Static light scattering for determination of physical parameters of macro- and nanoparticles

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Abstract. The work is dedicated to determination of physical parameters of micro- and nanoparticles by static light scattering method. We present static light scattering device and theory to determine sizes of particles in suspensions. We analyze calculated distributions of scattering intensity for particles of different sizes and compare it with experimental data, received for spherical particles of different sizes. We also suggest theory to calculate form factor of scattering intensity for micro- and nanoparticles of different shapes. We also demonstrated that Rayleigh scattering theory is better to be applied for small particles investigation.

1. Introduction
Micro- and nanoparticles are widely used in biomedical science [1], metalworking industry, researching of environment and a great variety of different nanotechnologies [2]. Methods of static light scattering (SLS) are being developed for more than a century and nowadays contain an amount of analytical solutions for different particle geometries. Low cost laser radiation sources, such as laser diodes, made light scattering technologies available for basic researches and education [2]. Nevertheless nowadays, this method is still not common if we need to analyze shapes of non-spherical particles with unknown sizes. We suggest the theory, which describes static light scattering by the particles of different shapes and sizes, and compare the theoretical considerations with experimental data received by designed SLS-device.

2. Theory
Particles interact with electromagnetic field of light, and scatter light in different directions. The relation between scattered and incident light can be presented by the following matrix equation [3].

\[
S_{\text{scattered}}(I_v, I_h, U, V)_{4 \times 1} = F_{4 \times 4} S_{\text{incident}}(I_{v0}, I_{h0}, U_0, V_0)_{4 \times 1} / k_0^2 r^2
\]

(1)

All 16 elements of transform matrix F are combinations of four complex amplitude functions S1, S2, S3, S4, which can be computed using different scattering theories.

2.1 Rayleigh theory
If particle size is much less than light wavelength, all elementary dipoles of particle emit coherently. This case of scattering is named after Lord Rayleigh who determined the dependence of the intensity of scattered light on the wavelength in 1871. Indicatrix can be described by the following expression [4]

\[
I(\theta) = \frac{24\pi^3 N V^2 (n_2^2 - n_0^2)^2 I_0}{L^2 (n_2^2 + 2n_0^2) \lambda_0^4} (1 + \cos^2 \theta)
\]

(2)
where \( n_0 \) – solvent refractive index, \( n_p \) – particle refractive index, \( I_0 \) – incident light intensity, \( \lambda_0 \) – incident light wavelength in vacuum, \( \theta \) – scattering angle, \( L \) – distance from the scattering volume to detection point, \( N \) – is concentration of particles, \( V \) – volume of the spherical particle.

With increasing particle size, dipole moments in different parts of it begin to emit in different phases, and interference will cause decrease of the total amplitude of electromagnetic radiation.

2.2 Scattering factors for particles of different shapes

When the dimension of particle is larger than that which can be treated as a single dipole, the approach is to treat the particle as an assembly of many tiny and structureless scattering elements. Each of these scattering elements gives rise to Rayleigh scattering independent of other scattering elements in the particle. The phase shift corresponding to any element in the particle is negligible and the phase difference between different elements in the particle is determined only by their positions and is independent of the material properties of the particle. Scattering in a given direction from all these elements results in interference because of the different locations of these elements in the particle. To satisfy the above assumptions, the particle has to have a refractive index close to 1 in addition to being small compared to the wavelength of light.

In the Rayleigh-Debye-Gans theory, the amplitude functions can be presented as [4]

\[
\begin{pmatrix}
    S_1 \\
    S_2 \\
    S_3 \\
    S_4
\end{pmatrix} = \frac{ik_0^2(n-1)}{2\pi} P^{1/2}(x) \begin{pmatrix} 1 & 0 \\ 0 & \cos \theta \end{pmatrix}
\]

Therefore scattering pattern can be described by the scattering factor \( P(x) \), which depends on a shape of the particle [4].

Thin disk:

\[
P(x) = \frac{2}{x^2} (1 - \frac{1}{x} J_1(2x))
\]

where \( x = K \cdot d/2 \), \( d \) – diameter, radius of gyration \( R_g = d^2/8 \).

Thin rod:

\[
P(x) = \int_0^{2\pi} \frac{sin \theta}{\theta} dt - \frac{sin^2 \theta}{x^2}
\]

where \( x = K \cdot l/2 \), \( l \) – length, \( R_g = l^2/12 \).

Ellipsoid of revolution:

\[
P(x) = \int_0^{\pi/2} \frac{\sin \beta}{\sin \beta + (\frac{b}{a} \sin \beta)^2} \cos \beta \ d\beta
\]

where \( x = Ka \cos^2 \beta + (\frac{b}{a} \sin \beta)^2 \)\(^{1/2} \), \( a, b \) – semiaxes, \( \beta \) is the angle between figure axis and bisectrix. More formulas for different shapes can be found in [5].

2.3 Mie theory

For bigger particles, we should also take into account primary wave reemission by elementary dipoles. When constructing the Mie theory, the Maxwell equations are solved inside and outside the scattering particle; therefore, it is necessary to introduce boundary conditions on the particle surface. For spherical particles, Gustav Mie in 1908 obtained an analytical solution. The original Mie theory is restricted to plane wave scattering by a homogeneous, isotropic sphere in a nonabsorbing embedding medium [6].

