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Magnetic fluids—suspensions of magnetic dipoles and their magnetic control

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Abstract
Suspensions of magnetic nanoparticles exhibit normal liquid behaviour coupled with superparamagnetic properties. This leads to the possibility to control the properties and the flow of these liquids with moderate magnetic fields. The magnetic control enables various experiments in fluid mechanics and gives rise to the development of numerous technical and medical applications. Ferrofluids and their general properties will be introduced and, as examples for the magnetic control of their flow and properties, thermomagnetic convection and magnetoviscous effects will be discussed in some detail.

1. Introduction

Colloidal suspensions containing small magnetic particles in appropriate carrier liquids represent a liquid system with strong magnetic dipoles which can be effectively influenced by magnetic fields. In contrast to paramagnetic salt solutions, which require extremely high magnetic fields on the order of several tesla to enable a magnetic influence on their behaviour, such suspensions allow significant control of their flow behaviour as well as of their properties by moderate fields of about several tens of millitesla. This magnetic control of flow or properties of a liquid material is a challenging possibility leading to interesting consequences for fluid mechanics, in general, and for application engineering in particular.

Stable suspensions of this kind were first synthesized in 1964 by Papell [1] and have since even reached technical importance in everyday life. In the following, the most important properties of these so called ferrofluids will shortly be summarized, including a short glance at the possibilities for applications of these liquids. Afterwards the magnetic flow control will be outlined on the basis of a discussion of heat transfer in ferrofluids under the influence of magnetic fields. The influence of magnetic fields on the suspensions' properties will then be discussed for the example of their viscous behaviour.

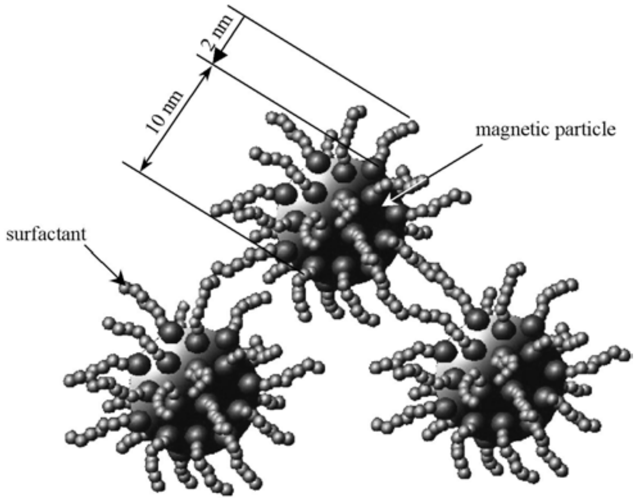

Figure 1. Schematic sketch of the magnetic particles including their surfactant. For reasons of clarity the surfactant and the particles are not drawn to scale.

2. Basic properties and applications of ferrofluids

As mentioned, ferrofluids contain colloidal magnetic particles in appropriate carrier liquids. The particles are usually made from magnetite (Fe_3O_4) and have a mean diameter of about 10 nm. With this size the particles can be treated as single domain particles [2], i.e. each of them is a small permanent magnetic dipole in the carrier liquid. While thermal energy prevents particles with a size of about 10 nm effectively from sedimentation in a gravitational field or from agglomeration due to magnetic dipole interaction, it does not prevent coagulation due to van der Waals attraction. To overcome this problem, the particles are coated with a surfactant made of long chained molecules, chosen so that their dielectric properties match those of the carrier liquid (see figure 1). The typical thickness of the surfactant layer is about 2–3 nm, the thickness being of importance for the hydrodynamic influence of the suspended particles on flows of the liquids. In this way it is possible to obtain stable suspensions of magnetic particles in carrier liquids like oil, water or kerosene. The typical volume fraction of the suspended magnetic material is about 7 vol% leading to a hydrodynamic volume fraction of the particles, including their surfactant, of approximately 23 vol%.

2.1. Magnetic properties

The behaviour of ferrofluids is mainly determined by their magnetic properties. As mentioned, each of the particles can be treated as a thermally agitated permanent magnet in the carrier liquid. In the presence of a magnetic field $\vec{H}$, the magnetic moment $\vec{m}$ of the particles will try to align with the magnetic field direction leading to a macroscopic magnetization of the liquid. The magnetization M of the liquid (see figure 2) behaves like the magnetization of a paramagnetic system and can thus be described by the well known Langevin law

