*Journal of Nano- and Electronic Physics*
Vol. **6** No 3, 03033(3pp) (2014)

*Журнал нано- та електронної фізики*
Том **6** № 3, 03033(3сс) (2014)

# Determination of Polydispersity of Magnetics Colloidal Nanopaticles by Optical Methods: Birefringence and Light Scattering Experiments

C.V. Yerin*

*North-Caucasian Federal University, 1, Pushkin Str., 355009 Stavropol, Russian Federation*

(Received 19 May 2014, revised manuscript received 02 July 2014; published online 15 July 2014)

Determination of particle size distribution of the magnetic colloids according to the static and dynamic light scattering and magnetic birefringence were produced. Shown that the magnetic colloids with a low concentration of the solid phase are characterized by steady bimodal distribution, including individual nanoparticles with a size of 10-20 nm and aggregates of particles with a size of 40-80 nm.

**Keywords**: Magnetic fluid, Light scattering, Translation and rotation diffusion coefficients, Aggregate of nanoparticles.

PACS number: 75.50.Mn

## 1. INTRODUCTION

Electromagnetooptical effects in magnetic colloids are very sensitive to the size of particles, especially in the low field region [1]. The reason of such distinction is that large particles and aggregates have more considerable moment (electrical or magnetic) and consequently interact with a field of small intensity more strongly. The polydispersity of particles and aggregates of magnetic colloids considerably influences their physical properties. Therefore in aggregated magnetic colloids particle size distribution definition represents the considerable interest. However the definition of a particles size distribution function in a colloid system demands the solution of integral Fredholm's equation. The solution of such integral equations is an incorrect or ill posed problem [2]. For the definition of particles size distribution functions of particles in magnetic fluids the wide range of regularization methods are used. One of the simplest procedures is histogram representations of an unknown distribution function or distribution function approximation a simple one or two-parameter function.

Electronic microscope data of magnetic fluids as a rule can be approximated by two-parameter distribution function similar to a log-normal distribution [3]. In this work we have tried to estimate the form of particles size distribution in kerosene based magnetic fluid on the basis of optical experiments: kinetics of a magnetic birefringence in a pulsed magnetic field as well as static and dynamic light scattering..

## 2. EXPERIMENT

For the measurement of birefringence the standard optical setup analogous to the one presented in [4] was used. The optical part of the setup included a He-Ne laser as a source of radiation, two crossed polaroids, and a glass cell with a specimen. A photomultiplier tube was used as a photodetector. The photocurrent was recorded by an analog-to-digital converter with subsequent computer processing of data arrays. A magnetic field with the strength up to 20 Oe was induced by Helmholtz coils. A colloidal solution of magnetite in kerosene stabilized by oleic acid with a magnetite volume concentration of 0.05 % was the object of our investigation. The low concentration of magnetite is caused by the necessity to conduct optical measurements in relatively thick layers. This concentration was obtained by diluting the initial magnetic fluid (from the Research and Production Institute of Gas Processing, Krasnodar, Russia) with a concentration of about 25 % by purified kerosene. The main parameter of the birefringence is the difference between the refractive indices of the extraordinary and ordinary rays. In investigations of this effect, the measured parameter is usually the intensity of the radiation passing through crossed polaroids placed on either side of a specimen. The intensity of the transmitted radiation in this configuration is determined by the optical density of a specimen $D$ and by the phase difference of the rays polarized along and across the optical axis (the field direction)

$$I = I_0 \exp(-2.3D)\sin^2(\delta/2). \qquad (1)$$

where $\delta$ is the phase difference of the extraordinary and ordinary rays, $l$ is the radiation path length in a cell, $\lambda$ is the radiation wavelength, and $I_0$ is the intensity of the incident radiation.

In the general case, the optical density of a specimen depends on both the field strength and the state of polarization of the incident radiation. However, if the transmittance of the system changes negligibly under the effect of a filed, the intensity of the radiation passing through crossed polarizers depends only on the phase difference of light oscillations and on the optical density in the absence of a field. The investigations have shown that the optical density of a specimen exposed to a magnetic field ranging from 0 to 25 Oe is independent of the field within the experimental error. The absolute value of the difference of the refractive indices was calculated by Eq. (1), in which the value of $D$ was calculated by photometering the cell with a specimen.

Figure 1 shows the experimental relaxation curve of birefringence in the magnetic colloid after the magnetic field (strength of 10 Oe) is switched off.

