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# Local arrangement of particles in magnetic fluids due to the measurement alternating field

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ABSTRACT

Changes in the magnetic susceptibility spectrum of ferrofluids, $\chi(\omega)$, due to the nanoparticle agglomeration are common when a static magnetic field is superimposed on the measuring field, but here we report on changes which occur in the absence of a static magnetic field, solely in the presence of the measuring field, over the frequency range of 50 Hz–13 MHz and irrespective of the colloidal stability of samples. The result is explained in terms of local rearrangement of particles within ferrofluids subjected to low frequency alternating magnetic field.



## 1. Introduction

Magnetic fluids or ferrofluids are ultra-stable colloidal systems consisting of single-domain magnetic particles dispersed in a carrier liquid. In order to prevent agglomeration, the particles are covered with a surfactant, which is compatible with the carrier liquid and with the material of particles [1].

The relaxation component of the frequency dependent magnetic susceptibility, $\chi(\omega)$, of such an assembly of single-domain magnetic particles is usually described by the Debye equation [2,3] with:

$$\chi(\omega) = \chi_\infty + \frac{\chi(0) - \chi_\infty}{1 + i\omega\tau} \quad (1)$$

where $\chi(0)$ is the static susceptibility, $\chi_\infty$ is the susceptibility at very high frequencies (but below resonance) and $\tau$ is the relaxation time.

The Debye spectrum (Eq. (1)) is valid for monodisperse ferrofluids with negligible interparticle magnetic dipole interactions. Expressions of the static susceptibility for monodisperse ferrofluids with weak interparticle interaction and for monodisperse ferrofluids with chain-like aggregates are given in Refs. [4,5] and generalization of expression (1) to the polydisperse case with weak interparticle interaction is given in Ref. [6].

Three relaxation processes influence the magnetic susceptibility of ferrofluids: i) the Brownian relaxation (associated with the rotation of particles in the carrier liquid [3]) ii) the Néel relaxation (correlated to the rotation of the magnetic moment of particles, inside the particles, by overcoming the energy barrier within particles [3]) and iii) the intra-well relaxation (in connection with the rotation of the magnetic moment of particles, inside the particles, but within the energy well [7,8]). However, at RF frequencies and below, only the Brownian and Néel relaxation mechanisms may manifest their presence in the magnetic susceptibility spectrum, $\chi(\omega)$ [3,7,8]. The Brownian relaxation time, $\tau_B$, is given by

$$\tau_B = \frac{4\pi\eta r_H^3}{k_B T} \quad (2)$$

where $\eta$ is the viscosity of the carrier liquid, $r_H$ is the hydrodynamic radius of a particle, $T$ is the temperature of the system and $k_B$ is the Boltzmann's constant.

The Néel relaxation time, $\tau_N$, is expressed by [3]:

$$\tau_N = \tau_D(1 + 2\sigma/5)\ \sigma < 1 \quad (3)$$

and

$$\tau_N = \frac{\sqrt{\pi}}{2}\frac{\tau_D}{\sigma^{3/2}}\exp(\sigma)\ \sigma \geqslant 2 \quad (4)$$

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where $\tau_D = \tau_0\sigma$ is referred as the rotational diffusion time, $\tau_0$, is the precessional decay time, $\sigma = Kv/k_BT$, $K$ is the effective anisotropy constant of particles and $v$ is the magnetic volume of a particle.

In given circumstances, the magnetic moment of the ferrofluid relaxes with the shortest relaxation time and the overall relaxation time, $\tau$, may be expressed as a function of both Brownian, $\tau_{B,}$ and Néel, $\tau_N$, relaxation times [9], where,

$$\tau = \tau_N\tau_B/(\tau_N + \tau_B) \quad (5)$$

Various theoretical models [4,5,10–14] and experimental results [15–21] have clearly shown that the magnetic susceptibility of ferrofluids is influenced by the presence of a static magnetic field, due to the changes in the local structure (i.e. formation of small aggregates, particle chains or large drop-like particle agglomerations). As a matter of fact, apart from magneto-optical investigations, complex magnetic susceptibility measurements are usually involved in the analysis of colloidal stabilization of ferrofluids [12,15,20,21].

Controlling the local structure and properties of ferrofluids with static magnetic field has been an attractive subject of research, but still little is known about the structural transformations in ferrofluids subjected to an alternating magnetic field. In an attempt of manipulation of ferrofluids using magnetic fields, in the Refs. [22,23], by means of magneto-optical investigations, the authors proved that particle agglomerations can be induced by alternating magnetic fields of various frequencies.

In the present paper we report on changes in the magnetic susceptibility spectrum of ferrofluids, $\chi(\omega) = \chi'(\omega) - i\,\chi''(\omega)$, in alternating magnetic field, over the frequency range of 50 Hz to 13 MHz, in a series of repetitive measurements and irrespective of the colloidal stability of magnetic fluid samples.