If we assume the field at a point inside the sphere is what it would be if the sphere were not present (Rayleigh-Debye approximation) [7]. Mie scattering of unpolarized light can be approximated by the following expression [7].
\[ I(\theta) = I_0 \left[ \frac{3|J_1(x)|}{x} + \gamma \right]^2 (1 + \cos^2 \theta)/2 \]  

(7)

where \( x = ka(1 + m^2 - 2m \cos \theta)^{1/2} \), \( J_1 = (\sin x - x \cos x)/x^2 - J_1 \) is often referred to as the 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, \( I_0 = c\varepsilon_0\epsilon_0(\text{m}^{-1})^2a^6k^4/18r^2 \), \( c \) – 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 \( x^{3/2} \).

Mic scattering theory has no size limitations and converges to the limit of geometric optics for large particles. In small particles limit it matches to Rayleigh theory.

2.4 Fraunhofer diffraction

When particle size is more than light wavelength, the main process is diffraction. When the particle dimension is much larger than the wavelength of light or the material is highly absorptive, the edge effect of particle contributes much more to the total scattered intensity. The interference effect now arises mainly from particle’s contour; i.e., diffraction produced by the bending of light at the particle boundary. In these instances, scattering from the inner part of the particle is less important and neglected as an approximation. The particle now behaves like a two-dimensional object instead of a three-dimensional particle. Only the projected area perpendicular to the light matters, not the volume of particle [4]. In this case scattering can be described by Fraunhofer diffraction theory.

3. SLS scattering measurements

The scheme of the SLS device is presented if Fig. 1. Light beam from semiconductor laser (wavelength 653 nm) is cleared by the diaphragm and focused to the center of cuvette. Measurements are consisted of two quantities: angle on the goniometer, which shows direction of dissipated radiation, and voltage from photomultiplier on the oscilloscope, which is proportional to the intensity of radiation scattered in this direction.

As a result, we have series of measurements, forming an indicatrix of light scattering, showing relative angular distribution of radiation energy. Main advantages of the actual method are simplicity, removability of the components of setup and non-invasiveness.

![Diagram](image-url)

**Figure 1.** The experimental setup: 1 — laser; 2 — diaphragm; 3 — cuvette with the studied suspension; 4 — goniometer; 5 — radiation inlet; 6 — optical fiber; 7 — photomultiplier; 8 — power supply for photomultiplier; 9 — oscilloscope.
4. Results and conclusions
In the experiment, we measured scattering curves for solutions of monodisperse spheres of polystyrene latex (refractive index \(n = 1.586\), relative to water refractive index \(m = 1.331 = 1.192\)) of the following diameters: 0.54 μm (solution concentration \(C = 0.2\) mg/ml), 2.1 μm (\(C = 0.1\) mg/ml), 11 μm (\(C = 0.012\) mg/ml).

Following figures present theoretical and experimental scattering patterns for considered latex particles in logarithmic scale. For particles, which size is smaller, than wavelength we considered both, Rayleigh and Mie theories.

**Figure 2.** Theoretical scattering curves, calculated for monodisperse microparticles with diameter of 0.54 μm

**Figure 3.** Experimental scattering curve, measured for monodisperse microparticles with diameter of 0.54 μm

**Figure 4.** Theoretical scattering curve, calculated for monodisperse microparticles with diameter of 2.1 μm

**Figure 5.** Experimental scattering curve, measured for monodisperse microparticles with diameter of 2.1 μm
It can be noticed that particle sizes can be distinguished using the level of scattered intensity in small angles. Concentration of solutions influence scattering, thus, method accuracy depends on accuracy of concentration measurements.

For small particles, with size lower than the light wavelength, we can conclude, that it is better to use Rayleigh theory for scattering curve approximation. Experimental scattering curve for solution of particles with size of 2.1 μm are not well approximated by Mie theory either. Therefore, we can conclude, that particles with sizes, which are close to the incident light wavelength are not well studied by SLS. In these cases, it is better to apply dynamic light scattering methods [8].

Scattering for 11 μm spheres fits Mie theory, because of the higher diameter/wavelength ratio. Mismatch of location of theoretical and experimental scattering extremums for it can be described, for example, by some polydispersity of solution.

Provided comparisons of theoretical and experimental data showed, that SLS could be successfully applied for solutions with microparticles with high diameter/wavelength ratio. In the next work, we will compare scattering curves for nonspherical particles with high diameter/wavelength.

References
[1] Dolgushin S A, Yudin I K, Deshabo V K, Shalaev P V, and Tereshchenko S A 2016 Biomedical Engineering 49 (6) 394–397
[2] Xu R 2015 Particuology 18 11–21
[3] David W H 2009 Light scattering theory, p 13
[4] Xu R 2002 Particle Characterization: Light Scattering Methods Kluwer (USA: Academic Publishers) p 397
[5] Pederson J S 1997 Advances in Colloid and Interface Science (Denmark: Elsevier) 70, 171-210
[6] Quinten M 2011 Optical properties of nanoparticle systems (Weinheim: Wiley-VCH)
[7] Drake R M, Gordon J E 1985 American Journal of Physics 53, 955
[8] Nenomnyashchaya E, Antonova E, 2018 IEEE International Conference on Electrical Engineering and Photonics 136–14