Max-Planck-Institut für Polymerforschung

Max Planck Institute for Polymer Research

BOOK of ABSTRACTS

8th German Ferrofluid Workshop MPI für Polymerforschung, Mainz

May 7-9, 2008

FIAS Frankfurt Institute for Advanced Studies

WEDNESDAY 7 MAY, 2008

12:30 *Registration*

13:00 - 13:40 **S. Odenbach** *"Yield stress in ferrofluids!?"*
13:40 - 14:05 D. Heinrich *"Time dependent NMR spectroscopy on ionic ferrofluids"*
14:05 - 14:30 R. Hentschke *"Gas-liquid phase behavior of dipolar fluids and beyond"*

14:30 - 15:20 *Coffee Break*

15:20 - 16:00 **P. J. Camp** *"Phase separation in model ferrofluids"*
16:00 - 16:25 E. Prinz *"Biomedical functionalization of magnetic nanoparticles"*
16:25 - 16:50 S. Beresnev *"Numerical study of the influence of diffusion of magnetic particle equilibrium shapes of a free magnetic fluid surface"*
16:50 - 17:15 G. Auernhammer *"Shear-induced structural changes in magnetic nanoparticle aggregates followed by x-ray microscopy"*

17:30 *Departure Excursion (Bus)*

18:00 - 20:00 *Excursion Kupferberg Sektkellerei*

THURSDAY 8 MAY, 2008

9:00 - 9:40 **Q. Pankhurst** *"Biomedical Applications of Magnetic Nanoparticles and Fluids"*
9:40 - 10:05 T. Friedrich *"Transport of ferrofluid due to traveling-stripe forcing"*
10:05 - 10:30 J. Cerda *"Structure formation and phase behavior in bidisperse ferrofluid monolayers-I: simulations"*

10:30 - 11:00 *Coffee Break*

11:00 - 11:40 **P. Martinoty** *"Mechanical properties of uniaxial magnetic gels"*
11:40 - 12:05 S. Klapp *"Field-induced and spontaneous structure formation in ferrofluid multilayer films"*
12:05 - 12:30 E. Heim *"Investigation of binding assays with streptavidin functionalized superparamagnetic nanoparticles and biotinylated analytes by fluxgate magnetorelaxometry"*

12:30 - 13:30 *Lunch (at conference site)*

13:30 - 14:10 **R. Perzynski** *"Vitreous transitions in a dense ferrofluid!"*
14:10 - 14:35 A. Erbe *"Frustration-induced magic number clusters of colloidal magnetic particles"*
14:35 - 15:00 A. Schmidt *"Magnetoactive liquid crystal elastomers"*
15:00 - 15:25 A. Ivanov *"Theoretical modeling of structure factor of ferrofluid under a magnetic field"*

15:30 - 16:00 *Coffee Break*

16:00 - 16:40 **Yu. Raikher** *"Field-induced behavior of fine magnetic particles embedded in polymeric matrices: some aspects"*
16:40 - 17:05 T. Kroll *"Nanoparticle driven imatinib delivery into cells with gold coated iron oxide particles"*

17:05 - 17:30 F. Ludwig *"Characterization of magnetic core shell nanoparticles - a comparative study"*
17:30 - 17:55 C. Gollwitzer *"The Rosensweig instability with a ferrogel"*

18:00 *Dinner (at conference site)*

19:00 - 21:00 *Poster Session*

FRIDAY 9 MAY, 2008

9:00 - 9:40 **J. Bibette** *"Experiments on self assemblies of magnetic colloids"*
9:40 - 10:05 H. Engler *"Investigation of the thermomagnetic convection in ferrofluid influenced by a time-modulated driving force"*
10:05 - 10:30 J. Wagner *"Magnetic nanorods in external fields"*

10:30 - 11:00 *Coffee Break*

11:00 - 11:40 **M. Zrinyi** *"From ferrofluids to ferrogels"*
11:40 - 12:05 V. Kancharla *"Fabrication and characterization of magnetorheological fluids for reconfigurable fixturing systems"*
12:05 - 12:30 B. H. Erne *"Microspheres with a Switchable Magnetic Remanence"*

12:30 - 12:45 *Closing Remarks*

WEDNESDAY, 7 MAY

Yield stress in ferrofluids!?

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It is well known, that the interparticle interaction between magnetic particles in a ferrofluid leads to strong changes in their rheological behavior. These changes are usually attributed to the formation of structures formed by the particles.
On the other hand magnetorheological (MR) fluids, containing micron sized magnetic particles with significantly higher interparticle interaction, are known to exhibit a strong yield stress forced by such structure formation of particles.
For ferrofluids the flow behavior at small shear rates, and in particular the question whether they show a yield stress is difficult to be clarified since the effects are orders of magnitude smaller than those in MR fluids. Therefore a specialized stress controlled rheometer has been build to enable an experimental clarification of this question. It could be shown that ferrofluids exhibit a field dependent yield stress which depends strongly on the microscopic make up of the fluids. Following this basic clarification various characteristics of the yield stress in ferrofluids have been investigated leading to a simple model for the description of the observed effects.
Within the talk the experimental techniques, the rheological findings for differently composed ferrofluids as well as the model describing them will be presented. In particular the prospects for future experiments need to shed a light on the physical meaning of the free parameters of the model will be discussed.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft under grant OD18/8 is gratefully acknowledged.

Time dependent NMR spectroscopy on ionic ferrofluids

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Magnetic nanoparticles colloidally suspended in a ferrofluid exhibit a tendency to form clusters and chain-like structures under the influence of an external magnetic field; an effect which in the past years has been extensively studied theoretically [1-3] as well as experimentally [4-7]. Recently we used Raman spectroscopy to monitor the metastable cluster formation and its dynamics in surfacted and ionic ferrofluids [5-7]. In this work we present results of a complementary study of the magnetic-field induced behavior of a water-based ionic ferrofluid (IFF) with a concentration of 1 vol.% using nuclear magnetic resonance (NMR) spectroscopy. For the measurements we used a low-resolution NMR spectrometer working at room temperature with an homogenous magnetic field of 400 mT.

In the experiments, an electrostatically stabilized ferrofluid which has not been exposed previously to any magnetic field is placed at 300 K in the bore of the NMR spectrometer. The NMR spectrum displays an asymmetric feature which is composed by two peaks of different intensity (Fig.1). The main peak is blue-shifted by approximately 17 kHz from the resonance frequency of "pure and free" water molecules [8]. The less intense peak appears to be centered at around 3 kHz above the pure water frequency. Both peaks are attributed to two different dynamic environments of water molecules in the ferrofluid [8], namely, molecules moving freely within the volume among the magnetic particles but far from them (3 kHz feature) and molecules from the solvation layers close around the magnetic grains (17 kHz structure). Clustering occurring in presence of an external magnetic field would manifest itself in shifts and change in intensity of the NMR features.

Figure 2 shows the time evolution of the peak amplitude of both peaks in a time scale of more than one hour. The amplitude of the NMR signal of the 17 kHz feature exhibits a slight increase in the first 300 s followed by a strong reduction in intensity, reaching its minimum after approximately 15 min. Simultaneously, the amplitude of the 3 kHz peak corresponding to the NMR signal stemming from water molecules far from the magnetic nanoparticles increases monotonically, saturating at times longer than one hour. This contrasting behavior of both NMR signals is readily understood by considering the dynamical processes within the ferrofluid triggered by an external magnetic field, as revealed by Raman spectroscopy [7]. The exponential decay of the amplitude of the 17 kHz feature is, thus, attributed to the field-induced clustering of the magnetic nanograins to form chain-like structures. As a result, the amount of water molecules in a salvation layer around the structures which are building up continuously decreases, leading to the observed reduction in peak intensity. In fact, a characteristic time constant of (150 ± 10) s is obtained for this decay, which is in very good agreement with the clustering times measured with Raman on the same IFF sample [7]. On the contrary, the much slower increase in amplitude of the 3 kHz

feature corresponding to water molecules far from the grains is taken as evidence of a sluggish long-ranged ordering of the chained structures with respect to each other, resulting in a sort of *superstructure* of the IFF in the homogeneous magnetic field of the NMR spectrometer. The characteristic time for this ordering obtained from a fit to the data points is (440 ± 50) s.

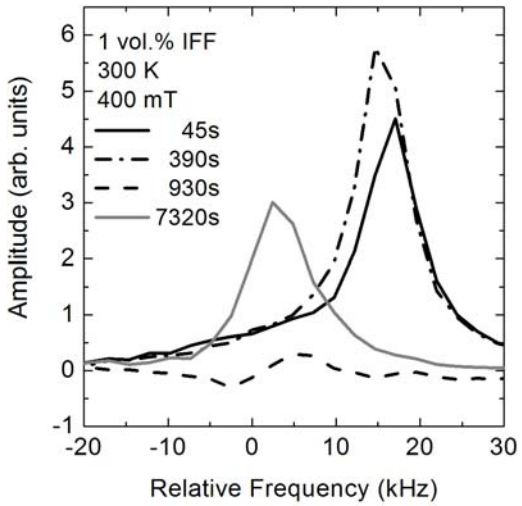

Fig.1 NMR spectra of an ionic ferrofluid at different times in a magnetic field of 400 mT.

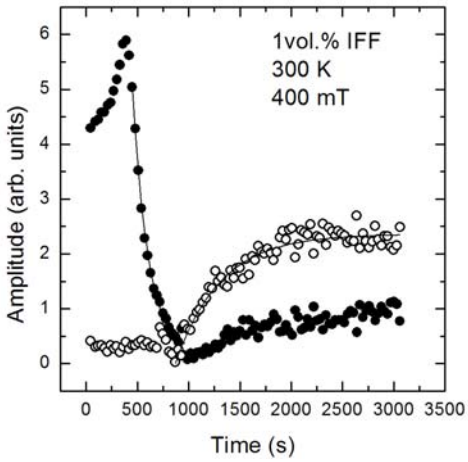

Fig.2 Time evolution of the amplitude of the 17 kHz (solid points) and the 3 kHz (open symbols) NMR peaks. Lines are fits using simple exponential functions.

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Gas-Liquid Phase Behavior of Dipolar Fluids and Beyond

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We discuss the phase behavior of two dipolar fluid models, the Stockmayer potential and a modification thereof with tunable orientation anisotropy of the dispersion attraction, mainly on the basis of recent Molecular Dynamics computer simulations [1, 2, 3, 4].
In the Stockmayer fluid we do not observe the disappearance of the isotropic gas-isotropic liquid coexistence at high dipole strength contrary to earlier findings based on Monte Carlo techniques. Even though the formation of reversible dipole chains strongly affects the location of the critical point, it does not lead to its disappearance. In addition to the simulation results we present a theory explaining the dependence of the gas-liquid critical point in the Stockmayer fluid on dipole strength. The theory is based on the Flory-Huggins lattice description for polymer systems in conjunction with a transfer matrix model for isolated chains of reversibly assembled dipolar particles. We find that the shift of the critical point as function of dipole strength, also observed in computer simulations, strongly resembles the critical point shift as function of chain length in ordinary linear polymer systems. In particular the decrease of the critical density with increasing dipole strength is a consequence of the existence of reversible chains near criticality. We also discuss the implication of our results on the question of existence or non-existence of a gas-liquid critical point at finite temperature and density in systems of dipolar soft spheres [5].
The second model, a coarse-grained molecular model for self-assembling semiflexible equilibrium polymers, is studied via Monte Carlo and Molecular Dynamics simulation in two and three dimensions. Here we investigate the transfer from ordinary gas-liquid coexistence to the appearance of liquid crystallinity driven by excluded volume interaction between rod-like aggregates. This is different from the isotropic liquid-to-ferroelectric liquid transition observed in the Stockmayer system. The transfer between the two types of phase behavior is governed by a tunable anisotropic attractive interaction between monomer particles. In two dimensions we observe additional network structures competing with nematic and columnar ordering. The interesting relation to dipolar fluid models like the Stockmayer fluid is discussed.

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Phase separation in model ferrofluids

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In 1970 de Gennes and Pincus studied theoretically the structural characteristics of strongly interacting ferrocolloids [1]. The primary focus was the formation of chain-like aggregates, stabilised by the 'nose-to-tail' conformation of the dipoles on neighbouring particles; see Figure 1. The following statement appears in Ref. [1].

Independently of the details of the magnetic arrangement, there is a significant attractive energy of magnetic origin (of order μ^2/a^3 *per* [colloidal particle] *at low temperatures) stabilizing the dense phase. Thus, on the whole, we expect in 0 field a mechanical phase diagram somewhat similar to that of a conventional Van der Vaals fluid, with a gas phase, a liquid phase and a solid phase.*

To determine the phase diagram of dipolar particles is, at first glance, a straightforward problem in statistical mechanics. But unfortunately, the nature and extent of particle aggregation greatly reduces the differences in enthalpy and entropy between dilute and dense phases; hence, the transition is expected to have a very small latent heat and be quite 'weak'. During the 1990s, computer simulations of simple ferrofluid models (such as the dipolar hard sphere fluid [2] and the Stockmayer fluid [3]) indicated that, under certain conditions, phase separation is preempted, and possibly precluded, by the strong association of particles to form chains. There are, however, several technical aspects of these simulation studies that may lead to the wrong conclusions.

In 2000, Tlusty and Safran proposed a defect-mediated theory for phase separation in which dilute and dense phases are distinguished by the connectedness of the chains [4]. In this scenario, the dilute phase is characterised by chain segments with 'dangling bonds' at each end of a chain, while the dense phase is described in terms of a branched, percolating network. Tlusty and Safran's work has reinvigorated the search for a phase transition in dipolar fluids.

In this contribution, I will present the results of recent simulation work in which advanced multicanonical and Wang-Landau Monte Carlo techniques were employed. The simulation methodologies obviate some of the problems associated with earlier simulation work. We have studied

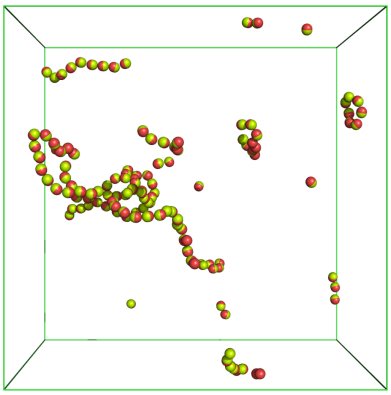

Figure 1: Snapshot of dipolar hard spheres in the dilute phase near coexistence, showing chain-like clusters (and one ring-like cluster).

both the dipolar hard sphere [5] and Stockmayer systems [6], and in each case, the results point towards the existence of a 'dipolar' phase separation. Appropriate comparisons between the two types of system [6, 7, 8] demonstrate consistency, and help strengthen this central conclusion.

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Biomedical Functionalisation of Magnetic Nanoparticles

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Biocompatible ferrites with the chemical composition $Mn_{0,8}Zn_{0,2}Fe_2O_4$ (diameter of the order 10-15 nm) are synthesized by the co-precipitation method. For application in biological organisms, these magnetic nanoparticles have been functionalised with the polysaccharide dextran. As a model chemotherapeutic drug doxorubicin, due to its auto fluorescence, has subsequently been bonded to the particles in two different ways. The first method is based on the synthesis of polyaldehyde dextran and the subsequent attachment of doxorubicin by its primary amine group. The second way is the synthesis of carboxymethyl dextran (CM-dextran). The attachment of doxorubicin to carboxymethyl dextran leads to a peptide bond with the primary amine group. Characterisation of the ferrite nanoparticles as prepared, functionalized with dextran, and additionally functionalized with doxorubicin was done by X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering (DLS), Zeta potential measurements, FTIR-, UV/VIS- and fluorescence spectroscopy, respectively.

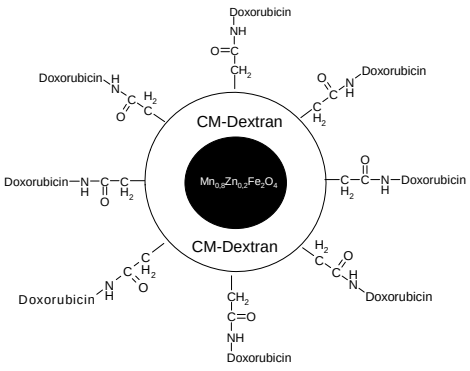

Fig. 1: Schematic illustration of doxorubicin-CM-dextran-coated nanoparticles

The so modified particles are intended to be used in adoptive cancer immunotherapy, a new approach where immune cells, especially T lymphocytes, will be exploited as autonomous drug delivery systems with high target specifity.

Therefore, the uptake efficiency of the modified ferrite particles into T lymphocytes was verified by fluorescence and confocal microscopy.
The functionality of the drug attached to the particles and internalized into cells was further characterised. Thus, among others, the cytotoxic effect evoked on T lymphocytes was determined as well as drug release kinetics monitored.

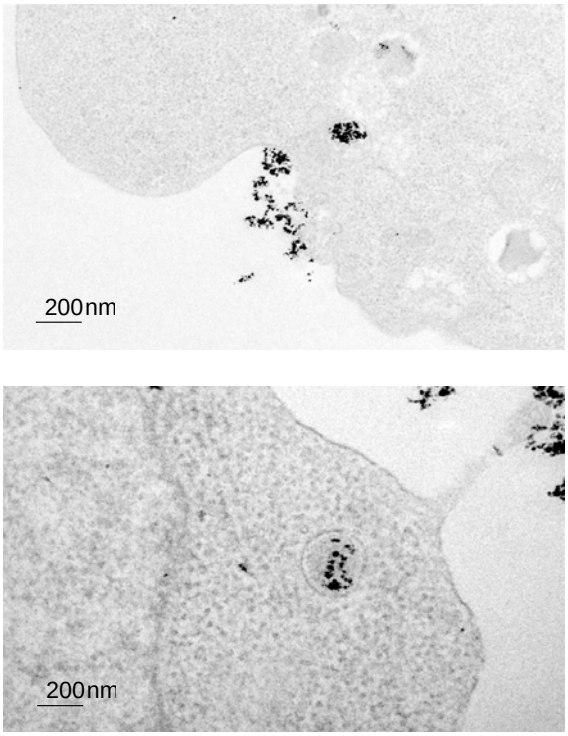

Fig. 2: TEM images of synthesized particles in T lymphocytes

Numerical Study of the Influence of Diffusion of Magnetic Particles Equilibrium Shapes of a Free Magnetic Fluid Surface

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Owing to the fact that the particle possess magnetic properties, not only Brownian motion but also a magnetophoresis diffusion process takes place in magnetic fluid [1,3]. The aim of our work is the investigation of the influence of the diffusion process on equilibrium free magnetic-fluid surface shapes.

We consider in particular the classical ferrohydrostatics problem on doubly-connected equilibrium shapes of a magnetic fluid located on a horizontal plate around a vertical cylindrical conductor with a direct current [1,2,4].

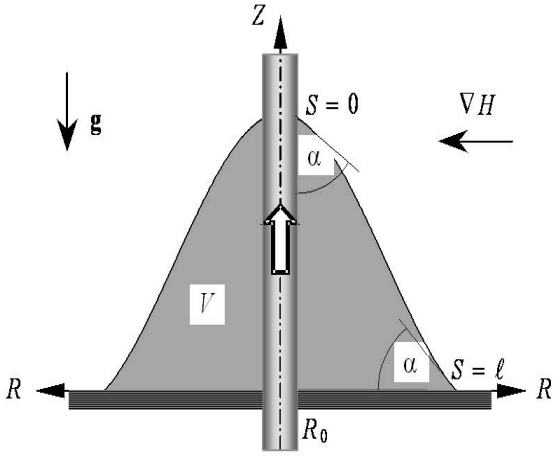

Fig1. Geometry of the problem

Assuming a linear magnetization law and neglecting the capillary pressure jump on the surface, the problem has been solved analytically, see [1,2]. A numerical solution for the more detailed problem of taking both the capillary jump but also the (nonlinear) Langevin's magnetization law into consideration, is given in [4]. However it should be emphasized that the simplest theoretical models studied in [1,2] and the more advanced in [4] are both based on the assumption of homogeneity of the magnetic fluid, i.e. the effect of magnetophoresis of ferromagnetic particles in the fluid has been completely neglected.

Our model is based on the Langevin's magnetization law for non-uniformly concentrated magnetic fluid defined in [1] as

$$M = M_S L(\xi H) C$$

where H is the magnetic field intensity, C the relative concentration of the particles in the magnetic fluid, M_S the magnetic-fluid saturation magnetization, L the Langevin function, and ξ a constant. It is shown in [6] that the steady-state concentration problem admits an analytical solution

$$C = \lambda \sinh(\xi H)/(\xi H)$$

with a constant λ depending on the shape of the fluid volume. The free surface is computed by starting with a uniform concentration field $C = C_0$ and solving the Young-Laplace equation to get an initial shape of fluid volume. Then, iteratively the concentration field for a known fluid volume and the free surface shape for a given concentration field are updated iteratively.

