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Investigation of the microscopic reason for the magnetoviscous effect in ferrofluids studied by small angle neutron scattering

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Abstract
Experimental studies made on different ferrofluid samples under shear flow have shown that an increase of magnetic field strength yields an increase of the fluid's viscosity, the so-called magnetoviscous effect, while increasing shear rate leads to a decrease of the viscosity. The change of the viscosity with magnetic field strength can be theoretically explained as an effect of chain-like structure formation and therefore can be related to the modification of the microstructure of ferrofluids.

Using a specially designed rheometer, ferrofluids having different magnitude of the magnetoviscous effect were investigated by small angle neutron scattering (SANS). Correlated to the structure formation in the fluid, the scattered intensity shows a variation with magnetic field and shear rate only for fluids with a high magnetoviscous effect. The results obtained show a good agreement with the qualitative model elaborated to explain the magnetoviscous effect, indicating a strong connection between the rheological behaviour of ferrofluids and their microstructure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The appearance of magnetic field-induced changes of viscosity of ferrofluids under shear stress was experimentally shown by McTague [1] in 1969 for a diluted suspension of cobalt nanoparticles. A theoretical explanation of the effect, given by Hall and Busenberg [2] in 1969 and completed in 1972 by Shliomis [3] is based on the concept of the hindrance of the free rotation of the particles in a shear flow under the influence of an external magnetic field. Considering a ferrofluid under shear flow, the velocity gradient in the flow will induce a rotation of the magnetic particles suspended in the ferrofluid. Thus, without influence of a magnetic field, the magnetic particles, considered to be spherical, rotate with their axis of rotation parallel to the vorticity of the flow.

Applying a magnetic field and assuming that the magnetic moments remain fixed within the particles, a tendency for the magnetic moments to orientate towards the field direction is expected. If the magnetic field is applied perpendicular to the vorticity of the flow the magnetic moments of the particles will tend to align parallel to the direction of the field. On the other hand, due to the viscous friction in the shear flow, a mechanical torque will act on each particle and will rotate it. For magnetic moments fixed within the particles, a rotation of the particles will cause a misalignment of the magnetic moments from the field direction. This leads to the appearance of a magnetic torque, trying to counteract the mechanical one and to realign the magnetic moments parallel to the magnetic field. Thus, the free rotation of the particles in the flow is hindered and an increase in the viscosity of the fluid is observed.

The explanation for the magnetoviscous effect described above applies only for large particles following the Brownian relaxation process of magnetization and thus having the magnetic moments fixed within. The small particles, relaxing by the Néel process, do not contribute to the change of viscosity of the fluid. Their magnetic moments can rotate inside the particles following the direction of the magnetic field, independent from the flow. Additionally, the model neglects the interaction between the particles and therefore it applies only for highly diluted ferrofluids.

In 1969, Rosensweig *et al* [4] measured the magnetoviscous effect in a concentrated fluorocarbon-based ferrofluid subjected to a uniform shear flow in the horizontal plane. Under the influence of a vertically orientated magnetic field, they measured increases of viscosity about two times higher than the viscosity without magnetic field. This is much stronger than the increase of viscosity predicted by Shliomis' single particle model of the magnetoviscous effect.

Experiments performed by other authors for commercial ferrofluids [5] have shown similar results. Consequently, the behaviour of concentrated ferrofluids has been attributed to chain-like clustering effects due to the strong interaction between the particles, which cannot be neglected in a more general theory. Additionally, in contrast to Shliomis' theory, in which the shear stress has negligible effect on the viscosity, a strong dependence of the magnitude of the magnetoviscous effect on the shear rate has been observed.

For the formation of clusters, the dipole–dipole energy of the particles has to overcome the thermal energy. Since the dipole–dipole energy increases with the size of the particles, only 'large' particles can form structures. For magnetite-based ferrofluids the particles must have diameters larger than about 12 nm, but only a small amount of the particles contained in commercial ferrofluids fulfils this requirement. Measurements performed in 2000 by Odenbach and Raj [6] have shown that a change of the concentration of the large particles strongly modifies the magnetoviscous effect. Moreover, not only can the magnetoviscous effect be correlated with the microscopical make-up of ferrofluids but also their viscoelastic behaviour, like, for example, viscoelasticity, shear-thinning and other non-Newtonian features, controlled by magnetic fields [7].

In this context various questions remain still open. For example, how can the microstructure of ferrofluids be described? How is the microstructure affected by a flow and a magnetic field and how does it react back onto the flow? What is the connection between the microstructural changes and their result on the magnetoviscous effect?

In spite of considerable research activities of various authors, these questions are still waiting to be answered. Since until now experimental data proving such a connection between the structure of ferrofluids and their viscous properties have been missing, the investigation of the microstructure of ferrofluids—for different magnetic field strengths and shear rates—and its consequences on the magnetoviscous effect has been the focus of recent research.

Since ferrofluids are opaque systems, the microstructural changes due to the magnetic field and shear rate variation cannot be directly observed. However, as proper tools for these investigations, small angle scattering methods like SAXS (small angle x-ray scattering) and SANS (small angle neutron scattering) can be used. While for energetical reasons (high brilliance of x-ray sources, high resolution and no restriction concerning the energy transfer) x-ray scattering seems to be more indicated, neutron scattering gains an advantage due to the weak interaction of neutrons with matter, but also due to the additional magnetic scattering, giving information about the magnetization state of the sample.

The functionality of SANS as a powerful tool for the characterization of ferrofluids has already been proved in former studies [8, 9]. For example, SANS experiments have been performed to investigate diffusion phenomena in magnetic fluids [10]. Since the magnetization of a ferrofluid is a measure of the concentration of the magnetic particles, it has been shown that by determination of the anisotropy of the magnetic scattering, it being proportional to the magnetization of the fluid, information about changes in particle concentration in a ferrofluid subjected to a magnetic field gradient can be obtained. Using small angle neutron scattering Cebula *et al* [11] have studied the aggregation process in cobalt-based ferrofluids, with concentrations between 0.27 and 2.14 vol%, under various conditions of temperature and externally applied magnetic field. A strong dependence of the scattering intensity on the volume concentration of magnetic particles has been observed, indicating for highly concentrated ferrofluids, even at zero field, cluster formation due to magnetic dipole–dipole interaction. By applying a magnetic field, interference peaks appear, corresponding to ordered structures such as chains aligned with the magnetic field direction.

Rosman *et al* [12] have studied the aggregation in magnetite-based ferrofluids with particle volume fraction varying between 0.02 and 7 vol%. It has been found that, in all fluids with concentration below 1 vol%, in the presence of an applied magnetic field of 0.1 T small chain-like aggregates are formed, aligned with the direction of the magnetic field. Three-dimensional aggregates, orientated and enlarged by application of magnetic fields, are formed at a higher volume concentration.

These results, together with additional information provided by various experiments in polymers [13], lead to the conclusion that SANS is a useful tool to study the formation and disruption of chains in usual ferrofluids under the influence of a magnetic field and obtain experimental access to an explanation of the magnetoviscous effect.