$$M = M_S\left(ctgh\alpha - \frac{1}{\alpha}\right) \tag{1}$$

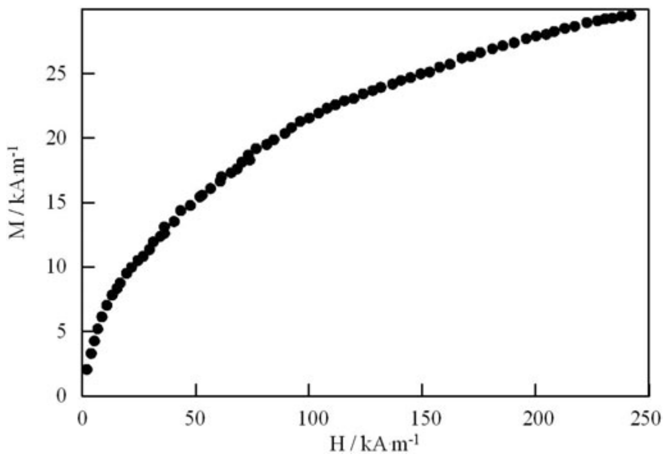

Figure 2. Typical magnetization curve of a ferrofluid.

with

$$\alpha = \frac{\mu_0 m H}{k_B T},$$

where $M_s = \phi M_0$ is the saturation magnetization of the liquid, which is determined by the volume concentration of the magnetic component ϕ and its spontaneous magnetization M_0. The constants μ_0 and k_B are the vacuum permeability and Boltzmann's constant respectively; T denotes the absolute temperature.

In contrast to paramagnetic salt solutions, the magnetic units interacting with the magnetic field are not single molecular magnetic moments but the particles, containing approximately 10^4 Bohr magnetons. This leads to a comparably strong increase of magnetization for weak magnetic fields, or in other words it causes an initial susceptibility of the liquids of the order of 1 compared to 10^{-4} for paramagnetic salt solutions. Since the force exerted by a magnetic field gradient on a magnetized system is proportional to its magnetization, ferrofluids experience strong magnetic forces even in weak magnetic fields due to their high initial susceptibility. This magnetic force enables an efficient control of the liquids' flow by moderate magnetic fields with strengths of less than 50 mT, as they can easily be produced by permanent magnets or small electromagnets as shown in figure 3.

An important aspect of the behaviour of ferrofluids is the type of relaxation of magnetization. Assuming a change in the applied magnetic fields' direction, the magnetization of the fluid has to change its direction too. This can principally take place in two different ways. On the one hand the magnetic moment of a particle can change its direction by a rotation of the moment inside the particle. On the other hand one can assume that the moment is spatially fixed inside the particle, resulting in the necessity of a rotation of the whole particle to enable an alignment with the magnetic field direction. Both processes are characterized by respective relaxation times. For the rotation of the moment inside the particle, a process called Néel relaxation, the Néelian relaxation time [3]

$$\tau_N = f_0^{-1} \exp\left(\frac{KV}{k_B T}\right) \tag{2}$$

applies. Here K is the anisotropy constant of the particles, V their magnetic volume and f_0 is the Larmour frequency of the magnetization vector in the anisotropy field of the particle, being

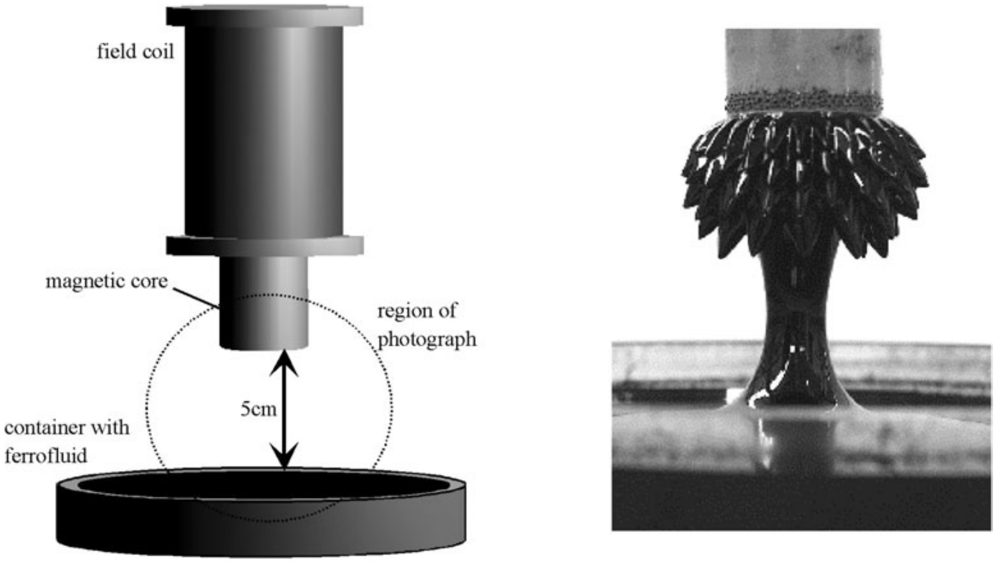

Figure 3. The magnetic force exerted by the electromagnet on the ferrofluid in the pool is strong enough to lift the fluid against the earth's gravitational field and to form the characteristic spike pattern.

