The Problem of Obtaining the Particle Size Distribution from the Correlation Function of Multiply Scattered Light

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Abstract

There are some methods and codes which allow obtaining the size distribution of particles suspended in liquids by means of dynamic light scattering. The solution of the problem is reduced to the decomposition of a singly scattered light correlation function into the sum of exponential functions. The optical method of the sizing based not on single, but multiple scattering just elaborated is described. Correlation times obtained by the fiber probe allow us to obtain the averaged value of the particle size. But the problem is to obtain the size distribution from the correlation function of multiply scattered light. An example of result of analysis of correlation function of light multiply scattered by bimodal suspension is represented. Several questions have been asked to mathematicians as a conclusion.

Keywords: Particle size distribution, multiple light scattering.

1. Introduction

The problem of particle sizing and obtaining the size distribution of particles suspended in liquids is very actual both as a scientific problem and for many industrial branches. These are the production of composite materials containing nanoparticles, petrochemical , paintwork industry, and others dealing with suspensions or emulsions.

The most reliable and non-disturbing methods are optical. Two main classes of the methods are particle sizing by the light scattering intensity dependence on the scattering angle or on the light wavelength [1-4] and by the width of the central polarized Rayleigh line of the singly scattered light spectrum using light beating spectroscopy (the dynamic light scattering, DLS) [5, 6]. The last is more widespread.

The solution of the problem of obtaining the size distribution of particles suspended in liquid is reduced to the decomposition of a singly scattered light correlation function into the sum of exponential functions. There are some well-known methods and codes which allow to solve the problem.

In its traditional form, however, the dynamic light scattering method requires:

1) suspension or emulsion sample placed in a special optical cuvette, 2) transparent suspension, and 3) no dust in the sample. A recently elaborated method of sizing based not on single, but multiple scattering [7] is free of the requirements.

The aim of the paper is to formulate the problems which are to be solved to obtain the size distribution of particles suspended in liquid from the form of intensity correlation function or of the central polarized Rayleigh line of the spectrum not of the single light scattering, but of the multiple one. This new problem is now still unresolved, as it was not formulated in general mathematically.

2. Traditional dynamic light scattering

In the traditional scheme of particle size measurements by the scattering spectrum, a focused laser beam passes through the cuvette with the examined sample, and the radiation scattered at an angle θ is fed to the quadratic photodetector (photomultiplier) with the help of an optical system. An additional reference laser beam of the same frequency or shifted in frequency can be introduced into the scheme to provide optical homodyning [8] or heterodyning [9].

Beatings of light frequency components generate intensity fluctuations on quadratic photomultiplier cathode, which are repeated in the detector current and are analyzed by the correlator or the spectrum analyzer. The photocurrent repeats the light intensity rather than the field. The intensity correlation function is related with the field correlation function $g^{(1)}(\tau)$ by the Ziegert relation:

$$g^{(2)}(\tau) = 1 + A\left|g^{(1)}(\tau)\right|^2 \tag{1}$$

Here A is a coefficient resulting from the space coherence of the light received by the photodetector. The function $g^{(1)}(\tau)$ is connected to the light spectrum by the Fourier transform.

The spectrum of light scattered by monodisperse particles has the form of Lorentzian with halfwidth Γ, and the time correlation function of the electric field of such light $g^{(1)}(\tau)$ is an exponent. In this case the intensity of the correlation function is an exponent with the damping rate of 2Γ on the incoherent background "substrate". The spectrum analyzer or the correlator determines the scattering spectrum line width Γ or the coherence time

$$\frac{\tau_c}{2} = \frac{1}{2\Gamma} \tag{2}$$

of the correlation function and with its help the particle radius r_p:

$$\Gamma = q^2 D = \frac{KT}{6\pi\eta r_p} q^2 \qquad \text{or} \qquad r_p = \frac{KTq^2}{6\pi\eta}\tau_c \tag{3}$$

and therefore

$$r_p = \frac{KT}{6\pi\eta\Gamma}\left(\frac{4\pi n}{\lambda}\sin\frac{\theta}{2}\right)^2 \tag{4}$$

as q is the scattering vector: $\vec{q} = \vec{k}_s - \vec{k}_L$ with $\vec{k}_s$, and $\vec{k}_L$ as the wave vectors of scattered

and incident light, as :

$$|q| = \frac{4\pi n}{\lambda} \sin\frac{\theta}{2}, \tag{5}$$

where n is the refractive index of the medium, λ is the wavelength of the incident light, θ is the scattering angle, K is the Boltzmann constant, T is the absolute temperature, η is the shear viscosity, and D is the particle diffusion coefficient.

When the suspension or emulsion includes particles of several sizes, the time correlation function turns out to be the sum of several exponents, and the spectrum in this case is the sum of Lorentzian functions.

