SZTE TTIK Környezettudományi Doktori Iskola
SZAB Kémiai Szakbizottság
Analitikai és Környezetvédelmi Munkabizottság

Magnetic nanofluids and composites: how to tailor their properties through composition for engineering and biomedical applications

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March 27, 2013, Szeged, Hungary

Short history

FLUIDITY + MAGNETIC PROPERTIES = ??

↓

New materials, new phenomena

Ferrofluids/Magnetic fluids

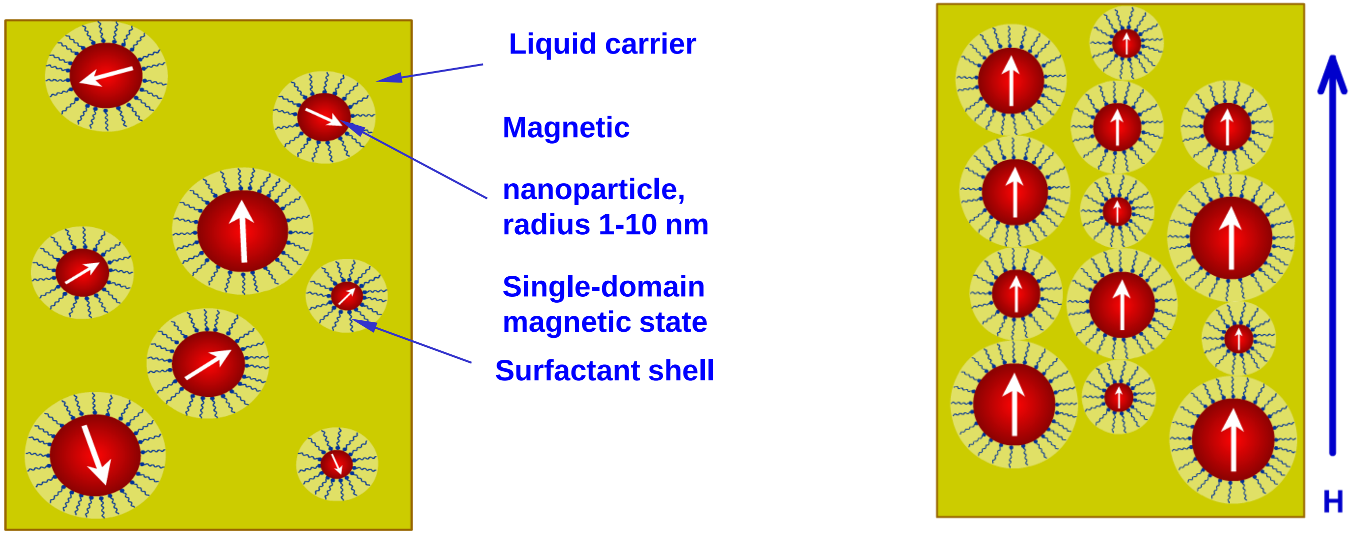
- T.L. O'Connor, Belgian Patent 613,716 (1962)
- **S. Papell (NASA), US Patent 3,215,572 (1965)**

Magnetorheological fluids

- National Bureau of Standards Technical News Bulletin 1948; 32(4): 54-60
- **J. Rabinow Proceedings of the AIEE Trans., 1948, 67, 1308-1315**

Magnetic nanofluid (ferrofluid)

Composition, magnetic behavior



Ultrastable colloidal suspension of magnetic nanoparticles (3-15 nm) in a carrier liquid

Langevin type magnetic behavior
Superparamagnetism

$$M_L = \phi_M M_d \left(\coth\xi - \frac{1}{\xi} \right) \qquad \xi = \frac{\pi \mu_0 M_d D_m^3 H}{6 k_B T}$$

Magnetic fluids

- First publications -

Magnetic suspensions:

- **G. Knight (1779) (Fe/water) F. Bitter (1932) (Fe_3O_4/water) W. C. Elmore (1938) (Fe_3O_4/water)...**

Magnetic fluids:

- **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**)

Ferrofluids in Romania

❖ Synthesis of first ferrofluids

Centre for Technical Physics, Iasi
… 1970-1975 …

❖ The first book on ferrofluids- worldwide (!)

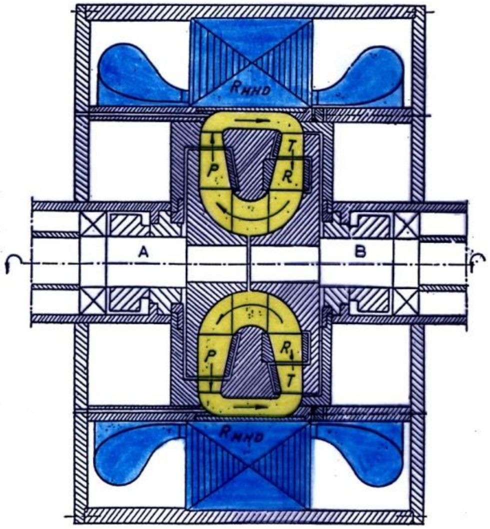
E. Luca, G. Calugaru, R. Badescu, C. Cotae, V. Badescu, **Ferofluidele si aplicatiile lor in industrie** (**Ferrofluids and their industrial applications**), Editura Tehnica, Bucuresti, **1978** (336 pages)

❖ The first dedicated laboratory in Romania

Laboratory of Magnetic Fluids from Timisoara
Dept. Hydraulic Machinery-Univ. "Politehnica" Timisoara
Prof. Ioan Anton, 1975

Mark Shliomis, **Magnitnie zhidkosti**, Usp. Fiz. Nauk, 1974

MHD turbotransformer



Patent RO Nr.57574
Prof. Ioan Anton 1971

Influence of the rotating magnetic field on the angular momentum of the liquid

Ferrohydrodynamics (FHD)

Equations of motion

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

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

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

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

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

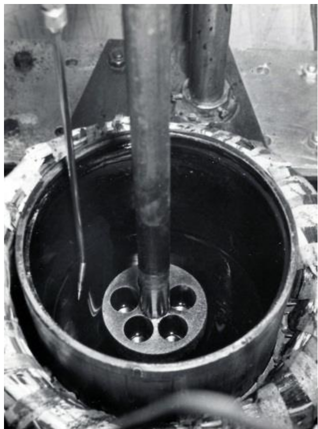
M. Shliomis, Magnitnie jidkosti, Usp.Fiz.Nauk, 1974
R. E. Rosensweig, Ferrohydrodynamics, Cambridge Univ. Press(1985)
L. Vekas, Magnetic nanofluids. Synthesis, structure, properties, applications, Romanian Academy Publ.House (in Romanian;to appear)

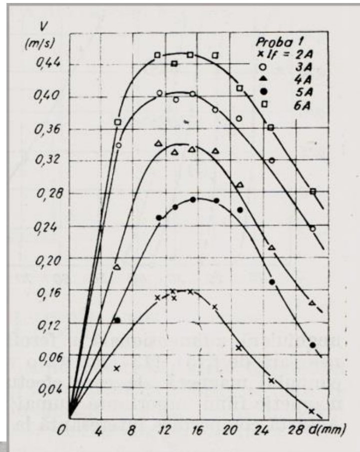
Volumic force: f=μoM(H)gradH for quasistatic conditions

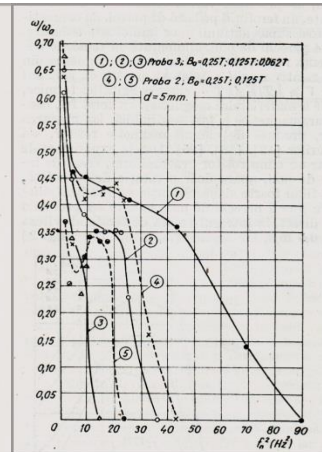
Ferrofluid flow in rotating magnetic field

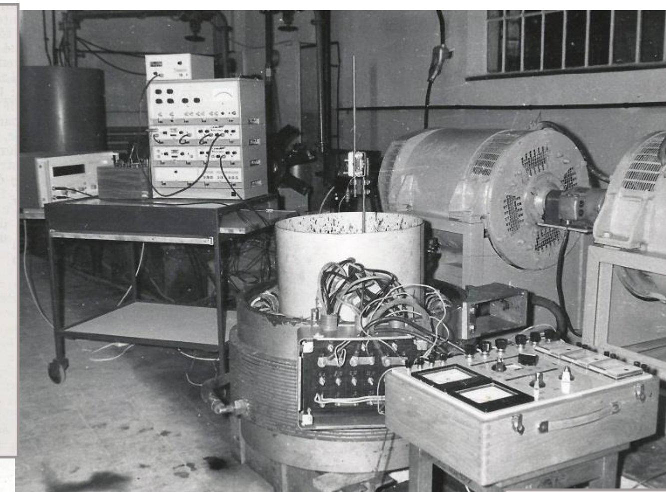
R.E. Rosensweig
M.I. Shliomis

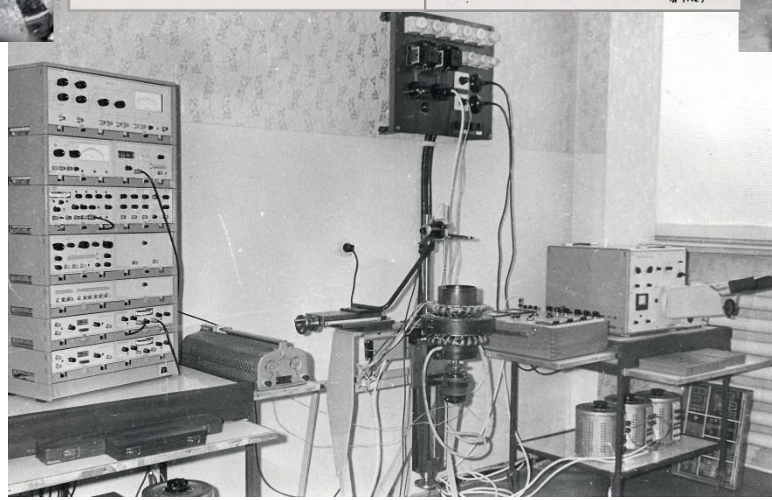
$$\rho \frac{d\vec{v}}{dt} = -\nabla p + \rho \vec{g} + \mu_0 (\vec{M}\nabla)\vec{H} + \frac{\mu_0}{2} \nabla \times (\vec{M} \times \vec{H}) + \eta \nabla^2 \vec{v}$$

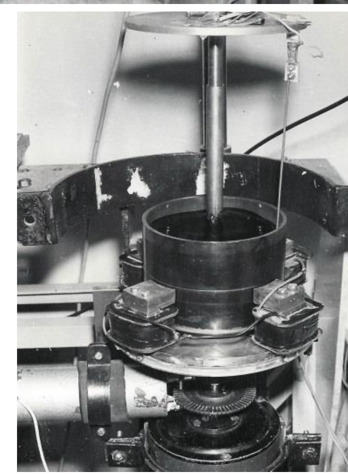


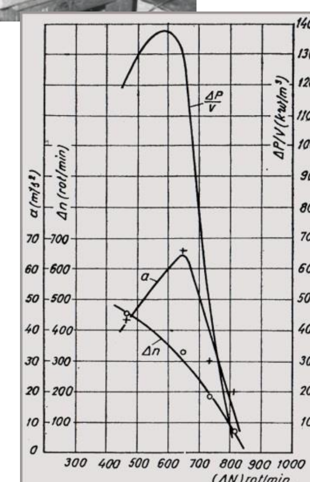












I.Anton, L. Vékás, I. Potencz, E. Suciu, *Ferrofluid flow under the influence of rotating magnetic fields*, IEEE Trans. on Magnetics (USA), MAG-16 (2) 283-287 (1980)

Introduction

Magnetic nanoparticles

Superparamagnetism

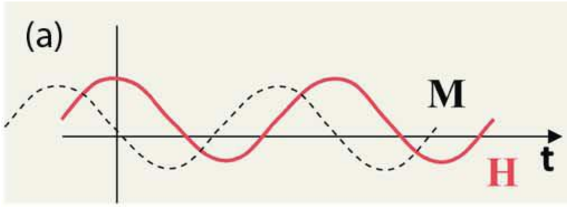
Colloidal stability

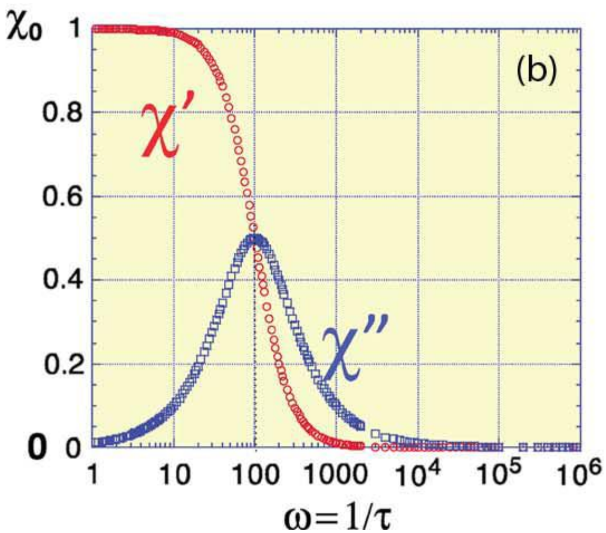
Magnetic force

Magnetically controllable fluids

Superparamagnetic particles – basic components of magnetic fluids

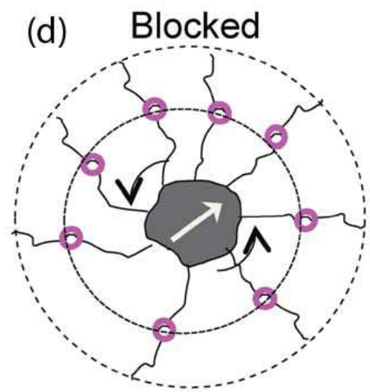
Relaxation of magnetization – response of MNPs to an a.c. magnetic field

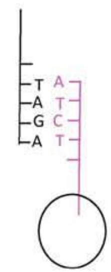




$$\tau_N = \frac{\sqrt{\pi}}{2}\tau_o \frac{\exp(KV_M/k_BT)}{(KV_M/k_BT)^{3/2}}$$

