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TOPICAL REVIEW

Recent progress in magnetic fluid research

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Abstract

Investigations of the properties, the flow and the application possibilities of suspensions of magnetic nanoparticles are an extremely lively research field nowadays. In particular, the biomedical application and the investigation of the rheological properties of these so-called ferrofluids gained high importance during the last years. Within this paper particular focus will be put on recent development in the field of rheological investigations of ferrofluids and their importance for the general treatment of ferrofluids. As will be outlined, recent experimental as well as theoretical investigations have shown that the formation of structures of magnetic nanoparticles has significant influence on the magnetoviscous behaviour of ferrofluids. The dependence of this structure formation on the magnetic field strength and shear stress applied to the fluid leads to strong changes of viscosity and to the appearance of viscoelastic effects in the fluids. The new findings have led to consistent microscopic models for the viscous properties of ferrofluids and they have driven the development of a macroscopic theory predicting new effects in ferrofluid dynamics.

Contents

1. Introduction

The specific research interest in suspensions of magnetic nanoparticles in appropriate carrier liquids is generated by the fact that such fluids combine normal liquid behaviour with the

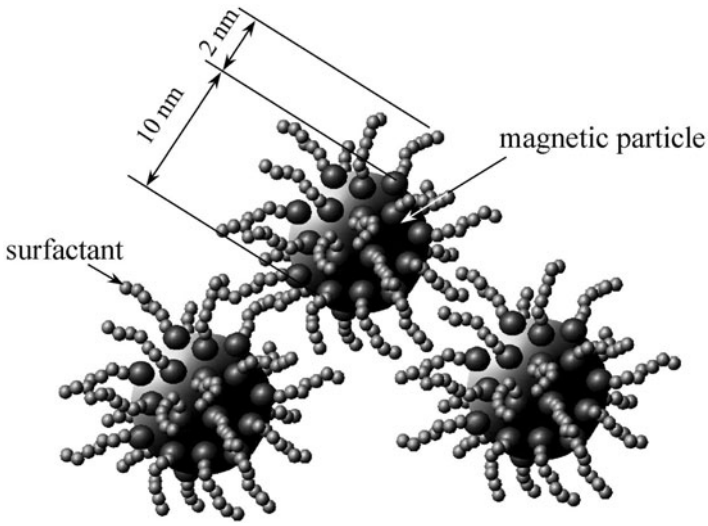

Figure 1. A schematic view of the coated magnetic particles in a ferrofluid.

possibility to control their flow and properties with moderate magnetic fields. Usually, these suspensions, commonly called ferrofluids, contain magnetic particles with a size of about 10 nm in diameter. The magnetic material most often used is magnetite (Fe_3O_4), and carrier liquids like water, kerosene or various oils are available. Due to their small size the magnetic particles neither form sediment in the gravitational field or in moderate magnetic field gradients nor do they agglomerate due to magnetic dipole interaction. Nonetheless a stable suspension can only be achieved if the particles are protected against agglomeration due to van der Waals interaction. This protection can be provided either by an electric charge stabilization or by coating the particles with long chained organic molecules (see figure 1). The molecules generate a repulsive force which prevents the particles from coming in contact and thus suppresses the destabilizing effect of the van der Waals interaction (for a review on ferrofluid synthesis see, for example, [1]). This form of stabilization is applied for the majority of ferrofluids used for scientific investigations as well as for technical applications, since it allows the synthesis of suspensions which are stable over years.

The peculiarity of ferrofluids is the combination of normal liquid behaviour with a magnetic control of their flow and properties. This possibility originates from the fact that each of the particles can be treated as a thermally agitated single domain particle in the carrier liquid. Thus each particle carries a magnetic moment of about 10^4 μ_B interacting with an applied magnetic field. Treating the particles as independent thermally agitated magnetic dipoles, the magnetization of the fluid can be described by the Langevin equation for paramagnetic systems. In contrast to paramagnetic salt solutions, for example, the initial susceptibility of ferrofluids is of the order of 1, and is thus 10^4 times larger than in normal paramagnetic systems (see figure 2). Since the force that can be exerted by a given magnetic field gradient to a magnetizable mass is proportional to the material's magnetization, strong magnetic forces can be generated for magnetic fluids with moderate magnetic fields due to this steep increase of the magnetization curve.

Stable ferrofluids were first produced in the early 1960s [2]. Thereafter the field of ferrofluid research developed quickly in chemistry (for the preparation of ferrofluids), physics (connected to the fundamental description and characterization) and engineering. In the

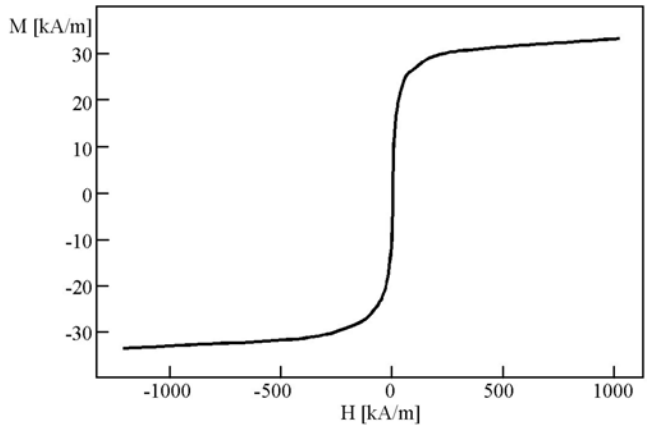

Figure 2. A typical magnetization curve for a standard ferrofluid containing 7.2 vol% of magnetite particles.

