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Hariharan Srikanth

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University of South Florida - Tampa
4202 East Fowler Ave.

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14. ABSTRACT
Ferrofluids are technologically important for a variety of applications ranging from biomedicine, hydraulics to power generation. They are also model systems for the investigation of physics of relaxation phenomena in magnetic nanoparticles. We have done systematic DC and AC magnetization studies of ferrofluids composed of Fe_3O_4 and $CoFe_2O_4$ nanoparticles (mean size ~ 14 nm) suspended in hexane and dodecane, respectively. The blocking temperature was just above (hexane) and much below (dodecane) the carrier fluid freezing temperatures providing interesting regimes to study the relaxation mechanisms associated with the fluid and frozen states. Frequency- and temperature- dependent AC magnetization were used to probe the

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Final Report: Static and Dynamic Magnetic Response in Ferrofluids

ABSTRACT

Ferrofluids are technologically important for a variety of applications ranging from biomedicine, hydraulics to power generation. They are also model systems for the investigation of physics of relaxation phenomena in magnetic nanoparticles. We have done systematic DC and AC magnetization studies of ferrofluids composed of Fe3O4 and CoFe2O4 nanoparticles (mean size ~ 14 nm) suspended in hexane and dodecane, respectively. The blocking temperature was just above (hexane) and much below (dodecane) the carrier fluid freezing temperatures providing interesting regimes to study the relaxation mechanisms associated with the fluid and frozen states. Frequency- and temperature- dependent AC magnetization were used to probe the Néel and Brownian contributions to the relaxation. Ferrofluids were also investigated under various flow conditions for possible electrokinetic battery applications. New instrumentation was developed for conducting these experiments.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. “Magnetoimpedance biosensor for Fe3O4 nanoparticles intracellular uptake evaluation” –A. Kumar, V. Fal-Miyar, J. A. Garcia, A. Cerdeira, S. Mohapatra, H. Srikanth, J. Gass and G. V. Kurlyandskaya, Applied Physics Letters 91, 143902 (2007)

2. “Transverse susceptibility as a probe of interface magnetism in functional multilayers and nanostructures” –N. A. Frey, M. B. Morales, H. Srikanth and S. Srinath, Encyclopedia of Advanced Materials: Science and Engineering (Pan Stanford Publishers, in press 2007)

3. “Static and dynamic magnetic properties of composite Au-Fe3O4 nanoparticles” –N. A. Frey, S. Srinath, H. Srikanth, T. Chao and S. Sun, IEEE Transactions on Magnetics 43, 3094 (2007)

4. “Synthesis and magnetic characterization of NiFe nanowires in nanoporous Si template” –S. Aravamudhan, K. Luongo, S. Bhansali, P. Poddar and H. Srikanth, Applied Physics A: Materials Science and Engineering (2007)

5. “Superparamagnetic polymer nanocomposites with Fe3O4 nanoparticle dispersions” –J. Gass, P. Poddar, J. Almand, S. Srinath and H. Srikanth, Advanced Functional Materials 16, 71 (2006)

Number of Papers published in peer-reviewed journals: 5.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. “Magnetic properties of Fe3O4 and CoFe2O4 based ferrofluids” –M. B. Morales, J. Gass, S. L. Morrow and H. Srikanth, APS March Meeting, Denver, CO (March 5-9, 2007)

2. “Synthesis and characterization of functional magnetic nanocomposites” –J. Gass, J. Sanders, S. Srinath and H. Srikanth, APS March Meeting, Baltimore, March 2006

3. “Sensor applications and spin transport measurements in carbon nanotube composites” –J. Sanders, J. Gass, H. Srikanth, F. K. Perkins and E. S. Snow, APS March Meeting, Baltimore, March 2006

4. “Exchange coupling, surface and configurational anisotropy in magnetic nanoparticles” –H. Srikanth, MRS Fall 2006, Boston, Nov. 2006

Number of Presentations: 4.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

1. “Magnetism and surface anisotropy in composite Au-Fe_3O_4 nanoparticles” –S. Srinath, N. A. Frey, H. Srikanth, C. Wang and S. Sun, Physical Review B (under review 2007)

