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# Study of interaction of laser radiation with scattering liquid media under conditions of a varying size distribution function of suspended particles

I.N. Shiganov, D.M. Melnikov, M.A. Yakimova

*Abstract.* **We report a study of laser radiation transfer processes in scattering media with a time-varying particle size distribution function. We consider the cases of a one-component solution, when the crystal growth occurs during freezing, and a solution with the addition of particles with a time-constant size. The results of the experimental validation of the developed mathematical model are presented. The possibility of using the obtained results to experimentally determine the concentration of metal particles in scattering liquids is considered.**

***Keywords:*** *light scattering, crystallisation, nephelometry, multicomponent scattering media.*

## 1. Introduction

A significant number of papers is devoted to the problems of propagation of laser radiation in scattering media [1–4]. As a rule, substances are considered whose properties are independent of time. However, in many cases, it is required to describe the radiative transfer process under varying physical, chemical and optical parameters of a medium.

In this paper, we study light scattering in a medium of scattering particles with a time-varying size by the example of solutions in which the crystal growth occurs during freezing. We also consider the case when the medium also has scattering centres whose size does not change with time. To describe the process of light scattering, we use a mathematical apparatus of Mie theory jointly with the Johnson–Mehl–Avrami–Kolmogorov theory. The scattering coefficient is thus a complex function whose argument is a time-dependent function describing the particle size.

The results can be applied both to study properties of a medium in the process of freezing and to improve the accuracy of rapid nephelometric analysis of substances. The use of liquid freezing in nephelometric studies is aimed at increasing the accuracy of rapid measurements (impurity concentration) and expanding the potential of the method for determining the performance properties of media. Increased accuracy is achieved due to the fact that the impurity concentration is calculated over the entire range of cooling temperatures, after which a series of the measurements obtained is appropriately processed.

**I.N. Shiganov, D.M. Melnikov, M.A. Yakimova** Bauman Moscow State Technical University, 2-ya Baumanskaya ul. 5, Bld. 1, 105005 Moscow, Russia; e-mail: daenoor@gmail.com

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The purpose of this paper is to test the possibility of using the method of laser nephelometry for investigation of scattering solutions in the process of their freezing at different parameters of impurity particles, as well as to determine the concentration of the added impurity.

Some adopted approximations make the mathematical model quite simple and convenient for determining the concentration of particles in a substance. A series of experiments is performed to test the suitability of the proposed mathematical model.

## 2. Theoretical study

In the simulation, we considered the following situation. A narrow collimated laser beam is incident along the normal onto a plane-parallel thin layer of the substance in question. The field of view of the radiation detector is limited by the diaphragm, due to which only the directly transmitted light and the light singly scattered in the forward direction are recorded. In this case, the intensity of the transmitted light can be determined using the Bouguer–Lambert–Beer equation in which the absorption coefficient is replaced by the extinction coefficient [1].

Attenuation of light was calculated for a sample, in which dispersed particles, i.e. crystals, grow upon cooling, and for a sample, in which apart from crystals there are other particles with the time-independent size, i.e. metal particles.

It is essential that the cross-sectional area of the laser beam incident onto the sample is sufficiently small so that it was possible to ignore the edge effects associated with a more intense growth of the crystals in the peripheral regions of the sample.

Simulation of a single-particle light-scattering coefficient was performed using Mie theory [2–4].

For a thin layer of a material, the intensity of the light transmitted through a scattering medium can be represented in the single-scattering approximation as

$$I = I_0 \exp(-lK_{\text{ext}}), \tag{1}$$

where $I$ is the intensity of the transmitted light; $I_0$ is the intensity of the incident light; $l$ is the optical thickness of the layer; and $K_{\text{ext}}$ is the extinction coefficient.