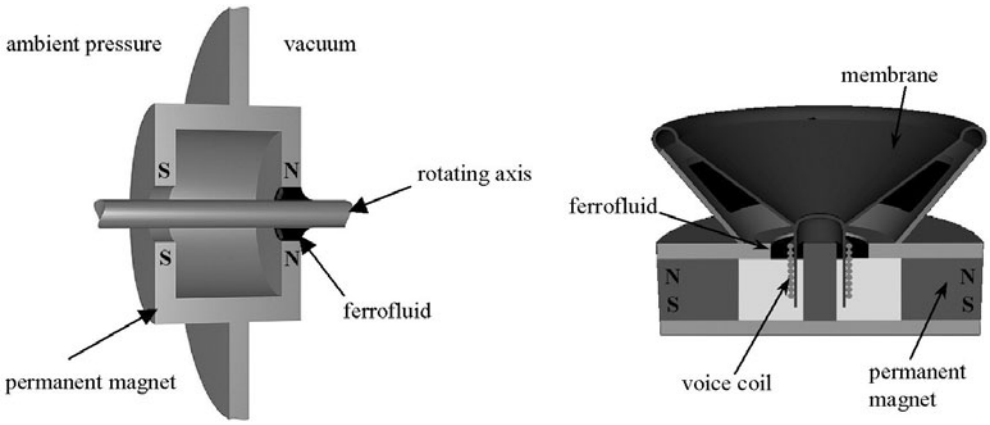

Figure 3. A schematic view of two important technical applications of ferrofluids: on the left-hand side the sealing of a rotary shaft and on the right-hand side the cooling of loudspeakers.

engineering field numerous applications [3] have been developed, some of them gaining high commercial value. As an example the sealing of rotary shafts and the cooling of loudspeakers will only briefly be mentioned. As depicted in figure 3, in both applications the magnetic fluid is positioned at a certain place inside the device by the magnetic field exerted by a permanent magnet system. In the case of the sealing, the rotating shaft is surrounded by a magnet creating a strong magnetic field in the small gap between the shaft and the magnet. The ferrofluid placed in this region seals the shaft with low friction, and the magnetic forces can easily be strong enough to keep the fluid in place against pressure differences of about 1 bar. For the loudspeaker system the generally present magnetic field is used to fix the ferrofluid in a way that helps to cool the voice coil. Both applications are nowadays widely used. In addition they are both examples for the typical use that has been made of ferrofluids in the past. In particular the field of applications has used only the possibility that magnetic fluids can be reliably positioned at a specified location while further field influences have been neglected.

But as mentioned above, magnetic fields cannot only be used for a positioning of the fluid but also for the modification of the fluid's properties or for the control of their flow. A

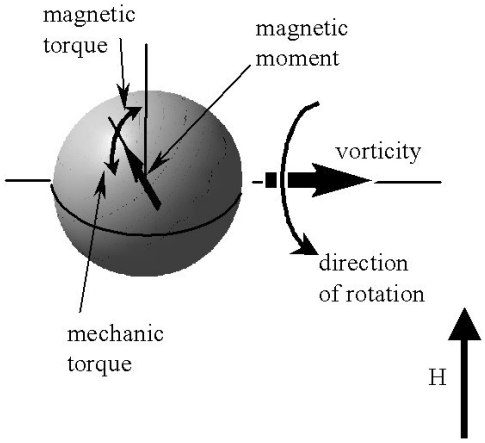

Figure 4. On the origin of a field dependent increase of viscosity in a ferrofluid. Explanations are given in the text.

prominent example for the modification of properties of ferrofluids in magnetic fields is the change of their viscous behaviour, which will be the main topic of this paper and which is, in addition, one of the most active research fields in ferrofluid research at present.

The second highly important branch of recent research on magnetic fluids is their use in biomedical applications. Especially cancer treatment by magnetic hyperthermia or magnetic drug targeting seem to be promising new therapeutic techniques. For information on these recent developments as well as on ferrofluids in general the interested reader is referred to [4–6], for example.

2. The magnetoviscous effect

As mentioned above, one of the well known phenomena generated by the influence of magnetic fields on ferrofluids is the change of their viscous behaviour. The first discovery of such changes was made by Rosensweig in 1969 [7] in concentrated magnetite-ferrofluids followed a few months later by an independent work by McTague [8] using highly diluted Co-ferrofluids. In both papers an increase of viscosity of ferrofluids with increasing magnetic field strength was observed, and McTague's experiments also showed a dependence of the effect on the relative angle between the magnetic field direction and the vorticity of the flow.

These phenomena can qualitatively be described by the following model. Assuming that the magnetic particles are not interacting with each other and that the magnetic moment is fixed within the particles, a shear flow will generate a rotation of the particles and thus also of the magnetic moment. The axis of rotation of the particles is aligned with the vorticity of the flow (see figure 4). If a magnetic field is applied to the system, the magnetic moments of the particles will tend to align with the magnetic field direction. If the moment is fixed inside the particle—as assumed above—the rotation caused by the viscous friction will lead to a disalignment of magnetic moment and magnetic field. This disalignment gives rise to a magnetic torque which counteracts the mechanic torque due to the shear flow. Thus the free rotation of the particles will be hindered and, macroscopically, an increase of viscosity will be observed.

If the fluid's vorticity is aligned with the field, the rotation of the particle will not force a disalignment of magnetic moment and field direction, and thus no magnetic torque will

counteract the free rotation of the particles. Therefore no increase of viscosity will be observed for this relative alignment of field and vorticity. Following the experiments by McTague—which come close to the above model assumption of a non-interacting system—Shliomis [9] derived a theoretical description which takes into account the magnetic and mechanic torques acting on the particles as well as their Brownian motion. In this concept the additional field dependent part of a ferrofluid's viscosity—which is called rotational viscosity η_r—can be written in the form

$$\eta_r = \frac{3}{2}\eta_0\tilde{\Phi}\frac{\alpha - \tanh\alpha}{\alpha + \tanh\alpha}\langle\sin^2\beta\rangle \tag{1}$$

where η_0 denotes the viscosity of the fluid for vanishing magnetic fields, $\tilde{\Phi}$ the volume concentration of the magnetic particles including their surfactant, β the angle between vorticity and magnetic field H, and $\alpha = \mu_0 mH/kT$ the ratio of magnetic and thermal energy of particles with magnetic moment m ($\langle\cdots\rangle$ devotes the spatial average, k is Boltzmann's constant and T the absolute temperature).