2. “Magnetization and relaxation effects in ferrofluids with Fe_3O_4 nanoparticle dispersions” –M. B. Morales, N. A. Frey and H. Srikanth, Journal of Applied Physics (under review 2007)

Number of Manuscripts: 2.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
Marienette Morales	0.50
James Gass	0.50
Jeff Sanders	0.25
FTE Equivalent:	**1.25**
Total Number:	**3**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Hariharan Srikanth	0.25	No
FTE Equivalent:	**0.25**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Jeff Sanders

Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress and Accomplishments (Final Report)
W911NF-05-1-0354

Hariharan Srikanth, University of South Florida, Tampa, FL

The goal of this research project was to synthesize and characterize the static and dynamic magnetic properties of ferrofluids and study the mechanism of energy conversion in flowing ferrofluids. The initial grant period was active from Aug. 2005 – July 2006 and the project was under no-cost extension from Aug. 2006 – July 2007.

During the grant period, work focused mainly on the following tasks:

1. Chemical synthesis of iron oxide and soft ferrite nanoparticles using co-precipitation, structural and magnetic characterization
2. Thermal CVD growth of carbon nanotubes using nanoparticle catalysts
3. Studies of magnetic properties of Au-Fe3O4 composite nanoparticles
4. Synthesis of ferrofluids and studies of the temperature and field-dependent magnetic properties, frequency-dependent response
5. Design and testing of several fluid flow measurement setups to test the kinetic battery properties of ferrofluids

We report on the scientific progress in these areas and describe some representative results.

1. Chemical synthesis of iron oxide and soft ferrite nanoparticles

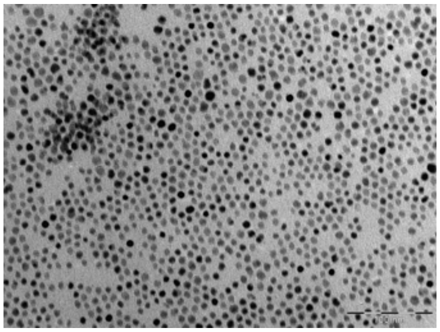


Fig. 1 TEM image of $CoFe_2O_4$ nanoparticles synthesized by chemical co-precipitation

The first task in preparation for making ferrofluids was to synthesize magnetic nanoparticles in the 5 to 20 nm size range. We used the chemical co-precipitation method to obtain nanoparticles of different materials (Fe_3O_4, $CoFe_2O_4$ and $NiFe_2O_4$). These materials were chosen because of their ease of production in the lab as well as their superparamagnetic characteristics expected at room temperature for the given size range. The as-synthesized particles were coated with oleic acid surfactant and extensively characterized using XRD, TEM. The magnetic properties of all the as-synthesized nanoparticles were measured with a Physical Property Measurement System. Fig. 1 shows a representative TEM image of one system (in this case, $CoFe_2O_4$ particles with average size ~ 10 nm). Different surfactant coatings were explored as it is vital to have uniform distribution of the nanoparticles after they are transferred to the fluid carrier. A simple test was to prepare vials with several nanoparticle concentrations (by volume) loaded into carrier fluids and left undisturbed for a few days (in some cases over a week). The quality of the suspension was checked using backlighting with a lamp and an optical microscope. Vials that showed settling/sedimentation of the particles at the bottom were discarded and further refinements were conducted in the surfactant coating process until suspensions that remained stable without settling for a period of a few days. Sedimentation (generally caused by dipolar interaction of the magnetic particles forming heavier clusters and settling under the influence of gravity) directly affects the flow properties of ferrofluids. So this important (and somewhat time consuming) phase of nanoparticle selectivity was requisite before ferrofluids used in the study were finalized.

