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Field-induced aggregates in a bilayer ferrofluid characterized by ultrasound spectroscopy

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Abstract
This paper presents dynamic changes in ferrofluid properties during a magnetic field sweep. The study reported was performed on a ferrofluid with a double layer of surfactant used to prevent aggregation of particles. The ferrofluid parameters (the radius and volume of the cluster, the elastic force constant) were studied by the ultrasound wave absorption method as a function of the dynamically changing magnetic field. During the application of the magnetic field from 0 to 100 kA m^{-1} the structure in the ferrofluid evolves and become anisotropic. The magnetic field was found to stimulate formation of micrometre clusters and exponential increase in the elastic force constant.

1. Introduction

A ferrofluid is a colloidal suspension of single-domain magnetic nanoparticles in a carrier liquid medium. The properties of ferrofluids are isotropic but the external magnetic field gives rise to anisotropy: the liquid undergoes restructuring by the formation of spherical and chain-like clusters.

Many applications of ferrofluids require stability of the structure, i.e. no formation of relatively large aggregates, even in a strong magnetic field. This property is of particular importance in medical applications in which a magnetic fluid is injected intravenously, and then blood circulation is used to transport the magnetic particles to the region of treatment. In such applications it is required that the particles do not aggregate and block their own spread [1]. One of the methods used to prevent aggregation is based on covering the ferrofluid particles with a single or double layer of a surfactant. This study was undertaken to determine by ultrasonic spectroscopy the properties of such a bilayer ferrofluid subjected to a magnetic field. In previous work [2–4] the magnetic field strength was obtained by increasing the field from 0 to H and then maintained at a constant value. After the ferrofluid structure reached equilibrium, the field-induced anisotropy of the ultrasonic wave absorption coefficient was measured. However, from a practical aspect, it is very important to develop the dynamic properties of the ferrofluid. Here, the ultrasound wave absorption coefficient was measured

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as a function of the sweep changes in the magnetic field for different angles between the wave propagation direction and the direction of the field.

2. Experimental details

The study was performed on a bilayer ferrofluid obtained by chemical precipitation of a mixture of ferric and ferrous salts in an alkaline aqueous medium [5]. To improve the stability of the ferrofluid the Fe_3O_4 magnetic particles were covered with a double layer of lauric acid and suspended in water. At $T = 40\,^{\circ}\mathrm{C}$ the density of the ferrofluid, ρ, was 1088.25 kg m^{-3} and the propagation velocity of the ultrasound waves, c, was 1477.5 m s^{-1}.

The anisotropy of the ultrasonic wave absorption was measured by the pulse method based on measurement of the intensity of the ultrasonic pulse passed through or reflected by the medium being studied. A detailed description of the measuring set-up is given in [2]. The frequency of the ultrasonic wave was 3.2 MHz. A changing magnetic field was obtained in an electromagnet controlled by a system with a programmable current source. It permitted an automatic sweep of the range of magnetic fields studied at a given rate $\mathrm{d}H/\mathrm{d}t$. The system is coupled with a computer which conducts a concurrent reading of the value of the ultrasonic wave absorption coefficient and the value of the external magnetic field.

2.1. Magnetic properties

In order to establish the dominant mechanism and to determine the mean particle radius, the measurements of differential magnetic susceptibility χ were performed in a constant magnetic field. The susceptibility measured in the direction perpendicular to the vector of the external magnetic field is described by the following theoretical function [6]:

$$\chi_{\perp} = 3\chi_0 \frac{L(\xi)}{\xi} = \frac{3\chi_0}{\xi}\left(\cosh\xi - \frac{1}{\xi}\right), \tag{1}$$

where χ_0 is the initial magnetic susceptibility for $H_{\mathrm{DC}} \longrightarrow 0$ and $f \longrightarrow 0$ and ξ is a Langevin function parameter.