## 2. Samples

The investigated samples, namely samples A, B and C, were water-based magnetic fluids with magnetite particles, supplied by the *Ferrotec Corporation*. Some basic characteristics of the samples are given in Table 1.

Initially, magneto-optical measurements were undertaken in order to investigate the colloidal stabilisation of the samples. When sample C was subjected to a static magnetic field, the particles agglomerated in elongated drops like aggregates (also known as "drops of condensed phase" [10]), parallel to the magnetic field lines. Fig. 1 shows an optical microscope photograph of aggregates formed in sample C when subjected to a static magnetic field, B = 10 mT.

In contrast, in the case of samples A and B, no drops of condensed phase were identified by the optical microscope, when a static field was applied. However, even if particles within these two samples agglomerate, the aggregates should be much smaller than in the case of sample C.

## 3. Results and discussions

Room temperature complex magnetic susceptibility measurements, $\chi(\omega) = \chi'(\omega) - i\,\chi''(\omega)$, over the frequency range of 50 Hz to 13 MHz, were made by means of the toroidal technique [24]

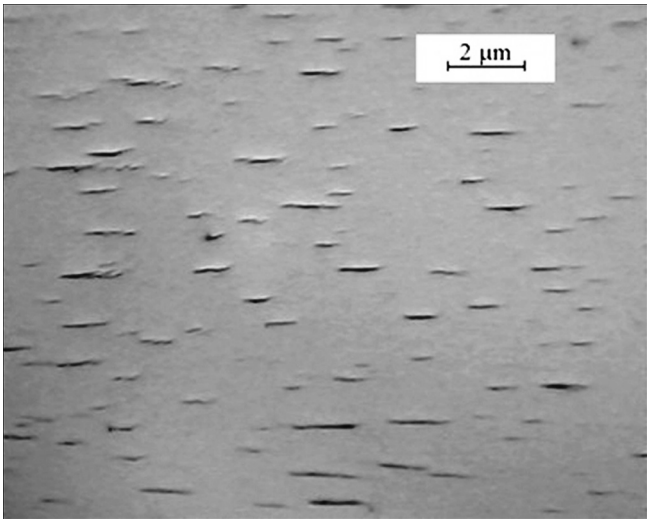


**Fig. 1.** Aggregates in sample C when subjected to static magnetic field, B = 10 mT.

in conjunction with a Hewlett Packard RF Bridge 4291A. The test cell consisted of a narrow slit, cut in a toroid of very high permeability and the probing field was in the order of 60 A/m. From the impedance measured across a number of excitation turns wound on the toroid, the $\chi'(\omega)$ and $\chi''(\omega)$ components were determined. Each logarithmic frequency sweep over the entire measurement range took about 2 min. After each sweep the sample remained in the sample holder (i.e. in the toroidal slit) for a predetermined ('rest') time; five minutes in the case of samples A and B, and four minutes in the case of sample C. The process was then repeated until the completion of the experiment.

The results are presented in Figs. 2–4, where the plots are normalized to the value of $\chi'$ measured at the beginning of the set of measurements (i.e. that corresponding to the time moment, $t = 0$ and frequency, $f = 50$ Hz).

As can be seen from Figs. 2 and 3, the frequency dependence of the $\chi''$ component does not exhibit a well-defined Brownian peak, but rather a shoulder at frequencies characteristic of the Brownian relaxation process. This means that the Brownian particles (i.e. large particles and aggregates, which can perform Brownian rotation when subjected to alternating measurement field) have a small volume concentration with respect to the particles, which perform only Néel rotation. This result is in agreement with that obtained by magneto-optical microscopy.

From Fig. 4, one can observe that the frequency dependence of the $\chi''$ component has a Brownian peak at a frequency of $f_{maxB} = 2.1$ kHz, indicating that the particle agglomeration phenomenon is significant in sample C. The frequency of $f_{maxB}$ decreases in time from 2.1 kHz to 1.4 kHz and since $\tau_B = 1/2\pi f_{max}$ [2], this result is indicative of an increase in the hydrodynamic radius of aggregates that can rotate in the carrier liquid, from 29 nm to 33.2 nm, respectively [17].

One of the most important features of the susceptibility measurements presented is that, irrespective of the degree of colloidal stabilization of particles within the investigated samples, the

**Table 1**
Characteristics of the samples.

| Sample | $4\pi M_\infty$ [G] | Viscosity [Pa·s] | Density [kg/m$^3$] | Average particle diameter [nm] | Standard deviation [nm] |
|---|---|---|---|---|---|
| A | 252 | $4.6 \cdot 10^{-3}$ | 1297 | 7.40 | 3.24 |
| B | 256 | $8.3 \cdot 10^{-3}$ | 1320 | 7.70 | 3.25 |
| C | 325 | $2.6 \cdot 10^{-3}$ | 1330 | 8.03 | 3.64 |