3rd German Ferrofluid Workshop

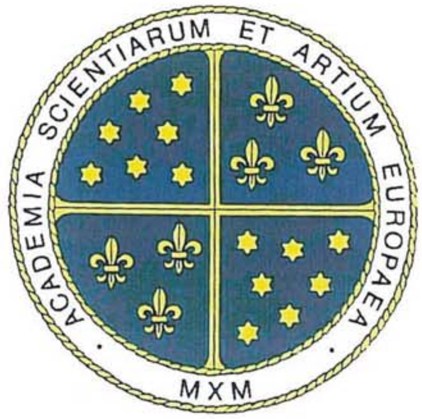
Benediktbeuern 2000

Oct. 31 – Nov. 2

Book of Abstracts

Workshop organized by: MPI for Polymer Research, Mainz ZARM, University of Bremen

The 3rd German Ferrofluid Workshop is organized under the auspices and with support of the Europäische Akademie der Wissenschaften und Künste



Ferrofluid Workshop 2000

The Ferrofluid Workshop 2000 is the third event in a periodical sequence of scientific meetings with the aim to promote the exchange among the German research groups working on the subject of magnetic liquids. For the first time this workshop also serves as a forum for the colloquium of the new DFG-priority program: *Colloidal magnetic fluids: Basics, development, and application of new ferrofluids.* This interdisciplinary program joins researchers from chemistry, physics and engineering sciences. Ferrofluids are an important sub field of nano-science technology with a broad potential of applications. This is reflected by the growing industrial interest in the ferrofluid workshop.

Besides the classical technical applications (liquid seals, dampers or lubricants) a new spectrum of examples of biological and medical use arises, such as cell sorting, drug targeting, cancer hyperthermia, or the clarification of immuno-chemical reactions. The preparation of ferrofluids for biological purposes necessitates control over the functionality of the particle coating. Accordingly, a considerable amount of workshop contributions is dedicated to new preparation and characterization techniques, the latter being sensitive to the hydrodynamic coating.

With regard to technical applications the interest is focused on rheological bulk properties, the dynamics of free liquid air interfaces, and the ability to manipulate these properties by means of external magnetic fields. These subjects are the domain of fundamental physical research, which is broadly represented by contributions of several experimental and theoretical research groups.

It would be most welcome if the discussions during this workshop would initiate an interdisciplinary cooperation among the involved researchers.

Der Ferrofluid-Workshop 2000 ist das dritte Meeting in dieser Reihe, mit dem Ziel, den wissenschaftlichen Austausch in Deutschland auf dem Forschungsgebiet der magnetischen Flüssigkeiten zu intensivieren. Der diesjährige Ferrofluid-Workshop dient erstmalig auch als Forum für das Kolloquium des von der DFG neu eingerichteten Forschungsschwerpunktes: *Kolloidale magnetische Flüssigkeiten, Grundlagen, Entwicklung und Anwendung neuartiger Ferrofluide*. Diese interdisziplinäre Einrichtung vereinigt Wissenschaftler aus den Bereichen Chemie, Physik und den Ingenieurwissenschaften auf einem Teilgebiet der Nanotechnologie mit hohem Anwendungspotential. Dies zeigt sich nicht zuletzt durch das zunehmende industrielle Interesse am Ferrofluid-Workshop.

Neben den klassischen technischen Anwendungen als flüssige Dichtungen, Dämpfer oder Schmiermittel hat sich in letzter Zeit das Feld der biologischen und medizinischen Anwendung etabliert. Dazu gehören z.B. Zellsortierung, Krebstherapie oder die Aufklärung von immunochemischen Reaktionen. Die Herstellung von biologisch verträglichen Ferrofluiden erfordert gezielte Kontrolle über die Funktionalität der Partikelumhüllung. Dementsprechend ist ein bedeutender Teil der diesjährigen Workshopbeiträge der Probenpräparation gewidmet. Darüber hinaus werden verstärkt solche Charakterisierungsmethoden diskutiert, die den Zugang zur sterischen Partikelhülle erlauben.

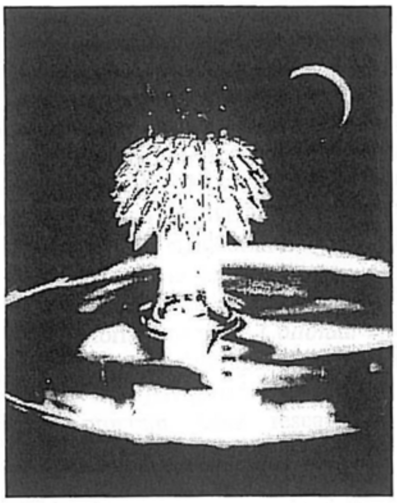
Bei den technisch orientierten Anwendungen konzentriert sich das Interesse v.a. auf rheologische Eigenschaften, die Dynamik freier Oberflächen und die Möglichkeit, diese Eigenschaften gezielt durch äußere Magnetfelder zu beeinflussen. An diesem Punkt setzt die physikalische Grundlagenwissenschaft an, die im Rahmen dieses Workshops breiten Raum einnimmt.

An ihr sind Experimentatoren und Theoretiker gleichermaßen beteiligt.

Wenn es gelänge, durch die Gespräche im Rahmen dieser Veranstaltung fachübergreifende Kooperationen zwischen den beteiligten Arbeitsgruppen zu initiieren, wäre das Ziel dieses Workshops erreicht.

The workshop is organized by: H.W. Müller, MPI for Polymer Research, Mainz
S. Odenbach, ZARM, University of Bremen

Financial support of the Deutsche Forschungsgemeinschaft (DFG) within the scope of the priority program SPP1104: *Kolloidale magnetische Flüssigkeiten, Grundlagen, Entwicklung und Anwendung neuartiger Ferrofluide* is gratefully acknowledged.



3rd German Ferrofluid workshop

Benediktbeuern

October 31 – November 2, 2000

Contents

New Problems of Heat and Mass Transfer in Magnetic Colloids

E. Blums

Institute of Physics, University of Latvia, Salaspils-1, LV-2169, Latvia

Magnetic fluids are new "intelligent" materials for various applications. In some technical devices the ferrofluid is exposed by strong temperature gradients which can influence its colloidal stability. The present paper deals with new problems of combined heat and mass transfer in ferrofluids under the effect of external magnetic field.

The hydrodynamic theory of mass transfer in ferrocolloids is based on calculations of the particle phoretic mobility. The magnetophoretic velocity of particles in colloids of uniform magnetization usually is calculated from the balance between the magnetic and viscous forces. If temperature and/or particle concentration gradients are present, it is necessary to reconsider the problem by taking into account for a non-potentiality of the magnetic driving force around particles. In the presence of a field **B** arbitrarily oriented to the ∇T or, more general, to the gradient of magnetic permeability $\nabla\mu$, the particles are transferred along $\nabla\mu$ as well as along **B** [1]. In two cases, $\nabla\mu /\!/ \mathbf{B}$ and $\nabla\mu \perp \mathbf{B}$, particles are moving along $\nabla\mu$ only. The $\nabla\mu$ depends on both the temperature and the particle concentration gradients. Therefore, the mass flux can be written in a classical form considering the magnetic summands as an additional part of the translation diffusion coefficient D and of the thermodiffusion ratio α_T [1]. Both these coefficients now depend on the orientation of magnetic field. If $\mathbf{B} /\!/ \nabla\mu$, the field causes an increase in D and a decrease in α_T (if the Soret coefficient in a zero field is positive), and opposite, if $\mathbf{B} \perp \nabla\mu$, a reduction of D and an increase in α_T takes place. The dependence $D=D(\mathbf{B})$ [1] calculated in one particle approximation agree well with theory [2] based on the Batchelor model accounting for magnetic interactions, as well with experiments [3] on particle optical grating and with the corresponding authors thermodynamic theory.

Conventional experimental techniques (for example, optical interferometry) can not be employed to examine the thermodiffusive separation in ferrocolloids because they are not transparent to the visible light. It is necessary to use various indirect methods, for example, the separation measurements in thermodiffusion column [4] or the optical measurements of particle grating in thin layers under the effect of a light absorption [5].

The thermodiffusion column consists of a long vertical flat channel and two separation chambers. Both, the particle transfer across the channel by thermodiffusion and the thermal convection of fluid in vertical direction cause a development of concentration difference in the upper and lower separation chambers. The Soret coefficient S_T can be evaluated from the unsteady separation curves. For colloids the column theory must be modified by account for the so-called "forgotten effect" (influence of the solutal buoyancy force on the thermal convection velocity) [6].

The Soret coefficient can be evaluated also from measurements of the optical grating in thin ferrofluid layers. Usually, in forced Rayleigh scattering experiments the one-dimensional grating is induced by an interference of two coherent optical beams [5]. To investigate the anisotropy of magnetic Soret effect, more preferable seem to be experiments on two-dimensional grating in optical image of a square-shaped grid focused on the ferrofluid layer [6].

First measurements indicate unusually high thermophoretic mobility of magnetic particles. From dynamic separation curves measured in the column experiments [4, 9] as well as from diffraction signals of the optical grating [5, 7, 8] it is found that in ferrofluids the thermal diffusion ratio $\alpha_T = S_T T$ exceeds 20. Surfacted nanoparticles in hydrocarbons are mowing toward the decreasing temperatures. Such direction of thermophoresis agrees with the Derjuagin's theory accounting for a slip velocity. According to the recent theoretic considerations the Soret coefficient of surfacted particles is proportional to the Gibbs absorption and the length of surfactant molecules as well as to the size of particles [10]. The measured values S_T qualitatively well agree with this theory. In some ionic ferocolloids particles are transferred toward increasing temperatures [7, 8]. Theory [11] trays to explain the reason of that. It is shown that the direction of thermodiffusive transfer of charged particles depends on electrochemical parameters of the colloid. If the Debye layer is very thin, independently of the surface potential the particles are transferred in a direction opposite to the temperature gradient, $S_T>0$. Increasing the thickness of double layer, at high values of ζ-potential it is possible to observe a reverse direction of particle transfer. The parameters of ionic ferrofluid used in the experiments [7] correspond to such requirements.

Separation measurements in thermodiffusion column confirm both the dependence of thermophoretic mobility of particles on magnetic flux density **B** and the theoretically predicted anisotropy of the magnetic Soret effect [12]. Nevertheless, the observed effects are significantly stronger than the theoretically evaluated ones. Recently, such disagreement between theory and measurements is observed also in optical grating experiments [13]. Obviously, the hydrodynamic theory [1] must be specified taking into account for slip characteristics and for a temperature jump on the particle solid-liquid interface. Besides, some other factors, for example, the polydispersity of colloidal particles, the formation of aggregates etc. also should be taken into account.

In recent thermodiffusion column experiments almost complete separation of the solid phase from the carrier liquid is achieved [14]. Thus, the Soret effect should be taken into account in the ferrofluid applications. Strong thermal diffusion in magnetic fluids evokes a great interest to some principally new research problems (free convection in thermally stratified colloids, magnetic Soret effect driven convection, double-diffusive convective instabilities etc. [15- 17]).

References

1. Blums, E., *JMMM* **149** (1995), 111-115.
2. Morozov, K.I., *JMMM* **122** (1993), 98-101.
3. Bacri, J.C. et all, *Phys. Rev.* E **52** (1995), 3936-3942.
4. Mezulis, A. et all, *Latvian J. Phys. and Techn. Sci.* (1995), 5, 37-50.
5. Langlet, L., Ph.D. Thesis, Univ. Denis Diderot Paris 7, (1996).
6. Blums, E., Odenbach, S., *Int. J. Heat and Mass Transfer* **43**, (2000), 9, 1637-1649.
7. Lenglet, J et all, Phys. *Rev. E*, (in press).
8. Mezulis, A., Ph.D. thesis, Univ. Denis Diderot Paris 7, (1999).
9. Blums, E. et all, *JMMM* **169** (1997), 220-228.
10. Morozov, K.I, *Proc. 3rd ASME/JSME Joint Fluids Engng. Conf.*, San Francisco, (1999).
11. Morozov, K.I., *JETF* **88** (1999), 944-946.
12. Blums, E. et all, *Phys. Fluids* **10** (1998), 2155-2163
13. Demouchy, G. et all, *Proc. 4th PAMIR Conf.*, Giens, (2000), (in press).
14. Völker, T., Blums, E., Odenbach, S., *Proc. 4th Int. Meeting on Thermodiffusion*, Bayreuth, (2000) (in press).
15. Brancher, J.P., Souhar, M., Shliomis, M.I., *Proc. 8th Int. Conf. Magnetic Fluids*, Timisoara, (1998), 302-303.
16. Shliomis, M.I., *Proc. 4th Int. Meeting on Thermodiffusion*, Bayreuth, (2000) (in press).
17. Kronkalns, G. et all, *Progress in Engineering Heat Transfer,* Eds: B. Grochal, J.Mikielewicz, B. Sunden, IFFM Publishers, Gdansk, (1999), 367-376.

