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Magnetic measurements on frozen ferrofluids as a method for estimating the magnetoviscous effect

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Abstract
Magnetic measurements on frozen ferrofluids with and without significant structure formation in an applied magnetic field have been performed. The results of these investigations were compared with the magnetic field dependent rheological properties for two different kinds of ferrofluids. Magnetic experiments performed similarly to conventional field cooled–field warming magnetic tests show the contribution of magnetic domain blocking and structure reorganization to the rheology of ferrofluids. Our efforts have shown the possibility of giving an estimate of the magnetoviscous effect by considering the temperature dependence of the magnetization of a frozen sample.

1. Introduction

The problem of structure formation in dispersions of single-domain magnetic nanoparticles in an applied magnetic field is nowadays intensively studied. Nanoparticles in such fluids, well known as ferrofluids, exposed to a magnetic field, can form structures like chains or columns. Experiments and numerical simulations [1] show the strong influence of structure formation on the rheological, magnetic, optical and other properties of these materials. Theoretical investigations on structure formation and on the influence of the structures on the rheological properties have been performed on the basis of microscopic assumptions, e.g. in [2], and on a macroscopic level, e.g. in [3]. In [4] it was shown that long chains can appear in ferrofluids under the action of an applied field when the temperature decreases. Here a magnetic field transformed the longest chains into dense globules. Magnetization measurements and rheological investigations on separated ferrofluid fractions with changed particle size distribution were performed in [5] and it has been found that mainly the larger particles show a significant magnetic field induced interparticle interaction leading to structure formation. Numerically, the polydispersity of the particles in ferrofluids has been considered in [6] and it was shown that the chains consist basically of the largest nanoparticles, and magnetic interaction between large and small particles reduces the size of the chains. In [7, 8] it has been shown that the appearance of chains of nanoparticles significantly increases the magnetization of the ferrofluid. Experimentally, the formation of structures in ferrofluids subjected to a magnetic field was observed by means of small-angle neutron scattering [9] and the relation of an increase of the fluid viscosity, the so-called magnetoviscous effect [10], with the structure formation was shown. Common ways of defining experimentally an ability of magnetic nanoparticles in ferrofluids to aggregate in an applied magnetic field are via rotational [11–13] or capillary rheology [14].

Our aim was to consider magnetization measurements on frozen ferrofluids as a method for estimating the ability of a fluid to show a magnetoviscous effect. A lot of magnetization measurements as well as theoretical techniques for interpreting experimental data on frozen ferrofluids were successfully performed before. The dynamical susceptibility of frozen ferrofluids has been obtained in [15, 16], and in [17] the presence of chains has been taken into account. Besides this, the local random anisotropy and dipole–dipole interaction were experimentally considered in [18]. Several years ago, novel strategies for magnetization measurements on frozen ferrofluids were presented [19, 20]. One should expect that, if a frozen ferrofluid is heated under a constant field, its magnetization $M(T)$ should display a change at a certain temperature forced by structural transformations of internal magnetic structures. This temperature is interpreted as a blocking of the superparamagnetic relaxation of the single

Table 1. Basic properties of the ferrofluid samples.

Sample	Magnetic material	d (nm)	ϕ (%)	Carrier liquid	$\eta_{20\,^\circ\mathrm{C}}$ (mPa s)	λ^*
APG513A	Fe_3O_4	10	0.8	Synthetic ester	120	0.5
VS1-017	Co	8	2.8	Silicon oil DC 702	65	2.5

particles [18, 21, 22]. The present study deals with magnetic measurements in the temperature region of the melting point of the carrier liquid. By means of such experiments it is possible to observe effects forced by structural changes inside the melting sample, since the magnetic properties of ferrofluids reflect their structural state. From the thermomagnetic curves obtained one is able to characterize the reorganization of the nanoparticles and structures. In that way it becomes possible to give an estimation of the ability of the fluid to exhibit a magnetoviscous effect.

2. Ferrofluid samples

Two different ferrofluids, the commercial magnetite based fluid APG513A manufactured by Ferrotec and a cobalt based fluid (VS1-017) prepared by S Behens and A Gorschinski at the Institute of Technical Chemistry of Forschungszentrum Karlsruhe, were used in the experiments. The basic parameters of both samples are listed in table 1, where d denotes the mean diameter of the magnetic particles, ϕ the volume concentration of the particles, η the dynamic viscosity of the fluid in the absence of a magnetic field and λ^* the modified interaction parameter, which quantifies the interparticle interaction and represents the ratio of the magnetic dipole interaction energy of two particles in contact to their thermal energy.

