Prospects of applying the elastic light scattering effect for the development of an optical method to the colloidal solutions diagnostic

M V Sapronov, N M Skornyakova

National Research University "Moscow Power Engineering Institute", Krasnokazarmennaya str. 14, Moscow, 111250, Russia

E-mail: maks-sapronov@yandex.ru, nmskorn@mail.ru

Abstract. In the paper the possibility of developing an optical method for colloidal solutions diagnostic based on elastic light scattering was investigated. The scheme of the experimental setup for light scattering indicatrix registration was presented, and the results of its work were demonstrated. The algorithm and the program of experimental data processing have been developed. Experimental light scattering indicatrices with 434, 546 and 656 nm wavelengths in a colloidal sulfur solution have been obtained. The scattering indicatrix models dynamics with changes in the scattering center size were presented. Qualitative comparison of the experimental and model results was carried out.

1. Introduction

The colloidal solution consists of dispersion medium and dispersed phase, which is suspended particles with the size in range from 1 to 1000 nm. The scope of application and use of colloidal solutions are numerous and diverse due to the unique nanoscale structures properties of the dispersed phase.

Traditionally, various colloidal solutions are widely used in medicine, pharmacology [1] and cosmetology. At the present stage of scientific and technical development substance nanoscale structures have been used in various narrow special areas. For example, on the basis of colloidal quantum dots receivers of thermal infrared radiation were developed [2], organic semiconductors for photovoltaic cells were created [3], colloidal nanoscale crystals of aluminum hydroxide AlOH are used for spectral radiation conversion [4], sulfur and carbon nanostructures are used for the production of lithium battery electrodes [5, 6, 7].

The challenges variety in which colloidal solutions are used requires qualitative and quantitative diagnostics methods of the colloidal solutions properties and parameters, such as the size, shape and concentration of the dispersed phase particles, the preparation time and the solution stability time. Among the existing diagnostic methods, the following are the most common. Nephelometry method [8, 9, 10], which allows to measure the dispersed phase concentration in a colloidal system based on the scattered light intensity measurement in it, optical [11] and electron [12] microscopy methods used to determine the nanometer-sized particles size and shape, a method based on dynamic light scattering, which is used to search for the size of nanoparticles [13, 14]. It should be noticed that these methods don't allow simultaneous concentration and size of the nanostructures measurement, in the present time, this is the most frequently used methods combination based on scattering G. the Mi and analytical ultracentrifugation [15, 16].
This paper discusses the prospects of using the elastic light effect to develop a method that will determine the particle size of the colloidal solution dispersed phase. The relative angular distribution of the scattered light intensity the scattering indicatrix is supposed to be used as the measured informative parameter.

2. Methodology

2.1. The experimental setup
For the light scattering indicatrix experimental determination by the colloidal solution dispersed phase, a model of the setup was developed; the scheme is shown in figure 1.

![Figure 1. The experimental setup scheme: 1 – cylindrical vessel with the investigated medium, 2 – the lens system, 3 – light source, 4 – matrix photodetector, 5 – movable rod, 6 – light filter.](image)

The incoherent light source (3) is a light-emitting diode lamp, which is placed in a light-tight housing with a round shape single outlet and adjustable size. The source spectral power density (3) has three maxima located in the blue, green and red regions of the visible spectrum. A narrow probing light beam is formed by the lens system (2) and directed to a cylindrical vessel (1) with colloidal solution of sulfur in water.

Recording of the scattered radiation is carried out on a camera (4) Nikon 1J5 [20]. The camera is mounted on a rod (5), which can rotate around the cylindrical vessel axis, with the optical axis of the lens crosses the axis of the vessel at any position of the rod. The lens focal length is chosen so that the image plane contains the axis of the cylindrical vessel. The experimental setup also provides a holder for band-pass filters (6), due to which the spectral selectivity of the detected light is provided. Three light filters with the maximum transmittance $\lambda_1 = 656 \text{ nm}$, $\lambda_2 = 546 \text{ nm}$, $\lambda_3 = 434 \text{ nm}$ wavelengths are provided for.

