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STUDY OF THE INTERPARTICLE MAGNETIC INTERACTION EFFECT ON MAGNETIC RESONANCE LINE IN FERROFLUIDS

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The dipolar magnetic interaction effect on magnetic resonance line in ferrofluids is analyzed. Starting from a ferrofluid with magnetite particles dispersed in kerosene and stabilized with oleic acid, three samples were obtained by successive dilution with kerosene. Magnetic resonance and light scattering measurements were performed for each sample of ferrofluid. The experimental results revealed that the resonance line has a two-line feature for all samples, the magnetic field at resonance slowly increases and the magnetic resonance linewidth decreases by dilution of the samples. In accordance with the light scattering measurements, this behaviour is interpreted as a magnetic interparticle interaction and particle agglomeration effect.

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1. Introduction

The ferrofluids are stable colloidal systems consisting of single-domain ferro-ferrimagnetic particles dispersed in a carrier liquid and coated with a surfactant in order to prevent agglomeration [1]. The magnetic properties of ferrofluids have been intensively studied because they have multiple applications ranging from instrumentation to medicine. Also, the ferrofluids seem to be an advantageous model system in order to simulate and study disordered systems, because their structure and particle concentration can be easily controlled depending on the obtaining process, temperature or presence of external fields [2].

V. K. Sharma and F. Waldner [3] have emphasized experimentally that the magnetic resonance line of ferrofluids is sensitive to the changes of the interparticle dipolar interaction upon dilution. Also, in papers [4] and [5] the effect of particle concentration within ferrofluids on magnetic resonance linewidth has been studied.

The aim of the present paper is to analyze the interparticle dipolar interactions and particle agglomeration effect on the resonance field, H_0, the linewidth, ΔH, and the shape of the magnetic resonance line of a ferrofluid, which has low stability in magnetic field.

2. Experimental

The investigated ferrofluid was a ferrofluid with magnetite particles dispersed in kerosene and stabilized with oleic acid. The colloidal particles of magnetite were obtained by chemical co-precipitation of Fe^{2+} and Fe^{3+} ions, in aqueous solution [6]. The mean physical diameter of the particles, $d_m=11.4nm$ was determined from electron microscope analysis of the investigated ferrofluid.

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The resolution of the electron microscope was *0.7 nm*. From the initial ferrofluid two other samples were obtained by successive dilution with kerosene, using a dilution ratio *2/3*. The samples were denoted sample 1, sample 2 and sample 3. The particle concentration within the samples are presented in Table 1 and were determined from saturation magnetization of each sample, using the mean magnetic diameter resulted from microscope electron picture. In order to determine the particle concentration, the thickness of the solid nonmagnetic shell was assumed as being *0.84 nm* [7]. The measured saturation magnetization of the initial sample was M_∞ = *148 gauss* and the saturation magnetization of the bulk material was considered M_S = *477.5 gauss* [8]. The static magnetization measurements were performed using the method of sample extraction.

The magnetic resonance measurements were performed at room temperature using an ESR spectrometer (ART-5 type), which works at the frequency *9060 MHz*. The resonance absorption signals were recorded using a data acquisition system.

In order to analyze the formation of particle agglomerations within the investigated samples of ferrofluid because of an external static magnetic field, light scattering measurements were performed. The details on experimental arrangement are presented in paper [9].

3. Results and discussions

In magnetic resonance spectrometers, the frequency of the microwave field usually remains constant and the static magnetic field increases slowly in a fixed range and in a settled time interval. For the above experimental arrangement, the occurring of particle agglomerations within ferrofluids in magnetic resonance measurements is possible. Therefore, light scattering measurements of the samples subjected to an external static magnetic field were performed. In Fig. 1 the time dependence of the scattered light intensity (normalized to the transmitted intensity in the absence of the field) is plotted for the most diluted sample (sample 3), at 23 °C, between the sudden onset and offset of the magnetic field, for several values of its magnitude in the range *20 Oe - 200 Oe*. The magnetic field transient time was less than one second.

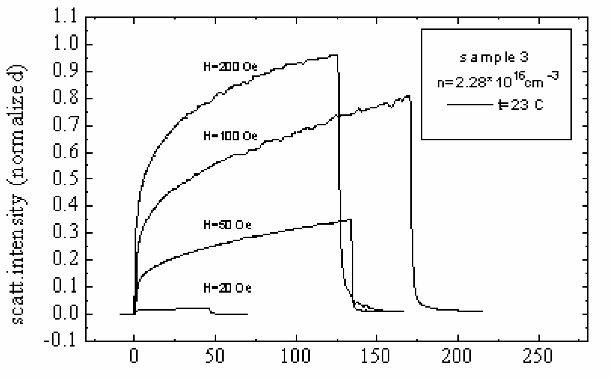

Fig. 1. Time dependence of the normalized scattered intensity in the most diluted sample (sample3) at 23 °C, for several values of the magnetic field intensity.