An interaction parameter for the magnetic nanoparticles was firstly introduced in [23] and modified in [10], taking into account the thickness of the surfactant layer coating the particles. One can calculate the modified interaction parameter as

$$\lambda = \frac{\mu_0 {M_0}^2 V^2}{2\pi d^3}\frac{1}{k_B T}\left(\frac{d}{d+2s}\right)^3 \tag{1}$$

where μ_0 denotes the vacuum permeability, M_0 the spontaneous magnetization of the magnetic material, V the volume of the magnetic material, k_B Boltzmann's constant and T the absolute temperature, d the mean diameter of the nanoparticles and s the coating thickness. According to [13] one can state that particles able to form structures should be larger than 16 nm for magnetite and larger than 6.5 nm for cobalt. Thus in the cobalt based ferrofluid VS1-017 all particles are large enough to form structures, whereas the magnetite based ferrofluid APG513A contains only small particles which are not able to form significant structures.

3. Rheological measurements

For the rheological investigation of the samples, the shear-controlled rheometer described in [11] with improved hardware and software was used. This rheometer uses a cone–plate geometry (opening angle 3°, cone diameter 70 mm) combined with a Couette region. The measured parameter is a rotational torque N, which depends linearly on the viscosity of the fluid. According to [10] the relative change of viscosity forced by the magnetic field can be calculated as

$$\Delta\eta = \frac{N_H - N_0}{N_0} \tag{2}$$

where N_0 and N_H are the torques measured for vanishing magnetic field and for magnetic field strength H respectively. In figure 1 the dependences of the relative change of viscosity on magnetic field strength measured for a shear rate of 0.3 s^{-1} are shown for both fluids.

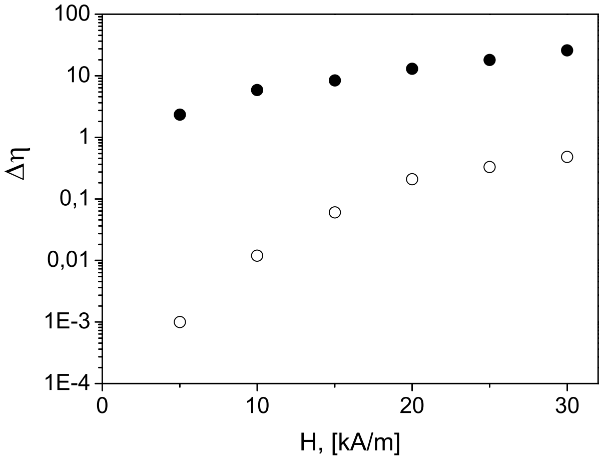

Figure 1. Relative change of viscosity for fluids APG513A (○) and VS1-017 (●) as a function of applied magnetic field strength for a shear rate of 0.3 s^{-1}.

Since the fluid APG513A contains mainly small particles, no significant structure formation should appear and the relative change of viscosity does not exceed the value of 0.5. In contrast, the cobalt based ferrofluid VS1-017 exhibits a significant magnetoviscous effect. This is commonly explained by the chain formation model [12] where the appearance of the magnetoviscous effect is attributed to strong interparticle interaction in the presence of a magnetic field.

As additional proof for the differences in structure formation in the samples investigated, yield stress measurements were carried out with a stress-controlled rheometer described in [24, 25].

Investigations of the sample APG513A were already performed in [13] and no yield stress was observed (sample 2 in [13]). In contrast to this, the ferrofluid VS1-017 exhibits a significant yield stress which grows quadratically with the strength of the applied field (figure 2).

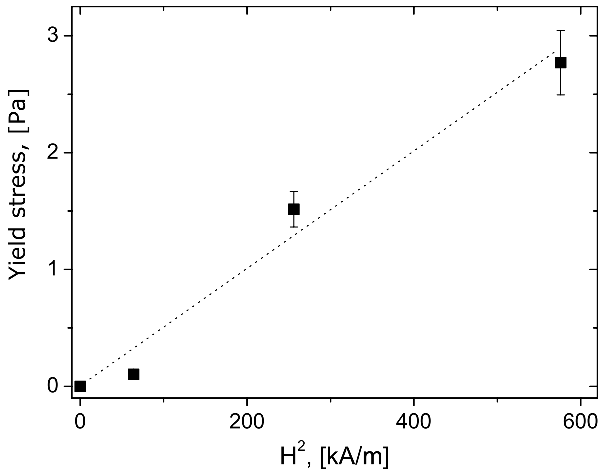

Figure 2. The magnetic field dependence of the yield stress for the fluid VS1-017 containing structure forming particles. The dotted line is a linear fit.

