On approximation and experimental accuracy in dynamic light scattering

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Abstract. The work is dedicated to estimation of accuracy of calculations in dynamic light scattering experiments, in particular approximation and size determination of nanoparticles in polydisperse solutions. In dynamic light scattering the proper approximation is crucial to final accuracy of sizes calculations, especially if we consider polydisperse solutions, such as biological fluids. Calculated and experimental errors have been compared.

1. Introduction
Dynamic light scattering is currently one of the few methods that allow non-destructive control of the size and shape of nanoparticles in liquids [1-4] and gases [5]. In this regard, dynamic light scattering and its modifications are widely used in industry [6], biology and medicine [7, 8]. It is much simpler then electron and atomic-force microscopes [9, 10], thought in comparison gives slightly less accurate results. Also it allows to determine concentrations and shapes of nanoparticles [11]. Industry uses devices by Malvern instruments, Photocor and others to determine sizes of nanoparticles in monodisperse solutions [12]. For biology and medicine it is important to determine size of nanoparticles in polydisperse suspensions, such as blood [7, 13, 14] or saliva [15].

For these type of applications we suggest the modification of standard dynamic light scattering device [16] and special algorithm of data analysis [12] presented in one hardware-software complex. In this work we analyze accuracy of the hardware-software complex in theory and experiment.

2. Experiment accuracy
In dynamic light scattering, the contribution to the noise component is generally made by laser radiation source [17, 18], photomultiplier and ADC [19]. The block diagram with main elements of the device is shown in figure 1.

We consider all noises of mentioned elements as additive, so it is possible to analyze them separately [20]. Final accuracy of the hardware-software complex depends on signal-to-noise ratio, discretization error and approximation validity.

Other elements, besides mentioned, also influence on measurement results. But we are going to consider their value to be insufficient. For instance, the light scattering in optical fiber should be mentioned only in case of long fiber [21, 22].
2.1. Laser instability
The laser instability caused by frequency and power fluctuations influence on the contrast of speckle pattern of scattering [23]. The more fluctuations, the less contrasting the speckle pattern will be [24]. This affects the signal-to-noise ratio in the recorded signal, since low contrast does not allow obtaining a high-intensity information signal [25, 26]. In previous works, it was shown that the signal-to-noise ratio in the detected signal affects the approximation error and, accordingly, the accuracy of the results [27]. To determine how the laser instability [28] influences the signal-to-noise it is possible to analyze it experimentally, which is done further.

2.2. Photomultiplier noise
A photomultiplier is characterized by different type of noises. The use of a photomultiplier in the conditions of a low signal makes it possible to achieve a high signal-to-noise ratio. The experiment uses a photomultiplier with a built-in amplifier and the following parameters. Control voltage 0.7 V, gain $10^5$, cathode radiant sensitivity 35 mA/W (on 650 nm), max dark current 10 nA, max average output signal current 100 µA.

Thus it is possible to calculate the minimum and maximum possible signal-to-noise ratio for the photomultiplier. In a real experiment, it is also necessary to take into account the background illumination, the level of which can be difficult to measure. In this regard, the signal-to-noise ratio for a particular experiment can be estimated as follows.

In the absence of a signal (switched off source of laser radiation), we register the voltage at the photomultiplier. In our experiment, the root-mean-square value of the voltage amplitude, recorded when the laser is off, was 5 mV. With the laser on and scattering on distilled water, the maximum recorded root-mean-square value of the voltage amplitude was 10 mV. In this value we include a laser instabilities as well.

Then we measure the scattering signal for a particular experiment. The average value of the voltage on the photomultiplier when the laser source is on corresponds to the signal value. In our case, the average value of the voltage in the study of the suspension was 120 mV. Thus, the signal-to-noise ratio was 21.6 dB, taking into account the presence of possible scattering of laser radiation on the circuit elements (cell, lenses).
2.3. **Analog-to-digital convertor error**

Errors in digitizing signals are related to the instrumental error of the analog-to-digital convertor. The quantization error depends on the number of ADC bits and for the device we use, the number of bits is 14 bits. The maximum detected voltage is 10 V, thus the quantization error = \( \frac{10}{2^{14}} = 0.61 \text{ mV} \), which is much less than noise level from the photomultiplier, so the quantization error can be neglected.

3. **Approximation error**

To analyze the accuracy of particle size measurements using the presented hardware-software complex, it is also necessary to take into account possible errors in the approximation. Analysis of the approximation error in model experiments for different signal-to-noise ratio was given in previous works [27]. It was shown that with a high signal-to-noise ratio, model signals are restored with an accuracy of close to 100%.

For the calculated signal-to-noise level within the framework of this work, the error of approximation for monodisperse solutions is 4%. As the number of components increases, the error also increases, and for 5 components it can achieve 20%. Nevertheless, this error is still very promising if we compare it with other dynamic light scattering spectrometers results [16].

4. **Experimental error and reliability assessment**

The accuracy of a real experiment in this work was estimated for a protein suspension with known size. We used protein albumin, which is a sphere with 6 nm diameter [29, 30]. The size distribution of albumin is shown in figure 2. The average size obtained in the experiment was 5.99 nm. The width of the distribution is ± 0.8 nm. Results are obtained by averaging a series of 10 experiments.

The theoretical width of the peak, taking into account the error, subject to unimodal distribution, should be ± 0.25 nm. The difference obtained in the experiment can be explained by the non-absolute equality of proteins in the test solution. We can admit that there are particles with sizes from 5.45 to 6.65 nm. In addition in this type of experiment we determine not real, but hydrodynamic radius of particles [31]. That can change the measured sizes two. Also aggregation [32] in time can possibly influence, but in this case it will change the central value of size distribution.

![Figure 2](image-url)  

**Figure 2.** Size distribution of protein nanoparticles in monodisperse suspension.
5. Conclusions

In this paper, we analyzed the accuracy of determining the size of nanoparticles in a liquid using the developed hardware-software complex. Separately, we estimated the signal-to-noise ratio in the hardware. The estimate of the approximation error was made using the results of previous model experiments and measured signal-to-noise ratio. It is shown that for the presented implementation of the scheme, the theoretical approximation error is 4% for unimodal distributions and 20% for solutions with 5 components. Due to the finite width of the particle size distribution (not the delta function), it is impossible to experimentally determine the exact value of the error. However, the accuracy of determining the distribution center was 0.15%. Thus, we can conclude that the real experimental error does not exceed the theoretically calculated value of 4% for monodisperse solutions. This promising result can be used for further modifications of the hardware-software complex to even further increase the signal-to-noise ratio and the accuracy for polydisperse solutions analysis.

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