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Shear dependence of field-induced contributions to the viscosity of magnetic fluids at low shear rates

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Abstract

Viscoelastic properties of ferrofluids are an upcoming field of scientific interest, since the magnetic control of the related fluid behavior would give rise to new applications as well as for new possibilities in basic research concerning viscoelasticity. We have constructed a specialized rheometer for the investigation of fluids under the influence of magnetic fields, to examine such effects in stable suspensions of magnetic particles. In particular we will report the change of field-induced increase of viscosity due to variation of the shear rate applied to the fluid. The results show that the available theoretical approach, namely the concept of rotational viscosity, is not valid for the description of the field-induced increase of viscosity in concentrated fluids at low shear rates. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Suspensions of nanosized magnetic particles stabilized by surfacting the particles with long chain molecules – so called ferrofluids – show normal liquid behavior coupled with superparamagnetic properties. This enables magnetic control of flow and properties of these fluids using magnetic fields in the order of 10–100 mT. The superparamagnetic behavior, and therefore the magnetic control are enabled due to the fact that the suspended magnetic particles are small enough to be treated as magnetic single domain particles. Commercially available ferrofluids contain approximately 10 vol% of magnetic material in various carrier liquids like water, kerosene or different oils (for further information on ferrofluids see, e.g. Refs. [1–3]).

Focusing on the control of the properties of magnetic fluids, an increase of viscosity of the fluids occurs. An applied magnetic field aligns the magnetic moment of the particle with the magnetic field direction. If a shear flow is applied in a way that the

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vorticity of the flow is not parallel to the magnetic field direction, the magnetic moment will be turned out of the field direction. The resulting angle between magnetic moment and magnetic field gives rise to a magnetic torque hindering the free rotation of the particle and therefore increasing the viscosity of the fluid. The field-induced viscosity increase, called rotational viscosity, was first predicted by Shliomis [4] and later on was verified experimentally by McTague [5] in diluted ferrofluids. Experiments with concentrated suspensions [6,7] using high shear rates showed a quantitative difference between experimental and theoretical results. This difference was explained by strong interactions between the magnetic particles forming agglomerates like chains, which are neglected in the theoretical approach. In the cited experiments [6,7] the particle interaction forced an increase of rotational viscosity by an order of magnitude compared with the theoretical values. Nevertheless, a principle explanation of the observed effects in the frame of the concept of rotational viscosity was possible.

Besides this increase due to rotational viscosity it can be expected that the reversible formation of agglomerates, chains and other structures due to the action of a magnetic field will give rise to additional changes of the viscous behavior of magnetic fluids. In particular the appearance of viscoelastic properties was predicted by Zubarev [8]. He calculated the components of the stress tensor of a magnetic suspension as a function of the lengths of chains formed by the suspended magnetic particles for the special situation of a channel flow. From the results it can be seen that, e.g. normal stress differences will appear in chain forming magnetic fluids. Experimental evidence for the existence of viscoelastic properties in suspensions of magnetic particles was given for magnetorheological fluids, i.e. fluids with micron-sized suspended magnetic particles (see, e.g. Refs. [9,10]).

Normal nanosized ferrofluids exhibit – in contrast to magnetorheological fluids – a much higher stability against sedimentation and therefore they enable systematic studies of new magnetic field-induced features without changes of the basic fluid properties. Thus the investigation of viscoelastic effects in such fluids is of particular interest for basic research since it may help to shed some light on the microscopic reasons for macroscopic changes of viscoelasticity. The resulting knowledge may then give rise to new development in application oriented investigations too. Usually the viscoelastic effects are weak in suspensions of nanosized magnetic particles, especially in those based on magnetite. The reason for this disadvantage is the small magnetic coupling between the particles and the resulting weak tendency of cluster formation. Therefore high-quality measuring facilities are necessary to investigate the viscoelasticity of magnetite ferrofluids. Nevertheless the advantage of systematic investigations overcomes the disadvantages due to small effects, since these fluids allow to obtain information from well-characterized systems. This information may also give rise to the design of new fluids with stronger viscoelastic properties.

As a first step in the examination of viscoelastic properties of ferrofluids we have started with the macroscopic measurement of influences of magnetic fields on their viscous behavior under the influence of variable shear using a specially designed rheometer. This rheometer and the results obtained for the shear dependence of the field-induced portion of viscosity will be presented in the following sections.