Abstracts

1. Preparation and Characterization

Anwendungsmöglichkeiten der Miniemulsion: Verkapselung von anorganischen Partikeln

D. Hoffmann, F. Tiarks, K. Landfester, M. Antonietti

Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Forschungscampus Golm, Am Mühlenberg, 14424 Golm

Miniemulsionen werden verstanden als wäßrige Dispersionen relativ stabiler Öltröpfchen, deren Größe zwischen 30 und 500 nm liegen. Hergestellt werden sie durch Scherung eines Systems bestehend aus Öl, Wasser, Tensid und Hydrophob. Die Polymerisation von Miniemulsionen erweitert die Möglichkeiten der Emulsionspolymerisation und verspricht dabei unter anderem Vorteile in bezug auf die Verkapselung hydrophoben Materials oder die Stabilität der gebildeten Latices.

Um z.B. Pigmente in einen Latex mit Hilfe der Miniemulsionspolymerisation zu verkapseln, ist es notwendig, die ausreichende Menge eines geeigneten Tensides zu finden, um Latexpartikel zu erhalten, deren Größe und Ladung Verkapselung ermöglicht. Um Miniemulsionen zu präparieren, müssen zwei Schritte kontrolliert werden: In einem ersten Schritt muß das hydrophobe oder hydrophobisierte Pigment, welches eingebaut werden soll, in der Monomerphase dispergiert werden, anschließend wird das Monomer mit dem Pigment in der Wasserphase miniemulgiert (siehe Abbildung 1). Bei der Verkapselung z.B. von Kohle ist die Art des Hydrophobs entscheidend, um die vollständige Verkapselung von nicht-agglomerierten Kohlepartikeln zu gewährleisten. Gleichzeitig dient das Hydrophob zur Stabilisierung, indem es die Ostwaldreifung der Tröpfchen unterdrückt. Der Einfluß unterschiedlicher Parameter auf die Verkapselung wurde mit Methoden der Transmissionselektronen-

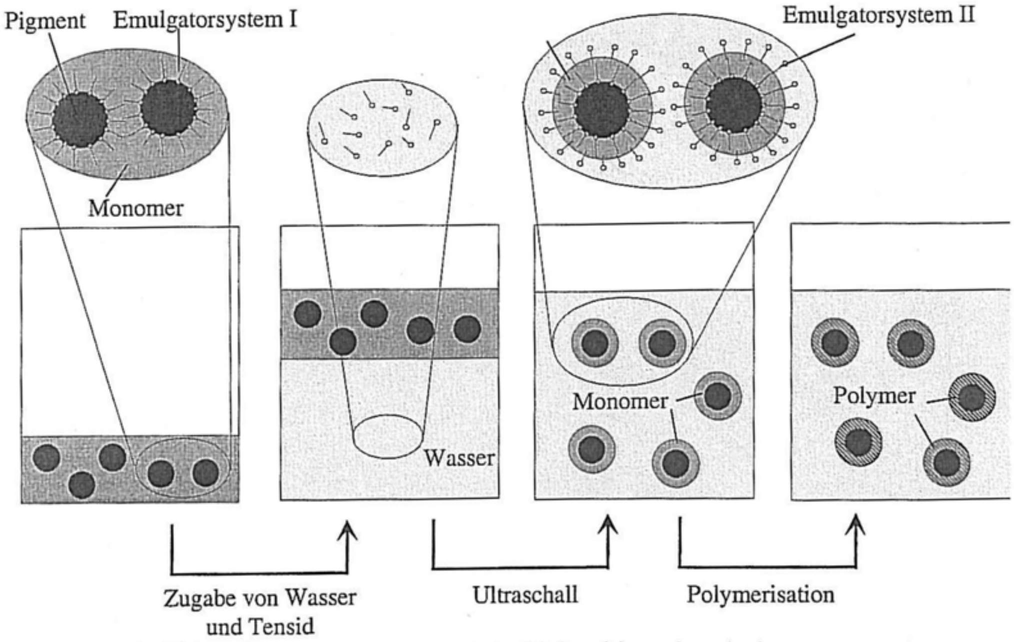


Abb. 1: Prinzip der Einkapselung von Pigmenten mittels der Miniemulsionspolymerisation.

Mikroskopie und Ultrazentrifugation charakterisiert [2].

In laufenden Arbeiten werden nun magnetische Materialien, wie z.B. Magnetit- oder Cobaltpartikel, effektiv in Polymerteilchen eingekapselt. Gleichzeitig werden die physikochemische Charakterisierung und die mechanistische Beschreibung der mit dem Miniemulsionsverfahren erhaltenen superparamagnetischer Nanopartikel in Polymerlatices durchgeführt. Für spätere biomedizinische Anwendungen sind folgende Punkte von Bedeutung:

- einstellbare Gesamtpartikelgröße im Bereich 50 – 250 nm bzw. im Bereich 1µm – 10 µm;
- enge Partikelgrößenverteilung der Gesamtpartikel;
- möglichst hoher Gehalt an magnetischer Komponente, angestrebt sind 60 – 80 Gew.-%;
- möglichst hohe Homogenität der Magnetisierung der Gesamtpartikel;
- vollständige Bedeckung der magnetischen Komponente durch das Polymer zur Vermeidung von Korrosion und anderen chemischen Reaktionen;
- möglichst variable chemische Struktur der Polymeroberfläche zur Einstellung von „Biokompatibilität", bzw. Vermeidung unspezifischer Erkennungsprozesse.

Literatur

[1] N. Bechthold, F. Tiarks, M. Willert, K. Landfester, M. Antonietti "Miniemulsion Polymerization: Applications and New Materials", *Macromol. Symp.*, 2000, *151*, 549-555.

[2] F. Tiarks, K. Landfester, M. Antonietti, "Encapsulation of carbon black by miniemulsion polymerization", eingereicht.

Structure Formation in Iron Nanocarpets and Nanobrushes

Helmut Wolf[1]

[1] *Universität des Saarlandes, FB 7.3 Technische Physik , Prof. Dr. R. Birringer 66123 Saarbrücken*

Chains of nanocrystalline iron

Collecting magnetic nanoparticles from a continuous aerosol flow in a homogeneous magnetic field, the particles arrange to chain-like threads on the substrate, growing in the direction of the applied magnetic field. During chain growth one observes a hierarchy of unexpected self organization phenomena that originate from structural instabilities. The substrate is first covered with a homogeneous carpet of nanoparticle chains with a diameter of $\sim$ 10nm (fig.1a).

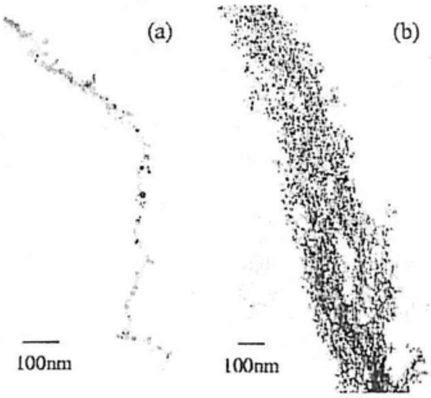


Figure 1: (a) Isolated thread of nanocrystalline iron particles; (b) Bundle of chain-like threads; (TEM-pictures)

Creation of bundles

At a chain length of about 100nm, the chains are rearranged to bundles, each consisting of a polymer-like network of 20 – 200 nanoparticle chains (fig.1b). These iron bundles whose diameter constantly ranges between 200 and 500nm repeat the carpet formation at a larger length scale.

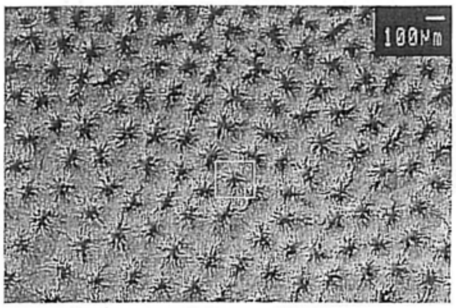


Figure 2: Triangular lattice of flower-like pores in a homogeneous carpet of bundles (REM, magnetic field perpendicular to substrate plain, topview)

Patterns in Nanocarpets

At a length of $\sim 40\mu$m this "supercarpet" develops new types of regularly evolving density patterns with a typical structure size of 100μm. The formation of triangular lattices of flower-like pores in the homogeneous supercarpet is observed as well as more complicated patterns (fig.2-4). The structure creation strongly resembles the Rosenzweig patterns in ferrofluids [1].

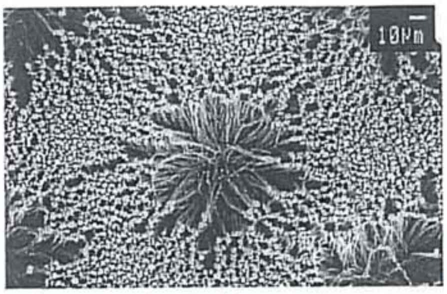


Figure 3: A pore represents a region of lowered magnetic field density because the iron bundles draw the magnetic field lines with them (REM, detail of fig.2)

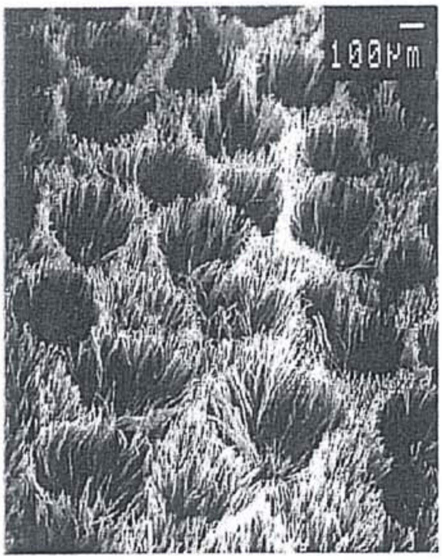


Figure 4: The carpet-patterns become more complicated as the length of the bundles grows (REM, sideview)

Nanobrushes

Collecting the iron particles in a magnetic gradient field, this type of spontaneous structure formation is not observed. In this way it is possible to grow homogeneous iron nanobrushes with a bundle length of 2mm and more.

Expected properties

Due to the unique material structure new magnetic and transport properties are expected, such as an anisotropic susceptibility and electric conductivity. A strong magnetoelastic effect and stress dependency of electric properties should be observed.

References

[1] R. E. Rosenzweig, Ferrohydrodynamics, (Cambridge University Press, New York, 1985).

Physical Methods for Physical/Chemical Characterization of Magnetic Core/Shell-Nanoparticles and Magnetic Fluids

N. Buske[1] and P.C. Morais[2]

[1]Mediport Kardiotechnik GmbH, Wiesenweg 10, D 122437 Berlin, Germany,
[2] Universidade de Brasília, Instituto de Física, Física Aplicada, 70919-970 Brasília-DF, Brasil

The growing interest for basic research as well as the demand for applications, such as in machinery as seal and damping tools, and in biomedicine for cancer diagnosis and therapy, have contributed enormously to push up the development of new magnetic fluids (MF's). Magnetic [1,2] and optical properties [3,4], particle-core [5] and hydrodynamic size distribution [6] core/shell composition [7], and colloidal stability [8], are physical/chemical parameters that need to be taken into account in tailoring new MF samples.

Mediport Kardiotechnik has prepared aqueous and non-aqueous MF's. The particles consist of magnetite/maghemite cores, synthesized in water by nucleation/crystal growth processes. Aliquots of the same stored MF were used for preparation of different core/shell-based MF's. The non-magnetic shells include ionic shell (OH_2^+ ions for instance), monolayer of oleoylsarcosine, dextran derivatives, oleic acid or dodecanoic acid, and bilayer comprising an inner layer of dodecanoic acid, and an outer layer of an ethoxylated C_{12} alcohol with 9mol/mol ethoxy groups.

In cooperation with the University of Brasilia (Brazil) the synthesized MF's were characterized using different physical methods, such as magnetic resonance (MR) [1], vibrating sample magnetometry (VSM) [2], Raman spectroscopy (RS) [3], static magnetic birefringence (SMB) [4], transmission electron microscopy (TEM) and atomic force microscopy (AFM) [5], photon correlation spectroscopy (PCS) [6], Mössbauer spectroscopy (MS) [7], and viscometry [9].