An observation of chain formation as well as structure destruction by means of shear influence for different combinations of magnetic field and shear rate would provide the necessary information to explain the connection between the macroscopical behaviour of ferrofluids and their microstructure. Understanding the mechanisms leading to the magnetoviscous effect together with the parameters that influence its magnitude will give the possibility for an optimization by the development of new types of ferrofluids. Starting from this insight, it will be possible that new ferrofluids are synthesized, exhibiting stronger changes of viscosity with the magnetic field and a higher shear stability of the effects, requirements that are necessary for applications.

2. Experimental data

2.1. Ferrofluid samples

According to the model which explains the magnetoviscous effect as a result of chain formation within the ferrofluids under magnetic field influence, an important parameter, determining the magnitude of the magnetoviscous effect, is the interaction parameter λ^* [14].

$$\lambda^* = \frac{\mu_0 M_0^2 V}{24 k_\mathrm{B} T}\left(\frac{d}{d+2s}\right)^3, \tag{1}$$

where M_0 denotes the spontaneous magnetization of the magnetic material, d the mean magnetic diameter of the particles and V their respective volume. The thickness of the surfactant layer is denoted by s. Defined as the ratio between the dipole–dipole interaction energy between two neighbouring particles and their thermal energy, λ^* describes the possibility that the particles contained in a ferrofluid interact and form chains.

The formation of the chains can appear only for values of the interaction parameter larger than unity, i.e. if the interaction between the particles is strong enough to keep the particles together and overcome their thermal motion. By comparing the values of λ^* calculated for magnetite and cobalt particles it has been obtained that in the case of magnetite the particles should be larger than 12 nm to contribute to the formation of structures whereas 6.5 nm cobalt particles are already able to form chain-like structures.

In order to observe the influence of the interaction parameter on the rheological behaviour of ferrofluids and on their microstructure respectively, fluids with different ability to form chains, two commercial ones, Ferrotec APG513A from two production lines, and an experimental one, Co87_03 (cobalt particles coated with an aluminium oxide shell, stabilized with korantin SH and suspended in kerosene) supplied by H Bönnemann (Mülheim/Karlsruhe), have been investigated.

The magnetite-based ferrofluid, APG513A_1, has a mean particle diameter (magnetic) of about 10 nm and a concentration ϕ of magnetic material of 7.2 vol%. The corresponding interaction parameter, considering a thickness of the surfactant layer of 2 nm, is calculated to be $\lambda^* = 0.5$ for the mean particle size. For the evaluation of the possibility of chain formation inside this fluid, it has to be taken into account that the particle diameters are distributed in a range between 3 and 20 nm [15]. Thus, only a small amount of particles is large enough to contribute to the magnetoviscous effect. Considering the mean diameter of these large particles to be about 16 nm, the interaction parameter for this fraction of particles is equal to $\lambda^* = 2.87$.

In addition to this fluid, another sample, APG513A_2, having the same basic characteristics as APG513A_1 but from a different production line, has been investigated. While the mean particle diameter and the concentration of the magnetic material remained the same as for APG513A_1, the particle size distribution has been changed. Comparative magnetization measurements (see figure 1) indicate a lower content of large particles in the APG513A_2 sample compared to APG513A_1. It is therefore expected that these two samples show different responses to the magnetic field influence.

The cobalt-based ferrofluid, Co87_03, having a mean particle diameter d of about 10 nm and full width at half maximum of the size distribution of 3.5 nm, contains only 0.35 vol% magnetic material. Nevertheless, since the particle sizes are distributed in the range of 7 nm to about 16 nm [16], all particles can contribute to chain formation and therefore strongly influence the magnitude of the magnetoviscous effect. Due to the larger spontaneous magnetization of cobalt compared to magnetite, the interaction parameter, calculated for a particle diameter d of 10 nm and a thickness s of the surfactant of 2 nm, is $\lambda^* = 5.26$.

2.2. Rheological characterization of the ferrofluid samples. The magnetoviscous effect

In figures 2 and 3 the dependence of the viscosity change for the APG513A_1 sample on magnetic field strength and shear rate is presented. As exemplified in figure 2, under the influence of a magnetic field of about 120 kA m^{-1} applied to the sample, its viscosity increases

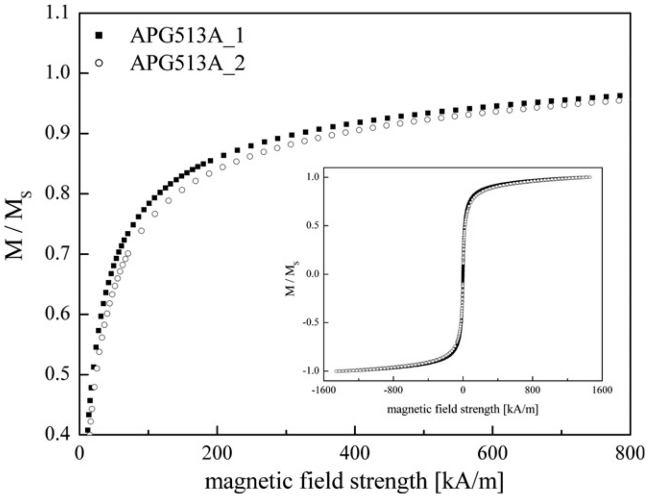

Figure 1. Magnetization curves for APG513A_1 and APG513A_2 normalized to the corresponding saturation magnetization.

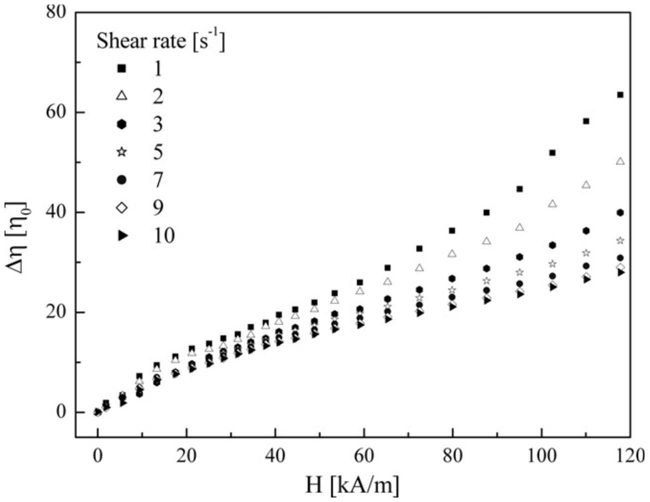

Figure 2. Magnetoviscous effect for APG513A_1 for shear rates between 1 and 10 s^{-1}. The field-induced change of the viscosity $\Delta\eta$ is expressed in units of the viscosity without magnetic field $[\eta_0]$. An increase of the magnetic field strength produces a stronger relative change of viscosity whereas higher shear rates lead to shear thinning.

about 60 times for the lowest shear rate presented here. Additionally, the shear dependence of the magnetoviscous effect can be observed. Increasing the shear rate from 1 to 10 s^{-1}, the relative change of the viscosity reduces by a factor of 3 at a magnetic field strength of 120 kA m^{-1}. Calculating the upper limit for the relative increase of the viscosity $(\Delta\eta/\eta_0)$ with the theory of rotational viscosity formulated by Shliomis, values of about two orders of magnitude lower than the experimentally determined ones are obtained, even assuming that all the particles contained in the ferrofluid can contribute to the effect. Thus, it is obvious that the Shliomis theory, explaining the increase of the viscosity as an effect of the hindrance of the free rotation of single particles in the flow, does not apply for this sample. The discrepancies