2. Magnetic fluid rheometer

The investigation of the influence of magnetic fields on the viscous and viscoelastic properties of ferrofluids requires a specially designed rheometer, which allows the application of a magnetic field. The rheometer discussed here (see Fig. 1) is of combined cone-plate and Couette type. The outer part of the fluid sample region is moved, while the torque transmitted to the cone is measured with a commercial torque sensor. Fig. 1 shows the most important parts of the rheometer in a schematic view, while Fig. 2 shows the details of the sample volume.

All mechanical parts within the fluid sample region are made from nonmagnetic materials. Therefore, it is possible to apply a magnetic field produced by two field coils arranged in a

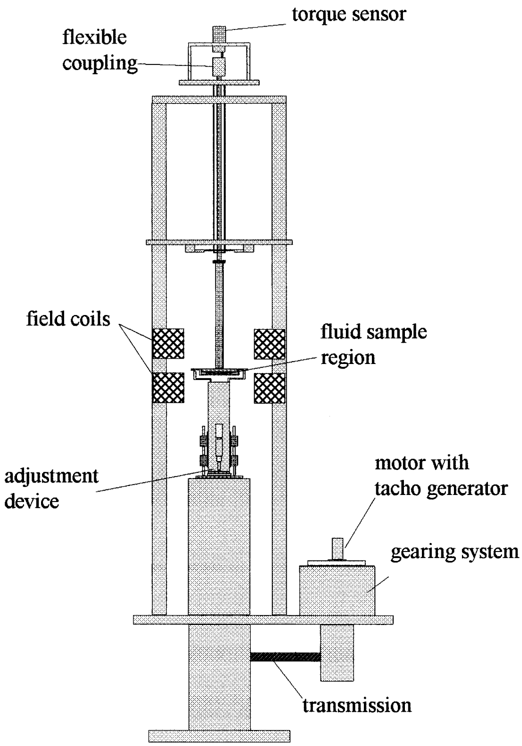

Fig. 1. Principal sketch of the magnetic fluid rheometer.

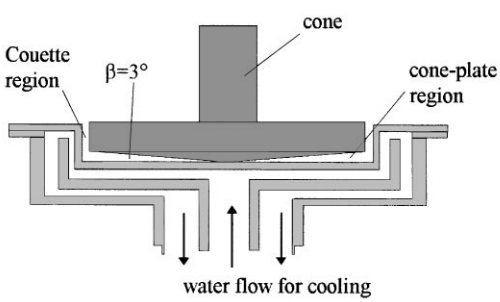

Fig. 2. The fluid sample region combined of a cone-plate and a Couette part.

Helmholtz-like system. With the currently available coil system magnetic fields with a strength of about 50 mT can be applied, showing a homogeneity better than 0.5% in the sample region. The field is parallel to the rotation axis and therefore vertical to the shear planes of the cone plate part of the rheometer. Therefore, the angle between the magnetic field direction and the vorticity of the flow is 90°. This maximizes the effect, e.g. of

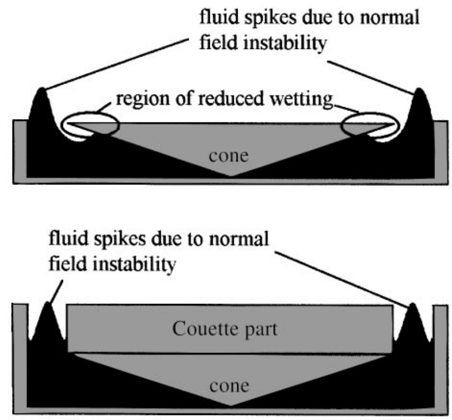

Fig. 3. Effect of normal field instability on wetting of the cone in pure cone plate (upper) and combined cone-plate and Couette systems (lower).

rotational viscosity, while the internal magnetic field is reduced to about 20% of the applied field strength due to demagnetization effects. This is accepted, since all other field geometries would reduce the angle between magnetic field direction and vorticity and therefore the magnetic influence on the fluids viscosity. In addition it would complicate a comparison of experimental results with existing theoretical approaches since the mean angle between the outstanding magnetic field and flow directions would have to be calculated.

Due to the use of a system combined from a cone-plate part and a Couette part, the possible appearance of normal field instability [1] does not affect the investigations. This effect giving rise to the appearance of fluid spikes on a free surface of magnetic fluid subjected to a magnetic field normal to the free surface would reduce the wetting of a pure cone plate system (see Fig. 3). For the combined system discussed here the change of wetting is transferred to the Couette part. The torque produced there is much smaller than that exhibited in the cone-plate region. Therefore, one can estimate that the influence of the spikes produced by normal field instability on the torque transmitted to the cone is less than 1% even for strong magnetic fields.