For weak magnetic field η_r increases as H^2, and for large magnetic fields a saturation value for the rotational viscosity is found with

$$\eta_r^{\max} = \tfrac{3}{2}\eta_0\tilde{\Phi}. \tag{2}$$

Thus for a commercial standard ferrofluid with 7 vol% of magnetic material, a mean particle diameter of about 10 nm and a surfactant layer thickness of 2 nm, resulting in a value of $\tilde{\Phi} = 19.2$ vol%, the maximum relative change of viscosity η_r/η_0 should be about 30%. This estimate is based on the assumption that all magnetic particles contribute to the viscosity changes. But—as mentioned before—only particles with a magnetic moment fixed inside the particle can contribute to the phenomenon. This condition depends on the magnetic relaxation behaviour of the particles. They can either align with the field by a rotation of the whole particle, a process called Brownian relaxation, or by a change of the direction of the magnetic moment inside the particle, the so-called Néel relaxation process. Both relaxation processes are characterized by respective relaxation times

$$\tau_B = \frac{3\tilde{V}\eta}{kT} \qquad \tau_N = f_0^{-1}\exp\left(\frac{K_a V}{kT}\right) \tag{3}$$

where the Brownian relaxation time τ_B is determined by the volume of the particles including the surfactant layer $\tilde{V}$ and the viscosity of the fluid, while the Néelian time τ_N depends on the volume of the magnetic core V and the anisotropy constant K_a of the particles; f_0 is the Larmour frequency of the magnetic moment in the anisotropy field of the particle. As is seen from (3), the time for the Brownian relaxation scales linearly with the particle volume, while the time for the Néel process grows exponentially with the particle size. Since the actual magnetic relaxation process of a particle takes place by the process with the shortest relaxation time, the small particles will follow the Néel process while the large ones behave in a Brownian manner. Commonly the Néel particles are called magnetically weak while the other ones are referred to as magnetically hard particles.

Coming back to the phenomenon of rotational viscosity, it is obvious that only magnetically hard particles will contribute to the effects. If one resumes the situation for a commercial standard ferrofluid containing magnetite particles, one has thus to observe that only sufficiently large particles have to be taken into account in the calculation of rotational viscosity. Looking at the particle size distribution in figure 5 one can see that particles with a diameter above approximately 13 nm—which is the critical diameter where the relaxation behaviour of the particles becomes Brownian—are present with a volume concentration of less than 1 vol% in total. Therefore the maximum change of viscosity following equation (2) should only be

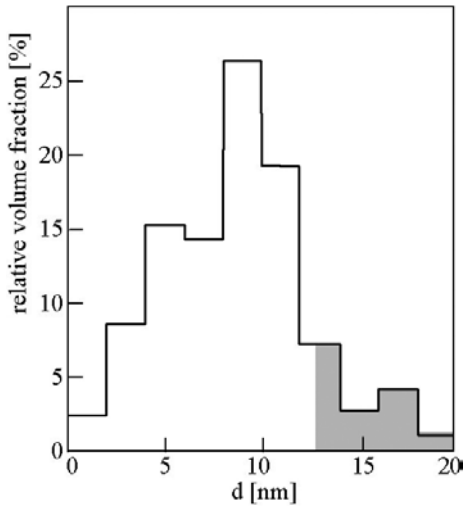

Figure 5. Particle size distribution for the ferrofluid APG513A used in the experiments discussed in the paper.

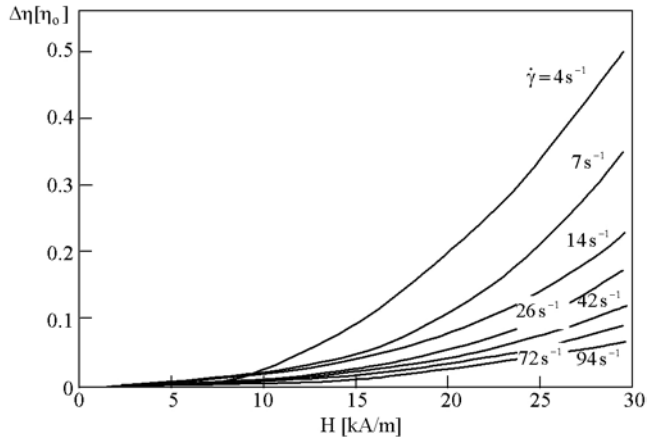

Figure 6. Change of viscosity of the magnetite based ferrofluid APG513A as a function of magnetic field strength for various shear rates $\dot{\gamma}$.

around 2%. Looking at the experimental data shown in figure 6 for a ferrofluid containing 7 vol% of magnetic particles, with the size distribution shown in figure 5, in an oily carrier liquid, it can be seen that changes of viscosity of more than 100% can already be achieved with moderate magnetic fields of the order of 30 kA m^{-1}.

In addition the data in figure 6 show a significant shear dependence of the increase of viscosity. This can obviously not be explained by the classical theory of rotational viscosity. Thus, to distinguish this phenomenon from the effect called rotational viscosity, the term 'magnetoviscous effect' has been introduced [10]. An approach to describe these effects using a master curve generated by plotting the viscosity changes against the relation of shear stress to magnetic interaction forces [11]—usually described by the Mason number—cannot be used for ferrofluids since the interparticle interaction is dominated by the particle size since the particles are single domain particles.