of the order $f_0 \approx 10^9\ \mathrm{s}^{-1}$. The second process, called Brownian relaxation [4] is characterized by

$$\tau_B = \frac{3\tilde{V}\eta}{k_B T}, \tag{3}$$

where $\tilde{V}$ denotes the hydrodynamic volume of the particle, i.e. including the surfactant layer, $\tilde{V} = \pi(d+2s)^3/6$ (d is the diameter of the particle and s the thickness of the surfactant layer) and η is the dynamic viscosity of the liquid.

The actual relaxation of magnetization takes place by the process with the shorter relaxation time. As seen from (3) and (4), both times scale with the size of the particles. But while the Brownian time increases only linearly with the particles' volume, the Néelian time rises exponential with increasing particle size. Thus for small particles, the Néelian process will dominate while large particles will relax following Brownian relaxation. For magnetite the critical size for the transition from Néel to Brown relaxation is about 13 nm. Looking to the size distribution in figure 4 it is clear that only a small portion of particles in a normal ferrofluid will follow the Brownian process, while the majority of the magnetic component will relax by the Néelian process. This is an aspect of high importance for the interpretation of experimental results obtained with such suspensions, as will be shown later in the example of magnetic control of the viscous properties of ferrofluids.

2.2. *Applications of ferrofluids*

Before we discuss the importance of the above mentioned strong control of magnetic fluids by moderate magnetic fields for basic research in fluid mechanics, we will shortly highlight the aspect of engineering and medical applications of ferrofluids. The feature of magnetic control forced strong efforts in the design of applications using the influence of a magnetic field, in particular the possibility of positioning the fluid inside a technical device, leading to

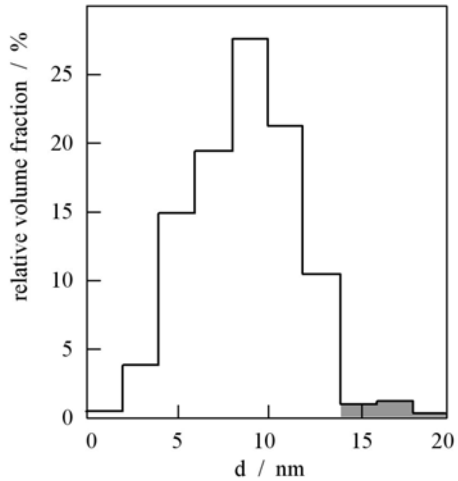

Figure 4. The size distribution of magnetic particles in a typical ferrofluid.

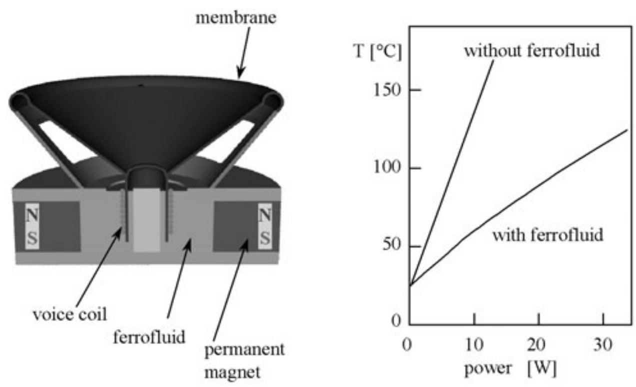

Figure 5. Schematic sketch of a ferrofluid cooled loudspeaker system (left) and a temperature versus power diagram for ferrofluid cooled and conventional speakers (after [3]).

several thousand application patents for ferrofluids [5]. Some of these reached commercial importance and are widely used in everyday life.

As an example the cooling of loudspeakers with magnetic fluids is shown in figure 5. This application is nowadays usual for high performance HiFi systems and represents the field of use of magnetic fluids with the largest commercial impact. A loudspeaker consists mainly of a membrane connected with the voice coil which is located in the magnetic field of a permanent magnet system. For high power loudspeakers or for smaller speakers, as in car HiFi systems, the ohmic heat produced in the voice coil leads to a critical limitation of the maximum power of the speaker. Placing a ferrofluid in the magnetic field around the voice coil increases thermal conductivity in this region and thus enables an increased heat transfer to the speakers' structure. This increases the cooling possibilities, and connected to increased cooling is increased maximum power of the system.