2. Growth and lateral manipulation of carbon nanotubes

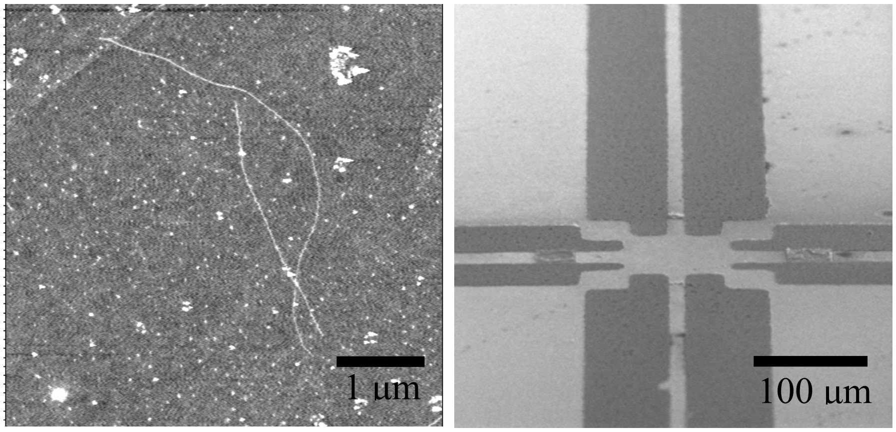


Figure 2 a) AFM image of SWNT and iron nanoparticle catalysts on Si/SiO$_2$ substrate. b) SEM image of carbon nanotubes selectively grown on patterened gold electrodes.

A simple CVD furnace available in the PI's laboratory was used to grow nanotubes from carbonyl precursors. Different strategies were experimented with to grow nanotubes horizontally on a substrate and also to bridge lithographically patterned gold electrodes. Fig. 2 shows our 'nanotube gallery'. The synthesis of these nanotubes and imaging were done by the PI's students in collaboration with Prof. Garrett Matthews and his graduate student in our Department. As demonstrated in the AFM and SEM images shown, we have been successful in growing fairly long nanotubes using Fe nanoparticle catalysts lying horizontally on Si/SiO2 substrates. We have also been able selectively lay arrays of nanotubes bridging patterned electrodes.

3. Studies of magnetic properties of Au-Fe3O4 composite nanoparticles

Nanoparticles of Fe$_3$O$_4$ and Au have been extensively studied as individual systems -Fe$_3$O$_4$ for its magnetic properties and Au for its optical and electronic properties as well as its desirable surface chemistry. We studied novel composite Au-Fe3O4 nanoparticles that were synthesized by collaborator Dr. Shouheng Sun and his co-workers at Brown University.

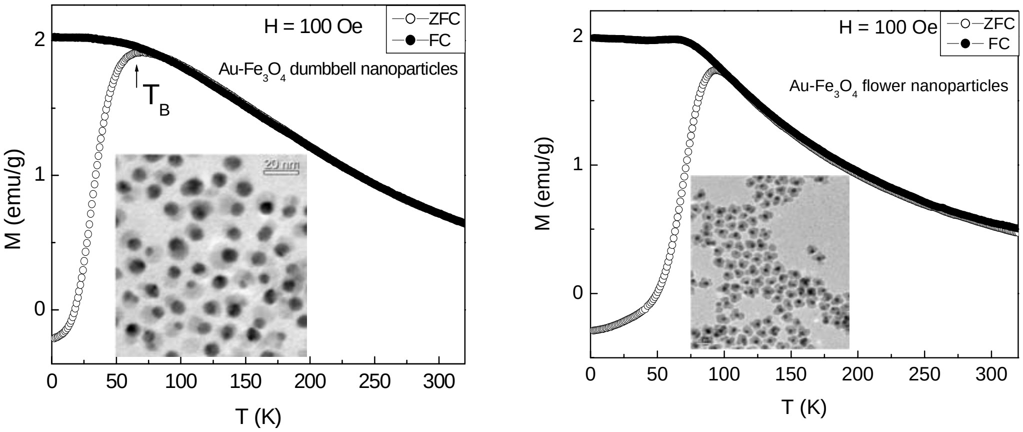


Fig. 3 Zero-field cooled (ZFC) and field-cooled (FC) magnetization in Au-Fe3O4 "dumbbell" and "flower" nanoparticle configurations. Inset shows TEM images of these composite particles

The interest in these composite structures stems from the fact that they are useful for biomedical applications. In terms of energy applications, the physical connection of Au to Fe3O4 might provide better transfer of heat and other give rise to novel interface electronic phenomena. Due to the lattice constant of Fe_3O_4 (a = 8.35A) being very nearly double that of Au (a = 4.08A), it turns out that Au and Fe_3O_4 can be grown as epitaxial composite nanoparticles. Based on the chemistry of the reaction, Fe_3O_4 can grow on one facet or multiple facets of an Au seed particle. The former results in a so-called “dumbbell-like” nanoparticle and the latter in a “flower-like” nanoparticle. We discovered dramatically different magnetic properties between these two configurations underlining the importance of surface and interface magnetism.

