtain information about mean-square shifts of nanoparticles. According to the well-known Einstein-Smoluchovskiy equation [7], Brownian particle mean-square shift during the time $t$ is in direct proportion to diffusion coefficient $D$ and it follows that

$$\sigma^2 = 2Dt = \frac{RTt}{2\pi rN_A}$$  

(9)

where $r$ - particle size, $R$ – universal gas constant, $T$ – temperature, $\eta$ - viscosity, $N_A$ - Avogadro's number. Substituting equation (9) into (8) we obtain

$$\rho = \sin^2 \left( k \frac{\sqrt{3} x RT}{f_0 \sqrt{3\pi rN_A} t} \right)$$  

(10)

As it follows from the current equation rate of change of correlation coefficient between intensity distributions increases for areas which are more distant from the center of the pattern. Thus, by measuring correlation coefficient between intensity distributions and by using equation (10) one can measure average size of particles. According to equation (10) dependencies $G(t)$ (5) for particles of a 40 nm size in distilled water solution ($\eta = 10^{-3}$ Pa·c) and vacuum oil solution ($\eta = 47 \cdot 10^{-3}$ Pa·c) at $T = 293$ K for different angles $\frac{x}{f_0}$ values were calculated. The results obtained are shown in Fig. 3.

3. **Experimental studies**

Experimental verification of the results obtained was carried out by using the setup shown in Fig. 1.

![Fig. 1 Experimental setup.](image)

Typical pattern of the intensity distribution of the scattered radiation at the output of the cuvette is shown in Fig. 2. From equation (10) follows that different scattering angles cause different dependencies $\rho(t)$. It was required to divide the intensity distribution pattern into areas corresponding to different angles $\frac{x}{f_0}$. Numbers in Fig. 2 correspond to sequence number
of areas in the intensity distribution pattern within which calculation of the correlation coefficient is performed.

![Image of intensity distribution pattern](image)

**Fig. 2.** Pattern of intensity of the radiation scattered by $TiO_2$ nanoparticles.

Dependence (5) measurement results obtained for $TiO_2$ nanoparticles in distilled water are shown in Fig. 3, a; results obtained for $TiO_2$ nanoparticles in vacuum oil are shown in Fig. 3, b.

![Graphs showing G(t) dependencies](image)

**Fig. 3.** $G(t)$ dependencies measured when $\frac{x}{f_0} = 0.045$, curve 1; $\frac{x}{f_0} = 0.037$, curve 2; $\frac{x}{f_0} = 0.012$, curve 3, calculated dependencies shown with solid lines.

As it follows from the figures above, rate of change of correlation coefficient between intensity distributions increases for areas which are more distant from the center of the pattern. It coincides with the theoretical results obtained above.

Relying on experimental results and using the expression (10) average size of $TiO_2$ nanoparticles in solution was determined. The average nanoparticles size was discovered to be $\sim 50$ nm, it corresponded to particles size in calibrated solutions under study.

4. **Conclusion**

Thus, in this paper correlation method based upon spatial averaging of the data on distribution of the radiation scattered by nanoscale objects in liquid media and CCD usage for the studies of characteristics of the objects was described.
References