According to Mie theory, the scattering cross section of a single particle is found from the expression [4]

$$C_{\text{sct}} = \frac{2\pi}{k^2} \operatorname{Re} \sum_{j=1}^{\infty} (2j+1)(a_j + b_j), \tag{2}$$

where $k$ is the wave number; and

$$a_j = \frac{m\psi_j(mx)\psi_j'(x) - \psi_j(x)\psi_j'(mx)}{m\psi_j(mx)\xi_j'(x) - \xi_j(x)\psi_j'(mx)}, \quad (3)$$

$$b_j = \frac{\psi_j(mx)\psi_j'(x) - m\psi_j(x)\psi_j'(mx)}{\psi_j(mx)\xi_j'(x) - m\xi_j(x)\psi_j'(mx)} \quad (4)$$

are the scattering functions. The functions in (3), (4) are determined from the relations

$$\psi_j(x) = xJ_j(x), \quad (5)$$

$$\xi_j(x) = xH_j(x) = x[J_j(x) + \mathrm{i}Y_j(x)], \quad (6)$$

$$m = n - \mathrm{i}\chi, \quad (7)$$

where $m$ is the complex refractive index of a substance; $n$ is the refractive index; $\chi$ is the absorption coefficient; $J_j(x)$ is the Bessel function of the first kind; $Y_j(x)$ is the Bessel function of the second kind; $H_j(x)$ is the Hankel function of the first kind;

$$x = 2\pi rm/\lambda; \quad (8)$$

and $r$ is the particle size.

The extinction coefficient for a group of particles has the form

$$K_{\mathrm{ext}} = N_0 \int_0^\infty C_{\mathrm{sct}}(r)g(r)\,\mathrm{d}r, \quad (9)$$

where $N_0$ is the concentration of crystalline particles in a layer; and $g(r)$ is the normalised density ($\mathrm{cm}^{-1}$) of the particle size distribution in the layer, which in this case is a function of time. In the calculations, the particle size distribution is assumed to be Gaussian.

The concentration of crystalline particles in the sample can be calculated as a ratio of the fraction of a crystallised volume to a volume of the sample involved in the attenuation of the beam. It depends on the cooling rate, composition and structure of the substance. For media with a complex chemical composition, there may be several freezing mechanisms [5]. In this paper we investigate only the crystallisation mechanism with a uniform growth of seeds prevailing in these substances. In this case, the crystal growth in a medium can be described by the classical Johnson–Mehl–Avrami–Kolmogorov scheme, according to which the fraction of the crystallised volume $q(t)$ is given by [6]

$$q(t) = \exp\left[-\int_0^t U(t')\,V(r(t,t'))\,\mathrm{d}t'\right], \quad (10)$$

where $t$ is the current point in time; $t'$ is the time corresponding to the beginning of the cooling process; $U(t')$ is the intensity ($\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$) of the appearance of a new phase (number of crystals) per unit volume of an uncrystallised medium per unit time, generally depending on time; and $V(r(t,t'))$ is the volume of an isolated seed of size $r$ emerging at a time $t'$ and at a time $t$.

This model adequately described the sample freezing process if the following conditions are met:

– due to the small thickness of the cell, the temperature gradients arising from the influence of its walls are small and the sample parameters can be considered constant in the volume filled with a light beam;

– the volume of the medium is small enough to considered the intensity of the appearance of crystals $U(t)$ constant over time and to assume that all the crystals originated at a time $t_0$;

– at a minimum temperature observed in the experiments the fraction of the solid phase is small, and therefore the interaction of crystals with each other and with the cell can be ignored;

– the shape of the crystals is the same and is independent of time;

– the light interacts only with the sample area remote from its side faces, and therefore the size of the crystal is a function of time and does not depend on the spatial position of the particles;

– metal impurities are not the centres of the crystal growth; and

– geometrical parameters of metal particles do not change with decreasing temperature.

The intensity of the appearance of the crystals, $U$, is given by [7]

$$U = \frac{v_{\mathrm{cool}}}{V_{\mathrm{sm}}\,T_0}, \quad (11)$$

where $v_{\mathrm{cool}}$ is the sample cooling rate ($^\circ\mathrm{C\ s}^{-1}$); $V_{\mathrm{sm}}$ is the volume of sample that interacts with the light; $T_0$ is the initial temperature.

The volume of the isolated crystal is determined by the formula

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(r_0 + at)^3, \quad (12)$$

where $r_0$ is the size of the crystal at the initial time; and $a$ is the crystal growth rate at a given cooling rate, which is a constant [8] for the medium in question.