Beside this thermal application, ferrofluids are used in mechanical systems like bearings as frictionless sealing [5] or even in medicine for drug targeting [6] and for magnetic hyperthermia [7] in cancer treatment. Further information on ferrofluids can be found, e.g., in [8, 9].

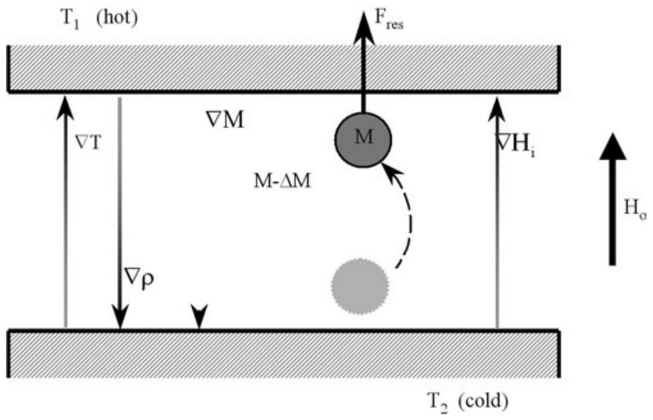

Figure 6. The origin of the magnetic driving force for thermomagnetic convection, explanations are given in the text.

3. Thermal transport in ferrofluids

The presence of a temperature difference in a fluid volume causes a density gradient which can lead to convective flow in a gravitational field. In a magnetic fluid the temperature gradient will additionally lead to a spatial difference in magnetization. In the further discussion we will now outline how this variation of magnetization can yield a magnetic force driving a convective flow independent from the action of gravitational forces. Let us consider a magnetic fluid enclosed by two horizontal flat walls (see figure 6) with infinite lateral extension. The walls are held at temperatures T_1 and T_2 and we assume that the temperature of the upper wall T_1 is higher than T_2. The resulting temperature gradient in the fluid causes a density gradient $\nabla\rho$ antiparallel to the temperature gradient. Even in a gravitational field this situation is obviously stable since the lighter fluid is at the top of the layer.

If a magnetic fluid is contained between the walls, a magnetic field gradient ∇H can give rise to a destabilizing magnetic force, which can drive a convective flow in the system, enhancing the heat transfer significantly. To see the origin of this force one can take a volume element of the fluid close to the cold lower wall and assume that it is displaced adiabatically in the direction of the temperature gradient, i.e. towards the hotter upper wall (figure 6). Due to the temperature dependence of magnetization this volume element has higher magnetization than its surroundings after the displacement. Thus, in the presence of the gradient of the magnetic field, it experiences a resulting magnetic force in the direction of the field gradient. This means that the force on the volume element is directed in the direction of the initial displacement. The same argument can be given for a volume element displaced from the upper towards the lower wall. In this case the displaced element has a magnetization lower than the surrounding and therefore experiences a force antiparallel to the field gradient.

As seen above, a displacement of a volume element ΔV of the fluid either parallel or antiparallel to the temperature gradient will always yield a resulting magnetic force in the direction of the initial displacement. Therefore this force has destabilizing character since it can amplify small disturbances of the fluid layer. This means that it is able to drive a convective flow controlled by the magnetic properties of the fluid and the strength of the applied field gradient.

The destabilizing force is counteracted by two stabilizing effects; the thermal conductivity and the viscous friction of the fluid. Both together provide the possibility that the temperature difference between the volume element and its surrounding equalizes faster than the element

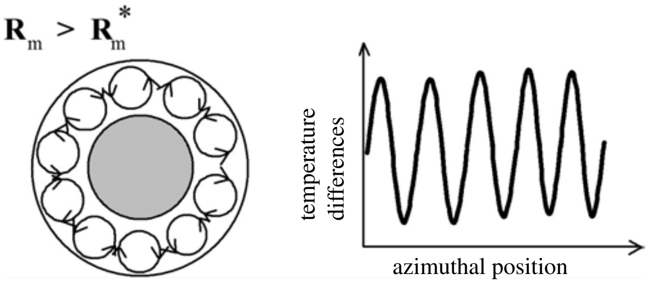

Figure 7. The detection of thermal flow of magnetic fluids can be maintained by means of the determination of the temperature distribution at a bounding wall. Further explanations are given in the text.

moves from one wall to the other. Equalizing of temperatures also means equalizing of magnetization of the volume element and the surrounding. Since the magnetization difference is the reason for the appearance of a destabilizing force, the equilibration of temperature leads to a reduction of the destabilizing effect and has thus stabilizing character. Therefore a convective flow, called thermomagnetic convection, will only appear if the destabilizing forces are strong enough to overcome the stabilizing effects. The actual situation of the system is characterized by a dimensionless number called the magnetic Rayleigh number [10, 11]

$$R_m = \frac{\mu_0 |\partial M/\partial T| \nabla H \Delta T h^3}{\kappa \eta} \tag{4}$$

where h denotes the thickness of the fluid layer, ΔT the temperature difference between the walls and κ and η the thermometric conductivity and the dynamic viscosity of the fluid respectively.