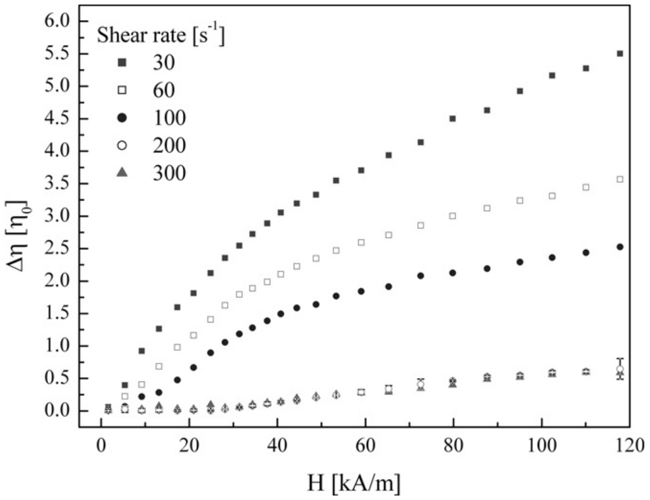

Figure 3. Magnetoviscous effect for APG513A_1 for shear rates between 30 and 200 s^{-1}.

between the model and the experimental results can therefore be considered as an effect of field supported particle–particle interactions within this ferrofluid sample [17]. By increasing the magnetic field strength, an alignment of the magnetic moments of the particles along a common direction is enhanced, encouraging magnetic interparticle interaction, i.e. the formation of chain-like structures. The competition between the mechanical and the magnetic torque acting on such structures determines their length as well as their orientation relative to the flow. Thus, each combination of magnetic field strength and shear rate leads to a specific magnitude of the magnetoviscous effect.

For low and medium shear rate regimes, up to 100 s^{-1}, a strong shear thinning can be observed (see figures 2 and 3). Shear rates larger than 200 s^{-1} do not produce significant changes of the magnitude of the magnetoviscous effect any more. Thus, it can be supposed that at high shear rates the field-induced changes of the viscosity for the APG513A_1 ferrofluid sample are mainly due to the hindrance of the free rotation of the large particles and permanent agglomerates in the flow.

Comparing the field-induced changes of viscosity for the magnetite-based ferrofluid, APG513A_1 ($\phi = 7.2$ vol%), and for the cobalt-based ferrofluid, Co87_03 ($\phi = 0.35$ vol%), it can be observed that the magnitude of the magnetoviscous effect is approximately equal, despite the different concentration of the magnetic material. This confirms the previous results concerning the dependence of the magnetoviscous effect on the content of the large particles [6].

Since the particle size distribution for the fluid Co87_03 is very narrow, it can be considered that most of the particles have diameters of about 10 nm, i.e. all particles are large enough to contribute to the formation of chains. In comparison, in the case of APG513A_1, only a small number of particles are larger than the critical diameter required to have an interaction parameter $\lambda^* > 1$, i.e. to form chain-like structures. Due to the reduced number of particles contributing to the chain formation, the resulting magnetoviscous effect in APG513A_1 is therefore comparable to the one measured for Co87_03 (see figures 2 and 4).

Peculiar to the Co87_03 fluid is its behaviour at high shear rates (see figure 5). Contrary to the magnetite-based ferrofluid treated above, the cobalt-based ferrofluid shows, at shear rates of about 200 s^{-1}, a magnetoviscous effect about three times stronger than for the APG513A_1

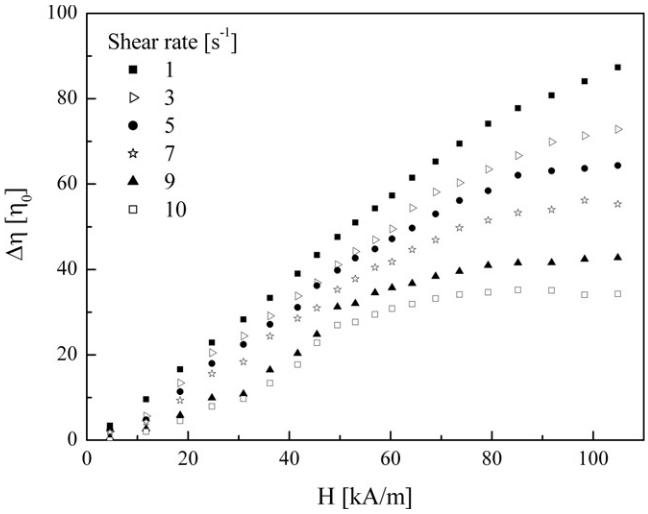

Figure 4. Magnetoviscous effect for Co87_03 for shear rates between 1 and 10 s^{-1}.

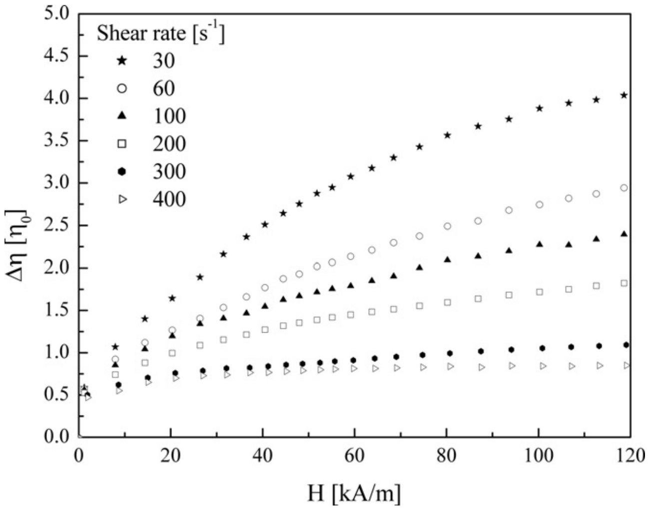

Figure 5. Magnetoviscous effect for Co87_03 for shear rates between 30 and 400 s^{-1}.

sample as well as a further shear thinning. Therefore, for the cobalt-based ferrofluids, even in the high shear rate regime it is expected that the particle chains are not destroyed.

The rheological investigation of the APG513A_2 sample (figures 6 and 7) shows low magnitudes of the magnetoviscous effect. This leads to the conclusion that the probability for the particles to form chains within this fluid is lower than in the APG513A_1 or Co87_03 fluids. Having a narrower particle size distribution function than APG513A_1 but the same mean particle diameter, the APG513A_2 sample contains a smaller number of large particles. Thus, the ability of the particles to organize themselves in chain-like structures is considerably reduced.