Fig. 3 show the ZFC and FC susceptibilities for the dumbbell and flower shaped nanoparticles indicating the classing signature of a sharp blocking transition in both cases. The insets show the TEM images for the two systems. While these appear relatively conventional and similar to what one would expect in typical spherical Fe3O4 nanoparticles, the M-H loops for the flower-like nanoparticles show surprising large exchange bias presumably resulting from complex interface magnetism as well as the interactions between multiple Fe3O4 particles within the clusters. The exchange bias in Au-Fe3O4 nanoparticles (seen as a loop shift in M-H loops) and the anomalously large coercivities and exchange fields measured as the temperature is lowered are shown in Fig. 4.

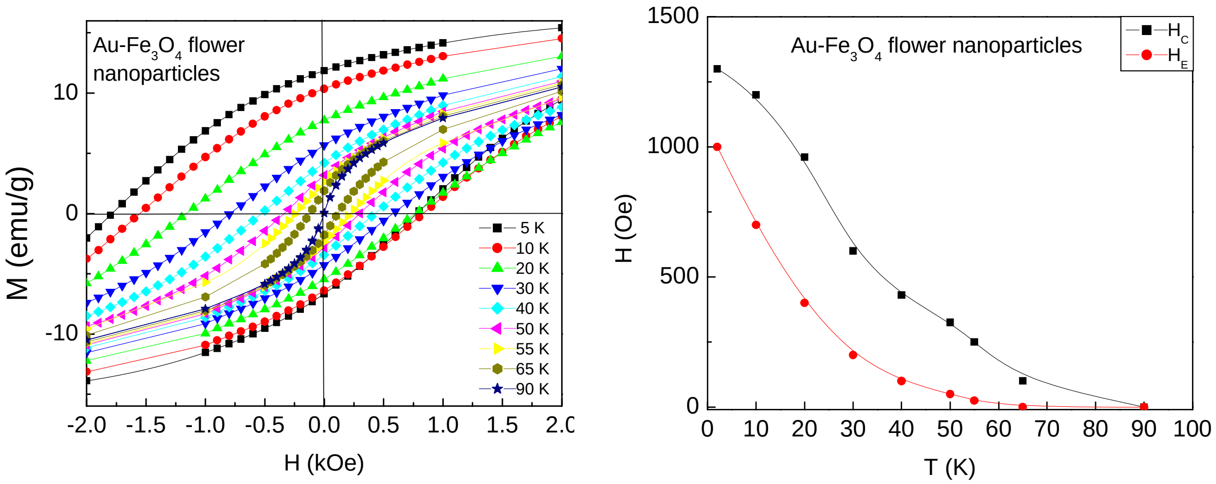


Fig. 4 The left panel shows the M-H data at different temperatures in the blocked state indicating exchange bias induced shift of the loops to the left. The coercivity also increases to large values. The right panel show plots of H_c and H_E extracted from the data of the left panel.

A comprehensive study of the DC, AC and RF magnetic susceptibilities has been reported by us in two publications:

1. “Static and dynamic magnetic properties of composite Au-Fe3O4 nanoparticles” –N. A. Frey, S. Srinath, **H. Srikanth**, T. Chao and S. Sun, **IEEE Transactions on Magnetics 43**, 3094 (2007)
2. “Magnetism and surface anisotropy in composite Au-Fe_3O_4 nanoparticles” –S. Srinath, N. A. Frey, H. Srikanth, C. Wang and S. Sun, **Physical Review B** (under review 2007)

4. Synthesis and magnetic properties of hexane and dodecane based ferrofluids

In this work, we synthesized and conducted a systematic comparative study of the magnetization and relaxation mechanisms in Fe_3O_4 nanoparticles in two different carrier liquids –hexane and dodecane -having different viscosities. In addition to the different viscosities of the fluids providing different environments for dipole-dipole interactions and chain formations, the characteristic temperatures in these two cases are such that the nanoparticle blocking temperature (~179K) is just above the freezing temperature of hexane (178 K) and much below the freezing temperature of dodecane (~264 K). Figure 5 shows a typical example system synthesized and investigated in this project.