Analysis of this monotonically decreasing function (1) shows that for $\xi_2 = \mu_0 m H_2/k_{\mathrm{B}}T = 4.733$ the magnetic susceptibility of the ferrofluid decreases by half: $\chi(\xi_2) = 0.5\chi_0$. Thus, from the experimental dependence $\chi_{\perp}(H)$ (figure 1) the mean magnetic moment of the ferrofluid particle was found as:

$$\langle m\rangle = \frac{4.733\cdot k_{\mathrm{B}}T}{\mu_0 H_2} = 3.15\times 10^{-19}\ (\mathrm{A\ m^2}). \tag{2}$$

The magnetic susceptibility was determined with the help of an RLC bridge MT-4080A used for measurements of the inductance of the cylindrical solenoid. The absolute error in the inductance measurement was $\triangle L = \pm 0.1\ \mu\mathrm{H}$. The ferrofluid sample assumed the shape of the cylinder (length $l = 75$ mm, radius $r = 5$ mm), specifically chosen in order to limit the effects related to demagnetization (demagnetizing factor = 0.01) [7].

Assuming the magnetic particles to have a spherical shape and taking into account the spontaneous magnetization of the material (for Fe_3O_4, $M_{\mathrm{g}} = 446$ kA m^{-1}), the radius of a magnetic grain is found from:

$$\langle r\rangle = \sqrt[3]{\frac{3\langle m\rangle}{4\pi M_{\mathrm{g}}}} = 5.5\ (\mathrm{nm}). \tag{3}$$

Figure 2 presents the magnetisation curve for the ferrofluid studied, the saturated state magnetization is marked as:

$$M_{\mathrm{S}} = M_{\mathrm{g}}\cdot\phi_{\mathrm{V}} = 5.04\ (\mathrm{kA\ m^{-1}}). \tag{4}$$

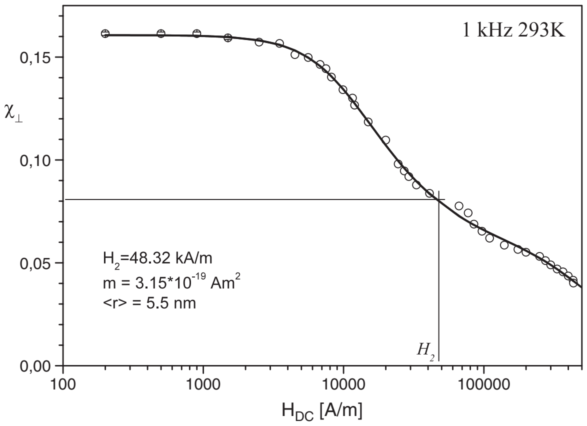

Figure 1. The magnetic susceptibility measured perpendicular to the direction of the constant magnetic field.

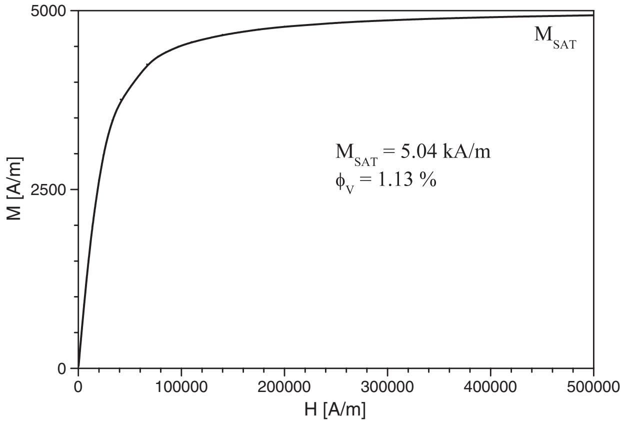

Figure 2. The magnetization of ferrofluid as a function of the constant magnetic field.

On the basis of equation (4) we could estimate the bulk concentration of magnetite particles as $\phi_V = 1.13\%$.

The Néel relaxation time τ_N is related to the magnetic radius of the grain r_m, the constant K and temperature T. For the following data—$\langle r \rangle = 5.5$ nm, $K = 23$ kJ m^{-3} [8], $k_B = 1.38 \times 10^{-23}$ J K^{-1}, $T = 300$ K, $\tau_0 = 1$ ns—we get $\tau_N = 48$ ns.