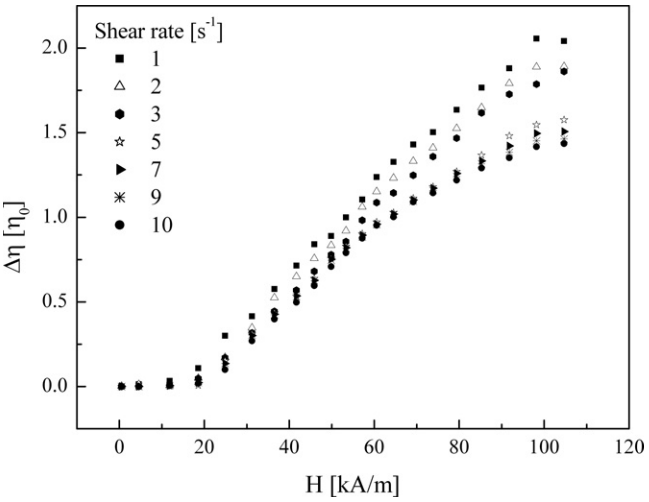

Figure 6. Magnetoviscous effect for APG513A_2 for shear rates between 1 and 10 s^{-1}.

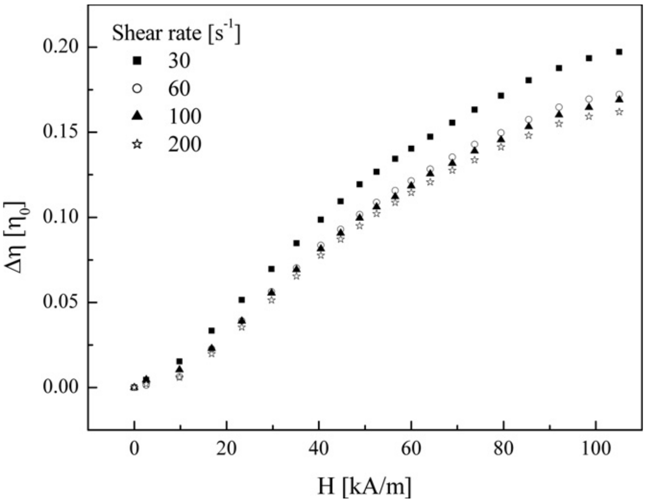

Figure 7. Magnetoviscous effect for APG513A_2 for shear rates between 30 and 200 s^{-1}.

2.3. SANS results

The selected results of the rheological characterization of the ferrofluid samples, presented above, have evidenced that the magnitude of the magnetoviscous effect depends as much on the interparticle interaction parameter as on the number of particles being able to form chains. To prove the connection between the magnetoviscous effect and the microscopic make-up of the ferrofluid samples, small angle neutron scattering investigations of the microstructure have been performed in the same experimental environment as the rheological measurements using a specially designed cone-plate rheometer (see figure 8) [18].

The SANS investigations have been carried out for shear rates and magnetic field strengths similar to those used for the rheological measurements. Additionally, in order to observe possible modifications of the microstructure at magnetic field values inaccessible for the

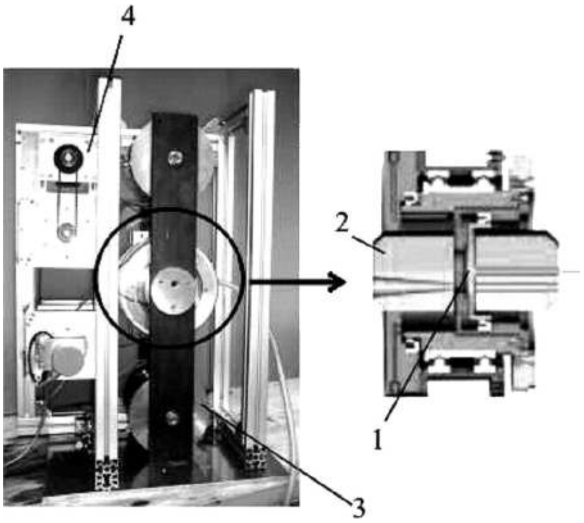

Figure 8. Photograph of the experimental setup for SANS (1—measuring cell, 2—pole shoe, 3—coil, 4—drive unit).

rheological measurements, the range of the magnetic field strengths has been extended up to 160 kA m^{-1}.

2.3.1. Qualitative model. Considering the ferrofluid sample as a single, noninteracting spherical paramagnetic particle system, it is expected that in the absence of a magnetic field no structures are formed. In a classical experiment using unpolarized neutrons the scattering intensity $I(\vec{q})$—which contains all the information on the shape, size and interactions of the scattering bodies (assemblies of scattering centres) in the sample—can be written as a sum of the nuclear component $I_{\text{nuc}}(\vec{q})$ and magnetic component $I_{\text{mag}}(\vec{q})$:

$$I(\vec{q}) = (I_{\text{nuc}}(\vec{q}) + I_{\text{mag}}(\vec{q})) = [A(\vec{q}) + B(\vec{q})\sin^2\alpha] \tag{2}$$

with $A(\vec{q})$ being the isotropic term of the scattering and $B(\vec{q})$ an anisotropic one; α is the angle between the projection of the magnetization of the sample in the detector plane and the scattering vector [19]. For example, for rotational symmetric particles, in the case of magnetic moments fully aligned along a magnetic field orientated perpendicular to the neutron beam, the isotropic term has a completely nuclear origin, while the anisotropic one represents the magnetic contribution.

Without the influence of a magnetic field, the magnetic moments of the particles are statistically distributed, leading to an isotropic appearance of the scattering intensity in the obtained SANS pattern. Applying a magnetic field to the ferrofluid sample, in the ideal case, chains aligned along the field direction are formed within the fluid. For the total magnetization of the chains fixed within and thus being also parallel to the magnetic field, it is expected that the scattering patterns are perfectly isotropic for the situation with magnetic field vector parallel to the neutron beam (0°-setup, see figure 9(a)) since no component of the magnetization appears in the detector plane (yz-plane).

In order to gain more information about the formation of chains and their organization in the flow, additional measurements with magnetic field nonparallel to the neutron beam have been performed. Because of magnetic field homogeneity considerations, a deviation of the magnetic field direction of 10° relative to the neutron beam has been chosen (10°-setup).

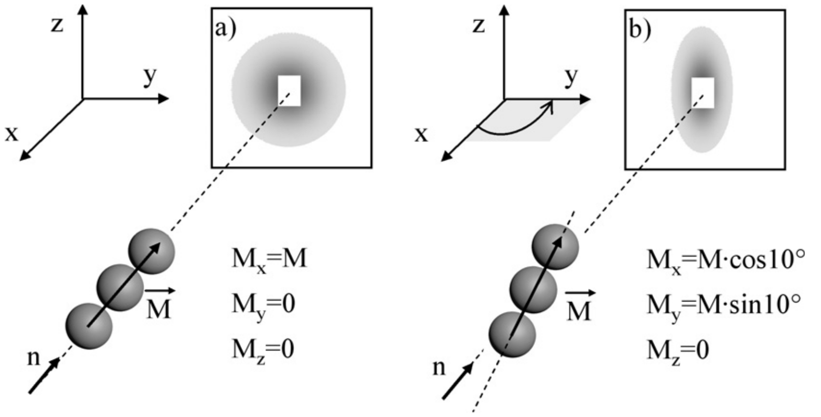

Figure 9. Qualitative model for SANS in ferrofluids in rest. The magnetic field is orientated parallel to the neutron beam (a) and with 10° between its direction and neutron beam (b) respectively.