* exiton@inbox.ru

*The article was reported at the International Conference «The Advanced Technology, Equipment and Analytical Systems for Materials», Kursk, 13-14 May, 2014*

 

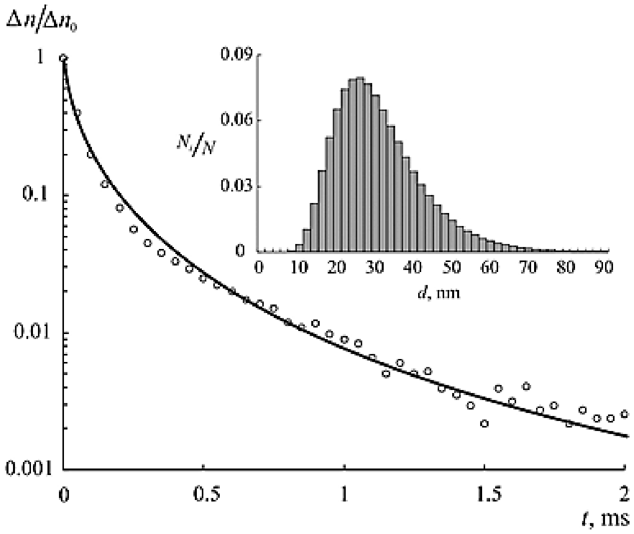


**Fig.** 1 – The decay of birefringence in magnetic colloid and histogram of particles sizes distribution calculated on this basis

The particle size of the colloids have a significant impact on their optical properties, including the parameters of the scattering of light. Fig. 2 shows the light scattering indicatrix for magnetic colloid concentration with solid phase 0.01 % for vertically light polarized with wavelength 650 nm. Indicatrix of the shows that its has little stretched forward, which means a slight deviation from Rayleigh particle size.

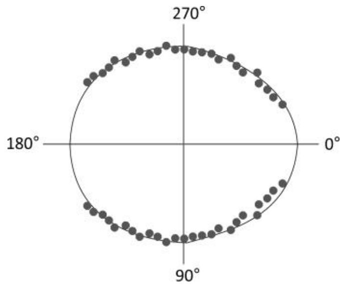


**Fig. 2** – Light scattering indicatrix of diluted magnetic colloid

According to the static light scattering determination of particle size distribution in colloids is a very complex task.

Now for the determination of particles sizes distribution of the colloid solutions of particles of the various nature the method of dynamic light scattering (DLS) is widely used [5]. At the heart of this method there is measuring of fluctuations of intensity of scattered light. Fluctuations of light intensity are related to the intensive Brownian motion of the colloidal particles. DLS-spectrometers autocorrelation function of the intensity fluctuations of the scattered light are measured (Fig. 3). The dispersion of particles sizes in kerosene based magnetic fluid has been measured by means of the Photocor Complex spectrometer which allows to make the automated examinations by the method of dynamic light scattering and to spot the form of particles size distribution. Distribution curve gained on the Photocor Complex spectrometer (Fig. 4) is the two-extreme function with the medial values of 13 and 53 nanometers corresponding to separate magnetite particles (10-20 nm) and to nanoparticles aggregate (40-80 nm).

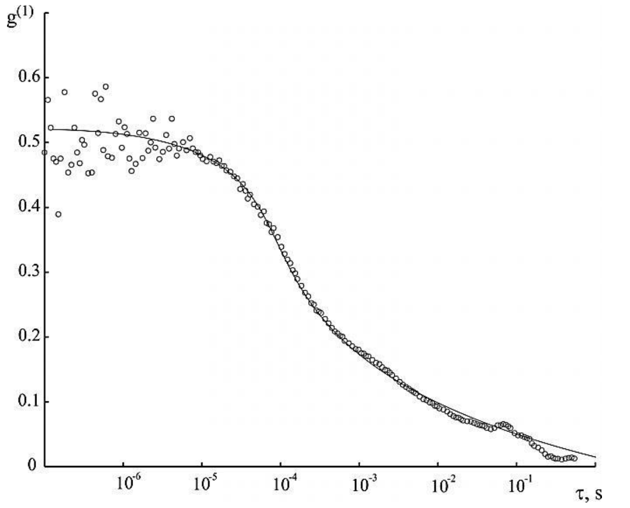


**Fig.** 3 – Autocorrelation function for magnetic colloid with concentration of 0.001 %

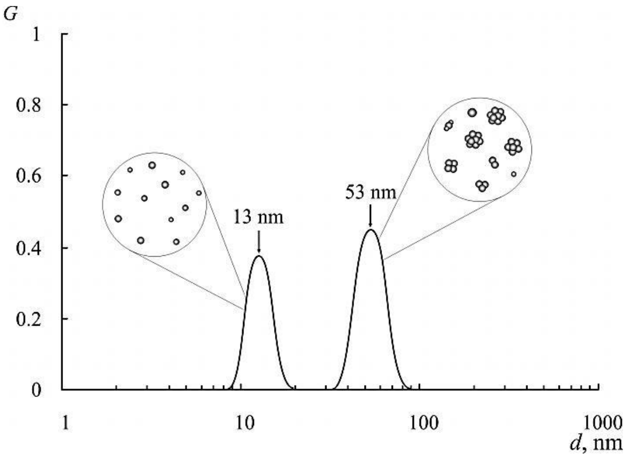


**Fig.** 4 – Particles sizes distribution determined by DLS on Photocor Complex spectrometer

## 3. DISCUSSION

Fredholm's equation that determines the relaxation of birefringence in a polydisperse system as follows.

