Advantages of the cross-correlation method for estimating nanoparticle sizes in suspensions

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Abstract. This article presents a cross-correlation method for estimation the size of nanoparticles in monodisperse colloidal solutions and suspensions. The original scheme of the experimental setup for carrying out cross-correlation experiments is presented. The results of measurements for a liquid sample with dispersed particles are presented for the cross-correlation method and the classical dynamic light scattering method, in which the autocorrelation function is calculated instead of the cross-correlation function of the scattering signals. The results obtained demonstrate the fact that for highly diluted samples, autocorrelation and cross-correlation produce the same result. Since the cross-correlation method is also applicable to turbid samples, this gives it a significant advantage over the dynamic light scattering method.

1. Introduction
The problem of estimating the size of dispersed particles in liquid media is relevant in many areas of production, quality control, medicine, etc. Among all existing methods for analyzing dispersed systems optical methods can be distinguished since they allow for remote studies without physical contact with the sample.

A convenient method for analyzing liquid samples is the method of dynamic light scattering. Currently, it is used for example in medicine to observe processes occurring in human blood plasma [1, 2]. But this method has the disadvantage that makes it is not applicable to turbid media investigation [3]. The need to dilute the sample can be a serious problem due to difficulties in selecting a solvent and changes in proteins interactions.

The cross-correlation method is based on dynamic light scattering. Coherent monochromatic radiation is scattered from nanoparticles in a cell with a sample without introducing perturbations. Considering that the cross-correlation method makes it possible to investigate even concentrated and turbid samples [3-5] it, possessing all the advantages of the method of dynamic light scattering, is more universal and can broader applicability limits.

The limitations of the cross-correlation method lie in the fact that the sample must be at least slightly transparent, and the dimensions of the diffusers must lie in the range from 1 nm to 10 μm [6].

2. Experimental setup
Scattered light is not coherent in nature. However, within a small angle, the single scattered light can still be considered coherent [7, 8]. Multiple scattering is incoherent and random. It is the single scattered light that carries information about the particle from which the laser radiation scattering occurred [9]. By calculating the cross-correlation function, we extract the single scattered light and suppress the contributions from multiple scattering.
Since the dynamic light scattering method uses one laser beam and one photodetector, it is not possible to suppress multiple noise scattering. Therefore, the dynamic light scattering method should be applied to sufficiently highly diluted samples [10, 11].

Figure 1 shows the scheme of the experimental setup which we developed for carrying out measurements by the cross-correlation method to study non-diluted samples. The method is based on the analysis of speckles formed as a result of laser radiation scattering from a random dispersed system, where the particles are in continuous chaotic motion. The speckle pattern is the result of coherent light scattering from particles. The character of the speckle pattern depends on the velocities of the particles which in turn depend on the size of the diffusers. The source of coherent monochromatic radiation is a semiconductor laser which is part of the laser module. The wavelength of the radiation is 650 nm. The lens built into the module helps to focus the laser beam in the sample volume where scattering is observed.

![Experimental setup](image)

**Figure 1.** Experimental setup. 1 — semiconductor laser module, 2 — beam splitter, 3 — collecting lens, 4 — scattering cell, 5 — multimode optical fibres, 6 — photomultiplier detectors, 7 — analog-to-digital convertor (ADC), 8 — computer.

The beam splitter divides one beam into two equal beams, which are focused by the lens (3) on the scattering volume in the cuvette. The scattering volume is formed by the intersection of two beams which have a waist in this region of space. The light scattered from the sample hits the input aperture of two multimode optical fibers that are connected to photomultiplier detectors [12]. The receiving ends of the optical fibers are located as close as possible to each other, so that the angle between the directions of reception of scattered light was as small [13].

Due to realized scattering geometry the obtained speckles are elongated in the vertical direction. Since the speckles of single scattered light are larger than the speckles of multiple scattered light, there is a higher probability that one single-speckle will hit the input aperture of both optical fibers at once [13].

The signals from photomultipliers are digitized by the analog-to-digital convertor (LCARD E20-10). It transmits the scattering data to a computer where the scattered light intensity normalized cross-correlation function is calculated. The use of the computer and ADC instead of the digital correlator made it possible to reduce the cost of the experimental setup and make it more compact and universal.