2.2. The experiment methodology
Previously, it was necessary to find the ratio between the values of the probing radiation spectral power density at wavelengths corresponding to the used light filters ($\lambda_1 = 656 \text{ nm}$, $\lambda_2 = 546 \text{ nm}$, $\lambda_3 = 434 \text{ nm}$). At first the light source images in the scattering medium absence through each of the filters were recorded, and then for each image the average pixel brightness was calculated. The obtained brightness values were used as normalization coefficients, taking into account the difference in the probing beam spectral power density, the photo detector sensitivity and the transmittance coefficients of light filters at different wavelengths.
At the experiment main stage, a colloidal solution was produced. For this, in 200 ml of distilled water H$_2$O was added 0.2 g sodium thiosulfate Na$_2$S$_2$O$_3$, there was a usual salt solution. Then 0.5 ml of 12% hydrochloric acid solution HCl was added to the obtained solution. After some time, sulfur began to be released in the suspended molecular clusters form – the dispersed phase, and the solution began to become cloudy.

The scattering indicatrix recording technique was to obtain a series of the digital probing beam images in scattered light at different camera positions. The light filter was placed in the holder, the camera was installed in such a way that the axis of the lens coincided with the axis of the probing radiation formation system. This position of the camera was taken as the reference angle beginning of the rod rotation. Then a series of images was recorded, in which each next frame differed from the previous one by that the rod with the camera rotates around the axis of the cylindrical vessel by five degrees clockwise from the start of the reference. A similar series of images was obtained with each of the three filters. All measurements were carried out in the external lighting absence. The dynamics of experimental probing beam images in scattered light with wavelengths $\lambda_1 = 656$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 434$ nm with increasing rod rotation angle is shown in figures 2-4, respectively.

2.3. The experimental results processing
First of all, the radiation source images were processed and the normalization coefficients of the scattered light relative intensity for different wavelengths were determined. The cylindrical vessel with the colloidal solution has an optical force and the scattered light refraction occurs on the vessel surfaces. The scattered radiation doesn't change its propagation direction after leaving the vessel, if it falls on its side wall normally. Therefore, only the part of the experimental image that contains the vessel axis was processed. In such area of each experimental image, the average pixel brightness was calculated, which is proportional to the scattered radiation intensity. The average value of the pixel brightness, taking into account the corresponding normalization factor, was compared with the rod rotation angle with the camera, at which the processed frame was obtained. After processing all the series images, light scattering indicatrix of certain wavelength is obtained.

3. Results
In the course of the experiment, after 30 and 60 minutes from the producing of the solution has been obtained three series of the probing beam images in scattered light, all three series were done with different filters. As the processing result of experimental images the scattering indicatrix presented in figures 5 and 6 were constructed.

The rod rotation angle with the camera when receiving each next shot in the series was chosen equal to 5 degrees. The constructive features of the setup allowed measurements in the angle range from 10 to 160 degrees, so the scattering indicatrices in figures 5 and 6 aren't closed and have two discontinuities.

4. Direct problem solution of elastic scattering in the framework of the G. Mi theory
The modeling 2D and 3D light scattering indicatrix program in the framework of G. Mi theory was developed by the authors [17, 18, 19]. It allows obtaining the scattering indicatrix of monochromatic unpolarized or linearly polarized radiation in dielectric or slightly absorbing spherical particles.

The particle shape limitation can be attributed to the calculating disadvantages of the scattering by the G. Mi formulas, but this calculation method has a significant advantage. The set of values that can take the initial data (the relative complex refractive index $m$ and the radius $r$ of the particle, the wavelength of the probing radiation $\lambda$) is practically limited only by the computer computational resources. The use of other methods for solving the direct problem of elastic light scattering is limited by the initial data permissible values. At the expense of the G. Mi theory noted advantage received program were universal, allowing to trace the light scattering dynamics when changing the relative size of $x = 2\pi r/\lambda$ or the particles refractive index in a wide range.

