Magnetic Fluids

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Lecture

in the framework of the topic

From fundamental properties of matter to magnetic materials and applications

2021 European School on Magnetism
Cluj-Napoca, September 12, 2021

Outline

Introduction

Synthesis

Particle sizes

Langevin model

Characterization

Ferrohydrodynamics

Applications

Kinetic arts

Magnetoresponsive liquids?

Magnetism and fluid behavior combined in one medium

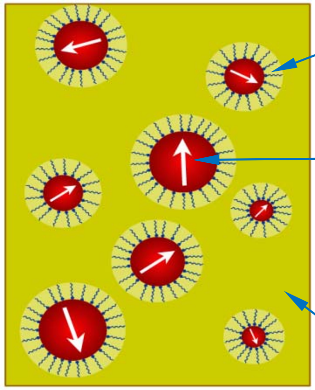
Paramagnetic salt solutions
(rare-earth salt solutions)
The ***magnetic force*** three orders of magnitude **smaller**
than the gravitational force
Too small for engineering applications

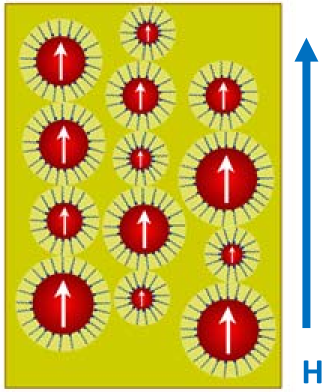
↓

FERROFLUIDS / MAGNETIC FLUIDS

Magnetic fluids/Ferrofluids

Composition and basic behavior





Ultrastable colloidal suspension of magnetic nanoparticles **(5-10 nm)** *in a carrier liquid*

Colloidal stability

ensured by
Brownian motion and
by screening
attractive interactions
between nanoparticles

$$\lambda_{\text{int}} = \frac{\mu_0 M_s^{\,2} \pi d^3 \varphi}{6 k_B T}$$

λ_{int}

the ratio between the dipole-dipole interaction energy and the thermal energy

(non-dimensional dipolar interaction energy)

Magnetizable fluid continuum- a valid approximation

$\lambda_{int} < 1$ ⇒ $d_m \leq 10$ nm (magnetite)

Newtonian flow behavior ⇐ **No particle clustering**

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

Magnetically controllable fluids

Particle size-an essential parameter

Colloidal suspensions of subdomain **nanometer size** magnetic nanoparticles

Magnetic fluids (ferrofluids)

$\lambda_{int} \leq 1$

Negligible attractive interactions

Suspensions of multidomain **micron size** magnetic particles

Magnetorheological fluids

$\lambda_{int} \gg 1$

Very strong attractive interactions

G. Bossis et al Magnetorheology: Fluids, Structures and Rheology, in: Lecture Notes in Physics, Springer-Verlag, 594, 202–232 (2002);
L. Vékás, *Ferrofluids and Magnetorheological Fluids*, Advances in Science and Technology, Vol. 54, 127-136 (2008)

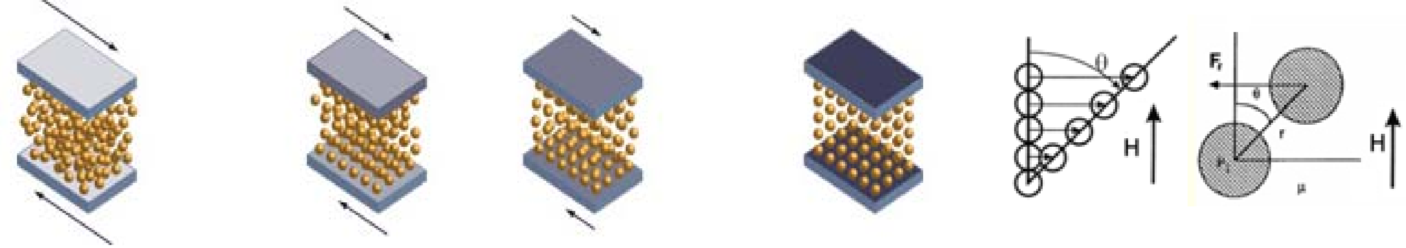
Magnetorheological Fluids

Composition and particle structuring mechanism

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)



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: $H \approx H_{sat}$
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 $\boldsymbol{m} = 4\pi\mu_0\,\mu_f\beta a^3\boldsymbol{H_0}$; $\beta = (\mu_p - \mu_f)/(\mu_p + 2\mu_f)$

Field dependent magnetic coupling parameter

$\lambda_{int}^{MR} = \pi\mu_0\,\mu_f\beta a^3\boldsymbol{H_0}^2/(2kT)$

$\lambda_{int}^{MR} = 1$ for $H_0 = 127$ A/m; $2a = 1\mu m$

$\boldsymbol{\lambda_{int}^{MR} \sim 10^8 \gg 1}$ ***for usual H values***

⇨

Intense particle clustering

Strongly non-Newtonian flow behavior

Yield stress: 50-100 kPa

Large MR effect: $10^2 - 10^3$ times increase of effective viscosity

J. Rabinow, The magnetic fluid clutch, AIEE Trans.,67, 1308-1315(1948)

G. Bossis et al Magnetorheology: Fluids, Structures and Rheology, in: Lecture Notes in Physics, Springer-Verlag, 594, 202–232 (2002)

Magnetic fluids/Ferrofluids-Early history

Patent filed in 1963 by Steven S. Papell of NASA: *Low viscosity magnetic fluid obtained by the colloidal suspension of magnetic particles*, US Patent 3.215.572 (1965).

Neuringer J L, Rosensweig R E, *Ferrohydrodynamics*, Physics of Fluids 7, 1927 (1964)

Rosensweig R.E., *Buoyancy and Stable Levitation of a Magnetic Body immersed in a Magnetizable Fluid*, Nature, 210, 613-614(1966)

Rosensweig R.E., *The Fascinating Magnetic Fluids*, New Scientist, 20, 146-148 (1966)

Rosensweig R.E., Kaiser R., *Study of ferromagnetic liquid*, Phase I. NASA Office of Advanced Research and Technology, Washington, D.C. (1967)

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

Kaiser R., Miskolczy G., *Magnetic properties of stable dispersions of subdomain magnetic particles*, J.Appl.Phys., 41(3)1064-1072(1970)

Rosensweig, R. E., *Magnetic fluid seals*. US Patent No. 3,620,584(1971)

Reimers G. W., Khalafalla S. E., *Preparing magnetic fluids by a peptizing method*, Bureau of Mines, US Dept.Int., Technical Progress Report-59(1972)

Shliomis M I, *Effective Viscosity of Magnetic Suspensions*, Sov. Phys. JETP 34, 1291-1294(1972)

Shliomis M.I., *Magnetic fluids*, Sov. Phys. Usp., 112, 153 (1974))

Chubachi R., Nakatsuka K., Shimoiizaka J., *Influence of Temperature and pH on the Dispersion Stability in Water Base Magnetic Fluids*, J-STAGE, 23(6)211-215(1976)

Rosensweig R. E., *Fluid dynamics and science of magnetic liquids*, in: Advances and Electronics and Electron Physics, vol.48, Academic Press, New York (1979)pp.103-199

Synthesis of magnetic fluids

Synthesis procedures

I. Synthesis of magnetic nanoparticles-bottom-up approaches

- **Chemical co-precipitation; thermal decomposition**

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

- **Steric stabilization (organic carriers)**
- **Electrostatic and electro-steric stabilization (water)**

III. Stabilization/dispersion in ionic liquids and liquid metals

⇩

Magnetic fluids/Ferrofluids-longterm colloidal stability

Charles S.W., **Preparation and magnetic properties of magnetic fluids**, Romanian Reports in Physics, 47, 249-264 (1995).

Massart R., Dubois E., Cabuil V., Hasmonay E., Preparation and properties of monodisperse magnetic fluids, J.Magn.Magn.Mater., 149, 1-5 (1995).

Charles S.W., **The preparation of magnetic fluids**, in: S. Odenbach (Ed) Ferrofluids. Magnetically controllable fluids and their applications, (Lecture Notes in Physics, 594; Springer-Verlag 2002) 3-18 (2002); .

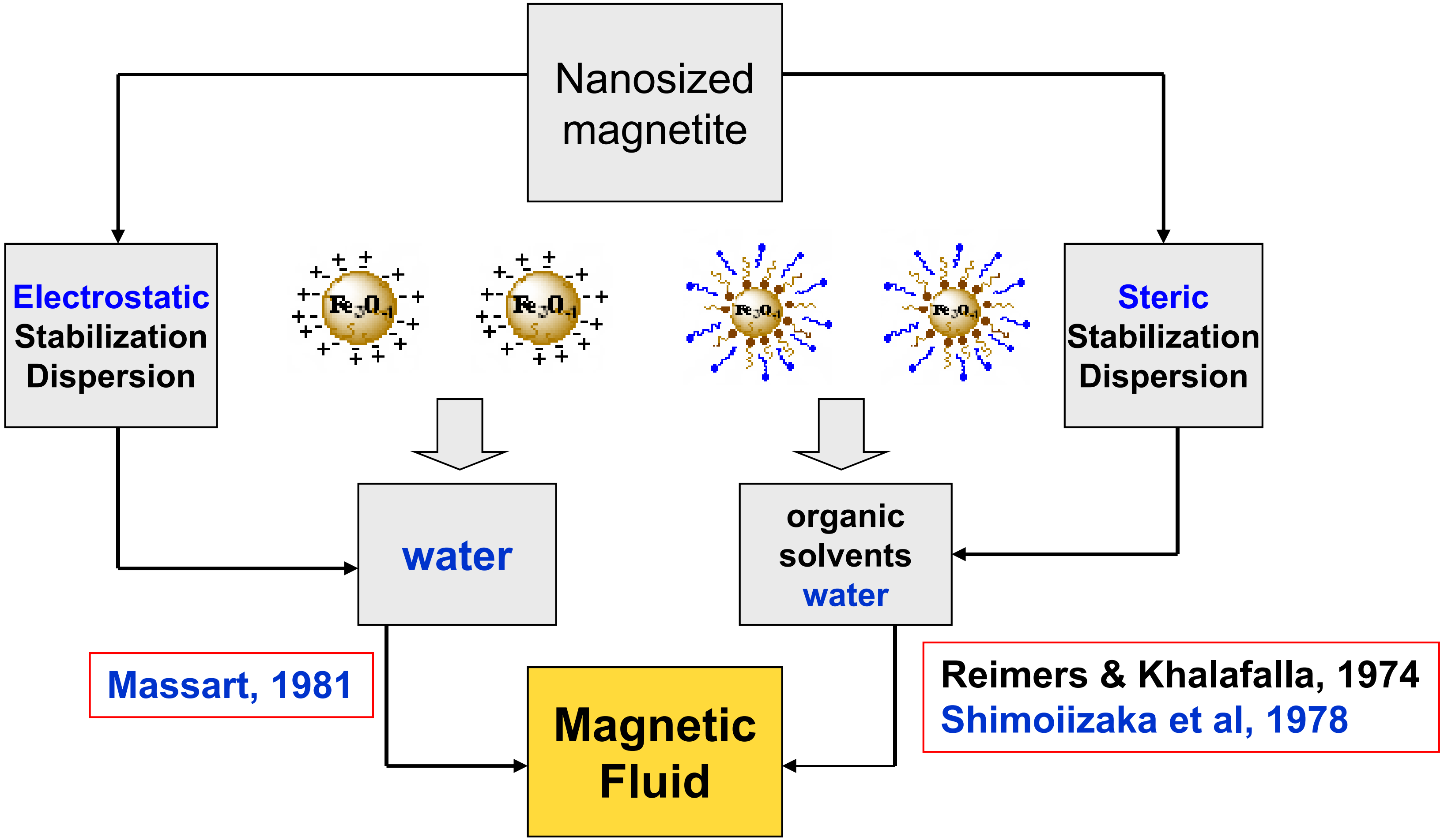
L. Vékás, M.V. Avdeev, Doina Bica, **Magnetic Nanofluids: Synthesis and Structure,** Chapter 25 in: **NanoScience in Biomedicine** (Ed. Donglu Shi) Springer (USA) 2009, pp.645-704

Riedl J.C., Sarkar M., Fiuza T., Cousin F., Depeyrot J., Dubois E., Mériguet G., Perzynski R., Peyre V., **Design of concentrated colloidal dispersions of iron oxide nanoparticles in ionic liquids: structure and thermal stability from 25 to 200◦C,** Journal of Colloid and Interface Science (2021)

Wang H, Chen S, Li H, Chen X, Cheng J, Shao Y, Zhang C, Zhang J, Fan L, Chang H, Guo R, Wang X, Li N, Hu L, Wei Y, Liu J, **A Liquid Gripper Based on Phase Transitional Metallic Ferrofluid**, Adv. Funct. Mater., 2100274 (2021)(9pg)

Magnetic fluid preparation by chemical co-precipitation

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow \mathbf{Fe_3O_4} + 4H_2O$$



Charles, S. W., in: S. Odenbach (Ed) *Ferrofluids. Magnetically controllable fluids and their applications* (Lecture Notes in Physics; **594**; Springer-Verlag 2002)

Good vs bad ferrofluid

Stability in magnetic field

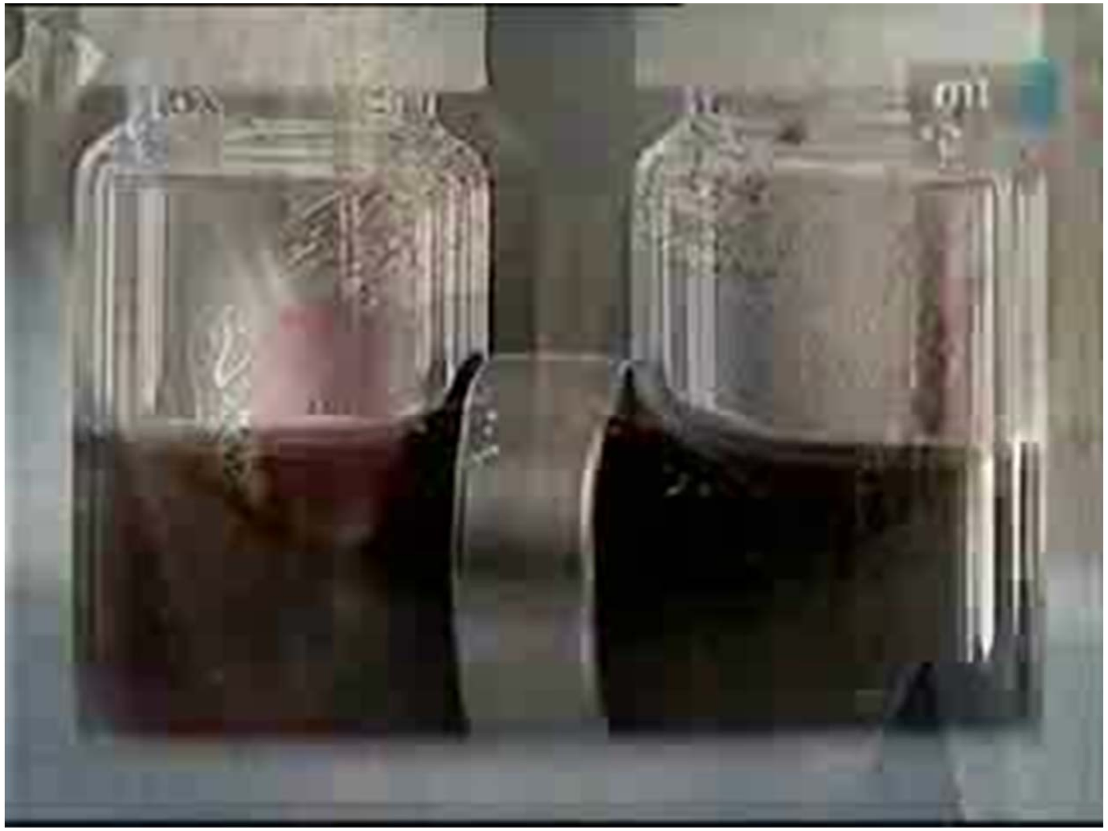
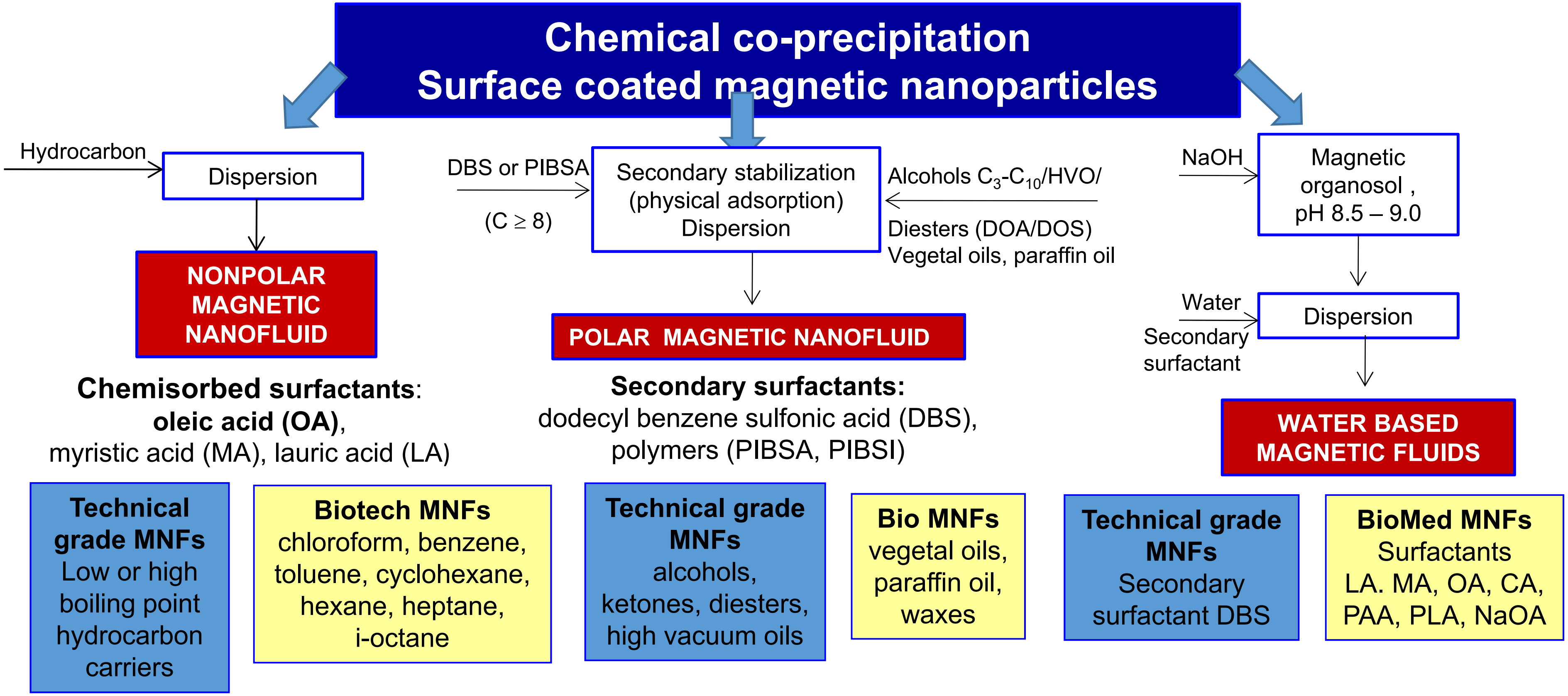


Illustration from Prof. Etelka Tombácz-Physical chemistry of colloids-Univ. of Szeged

Engineering and bio-ferrofluids

Synthesis



Laboratory of Magnetic Fluids Timisoara (Romania)

Over 50 types of ferrofluids

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)

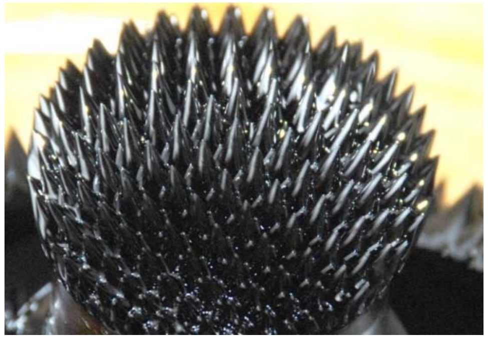
Doina Bica, Rom.Rep.Phys.(1995);E. Tombácz, Doina Bica et al., J Phys Condensed Matter(2008); L.Vékás, Doina Bica, M.V. Avdeev,*China Particuology* 5 (2007); L.Vékás, M.V. Avdeev, Doina Bica, in: D. Shi (Ed) NanoScience in Biomedicine (Springer, 2009); E.Tombácz et al COLSU A (2013); Vasilescu et al Soft Matter(2018)

An example of "long-term high colloidal stability" magnetic fluid….