The nanoparticles themselves have been characterized by TEM [5], AFM [5], and MS [7]. Concentrated MF's have been characterized by MR [1], VSM [2], TEM and AFM, and viscometry [9]. However, for the purpose of the optical characterization of MF's the samples need to be diluted.
Conclusions obtained from the characterization of the nanoparticles themselves or from highly diluted MF's can not be fully transferred to usual MF samples containing higher particle concentration.

In this paper, an overview of the advantages and disadvantages of the physical characterization methods will be given, and the first results presented. Especial emphasis will be given in the methodology used to investigate the biodistribution of dextran-coated MF in mice using MR [10].

References

[1/] L.M. Lacava, R.B. Azevedo, Z.G.M. Lacava, N. Buske, A.L. Tronconi, and P.C. Morais, **Nanoparticle sizing: A comparative study using atomic force microscopy, transmission electron microscopy, and ferromagnetic resonance**, 3rd International Conference on the Scientific and Clinical Applications of Magnetic Carriers, May 3-6, 2000 – Rostock, Germany; A.L. Tronconi, P.C. Morais, K. Skeff Neto, F. Pelegrini, and N. Buske, **Magnetic resonance study of single and double layered magnetite-based magnetic fluids**, 4th

Liquid Matter Conference, July 3-7, 1999 – Granada, Spain.

[2] P. Killat, H. Heinze, and N. Buske, **Novel Equipment for determination of magnetization curves of magnetic fluids,** 2nd German Workshop on Magnetic Fluids, 1999 – Magdeburg – Germany; N. Buske and C. Gansau, **Size and Magnetic Properties of Magnetite and Cobalt Nanoparticles**, 9th European Congress on Biotechnology, July 11-15, 1999 – Brussels, Belgium.

[3] P.C. Morais, S.W. da Silva, M.A.G. Soler, and N. Buske, **Raman spectroscopy in oleoylsarcosine-coated magnetic fluids: a surface grafting investigation**, Intermag 2000, April 9-13, 2000 – Toronto, Canada; S.W. da Silva, P.C. Morais, M.A.G. Soler, N. Buske, and C. Gansau, International Conference on Magnetism, August 6-11, 2000 – Recife, Brazil; P.C. Morais, S.W. da Silva, M.A.G. Soler, and N. Buske, **Raman investigation of uncoated and coated magnetic fluids**, J. Phys. Chem. A **104**, 2894 (2000).

[4] M.F. da Silva, J.A. Goulart, K. Skeff Neto, P.C. Morais, and N. Buske, **Birefringence characterization of magnetite-based magnetic fluids in the low-field regime**, 4th Liquid Matter Conference, July 3-7, 1999 – Granada, Spain.

[5] P.C. Morais, B.M. Lacava, A.F. Bakuzis, L.M. Lacava, L.P. Silva, R.B. Azevedo, Z.G.M. Lacava, N. Buske, M.A. Novak, and W.C. Nunes, **Atomic force microscopy and magnetization investigation of water-based magnetic fluids**, International Conference on Magnetism, August 6-11, 2000 – Recife, Brazil.

[6] N. Buske, T. Rheinlaender, and C. Gansau, **Separation of Magnetizable Core/Shell Nanoparticles in gradH,** 3rd International Conference on the Scientific and Clinical Applications of Magnetic Carriers, May 3-6, 2000 – Rostock, Germany.

[7] P.C. Morais, E.C.D. Lima, A.M.L. Silva, A.F. Bakuzis, and K. Skeff Neto, **Synthesis and characterization of cobalt ferrite-based ionic ferrofluids: A nanoparticle size control approach**, 3rd International Conference on the Scientific and Clinical Applications of Magnetic Carriers, May 3-6, 2000 – Rostock, Germany.

[8] Fanyao Qu and P.C. Morais, **Energy levels in metal oxide semiconductor quantum dots in water-based colloids**, J. Chem. Phys. **111**, 8588 (1999); Fanyao Qu and P.C. Morais, **Oxide semiconductor nanoparticle in aqueous medium: A surface charge density investigation, J. Phys. Chem. B 104, 5232 (2000).**

[9] N. Buske P. Killat and J. Müller, **Ferrofluids of high Saturation Magnetization and low Viscosity: Calculations and Experiments,** ICMF 8, Timisoara (1998), Romania

[10] M.F. Da Silva, P.C. Morais, L.M. Lacava, K. Skeff Neto, O. Silva, F. Pelegrini, R.B. Azevedo, C. Gansau, N. Buske, and Z.G.M. Lacava, **Use of the ferromagnetic resonance to investigate the time decay of magnetic fluids endovenously administrated in mice**, 3rd International Conference on the Scientific and Clinical Applications of Magnetic Carriers, May 3-6, 2000 – Rostock, Germany; Z.G.M. Lacava, L.M. Lacava, P.C. Morais, M.F. Da Silva, K. Skeff Neto, O. Silva, F. Pelegrini, R.B. Azevedo, C. Gansau, and N. Buske, **Distribution of a dextran-coated magnetic fluid in mice tissues investigated by ferromagnetic resonance measurements**, 3rd International Conference on the Scientific and Clinical Applications of Magnetic Carriers, May 3-6, 2000 – Rostock, Germany.

Untersuchung von Kern und Hülle in Ferrofluiden durch Neutronen-Kleinwinkelstreuung.
I. Anwendung polarisierter Neutronen in Cobalt-Ferrofluiden

A. Wiedenmann, A. Hoell

Hahn-Meitner Institut, Bereich Strukturforschung , Glienickerstrasse 100, 14109 Berlin
e-mail: Wiedenmann@hmi.de

Die Nutzung polarisierter Neutronen bietet die umfassendste Möglichkeit einer Strukturuntersuchung von Kern und Hülle als auch der magnetischen Nanostruktur durch eine zusätzliche Kontrastvariation (SANSPOL). Im Falle polarisierter Neutronen tritt neben den beiden Beiträgen der Amplitudenquadrate $F_N^2(Q)$ für reine nucleare Streuung und $F_M^2(Q)$ für reine magnetischen Streuung ein Interferenzterm $F_N(Q)\ F_M(Q)$ auf, der je nach Vorzeichen des Neutronenspins (+ oder -) addiert oder subtrahiert wird:

$$I^+(Q,\alpha) = F_N^2 + \{F_M^2 - 2\,P\,F_N\,F_M\}\,\sin^2\alpha$$
$$I^-(Q,\alpha) = F_N^2 + \{F_M^2 + 2\,P\varepsilon\,F_N F_M\}\,\sin^2\alpha.$$

α stellt den Winkel zwischen dem Streuvektor Q und dem Magnetfeldvektor H dar. Die Streusignale für beide Polarisationsrichtungen I^+ und I^- sind ausgeprägt anisotop (Abb. 1) Der Interferenzterm, der aus den Differenzen der beiden Spektren $I^+(Q,\alpha)$ und $I^-(Q,\alpha)$ gewonnen wird, ist linear in den Amplituden und erlaubt damit prinzipiell die Ermittlung des Vorzeichens von magnetischem und nuklearem Streukontrast. Daher können mit SANSPOL sehr präzise schwache magnetische Kontraste neben starken nuclearen Streukontrasten (oder *vice versa*) nachgewiesen werden .

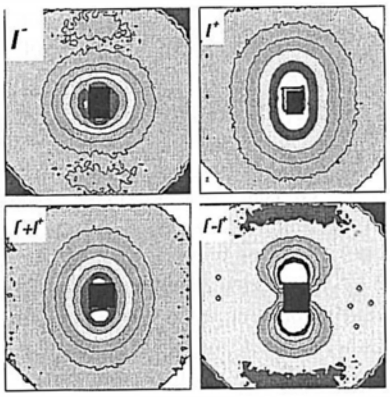


Abb. 1: SANSPOL-Intensitäten in Co-ferrofluid

In einer ersten Serie haben wir SANSPOL auf eine sehr verdünnte Cobalt-Ferrofluid Lösung von Co-(C_{21}-H_{39}-N-O_3) [1] in einer Mischung von protoniertem und deuteriertem Toluol angewandt [2, 3]. Während $I^+(\perp)$ kontinuierlich mit wachsendem Q abnimmt (Abb. 2a). weist $I^-(\perp)$ ein deutliches Maximum bei Q=0.68 nm auf, bei dem auch der Intererferenzterm sein Vorzeichen wechselt. Die deutlich verschiedenen Intensitätsverläufe für beide Polarisationsrichtungen müssen mit dem selben Formfaktor erklärbar sein, der die Partikel beschreibt, wobei nur die Kontraste polarisationsabhängig verschieden sein können. Dies ist nur möglich mit den in Abbildung 2c gezeigten Streulängenprofilen: Der magnetisierte Kern ist in einer vom Lösungsmittel undurchdringbaren Hülle eingekapselt, wobei die Kompositpartikel die in Abbildung 1d gezeigten Volumenverteilung aufweist.

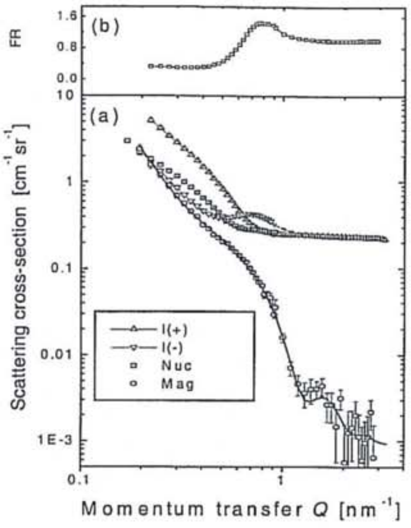


Abb. 2: SANSPOL in einem Co-Ferrofluid.

a) Streukurven für polarisierte und unpolarisierte Neutronen. Die durchgezogene Linien repräsentieren Fits mit den Parametern der Abb. 2c und 2d.

b) Flip-Verhältnis FR

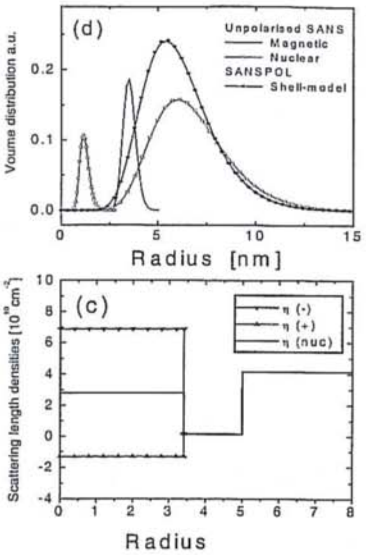


Abb. 2c) Streulängendichten für SANSPOL in Kern, Hülle und Lösungsmittel.

2d) Volumengrößenverteilung der Kompositpartikeln

Dieses Beispiel zeigt wie mit SANSPOL Dichteprofile sehr präzise nachgewiesen werden können, und verlässliche Aussagen über Kernradien als auch Hüllendicken erlauben.

Die eingeschränkte Empfindlichkeit der unpolarisierten Neutronen hätte dagegen die in Abbildung 2d gezeigten bimodale Größenverteilung der Partikel suggeriert.

Danksagung

Die Co-Ferrofluide wurden uns freundlicherweise von der Fa Mediport Kardiotechnik Berlin, GmbH zu Verfügung gestellt.

Literatur

[1] A. Wiedenmann, Mat. Science Forum,312-314 (1999), 315. J. Metastable and Nanocrystalline Materials, 2-6 (1999) 315.

[2] A. Wiedenmann, J. Appl. Cryst, **33**(2000), 428-532

[3] M. Giersig, M. Hilgendorff, J. Phys. **D** **32** (1999) L1.

SQUID-Messsystem für den Nachweis von magnetisch markierten Immunoassays in magnetisch ungeschirmter Umgebung#

A. Haller [1], H. Matz [1], S. Hartwig [1], T. Kerberger [1], H. Atzpadin [2], L. Trahms [1]

[1] *Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, 10587 Berlin*
[2] *Technische Universität Berlin, Einsteinufer 17, 10587 Berlin*

Einleitung

Eine neuartige Technik zum Nachweis von immunchemischen Reaktionen (z.B. Immunoassays in der medizinischen Labordiagnostik) auf der Basis von magnetischen Nanopartikeln und empfindlichen SQUID-Messsystemen wurde kürzlich entwickelt. Dabei werden die Reaktionspartner einer solchen Reaktion durch magnetische Nanopartikel markiert. Nach der immunchemischen Reaktion sind die magnetischen Nanopartikel an den nachzuweisenden Analyten gebunden. Durch diese Mobilitätseinschränkung zeigen sie ein verändertes magnetisches Relaxationssignal. Idealerweise sollte die Néelsche Relaxationszeit der Partikel im Bereich von 10 ms liegen, während die Reorientierung der magnetischen Nanopartikel aufgrund von Brownscher Bewegung 100-fach schneller ablaufen sollte. Wegen der hohen Polydispersität der verfügbaren Ferrofluide ist das Nachweisverfahren noch nicht optimiert.