$$\Delta n(t) = \int_0^\infty \Delta n(r) f(r) \exp\left(-6D_r(r)t\right) dr \qquad (2)$$

When the solution is not monodiperse the description of the magnetooptic effect is much more complex:

$$\frac{\Delta n(t)}{\Delta n_0} = \frac{\sum_i C_{Vi} \cdot \Phi_i \cdot \exp\left(-6\left(D_r\right)_i t\right)}{\sum_i C_{Vi} \cdot \Phi_i} \qquad (3)$$

where $C_{Vi}$, $\left(D_r\right)_i$ are the volume concentration, rotation diffusion constant and orienatational function respectively. In low field orientational function is given by the expression:

$$\Phi_i = \frac{kT \cdot \Delta\chi_i + m_i^2}{15(kT)^2} H^2 \qquad (4)$$

where $m$, $\Delta\chi$ - are permanent dipole and anisotropy of magnetic susceptibilities of particles of fraction $i$.

For the description of the particle size distribution of various colloids (including magnetic fluids) the log-normal distribution function often is used [3]:

$$f(y) = \frac{1}{\sigma y\sqrt{2\pi}} \exp\left(-\frac{(\ln y)^2}{2\sigma^2}\right) \qquad (5)$$

where and $\sigma$ – is standard deviation in ln($y$). Taking into account the peculiarities of the log-normal distribution function the relaxation of birefringence effect for aggregates of magnetic particles with an induced magnetic moment looks as follows:

$$\frac{\Delta n(t)}{\Delta n_0} = \exp\left(-18\sigma^2\right)\int_0^\infty f(y) y^6 \exp\left(-\frac{6kT}{\pi\eta\, y^3 \bar{d}^3} t\right) dy \qquad (6)$$

And for aggregates with permanent magnetic moment:

$$\frac{\Delta n(t)}{\Delta n_0} = \exp\left(-40.5\sigma^2\right)\int_0^\infty f(y) y^9 \exp\left(-\frac{6kT}{\pi\eta\, y^3 \bar{d}^3} t\right) dy \qquad (7)$$

The histogram of particle sizes distribution which was calculated by Eq. (6) is presented in fig. 2. The dispersion of particles sizes on these data is from 10 to 80 nanometers. The electronic microscopy gives the sizes of particles of a magnetite in the range of 7-20 nanometers. It allows speaking about the considerable role of nanoparticles aggregates in magnetooptical effects in magnetic colloids.

The comparison of the equations (6) and (7) shows, that the solution of the problem of defining the distribution function of particles in the sizes from data of the magnetic birefringence essentially depends on the physical mechanism of particles orientation accepted in calculations (the presence of prevailing permanent or induced magnetic moments). The additional information on the type and quantity of magnetic moments of particles and aggregates is necessary for the correct solution of the problem.

Current experimental devices for dynamical light scattering determine usually the autocorrelation function of the photocurrent:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I^2\rangle} = \frac{1}{\langle I^2\rangle} \lim_{N\to\infty} \sum_{i=0}^{N} I(t_i) I(t_i+\tau) \qquad (8)$$

To calculate the particle size r is necessary to determine the autocorrelation function of the light field $g^{(1)}(t)$ which is determined by the configuration of the optical experiment (wavelength, scattering angle) and the constant of translational diffusion $D_t = kT/6\pi\eta r$. In the case of a polydisperse system the autocorrelation function has the form [5]:

$$g^{(1)}(t) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)\, d\Gamma,\ \Gamma = q^2 D_t,\ q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}. \qquad (9)$$

This equation is also a Fredholm's equation but with a fairly simple exponential kernel. For recovery of the distribution function of particles disperse systems in size according to the dynamic light scattering there is a set of special methods.

## 4. CONCLUSION

Thus optical methods give the considerable possibilities on the definition of particles sizes distribution of magnetic colloids and its magnetic moments. Optical investigations of the magnetic birefringence, dynamic and static light scattering in the magnetic colloids show the presence of a magnetic colloid of magnetite along with individual nanoparticles 8-20 nm in size, and also aggregates of particles with a size of 30-80 nm, with aggregates present in the sample, even in the absence of a magnetic field. The question on the possibility of the smooth transition of a particle size distribution in the distribution of aggregates (fig 1) or disrupture between them (fig. 3) demands additional investigation.


### ASKNOWLEGMENTS

This work was supported by the Russian Foundation for Basic Researches (grant No 14-03-00312).


### REFERENCE


1. S.P. Stoylov, *Colloid Electro-Optics: Theory, Techniques, Applications* (Acad. Press: London: 1991).
2. A.N. Tikhonov, V.Y. Arsenin, *Solutions of Ill Posed Problems* (Wiley: New York: 1977).
3. S.R. Wilson, P.J. Ridler, B.R. Jennings, *J. Phys. D: Appl. Phys.* **29**, 885 (1996).
4. K.V. Erin, *Opt. Spectrosc.* **106**, 858 (2009).
5. R. Pecora, *J. Nanoparticle Res.* **2**, 123 (2000).