Long-term highly stable magnetic fluid in non-uniform magnetic field

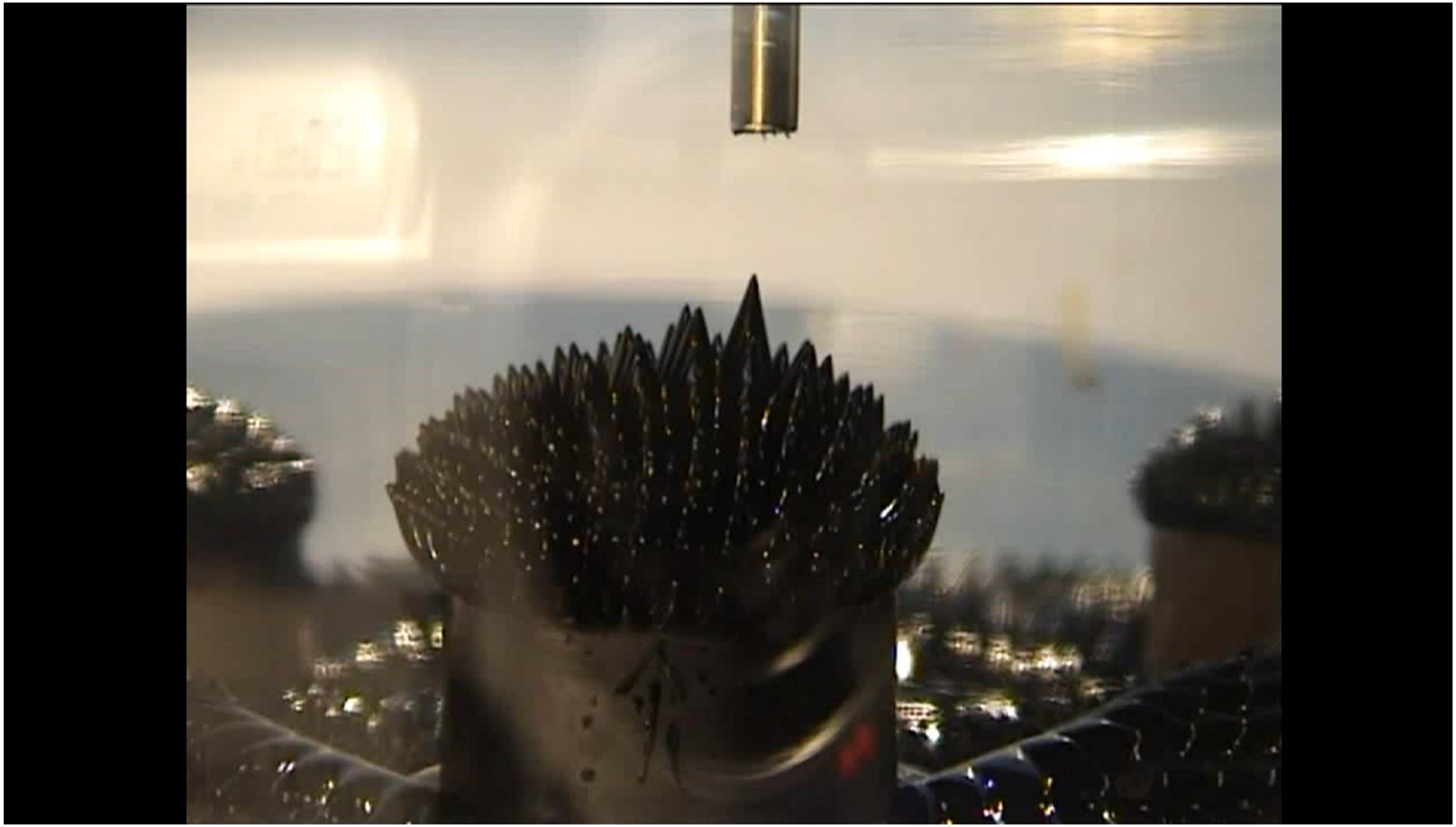
…stable over 39 years in non-uniform magnetic field…

About **one liter** sealing MF:
Low vapor pressure organic carrier
Saturation magnetization Ms≈ 500 G



Laboratory of Magnetic FluidsTimisoara

Synthesis

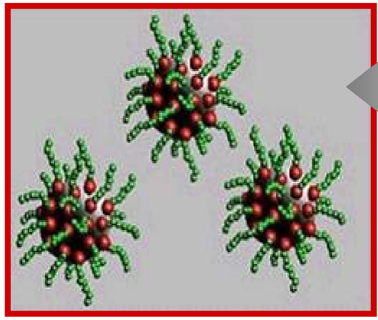


Particle sizes

Particle sizes and colloidal stability

Size of magnetic nanoparticles-an essential parameter

Optimal particle size and adequate stabilizing layer prevent gravitational settling and agglomerate formation by magnetic and van der Waals interactions



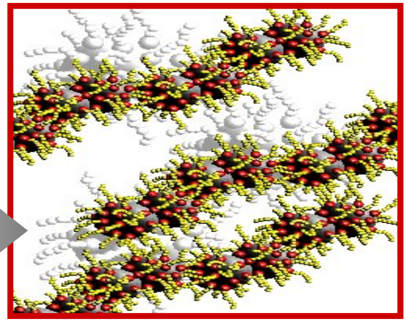
Stable FF, no agglomerates

$\lambda_{int} < 1$

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

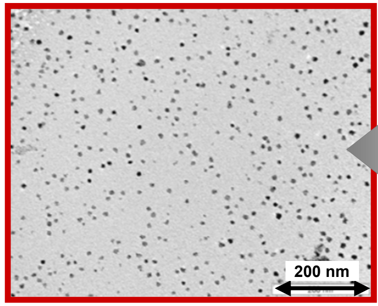
Non-dimensional dipolar interaction energy

$\lambda_{int} > 1$



Unstable FF, agglomerate formation

Magnetite nanoparticles

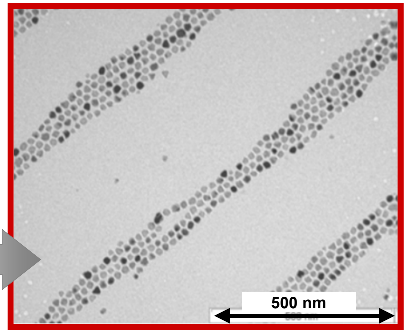


d_{TEM} = 9.0 nm
λ_{int} = 0.5

Cryo-TEM: FF/Decalin (OA)

LMF Timisoara

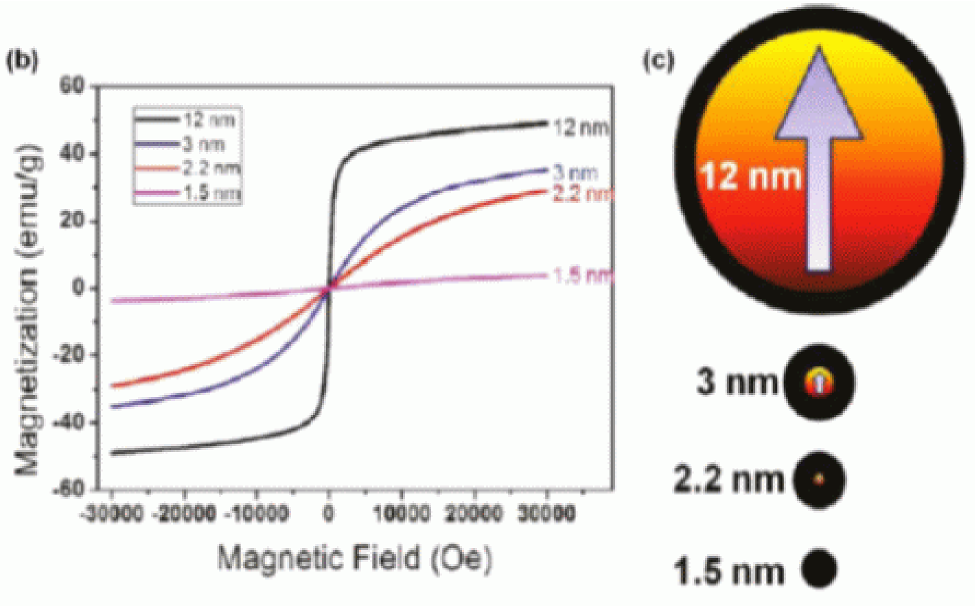
d_{TEM} = 18.6 nm
λ_{int} = 4.4



Cryo-TEM: FF/Decalin (OA)

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

Particle size and magnetic properties
"Magnetic" size of nanoparticles



Physical size
vs.
Magnetic size

Size-dependent magnetization – the spin-canting effect

(b) Field-dependent magnetization curves for various-sized NPs. The iron oxide USNPs were nearly paramagnetic

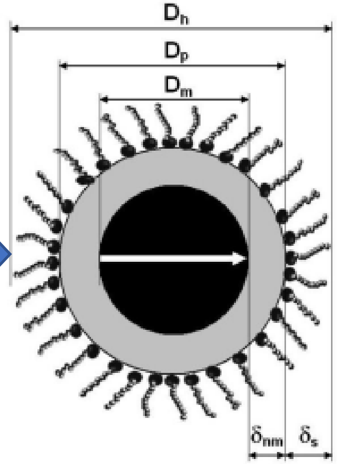
(c) Schematic illustration of the **spin-canting effect**. The spin-canted surface layers are assumed to be 0.9 nm thick, therefore **the magnetic size is less than the physical size** (TEM) of magnetic nanoparticles

Kim B.H., Hackett M.J., Park J., **Hyeon T.**, Synthesis, Characterization, and Application of Ultrasmall Nanoparticles, Chemistry of Materials, 26(1), 59-71 (2014).

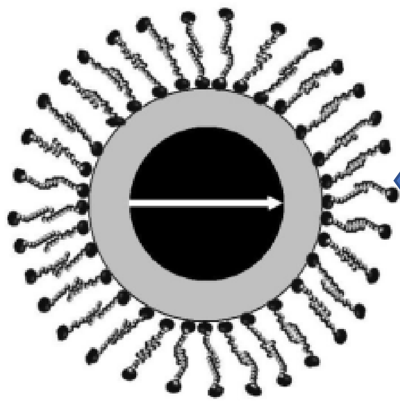
Characteristic particle sizes

Magnetic, physical and hydrodynamic sizes of dispersed magnetic nanoparticles

Stabilizing surfactant monolayer



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



Stabilizing surfactant bilayer

Ferrofluids-nonpolar carrier

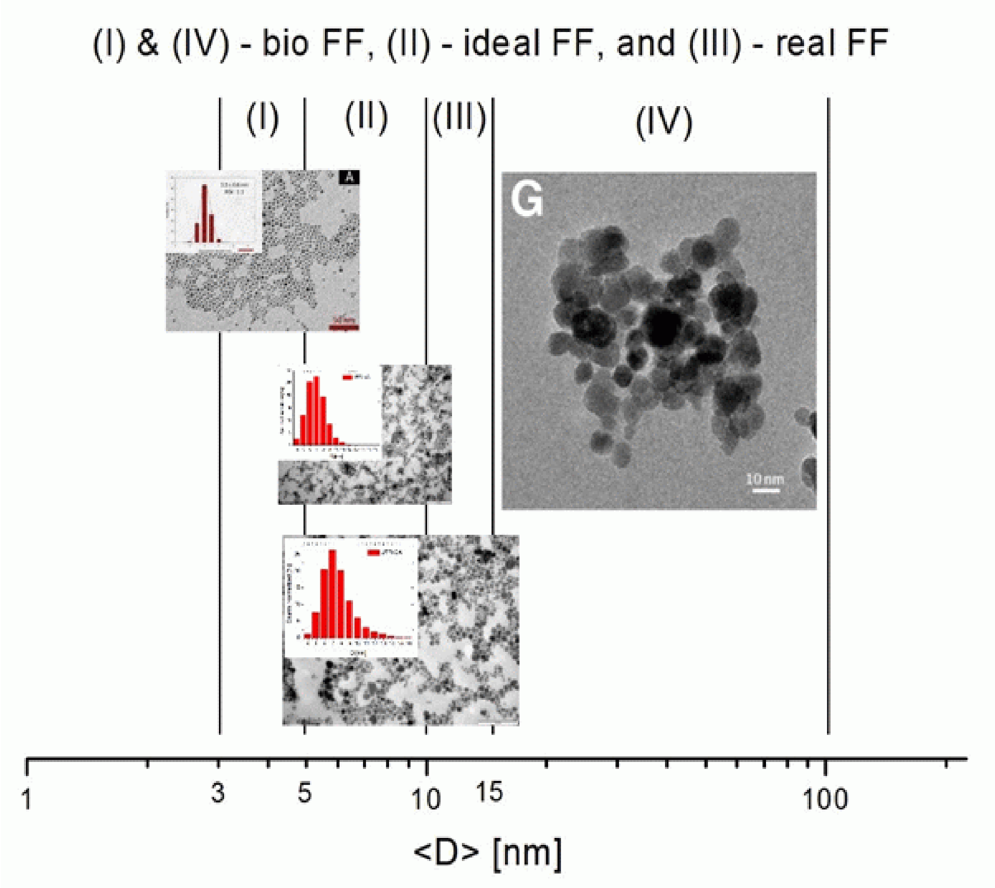
Ferrofluids-polar carrier

Magnetic size → Magnetic properties

Hydrodynamic size → Flow properties

Particle sizes and classification of ferrofluids

Engineering and bio-ferrofluids



Characteristic physical particle size ranges:

(I)**bio-ferrofluids** (**2-5 nm**) [Vangijzegem et al,NANOMATERIALS 10 (2020) 757(pp.17)];

(**II**) **ideal ferrofluids** (**5-10 nm**) and

(**III**) **conventional (real) ferrofluids** (**5-15 nm**) [Socoliuc et al 2021 (to be published)];

(**IV**) **bio-ferrofluids** (**15-100 nm**) [Ludwig et al, IEEE TRANSACTIONS ON MAGNETICS, VOL. 50(2014)]

Langevin model

Ideal ferrofluids-Monodisperse Langevin model

Magnetostatic properties

Identical size non-interacting MNPs dispersed in the carrier liquid; ***n*** particles in unit volume

Superparamagnetic gas approximation

$$U = -\mu_0 mH \cos\theta \quad \langle m\cos\theta\rangle = mL(\xi)$$

Particle with magnetic moment *m* in magnetic field *H*

$$L(\xi) = \coth\xi - \frac{1}{\xi} \qquad \xi = \frac{\mu_0 mH}{k_B T}$$

Langevin function; Langevin parameter

$$M = n\langle m\cos\theta\rangle$$

Magnetization of FF in magnetic field H
n-number density of MNPs

$$M_s = nm$$

Saturation magnetization

$$\phi_M = \frac{M_s}{M_d}$$

Volume fraction of magnetic NPs

$$M_L = \phi_M M_d\left(\coth\xi - \frac{1}{\xi}\right)$$

Langevin formula FF magnetization

$$\xi = \frac{\pi\mu_0 M_d D_m^3 H}{6k_B T}$$

D_m **Magnetic diameter**

$$L_\xi \to \frac{\xi}{3}$$

weak magnetic field

$$\chi_{iL} = \frac{\pi\mu_0 M_d^2 D_m^3 \phi_m}{18k_B T}$$

initial susceptivity

$$L_\xi \to 1 - \frac{1}{\xi}$$

strong magnetic field

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

magnetization

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

Real ferrofluids-polydisperse approximation

Magnetic granulometry-Chantrell model, 1978

Log-normal distribution of magnetic size x

$$f(x) = \frac{1}{xS\sqrt{2\pi}} exp\left(-\frac{ln^2 \frac{x}{D_0}}{2S^2} \right)$$

$$ln(D_0) = \langle ln(x) \rangle$$

S is the deviation of $ln(x)$ from $ln(D_0)$

$$S = \frac{1}{3}\sqrt{ln\frac{3\chi_{iL}H_0}{M_S}}$$

$$D_0^3 = \frac{18k_BT}{\mu_0\pi M_d}\sqrt{\frac{\chi_{iL}}{3H_0M_s}}$$

$$M_L = M_S\int_0^\infty L(\xi)f(x)dx$$

$f(x)dx$ probability to have the magnetic size $(x, x+dx)$

Chantrell R.W., Popplewell J., Charles S.W., Measurements particle size distribution parameters in ferrofluids, IEEE Trans.Magn., 14, 975-977 (1978).