Material

Die zur Zeit eingesetzten magnetischen Nanopartikel sind nicht optimal in Bezug auf die gewünschte Relaxationszeit nach dem Néel-Prozess von ca. 10 ms.

Zur Bestimmung der damit erreichten Nachweisempfindlichkeit des Verfahrens wurden gefriergetrocknete Proben eines kommerziellen Ferrofluids (Hersteller Meito Sangyo, Japan) untersucht.

Methode

Nach Magnetisierung der Proben in Feldern bis zu 1 kA/m wird das Relaxationssignal der Proben aufgezeichnet. Die Relaxationsprozesse aufgrund von Brownscher Bewegung und durch den Mechanismus nach Néel werden im aufgenommenen Zeitsignal analysiert. Zur Unterscheidung von gebundenen, magnetischen Nanopartikeln und solchen, die keine immunchemische Bindung eingegangen sind, wird die unterschiedliche Relaxationszeit beider Prozesse genutzt.

Für die praktische Einsetzbarkeit als medizinisches Labordiagnostikverfahren ist ein Betrieb des Messsystems in magnetisch ungeschirmter Umgebung wünschenswert. Das hier vorgestellte Messsystem wurde für den Betrieb in ungeschirmter Laborumgebung entwickelt und zur Messung von Relaxationssignalen an Ferrofluidproben eingesetzt. Die Signale hoher Störpegel magnetischer Umgebungsfelder wurden durch Verwendung eines elektronischen Gradiometers, das aus sechs SQUID-Magnetometern gebildet wird, reduziert.

Ergebnis

Die gemessenen Relaxationsamplituden wurden als Mittelwerte über 5 Aufmagnetisierungen bei einer Gesamtmesszeit von 7.5 s bestimmt. Die minimal nachweisbare Menge an γ-Fe_2O_3-Partikeln eines kommerziellen Ferrofluids entspricht einer Stoffmenge Eisen von 600 pmol bzw. 50 ng γ-Fe_2O_3.

#gefördert durch das Bundesministerium für Wissenschaft, Bildung, Forschung und Technologie unter dem Kennzeichen 13N7005/1

Magnetic Iron-Nitride Nanoparticles

N. Buske[1] and M. Wagener[2]

[1] Mediport Kardiotechnik GmbH, Wiesenweg 10, D-12247 Berlin, Germany
[2] Fraunhofer-Institute for Manufacturing and Advanced Materials (IFAM),
Wiener Str. 12, D-28359 Bremen,

Motivation:

Long term stable magnetic fluids (MF) of high saturation magnetization at a relatively low viscosity are smart raw materials for the MF technology, such as for MF-radial and axial (ultra high vacuum) seals in machinery or for use in innovative electromagnetic pump systems or in MF-sensors.
Iron-nitride (ε-Fe_3N or/and Fe_4N) particles are potential magnetic components due to its bulk saturation magnetization J_s of at least 1200 mT, which is situated between pure iron (J_s = 2100mT) and magnetite (J_s = 600mT). Furthermore, NAKATANI [1] already described iron nitride MF of saturation magnetizations by 233mT, but without any remarks to the bulk viscosity and long-term stability.
In this paper iron-nitride MF and particles of different core sizes will be tested due to their oxidation stability (long-term magnetic stability) and their optimum relation of saturation polarization and viscosity.

Materials/Methods:

Distilled iron pentacarbonyl ($Fe(CO)_5$, BASF) was dissolved in decane and/or petroleum which already contains the surfactant. This mixture was heated one hour at 90°C to obtain a non magnetic intermediate, and then heated again for some hours at 150°C in order to finish the thermolysis of the iron pentacarbonyl. The particle formation was checked by interruption of the preparation process 10 times within some days. Dry Argon (grad 6) and/or ammonia (grade 5) passes the solution during the whole procedure. As surfactant Polyisobutenylsuccinimide (PIBSI), M=1300 (BASF) was used.

After the preparation process the core/shell particles were more or less homogenously dispersed in the carrier liquid. Both the carrier free particles(cf. table) and the dispersions were characterized due to crystal structure by XRD (Seifert C3000), particle size and chemical composition REM with EDX (Philips XL20), TEM (Philips CM30) and elemental analysis by hot gas extraction at 2000°C .

A magnetic balance developed by the authors was used to measure the loss of magnetic power as a function of time.

Results:

µm-iron nitride particles (ALFA) and more than 50nm particles prepared in the lab. were stable against oxidation, but can not be used as solids for MF.
Contrary, PIBSI modified iron nitride sub-6nm particles are useful for preparation of MF, but the MF are .not long term magnetic stable. The particles are oxidized to non magnetic particles depending on its core size and the exposed time to oxidizers.

Conclusions:

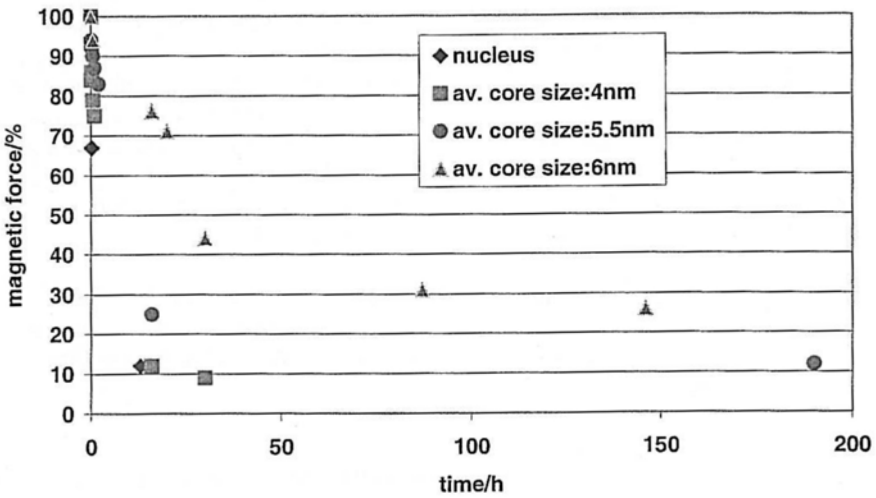
PIBSI covered ε-Fe_3N/ γ-Fe_4N sub-6nm particles are <u>not</u> stable against oxidation. Magnetic fluids containing such particles loss their magnetic power in some days when the MF is kept under ambient conditions.

The highest saturation polarization of a MF having a viscosity of 4 Pa s (27°C) which was prepared in this work was 110mT. The corresponding best values of MF containing magnetite nanoparticles and Co-nanoparticles are in order of 130mT and 220mT, respectively.

References:

[1] I. Nakatani, M. Hijikata and K. Ozawa: JMMM 122 (1993), 10-14

Decrease of magnetic interaction force of iron nitride-MF with different solid core sizes as function of time



Magnetic Sizing of Magnetic Nanoparticles

N. Buske, C. Gansau, T. Rheinländer and B. Kroll

Mediport Kardiotechnik GmbH, Wiesenweg 10, 12247 Berlin

Motivation:

Coated magnetic nanoparticles stably dispersed in polar or non polar fluids represent dispersions with superparamagnetic bulk properties (magnetic fluids) which were more and more used in science, technique, biology and medicine, i.e. for cell sorting, drug delivery and hyperthermia. Measurements of the hydrodynamic diameter of these core/shell nanoparticles by photon correlation spectroscopy (PCS) often show broad particle size distributions or particle size fractions that generally the scientific interpretation of MF properties hinders and an optimal application often limits. Therefore, novel methods for a sizing of core/shell-nanoparticles are an important goal for the future.

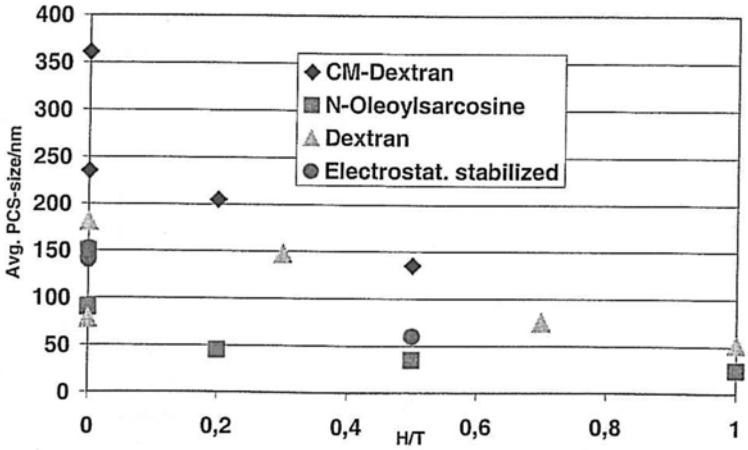
Materials/Methods:

Magnetite nanoparticles prepared at similar conditions at Mediport Kardiotechnik were used. The particles were stable dispersed in aqueous carriers at state of the art. The shell was on the one hand an electrochemical double layer of ions (surfactant free) and on the other hand, biocompatible polysaccharides (dextran, mw = 10 000, FLUKA, CM-dextran, mw. 15 000, FLUKA , N-oleoylsarcosine , SIGMA, [1]

The magnetic sizing in presence of an external magnetic field gradient was execute by an magnetic separator of GMW Associates (USA) combined with a bed of soft iron mm-spheres at using a similar procedure as described in [2].

Furthermore, magnetization curves of the MF´s were taken to determine the saturation polarization of the MF /Is(MF)/, additionally the total iron concentration fracture φ and the Fe^{2+}/Fe^{3+} relation or the investigated magnetic fluids was experimentally determined by physico-chemical methods.

Fig. 2: Hydrodynamic unimodal PCS-size of coated magnetic nanoparticles as function of the magnetic field strength H



Results and Discussion:

First results are shown in Fig. 2:

Generally, by three particle size fractions per MF sample could be separated. Surprisingly, the electrostatically stabilized particles could be classified as well. As to expect [3] the particles were more or less aggregated (PCS-size: 130 ... 60nm).
As known the coated sterically stabilized particles are better stabilized towards aggregation.
Average medium PCS sizes from 200 to 17nm were observed. The last fraction could be consist of primary particles only. This is in overestimation with a size evaluation: they are designed by the magnetite core size between 5 and 15nm (by TEM) and the calculated layer thickness of 2 -3.5nm.
The values of the saturation polarization of the MF /Is(MF)/ and the volume fracture of the core was used for estimation of the saturation polarization of the particles (Is(p): Is(p) = φ x Is(MF). The values kind of stabilizer, the age of the samples and the store conditions. Bulk material has a value of 600mT.

Conclusions:

Magnetic nanoparticles dispersed in aqueous carriers can be sorted by external magnetic field gradients by three or four fractions. The smallest fraction of sterically stabilized magnetite particles seems to be present the PCS-hydrodynamic size of primary (not aggregated) particles. The other fractions, including all fractions of electrostatically stabilized particles present PCS values of aggregated particles.

References:

[1] N Buske; DE pat 198 52 152 (1997)
[2] T. Rheinländer, R. Kötitz, W. Weitschies and W. Semmler; Colloid Polym Sci:278:259-63 (2000)
[3] N Buske; Progr Colloid Polym Sci:95:175-180 (1994)

Untersuchung von Kern und Hülle in Ferrofluiden durch Neutronen-Kleinwinkelstreuung

II. Magnetitferrofluide mit unterschiedlichen organischen Hüllen

A. Hoell, A. Wiedenmann, M. Kammel

Hahn-Meitner-Institut, Bereich Strukturforschung, Glienicker Straße 100, 14109 Berlin.
email: hoell@hmi.de

Nanokristalline Magnetitteilchen, Fe_3O_4, sind biologisch verträglich, nicht toxisch sowie abbaubar und in einigen Punkten bereits medizinisch getestet. Damit ist Magnetit prädestiniert für die Entwicklung biokompatibler magnetischer Flüssigkeiten und deren Einsatz in der Humanmedizin (Hypertermie, drug carrier) [1-3].