3. Results and discussion

Dynamic measurements of the ultrasound wave absorption coefficient α were made at a constant rate of increase of the magnetic field $\mathrm{d}H/\mathrm{d}t = 200$ A m^{-1} s^{-1}, for different angles φ of the direction of propagation of the acoustic waves, **k**, to the direction of the magnetic field, H. The results are presented in figure 3. The values of α were different for different angles φ (in the field $H = 0$ kA m^{-1} the ferrofluid is isotropic—the same value α for each angle). The greatest increase in the ultrasound wave absorption caused by the magnetic field was noted at $\varphi = 0°$. With increasing φ the effect of the magnetic field on the acoustic properties of

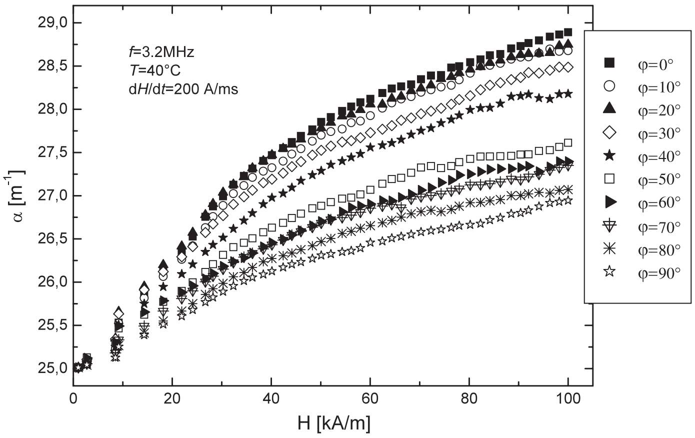

Figure 3. Ultrasound wave absorption coefficient as a function of the magnetic field for different angles φ between the direction of the field and the wave propagation direction.

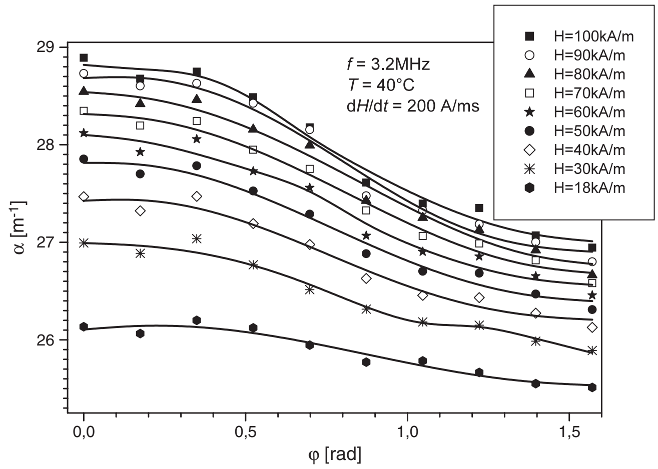

Figure 4. Anisotropy of the ultrasound wave absorption coefficient in the ferrofluid, at different magnetic field values (solid lines are theoretical Taketomi functions).

the ferrofluid decreased. The above results indicate that the field-induced anisotropy of the ultrasound wave absorption coefficient is a consequence of joining the magnetic particles into first spherical and later chain clusters arranged along the magnetic field lines. The effect is clearly visible in figure 4 showing anisotropy α determined at different values of the magnetic field.

According to Taketomi [9], the amplitude of ultrasonic attenuation, α, of an ultrasonic wave propagating in the ferrofluid under the effect of an external magnetic field consists of two parts, related, respectively, to the rotational motion of the clusters, α_{rot}, and their translational motion, α_{tr}. In his theory, the clusters, activated by the acoustic field, perform translational and rotational motions simultaneously. This is an irreversible process dissipating the energy of the acoustic wave into heat. The two mechanisms affecting the absorption coefficient are described as [9]:

Table 1. Values of the selected parameters $\frac{4}{3}\eta_S + \eta_V$, α_5, α_1, k and r_{cl} obtained from the fit of the function describing the anisotropy of the ultrasonic absorption coefficient to the experimental points using the least-squares method.

H (kA m^{-1})	$\frac{4}{3}\eta_S + \eta_V$ (N s m^{-2})	α_5 (N s m^{-2})	α_1 (N s m^{-2})	k (N m^{-1})	r_{cl} (μm)
100	0.469	0.014 79	0.001 78	77.7	1.55
90	0.4182	0.050 7	−0.028 36	37.5	1.897
80	0.462	0.018 4	−0.005	14.8	1.89
70	0.452	0.021 5	−0.061	8.55	1.2
60	0.461	0.011 8	0.003 14	6.96	0.777
50	0.4346	0.023 2	−0.003 8	7.18	1.174
40	0.4188	0.028 6	−0.007 73	2.24	0.782
30	0.4403	0.022 5	−0.016 62	2.21	0.625
18	0.415	0.011 4	−0.000 94	0.74	0.706