For solving the Young Laplace equation we use the finite difference and the tangential method, respectively, described in [7] on a uniform mesh size with 4000 grid points.

The numerical results, see Fig.2, show that the diffusion of ferromagnetic particles in a magnetic fluid under the action of a non-uniform magnetic field greatly influences the free magnetic-fluid surface shape. The attachment point of the fluid at the conductor is about two times higher for a nonuniform concentration in comparision to a uniform distribution of particles.

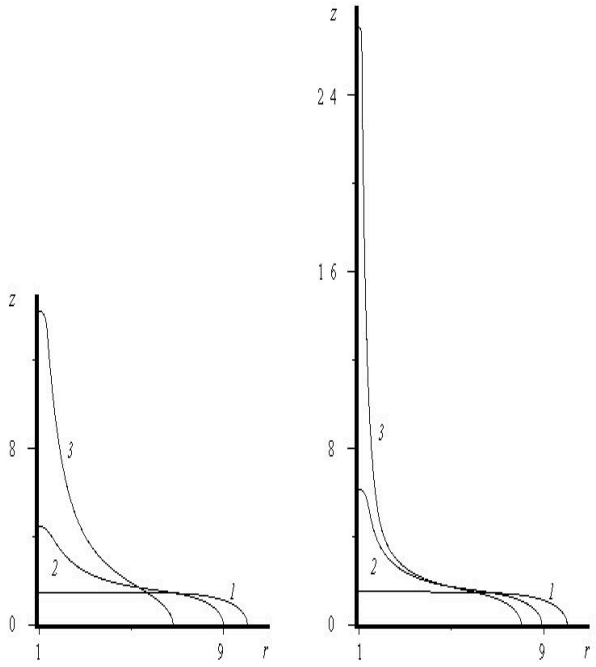

Fig2. Free surface shapes at current intensity. Uniform particle concentration (left) and nonuniform particle concentration (right).

Parameter studies demonstrate that in high gradient fields large differences appear, both qualitatively and quantitatively. As a consequence, the approximation by a uniform particle concentration, used often in the applications, seems to be applicable only on ferrohydrostatic problems with nearly uniform magnetic fields.

Acknowledgments

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Shear-induced structural changes in magnetic nanoparticle aggregates followed by x-ray microscopy

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X-ray microscopy is an imaging technique which allows for a spatial resolution below 35 nm. Can it also be used to investigate shear-induced structural dynamics? We accomplished this by inserting a piezo actuator-driven shear cell into the focal plane of the x-ray microscope.
To demonstrate the possibilities of this novel device, we investigate shear-induced reorganization of 50 nm sized magnetite particles embedded in a polymer melt. We find two contributions to the reorganization of these particle aggregates. While applying large amplitude oscillatory shear, the aggregates strongly move and reorganize. After stopping the shear, a slow reorganization persists over several minutes.
The high electron density of the iron containing colloids, allows measuring with a low X-ray dose and thus repeated imaging of the same region without significant changes due to beam damage. We compare our results to experiments with non-magnetic colloids.

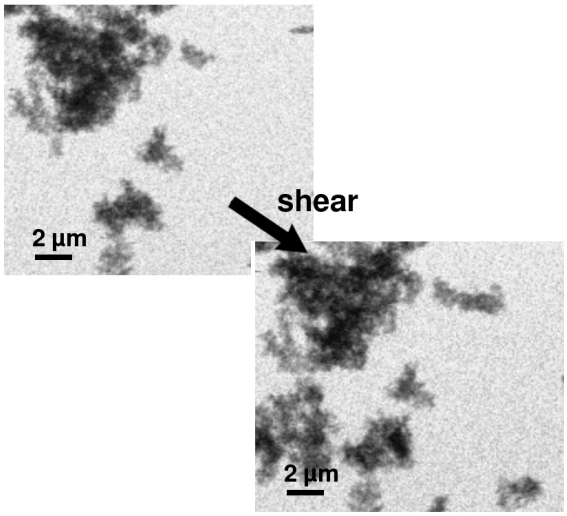

Figure 1: Shear-induced reorganization of colloidal aggregates.

THURSDAY, 8 MAY

Biomedical Applications of Magnetic Nanoparticles and Fluids

Quentin Pankhurst

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The emerging field of 'endomagnetics' – the sensing, moving and heating of magnetic nanoparticles in the human body for diagnostic and therapeutic purposes - will be reviewed. Examples will be given for each of the modalities: ***Sensing:*** A high-Tc SQUID based sensor system, with a room temperature hand-held probe, designed for use in a hospital operating theatre to detect breast cancer sentinel lymph nodes (Figure 1). The system is currently being evaluated in patients, and has been used successfully in seven operations.

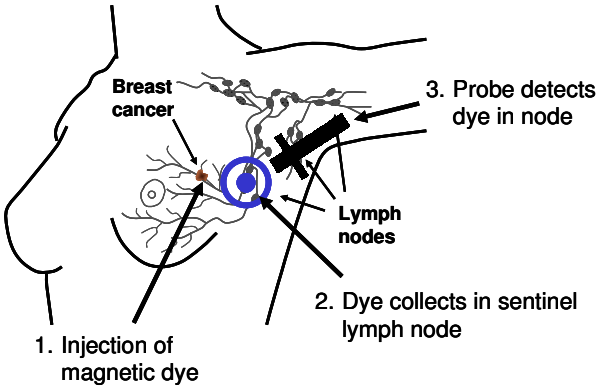

Figure 1: An intra-operative medical device for breast cancer surgery which uses a high-sensitivity, high-T_c SQUID based probe.

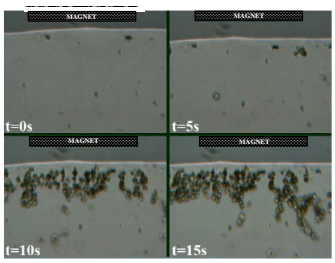

Figure 2: Actuation of magnetically labelled CD133 stem cells.

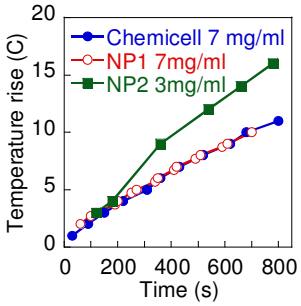

Figure 3: Magnetic heating of magnetite/maghemite nanoparticles in a 140 Oe field at 138 kHz.

Moving: A high field-gradient magnetic actuator designed to capture magnetic nanoparticle loaded haematopoetic stem cells for the treatment of atherosclerosis. Bench-top (Figure 2) and animal trials are under way to establish the efficacy of such a therapy, with promising results. ***Heating:*** Magnetic field hyperthermia treatment for superficial and, as a long term goal, metastatic cancer, using antibody-targeted magnetic nanoparticles. Work is progressing on several fronts: the synthesis of improved magnetic particles for heat transduction (Figure 3), the engineering of new high-frequency drive circuits to produce rf fields in controlled geometries, and cell and animal studies of antibody-nanoparticle conjugation and tumour targeting.

Transport of ferrofluid due to travelling-stripe forcing

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Introduction

Transport of a ferrofluid has been achieved by rotating [1], but also by travelling magnetic fields [2, 3]. As described in [4] the surface of a magnetic liquid shows quite a number of phenomena in the vicinity of the Rosensweig instability [5, 6]. We found, that forcing by an undercritical spatiotemporally modulated magnetic induction does not just cause surface-waves to travel along the fluids surface, but also shows a transport of the liquid. For high subcritical magnetic fields the increase of the forcing frequency can lead the fluid to form rosensweig cusps in different patterns. A further increase of the magnetic field strength up to the subsequent overcritical regime changes the spectrum of surfacepatterns, and therefore also the effect of locomotion.

Experimental Setup

In order to measure the transport of ferrofluid we capture the surface profile of the fluid by means of X-ray imaging [7] (see Fig. 1) while the iron rods within the conveyor belt impress a travelling sinusoidal modulation to the magnetic field. The wavevector $\vec{k}$ of the travelling magnetic-field-wave is given by the distance between the iron rods in the belt, while the frequency ω can be adjusted by controlling the driving speed of the motor via a computerinterface. This way the magnetic induction can be assumed to be

$$\vec{B}(x,t) = \vec{B_0}\left(1 + \alpha e^{i\left(\omega t - \vec{k}\vec{x}\right)}\right)$$

for $\alpha \approx \frac{1}{20}$.

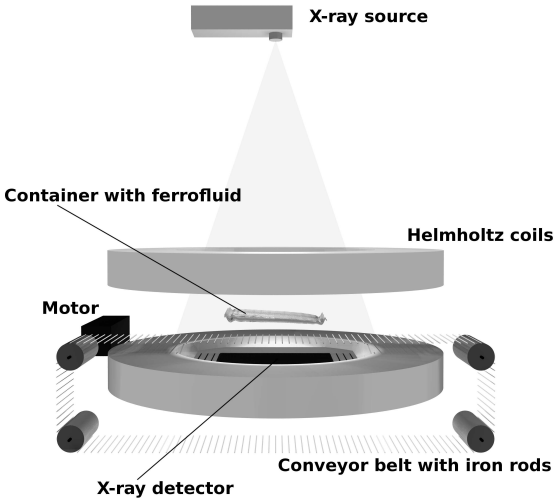

Figure 1: X-ray setup

Experimental Results

In order to get a value for the amount of pumping that occurs in this special (rectangular) geometry we will introduce the angle of surface inclination between the two averaged surface profiles for driving the belt either forward or backward as shown in Fig. 2.
By repeating this process, we obtain a series of angels for varying driving frequencies and magnetic field-strengths (see Fig. 3). For varied driving frequency the surface forms different structures including different patterns of Rosensweig

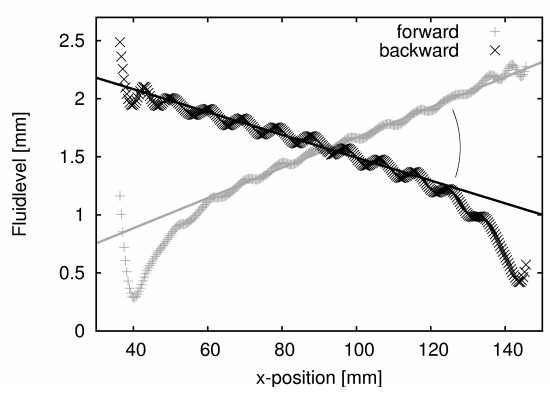

Figure 2: Angle of surface inclination

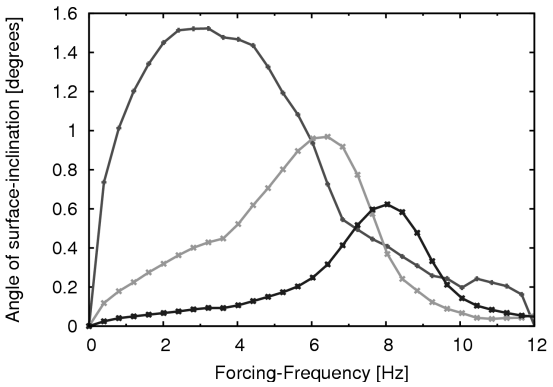

Figure 3: Angle of surface inclination as a function of driving frequency for different magnetic inductions

cusps which have a strong influence on the pumping-effect. A change of the magnetic field shifts the frequency ranges for different surface-patterns or even suppresses some of them. We discuss the results in terms of [8].

Further Issues

If you are interested in more details and nice pictures, see me at the workshop...

Acknowledgments
We thank our great mechanician Klaus Oetter for all the technical assistance with the setup.

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Structure formation and phase behaviour in bidisperse ferrofluid monolayers - I : simulations.

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Molecular dynamics (MD) is used to study thoroughly the mircrostructure formation of bidisperse ferrofluid monolayers. Long-range dipolar interactions are computed using a recently developed dipolar-P3M-layer correction algorithm. In comparison to the traditional Ewald sum methods, this approach allows to handle and characterize larger systems. An extensive comparison with theoretical density functional theory, and experimental results from in situ cryogenic tansmission electron microscopy [1] will be also presented. The effects induced by the presence of external fields applied to the ferrofluid monolayers are also studied in detail.

Acknowledgments

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Mechanical properties of uniaxial magnetic gels

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We study the formation kinetics and the mechanical response of uniaxial magnetic gels submitted to a sinusoidal shear deformation. These materials are composed of magnetic particles embedded in a polymeric network and aligned along the magnetic field direction during the growing of the gel. They react not only to magnetic field gradients, like the isotropic magnetic gels, but also to homogeneous magnetic fields. This study was carried out using a piezoelectric rheometer we have recently developed. This apparatus enables to take measurements of the complex shear modulus in a wide frequency range (from ~ 0.1 Hz to ~ 10 kHz), and, thanks to the very weak strains applied to the sample (~ 10^{-4}), to follow a gelation mechanism without perturbing it. As a result of its small size, the measuring cell was placed in the air-gap of an electromagnet to follow the kinetics of formation of the gel, and, after the gel formation, under the objective of an optical microscope to determine the organization of the magnetic particles. For all the samples studied, the compound was introduced in the measuring cell in the sol phase and the gel was formed in situ. The experiments were performed without the magnetic field (isotropic gel), or with a magnetic field oriented in a direction parallel or perpendicular to the shear (uniaxial gel). Two types of uniaxial magnetic gel were studied. An aqueous gel using a commercial ferrofluid, and an organic gel containing magnetite particles. The similarities and the differences between the mechanical behaviors observed for the two gels will be discussed.

Field-induced and spontaneous structure formation in ferrofluid multilayer films

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Using computer simulations (Monte Carlo and Molecular Dynamics) we investigate the structure formation and phase behavior of ferrofluids confined to film-like geometries. The ferrofluids are modelled as monodisperse dipolar soft spheres with diameters σ and dipolar coupling strengths $\lambda = \mu^2/k_BT\sigma^3$ (with μ and T being the magnitude of the dipole moment and the temperature, respectively).

Confinement alone induces a layering of the particles combined with a preferred in-plane orientation of the dipole moments already at moderate coupling strengths ($\lambda \approx 3$) [1, 2]. We find that both the translational and the orientational microstructure in the resulting ferrofluid multilayer films is strongly influenced by homogeneous external magnetic fields [3]. In particular, for suitable film thicknesses strong fields directed perpendicular to the film plane do not only orient the particles, but also generate an additional layer in the system, combined with structural rearrangements within the layers (see Figure 1). In the limiting case of only one surface we find an field-induced smectic-like ordering, in agreement with recent experiments of ferrofluids at surfaces [4]. For confined films, the reverse effect occurs with an in-plane field which can actually reduce the number of layers.

We also discuss the case of strong dipolar coupling ($\lambda \approx 7$) where the bulk ferrofluid and corresponding films of mesoscopic thicknesses [1] display spontaneous ferromagnetic ordering. We demonstrate that the ordering persists down to nanoscopic wall separations where the system consists of only three monolayers. For smaller thicknesses we observe stripe-like defects (domains) and finally the breakdown of ferromagnetic ordering for systems close to the two-dimensional limit [5].

Acknowledgments
We gratefully acknowledge financial support via the Emmy-Noether-Programme and the Sonderforschungsbereich 448 "Mesoscopically structured composites" (project B6).

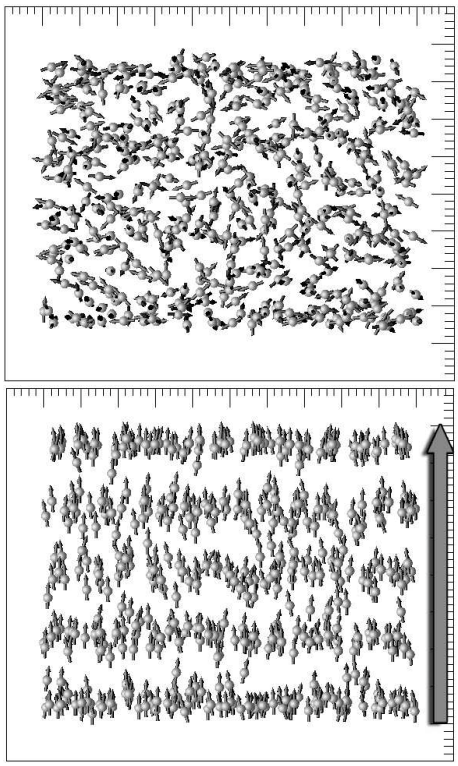

Figure 1: Snapshots of a confined ferrofluid system in the absence (top) and presence (bottom) of a strong vertical magnetic field (thick arrow). The magnetic dipole moments in the (spherical) particles are represented by small arrows.

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Investigation of binding assays with streptavidin functionalized superparamagnetic nanoparticles and biotinylated analytes by fluxgate magnetorelaxometry

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Introduction

Magnetorelaxometry (MRX) has been introduced using superconducting quantum interference devices (SQUIDs) [1]. In our measurement system we use a differential fluxgate arrangement to measure the magnetic stray field of a sample at room temperature [2]. MRX was proposed to perform magnetic relaxation immunoassays [3]. In this work we present binding measurements of streptavidin coated magnetic nanoparticles and two types of biotinylated analytes which essentially differ in size. To quantify the different assay results we discuss different analysis methods.

Materials

For all experiments we use the specific streptavidin and biotin binding system which is one of the strongest non-covalent binding known. As magnetic markers we use fluidMAG/BC-Streptavidin nanoparticles (MNP-StAv) produced by chemicell GmbH. The two analytes are biotinylated agarose beads (~5µm diameter) and biotinylated BSA proteins (~6nm diameter) and were obtained from Sigma-Aldrich Co..

Method

In a MRX experiment the sample is magnetized by a magnetic field in the order of 2mT for about 2 seconds. After switching off the magnetizing field, the stray field of the MNPs relaxes either via the Brownian or Néel relaxation mechanism. The Brownion relaxation takes place due to particle rotation and in case of Néel relaxation the inner magnetic moment of the particle rotates. In the former case the relaxation behavior of a polydisperse ensemble can be phenomenologically described by [4,5]

$$B_{Brown}(t) = B_{off,B} + B_{0,Brown} \cdot \exp\left(-\left(\frac{t}{\tau_B}\right)^{\beta}\right) \quad (1)$$

and in the latter case by [4,5]

$$B_{Néel}(t) = B_{off,N} + B_{0,Néel} \cdot \ln\left(1+\frac{\tau_N}{t}\right). \quad (2)$$

Here $B_{0,Brown}$ and $B_{0,Néel}$ are measures for the content of MNPs relaxing via the Brownian and Néel mechanism, respectively. The quantities τ_B, β, τ_N are characteristic for a given ferrofluid and should not depend on MNP concentration. They can be determined from aqueous and freeze-dried reference samples.

Experiments and Discussions

In the first experiment 6 samples were prepared each with 19 pmol of MNP-StAv and an increasing amount of washed biotinylated agarose beads ranging from 40 µL to 140 µL. The MNP-StAv were bound to the big agarose beads and were instantly immobilized switching their relaxation behavior from Brownian to Néel type. This situation can be perfectly analyzed by fitting the superposition of (1) and (2) to the relaxation curves. In Fig. 1 the fraction of immobilized MNPs vs. the agarose bead content is depicted calculated from $B_{0,Néel}$ refered to the value of a freeze-dried reference sample. In addition, the curves were fitted with different numbers of fixed parameters determined from reference samples showing that only knowing the charac-

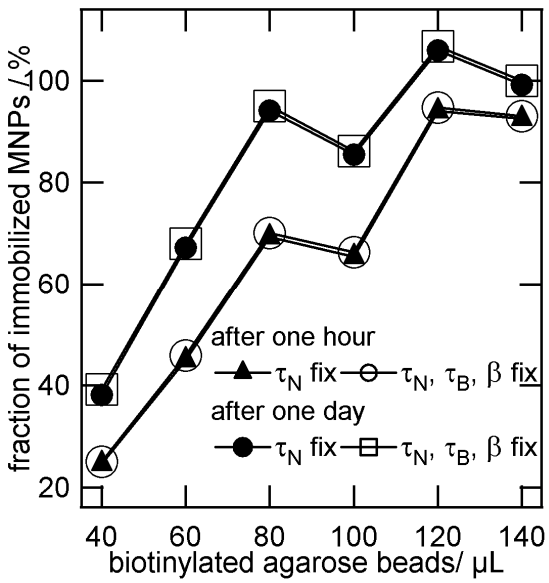

Fig. 1: Evolution of the immobilization of 6 samples with 19 pmol immobilized streptavidin functionalized MNPs and increasing amount of biotinylated agarose beads.

teristic parameter τ_N is sufficient to accurately quantify the $B_{0,Néel}$ values. At a content of 120 µL agarose beads all MNP-StAv are bound. The reaction is not finished after one hour because of the long diffusion time of the reactants.