Ferrofluide mit Fe_3O_4 als magnetische Teilchenkerne werden durch Fällung von Fe-III/Fe-II-Chloriden in wässriger Lösung hergestellt [1,4]. Dabei entstehen Partikel mit einer Größenverteilung im Bereich von 3 bis 20 nm die bei Raumtemperatur superparamagnetisch sind. Diese Magnetitteilchen werden mit unterschiedlichen organischen Hüllenmaterialien (Einfach- und Doppelschichten) umgeben, wobei in der Regel eine wässrige Trägerflüssigkeit verwendet wird. Für potentielle Anwendungen ist neben der Größenverteilung der Magnetitteilchen die organische Hülle entscheidend. Entscheidende Parameter der Hülle sind die Hüllendicke, ihre Wechselwirkung mit der Trägerflüssigkeit als auch die mit der Oberfläche des Magnetitkerns.

In dieser Arbeit werden erste strukturelle Ergebnisse zu den Magnetitkompositteilchen in verdünnten Ferrofluiden im wässrigen Medium vorgestellt, die alle Magnetitkerne vergleichbarer Chargen besitzen, deren Volumenanteil etwa 1 vol% beträgt. Neutronen-Kleinwinkelstreuung mit magnetischer Kontrastvariation unter Anwendung der Technik polarisierter Neutronen (SANSPOL) wird angewendet, um vier Ferrofluide mit unterschiedlichen Hüllenmaterialien und ein elektrostatisch stabilisiertes Magnetitfluid ohne organische Hülle zu untersuchen (Abb. 1 und 2). Die Methode SANSPOL und deren strukturelle Aussagemöglichkeiten werden in [5,6] beschrieben. Die vier Ferrofluide besitzen Hüllen aus den folgenden chemischen Bestandteilen:

a.) Doppelhülle aus Dodekansäure
b.) Doppelhülle aus Dodekansäure und N-Oleoylsarkosin
c.) Einfachhülle aus Dextran
d.) Einfachhülle aus Dextran, karamellisiert.

Um alle stukturellen Details aufzuklären, wird die Streulängendichte der Trägerflüssigkeit durch Mischung von H_2O und D_2O variiert, und damit der Kontrast zu Kern und Hülle verändert. Neben der Teilchengrößenverteilungen, können die Hüllendicken als auch die magnetisierbaren Nanostrukturen der Kompositteilchen angegeben werden.

Danksagung

Alle Magnetitferrofluidmuster wurden uns freundlicherweise von der Fa. Mediport Kardiotechnik GmbH, Berlin zur Verfügung gestellt.

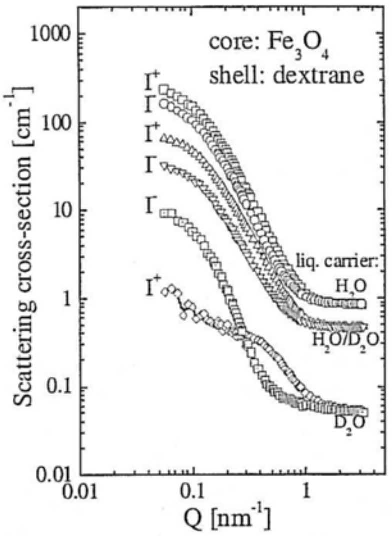


Abb.1: Neutronen-Kleinwinkelstreukurven eines Magnetitferrofluids mit karamellisierter Dextranhülle in unterschiedlichen Mischungen von H_2O und D_2O. Dargestellt sind die Streuintensitäten $I^+(Q \perp H)$ und $I^-(Q \perp H)$.

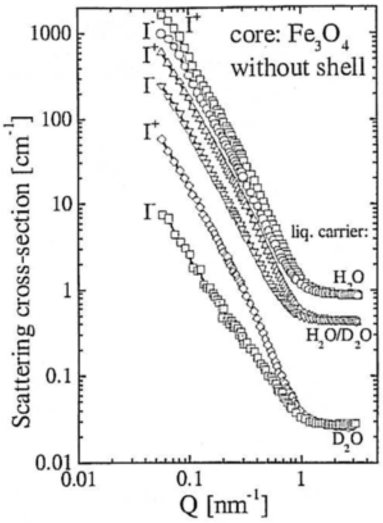


Abb.2: Neutronen-Kleinwinkelstreukurven eines elektrostatisch stabilisierten Magnetitferrofluids ohne organische Hülle in unterschiedlichen Mischungen von H_2O und D_2O. Dargestellt sind die Streuintensitäten $I^+(Q \perp H)$ und $I^-(Q \perp H)$.

Literatur

[1] P. Görnert, N. Buske: presentation on the 5th INTERTECH Conference, Berlin, März 2000.

[2] Magnetism in Medicine, eds. W. Andrä and H. Nowak, WILEY-VCH Berlin, 1998.

[3] R. Hergt et al, IEEE Trans. Magn., 34 (1998) 3745.

[4] N. Buske, DE pat. 197 58 350 (1997).

[5] A. Wiedenmann, Mat. Sci. For. 312-314, 1999, 315-324.

[6] A. Wiedenmann, J. Appl. Cryst. 33, 2000, 428-432.

Untersuchung von Kern und Hülle in Ferrofluiden durch Neutronen-Kleinwinkelstreuung
III. Ferrofluide mit Bariumhexaferritpartikeln als schwach magnetische Kerne

A. Hoell[1], A. Wiedenmann[1], R. Müller[2], W. Gawalek[2]

[1] Hahn-Meitner-Institut, Bereich Strukturforschung, Glienicker Straße 100, 14109 Berlin.
[2] Institut für Physikalische Hochtechnologie, Winzerlaer Straße 10, 07745 Jena.

Magnetische Flüssigkeiten mit Bariumhexaferrit $BaFe_{12-2x}Ti_xCo_xO_{19}$ ($x \geq 0.8$) als magnetische Partikel [1], die bei Raumtemperatur superparamagnetisch sind, wurden unter Nutzung eines modifizierten Glaskristallisationsverfahrens [2] zur Partikelherstellung entwickelt. Im Vergleich zu Magnetit hat Bariumhexaferrit eine sehr hohe uniaxiale Kristallanisotropieenergie und verspricht damit besondere Anwendungsgebiete abzudecken. Diese nanokristallinen Bariumhexaferritpartikeln, deren mittlerer Durchmesser ca 8 nm (TEM) beträgt, haben eine nichtmagnetische Oberflächenschicht (eine sogenannte Totschicht), die nicht mit der organischen Hülle der Partikeln zu verwechseln ist. Die Existenz dieser Schicht wurde indirekt durch magnetische Messungen nachgewiesen [3].

Bariumhexaferrit-Ferrofluide wurden mittels $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (Ölsäure) als Hüllenmaterial und Dodecan als Trägerflüssigkeit hergestellt. Die Agglomeratanzahl wurde durch zentrifugieren (5000 g) reduziert. Die überstehende konzentrierte Flüssigkeit ist das Ausgangsferrofluid, aus dem Ferrofluide mit verschiedenen Konzentrationen herstellbar sind.

Neutronen-Kleinwinkelstreuuntersuchungen (SANS) werden direkt an verdünnten flüssigen Proben mit magnetisierbaren Partikelanteilen von 1 – 4 vol% (VSM-Messungen) durchgeführt, um die Struktur der vereinzelten Partikeln und eine evt. Aggregation zu untersuchen.

SANS liefert Strukturparameter wie die Teilchengrößenverteilungen für die Kern-Hülle Kompositpartikeln im Größenbereich von ca 1 bis 100 nm mit hoher statistischer Sicherheit, für den Fall das Streulängendichteunterschiede zwischen den einzelnen Strukturelementen vorliegen (Abb. 1). Die Streulängendichte der Trägerflüssigkeit wird durch Mischung von undeuteriertem und deuteriertem Dodecan $xC_{12}H_{26}$ - (1-x) $C_{12}D_{26}$) variiert, um neben der Dicke der organischen Hülle auch zu klären, ob die Trägerflüssigkeit in die Hüllenschicht eindringen kann (Abb. 1).

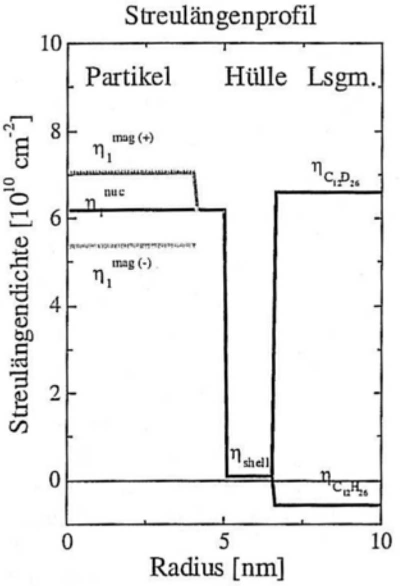


Abb. 1: Theoretische Streulängendichten für Kern, org. Hülle und Lösungsmittel, sowie magnetische Streulängendichten für SANSPOL. Der magnetische Kern ist mit einer nichtmagnetischen Oberflächenschicht dargestellt.

Neutronen-Kleinwinkelstreuung mit polarisierten Neutronen (SANSPOL) gestattet durch eine zusätzliche magnetische Kontrastvariation die Untersuchung der magnetisierbaren Nanostrukturen und ist damit die umfassenste Möglichkeit Struktur als auch magnetische Eigenschaften aufzuklären und beide miteinander in Beziehung zu setzen [4].

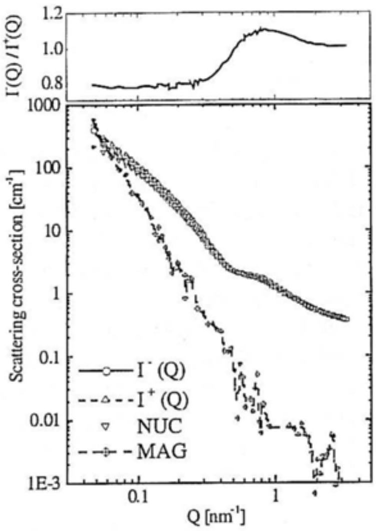


Abb.2: Mit Sanspol ermittelte Streukurven eines Bariumhexaferrit-Ferrofluids. Die obere Abb. zeigt das Flipping Verhältnis zwischen den beiden Polarisationsrichtungen.

Erste Messungen zeigten nur schwach anisotrope zweidimensionalen Streudiagramme für die beiden Polarisationsrichtungen. Die daraus extrahierten Streukurven für die beiden Polarisationsrichtungen $I^-(Q)$ und $I^+(Q)$ für **Q** ⊥ **H** zeigen nur geringe Unterschiede (Abb. 2). Dies deutet auf einen im Vergleich zum nuclearen geringen magnetischen Streukontrast hin. Gerade für derartige Kontrastverhältnisse werden mit polarisierten Neutronen Resultate erzielt die im unpolarisierten Fall kaum zugänglich sind [5]. Das Flippingverhältnis (Abb. 2 oben) zeigt eine starke Q-Abhängigkeit. Alle vier in Abb. 2 gezeigten Streukurven werden durch dieselbe Struktur verursacht, wobei sich nur die Kontrastverhältnisse (Abb. 1) unterscheiden. Aus der Strukturmodellanpassung erwarten wir auch eine Aussage über die mögliche Existenz der unmagnetischen Oberflächenschicht der Bariumhexaferritpartikeln abzuleiten, wie es an Magnetitpartikeln in einer Silicatglasmatrix gezeigt wurde [6].

Literatur

[1] R. Müller et al, J. Magn. Magn. Mater. 201, 1999, 34-37.
[2] R. Müller et al, Proceed. ELECTROCERAMICS IV Conf. 5. - 7.9.1994 Aachen, vol. II p. 1183-85.
[3] S. Kirusu et al, IEEE Trans. Magn. 23, 1987, 3137.
[4] A. Wiedenmann, Mat. Sci. For. 312-314, 1999, 315-324.
[5] A. Wiedenmann, J. Appl. Cryst. 33, 2000, 428-432.
[6] U. Lembke, A. Hoell, A. Wiedenmann et al, J. Appl. Phys. 85, 1999, 2279-2286.

2. Bulk properties

The Langevin-dynamics simulation of interacting fine magnetic particle systems

D.V.Berkov, N.L.Gorn, P.Görnert

INNOVENT e.V., Felsbachstr. 5, D-07745, Jena, Germany

The most challenging problem in physics of disordered systems of magnetic particles is the investigation of their dynamical properties; the major difficulty here is due to the long-range and anisotropic dipolar interparticle interaction. The most direct theoretical method to study the corresponding dynamics is based on numerical solution of stochastic Langevin equations [1]. In this paper we present novel results obtained using this method for the *ac*-susceptibility χ of such systems.