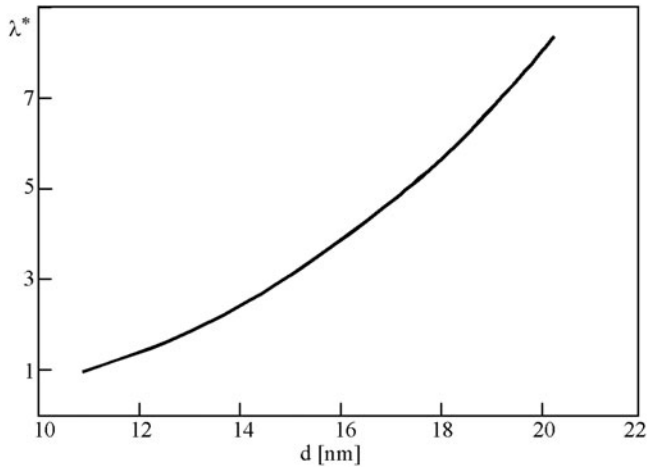

Figure 7. The interaction parameter λ* for particles with a 2 nm thick surfactant as a function of the particle size.

To find a microscopic approach to understand the reason for the observed changes of the magnetoviscous effect one can describe the ferrofluid as a bidisperse system with a large fraction of small particles and a small fraction of large particles. As discussed before, this small fraction of magnetic hard particles cannot explain the strong magnetoviscous effect just by a hindrance of their free rotation due to the magnetic field influence. So it has to be assumed that the magnetic interparticle interaction leads to the formation of structures formed by the particles. In the easiest case the structures could be rigid straight chains. To enable the appearance of such internal structures, the interaction parameter

$$\lambda = \frac{\mu_0 M_0^2 V}{24kT}, \tag{4}$$

where M_0 denotes the spontaneous magnetization of the magnetic material, has to be greater than one. Since λ is calculated from the ratio of the interparticle interaction of two magnetic particles in contact to thermal energy, it is obvious that for a ferrofluid with coated particles a modified interaction parameter

$$\lambda^* = \left(\frac{d}{d+2s}\right)^3 \lambda \tag{5}$$

has to be used [12]. Here s denotes the thickness of the surfactant layer. For a value of $s = 2$ nm this change means a reduction of λ by a factor of approximately 2.

For the large particles with diameters above 13 nm the magnetic dipole interaction is so strong that the parameter clearly exceeds 1 (see figure 7), and thus these particles are able to form chain-like structures. Here the value of the spontaneous magnetization of magnetite $M_0 = 4.5 \times 10^5$ A m^{-1} has been used for the calculation.

The influence of the hindrance of rotation of these structures in the flow has been assumed to be the reason for the strong increase of viscosity with magnetic field strength, and the breakage of the chains in a shear flow [13] provides an explanation for the reduction of the effect with increasing shear rate. The major remaining question at this point is whether the small amount of large particles can give rise to the observed strong effects.

To obtain a quantitative proof for the model, Zubarev [14] developed a theoretical approach calculating the viscosity changes in a ferrofluid with chain formation. For the theory it is

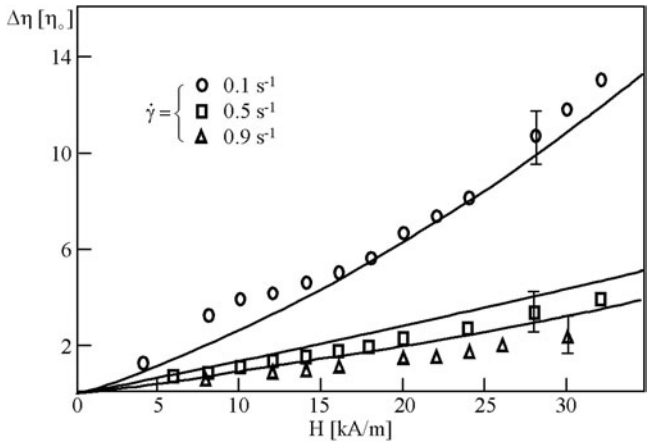

Figure 8. The magnetoviscous effect for APG513A for low shear rates with fits from the theory in [13]. Further explanations are given in the text.

assumed that the chains are rigid, straight and do not interact with each other. Then one can calculate the free energy of an ideal gas of such chains in a magnetic field, and a minimization of this free energy provides a chain length distribution function. With this chain length distribution it is possible to calculate the stress tensor of the fluid and therefore its viscosity. Since the theoretical approach is set up for vanishing shear rate, the fit to experimental data has to be undertaken for very low shear rates. The free parameters of the fit are the size and the volume concentration of the large particles. Figure 8 shows experimental data on the magnetoviscous effect for the same fluid as in figure 6 for a shear rate of $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$ together with a fit of the theory in [14]. The theoretical curve—which obviously fits well to the experimental data—was obtained with a mean size of the large particles of $d_{\mathrm{ml}} = 16.5$ nm and a magnetic volume fraction of these particles of 0.7 vol%. These values obviously correspond well to the size distribution in figure 5.

To include the effect of shear rate in the theory, all summations over the chain length distribution function have been terminated at a maximum chain length obtained from an equilibrium of magnetic interaction keeping the chains together and shear forces breaking them up [13]. As is seen in figure 8, this concept works well for relatively small shear rates, providing a proof for the validity of the model assumption, that formation and breakage of chains are the determining processes for the magnetoviscous effect.