To find the particles size distribution it is necessary to decompose our correlation function into the sum of exponents. This decomposition gives us the distribution of intensity of light scattered by the particles of a given size. The knowledge of the indicatrix of the light scattered by particles (e.g. the Rayleigh - Gans -Debye's approximation) allows us to get the particle size distribution easily.

The problem of the decomposition of the functions into the sum of exponents is mathematically incorrect, but the methods developed at present, e.g. the regularization by Tikhonov, have provided the decision of the problem.

At present time there are many methods and codes providing the decomposition of the correlation function into exponents, many different "Sizers" operating on the principle of the dynamic light scattered and using such codes.

However all stated above pertains to single light scattering. Therefore the sample of the suspension or emulsion under investigation by means of traditional "Sizer" must be: 1) diluted up to transparency; 2) put into a special optical cell; 3) dust must be removed.

This creates difficulties in the use of dynamic light scattering for checking emulsion and suspension quality in industry, as they often are turbid, impure and dust-laden.

Great efforts were undertaken for separation single scattered light from whole of light scattered by turbid solution [10,11]. These devices are intended for multiple scattering inhibition using a light source with a small coherence length. The devices provide radiation input into an examined volume and scattered light output through the same single-mode optical fiber. A small coherence length of the source is supposed to provide the correlation function of light scattered in only a small volume limited to the coherence length of the source. However, the correlation function in the case will have a small amplitude compared to the background (and, therefore, a low accuracy). Moreover all these methods have their own restrictions of maximum permissible turbidity of the liquid under investigation.

3. DLS of multiple scattering by the fiber probe

Last time, however, the simple way of emulsion drop sizing from the width of the spectral line of scattered light using an optical fiber probe immersed in the examined medium was elaborated and realized, that admits measurements in transparent and very turbid (milk-like) and dusty media [7]. The method is based on measurements not only single, but multiple scattering spectra too. While usually only the single scattered was used.

The essence of the elaborated methods consists in the fact that in turbid emulsions the particle size is determined by the spectral line width of a not single but multiple scattering. For this purpose, a fiber probe was used consisting of one illuminating and two collecting optical fibers. The laser light was fed into the illuminating fiber whose output end was embedded into one thin cylindrical probe block together with the input ends of two collecting fibers. These optical fibers were parallel. The first (base) collecting fiber was placed in immediate proximity to illuminating one, the second (auxiliary) fiber was fixed at a certain distance from illuminating and base fibers.

The light scattered back by particles (more precisely, at the scattering angle $\theta = 178$-$180°$), gets into the collecting fibers and through the one of collecting fibers and spatial coherence unit is sent to the photomultiplier. The signal from the photodetector goes onto the correlator or spectrum analyzer (CSA).

When measurements using the proposed device are taken in very turbid media, like milk or 5% Emulsol EMU-1 (lubricoolant, self-emulsifying oil) suspension the correlator fixes the correlation function of multiply, not singly scattered light for which eqs.1, 2 hold.

The correlation function has in this case a graph which nearly matches an exponential function, but its width

$$\Gamma_m = \overline{\Gamma} \tag{6}$$

may differ several times from the width of the correlation function of singly scattered light [12]. N is the number of scattering acts averaged over all possible trajectories, and the average line width $\overline{\Gamma}$ in each scattering act is

$$\overline{\Gamma} = \lim_{N\to\infty} \frac{\sum_{i=1}^{N} \Gamma_i}{N} = \int_{4\pi} |G(\theta,\psi)|^2 \, \Gamma(\theta) \, d\omega \quad . \tag{7}$$

Here Γ_i is the spectral line width in the i-th scattering act, $G(\theta,\psi)$ is the form factor of scattering by particles, $\Gamma(\theta)$ is the angular dependence (3) of Γ for a single scattering, and $d\omega$ is the element of the solid angle. From eq. (3) and (7) we deduce [12] that

$$\overline{\Gamma} = \Gamma_{90} \cdot \left(1 - \overline{\cos\theta}\right) \quad , \tag{8}$$

where

$$\Gamma_{90} \equiv \Gamma(90°), \tag{9}$$

and $\overline{\cos\theta}$ is defined as

$$\overline{\cos\theta} = \int_{4\pi} |G(\theta,\psi)|^2 \cos\theta \, d\omega \quad . \tag{10}$$

Within such an approach it turns out that for spherical particles and the scattering angle ~180° we have

$$\Gamma_m = N\Gamma \approx \Gamma_{90} (d^2/l^2) \cdot (1 - \overline{\cos\theta})^2 / (1 + \overline{\cos\theta}) \, . \tag{11}$$

In [12] d is the cuvette diameter, and in our case it must be the size of the illuminated region, and l is the photon path in the medium. Then Γ_m depends on l or on the extinction coefficient σ

$$\sigma = 1/l, \tag{12}$$

σ and l are uniquely related to the scattering coefficient R and, at first glance, it seems that one can find the scattering multiplicity and Γ and r_p, knowing only σ and Γ_m . The actual situation turns out to be a little more sophisticated.