For the second experiment 9 samples were prepared each with 19 pmol of MNP-StAv and an increasing amount of biotinylated BSA protein ranging from 2.1 nmol to 10.7 nmol. Here the BSA protein acts as a linker that cross-links the MNP-StAv. The formation of clusters of different sizes takes place during the cross-linking process. As a consequence, the analysis of the relaxation curves with a superposition is not feasible. For a simple analysis the area under the relaxation curves was calculated and related to the area of the immobilized reference sample. The size of the area is a measure of the cluster size and thus for the cross-linked MNP-StAv. Fig. 2 shows the evolution of the cross-linking state. By increasing the amount of BSA linkers the cross-linking has a maximum at 4.3-5.3 nmol of biotinylated BSA. By further increasing the BSA linker concentrations the cross-linking decreases again.

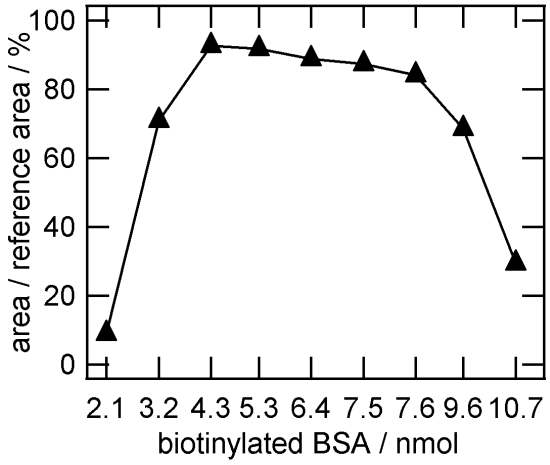

Fig. 2: Evolution of the cross-linking state of 9 samples with 19 pmol streptavidin functionalized MNPs and increasing amount of biotinylated BSA.

This is due to the occupation of all binding sites of the MNP-StAv by the BSA linker. The curve from Fig. 2 can be used as a calibration curve to analyze an unknown amount of biotinylated BSA proteins.

Acknowledgments

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Vitreous transitions in a dense ferrofluid

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An experimental study of glass transitions in colloidal dispersions of charged and magnetic nanoparticles (ferrofluids) is presented here.

The colloidal glass transition, observed at high concentrations, leads to an amorphous solid state out of the thermodynamical equilibrium. The charged particles are then strongly interacting, in a potential where the electrostatic repulsion prevails. Thanks to the original properties of ferrofluids, the complete structural degrees of freedom of the particles are considered. Positional ones are probed using static and dynamic scattering techniques (X-rays and Neutrons). Glassy dynamics (non-diffusive, aging and intermittency) are reported at nanometric length-scales. When a magnetic field is applied, the structure of the dispersion becomes anisotropic, as well as the translational dynamics of the particles and its aging. The rotational dynamics of the nanoparticles are probed using magneto-induced birefringence measurements. The rotational dynamics drastically slow down above a volume fraction threshold, which depends on the intensity of the repulsion between nanoparticles. Its aging is studied on long time-scales. An effective age is introduced to unite aging properties at different concentrations.

At low temperatures, the frozen dispersion constitutes an assembly of disordered giant spins, which present some analogies with atomic spin glasses. Using SQUID magnetometry, we study the orientational dynamics of these superspins. We use a method borrowed from spin glasses to extract a dynamical correlation length between superspins; its size increases during the aging.

Frustration-induced magic number clusters of colloidal magnetic particles

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Colloidal particles can be used as model systems for a large variety of interactions. Superparamagnetic particles, for example, have been used to study the phase behavior of interacting particles in 2 dimensions. Antiferromagnetic interactions, on the other hand, cannot be investigated with these particles, because the direction of the magnetic moments of the particles is always parallel to their polarizing field. Particles with fixed magnetic moments are therefore interesting to study configurations, which arise due to antiferromagnetic interactions on various lattice geometries.

Here we report the formation of stable two-dimensional clusters consisting of long-range interacting colloidal particles with predefined magnetic moments. The symmetry and arrangement of the particles within the cluster is imposed by magnetic frustration, which arises because the particles are close packed on a triangular lattice. By satisfying the criteria of stability, a series of stable “magic number” clusters is formed. The stable clusters have compensated magnetic moment and chirality. Thus, the system can be regarded as a classical mesoscopic model for spin arrangements in two-dimensional triangular antiferromagnet, although the exact nature of the interactions between macroscopic magnetic moments is different.

Magnetoactive Liquid Crystal Elastomers

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Liquid crystal elastomers (LCEs) offer an interesting spectrum of properties, including temperature induced, fully reversible shape changes connected with considerable development of pulling force, and synthetic diversity. In order to take advantage of LCEs for an extended number of viable devices, it is desirable to trigger such shape changes with electromagnetic fields rather than temperature changes. In this work we present an access to magnetoactive LCEs by the incorporation of superparamagnetic Fe_3O_4 nanoparticles into oriented nematic side-chain LCEs and offer a contactless activation pathway to for the nematic-to-isotropic transition by local magnetic heating in external fields due to relaxational processes.

Magnetic Fe_3O_4 particles with an average core diameter of 12 nm are stabilized in toluene by surface-functionalization with N-oleylsarcosine and incorporated into nematic side-chain liquid crystal elastomers in situ during the hydrosilylation crosslinking reaction. In order to introduce nematic anisotropy, the slightly crosslinked LCE materials are loaded during the final crosslinking process at 70 °C. By this pathway, magnetoactive LCEs are accessible with particle contents up to 10 mass-%. Transmission electron microscopy (TEM) (Figure 1) reveals a homogeneous particle distribution, and we find no influence of the particles on the nematic-to-isotropic phase transition temperature T_{NI} found between 69 °C – 73 °C..

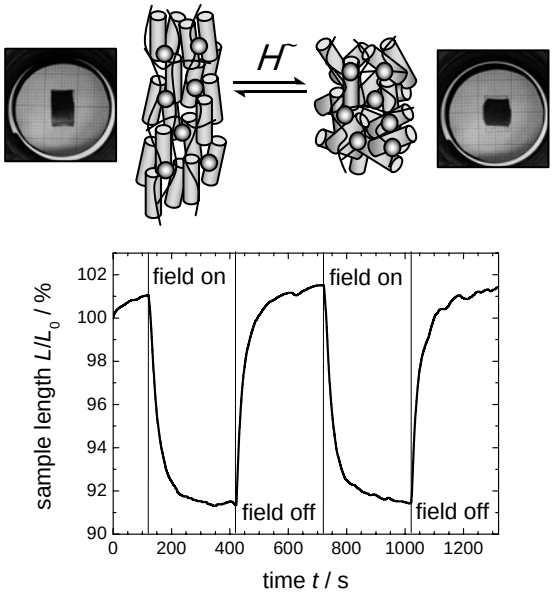

Figure 1: Length contraction in magnetoactive LCEs.

Mechanical properties of the samples in dependence of the temperature and in the presence of a electromagnetic field are investigated with in a tensile tester setup either equipped with a thermochamber, or an inductor coil coupled to a HF generator for the generation of the AC field. Under field influence, a sample contraction up to 27 % is observed, that is fully released when the field is switched off. The load evolved reaches 70 kPa and more.

The materials' ability to respond to a contactless electromagnetic stimulus with a well-defined contraction can be of use for various actuator applications.

Theoretical modeling of structure factor of ferrofluid under a magnetic field

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The structure of ferrofluid is investigated using SANS and SAXS methods. Intensity of scattering experimentally measured allows to obtaine the so-called structure factor, which is actually the Fourier transform of the pair correlation function of the ferroparticle system. The structure factor describes the contribution to scattering from microstructure correlations. A lot of works are known to be devoted to determination of structural factor for both ionic ferrofluids [1,2] and sterically stabilized magnetic fluids [3]. The fact that the structure factor of a magnetic fluid under external magnetic field can be anisotropic was demonstrated in experiments and computer simulations many times (e.g. [2]). Nonetheless, no theoretical or definitive physical explanation of this anisotropy has been given until now. This report is devoted to theoretical study of the structure factor of ferrofluids under a static magnetic field.

The ferrofluid is modeled as a system of monodisperse dipolar hard spheres containing the constant magnetic moment. Each ferroparticle *i* is characterized by a radius vector $\mathrm{r}_i(r_i,\theta_i,\varphi_i)$ and by a vector $\Omega_i(\omega_i,\varsigma_i)$, describing the orientation of its magnetic moment. The radial distribution function is calculated on the basis of a power series expansion in terms of the volume ferroparticle concentration. In this case the power-series coefficients correspond to virial coefficients. We consider the first-order approximation ($\sim\varphi$) of radial distribution function. The interparticle potential energy formed as a sum of hard-sphere repulsion $U_{hs}(i,j)$ and dipole-dipole interaction $U_d(i,j)$. Under external magnetic field it is nessesary to avarege $U_d(i,j)$ over all positions of the *i*th particle in the ferrofluid volume and over all orientations of the *i*th magnetic moment. Take into account foregoing model foundation the radial distribution function is gain. Then using Fourie transform of the theoretically predicted radial distribution function we get the structure factor.

Thus, the theoretical model describing influence of system parameters on ferrofluid structure factor is obtained. The anisotropy of structure factor under a magnetic field is observed.

Acknowledgments

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Field-induced behavior of fine magnetic particles embedded in polymeric matrices: some macroscopic and mesoscopic aspects

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Embedding of fine magnetic particles in polymeric matrices results in a wide variety of materials and systems. In this family the properties of one material differ greatly from those of another, but always a lot of new physics turns up and fascinating applicational prospects open.

In the talk only two species from this new "densely-populated" world would be discussed. As the first example we take the dispersions of fine particles in the matrices possessing equilibrium elasticity, i.e., in rubber or gel macromolecular networks. These materials are known as magnetorheological polymers, ferrogels and under a number of other names none of which nevertheless can describe exhaustively their specifics. We clarify physical mechanisms controlling the equilibrium field-induced behavior of those systems and present some successful attempts to predict the stress-strain effects under field. The problem is approached from two angles. One is continuum modeling where the material is treated as a uniform medium that is simultaneously elastically deformable and magnetizable; in this statement the particle volume distribution in the matrix is fixed and unchangeable. Field-induced shape changes of spheres, cylinders and membranes are considered for the cases of small and finite deformations.

In soft magnetic elastomers two notable effects are observed, however, which are essentially inexplicable in the continuum framework. Those are a large field-induced change of the elastic modulus and the magnetic shape memory effect. For their understanding the self-organization of the particles should be taken into account. This implies a two-phase model where the particles are able to move with respect to one another and to the matrix. Via appropriate numeric simulation one "gets hold" of the mechanisms of these effects which turn out to be strongly dependent on the particle concentration.

The second example to be presented concerns the theory of Brownian motion of a solid particle in a non-Newtonian fluid. The subject is closely connected to microrheology. We take two model types of matrices, viz. Maxwell (two-parameter) and Jeffreys (three-parameter), both of which lack equilibrium elasticity. Notably, if one does not neglect the particle inertia, the set of corresponding Langevin equations could be derived easily but turns out

to be immensely difficult to solve. A natural way of simplification is a passage to the non-inertia limit that is well justified since for fine particles the viscous forces are always far greater than the inertia ones. Surprisingly, this step turns out to be non-trivial. Our analysis shows that for Maxwell model the way out goes through the so-called "thermal drift" or multiplicative noise, while for Jeffreys model a correct route to the non-inertial limit requires a “multi-component noise”. In the built-up frameworks we obtain (through Kubo theorem or by solving Fokker-Planck equations) simple expressions for the dynamic magnetic susceptibilities and analyze them. An important contribution to the latter comes from the mechanical impedance of an AC-field driven Brownian ferroparticle. Due to that, such magnetic tests allow to characterize the internal rheology of the suspending non-Newtonian fluids.

Nanoparticle driven imatinib delivery into cells with gold coated iron oxide particles

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Introduction

The targeted delivery of therapeutics into relevant cells and tissues is still of major concern. We present a simple straight forward strategy of binding a therapeutic drug onto magnetic nanoparticles. The magnetic core of the nanoparticles allows the precise localization of the nanoparticles and the release of the drug at the desired destination.

We choose imatinib (syn.: STI571) as a model substance, because it is well defined and shows a distinct molecular action by inhibiting the kinase activity of the bcr/abl fusion protein in chronic myeloic leukemia (CML). Therefore we used the CML cell line K562 as a model system. For preparing the delivering nanoparticles, iron oxide particles were coated with gold. Finally, the drug was adsorbed to the gold surface of the nanoparticles.

Results

The imatinib loaded nanoparticles have the same effect onto the leukemia cells as the pure drug itself. K562 cells exhibited a dramatic reduction in cell proliferation depending on the concentration of the nanoparticles and subsequently the transferred drug. Cell cultures incubated with nanoparticle preparations without imatinib showed no effect and exerted a comparable proliferation as untreated K562 cells.

Bcr/abl negative cells were not affected by the imatinib loaded nanoparticles.

Summary

In conclusion, we could prepare gold coated magnetic iron oxide nanoparticles with adsorption properties for imatinib. This approach allows the use of these imatinib loaded nanoparticles as a particle assisted delivery system to selected target cells. These results encourage us to use magnetic nanoparticles as vehicles for other drugs and as drug locating system.

Acknowledgments

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Characterization of magnetic core-shell nanoparticles by magnetorelaxometry, ac susceptibility, TEM and photon correlation spectroscopy – a comparative study

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Magnetic nanoparticles (MNPs) find wide application in medicine and bioanalytics. For the various applications like MRI-contrast enhancement, magnetofection, drug delivery, hyperthermia, protein and cell separation, as well as immunoassays, the requirements on the particles are quite different. In addition, for in-vivo applications one has to guarantee that the MNPs do not aggregate in the given medium. For applications, such as the magnetic relaxation immunoassay (MARIA), only specific bindings of the functionalized MNPs may occur. Consequently, there is a strong need for a fast, reliable and inexpensive technique for the MNP characterization which is important for both manufacturers and users of core-shell MNPs.

As has been demonstrated in [1-3], the measurement of the magnetorelaxometry (MRX) and the analysis of the experimental curves with the moment superposition model is a quick and powerful tool for the estimation of structure parameters like core and hydrodynamic size distributions as well as anisotropy constant. Generally, the relaxation signal can be described by [1,2]

$$m_r(t) = M_s \int_0^\infty f(d_h) \int_0^\infty f(d_c) \frac{\pi}{6} d_c^3 L(d_c) \times \left\{ 1 - \exp\left[-\frac{t_{mag}}{\tau_{eff}} \right] \right\} \exp\left[-\frac{t}{\tau_{eff}} \right] dd_c dd_h$$

where $f(d_c)$ and $f(d_h)$ are the distribution of core and hydrodynamic diameters, $L(d_c)$ is the Langevin function, d_c is the core diameter and $\tau_{eff} = \tau_B \tau_N / (\tau_B + \tau_N)$ is the effective relaxation time. To determine the MNP core parameters, one generally immobilizes the MNPs, e.g., by freeze-drying. Consequently, Brownian relaxation is inhibited, so that τ_{eff} can be replaced by τ_N and integration has to be performed only over d_c. Fig. 1 depicts the distribution of core sizes determined from MRX curves measured on freeze-dried Fe_3O_4 MNPs from chemicell GmbH with the assumption that the MNP cores are lognormal distributed. For comparison, the core size distribution from TEM measurements is shown.

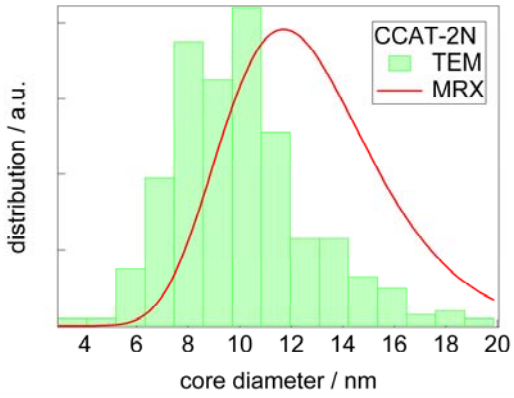

Fig. 1: Distribution of core diameters determined from MRX and TEM measurements (number of samples: 411) on freeze-dried Fe_3O_4 MNP sample.

To reduce the number of fit parameters when analyzing MRX curves measured on MNP suspensions, it is recommended to first estimate the core parameters on a freeze-dried reference sample. Fig. 2 shows the normalized relaxation curve measured on an aqueous suspension of the same MNPs as in Fig. 1. The best fit is obtained for a mean and standard deviation of the lognormal distribution of hydrodynamic diameters of $\mu_h = 96.5$ nm and $\sigma_h = 0.38$,

respectively. Photon correlation spectroscopy (PCS) measurements performed on the same MNP sample provided a comparable mean value.

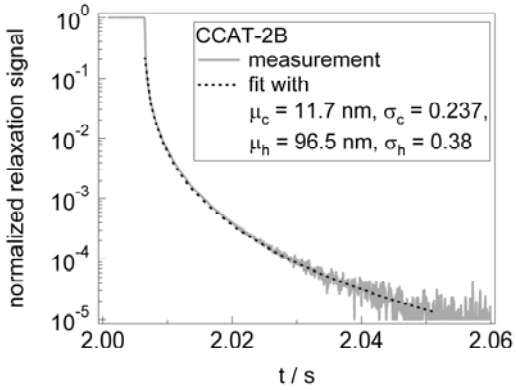

Fig. 2: MRX curve measured on Fe_3O_4 MNP suspension along with best fit.

We also applied ac susceptometry to get information on the distribution of hydrodynamic sizes. Taking both Brownian and Néel relaxation into account, real and imaginary part of the ac susceptibility of a MNP suspension with a distribution of core and hydrodynamic diameters are given by [4]

$$\chi'(\omega) = \chi_0^* \int_0^\infty f(d_h) \int_0^\infty \frac{d_c^6 f(d_c)}{1+(\omega\tau_{eff})^2} dd_c dd_h$$

and

$$\chi''(\omega) = \chi_0^* \int_0^\infty f(d_h) \int_0^\infty \frac{d_c^6 f(d_c) \omega\tau_{eff}}{1+(\omega\tau_{eff})^2} dd_c dd_h$$

with

$$\chi_0^* = \frac{\mu_0 n M_s^2}{k_B T} \left(\frac{\pi}{6}\right)^2 .$$

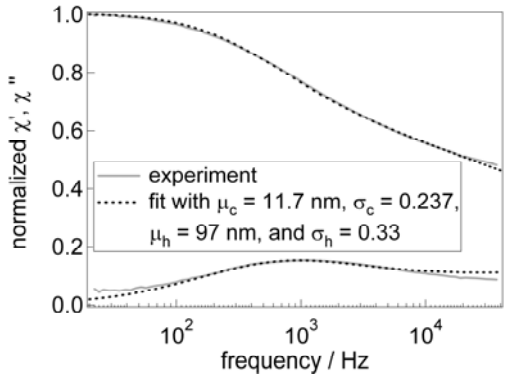

Fig. 3: Normalized real and imaginary part of the ac susceptibility measured on Fe_3O_4 MNP suspension along with best fit.

Fig. 3 depicts χ' and χ'' measured on the same sample as in Fig. 2 together with the best fit. As for Fig. 2, the values for the core parameters were taken from the MRX measurement on a freeze-dried reference sample. The fit parameters for μ_h and σ_h are in excellent agreement with the values estimated from the MRX curves. Note that the mean value $\mu_h = 97$ nm significantly differs from the value that one obtains by assuming that the maximum in χ'' occurs at $\omega \cdot \tau_B = 1$. The deviation is caused by the factor of d_c^6 in the numerator which is caused by the m^2 dependence of χ_0 in the Debye model.

As we have demonstrated the structure parameters of MNPs estimated from MRX measurements agree well with the values estimated by other methods such as TEM, PCS or ac susceptibility. Based on the MRX technique and the tested model, we are currently developing a compact, fluxgate-based MRX measurement system placed in a 19'' housing which could be an important tool for both manufacturers and users of MNP.

Acknowledgments

This work was financially supported by the DFG via SFB 578 and by the BMBF under contract number 13N9174.