$$\alpha_{rot}(\varphi) = \frac{\varpi^2}{2\rho_0 c^3}\left[\left(\frac{4}{3}\eta_S + \eta_V\right) + 2\alpha_5\cos^2\varphi + \alpha_1\cos^4\varphi\right], (\mathrm{m}^{-1}) \quad (5)$$

$$\alpha_{tr}(\varphi) = \frac{1}{c}\frac{3\pi\eta_0 r_{cl}\varpi^3 V_{cl} N(6\pi\eta_0 r_{cl} + \varpi V_{cl}\rho_0)}{(k\sin\varphi - \rho_m V_{cl}\varpi^2)^2 + (6\pi\eta_0 r_{cl}\varpi)^2}, (\mathrm{m}^{-1}) \quad (6)$$

where c is the velocity of the ultrasonic wave propagating at an angular frequency ϖ, ρ_0 and ρ_m are the densities of the carrier fluid and magnetic particles, η_0 is the viscosity of the carrier fluid, η_S and η_V are the dynamic and volume viscosities of the ferrofluid, r_{cl} and V_{cl} are the radius and volume of the cluster, N is the number of clusters per unit volume, k is the elastic force constant, φ is the angle between the magnetic field strength vector and the propagation vector of the ultrasonic wave and α_1, α_5 are the Leslie coefficients appearing in the theory of liquid crystals [10].

Note that the first (isotropic) term in the square brackets of equation (5) bears no relation to the particle or cluster rotation. It represents the ordinary viscous dissipation of sound waves:

$$\alpha_{rot} = \frac{\varpi^2}{2\rho_0 c^3}\left[\left(\frac{4}{3}\eta_S + \eta_V\right)\right]. \quad (7)$$

In the absence of an applied magnetic field, when the elastic force constant $k = 0$ equation (6) also becomes isotropic:

$$\alpha_{tr} = \frac{3\pi\eta_0 r_{cl}\varpi V_{cl} N(6\pi\eta_0 r_{cl} + \varpi V_{cl}\rho_0)}{c[(\rho_m V_{cl}\varpi)^2 + (6\pi\eta_0 r_{cl})^2]}. \quad (8)$$

The theoretical Taketomi functions fitted to the experimental data are presented in figure 4. Figure 5 shows the anisotropy of the ultrasound wave absorption coefficient in the ferrofluid and the components ($\alpha_{rot} + \alpha_{tr}$) of the Taketomi functions for an exemplary value of the magnetic field $H = 18$ and 70 kA m^{-1}. It is evident that the ultrasound wave absorption is mostly dependent on the rotational movements of the clusters as their contribution is many times greater than that of the translational movements. The measurements of $\alpha(\varphi)$ provide important information on the structure of a ferrofluid in a magnetic field. Selected parameters are shown in table 1.

According to the results, in a ferrofluid subjected to an external magnetic field micrometre-sized spherical clusters appear, later arranging in chains along the direction of the field. With increasing magnetic field the number of particles participating in cluster formation increases and hence the radius of the spherical clusters increases, as shown in figure 6. At a magnetic