The scattering indicatrix 2D-models dynamics of nonpolarized monochromatic light for three wavelengths $\lambda_1 = 434$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 656$ nm on a particle with the relative refractive index $m = 1.532$ when changing its radius $r$ in the range from 1 to 11 nm is shown in figure 7, in the range
from 11 to 22 nm – in figure 8, in the range from 22 to 33 nm – in figure 9, in the range from 50 to 90 nm – in figure 10 and in the range from 100 to 245 nm – in figure 11.

**Figure 2.** Dynamics of the experimental probing beam images in scattered light with 434 nm wavelength (avi file).

**Figure 3.** Dynamics of the experimental probing beam images in scattered light with 546 nm wavelength (avi file).

**Figure 4.** Dynamics of the experimental probing beam images in scattered light with 656 nm wavelength (avi file).
Figure 5. Experimental light scattering indicatrices with wavelengths $\lambda_1 = 434$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 656$ nm by colloidal sulfur particles 30 minutes after the solution was produced: a) in a grid with conventional scale; b) in a grid with logarithmic scale.

Figure 6. Experimental light scattering indicatrices with wavelengths $\lambda_1 = 434$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 656$ nm by colloidal sulfur particles 60 minutes after the solution was produced: a) in a grid with conventional scale; b) in a grid with logarithmic scale.
Figure 7. Two-dimensional light scattering indicatrix models with wavelengths $\lambda_1 = 434$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 656$ nm on a particle with the relative refractive index $m = 1.532$ when changing its radius $r$ from 1 to 11 nm: a) in a grid with constant scale; b) in a grid with variable scale (avi file).

Figure 8. Two-dimensional light scattering indicatrix models with wavelengths $\lambda_1 = 434$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 656$ nm on a particle with the relative refractive index $m = 1.532$ when changing its radius $r$ from 11 to 22 nm: a) in a grid with constant scale; b) in a grid with variable scale (avi file).
Figure 9. Two-dimensional light scattering indicatrix models with wavelengths $\lambda_1 = 434$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 656$ nm on a particle with the relative refractive index $m = 1.532$ when changing its radius $r$ from 22 to 33 nm: a) in a grid with constant scale; b) in a grid with variable scale (avi file).

Figure 10. Two-dimensional light scattering indicatrix models with wavelengths $\lambda_1 = 434$ nm, $\lambda_2 = 546$ nm, $\lambda_3 = 656$ nm on a particle with the relative refractive index $m = 1.532$ when changing its radius $r$ from 50 to 90 nm: a) in a grid with constant scale; b) in a grid with logarithmic scale (avi file).

Conventionally, three particle sizes ranges can be distinguished, for each of which the scattering features have significant differences. When the particle is small ($x \ll 1$), we talk about the light elastic scattering in the Rayleigh approximation. This case corresponds to the scattering indicatrix in figures 7...
and 8. Presented in figures 9 and 10 of the scattering phase function correspond to the Rayleigh–Gans approximation \((x \sim 1)\), the features of which can be attributed to the pronounced scattering forward and the emergence of a small number the interference of the "petals" in the scattering phase function. Figure 11 shows the scattering indicatrices corresponding to the approximation of large particles \((x >> 1)\), when the interference of scattered light is manifested in the form of a significant maxima and minima number in the angular intensity distribution. The number of interference "petals" increases with increasing particle radius.

![Figure 11](image.png)

**Figure 11.** Two-dimensional light scattering indicatrix models with wavelengths \(\lambda_1 = 434\) nm, \(\lambda_2 = 546\) nm, \(\lambda_3 = 656\) nm on a particle with the relative refractive index \(n = 1.532\) when changing its radius \(r\) from 100 to 245 nm in a grid with logarithmic scale (avi file).