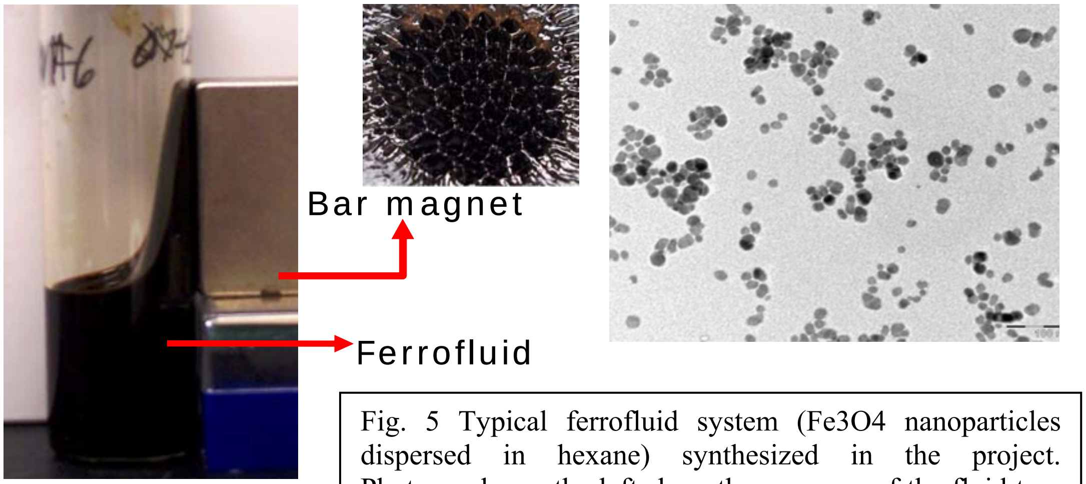


Fig. 5 Typical ferrofluid system (Fe3O4 nanoparticles dispersed in hexane) synthesized in the project. Photographs on the left show the response of the fluid to a bar magnet. TEM image of mean size 14nm Fe3O4 nanoparticles used in the ferrofluids is also shown.

Fe_3O_4 nanoparticles were synthesized by following the chemical co-precipitation method described in the literature. The surfactant coating used was oleic acid, which enables the particles to remain well-suspended and stable in the nonpolar carrier liquid. The ferrofluids were prepared by dispersing the particles in hexane and dodecane with room temperature viscosities of 0.294 cP and 1.35 cP, respectively. The DC susceptibilities for the as-synthesized nanoparticles in powder form, dispersed in hexane and dodecane respectively are shown in Figure 6.

The hexane and dodecane fluids provide interesting perspectives as in the former case, the nanoparticle blocking and carrier fluid freezing temperatures almost coincide whereas in the latter case, they are well separated.