We simulate a system of randomly placed non-overlapping spherical single-domain magnetic particles. To calculate $\chi(T)$ we integrate numerically the stochastic Landau-Lifshitz-Gilbert equation [1] for the motion of the particle magnetic moments μ_i in the deterministic $\mathbf{H}_i^{\mathrm{eff}}$ and random $\mathbf{H}_i^{\mathrm{fl}}$ fields; the latter is assumed to represent the influence of thermal fluctuations [1].

The field $\mathbf{H}_i^{\mathrm{eff}}$ includes the external, anisotropy and interparticle interaction fields. We assume that all particles possess the uniaxial anisotropy with the reduced anisotropy constant $\beta = 2K/M_S^2$, where K is the 'usual' anisotropy constant and M_S the saturation magnetization. The dipolar interparticle interaction field is evaluated using the Lorentz cavity method.

The real $\chi'(\omega,T)$ and imaginary $\chi''(\omega,T)$ parts of the *ac*-susceptibility are calculated in a standard way applying an oscillating field $h_z = h_0 \cos \omega t$ and measuring in- and out-of-phase magnetization components. The reduced temperature used below is defined in units of the stray field energy as $\Theta = kT/ M_S^2V$ (V being the particle volume), the reduced frequency is $w = \omega/\gamma M_S$ (γ is the gyromagnetic ratio). The measurements were performed for a system of $N_p = 256$ particles. The program was successfully tested on non-interacting particles using both analytical and numerical results (see [1] and Ref. therein).

The most interesting question concerning the behaviour of the system under study is the influence of the interparticle interaction on its *ac*-susceptibility $\chi(T)$. To study this problem we have performed simulations for various particle volume concentrations c. Typical results are shown in Fig.1 and 2, where it can be clearly seen that changes in the $\chi(\Theta)$-curves with increasing concentration depend *qualitatively* on the single-particle anisotropy β.

For high and moderate anisotropies ($\beta > 1$) the peak on the $\chi(\Theta)$-dependencies shifts towards *lower* temperatures when the particle concentration (and the interaction strength) increases. This shift is pronounced quite well for low dissipation (see Fig. 1, where $\beta = 2.0$ and the damping constant $\lambda = 0.1$) and is getting weaker when the dissipation increases. This means that the dipolar interaction leads to the *decrease* of the free energy barriers in systems of fine particles with *high* and *moderate* anisotropies and this effect is stronger in the low damping case. This result is in agreement with (i) the Mössbauer experiments of Morup et al. and his theoretical predictions [2] (where the interaction is treated as a small perturbation) and (ii) our recent numerical results for the energy barrier distribution density in such systems [3].

For sufficiently small anisotropy values (how small - depends on λ) the $\chi(\Theta)$-peak shifts towards *higher* temperatures with increasing concentration - see Fig.2 ($\beta = 0.5$ and $\lambda = 1.0$). This can be easily understood, because the low anisotropy β means that already for moderate particle concentration the interparticle interaction makes the dominant contribution to the energy barrier height. Hence the average barrier height increases when the particle concentration increases.

Such a behaviour (shift of the $\chi(T)$-peak towards *higher* temperatures with increasing concentration) was found in most experiments on standard magnetite or maghemite ferrofluids [4,5,6,7]. However, there exists an important disagreement between our simulations and experimental results: the anisotropy (calculated from K- and M_S-values reported, e.g., in [4,7]) for these measurements is $\beta \approx 1.5 \div 2.0$ so that the opposite shift of the $\chi(T)$-peak with increasing concentration should be observed according to our simulations.

The most probable reason for this discrepancy is the following. The average value of the anisotropy constant K for a ferrofluid sample is usually obtained from its low-T hysteresis loop $M(H)$ [8], where the contributions of different particles to the sample magnetization M are proportional to their moments μ. By the susceptibility measurements, however, particle contributions are $\sim \mu^2$, which means that the contribution of larger particles is much more significant for the χ-measurements. At the same time, it is well known that the total effective anisotropy of fine particles made of the material with the relatively weak cubic crystallograhic anisotropy *decreases* with the growing particle size (see, e.g, [9]). Hence larger particles with larger moments which contribute significantly more to the susceptibility than to the magnetization itself have a much lower anisotropy value β. Hence the peak of the total *ac*-susceptibility shifts towards *higher* temperatures with increasing particle volume fraction, as it should be for the low anisotropy case.

[1] J.L.Garcia-Palacios, F.J.Lazaro, *Phys. Rev.*, **B58** (1998) 14937

[2] M.F.Hansen, S.Morup, *J. Magn. Magn. Mat.*, **184** (1998) 262

[3] D.V.Berkov, *J. Magn. Magn. Mat.*, **186** (1998) 199

[4] T.Jonsson, J.Mattson, C.Djurberg, F.A.Khan, P.Nordblad, P.Svendlindh, *Phys. Rev. Lett.*, **75** (1995) 4138

[5] J.Zhang, C.Boyd, W.Luo, *Phys. Rev. Lett.*, **77** (1996) 390

[6] S.Taketomi, *Phys. Rev.*, **B55** (1997) 3073

[7] T.Jonsson, P.Nordblad, P.Svendlindh, *Phys. Rev.*, **B57** (1998) 497

[8] T.Jonsson, J.Mattson, P.Nordblad, P.Svendlindh, *J. Magn. Magn. Mat.*, **168** (1997) 269

[9] F.Gazeau et al., *J. Magn. Magn. Mat.*, **186** (1998) 175

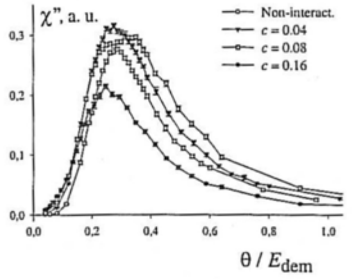


Fig.1. Temperature dependencies $\chi''(\Theta)$ for a system of particles with the anisotropy $\beta = 2.0$ and damping $\lambda = 0.1$ for various particle volume fractions c as shown in the legend

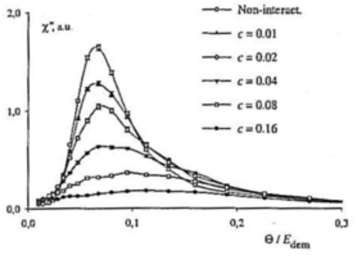


Fig.2. The same as shown in Fig.1 for $\beta = 0.5$ and $\lambda = 1.0$

Struktur und viskose Eigenschaften von Ferro-Fluiden und magneto-rheologischen Fluiden. Nicht-Gleichgewichts-Molekular-Dynamik (NEMD) Studien für einfache Modellsysteme

Siegfried Hess[1] und Martin Kröger[1,2]

[1] *Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, D – 10623 Berlin, Germany. Email: S.Hess@physik.tu-berlin.de*

[2] *Polymerphysik, Institut für Polymere, ETH Zürich, Sonneggstr. 3, CH – 8092 Zürich, Schweiz*

Ein einfaches Modell zur theoretischen Behandlung von Ferro-Fluiden und magneto–rheologischen Fluiden wird vorgestellt. Ergebnisse analytischer Rechnungen und insbesondere von NEMD–Computer-Simulationen liegen vor zur Struktur [1] von Fluiden, die colloidale Teilchen mit (perfekt) orientierten magnetischen Dipolen enthalten, ferner zur Anisotropie der Viskosität [2, 3], zum rheologischen Verhalten dieser Systeme [3, 4] und der durch die Strömung bedingten Veränderung der Struktur [4].

References

[1] S. Hess, J.B. Hayter, and R. Pynn, *A comparison of molecular dynamics and analytic calculations of correlations in an aligned ferrofluid*, Molec. Phys. **53**, 1527 (1984);
S. Hess, *Structure and dynamics of oriented ferrofluids* in: Physics of Complex and Supermolecular Fluids, eds. S.A. Safran and N.A. Clark, J. Wiley, New York 1987, p. 631

[2] S. Hess, J.F. Schwarzl and D. Baalss, *Anisotropy of the viscosity of nematic liquid crystals and of oriented ferrofluids via nonequilibrium molecular dynamics*, J. Phys. Condens. Matter 2, 8A, 279 (1990)

[3] S. Hess, M. Kröger, W. Loose, C. Pereira Borgmeyer, R. Schramek, H. Voigt, and T. Weider, *Simple and Complex Fluids under Shear*, in K. Binder and G. Ciccotti (eds.) *Monte Carlo and Molecular Dynamics of Condensed Matter Systems*, IPS Conf. Proc. **49**, Bologna 1996, p. 825 - 841;
S. Hess, C. Aust, L. Bennett, M. Kröger, C. Pereira Borgmeyer, T. Weider, Physica A **240** (1997) 126;
S. Hess, *Flow properties and structure of anisotropic fluids studied by Non-Equilibrium Molecular Dynamics and Flow properties of other complex fluids: polymeric liquids, ferro-fluids and magneto-rheological fluids* in: P. Parisi and C. Zannoni (eds.) *Advances in the computer simulation of liquid crystals* (Kluwer, Dordrecht, 2000)

[4] S. Hess and T. Weider, *Flow properties and structural changes in magneto-rheological fluids via non-equilibrium molecular dynamics*, Proc. XIIth Int. Congr. Rheol. eds. A. Ait-Kadi, J.M. Dealy, D.F. James and M.C. Williams, Can. Rheol. Group, Quebec 1996, p. 313-314

Magnetization of ferrofluids with dipolar interactions - a Born Mayer expansion

Björn Huke[1], Manfred Lücke[1]

[1] *Universität des Saarlandes, Insitut für Theoretische Physik, Postfach 151150, D-66041 Saarbrücken, Germany*

We are concerned with the equilibrium magnetization M as a function of the internal magnetic field H for given temperature and particle concentration. Ferrofluids with high particle concentration or with particles consisting of ferromagnetic material with a large bulk magnetization show strong deviations from the simple Langevin behavior of the magnetization due to particle–particle interaction effects.

Our approach assumes the magnetic particles in the ferrofluid to be hard spheres with a common diameter D and dipolar moment m. We use the technique of the Born–Mayer expansion together with an expansion in the strength of the dipolar coupling to get analytical approximations. They are obtained via series expansions of the free energy in terms of two parameters: (i) the volume fraction of the hard core particles ϕ and (ii) a dimensionless dipolar coupling constant ϵ, given by the ratio between a typical dipolar energy for particles in hard core contact and the thermal energy kT.

The long range character of dipolar forces requires great care when invoking the thermodynamic limit. To solve the problem we describe the dipolar fields that are generated by distant particles by a magnetic continuum field while incorporating explicitly the near field contributions from a sufficiently large region in a statistical mechanical description. The inconsistencies of the Weiss model in treating the transition from a continuum to fields on the particle scale are thus avoided. The statistical mechanics of the dipoles in the near region is influenced by the far field contribution entering into an effective field that contains the sought after M. Thus, the latter is determined selfconsistently.

We present two different expansions in ϵ and ϕ, one containing only linear terms in ϕ, the other also second order ϕ terms, but only up to $O(\epsilon^2)$ and discuss the range of applicability in the ϕ–ϵ plane. We compare the results to those of existing models.

Real ferrofluids show a polydisperse distribution of the particle diameters. The effects of polydispersity on the equilibrium magnetization are comparable to those of the particle–particle interaction. We discuss the necessary modifications of our theory to incorporate the polydispersiveness.

We also touch the question if short range interactions other than hard core repulsion have an significant effect on the magnetization.

Acknowledgements

The support by the Deutsche Forschungsgemeinschaft (SFB 277) is gratefully acknowledged.