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The Rosensweig Instability with a Ferrogel

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Ferrogels

Ferrogels are an interesting new class of materials that enhance the properties of magnetic fluids by elastic components [1]. Due to the coupling of magnetic and elastic energies, they are able to change their shape and exert forces in response to external magnetic fields [2]. Large deformations could be achieved by gradient magnetic fields, utilizing the Kelvin force [3]. The deformation in homogeneous magnetic fields has not been studied to the same extent [4, 5].
When applying a homogeneous magnetic field to a layer of ferrofluid, the surface becomes instable to liquid crests (the famous Rosensweig instability). This instability should also be possible in ferrogels. From a linear stability analysis [6], the critical magnetization is given by

$$M_c^2 = \frac{2}{\mu_0}\frac{1+\mu}{\mu}(\sqrt{\rho g \sigma} + G) \qquad (1)$$

where G is the shear modulus. For $G = 0$ this coincides with the critical magnetization for a ferrofluid, i. e. the critical field is shifted to higher values due to the elastic forces. The critical wavenumber is predicted to remain the same.

Experiment

We use a thermoreversible ferrogel [7] and expose it to a homogeneous magnetic field. By controlling the temperature we can easily change the elastic modulus over several orders of magnitude. The surface topography of the ferrogel is then recorded using an X-ray technique [8] (see figure 1). Because our ferrogel has no elasticity in the static limit, the instability is driven by a static field plus a sinusoidal modulation. We measure both amplitude (see figure 2) and phase of the modulated surface deflection and compare it with the theory.

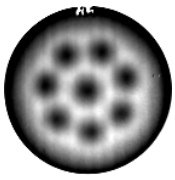

Figure 1: Radioscopic image of the Rosensweig peaks in our ferrogel.

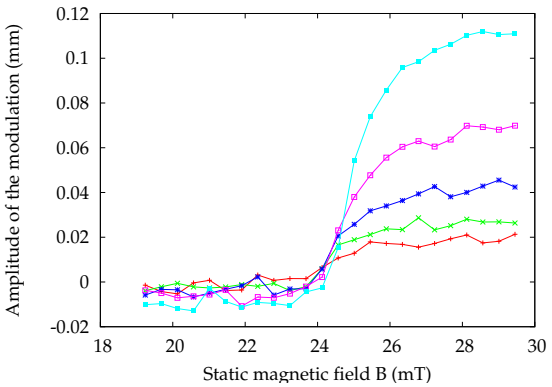

Figure 2: Amplitude of the modulation of the surface deflection in response to a modulated magnetic field

Acknowledgments

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FRIDAY, 9 MAY

Experiments on self assemblies of magnetic colloids.

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This talk will review some results obtained on self-assembled colloids. We first present a new approach to study both the kinetic of bio-complexes formation and their mechanical properties (bending, streching and compression). Self-assembling of magnetic colloids under magnetic field allows to impose colloidal distances and forces.Therefore the distance between grafted biomolecules can be monitored during contact duration and the corresponding average time scale of the complex formation can be directly measured. Then we show how long magnetic filaments made of linked magnetic particles may be used to measure the bending rigidity of linkers as well as their force distance behavior, at a single link level. Dynamical properties of these flexible filaments, and particularly their ability to swim and transport colloidal objects or cells will be discussed. Finally this talk will introduce some new magnetic colloids that depending on both their shape and their spontaneous direction of magnetization are able to self-assemble with controlled isomery. We will present three types of mesopolymers: syndiotactic, isotactic and double helical structures.

Investigation of the thermomagnetic convection in ferrofluid influenced by a time-modulated driving force

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This work considers heat and mass transfer phenomena in a horizontal ferrofluid layer influenced by a time-modulated magnetic field.

Theoretical investigations of thermal convection [1-3] have shown that the stability point for the transition from conduction to convection depends on temperature difference and the frequency of the driving force. The driving force for a "classical" thermal convection is the buoyancy force resulting from a density gradient in the system due to an applied vertical temperature difference. The status of thermal convection can be described by the dimensionless Rayleigh number *Ra*, which is given by

$$\mathrm{Ra} = \frac{\beta_T \cdot g \cdot \rho \cdot \Delta T \cdot d^3}{\kappa \cdot \eta} \qquad (1)$$

For a horizontal fluid layer within two rigid boundary plates of high heat conductivity, the critical Rayleigh number for a driving force, constant in time, is 1708 [6]. Eq. 1 shows that the Rayleigh number, and therefore the buoyancy force can be time-modulated either by altering the temperature difference over the gap or the gravitational acceleration. Both possibilities to achieve a time-dependent driving force require an immense technical effort which hinders the practical realization of these options.

The chance to influence the material- and flow properties of a ferrofluid by means of an external magnetic field makes it possible to overcome these experimental difficulties. The magnetic force [4] which arises within a horizontal fluid gap subjected to an external magnetic field and a temperature gradient is able to drive a convective flow in the system. This effect driven by the magnetic force is called thermomagnetic convection [5] and can be described by the dimensionless magnetic Rayleigh number Ra_m, which is given by

$$\mathrm{Ra}_m = \frac{\mu_0 \cdot K \cdot \nabla H \cdot \Delta T \cdot d^3}{\kappa \cdot \eta} \qquad (2)$$

The magnetic Rayleigh number Ra_m, and therefore the magnetic force, can be time-modulated by a temporal variation of ∇H realized by a time-modulated external magnetic field. The difficulties to build an experimental setup to generate a time-modulated magnetic field which provides the required frequencies are comparably easy to handle.

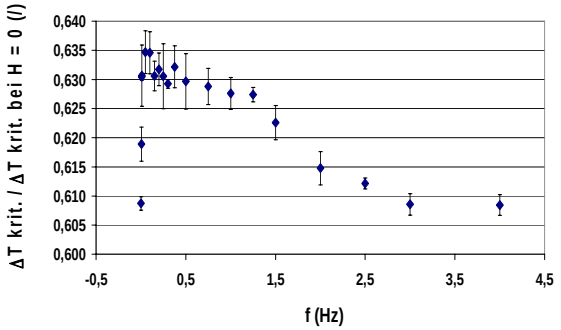

Figure 1: Critical temperature difference versus frequency of the driving force in a system subjected to both magnetic and buoyancy forces.

Magnetic Nanorods in External Fields

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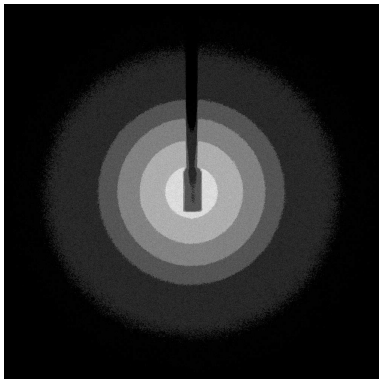
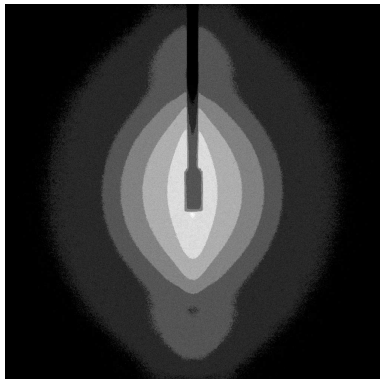
Suspensions of magnetic nanoparticles are interesting colloidal model systems to investigate the structural and dynamic response to external fields [1-3]. Due to the availability of defined rodlike particles with tunable aspect ratio, the complexity of the model system can be increased compared to conventional spherical ferrofluids.
As a model system, rhombohedral hematite (α-Fe_2O_3) particles are prepared, whose aspect ratio is varied by the concentration of NaH_2PO_4 selectively covering one crystal surface and thus enabling anisotropic growth [4]. We obtain particles with a median length of typically $L_0 = 200 - 400$nm and a median diameter of $D_0 = 50 - 100$nm. The polydispersity of the particles expressed as the geometric standard deviation of $\sigma_D \approx 1.05$ and $\sigma_L \approx 1.10$ for the length and diameter, respectively, is considerably small. For electrostatic stabilisation, the nanorods are covered by a silica shell. Due to the form anisotropy with large accessible aspect ratio, even weakly magnetic particles can be aligned in moderate magnetic flux densities in the range of several $10^{-2}\,T$. The angular correlation of both silica coated and uncoated nanorods with different aspect ratios in an external magnetic field is investigated by means of synchrotron small angle scattering experiments in dependence of the strength and orientation of an external magnetic field. The orientation of the rodlike particles can easily be seen from 2d-scattering patterns.



Scattering pattern without external magnetic field.



Scattering pattern with external magnetic field ($B_0 = 0.1\,T$) perpendicular to the primary beam.

The rotational diffusion of such nanorods is determined via depolarized light scattering experiments using highly dilute suspensions. A significant increase of the magnetic moment can be achieved by reduction of hematite (α−Fe_2O_3) to magnetite (Fe_3O_4) by hydrogen at 350°C. Hereby the form of the particles remains stable.

Acknowledgments

The authors thank M. Sztucki for support during the SAXS experiments at the ESRF.

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In this work, a horizontal ferrofluid layer subjected to a vertical time-modulated external field is considered. The fluid layer is heated from below so that both, the magnetic and the buoyancy mechanism, are working simultaneously. In this case the Rayleigh number is the sum of Ra and Ra_m where Ra_m is time-dependent.
Figure 1 shows that the critical Rayleigh number, therefore the critical temperature difference, depends on the frequency of the driving force. For low frequency, the critical temperature difference increases and reaches a maximum for a certain value of the frequency. With a further increase of the frequency, the critical temperature difference decreases. That means the system is stabilized by low frequencies of the driving force and destabilized for higher frequencies.
Within the presentation a modified experimental setup which permits to indicate the critical temperature difference where the state of heat flux changes from conduction to convection will be presented as well as first results on the shift of the critical temperature difference.

Acknowledgments

We are grateful to Prof. M. Luecke (Universitaet des Saarlandes) for enlightening discussions.
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FROM FERROFLUIDS TO FERROGELS

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Polymer gels contain substantial amount of liquid as swelling agent. A ferrogel is a chemically cross-linked network swollen by a by a ferrofluid. The incorporated magnetic particles, characterized by strong adsorptive interactions with polymer chains, couple the shape and physical properties of the gel to the external field. Since the particles cannot leave the polymer matrix, so that all of the forces acting on the particles are transmitted directly to the polymer chains resulting in either locomotion or deformation. Shape distortion occurs instantaneously and disappears abruptly when external fields are applied or removed, respectively. Combination of magnetic and elastic properties leads to a number of striking phenomena that are exhibited in response to impressed magnetic fields. Giant deformational effect, tunable elastic modulus, non-homogeneous deformation and quick response to magnetic field (Fig. 1) open new opportunities for using such soft materials for various technical and biomedical applications.

Synthesis of ferrogels in uniform magnetic field can be used to prepare anisotropic samples. The anisotropy manifest itself in both direction dependent elastic modulus as well as direction dependent swelling. The magnetic field responsive gels have shown a change in compressive modulus under uniform magnetic field.

Depending on the orientation of particle chains in the network as well as on the strength of magnetic field, the induced temporary reinforcement may exceed one order of magnitude. These results suggest that magnetic field responsive gels have several potential applications as tuned vibration absorbers, stiffness tuneable mounts and suspensions. Since the magnetic fields are convenient stimuli from the point of signal control, therefore it is of great importance to develop and study such soft and flexible magnetic systems.

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Fig. 1 Snapshot of shape change of a magnetite-loaded PDMS gel due to modulated magnetic field. The frequency of the field is 40 Hz.

Fabrication and characterisation of Magnetorheological materials for reconfigurable fixturing applications

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Abstract

Magnetorheological (MR) fluids are suspensions of magnetic particles in carrier fluids, whose rheological properties can be controlled by the application of external magnetic field [1]. Currently, MR fluids are being used in a variety of applications such as semi-active shock absorbers, valves, clutches, brakes, and dampers for vibration reduction in automobile and machineries [2, 3]. However, the use of MR fluids in fixturing applications has been very limited. The focus of this work is to develop a MR fluid suitable for fixturing applications and to design a reconfigurable fixturing system for holding irregular or complex shaped geometry during different manufacturing processes.

For an application like reconfigurable fixturing, it is important that an MR fluid possesses the following characteristics: high yield strength, low off-state viscosity, and low sedimentation rate of the particles. A new type of MR fluid was prepared using blend of polymeric matrix – hydrocarbon oil mixture [4]. A systematic rheological characterization was carried out to evaluate the effect of particle content in the polmeric matrix under steady state flow in a custom made Couette geometry, exposed to varying external magnetic field. Indeed, we compare the rheological properties and the sedimentation behaviour of the new type MR fluid with a commercially available MR fluid.

We found that the off state viscosity of the commercially availably MR fluid was slightly lower than that of the new type MR fluid. However, when exposed to a magnetic field of 0.26T, the new type MR fluid showed higher magnetorheological response compared to the commercial one. Also, it is interesting to note that the sedimentation rate of the new type MR fluid was significantly lower than the commercial one. These findings make the new type MR fluid attractive to MR applications requiring high yield stress and low sedimentation rate such as reconfigurable fixturing. The results to date are used in designing a reconfigurable fixturing system and performance of the fixture using new type of MR fluid is currently being tested.

Keywords: Magnetorheological fluids, Polymeric Matrix, Magnetorheological Behaviour, Sedimentation Behaviour

Acknowledgments

The authors gratefully acknowledge financial support form the EPSRC for supporting this project through Nottingham Innovative Manufacturing Research Centre.

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Microspheres with a Switchable Magnetic Remanence

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Silica microspheres with embedded cobalt ferrite nanoparticles have a permanent magnetic dipole moment that can be switched on or off. This will be demonstrated on the basis of complex magnetic susceptibility spectra measured at exceptionally low frequencies in the weak-field limit. In a colloidal dispersion, the microspheres affect each other's rotational diffusion by magnetic and hydrodynamic interactions. Whereas related particles are being developed for biomedical applications, our first aim is to prepare new model particles that interact as dipolar hard spheres and can be studied in situ in real time with single-particle resolution using optical microscopy, as opposed to our magnetic nanoparticle model systems. The ultimate question is whether liquid-gas coexistence is possible in monodisperse dipolar hard sphere fluids.

POSTER SESSION

LIST OF POSTERS

Behrens, Silke, Forschungszentrum Karlsruhe silke.behrens@toc.cpv.fzk.de	**P01**	**Poster** (with Gorschinski): "Synthesis of magnetic metal nanocomposite particles"
Bohlius, Stefan, MPI für Polymerforschung, Mainz bohlius@mpip-mainz-mpg.de	**P02**	**Poster:** "The amplitude equation for the Rosensweig instability"
Borin, Dmitry, TU Dresden dmitry.borin@tu-dresden.de	**P03**	**Poster:** "Experimental study of dynamics of changes of viscosity in magnetically controlled fluids under shear flow"
Dutz, Silvio, Inst. of Photonic Technology, Jena silvio.dutz@ipht-jena.de	**P04** **P05**	**Poster 1**: "Effect of package density on magnetic properties of iron oxide nanoparticles" **Poster 2:** "Magnetische Eigenschaften wasserbasierter Citrat-Magnetit Magnet-flüssigkeiten mit hoher Partikelkonzentration"
Elfimova, Ekaterina, Ural State University, Ekaterinenburg ekaterina.elfimova@usu.ru	**P06**	**Poster:** "Ionic stabilized ferrofluid: anisotropy of the structure factor under external magnetic field"
Feyen, Mathias, MPI für Kohleforschung, Mülheim an der Ruhr feyen@mpip-muelheim.mpg.de	**P07**	**Poster:** „Encapsulation of Fe_30_4 nanoparticles in cross-linked polystyrene spheres"
Gollwitzer, Christian, Univ. Bayreuth christian.gollwitzer@uni-bayreuth.de	**P08**	**Poster:** "Measuring the deformation of a ferrogel sphere in a homogeneous magnetic field"
Gorschinski, Angelika, Forschungszentrum Karlsruhe angelika.gorschinski@itc-cpv.fzk.de	**P09**	**Poster**: „Synthesis of magnetic metal nanocomposite particles" (with Behrens)
Gürler, Celin, Univ. Düsseldorf celin.guerler@uni-duesseldorf.de	**P10**	**Poster:** „Electromagnetically driven nanorotors and –heaters"
John, Thomas, Univ. Magdeburg thomas.john@physik.uni-magdeburg.de	**P11**	**Poster:** "Measurements and calculations of torques on a ferrofluid sphere under time asymmetric magnetic fields"
Kantorovich, Sofia, MPI-P Mainz, FIAS Frankfurt, Ural State University kantorovich@fias.uni-frankfurt.de	**P12**	**Poster:** "Ground state structures in ferrofluid monolayers"
Krekhova, Marina, Univ. Bayreuth marina.krekhova@uni-bayreuth.de	**P13**	**Poster:** "Morphological and rheological properties of thermoreversible organoferrogels"
Lange, Adrian, TU Dresden adrian.lange@tu-dresden.de	**P14**	**Poster:** "Thermomagnetic convection in magnetic fluids influenced by time-modulated magnetic fields: experiment and theory"
Leschhorn, Andreas, Univ. des Saarlands, Saarbrücken andy@lusi.uni-sb.de	**P15**	**Poster:** "Stability of the Couette flow of a ferrofluid in an axial magnetic field: influence of polydispersity"

LIST OF POSTERS

Matura, Pascal, Univ. des Saarlands, Saarbrücken p.matura@lusi.uni-sb.de	**P16**	**Poster:** "Magnetically driven convection in ferrofluids"
Messing, Renate, Univ. Düsseldorf, renate.messing@uni-duesseldorf.de	**P17**	**Poster:** "Heat Transfer at the Nanoscale"
Rahn, Helene, TU Dresden helene.rahn@tu-dresden.de	**P18**	**Poster:** „Magnetic nanoparticles used as drug carriers for minimally invasive cancer treatment"
Reindl, Matthias, TU Dresden matthias.reindl@tu-dresden.de	**P19**	**Poster:** "Flow control of magnetic fluids exposed to magnetic fields"
Richter, Reinhard, Univ. Bayreuth reinhard.richter@uni-bayreuth.de	**P20**	**Poster:** „Why does a ferrofluidic pendulum FLIP at a critical driving frequency""
Wiesen, Leonhard, Univ. Bayreuth leonhard.wiesen@uni-bayreuth.de	**P21**	**Poster:** "Hexagon-square transition of the Rosensweig instability in the presence of a magnetic ramp"
Wu, Zhenyu, Univ. Ulm zhenyu.wu@uni-ulm.de	**P22**	**Poster:**"Synthesis of Nanotube Ferrofluids by Virus Templating"
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Interaction of tumor cells and peripheral blood cells with magnetic nanoparticles coated with tailored dextran-based shells

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It is known, that most of the cancer patients do not die from the primary tumor but from distant metastases. Once the primary tumor is formed, cells may begin to dissociate from the tumor and spread to other parts of the body via the circulatory or lymph system. These disseminated tumor cells are able to form metastases. To prevent a spreading of tumor cells to other parts of the body and forming metastasis, it is necessary to eliminate the tumor cells out of the blood quantitatively.

In hematology and oncology magnetic nanoparticles are regularly used for labeling and detection of cells. In addition to antibodies, the diversity of the shell surface is a promising opportunity to get a pure fraction. It has been shown that magnetic nanoparticles with a dextran-based shell interact with living cells in a cell type specific manner. Pure dextran (D), carboxy dextran (CD) and carboxymethyl dextran (CMD) were studied as coating materials. The carboxymethyl dextran shell is most efficient in the separation of tumor cells from leukocytes. Tumor cells showed an intense interaction with CMD coated particles whereas the leukocytes exhibited a lower tendency to interact. To achieve a more pronounces discrimination between cancer cells (MCF-7 cells) and leukocytes, the influence of the structure of the CMD coating material was investigated. Neither variation of the degree of carboxymethylation nor the molecular masses of the dextran did yield coating materials with an increased difference in the interaction with the two cell types.

Thus, the pattern of functionalization of the CMD was modified. Using different synthesis paths for the carboxymethylation of dextran, it is possible to obtain CMD with a statistic pattern of carboxymethyl groups along the dextran chain or a non-statistic distribution of the substituents. Interestingly, first experiments show that a non-statistical distribution of carboxymethyl groups intensifies the difference of interaction with the cells. MCF-7 cells are only slightly affected in their interaction with CMD coated nanoparticles whereas the leukocytes exhibited a significant decrease of interaction.

