European School of Magnetism

New magnetic materials and their functions

September 9-18, 2007 in Cluj-Napoca, Romania

FERROFLUIDS

Synthesis, structure, properties and applications

Lecture prepared by

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With the support of

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[6]Nat.Inst.R&D for Physics of Lasers and Radiation, Bucharest, Romania

12th September, 2007

OUTLINE

- ***Short history of the field***
- **Magnetically controllable fluids- a new MHD**
- **Magnetic nanoparticles and magnetic nanofluids, application orientated synthesis**
- **Colloidal stability and structural investigations**
- **Magnetic and flow properties**
- **Magnetic nanofluids & new nanomaterials**
- **Magnetically controllable fluids:**

Engineering &biomedical applications

Ferrofluids, magnetic (nano)fluids

What are they?

The beginning…

FLUIDITY + MAGNETIC PROPERTIES=??

↓↓

New kind of materials, new phenomena

Ferrofluid/Magnetic fluid

T.L. O'Connor, Belgian Patent 613,716 (1962)

S. Papell (NASA), US Patent 3,215,572 (1965)

Ultrastable colloids of magnetic nanoparticles in water and organic carriers

Ferrofluids, magnetic (nano)fluids Behavior & use

Early history - a few data…(1)

New phenomena new applications

G. Knight (1779) (Fe/water) F. Bitter (1932) (Fe3O4/water) W. C. Elmore (1938) (Fe3O4/water)...

J.L. Neuringer, R.E. Rosensweig, *Ferrohydrodynamics,* Phys. Fluids, 7(**1964**)1927

R.E. Rosensweig, *Fluidmagnetic buoyancy,* AIAA J., 4 (**1966**)1751

R.E. Rosensweig, *Buoyancy and stable levitation of a magnetic body immersed in a magnetizable liquid*, Nature (London), 210 (**1966**)613

R.E. Rosensweig, *The fascinating magnetic fluids*, New Scientist, 20th January, **1966**

R.E. Rosensweig, *Magnetic fluids,* Int.Sci. Tech.48-56 (**1966**)

E.L.Resler, R.E. Rosensweig,*Magnetocaloric power*, AIAA J. 2 (8)1418 (**1964**)

…a magnetocaloric thermodynamic cycle to efficiently convert heat to electricity with **no moving mechanical** parts to be used on spacecraft…

Ferrofluids, magnetic (nano)fluids

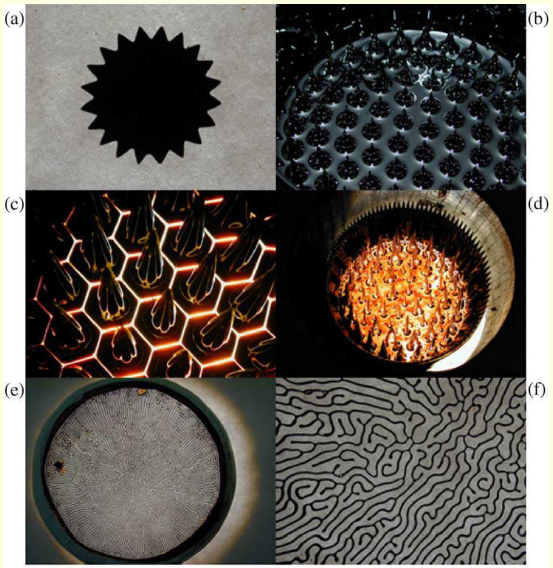
Behavior & use

Early history - a few data…(2)

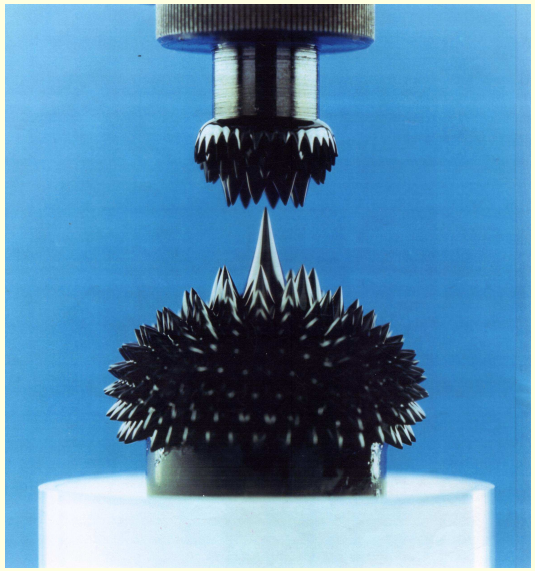
New phenomena & new applications

M.D. Cowley, R.E. Rosensweig, ***The interfacial stability of a ferromagnetic fluid***, J. Fluid Mechanics, 30 (**1967**)671-688

A themed session at **Dynamics Days Europe 2007**, Loughborough, England was held on this phenomenon **in honor of the 40th anniversary publication of the paper**. **The phenomenon furnishes a singular example of fluid patterning in the absence of a dissipative process**.
Both authors participated. A publication of the session papers is forthcoming by Springer



C. Rinaldi,…, M.Zahn /Current Opinion in Colloid & Interface Science,10 (2005) 141– 157



Lab. Magnetic Fluids Timisoara

Ferrofluids, magnetic (nano)fluids

Behavior & use

Early history - a few data…(3)

New phenomena & new applications

Magnetic fluid in time-varying non-uniform magnetic field

Dynamical surface instabilities

Lab. Van't Hoff of Colloids- 100 years anniversary

Exhibition at Univ. Utrecht 2004- A. Philipse (Utrecht), Doina Bica(Timisoara)

Ferrofluids, magnetic (nano)fluids

Behavior & use

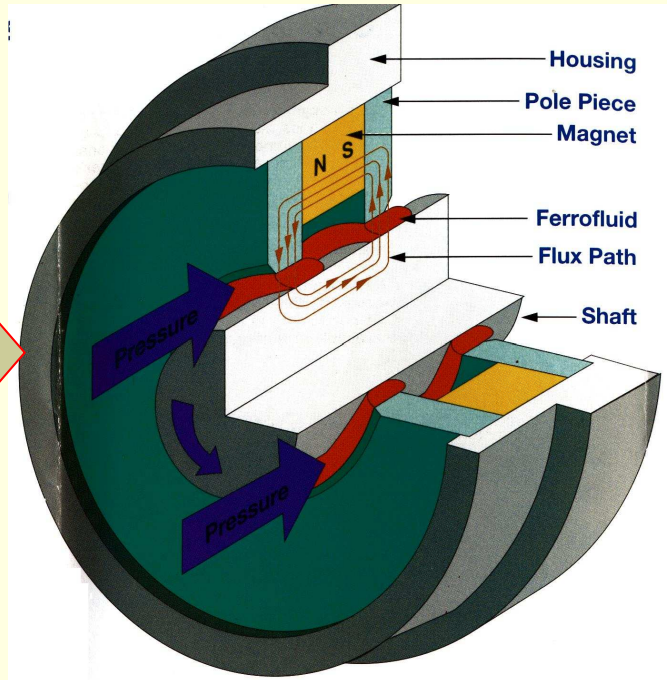
Early history - a few data…(4)

New phenomena new applications

Establishment of the commercial enterprise, **Ferrofluidics** Corporation (USA) in Massachusetts in **1968** by R. E. Rosensweig with colleague R. Moskowitz

R. E. Rosensweig, ***Magnetic fluid seals***
US Patent 3,260,584 **(1971)**

The invention discloses a means for constructing **compact rotary shaft seals** in which a single magnet supplies magnetic field to a multiplicity of discrete stages,each retaining a **liquid O-ring of magnetic fluid**, such that the device is capable of sustaining large pressure differences without leakage.
The seals are hermetic and utterly free of mechanical wear.
Described as 'a modern machine element'the seals furnished **the most important product line of the Ferrofluidics Corporation** (from **2000** on a multi-national company **Ferrotec**-headquarters in **Japan)** and have been widely copied around the world.



Ferrofluids, magnetic (nano)fluids

Behavior & use

Early history - a few data…(5)

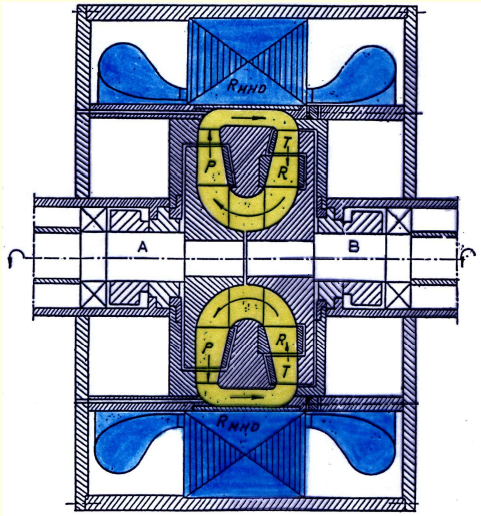
New phenomena new applications

Magnetic fluids in Romania-the beginning…

Preparation of first ferrofluid samples
Institute of Technical Physics, Iasi
…early '70th…

E. Luca, G. Calugaru, R. Badescu,
C. Cotae, V. Badescu,
Ferofluidele si aplicatiile lor in industrie
(*Ferrofluids and their industrial applications*)
Editura Tehnica, Bucuresti, **1978** (336 pages)
…the first book on magnetic fluids!!

MHD torque converter



RO Patent Nr.57574
Prof. I. Anton 1971
Dept. Hydr. Machines UP Timisoara

Magnetohydrodynamics

- **Classical MHD** – hydrodynamics of electroconducting fluids under the action of an applied magnetic field

electrical conductivity $\sigma \geq 0$
magnetic permeability $\mu = \mu_0$

- **New MHD:*Ferrohydrodynamics*-** hydrodynamics of ferrofluids (magnetic fluids) under the action of an applied magnetic field

Neuringer-Rosensweig (**USA**) 1964 and Shliomis (**USSR**) 1974

electrical conductivity $\sigma = 0$
magnetic permeability $\mu \geq \mu_0$

Classical Magnetohydrodynamics (MHD) and Ferrohydrodynamics (FHD)

Equations of motion

Electroconductive fluid

$$\rho\frac{d\vec{v}}{dt}=-\nabla p+\rho\vec{g}+\vec{j}\times\vec{B}+\eta\nabla^2\vec{v}$$ MHD

Magnetic fluid – fluid with internal rotation, non-symmetric stress tensor

$$\rho\frac{d\vec{v}}{dt}=-\nabla p+\rho\vec{g}+\mu_0\left(\vec{M}\nabla\right)\vec{H}+\frac{\mu_0}{2}\nabla\times\left(\vec{M}\times\vec{H}\right)+\eta\nabla^2\vec{v}$$ FHD

$$\frac{d\vec{M}}{dt}=-\frac{1}{\tau_B}(\vec{M}-\vec{M}_0);\quad \vec{M}_0=nmL(\xi)\frac{\vec{\xi}}{\xi}$$ Relaxation of magnetization

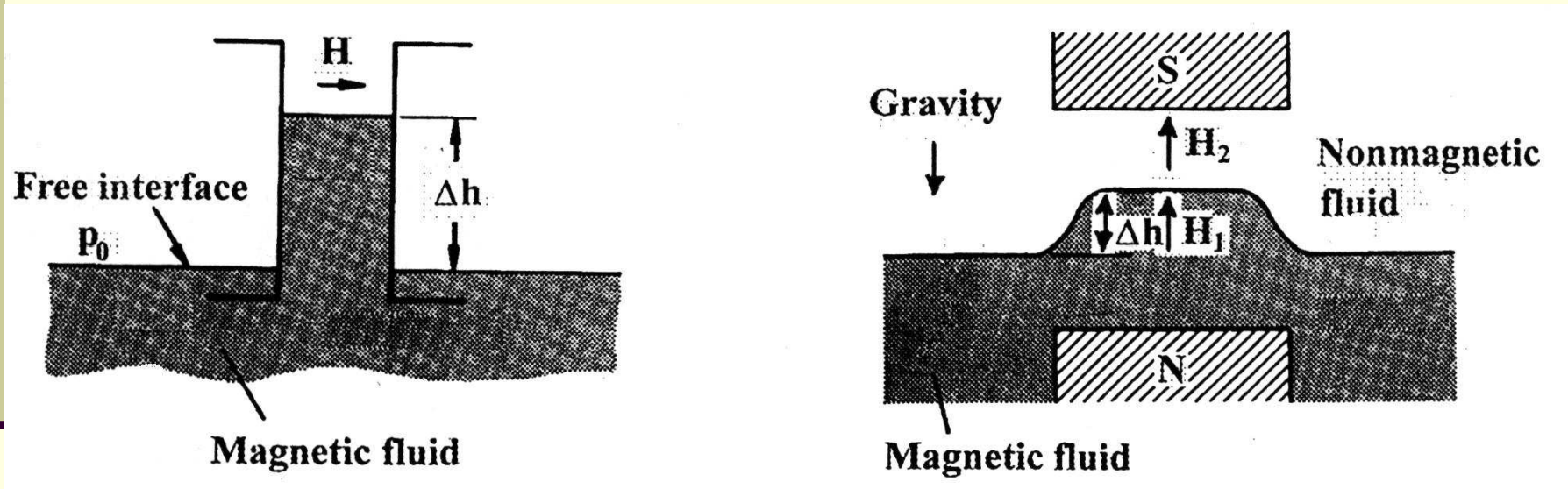
$$\vec{\xi}=\frac{\mu_0 m\vec{H}}{k_B T};\qquad \tau_B=\frac{3\eta V}{k_B T}$$

$$\nabla\vec{v}=0;\qquad \vec{M}=f(\vec{H})$$

M. Shliomis, Magnitnie jidkosti, Usp.Fiz.Nauk, 1974
R. E. Rosensweig, Ferrohydrodynamics, Cambridge Univ. Press(1985)
E. Luca,et al, Ferofluidele si aplicatiile lor in industrie, Ed. Tehnica, Bucuresti (1978) !

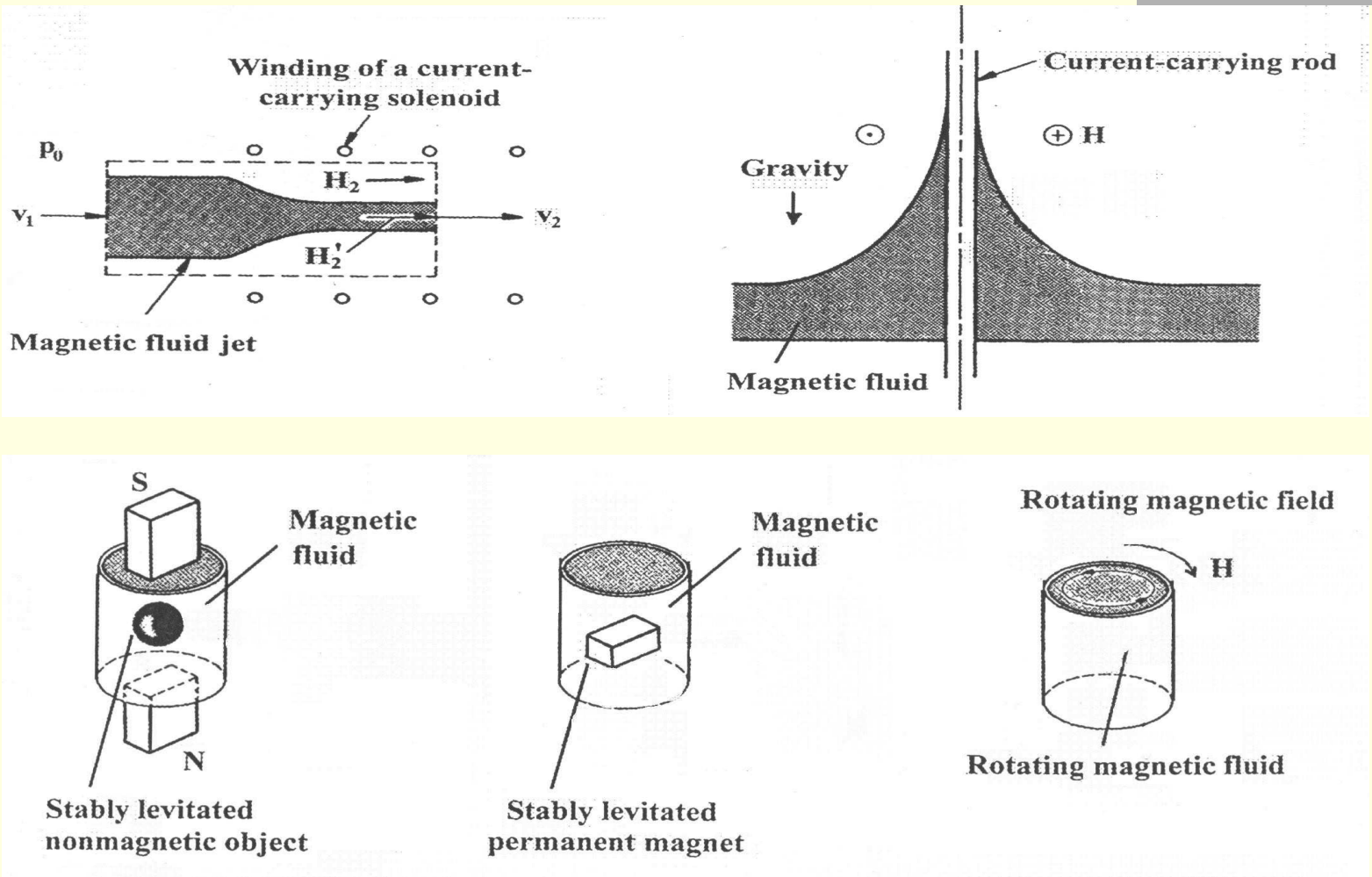
Volumic force: f=μoM(H)gradH for quasistatic conditions

Typical phenomena in ferrohydrodynamics (1)



R. E. Rosensweig, Ferrohydrodynamics, Cambridge Univ. Press(1985)

Typical phenomena in ferrohydrodynamics (2)



R. E. Rosensweig, Ferrohydrodynamics, Cambridge Univ. Press(1985)

After 40 years…
MAGNETICALLY CONTROLLABLE FLUIDS

- **Ferrofluids, magnetic (nano)fluids- the main topic of the present lecture**

  Ultrastable colloidal suspensions of magnetic nanoparticles in a carrier liquid

  Quasihomogeneous magnetizable liquids

  Approximatively Langevin type magnetic behavior and Newtonian flow properties, small magnetoviscous effect
- **Magnetorheological fluids**

  Suspensions of micronsized ferromagnetic particles in a carrier liquid

  Non-newtonian behavior, strongly magnetic field dependent yield stress and effective viscosity (about 100-1000 times increase)
- **Magnetizable gels&elastomers**

  Nano- or micrometer range magnetic particles dispersed in a polymer matrix

  Field dependent size and mechanical properties, tuneable elastic properties

Synthesis of magnetic nanofluids

Two-step procedure

A. Synthesis/preparation of magnetic nanoparticles

- Chemical procedures: co-precipitation, micro-emulsion techniques
  Physical procedures: wet grinding
- Physical-chemical methods: decomposition of organo-metallic compounds (e.g., laser-pyrolisis)

B. Stabilization/dispersion of nanoparticles in a liquid carrier

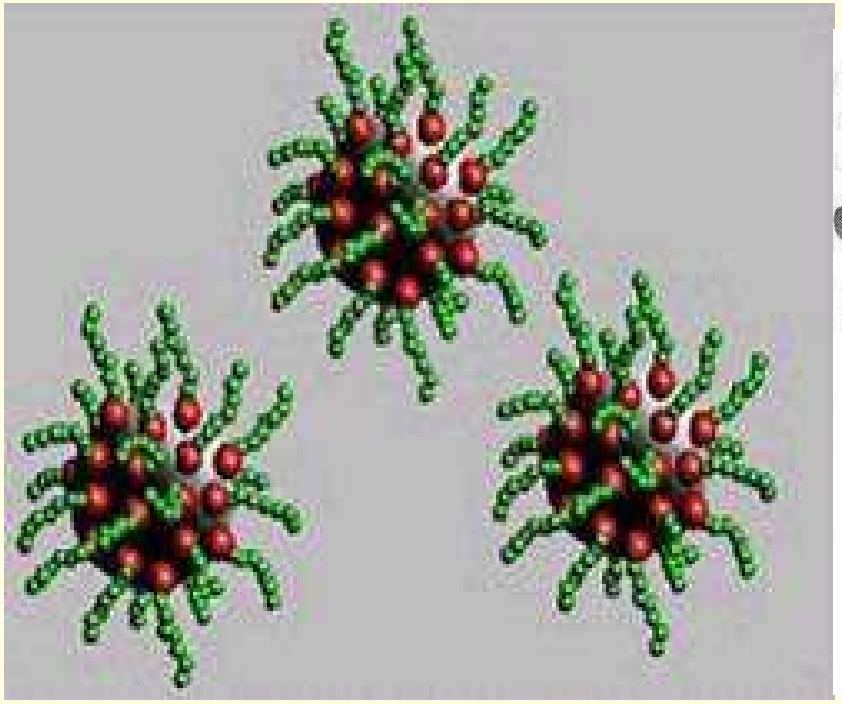
- Non-polar carriers
- Polar carriers

S. W. Charles, The preparation of magnetic fluids,
In: S. Odenbach (ed.),
Ferrofluids. Magnetically Controllable Fluids and Their Applications,
Springer Verlag(2002)pp.3-18

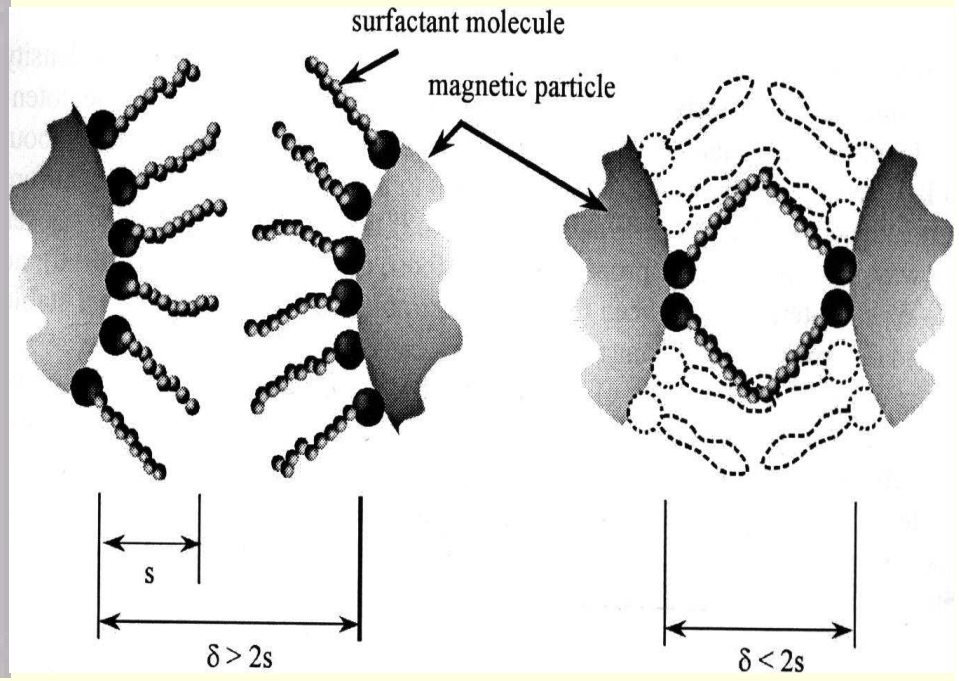
Synthesis of magnetic nanofluids

Composition&Mechanism of sterical stabilization

S. Odenbach, JoP Condens.Matter,16(2004)



R. E. Rosensweig, Ferrohydrodynamics, Cambridge Univ. Press(1985)

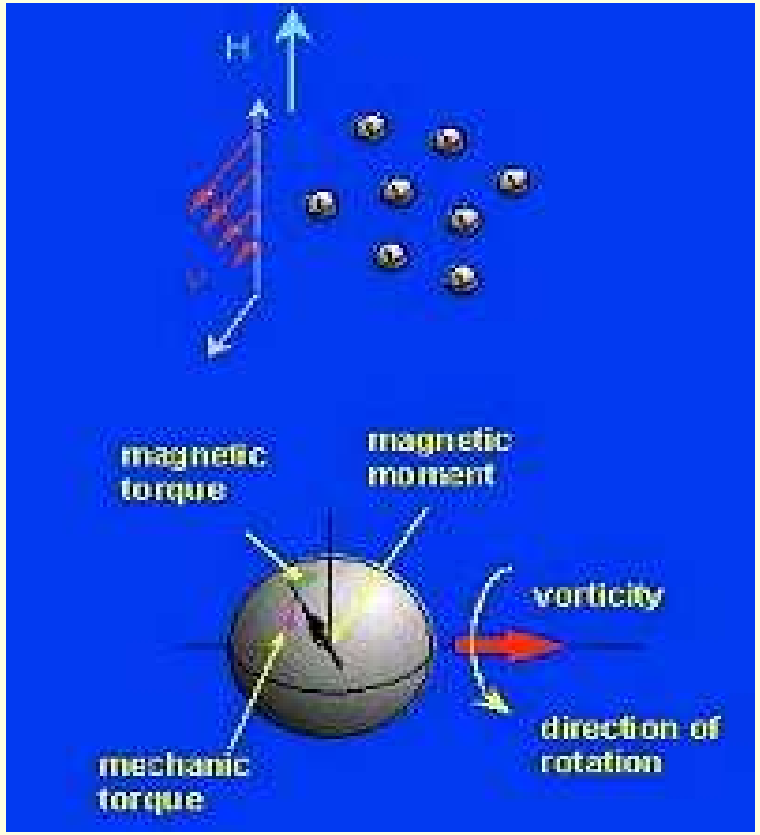


Magnetic nanoparticles(MNP) dispersed in a carrier liquid(CL) are coated with mono- or double-layer of organic surfactant(S) molecules in order to prevent their agglomeration