Characterization

Characterization methods and equipments
Measurement & evaluation of properties

Particle size distributions:

TEM, HRTEM, XRD

Composition, stabilization procedures, colloidal stability, structural processes in magnetic field

SANS, SANSPOL, SAXS, XPS

Dilution stability, phase transition, stability in intense magnetic field

magneto-optical investigations, DLS, SLS

Flow properties in magnetic field:

Magnetorheological investigations

Rheometer MR

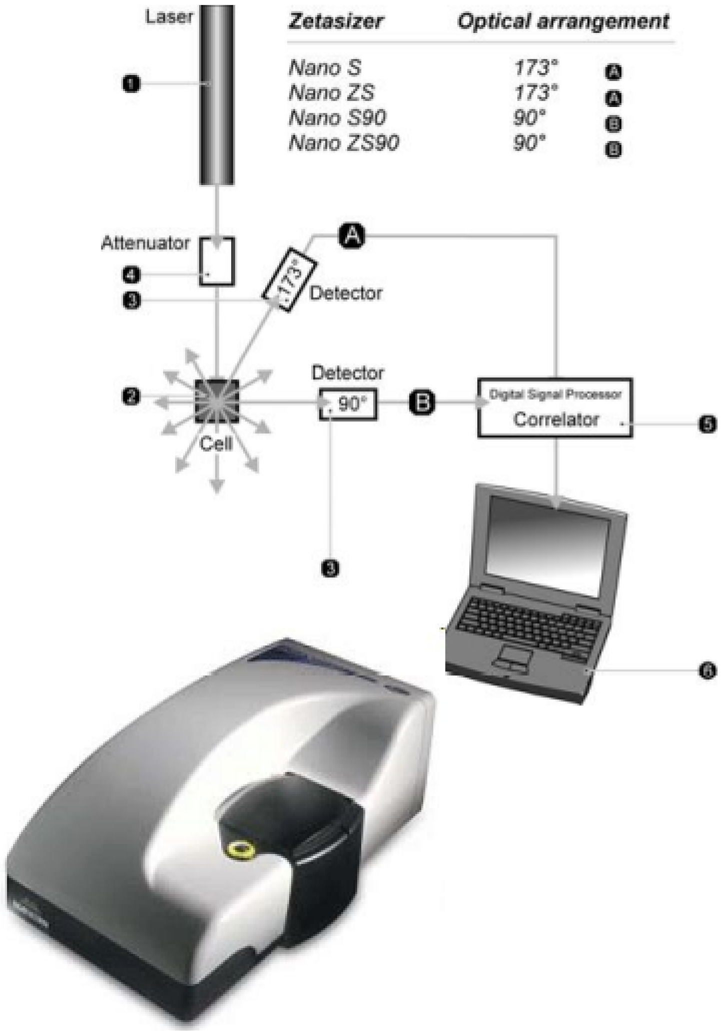
Magnetic properties vs. MNP volume fraction: **magnetometry *VSM, Mössbauer spectroscopy***

Radiation and thermal resistance

Chemiluminiscence, Differential scanning calorimetry

Application orientated selection of magnetic fluids

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:

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

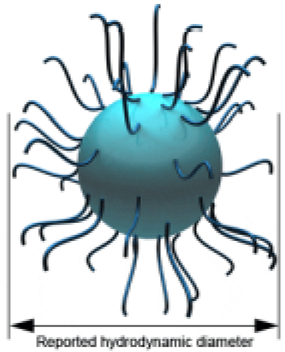
d(H) = hydrodynamic diameter

D = translational diffusion coefficient

k = Boltzmann's constant

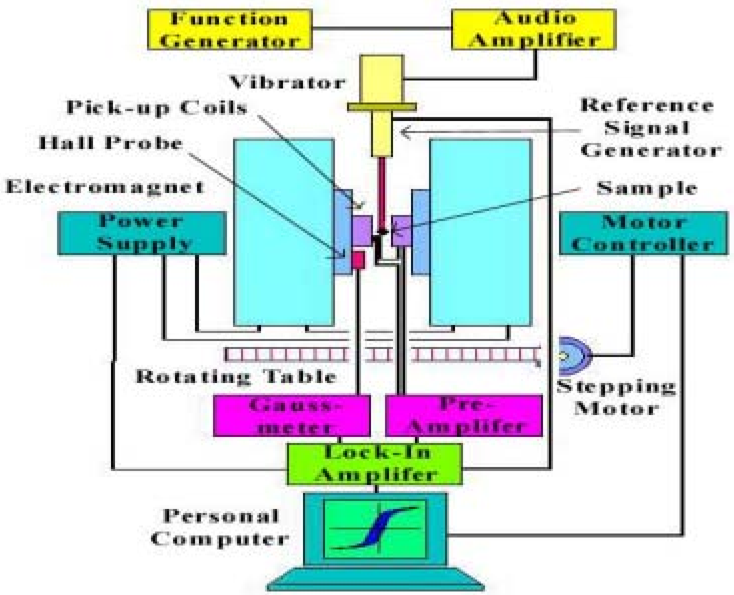
T = absolute temperature

η = viscosity



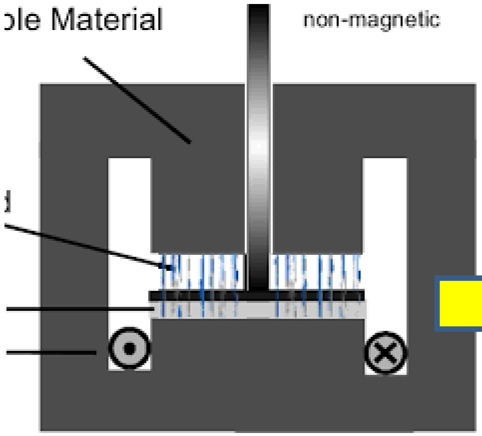
The method is applicable only for relatively dilute samples!

Vibrating sample magnetometer

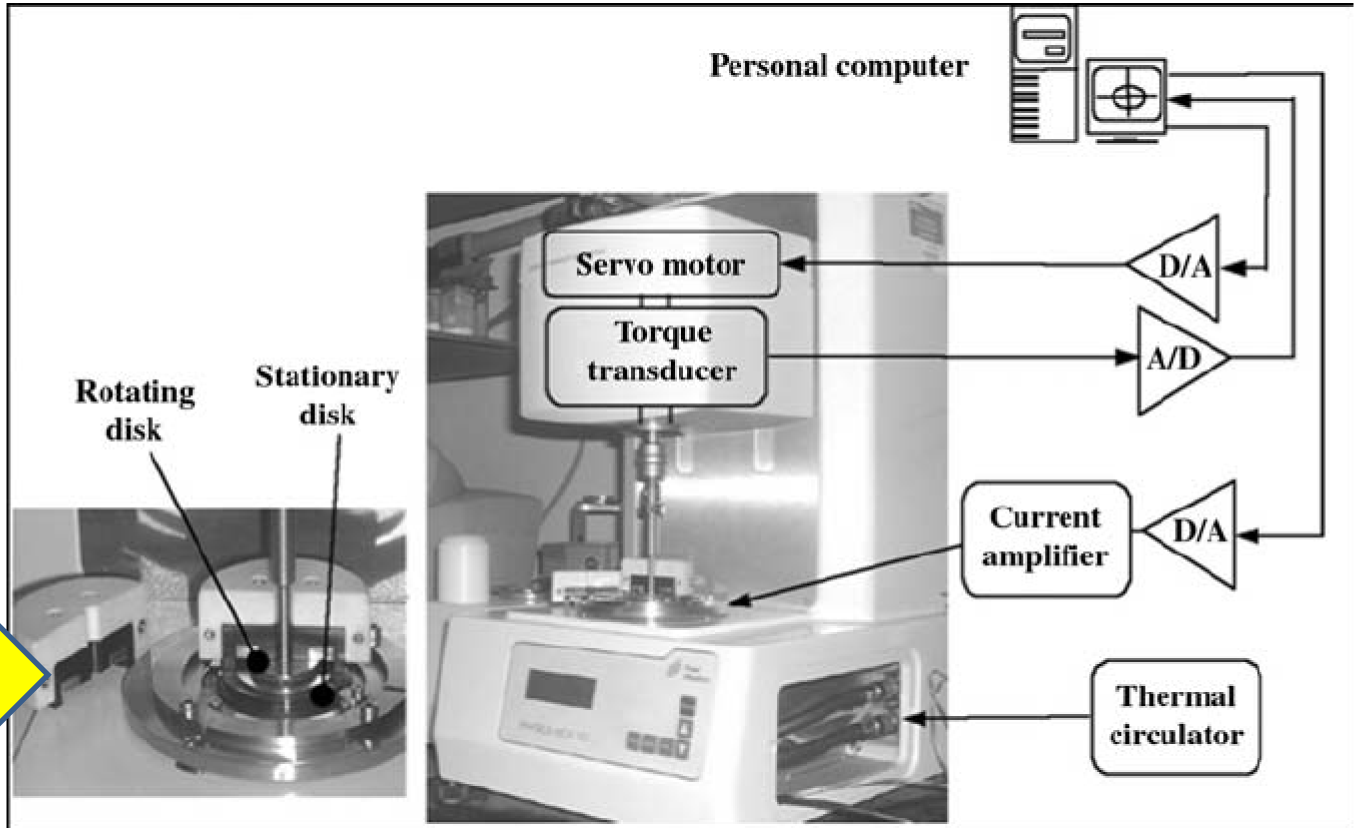


System diagram of Vibrating Sample Magnetometer

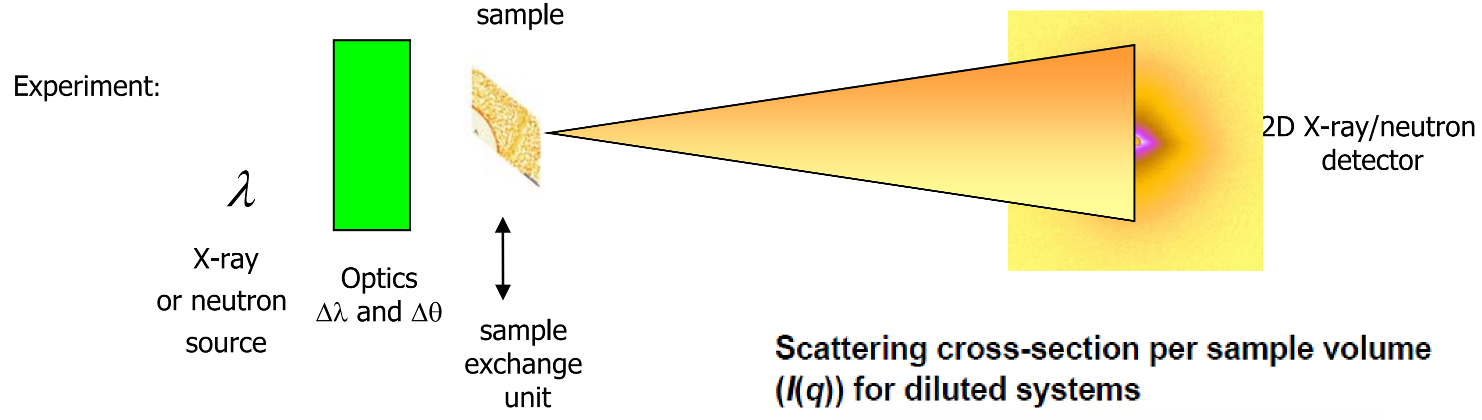
Rotational rheometer with magnetorheological cell



MR cell



Small Angle Neutron and X-ray Scattering facilities for structural investigations



Scattering wave vector q

$$q = \frac{4\pi \sin\theta}{\lambda}$$

Scattering cross-section per sample volume (*I*(*q*)) for diluted systems

$$\frac{d\Sigma}{d\Omega} = n\, V^2\, \Delta\rho^2\, P(q)$$

particle concentration (n), particle volume (V), particle contrast ($\Delta\rho$), particle form-factor ($P(q)$)

Structural investigations up to high volume concentration of as-prepared samples
These techniques evidence nanoparticles and agglomerates in the size range 1-100 nm

Important! The samples do not need any previous treatment (e.g., diluting and drying as for TEM)
"In vivo" investigations of magnetic fluids

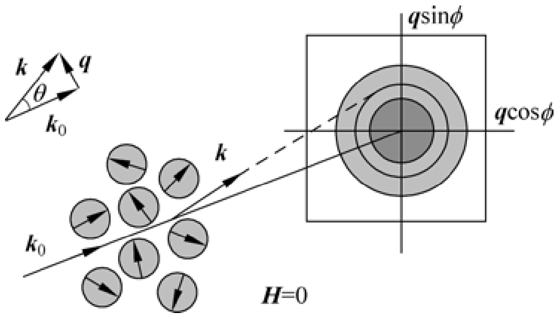
SANS: Particle interactions & structure formation

Particle structure

Particle interactions

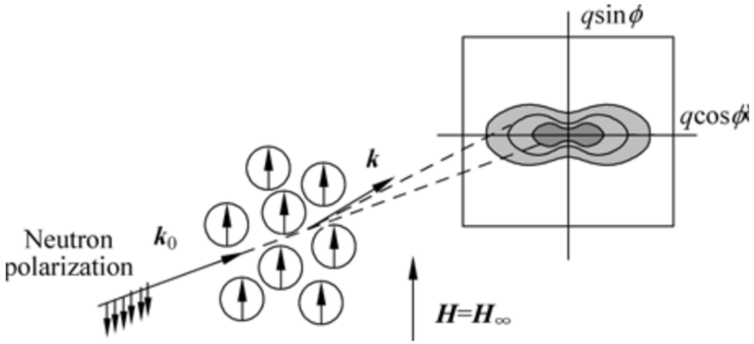
Cluster formation

FFs in zero field (B=0) conditions



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

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



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

M.V. Avdeev, V.L. Aksenov, **SANS in structure research of magnetic fluids**, Physics-Uspekhi 2010

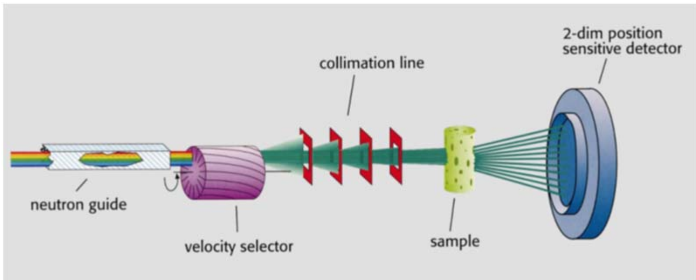
L. Vékás, M.V. Avdeev, Doina Bica, ***Magnetic Nanofluids: Synthesis and Structure***, Ch25 in: **NanoScience in Biomedicine** (Ed. Donglu Shi) Springer (USA) 2009

Neutron scattering facilities used (1)

(with applied magnetic field)

SANS-1 GKSS Geesthacht

SANS SzFKI Budapest



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

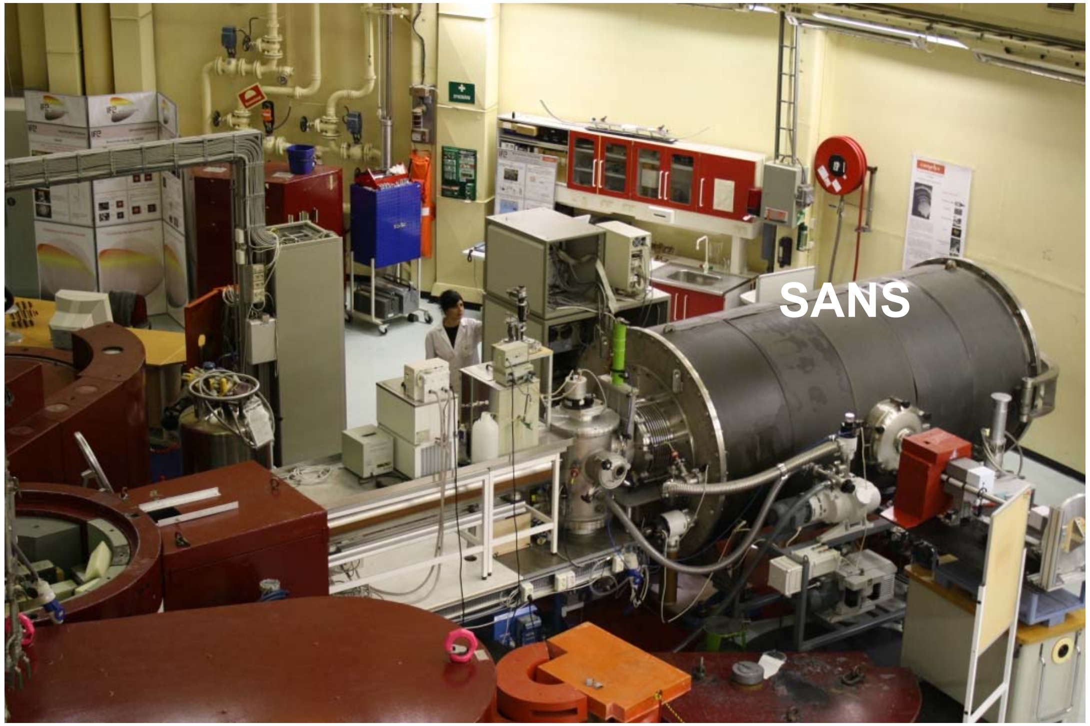
B= 2.5T

Budapest Neutron Center
“Yellow Submarine”

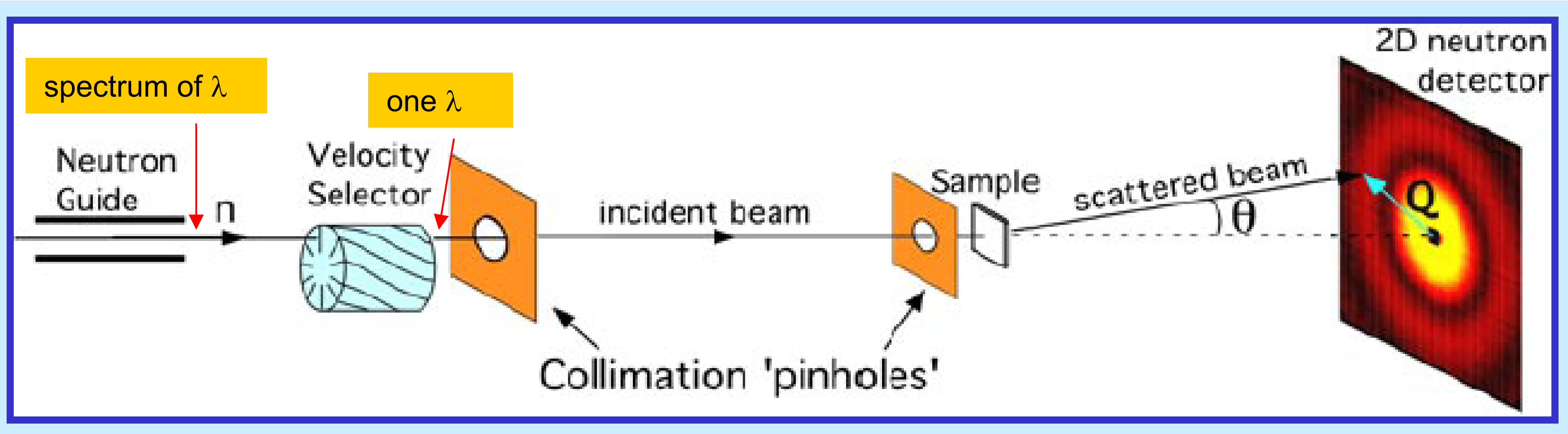
B= 1.7 T

SANS facilities used (2)

IFE Kjeller-Norway



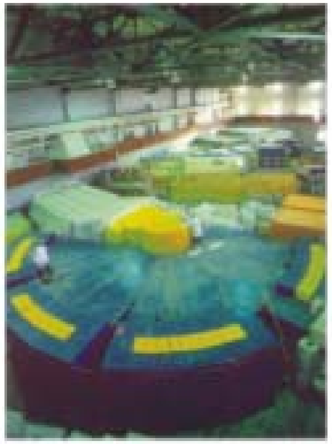
- Liquid H_2 cold source
- Long wavelengths (5-10 Å)
- Q-range: 0.008-0.35 $Å^{-1}$
- 7-position sample chamber

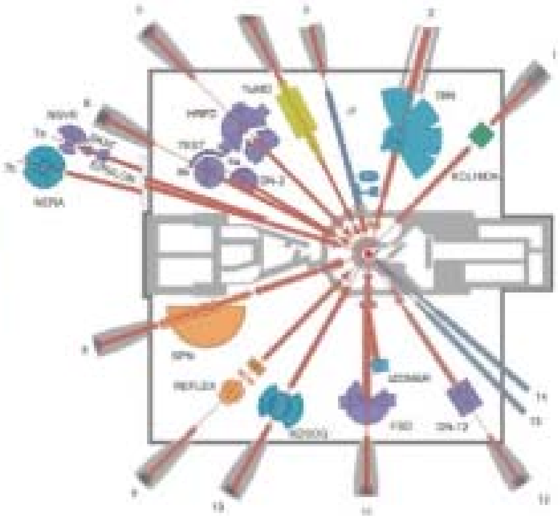


SANS facilities used (3)