Measurements of the rotational viscosity of ferrofluids

J. P. Embs[1,3], H. W. Müller[2], K. Knorr[1], M. Lücke[3]

[1] *Universität des Saarlandes, Technische Physik, D-66041 Saarbrücken*
[2] *Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz*
[3] *Universität des Saarlandes, Theoretische Physik, D-66041 Saarbrücken*

One of the interesting properties of ferrofluids is their tunable viscosity [1], which can be controlled by an external magnetic field $\mathbf{H}_0$. In our experiment [2] we measure the field induced magneto-viscous damping by means of a torsional pendulum, which executes oscillations around the z-axis with an angular frequency $\Omega(t) = \Omega_0 \cos(\omega t)$. In order to guarantee a solid body rotation and to avoid a disturbing dissipative shear within the probe the cylindrical container is densely packed with plastic straws. The rigid motion of the ferrofliud creates an off-equilibrium situation, in which the magnetization $\mathbf{M}$ is forced out of the field direction $\mathbf{H}_0 \parallel \mathbf{e}_x$. This generates a dissipative torque

$$\mathbf{N} = \mu_0 \int_V (\mathbf{M} \times \mathbf{H}) \mathrm{d}V, \qquad (1)$$

where $\mathbf{H} = \mathbf{H}_0 - \bar{N}\mathbf{M}$ is the macroscopic field within the probe, $\bar{N}$ the geometrical demagnetization factor and V the volume. Due to the tiny deflection angle $\Omega_0/\omega < 1^\circ$ the off-equilibrium component of the magnetization $\mathbf{m} = \mathbf{M} - \mathbf{M}_{\mathrm{eq}}$ is also small and therefore approximately governed by the relation

$$[\partial_t - \mathbf{\Omega}\times]\mathbf{M} = -\frac{\mathbf{m}_\parallel}{\tau_\parallel} - \frac{\mathbf{m}_\perp}{\tau_\perp}. \qquad (2)$$

Here $\tau_\parallel(H)$ and $\tau_\perp(H)$ are respectively the relaxation times parallel and perpendicular to the applied field. Since in our experiment the low frequency condition $\omega\tau_\perp \ll 1$ and the weak flow approximation $\Omega\tau_\perp \ll 1$ both are valid one can easily solve Eq. 2 for $\mathbf{m}_\perp$ and evaluate the dissipative torque $\mathbf{N}$. The latter is proportional to the measured damping increment

$$\Gamma_{FF}(H_0) = \frac{-N}{\Omega\Theta} = \mu_0 \frac{V}{\Theta} \tau_\perp M_{\mathrm{eq}} H_0, \qquad (3)$$

where Θ is the moment of inertia of the oscillating body and $\mathbf{M}_{\mathrm{eq}}$ denotes the equilibrium magnetization at the applied field strength. The experimental data on the field dissipation are shown in Fig.1. They can be used in combination with the recorded magnetization curves $M_{\mathrm{eq}}(H)$ to determine the field dependence of the transverse relaxation time $\tau_\perp(H)$ as depicted in Fig.2.
Microscopic information on the investigated samples can be obtained from our experiment under special assumptions upon the microstructure of the probe: Assuming that the ferrofluid is a monodispersed suspension of non-interacting spherical rigid dipoles the following dependencies have been deduced [3, 4]

$$\tau_\perp(H_0) = 2\tau_B \mathcal{L}(\alpha)/[\alpha - \mathcal{L}(\alpha)]. \qquad (4)$$

Here τ_B is the Brownian relaxation time being proportional to the hydrodynamic particle volume $\frac{\pi}{6}d_h^3$ (magnetic core plus surfactant coating). Moreover, $\mathcal{L}$ is the Langevin function and $\alpha = \mu_0 m H_{loc}/k_B T$ the dimensionless field strength, where m

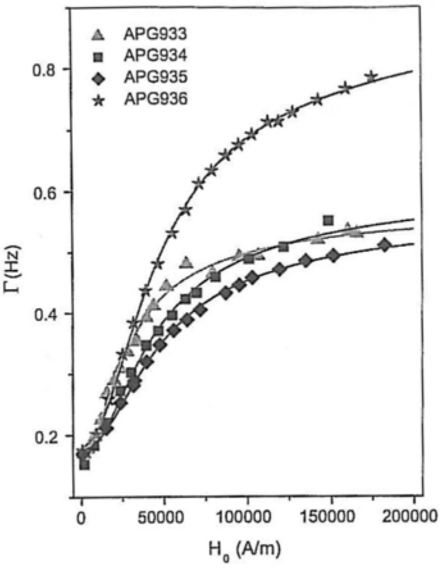


Figure 1: The measured damping $\Gamma(H_0) = \Gamma_{FF}(H_0) + \Gamma_p$, where Γ_p is a parasitic contribution due to air friction and mechanical losses within the torsional wire. Solid lines are fitted curves by use of the microscopic relationships (??,4).

is the particle's magnetic moment being proportional to the core volume $\frac{\pi}{6}d_m^3$ and H_{loc} is the local field felt by an individual dipole.

Sample	d_m[nm]	d_h [nm]
APG 933	10.1	16.1
APG 934	8.5	11.3
APG 935	8.5	9.4
APG 936	8.2	9.6

Table 1: Values for the particle core diameter d_m and the hydrodynamic diameter d_h as obtained by fitting the measured magneto-viscous dissipation $\Gamma(H_0)$.

Using Eq. (4) with d_m, d_h, and Γ_p to fit the experimental curves yields the solid lines in Fig.1 and the values for the particle size given in Tab. 1. To estimate the reliability of this method these values are compared with the outcomes of different complementary characterization techniques.

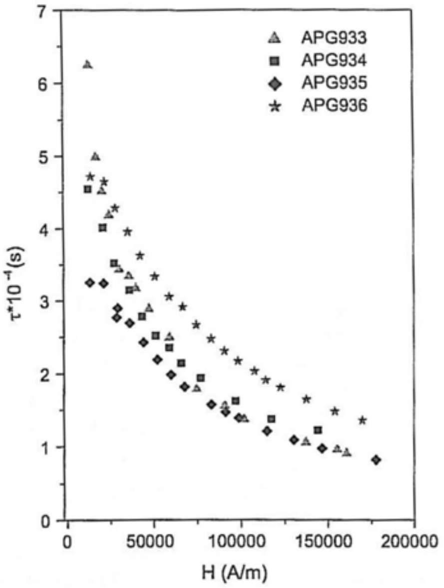


Figure 2: Combining the meausred damping (see fig. 1) and the recorded magnetization we found, using eq. 3, the relaxation time $\tau = \tau_\perp(H)$.

References

[1] M. I. Shliomis, Sov. Phys. JETP **34**, 1291 (1972).

[2] J.P. Embs, H.W. Müller, C. Wagner, K. Knorr, M. Lücke, Phys. Rev. E, **61**, R2196 (2000).

[3] J.T. Waldron, Y.P. Kalmykov, W.T. Coffey, Phys. Rev. E, **49**, 3976 (1994).

[4] M. Shliomis, Chem. Eng. Commun., **67**, 275 (1988).

Magnetoviscosity and relaxation in ferrofluids

B.U. Felderhof

Institut für Theoretische Physik A, RWTH Aachen, Templergraben 55, D-52056 Aachen

Abstract

The increase in viscosity of a ferrofluid due to an applied magnetic field is discussed on the basis of a phenomenological relaxation equation for the magnetization. The relaxation equation was derived earlier from irreversible thermodynamics, and differs from that postulated by Shliomis. The two relaxation equations lead to a different dependence of viscosity on magnetic field, unless the relaxation rates are related in a specific field-dependent way. Both planar Couette flow and Poiseuille pipe flow in parallel and perpendicular magnetic field are discussed. The entropy production for these situations is calculated and related to the magnetoviscosity.

Magnetische Separation von Ferrofluiden

S. Thurm[1], S. Odenbach[1]

[1] *ZARM, Universität Bremen, Am Fallturm, 28359 Bremen*

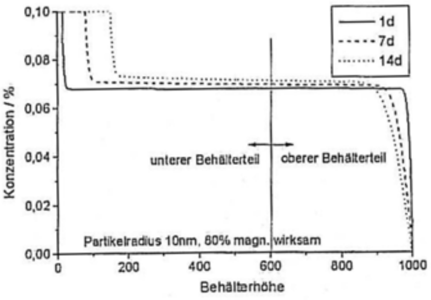
Einleitung

Im Rahmen dieses Projekts soll die Ursache für das Auftreten starker magnetoviskoser Effekte in kommerziellen Ferrofluiden untersucht werden. Die existierende Theorie geht von unabhängigen, nichtwechselwirkenden Teilchen aus, deren Rotation in einer Scherströmung durch die Wirkung eines senkrecht zur Vortizität der Srömung stehenden Magnetfeldes gehemmt wird. Die Stärke dieses Effektes kann jedoch mit der bisher existierenden Theorie zur Rotationsviskosität nicht erklärt werden. Da nur große Partikel mit "eingefrorenem" magnetischen Moment zur Rotationsviskosität beitragen, der Anteil dieser Partikel in kommerziellen Fluiden aber sehr klein ist, vermuten wir die Existenz sogenannter *primärer Agglomerate [1]*. Diese Agglomerate bestehen aus zwei bis drei einzelnen Partikeln, die während des Herstellungsprozesses mit einer gemeinsamen Polymerhülle umgeben werden. Aktuelle molekulardynamische Rechnungen von Satoh und Chantrell [2] zeigen, daß diese primären Agglomerate Anlaß zur Kettenbildung in magnetischen Feldern geben können, wodurch die experimentell gefundene Scherverdünnung und die extrem großen magnetoviskosen Effekte bei niedrigen Scherraten erklärbar wären.

Durch magnetische Separation sollen Ferrofluide in Fraktionen mit niedrigem und hohen Agglomeratanteil aufgetrennt werden. Durch sukzessive Auftrennung der Franktionen in anschließenden Separationsstufen können Informationen über die Rolle primärer Agglomerate und großer Teilchen auf das magnetoviskose Verhalten erhalten werden.

Numerische Simulation

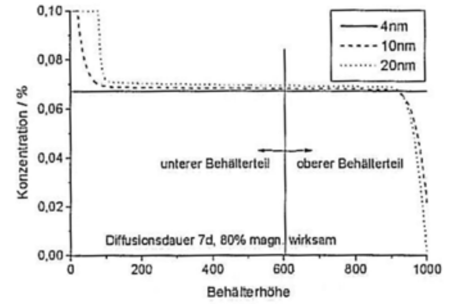
Kenntnisse vom zeitabhängigen Konzentrationsprofil im Behälter waren von fundamentaler Bedeutung für die Konstruktion der Separationsanlage. Zur Generierung dieser Daten wurde eine numerische Simulation entwickelt, die die Diffusionsvorgänge in der gewünschten Behältergeometrie berechnet. In Grafik 1 ist die Konzentrationsverteilung für Partikel mit einem Durchmesser von 10nm bei unterschiedlichen Zeiten zu sehen.



Grafik 1: Konzentrationsverteilung

Durch die Konzentrationserniedrigung im oberen Teil und –erhöhung im unteren Teil des Behälters ist eine Auftrennung in zwei unterschiedlich konzentrierte Chargen möglich. [3, 4, 5]

Grafik 2 verdeutlicht die Selektivität der magnetischen Separation. Aufgetragen ist die Konzentrationsverteilung verschiedener Partikelradien nach einer Zeitdauer von 7 Tagen. Während große Partikel relativ schnell in Bereiche größerer Feldstärke wandern, werden kleinere Partikeln in nur geringem Maße beeinflußt.



Grafik 2: Einfluß des Partikeldurchmessers

Magnetische Separationsanlage

Zentrale Elemente der Anlage sind die gradienterzeugenden Polschuhe mit $\nabla H \geq 10^7\,\mathrm{Am}^{-2}$ und eine in-situ Konzentrationsmesseinrichtung auf induktiver Basis. Um den Konzentrationsverlauf im Behälter möglichst genau verfolgen zu können, sind 3 Meßspulen in unterschiedlicher Höhe plaziert (vgl Bild 1).

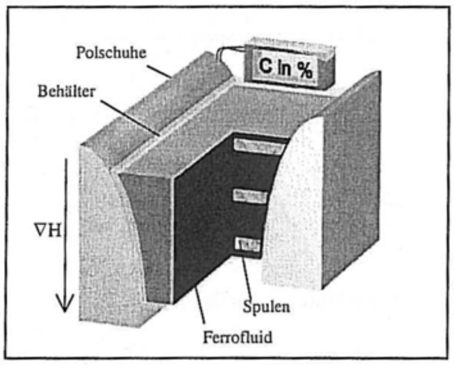


Bild 1: Versuchsaufbau

Verfolgt wird die Veränderung der Induktivität der Spulen in Abhängigkeit der Konzentration. Je höher die Konzentration, desto größer die Induktivität der Spulen.

Ergebnisse

Präsentiert werden Magnetisierungsmessungen, Sedimentationsmessungen und Ergebnisse aus magnetischen Separationsmessungen von verschiedenen Flüssigkeiten.

Flüssigkeiten:

- Kerosinbasiertes Ferrofluid, η=5 mPas
- Auf synthetische Ester basiertes kommerzielles Ferrofluid (APG513A), η=138 mPas

Aus den rheometrischen Untersuchungen der aufgetrennten Fraktionen wird der Einfluß primärer Agglomerate auf den magnetoviskosen Effekt beschrieben und diskutiert.