Néel





$$\tau_B = \frac{3\eta V_H}{k_B T}$$

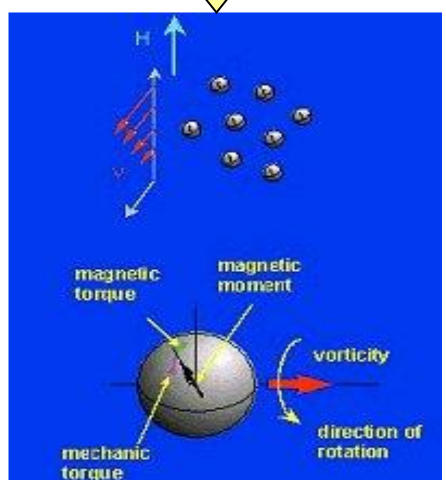
Brown

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_N}$$

τ - effective relaxation time

χ' –real (in phase) component

χ'' – imaginary (loss) component



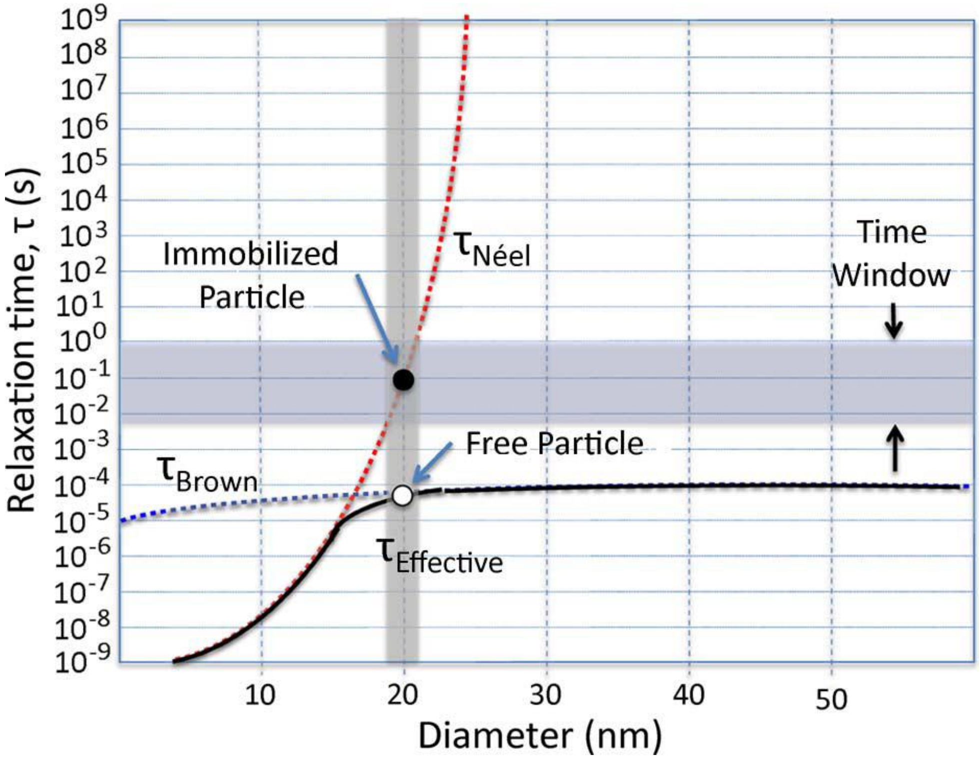
Microvortices
in a viscous carrier
--“rigid” dipoles--

K.M. Krishnan
IEEE Trans Magn 2010

S. Odenbach in: Handbook of Magnetic Materials, vol. 16 (2006)

Superparamagnetic particles

Dependence of relaxation time on MNP size



The dependence of the Brownian, Néel and effective relaxation time on the particle “magnetic” diameter. Liquid carrier: water ($\eta = 10^{-3}$ Ns/m^2). The time window is set by the measurement. A coating thickness of 15 nm, anisotropy constant K=20 kJ/m^3 and T= 300 K is assumed. (Kotitz et al. JMMM (1999))

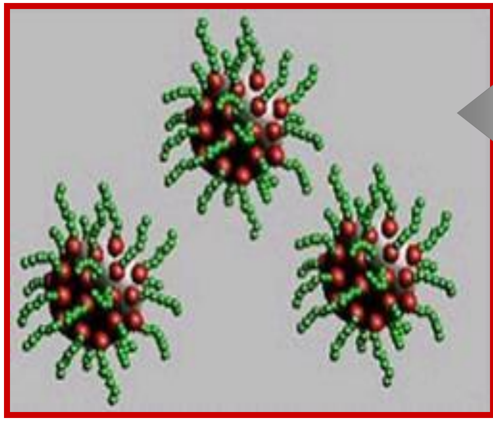
K.M. Krishnan
IEEE Trans Magn 2010

Magnetic nanofluids-Colloidal stability

Individual particles vs. clusters

Dependence on the size of magnetic nanoparticles

Stabilization procedures prevent gravitational settling of MNPs, agglomerate formation by magnetic and van der Waals interactions



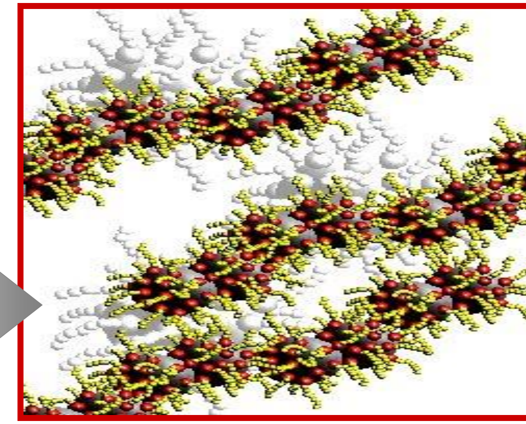
Stable FF, individual particles
no clusters!

$\lambda_{int} < 1$

$$\lambda_{int} = \frac{\mu_0 \cdot M_d^2 \cdot d_m^3}{72\, k_b \cdot T}$$

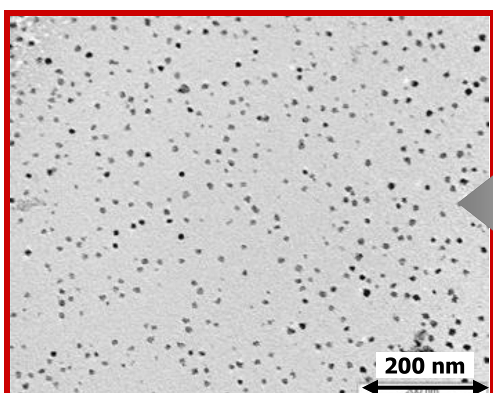
Non-dimensional dipolar interaction energy

$\lambda_{int} > 1$



Unstable FF, cluster formation!

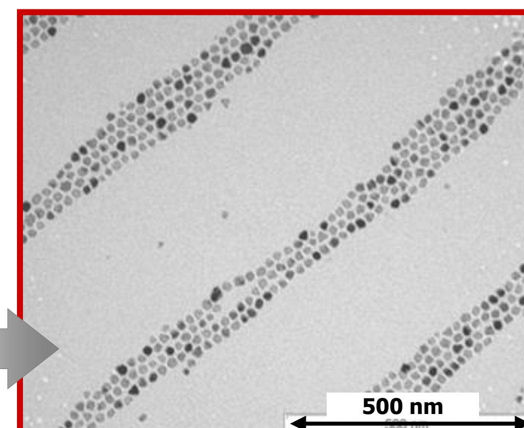
Magnetite nanoparticles



Cryo-TEM: FF/Decalin (OA)

d_{TEM} = 9.0 nm
λ_{int} = 0.5

d_{TEM} = 18.6 nm
λ_{int} = 4.4



Cryo-TEM: FF/Decalin (OA)

S. Odenbach, Ferrofluids, 2006
M. Klokkenburg et al., JoPhys CM, 2008

Well stabilized magnetic fluid vs. usual magnetic suspension

Behavior in non-uniform magnetic field

The utmost significance of stabilization procedure applied

Group Prof. Etelka Tombácz-Univ. Szeged (www.magneticmicrosphere.com)

Magnetic force: magnetic fluid ''flows upward''

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

Magnetic force about $\mathbf{10^4}$ times greater than gravitational force

Demo- Exhibition_*100 years anniversary of Laboratory Van't Hoff,* Univ Utrecht
Prof. A.P. Philipse (Utrecht), Dr. Doina Bica (Timisoara) (2001)

MAGNETICALLY CONTROLLABLE FLUIDS

- Ferrofluids, magnetic nanofluids
- 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 micron sized ferromagnetic particles in a carrier liquid

  Non-newtonian behavior, strongly magnetic field dependent yield stress and effective viscosity (about 100-1000 times increase)
- Nano-micro structured composite magnetizable fluids

  Micron-sized ferromagnetic (Fe) particles suspended in a high magnetization ferrofluid carrier

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

  Excellent sealing fluids & MR fluids

Synthesis and characterization

How to obtain highly stable magnetic colloids?

Synthesis & stabilization procedures

I. Synthesis of magnetic nanoparticles

- **Chemical co-precipitation**
- **Thermal decomposition**

II. Stabilization/dispersion in non-polar or polar carrier liquids

- **Steric stabilization (organic carriers)**
- **Electro-steric stabilization (water)**

↓

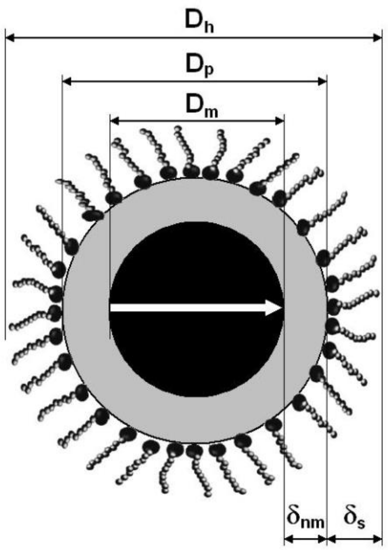
Magnetic nanoparticles dispersed in various carriers
Magnetic nanofluids

L. Vékás, Doina Bica, M.V. Avdeev, *China Particuology* 5 (2007)
E. Tombácz, Bica D., Hajdú A., Illés E., Majzik A., Vékás L., *J.Phys.:Condens.Matter*., 20(2008)
L.Vékás, M.V. Avdeev, Doina Bica, ch.25 in: D. Shi (Ed) *NanoScience in Biomedicine (*Springer, 2009)

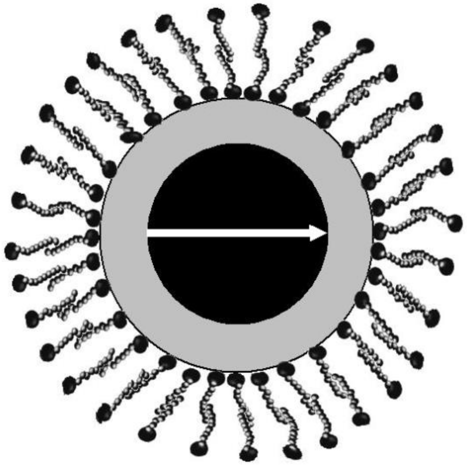
Hydrophobic and hydrophilic magnetite nanoparticles

Structure&characteristic sizes

Magnetic, physical and hydrodynamic size



D_m – magnetic diameter
D_p – physical diameter
D_h – hydrodynamic diameter
δ_m – thickness of the nonmagnetic layer
δ_s – thickness of the surfactant layer



Magnetite NP with *hydrophobic* coating (e.g.Fe3O4.OA)

Magnetite NP with *hydrophilic* coating (e.g.Fe3O4.(OA+OA))

Synthesis of magnetic nanoparticles

Chemical co-precipitation

Surface coated hydrophilic / hydrophobic MNPs

Aqueous solutions Fe^{3+}, Fe^{2+} 80 - 82ºC → **Coprecipitation** ← NH_4OH (solution 25%)

↓

Subdomain Fe_3O_4 nanoparticles

↓

Surfactant (LA, MA or OA) → **Sterical stabilization (chemisorption)**

↓

Phase separation

↓

Magnetic decantation → Aqueous solution of

↓

Surface covered magnetic nanoparticles

↓

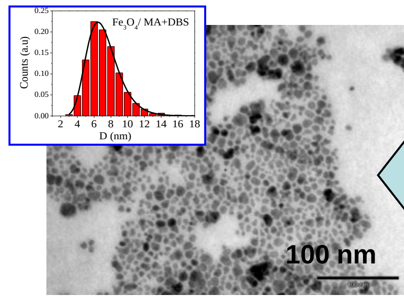
Distilled water 70 - 80ºC → **Repeated washing**

↓

Magnetic decantation → Aqueous solution of residual salts

↓

Surface covered magnetic nanoparticles Hydrophilic



Mean size 6-9 nm

↓

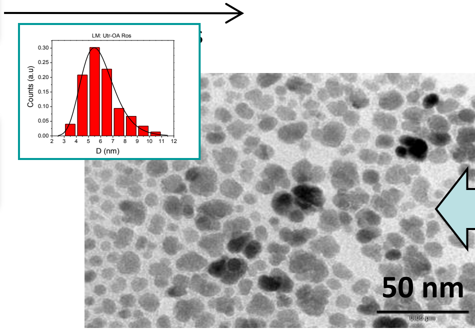
Acetone → **Repeated floculation, extraction, redispersion**

↓

Magnetic decantation → Acetone, water, free oleic acid

↓

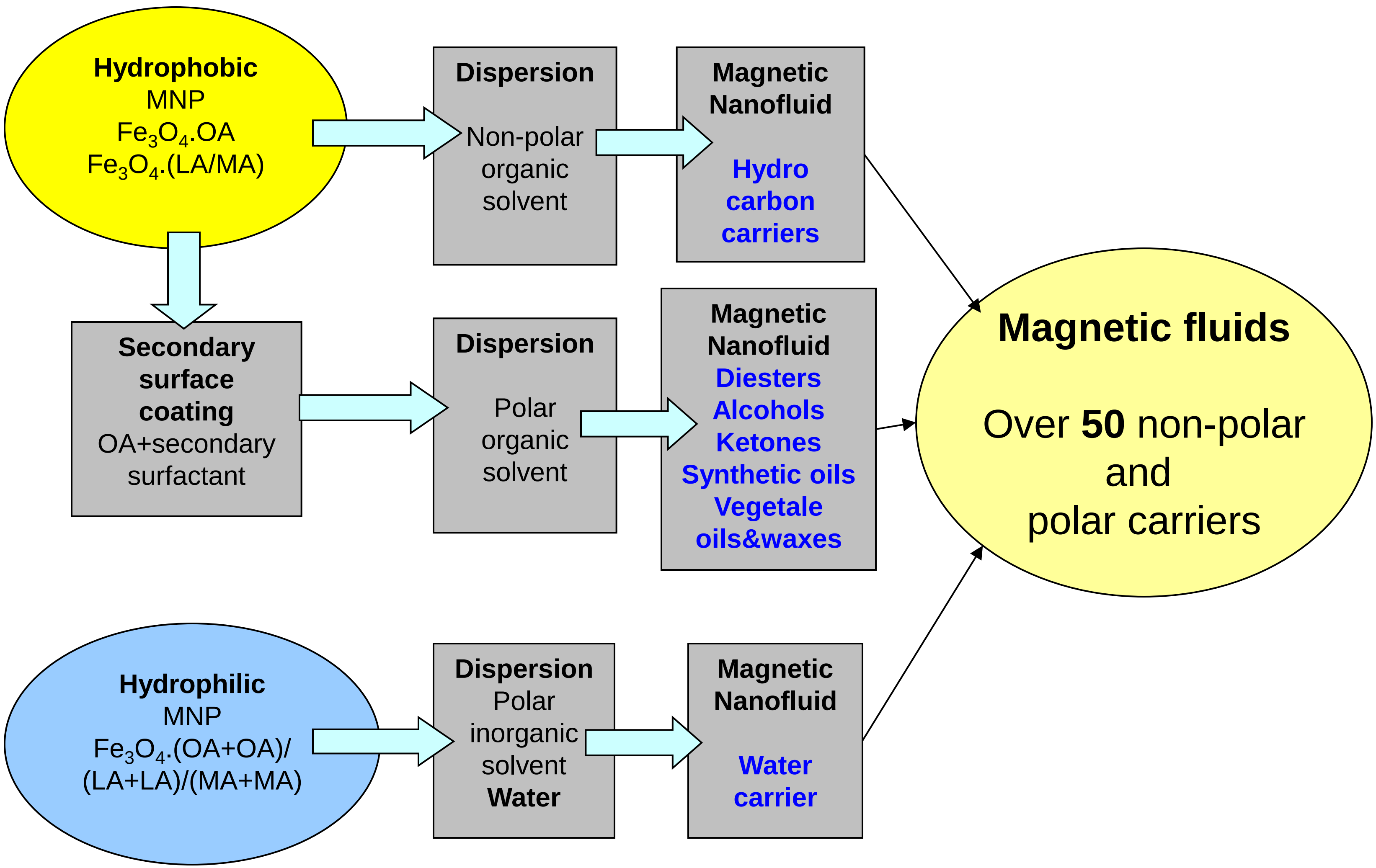
Surface coated magnetic nanoparticles Hydrophobic