From the results of one measurement it is impossible to obtain the scattering multiplicity N and, therefore, one can't determine single scattering linewidth Γ from the multiple scattering linewidth Γ_m and finally to determine the scattering particles size.

Fortunately a universal dependence of Γ/Γ_{mbase} on the ratio $\Gamma_{mbase}/\Gamma_{maux}$ turned out to exist [12]. Such a dependence is universal for particles having different radii and consisting of different materials, but it changes with varying distance between the illuminating, collecting, and auxiliary optical fibers, and should therefore be measured separately for each probe.

Thus, after we have manufactured the optical fiber probe as described in [12] and determined for it the universal dependence of the ratio Γ/Γ_{mbase} on $\Gamma_{mbase}/\Gamma_{maux}$, we can find the true average size r_p of particles from the measured Γ_{mbase} and Γ_{maux} values in the collecting base and auxiliary fibers in both transparent and cloudy emulsions and suspensions.

The proposed method of measurements has several major advantages over the traditional scheme and schemes involving single-mode fibers [10,11].

It does not require that the examined liquid be placed into a special optical cuvette. The fiber probe (the illumination - scattered light collection unit) can be placed into any reservoir, a barrel, a cistern, and others with finished product, into chemical reactors, tanks and wash-tubs of processing machines, etc., where particle sizes should be measured.

This probe does not require alignment of the optical system connected with the sample, and the system that provides spatial coherence conditions can be aligned and fixed before exploitation. This alignment is simple and reliable, owing to the use of multimode fibers.

Measurements using this probe can be taken in both transparent and very turbid media such as milk or 5-10 % colloidal solution of Emulsol. In this case the correlation function of not single but multiple light scattering is fixed, the coherence time of which

$$\tau_m=1/\Gamma_m \tag{13}$$

is related to

$$\tau=1/\Gamma \tag{14}$$

by the coefficient determined from the line width ratio in the base and auxiliary collecting fibers.

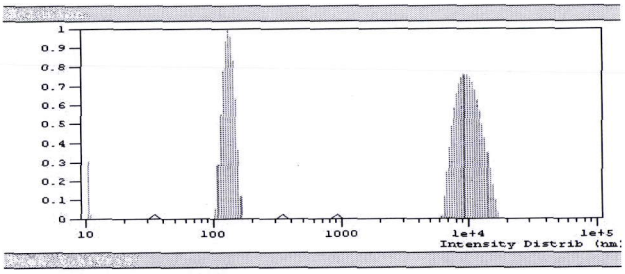
The method elaborated exhibits very high resistance to dust in the sample.

The knowledge of the mean radius proves as a rule to be sufficient for practical application in the control over production quality or reaction run. However in a whole row of cases, including sometimes the control in the course of some production processes, it is necessary to have information about the size distribution of particles or drops in a turbid emulsion.

For present day the theory of the information obtaining from multiple scattering spectra or correlation function is absent.

4. Experimental examples

It is obvious that if the suspension contains particles of different sizes then in course of multiple scattering the scattering occurs at particles of different sizes in sequence. For example, when the suspension contains particles of two sizes, τ distribution of the multiply scattered light spectra may be not bimodal, but wide monomodal. It is the case what is illustrated by Fig. 1-3.



Distribution analysis

Fitting range : [50; 215] channels
Number of Intervals : 200
Boundaries : [10.00; 1e+5]
Resolution : 0

Peak Num	Area	Mean	Position	STD
1	0.019	10.26	10.24	0.178
2	0.374	130.5	128.9	13.76
3	0.608	1.0e+4	9775.	2309.

χ^2 : 0.001

Cumulant Analysis

Mean : 333.7
Standart deviation : 556.5
Polydispersity : 2.781 (Standard Deviation / Mean)^2

Figure 1: Particle size distribution (intensity distribution) obtained by the dynamic light single scattering in the water-in-oil suspension (30 times diluted).

Measurements were performed in water-in- transformer oil emulsion with addition of AOT (surfactant, sodium bis(2-ethilhexil)sulfosuccinate). The suspension contained 2.34 % H_2O and 0.089 % AOT. The suspension was at rest two weeks after mixing, then it was shaked up, and particle size distribution was determined by means of traditional dynamic light scattering scheme with correlator "Photocor-FCm" and code "DynaLS". To provide the last single-scattering measurement the suspension was 30 times diluted.

The Fig. 1 shows the obtained size distribution with the Y axis as the intensity of light scattered by the particles and the X axis as the particle size. The distribution indicates particle radii 130 nm and 10^4 nm. The scattering intensity ratio of the size modes is 0.615. The cumulant analysis was provided up to a second cumulant.

