Combined technique based on light scattering for investigation of the colloid's parameters

E A Savchenko¹, E K Nepomnyashchaya¹

¹Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya str., 29, St. Petersburg, Russia, 195251
e-mail: savchenko-spbstu@mail.ru

Abstract. The determination of colloid’s parameters is important issue in different fields of science and industry. The purpose of this work is investigation of the physical and dynamical parameters of colloid’s parameters. This paper offers new experimental setup of combined method based on light scattering techniques (dynamic light scattering and electrophoretic light scattering). Distinctive features of these methods are simplicity, informativeness, non-destructiveness and high accuracy of obtained results. Light scattering techniques are based on the correlation function of fluctuations of the intensity of scattered light calculation. The analysis of correlation function allows one to obtain the size distribution, translational diffusion coefficients and the molecular weight of biomolecules. In addition when an electric field is applied, we can determine electrophoretic mobility, zeta potential and the degree of intermolecular interaction directly in the liquid. In this paper, results of different types of colloid’s parameters are presented. The obtained results can be used, for example, in medical application for investigation of aggregation processes of proteins with nanoparticles (gold, magnetic, carbon and others), which may be useful in the diagnosis and treatment of various diseases.

1. Introduction
Currently, researchers have a great interest in studying the parameters of colloidal particles in aqueous solution due to their possible use in medicine, cosmetology, food industry, pharmaceuticals and other fields [1]. As is known, colloidal systems are mixtures of two or more components, in which discrete particles with size in at least one dimension from 1 to 1000 nm are distributed in another phase, usually continuous, different from the first in composition or aggregative state and referred to as dispersion medium [2-6]. The state of colloidal systems at any time is characterized by a set of qualitative and quantitative parameters. Liquid colloidal systems are characterized by a variety of state parameters, which are usually instable in time and with changing external conditions. At the same time, there are many methods to investigate the physical and dynamic parameters of liquid colloidal systems [3-9]. Figure 1 shows the main parameters of colloidal particles and methods for their study.
Figure 1. Parameters of colloidal particles and methods for their investigation.

Methods based on light scattering are the most common methods for studying the parameters of colloidal particles. In comparison with other methods (electrophoresis, optical and electron microscopy, Raman spectroscopy) methods of light scattering are [10]:

- simple (use the minimum number of elements of the optical scheme) [11],
- cheap (do not require expensive equipment),
- high-speed (signal pickup time is about one minute),
- informative (measurements simultaneously from 4 parameters) [12].

In this paper, a combination of two light scattering techniques is used: dynamic light scattering and electrophoretic light scattering.

2. Theory of the combined method of colloids investigation

The combined method of measuring parameters of colloids is based on measuring the correlation function of the intensity fluctuations of scattered light.

Scattered radiation is detected at the angle \( \theta \). The wave vectors of the incident and scattered radiation are denoted as \( k_0 \) and \( k_s \) respectively. The coordinates of the j-th diffuser are taken as the origin. The scattered light wave field is generally written as

\[
E_s(t) = \sum_j A_j e^{i\varphi_j} e^{-i\omega_0 t_j}
\]

where \( A_j \) – amplitude of scattered field by the j-th diffuser, \( \varphi_j = (k_0 - k_s)r_j = qr_j \) is the corresponding phase of the field.

The wave scattering vector \( q \) for the detected radiation will be equal to

\[
|q| = 2|k_0| \sin \left( \frac{\theta}{2} \right) = \frac{4\pi n_0 \lambda_0 \sin \left( \frac{\theta}{2} \right)}{\lambda_0}
\]

where \( n_0 \) – the refractive index of the medium (solvent), \( \lambda_0 \) is the wavelength of laser in vacuum.