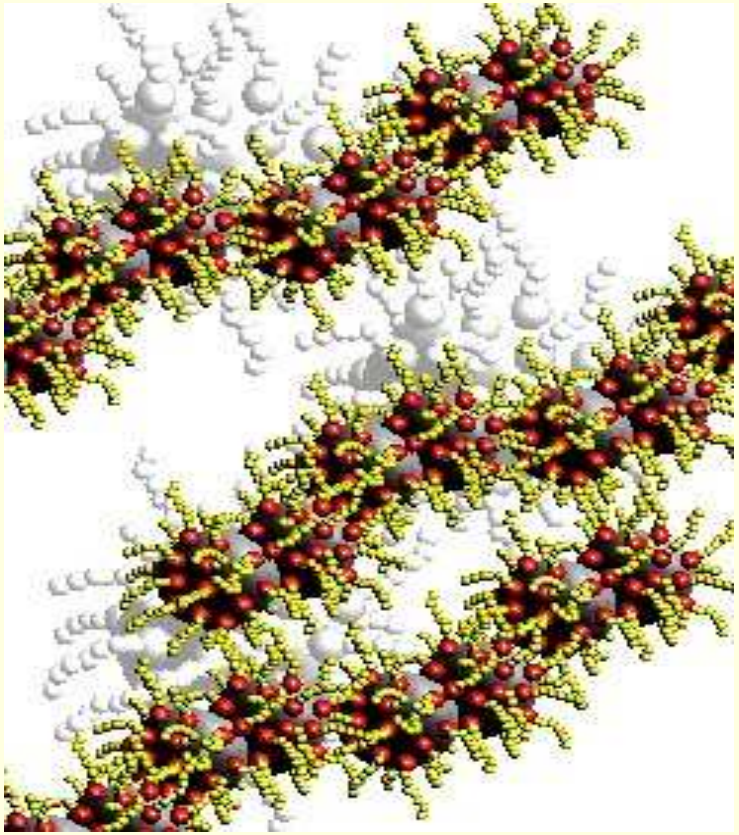
Composition: MNP-magnetite, maghemite, cobalt-ferrite, iron, cobalt CL- non-polar and polar organic solvents, water S- carboxylic or sulphonic acids, polymers

Synthesis of magnetic nanofluids

Structural processes under the influence of applied magnetic field



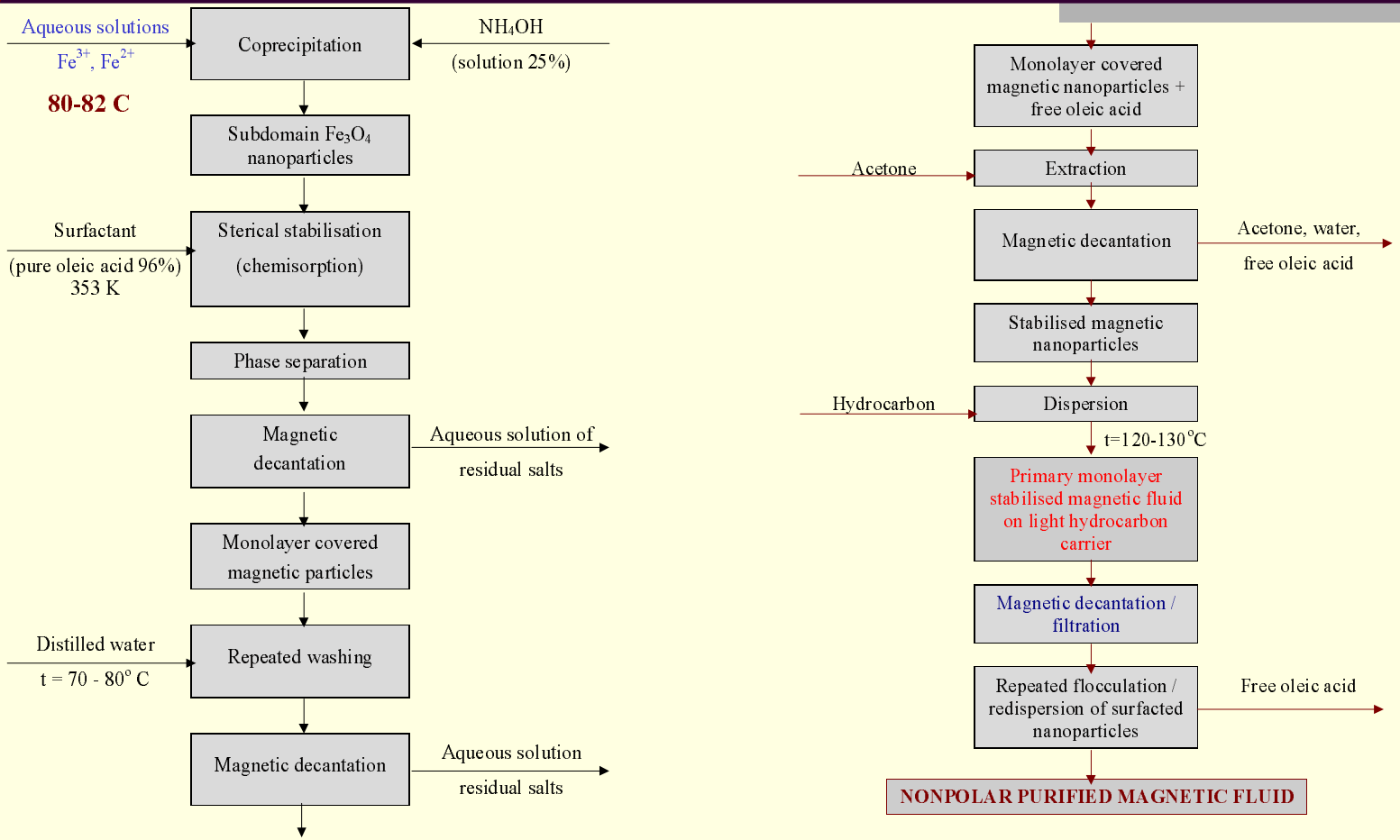
Rotational motion of a nanoparticle in the liquid-vorticity



Agglomerate formation under the influence of magnetic field

Procedure of synthesis of magnetic nanofluids with organic non-polar carrier liquids

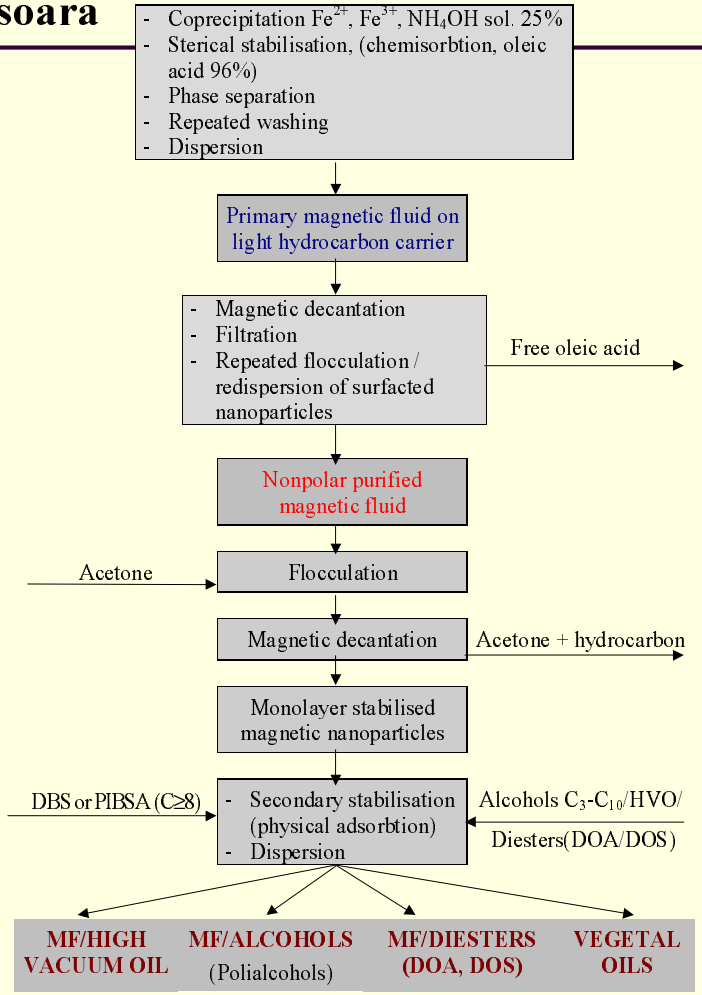
Lab. Magnetic fluids-Timisoara



Surfactants: **oleic acid (OA)**, stearic acid (SA), palmitic acid (PA), **myristic acid (MA), lauric acid (LA)**
Carriers : hydrocarbons (H), deuterated hydrocarbons(D-H), halogenated compounds(Hal)
MF/H/OA: D.Bica,R.Minea, Patent RO 97556(1989); D.Bica, Rom.Rep.Phys., 47(1995)265 ;
MF/H/LA; MA : L.Vekas et al.Rom.Rep.Phys., 58(2006); M.V. Avdeev, D.Bica et al. JMMM, 311 (2007)

Procedure of synthesis of magnetic nanofluids with organic polar carrier liquids

Lab. Magnetic fluids-Timisoara



DBS-dodecyl-benzen-sulphonic acid
PIBSA-poly-izobutylen-succin-anhydride

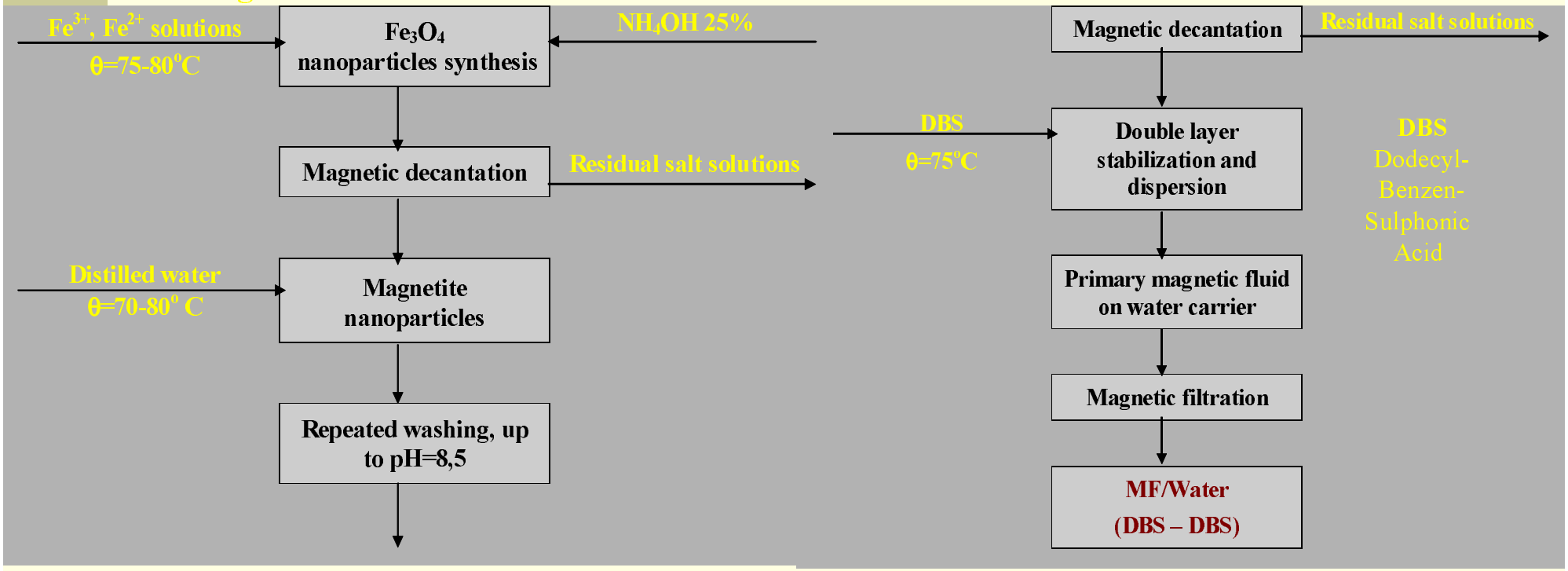
D.Bica et al.Patents RO 93107 (1987), 93162 (1987), 97224 (1989),97599(1989), 105048 (1992), 115533 (2000); D.Bica, Rom.Rep.Phys.,47(1995)265
D.Bica, L.Vekas, M.Rasa, J.Magn.Magn.Mater, 252 (2002)10

Preparation of water based magnetic fluids (1)

Double layer sterical stabilization of magnetite nanoparticles in water carrier

Sterical stabilization applied to MF/water:
Shimoiizaka et al (1980), Khalafalla,Reimers(1980), Doina Bica (1985), Wooding, Kilner, Lambrick(1991), Shen, Laibinis, Hatton (1999)

Lab. Magnetic fluids-Timisoara

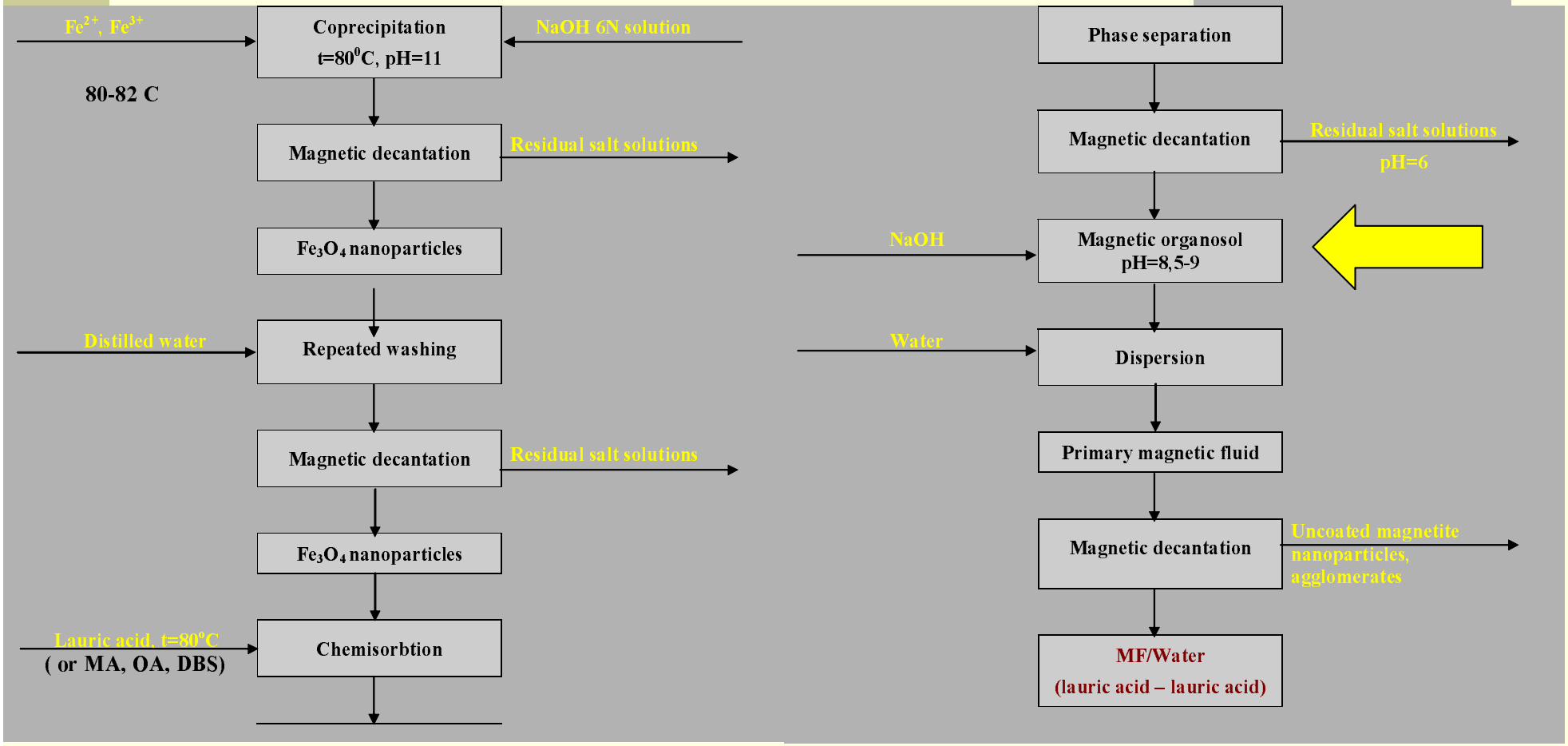


D.Bica, Patent RO 90078 (1985); Rom.Rep.Phys., 47(1995)265
D.Bica. L. Vekas, M. Rasa, J. Magn.Magn.Mater., 252(2002)10

Preparation of water based magnetic fluids (2)

Double layer sterical stabilization using various chain length surfactants

Lab. Magnetic fluids-Timisoara



MF/water samples with LA+LA, MA+MA,OA+OA, LA+DBS, MA+DBS, OA+DBS double layer sterical stabilization

D.Bica, L. Vekas, M.V.Avdeev, Oana Marinica, V. Socoliuc, Maria Balasoiu, V.M.Garamus, J.Magn.Magn.Mater. 311 (2007)

Synthesis of surface protected iron and iron oxide nanoparticles by laser pyrolisis for biocompatible and high magnetization nanofluids

INFLPR Bucuresti - I. Morjan and collab.

- Fe-C, Fe- Fe3O4 and γ-Fe2O3 nanoparticles produced by laser pyrolisis

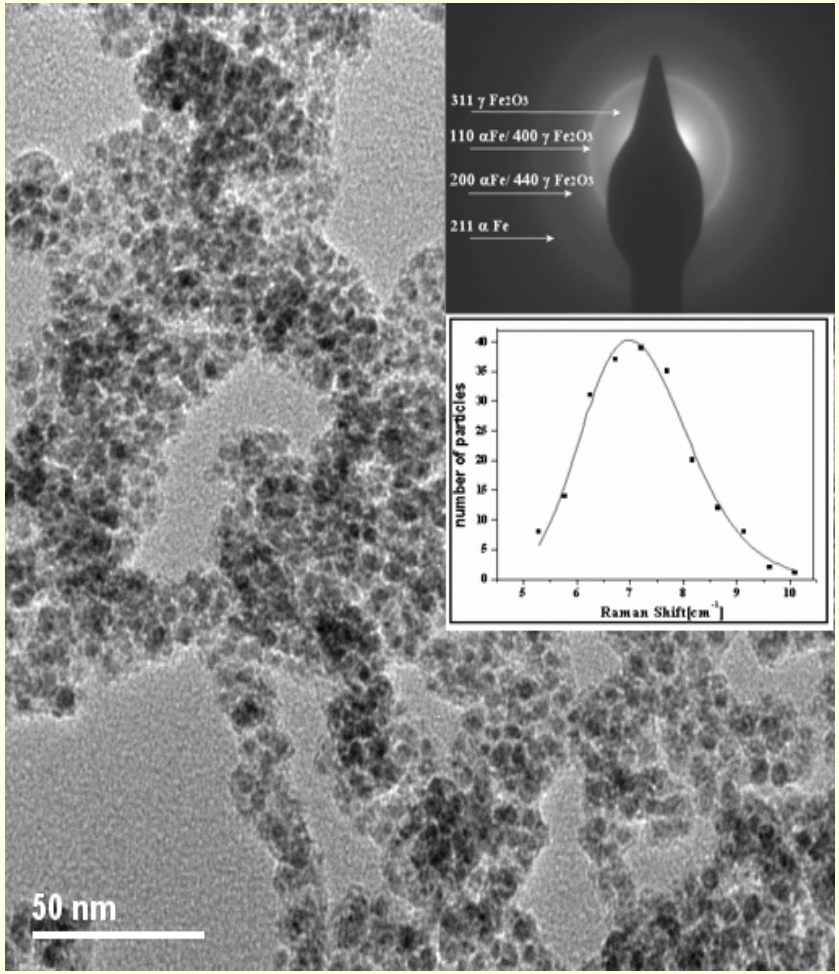
  I. Morjan et col. INFLPR Bucharest

- Dispersion/ stabilization of iron or iron oxide nanoparticles in water and various organic carriers by sterical stabilization

  D. Bica Lab. MF-CFATR Timisoara

Fe-C or γ- Fe2O3 nanoparticles in water carrier for biomedical applications

MFs with M~2000 G for high pressure rotating seals?

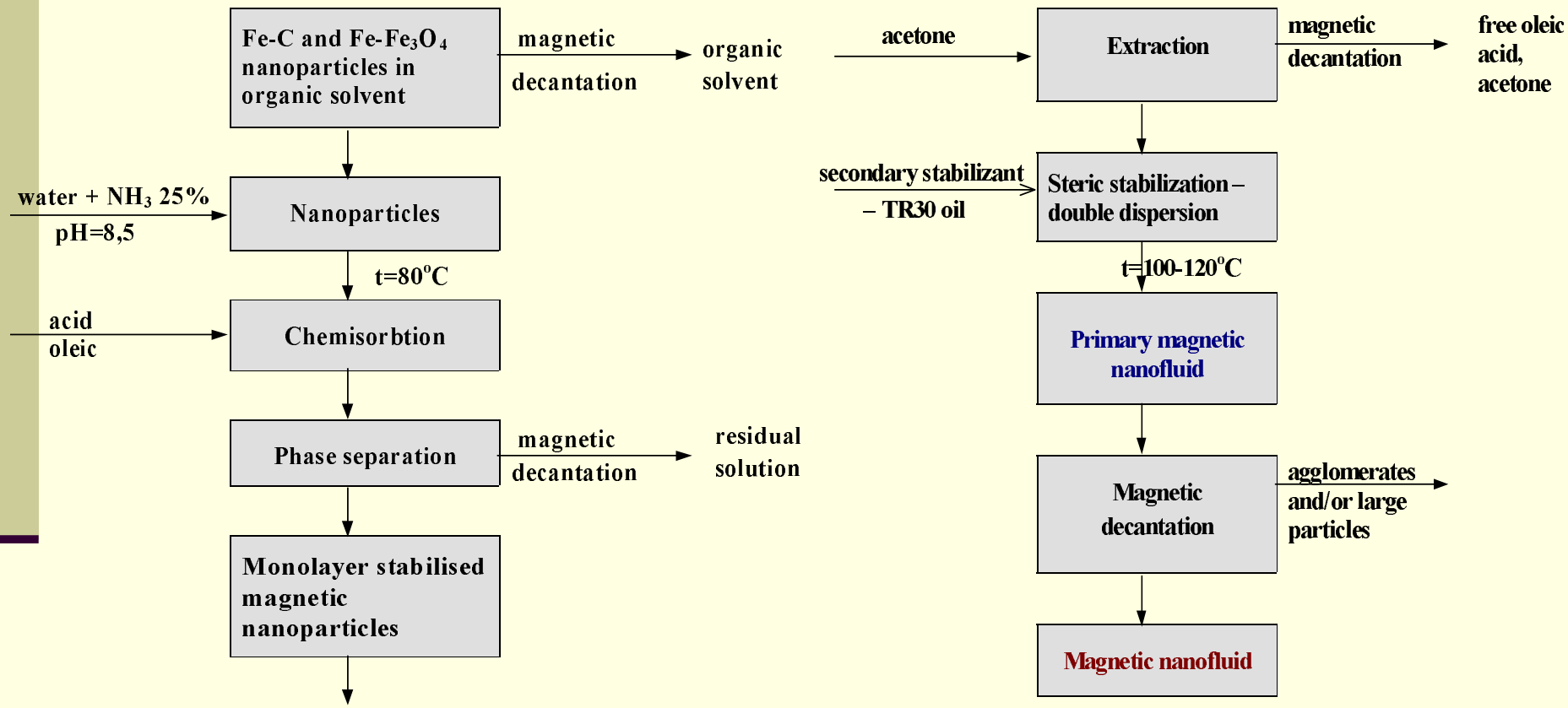


I.Morjan et col. INFLPR Bucharest, V. Ciupina et col. Univ. Ovidius Constanta

Dispersion/stabilization of surface protected iron nanoparticles obtained by laser pyrolisis in various organic carriers and water

Lab. Magnetic fluids-Timisoara-INFLPR Bucuresti - I. Morjan and collab.