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The amplitude equation for the Rosensweig instability

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Introduction

Since its discovery in 1967 [1], the normal field or Rosensweig instability attracted the attention of experimentalists and theoreticians, alike. The phenomenon describes the transition of an initially flat ferrofluid surface to hexagonally ordered surface spikes as soon as an applied magnetic field exceeds a certain critical value. Ferrofluids are suspensions of magnetic nanoparticles in a suitable carrier liquid. One of the most prominent properties is the superparamagnetic behavior in external magnetic fields, which accounts for the large magnetic susceptibility and the high saturation magnetization in rather low magnetic fields. If one starts to crosslink a mixture of a ferrofluid and a polymer solution with cross-linking agents, a superparamagnetic elastic medium, also called ferrogel, is obtained [2]. As in usual ferrofluids, the initially flat surface of ferrogels becomes linearly unstable beyond a critical magnetic field [3]. A nonlinear analysis of the Rosensweig instability, however, turned out to be very complicated mainly due to the fact that the instability necessarily involves a deformable surface. In addition, the driving force is provided by the boundary conditions at the deformed surface and not by the bulk equations. A second problem arises by the fact that this instability is intrinsically dynamic in nature, although the linear threshold and the critical wavelength can be obtained in a static description (as an energetic minimum neglecting viscous effects). A nonlinear description, however, has to treat this instability as a breakdown of traveling surface waves.

Results

We have succeeded in deriving from the basic hydrodynamic and magnetic equations and boundary conditions an amplitude equation for the Rosensweig instability. Starting from the linear solution, a systematic expansion of those equations and boundary conditions in terms of the normalized distance to the threshold is the standard procedure of the weakly nonlinear analysis. To adapt this method to the Rosensweig instability, the adjoint linear eigenvectors in the presence of a deformable surface are needed to satisfy Fredholm's theorem. This has been achieved recently [4] and is useful for other instability problems involving deformable surfaces, like the Marangoni instability. This enabled us to perform the usual expansion procedure for the full dynamic problem up to third order, which in the limit of vanishing frequency gives the desired amplitude equation for the stationary instability. It contains cubic and quadratic nonlinearities as well as a first and, in the case of a finite elastic shear modulus, a second order time derivative of the pattern amplitudes. The quadratic nonlinearity guarantees the hexagonal pattern to be stable at the linear onset and renders the bifurcation transcritical. For higher magnetic fields the hexagonal pattern transforms into a square pattern accompanied by a second hysteretic regime. Both findings are qualitatively verified by experiments. Comparison will be made to corresponding results obtained by the so-called energy method [6], which is approximative and unsystematic.

Acknowledgments

This work is supported by the DFG priority program 1104 "Kolloidale magnetische Flüssigkeiten". HRB thanks the Deutsche Forschungsgemeinschaft for partial support through the Forschergruppe FOR 608 "Nichtlineare Dynamik komlplexer Kontinua".

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Experimental study of dynamics of changes of viscosity in magnetically controllable fluids under shear flow

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The dynamics of changes of viscosity in magnetically controllable fluids, such as ferrofluids (FF) and magnetorheological fluids (MRF), under action of external magnetic fields and shear stress is a significant characteristic, which is necessary for the understanding of effects occurring in these fluids.

A lot of theoretical models and predictions for the dynamical behavior of the structure formation of magnetic particles in a liquid medium under the action of external excitations are known, e.g. [1-4]. However, there are only a limited number of experimental investigations dedicated to this problem for the case of mechanical stresses applied to the medium. It has been shown in [5], that FF show a long time reaction to a stepwise change of shear stress at constant magnetic field strength, as well as to a stepwise change of magnetic field strength at constant shear rate. To shed some light on this unusual temporal behavior we are actually investigating stepwise changes of shear rate and field strength on magnetic suspensions of different composites (MR as well as FF).

To investigate the transient dynamics in FF and MRF the shear-controlled rheometer described in [6] with actually improved hardware was used. The rheometer uses a cone-plate geometry and allows to vary shear rate in the range between 10^{-4} s^{-1} and 10^{3} s^{-1} and to apply an external magnetic fields up to 40 kA/m with a homogeneity better than 95%. As a reference device for calibration, as well as for the validation of the experimental results in the absence of magnetic field, a commercial rheometer (Anton Paar MCR 301) was used.

Figure 1 shows an example of a long-time change of torque to a stepwise shear stress change for a magnetite based FF (TTR).

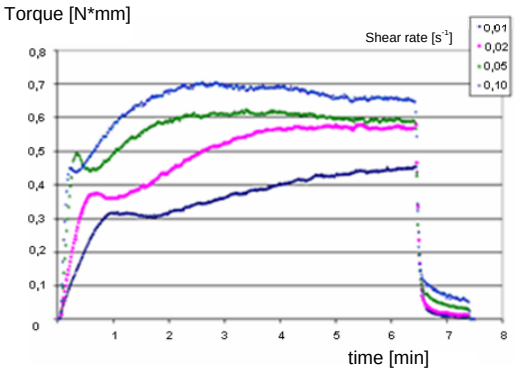

Figure 1. A long-time reaction of rheometers torque sensor to the shear stress stepwise change [5].

Preliminary experimental results for the magnetic field and shear rate dependence of the transient behavior will be presented at the workshop.

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Effect of package density on magnetic properties of iron oxide nanoparticles

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Magnetic iron oxide nanoparticles are interesting materials for a variety of biomedical and technical applications. Each application requires magnetic nanoparticles (MNP) with magnetic properties adapted to the specific task of the considered application. In the literature, a strong influence of the package density on the magnetic properties of a magnetic nanoparticle powder is described theoretically [1]. Aim of this study is the experimental investigation of the correlation between package density and magnetic properties, e.g. coercivity (H_C), relative remanence (M_R/M_S), and specific hysteresis losses (SHL).

For this aim, the package density of a pure MNP powder (18 vol.-%) was decreased by dilution of the MNP with a dry non-magnetic substance (matrix) down to 0.25 vol.-%. As matrix material, hydrophilic SiO_2 powder with a specific surface area of 130 m^2/g and a primary particle diameter of 16 nm was used. To obtain a preferably homogeneous distribution of single MNP in the matrix, MNP with a low agglomeration trend are required. To this end, the MNP used for this investigation were prepared by laser evaporation as described before [2]. These particles with a mean diameter of about 20 nm show a relative remanence of 0.21 which indicates only weak agglomerates in the powder.

An increased package density (67 vol.-%) compared to the mean density of the pure MNP powder could be obtained by compression of the sample at a pressure of about 350 MPa in an uniaxial press.

For the investigation of the magnetic properties, the hysteresis curves at saturation field amplitude (1275 kA/m) as well as at a lower field amplitude (11 kA/m) were measured by vibrating sample magnetometry (VSM). The SHL of the samples were calculated by integrating the areas of the measured hysteresis curves.

The magnetic characterization shows a strong correlation of the package density and the magnetic properties of the MNP. With decreasing package density, an exponential increase of H_C as well as M_R/M_S could be observed at low field amplitudes and at magnetic saturation field amplitudes. Due to these results, an exponential increase of the SHL for decreasing package density could be observed for the two investigated field amplitudes. In the Henkel-Plot [3] an increase of the magnetic interactions between the single particles of the nanoparticle powder for increasing package densities was found.

The results of the magnetic characterization are in good agreement with the theoretical estimations [1].

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Magnetische Eigenschaften wasserbasierter Citrat-Magnetit-Magnetflüssigkeiten mit hoher Partikelkonzentration

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Wasserbasierte Ferrofluide finden aktuell verstärkten Einsatz bei verschiedenen biomedizinischen und technischen Anwendungen. Für die meisten Anwendungen ist es dabei von Vorteil, dass das Ferrofluid eine hohe Konzentration an magnetischem Material aufweist. Bisherige Ferrofluide zeigen allerdings die Tendenz, dass mit steigender Partikelkonzentration die Sedimentationsstabilität abnimmt. Vor diesem Hintergrund wurde ein Ferrofluid synthetisiert, welches bei hoher Partikelkonzentration eine sehr gute Stabilität gegen Sedimentation aufweist.

Die Primärpartikel (Magnetit/Maghemit) wurden nach der Khalafalla-Methode durch Kopräzipitation aus Eisen(II)- und Eisen(III)-Salzen mittels Ammoniumhydroxid im nm-Bereich gefällt. Diese wurden anschließend mittels Citronensäure komplexiert und im pH-Bereich zwischen 6,5 und 8 in wässeriger Lösung stabilisiert. Die aus Ammoniumsalz gebildeten Nebenprodukte und überschüssige Citronensäure wurden aus dem Dispersionsmedium durch Waschen entfernt.

Es bildeten sich zwei Phasen: ein an Teilchen konzentriertes, teilweise aggregiertes Sediment und ein weniger konzentrierter, aber kolloidal stabiler Überstand. Nur letzterer wurde verwendet und weiterhin durch Entzug von Wasser bis auf 10 vol% an Magnetteilchen konzentriert. Teilchenaggregate wurden durch Ultraschall teilweise redispergiert und der Rest mittels Filtration durch Glaswolle entfernt.

Die niedrig viskose MF diente als Stammlösung, aus der durch Verdünnen mit destilliertem Wasser Verdünnungsreihen hergestellt wurden, um an denen die strukturellen und magnetischen Messungen durchzuführen.

Die Untersuchung im TEM lieferte Kernteilchengrößen im Bereich von 4 bis 15 nm, welche in guter Übereinstimmung mit den mittels EDX bestimmten Werten von 10 nm sind. Anhand Rückstreu-PCS wurde ein volumengewichteter mittlerer hydrodynamischer Teilchendurchmesser von 7,5 nm gemessen.

Bei quasistatischen Messungen der Magnetisierungskurve am VSM wurde für das Fluid eine spez. Sättigungsmagnetisierung von rund 31 $A*m^2*kg^{-1}$ festgestellt, woraus eine Partikelkonzentration von etwa 41 m% abgeleitet werden kann. Die immobilisierten Partikel besitzen ein H_C von 0,07 kA/m bei einer relativen Remanenz von 0,0011. Somit wurde für die einzelnen Partikel superparamagetisches Verhalten angenommen und nach der Chantrell-Methode ein Partikeldurchmesser von 7,5 nm aus den magnetischen Daten ermittelt.

Die spezifische Heizleistung der Partikel wurde für bis zu 100fache Verdünnung des Fluides mit konstant 50 W/g (bei f = 410 kHz und H = 11 kA/m) bestimmt. Dies bestätigt die Vermutung, dass die Partikel größtenteils einzeln im Fluid vorliegen und nur wenige Agglomerate auftreten.

Es ist also gelungen, ein hochkonzentriertes wasserbasiertes Ferrofluid herzustellen, welches bei starken Verdünnungen noch sedimentationsstabil bleibt und konstante magnetische Eigenschaften aufweist. Potentielle Anwendungen werden momentan im Drug-Targeting, in der Magnetseparation und in der Hyperthermie gesehen, wobei für die Hyperthermie die Heizleistung der Partikel noch erhöht werden muss.

Ionic stabilized ferrofluid: anisotropy of the structure factor under the external magnetic field

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There are two methods of magnetic fluids stabilization: sterical cover creation on the surface of ferroparticles and stabilization thanks to formation of double electric layers. In particular, the last one allows synthesizing magnetic nanocolloid on water base, usage of it is acceptable in medical practice [1]. Obvious, the research of behaviour and properties of that ferrofluids is very important. The theoretical model which describes interparticle correlations and the structure factor of ionic-stabilized ferrofluids is offered in our research.

Fundamental ideas of our model is based on ferroparticles consideration as a system of dipolar soft monodisperse spheres with diameter d. Repulsion of double electric layers ith and jth ferroparticles is modeled by the Yukawa potential:

$$U_e(ij) = U_0 \frac{1}{\kappa r_{ij}} e^{-\kappa(r_{ij}-d)},$$

where r_{ij} is the distance between the centers of particles ith and jth, κ^{-1} is a characteristic repulsion length, and $U_0/\kappa d$ corresponds to the large volume of the energy. To describes the magnetic interaction, the system of the elastic repulsion particles is replaced on the system of solid spheres [2], that have some effective diameter d_e:

$$d_e = \int_0^\infty \left[1 - \exp\left(-\frac{U_e(r)}{k_B T}\right)\right] dr,$$

where $k_B T$ is the thermal energy. Whereupon the magnetic interaction of ith and jth particles with the effective diameter d_e is defined of dipole-dipole interaction. The radial distribution function is built on the base of thermodynamic theory of perturbations on concentration and interparticle intensity of ferroparticle magnetic moments. Correlations of two and three particles in locations and orientations of ferroparticles in the magnetic field are taken into account in this method. The theoretical predictions of pair correlation function in different concentrations of ferroparticles in ferrofluid correspond well with the computer simulation data [3].

Fourie transform of the pair correlation function allows to define the structure factor of ferrofluid. We have observed anisotropy of the structure factor under external magnetic field.

As a result, we have constructed the interparticle interaction model in the ionic-stabilized magnetic fluid and have found the structure factor for various physico-chemical parameters of the system with and without the external magnetic field.

Acknowledgments

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Encapsulation of Fe_3O_4 Nanoparticles in Cross-Linked Polystyrene Spheres

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Introduction

Magnetic nanoparticles are of great interest for researchers from a wide range of disciplines, including magnetic fluids catalysis, biotechnology/ biomedicine, magnetic resonance imaging, data storage, and environmental remediation.[1] The long term stability and dispersity of magnetic nanoparticles in a medium are important issues for those application areas. Thus, coating magnetic nanoparticles with inorganic or organic layers is necessary for the aim of protection and to receive stable monodisperse systems. We developed a simple and fast method to synthesize and encapsulate Fe_3O_4 nanoparticles in high yields with a tailored cross linked polystyrene shell below 100 nm.

Experimental:

Fe_3O_4 nanoparticles are prepared by the coprecipitation of ferrous and ferric chlorides in aqueous solution of NH_4OH.[2] Stabilizing the particles and immobilizing vinyl groups on the surface 16-heptadecenoic acid (HDA) is added into the running batch. The as-prepared homogeneous dispersion is first diluted in 1.3 % NH_4OH in H_2O and then mixed together with styrene, glycidyl methacrylate and divinylbenzene. The emulsion polymerization is initiated by the water soluble initiator $(NH_4)S_2O_8$ to receive encapsulated Fe_3O_4 particles after 16 h reaction time.

Results and Discussion:

The synthesized single crystalline Fe_3O_4 nanoparticles are well dispersed in H_2O after the treatment with HDA.

The successful adsorption of HDA on Fe_3O_4 was verified by the ATR-IR-spectroscopy of a carefully washed and dried sample. Signals which are characteristic for chelating bidentate interaction between the iron ions on the surfaces and the COO^- groups of the surfactant and immobilized terminal vinyl groups were observed. This result is consistent with the increasing amount of organic material in the sample measured by TGA.

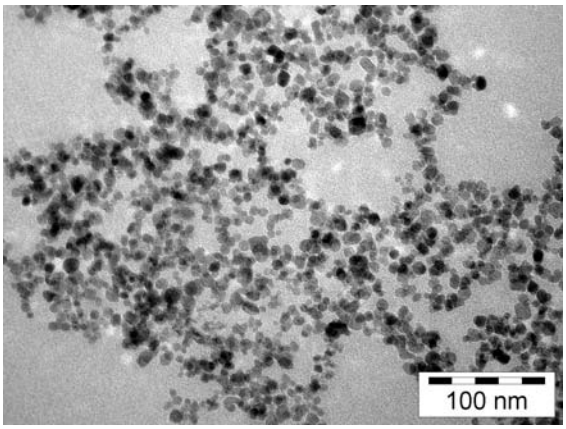

Fig. 1 HR-TEM image of Fe_3O_4 nanoparticles functionalized with HDA

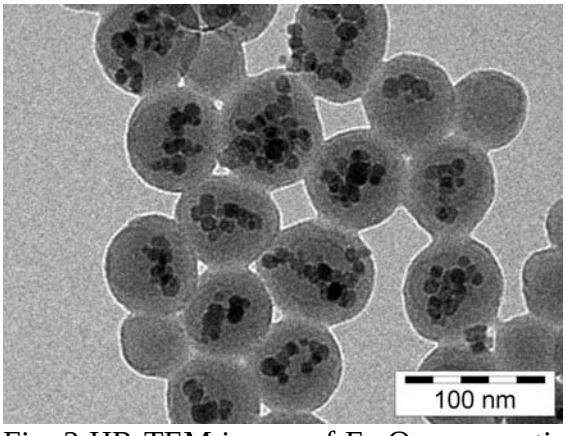

Fig. 2 HR-TEM image of Fe_3O_4 nanoparticles encapsulated in cross-linked polystyrene

HR-TEM images and DLS-Measurements further show the arrangement and size of

the functionalized materials before and after the encapsulation with polystyrene. Fig.1 exhibits the randomly distributed nanoparticles on a copper grid with diameters 10.0 nm ±2.5 nm. Following the polymerization, the encapsulated nanoparticles (Fig. 2) form small clusters in the middle of the well defined polymer spheres with sizes below 100 nm. Finally, SQUID measurements were performed on the dried samples to confirm the superparamagnetic properties of the pure Fe_3O_4 and the encapsulated particles at room temperature.

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Measuring the deformation of a ferrogel sphere in a homogeneous magnetic field

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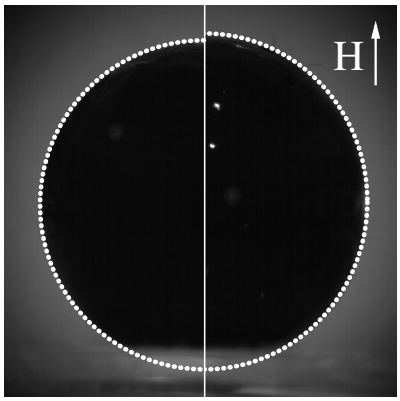

Figure 1: Image of the symmetrical (left) and distorted ball (right). The dotted line displays a fit with a circle (left) and an ellipse (right).

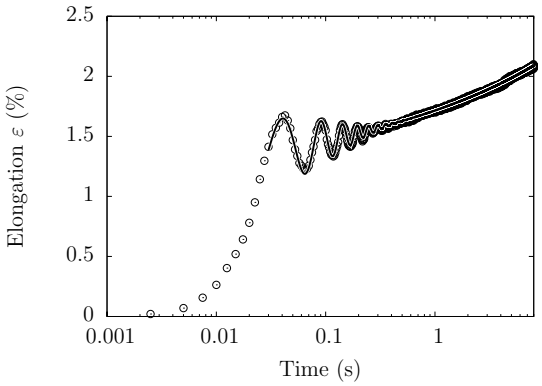

Figure 2: Elastic response of the ball, when a magnetic field is suddenly applied. The solid line represents a fit with a harmonic oscillator.

Introduction

Ferrogels are an interesting class of new intelligent materials that arise as a combination of soft matter and ferrofluids [1]. In contrast to merely combining the properties of both materials, they also exhibit new qualitative behaviour: the coupling of the magnetic particles to the gel network introduces the ability to convert a magnetic stress into a mechanical force. Macroscopic deformations have only been observed in gradient magnetic fields so far [2], because this effect is much larger than in uniform fields[3]. However, theoretical estimates of the elongation of a magnetizable, elastic sphere in a homogeneous magnetic field date back to 1960 [4], where an ellipsoidal shape of the distorted sphere was assumed. Recently, it has been recomputed for the case, that the shape is not constrained to an ellipsoid[5, 6]. According to both models the dependence of the relative elongation ε on the magnetization M and the shear modulus G is given by

$$\varepsilon = \kappa M^2/G, \qquad (1)$$

where $\kappa = 1/15 \quad (5/57)$ for Landau's (Raikher's) model, respectively.