According to (10)–(12) the concentration of crystal particles has the form

$$N_0(t) = \left[1 - \exp\left(-\frac{4}{3}\pi t r^3 \frac{v_{\mathrm{cool}}}{V_{\mathrm{sm}}\,T_0}\right)\right] V_{\mathrm{sm}}^{-1}. \quad (13)$$

The total extinction coefficient of the light by the initial solution and the solution with metal particles is determined as the sum of each component:

$$K_{\mathrm{ext}}^{\Sigma} = K_{\mathrm{ext}}^{\mathrm{cr}} + K_{\mathrm{ext}}^{\mathrm{me}} = N_0 \int_0^\infty C_{\mathrm{sct}}^{\mathrm{cr}}(r)g(r)\,\mathrm{d}r + N_{\mathrm{me}}C_{\mathrm{sct}}^{\mathrm{me}}, \quad (14)$$

where $K_{\mathrm{ext}}^{\mathrm{cr}}$ and $K_{\mathrm{ext}}^{\mathrm{me}}$ are the extinction coefficients of crystals and metal particles, respectively; $C_{\mathrm{sct}}^{\mathrm{cr}}$ and $C_{\mathrm{sct}}^{\mathrm{me}}$ are the light scattering cross sections of the crystal and a single metal particle, respectively; and $N_{\mathrm{me}}$ is the concentration of metal particles. As mentioned above, the geometrical and optical parameters of metal particles in the temperature range under study do not noticeably change, and so their contribution to the total extinction coefficient $K_{\mathrm{ext}}^{\Sigma}$ will be constant while the contribution of growing crystals will be variable [9].

Figure 1 shows the dependence of the extinction coefficient of the light by particles (crystals) of a scattering solution when their size varies from 100 to 280 nm. To estimate the contribution to the total scattering coefficient, we can use relations (1) and (14) and plot the dependences of changes in

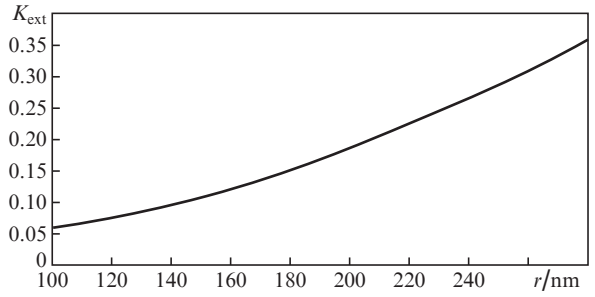


**Figure 1.** Extinction coefficient of the 532-nm radiation as a function of the particle size.

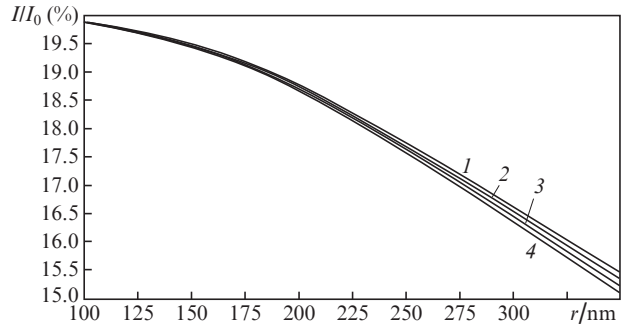


**Figure 2.** Laser light intensity after interaction with (*1*) a pure sample and samples with a concentration of metal particles of (*2*) 1%, (*3*) 2% and (*4*) 3% vs. crystal size. The size of the metal particles is 300 nm.

the light intensity for different impurity concentrations. These dependences are shown in Fig. 2.

Expression (1) in view of (14) takes the form

$$I = I_0 \exp\left\{-l\left[N_0 \int_0^\infty C_{\text{sct}}^{\text{cr}}(r) g(r)\,\mathrm{d}r + N_{\text{me}} C_{\text{sct}}^{\text{me}}\right]\right\}. \qquad (15)$$

Let us denote the intensity of the light transmitted through a pure sample by $I_1$ and through a sample with an impurity by $I_2$. Then, using the above dependences, we write the desired expression for the experimental determination of the concentration of metal particles:

$$N_{\text{me}} = \frac{\ln(I_1/I_0) - \ln(I_2/I_0)}{l C_{\text{sct}}^{\text{me}}}. \qquad (16)$$

This expression is used to calculate the concentration of metal particles in the entire range of cooling temperatures. The concentration $N_{\text{me}}(t)$ remains constant if metal impurities are not crystal growth centres.