IBR-2 Reactor Spectrometers Complex – the main JINR basic facility for condensed matter physics research with neutrons

JINR Dubna-Frank Laboratory of Neutron Physics

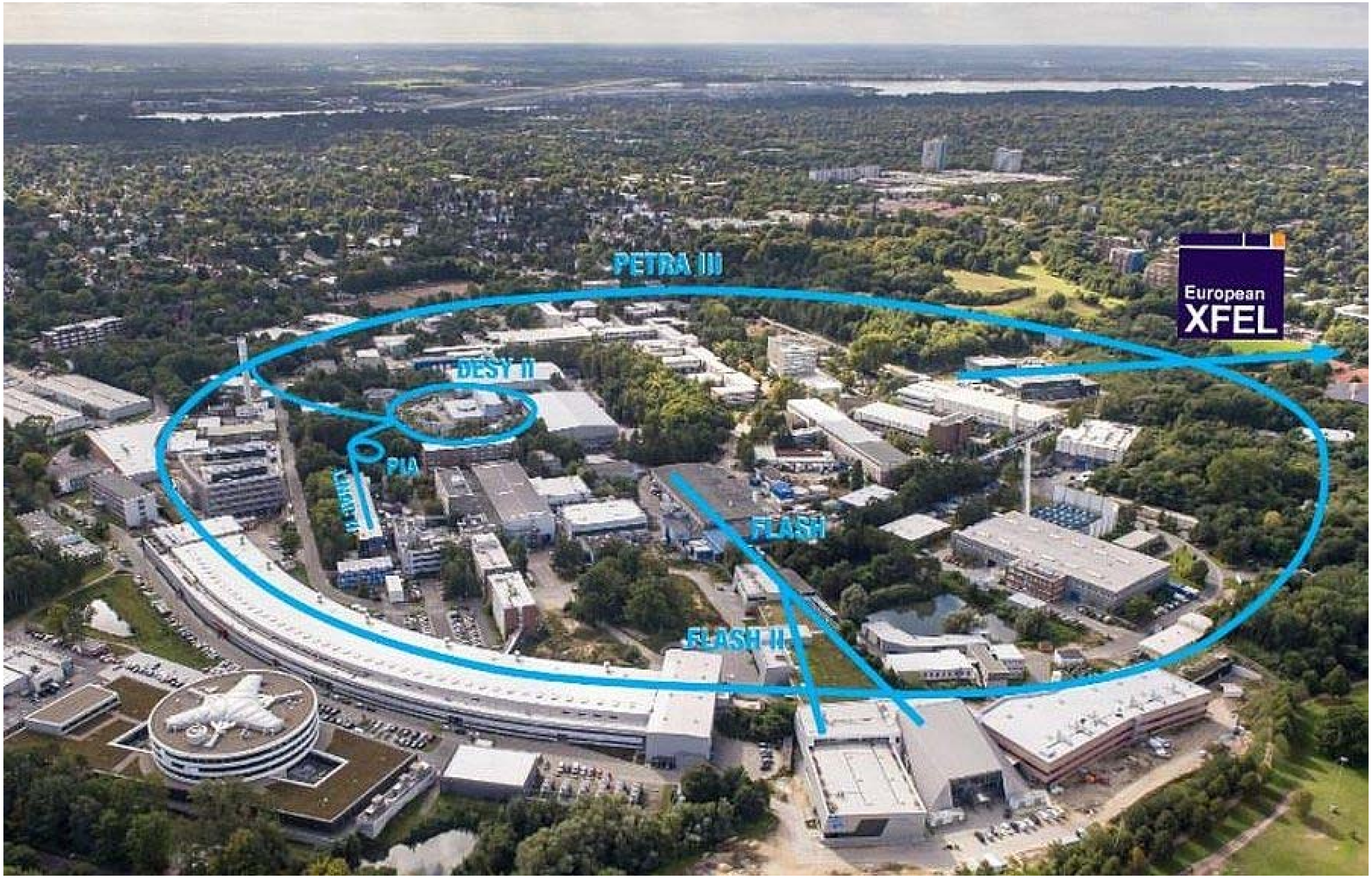




YuMo SANS facility; neutron reflectometer GRAINS

http://flnph.jinr.ru/en/facilities/ibr-2

German Electron Synchrotron-DESY Hamburg



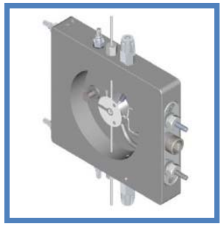
Small Angle X-ray Scattering (SAXS)

P12 BioSAXS facility at PETRA 3
HZG/EMBL/DESY Hamburg

- **photon energy** 4-20 keV
- **flux** ~10^{13} ph/s
- **beam size on sample** 200 x 110 μm^2

- **sample volume** ~ 20 μL
- **typical measurement time** 1 s
- **check of radiation damage**

Automatic sample changer, 1 min per sample including cleaning and drying



Controlling heating and cooling with rate up to 20 °C/min (Linkam Heating Stage)

Variable sample to detector distance from 1.5 m to 6 m
for length scale of studied objects from about 1000 to 0.1 nm

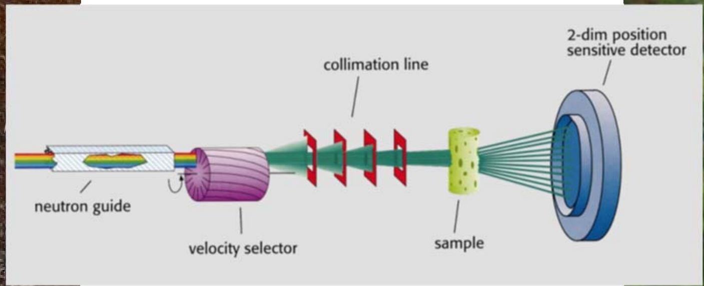
https://www.desy.de/index_eng.html
https://www.embl-hamburg.de/biosaxs/p12/

A joke! …. about the PRECISION of scattering techniques

Material supposed to nuclear scattering

Result of scattering data interpretation

Venus from Milo
The Louvre Museum

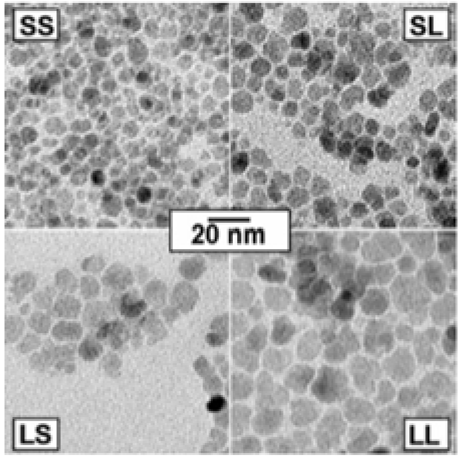


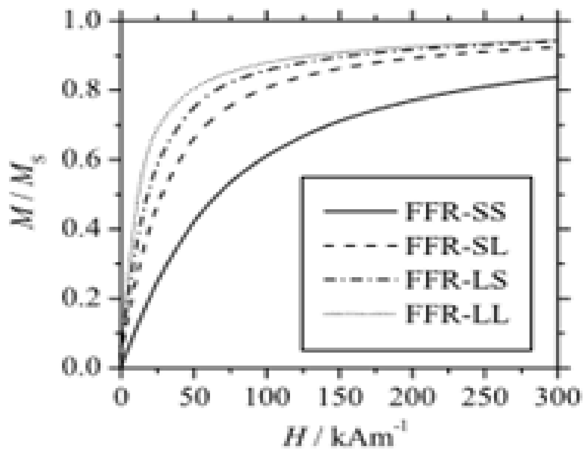
CERN preprint
Early sixties
last century
(adapted)

Statue at Devil's Hole in Jersey, the largest of the Channel Islands between England and France

Polydisperse real ferrofluid
Particle size analysis-an example

High colloidal stability cyclohexane based ferrofluid (FFR)





Sample	$d_c(nm)^a$	$d_{M\,(nm)}{}^b$	$\rho_{dry}(kg\ m^{-3})$	λ
Unfractionated FFR	9.1	11.3	2900	0.40
Fraction FFR-SS	7.9	7.7		0.25
Fraction FFR-SL	9.7	9.9		0.55
Fraction FFR-LS	11.4	11.7		1.0
Fraction FFR-LL	15.0	15.22	3630	2.7

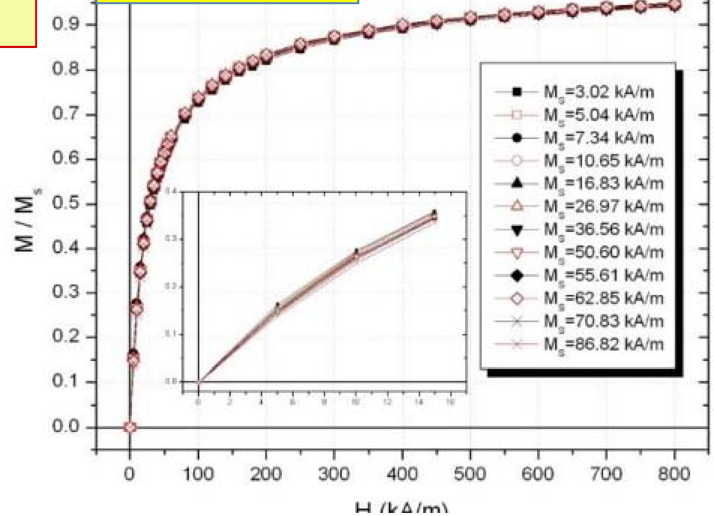
van Ewijk G A, Vroege G J, Philipse A P, Susceptibility measurements on a fractionated aggregate-free ferrofluid,
J. Phys.: Condens. Matter. 14 (2002) 4915–4925

Van’t Hoff lab of Colloids
Univ. Utrecht

Real ferrofluids
Magnetization curves-influence of particle agglomerates

Well screened particle interactions

no agglomerates evidenced

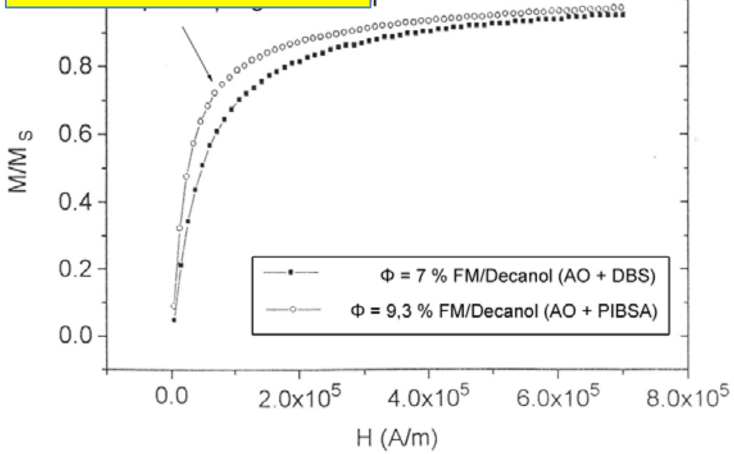


High colloidal stability magnetic fluid (non-polar hydrocarbon, low vapor pressure). Non-dimensional magnetization curves for samples having different values of saturation magnetization Ms = 3.02–86.82 kA/m

Raşa M., Bica D., Philipse A., Vékás L., Dilution series approach for investigation of microstructural properties and particle interactions in high-quality magnetic fluids, Eur.Phys.J.E, 7, 209-220 (2002).

Irreversible particle agglomerates Practically absent up to close packing

agglomerates evidenced



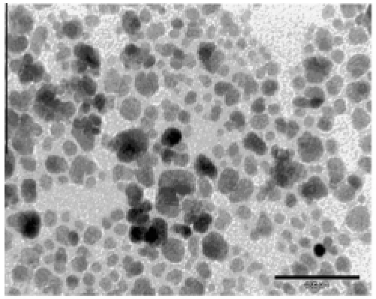
Polar (decanol) based FFs
Oleic acid (AO) + dodecylbenzene sulphonic acid (DBS) double layer; physical vol fraction 7%
Oleic acid (AO) + Polyisobutylene Succinic Anhydride (PIBSA) double layer; physical vol fraction 9.3%
Secondary stabilizant PIBSA less efficient than DBS

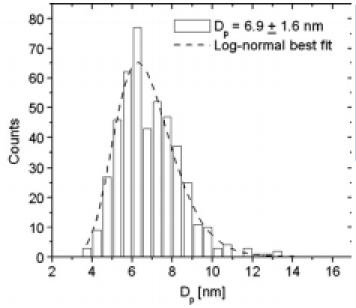
Effect of less efficient stabilization

Real ferrofluid-magnetic, physical and hydrodynamic sizes

Transformer oil based ferrofluids-about the quality of particle surface coating
Micropilot scale samples (13) (ROSEAL Co-Romania)

Physical vol fraction = 0.8% ... 21% (magnetite NPs)
Carrier liquid: transformer oil (MOL TO 40A)
Surfactant: **vegetable oleic acid**, product 100471 Merck,
approx. 10% saturated carboxylic acids (stearic, palmitic)





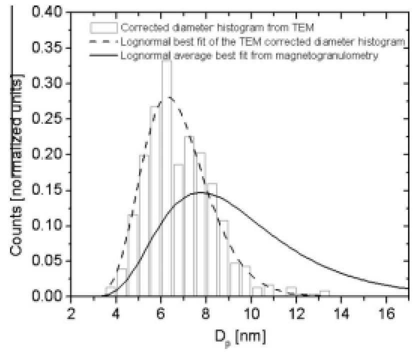
The use of
a relatively
cheap surfactant

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

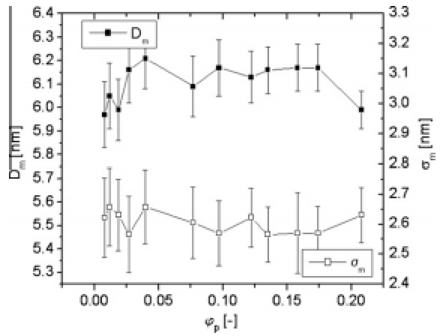
The mean hydrodynamic diameter obtained
from DLS is between 17.4-18.9 nm

Reduced
particle clustering
approx. 2 particles/cluster

Susan-Resiga D., Socoliuc V., Boros T., Borbáth T., Marinică O., Han A., Vékás L., The influence of particle clustering on the rheological properties of highly concentrated magnetic nanofluids, J. Coll. Interface Sci., 373, 110-115 (2012).



Physical diameter distributions as obtained
from TEM and magnetogranulometry

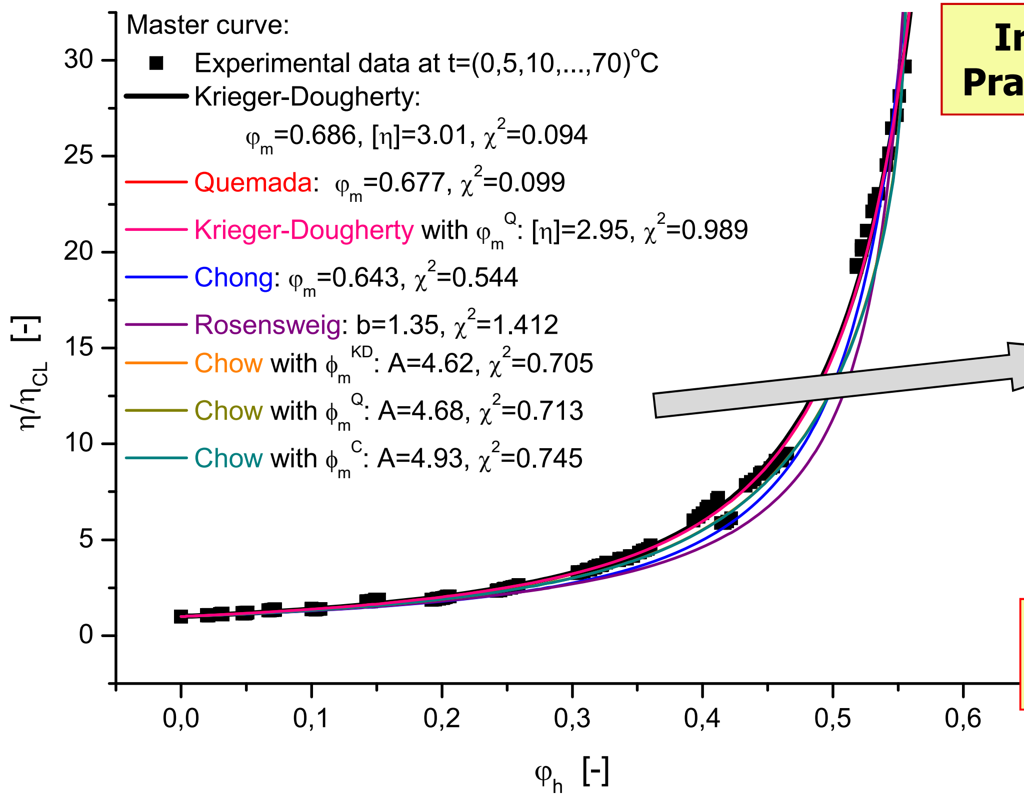


Fit results for the magnetic diameter distribution
(the bars represent the fit errors)

Real ferrofluids-Flow test
Efficiency of stabilization

Ferrofluid samples/Hydrocarbon carrier (transformer oil; tehnical oleic acid surfactant)

Non-dimensional dynamical viscosity vs. hydrodynamic volume fraction: 0 - 0.60
Saturation magnetization: M_s= 40 -1100 G Temperature range t = 0 – 70 ^{0}C



Irreversible particle agglomerates Practically absent up to close packing

A_{theor} = 4.67
A_{exp} ≈ 4.70

Negligible magnetic interaction between particles

Long-term high colloidal stability

Formula of Chow, PhysRev E 1994

$$\eta = \eta_{CL}\left[exp\left(\frac{2.5\,\varphi_h}{1-\varphi_h}\right)+\frac{A\varphi_h^2}{1-A\varphi_h^2\,\varphi_m}\right]$$

Daniela Susan-Resiga, L. Vekas, RomRepPhys 2018

Susan-Resiga D. et al, J. Coll. Interface Sci (2012)

Concentrated aqueous ferrofluids

An example of manifold comparative analysis

Electrostatic vs electrosteric stabilization

Chemical coprecipitation
Atmospheric conditions

Electrostatic stabilization
Massart 1981

XPS analysis
Fe^{3+}/Fe^{2+} = **2.08** for Fe_3O_4/CA
Fe^{3+}/Fe^{2+} = **2.20** for Fe_3O_4/OA+OA

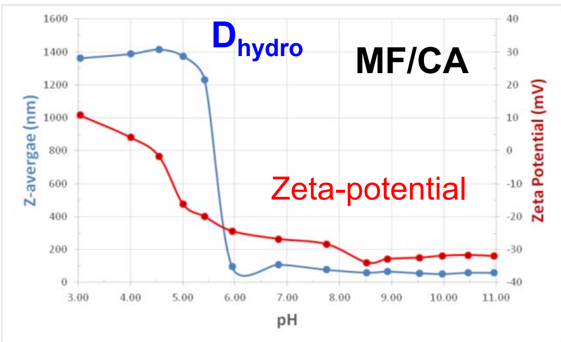
Electrosteric stabilization
Shimoiizaka et al 1980