To get a further proof for the fact that the small amount of large particles in magnetite ferrofluids plays the dominant role for the appearance of magnetoviscous effects in magnetic fluids, experiments with ferrofluids with variable content of large particles have been performed [12, 15]. In these investigations it was clearly shown that the strength of the magnetoviscous effect depends directly on the content of large particles in the fluid. As an example figure 9 shows the change of viscosity again for the fluid APG513A together with two modifications of the same fluid obtained by a magnetic separation technique [16]. Obviously the fluid with increased content of large particles shows a strongly enhanced magnetoviscous effect, while the change of viscosity in the fluid with a reduced fraction of large particles shows only a very weak dependence of viscosity on magnetic field strength.

The solid curves are again fits of the theory [14] to the experimental data. From the fit parameters shown in the figure it is clear that the change of the magnetoviscous effect can directly be explained by a change of the volume fraction of sufficiently large particles.

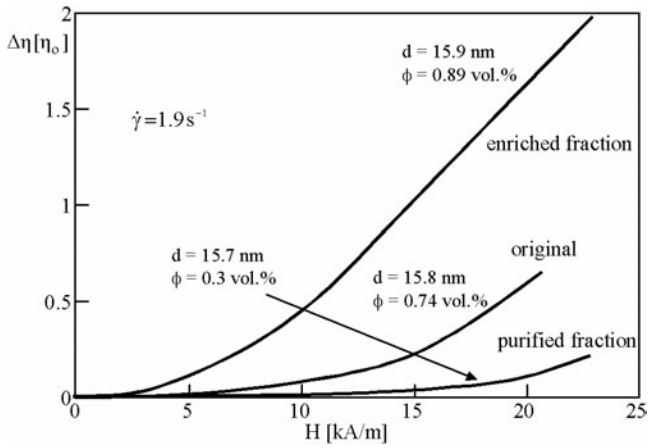

Figure 9. The magnetoviscous effect for three modifications of APG513A obtained by a magnetic separation process. The three fluids differ only in the content of the large particles.

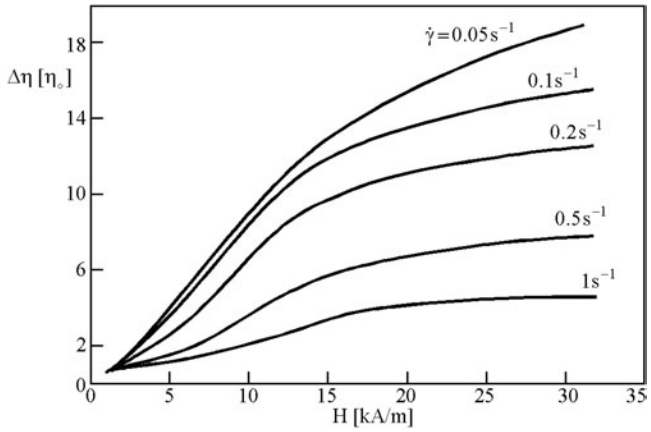

Figure 10. The magnetoviscous effect for a ferrofluid containing approximately 0.4 vol% of 9 nm Co-particles.

Recently, new ferrofluids containing cobalt particles [17] have become available. For cobalt the critical diameter for the transition from magnetic hard to magnetic soft particles as well as for an interaction parameter λ^* significantly larger than 1 is about 6 nm. Thus fluids containing cobalt particles with diameters about 10 nm will show a strong tendency for chain formation. As is seen in figure 10, a magnetic fluid with a very small content of these particles shows a magnetoviscous effect comparable to the findings in figure 6. The fluid used contained particles with a diameter of 9 nm having an interaction parameter $\lambda^* \approx 5$, which corresponds to a diameter of 17 nm for magnetite particles. This is obviously in good agreement with the fit results in figure 8.

These experimental findings together with the mentioned agreement with the theoretical model [14] as well as numerical studies [18–20] and neutron scattering experiments [21] confirm the model of chain formation of magnetic particles as an explanation for the magnetoviscous effect. Thus it is reasonable to discuss further consequences of the formation of internal structures. This discussion will be split up into two major parts. On the one hand one has to look for further rheological consequences of the chain formation, like for example

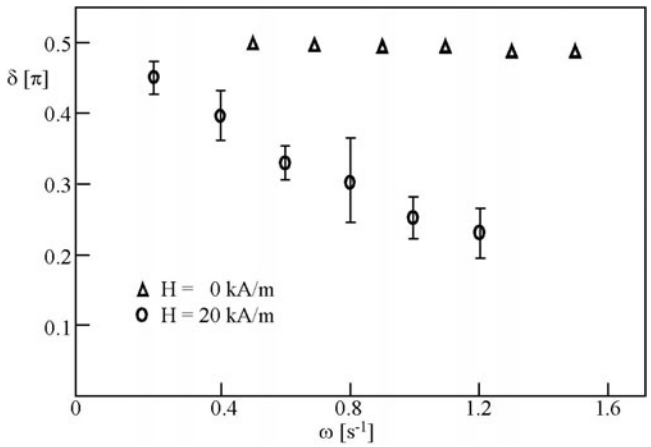

Figure 11. The phase shift δ between shear and stress for APG513A as a function of the frequency of the oscillating load ω for $H = 0$ and 20 kA m^{-1}.

magnetic field dependent viscoelastic effects. On the other hand the findings made above show that the behaviour of a ferrofluid with interacting particles cannot be described by the theory of rotational viscosity [9]. Since this theory is a direct consequence of an expression for the relaxation of magnetization, which itself is the basis for the general description of ferrofluids, and which relies on the fundamental assumption of non-interacting particles, it has to be clarified how far the description of relaxation of magnetization has to be extended, and whether this extension has consequences for the general treatment of ferrofluids.

3. Rheological consequences of the formation of internal structures

A deeper insight to the field dependent changes of the rheological behaviour of ferrofluids can be obtained by subjecting them to an oscillating load [22]. From such investigations one can derive for example the complex viscosity of the fluids, and information about the phase shift between shear and stress or about the first normal stress coefficient. Altogether, these measurements thus give an insight to the viscoelastic properties of the fluids.