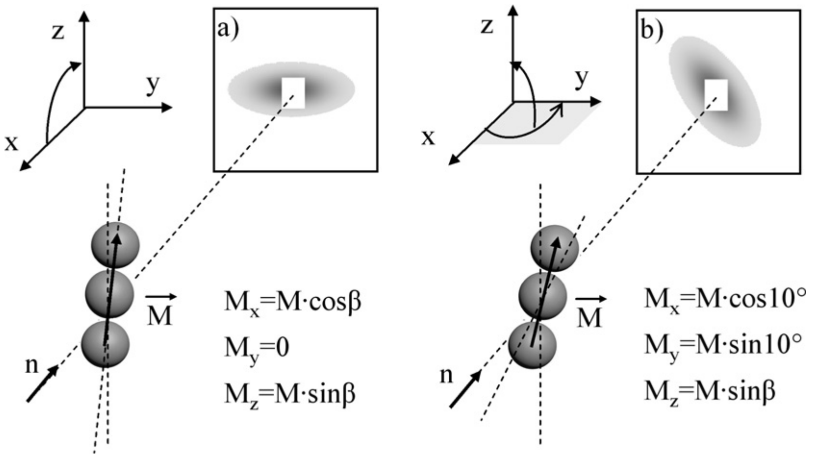

Figure 10. Qualitative model for SANS in ferrofluids under shear flow. The magnetic field is orientated parallel to the neutron beam (a) and with 10° between its direction and neutron beam (b) respectively.

For this situation (figure 9(b)), there will be a component of the total magnetization of the sample in the detector plane ($M_y \neq 0$), resulting in an anisotropy of the scattering pattern. Because of the $\sin^2\alpha$ dependence of the anisotropic term of the scattering (see equation (2)) the anisotropy of the scattering patterns should reach a maximum in the vertical direction (z-direction).

A shear flow applied to the fluid sample by rotating the plate while the cone remains fixed should produce a misalignment of the chains from the direction of the magnetic field. The chains will be locally deviated towards the z-direction (see figure 10). Thus, in the shear flow, it is expected that the local magnetization of the deviated chains will have a component along the z-direction, leading to the appearance of an anisotropy in the scattering pattern. For a magnetic field orientated parallel to the neutron beam, the anisotropy of the scattering patterns shows a maximum in the horizontal direction, i.e. $\sin^2\alpha = 1$ (see figure 10(a)). For the setup with an angle of $\delta_{\mathrm{MF}} = 10°$ between the magnetic field and neutron beam the vertically disposed anisotropy—due to the position of the rheometer relative to the neutron beam (see figure 9(b))—combines with the horizontal anisotropy term caused by the deviation of the chains in the shear flow (figure 10(a)). The resulting deviation of the anisotropy from the vertical direction (figure 10(b)) is therefore related to both the length and deviation of chains in the flow.

2.3.2. *Ferrofluids with strong magnetoviscous effect.*

From the SANS investigations, performed at Hahn Meitner Institute in Berlin, two-dimensional data sets have been obtained for each combination of magnetic field strength and shear rate. The measurements have been carried out for various sample–detector distances, covering a q-range (with q being the scattering vector) between 0.05 and 0.325 nm^{-1} and between 0.123 and 1 nm^{-1} respectively. This allows an investigation of inhomogeneities on scales in the interval from 6 to 130 nm.

The measurements for the magnetite-based ferrofluid APG513A_1 have shown no modification of the microstructure at low values of the scattering vector, i.e. for large dimensions in real space. Therefore, only the results for large q-vectors—for a structure size range between 6 and 50 nm—exhibiting changes of the scattered intensity with magnetic field strength and shear rate variation are presented.

The resulting scattering patterns contain not only information about the formation of chains in the sample, but also contributions from the carrier liquid, the surfactant and the small particles which do not take part in the structure formation process. Thus, in order to observe only the modification of the microstructure under the influence of different magnetic field strengths and shear rates, a reference scattering pattern has been considered.

As has been discussed in section 2.2, the rheological measurements for the magnetite-based ferrofluids have shown that the slight increase of the viscosity at high shear rates is mainly due to the hindrance of the free rotation of single particles in the flow. Therefore, for each magnetic field strength used in the experiments, the reference scattering pattern ($\dot{\gamma} = 200\ \mathrm{s}^{-1}$), corresponding to the single particle system, has been subtracted from the scattering patterns obtained for all other measured shear rates. The difference patterns will thus contain only information about relevant changes in the microstructure, corresponding to the chain-like ordering. The difference patterns obtained for the fluid with high magnetoviscous effect, APG513A_1, indicate a dependence of the scattered intensity on the shear rate and the magnetic field strength (figure 11).

For a high magnetic field strength and a low shear rate ($H = 160\ \mathrm{kA\ m}^{-1}$, $\dot{\gamma} = 1\ \mathrm{s}^{-1}$) the difference pattern is almost zero. Due to the high magnetic field, segments of chains are formed, but their deviation from the initial direction is very small. Thus, the situation is similar to the static case. Since the cross sections have almost the same size as those in a single particle system, the difference between this situation and the reference scattering pattern is merely given by a lower concentration of the scattering centres, due to the structure formation in the ferrofluid sample. For higher shear rates, the deviation of the chains from the magnetic field direction becomes larger and therefore their projection, as seen by neutrons, increases. The difference is maximal for the highest shear rate shown here ($\dot{\gamma} = 10\ \mathrm{s}^{-1}$), where the magnetic field is still strong enough to keep the particles together. With decreasing magnetic field strength and low shear rate ($H = 80\ \mathrm{kA\ m}^{-1}$, $\dot{\gamma} = 1\ \mathrm{s}^{-1}$), both the magnetic and mechanical influences on the chains reduce, leading to a different length as well as to a different deviation angle of the chains in the flow. Therefore, the difference between the scattering patterns and the reference becomes nonzero and shows a minimum for the lowest magnetic field strength presented here. Keeping the magnetic field strength constant and increasing the shear rate, the deviation of the chains increases, resulting in a further change in the difference scattering patterns. For low