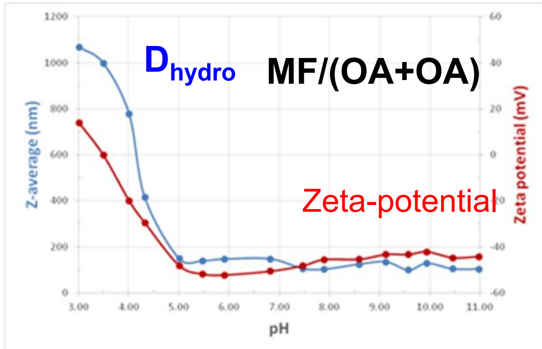
Aalto Univ.
Finland

Magnetic nanoparticles: **magnetite**
Physical vol fraction: 20% v/v
Particle size: 5.9±2.5 nm
Stabilizant: citric acid (CA)
Stabilizant layer thickness: approx 0.5 nm
Hydrodynamic vol fraction: approx **30%** v/v
Saturation magnetization: 78.20 kA/m (**982 G**)
Timonen J V I et al., Science 2013
Sahoo Y et al., J. Phys. Chem. B 2005

Lab MF
Timisoara
Romania

Magnetic nanoparticles: **magnetite**
Physical vol fraction: 14% v/v
Particle size: 7.8±1.9 nm
Stabilizant: oleic acid double layer (OA+OA)
Stabilizant layer thickness: approx 3.5 nm
Hydrodynamic vol fraction: approx **30%** v/v
Saturation magnetization: 48.73 kA/m (**612 G**)
Bica D et al., J Magn Magn Mater2007
Tombácz E, Bica D et al., J Phys Condens Matter2008

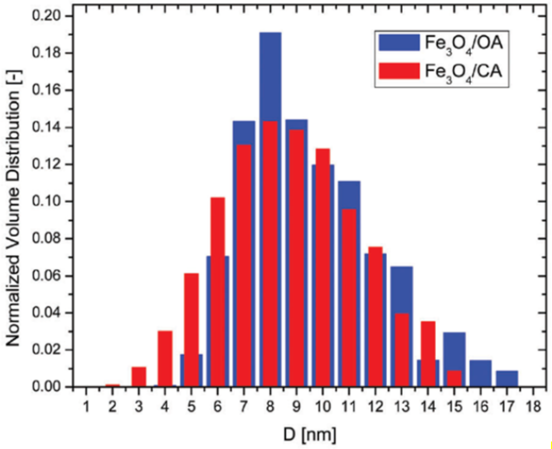


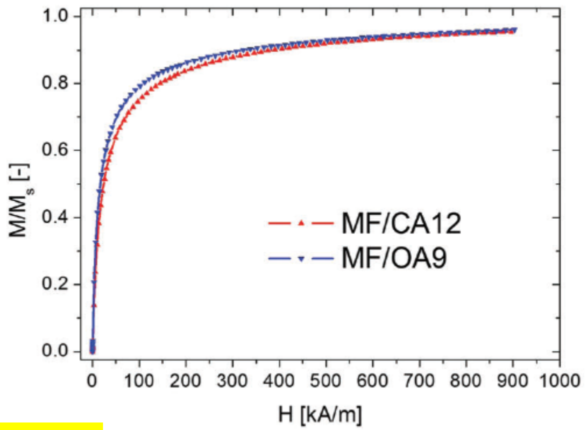


Dynamical Light Scattering investigation

Concentrated aqueous ferrofluids

MF/CA and MF/OA+OA – Magnetization & Particle sizes





Physical size

Sample	Number of particles	Mean [nm]	St.Dev [nm]	Skewness [-]
Fe_3O_4/CA	1215	**5.9**	2.5	0.6
Fe_3O_4/OA+OA	1014	**7.8**	1.9	1.0

Magnetic size

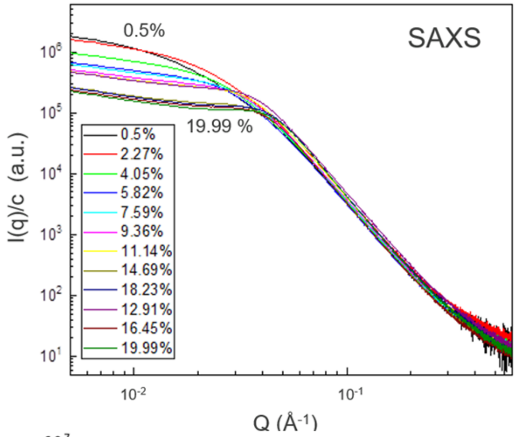
Sample	χ_0 [-]	M_S [kA/m]	M(1/H) Lin. Fit R^2	n [x10^{22} part/m^3]	D_0 [nm]	σ [-]	Fit R^2	Φ_m [-]	<D_m> [nm]	δ_m [nm]
MF/CA12	3.0	**78.20**	0.996	86.72	5.35	0.39	0.9999	0.14	**5.8**	2.3
MF/OA9	3.6	**48.73**	0.991	39.91	6.23	0.39	0.9997	0.10	**6.7**	2.7

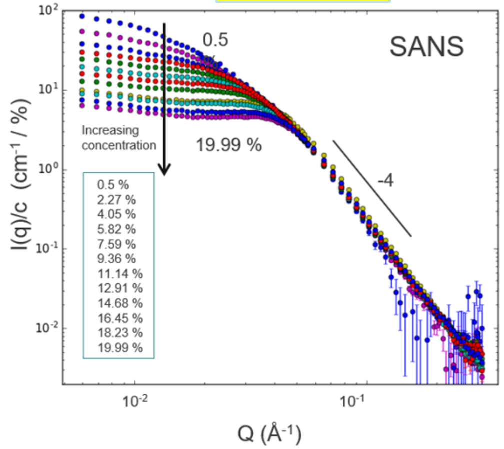
Concentrated aqueous ferrofluids

Particle interactions-SAXS and SANS investigations

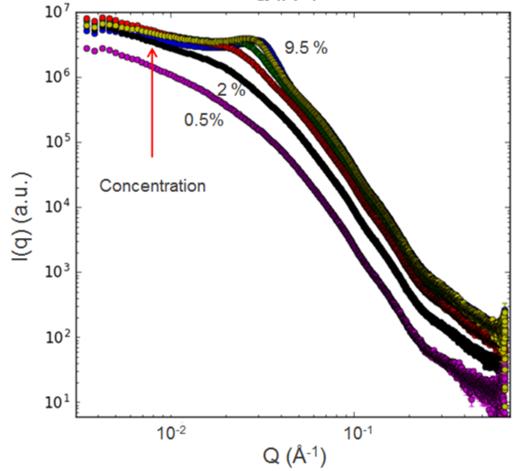
SAXS **SANS**

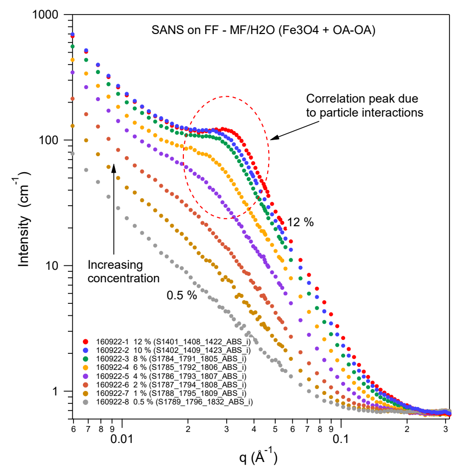
Electrostatic stabilization
MF/Citric Acid
No agglomerates





Electrosteric stabilization
MF/oleic acid double layer
Agglomerates evidenced





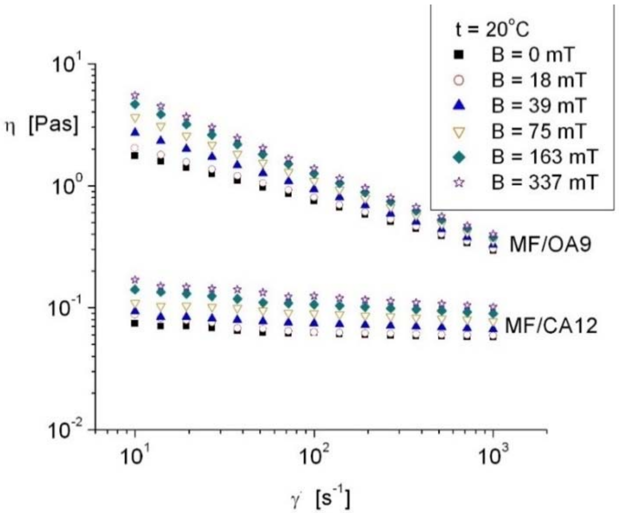
SAXS-DESY Hamburg

SANS-IFE Kjeller

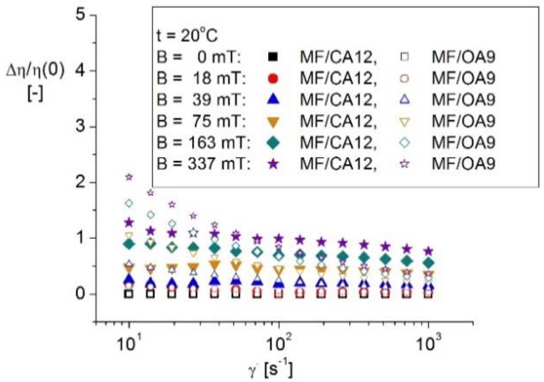
Concentrated aqueous ferrofluids

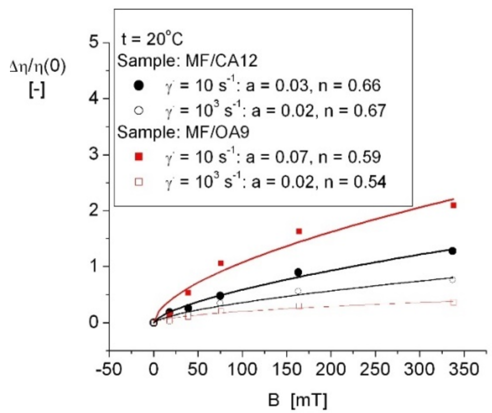
Particle interactions-Magnetorheological investigations

The role of stabilization mechanism-MF-water/CA and MF-water/(OA+OA)



Magnetorheology clearly differentiate between electrostatic (citric acid-electric double layer) and electrosteric stabilization (oleic acid double layer)



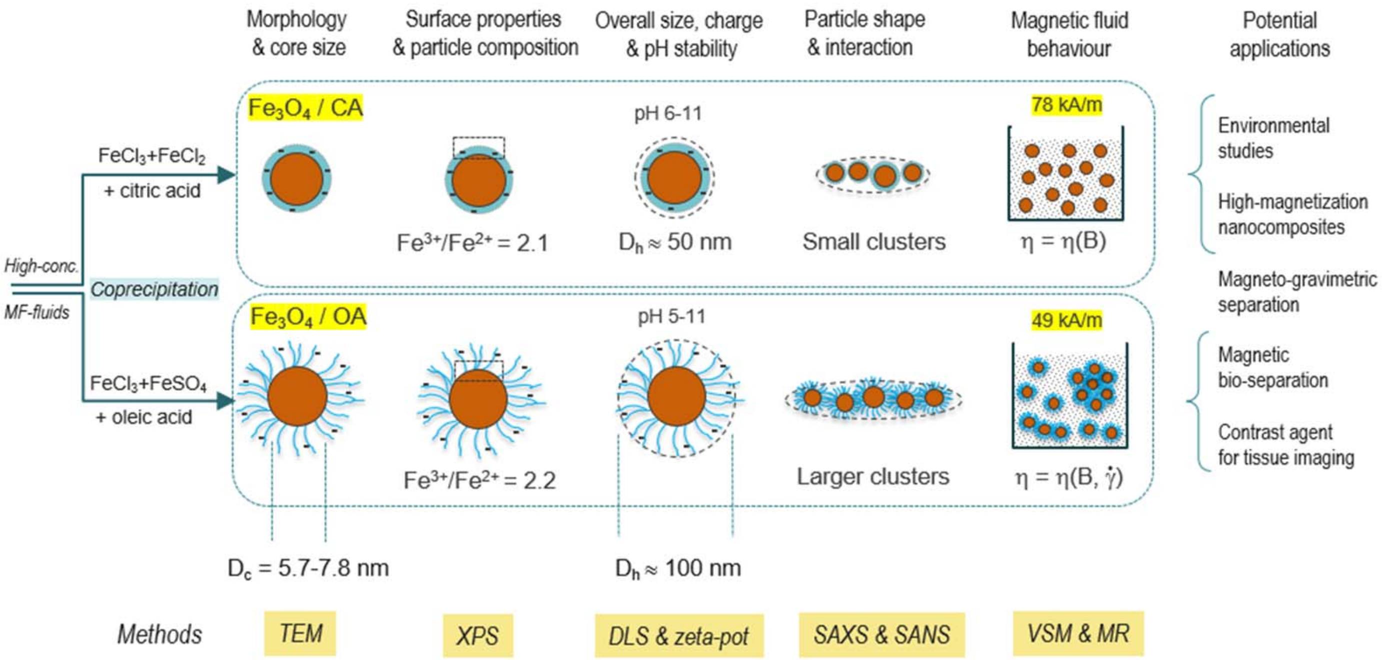


Viscosity curves and magnetoviscous effect for the highest concentration MF/CA (physical vol fraction 20%) and MF/(OA+OA) (physical vol fraction 14%) samples at different magnetic field strengths

Concentrated aqueous ferrofluids

Electrostatic vs electrosteric stabilization

Manifold comparison



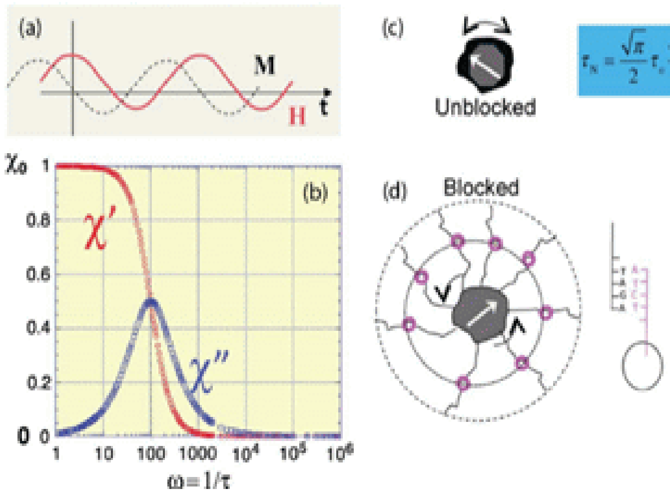
Corina Vasilescu, M. Latikka, K. D. Knudsen, V.M. Garamus, V. Socoliuc, Rodica Turcu, Etelka Tombácz, Daniela Susan-Resiga, R.H.A. Ras, L. Vékás, Soft Matter (2018)

Ferrohydrodynamics

Relaxation of magnetization

Response of MNPs suspended in a viscous carrier to a.c. magnetic fields

Orientation of magnetization vector **M** relative to the a.c. applied field **H** strongly dependent on magnetic material, particle size and carrier viscosity



$$\tau_N = \frac{\sqrt{\pi}}{2}\tau_0 \frac{\exp(KV_M/k_BT)}{(KV_M/k_BT)^{1/2}}$$

Néel relaxation time

$$\tau_N = \tau_0 e^{\sigma}$$

$$\sigma = \frac{KV_m}{k_BT}$$

$$\tau_B = \frac{3\eta V_H}{k_BT}$$

Brown relaxation time

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

Effective relaxation time

χ'- real (in phase) component
χ''- imaginary (loss) component

K-magnetic anizotropy constant
η- carrier liquid viscosity

R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ Press1985
K. M. Krishnan, *Biomedical Nanomagnetics*: A Spin Through Possibilities in Imaging, Diagnostics, and Therapy, IEEE Trans Magn 2010;
Stierstadt K, Liu M, Maxwell's stress tensor and the forces in magnetic liquids, ZAMM•Z. Angew. Math. Mech., 1–34 (2014);
Shliomis M I, Ferrohydrodynamics: Retrospective and Issues, in: S. Odenbach, Ed., Ferrofluids. Lecture notes in Physics 594 (Springer Verlag, 2002) pp.85-111

Quasistationary appproximation

$$\vec{M} \; II \; \vec{H}$$

Relaxation time-
Negligible/very short

$$\overline{f}_v = \mu_0 M \nabla H$$

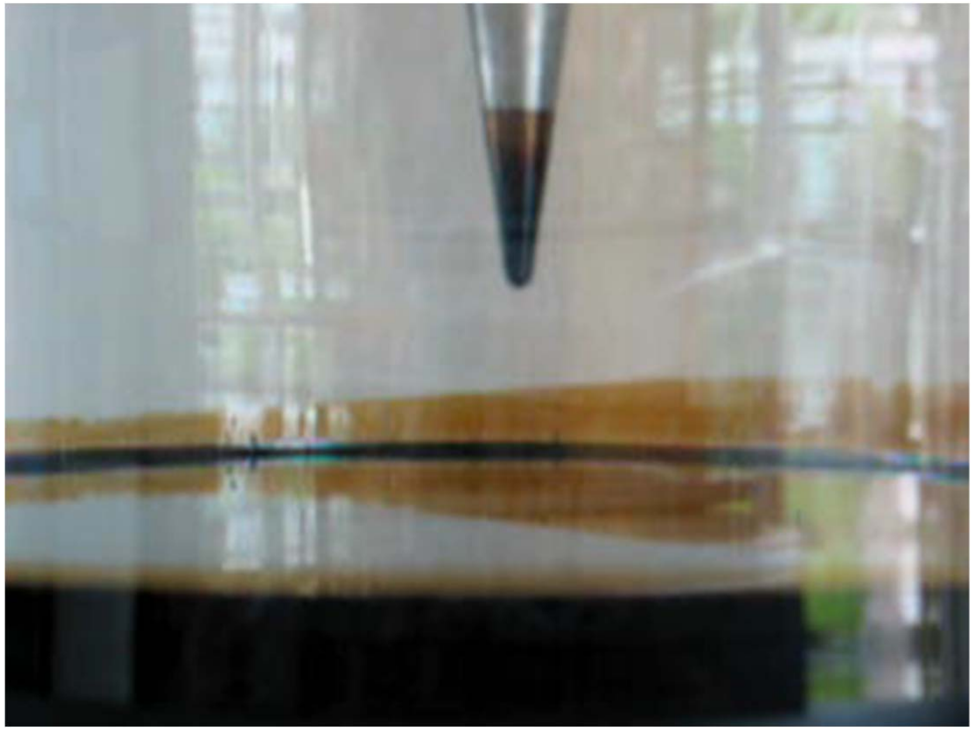
Magnetic force/ unit volume

$$\rho\left[\frac{\partial \overline{v}}{\partial t} + \left(\overline{v}\nabla\right)\overline{v}\right] = -\nabla p + \mu_0 M \nabla H + \rho \overline{g} + \eta \nabla^2 \overline{v}$$