Light scattering in ferrofluids with drop-like aggregates originates from the light diffraction on the stretched drops of condensed phase aligned in the field direction. Since their particle density is much greater than in the uncondensed state, the ferrofluids are opaque to visible light [9], [10]. Under the assumption of incoherent scattering, the intensity of the scattered light is proportional with the density of the condensed phase drops. From the data plotted in Fig. 1, one can conclude that the external magnetic field induces the phase condensation phenomena. For samples 1 and 2, which are more concentrated, similar behaviour was found. Therefore, we can conclude that all investigated samples present large particle agglomerations stretched in the direction of the external magnetic field.

The magnetic resonance spectra for the investigated samples are presented in Fig. 2. The external magnetic field at resonance H_0 was experimentally evaluated as $(H_1+H_2)/2$ and the linewidth ΔH was experimentally determined as H_2-H_1, were H_1 and H_2 are values of the external magnetic field corresponding to the maximum and the minimum of the resonance lines respectively. The experimental results of the external magnetic field at resonance and of the linewidth for the investigated samples are presented in Table 1. As it can be observed from Fig. 2 and Table 1, the resonance line has a two-line pattern for all samples, the magnetic resonance field slowly increases and the linewidth decreases by dilution of the samples.

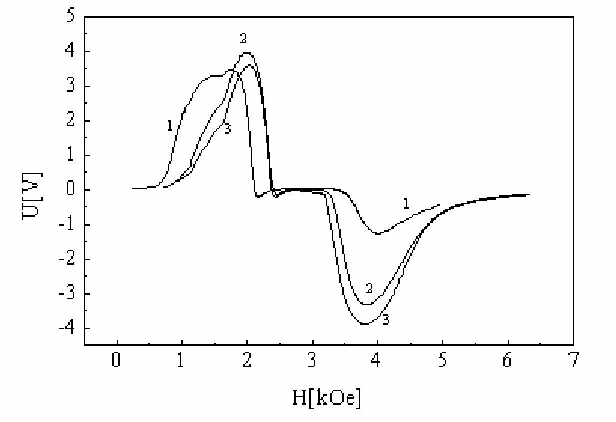

Fig. 2. The magnetic resonance spectra for the investigated samples.

Table 1. The magnetic resonance data on ferrofluid samples

Sample	n[cm^{-3}]	H_0[kOe]	ΔH[kOe]
1	$5.13\cdot10^{16}$	2.888	2.241
2	$3.42\cdot10^{16}$	2.904	1.847
3	$2.28\cdot10^{16}$	2.928	1.762

The theoretical description of the magnetic resonance condition for a system consisting of single domain particles is based on the analysis of the free energy per unit volume of a representative particle. As it is shown in [11], the resonant pulsation, ω, is given by the relation:

$$\frac{\omega}{g\gamma} = \frac{1}{M_S \sin\theta_0}\left(F_{\theta\theta}F_{\varphi\varphi} - F_{\theta\varphi}^2\right)^{1/2} \tag{1}$$

where (1), M_S is the saturation magnetization of the bulk material of the particle, g is the spectroscopic splitting factor and γ is the gyromagnetic electronic ratio. Also, φ and θ are the angular coordinates of the magnetization of the particle; $F_{\theta\theta}$, $F_{\varphi\varphi}$ and $F_{\theta\varphi}$ are the second derivatives of the free energy per unit volume of the representative particle, at the equilibrium position of magnetization of the particle, where F has a minimum. The free energy per unit volume of the representative particle is:

$$F = -M_S H_0\left(\vec{e}\vec{e}_H\right) - M_S H_D\left(\vec{e}\vec{e}_D\right) - K\left(\vec{e}\vec{e}_A\right)^2 \tag{2}$$

where H_o is the intensity of the static external magnetic field; H_D the intensity of the dipolar magnetic field acting on the representative particle due to all others particles from the sample, K represents an uniaxial effective anisotropy constant, $\mathbf{e}$, $\mathbf{e}_H$, $\mathbf{e}_D$ and $\mathbf{e}_A$ are the unit vectors which define the direction of magnetization, of the static external magnetic field, of the dipolar magnetic field and of the anisotropy axis respectively.