Experiment

We produce a spherical sample of a thermoreversible ferrogel [7] by vacuum casting the gel into an aluminium mould. The ferrogel has a density of $\rho = 1.085\,\mathrm{g/cm^3}$ and is superparamagnetic. To minimize the influence of gravity on the shape, the ferrogel ball is immersed into water and observed laterally by means of a highspeeed camera. The contour of the sample, as seen by the camera (figure 1), is locally fitted with a circular arc to determine its position. When exposed to a sudden increase of the magnetic field, the ball is stretched in the direction of the field, and shrinks perpendicular to it (figure 1, r.h.s), performing uniaxial damped vibrations (figure 2), which can be described by a harmonic oscillator model (solid line in figure 2).
In order to compare the result with the theoretical models, we measure the magnetization curve $M(H)$ (figure 3) and the time-dependent shear modulus $G(t)$ (figure 4). To measure $G(t)$, we perform a purely mechanical creep experiment, where we apply a constant shear deformation to the sample and measure the stress over time. The shear modulus $G(t)$ can be described by a stretched exponential with good accuracy

$$G(t) = G_{\mathrm{rheo}} \exp\left(-(t/t_0)^{\beta}\right). \qquad (2)$$

By extrapolating the complex creep response $G(t)$

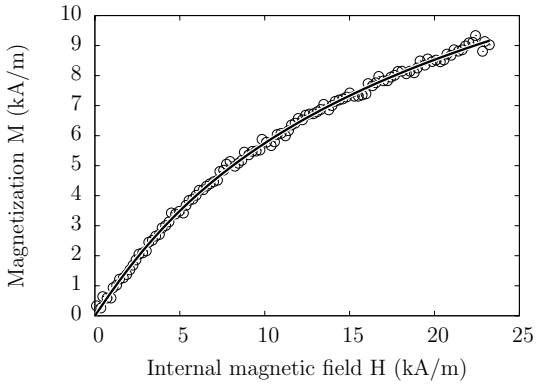

Figure 3: Magnetization curve of the ball.

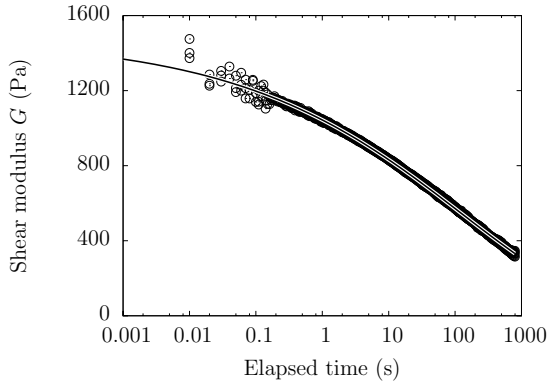

Figure 4: The force response to a jump in the deformation. The solid line displays a fit to Eq. (2) with the parameters $G_{rheo} = 1480\,\mathrm{Pa}$, $t_0 = 127$ s and $\beta = 0.218$.

to the time $t = 0$, we are able to compare the observation with the theoretical models. Further, the ratio of the elongation parallel and perpendicular to the field enables us to measure Poisson's ratio σ of the gel, which is close to the limit $\sigma = 1/2$ for an incompressible material.
In summary, we propose a simple testbed for the magnetoelastic response of ferrogels. The results indicate, that the complex elasticity of this new kind of smart material has to be taken into account for a proper theoretical description. For details see reference [8]

Acknowledgments

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Synthesis of magnetic metal nanocomposite particles

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One challenge in synthesizing multicomponent nanostructures, e.g. of core-shell type is understanding how to form an interface between the different materials which may exhibit very different crystallographic structures, lattice dimensions, chemical stability, or reactivity. The synthesis of cobalt nanoparticles applying dicobalt octacarbonyl with organometallic precursors (aluminium trialkyls) or polysiloxane micelles has been previously reported by Bönnemann et al. [1,2] and Riffle et al. [3], respectively. We report the synthesis of monodisperse cobalt nanoparticles by thermolysis of a dicobalt octacarbonyl precursor in the presence of simple aminofunctionalized siloxanes. The aminofunctionalized siloxane controls particle formation by complexation of cobalt and mediates further deposition of silica. The particles were passivated with low doses of oxygen, resulting in good stability towards air and moisture. The amount of siloxane, the temperature, as well as the heating rate affect the monodispersity and the size of the particles. When tetraethoxysilane is added and hydrolyzed, the amino functionalized siloxane serves as a coupling agent for further deposition of silica. Alternatively, a peptizing agent (KorantinSH) may be applied to form colloidal solutions or magnetic fluids.

The presented procedure opens a new and simple synthetic pathway for the production of hybrid particles of various nature exhibiting multifunctional behavior and new surface functionalities. The combination of materials exhibiting different physical phenomena is manifold, including optical/magnetic, optical/catalytic, magnetic/ferroelectric etc.

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Electromagnetically driven nanorotors and –heaters

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Motivation

Molecular motors play an important role in biological systems, and much effort is conducted to construct artificial objects that are capable to convent chemical or electrochemical fuels as well as electromagnetic energy into a specific, predetermined motion on the nanoscale.

Results

We present results on the selective activation of nanoparticle rotation by the application of electromagnetic energy in the kHz regime with wide application potential in nanoscience and –technology. The nanorotors implied in this study are based on cobalt nanosheres decorated with a stabilizing shell, showing an extrinsic superparamagnetic behaviour that is a dynamic magnetic behaviour ruled by Brownian rotation of the particles.

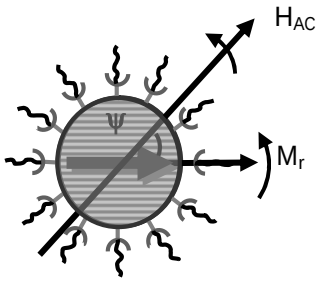

Figure 1: The remagnetization of a magnetically blocked single-domain nanoparticle occurs by Brown rotation and is thus dominated by the hydrodynamic properties of the particle.

By proper adjustment of the shell thickness and dispersion characteristics, a predetermined relaxation frequency can be achieved and adjusted to the applied radiation frequency, offering the possibility to address a selective particle motion that may lead to molecular transport and the generation of local heat. Possible applications involve electromagnetically driven transport across interfaces and membranes as well as the induction of thermally activated chemical reactions, i.e. polymerizations, for the creation of a well-defined polymeric particle shell.

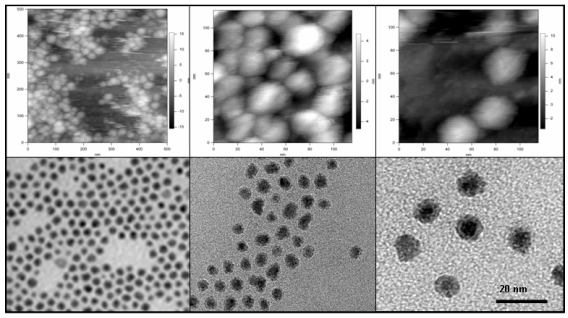

Figure 2: AFM- and TEM images of cobalt nanoparticles coated with polycaprolactone.

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Ground state structures in ferrofluid monolayers: Theory and Simulations.

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A combination of analytical calculations and Monte Carlo simulations was used to find the ground state structures in ferrofluid monolayers. Taking into account the magnetic dipole-dipole interaction between all particles in the system, and treating ferroparticles as hard spheres, we found different topological structures that were probable for low temperatures. It turned out that among the most energetically advantageous are rings, double rings and vortex structures. However, we have shown a single ideal ring to be the most probable ground state structure for a ferrofluid monolayer. We compared extensively theoretical predictions to the results of computer simulations and found them to be in a very nice agreement.

Morphological and rheological properties of thermoreversible organoferrogels

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Thermoreversible organoferrogels have been prepared by physical gelation of ferrofluids (FF) with two kinds of gelators of the type SEBS triblock copolymer, i.e., poly(styrene-b-(ethylene-co-butylene)-b-styrene) from the series Kraton G (G 1650, M_w = 104,000; G 1652, M_w = 80,000). The original FF consist of magnetite colloidal nanoparticles stabilized with oleic acid in two types of paraffin oil (Finavestan A 50B with η = 13.6 $mm^2 \cdot s^{-1}$ at 20 °C and M = 280 $g \cdot mol^{-1}$, Finavestan A 80B with η = 34 $mm^2 \cdot s^{-1}$ at 20 °C and M = 350 $g \cdot mol^{-1}$ (manufacturer information)).

The gelator concentration range, where stable, uniform organoferrogels are formed, is for both types of gelators c_{gel} = 4 - 10 wt.% per paraffin oil. The magnetite concentration can be varied from c_{FF} = 20 - 26 wt.% magnetite per paraffin oil.

Magnetic measurements of ferrogels, based on FF with 21 wt.% magnetite in A 50B, reveal a typical super-paramagnetic behaviour at room temperature without any hysteresis loop. The saturation magnetization (averaged over three measurements) at gels with both gelators is similar within the experimental error range and equal $M_s \approx 13$ A/m for c_{gel} = 5 wt.%.

We investigated the influence of the gelator type, paraffin oil type and their concentrations on the morphological, thermal and mechanical properties of the ferrogels (FGs) in comparison with their underlying magnetite-free precursor neat gels (NGs). The transition electron microscopy (TEM, cryo-TEM, CRF-TEM (cryo fracture replica TEM)) analysis, falling ball method measurements and rheological studies have been performed.

As revealed by TEM, both NGs and FGs exhibit a cluster network in the concentration range of c_{gel} = 4 - 10 wt.%. Magnetite particles are located in the "free" paraffin oil between the clusters of the gelator micelles.

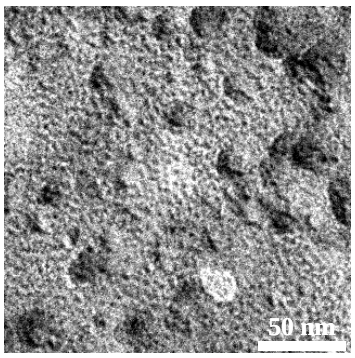

Fig. 1. CRF-TEM image of FG with c_{FF} = 21 wt.% magnetite in A 80B and c_{gel} = 5 wt.% G 1650 per paraffin oil: small bumps of magnetite and large bumps of PS micellar cores.

The diameter of the PS micellar cores is increasing with increasing molar mass of the gelator, as well as of the viscosity of the paraffin oil.

As revealed by rheological oscillatory shear experiments, the softening temperatures increase in general with increasing molar mass of the gelator as well as of the viscosity of the paraffin oil.

The FGs soften mostly at higher temperatures than the NGs. Thus, magnetite nanoparticles exhibit a stabilizing effect on the gel phase. That phase, where the storage modulus *G'* is frequency independent over the whole range 0.01 - 100 Hz, exists at 25 – 45 °C for gels with G 1650 and at 10 – 30 °C with G 1652. All gels exhibit a very wide

transition temperature region over ~ 40°C with an elasto-viscous or visco-elastic fluid behaviour. The flow temperature on which gels become liquids (T_{liq}) is also higher for FGs in comparison with NGs (Fig.2).

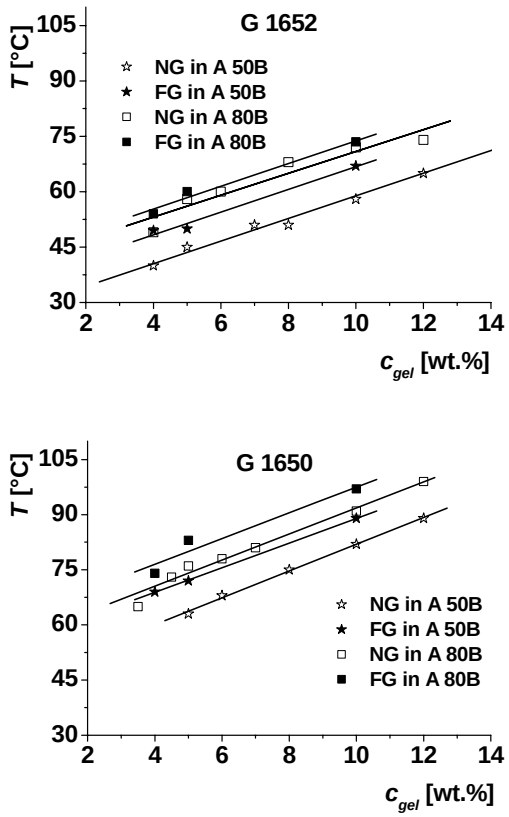

Fig. 2. T_{liq} for NGs and FGs (c_{FF} = 21 wt.% magnetite in paraffin oil).

All prepared FGs have been found homogeneous under optical microscopy observations and stable during at least 1 year.

Acknowledgments

Financial support from the DFG (Research Group FOR 608, project 5) is gratefully acknowledged.

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Thermomagnetic convection in magnetic fluids influenced by time-modulated magnetic fields: experiment and theory

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The influence of a time-modulated magnetic field on the convection in a horizontal layer of magnetic fluid bounded by isothermal non-magnetic boundaries is analysed.
For a horizontal layer of a non-magnetic fluid subjected to a vertical temperature difference ΔT, the transition from the quiescent state to that of thermal convection sets in at a critical Rayleigh number $Ra_c = 1708$ [1], where

$$Ra = \frac{\beta_T g \rho \Delta T d^3}{\kappa \eta} \ . \qquad (1)$$

This critical number applies if the driving, i.e. the temperature difference, is constant in time. Theoretical investigations on thermal convection with a time modulation of either the temperature [2] or the gravitational acceleration [3] show a shift of Ra_c depending on the strength and the frequency of the modulation. Contrary to the theoretical results, experimental ones are missing since the realisation of both systems requires tremendous technical efforts.
The study of thermal convection in magnetic fluids comes here as a rescue. The magnetic force [4] present in a horizontal layer subjected to an external magnetic field and a vertical temperature gradient admits a convective flow in the layer. This magnetically driven convection is called thermomagnetic convection characterised by the magnetic Rayleigh number

$$Ra_m = \frac{\mu_0 K \mathrm{grad} H \Delta T d^3}{\kappa \eta} \ , \qquad (2)$$

where K is the pyromagnetic coefficient of the fluid. The magnetic Rayleigh number and therefore the magnetic driving can be time-modulated by a temporal variation of the field gradient $\mathrm{grad} H$. The uncomplicated technical realisation of sudden changes in the magnetic field had been shown in [5, 6, 7] and allows the measurement of the critical quantities for the onset of convection (see contribution of Harald Engler). For a comparison with these results, a linear stability analysis of the described system is performed. The possibilities of different time modulations of the external magnetic field are discussed.

Acknowledgments

Financal support by the Deutsche Forschungsgemeinschaft under grand Od 18/7-1 and DLR 50 WM 0639 is grateful acknowledged.

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Stability of the Couette flow of a ferrofluid in an axial magnetic field: Influence of polydispersity

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The gap between two concentric rotating cylinders is filled with a ferrofluid. A homogeneous magnetic field is applied parallel to the cylinder axis. The stability of the Circular Couette flow is analysed with different models that take into account the polydispersity of the ferrofluid to a varying degree.

Magnetically driven convection in ferrofluids

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The effect of an alternating magnetic field on the linear stability properties and on the nonlinear convective states of a ferrofluid in the well-known Rayleigh-Bénard geometry is investigated numerically.
We impose a temperature gradient and a homogeneous time-dependent periodic magnetic field on the fluid layer. A competition between stabilizing thermal and viscous diffusion and destabilizing buoyancy and Kelvin forces occurs.
We determine the stability boundaries and the type of the response - harmonic or subharmonic. The effect of low and high frequency forcing on the stability boundaries as well as on the nonlinear oscillations that may occur is investigated.

Heat Transfer at the Nanoscale

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Motivation

The property to transfer electromagnetic energy into heat is an interesting feature in nanoparticles with permanent or inducible dipoles, such as metal, semiconductor or magnetic colloids. Upon irradiation with electromagnetic waves of appropriate frequency, heat loss is achieved locally and specifically, being of potential for biomedical applications in hyperthermia and drug delivery, as well as for technical use in adhesives. An issue of great significance is the transfer of the loss power from the particle to the surrounding medium. Macroscopic models are found to give an incomplete image of the heat transfer on the nanoscale, due to a high surface-to-volume ratio and the impact of a hydrodynamic interface. A main hypothesis is that the heat transport results in a temperature gradient on the interface between the particle surface and the medium.[1]

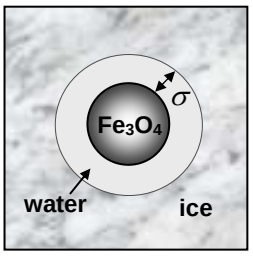

Figure 1: Schematic of a magnetic nanoparticle embedded in ice. Heat released from the particle creates a spherical shell of liquid.

Results

We report on detailed investigations on the electromagnetic heatability of nanoparticles in AC magnetic fields of the kHz regime in a model system composed of magnetic nanoparticles embedded in an ice matrix.[2]

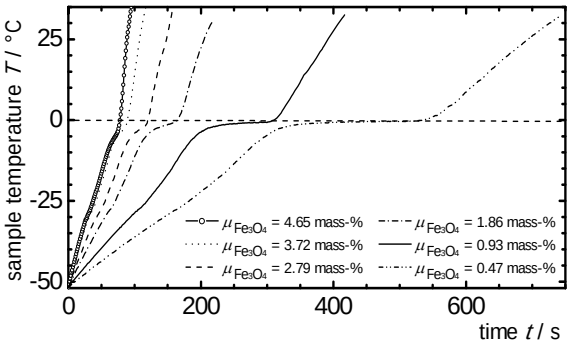

Figure 2: Magnetocalorimetric heating curves of frozen water-based ferrofluids with different magnetite content.

The developed experimental setup of magnetocalorimetry allows the detection of energy consumption connected with the endothermic transition in terms of transition temperature and enthalpy in AC magnetic fields. The comparison of MC results with respective behavior by conventional (extrinsic) heating in differential scanning calorimetry (DSC) shows significant differences between these two heating methods.

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Magnetic nanoparticles used as drug carriers for minimally invasive cancer treatment

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Ferrofluids are being investigated for minimally invasive cancer treatment procedures. Thereby the biocompatibility of these suspensions is an important aspect for their medical applications.

Conventional cancer treatment methods such as chemotherapy can be improved to become a local therapy by using the magnetic nanoparticles. For chemotherapy the particles are used to carry drugs to the desired area – the tumour tissue. This method is called magnetic drug targeting (MDT) and is performed as follows. The chemotherapeutic agent mitoxantrone is ionically bound on the nanoparticles and injected into the artery which supplies the tumour. A strong magnetic field gradient is used to lead the nanoparticles acting as drug carriers to the tumour tissue and to keep them there for approximately one hour.

Experiments proving this therapeutic approach are performed on tumours which have been grown on rabbits. After the treatment the animals are sacrificed, the tumours resected, fixated in formalin and embedded in paraffin [1-4]. For the analysis of these tumour samples we are applying a method for 3-dimensional imaging – the micro-computed tomography (µCT) - using a cone beam X-ray source which is placed at TU Dresden as well as and a second setup based on synchrotron radiation at DESY/HASYLAB.

The results obtained with both equipments have shown that the nanoparticles are agglomerated within the vascular system of the tumour. Furthermore an enrichment of nanoparticles within the surrounding areas of the veins could be detected (see Figure 1). Thus, the delivered drugs bonded on nanoparticles have been transferred through the membrane of the cells into the tumour tissue by the magnetic force [5, 6].

Using image processing techniques, the distribution of particles can be examined and related to experimental conditions used during the MDT process.

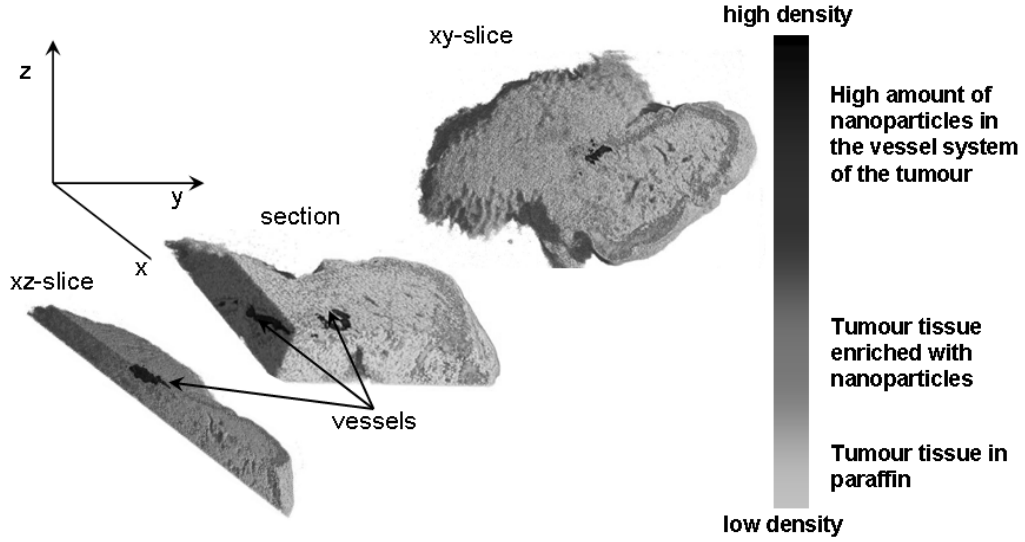

Figure 1: 3-D Representation of a 1.2 mm high and 16 mm wide slice of a tumour sample and frontal and axial cross sections.