Mean size 6-7 nm

Bica Doina et al., *RO Patents* 90078(1985); 97556(1989)
Bica Doina, *Rom.Rep.Phys.* (1995)
Vekas L., Bica D., Avdeev M.V., *China Particuology* 5 (2007)

Dispersion of surfacted MNPs in various carriers



Synthesis of magnetic nanofluids

Monolayer coated magnetic nanoparticles

Hydrocarbon → Dispersion → **NONPOLAR MAGNETIC NANOFLUID**

Chemisorbed surfactants:
oleic acid (OA),
myristic acid (MA), lauric acid (LA)

Technical grade MNFs
Low or high boiling point
Hydrocarbon carriers

Biotech MNFs/low boiling point
non-polar organic solvents
Primary materials for
bio-nano-materials preparation :
MNF/chloroform, benzene, toluene,
cyclohexane, hexane, heptane, i-octane

DBS or PIBSA (C ≥ 8) → Secondary stabilisation (physical adsorption) Dispersion ← Alcohols C_3-C_{10}/HVO/ Diesters (DOA/DOS) Vegetal oils, paraffin oil

→ **POLAR MAGNETIC NANOFLUID**

Secondary surfactants:
dodecyl benzene sulphonic acid (DBS),
polymers (PIBSA, PIBSI)

Technical grade MNFs
alcohols, ketones, diesters,
high vacuum oils

Biotech MNFs
vegetal oils,
paraffin oil,
waxes

NaOH → Magnetic organosol , pH 8.5 – 9.0

→ Water, Secondary surfactant → Dispersion

→ Primary magnetic fluid

→ Magnetic decantation → Uncoated magnetite nanoparticles, agglomerates

→ **WATER BASED MAGNETIC FLUIDS**

Technical grade MNFs
Secondary surfactant DBS

BioMed MNFs
Surfactants
LA. MA, OA, CA,
PAA, PLA, NaOA

Doina Bica et al., Romanian Patents: 90078 (1985); 93107 (1987); 97224 (1989); 97559 (1989); 107547 B1(1989); 107548 B1(1989); 105048 (1992) ; 105049 (1992); 115533 B1(2000); 122725 (2009)

Doina Bica, Rom.Rep.Phys.(1995);E. Tombácz, Doina Bica et al., JoPhys Condensed Matter(2008);
L.Vékás, Doina Bica, M.V. Avdeev,*China Particuology* 5 (2007) (review)
L.Vékás, M.V. Avdeev, Doina Bica, chap 25 in: D. Shi (Ed) NanoScience in Biomedicine (Springer, 2009)

Application orientated evaluation of magnetic nanofluids and suspensions

- **Size distribution** of magnetic nanoparticles: TEM, HRTEM
- **Mechanism of stabilization** and "chemical" size selection of dispersed magnetic particles
- Composition and magnetic field dependent **structural processes**, sterical stabilization and **long-term colloidal stability**: SANS, SANSPOL (B = 0-2.5 T);DLS
- **Dilution stability** and phase transition phenomena: magneto-optical investigations, DLS,SLS
- **Magnetic properties** vs. concentration: VSM measurements
- **Flow properties** under the influence of applied magnetic field: MR investigations

Evaluation and selection of MNP/MFs for various applications

MNF for rotating seals, bearings, sensors, dampers

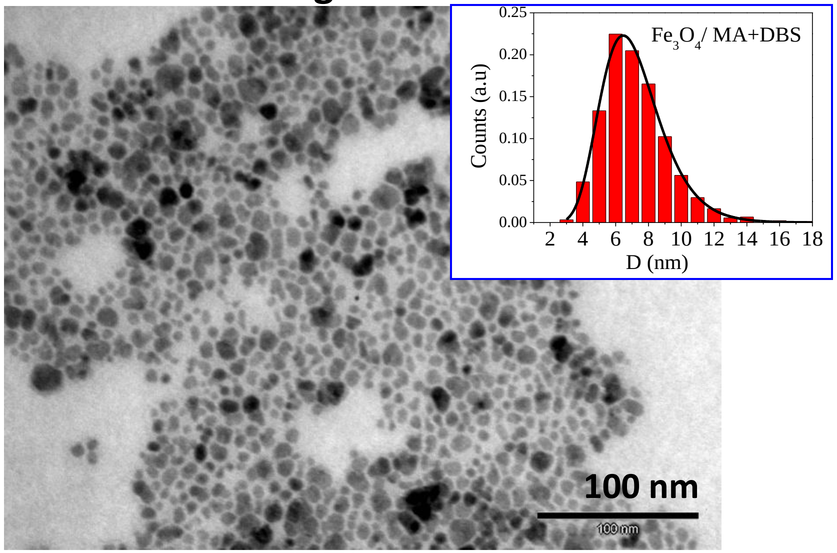
- high magnetization
- organic carrier liquids
- excellent stability in intense and strongly non-uniform magnetic fields

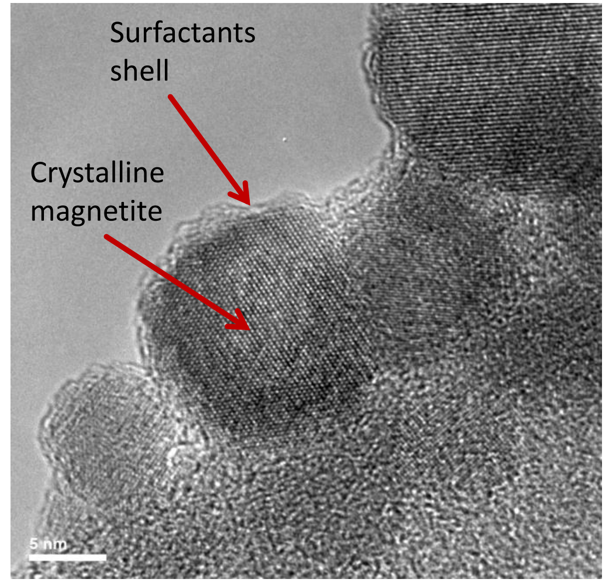
MNP and MNF for Biotechnologies&medical applications

- biocompatible surface coating/functionalization
- water and organic carrier liquids
- excellent stability in biologically relevant media

Particle size distributions-physical size-TEM

Water based magnetic fluid



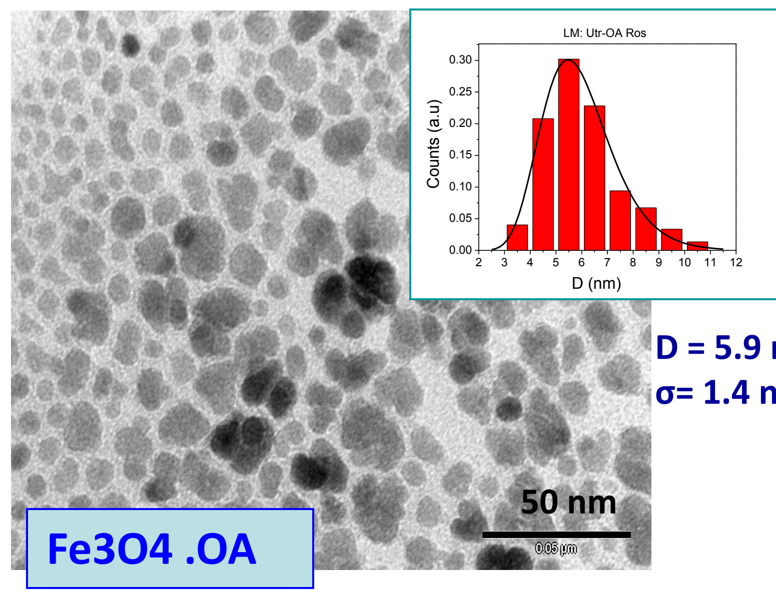


- **Log-normal size distribution of particles;**
- **Size selective stabilization / dispersion of magnetic nanoparticles.**

Sample	Mean diameter (nm)	Standard deviation (nm)
MF/MA+MA	**4.3** ± 0.08	1.3 ± 0.07
MF/LA+LA	6.1 ± 0.15	2. 4 ± 0.13
MF/MA+DBS	5.8 ± 0.03	1. 1 ± 0.02
MF/LA+DBS	6.6 ± 0.12	1. 7 ± 0.13
MF/DBS+DBS	**8.0** ± 0.16	2. 2 ± 014

Mean solid size below 10 nm

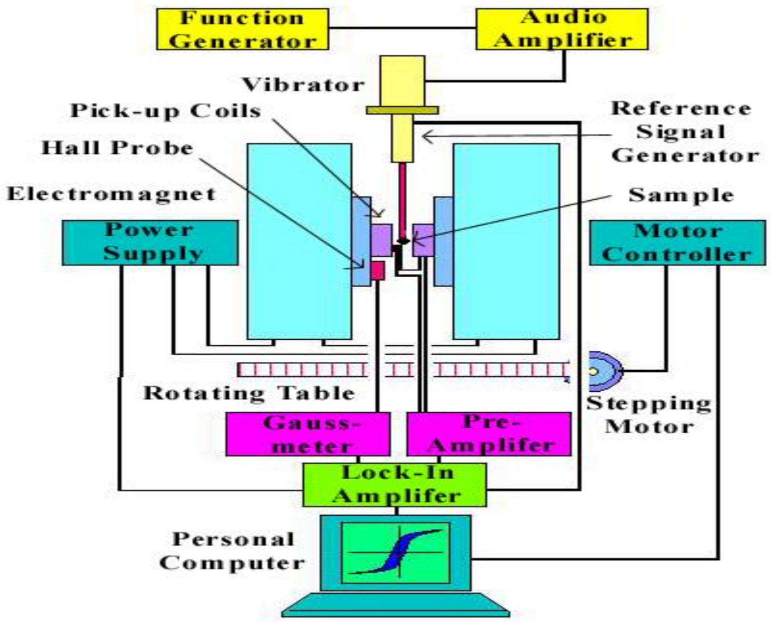
Hydrocarbon based magnetic fluid-micropilot scale



D = 5.9 nm
σ= 1.4 nm

Magnetic size

Vibrating sample magnetometer-VSM



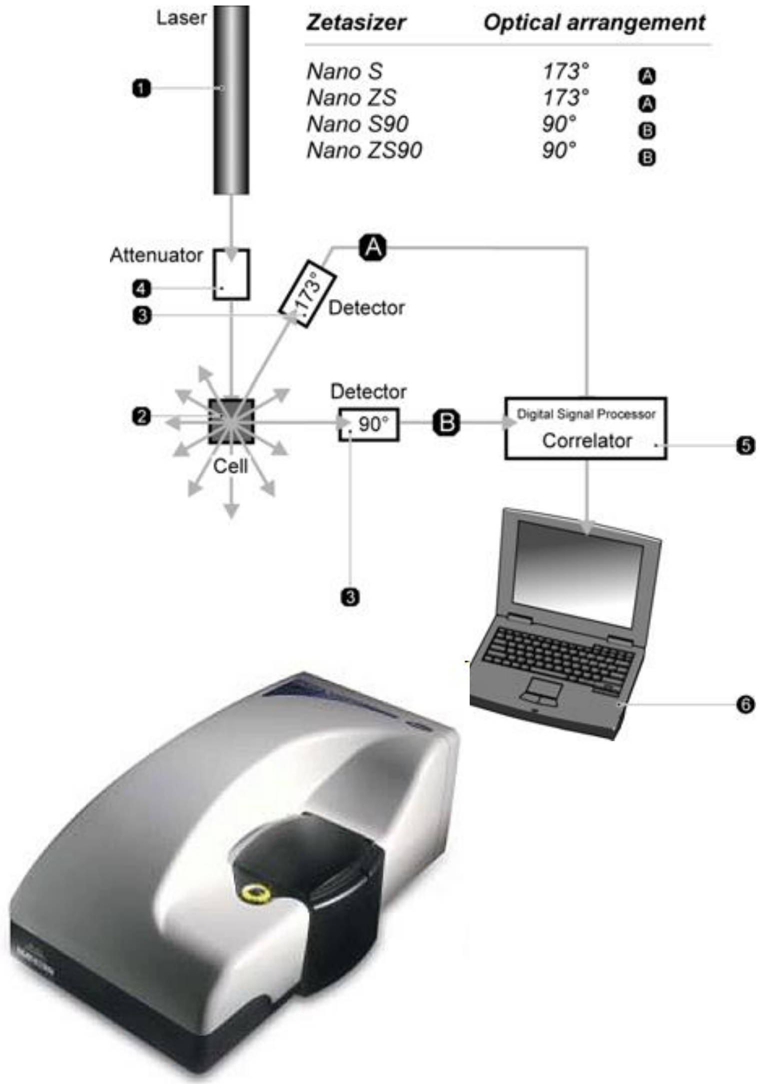
System diagram of Vibrating Sample Magnetometer

Full magnetization curves, magnetostatic properties, magnetogranulometry- ”magnetic size “distributions

Hydrodynamic size

Dynamical Light Scattering (DLS) investigations

Nano Zetasizer-Malvern



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:

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

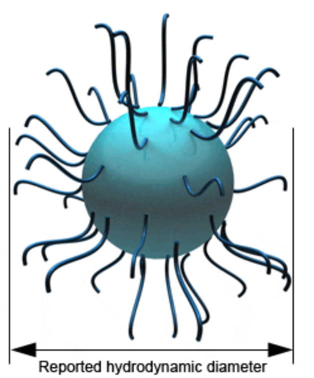
d(H) = hydrodynamic diameter

D = translational diffusion coefficient

k = Boltzmann's constant

T = absolute temperature

η = viscosity



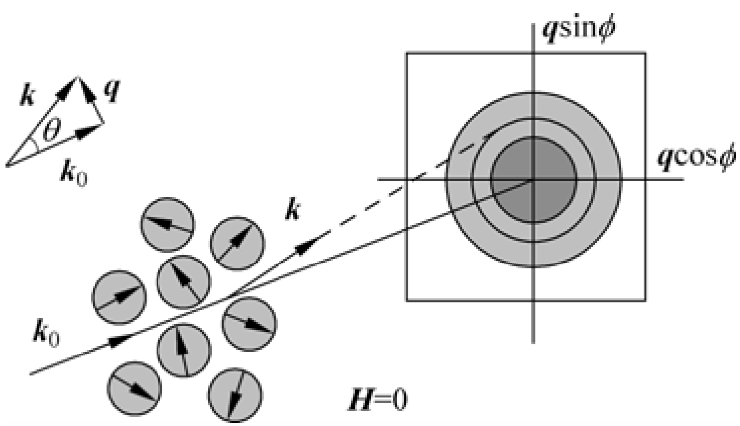
Particle interactions & structures in magnetic fluids