As a first approach, figure 11 shows the phase shift δ between shear and stress as a function of the frequency of the oscillating load ω for different magnetic fields. For a Newtonian fluid the phase shift is independent from ω and equal to $\pi/2$, while a pure elastic system would give $\delta = 0$. Viscoelastic materials show an ω-dependence of δ with a decrease to higher values of ω where the elastic components dominate the behaviour. As is seen in figure 11, the ferrofluid used shows the expected Newtonian behaviour for vanishing magnetic field and a significant appearance of elastic components of its properties with rising field strength.

This existence of viscoelastic properties of ferrofluids in the presence of magnetic fields is also obvious from the imaginary part of the complex viscosity plotted in figure 12. Again for $H = 0$ the imaginary part of the complex viscosity vanishes and with increasing field η'' becomes non-zero. The maximum of η'' provides a frequency ω of the load which is inversely proportional to the relaxation time of the system. For the highest field used here this relaxation time equals approximately 10 s. This high relaxation time is probably a hint for the fact that—for small shear rate—a significant interaction of the chains appears.

A deeper insight to the viscoelastic behaviour can be obtained from the storage module G' shown in figure 13. For vanishing field G' is more than an order of magnitude smaller than

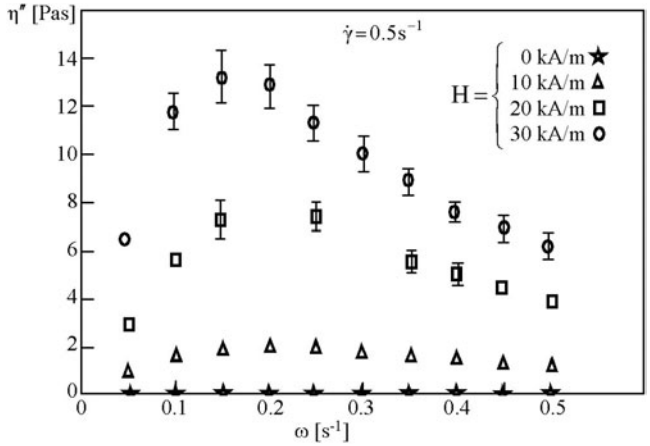

Figure 12. The imaginary part of the complex viscosity of APG513A as a function of the frequency of the oscillating load ω for different magnetic fields.

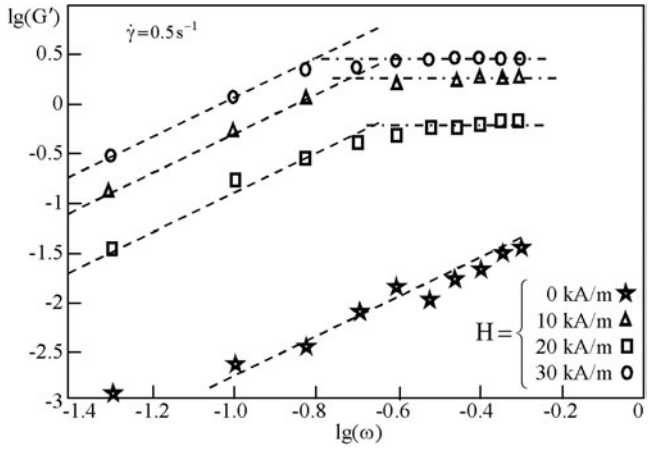

Figure 13. The storage module for APG513A as a function of the frequency of the oscillating load ω for different magnetic fields.

in the presence of the weakest field applied. The fact that even for $H = 0$ a square dependence of G' on ω over the whole frequency range investigated is found may be a hint for very weak non-Newtonian properties due to interparticle interactions being present in the absence of a magnetic field too. For $H > 0$ a square dependence for small values of ω and a plateau for larger values of the frequency—a behaviour which is typical for a fluid that can be described by the Maxwell model [23]—are found.

The solid lines in the figure represent a fit of the Maxwell model with a single pair of relaxation time—which is equal to the value obtained from the imaginary part of the complex viscosity in figure 12—and relaxation module. For this comparison to the Maxwell model it has been assumed that the measurements took place in the linear regime. Future investigations will have to clarify whether the deviations seen are a result of a nonlinear influence in the measurements, but for the actual status the good agreement with the Maxwell model is a good hint that this description is valid as a first approximation for the ferrofluid investigated.

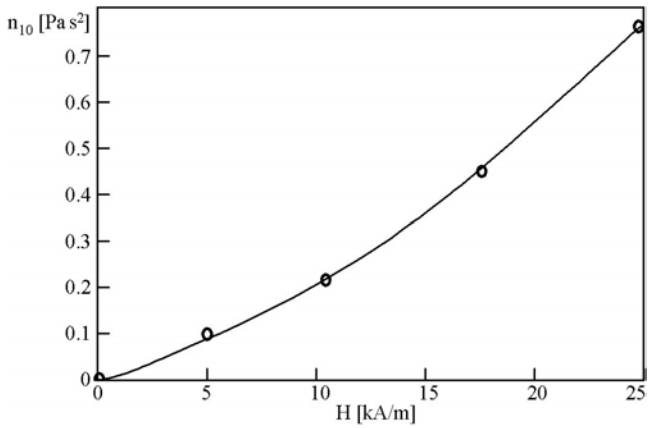

Figure 14. The first normal stress coefficient for APG513A as a function of the magnetic field strength.

It is interesting to note that the fit cannot be improved by adding further parameter pairs and thus extending the description to a generalized Maxwell model. This can be a hint that, despite the fact that the single particles have a size distribution, the chains formed from these particles have a relatively small distribution concerning their overall elasticity and size.