Example: Dispersion/stabilization of Fe-Fe3O4 and Fe-C nanoparticles in transformer oil



Main objectives:

High magnetization nanofluids with non-polar organic carrier

Water based biocompatible magnetic nanofluids; Nanocomposites

Results of preparation procedures

- Synthesis of **magnetite, maghemite, cobalt-ferrite, surface protected iron nanoparticles**
- Rich scientific background and know-how in physical-chemical synthesis of **magnetically controllable nanofluids and composites**: magnetic nanofluids, emulsions, magnetofluidic composites, magneto-rheological fluids, polymeric nanocomposites
- Large variety of **carrier matrices: over 50** non-polar and polar liquids, polymers (hydrocarbons, synthetic oils, alcohols, ketones, water, styren, resins etc., including deuterated carriers)
- Different chain length surfactants for **size selective dispersion/stabilization** of magnetic nanoparticles in non-polar and polar carriers, e.g. mono-carboxylic acids, sulphonated acids, polymers, used as mono-layer or double- layer coating of nanoparticles
- Efficient stabilization methods : entropic driven **steric** and **combined electrostatic + steric**
- **Dilution stability**
- **High quality magnetic nanofluids** tailored for engineering and biomedical researches and applications, with saturation magnetization up to approx. **90 kA/m (~1150 G):**

High colloidal stability magnetic fluids with organic carriers for leakage-free rotating seals

Water based magnetic nanofluids for biomedical applications

Application orientated evaluation of magnetic fluids

Manifold characterization of magnetic fluids

- Size distribution of magnetic nanoparticles: TEM, HRTEM
- Dilution stability
- Composition and magnetic field dependent structural processes, long-term colloidal stability: SANS, SANSPOL (B= 0-2.5 T)
- Mechanism of stabilization and “chemical” size selection of dispersed magnetic particles
- Phase transition phenomena: magneto-optical investigations
- Magnetic properties vs. composition: VSM measurements
- Mössbauer spectroscopy
- Flow properties under the influence of applied magnetic field: MR investigations

Evaluation and selection of MFs for various applications

- **Separation processes, magnetic fluid devices: rotating seals, sensors**

New type of nanostructured composite materials for:

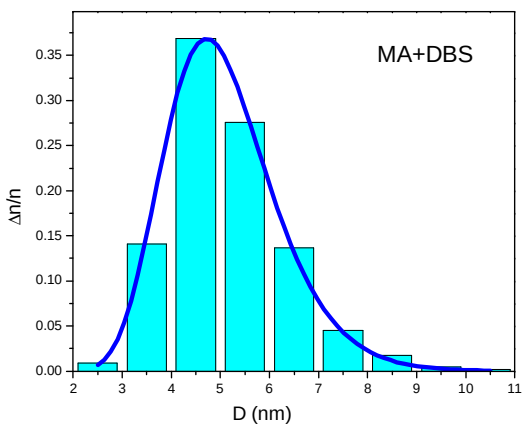
- Biomedical uses
- Engineering applications

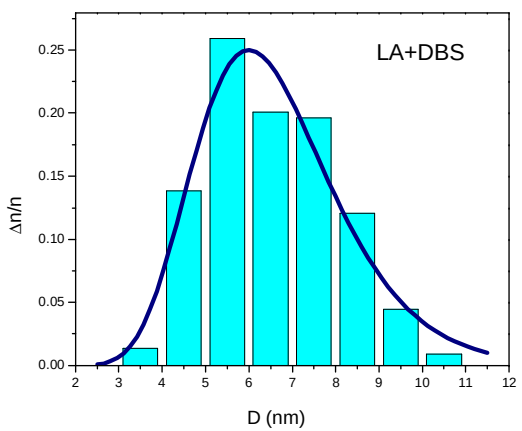
TEM Size distribution of Fe_3O_4 nanoparticles

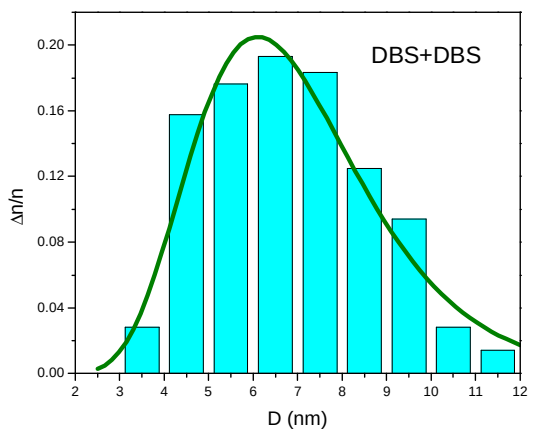
The log-normal probability function for the size distribution of magnetic nanoparticles:

$$f(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln^2 D/D_0}{\sigma^2}\right)\right] \qquad (1)$$

Magnetite nanoparticles stably dispersed in water with different surfactants

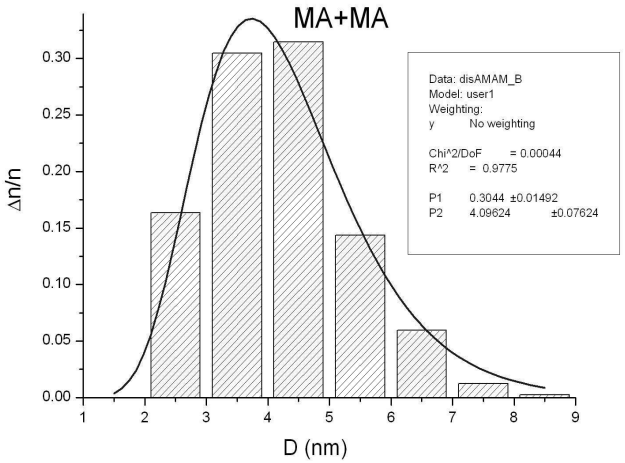


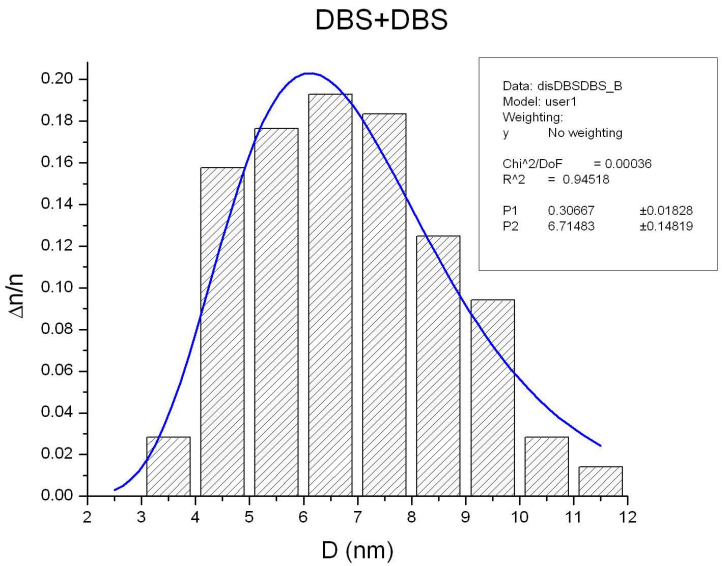




TEM Water based MFs

Influence of surfactant double layer





Sample	Mean diameter (nm)	Standard deviation (nm)
MF/W/MA+MA	**4.3** ± 0.08	1..3 ± 0.07
MF/W/LA+LA	6.1 ± 0.15	2. 4 ± 0.13
MF/W/MA+DBS	5.1 ± 0.03	1. 1 ± 0.02
MF/W/LA+DBS	6.6 ± 0.12	1. 7 ± 0.13
MF/W/DBS+DBS	**7.0** ± 0.16	2. 2 ± 014

Log-normal size distribution of particles

Size selective stabilization/dispersion of magnetic nanoparticles

Significant reduction of mean size and standard deviation with MA, compared to DBS double layer

Similar for organic non-polar MFs (DHN,Utr): **4-8 nm** mean size variation for MA to OA coating

SANS investigations

Cooperation with JINR Dubna, BNC-KFKI Budapest, GKSS Geesthacht

Bulk nuclear structure

parameters of the particle size distribution
thickness and composition of the surfactant shell
micelle formation in ferrofluids
interparticle interaction
particle aggregation in different conditions
chains formation and interaction

Bulk magnetic structure

magnetic size of particles and aggregates
magnetic correlation between particles
magnetization in bulk and interface

Size range investigated: 1- 100 nm

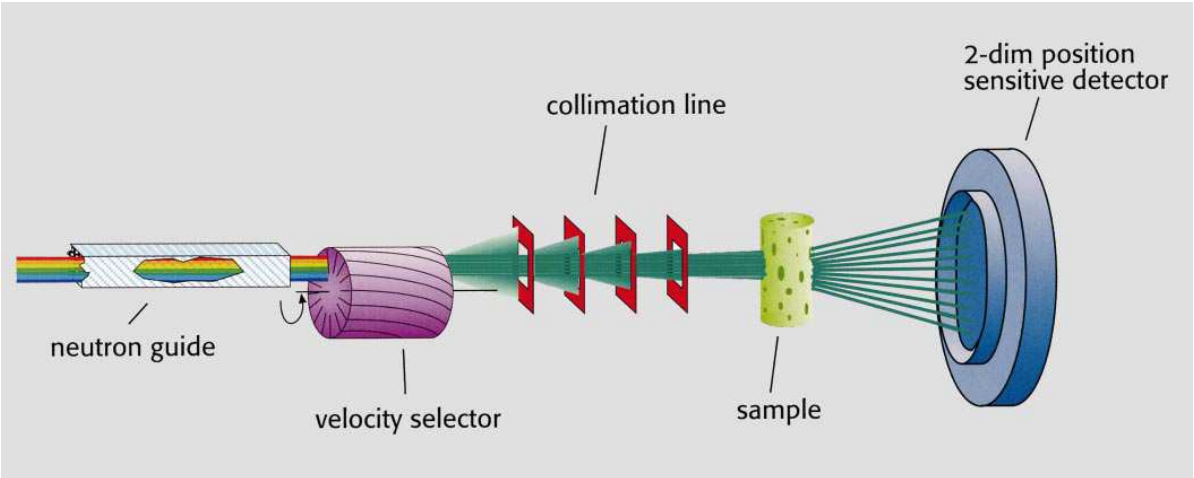
EMS 2007 Cluj-Napoca Romania

Structural investigations on magnetic nanofluids by Small Angle Neutron Scattering (SANS)- **Coop. GKSS Geesthacht, BNC Budapest, JINR Dubna, Lab. MF Timisoara**

SANS 1 and SANS 2 facilities at GKSS Geesthacht (Germany)

General view on SANS 1 and SANS 2

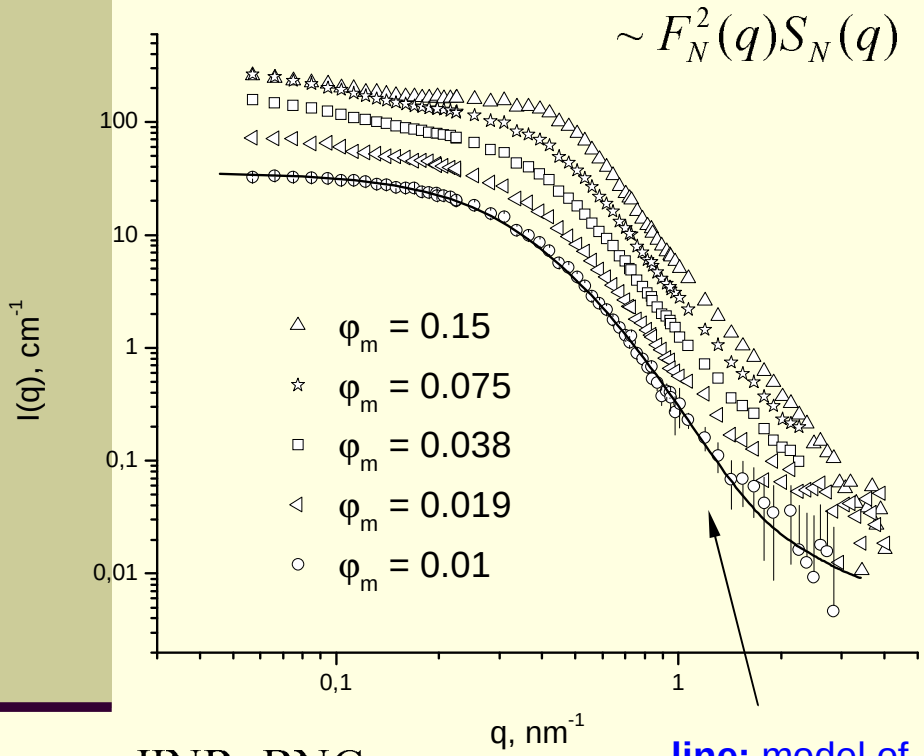
SANS-1: NanoMF sample positioning in the working gap **detail**



Main components of SANS facilities at GKSS schematic view

SANS investigations(1):Interparticle interaction. Non-polar ferrofluids

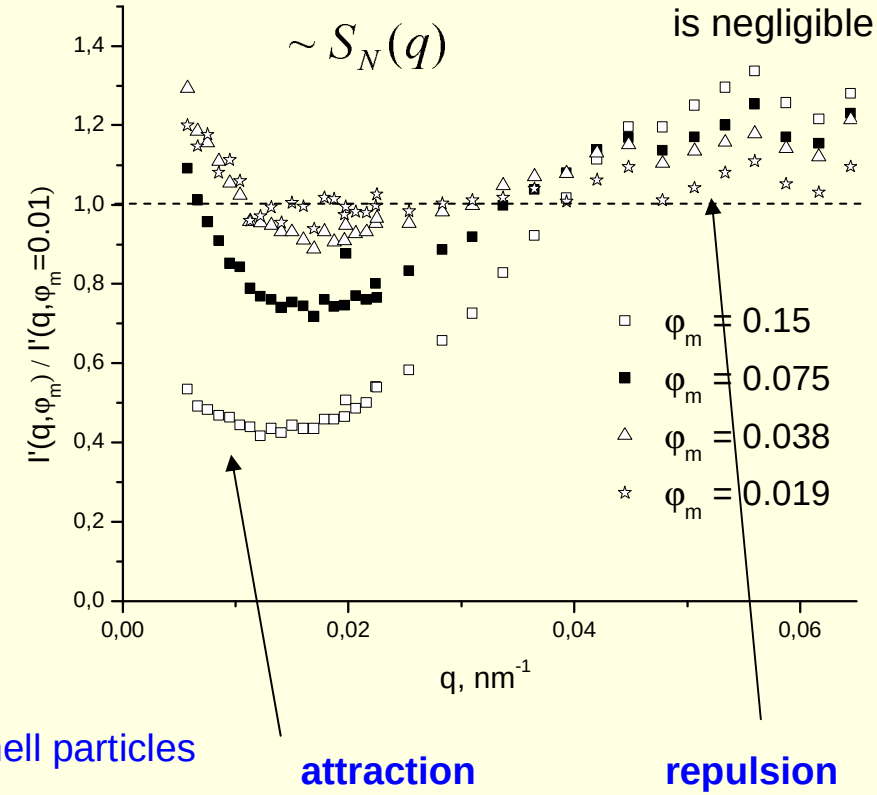
magnetite/oleic acid/H-benzene



JINR, BNC

line: model of polydisperse core-shell particles

magnetic scattering (correlation) is negligible



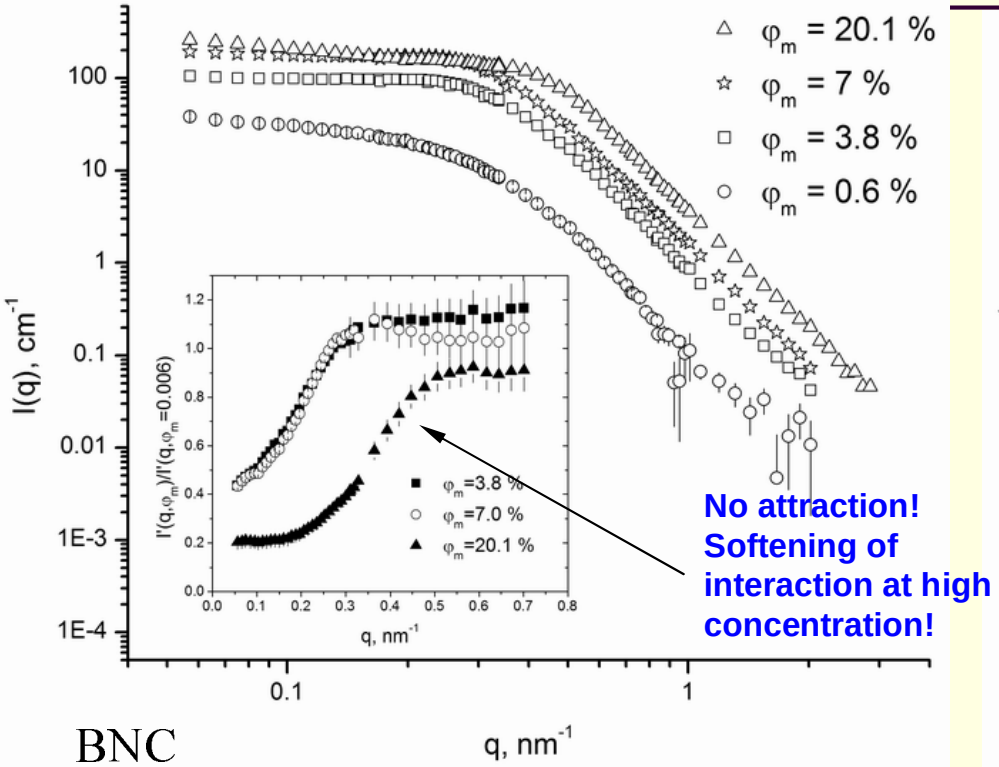
attraction **repulsion**

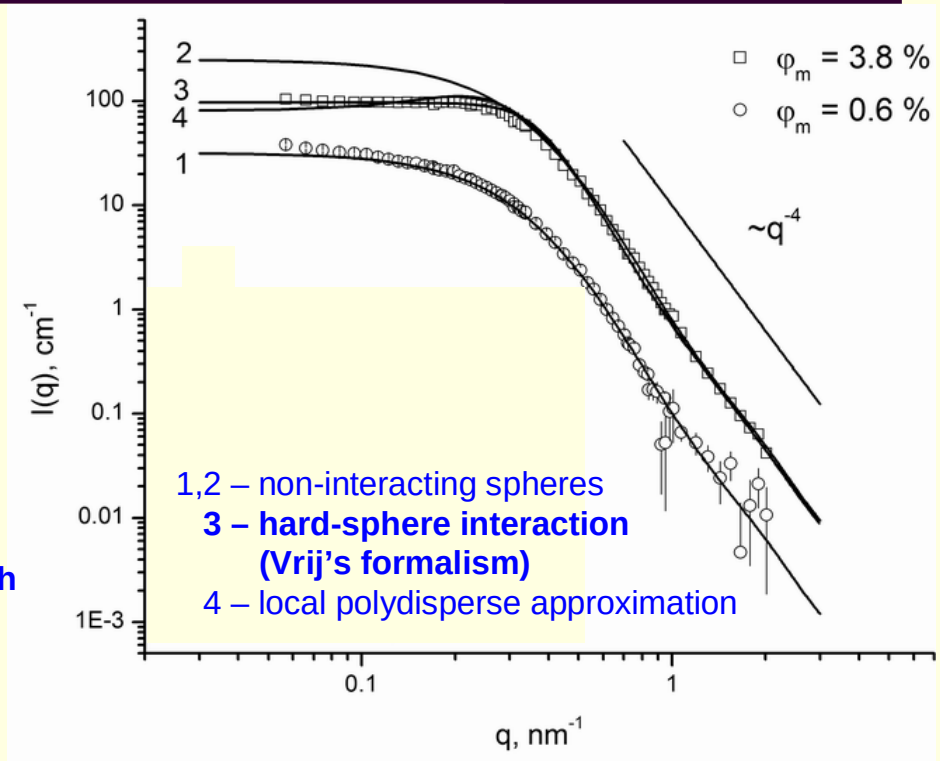
Type of structure-factor:

long-range attraction with short-range (contact) repulsion !

SANS investigations (2):Interparticle interaction. Polar ferrofluids

magnetite/oleic acid + DBS/H-pentanol





curve 1 (non-interacting particles) $\rightarrow R_0$ = 3.4 nm; S = 0.38

curve 3 (hard-spheres interaction) $\rightarrow \delta$ = 2.3 nm < 2 $\times$ 1.8 nm $\rightarrow$
$\rightarrow$ significant overlap of surfactant sublayers in the double layer

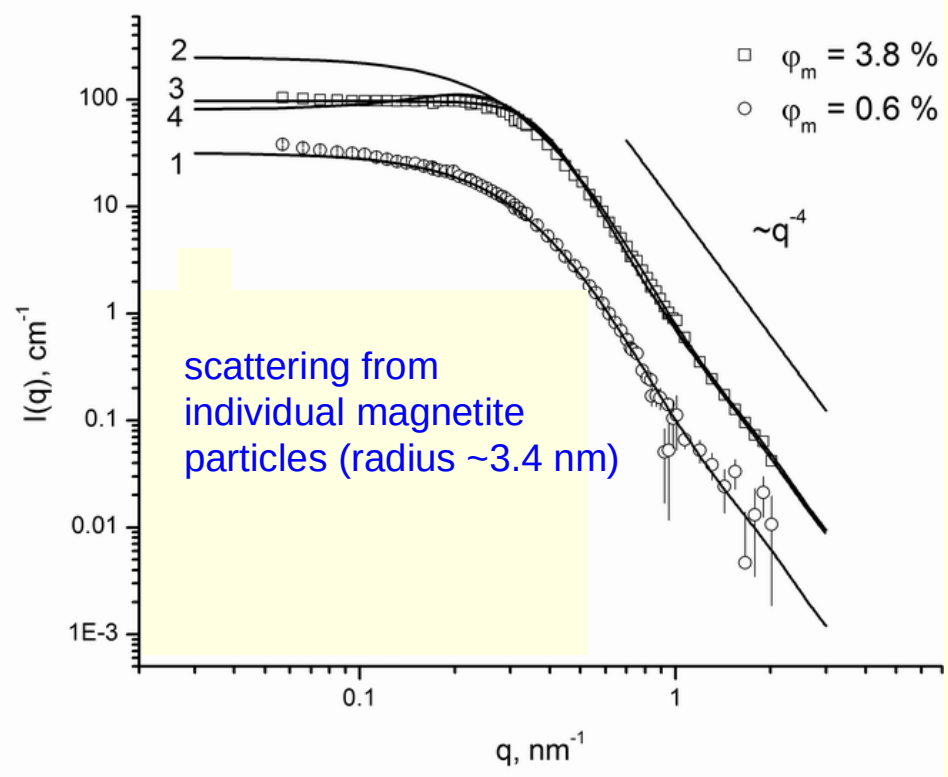
Type of structure-factor: hard spheres (φ_m< 5%) $\rightarrow$ soft spheres (φ_m> 5%)!

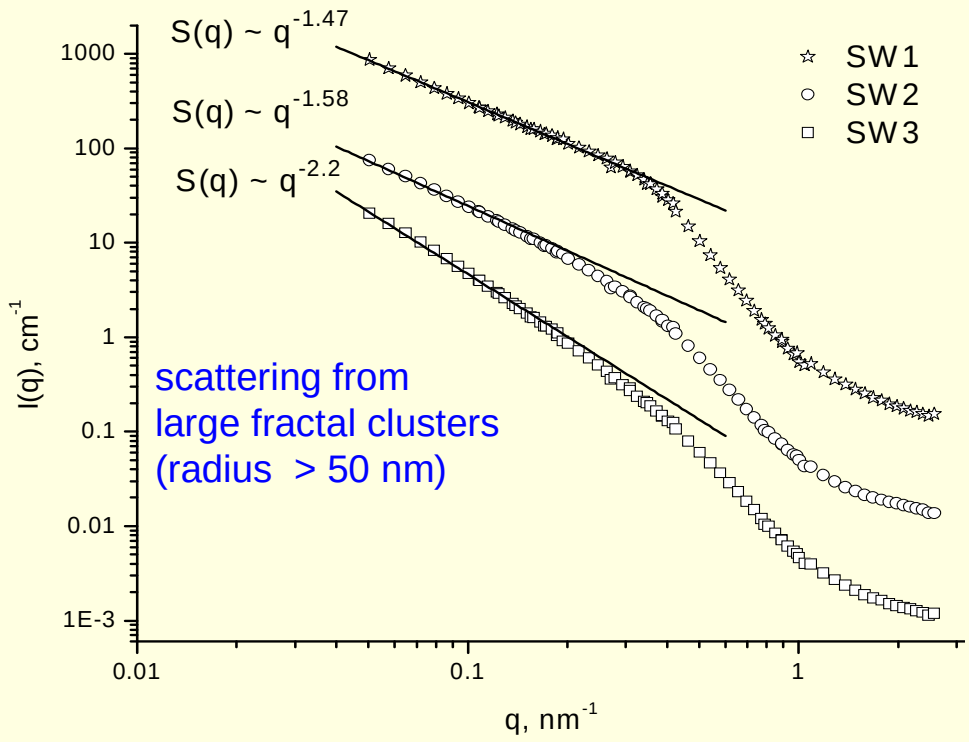
SANS investigations (3)

Comparison of two polar MFs --M.V.Avdeev et col.