## 3. Experimental

As a model medium, we used mineral oil in the experiment. In the process of cooling in media of this type there occurs a growth of nucleation centres, i.e., crystals of the wax fraction, which makes it possible to consider them to be colloidal solutions in a certain (according to the size of the crystals) temperature range [5].

The experimental setup (laser nephelometer) is shown in Fig. 3. Radiation of a 532-nm cw laser (the second harmonic

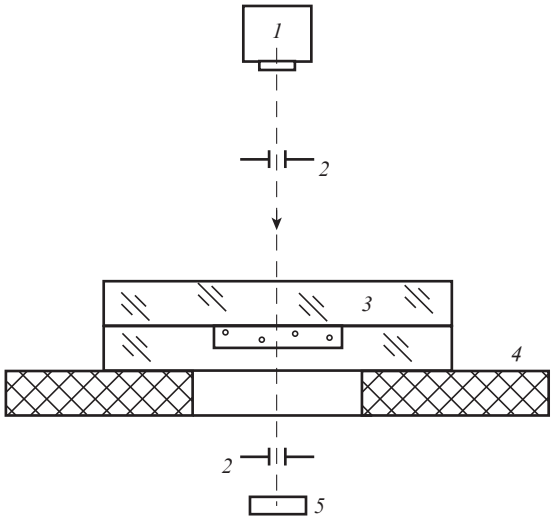


**Figure 3.** Scheme of the experiment:
(*1*) laser source; (*2*) diaphragm; (*3*) cell with the sample; (*4*) thermocouple; (*5*) photodiode.

of the Nd : YAG laser) (*1*) after passing through a diaphragm (*2*) is incident along the normal onto a cell (*3*) with an optical path length of 30 μm. The sample temperature is varied using a built-in ring Peltier element (*4*). The diaphragm (*2*) transmits radiation propagating in a small solid angle, which allows one not to take into account the scattering of any multiplicity higher than the first. Radiation is detected by a photodiode (*5*). A thermocouple is used to measure the sample temperature. Based on the data [10], the sample cooling rate is set equal to 7 °C min$^{-1}$. At this rate there occurs a fairly uniform solidification of the substance. Accuracy of the measurement of the scattered radiation power is ~5%, which is a good result for nephelometric measurements.

The small cell thickness makes it possible to compensate for spatial inhomogeneity of the liquid solidification. At a rate 7 °C min$^{-1}$, the oil cooling front is distributed along the glass (the cell material), i.e. from the periphery to the sample centre. When the cell boundaries are maximally close to each other, the cooling fronts overlap, which reduces the effect of solidification inhomogeneity.

Experiments were carried out with standard samples of mineral oil and similar samples, into which an impurity, metal (steel) particles, was added. The particle size distribution analysis was performed using a Microtrac BlueWave laser diffractometer (Microtrac Inc., USA). The results showed that the particle size distribution is Gaussian with a mean particle diameter of 300 nm and a standard deviation of 30 nm. The mineral oil samples with added particles were subjected to ultrasonic homogenisation. Observations carried out using phase-contrast microscopy showed that in the experiments metal particles did not precipitate on the cell walls.

## 4. Discussion of the results

In this work, we performed a series of experiments for determining the scattering coefficient of the light by samples of pure mineral oil and mineral oil with monodispersed metal particles at a concentration of 1% and 2%. The aim of our experiments was to test the correctness of the proposed mathematical model, namely, the acceptability of assumptions that the light is singly scattered, the crystal growth rate

is independent of the position of the laser beam in the cell plane and the impurities are not the centres of the crystal growth, etc. The agreement of theoretical and experimental results indicated the validity of the assumptions. Furthermore, we investigated the possibility of practical application of the described method for analysing colloidal solutions and solutions with mechanical impurities.