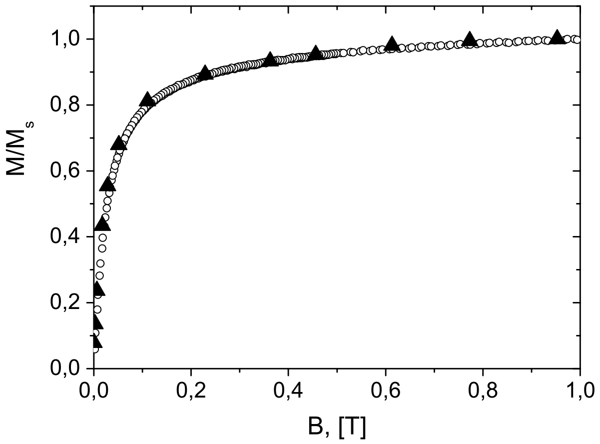

Figure 3. Normalized magnetization curve of APG513A at room temperature: ○—before NFC–FW and ▲—after NFC–FW.

4. Magnetization measurements

The magnetic measurements were performed with a vibrating sample magnetometer (Lake Shore 7407) equipped with a cooling stage using liquid nitrogen.

The cooling stage allows a temperature control with a precision of ±0.1 K. As the cooling sequence, a procedure analogous to the negative high field cooling–field warming (NFC–FW) procedure [19] was used. A sample was subjected to a uniform constant magnetic field B_c providing a magnetization of the fluid equal to 95% of its saturation magnetization M_s at room temperature. In this magnetic field the sample was frozen by cooling to the temperature T_f with a cooling speed of 5 K min^{-1}. After freezing, the sample was oriented perpendicular to its initial position with respect to the magnetic field direction. Afterwards, field warming was performed at a magnetic field strength B_{fw} corresponding to a field that provides $M = 0.5M_s$. The speed of warming was about 2 K min^{-1}. Prior to the NFC–FW procedure, magnetization curves for both samples were measured at room temperature. The results of these measurements are presented in normalized form in figures 3 and 4 for APG513A and VS1-017 respectively.

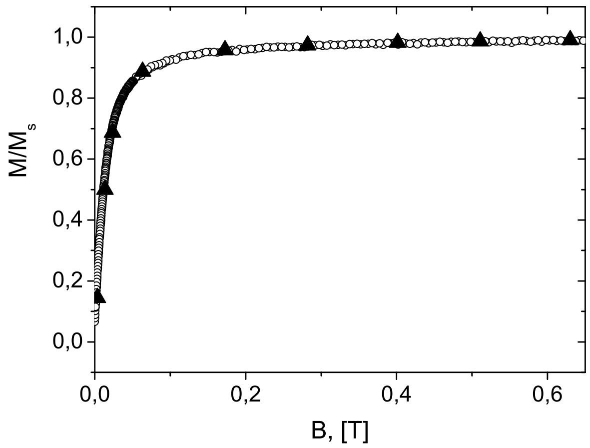

Figure 4. Normalized magnetization curve of VS1-017 at room temperature: ○—before NFC–FW and ▲—after NFC–FW.

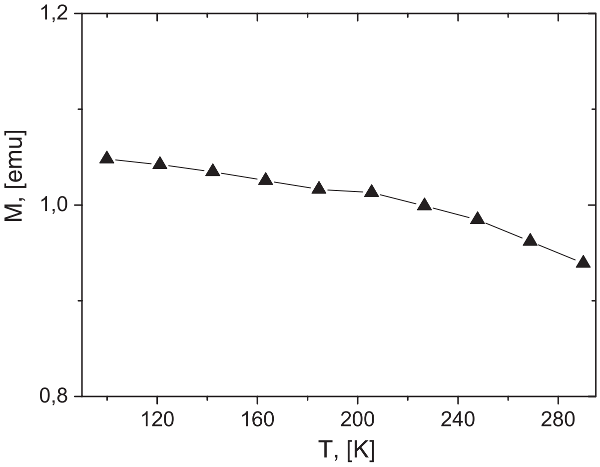

Figure 5. Thermomagnetic NFC–FW measurement for APG513A. An explanation is given in the text. The line serves as a guide for the eye.

Table 2. Parameters of the experimental procedure.

Sample	T_f (K)	B_s (290 K) (T)	B_{fw} (mT)
APG513A	170	1	50
VS1-017	190	0.3	30

These measurements were repeated after each NFC–FW experiment to ensure that the cooling and heating procedure has not changed the basic properties of the fluids. Beside this, the weight of the samples was controlled before and after each procedure. The experimental parameters for the NFC–FW procedures are collected in table 2.