Substituting the value of the field in the definition of the autocorrelation function for the field

\[
G^{(1)}(\tau) = \sum_j A_e^{-iqr_j(0)} \sum_j A_e^{-iqr_j(\tau)} > e^{-i\omega_0 \tau}
\]

In the absence of interaction between particles, the cross terms in the formula disappear and equation (3) is simplified to the form

\[
G^{(1)}(\tau) = N|A|^2 < e^{iqr(\tau)-r(0)} > e^{-i\omega_0 \tau} =
\]

\[
N|A|^2 e^{-i\omega_0 \tau} \int P(r, \tau) e^{iqr(\tau)} d^3r
\]

where \( P(r, \tau) \) is the probability of the particle to be in the position \( r \) at the time \( \tau \). In the approximation of spherical scatterers that do not interact with each other, equation (3) is simplified to the form...
\[ G^{(1)}(\tau) = N|A|^2 e^{-i\omega_0 \tau} \int P(r, \tau) e^{iqr(\tau)} d^3r = N|A|^2 e^{-i\omega_0 \tau} e^{-Dq^2 \tau} \]  

(5)

where \( D \) is the translational diffusion coefficient, which is responsible for the movement of a particle in space, is written in mm²/s. This simplification is possible, since the probability of finding a particle in position \( r \) for the described conditions satisfies the equation

\[ \frac{\partial P}{\partial \tau} = D \nabla^2 P \]  

(6)

Thus, we can write simplified expressions for the autocorrelation functions of spherical non-interacting scatterers, the dimensions of which are much smaller than the wavelength

\[ G^{(1)}(q, \tau) = A \exp(-Dq^2 \tau) \]
\[ G^{(2)}(q, \tau) = 1 + A \exp(-2Dq^2 \tau) \]  

(7)

where \( A \) is a certain constant determined by the concentration of scatterers, radiation intensity, etc.

In accordance with the Stokes-Einstein equation, the translational diffusion coefficient [13] is determined by

\[ D = \frac{kT}{6\pi \eta R} \]  

(8)

Here, \( \eta \) is the viscosity of the fluid, \( k \) is the Boltzmann constant, \( T \) is the temperature, and \( d \) is the size of nanoparticles.

The probability of finding a particle in position \( r \) at the time \( \tau \) when applying an electric field can be calculated using the following expression

\[ \frac{\partial P(r, \tau)}{\partial \tau} = D \nabla^2 P(r, \tau) \pm \theta \left( \frac{\partial P(r, \tau)}{\partial x} \right), \]  

(9)

where \( \theta \) is the velocity of the particles in the solution. The second term in the expression (9) can be either negative or positive, depending on the direction of the particle movement in an electric field. Expression (9) is solved using the Fourier transform [14-16]. The result will be the Gaussian distribution function

\[ P(r, \tau) = \left( \frac{1}{4\pi DT} \right)^{3/2} e^{-\left(\frac{x^2 + y^2 + z^2}{4DT}\right)}, \]  

(10)

Substituting expression (10) into (5) and taking into account that particles in electric field move to an oppositely charged electrode with a speed [17]

\[ \theta = \mu E, \]  

(11)

where \( \mu \) is the electrophoretic mobility, \( E \) is the strength of the applied field and it is possible to calculate the autocorrelation function [12]

\[ G^{(1)}(\tau) = N|A|^2 e^{-i\omega_0 \tau} e^{-iq\theta \tau} e^{-q^2 D \tau} \]  

(12)

In an electric field, the correlation function will be modulated by a cosine function, the frequency of which is determined by the electrophoretic mobility, and the damping rate is determined by the diffusion coefficient. The electrophoretic mobility in the case of a monodisperse solution can be calculated according to the relation [18-23]

\[ \Delta t = \frac{2\pi}{\mu q \cos \varphi / 2}, \]  

(13)

where \( \Delta t \) is the oscillation period of the autocorrelation function, the value of which can be found from the obtained experimental dependences, \( q \) is scattering vector, \( \varphi \) is the angle at which scattered radiation is recorded. The electrophoretic mobility of the particles is also calculated as the zeta potential on the base of the Smoluchowski theory, taking into account the introduction of corrections for the thickness of the double electric layer [23]

\[ \zeta = \frac{3\pi \mu}{2\varepsilon \varepsilon_0}, \]  

where \( \zeta \) – zeta potential, \( \varepsilon \) – permittivity, \( \eta \) – viscosity.

3. Experimental setup

In this paper, an experimental setup of a combined technique based on light scattering was developed. The experimental setup is shown in Fig.2.
Figure 2. The scheme of the combined experimental setup of measuring the parameters of colloidal particles: 1 — semiconductor laser $\lambda=650\text{ nm}$, 2 — lens, 3 — cuvette with electrodes, 4 — voltage source, 5 — diaphragm, 6 — photomultiplier, 7 — ACD converter, 8 — computer.