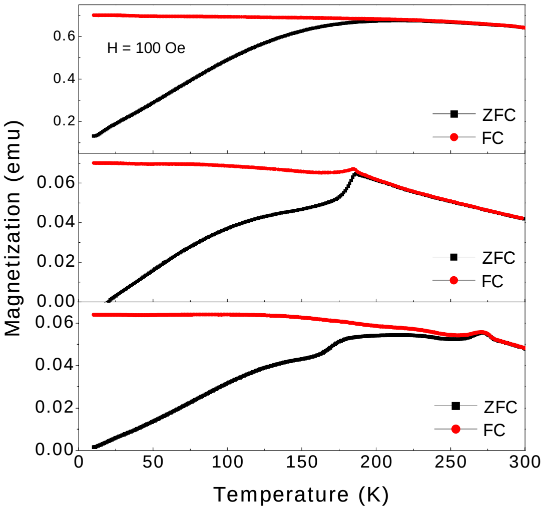
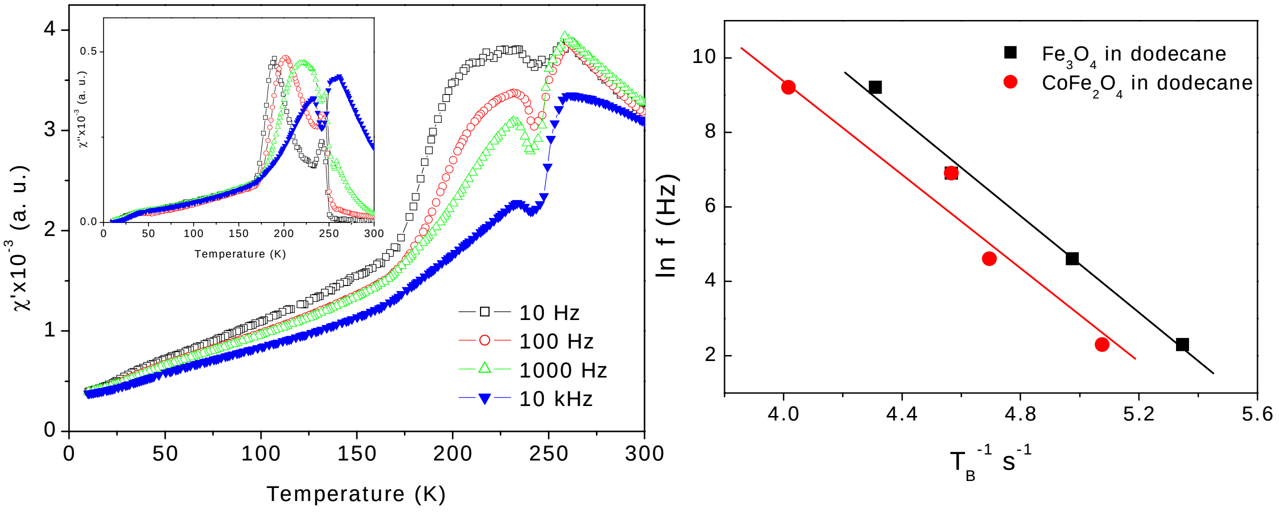
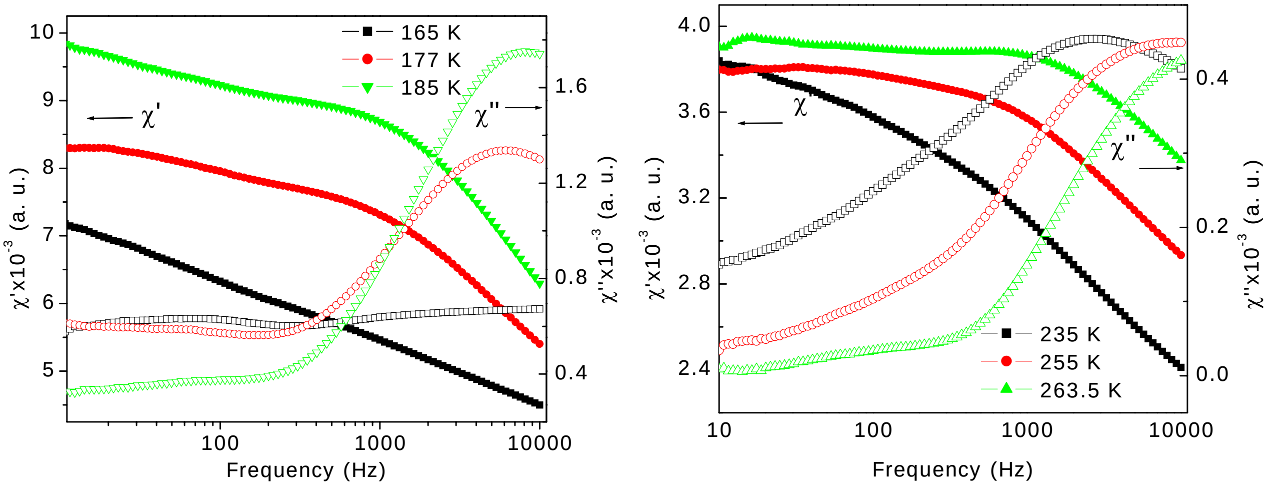