5. Discussions

The size increase of the colloidal sulfur particles over time after the solution was produced should have caused a change in the scattering indicatrix shape. Indeed, the light scattering nature of different wavelengths after 30 (figure 5) and 60 (figure 6) minutes after the solution was produced is different. Figure 5 shows that in the entire angles range at which measurements were made, the light with 546 nm wavelength experiences the greatest scattering, and the light with a wavelength of 656 nm undergoes the least scattering. From the figure 11 it can be seen that at angles from 10 to 50 degrees, light with a wavelength of 656 nm is more scattered, and light with wavelengths of 434 and 546 nm is scattered weaker, at angles from 85 to 160 degrees, the intensity of the scattered light at each wavelength differs slightly. Shown in figure 10 the scattering phase function doesn't have intersection points, while the scattering phase function in figure 11 cross each other.
The light scattering indicatrix shape of different wavelengths in each of the figures 10 and 11 is also different. But all the curves have common features: a pronounced maximum in the "forward" direction; a dip near the angle of 100 degrees. The "petals" at the experimental distributions aren't available, but the interference effects are manifested in the fact that most of the scattering light isn't experiencing the shortest wavelength, which is scattering characteristic in the absence of interference phenomena. All these features indicate the scattering in the Rayleigh-Gans approximation, qualitatively the experimentally obtained scattering phase function correspond to the models presented in figure (10).

6. Conclusion
On the comparison basis of experimental and calculated light scattering indicatrices it was concluded that their qualitative coincidence, which means that the elastic light scattering phenomenon can be used to develop an optical method for the diagnosis of colloidal solutions.

The paper shows the difference between experimental light scattering indicatrix with different wavelengths on the same particle system, as well as their change over time. Provided that the wavelengths of the detected scattered light are known, the scattering indicatrix can be used as measured informative parameters to determine the scattering particles size. If on the basis of the considered experimental scheme to produce an automated system for measuring the scattering indicatrix, it will be possible to trace the dynamics of the scattering indicatrix in time and, based on it, to determine the preparation time and the stability time of the colloidal solution.

Acknowledgments
The work was supported by the Ministry of higher education and science of the Russian Federation (project 3.8009.2017/BCh).

References
[1] Wongmekiat A, Tozuka Y, Moribe K, Oguchi T and Yamamoto K 2007 Chem. and Pharmac. Bull. 5 359-363
[2] Hafiz S, Scimeca M, Sahu A and Ko D-K 2019 Nano Converg. 6 1
[3] Luo K, Wu W, Xie S, Jiang Y, Liao S and Qin D 2019 Appl. Sci. (Switzerland) 9 1885
[4] Kim M, Lee D, Woo H-Y, Kim T-H, Paik T and Kim K-S 2019 Materials and Design 175 107800
[5] Zheng G, Yang Y, Cha J, Hong S S and Cui Y 2011 Nano Lett. 11 4462-67
[6] Guo J, Xu Y and Wang C 2011 Nano Lett. 11 4288-94
[7] Ji L, Rao M, Aloni S, Wang L, Cairns E J and Zhang Y 2011 Energy and Envr. Sci. 4 5053-59
[8] Jakuneej U, Dnan Y, Morrison R, Beckett R, McKinnon I and Grudpan K 2003 Analytical Sci. 19 1495-98
[9] Matsuzaki K, Murase O, Sugishita K, Yoneyama S, Akada K, Ueha M, Nakamura A and Kobayashi S 2000 Biochimica et Biophysica Acta – Biomembranes 1467 219-226
[10] Gimeno-Furio A, Hernandez L, Navarrete N and Mondragon R 2019 Renewable Energy 140 493-500
[11] Attota R, Kavuri P P, Kang H, Kasica R and Chen L 2014 Appl. Phys. Let. 105 163105
[12] Boyd R D, Gunnarsson R, Pilch I and Helmersson U 2014 J. of Phys.: Conf. Series 522 012065
[13] Beliciu C M and Moraru C I 2009 J. of Dairy Sci. 92 1829-39
[14] Nobbmann U and Morfesis A 2009 Materials Today 12 52-54
[15] Mächtle W 1999 Biophysical J. 76 1080-91
[16] Lechner M D 2005 J. of the Serbian Chem. Society 70 361-369
[17] Saponov M V and Skornyakova N M 2017 Scientific Visualization 9 42-53
[18] Saponov M V and Skornyakova N M 2017 Optical Methods of Flow Investigation: Proc. XIV Sci.-Tech. Int. Conf. (Electronic Materials) (Moscow: «Pero») pp 243-250