As a source of radiation, we used a solid-state laser module with the power 2.5 mW and 650 nm wavelength [24-26]. The diaphragm was used to narrow the laser beam. The radiation is focused by the aspheric short-focus lens built in the module on the cuvette with the test object, on the side faces of which are deposited electrodes. A constant voltage from a constant current source of various sizes was applied to the electrodes. The scattered radiation is registered under fixed angles and transferred to the photomultiplier by means of an optical fiber. The signal from the photomultiplier is digitized by the ADC converter at the frequency 50 kHz and processed with a computer.

To define the scattering angle we used the Mie theory [27-31]. Mie scattering of unpolarized light can be approximated by the following expression [27]

$$I(\theta) = I_0 \left[ \frac{3J_1(x)}{x} + \gamma \right]^2 \frac{1 + \cos^2 \theta}{2}$$

(15)

where $x = ka(1 + m^2 - 2m \cos \theta)^{1/2}$, $J_1 = (\sin x - x \cos x)/x^2$ — first-order spherical Bessel function of the first kind, $m$ — real relative index of diffraction, $a$ — radius of a single sphere, $k = 2\pi\lambda$ — wave vector, $I_0 = c\varepsilon_0 E_0^2 (m^2-1)^2 a^4 k^4 / 18 r^2$, $c$ — velocity of light, $\varepsilon_0$ — permittivity of a free space; $\gamma$ — parameter of approximation, which is necessary, when $ka>1$. For our experimental situation $\gamma$ can be chosen as a function $x^{-3/2}$.

In this work we demonstrated possibilities of developed combined method and setup on the example of microspheres with diameters of 0.97 μm. For these particles we calculated scattering indicatrix using Mie theory (figure 3).

Figure 3. Theoretical scattering curve, calculated for monodisperse microparticles with diameter of 0.97 μm.

As it can be noticed the best angles to detect scattering are 5-20°. At these angles we can provide maximum signal-to-noise ratio. In this work we choose the scattering angle equal to 10°.
4. Results
The silicon oxide spheres suspended in deionized water with diameter of 0.97 μm were used as a test sample. Fig. 4 shows the autocorrelation function calculated for the case of Brownian motion of microspheres and electric field of 5 V/cm.

![Figure 4](image)

**Figure 4.** Autocorrelation functions of monodisperse microparticles with diameter of 0.97 μm in electric field. (a) 0 V/cm; (b) 5 V/cm.

With the help of a special signal processing program that was developed in our laboratory [12], the following parameters were calculated: diffusion coefficient, hydrodynamic radius, electrophoretic particle mobility, and zeta potential. The obtained parameters are presented in table 1.

| Parameters               | Data calculated using a combined technique |
|--------------------------|--------------------------------------------|
| Diffusion coefficient    | $3.9 \times 10^{-12}$ m$^2$/s-V             |
| Hydrodynamic radius      | 0.508 μm                                   |
| Electrophoretic mobility | $1.4 \times 10^{-7}$ m$^2$/s-V              |
| Zeta potential           | 31.2 mV                                    |

5. Conclusions
The obtained results indicate the applicability of this method in studies of the physical and dynamic parameters of colloidal systems. Combining electrophoretic and dynamic scattering methods in one device, as well as high sensitivity (measurement of sample parameters with a percentage concentration of about $4 \times 10^{-3}$%), informativeness of the methodology (simultaneous measurement of four parameters) and quick analysis (measurement during one minute) create competition for existing commercially available instruments.

6. References
[1] Babick F 2016 Suspen. of Coll. Part. and Aggreg. 7
[2] Grebenikova N M, Myazin N S, Rud V Y, Davydov R V 2018 Proc. of the 2018 IEEE Int. Conf. on Electrical Engineering and Photonics p 295
[3] Nepomnyashchaya E K, Velichko E N, Aksenov E T and Bogomaz T A 2018 Proc. of Intern. Conf. Las. Opt. p 561
[4] Baranov M A, Klimchitskaya G L, Mostepanenko V M and Velichko E N 2019 American Physical Society 99 2
[5] Baranov M A, Alekseenko A P and Velichko E N 2018 J. Phys.: Conf. Ser. 1124 031018
Acknowledgments
This work is supported by State Assignment in science activity for universities (project № 3.5469.2017).