This phenomenon was first investigated under terrestrial conditions in flat fluid layers by Schwab [10, 12], showing a variety of different flow structures induced by an interaction of normal buoyancy driven convection and thermomagnetic flows. These experiments showed clearly that a detailed investigation of thermomagnetic convection would require an efficient suppression of the buoyancy driven flows. These are, in the majority of cases, much stronger than the magnetically driven ones and thus the magnetic effects just modify the thermal main flow.

The only way to suppress the buoyancy effects appropriately is by carrying out experiments under reduced gravity conditions, e.g. in drop tower or sounding rocket experiments. In a cylindrical geometry such experiments have the additional advantage that periodic boundary conditions, being preferable for the comparison with theoretical work, can be applied (see e.g. [13, 14]). In such geometry the inner cylinder bounding the ferrofluid is heated and the outer one is cooled while the whole system is under the influence of an azimuthal field with a radial field gradient driving the convective flow. The major problem in the investigation of thermomagnetic convection is the detection of the flow profile since magnetic fluids are optically opaque. A way out of this complication is the investigation of the temperature distribution inside the fluid at the outer boundary of the cylindrical fluid layer. As shown in figure 7 the convective flow will create a sinusoidal temperature distribution from which the flow profile can be reconstructed; positions where the fluid flows from the heated inner to the cooled outer cylinder will be characterized by a temperature maximum, while reverse flow will lead to a minimum in the temperature distribution. Using this method the temperature distribution in figure 8 can be related to a temperature profile consisting of counter-rotating vortices with a diameter equal to the thickness of the fluid layer. Measuring the amplitude of this

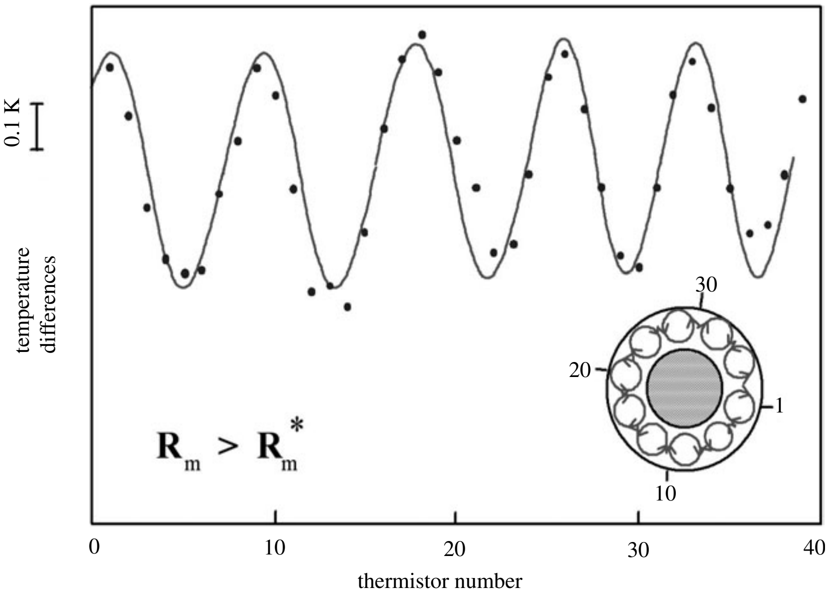

Figure 8. The measured temperature distribution of pure thermomagnetic convection [13] together with the corresponding flow pattern.

temperature distribution as a function of the magnetic Rayleigh number one can furthermore determine the critical magnetic Rayleigh number for the onset of the convective flow. In [13, 14] these investigations lead to $R_m^* = 1820 \pm 100$, being in excellent agreement with theoretical calculations performed independently by Polevikov and Fertman [15, 16].