Pentanol OA+DBS

Water 1-OA+DBS
Water 2-DBS+DBS
Water 3-OA+OA



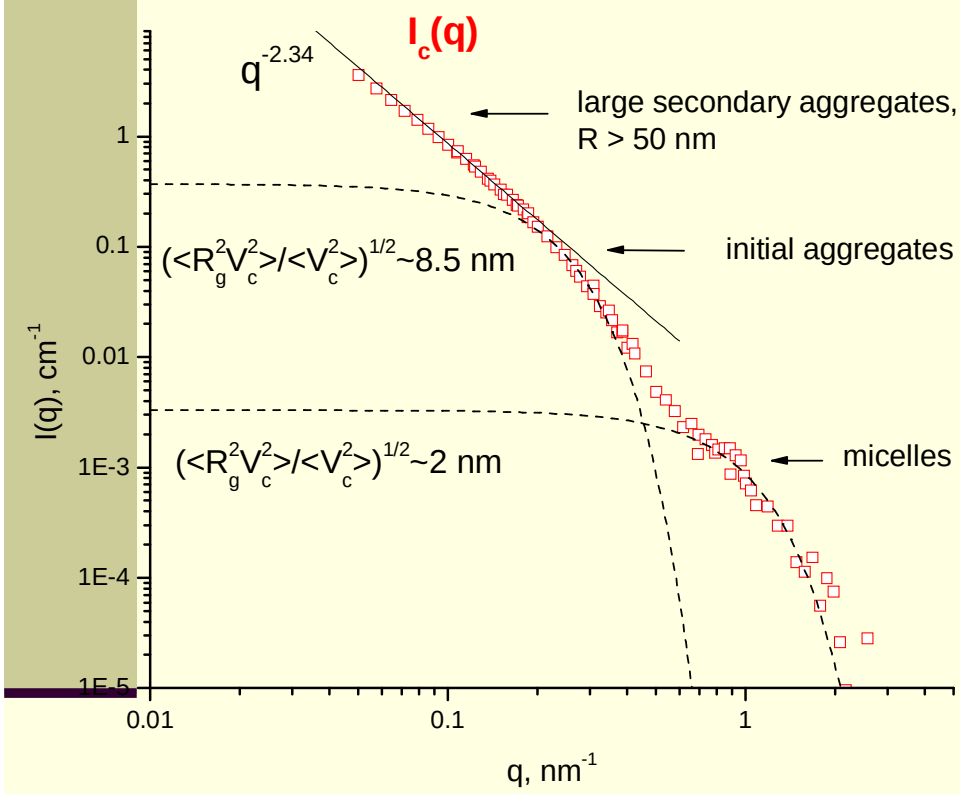


Effective "hard radius"
of whole particles R ~ 5.7 nm →
thickness of surfactant shell δ = 2.3 nm

Cluster fractal dimension D ~ 1.5 - 2.5;
Mean radius of cluster units R ~ 10 nm

SANS investigations(4): Water-based magnetic fluids

Shape scattering
Fe_3O_4 / DBS + DBS / water



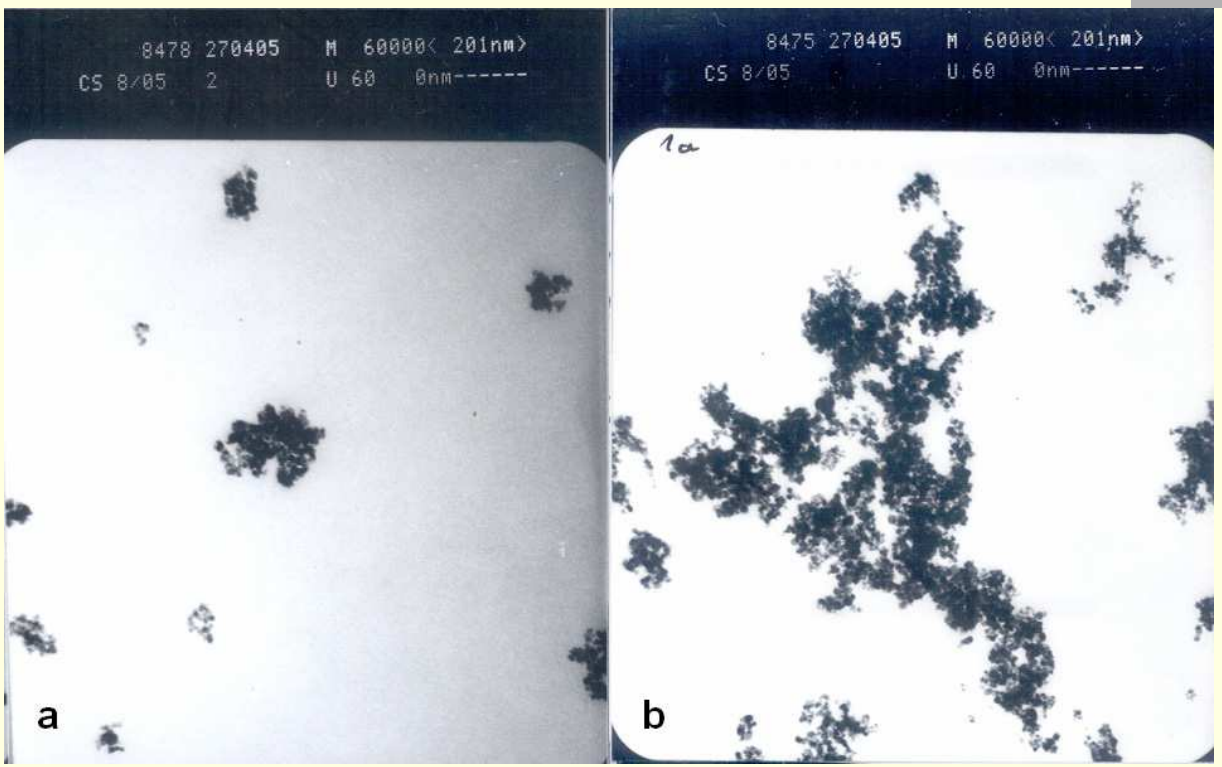
- initial tight aggregates with size of ~20 nm present; content of magnetite ~ 26 %
- secondary fractal clusters form in time; *D*-value changes with the contrast from 1.58 at 0 % of D_2O up to 2.5 at 80 % of D_2O; D-value from the shape scattering is 2.3;
- secondary fractal clusters can be destroyed by temperature increase
- micelles of DBS are in solution (size ~ 5 nm)

M.Balasoiu, M.V.Avdeev, V.L.Aksenov, D.Hasegan, V.M.Garamus, A.Schreyer, D.Bica, L.Vékás , JMMM (2006)

Colloidal stability of water based magnetic fluids

Biocompatible/bioactive magnetic nanofluids

Magnetic (iron oxide)nanoparticles manufactured by **Chemicell (Berlin, Germany)** covered by phosphated starch polymers for colloidal stabilization in deionized water.



Electron microscopy of magnetic nanoparticle suspension in deionized water (a) and in 0.9% NaCl (b)- **Destabilization of suspension under physiological conditions- Formation of large agglomerates**

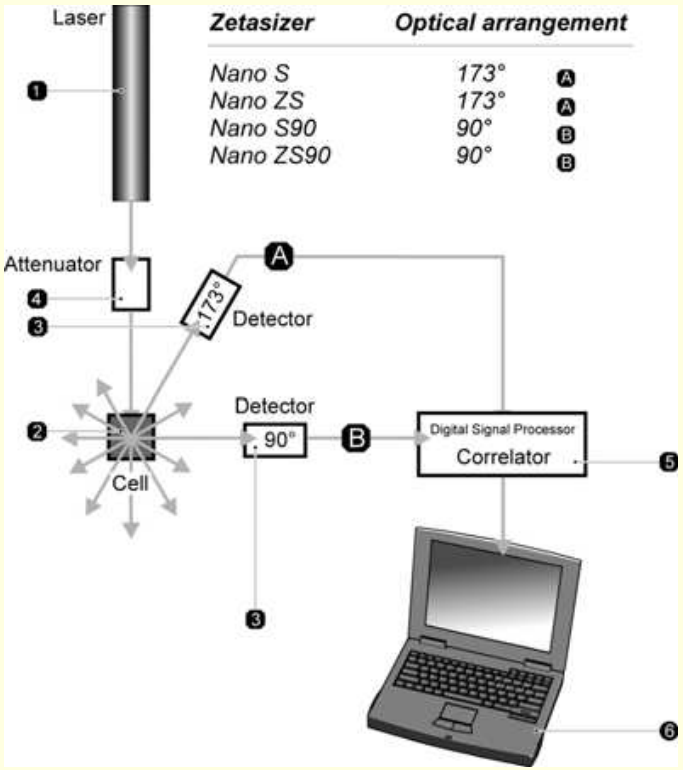
R. Jurgons et al., Drug loaded magnetic nanoparticles for cancer therapy, J Phys Condensed Matter, 28(2006)S2893-S2902

EMS 2007 Cluj-Napoca Romania

Colloidal stability of water based magnetic fluids

Dynamical Light Scattering (DLS) investigations (1)

Nano Zetasizer-Malvern



Optical configurations of the Zetasizer Nano series for Dynamic Light Scattering (DLS) measurements (Malvern, UK)

Principle of DLS

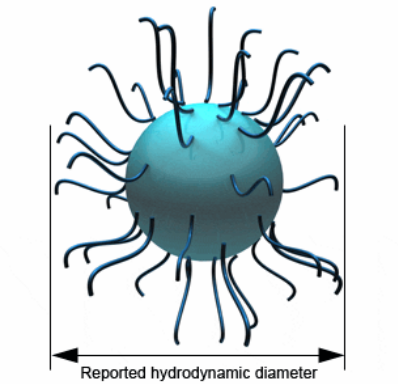
Particles in suspension undergo Brownian motion.This is the motion induced by the bombardment by solvent molecules that themselves are moving due to their thermal energy.

If the particles are illuminated with a laser,**the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles** as smaller particles are "kicked" further by the solvent molecules and move more rapidly.

Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the **Stokes-Einstein** relationship:

$$d(H) = kT/(3\pi\eta D)$$

d(H) = hydrodynamic diameter
D = translational diffusion coefficient
k = Boltzmann's constant
T = absolute temperature
η = viscosity

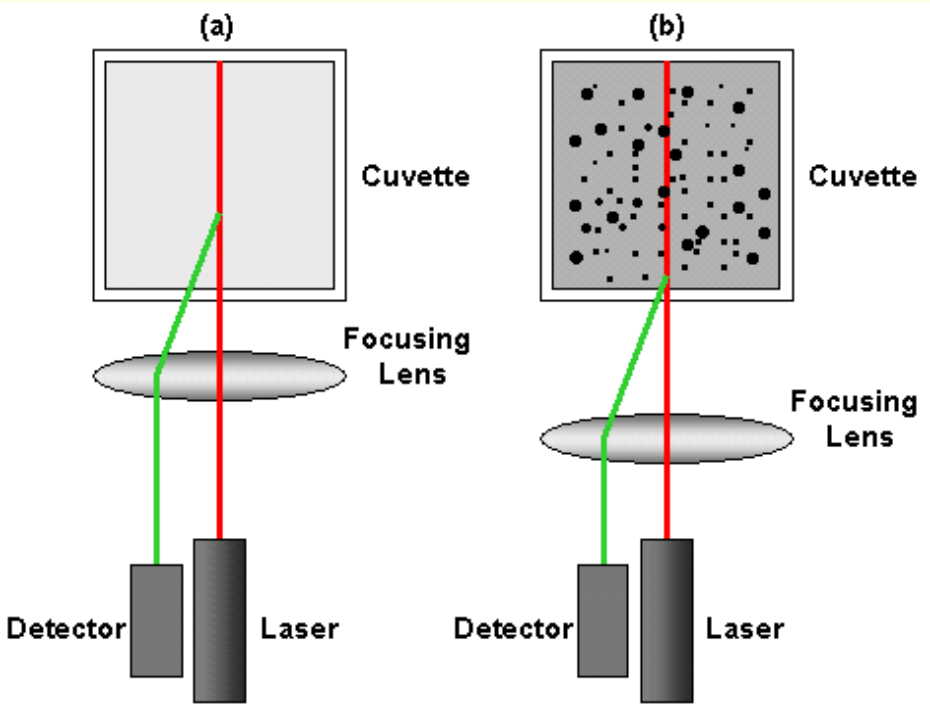


Colloidal stability of water based magnetic fluids

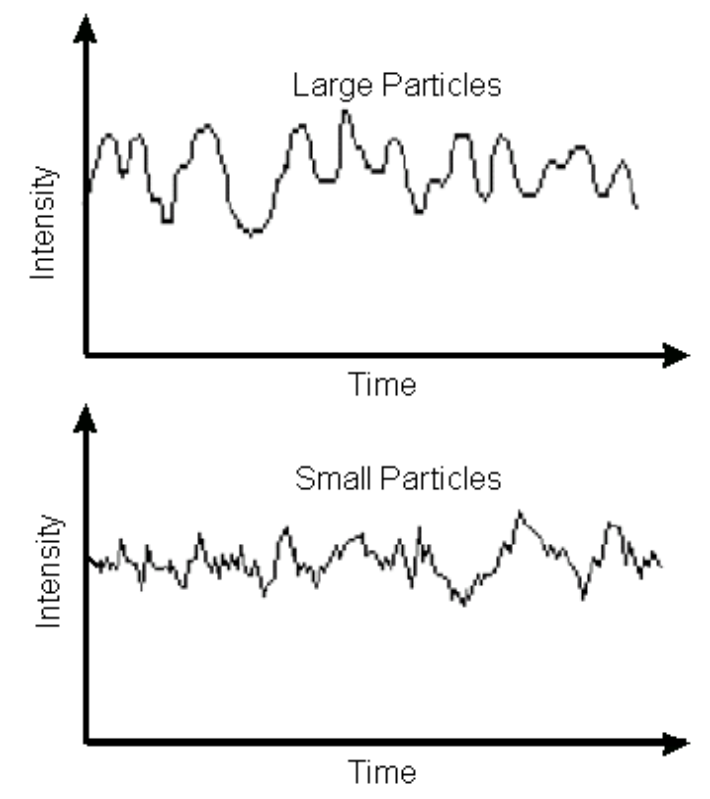
Dynamical Light Scattering (DLS) investigations (2)

Nano Zetasizer-Malvern

Principle of DLS



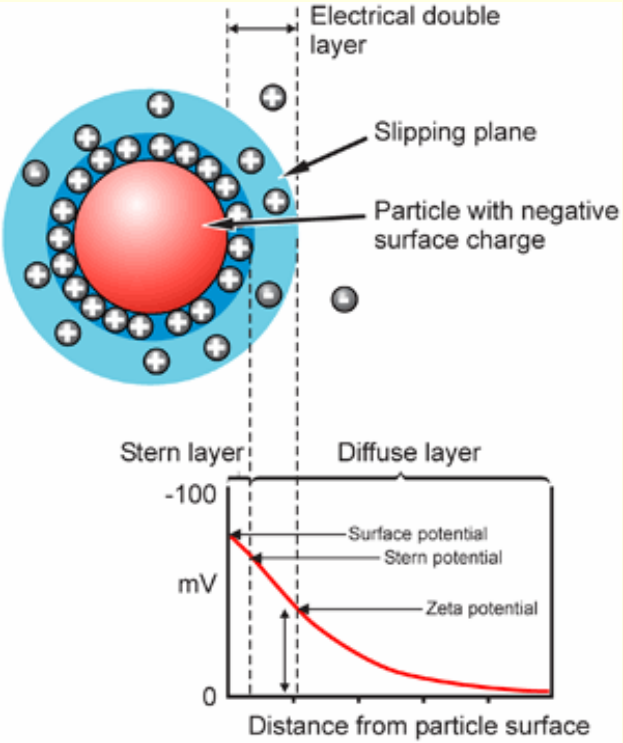
Schematic diagram showing the measurement position for (a) small,weakly scattering samples and for (b) concentrated, opaque samples. The change in measurement position is achieved by moving the focusing lens accordingly



Typical intensity fluctuations for large and small particles

Colloidal stability of water based magnetic fluids

Dynamical Light Scattering (DLS) investigations (3)



What is zeta potential?

Most particles dispersed in an aqueous system will acquire a surface charge, principally either by ionization of surface groups, or adsorption of charged species. These surface charges modify the distribution of the surrounding ions, resulting in a layer around the particle that is different to the bulk solution. If the particle moves, under Brownian motion for example, this layer moves as part of the particle. The zeta potential is the potential at the point in this layer where it moves past the bulk solution. This is usually called the slipping plane. The charge at this plane will be very sensitive to the concentration and type of ions in solution.

Zeta potential is one of the main forces that mediate interparticle interactions. Particles with a high zeta potential of the same charge sign, either positive or negative, will repel each other. Conventionally a high zeta potential can be high in a positive or negative sense, i.e. <-30mV and >+30mV would both be considered as high zeta potentials. For molecules and particles that are small enough, and of low enough density to remain in suspension, a high zeta potential will confer stability, i.e. the solution or dispersion will resist aggregation.

Zeta potential is measured by applying an electric field across the dispersion. Particles within the dispersion with a zeta potential will migrate toward the electrode of opposite charge with a velocity proportional to the magnitude of the zeta potential. This velocity is measured using the technique of laser Doppler anemometry.

Colloidal stability of water based magnetic fluids

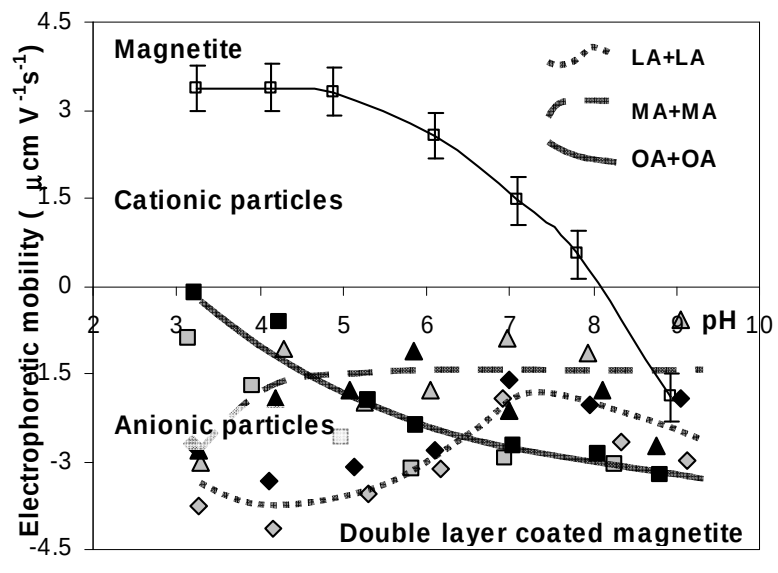
Dynamical Light Scattering investigations(4)

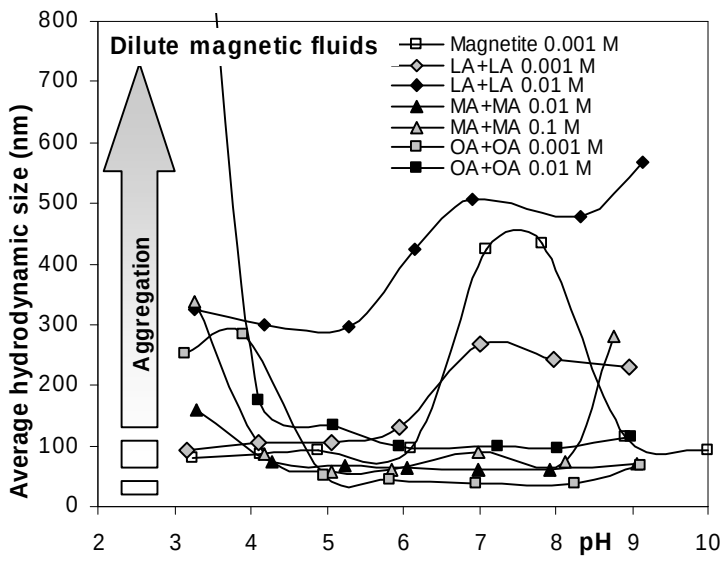
Double layer sterical stabilization using ***different chain length surfactants***

Biocompatible magnetic nanofluids

DLS experiments with NanoZS (Malvern)

E. Tombácz, Univ. Szeged -D. Bica, LMF Timisoara





Effect of anionic surfactant double layer coating on the pH-dependent charge state (left) and aggregation (right) of magnetite particles in 0.001, 0.01 and 0.1 M NaCl solutions at 25+0.10°C.

OA+OA and MA+MA stabilized MF/water samples keep their colloidal stability in the physiological range of pH (6-8)

E. Tombácz, D. Bica, A. Hajdú, E. Illés, A. Majzik, L. Vékás, *Surfactant double layer stabilized magnetic nanofluids for biomedical applications* (2007, submitted)

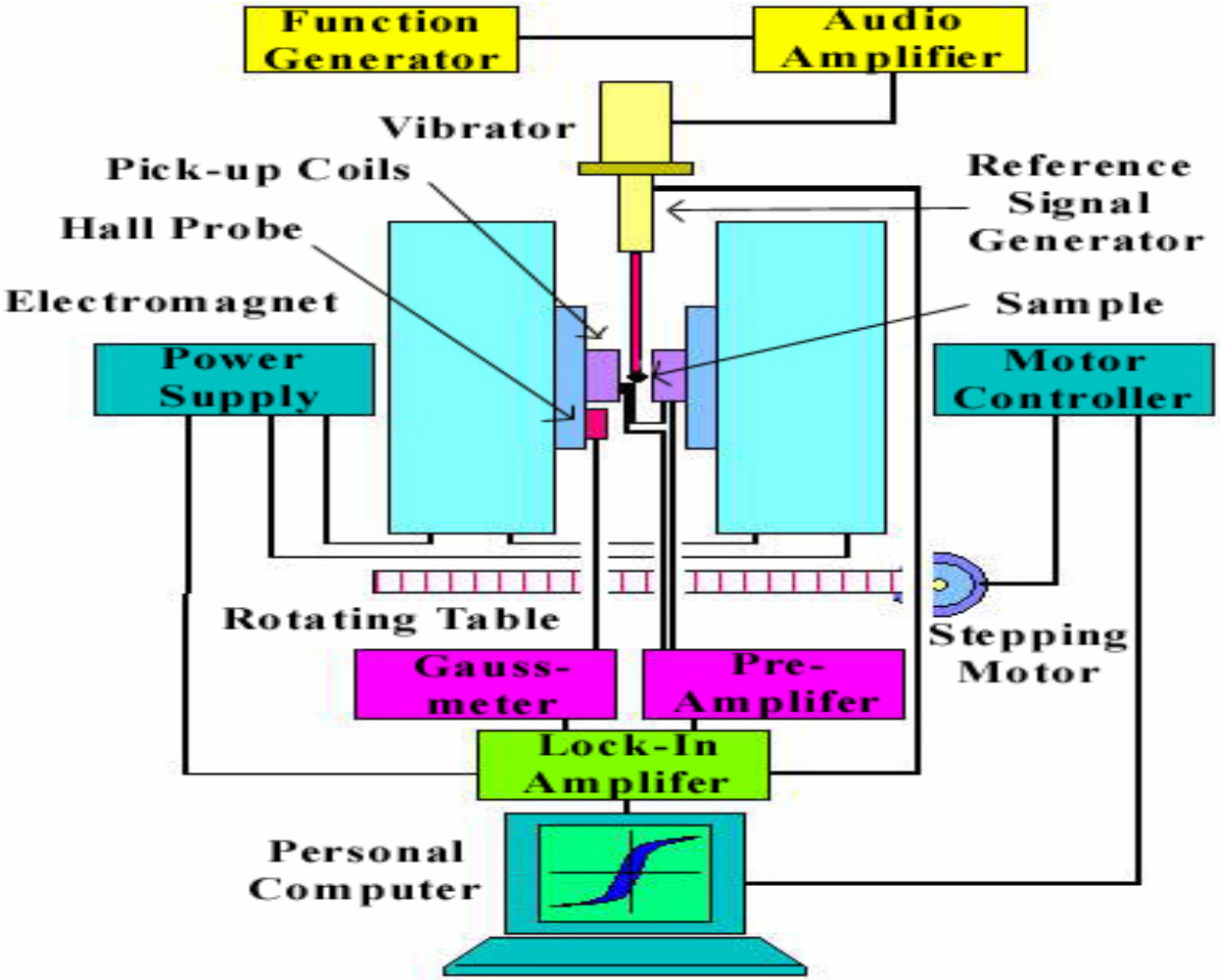
Magnetic and rheo-magnetorheological characterization of MFs

National Center for Engineering of Systems with Complex Fluids
Univ. Politehnica Timisoara