Under assumption of small anisotropy field and small interactions (conditions fulfilled for magnetite particles within ferrofluid at resonance, even in the case of particle agglomeration occurrence) the magnetization of the representative particle at equilibrium position is approximately parallel to the static magnetic field and the terms $(H_D/H_0)^2$, $2KH_D/(M_SH_0^2)$ and $(2K/H_0M_S)^2$ can be neglected. Also, assuming that the static magnetic field is parallel to the *oy* direction and using the approximation $(1+x)^{1/2} \cong 1 + x/2$, the relation (1) becomes:

$$H_0 = \frac{\omega_{res}}{g\gamma} - H_D \sin\theta_D \sin\varphi_D - \frac{K}{M_S}\left(2\sin^2\theta_A \sin^2\varphi_A - \cos^2\theta_A - \cos^2\varphi_A \sin^2\theta_A\right) \tag{3}$$

Because large particle agglomerations occur in the presence of a static magnetic field, we can assume an orientation distribution of the anisotropy axes of particles. Also, the magnetic particles within ferrofluid obey a dimensional distribution and because the neighbors of first order give the most important contribution to the dipolar field, we can assume an orientation distribution of the dipolar field. In relation (3), averaging over all particle sizes, over all orientations of the anisotropy axes and over all orientations of the dipolar field, the mean value of the static magnetic field at resonance, for the ferrofluid, can be written as:

$$H_0 = \frac{\omega_{res}}{g\gamma} - \frac{m}{d^3}\alpha - \frac{K}{M_S}\beta \tag{4}$$

whose m is the mean magnetic moment of a particle, d is the mean distance between the particles α is a constant depending on the local structure of the system and β is a constant depending on the orientation of the anisotropy axes. Taking into account the relation (4), it results that the dilution of a sample lead to an increase of the mean distance between the particles, then to an increase of H_0, in accordance with the experimental results (Fig. 2 and Table 1).

From relation (4) it can be observed that the resonance condition depends on the orientation of the anisotropy axis, on the dimensional distribution of the particles and on the local structure of the system. As a consequence, an extrinsic enlargement of the resonance linewidth of ferrofluids occurs due to the spread of the resonance magnetic field. Based on Van Vleck's method of moments [12], the resonance linewidth (i.e. the difference between the magnetic field corresponding to the maximum and the minimum of the resonance lines) is given by:

$$\Delta H = 2\left(\left\langle H_0^2\right\rangle - \left\langle H_0\right\rangle^2\right)^{1/2} \tag{5}$$

Averaging H_0^2 and H_0, the magnetic resonance linewidth of ferrofluid will have a value directly proportional with the anisotropy field and with the interaction term m/d^3:

$$\Delta H \approx f\left(\frac{m}{d^3}, \frac{K}{M_S}\right) \tag{6}$$

A linear dependence of the magnetic resonance linewidth on the interaction term m/d^3 was pointed out in paper [4] and [5]. Based on relation (6) the decrease of the magnetic resonance linewidth with dilution of the samples can be explained as a result of increase of mean distance between the particles.

As it was shown in [13], the anisotropy and the interaction terms can be expressed as a result of thermal fluctuations of the magnetic moment of the particle, as follows:

$$\frac{K}{M_S} = \frac{K_0}{M_{S0}} \frac{1 - 3x^{-1}\coth x + 3x^{-2}}{\coth x - x^{-1}} \tag{7}$$

$$\frac{m}{d^3} = \frac{M_{S0}V}{d^3}\left(\coth x - x^{-1}\right) \tag{8}$$

where $x=(M_{S0}VH_0)/(k_BT)$, K_0 and M_{S0} are the anisotropy constant and the magnetization of bulk material in the absence of thermal fluctuations respectively. Therefore, based on relations (7) and (8), from relation (4) and (6) it results that if the volume of a particle decreases then ΔH decreases and H_0 becomes closer to the value $\omega_{res}/g\gamma$. Consequently, the small particles give narrow lines in the vicinity of $\omega_{res}/g\gamma$ and the large particles give lines having large values of linewidth at different values of H_0. Moreover, the particles from particle agglomerations will give lines having larger values of linewidth as results from relation (6). The superposition of all contribution of resonant lines leads to a two-line pattern: the narrow one corresponding to the small particles in superparamagnetic state and the width one corresponding to the large particles and to the particles from particle agglomerations. Therefore, two-line pattern and large value of the resonance linewidth as we have determined for the investigated samples, are signs of low stability of ferrofluids, result that is in agreement with light scattering measurements.

4. Conclusion

The magnetic resonance line is sensitive to the changes of interparticle interactions and to particle agglomeration occurrence. Therefore the magnetic resonance measurements can be used in for the quantitative analysis of the stability of ferrofluids.

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