In figures 5 and 6 we have plotted the magnetization of the fluids as a function of temperature. Figure 5 shows that the fluid APG513A undergoes a smooth decrease of magnetization with increasing temperature, as is expected for independent superparamagnetic particles. At about $T = 196$ K (the

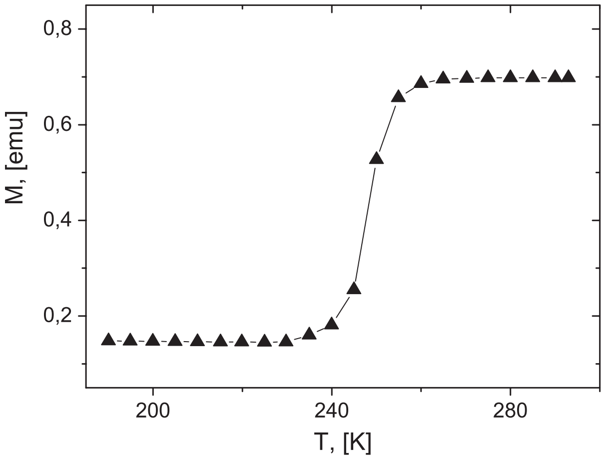

Figure 6. Thermomagnetic NFC–FW measurement for VS1-017. An explanation is given in the text. The line serves as a guide for the eye.

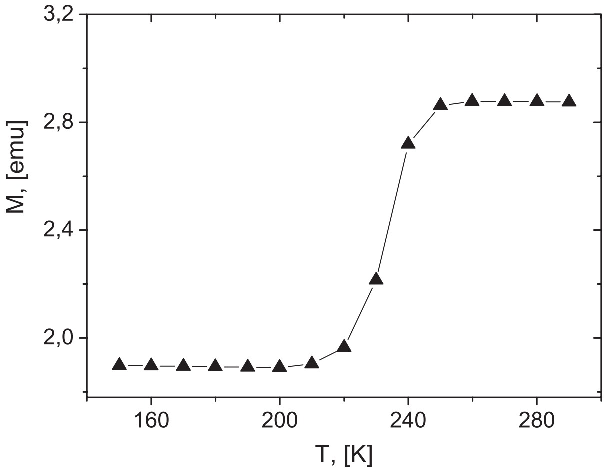

Figure 7. Thermomagnetic NFC–FW measurement for a magnetorheological fluid. An explanation is given in the text. The line serves as a guide for the eye.

melting point of the carrier liquid) a slight change of the slope of the curve seems to be detectable, which could be connected to the release of Brownian motion of the particles. The thermomagnetic curve for the cobalt based fluid VS01-017 shown in figure 6 exhibits, in contrast to the curve measured for APG513A, a strong change of M at the melting temperature of the carrier liquid. With melting of the carrier liquid the magnetization increases by about a factor of 6. The difference between this behaviour and that found for the magnetite based fluid is a result of the formation of structures of the particles in the VS01-017 fluid. The structures formed in a strong field and afterwards fixed by freezing remain stable after changing the field direction. Due to the strong interparticle interaction between the Co particles, the magnetization of the structures is frozen and the comparably weak external field cannot change it. At the melting point the particles regain their mobility and orient within the applied field, resulting in the strong increase of magnetization observed. The relatively wide temperature range in which the magnetization relaxes towards the field direction can be attributed to the high viscosity of the carrier fluid close to the melting point, hindering the motion of the particles on the comparably short timescale given by the speed of heating.

As additional proof for the fact that structure formation of the magnetic particles leads to the characteristic change in the thermomagnetic curve in figure 6 we have repeated the NFC–FW experiment with a magnetorheological fluid. These suspensions of micron sized magnetic particles are known to form large structures [1]. The MR fluid sample used consists of spherical Fe_2O_3 particles with a mean diameter of 5 μm suspended in mineral oil with a volume concentration of about 20%. As seen from figure 7, the characteristics of the curve are identical to those in figure 6.

5. Conclusion and outlook

It has been shown that structure formation of magnetic nanoparticles leads to a characteristic change of the magnetization in the thermomagnetic curve obtained from a NFC–FW experiment. This change allows a clear discrimination between fluids with internal structure formation due to field induced interparticle interaction and those without. Since the structure formation is the basis for the magnetoviscous effect, experiments like those described here allow a preselection of fluids used for rheological experiments without time-consuming and fluid-consuming magnetorheological measurements. Further investigations will have to prove whether a quantitative interpretation of the thermomagnetic curves with respect to the strength of the magnetoviscous effect is possible.

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