Navier-Stokes equation in quasistationary ferrohydrodynamics

R.E. Rosensweig, Ferrohydrodynamics,
Cambridge Univ Press1985

Magnetic force much higher than gravitational force



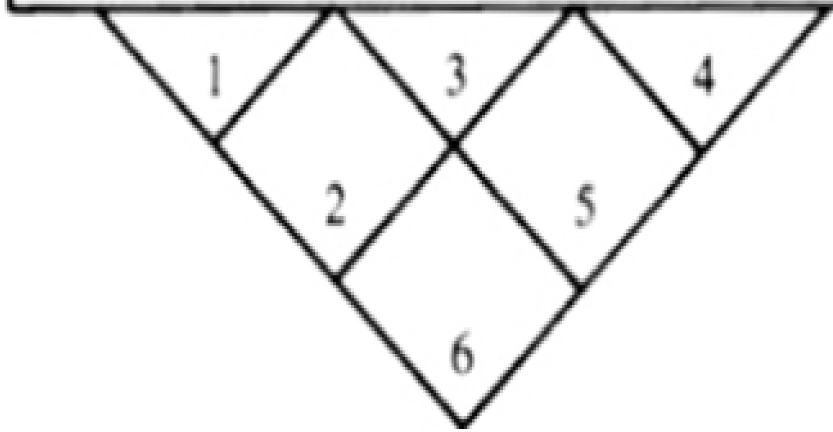
Normal field instabilities induced by a magnetic field
mineral oil based Ferrofluid-Doina Bica-Lab MF Timisoara
Exhibition-100 years anniversary of the van't Hoff laboratory-University Utrecht-2004
Courtesy of Prof. Albert Philipse

Bernoulli relationship in ferrohydrodynamics

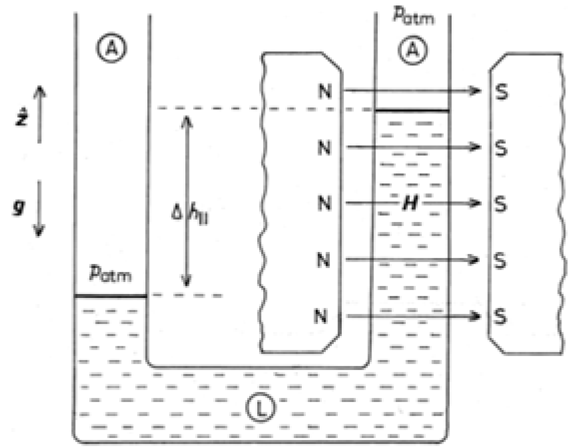
Magnetic pressure

$$p_m = \mu_0 \int_0^H M\,dH = \mu_0 \bar{M} H$$

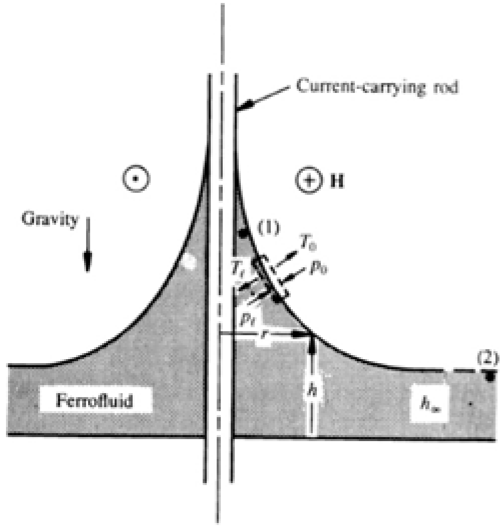
$$p^* + \rho \frac{v^2}{2} + \rho g h - \mu_0 \bar{M} H = \text{constant}$$

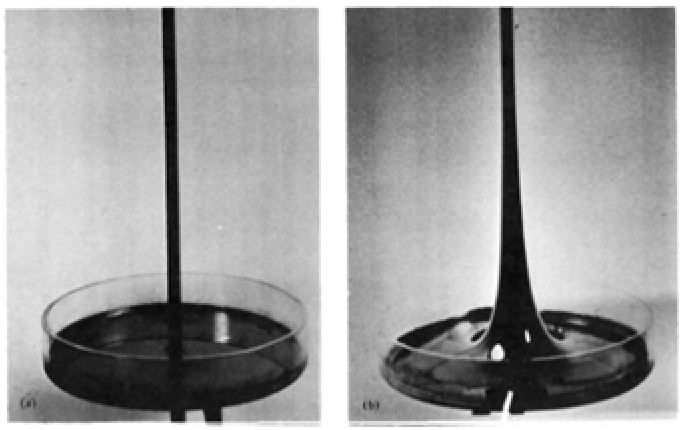


R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ Press1985



The classical **Quincke experiment**
(magnetic susceptivity of liquids)
Rise of magnetic fluid between the poles
of a magnet-category 4 of FF behavior



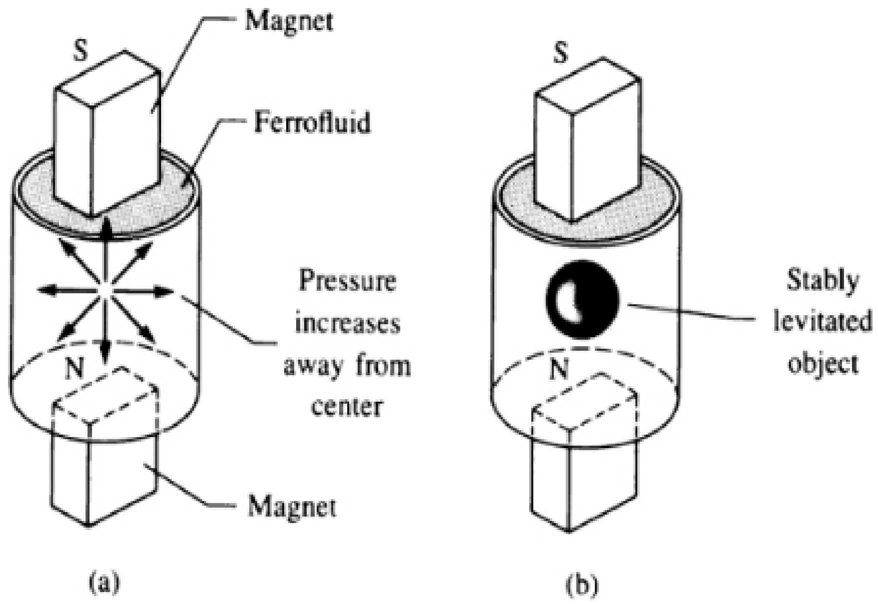


The conical meniscus in ferrohydrostatic equilibrium (scheme). Balance of magnetic and gravitational energies at any point on the free liquid surface is demonstrated when an electric current is passed through a vertical rod running through a pool of ferrofluid:

At each point in the bulk ferrofluid, the sum of the magnetic, gravitational, and pressure terms in the ferrohydrodynamic Bernoulli equation equals the same constant

R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ Press1985

First order levitation effect

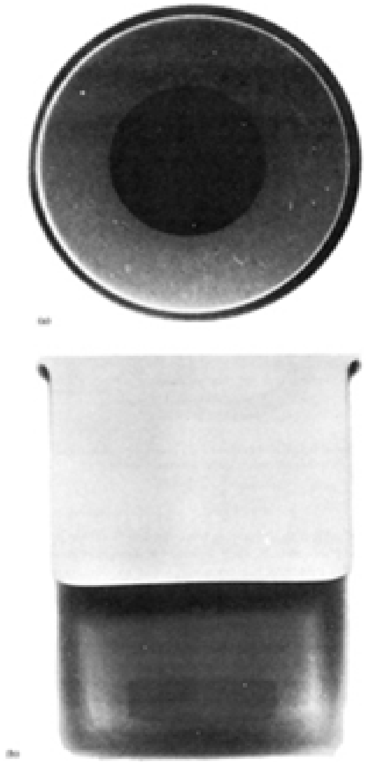


Levitation of a nonmagnetic body in a magnetized fluid

is a demonstration of the generalized Bernoulli equation:
(a) pressure in the fluid is lowest at the center and increases with distance from it;
(b) when a **nonmagnetic object** is placed in the container,
it moves to the center and remains there in equilibrium

R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ Press1985

Second order levitation effect

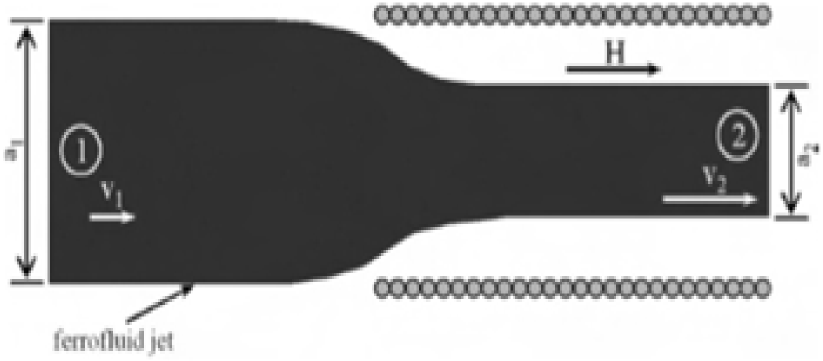


Self-levitation of a magnetic object in magnetic fluid

The X-ray images show a disk magnet stably suspending itself in a baker of ferrofluid.
The magnet, which is nearly four times as dense as the fluid,
is seen hovering above the bottom of the beaker in the side view (b).
As the plan view illustrates, the magnet is repulsed from the surrounding beaker wall

R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ Press1985

Horizontal ferrofluid jet



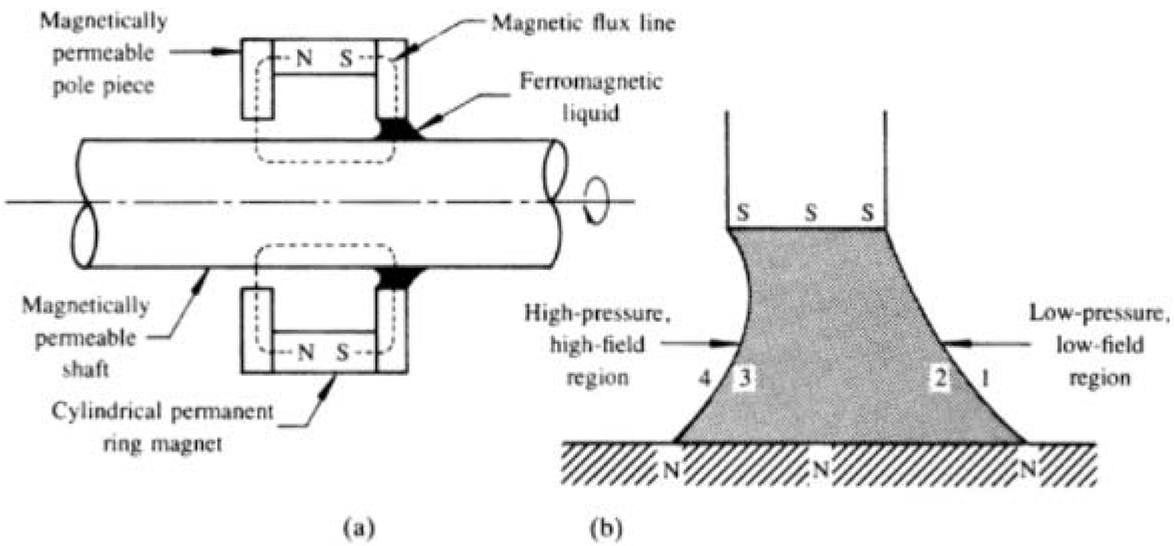
Magnetic nozzle: reduction of the cross section of jet entering in non-zero magnetic field region

R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ Press1985

Applications

Leakproof dynamic sealing

Operating principle-1

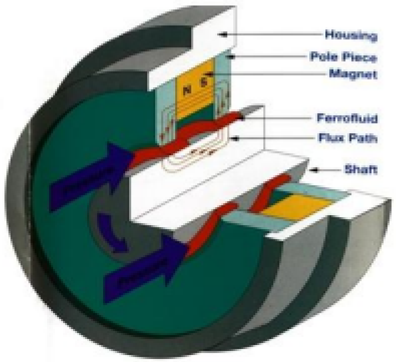


The only leakproof rotating seal on the market

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

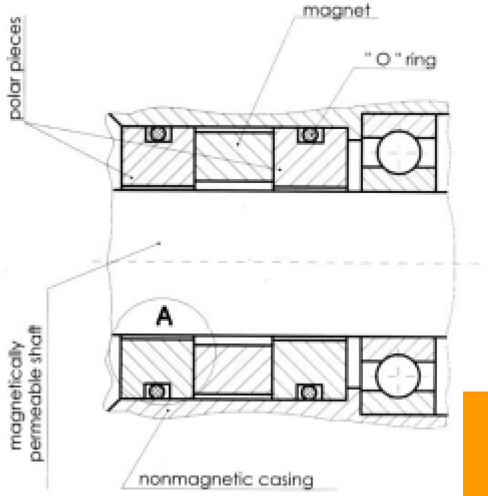
R.E. Rosensweig, *Ferrohydrodynamics*, Cambridge Univ Press1985

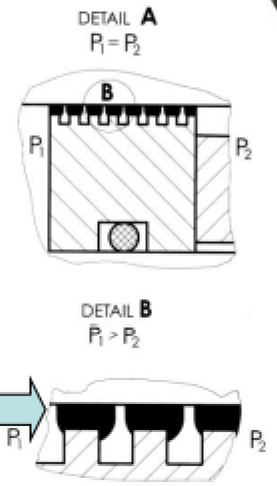
Operating principle-2



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

Magnetofluidic rotating seals





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
$|gradH|$ ~ $10^9 A/m^2$

MF rotating seals in high-tech processes and devices
A highly successful commercial application

Semiconductor industry - Fabrication of high quality silicon integrated circuits for **electronic devices sputtering systems** (**vacuum integrity** up to 10^{-7}-10^{-9} torr), **crystal growing systems** (e.g., defect-free mono-crystalline silicon); X-ray rotating anode, tire pressure for **all-terrain vehicles**, production of **optical fibers**, high altitude **telescope** for deep **space exploration**, excimer laser systems, electron beam evaporators, **computer memory drives**, **bearing protection**, **angle of attack sensor of aircrafts**, airborne infrared **imaging cameras**, manipulators for **robotics**, fabrication and handling of **nuclear fuel assemblies**, precision ball bearing and **disk drive spindles**

Ferrotec Company, the largest manufacurer: “The Ferrofluid That We Use in Our Ferrofluidic Seals is not Available for Purchase as a Stand-alone Product”

https://seals.ferrotec.com/technology/

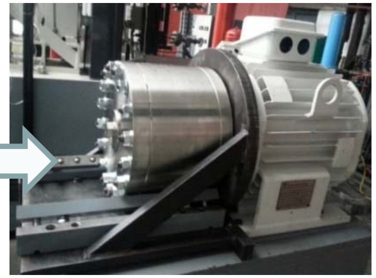
Leakage-free magneto-fluidic rotating seals Manufactured in Romania

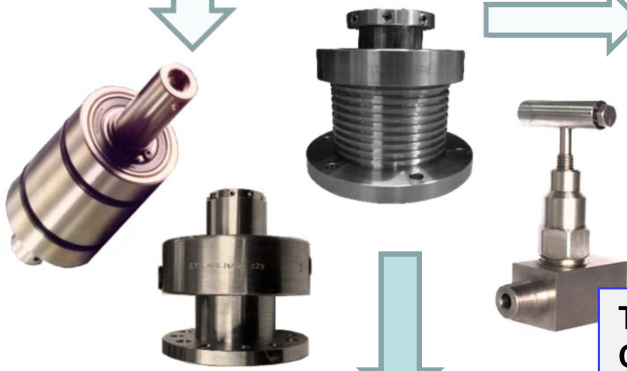
Lab MF

ROSEAL Co

Technology Transfer

Magnetic fluids for seals
Qualification for Environment, Radiation and Thermal resistance





Projects

- *NanoMagneFluidSeal* (2006-2008)
- *Semarogaz* (2007-2009)
- *MagNanoMicroSeal* (2012-2016)
- *HiSpeedNanoMagSeal* (2014-2017)

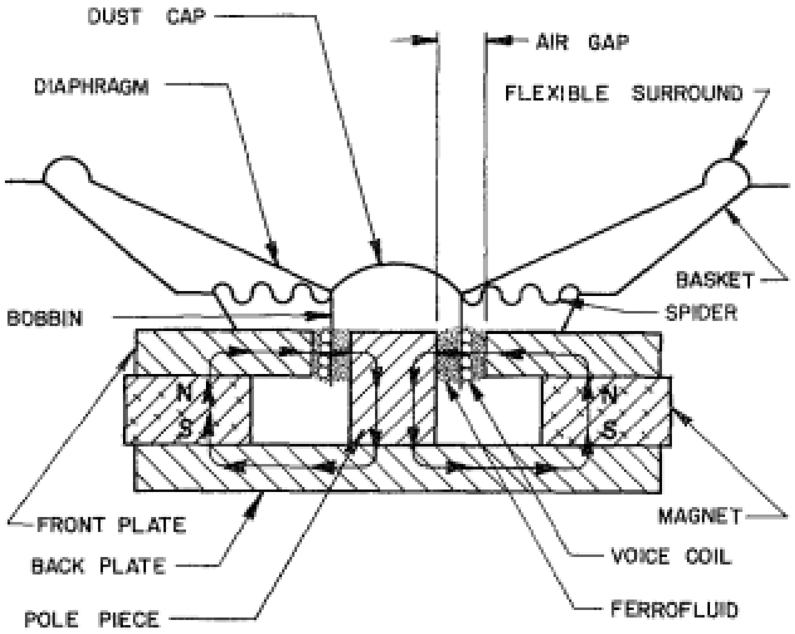
T. Zaharescu, R. Setnescu, I. Borbath, Cent.Eur.J.Chem.12(2014); T. Borbath et al, Int.J. Fluid Machinery and Systems, 4(2011)

Nuclear Power Units (2012-)
High power electric switches
Vacuum technology
Gas compressors

Helium leakage less than 10^{-7} cm^3/sec

Highly limiting any radioactive escape much below the admissible level, resistance to radiation, several years long maintanence-free operation

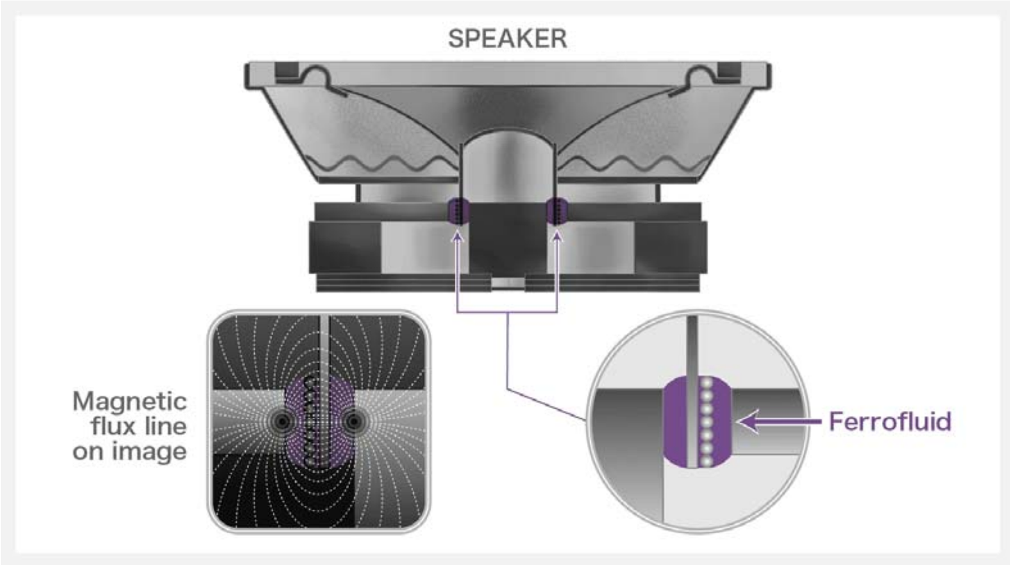
Ferrofluid improved loudspeakers
Another highly successful application



Bottenberg et al 1980;Raj and Moskowitz 1980

Improvements by displacement of a small volume of ferrofluid in the air gap:
a) cooling (ferrofluid is 4-5 times more thermally conductive as the air, lowering the voice coil operating temperature under both transient and steady state conditions); (b) **damping** (proportional to the viscosity of ferrofluid); (c) **voice coil centering** (the restoring force is enough to ensure the centering the coil ; the first order levitation force constant is proportional to the ferrofluid magnetization and the maximum field strength in the gap);
(d) **reduced harmonic distortion** and spectral contamination due to centering force;
(e) reduced thermal power compression effects and **better linearity**.