Fig. 6 Comparison of ZFC, FC magnetizations for (top) nanoparticles (middle) hexane ferrofluid and (bottom) dodecane ferrofluids is shown. Note the distinct carrier liquid freezing cusps in the ferrofluids



The AC susceptibility for dodecane ferrofluids is shown in Fig. 7. In this case, the two peaks (freezing and blocking) are clearly resolved in the real part of the susceptibility (main panel) and χ'' (inset). Frequency dependent data of the blocking peak (shown in the right panel) were fit to the Neel-Arrhenius model $\ln(f) = \ln(f_o) - E_a/k_BT$. From the fit, the calculated values of the activation energy E_a/k_B and Larmor frequency, f_o are 3171 K and 3.24 x 10^{10} Hz, respectively.

An important study from the fundamental physics perspective as well as commercial applications of ferrofluids is to probe the time scales of the Brownian and Neel relaxation effects. Our experiments with hexane and dodecane based ferrofluids (with dispersed Fe3O4 nanoparticles) revealed new and important effects associated with the relaxation times. In Fig. 8, we have shown the frequency dependent magnetization spanning the freezing transitions in both the ferrofluids. For the hexane ferrofluids, conventional behavior is observed –the two-slope feature in complex susceptibility represents the crossover from Brownian to Neel mechanism. In the frozen state (see data for 165K in left panel), Brownian processes are no longer present so a single monotonic slope due to Neel relaxation is noted. However, in the case of dodecane (right panel), the data even below the carrier fluid freezing temperature maintains a nonlinear variation



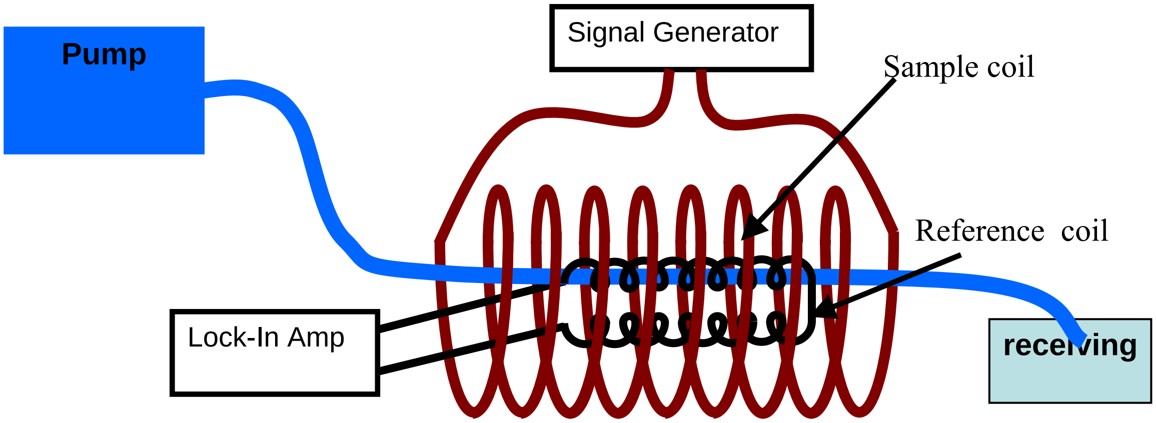
pointing to a more complex scenario in terms of the Brownian and Neel relaxation effects. We have interpreted this in terms of non-local freezing in dodecane ferrofluids which would preserve some orientational degree of freedom of the particles and clusters.

A paper summarizing our studies -"A comparative study of magnetic properties of hexane and dodecane ferrofluids with Fe3O4 nanoparticle dispersions" –M. B. Morales, N. A. Frey and H. Srikanth –has been communicated to Journal of Applied Physics. This work has been presented at the 2007 APS March meeting in Denver and is also scheduled to be presented at the 52nd annual Magnetism and Magnetic Materials (MMM) conference in Tampa in November 2007.