The driving system of the rheometer allows rotating as well as oscillating movements of the outer wall of the cell. In the rotating mode shear rates ($\dot{\gamma} = \mathrm{d}v/\mathrm{d}r$) between 16 and 240 s^{-1} can be

Table 1
Characterizing parameters of the rheometer

Diameter of cone	76 mm
Diameter of moved cell	80 mm
Cone-plate angle	3°
Torque range	10^{-5}–10^{-2} Nm
Frequency range rotating	0.13–2 Hz
Frequency range oscillating	0.0035–1 Hz

reached. The oscillating mode allows shear amplitudes between 0.5° and 2.5° with oscillation frequencies from 3.5 mHz to 1 Hz.

With the currently available torque sensor transmitted torques on the inner cone in the range 10^{-5}–10^{-2} Nm can be measured. Therefore, the rotating mode allows the measurement of dynamic viscosities from 0.3 to 3700 mPa s, while oscillating motion gives information of complex viscosities between 11 mPa s and 13 000 Pa s. The whole system can be thermostated with different methods to an accuracy better than 0.1 K.

A selection of the most important parameters of the rheometer is given in Table 1. The measuring ranges and accuracies of the apparatus are slightly better than those of commercially available systems. In addition it allows the application of magnetic fields, which is usually impossible for commercial rheometers.

3. Shear dependence of magnetic-field-induced viscosity

With the magnetic fluid rheometer described above we have investigated the shear dependence of magnetic-field-induced viscosity portion in a commercial ferrofluid of magnetite type. The fluid contains about 6.7 vol% of magnetite in a carrier liquid with a kinematic viscosity of about 100 mm^2/s at 20°C. The particles have a mean size of 10 nm and they are covered with a surfactant layer of about 3 nm thickness. Their size distribution ranges from 3 to 17 nm, with a remarkable amount of particles larger than 10 nm [7]. Those particles are of particular importance for cluster formation due to their high magnetic moment [11]. Detailed information on the properties of the fluid, which was also used in experiments for the determination of rotational viscosity at high shear rates using our Taylor–Couette system [6,7], are given in Table 2.

To obtain the lowest shear rates available with our magnetic fluid rheometer, we have carried out the investigation of field-dependent increase of viscosity of the fluid by means of the oscillating mode of the rheometer. Fig. 4 shows the measured torque transmitted to the cone by means of the fluid for a given shear rate and different magnetic field strengths. The change of the maximum amplitude of the torque signal is a direct measure for the change of the mean viscosity in the fluid induced by the magnetic field. The shear rate amplitude $\dot{\gamma}$ in oscillating mode is given by

$$\dot{\gamma} = \omega\gamma = \omega\,\frac{\varphi_0}{\beta}, \tag{1}$$

where ω denotes the frequency of oscillation, φ_0 its angular amplitude, and β the angle between the cone and the plate (see Fig. 2). The variation of shear amplitude in oscillating mode is performed

Table 2
Properties of the magnetic fluid

Volume concentration of magnetic particles	Φ	6.7%
Volume concentration of particles with surfactant	$\acute{\Phi}$	27%
Mean particle diameter	d	10 nm
Thickness of surfactant	s	3 nm
Kinematic viscosity (20°C)	ν	125 mm^2/s
Density	ρ	1.28×10^3 kg/m^3
Saturation magnetization	M_s	3.0×10^4 A/m
Dynamic viscosity of carrier liquid	η_0	0.12 kg m/s
Magnetization of the magnetic particles	M_d	4.5×10^5 A/m

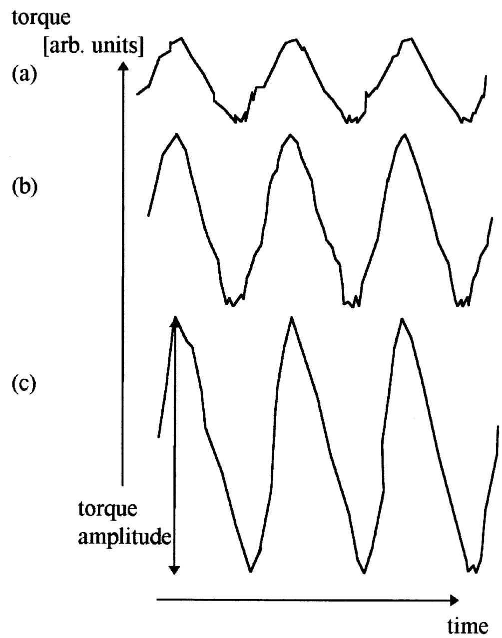

Fig. 4. The oscillating torque signal measured for (a) $H = 0$ A/m, (b) $H = 4000$ A/m and (c) $H = 4800$ A/m for a shear rate of $1.05\ s^{-1}$.