Ferrofluid improved loudspeakers
A highly successful commercial application



https://ft-mt.co.jp/en/product/electronic_device/ferrofluid/audio/

Multi-media computers, laptops, cellular phones,
portable DVD player and headphones,
imposed significant size reduction of the dynamic speaker,
while keeping high the requirements on sound quality:
cellular phones or hearing aids which employ
a few millimeter size speakers with tight radial gap

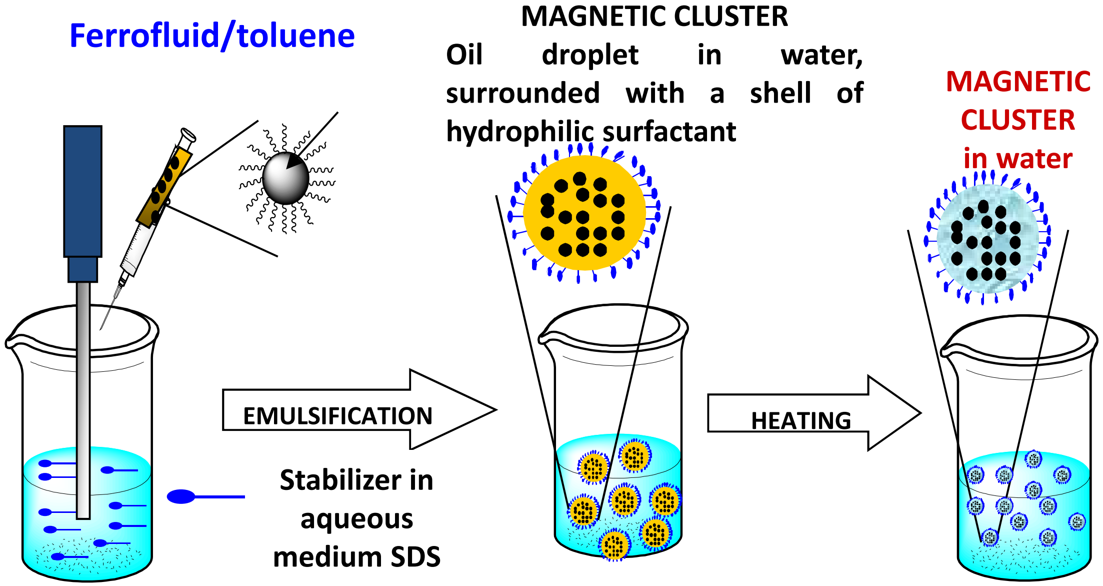
https://www.sony.com/electronics/support/articles/00045726

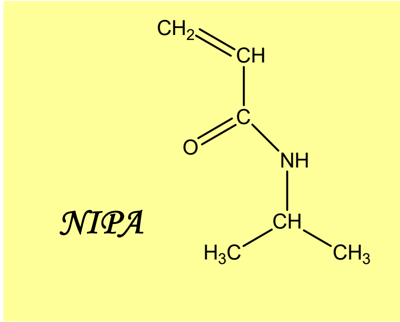
Tunable and adaptive multifunctional materials derived from ferrofluids

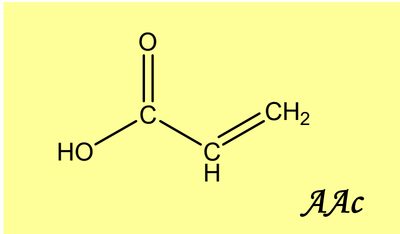
Magnetic microgels-1

-preparation by ferrofluid-in-water miniemulsion method-

1st step: Nanoparticle clusters (NPCs) by toluene FF in water miniemulsion







2st step: Encapsulation of NPCs into cross-linked polymers by free radical polymerization in water (p-NIPA, pNIPA-pAAc, pAPTAC) → magnetic microgels

E.g., Magnetite NP clusters encapsulated in poly(N-isopropylacrylamide-co-acrylic acid

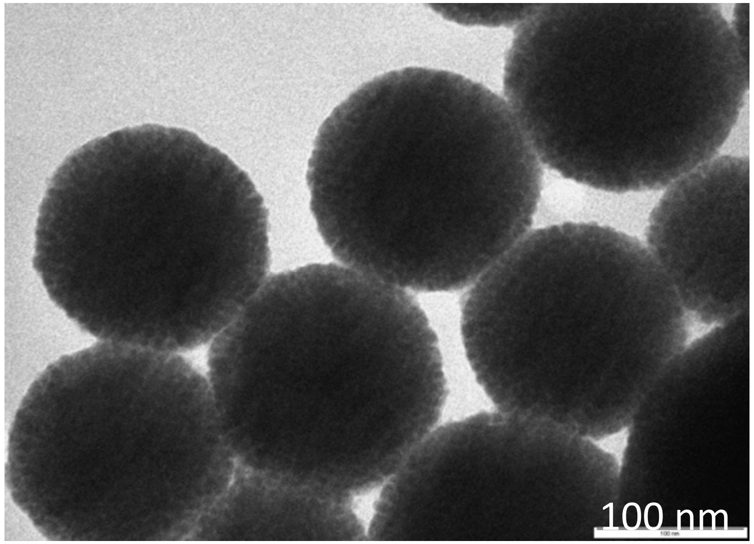
INCDTIM Cluj-Napoca

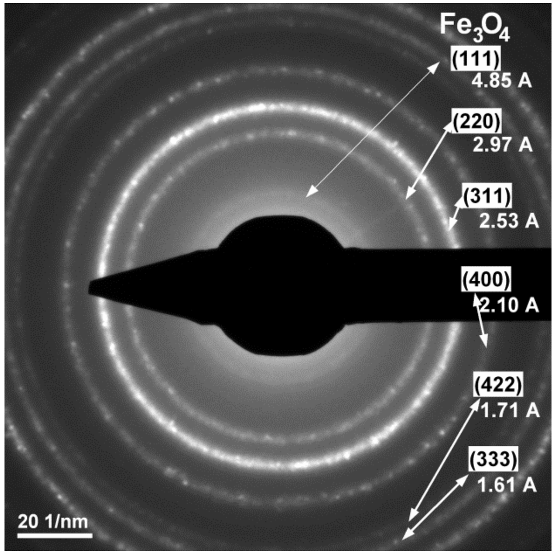
R. Turcu, I. Craciunescu, A. Nan, in: Upscaling of Bio-Nano-Processes, H. Nirschl and K. Keller (Eds.) Springer-Verlag Berlin Heidelberg 2014, pp.57-76

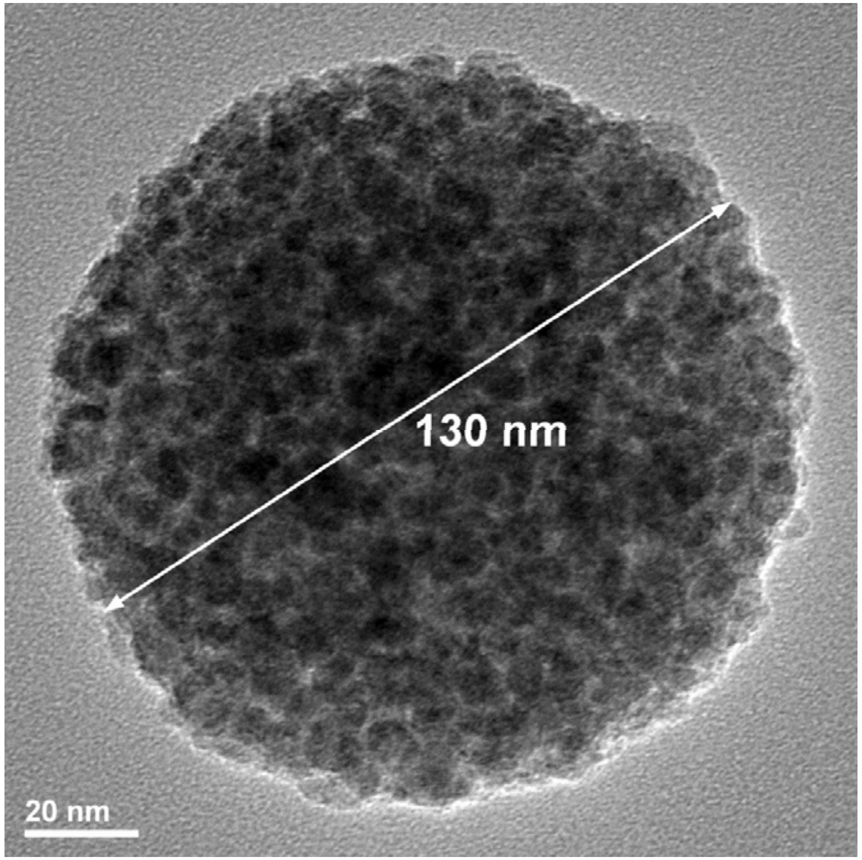
Magnetic microgels-2

Morphological characterization

NPCs stabilized with SDS prepared by oil-in-water miniemulsion method



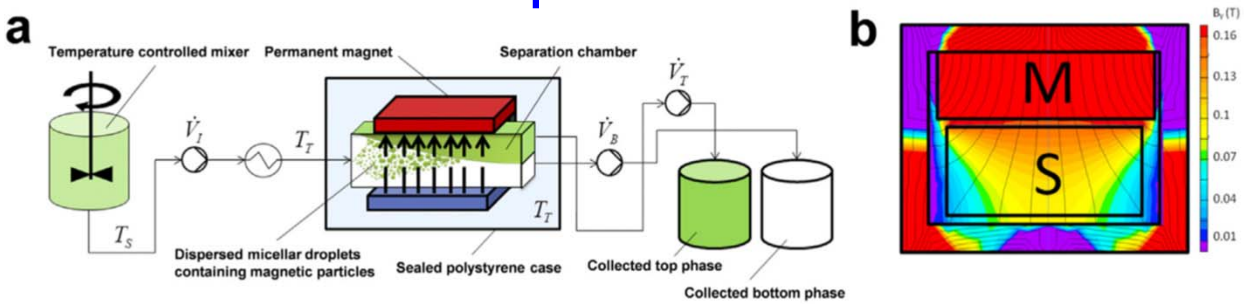




R Turcu, V Socoliuc, I Craciunescu, A Petran, A Paulus, M Franzreb, E. Vasile, L. Vékás, Soft Matter 11(2015)

E. Tombácz, R. Turcu, V. Socoliuc, L. Vékás, Biochem.Biophys.Res.Comm. 468(2015)

Magnetic microgels for Magnetic bioseparation
Comparative tests



Continuous magnetic extraction (CME) using cation exchange functionalized magnetic particles. The magnet consists of the magnetic ferrite material (M) and a surrounding pole shoe, imposing a lifting force on any magnetic particles within 'S'.

Institute of Functional Interfaces - Karlsruhe Institute of Technology

Magnetic support (Manufacturer)	Description of particle materials	Mean size (nm)	Flow rate (L/h)	Separation efficiency (%)
MagPrep Silica 25 (Merck KGaA)	Magnetite crystals coated with a thin layer of silica	25	5	>95
MagPrep SO_3 100 (Merck KgaA)	Magnetite crystals coated with a thin layer of silica	100	5	>99
Poly(NIPA-co-AAc) (**INCDTIM Cluj-Napoca, Romania**)	Magnetite embedded within a poly(N-isopropylacrylamide-co-acrylic acid) matrix	200	9	**>99**
M-PVA-DEAP (PerkinElmer Chemagen Technologie GmbH)	Spherical beaded polyvinyl alcohol – magnetite composite particle functionalized with diethylaminopropyl groups	2000	9	>99

Fischer I., Hsu C.-C., Gärtner M., Müller C., Overton T. W., Thomas O.R.T., Franzreb M., *Continuous protein purification using functionalized magnetic nanoparticles in aqueous micellar two-phase systems*, Journal of Chromatography A, 1305, 7– 16(2013)

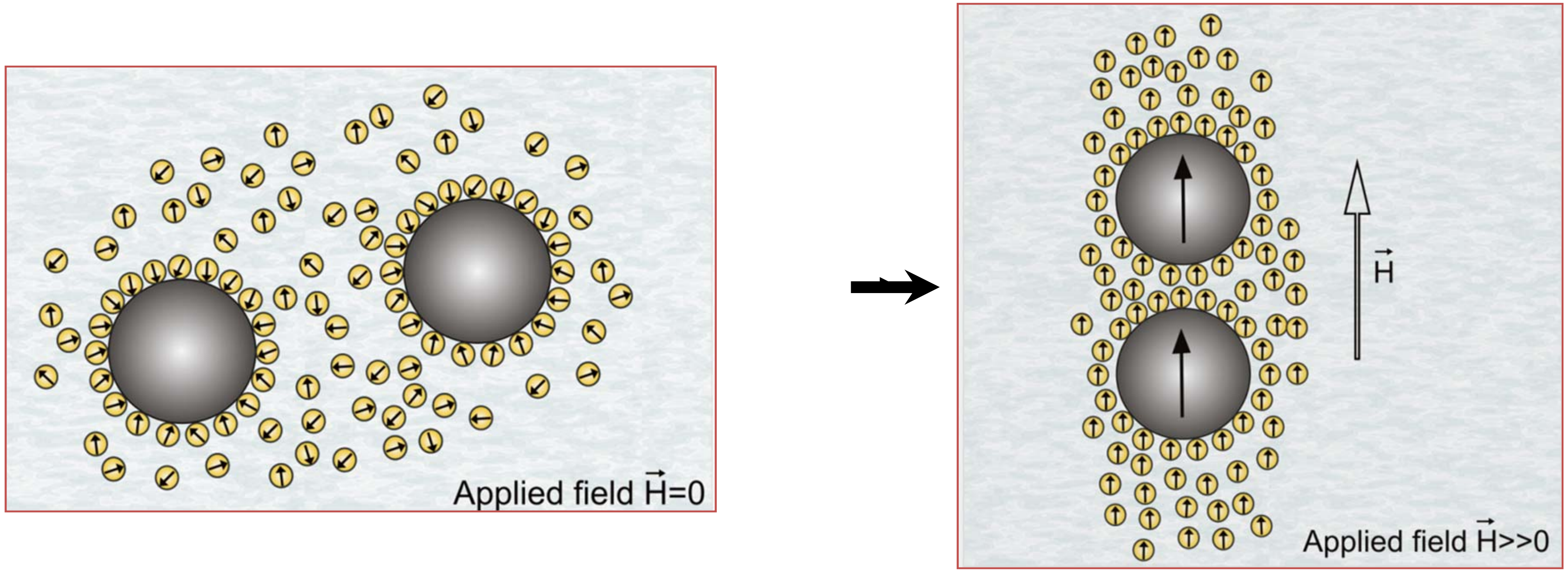
Useful supplementary information on magnetoresponsive nanocomposite manufacturing for biotechnology and nanomedicine

Theodora Krasia-Christoforou, Vlad Socoliuc, Kenneth D. Knudsen, Etelka Tombácz, Rodica Turcu, Ladislau Vékás, *From single-core nanoparticles in ferrofluids to multi-core magnetic nanocomposites: Assembly strategies, structure and magnetic behavior* (review; feature paper), Nanomaterials, **10**, 2178(2020)

Vlad Socoliuc, Davide Peddis, Viktor I. Petrenko, Mikhail V. Avdeev, Daniela Susan-Resiga,Tamas Szabó, Rodica Turcu, Etelka Tombácz, Ladislau Vékás, *Magnetic Nanoparticle Systems for Nanomedicine—A Materials Science Perspective* (review; feature paper), Magnetochemistry, 6, 2(2020)

Ferrofluid based very high magnetization nano-micro fluids

Micrometer size Fe particles dispersed in a ferrofluid carrier
Extremely bidisperse magnetizable suspensions



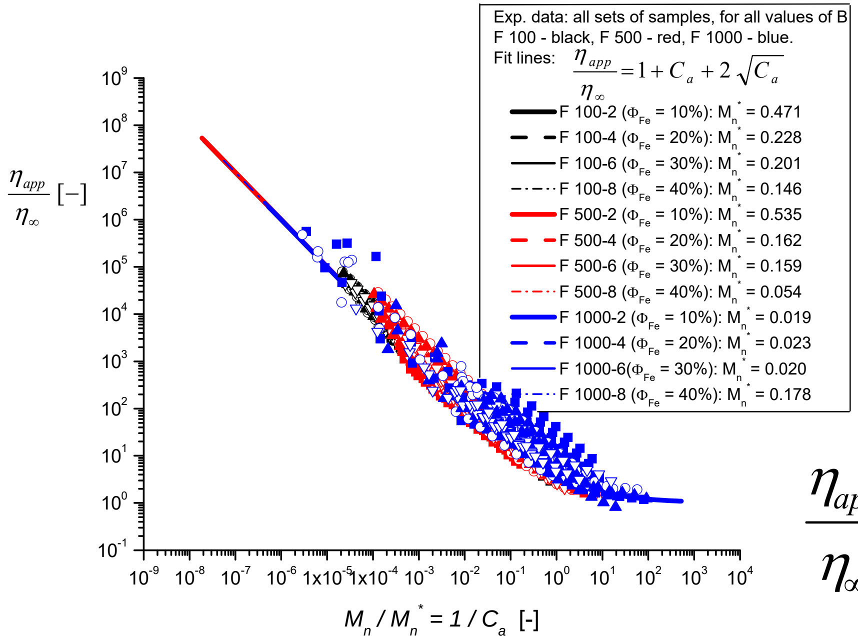
The magnetic nanoparticles – *tiny permanent magnets* – cover the surface of the micrometer size Fe particles and impede their direct surface-to-surface contact => **increased sedimentation stability and very high magnetization**

Excellent sealing and magnetorheological fluids

Doina Bica et al. Patent RO 122725(2009); Tünde Borbáth et al Int J Fluid Machinery and Systems, 2011; Daniela Susan-Resiga et al J Magn Magn Mater 2010; Rheol. Acta 2014; Rheol. Acta 2016; J. Rheology 2017