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Flow control of magnetic fluids exposed to magnetic fields

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Motivation

To describe the influence of magnetic fields on the flow of ferrofluids is a major goal of magnetic fluid research. In former investigations this has been done on the basis of [1-3]. However, microscopic parameters like the mean particle size, the particle size distribution, the volume concentration of particles and the magnetic anisotropy are difficult to obtain.

Within a current research project, a new approach to describe ferrofluid behaviour will be attempted: A theory solely based on macroscopic parameters, like the dynamic viscosity μ or the coupling coefficient between magnetization dynamics and the symmetric velocity gradient λ_2, shall be able to describe the behaviour of magnetic fluids under magnetic field influence.

Within the frame of a larger cooperation project, the group of M. Lücke (Saarbrücken) investigates the flow of a magnetic fluid between rotating concentric cylinders known as Taylor vortex flow. Using different models for the relaxation of magnetisation-including the one established by M. Liu (Tübingen)-a way to distinguish the adequate description of ferrofluid dynamics is achieved. At our institute, we do the experimental work by building a Taylor-Couette setup in order to analyze the flow phenomena appearing in the gap between the two rotating cylinders, thus being able to validate the simulated flows.

Experiment

A Taylor-Couette-Setup has been built with a gap height of 20 cm, a radius of the inner cylinder of 1 cm and a gap width of 1 cm, resulting in an aspect ratio of Γ=20 and a radius ratio of η=0.5. Either of the two cylinders may rotate in both directions. The magnetic field is generated by Helmholtz-coils in Fanselau arrangement with a peak field strength of 40kA/m in the homogeneous area.

The axial velocity component of the flow modes is measured by means of Ultrasound-Doppler-Velocimetry, whereas the transducer is placed on either one side of the gap. An example for a velocity profile of TVF is given in Fig. 1.

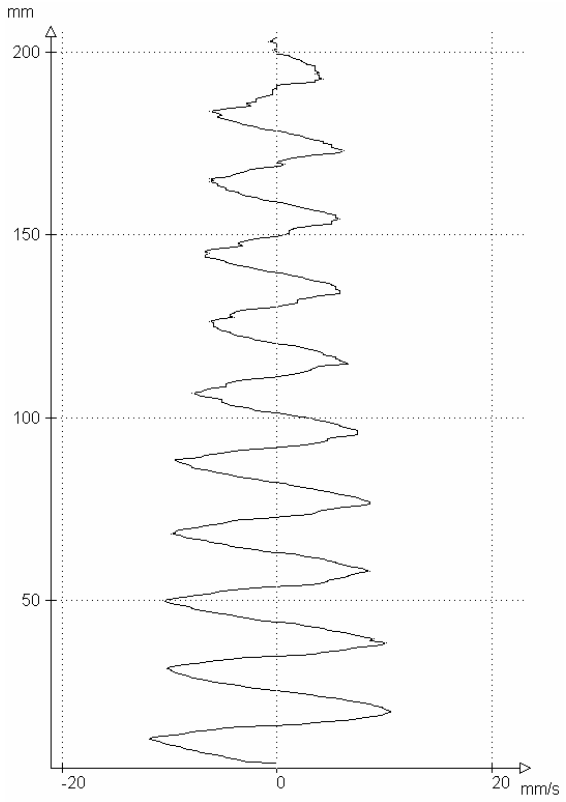

Fig. 1: Axial sinusoidal velocity profile for Re=118 for the inner cylinder, Re=0 for the outer cylinder and the US-transducer being placed at the outer cylinder wall.

As may be seen in Fig. 1, the peak velocities decrease with increasing depth. This might be due to a beam widening of the ultrasound signal, but is still subject to further investigation and discussion.

Also other flow modes show their characteristic axial velocity profiles, as pictured in Fig. 2a and Fig. 2b. The flow is time-periodically alternating between the two axial velocity profiles.

The sinusoidal velocity profiles get analyzed by FFT. As expected, for TVF, the predominant peak of the power density spectrum showed to be at a wavelength of twice the gap width.

Currently, the system is validated with various silicon oils and the phase transitions being checked. The experimental setup and first results of experiments done with ferrofluids exposed to magnetic fields shall be presented at the workshop.

Acknowledgments

This project is funded by DFG under grant no. OD18/11

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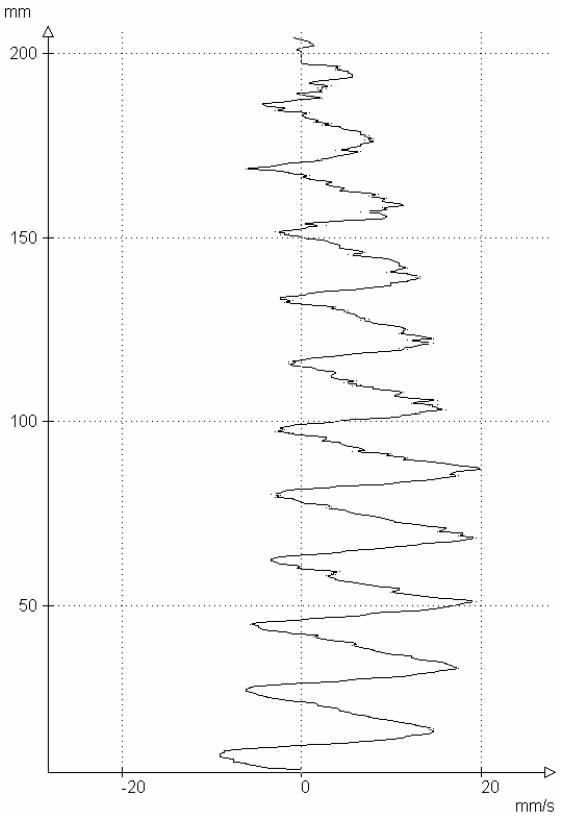

Fig. 2a: Snapshot 1 of a wavy vortex flow (WVF) at Re=160 for the inner cylinder and Re=45 for the counter rotating outer cylinder.

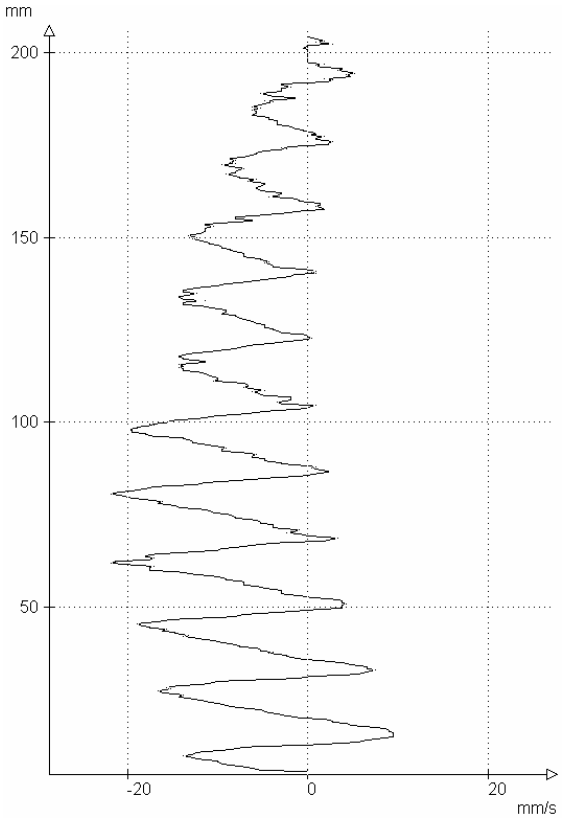

Fig. 2b: Snapshot 2 of WVF at the same Reynolds numbers as in Fig. 2. The time delta between the two snapshots is 1625ms.

Why does a Ferrofluidic Pendulum FLIP at a Critical Driving Frequency

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Recently a new type of torsional pendulum was proposed [1] which we realize by suspending a DISC SHAPED container in a Helmholtz pair of coils driven by an alternating sinusoidal current. The container is suspended with its long axis in line with the fiber. In contrast to a spherical pendulum [2, 3] the orientation of the disc is sensitive both to the field direction and the field frequency: As sketched in Fig. 1 it should expose its edge to the field vector of low oscillating field and its broad side to the field vector of high frequency.

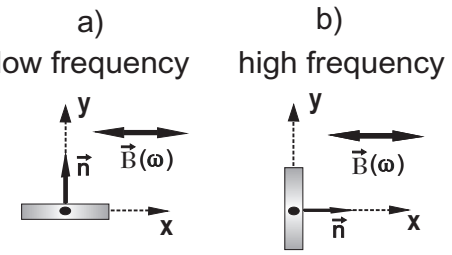

Figure 1: The two different orientations of the pendulum for low and high driving frequencies.

Unfortunately, this reorientation (FLIP) does not occur for available ferrofluids because of their polydispersity. But with help of an additional constant magnetic field $B_{\rm help}$, which is orientated perpendicular to the oscillating one, the FLIP of the pendulum can be observed. Figure 2 displays the pendulum frequency f_P versus the driving frequency f. The flip occurs at $f_P = 0\,$Hz. The mechanism for the flip is intrinsically connected with the frequency dependence of the generalized ac-susceptibility $\chi'_\parallel(f)$ for a field parallel, and $\chi'_\perp(f)$ for a field orthogonal to the symmetry axis of the filled pendulum. The solid line in Fig. 2 gives our theoretical estimate for the pendulum frequency according to

$$\hat{f_P}^2 = B_0 V \frac{\chi'_\perp(f) - \Big(\chi'_\parallel(f) + h(\gamma)\Big)}{4\pi\,\mu_0 J} + f_{\rm mech}^2.$$

Here B_0 denotes the amplitude of the oscillating field, V the volume of the disc-shaped body, J the moment of inertia of the pendulum and

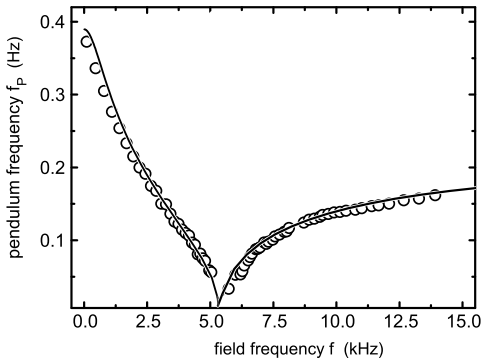

Figure 2: Pendulum frequency versus driving frequency for a constant driving amplitude. The flip occurs for $f_P = 0$ at $f \approx 5.2$ kHz. From [4].

$f_{\rm mech}$ its frequency without any magnetic field. Moreover we use the abbreviation

$$h(\gamma) = \frac{\gamma}{\mu_0} V \left(\chi'_\perp(0) - \chi'_\parallel(0)\right),$$

with $\gamma = 2B_{\rm help}^2/B_0^2$. We have measured the variation of f_P for different values of $B_{\rm help}$, and find again a convincing agreement with the model.

The observed effect is a physical mechanism in principal which should occur not only for oblate magnetizable bodies like the disc, but also for prolate bodies, like rods. Moreover it should be observed in electrical polarized matter, too.

Acknowledgments
The authors thank M. Zaks for helpful advice.

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Hexagon–Square Transition of the Rosensweig Instability in the presence of a magnetic ramp

Leonhard Wiesen[1], Christian Gollwitzer[1], Reinhard Richter[1], Ingo Rehberg[1]

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Introduction

The Rosensweig instability has been predicted [1] and found experimentally [2] to show a transition from a hexagonal arrangement of the peaks to a square one. In a recent experiment we unveiled that this transition does show an inverse hysteretic character (proteresis) [3]. In our contribution we reinvestigate this transition in a container with larger aspect ratio and under the influence of a magnetic ramp to minimize the influence of the boundary.

Experiment

The experimental setup consists of a flat aluminum pan with a diameter of ca 40 cm (see figure 1), positioned in the center of a Helmholtz pair of coils (see figure 2). The magnetic field is overcritical in a circular area with diameter of ca 24cm. To analyze the surface structure of the fluid we use the attenuation X-rays, as shown in figure 2 [4].

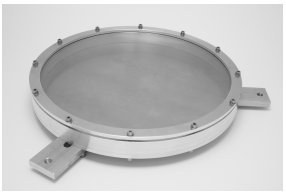

Figure 1: Aluminum pan with diameter of 40 cm.

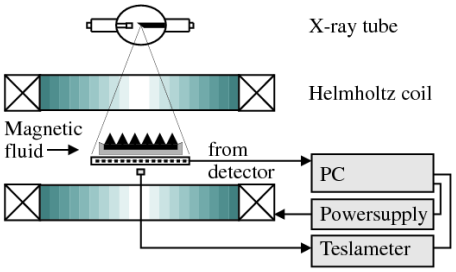

Figure 2: Experimental setup.

Starting at subcritical values we increase the induction B quasi adiabatically, and observe the well known subcritical transition to a hexagonal pattern. Increasing B further we measure a transition to squares. Figure 3 shows an radioscopic image as an example. From these pictures we extract the peak to peak distance from the real space and the amplitude, the wavelength and the angular correlation function from the fourier space. Figure 4 displays the evolution of the wavelength under increase and decrease of the order parameter B.

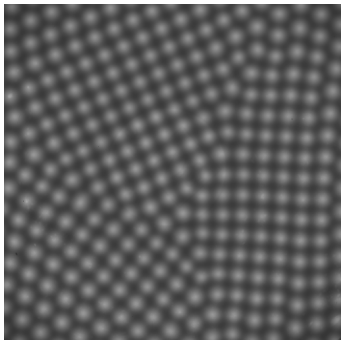

*Figure 3: Radioscopic image of the Rosensweig peaks in our ferrogel (19*19cm).*

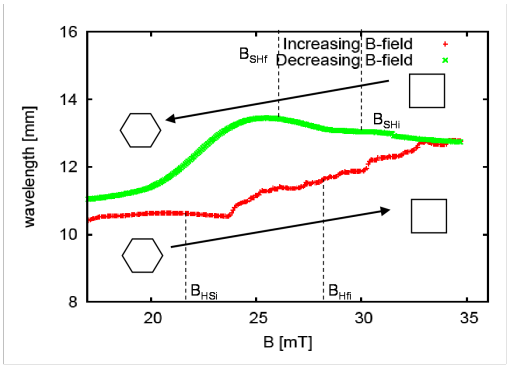

Figure 4: Wavelength of the peaks by analyzing the average distance of the peaks in fourier space.

References

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Nanoparticle driven imatinib delivery into cells with gold coated iron oxide particles

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[3)]*Institut für Anatomie, Universitätsklinikum Jena, Teichgraben 7, D-07743 Jena*

Introduction

The targeted delivery of therapeutics into relevant cells and tissues is still of major concern. We present a simple straight forward strategy of binding a therapeutic drug onto magnetic nanoparticles. The magnetic core of the nanoparticles allows the precise localization of the nanoparticles and the release of the drug at the desired destination.

We choose imatinib (syn.: STI571) as a model substance, because it is well defined and shows a distinct molecular action by inhibiting the kinase activity of the bcr/abl fusion protein in chronic myeloic leukemia (CML). Therefore we used the CML cell line K562 as a model system. For preparing the delivering nanoparticles, iron oxide particles were coated with gold. Finally, the drug was adsorbed to the gold surface of the nanoparticles.

Results

The imatinib loaded nanoparticles have the same effect onto the leukemia cells as the pure drug itself. K562 cells exhibited a dramatic reduction in cell proliferation depending on the concentration of the nanoparticles and subsequently the transferred drug. Cell cultures incubated with nanoparticle preparations without imatinib showed no effect and exerted a comparable proliferation as untreated K562 cells.

Bcr/abl negative cells were not affected by the imatinib loaded nanoparticles.

Summary

In conclusion, we could prepare gold coated magnetic iron oxide nanoparticles with adsorption properties for imatinib. This approach allows the use of these imatinib loaded nanoparticles as a particle assisted delivery system to selected target cells. These results encourage us to use magnetic nanoparticles as vehicles for other drugs and as drug locating system.

Acknowledgments

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Synthesis of magnetic metal nanocomposite particles

A. Gorschinski,[a] G. Khelashvili,[a] D. Schild,[b] W. Faubel,[a] S. Heissler,[a] H. Bönnemann,[a,c] E. Dinjus,[a] S. Behrens[a,]*

Institut für Technische Chemie[a] and Institut für Nukleare Entsorgung[b], Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe and Max- Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim[c]

One challenge in synthesizing multicomponent nanostructures, e.g. of core-shell type is understanding how to form an interface between the different materials which may exhibit very different crystallographic structures, lattice dimensions, chemical stability, or reactivity. The synthesis of cobalt nanoparticles applying dicobalt octacarbonyl with organometallic precursors (aluminium trialkyls) or polysiloxane micelles has been previously reported by Bönnemann et al. [1,2] and Riffle et al. [3], respectively. We report the synthesis of monodisperse cobalt nanoparticles by thermolysis of a dicobalt octacarbonyl precursor in the presence of simple aminofunctionalized siloxanes. The aminofunctionalized siloxane controls particle formation by complexation of cobalt and mediates further deposition of silica. The particles were passivated with low doses of oxygen, resulting in good stability towards air and moisture. The amount of siloxane, the temperature, as well as the heating rate affect the monodispersity and the size of the particles. When tetraethoxysilane is added and hydrolyzed, the amino functionalized siloxane serves as a coupling agent for further deposition of silica. Alternatively, a peptizing agent (KorantinSH) may be applied to form colloidal solutions or magnetic fluids.

The presented procedure opens a new and simple synthetic pathway for the production of hybrid particles of various nature exhibiting multifunctional behavior and new surface functionalities. The combination of materials exhibiting different physical phenomena is manifold, including optical/magnetic, optical/catalytic, magnetic/ferroelectric etc.