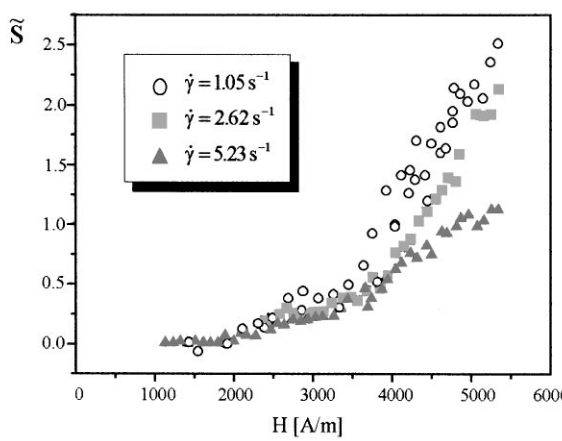

Fig. 5. Relative field-induced viscosity increase of a magnetite based ferrofluid as a function of the strength of the internal magnetic field in the fluid and of shear rate.

by varying either the amplitude or the frequency of the oscillation of the plate. During the investigation, the temperature of the fluid has been held at a temperature of 22.2°C constant to 0.1 K by use of a water flow cooling system directly tempering the fluid cell (see Fig. 2).

The amplitude of the torque signals was determined by averaging single amplitudes over 40 oscillation cycles to reduce errors due to electronic noise and mechanical disturbances. Fig. 5 shows the relative field induced increase of the viscosity of the fluid

$$\tilde{S} = \frac{\eta(H) - \eta(H=0)}{\eta(H=0)} \tag{2}$$

as a function of the magnetic field inside the fluid for different shear rates obtained from torque signals like those shown in Fig. 3. First of all it is clearly seen that the viscosity increases as a function of magnetic field strength. An increase is generally expected, as discussed in Section 1. But if one tries to compare the experimental results shown in Fig. 5 with the theoretical approach made by Shliomis [4] for rotational viscosity, it becomes obvious that the phenomenon observed here can no longer be described by the simple hindrance of rotation of single magnetic particles. The description of the relative rotational viscosity is given in Ref. [4] by

$$S = \frac{3}{2}\,\Phi' \frac{\alpha(H) - \tanh\alpha(H)}{\alpha(H) + \tanh\alpha(H)} \langle \sin^2 \vartheta \rangle, \tag{3}$$

where Φ' denotes the volume fraction of the magnetic particles including the surfactant, $\langle \sin^2 \vartheta \rangle$ the time average of the squared sine of the angle between vorticity of the flow and magnetic field direction and $\alpha(H) = \mu_0 mH/kT$ (μ_0 vacuum permeability, m magnetic moment of the particles, H applied magnetic field strength, T absolute temperature and k Boltzmann's constant) the relation of magnetic and thermal energy of the particles, respectively. Since we have chosen the geometry of our rheometer in a way that $\vartheta = 90°$, the factor $\langle \sin^2 \vartheta \rangle$ equals 1. The limit of the expression $(\alpha(H) - \tanh\alpha(H))/(\alpha(H) + \tanh\alpha(H))$ is also one, therefore the maximum of S is given by the volume fraction of the magnetic particles including their surfactant layers

$$S_{max} = \tfrac{3}{2}\Phi'. \tag{4}$$

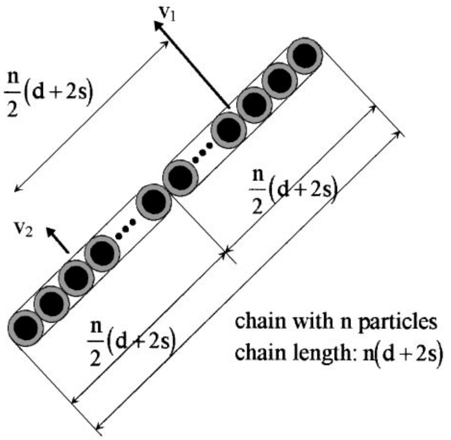

Fig. 6. Principle explanation for the observed shear thinning by breakage of chains of magnetic particles.