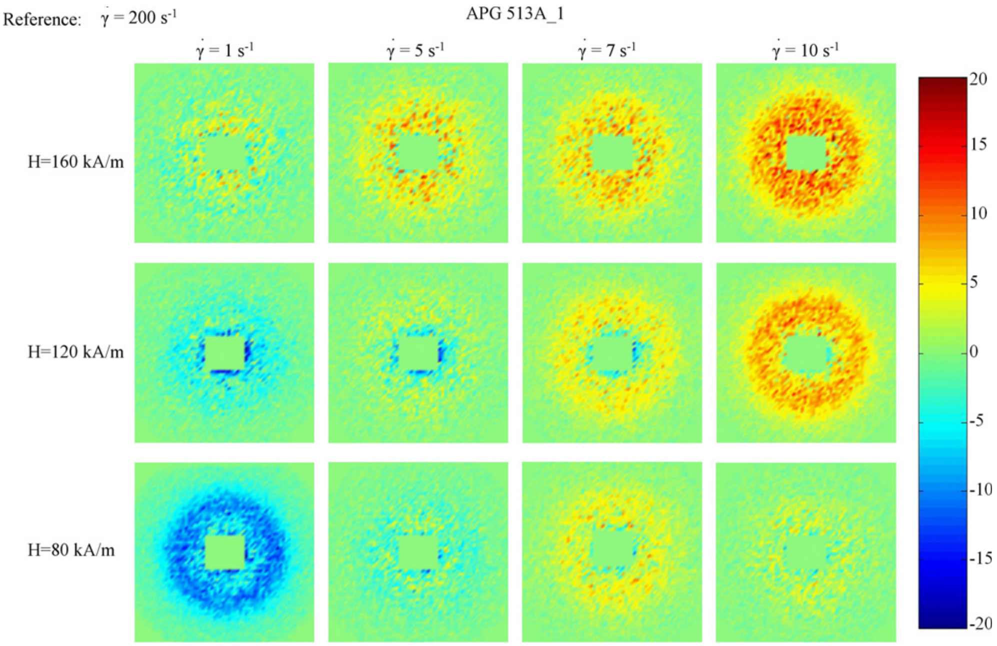

Figure 11. Difference scattering patterns for APG513A_1 for the 0°-setup (magnetic field aligned parallel to the neutron beam). The scattering pattern obtained for $\dot{\gamma} = 200\ \mathrm{s}^{-1}$ has been used as reference [20].

magnetic field strength and high shear rate ($H = 80\ \mathrm{kA\ m}^{-1}$, $\dot{\gamma} = 10\ \mathrm{s}^{-1}$), the chains are broken, the particles are homogeneously distributed in the sample, and hence the difference scattering pattern is again almost zero.

According to the qualitative model described at the beginning of this section, with increasing shear rate, i.e. with rising deviation of the chains, an anisotropy of the scattering patterns is expected. For the case of magnetite particles, the magnetic component of the scattering is weak. The magnetic scattering length density ($\eta_M = 1.36 \times 10^{14}\ \mathrm{m}^{-2}$) is about five times smaller than the nuclear scattering length density ($\eta_N = 6.95 \times 10^{14}\ \mathrm{m}^{-2}$). Thus, the magnetic contribution to the anisotropic term of the scattering intensity cannot be observed. Nevertheless, long structures with strong form anisotropy should also provide an anisotropic nuclear component of the scattering. In conclusion, the experimental results obtained for the APG513A_1 sample indicate the presence of short chains only. This agrees with the analytical results of the chain formation theory, formulated by Zubarev, which predicts a mean length of the chains between 2 and 4 particles [21].

The difference scattering patterns obtained in the case of a magnetic field orientated parallel to the neutron beam (figure 11) have shown a variation of the scattering intensity relative to the reference patterns with increasing shear rate. For the 10°-setup, the situation is found to be dissimilar. The difference scattering patterns presented, on the same scale, in figure 12, do not show a significant modification with either the variation of magnetic field or with increasing shear rate in the range between 1 and 10 s^{-1}. The shear effect can only be observed at the transition between the medium and high shear rate regimes and is not modified by the magnetic field variation.

In conclusion, the measurements presented above for APG513A_1, performed for the orientation of the rheometer with a 10° angle between the magnetic field direction and neutron

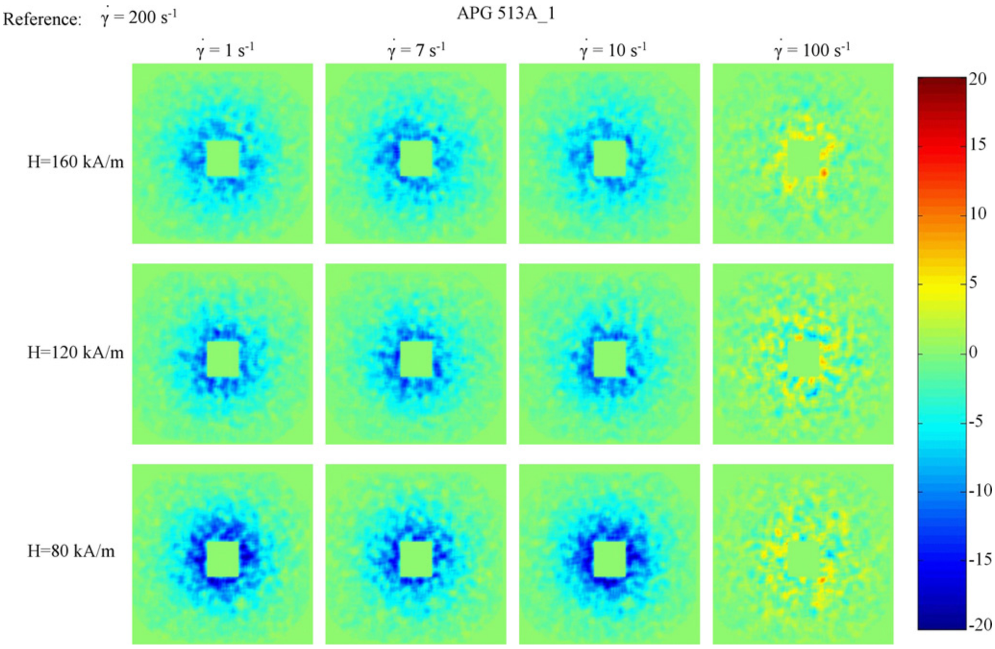

Figure 12. Difference scattering patterns obtained for APG513A_1 for the 10°-setup. The scattering pattern obtained for $\dot{\gamma} = 200$ s^{-1} has been used as reference.

beam, do not introduce additional information like, for example, the variation of the length of the chains with magnetic field. Due to the orientation of the magnetic field, only the cross section of the 10° projection of the chains in horizontal direction (see figures 9(b) and 10(b)) can be seen by the neutrons. Additionally, for the magnetic moments deviated from the neutron beam direction, the isotropic component of the magnetic scattering is reduced, while the anisotropic term is too small to enable an observation of its variation with magnetic field strength. The absolute intensity is also reduced due to the slightly increased volume of the sample in the neutron beam from 0.0564 cm^3 for the 0°-setup to 0.0580 cm^3 for the 10°-setup respectively. Nevertheless, the results obtained for the 10°-setup confirm the hypothesis of short lengths of the chains, formulated as a result of the observations made for a magnetic field parallel to the neutron beam.

Due to the weak magnetic scattering of magnetite, no anisotropic scattering patterns have been obtained for the APG513A_1 sample. Thus, even if the SANS results presented above can be related to the changes of the microstructure they do not give information about the length and orientation of the chains. Therefore, investigations using another magnetic material have to be made. Comparing the properties of cobalt bulk material with the properties of magnetite it is found that the magnetic scattering length density of cobalt is about a factor of three larger than for magnetite ($\eta_M = 4.14 \times 10^{14}$ m^{-2}). Additionally, due to the increased spontaneous magnetization of cobalt, the magnetic moments of the cobalt particles are, for the same particle size, about three times larger than for magnetite ($Ms_{\mathrm{Co}}/Ms_{\mathrm{magnetite}} = 3.24$). Thus, the dipole–dipole energy, i.e. the interaction parameter λ^*, is also larger, favouring the formation of chains.