Small Angle Neutron Scattering(SANS) -*in vivo* structural investigations

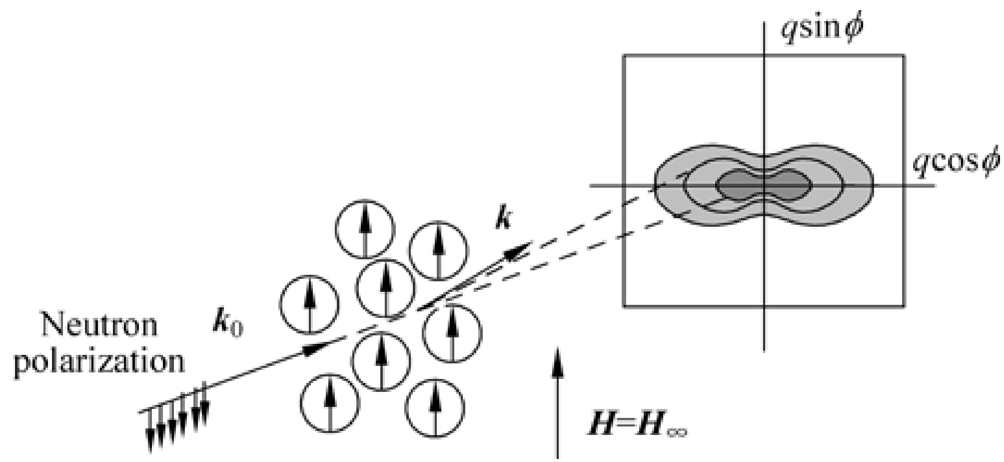
Particle structure | **Particle-particle interaction** | **Cluster formation**

MFs in zero field (B=0) conditions

MFs under the influence of applied magnetic field (B>0)



Schematic view of SANS experiment on system of magnetic nanoparticles. In case of unmagnetized system scattering pattern is isotropic over radial angle φ on detector plane



Schematic view of SANSPOL experiment on system of magnetic nanoparticles. Anisotropy in the scattering pattern over radial angle φ is caused by magnetization of the system

1-100 nm range

GKSS Geesthacht BNC KFKI – Budapest JINR Dubna

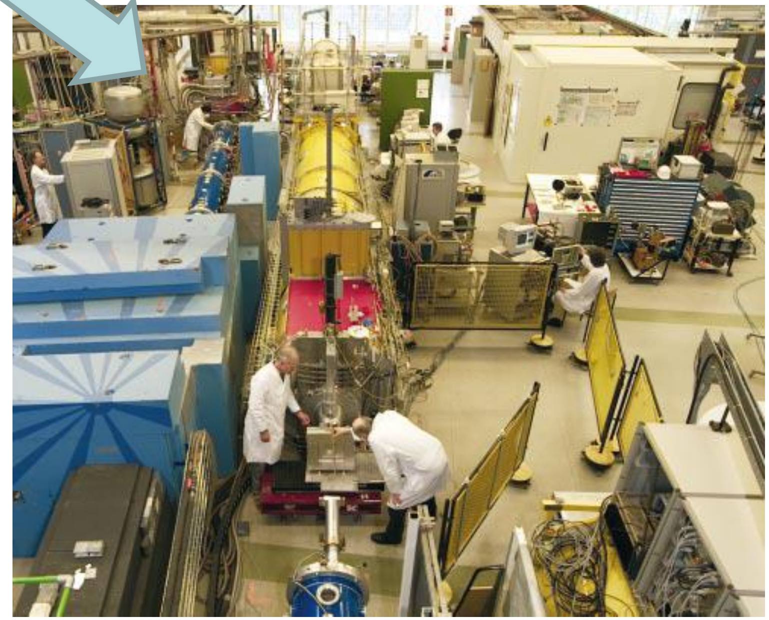
M.V. Avdeev, V.L. Aksenov, Physics-Usp. 2010

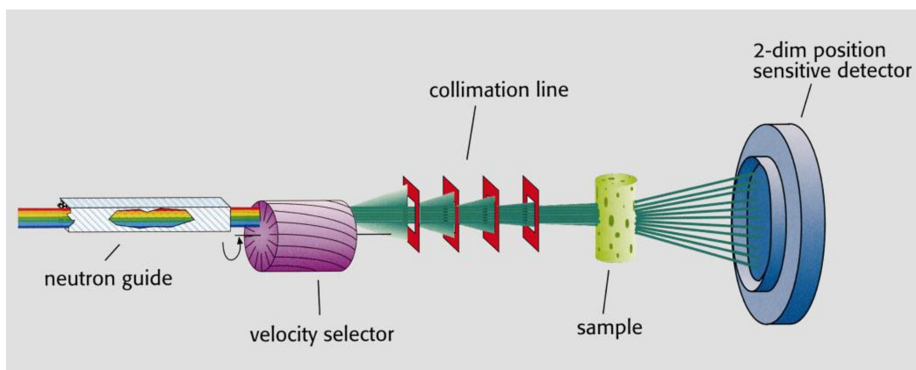
L. Vékás, M.V. Avdeev, Doina Bica, ***Magnetic Nanofluids: Synthesis and Structure***, Chapter 25 in: **NanoScience in Biomedicine** (Ed. Donglu Shi) Springer (USA) 2009

Structural investigations

Small Angle Neutron Scattering facilities used

SANS-1





GKSS Research Center, Geesthacht
SANS-1 and SANS-2

B= 2.5T

Budapest Neutron Center
“Yellow Submarine”

B= 1.7 T

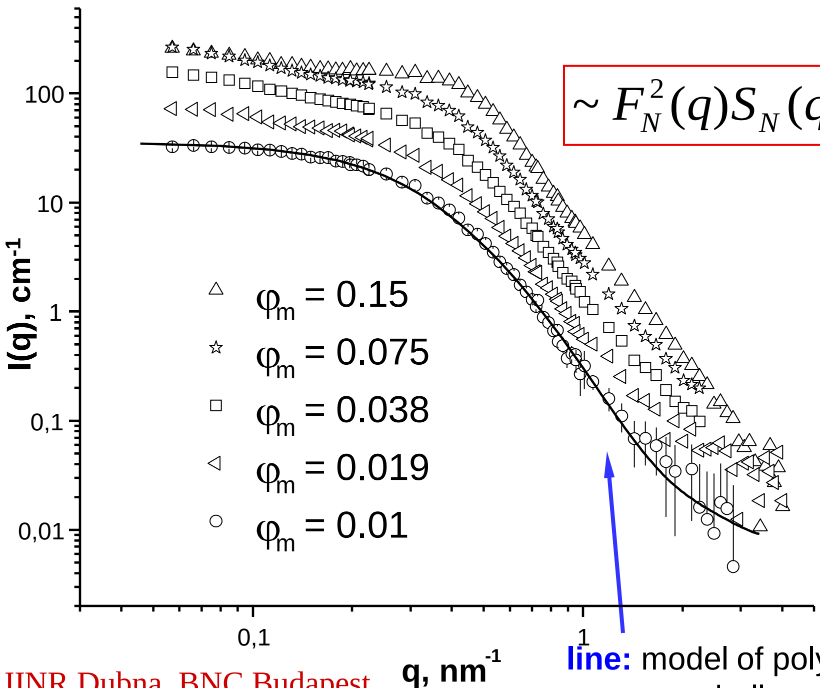
Particle interactions

Highly and weakly stable colloidal MFs

SANS investigations

Highly stable magnetic fluid

magnetite/H-benzene: oleic acid (OA)

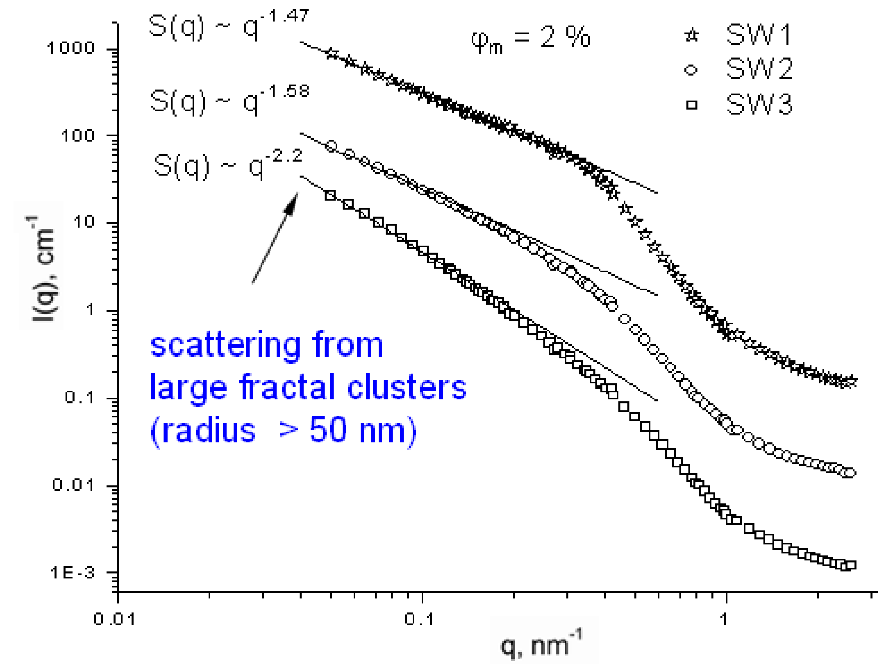


JINR Dubna, BNC Budapest

line: model of polydisperse core-shell particles

Weakly stable magnetic fluids

magnetite/water: OA+DBS, DBS+DBS, OA+OA



Type of structure-factor: **long-range attraction with short-range (contact) repulsion**

Cluster fractal dimension **D ~ 1,5 – 2.5**
Mean radius of cluster units **R ~ 10 nm**

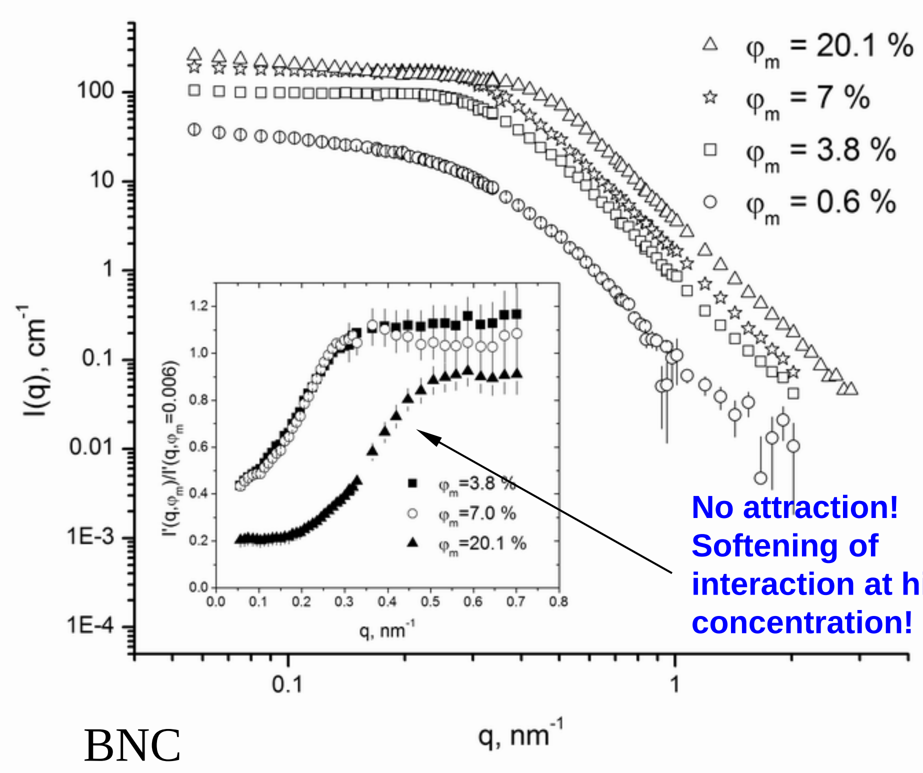
M.V. Avdeev, V.L Aksenov, M. Balasoiu et al. J. Coll. Interface Sci, 2006
L. Vekas, M.V. Avdeev, D. Bica, Magnetic fluids: Synthesis and Structure (Donglu Shi (Ed),Springer,2009)

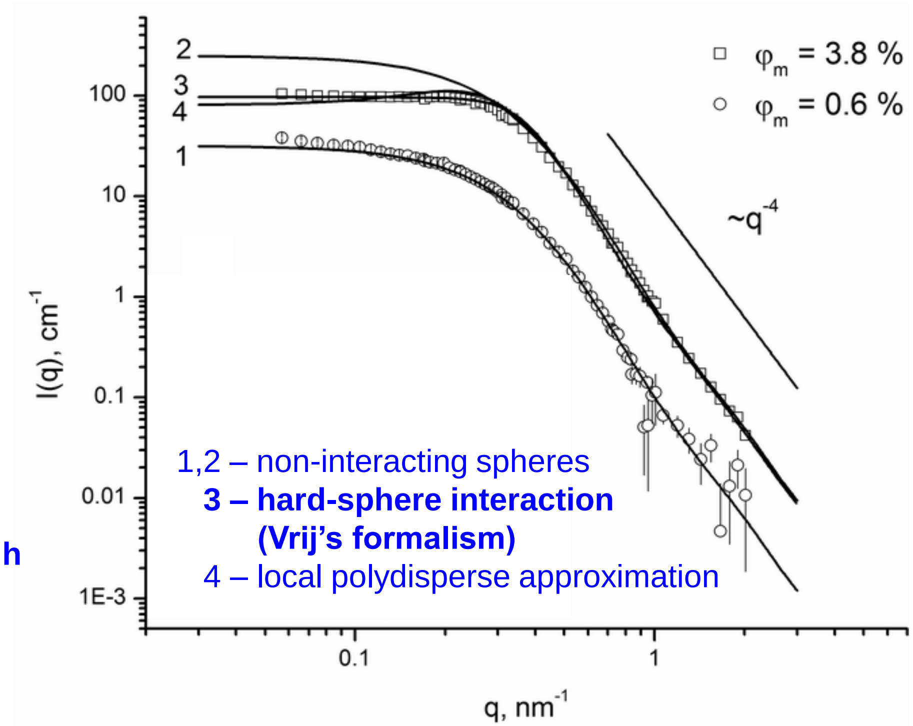
Particle interactions

Highly stable polar MNF

SANS

MNF/pentanol:magnetite/OA + DBS





curve 1 (non-interacting particles) → R_0 = 3.4 nm; S = 0.38

curve 3 (hard-spheres interaction) → δ = 2.3 nm < 2 × 1.8 nm →
→ significant overlap of surfactant sub-layers in the double layer

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

Structural investigations on the efficiency of different chain length surfactants