Fig.2 and 3 show correlation time distributions obtained by the same correlator and code by means of the fiber probe described above through base (Fig.2) and auxiliary (Fig 3.) fibers. As the code "DynaLS" normalizes correlation times by the value $\frac{6\pi\eta}{KTq^2}$, these figures are shown with X axis as effective particle radii r_{eff} (in nanometers):

$$r_{eff} = \tau / \left(\frac{6\pi\eta}{KTq^2} \right). \qquad (15)$$

It must be noted once more that the value r_{eff} is not a particle radius, but it is only normalized correlation time.

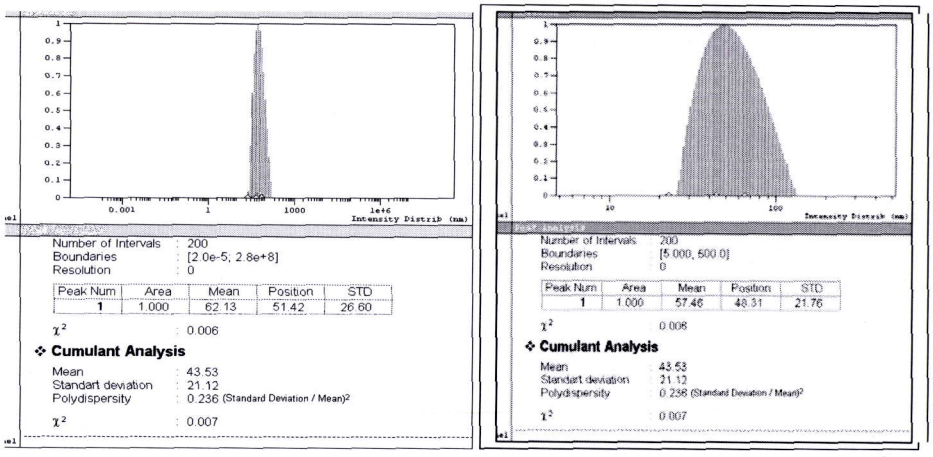


Figure 2: The distribution of correlation times normalized by the value $\frac{6\pi\eta}{KTq^2}$ of multiply scattered in water-in-oil suspension light got through base fiber of probe.

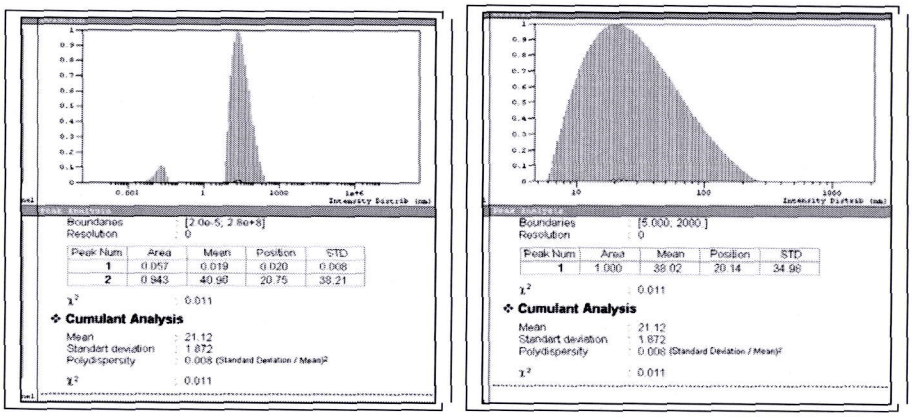


Figure 3: The distribution of correlation times normalized by the value $\frac{6\pi\eta}{KTq^2}$ of multiply scattered in water-in-oil suspension light got through auxiliary fiber of probe.

Fig. 2 and 3 show the distributions obtained in wide limits on the left part, and the main peaks in narrow limits on the right part.

The multiple scattering gives one-mode correlation time distribution. Effective

particle size distribution peaks achieved from these times are positioned at 57.5 nm for base collecting fiber and at 38 nm for auxiliary one. Widths of the peaks are 21.8 and 35.0 nm respectively.

5. Conclusion

Thereby, here we have explained the problem of obtaining the particle size distribution from the form of intensity correlation function of the multiple light scattering, not of the single one. This new problem is now still unresolved, as it was not formulated in general mathematically. But we hope that the problem can be solved by means of anticipatory computing.

Most likely, the two collecting fibers in the fiber probe are sufficient to determine the average particle radius, but is it enough to obtain the particle size distribution ? – it is the question. May be must we add a third collecting fiber ? And how have we to approach the elaboration of methods of obtaining size distribution from multiple light scattering correlation functions ? All the questions must be addressed rather to mathematicians than physicists, and the aim of the paper was to formulate the questions.

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