In the case of the cobalt-based ferrofluid, the scattering at large q-vectors—corresponding to structure sizes between 6 and 50 nm—shows an evolution of the scattering patterns comparable with the results for the magnetite-based sample, APG513A_1. The measurements

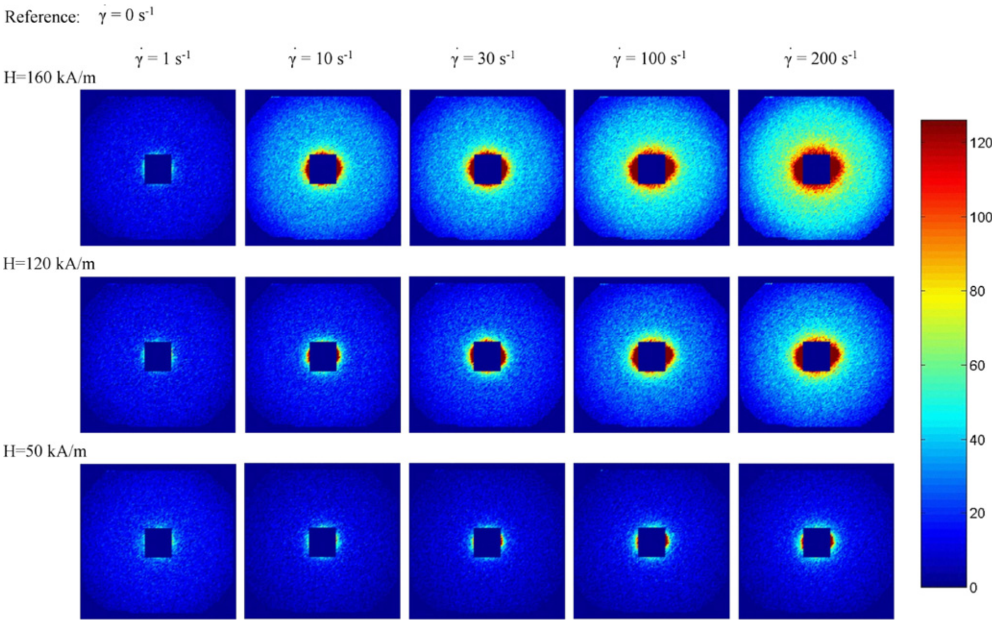

Figure 13. Scattering patterns obtained for Co87_03 for the 0°-setup (magnetic field aligned parallel to the neutron beam) for different magnetic field strengths and shear rate varied between 0 and 200 s^{-1}.

on this scale reveal only the interaction between neighbouring particles and the presence of short chains within the fluid. Nevertheless, the rheological measurements for the Co87_03 ferrofluid show a strong increase of the magnetoviscous effect with increasing magnetic field strength, despite the relatively low concentration of the cobalt material. Thus, due to the strong change of viscosity under the influence of a magnetic field it is to be expected that the chains formed within this fluid are large compared with the structures formed in the magnetite-based ferrofluid, APG513A_1. Special attention has therefore been given to the investigations at low q-vectors, corresponding to inhomogeneity/structure sizes between 50 and 130 nm.

The rheological measurements for the cobalt-based ferrofluid have shown that even at high shear rates there should be chains within the fluid sample, contributing to the field-induced increase of viscosity. Thus, for the case of the cobalt-based ferrofluid, the static case ($\dot{\gamma} = 0\ s^{-1}$) has been considered as reference and has been subtracted from the scattering patterns obtained for the other shear rates.

From the difference scattering patterns presented in figure 13 it can be seen that at low shear rates, for all the magnetic fields illustrated here, the deviation of the chain-like structures is too low to produce a significant change of the scattering intensity.

At low magnetic field strengths (here $H = 50\ \mathrm{kA\ m^{-1}}$) an anisotropy of the scattering patterns can be observed only at relatively high shear rates, for this case beginning with $\dot{\gamma} = 30\ s^{-1}$.

An increase of the magnetic field strength leads to a stronger magnetic torque acting on the magnetic particles. Thus, a larger number of particles tend to orientate their magnetic moments along a common direction. In consequence, the chains formed are longer compared to the situation with a weak magnetic field. Additionally, with increasing length of the chains, there will be an increase in the viscous torque acting on the structures formed. The length and the deviation of the chains in the flow will therefore be determined by the equilibrium between

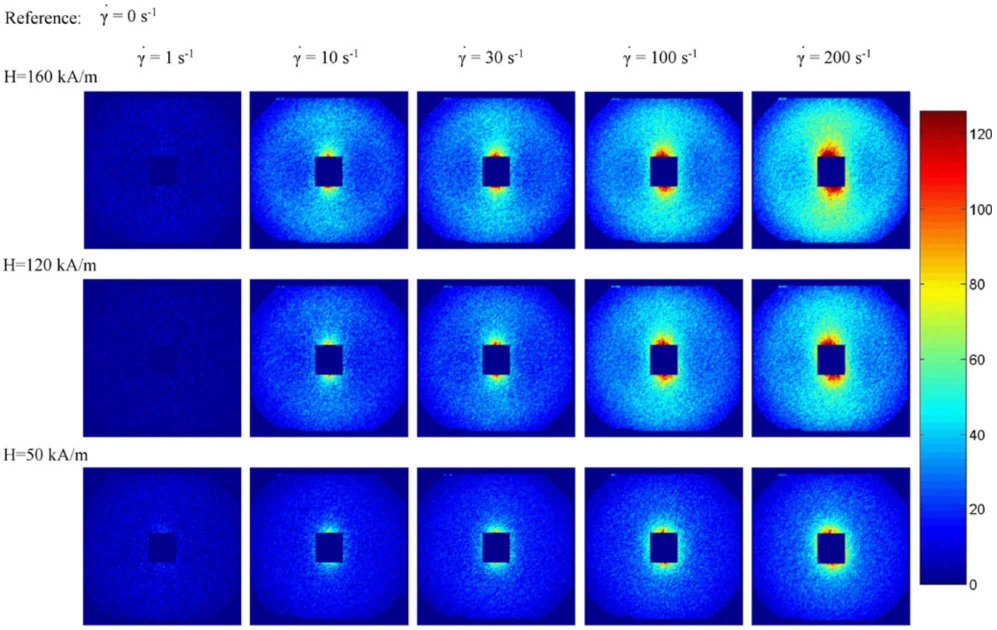

Figure 14. Difference scattering patterns obtained for Co87_03 for 10° between magnetic field direction and neutron beam for different magnetic field strengths and shear rate varied between 0 and 200 s^{-1}.

the two torques, the magnetic one and the mechanical one, acting on the chains. Nevertheless, from the anisotropy of the difference scattering patterns presented above it can be concluded that for shear rates being large enough to produce a deviation of the chains, the projection of the chains—as it can be seen by the neutrons—increases with increasing magnetic field strength. For each magnetic field presented in figure 13 a higher shear rate leads to a higher deviation of the chains which is evidenced by a stronger anisotropy of the scattering patterns relative to the reference.