4. Magnetoviscous effects

4.1. Rotational viscosity and the magnetoviscous effect

As an example of the influence of magnetic fields on the properties of magnetic fluids, the change in the rheological properties will now be discussed. Assuming a magnetic fluid in a shear flow, the particles inside the fluid will start to rotate in the flow with the axis of rotation parallel to the vorticity of the flow. Applying an external magnetic field to the system, and assuming that the field is collinear with the vorticity of the flow, the magnetic moment of the particle will align with the field and the particle will rotate around the field direction; no influence on the flow will appear (see figure 9(b)). In contrast, if the field is perpendicular to vorticity as shown in figure 9(a), the viscous friction will tilt the particle's magnetic moment against the field direction, if the moment is spatially fixed in the particle. The resulting finite angle between the magnetic moment and the field direction will give rise to a magnetic torque counteracting the viscous torque and will try to realign the moment with the field. The counteraction of the torques results in a hindrance of the free rotation of the particles in the flow, and thus in an increase in the fluid's viscosity. This phenomenon, called rotational viscosity, was first observed experimentally by McTague [17] and theoretically described by Shliomis [18].

Following [18] the increase in viscosity over the zero field value η_r can be written in the form

$$\eta_r = \frac{3}{2}\phi' \eta_0 \frac{\alpha - \tanh\alpha}{\alpha + \tanh\alpha} \langle \sin^2 \beta \rangle, \tag{5}$$

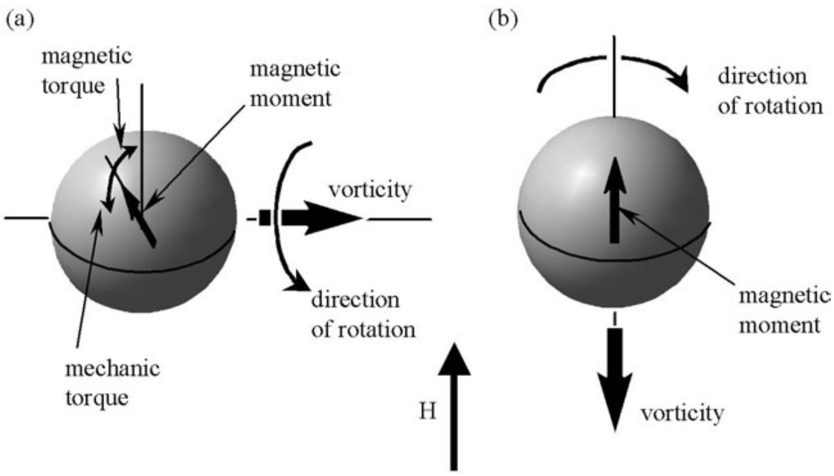

Figure 9. The origin of magnetic influences on the viscous properties of ferrofluids, explanations are given in the text.

where ϕ' denotes the volume fraction of the particles including the surfactant, β is the angle between vorticity of the flow and magnetic field direction and $\langle \cdots \rangle$ denotes the spatial average of the respective quantity. This description is based on two fundamental assumptions: first, that, as used above, the magnetic moment is spatially fixed in the particle, and second, that no interaction between the particles occurs.

The first assumption is valid for magnetic particles with a certain minimum size only as discussed in section 2. As mentioned there, for commercial ferrofluids containing magnetite particles with a mean diameter of about 10 nm only very weak magnetoviscous effects would be expected from this theory, since only a few large particles contained in the fluid would be able to contribute to magnetoviscosity. On the other hand the volume concentration of about 7 vol% implies that interaction between the particles may occur, forming agglomerates like chains or clusters, strongly affecting the fluids' viscous behaviour.

In experiments using a specialized rheometer for magnetic fluids [19], it was found that commercial ferrofluids indeed show a strong magnetoviscous effect, which can only be explained by the formation of magnetic structures, built up by numerous particles. In addition significant field dependent shear thinning was observed (see figure 10), leading to the assumption that the magnetic structures are broken by shear reducing their hydrodynamic size and therefore their influence on the flow [20, 21]. In this context it has to be observed that the magnetic dipole interaction energy of particles with a diameter below 13 nm is less than their thermal energy, and thus such particles cannot form permanent structures. Therefore, again, only the large particles contained in the fluid can contribute to the effects observed.

To prove that just a small fraction of large particles in a ferrofluid gives rise to the strong observed magnetoviscous effects we have investigated a series of fluids with different content of large particles [22]. All fluids originated from the same production process and were subjected to different purification processes to change their content of large particles without changing their other properties. Figure 11 shows the magnetoviscous effect for these fluids where the different fluids are indicated by F1–F5 with increasing content of large particles indicated by increasing ordinal number. Obviously a reduction in the large particle content leads to a dramatic decrease in the magnetoviscous effect, giving an additional indication that the magnetoviscous effect in commercial ferrofluids is dominated by the action of large particles.