The calculated cross-correlation function is influenced by only by the single-scattered light because the same single scattering speckles can be received at once by two photodetectors due to the arrangement of optical fibers.

It is possible to improve the effectiveness of the cross-correlation method in several ways. First, the equality of the modules of the scattering vectors must be maintained, that is, the system of incident laser beams and the free ends of the optical fibers must be symmetrical with respect to the horizontal plane. Accurate alignment of setup elements will help to improve the quality of received signals. Second, it is possible to stabilize the measurement results by providing a mechanism for thermal stabilization of the sample. Third, depending on the degree of sample turbidity, it is possible to change
the path length of the rays inside the cuvette by shifting the cuvette [14]. That is why it is convenient to use in experiments a cuvette with a rectangular or square cross section, and not with a circular one.

3. Signal processing and results

We carried out measurements for aqueous solutions and suspensions with particles of different sizes and different concentrations. Figure 2 shows an example of experimental auto-correlation and cross-correlation functions graphs. We used rhodamine solution as a sample.

![Graphs of autocorrelation and cross-correlation functions obtained by processing the scattering signals from a solution of rhodamine.](image)

The graphs show that both functions are smooth and similar in shape. The method of dynamic light scattering which includes the analysis of the autocorrelation function is well developed and successfully applied to research, for example, in the field of medicine. The fact that the cross-correlation function coincides with the autocorrelation function gives great promise to the cross-correlation method. In our sample, the concentration of particles was low, and therefore the intensity of the multiple scattered light in the recorded signals was absent. In the case of large colloidal particles or a high concentration of scatterers, the method of dynamic light scattering will give incorrect results because of the strong noise associated with multiple scattering. The fact that we obtained such functions that are similar in form indicates that due to the presence of two laser beams and two photodetectors in the system and due to the selection of geometrical parameters of the setup, we were able to detect correct cross-correlation function.

The calculated cross-correlation function for a monodisperse system can be approximated by a curve, which is described by following expression [15].

\[ g_{12} = A \exp(-2K_1 \tau + K_2 \tau^2) \]  

(1)

here \( A \), \( K_1 \) and \( K_2 \) are fitting coefficients. The first cumulant \( K_1 \) is related to the diffusion coefficient \( D \) by formula

\[ K_1 = D q^2 \]  

(2)

The absolute value of the scattering vector \( q \) can be calculated in advance by the formula (3), if we know the refractive index of the solvent \( n \), the laser wavelength \( \lambda \) and the scattering angle \( \theta \).

\[ q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \]  

(3)
The hydrodynamic particle radius $r$ can be estimated from the Stokes-Einstein relation (4) [15], where $T$ is the absolute temperature, $k_B$ is the Boltzmann constant and $\eta$ is the solvent viscosity.

$$D = \frac{k_B T}{6 \pi \eta r}$$ (4)

Thus, choosing the fitting coefficients for the approximating curve, one can estimate the size of the particles in the liquid monodisperse sample.

4. Conclusions
The method of cross-correlation, as well as the method of dynamic light scattering, allows rapid analysis of liquid samples with particle sizes of the order of units or hundreds of nanometers. The autocorrelation approach is currently used in various fields and it is implemented in instruments. It is used for nanoparticle sizing in polydisperse samples or estimating the sizes in monodisperse samples. But since the method of dynamic light scattering cannot be used to study turbid media and the selection of a suitable solvent for diluting and increasing transparency can be difficult, the cross-correlation method is more relevant than ever.

Our idea is that the multiple scattering that occurs in turbid samples, creating the background noise for the useful signal, should be excluded from consideration by optimal selection of the experimental setup parameters and calculation of the mutual correlation function of two signals corresponding to intensity fluctuations at two different points of the speckle pattern instead of the autocorrelation function of a single signal. It remains only to apply the algorithm for processing the correlation function already developed for the method of dynamic light scattering [16-24].

At this stage of work, we selected angles and distances in our setup in order to increase the signal-to-noise ratio [21, 22]. In the future, it is planned to refine the cross-correlation method so that it can be used to accurately determine the size distribution of particles in liquid samples.

Acknowledgments
This work is supported by State Assignment in science activity for universities (project № 3.5469.2017).

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