Figure 4 shows the experimental dependences of the intensity of the light transmitted through the sample on the temperature. One can see that the difference in the dependences for pure samples and samples with metal particles is observed when the temperatures start to exceed the phase transition temperature (this is important for the practical application of the method, since it can be used to monitor the purity of liquid media without deep cooling, which reduces the time spent and energy). Then, the intensity of the directly transmitted light decreases significantly slower for the pure sample than for the contaminated samples, which is apparently due to a smaller scattering coefficient. The curves for samples with different concentrations of particles virtually coincide down to a temperature of about 0 °C. Upon further cooling, the differences in the intensities become significant, thereby providing a high resolution of the method and the possibility of determining the concentration of impurities with great accuracy. Thus, a temperature below –8 °C is optimal for these purposes.

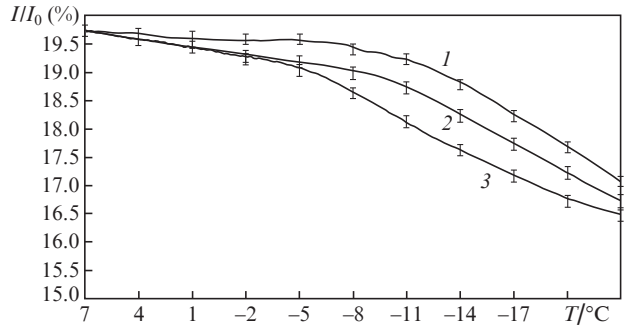


**Figure 4.** Laser light intensity after interaction with (*1*) a pure sample and samples with a concentration of metal particles of (*2*) 1% and (*3*) 2% vs. sample temperature.

We have compared the experimental data (Fig. 4) with the theoretical values given in Figs 1 and 2. In order to establish a correspondence between the values given in these figures, we used expressions (12)–(16). The experimental curves qualitatively and quantitatively coincide with the theoreticalones. At the beginning of the cooling process, at positive temperatures, some discrepancies between the theoretical and experimental results can be explained by the influence of freezing mechanisms that are not taken into account in constructing a mathematical model. At low temperatures (below –18 °C) the deviation from the theoretical data is due to the fact that the concentration of the crystals becomes so high that the light is multiply scattered, and the Bouguer–Lambert–Beer law turns out inapplicable. In addition, the high concentration of crystals leads to the fact that we cannot ignore their mutual influence. As a result, one can limit the optimal temperature range from –8 °C to –18 °C.

Based on the results of the experiments we calculated the concentration of particles added to the sample. To this end, we plotted the dependences of $I_1/I_0$ and $I_2/I_0$ on time (which in the experiment is linearly related to the temperature of the substance). After substituting these dependences into (16), the function $N_{me}(t)$ was determined. The value of the concentration of metal particles $N_{me}$, found in the entire investigated temperature range, remains constant (with an error of no more than 2%). This suggests that in the described experimental conditions, the metal particles are not crystal growth centres, i.e. the initial assumption is correct and the proposed mathematical model is valid under these conditions.

Deviation of the measured particle concentrations from the true value was 8% (for the impurity concentrations of 1% and 2% in the sample), which is a good result for nephelometric measurements.

## 5. Conclusions

We have studied the interaction of laser light with scattering liquid media under conditions of their solidification according to the crystallisation mechanism. The extinction coefficient of light is considered as a function of time. We have analysed the effect of particles having a constant size on the scattering coefficient of the solution in the process of its solidification and derived a dependence to calculate the concentration of metal particles (impurities) with a size of 100 to 280 nm in the solution. Calculations have been performed using the results of the experiment, in which the solution is cooled prior to the crystal growth therein under its simultaneous illumination by the laser light.

Based on the results of the study we have proposed a calculation method for determining the concentration of metal particles in liquid scattering media under their cooling by laser nephelometry. It is shown that in this case, use can be made of the mathematical apparatus of Mie theory jointly with the Johnson–Mehl–Avrami–Kolmogorov theory, which allows one to measure, in a single cycle of sample cooling, the concentration with an accuracy suitable for rapid methods. Comparison of the results of calculations and experiments has shown that the relative accuracy of the procedure is about 8%.

Thus, the described method and the experimental setup can be used to determine the concentration of mechanical impurities in liquid scattering media. In addition, the setup can be used to study the process of cooling of liquid scattering media, because in this case the impact of external factors on the results of experiments is minimised.

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