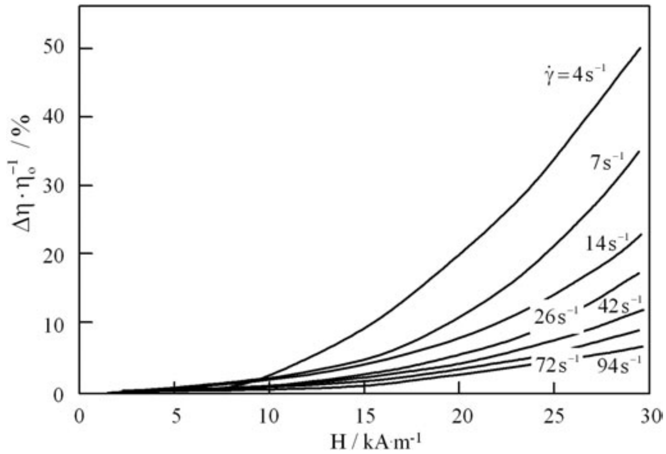

Figure 10. The magnetoviscous effect in a commercial magnetite based ferrofluid for various shear rates.

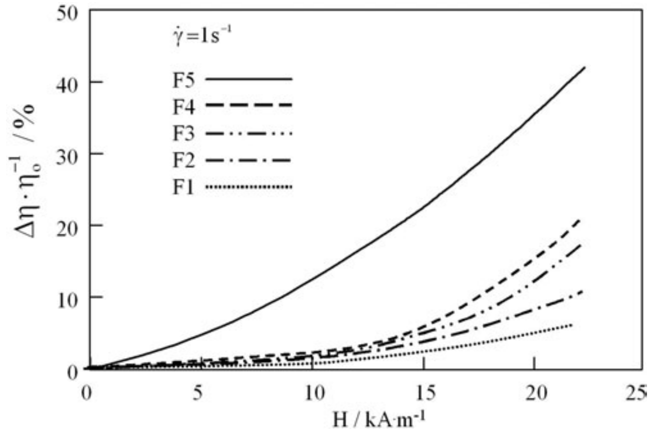

Figure 11. The magnetoviscous effect for five fluids differing in the content of large particles (increasing ordinal number corresponds to an increasing number of large particles).

4.2. A model for magnetoviscous effects in commercial ferrofluids

Based on the above experimental findings a model for the description of the magnetoviscous effect in commercial ferrofluids has been developed [20, 21, 23]. In this model it is assumed that the ferrofluid can be described in a first approximation as a bidisperse system containing a large fraction of small particles not contributing to the magnetoviscous effects and a small fraction of relatively large particles able to form agglomerates. This assumption is clearly validated by the fact that the extraction of large particles from the fluid leads to a significant reduction of the magnetoviscous effect. Furthermore particles with diameters below 13 nm likewise do not contribute to rotational viscosity since their magnetic moment is not fixed inside the particles, nor is their magnetic dipole interaction strong enough to allow chain formation of such particles. Thus all these particles can be assumed to be part of the small fraction having a certain mean diameter. On the other hand particles with larger diameter have sufficient dipole interaction to form chains and are thus part of the large fraction with a certain larger mean diameter assumed

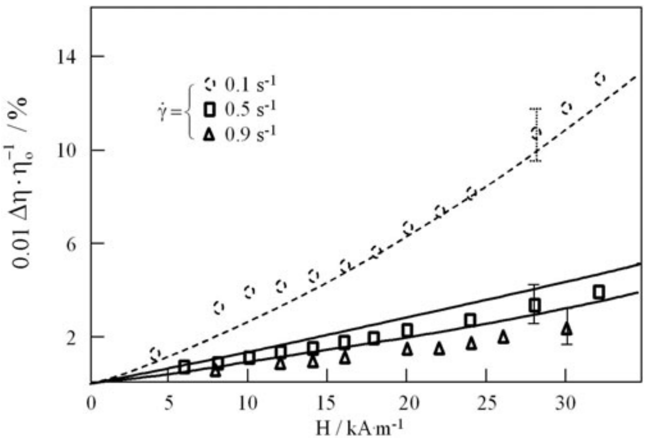

Figure 12. The magnetoviscous effect at low shear rates together with the results of the theoretical model of a bidisperse system.

