Field dependence of magnetooptic effect in magnetic colloid with superparamagnetic particles

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Abstract. The field dependences of magnetic birefringence in two samples of magnetic fluid with different average particle size are investigated. It is established that the dependences of magnetic birefringence are parabolic. Significant difference in experimental data and calculations using the single-particle birefringence model was found. The experimental results are interpreted by the polydispersity of the particles in the samples, as well as by the presence of small aggregates with a partially compensated magnetic moment.

1. Introduction
The birefringence in ferrofluids under the influence of a magnetic field has been studied for about 50 years [1], however, a generally accepted physical mechanism explaining all the experimental features has not been proposed to date. Apparently, the reason for this is the significant effect on the optical properties of the effects of magnetic dipole-dipole interaction and the formation of structures from magnetic nanoparticles. Usually, for weakly concentrated samples, the single-particle model [2] is used, according to which the optical anisotropy in a colloid arises due to the orientational ordering of the long axes of non-spherical nanoparticles under the action of an external field. However, there are other models that take into account the presence in the magnetic fluid of aggregates of particles of various types, as well as anisotropic spatial arrangement of particles. The study of the field dependence of the optical anisotropy allows one to obtain a certain amount of useful information about the system. Most often, field dependence is used to determine the magnetic moments of particles, but on the basis of these data it is possible to study aggregation processes in the colloid, as well as to determine the optical characteristics of the material of colloidal particles. In this paper, we present the results of studying the field dependence of birefringence for two samples of magnetic fluids with significantly different particle sizes.

2. Experiment
The samples were kerosene based magnetic fluids with magnetite particles. Sample 1 was a magnetic fluid produced by Research and Development Institute Gazpererabotka (Krasnodar, Russia), sample 2 was a magnetic fluid produced by STC Magnetic Fluids (Naro-Fominsk, Russia). The original concentrated liquids were diluted with kerosene to a volume concentration of 0.01%. The particle size distribution is determined by the method of dynamic light scattering on the PhotocorComplex instrument. The particles size distributions for samples are shown in figure 1. In sample 1, the average radius is about 6.5 nm, and in sample 2 it is about 11.5 nm.
For studies of the field dependence of magnetic birefringence, an ellipsometer "Ellips-1891" was used in the mode of measuring ellipsometric parameters $\Delta$ and $\Psi$ in transmitted light. The magnetic field was created by electromagnet mounted on an ellipsometer. The relationship between the ellipsometric parameter $\Delta$ and the main parameter of birefringence – the difference between the extraordinary and ordinary rays $\Delta n = n_\parallel - n_\perp$ given by the ratio:

$$\Delta n = \frac{\lambda \Delta}{2\pi l}.$$  \hspace{1cm} \text{(1)}$$

where: $\Delta$ – phase difference of extraordinary and ordinary rays, $l$ – path length of the light in the cell, $\lambda$ – wavelength of light.

The use of a specialized ellipsometric device made it possible to significantly increase the sensitivity of measurements of a magnetic birefringence. It was possible to confidently register the values of birefringence $\Delta n \approx 10^{-10} - 10^{-9}$, which are two to three orders of magnitude less than in known literary sources [3-4].
3. Results and Discussion

The samples were kerosene based magnetic fluids with magnetite particles. Sample 1 was a magnetic fluid produced by Research and Development.

In orientational models of optical anisotropy of magnetic colloids equilibrium the orientation-dependent part of the magnetic energy of the particle in the external field is used [5]:

\[ U = -mH(e \cdot h) - KV(e \cdot n)^2, \] (2)
where \( m \) is the magnetic moment of the particle, and \( e, h, n \) are unit vectors of the magnetic moment, field and easy magnetization axis of the particle, \( V \) is the volume of the ferromagnetic core of the particle.

The anisotropy constant \( K \) is the sum of the magnetocrystalline anisotropy constant (for magnetite \( K \approx 10^4 \text{ erg/cm}^3 \)) and the particle shape anisotropy constant \( K_\Delta = 2\pi M_s^2 \Delta N \), which is determined by the degree of non-sphericity of the particle and is comparable in order of magnitude to the magnetocrystalline anisotropy constant. The birefringence of a dilute suspension of anisotropic particles is determined by the orientational order tensor. The stationary distribution function of an assembly of noninteracting magnetic moments in a constant field is determined by the Gibbs distribution.