Unsaturated mono-carboxylic acid

double bond kink

oleic acid (OA)
$C_{18}H_{34}O_2$

Excellent stabilizer due to high solvation

Saturated mono-carboxylic acids

stearic acid (SA)
$C_{18}H_{36}O_2$

palmitic acid (PA)
$C_{16}H_{32}O_2$

Non-efficient stabilizers because of worse solvation

myristic acid (MA)
$C_{14}H_{32}O_2$

lauric acid (LA)
$C_{12}H_{32}O_2$

Good stabilizers limited to small particle sizes

R. Tadmor, R. E. Rosensweig, J. Frey, J. Klein, *Resolving the Puzzle of Ferrofluid Dispersants*, Langmuir 16 (2000)

M.V. Avdeev, D. Bica, L. Vekas, V.L. Aksenov, A.V. Feoktystov, L. Rosta,V.M.Garamus, R. Willumeit , *Comparative structure analysis of non-polar organic ferrofluids stabilized by saturated mono-carboxylic acids*, JColl&Int Sci 334(2009)

Particle sizes - Influence of surfactant chain length

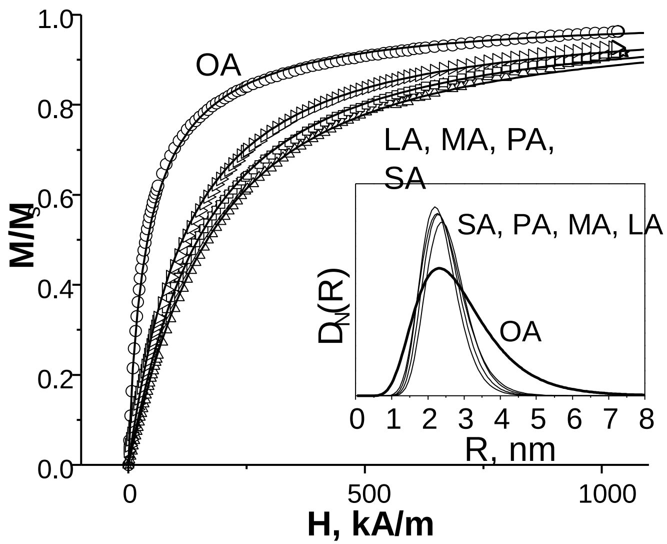
Magnetite NPs stabilized in organic non-polar carrier

DHN-decahydronaphtalene

SANS and VSM analyses

Lab. Magnetic Fluids Timisoara

GKSS Geesthacht
BNC Budapest



SANS

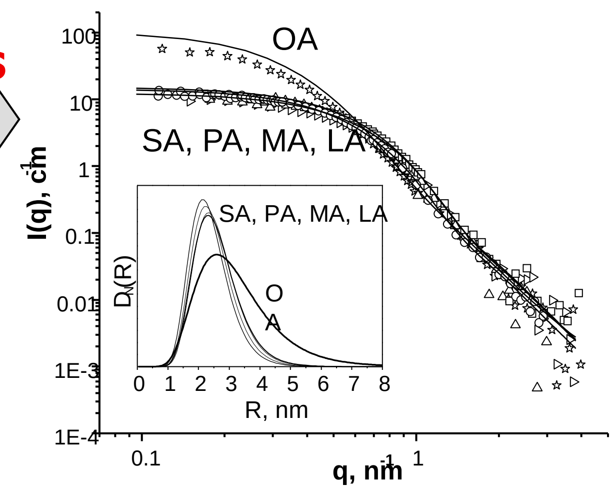
OA
R_0 = 3 nm, S = 0.38

LA, MA, PA, SA
$\langle R_0 \rangle$ = 2.4 nm, $\langle S \rangle$ = 0.28

VSM

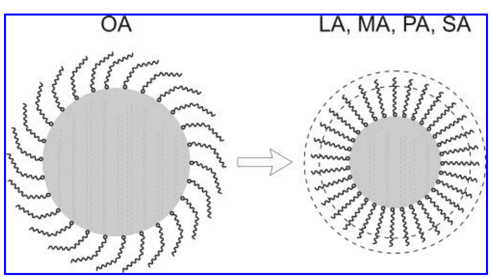
OA
R_0 = 2.7 nm, S = 0.39

LA, MA, PA, SA
$\langle R_0 \rangle$ = 2.4 nm, $\langle S \rangle$ = 0.27



Magnetization curves (points) for ferrofluids/ DHN, φ_m = 1.5 %. Lines are the results of the polydisperse Langevin approximation.
Inset : particle size distributions of magnetite (magnetic size)

SANS curves (points) FFs in DHN normalized to φ_m = 1.5 %. Lines : results of approximation by the model of polydisperse independent spheres
Inset : particle size distributions of magnetite (atomic size)



- Magnetic size smaller than scattering size
- Non-magnetic layer ~ 0.8-1.0 nm
- Saturated surfactants "select" smaller sizes
- **Oleic acid (OA) is the most efficient stabilizer in non-polar organic carriers**
- VSM and SANS data are in excellent agreement

M.V. Avdeev, D. Bica, L. Vekas, V.L. Aksenov, A.V. Feoktystov, L. Rosta, V.M. Garamus, R. Willumeit JColl&Int Sci 2009

Surface coated magnetite NPs for biotech applications

Efficiency of biocompatible surfactant-TEM, VSM & rheological investigations

MF Samples investigated: 13, with different volume fraction of MNPs

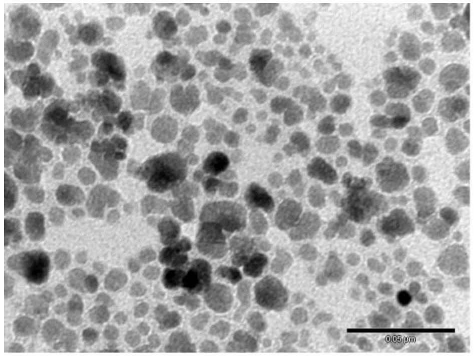
Physical (solid) volume fraction of magnetite nanoparticles: **0.8-21%**
Carrier: hydrocarbon (transformer oil)

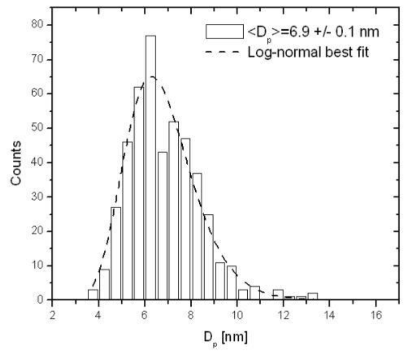
Surfactant: oleic acid vegetable (product of Merck)- a mixture of unsaturated and saturated carboxylic acids

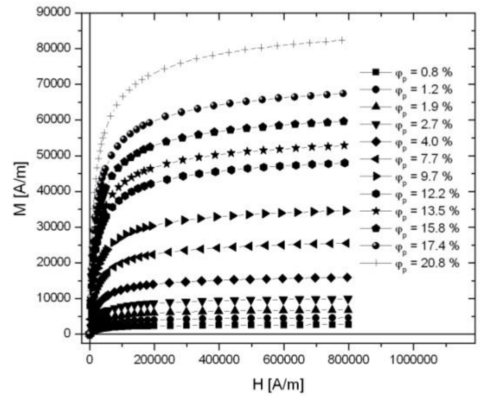
Composition of fatty acids
-**Oleic acid (C18:1) 65-88%**
- Myristic acid (C14:0) ≤ 5.0 %
- Palmitic acid (C16:0) ≤ 16.0 %
- Palmitoleic acid (C16:1) ≤ 8.0 %
- Margaric acid (C17:0) ≤ 0.2 %
- Stearic acid (C18:0) ≤ 6.0 %
- Linoleic acid (C18:2) ≤ 18.0 %
- Linolenic acid (C18:3) ≤ 4.0 %
- Fatty acids of chain length > C18 ≤ 4.0 %

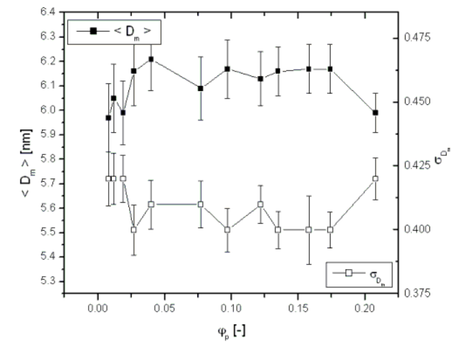
Relatively large amount of saturated carboxylic acids, besides oleic acid
How this composition influence colloidal stability? Formation of clusters?!

Size distributions of MNP









TEM picture of the magnetite nanoparticles and the physical diameter distribution of the magnetite nanoparticles

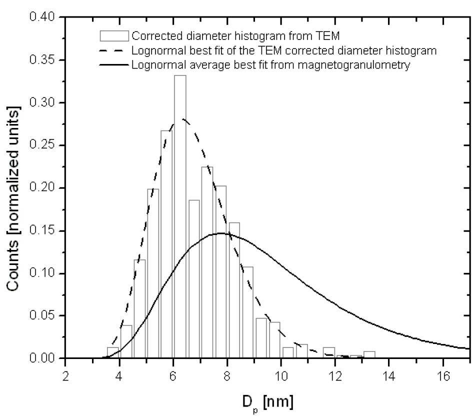
$\mathbf{D_{pTEM} = 6.9\ nm;\ \sigma = 1.5\ nm}$

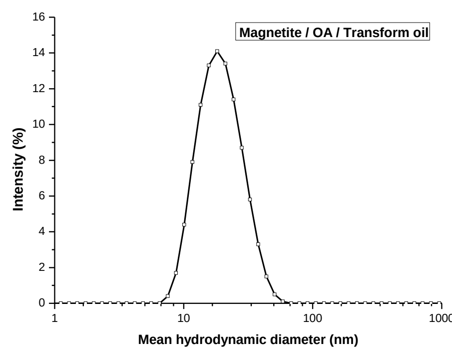
M=M(H) fitted with the model Ivanov&Kuznetsova Phys Rev E (2001)

$\mathbf{D_m = 6.1\ nm;\ \sigma_m = 2.6\ nm}$

(practically no influence of volume fraction)

Weak clustering





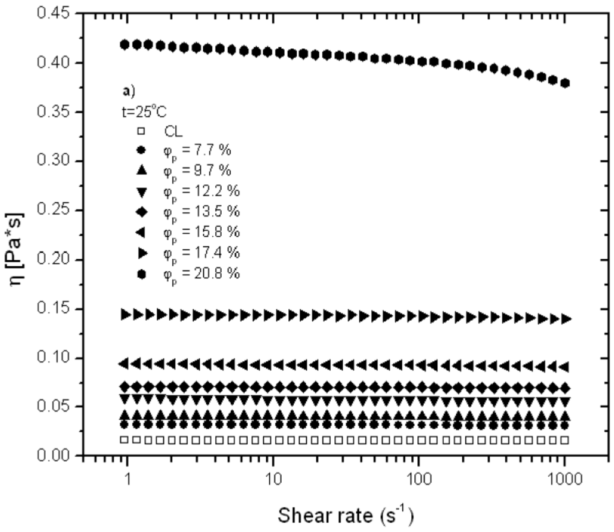
Daniela Susan-Resiga, V. Socoliuc, T. Boros, Tunde Borbáth, Oana Marinica, Adelina Han,L. Vékás, *The influence of particle clustering on the rheological properties of highly concentrated magnetic nanofluids*, J. Coll.& Int. Sci., 373 (2012) 110–115

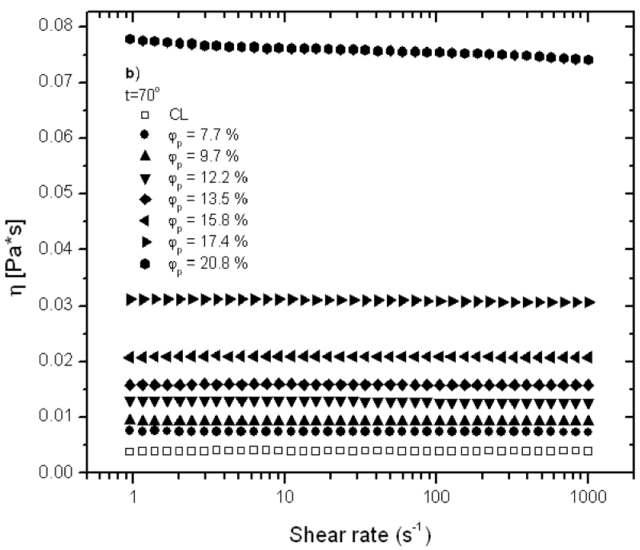
$D_{pTEM} - D_m$ = 0.8 nm< 1.7 nm

D_h= 18 nm (> 11 nm)

Viscosity curves

Influence of the physical volume fraction φ_ρ



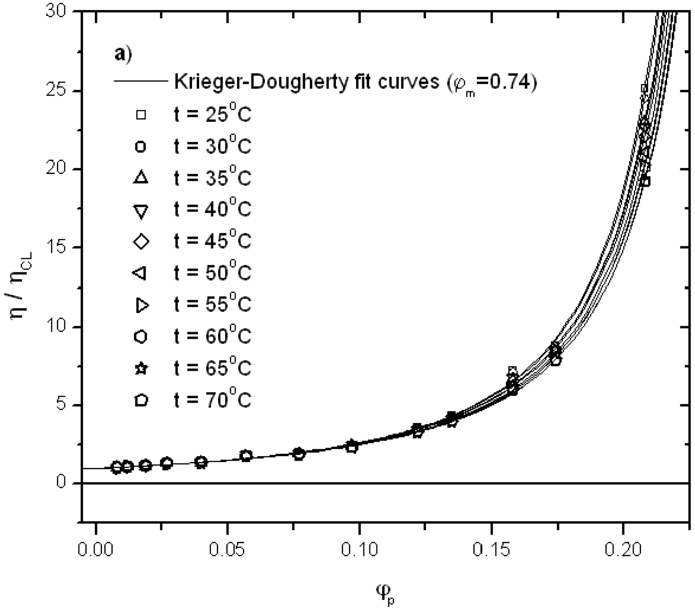


Viscosity curves of the carrier liquid (CL)
and
Magnetic nanofluid samples at
a) 25°C and b) 75°C

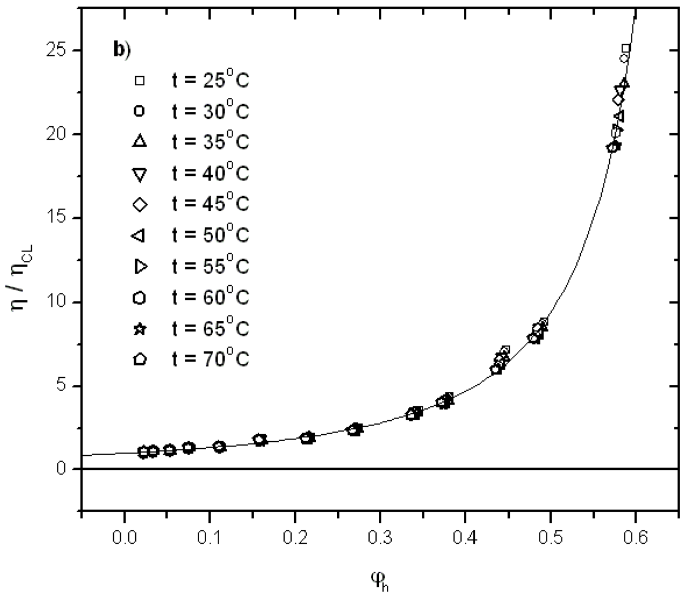
Volume fraction dependence of relative viscosity