The effect of the magnetic field and shear rate variation on the microstructure of the ferrofluid sample can be also observed in the difference scattering patterns presented in figure 14, for the 10°-setup. It can be seen that low shear rates yield no modification relative to the reference while, for shear rates higher than 10 s^{-1}, strong changes of the difference scattering patterns appear. First, with increasing magnetic field strength, the anisotropic part of the difference scattering patterns increases, confirming, at a given shear rate, an increase of the chain lengths. For a constant magnetic field strength, with increasing shear rate the chains are more deviated. This results in a deviation of the anisotropy from the vertical direction, confirming the assumption made in the qualitative model that the chains, initially aligned parallel to the direction of magnetic field ($\dot{\gamma} = 0\ s^{-1}$), are deviated in a shear flow. The resulting anisotropy reaches a maximum in the direction perpendicular to the chain direction.

2.3.3. Ferrofluids with low magnetoviscous effect. Further measurements have been performed for the magnetite-based ferrofluid sample with low magnetoviscous effect, APG513A_2 (figure 15).

Comparing the difference scattering patterns for APG513A_2 (see figure 15) and for APG513A_1 (cf figure 13), it can be observed that there is a reasonable connection between

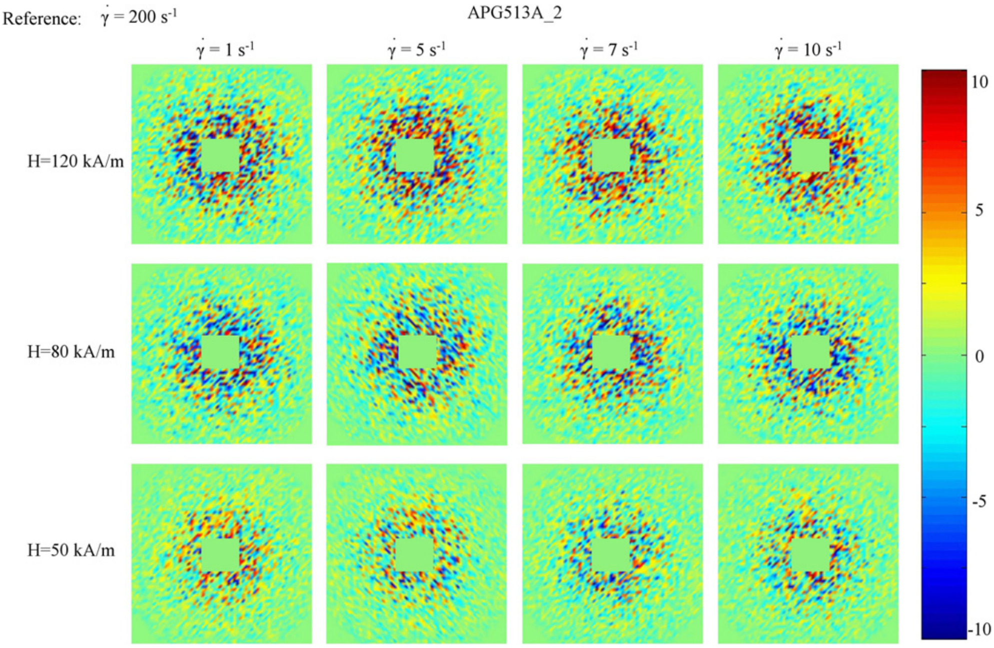

Figure 15. Difference scattering patterns for APG513A_2 for the 0°-setup (magnetic field aligned parallel to the neutron beam). The scattering pattern obtained for $\dot{\gamma} = 200$ s^{-1} has been used as reference.

the rheological measurements of the magnetoviscous effect and the modification of their microstructure probed by SANS. Even on reducing the intensity scale by a factor of two for the APG513A_2 fluid no modification of the difference scattering patterns with increasing shear rate has been observed. Thus, it can be considered that no chain formation occurs. The measured weak increase of the viscosity for APG513A_2 is merely due to the hindrance of the free rotation of the single particles, i.e. small permanent structures, in the flow, by means of magnetic fields.

The slight modification of the difference scattering patterns with magnetic field strength is most likely only an orientation effect of the magnetic moments of the single particles. For a low magnetic field strength, the magnetic moments of the particles are randomly distributed in the ferrofluid sample. For higher magnetic field strength, the magnetic moments of the single particles tend to be orientated closer to the direction of the magnetic field. This orientation process induces a change of the resulting magnetic moment of the sample. Thus, due to the increased magnetic scattering contribution a marginal modification with the magnetic field strength can be observed in the difference scattering patterns.

3. Conclusions

To gain a deeper insight into the microstructure of ferrofluids under shear flow and magnetic field influence, measurements by means of small angle neutron scattering have been performed, using a specially designed rheometer. The investigations of the microstructure could thus be carried out under the same experimental conditions as the rheological measurements. Using this setup, magnetite- and cobalt-based ferrofluids have been subjected to rheological and small angle neutron scattering investigations. In order to observe the changes of the microstructure under external influences two main parameters have been varied. The ferrofluid samples have been subjected to shear rates between 0 and 200 s^{-1} and magnetic field strengths up to 160 kA m^{-1}.

Concerning the fluids with strong magnetoviscous effect, in the case of the magnetite-based ferrofluid, the relatively weak changes in the two-dimensional scattering patterns measured under the influence of magnetic field and shear rate indicate the formation of short chains only. Since the magnetic scattering length density of magnetite is small compared to the nuclear scattering length density, the orientation of the chains in the flow could not be monitored. Further experiments performed for cobalt-based ferrofluids have evidenced the formation of chain-like structures, orientated in a shear flow. In order to distinguish between the variation of the length of the chains and of their orientation, SANS experiments have been carried out under two different geometric configurations. Thus, for the arrangement with magnetic field parallel to the neutron beam, the appearance of an anisotropy and its increase with rising shear rate indicates a larger deviation of the chains from the magnetic field direction. Using the configuration with 10° between magnetic field and neutron beam, the results obtained for the static case confirm the variation of the length of the chains with modification of the magnetic field strength. Additional information concerning the deviation of the chains in the shear flow could be obtained. The appearance of a vertical orientated anisotropy of the scattering patterns, as well as its evolution with changing magnetic field strength, is in a good agreement with the qualitative model developed for the interpretation of the SANS data. Final evidence for the validity of the chain formation model is given by the deviation of the anisotropy from the vertical direction due to the influence of a shear flow.

Evidences of the chain-like structure formation in ferrofluids under magnetic field influence and shear flow have also been obtained by molecular dynamic simulations [22]. A preliminary comparison of the simulated values and experimental data for the cobalt-based ferrofluid, Co87_03, shows promising results [23, 24], thus encouraging further common efforts for the investigation of the microstructure of ferrofluids and its consequences on the magnetoviscous effect.

Nevertheless, concerning the fact that in static experiments other types of ordering than chains have also been reported [25] and that for example field-induced ordered lamellar structures might show qualitatively the same behaviour as chains in the present scattering geometry, a variation of fluid sample parameter as well as SANS experiments using polarized neutrons are foreseen. Information obtained by combining static and dynamic SANS experiments in different geometries will enable a two-dimensional quantitative analysis [26] of the scattering patterns. These results, together with molecular dynamic simulations and analytical approaches, will lead to a more detailed understanding of the magnetoviscous effect and will open the way to new technologically useful applications.

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