here. The agglomerates are assumed to be straight chains and interaction is only taken into account between neighbouring particles in the chains, while interaction of chains, or of small particles with the chains, is neglected. The latter assumption can easily be proved to be valid by calculating again the magnetic interaction energies which differ approximately by an order of magnitude. Under these assumptions the free energy of the system can be written as the free energy of an ideal gas of chains with a certain chain length distribution. From a minimization of the free energy one obtains this chain length distribution which can be used to calculate the stress tensor of the fluid and therefore its field dependent viscosity. The calculations can only be performed for zero shear rate. Shear can be taken into account by cutting all summations over the chain length distribution at a maximum chain length obtained from an equilibrium of the magnetic dipole interaction forces inside the chain and viscous forces trying to rupture the structures [20]. Figure 12 shows the measured magnetoviscous effect for the lowest shear rate available with our rheometer, together with a fit of the theory to the experimental data. The free fit parameters are the mean size of the large particles and their volume concentration. As a result one obtains a mean particle size of about 16 nm and a volume concentration of about 1%, which corresponds well with the size distribution obtained from magnetic measurement shown in figure 4. The lines for the data with higher shear rates were obtained without an additional fit by the method described above.

5. Conclusion

It has been discussed that suspensions of magnetic nanoparticles called ferrofluids exhibit magnetic properties enabling magnetic control of their properties and flows. It has been shown as an example that the viscosity of the fluids can strongly be influenced by magnetic fields. Taking into account the interaction between the magnetic particles, a quantitative description of the magnetoviscous effects is obtained, showing that a small fraction of large particles in the fluid forms chains dominating the rheological properties of the fluids in the presence of magnetic fields. In addition, the importance of these large particles has been proved by experiments using fluids with different volume concentrations of large particles. As an example of a flow driven and controlled by magnetic forces, the phenomenon of thermomagnetic convection has been discussed, and it has been outlined that a thermal flow can be driven in a ferrofluid purely by the action of magnetic forces.

In general one can state that the future development of the application of magnetic fluids will strongly depend on the understanding of processes like those described above. The field of applications, which has been more or less restricted to the positioning of the fluids by means of magnetic fields, could be strongly extended if magnetic flow and property control could be technically used.

References

[1] Papell S S 1964 Low viscosity magnetic fluid obtained by the colloidal suspension of magnetic particles. *US Patent Specification* 3 215 572
[2] Kneller E 1962 *Ferromagnetisms* (Berlin: Springer)
[3] Néel L 1949 *C. R. Acad. Sci., Paris* **228** 664
[4] Brown W F 1963 *Phys. Rev.* **130** 1677
[5] Berkovsky B M and Bashtovoy V 1996 *Magnetic Fluids and Applications Handbook* (New York: Begell House Inc.)
[6] Alexiou Ch, Arnold W, Hulin P, Klein R, Schmidt A, Bergemann Ch and Parak F G 2001 *Magnetohydrodynamics* **37** 3
[7] Hergt R, Andrä W, d'Ambly C G, Hilger I, Kaiser W A, Richter U and Schmidt H G 1998 *IEEE Trans. Magn.* **34** 3745
[8] Rosensweig R E 1985 *Ferrohydrodynamics* (Cambridge: Cambridge University Press)
[9] Blums E, Cebers A and Maiorov M M 1997 *Magnetic Fluids* (Berlin: Walter de Gruyter)
[10] Schwab L, Hildebrandt U and Stierstadt K 1983 *J. Magn. Magn. Mater.* **39** 113
[11] Finlayson B A 1970 *J. Fluid Mech.* **40** 753
[12] Schwab L 1987 *J. Magn. Magn. Mater.* **65** 315–6
[13] Odenbach S 1993 *Microgravity Sci. Technol.* **4** 161
[14] Odenbach S 1995 *J. Magn. Magn. Mater.* **149**
[15] Polevikov V and Fertman V E 1977 *Magnetohydrodynamics* **1** 15
[16] Berkovsky B M and Polevikov V 1988 *Numerical Experiments in Convection* (Minsk: Minsk Universitetskoy) (in Russian)
[17] McTague J P 1969 *J. Chem. Phys.* **51** 133
[18] Shliomis M I 1972 *Sov. Phys.–JETP* **34** 1291
[19] Odenbach S, Rylewicz T and Heyen M 1999 *J. Magn. Magn. Mater.* **201** 155
[20] Odenbach S 2002 *Magnetoviscous Effects in Ferrofluids (Springer LNP)* (Heidelberg: Springer)
[21] Odenbach S and Störk H J 1998 *J. Magn. Magn. Mater.* **183** 188
[22] Odenbach S and Raj K 2000 *Magnetohydrodynamics* **36** 379
[23] Zubarev A Yu 2002 *Ferrofluids—Magnetically Controllable Fluids and their Applications (Springer LNP 594)* ed S Odenbach (Heidelberg: Springer)