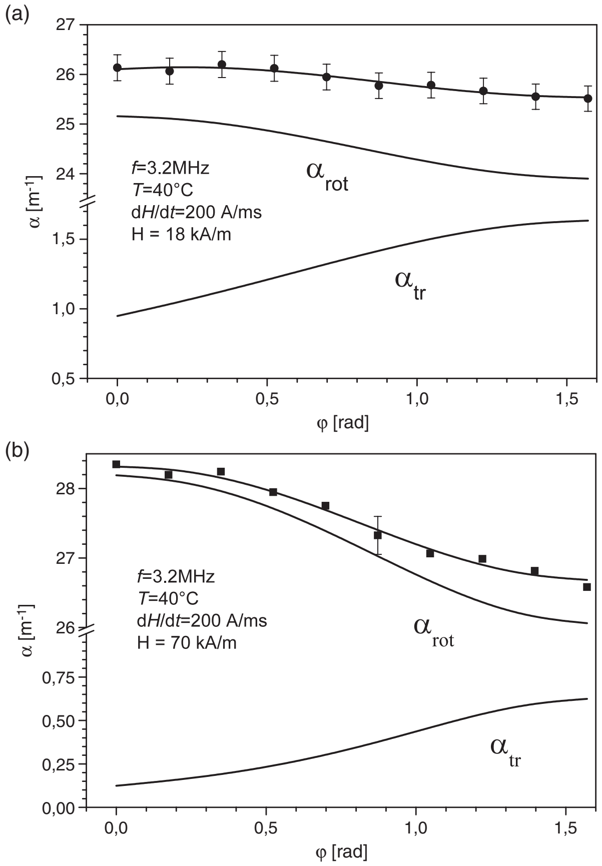

Figure 5. Anisotropy of the ultrasound wave absorption coefficient in the ferrofluid and the components ($\alpha_{\rm rot} + \alpha_{\rm tr}$) of the Taketomi functions for (a) 18 kA m^{-1} and (b) 70 kA m^{-1}.

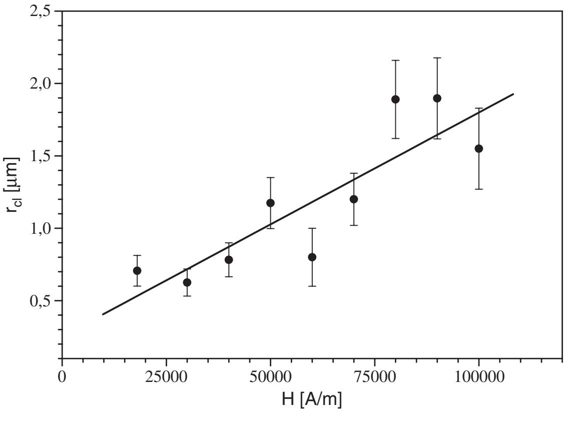

Figure 6. The radius of clusters as a function of magnetic field.

particle concentration of 1.13% the use of a double layer of a surfactant does not prevent cluster formation. A probable reason for this is too high a concentration of nanoparticles. In

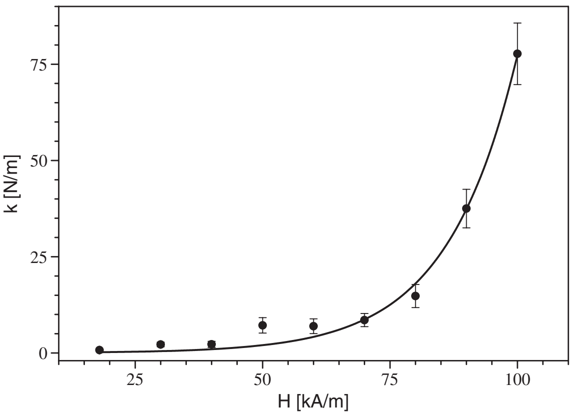

Figure 7. Elastic force constant as a function of magnetic field.

ferrofluids with a lower concentration of magnetic particles (weaker magnetic properties) with a surfactant bilayer the effect of the magnetic field on the ultrasound wave absorption coefficient was very small [11]. Measurements of ultrasonic wave propagation also confirmed the effect of the ferrofluid concentration on the structure of a ferrofluid subjected to an external magnetic field. The changes in the ultrasonic wave absorption coefficient decrease with decreasing concentration of the ferrofluid, which can be interpreted as being due to the formation of a lower number of smaller clusters [12]. Therefore, ferrofluids with a lower concentrations of magnetic particles can be used for biomedical applications. The formation of clusters and the arrangement of their magnetic moments along the direction of the field (according to the Néel and Brown mechanisms) is also responsible for an increase in the elastic force constant. As shown in figure 7, the elastic force constant increases exponentially with increasing magnetic field.

4. Conclusion

According to the above-discussed results, the ultrasound wave absorption coefficient increases with increasing magnetic field and its value depends on the angle between the propagation vector and the direction of the magnetic field. This dependence means that in the ferrofluid studied with a magnetic particle concentration of $\phi_V = 1.13\%$ the process of particle aggregation takes place despite the surfactant bilayer.

The presence of micrometre-sized clusters was detected and their size increased with increasing magnetic field. The ultrasound wave energy is used mainly for the rotational motions of the clusters. The magnetic field sweep is also responsible for an exponential increase in the elastic force constant of the ferrofluid studied.

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