Physica MCR 300
Rheometer

VSM 880
Magnetometer

Main components of VSM

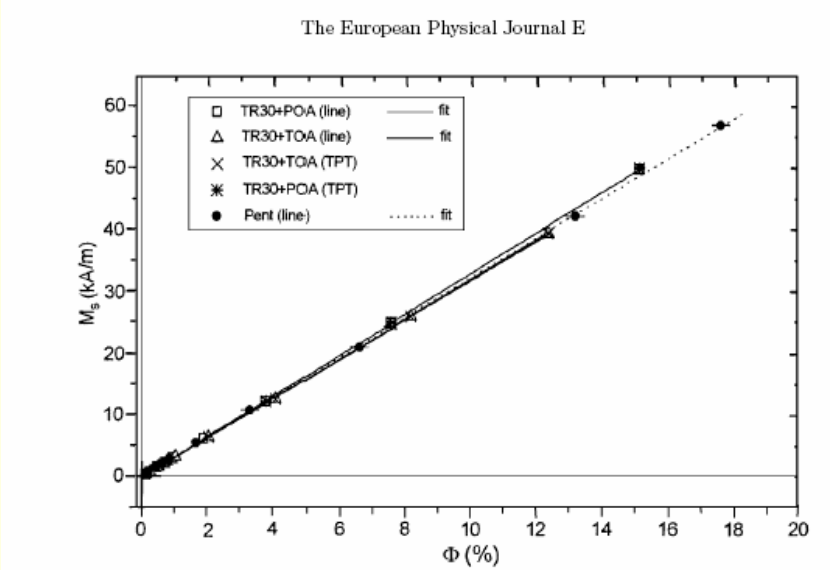


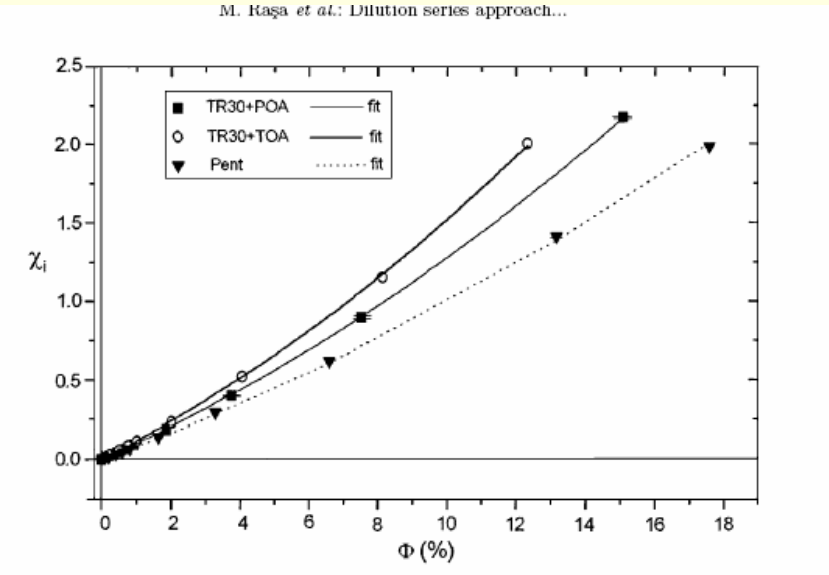
System diagram of Vibrating Sample Magnetometer

Dilution stability of magnetic fluids with organic carrier

High colloidal stability MFs: magnetic investigations

Saturation magnetization M_s and initial susceptivity χ_i vs. volume fraction Φ for various **Transformer oil (TR30)** and **Pentanol (Pent)** based magnetic fluids





Ms is determined from a linear fit to the quasisaturation part of magnetization curves and it is compared to a fit to MF model with Thermodynamic Perturbation Theory(TPT):

$$M \approx M_s - c/H + M_s\, c/(3H^2) - c^2/(3H^3) \sim M_s - c/H$$

In case of initial susceptivity χ_i the degree of **non-linear behavior is a result of both particle interaction and aggregate formation** in samples: $\chi_i \approx \chi\,(1 + \chi/3 + \chi^2/144)$ (TPT)

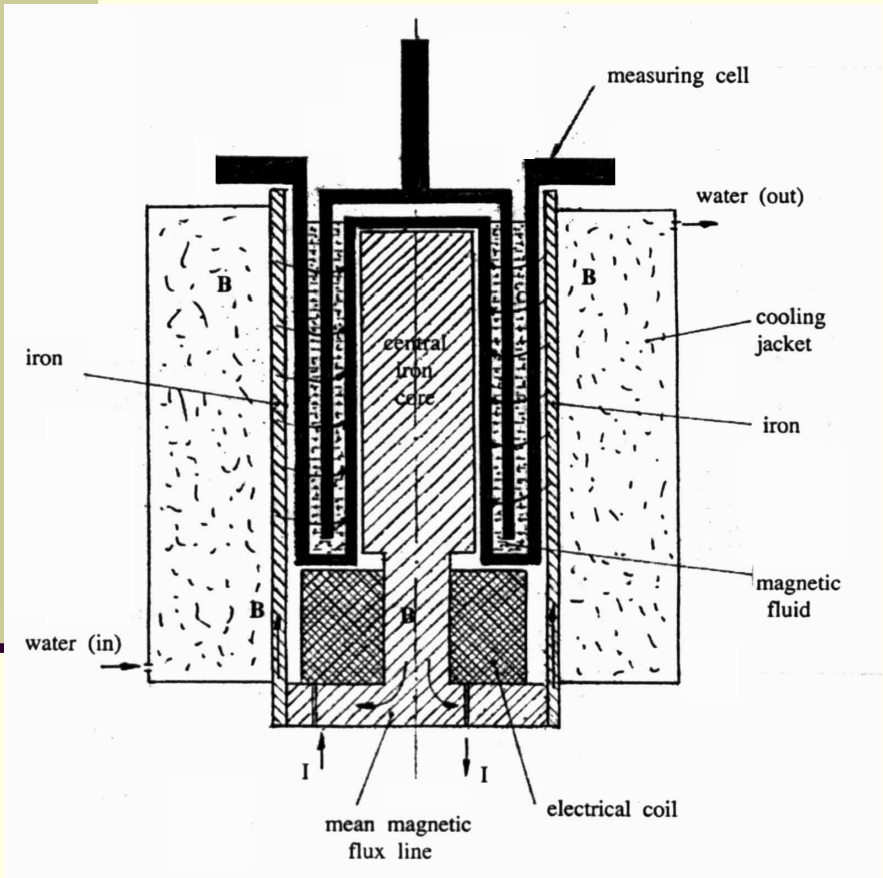
MF/Pentanol is practically free of aggregates up to high volume fraction of MNPs

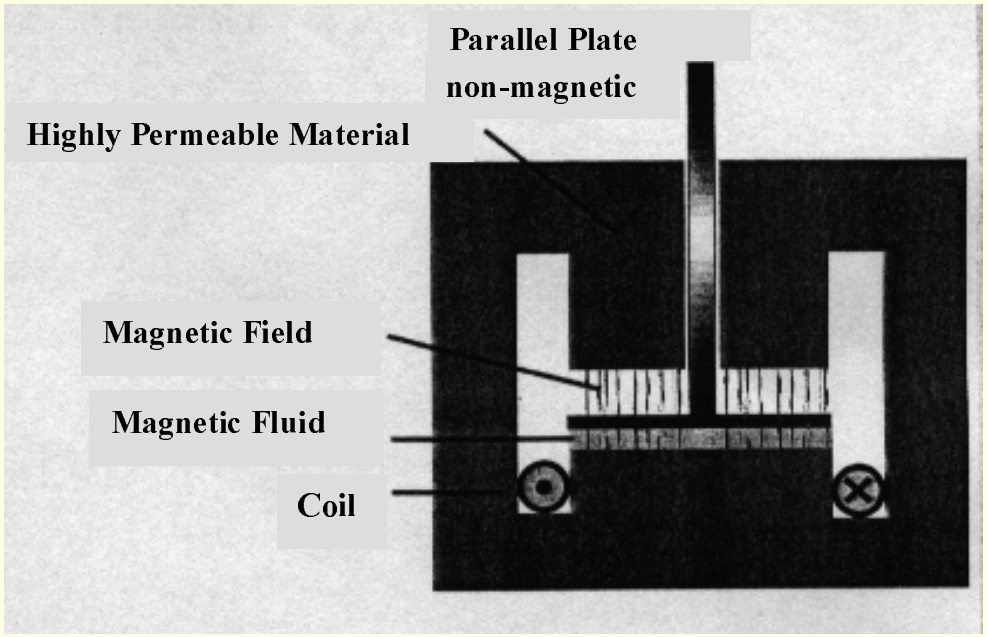
M. Rasa, D. Bica, A.P. Philipse, L. Vekas, Eur.J.Phys., E (2002)

MAGNETORHEOLOGICAL INVESTIGATIONS

MR cells

National Center for Engineering of Systems with Complex Fluids
Univ. Politehnica Timisoara



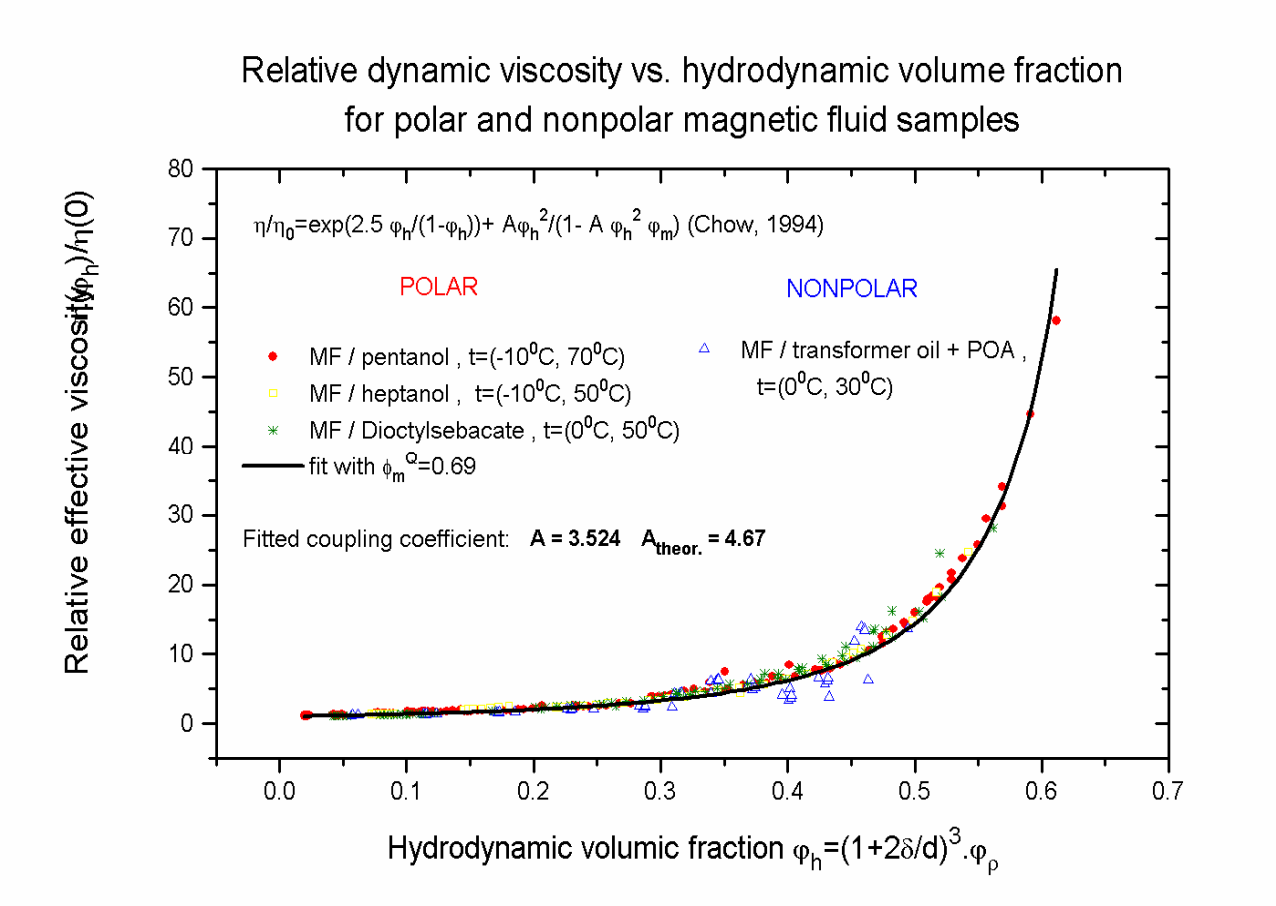


PHYSICA MCR 300

RHEOTEST - 2

Effective viscosity vs. hydrodynamic volume fraction

High colloidal stability MFs: ***flow properties in the absence of the field***



Good correspondence with the theoretical formula of Chow (Phys.Rev. E (1994))

Influence of dipolar interactions beside the hard sphere ones: A(fit) = 3.5 < 4.6(theor)

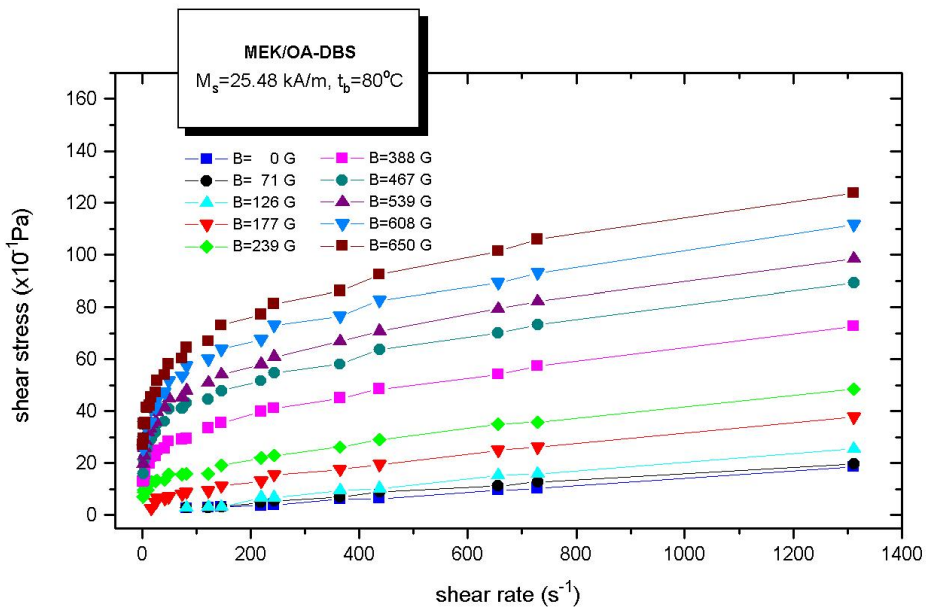
L.Vekas, D. Bica, D. Gheorghe, I. Potencz, M. Rasa, JMMM 201(1999)

Flow properties of MFs with short chain length organic carriers

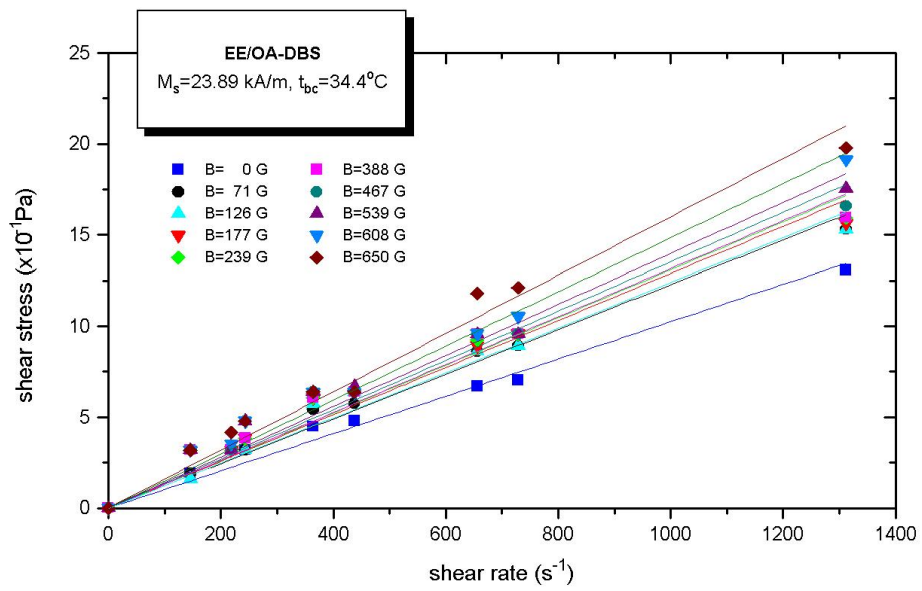
Flow curves in applied magnetic field

RHEOTEST-2, cylindrical MR cell

MF/MEK(Methyl-ethyl-ketone)



MF/EE(Ethylic ether)



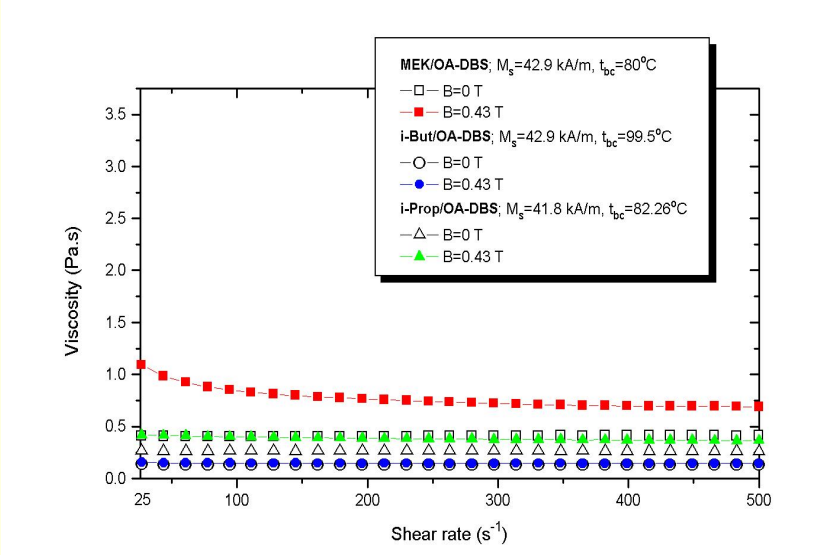
Field induced non-Newtonian behaviour

Roughly Newtonian behaviour

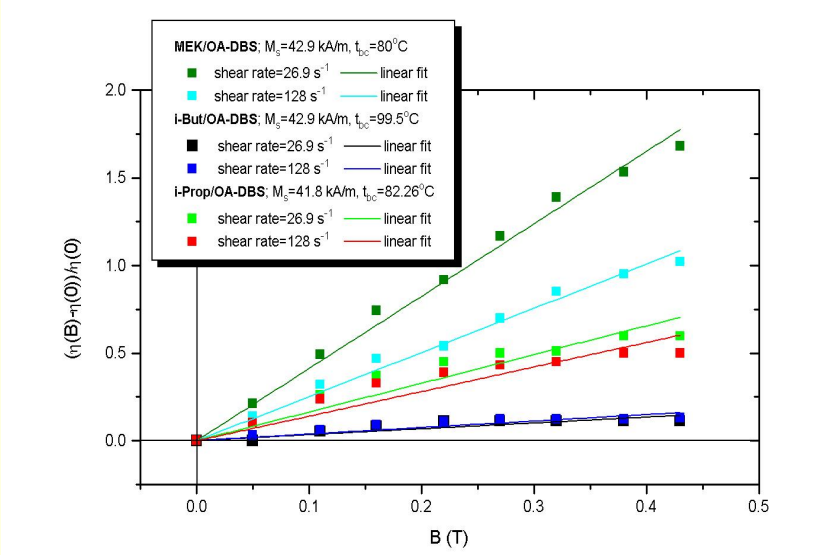
Effective viscosity increase due to magnetic field induced agglomerate formation in strongly polar MF/MEK sample L. Vekas,D.Bica, O. Marinica, M. Rasa, V. Socoliuc, F.D. Stoian JMMM 289(2005)

Flow properties of polar MFs: Dependence of viscosity on shear rate under the influence of magnetic field for MF/MEK, MF/Prop, MF/But

(PHYSICA MCR300, plate – plate MR cell)



Viscosity vs. shear rate under applied magnetic field (B)



MR effect vs. magnetic induction B

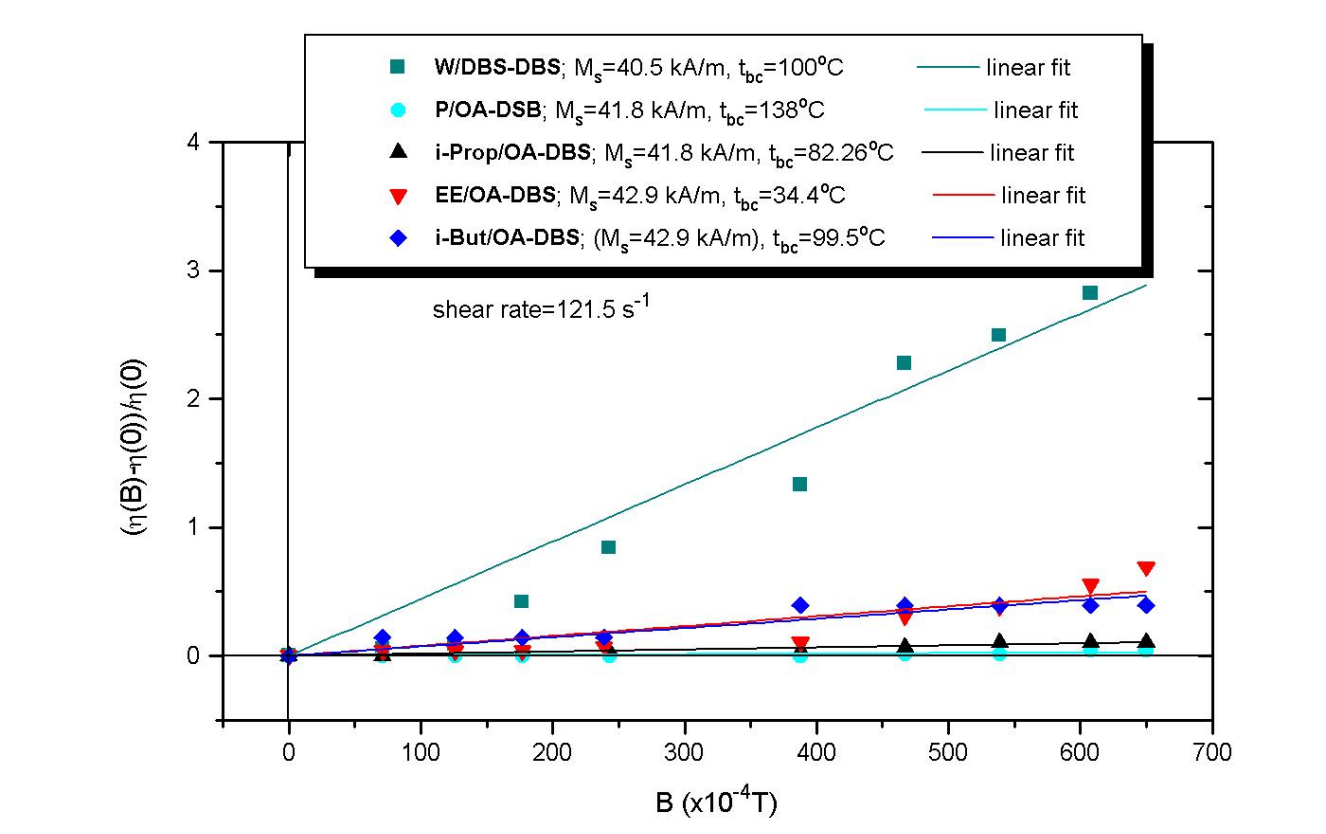
MF/But: Newtonian behavior in magnetic field
Negligible MR effect

MF/MEK: Field induced non-Newtonian behavior
Strong MR effect

Relative increase of viscosity in magnetic field of high magnetization MFs

Water and organic polar carriers

(cylindrical MR cell)



MF/pentanol (P): negligible MR effect

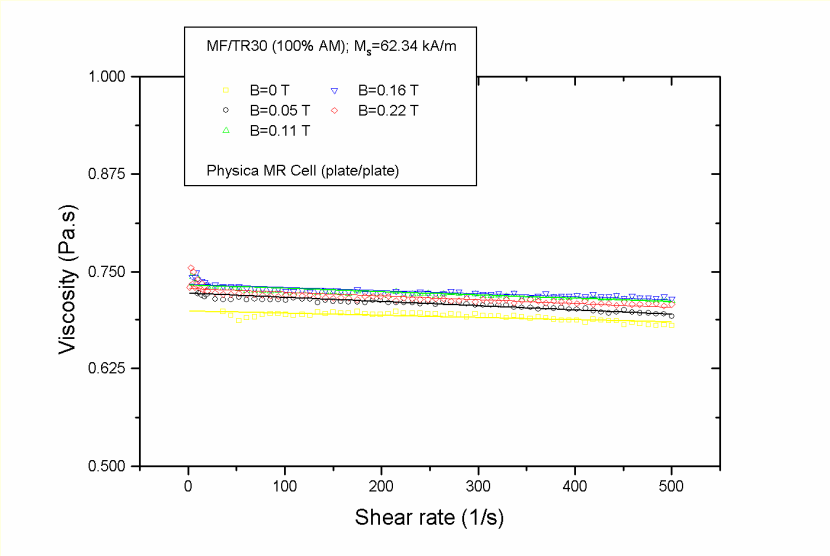
MF/water (DBS+DBS): largest MR effect

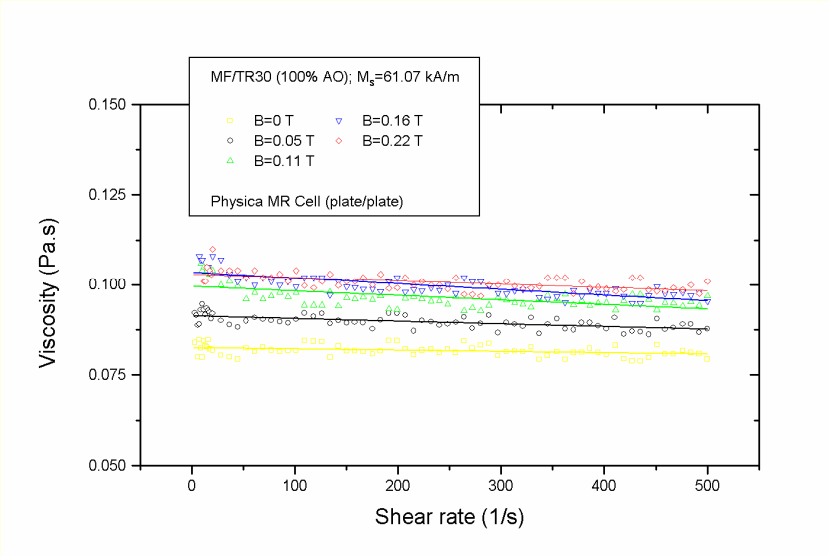
Stabilization/dispersion of magnetic nanoparticles in organic carriers with different chain length surfactants MA (C14) and OA(C18)