[1] H. Bönnemann, K.S. Nagabhushana, R.M. Richards, "Colloidal Nanoparticles Stabilized by Surfactants or Al-organic Derivatives: Preparation and Use as Catalyst Precursors", Chapter 2 in: D. Astruc (ed), Nanoparticles and Catalysis, Wiley-VCH p. 49 - 91 (2007) (ISBN 3-527-31572-7)

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LIST OF PARTICIPANTS

Participants

Auernhammer, Günter K., MPI für Polymerforschung, Mainz auhammer@mpip-mainz.mpg.de	**16:50-17:15 07.05**	**Talk:** "Shear-induced structural changes in magnetic nanoparticle aggregates followed by x-ray microscopy"
Behrens, Silke, Forschungszentrum Karlsruhe silke.behrens@toc.cpv.fzk.de	**P01**	**Poster** (with Gorschinski): "Synthesis of magnetic metal nanocomposite particles"
Beresnev, Sergey, Univ. Magdeburg sergey.beresnev@mathematik.uni-magdeburg.de	**16:25-16:50 07.05**	**Talk:** "Numerical study of the influence of diffusion of magnetic particle equilibrium shapes of a free magnetic fluid surface"
Bibette, Jerome, ESPCI, Paris jerome.bibette@espci.fr	**9:00-9:40 09.05**	**Inv. Speaker:** "Experiments on self assemblies of magnetic colloids"
Bohlius, Stefan, MPI für Polymerforschung, Mainz bohlius@mpip-mainz-mpg.de	**P02 08.05**	**Poster:** "The amplitude equation for the Rosensweig instability"
Borin, Dmitry, TU Dresden dmitry.borin@tu-dresden.de	**P03 08.05**	**Poster:** "Experimental study of dynamics of changes of viscosity in magnetically controlled fluids under shear flow"
Buske, Norbert, MagneticFluids, Berlin n.buske@magneticfluids.de		
Camp, Philip J., Univ. of Edinburgh philip.camp@ed.ac.uk	**15:20-16:00 07.05**	**Inv. Speaker:** "Phase separation in model ferrofluids"
Cerda Pino, Juan Jose, FIAS Frankfurt jcerda@fias.uni-frankfurt.de	**10:05-10:30 08.05**	**Talk:** "Structure formation and phase behavior in bidisperse ferrofluid monolayers-I: simulations"
Dutz, Silvio, Inst. of Photonic Technology, Jena silvio.dutz@ipht-jena.de	**P04 08.05 P05 08.05**	**Poster 1**: "Effect of package density on magnetic properties of iron oxide nanoparticles" **Poster 2:** "Magnetische Eigenschaften wasserbasierter Citrat-Magnetit Magnet-flüssigkeiten mit hoher Partikelkonzentration"
Elfimova, Ekaterina, Ural State University, Ekaterinenburg ekaterina.elfimova@usu.ru	**P06 08.05**	**Poster:** "Ionic stabilized ferrofluid: anisotropy of the structure factor under external magnetic field"
Engler, Harald, TU Dresden harald.engler@tu-dresden.de	**9:40-10:05 09.05**	**Talk:** „Investigation of the thermomagnetic convection in ferrofluid influenced by a time-modulated driving force"
Erbe, Artur, Univ. Konstanz artur.erbe@uni-konstanz.de	**14:10-14:35 08.05**	**Talk:** „Frustration-induced magic number clusters of colloidal magnetic particles"

Participants

Erné, Ben, Van't Hoff Lab., Utrecht University b.h.erne@uu.nl	**12:05-12:30 09.05**	**Talk:** Microspheres with a Switchable Magnetic Remanence“
Fahmi, Amir, The Univ. of Nottingham amir.fahmi@nottingham.ac.uk		
Feyen, Mathias, MPI für Kohleforschung, Mülheim an der Ruhr feyen@mpip-muelheim.mpg.de	**P07 08.05**	**Poster:** „Encapsulation of Fe_30_4 nanoparticles in cross-linked polystyrene spheres“
Friedrich, Thomas, Univ. Bayreuth thomas.friedrich@uni-bayreuth.de	**9:40-10:05 08.05**	**Talk:** „Transport of ferrofluid due to travelling-stripe forcing“
Gollwitzer, Christian, Univ. Bayreuth christian.gollwitzer@uni-bayreuth.de	**17:30-17:55 08.05** **P08 08.05**	**Talk:** „The Rosensweig instability with a ferrogel“ **Poster:** “Measuring the deformation of a ferrogel sphere in a homogeneous magnetic field”
Gorschinski, Angelika, Forschungszentrum Karlsruhe angelika.gorschinski@itc-cpv.fzk.de	**P09 08.05**	**Poster**: „Synthesis of magnetic metal nanocomposite particles“ (with Behrens)
Gürler, Celin, Univ. Düsseldorf celin.guerler@uni-duesseldorf.de	**P10 08.05**	**Poster:** „Electromagnetically driven nanorotors and –heaters“
Heim, Erik, TU Braunschweig e.heim@tu-bs.de	**12:05-12:30 08.05**	**Talk:** „Investigation of binding assays with streptavidin functionalized superparamagnetic nanoparticles and biotinylated analytes by fluxgate magnetorelaxometry“
Heinrich, Dirk, TU Berlin dhein@physik-tu-berlin.de	**13:40-14:05 07.05**	**Talk:** „Time dependent NMR spectroscopy on ionic ferrofluids“
Hempelmann, Rolf, Univ. des Saarlandes, Saarbrücken r.hempelmann@mx.uni-saarland.de		
Hentschke, Reinhard, Univ. Wuppertal hentschk@uni-wuppertal.de	**14:05-14:30 07.05**	**Talk:** “Gas-liquid phase behavior of dipolar fluids and beyond”
Heritier, Luis, MPI for Polymer Research, Mainz heritier@mpip-mainz.mpg.de		
Holm, Christian, FIAS Frankfurt, and MPI for Polymer Research, Mainz c.holm@fias.uni-frankfurt.de		**Organizer**
Ivanov, Alexey, Ural State Univ., Ekaterinenburg alexey.ivanov@usu.ru	**15:00-15:25 08.05**	**Talk:** “Theoretical modeling of structure factor of ferrofluid under a magnetic field“

Participants

John, Thomas, Univ. Magdeburg thomas.john@physik.uni-magdeburg.de	**P11** **08.05**	**Poster:** "Measurements and calculations of torques on a ferrofluid sphere under time asymmetric magnetic fields"
Kancharla, Venkata, The Univ. of Nottingham epxvsk@nottingham.ac.uk	**11:40-12:05** **09.05**	**Talk:** "Fabrication and characterisation of magnetorheological fluids for reconfigurable fixturing systems"
Kantorovich, Sofia, MPI-P Mainz, FIAS Frankfurt, Ural State University kantorovich@fias.uni-frankfurt.de	**P12** **08.05**	**Poster :** "Ground state structures in ferrofluid monolayers"
Klapp, Sabine, TU Berlin, sabine.klapp@fluids.tu-berlin.de	**11:40-12:05** **08.05**	**Talk:** "Field-induced and spontaneous structure formation in ferrofluid multilayer films"
Kochinke, Korinna, KIST Europe, Saarbrücken kkochinke@freenet.de		
Kraupner, Alexander, Bayer Schering Pharma AG, Berlin alexander.kraupner@bayerhealthcare.com		
Krekhova, Marina, Univ. Bayreuth marina.krekhova@uni-bayreuth.de	**P13** **08.05**	**Poster:** "Morphological and rheological properties of thermoreversible organoferrogels"
Krill, Carl, Univ. Ulm carl.krill@uni-ulm.de	**P22** **08.05**	**Poster:** "Synthesis of Nanotube Ferrofluids by Virus Templating" (presented by Z. Wu)
Kroll, Torsten, Universitätsklinikum Jena torsten.kroll@med.uni-jena.de	**16:40-17:05** **08.05**	**Talk:** "Nanoparticle driven imatinib delivery into cells with gold coated iron oxide particles"
Lange, Adrian, TU Dresden adrian.lange@tu-dresden.de	**P14** **08.05**	**Poster:** "Thermomagnetic convection in magnetic fluids influenced by time-modulated magnetic fields: experiment and theory"
Leschhorn, Andreas, Univ. des Saarlands, Saarbrücken andy@lusi.uni-sb.de	**P15** **08.05**	**Poster:** "Stability of the Couette flow of a ferrofluid in an axial magnetic field: influence of polydispersity"
Ludwig, Frank, TU Braunschweig f.ludwig@tu-bs.de	**17:05-17:30** **08.05**	**Talk:** "Characterization of magnetic core shell nanoparticles … - a comparative study"
Martinoty, Philippe, Univ. of Strasbourg philippe.martinoty@ldfc.u-strasbg.fr	**11:00-11:40** **08.05**	**Inv. Speaker:** "Mechanical properties of uniaxial magnetic gels"
Matoussevitch, Nina, Qiagen GmbH, Hilden nina.matoussevitch@qiagen.com	**P10** **08.05**	**Poster:** „Electromagnetically driven nanorotors and –heaters"(Presented by **Gürler**)
Matura, Pascal, Univ. des Saarlands, Saarbrücken p.matura@lusi.uni-sb.de	**P16** **08.05**	**Poster:** "Magnetically driven convection in ferrofluids"

Participants

Messing, Renate, Univ. Düsseldorf, renate.messing@uni-duesseldorf.de	**P17 08.05**	**Poster:** "Heat Transfer at the Nanoscale"
Modahl, Grete Irene, Invitrogen Corporation, Lillestrom grete.modahl@invitrogen.com		
Odenbach, Stefan, TU Dresden stefan.odenbach@tu-dresden.de	**13:00-13:40 07.05**	**Inv. Speaker**: "Yeld stress in ferrofluids!?"
Pankhurst, Quentin, Univ. College London q.pankhurst@ucl.ac.uk	**9:00-9:40 08.05**	**Inv. Speaker:** "Biomedical Applications of Magnetic Nanoparticles and Fluids"
Perzynski, Regine, LI2C - UPMC and Univ. Paris 6 rperz@ccr.jussieu.fr	**13:30-14:10 08.05**	**Inv. Speaker:** "Vitreous transitions in a dense ferrofluid!"
Pleiner, Harald, MPI for Polymer Research Mainz pleiner@mpip-mainz.mpg.de		**Organizer**
Prinz, Eva, Univ. des Saarlandes, Saarbrücken e.prinz@mx.uni-saarland.de	**16:00-16:25 07.05**	**Talk:** „Biomedical functionalisation of magnetic nanoparticles"
Polevikov, Viktor, Univ. Magdeburg		
Queralto, Nuria Gratacos, MPI for Polymer Research, Mainz queralto@mpip-mainz.mpg.de		
Raikher, Yuriy L., Inst. of Continuous Media Mechanics, Russian Acad. of Sciences, Perm raikher@icmm.ru	**16:00-16:40 08.05**	**Inv. Speaker:** "Field-induced behavior of fine magnetic particles embedded in polymeric matrices: some … aspects"
Rahn, Helene, TU Dresden helene.rahn@tu-dresden.de	**P18 08.05**	**Poster:** „Magnetic nanoparticles used as drug carriers for minimally invasive cancer treatment"
Reindl, Matthias, TU Dresden matthias.reindl@tu-dresden.de	**P19 08.05**	**Poster:** "Flow control of magnetic fluids exposed to magnetic fields"
Richter, Reinhard, Univ. Bayreuth reinhard.richter@uni-bayreuth.de	**P20 08.05**	**Poster:** „Why does a ferrofluidic pendulum FLIP at a critical driving frequency""
Schmidt, Annette M., Univ. Düsseldorf schmidt.annette@uni-duesseldorf.de	**14:35-15:00 08.05**	**Talk:** „Magnetoactive liquid crystal elastomers"
Steinfeld, Ute, KIST Europe, Saarbrücken steinfeld@kist-europe.de		

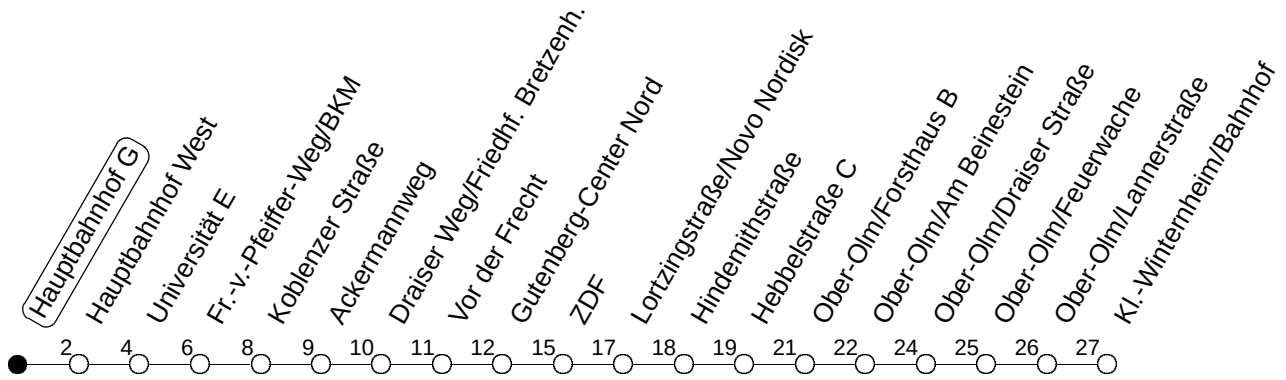
Participants

Wagner, Joachim, Univ. des Saarlandes, Saarbrücken j.wagner@mx.uni-saarland.de	**10:05-10:30 09.05**	**Talk:** „Magnetic nanorods in external fields“
Wagner, Kerstin, INNOVENT e. V., Jena kw@innovent-jena.de		
Wiesen, Leonhard, Univ. Bayreuth leonhard.wiesen@uni-bayreuth.de	**P21 08.05**	**Poster:** “Hexagon-square transition of the Rosensweig instability in the presence of a magnetic ramp”
Wu, Zhenyu, Univ. Ulm zhenyu.wu@uni-ulm.de	**P22 08.05**	**Poster:**“Synthesis of Nanotube Ferrofluids by Virus Templating” ”
Wotschadlo, Jana, FSU Jena jana.wotschadlo@med.uni-jena.de	**P23 08.05**	**Poster:** „Interaction of tumor cells and peripheral blood cells with magnetic nanoparticles coated with tailored dextran-based shells“
Zeidis, Igor, TU Illmenau igor.zeidis@tu-illmenau.de	**P24 08.05**	**Poster:** “Locomotion of a magnetizable worm in a magnetic field”
Zrinyi, Miklos, Budapest Univ. Of Technology and Economics zrinyi@mail.bme.hu	**11:00-11:40 09.05**	**Inv. Speaker:** „From ferrofluids to ferrogels“

PRACTICAL INFORMATION

68

Haltestelle : **Hauptbahnhof G**
Fahrtrichtung : **KLEIN-WINTERNHEIM**



Fahrzeitangabe in Minuten

	Montag-Freitag			Samstag			Sonn- und Feiertag
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6	29	49					
7	09⬓	29	49				
8	09	29B	49	00	30	59	
9	09	29	59	29	59		
10	29	59		29	59		
11	29	59		29	59		
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17	09	29	49	29	59		
18	09	29	59				
19	29	59					

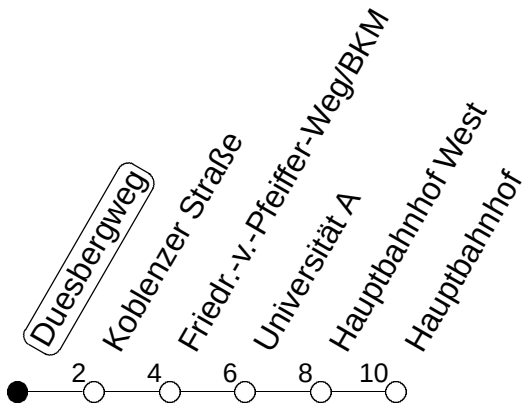
⬓ : Hochflurbus

B : Nur bis Mainz/Hindemithstraße

Ferien in Mainz: 24.12.07-8.01.08/4.-5.02./12.03.-28.03./2.05./23.05./23.06-1.08./6.10.-17.10.08

69

Haltestelle : **Duesbergweg**
Fahrtrichtung : **HAUPTBAHNHOF**



Fahrzeitangabe in Minuten

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9	07v 17v 27v 37v 47v 52v 57v		
10	02v 07v 17v 37v 57v		
11	17v 37v 47v 57v		
12	07v 17v 37v 57v		
13	17v 37v 57v		
14	17v 37v 57v		
15	17v 37v 47v 57v		
16	07v 17v 27v 37v 57v		
17	17v 37v 47v 57v		
18	17v 37v		

v : Nur an Vorlesungstagen der Universität Mainz

Vorlesungsfreie Tage: 24.12.07-5.01.08 / 18.02.-12.04. / 14.07.-18.10. / 22.12.-31.12.08

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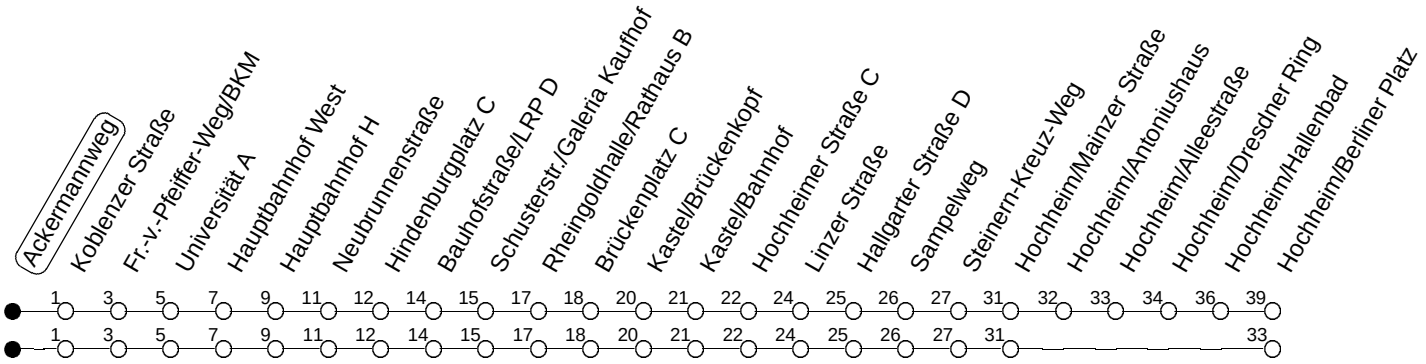
Haltestelle : **Ackermannweg**
Fahrtrichtung : **HOCHHEIM**



Fahrzeitangabe in Minuten

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8	07r	27B	47r		47r		
9	17r	47r			17r	47r	
10	17r	47r			17r	47r	
11	17r	47r			17r	47r	
12	17r	47			17r	47r	
13	07	27	47		17r	47r	
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15	07	27	47		17r	47r	
16	07	27	47		17r	47r	
17	07	27	47A		17r	47r	
18	07	27	47A		17r	50H	
19	17r	47r					
20	17r	50H					

r : Über Hochheim/Wiesbadener Straße
⬓ : Hochflurbus
B : Nur bis Brückenplatz
S : Nur an Schultagen in Mainz
A : Ab Berliner Platz weiter über Goethestr. - Altenwohnheim nach Altkönigstr.
H : Nur bis Hauptbahnhof

Ferien in Mainz: 24.12.07-8.01.08/4.-5.02./12.03.-28.03./2.05./23.05./23.06-1.08./6.10.-17.10.08

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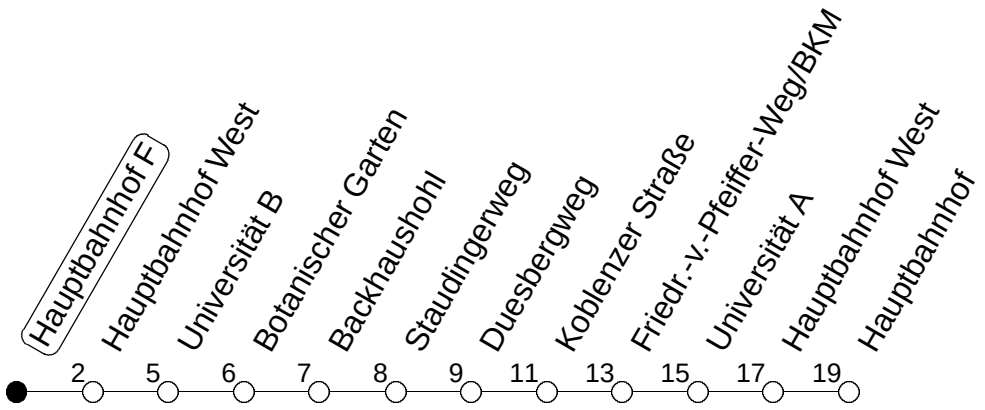
Haltestelle : **Hauptbahnhof F**
Fahrtrichtung : **UNIVERSITÄT/CAMPUS**



Fahrzeitangabe in Minuten

	Montag-Freitag								Samstag	Sonn- und Feiertag
Std.	**Minuten**								**Minuten**	**Minuten**
7	36v	40v	44v	48v	52v	56v				
8	00v	04v	08v	18v	28v	38v	48v	58v		
9	08v	18v	28v	38v	43v	48v	53v	58v		
10	08v	28v	48v							
11	08v	28v	38v	48v	58v					
12	08v	28v	48v							
13	08v	28v	48v							
14	08v	28v	48v							
15	08v	28v	38v	48v	58v					
16	08v	18v	28v	48v						
17	08v	28v	38v	48v						
18	08v	28v								

v : Nur an Vorlesungstagen der Universität Mainz

Vorlesungsfreie Tage: 24.12.07-5.01.08 / 18.02.-12.04. / 14.07.-18.10. / 22.12.-31.12.08

Staudinger Hörsaal

Haupteinfahrt

Ackermannweg

68

MPI fuer Polymerforschung

P MPI

P Studenten

Koblenzer Straße

Bretzenheim, Lerchenberg

Finthen

Münchfeld
Gonsenheim

NORD

0 100m

© Uni Mainz, Stand: Juni '96

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Duesbergweg

Ackermannweg

Chemie

Mensa

Studentenhaus

Physik

AB Darmstadt, Frankfurt, Wiesbaden

Pizzeria Campus

Wohnheime u.
Kindergarten

Staudingerweg

Physik

Bechenweg

Weiderweg

Wittichweg

54, 55,
58, 68

Pfeifferweg

Fußgänger-Überweg
pedestrian bridge

Pfeiffer-
weg

Straß-
mannweg

Bentzel-
weg

Saarstraße

Fußweg

Botanischer
Garten

Dalheimer Weg

Bentzelweg

MPI f. Chemie

„Muschel"

Naturwiss.
Fakultät

Col.-Klein-
mann-Weg

Weiderweg

Philosophicum

Universitäts-
Bibliothek

Wittichweg

Innenstadt/Hauptbahnhof

Fußweg

Stadion

SB II

Bechenweg

ReWi

Müllerweg

Studierenden-
Sekretariat

Bretzenheim

Backhaushohl

Sport-
Institut

Bentzelweg

Müllerweg

Forum

Eingang für
Fußgänger

ESG

Einfahrt Sport

Gieseum und-
weg

Alte Mensa

Albert-Schweitzer-Straße

KHG

Xaverius weg

Innenstadt/
Zahlbach

Einfahrt
nur nach 19 Uhr,
an Wochenenden
oder mit Codekarte