Finally, one can derive the first normal stress coefficient ν_{10} from the extrapolation of G'/ω^2 to $\omega = 0$. The result, as a function of the magnetic field strength, is shown in figure 14. If one combines the result for ν_{10} with the experiments on the Weissenberg effect [24] carried out earlier with the same fluid and which provide the combination $\nu_{10}+4\nu_{20}$ of the first and second normal stress coefficient, one can also derive the second normal stress coefficient. For a magnetic field of $H = 25$ kA m^{-1} as has been used in [24], the results in figure 14 give $\nu_{10} = 0.75$ Pa s^2, while the experiments on the Weissenberg effect lead to $\nu_{10}+4\nu_{20} = 0.04$ Pa s^2. Therefore one finds $\nu_{20} = -0.18$ Pa s^2. At this point one can note that the second normal stress coefficient is negative and significantly smaller than ν_{10}—a behaviour which is common from the investigation of polymer solutions. But in contrast to polymers where the ratio $|\nu_{10}/\nu_{20}|$ is about 10:1 one obtains for the fluid investigated here a value of 4.2:1. Recent numerical studies [25] have predicted that this ratio should take values $|\nu_{10}/\nu_{20}| \leqslant 4{:}1$ for ferrofluids with an interparticle interaction like there is present in APG513A.

To conclude this part of the discussion, one can state that the formation of internal chain-like structures gives rise to a field dependent viscoelastic behaviour of ferrofluids which shows similarities to dilute polymer solutions and which can be described in a first approximation by the Maxwell model.

4. Consequences of the internal structures for the basic description of ferrofluids

As mentioned earlier, the general description of ferrofluids is based on an equation for the relaxation of magnetization [26] which assumes that a ferrofluid can be treated as a system of non-interacting, spherical, magnetically hard particles. It has the form

$$\frac{\mathrm{d}M}{\mathrm{d}t} - (\Omega \times M) = -\frac{1}{\tau}(M - M_{\mathrm{eq}}) \tag{6}$$

where M_{eq} denotes the equilibrium magnetization and τ the relaxation time for the relaxation of magnetization.

It has been seen from the results of the rheological investigations that real ferrofluids exhibit a significant amount of interparticle interaction which gives rise to severe changes of their properties. Thus it has to be reconsidered, whether the classical approach for the magnetization relaxation [26] provides a complete description of the behaviour of ferrofluids with non-vanishing interaction, or whether an extension becomes necessary. To do so, one can in principle try to formulate an extended equation for the relaxation of magnetization on the basis of a more complex microscopical description of ferrofluids taking internal structures into account. The obvious disadvantage of such an approach is on the one hand the complexity of such a description and the resulting neglects that have to be made, and on the other hand the lack of knowledge about the definite details of the microstructural composition of a sheared ferrofluid in the presence of a magnetic field. Moreover such an extension would not hold if new ferrofluids, for example with stronger interparticle interaction giving rise to different internal structures like rods [27] or droplets [28], become available.

Therefore Müller and Liu [29] derived an equation for the relaxation of magnetization of ferrofluids on the basis of the principles of irreversible thermodynamics. In this approach the ferrofluid is treated as a magnetizable continuum. Taking the conserved quantities—the electromagnetic field, the magnetization of the fluid, the density of the fluid, the concentration of particles and the momentum density—as variables for the thermodynamic energy density they have derived equations for the energy and momentum flux and the entropy production. These equations, together with the material dependent parameters like susceptibilities and transport coefficients, provide a full description of the dynamics of ferrofluids.

The central advantage of this approach is that it does not need any microscopical assumptions about the structure of the fluid, which is a clear distinction from other models for magnetic influence on viscous properties of suspensions of magnetic particles like for example in [30]. The properties of the fluid—which are indeed determined by their microscopic structure—are included in the mentioned material parameters which have to be determined experimentally by appropriate measurements. Thus a change of the fluid system will generate a change in the parameters only, but the theory itself—and its consequences—remain unchanged. Just the microscopic interpretation of the various parameters would have to be reconsidered, but this does not affect the overall predictions of the theory.

From the general structure of ferrofluid dynamics Müller and Liu derived an equation for the relaxation of magnetization [29] which reads in the reduced form needed here

$$\frac{\mathrm{d}}{\mathrm{d}t}M_i + \lambda_1 M_i(\vec{\nabla}\vec{v}) + \lambda_2(\nabla_i v_j + \nabla_j v_i) - (\Omega \times M)_i = \frac{1}{\tau}(H - H_{\mathrm{eq}}). \tag{7}$$

It contains first of all those terms already known from Shliomis' equation, namely the term with the vector product of viscosity and magnetization which is the basis for the appearance of rotational viscosity. But in addition two further terms appear, one connected to the divergence of the velocity field—that means to sound propagation in ferrofluids—and the other related to the symmetric velocity gradient $\nabla_i v_j + \nabla_j v_i$.

To solve the question whether this approach gives a new insight to the behaviour of ferrofluids with a microstructure that does not fit to the assumption of Shliomis, it is necessary to check whether at least one of the parameters λ_1 and λ_2 does not vanish in such a fluid. For this purpose an experiment which allows one to measure the parameter λ_2 has been set up [31]. The experiment allows the independent variation of the symmetric and the antisymmetric velocity gradient. As is depicted in figure 15, it consists of two independently rotating cylinders forming a gap which contains the ferrofluid. If both cylinders rotate with the same angular velocity,

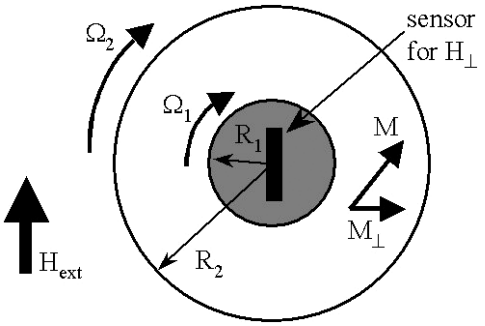

Figure 15. The principle of the experimental setup for the determination of the coupling parameter λ_2. Details are given in the text.