Influence of temperature

Dependence on solid volume fraction



Dependence on hydrodynamic volume fraction



$$\frac{\eta}{\eta_{CL}}\left(\varphi_p,\{p,[\eta]\}\right) = \left(1 - \frac{p \cdot \varphi_p}{\varphi_m}\right)^{-[\eta]\cdot\varphi_m}$$

$$p = \frac{\varphi_h}{\varphi_p}$$

$\varphi_m = \varphi_{hmax} = 0.74$

Krieger-Dougherty formula

η and η_{CL} values extrapolated to zero shear rate

Relatively moderate increase of viscosity up to the highest hydrodynamic volume fraction 0.6

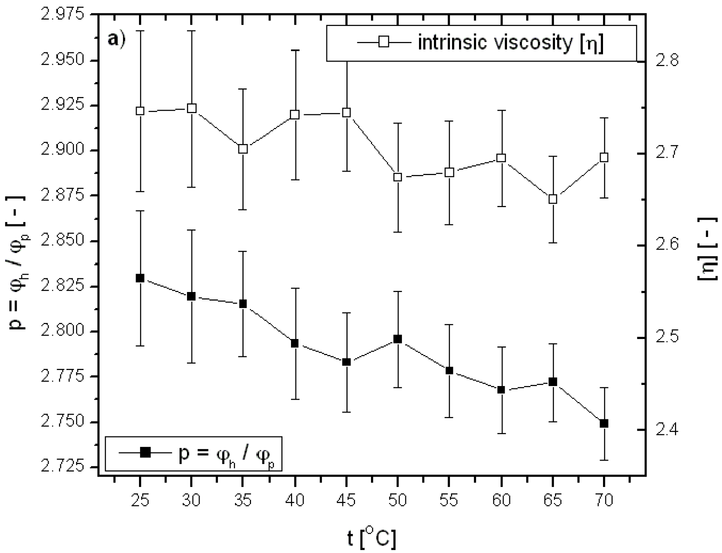
Experimental points of relative viscosity fall on a master curve for t=25-70 ^{0}C

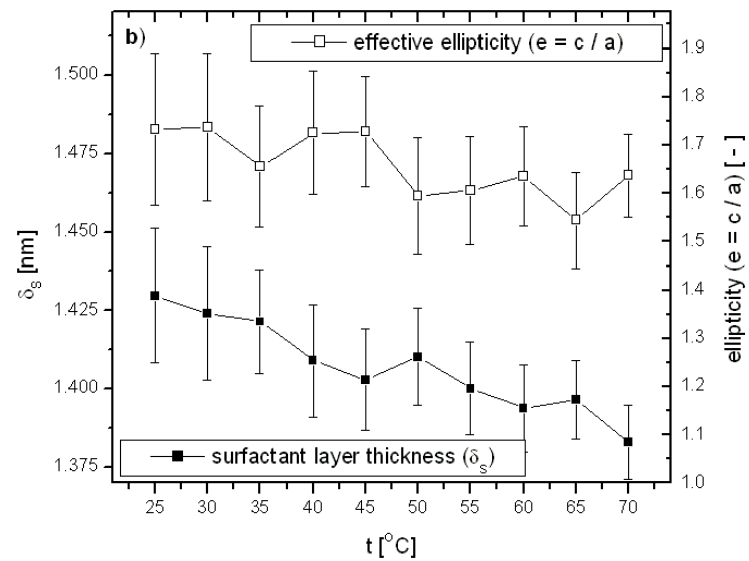
Evaluation of characteristic sizes & particle clustering

Fit parameters of the Krieger-Dougherty equation

Volume fractions ratio **p**, intrinsic viscosity **[η]**

particle mean ellipticity **e** and mean effective surfactant layer thickness $\boldsymbol{\delta_s}$





$$p = \frac{\varphi_h}{\varphi_p} = \left(\frac{\bar{D}_p + \delta_s}{\bar{D}_p}\right)^3$$

D_p = 6.9 nm ⇨ Surfactant layer thickness δ_s= 1.38-1.43 nm

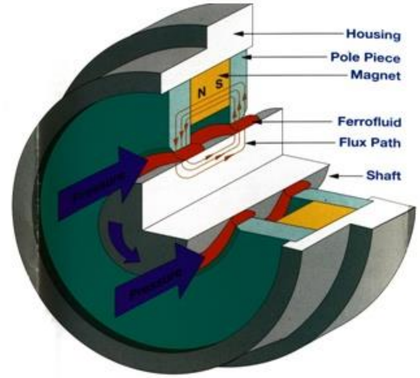
SANS: $\delta_s \approx$ 1.4nm; Avdeev et al. JCIS 2009

[η] ≈ 2.8 ⇨ e ≈ 1.65   e(TEM) ≈ 1.3 ⇨ **1.3 part/cluster**

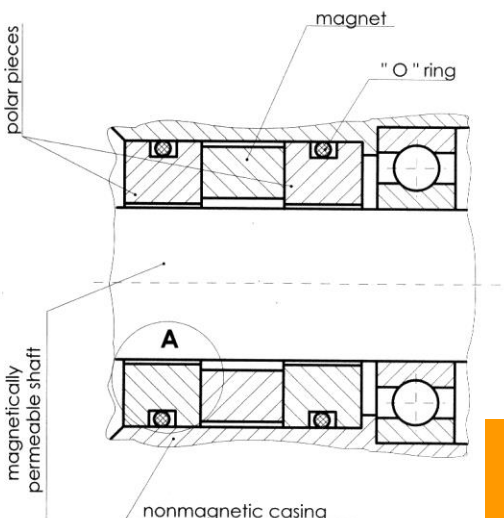
Daniela Susan-Resiga, V. Socoliuc, T. Boros, Tunde Borbáth, Oana Marinica, Adelina Han, L. Vékás, *The influence of particle clustering on the rheological properties of highly concentrated magnetic nanofluids*, J. Coll.& Int. Sci., 373 (2012) 110–115

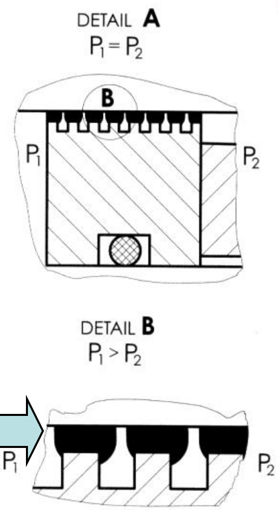
Why high magnetization MFs?

Magnetofluidic rotating seals



Sealed medium: gas
Friction: only viscous
No leakage
No wear
Years long operating life





MF "O" rings

Sealing capacity ~ M_s

$$\Delta p = n\mathbf{M_s}(B_{max} - B_{min})$$

10^{-8} mbar – 50 bars

Main requirements for sealing MFs

- **Magnetization: high / very high**
- Viscosity: as low as possible
- Magnetoviscous effect: reduced, below 50%
- Evaporation rate: low/very low

Long-term colloidal stability in strong non-uniform magnetic field

B_{max} ~ 1-1.5T
$|\mathrm{grad}H|$ ~ 10^9 A/m^2

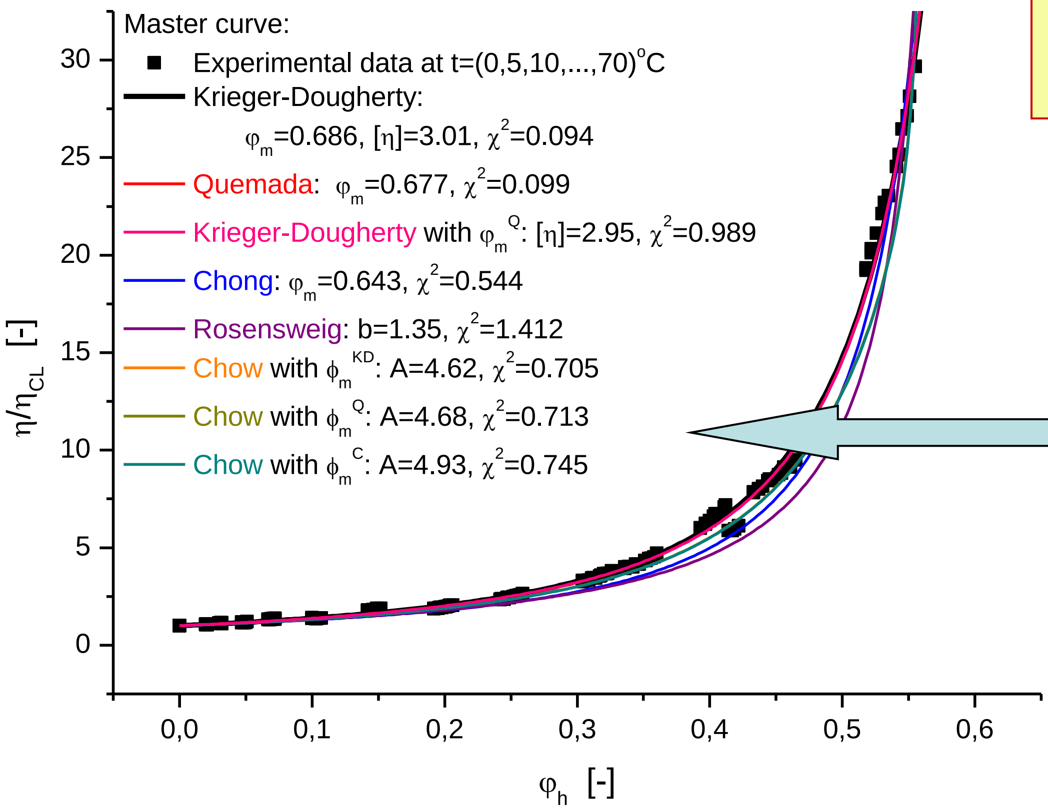
High magnetization MNF for seals/ non-polar organic (OA)

Testing of performances:Volume fraction dependence of effective viscosity

Non-dimensional dynamical viscosity vs. hydrodynamic volume fraction: 0 - 0.65

Saturation magnetization: M_s=0 -**1000 G**; Temperature range t = 0 – 70 ^{0}C

M_s = 1000 G – a reasonable upper limit for magnetite magnetic nanofluids



Irreversible particle agglomerates
Practically absent

$$\frac{\eta}{\eta_o} = \exp\left(\frac{2.5\varphi_h}{1-\varphi_h}\right) + \frac{A\varphi_h^2}{1-A\varphi_h^2\varphi_{hm}}$$

T.S. Chow
Phys.Rev. E
1993, 1994

Particle interaction Parameter A

A_{theor}= 4.67
A_{fit} ≈ 4.70

Long-term high colloidal stability

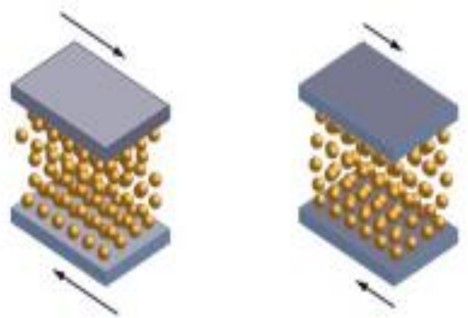
Daniela Gheorghe (Resiga), PhD thesis, 2001
Resiga D., Vékás L., Bica D., Chiriac A.,
Comportarea reologică a fluidelor magnetizabile,
Ed. Orizonturi Universitare Timişoara (2002) 184 p.

Magnetorheological(MR) Fluids-*commercial products*

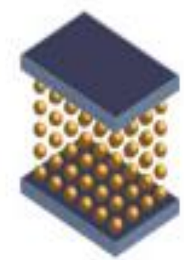
Composition & intense field induced structuring: large elongated clusters!

Magnetic particles: magnetically soft **multi-domain** Fe, Fe alloys of **1-10 μm**
Carrier liquids: petroleum based oils, silicon oils, mineral oils, synthetic oils, water
Suspension agents: thixotropic and surface active agents (e.g., carboxylic acids, stearats, polymers, organoclays) (in use thickening--significant aging observed!)
Characteristic time of field induced structural changes: ~ msec

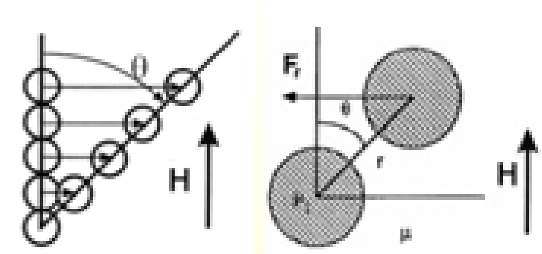
No field: H=0
Fe particles diffusing randomly; blades moving freely



Increasing field: H > 0
Fe particles start forming chains; resistance between blades increases



Saturating field: H ≈ H_{sat}
Strong field forms continuous chains-**quasi-solid state**; blades movement restricted



Restoring force F_r
induced by magnetic field *H* in shearing flow

Field dependent magnetic moment of particles $\boldsymbol{m} = 4\pi\mu_0 \mu_f \beta a^3 \mathbf{H_0}$; $\beta = (\mu_p - \mu_f)/(\mu_p + 2\mu_f)$

Field dependent magnetic coupling parameter
$\lambda_{int}^{MR} = \pi\mu_0 \mu_f \beta a^3 \mathbf{H_0}^2/(2kT)$
$\lambda_{int}^{MR} = 1$ for $H_0 = 127$ A/m; $2a = 1\mu m$
$\lambda_{int}^{MR} \sim 10^8 \gg 1$ *for usual H values !!!*