Literatur

[1] O'Grady, K., Stewardson, H.,Chantrell, R.W., Fletcher, D., Unwin, D.,Padur, M.; *Magnetic filtration of ferrofluids*, IEEE Trans. Magn. **22**, 5 (1986) 1134

[2] Satoh, A., Chantrell, R.; Coverdale, G.N., Kamiyama, S.; *Microsimulations of ferromagnetic colloidal dispersions in a simple shear flow*, Proceedings of the International Symposium of Hydrodynamics of Magnetic Fluids and ist applications, Sendai 1997

[3] Gerber, R., Takayasu, M., Friedlaender, F.J.; *Generalization of HGMS theory: the capture of ultra-fine particle,*. Transactions on magnetics, vol.mag-19, no.5 1983

[4] Gerber, R.; *Magnetic filtration of ultra-fine particles.* Transactions on magnetics, vol.mag-20, no.5 1984

[5] Odenbach, S.; *Forced diffusion in magnetic fluids under the influence of a strong magnetic field gradient.* Zeitschrift für Physik B, 1994

Danksagung:
Dieses Projekt wird von der DFG unter dem Kennzeichen OD18/3-1 gefördert.

Convection and Thermal Diffusion in a Two-dimensional System of Ferrofluid

Adrian Lange

Institut für Theoretische Physik, Universität Magdeburg, Postfach 4120, D-39016 Magdeburg

Motivation

For a thin ($h = 100\mu$m) horizontally extended (2×2 cm) layer of magnetic fluid subjected to local heating by a laser beam and to a constant vertical magnetic field, a novel convective instability was observed [1]. Below a critical magnetic field the far-field diffraction pattern shows concentric rings. Above a critical magnetic field an instability occurs in which the circular rings are replaced by "polygons". In [1] these polygonal diffraction patterns are attributed to the appearance of an even number of convection rolls. Additionally, the crucial roll of the thermal diffusion mechanism (Soret effect) was emphasized.

Linear Stability Analysis

An incompressible, nonconducting, and viscous magnetic fluid in a plane cylinder geometry (r, ϕ) between two concentric circles with the radii $R_1 < R_2$ is considered. It is assumed that the magnetization M of the magnetic fluid depends linearly on the applied magnetic field **H**, $\mathrm{M} = \chi\mathbf{H}$, where χ is the susceptibility of the fluid. With respect to the discussion about the validity of the Kelvin force [2], it is also assumed that the susceptibility depends linearly on the volume concentration of magnetic particles.

The system is governed by the Navier-Stokes equation, the thermal conduction equation, the diffusion equation, and the equation of continuity which have to be supplemented with the appropriate boundary conditions. The stationary basic state between the inner and outer radius is given by the zero flow field $\mathbf{v} = 0$, a nonlinear temperature profile, and a nonlinear, *temperature difference* dependent concentration profile

$$c_G(r) \quad = \quad \frac{c_0}{c_0 + (1 - c_0) r^{\gamma}} \qquad (1)$$

$$\gamma = \frac{\mathcal{S}\,(T_1 - T_0)}{\mathcal{L} \ln \eta} ,$$

where $c_0 = c_G(T_0)$ is the concentration at room temperature $T_0 < T_1$ at the outer radius. The Soret number $\mathcal{S}$ is proportional to the temperature difference, i.e., proportional to the external driving whereas the Lewis number $\mathcal{L}$ is determined by material parameters of the magnetic fluid. The dimensionless radial distance r runs from $\eta = R_1/R_2$ to 1. Depending on the size of the temperature difference the concentration profile can be either convex or concave (see Fig. 1). Since no *measurements* of the basic state with respect to the concentration of the magnetic particles have yet been undertaken, such measurements would offer a first opportunity to determine the role of thermal diffusion in such a system.

Motivated by Chandrasekhars solution for the Taylor-Cuette system [3], the linearized differential equations for small deviations in the velocity, the temperature, and concentration from the basic state

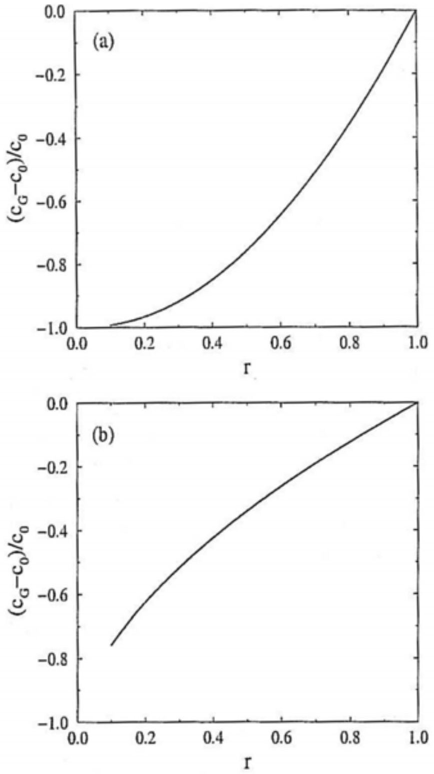


Figure 1: Particle concentration as a function of the radial distance r for $c_0 = 0.1$, $\eta = 0.1$, and different temperature differences δT. (a) $\delta T = 50$ K, (b) $\delta T = 15$ K

are solved in a similar way. Results will be presented for the stability of the basic state depending on the temperature difference, the strength of the magnetic field, and the thermo diffusion effect.

References

[1] T. Du and W. Luo, Appl. Phys. Lett. **72**, 272 (1998); W. Luo, T. Du, and J. Huang, Phys. Rev. Lett. **82**, 4134 (1999).

[2] M. Liu, Phys. Rev. Lett. **84**, 2762 (2000); W. Luo, T. Du, and J. Huang, Phys. Rev. Lett. **84**, 2763 (2000).

[3] S. Chandrasekhar, *Hydrodynamic and Hydromagnetic Stability*, (Dover Publication, New York, 1970).

Field-induced Ordering of superparamagnetic Colloids in 2D

K. Zahn, P. Keim, H. König, A. Wille, G. Maret

Universität Konstanz, Fachbereich für Physik, Universitätsstr. 10, 78464 Konstanz

Recently we proposed a novel experimental setup to model ordering phenomena of microscopic magnetic particles in an external field [1]. We use polystyrene spheres confined to an air-liquid interface of a water drop hanging from a glass plate. The particles are paramagnetic due to Fe_2O_3 doping. Thus an external magnetic field B induces a dipole moment $M = \chi \cdot B$ in the spheres, with an effective magnetic susceptibility χ of the particles. The interaction strength $\Gamma = \mu_0/4\pi \cdot (\chi \cdot B)^2 \cdot \rho^{3/2}/kT$, ρ denoting the mean 2D particle concentration, can conveniently and reversibly be controlled through B, its value ranging from 0 to 10^3. In addition, Γ was precisely calibrated and therefore quantitative comparison with theory was possible [1]. Using video-microscopy the particle structure and dynamics can be evaluated on all relevant length and time scales.

If B is applied perpendicular to the interface a crystalline phase is found at high Γ (Fig.1) [2]. If the magnetic field is applied parallel to the particle plane an aggregation of the colloids into straight chains is observed (Fig.2). At distances large compared to the length of the chains they repel each other. However, at smaller distances an attractive force is observed and the chains can be further aggregated into a dense 2D (single-) layer (Fig.3).

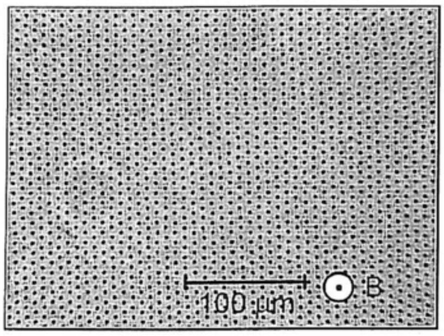


Fig.1: *2D colloidal crystal consisting of paramagnetic latex spheres at a water air interface.*

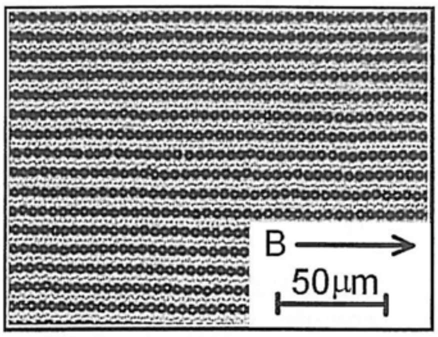


Fig.2: *Magnetic colloids aggregated in straight chains in an external field B.*

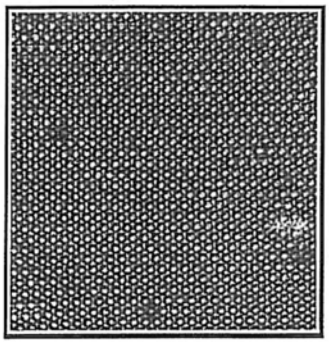


Fig.3: *Mono-layer of magnetic colloids in 2D.*

References

[1] K. Zahn, J. M. Méndez-Alcaraz, and G. Maret, Phys. Rev. Lett. **79**, 175 (1997).

[2] K. Zahn, R. Lenke, and G. Maret, Phys. Rev. Lett. **82**, 2721 (1999).

Magnetic Force in Ferrofluids

Mario Liu[a] and Klaus Stierstadt[b]
[a]Institut für Theoretische Physik, Universität Hannover,
30167 Hannover, Germany
[b]Sektion Physik, Universität München,
80539 München, Germany

September 11, 2000

While the electromagnetic force is a simple and unique quantity in microscopic physics, given by the Lorentz force, it is a multi-faceted, heuristic concept in macroscopic physics. Not aware of the fact, and possibly for want of something better, we tend to take the Kelvin force, $\mu_0 M_i \nabla H_i$, with its curious preference of H over B, as *the* magnetic force density. (There is of course also the macroscopic Lorentz force, which is however zero if the system is neutral and insulating).

To understand why this is a conceptual pitfall, consider the hydrodynamic theory for ordinary fluids, such as water or air, in the absence of fields. It consists of a set of partial differential equations including the Navier-Stokes equation. By solving these equations with the appropriate initial and boundary conditions, one is in principle able to predict any experimental outcome – say the trajectory of an airplane – without ever the need to introduce the concept of force. For the convenience of reasoning and arguing, however, we do label certain terms as force densities: in the differential equations, boundary conditions, or the solution under consideration. As a result, these forces depend on the context and geometry – take the form of the airfoil and the associated lift.

Circumstances are similar in the hydrodynamic theory of ponderable systems, and there is just as little reason to expect the existence of a unique electromagnetic force that is independent from geometry and context. But we do also need the concept of force: Physics does not comprise solely of mathematics, and clear thinking about the valid expressions for the electromagnetic force under given conditions will give us considerable heuristic power in prediction — without having to solve the set of partial differential equations each and every time. A simple question about the deflection of a pendulum in response to a field should be answerable by considering an elementary force equilibrium, between the strain in the string, the gravitational and the electromagnetic force. Solving the hydrodynamic theory with appropriate boundary conditions, the magnetic force is found to be[1]

$$\mathcal{F} = \tfrac{1}{2} \oint [\mu_0 \chi H_t^2 + \chi B_n^2/(1+\chi)\mu_0] \, \mathrm{d}\mathbf{A}, \tag{1}$$

where the surface integral is to be taken over the surface of the magnetizable body. The subscripts t and n denote the tangential and normal field component with respect to the surface. As the above fields are continuous across the interface, they may be both the external or the internal field. Eq (1) is rather generally valid, it holds irrespective of χ's size, or of its dependency on the density ρ_1 of magnetic particles in ferrofluids; it is also easily generalized for nonlinear constitutive relations, though equilibrium is an essential requirement.

Employing the Gauss law, and provided χ is spatially constant, with $M = \chi H = \chi B/\mu_0(1+\chi)$, we may rewrite Eq (1) as a volume integral,

$$\mathcal{F} = \int (\mu_0 M_t \boldsymbol{\nabla} H_t + M_n \boldsymbol{\nabla} B_n) \, \mathrm{d}^3 r. \tag{2}$$

If the field is normal to the surface, the first term vanishes, and $\mathcal{F} = \int M_i \boldsymbol{\nabla} B_i \, \mathrm{d}^3 r$ is retrieved; if the field is tangential to the surface, the Kelvin form $\mathcal{F} = \int \mu_0 M_i \boldsymbol{\nabla} H_i \, \mathrm{d}^3 r$ holds.

(1)*Mario Liu and Klaus Stierstadt, submitted*