Comparative magnetorheological analysis (MCR 300 Physica rheometer)

Non-polar carrier**, mono-layer sterical stabilization with **MA (14)** and **OA (C18)

Flow properties under the infuence of applied magnetic field



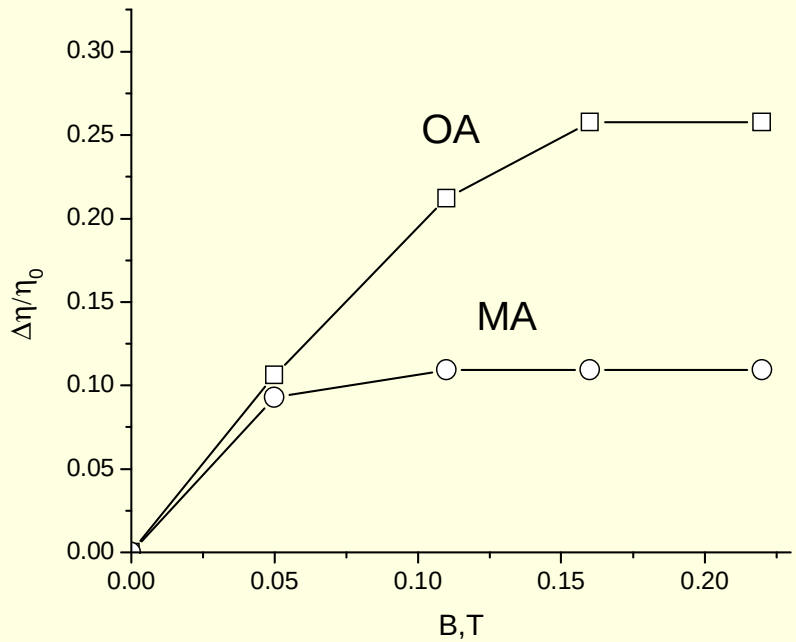


Concentrated (M= 62 kA/m)
MA stabilized MF/Utr sample
Large viscosity,
reduced MR effect
(≤10%; at higher shear rate)

Concentrated (M= 61 kA/m)
OA stabilized MF/Utr sample
Moderate viscosity,
relatively large MR effect (~20-30%)

Stabilization/dispersion of magnetic nanoparticles with various chain length surfactants in non-polar carrier

Dependence of magnetoviscous effect on the nature of surfactant MF/Utr samples with OA and MA surfactant layers



Due to particle size selection by surfactants, the magnetoviscous effect **Δη/η** is approx. 50 % smaller for **MA** stabilized sample, compared to that with **OA**

L.Vekas, D. Bica, O.Marinica, Rom.Rep.Phys. 58(2006)

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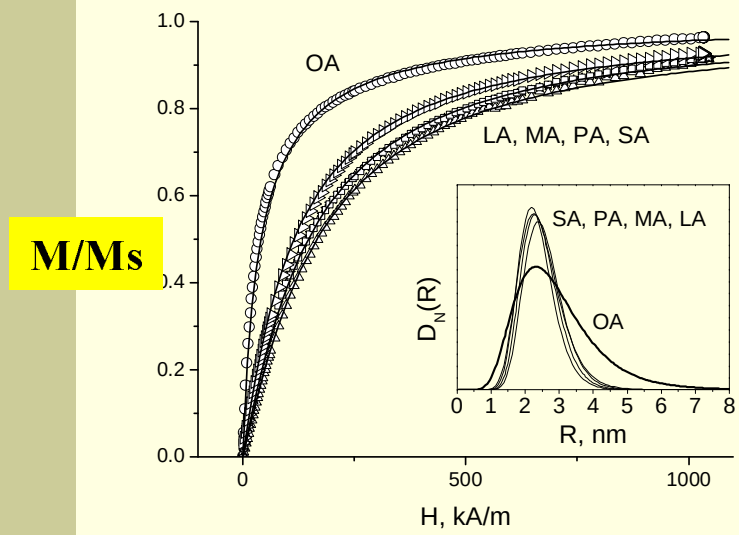
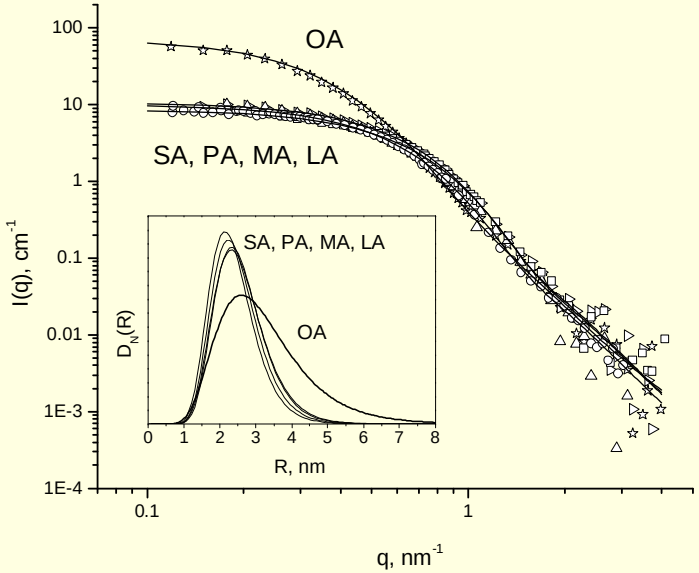
Stabilization/dispersion of magnetic nanoparticles with different chain length surfactants in non-polar organic carrier

OA (C18), SA(C18), PA(C16), MA (C14) and LA(C12) stabilized MF/DHN samples

Comparative magnetogranulometric and SANS analyses

Mikhail V. Avdeev, Doina Bica, Ladislau Vékás, Oana Marinica, Victor L. Aksenov, Vasyl M. Garamus, Regine Willumeit, Laszlo Rosta, Alexey O. Ivanov, Valentin S. Mendelev (2007; in preparation)





Non-dim magnetization curves (points) for magnetic fluids stabilized by various mono-carboxylic acids in DHN, φ_m = 1.5 %. Lines are the results of the polydisperse Langevin approximation with log-normal particle size distribution. Inset shows the corresponding particle size distributions of magnetite (**magnetic size**). Parameters of the $D_n(R)$ function in the OA case are R_0 = 0.27 nm, S = 0.39.
Parameters of the $D_n(R)$ function averaged over the cases SA, PA, MA, LA are R_0 = 0.24 nm, S = 0.23.

SANS curves (BNC Budapest) for magnetic fluids stabilized by various mono-carboxylic acids in DHN, φ_m = 1.5 %. Lines are the results of approximation by the model of polydisperse non-interacting spheres with log-normal particle size distribution.
Inset shows the corresponding particle size distributions of magnetite (**atomic size**). Parameters of the $Dn(R)$ function in the OA case are R_0 = 0.30 nm, S = 0.38.
Parameters of the $D_n(R)$ function averaged over the cases SA, PA, MA, LA are R_0 = 0.24 nm, S = 0.28.

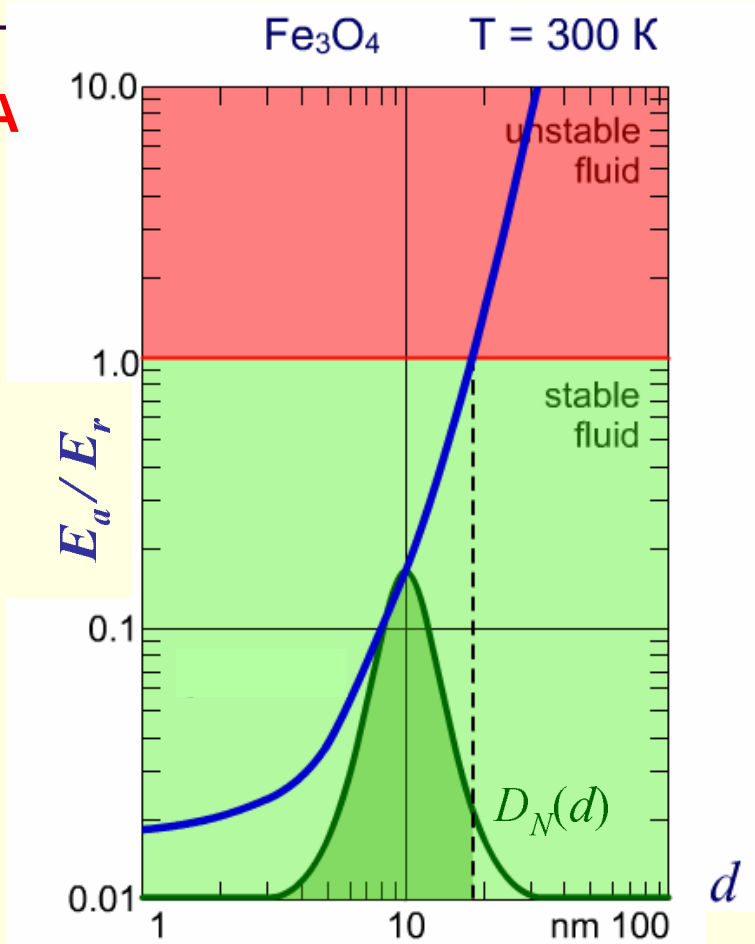
$$D_n(R)=(1/(2\pi)^{1/2}SR)\exp[-\ln^2(R/R_0)/(2S^2)]$$

Magnetic nanofluids with " chemically tailored" magnetic nanoparticles(1)

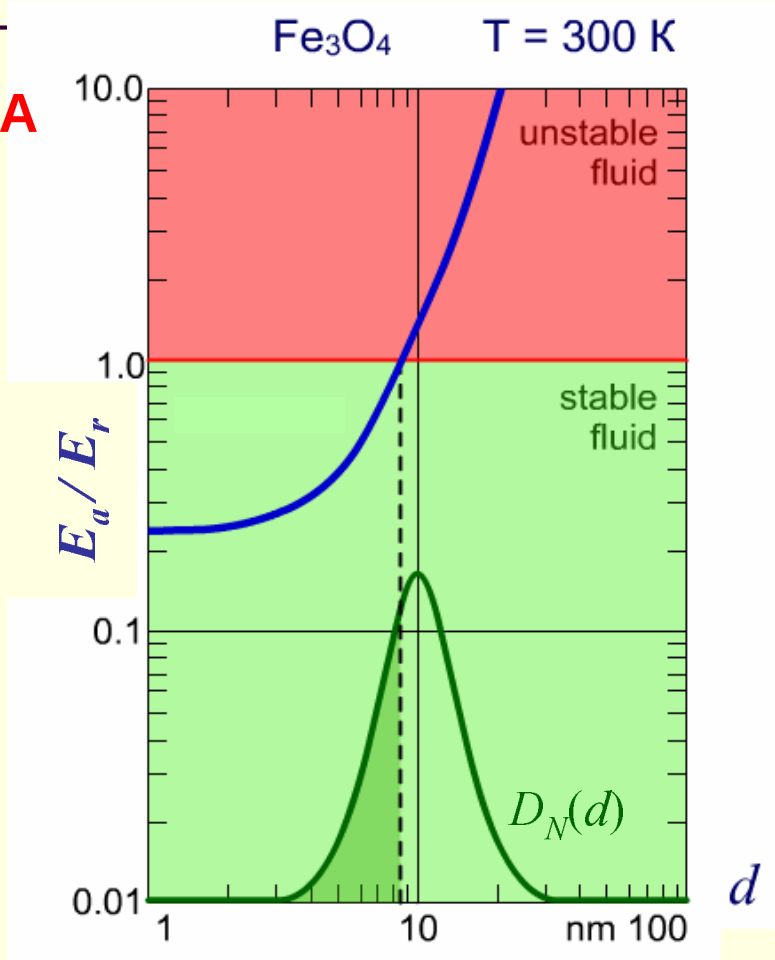
Size selective synthesis of surfactant covered magnetic nanoparticles

Type of surfactant regulates dispersed particle size during the MF stabilization

OA



MA



Qualitative scheme of the size regulation effect. Restriction on the particle size from the energetic condition of stability for two surfactants is compared with the particle size distribution of nanomagnetite

Mikhail V. Avdeev, Doina Bica, Ladislau Vékás, Oana Marinica, Victor L. Aksenov, Vasyl M. Garamus, Regine Willumeit, Laszlo Rosta, Alexey O. Ivanov, Valentin S. Mendelev (2007; in preparation)

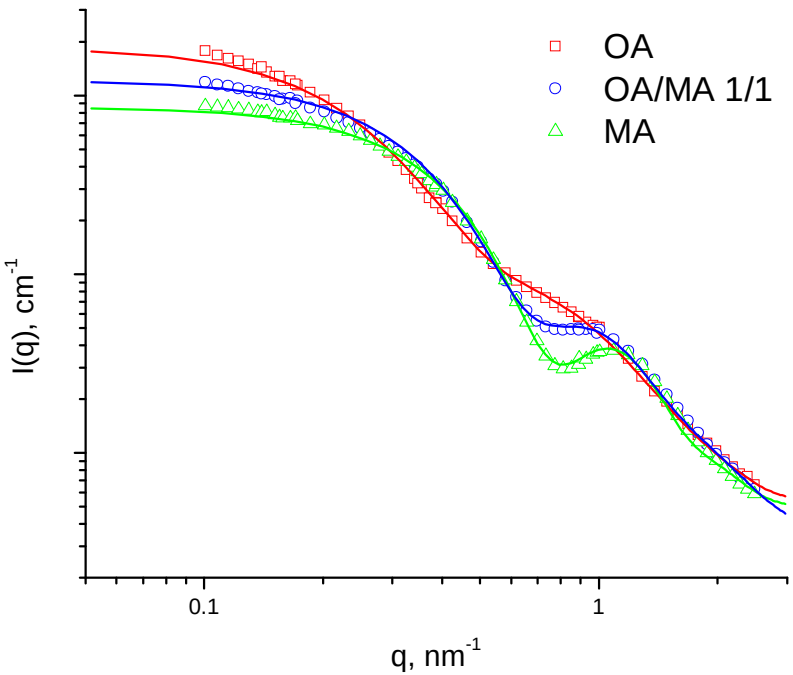
Magnetic nanofluids with " chemically tailored" magnetic nanoparticles(2)

Size selective synthesis-stabilization of magnetic nanoparticles with mono-layer of mixed surfactants

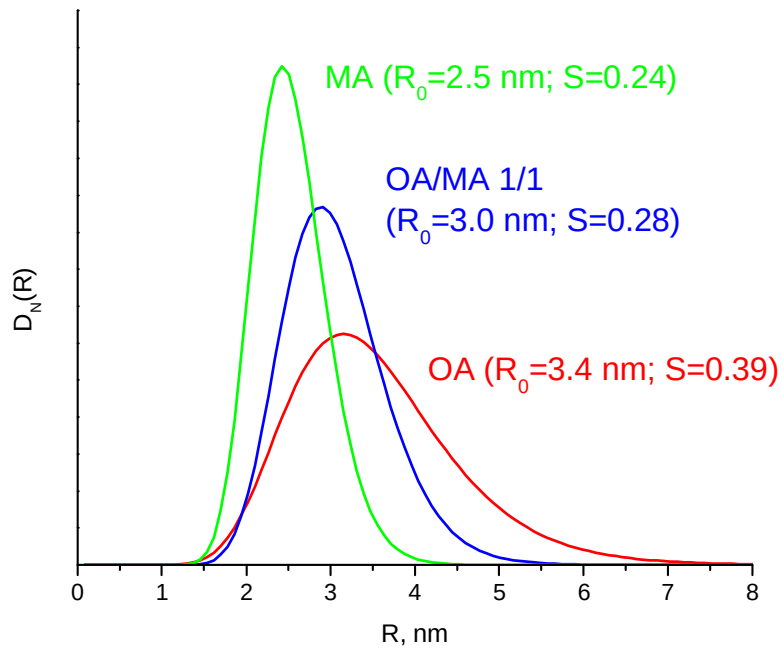
Non-polar carrier (D-benzen)), φ=1.1 %

SANS curves and resulting size distributions

Mixed surfactants monolayer (MA + OA) with 1:0, 1:1 and 0:1 mixing ratios



Nuclear scattering contribution. Solid lines are fits of the core-shell model.



Resulting log-normal size-distribution functions.

Increased MA content, more reduced diameter and standard deviation

M.V. Avdeev, D. Bica et al (2007, in preparation)

TOWARDS NEW TYPE OF SMART NANOMATERIALS

Magnetic fluid initiated nanocomposites

- Core-shell structures
- CNTs + magnetite+PPy hybrid structures
- Multi-layered structures
- Resin-based composites
- Magnetic gels&elastomers

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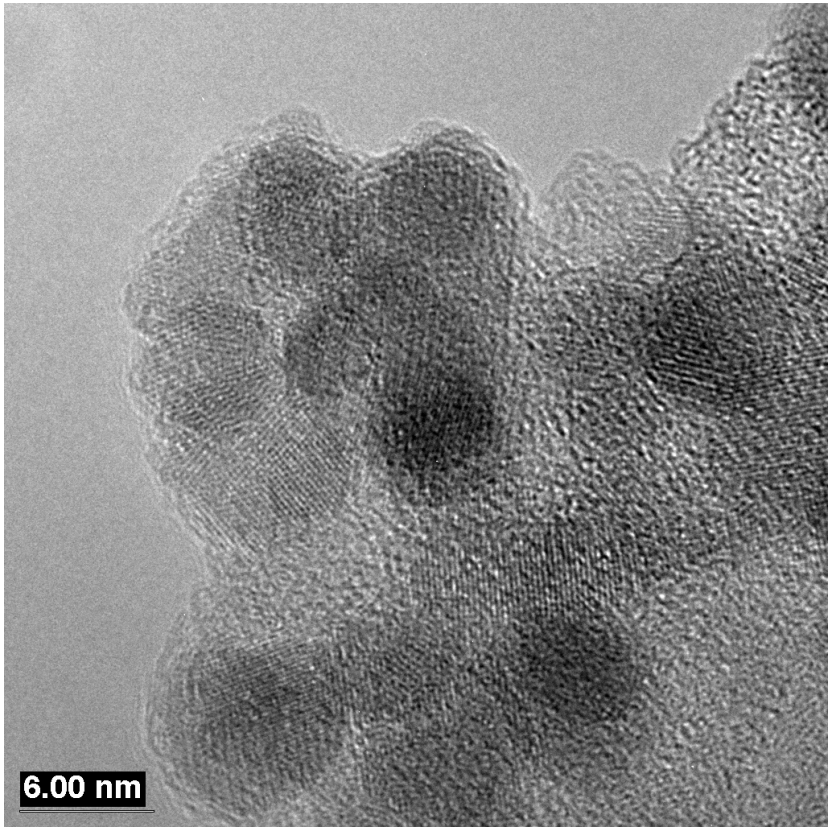
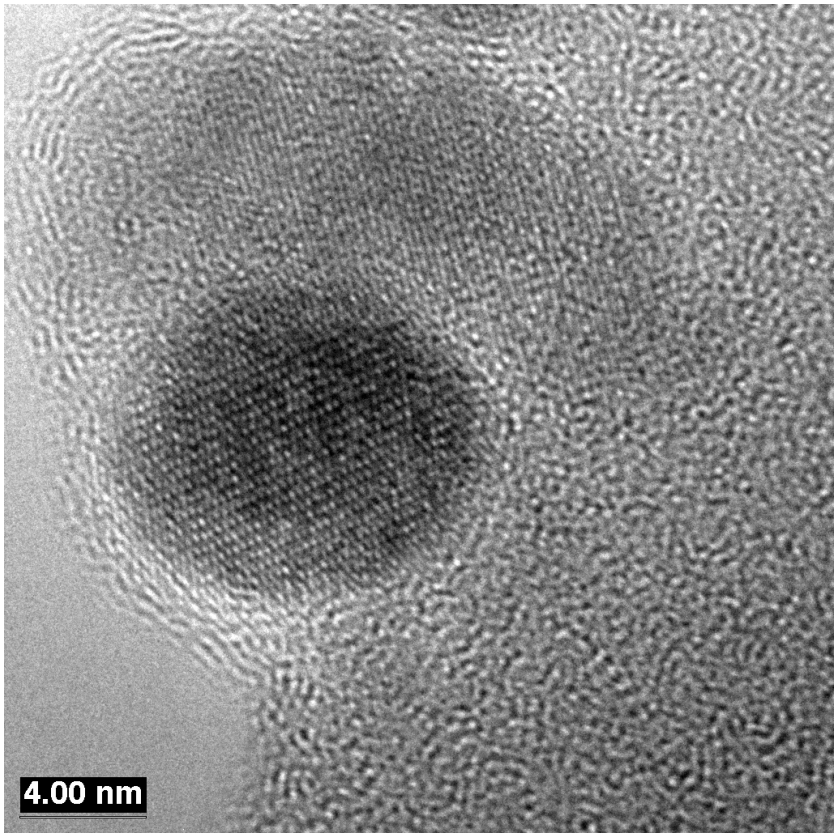
Magnetite-polypyrrole Core-shell nanostructures

Lab.MF Timisoara- INCDTIM Cluj-Napoca- Inst. of Materials Nantes
Dr. Rodica Turcu and collab (NanoFunc- project CEEX)

Primary components: MF/water and PPy

Hybrid nanostructure: Magnetic core-electroconducting shell





HRTEM images of magnetite nanoparticles coated with PPy
R. Turcu, O.Pana, D. Bica, L. Vekas, A. Nan, I. Craciunescu, O. Chauvet, C. Payen (2007; in preparation)

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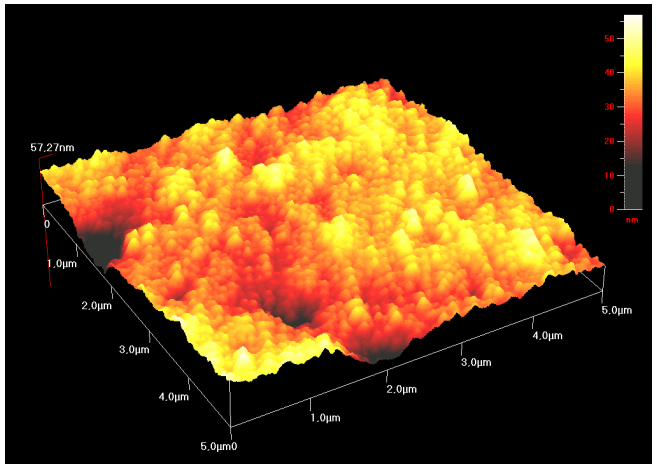
Polymeric nanocomposites with magnetite nanoparticles

PVC Nanocomposites layer/thin multi-layer

Coop. Lab. MF Tms-- Univ. Cyprus

A. Christophidou, D. Bica et al. Proc.ISNM2006 (MIT)

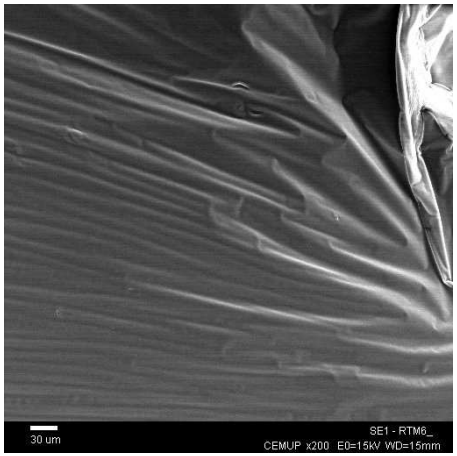


AFM image of spin-coated PVC film with magnetic nanoparticles

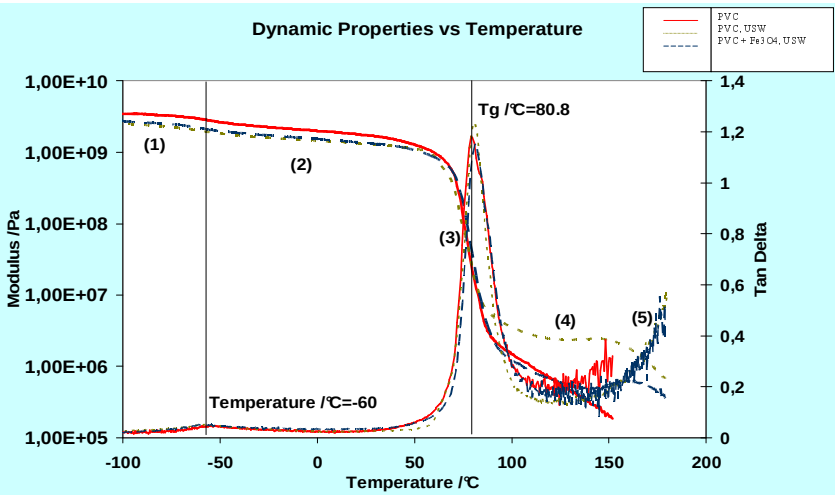
Resin based magnetizable nanocomposites

Coop. CNISFC Tms--Univ. Porto

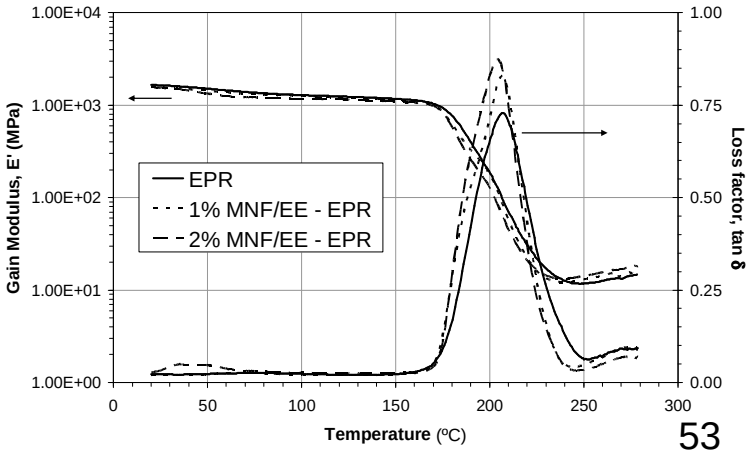
N. Crainic, D.Bica, A.T. Marques et al Proc.ISNM 2006(MIT)



RTM 6 resin in the fracture zone [x 200].