5. Ferrofluids flow experiments

The ferrofluid flow experiments and our attempts to obtain reliable data on energy conversion unfortunately did not yield positive results. We tried several schemes and built our own experimental setups to investigate ferrofluids flowing in linear and rotating geometries. Basically, there are several challenges in measurement of the permeability and/or the induced emf in flowing ferrofluids. Sensitivity of the instrument in being able to detect small induced signals is an issue and we spent some time analyzing different methods. For the linear flow, the schematic of the experimental set-up built in this project is shown in Fig. 9.

Since the change in the susceptibility of superparamagentic ferrofluids under flow conditions is not expected to be very high, we decided on using an inductive balance configuration. The idea behind the inductive balance is to create two perfectly balanced coils of opposite polarity inside a single larger coil. It is like a transformer where half the coils in the secondary generate an EMF that opposes the EMF generated in the other half of the coils. In this set up the two empty coils would always add to zero voltage. If a sample is placed in one of the coils its susceptibility would cause the flux through that coil to increase, thereby increasing the EMF produced in that coil. The two coils would no longer balance and a voltage would be measured.



The voltage in a single empty coil is given by:

$V_e = N\frac{d\phi}{dt}$ for empty coil.

Inserting a sample changes the flux by a factor of μ making the new equation

$V_s = N\mu \frac{d\phi}{dt}$ for a coil completely filled with sample.

With some manipulation the permeability of the material can be found by:

$$\mu = \frac{V_e - V_d}{V_e}$$

where N is the number of turns, V_e is the induced voltage of a single empty coil V_s is the voltage of a coil with a sample in it, and V_d is the voltage difference generated by the two coils set in opposite polarity. This assumes that the material completely fills the coil space. A similar equation can be obtained using a filling fraction coefficient.

This method should be sensitive enough to detect the susceptibility of the ferrofluid even though the susceptibility might be somewhat low. Since we are not just interested in the susceptibility of the ferrofluid but also in its change in susceptibility under flow conditions, this concept can be further adapted. The reference coil could be filled with static ferrofluid. In this setup the background susceptibility of the static material will effectively be subtracted out so that only a difference from the static susceptibly will generate a voltage.

Although the sensitivity of the setup was demonstrated reasonably well with moving bulk magnets, we were unable to detect reliable changes in emf under various flow conditions of the ferrofluids.

Ferrofluid rotation experiments:

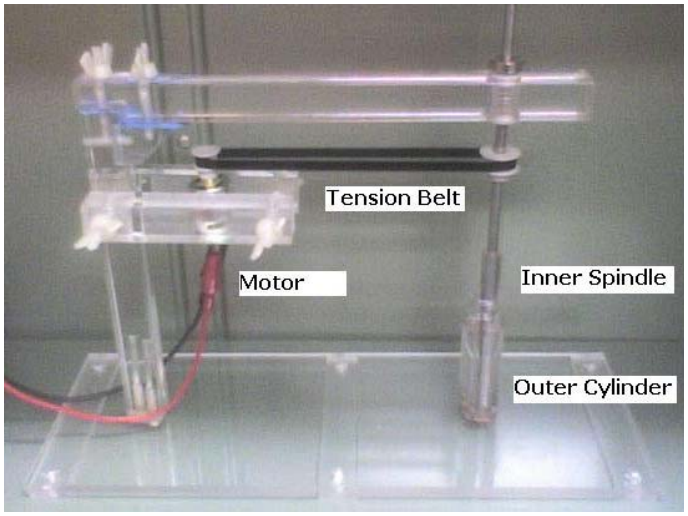


Fig. 10 shows the photograph of a ferrofluid cell we built in the project. A rotating spindle controlled by a stepper motor causes the ferrofluid to undergo Couette flow between two cylinders. We attempted a novel design wherein the transverse susceptibility component due to the magnetic torque generated could be measured sensitively using a resonant method. In this case, a copper coil was wound around the outer cylinder and the change in resonant frequency of the coil under various rotational frequencies of the ferrofluid would be monitored. At the time of writing this final report, these experiments are still under progress and any new results would be communicated for publication in the future with due acknowledgement of the grant support.

In summary, this project supported by ARO has yielded several new results on magnetic nanoparticles and ferrofluids. The intended tasks were successfully completed except for the flow experiments which turned out to be somewhat challenging given the short duration of the project.