According to [3,4], the dependence of the magnitude of magnetic birefringence in a colloidal system of single-domain magnetic nanoparticles with an arbitrary value of magnetic anisotropy:

\[
\Delta n = \frac{3\pi C_V}{n_0} (g_1 - g_2) \Phi(\xi, \sigma),
\]

where \( C_V \) - volume concentration of magnetite, \( g_{1,2} \) - optical polarizability of a particle, \( \Phi(\xi, \sigma) \) is the component of orientational tensor along the direction of the applied field (orientational function). The function \( \Phi(\xi, \sigma) \) contains dimensionless parameters:

\[
\xi = \frac{mH}{kT}, \quad \sigma = \frac{KV}{kT},
\]

where \( \xi \) (the Langevin parameter) and \( \sigma \) being respectively the magnetic energy and the anisotropy energy of one grain normalized to the thermal energy \( kT \).

For arbitrary parameter values \( \xi \) and \( \sigma \), the orientation function \( \Phi(\xi, \sigma) \) may be written as [4]:

\[
\Phi(\xi, \sigma) = \frac{3}{2} \left(1 - \frac{3L(\xi)}{\xi} \right) \left[ \frac{d}{d\sigma} \ln R(\sigma) - \frac{1}{3} \right],
\]

where \( L(\xi) \) is the Langevin function and

\[
R(\sigma) = \int_0^1 \exp(\sigma \alpha^2) d\alpha.
\]

It is believed that when \( \sigma < 1 \) particles behave like superparamagnetic, and in the opposite case as hard-dipole particles [5].

Calculations without taking into account the anisotropy of the form give for sample 1 \( \sigma \approx 0.3 \), and for sample 2 \( \sigma \approx 1.6 \). This suggests that the particles in the samples should differ significantly in the relaxation time of the magnetic moment, namely: in sample 1 they should be mainly superparamagnetic dipole, and in sample 2 they should be hard magnetic dipole.

The asymptotic forms for the particle-size dependent factors entering expression (5) are [4]:

\[
1 - \frac{3L(\xi)}{\xi} = \begin{cases} \frac{\xi^2}{15} & \text{if } \xi << 1 \\ 1 - \frac{3}{\xi} & \text{if } \xi >> 1 \end{cases},
\]

\[
\frac{3}{2} \left[ \frac{d}{d\sigma} \ln R(\sigma) - \frac{1}{3} \right] = \begin{cases} \frac{2\sigma}{15} & \text{if } \sigma << 1 \\ 1 - \frac{2}{3\sigma} & \text{if } \sigma >> 1 \end{cases}.
\]
Thus, the field dependence of magnetic birefringence in weak field is parabolic \( \Delta n = Z(C, n, m, \sigma, kT) H^2 \). The proportionality coefficient \( Z = \partial(\Delta n)/\partial(H^2) \) or the tangent of the angle of inclination of the field dependence in weak fields depends on the concentration of particles, their optical characteristics, magnetic moment and magnetic anisotropy energy. The dependence of the slope of the field depending on the particle size should be the most significant. For small superparamagnetic particles, the ratio of the tangents of tilt angles for particles of different sizes should be \( Z_1/Z_2 = (r_1/r_2)^9 \). For the studied samples, the average particle sizes differ by about 1.5 times and we should expect a difference of proportionality coefficients by more than an order of magnitude (30-40 times). However, the experimental data give a maximum difference of about 1.7 times. In the figure 5 the spectral dependence of the ratio \( Z_2/Z_1 \) is shown.

![Figure 5. Spectral dependence of the \( Z_2/Z_1 \) ratio.](image)

The presence of a maximum in the spectral dependence can be explained by the features of the spectrum of the refractive index of the magnetic fluid [6], which also has a maximum in this region.

4. Conclusion

Significant difference in experimental data and calculations using the single-particle birefringence model can be explained on the one hand by the polydispersity of particles, and on the other by the presence of small particle aggregates in samples. Since the late 1980s [7, 8], a model of short chain aggregates for magnetic birefringence has been discussed. In [9], a simulation of the effect of short chains in magnetic birefringence of bidisperse magnetic fluids was performed. The application of this mechanism to interpret the results of our experiments is ambiguous and requires discussion. Magnetic moment of a chain significantly exceeds the moment of a single nanoparticle. The formation of chains in magnetic fluids with larger particles, in which a stronger magnetic dipole-dipole interaction, will lead to a more significant value of the parameter \( \xi \) and proportionality coefficient \( Z = \partial(\Delta n)/\partial(H^2) \). However, this is not observed experimentally. The difference in proportionality coefficients is even smaller than follows from the single-particle birefringence model. A more realistic explanation of the effect is the formation of small aggregates with a partially compensated magnetic moment. Such aggregates can be ring-like structures. The model of ring-like aggregates was applied in [10] to interpret the low-temperature dependence of the magnetic susceptibility of magnetic fluids. The possibility of the formation of such aggregates at room temperatures and in diluted magnetic colloids requires special study.

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