Dynamic properties versus Temperature (a) PVC (b) PVC ultrasonically welded, (c) PVC + Fe_3O_4, ultrasonically welded



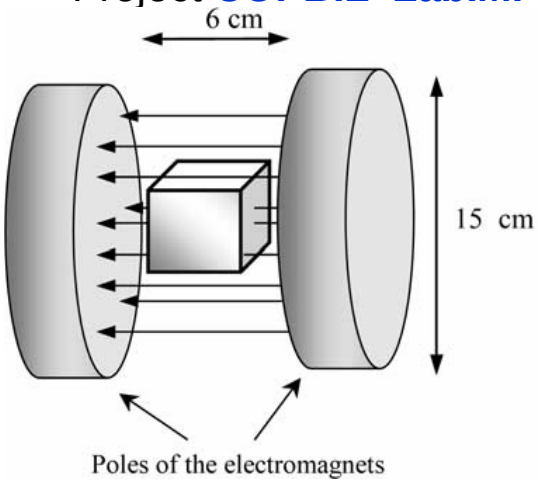
DMTA test results for RTM 6 + 1 % MNF / EE.

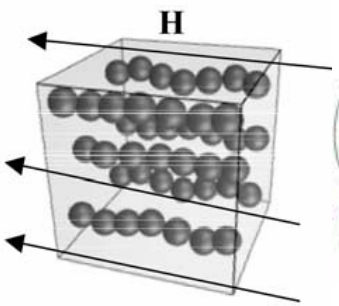
Polymeric composite with field induced uniaxial ordered structure

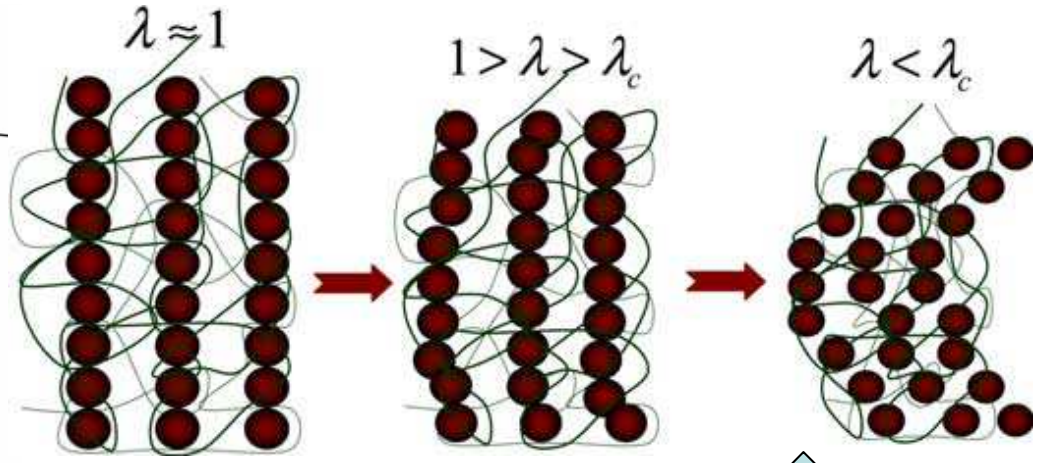
Smart composites with controlled anisotropy Zsolt Varga, Genovéva Filipcsei, Miklós Zrínyi*

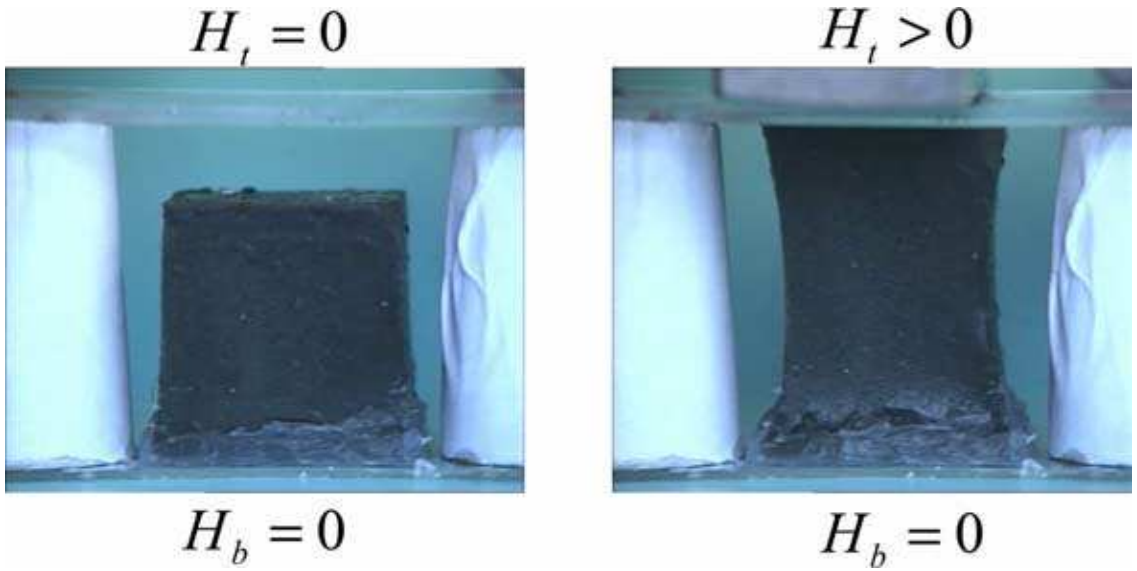
HAS-BUTE Laboratory of Soft Matters, Department of Physical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary (POLYMER, 2007 (to appear))

Project **COPBIL Lab.MF Timisoara-Dept. Phys. Chem.-BUTE**







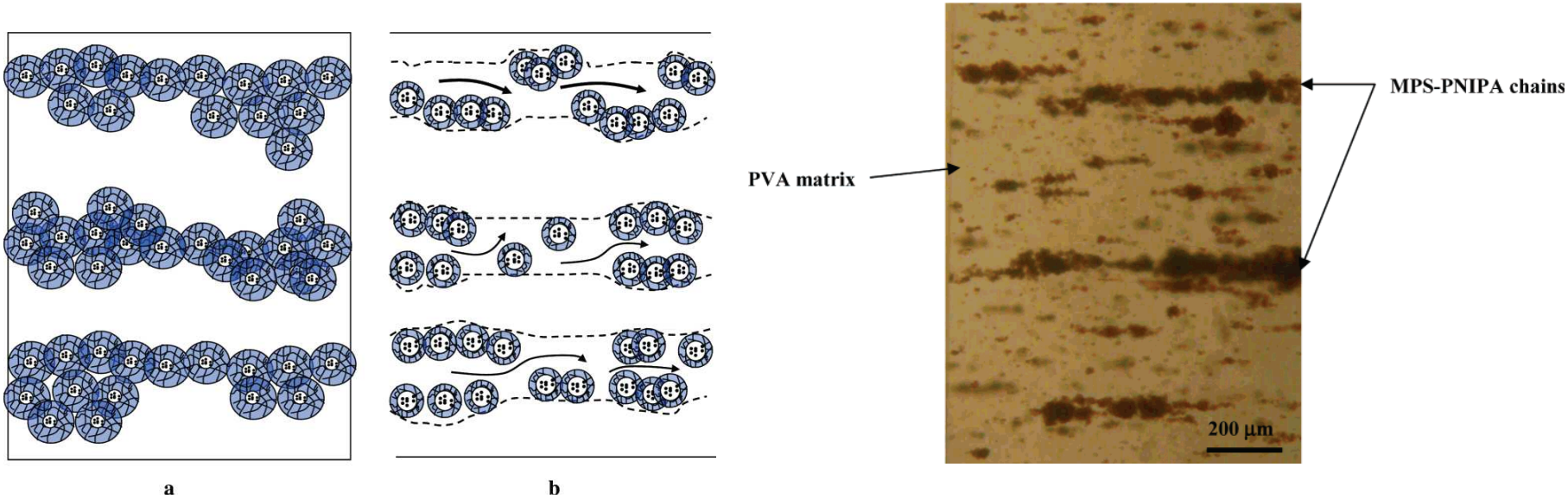


Schematic picture of the bending of the magnetic PVA gels under compression.

The **new generation of magnetic elastomers** represents a new type of composites, consisting of small (mainly nano- and micron-sized) magnetic particles dispersed in a high elastic polymeric matrix

Intelligent polymeric nanocomposite membrane

Macromolecules **2006,** *39,* 1939-1942 Ildiko´ Csetneki, Genove´va Filipcsei, and Miklo´s Zrı´nyi**Department of Physical Chemistry, Budapest UniVersity of Technology and Economics,HAS-BME Laboratory of Soft Matters, H-1521 Budapest, Hungary*



Ordered nanochannels can act as "on-off"switches or "permeability valves"

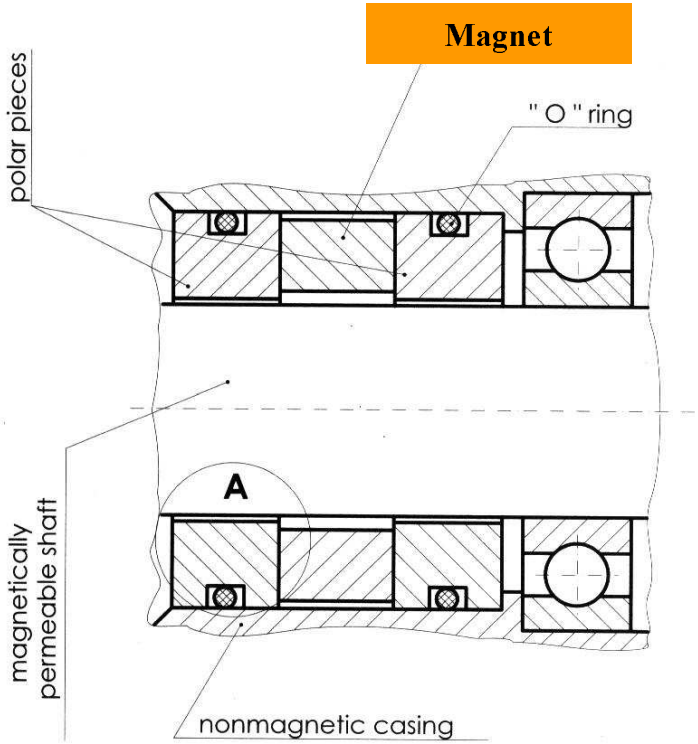
Poly(*N*isopropyacrylamide)gel-----PNIPA gel Magnetic polystyrenelatex ---MPS

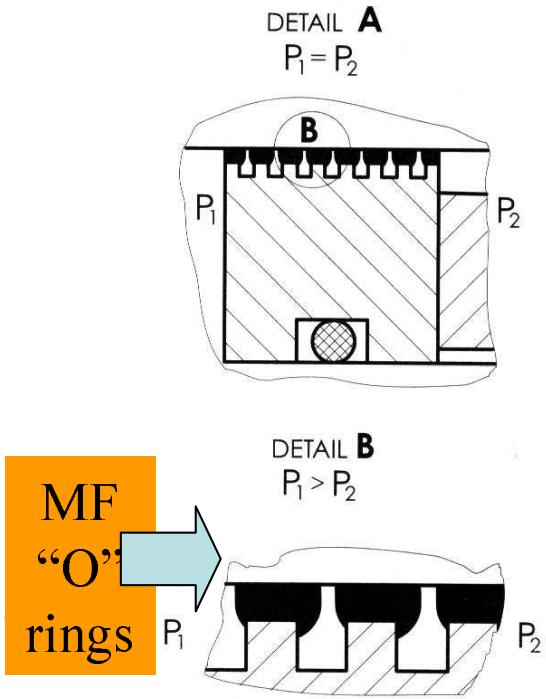
Schematic representation of channels made of MPS-PNIPA latex built in the PVA gel matrix: (a) "off" state below the collapse transition temperature; (b) "on" state above the collapse transition temperature.
Arrows indicate the diffusive mass transfer in the channels of PVA membrane.

MF and MRF applications

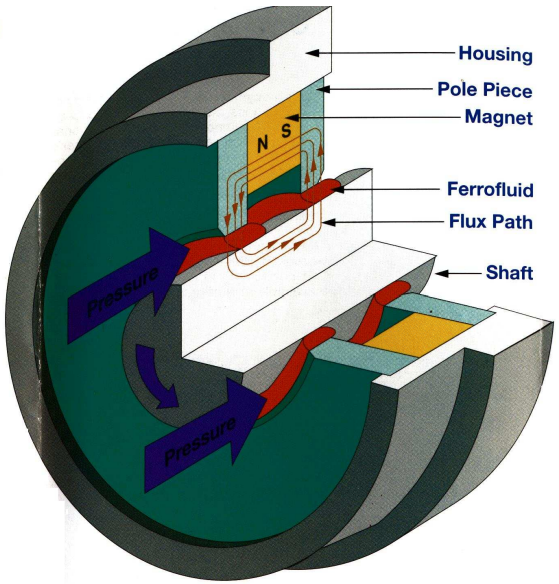
- Leakage-free rotating seals
- Sensors and transducers
- Semi-active dampers
- Biomedical applications

Leakage-free rotating seals





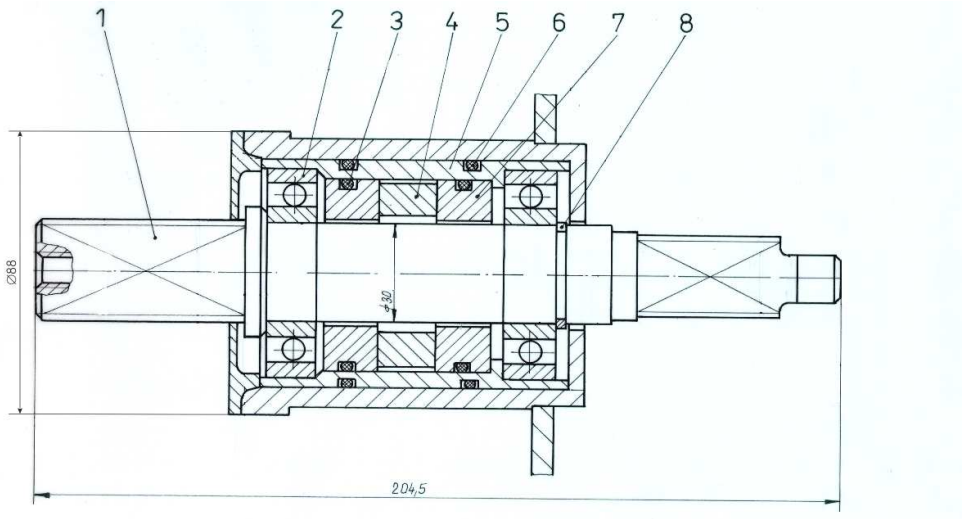
General view



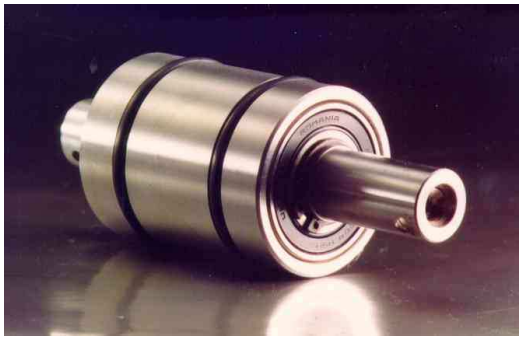
$$\Delta p = nMs(B_{max} - B_{min})$$

Construction&Operating principle

Leakage-free rotating seals



a



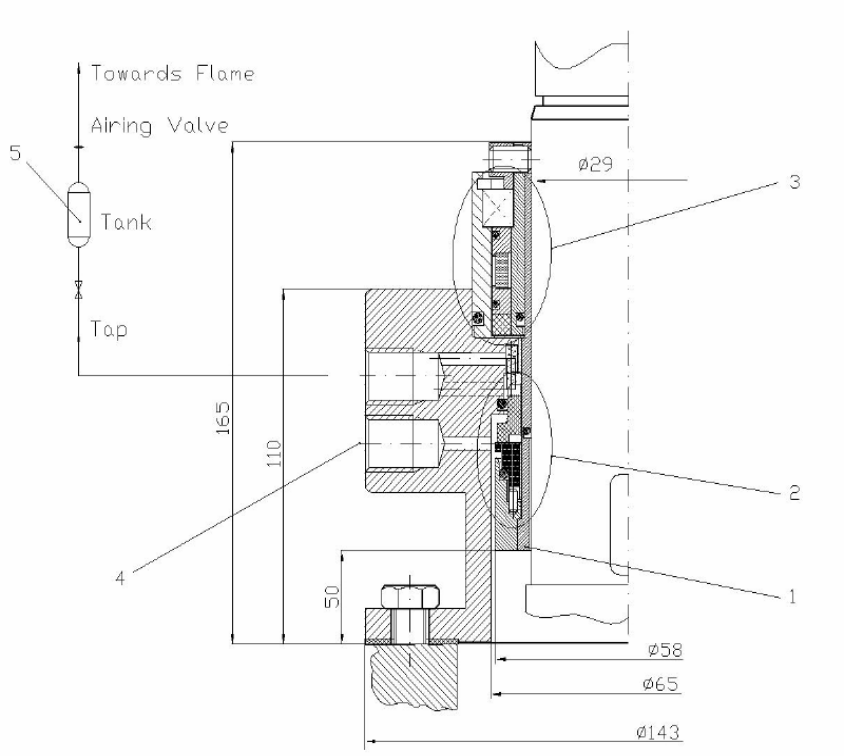
b

Manufacturer ROSEAL Co. Romania

Magnetic fluid feedthrough for
a)high vacuum b)high power electric switches with SF6

Components: 1- shaft; 2- ball bearing; 3,6- “O” ring; 4- permanent magnet; 5- non-magnetic casing; 7- polar piece; 8- safety ring.

Leakage-free rotating seals



Manufacturer ROSEAL Co. Romania

Mechanical- magnetic fluid combined seal for liquefied gas pump shaft

1- shaft; 2- mechanical seal; 3- magnetic fluid seal;

4- inlet for cooling and lubrication fluid;

5- system for escaped process fluid evacuation

Differential pressure transducer for gases

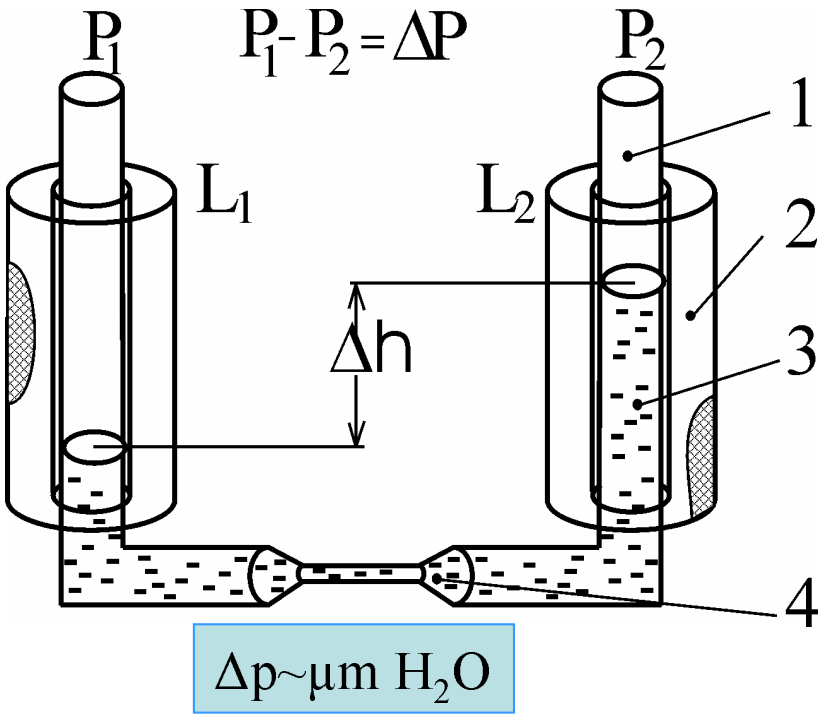
1 – U-shaped tube;

2 - two identical electrical coils (L_1 and L_2);

3 – MF;

4 – strangulation for damping of the MF column oscillatory motion; $P_{1,2}$ – pressures;

h – level gap



I. Potencz, N.C. Popa, et al, **RO Patent 98431 (1989)**

I.De Sabata, N.C. Popa, I. Potencz, L. Vekas,

Inductive transducers with magnetic fluids

Sensors and Actuators, A 32(1992)678

Flow rate and inclination transducers

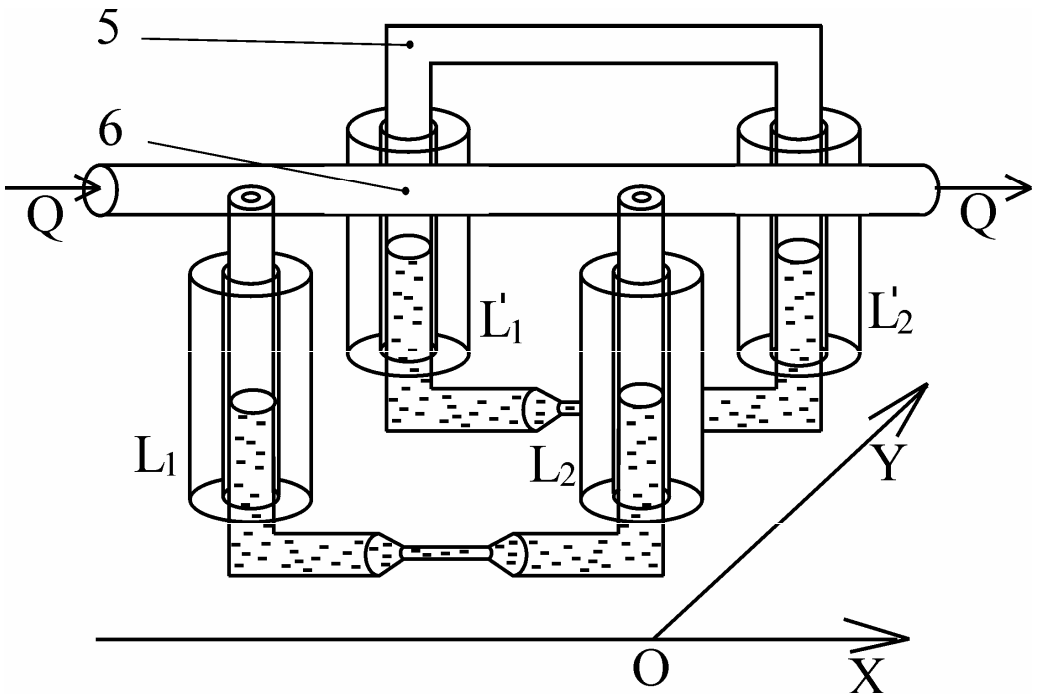
Flow rate transducer

Inclination correction of the differential pressure transducer is made using an identical MF inclination transducer

5 - tube joining the top ends;

6 - laminar flow-measuring element;