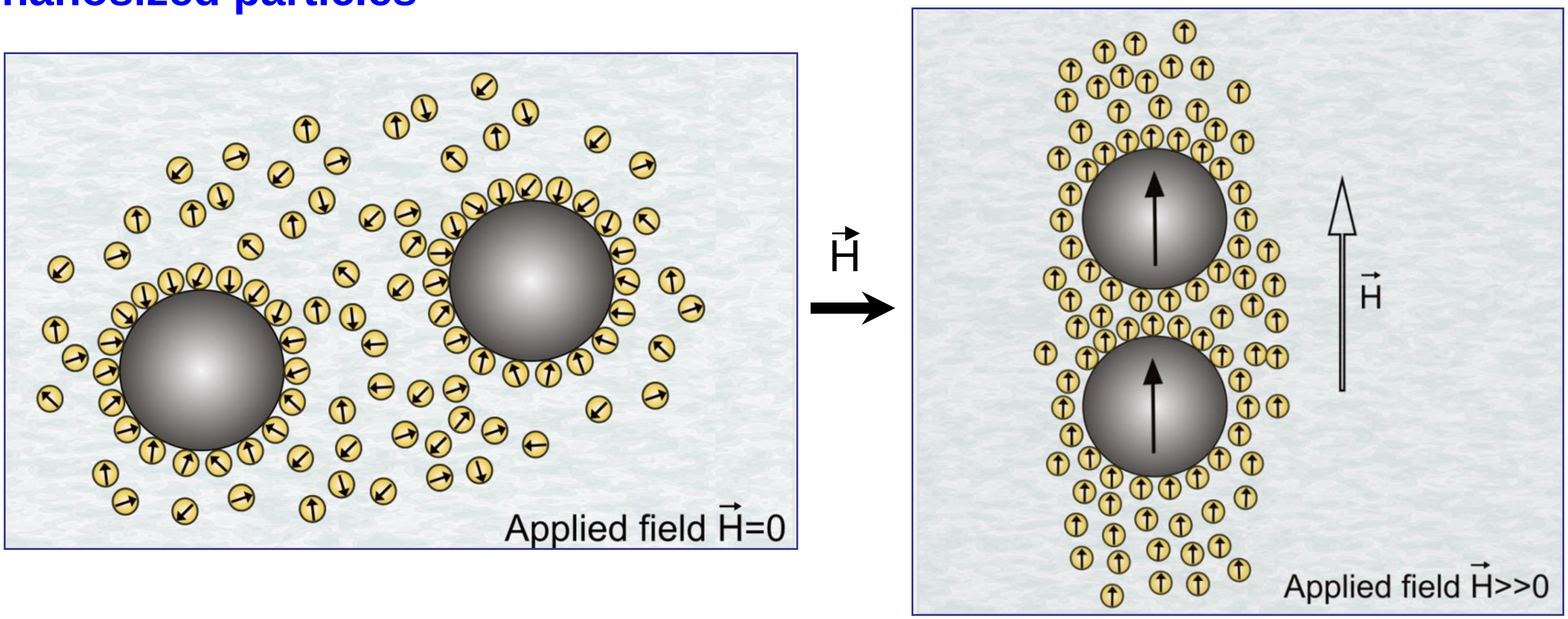
Strongly non - Newtonian behavior
High yield stress: 50-100 kPa
Large MR effect: $10^2 - 10^3$ times increase of effective viscosity

Sedimentation and aging problems

Nano-micro composite magnetic fluids

Field controlled clusterization of micron and nanosized particles

Micrometer size Fe particles dispersed in high concentration magnetic nanofluids-D fluids
No special additives dissolved in the carrier



The magnetic nanoparticles – *tiny permanent magnets* – cover the surface of the micrometer size Fe particles and impede their direct surface-to-surface contact => **negligible aging, increased sedimentation stability&redispersability and very high magnetization**

Excellent sealing and magnetorheological fluids

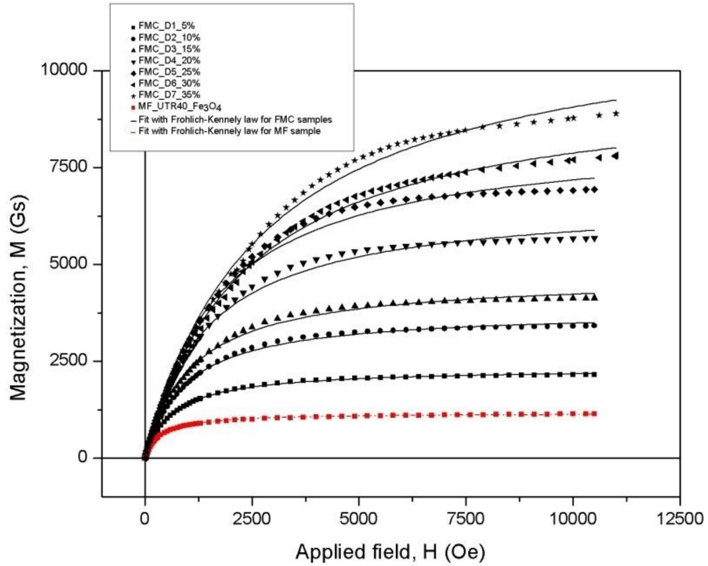
• G.Bossis et al in: S. Odenbach(Ed): Ferrofluids (Springer,2002); M.V.Avdeev et al JMMM 2004
•Doina Bica et al. Patent RO 122725(2009); Daniela Resiga et al J Magn Magn Mater 2010

Nano-micro composite magnetic fluids-D fluids

Influence of micrometric Fe content

Magnetization curves for **D fluids**; Φtotal ≈ 0.27-0.57; Φmicro ≈ 0.05-0.35; Φ nano ≈ 0.22 (const)

The Langevin-type magnetic behavior is no more valid !



$$M = \frac{M_s \cdot H}{\dfrac{M_s}{\chi_{init}} + H}$$

Frölich-Kennelly formula

Nr.crt.	Sample	Fe_3O_4 volume fraction (%)	Iron volume fraction (%)	χ_{init}	M_s (Gs)
1.	FMC_D1_5%	22	5	3.53±0.02	2317± 3
2.	FMC_D2_10%	22	10	4.07±0.05	3803± 14
3.	FMC_D3_15%	22	15	4.34±0.06	4688± 22
4.	FMC_D4_20%	22	20	4.69±0.09	6681± 46
5.	FMC_D5_25%	22	25	4.93±0.10	8407± 72
6.	FMC_D6_30%	22	30	4.14±0.05	9727± 54
7.	FMC_D7_35%	22	35	4.23±0.06	**11540± 95**
8.	**MF_UTR40_Fe_3O_4**	22	0	3.18±0.02	**1166± 2**

An order of magnitude increase of the saturation magnetization!

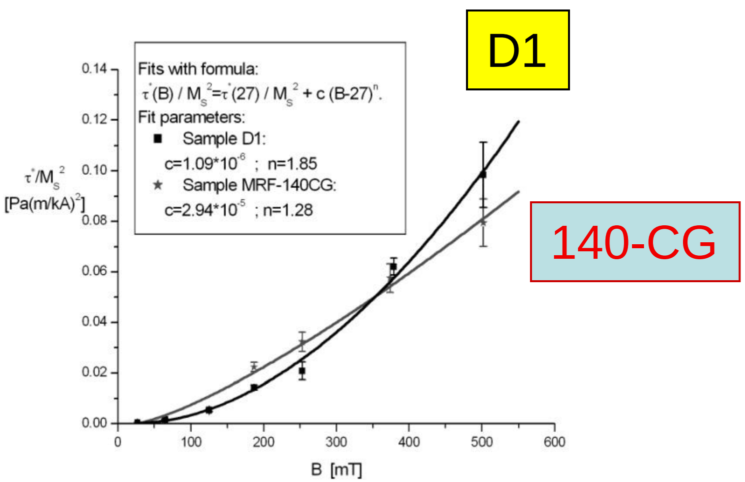
Nano-micro magnetizable fluids vs. commercial MR fluids

Effect of nanosized magnetic particles on MR effect

D1 sample :$\Phi_{micro} \approx 0.2$; $\Phi_{nano} \approx 0.2$; $\Phi_{total} \approx$ 0.4

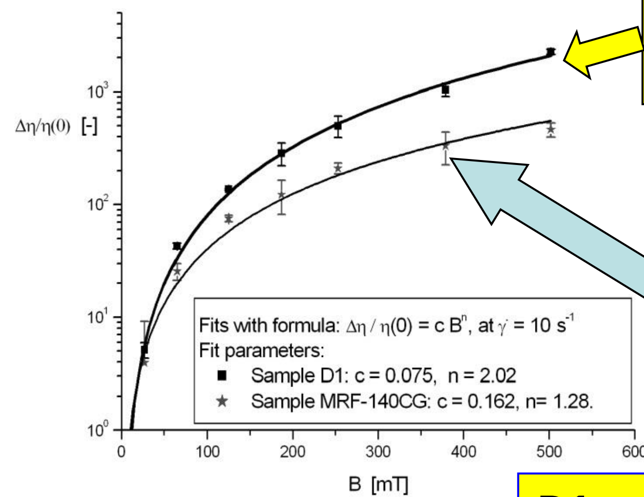
140 CG(LORD sample): $\Phi_{micro} \approx$ 0.4

$$[\eta(B)-\eta(0)]/\eta(0) = f(B)$$



Apparent yield stress normalized by the square of saturation magnetization versus magnetic flux density

Shear rate 10 s^{-1}



D1 – nano-micro lab sample

MRF-140CG – commercial sample-LORD Co (USA)

Relative increase of viscosity versus magnetic flux density

D1 nano-micro fluid

Reduced sedimentation

Higher MR effect

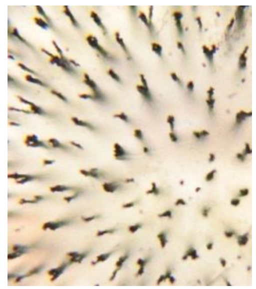
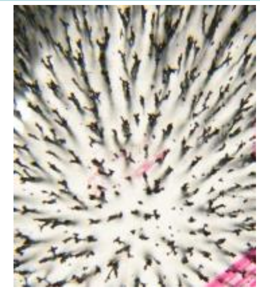
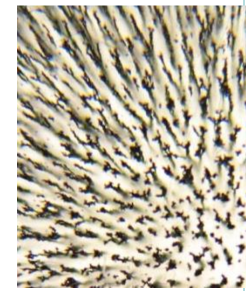
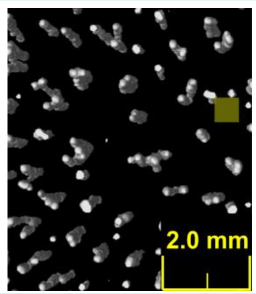
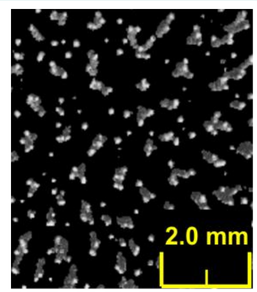
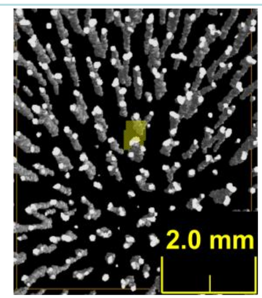
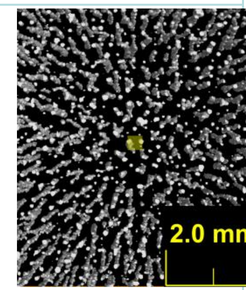
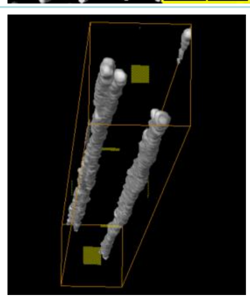
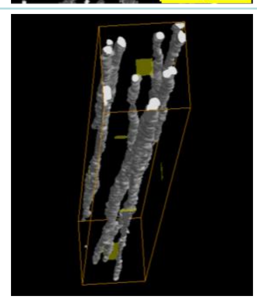
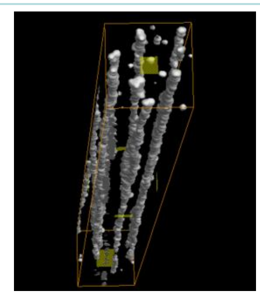
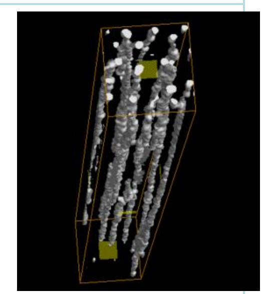
No long chain polymer additives

No thickening in use

Relatively high costs

Daniela Susan-Resiga, Doina Bica, L. Vékás, J Magn Magn Mater., 2010

Magnetic Elastomers
" MR fluids" - no sedimentation!

	H = 220 kA/m	H = 70 kA/m	H = 30 kA/m	H = 8 kA/m
Picture of the bottom of the sample				
Bottom view of the reconstructed tomography image				
Extracted columns from the reconstructed tomography image				

Tünde Borbáth (ROSEAL Co), PhD Thesis , Univ Politehnica Bucharest, 2012

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Smart Materials and Structures

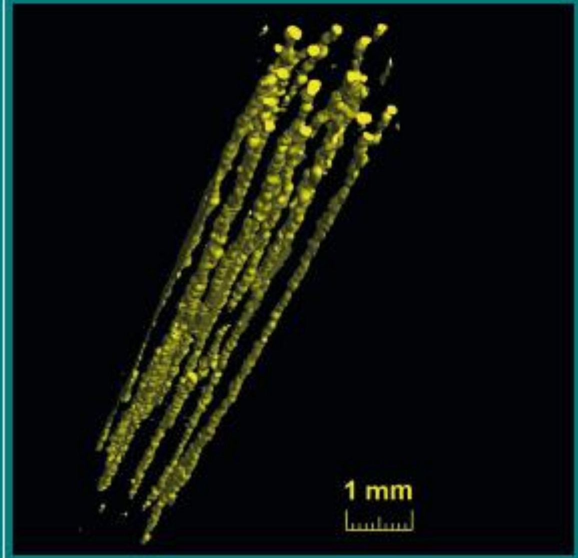
Systems from nano- to macroscale

Volume 21 Number 10 October 2012

Featured article

XµCT analysis of magnetic field-induced phase transitions in magnetorheological elastomers

T Borbáth, S Günther, D Yu Borin, Th Gundermann and S Odenbach



iopscience.org/sms

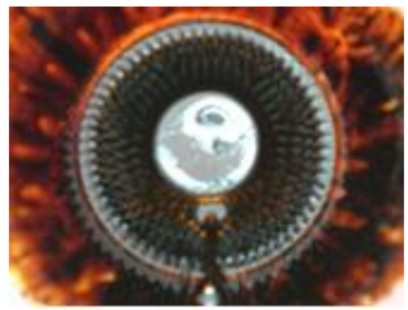
IOP Publishing

Micro-pilot scale synthesis of magnetic fluids

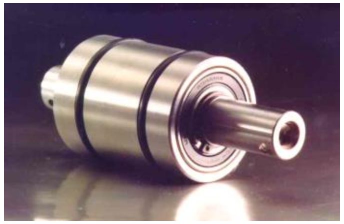
Procedures developed by Doina Bica† - Romanian Academy-Timisoara Branch