Therefore the maximum value of pure relative rotational viscosity in our fluid would be of the order of 40% compared with the experimental findings upto 250%. From this discrepancy we conclude that agglomerates of magnetic particles must have been formed in the fluid changing its viscosity in a way that cannot be described by assuming the agglomerates as rotating spheres using the theories on rotational viscosity.

In addition the experimental results in Fig. 5 show that the field-induced viscosity portion is reduced with increasing shear rate. That means that an observation of viscosity of the fluid as a function of shear rate at a given magnetic field strength shows shear thinning of the fluid. As a possible explanation for this behavior one can assume once more the formation of agglomerates of magnetic particles in the fluid under the influence of a magnetic field. To give a first approximation for the possibility of a breakup of a chain due to viscous forces one can assume a chain like that is shown in Fig. 6 consisting of n particles thus having a length of $n(d + 2s)$ (d particle diameter, s thickness of surfactant layer).

As a first approximation the chain is assumed to be rigid and having a fixed orientation vertical to the flow of the fluid. If now a breakup in the middle of the chain is considered, one can calculate the magnetic force between the two particles in the middle of the chain as the force holding both parts of the chain together. It is given by the force between two aligned magnetic dipoles (the particles in the center of the chain) at a distance of $d + 2s$, and it can be written for the magnetic particles considered here in the form [12]:

$$F_{\text{magnetic}} = \frac{\mu_0 M_d^2 \pi d^6}{24(d + 2s)^4}, \tag{5}$$

where M_d denotes the spontaneous magnetization of the magnetic material of the particles.

The viscous force trying to disrupt the chain can be estimated using Stokes' law for the two half parts of the chain using the velocities in the middle of each chain part (see Fig. 6). Then one can write for the disrupting force

$$F_{\text{viscous}} = 6\pi\eta_0 \frac{n}{2}\frac{(d + 2s)}{2}(v_1 - v_2), \tag{6}$$

where η_0 is the dynamic viscosity of the carrier liquid. This can be rewritten using the shear rate $\dot{\gamma}$ in the form

$$F_{\text{viscous}} = 6\pi\eta_0\dot{\gamma}\,\frac{1}{2}\left[\frac{n}{2}(d + 2s)\right]^2. \tag{7}$$

For the following it will be assumed that the chains are formed by agglomerates of particles with a diameter of about $d = 16$ nm, as they have been mentioned in the explanation of the rotational viscosity in Ref. [6]. Such agglomerates – usually called primary agglomerates – are formed during the production of the suspension, and are therefore present in any ferrofluid [11]. In addition Coverdale et al. [13] showed that such agglomerates have a tendency to form chains under the influence of magnetic fields. Comparable results were also obtained by Jordan [14] for single particles in this size range.

From Eqs. (6) and (7) using the characteristic data of the fluid from Table 2 and assuming a particle diameter in the chain as discussed before, one can calculate that magnetic and viscous force become comparable for a chain length of about 130 particles for $\dot{\gamma} = 1$; 80 particles for $\dot{\gamma} = 2.6$ and 60 particles for $\dot{\gamma} = 5.2$. Chains containing a number of particles in this order of magnitude have already been observed experimentally [15,16] for slightly larger particles. So the consideration has a realistic basis. Thus the observed shear thinning can be explained in a first consideration as process of breakups of chains of magnetic particles due to the viscous friction exhibited by the fluid.

4. Conclusions

A rheometer allowing the investigation of magnetic fluids under the influence of magnetic fields has been constructed. The combination of its features, especially the different driving modes enables the measurement of a variety of viscoelastic features of magnetic liquids. Due to the high-precision measuring system, it becomes possible to observe in particular such effects in stable fluids with nanosized particles, which usually exhibit only weak viscoelasticity. The investigation of such fluids will provide data that may enable microscopic explanations for viscoelastic properties. Using this new measuring device we have investigated the field-induced increase of viscosity in a magnetite type ferrofluid as a function of shear rate. The fluid shows shear-dependent decrease of the field-induced viscosity portion. The comparison of the results with the theory of rotational viscosity shows that the description of field-induced viscosity in concentrated magnetic fluids at low shear rates is outside the range of validity of this theory. Therefore, a new theory will have to be formulated to give a quantitative explanation of the hydrodynamic reasons of the observed phenomena. Such a theory will have to take interactions of the particles and the resulting formation of chains and clusters into account. For a first qualitative explanation a breakup of chains of magnetic particles formed by the influence of the magnetic field can be considered.

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