Q – gas flow

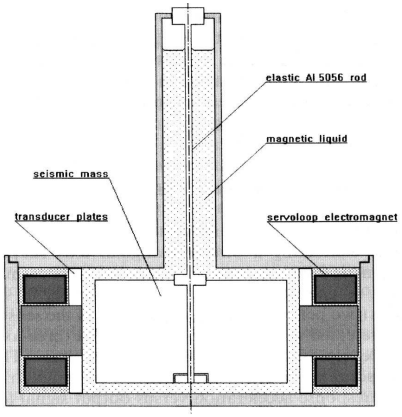


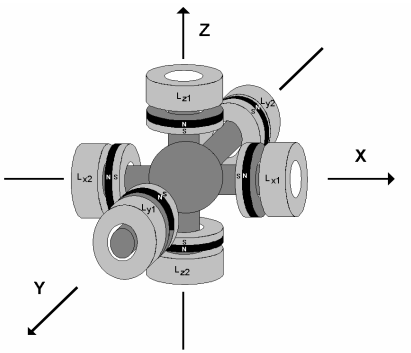
Q~ $cm^3/min \rightarrow 100 m^3/min$

N.C. Popa, I. Potencz, L. Vekas, *Magnetic fluid flow meter for gases*, **IEEE Trans. Magnetics, 30(1994)936**

Magnetic fluid acceleration sensors

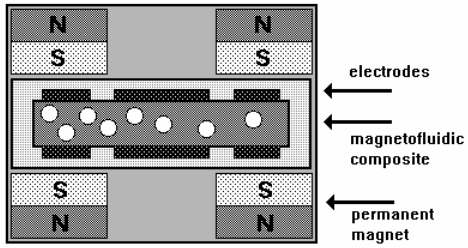
APPLICATIONS BASED ON THE MAGNETIC FLUID LEVITATION EFFECT

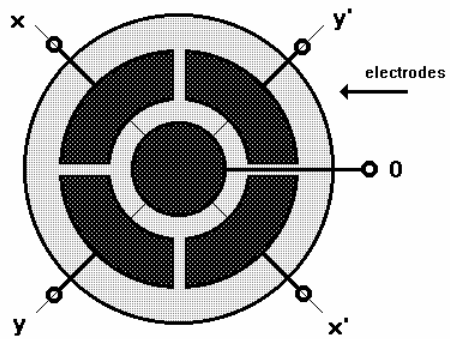




Bi- and three-axial accelerometers

Sensitivity from 10^{-6} up to 10^{-9} m/s^2



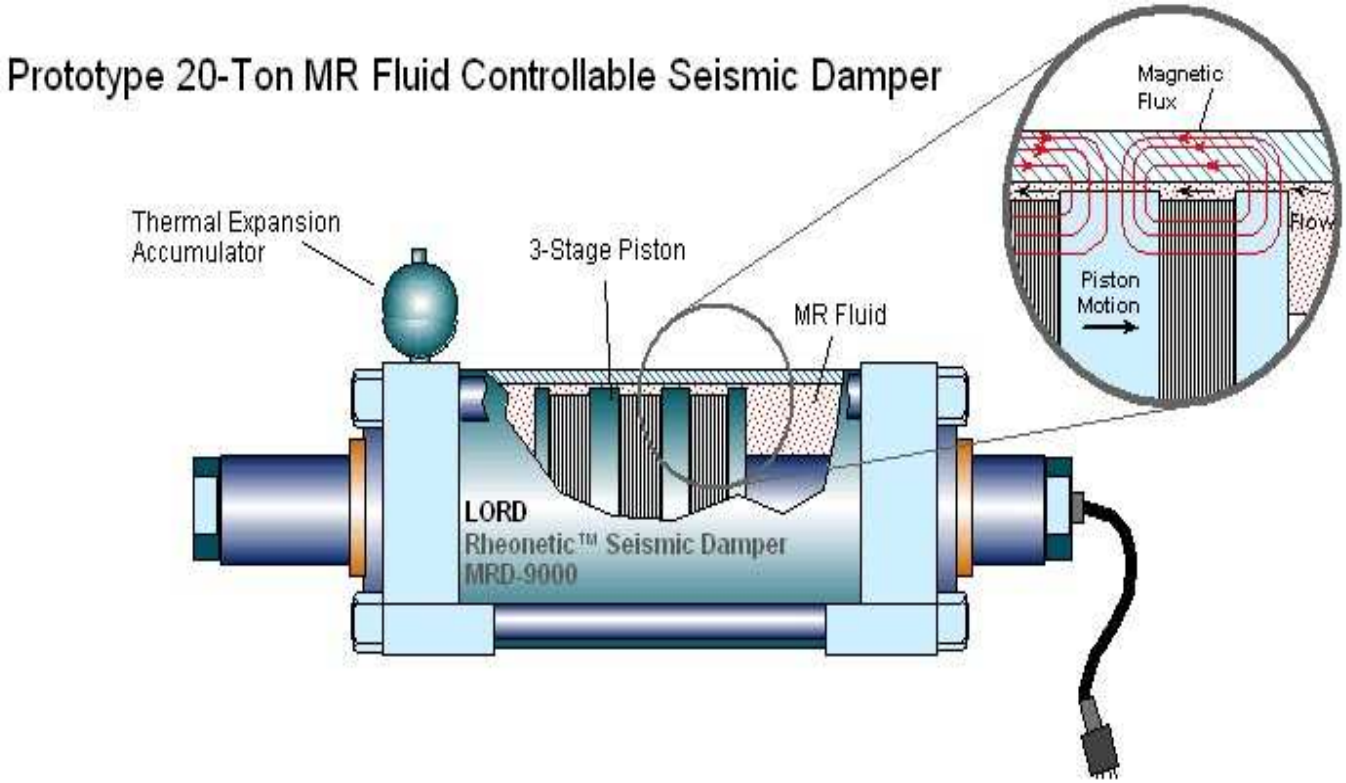


Magnetic fluid composite accelerometer

Wide sensitivity range, between 10^{-3} to 10 m/s^2

M.I. Piso, **RO Patents** 98569(**1990**),99568 (1990), 99036 (**1992**), 100632(**1991**)
M.I. Piso, *Magnetofluidic inertial sensors*, Rom.Rep.Phys.47(**1995**)437

Applications of MR fluids



Semi-active MR damper for buildings

LORD Co., USA

Applications of MR fluids

Semi-active dampers for large constructions

Rheonetic™ Lord Co. – U.S.A.

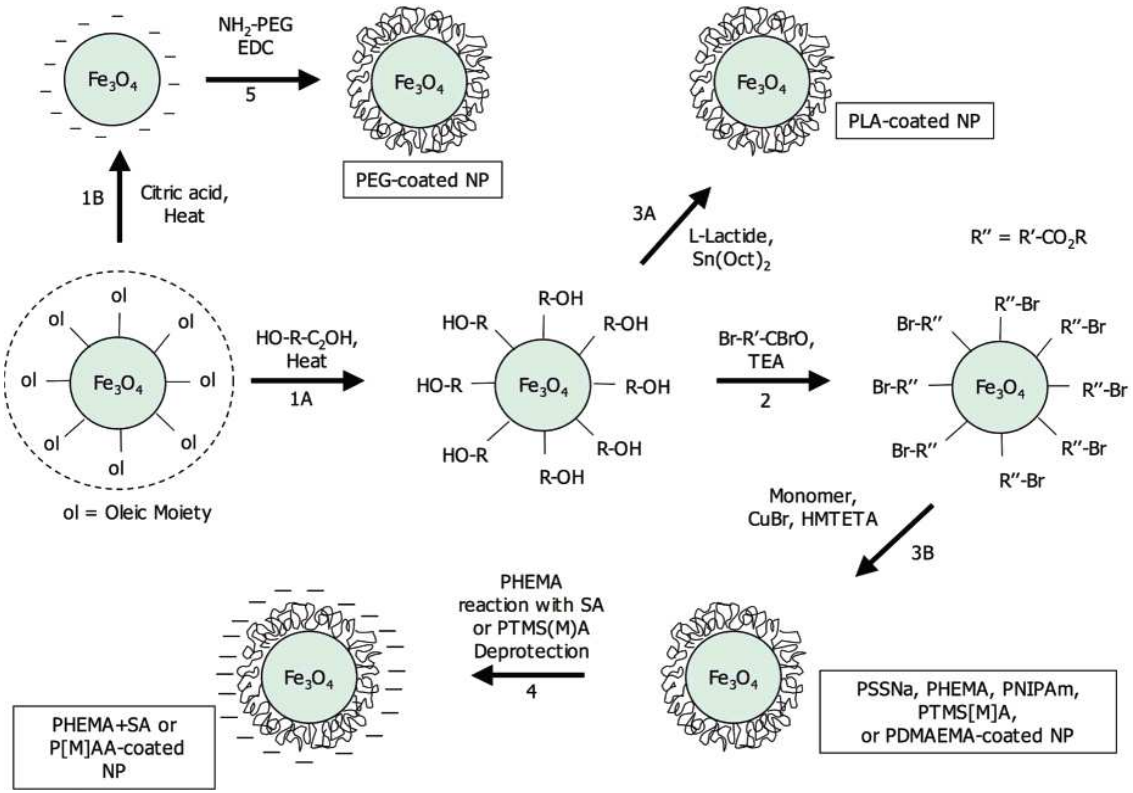
Japan's National Museum of Emerging Scince and Innovation - Tokyo

Dong Ting Bridge, Dong Ting Lake - Changsha, China

Biomedical applications

***Functionalization of Monodisperse Magnetic Nanoparticles*, Langmuir vol.23, 2158-2168 (2007)**

Marco Lattuada† and **T. Alan Hatton***
Department of Chemical Engineering, Massachusetts Institute of Technology (MIT)

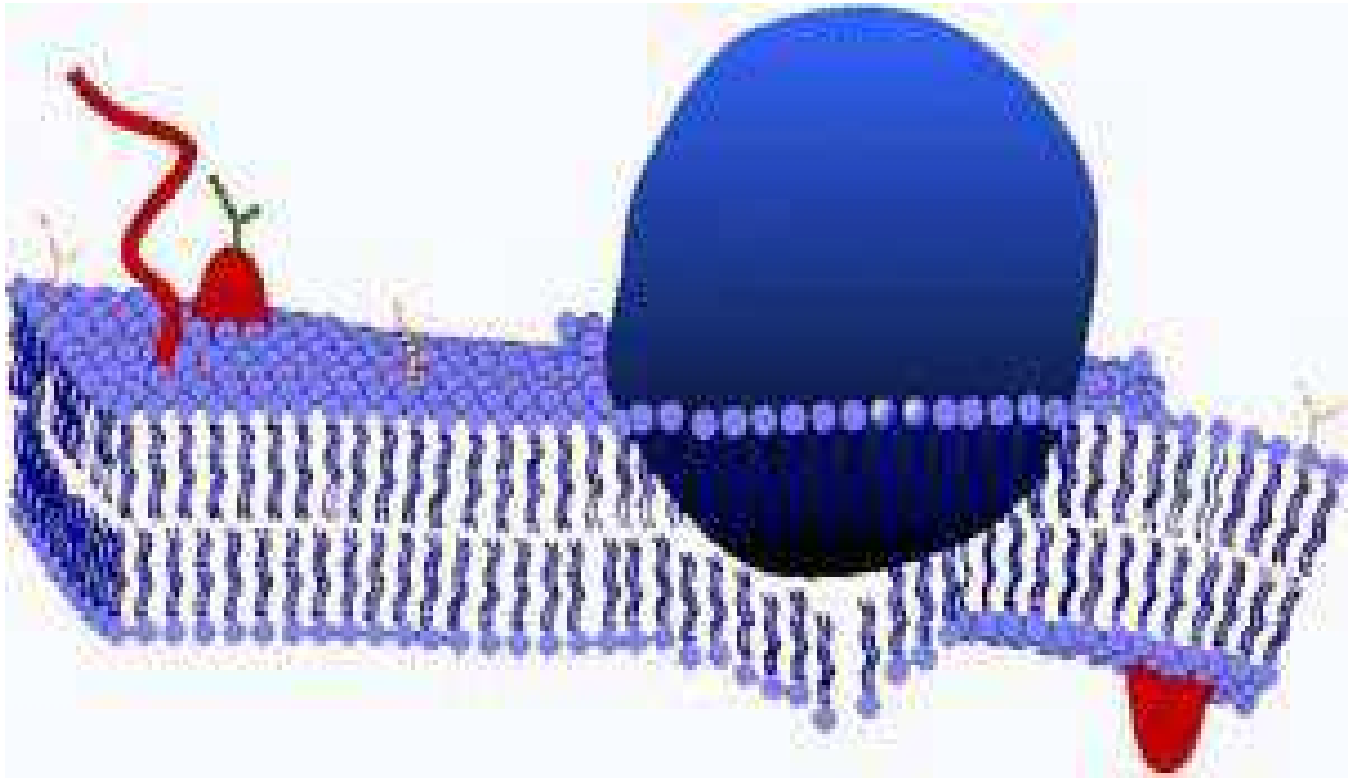


ATRP- atom transfer radical polymerization
CA-citric acid; *N,N,N,N¢,N¢,N¢*-Hexamethyltriethyltetramine(HMTETA; 97%)
PEG- polyethylene glycole;
Poly-Hydroxyethylmethacrylate (PHEMA; 97%)
Trimethylsilyl methacrylate (TMSMA)
Succinic anhydride (SA; 99%)
4-styrenesulfonic acid sodium salt hydrate (SSNa; 98%); *N*-isopropylacrylamide (NIPAm; 97%)
Dimethylaminoethyl methacrylate (DMAEMA; 98%)
Amino end-functionalized polyethylene glycol (NH2-PEG, 10 kDa)
N-isopropylacrylamide (NIPAm; 97%)
Poly(methacrylic acid) (PMAA)

Steps 1A and 1B: ligand exchange reactions. Step 2: acylation of hydroxyl groups to prepare ATRP surface initiators. Step 3A: surface-initiated ring opening polymerization of L-lactide. Step 3B: surface-initiated ATRP. Step 4: deprotection or additional reaction after polymerization. Step 5: grafting of endfunctionalized PEG chains onto the nanoparticle surface using amidation chemistry.

Biomedical applications

Magnetic nanoparticles and biological cells

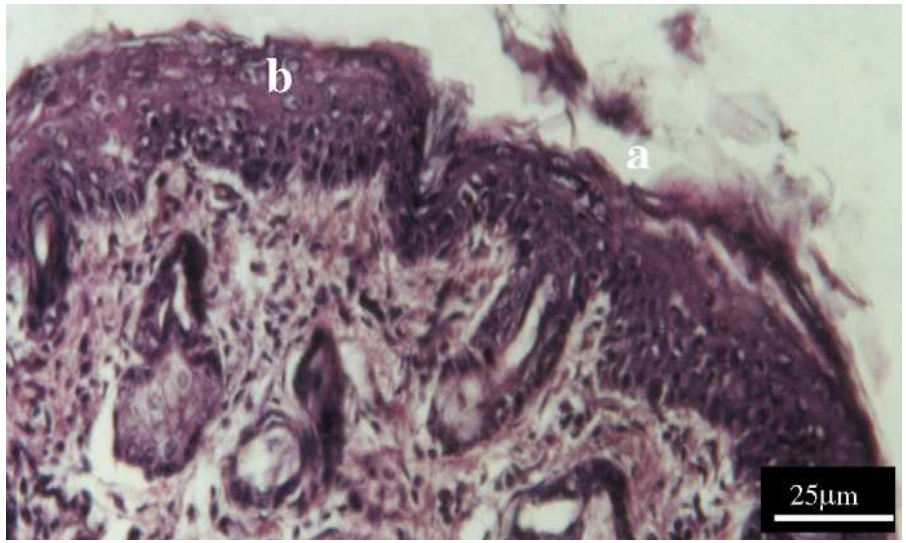


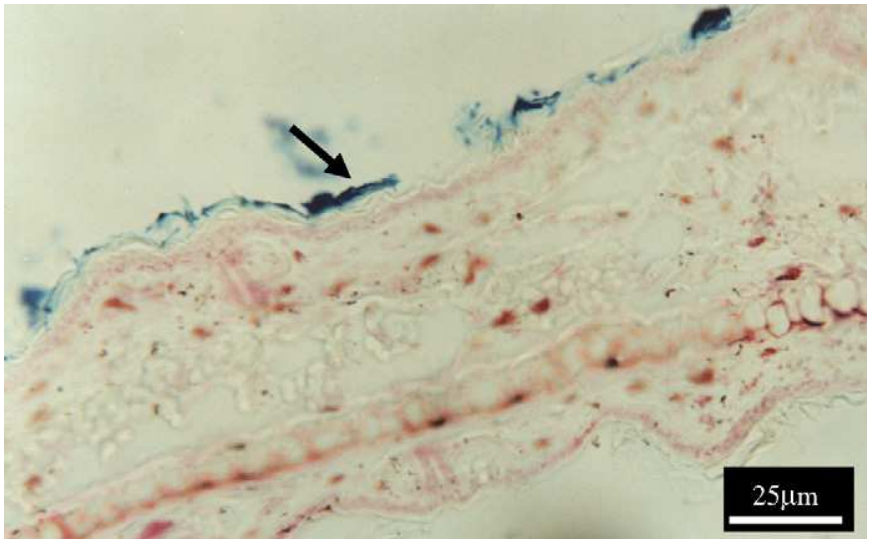
Magnetic nanoparticle moving through the cell wall

Biomedical applications

Magnetic nanofluid composites for UV protection of skin

Mice auricles





Changes in the control mice auricles, **unprotected by magnetic nanocompounds** Aspect after *prolonged exposure to UV radiations*:

(a)hyperkeratosis and

(b) vacuolar keratinocytes in epidermis

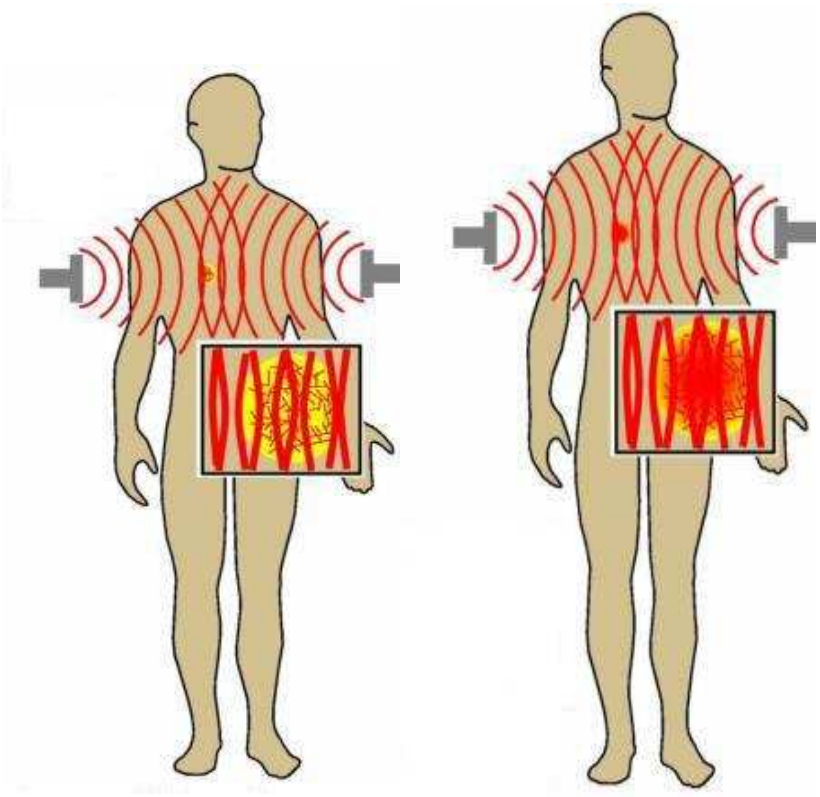
Normal aspect of the skin in mice auricles **protected with magnetic nanocompound** with lanoline, after *prolonged exposure to UV radiations:*

arrow—**magnetic fluid**

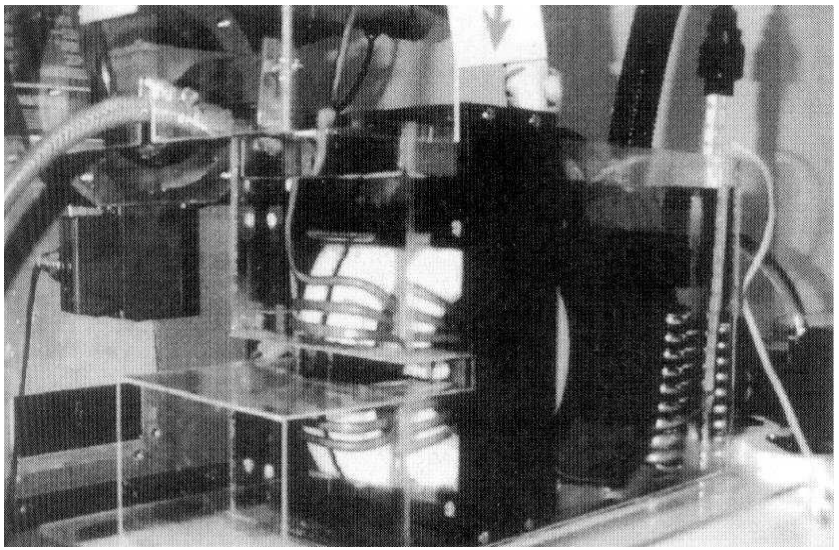
M. Sincai, D. Argherie, D. Ganga, D. Bica, L. Vekas, *Application of some magnetic nanocompounds in the protection against sun radiation*, JMMM 311(2007)363

Biomedical applications

Magnetic hyperthermia of tumors



(a) (b)



(a) Magnetic nanofluid introduced in tumor is heated by a high frequency e.m. field
(b) Temperature of cells is increasing-hyperthermie

Hospital Charité, Berlin-
Dr.Andreas Jordan

First clinical case- Charité Berlin, September, 2003

Pilot-scale production of magnetic nanoparticles and nanofluids

SC ROSEAL SA-Romania – http://roseal.topnet.ro/

Contact person:I. Borbáth

a

MNF synthesis-pilot scale installation –
a-detail; **b**-general view

b

N A N O M A G N E F L U I D S E A L

c

MNF synthesis-pilot scale installation
c- magnetic nanoparticle synthesis; **d**-auxiliary equipments

d

Research partners

⇒Ion Morjan-Nat.Inst. R&D Laser Physics and Radiation, Bucharest
⇒Rodica Turcu-Nat.Inst.R&D for Isotopic&Molecular Technologies, Cluj
⇒Victor Kuncser- Nat.Inst.R&D for Physics of Materials, Bucharest
⇒Marius-Ioan Piso - Romanian Space Agency, Bucharest
⇒Maria Balasoiu - Nat.Inst.R&D for Nuclear Physics, Bucharest
⇒Petre Patrut- Univ. Civil Engineering, Bucharest
⇒Jenica Neamtu-Nat.Inst.R&D Electrical Engng.-ICPE CA, Bucharest
⇒Mikhail Avdeev-Frank Lab.Neutron Physics – JINR-Dubna
⇒László Rosta- Budapest Neutron Center
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⇒Miklós Zrinyi-Dept.Physical Chemistry, Budapest Technical University
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Industrial partner
ROSEAL Co., Odorhei: Istvan BORBATH, General Manager

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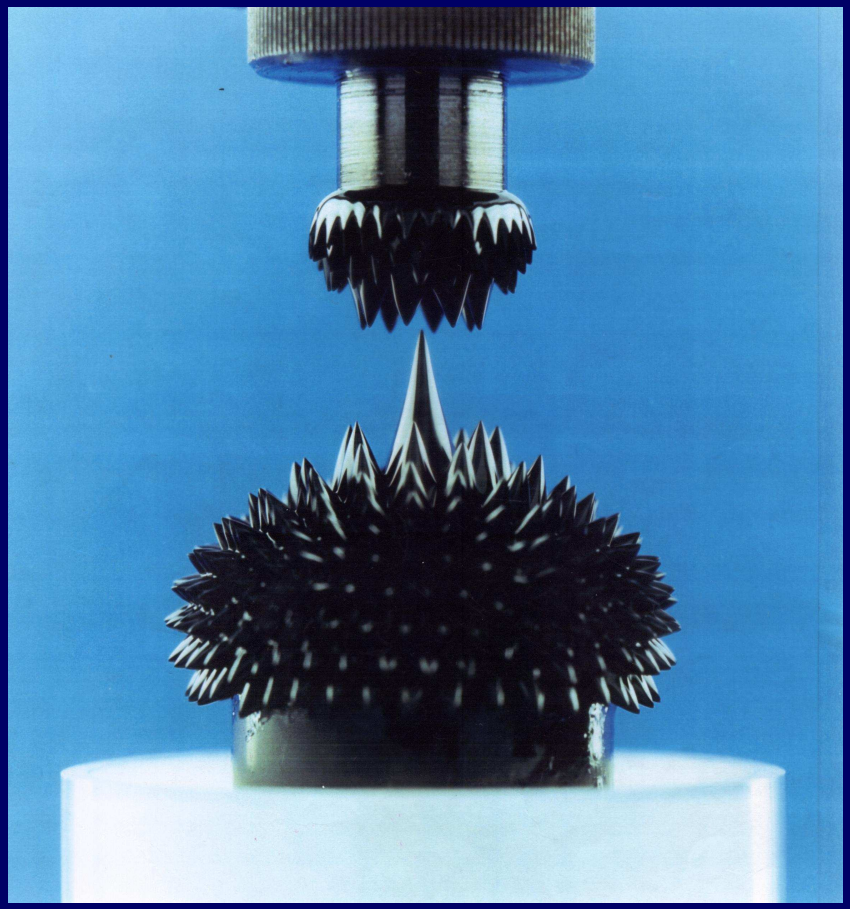
THANK YOU FOR YOUR ATTENTION!



Laboratory of Magnetic Fluids Timisoara