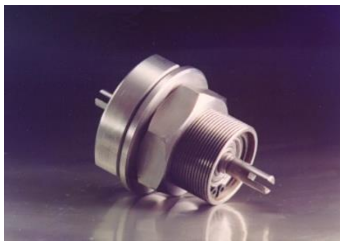
SC ROSEAL SA
Odorheiu Secuiesc

CEEX *NanoMagneFluidSeal*
2006-2008



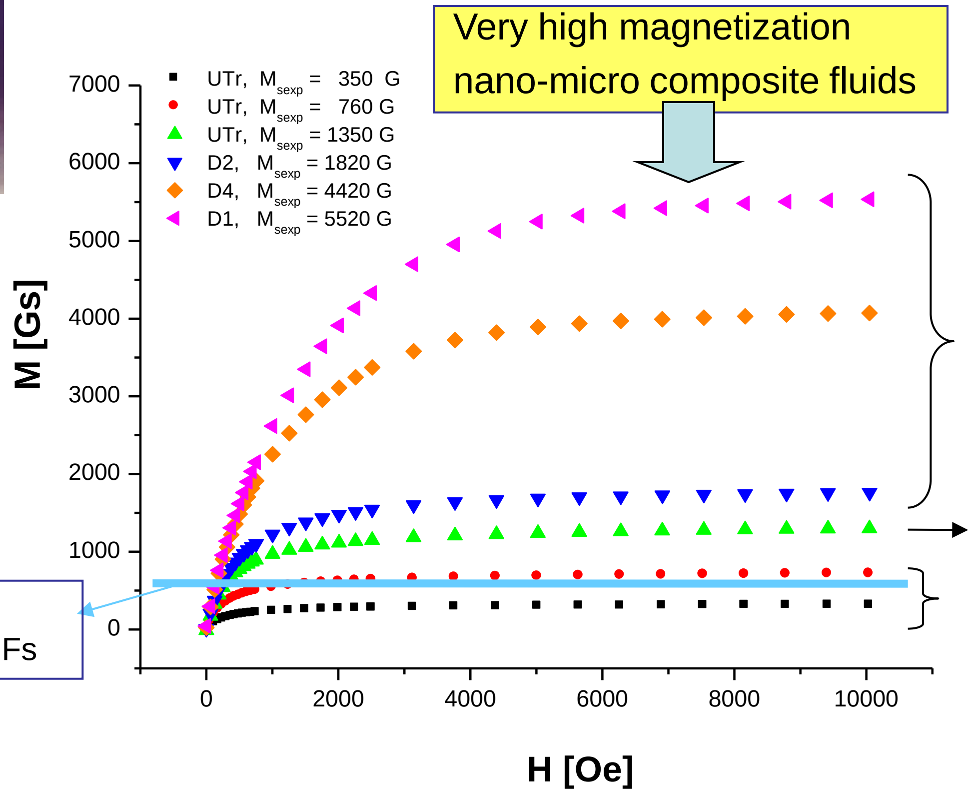
High Magnetization Sealing and MR Fluids
MF rotating seals manufacturing



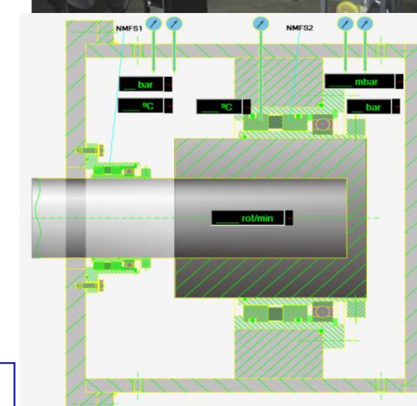


ROSEAL Co.& Lab MF Timisoara-microproduction
http://roseal.topnet.ro/ang/index1.html

Saturation magnetization of MNFs and nano-micro composite fluids



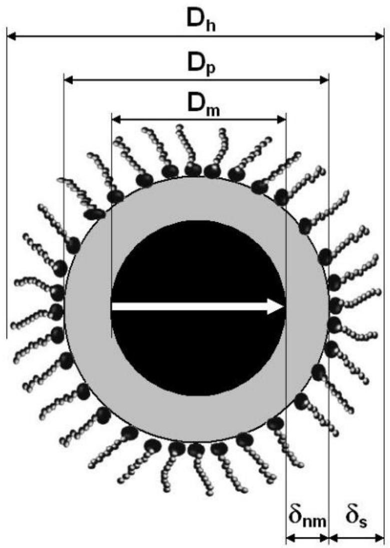
Usual limit of commercial MNFs



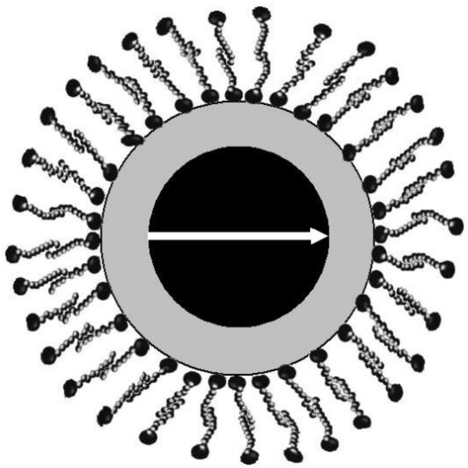
Doina Bica et al. Patents RO 115533 B1(2000); RO122725 (2009)
T. Borbáth et al. Int. J. Fluid Machinery and Systems (2011)

Magnetic nanoparticles, magnetic nanofluids and magnetic nanocomposites for biomedical applications

Hydrophobic and hydrophilic magnetite nanoparticles for fabrication of functionalized magnetic nanocomposites



D_m – magnetic diameter
D_p – physical diameter
D_h – hydrodynamic diameter
δ_m – thickness of the nonmagnetic layer
δ_s – thickness of the surfactant layer



Magnetite NP with *hydrophobic* coating Fe3O4.OA

Magnetite NP with *hydrophilic* coating Fe3O4.(OA+OA)

ROSEAL Co. supplier: http://www.magneticmicrosphere.com/suppliers.php?category=2

Functionalized magnetic nanocomposites for biotech & biomedical applications-*flow chart*

Coprecipitation
Fe^{3+}, Fe^{2+} sol.
NH_4OH 25%
pH=11; 80^{0}C
Magnetite NP

→

Surface coating
of MNP
OA (or LA;MA)
or
(OA+OA)
(LA+LA);(MA+MA)

→

Advanced purification
Washing
Decantation
Filtering

→

Hydrophobic
MNP
Fe_3O_4.OA

Hydrophilic
MNP
Fe_3O_4.(OA+OA
)

→

Controlled clusterization in organic matrix

→

Magnetic micro-gels

“Magnetic nanocontainers”

Superparamagnetic behavior, high specific magnetic moment (20-50 emu/g)

Multiresponsive CEX magnetic microgels
- preparation procedure using hydrophilic magnetite -

Group of Dr. Rodica Turcu
Nat.Inst. Isotopic and Molecular Technologies
Cluj-Napoca, Romania

Water based magnetic nanofluid Fe_3O_4/OA+OA

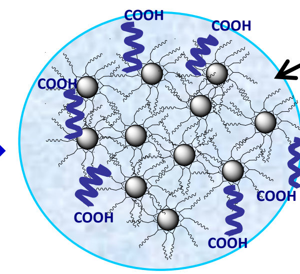
+

Monomers: **NIPA, AAc**

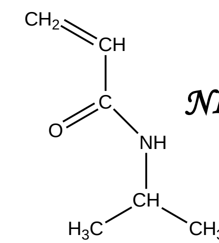
Crosslinker: BIS

Oxidant: APS

1 step copolymerization method

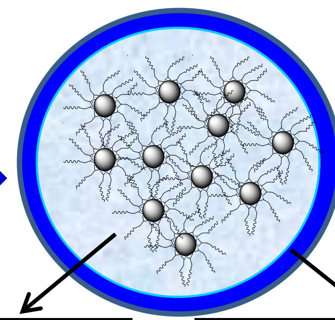


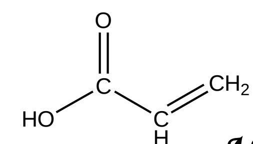
Controlled clustering of MNP into copolymer p(NIPA-Aac)



NIPA

2 steps, layer by layer polymerization method





AAc

1 step: control clustering of MNP into pNIPA

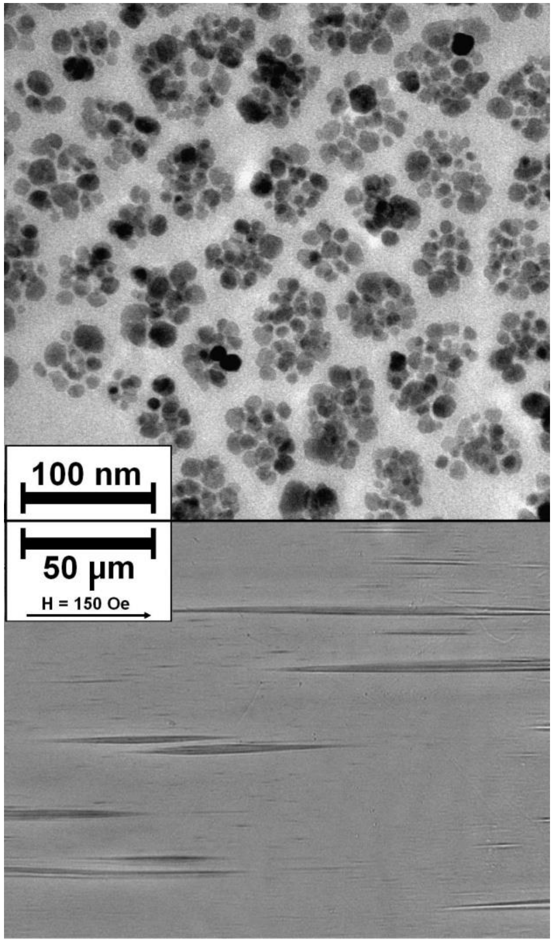
2-nd step: pAAc coating of microgel particles

NIPA – N-isopropylacrylamide
AAc – acrylic acid
BIS - N,N’-methylenbisacrylamide
APS – ammonium persulfate

Control of functional groups distribution
High concentration of COOH on the surface

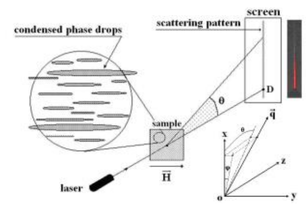
Behavior of magnetic microgels in magnetic field

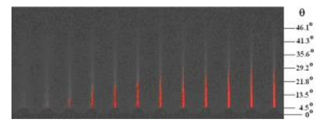
Magnetic field induced phase condensation in a water based suspension of magnetic microgels

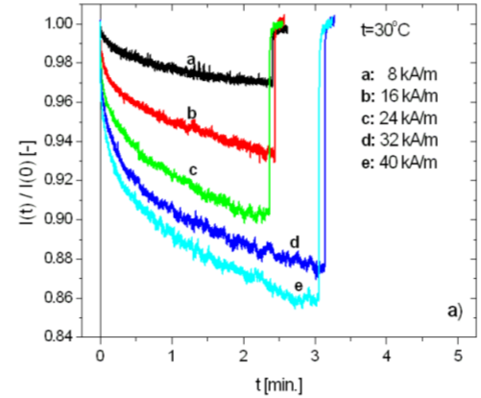


Magnetic field induced phase condensation:
the specific surface aria of the colloid decreases with approx. three orders of magnitudes!
the decrease of adsorbtion capacity influences the separation efficiency of magnetic beads

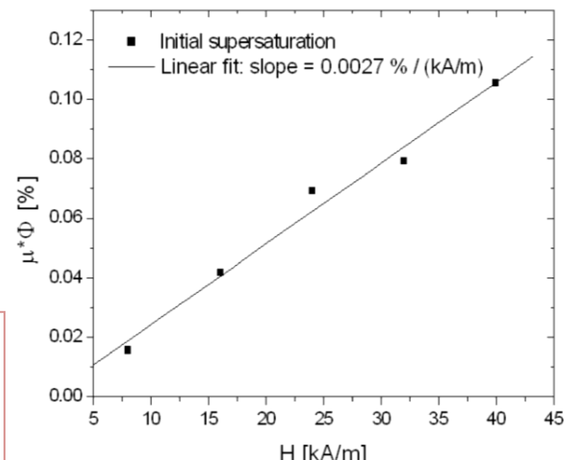
Light scattering on the condensed phase drops-time evolution







Increase of the degree of condensation by increasing the intensity of applied field



V. Socoliuc, L. Vekas, Rodica Turcu: *"Magnetically induced phase condensation in an aqueous dispersion of magnetic nanogels"*, Soft Matter (2013)

Applications in biology and medicine

- MRI contrast
- Magnetic bioseparation (proteins, enzymes…)
- Magnetic drug targeting
- Magnetic hyperthermia
- Catalysis

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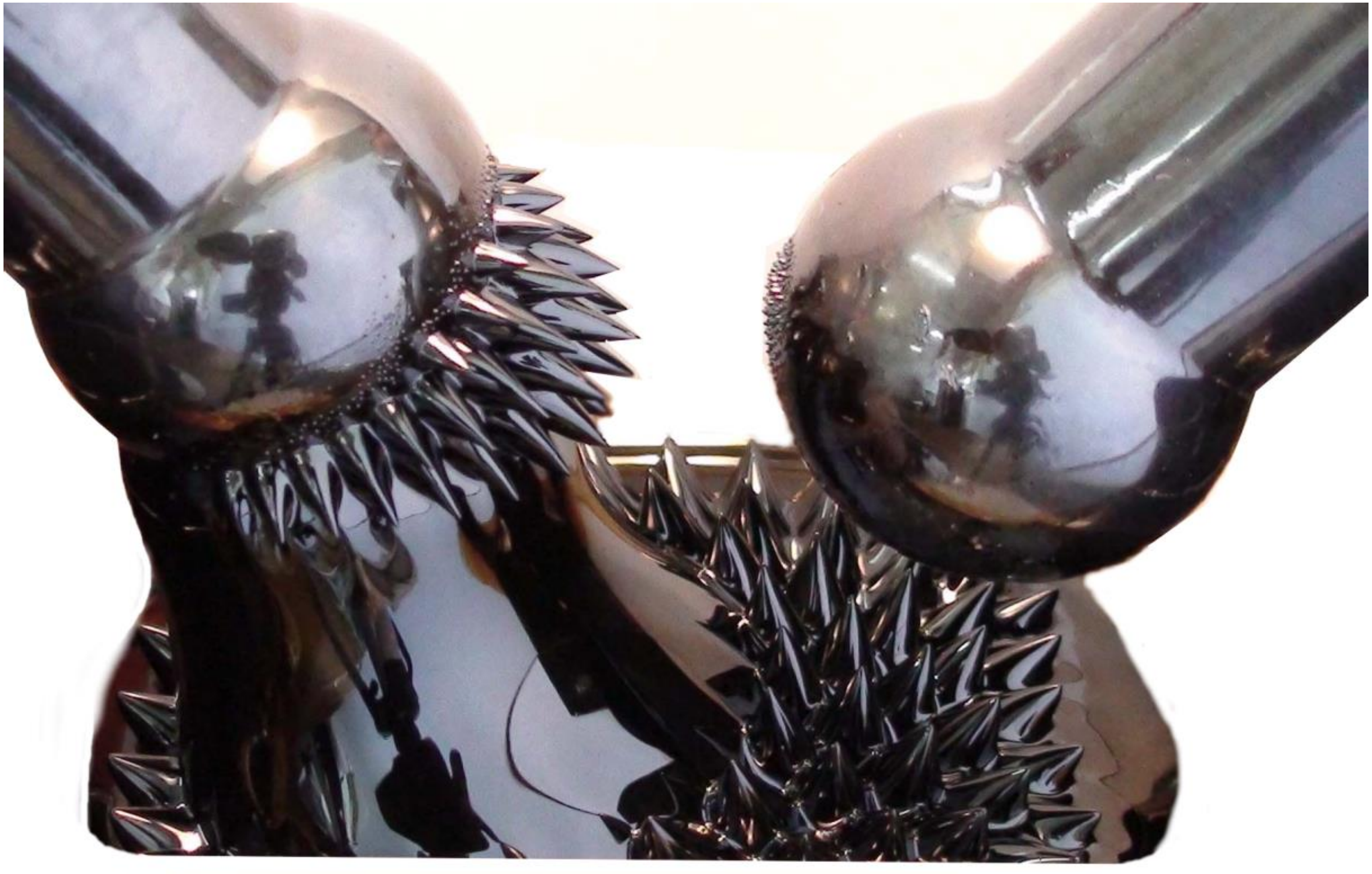

Thank you for your attention!