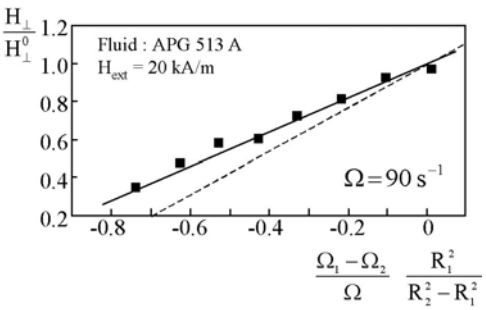

Figure 16. The determination of the coupling parameter λ_2 from the slope of the change of the off-equilibrium component of magnetization with the shear parameter s.

the fluid experiences a vorticity

$$\Omega = \frac{\Omega_2 R_2^2 - \Omega_1 R_1^2}{R_2^2 - R_1^2}, \tag{8}$$

but the symmetric velocity gradient—and thus the shear rate—is zero. If a magnetic field is applied perpendicular to the axis of rotation, the magnetization of the fluid will be tilted against the field direction due to the action of the viscous torque acting on the particles. This deviation from the equilibrium magnetization can be measured by detecting the magnetic field component $H_\perp$ perpendicular to the direction of the applied field H_0 by means of a Hall sensor inside the inner cylinder.

As is seen from equations (6) and (7), both relations for the relaxation of magnetization will provide identical results for the perpendicular component of magnetization in this situation. In contrast, if the angular velocities of the cylinders are varied in a way that the vorticity is constant, but a symmetric velocity gradient appears, both theories predict different changes of the magnetization behaviour. Due to demagnetization effects in both cases a linear dependence of the perpendicular magnetization component on the dimensionless shear parameter

$$s = \frac{\Omega_1 - \Omega_2}{\Omega} \frac{R_1^2}{R_2^2 - R_1^2} \tag{9}$$

is found. The slope of the change of $M_\perp$ versus s depends on the theoretical approach. Generally the slope is given by

$$\frac{H_\perp}{H_\perp^0} = 1 + \dot{\gamma}(\mathsf{F}(R_i) - \lambda_2 \mathsf{G}(R_i, \chi)) \tag{10}$$

where $H_\perp$ denotes the magnetic field component perpendicular to H_0 for the shear-free situation. The functions G and F result from the mentioned demagnetization effects. Obviously finite values of λ_2 will result in a change of the slope compared to the Shliomis model ($\lambda_2 = 0$). Figure 16 shows for the fluid APG513A—which has also been used for the rheological experiments discussed in sections 2 and 3—the change of the normalized perpendicular component of the magnetic field measured in the centre of the cylindrical setup as a function of s for $\Omega = 90\ \mathrm{s}^{-1}$. The dashed line is the expectation from Shliomis' theory, which means for $\lambda_2 = 0$ taken from equation (10), while the solid line is a linear fit to the experimental data. From the slope found in the fit one can deduce with equation (10) that the parameter λ_2 takes the value $\lambda_2 = 0.2$. So it is significantly different from zero, giving a clear proof of the validity

of the new equation of magnetization relaxation. Using a relation given by Brenner [32] for the orientational distribution of ellipsoidal particles in a pure elongational flow, one can relate λ_2 to the axis ratio of the structures being responsible for the magnetization signal [31]. For $\lambda_2 = 0.2$ one obtains an axis ratio of 2, which corresponds to a mean chain length of $\bar{n} = 2$ particles per chain. The same result for the mean chain length is found from [14] for the rheological investigations where $\bar{n} = 2.5$ has been calculated.

More recent experiments, carried out with a cobalt-ferrofluid, have shown that fluids with a stronger tendency of chain formation show a shear rate dependent value of λ_2 which again can be related to a mean chain length of chains of particles in the system corresponding well to the findings from rheological measurements.

5. Conclusions and outlook

To conclude, one can first of all state that suspensions of magnetic nanoparticles exhibit the possibility to modify their properties and to control their flow by moderate magnetic fields. This fact creates a research field which is actually strongly developing. Focusing on the rheological properties of the system, the main attraction of ferrofluids is obviously the possibility to control the interparticle interaction by a modification of their microscopic composition as well as by the applied magnetic field. Thus magnetic fluids are an interesting model substance for the investigation of the influence of interparticle interaction on the rheological behaviour of suspensions and for the determination of a connection between the microstructure forced by interparticle interaction and the macroscopic properties.

Besides the basic scientific interest, a deeper understanding of the rheological behaviour of magnetic suspensions themselves can also give rise to the development of new ferrofluids exhibiting magnetoviscous effects strong enough to allow the design of applications making use of the magnetic control of the properties of the fluid.

Furthermore, the recent development of strongly interacting ferrofluids, exhibiting significant changes of their microstructure, enhances the importance of the newly formulated basic description of ferrofluids. As discussed above, abandoning the strong restraint that a ferrofluid has to be a system of non-interacting spherical objects leads to the introduction of new coupling parameters between certain flow properties and the magnetization behaviour. As has been shown, the formation of even small ellipsoidal structures in the fluid gives rise to a significant coupling of the symmetric velocity gradient to the magnetization dynamics, and stronger interacting particles can make this effect dominant. Since this theoretical approach is quite new, it can be expected that a further development of the new ferrofluid dynamics [29] will give rise to the prediction of numerous new effects like, for example, the influence of magnetic fields on sound propagation in magnetic fluids [33].

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