Ferrofluid based MRF-tuning the composition

Non-dimensional apparent viscosity vs. Mason Mn/Casson Ca number



$$\frac{\eta_{app}}{\eta_\infty} = f\left(\frac{M_n}{M_n^*} = \frac{1}{C_a}\right)$$

$$M_n = 72 \frac{\eta_{FF}\,\dot{\gamma}\,\Phi^2}{\mu_o\,\mu_{r\,FF}\left[\langle M_{FF-MRF}\rangle - \langle M_{FF}\rangle\right]^2}$$

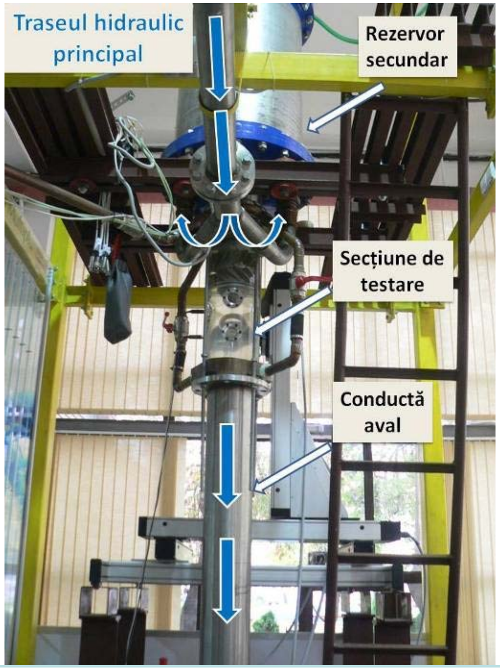
$$\frac{\eta_{app}}{\eta_\infty} = C_a + 2\sqrt{C_a} + 1 \qquad C_a = \frac{\tau_C}{\eta_C\,\dot{\gamma}} = \frac{\tau_C}{\eta_\infty\,\dot{\gamma}};$$

Collapse of experimental points on a **master curve**
for different values Fe **micro**particle volume fraction **ϕ**
and magnetite **nano**particle volume fraction φ .
(yield stress; shear rate)

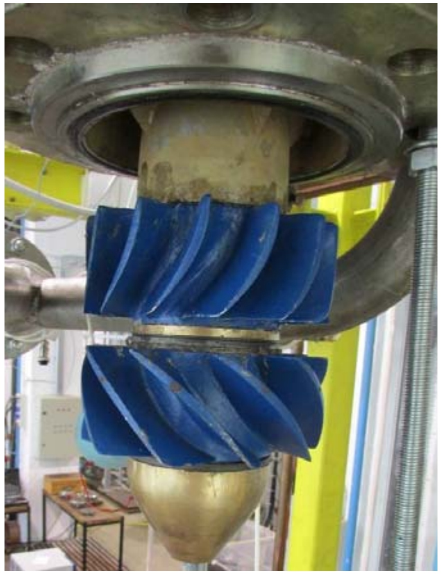
Basics for design of MR devices

Daniela Susan-Resiga, L. Vékás, *Ferrofluid based composite fluids: magnetorheological properties correlated by Mason and Casson numbers*
J of Rheology, 2017

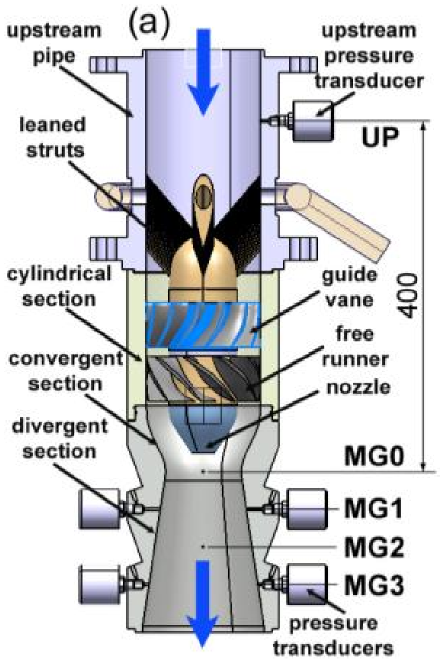
MR controller devices in hydraulic machinery

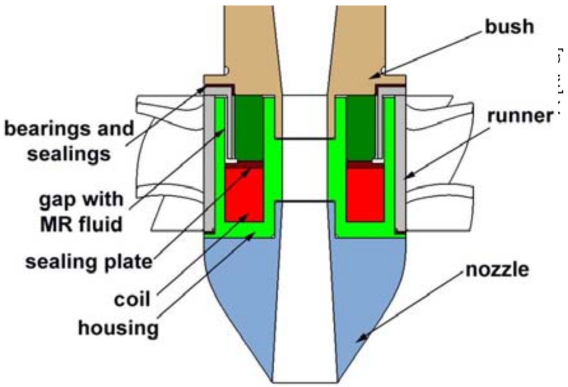


Lab Hydraulic Machines-Timisoara

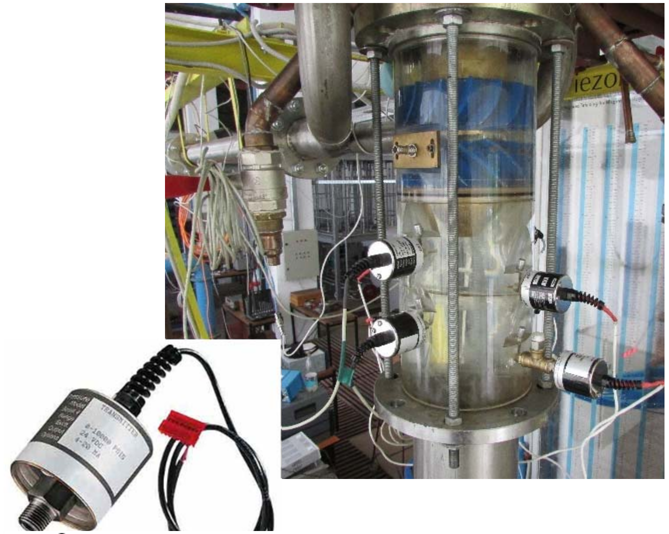


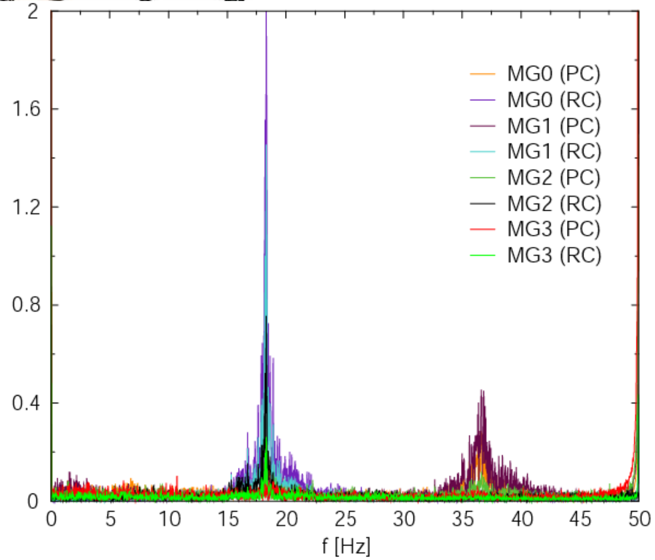
Testing an MR brake





Swirl generator



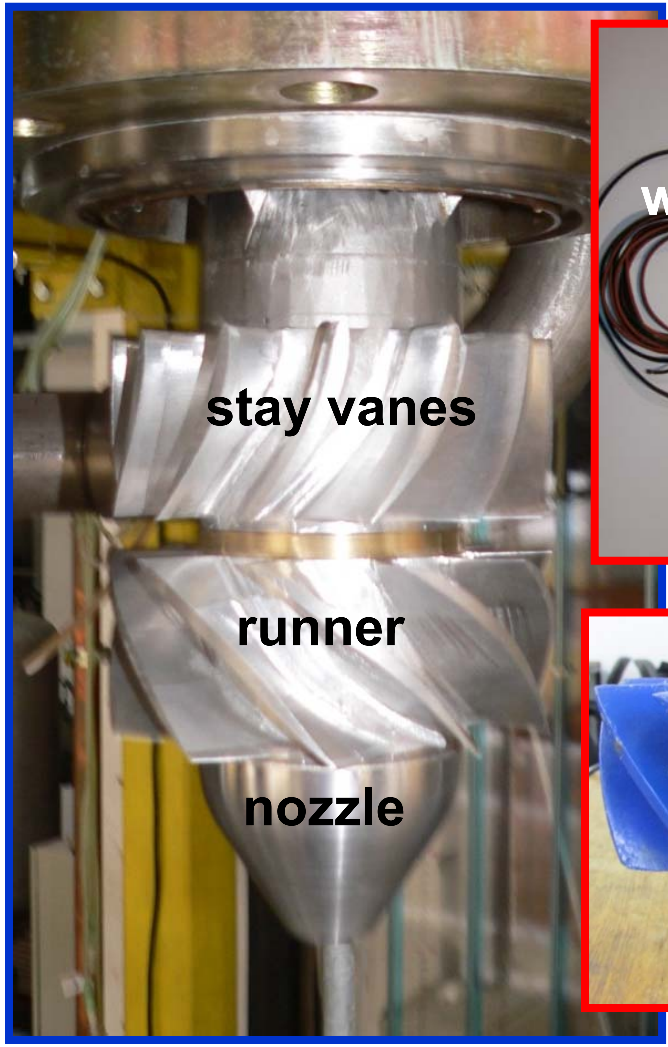


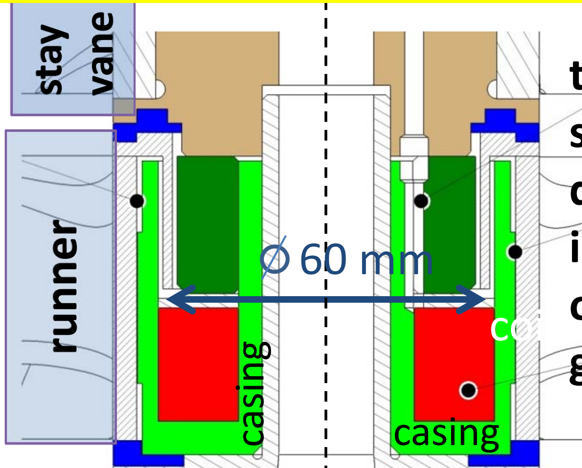
Fourier transform of pressure signals (amplitude&frequency) associated with free runner rotation **without MR brake**- at **1020 rpm**
Intense vibrations are induced

MR controller devices in hydraulic machinery

MR brake implemented on swirl generator

→ slow down runner speed → control hydrodynamic instabilities



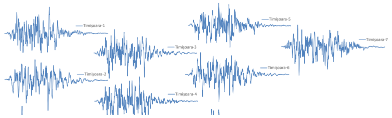


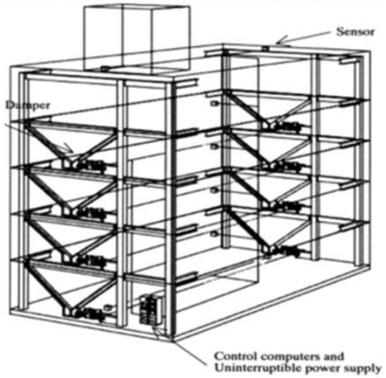
technical solution designed and implemented on swirl generator

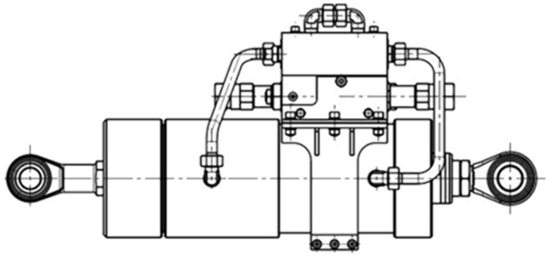
without / with MR brake control

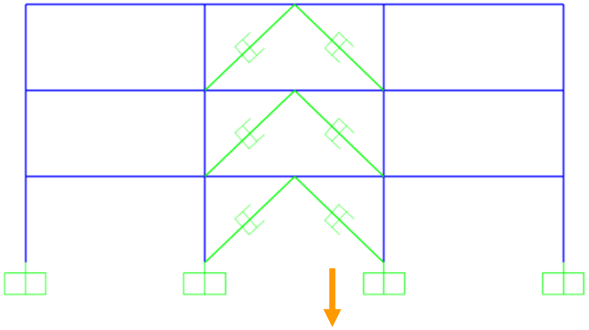
S. MUNTEAN, A.I. BOSIOC, R.A. SZAKAL, L. VEKAS, R. SUSAN-RESIGA, 2016, Hydrodynamic investigations in a swirl generator using a magneto-rheological brake, 1st International Conference on Materials Design and Applications MDA2016, in Advanced Structured Materials (SPRINGER), vol. 65.(2017)

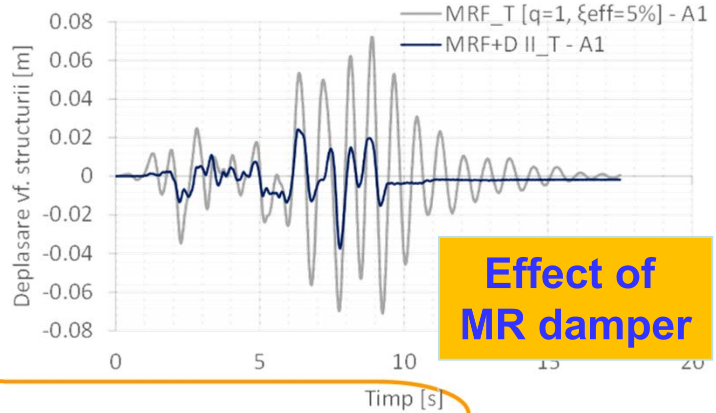
Semi-active MR dampers for seismic protection



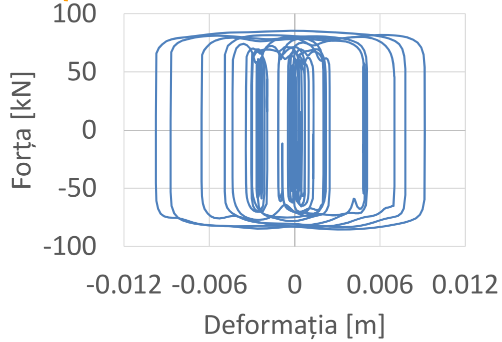


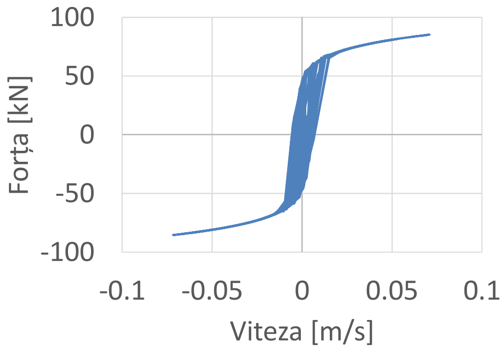




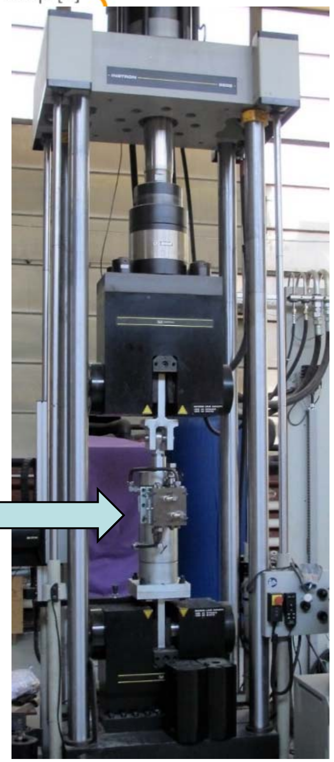


Effect of MR damper





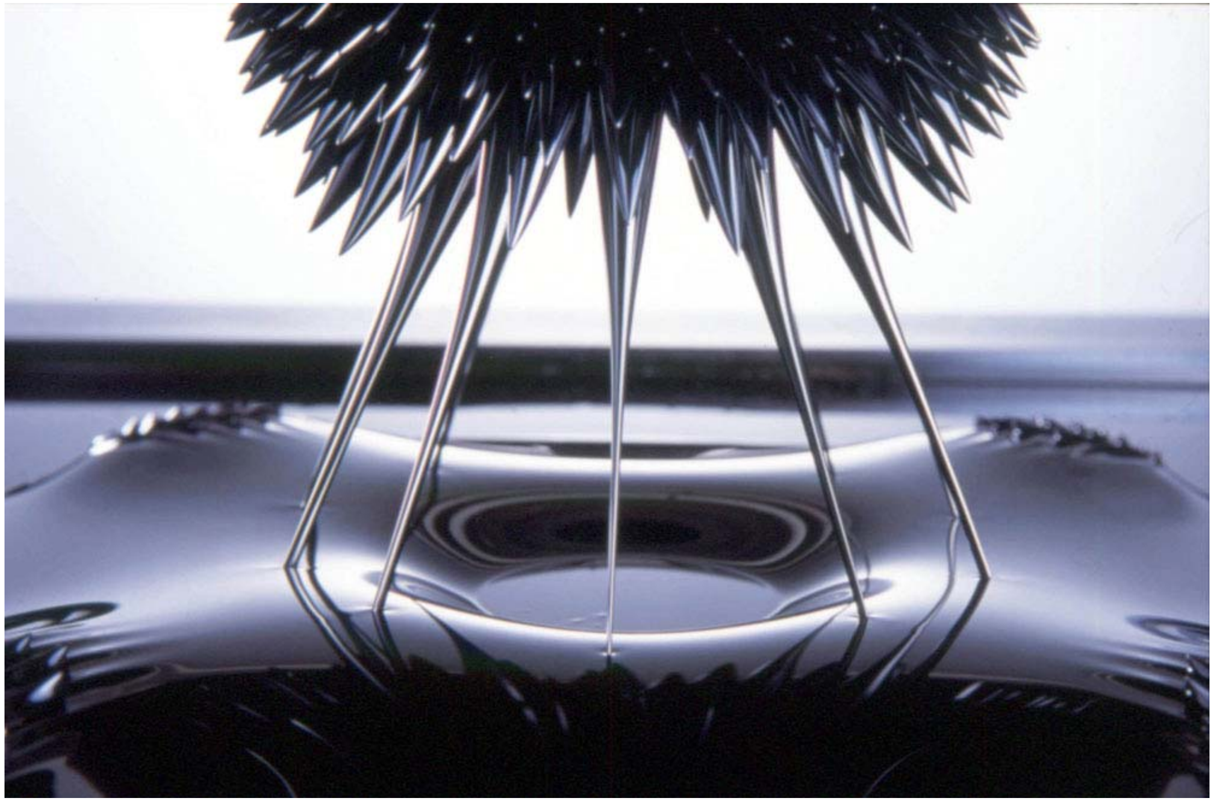
Set-up for the experimental investigation of an **MR damper** of **10 tf** capacity



C. Vulcu, D. Dubina et al, *Hybrid Seismic Protection System: Buckling Restrained Brace of Nano-Micro Composite Magneto Rheological Damper*,EUROSTEEL 2017, Copenhagen, ce/papers vol.1(2-3)2936-2045(September, 2017)

SEMNAL-MRD Project PN II 77/2014
UPTimisoara and partners (2014-2017)

Ferrofluids in kinetic arts



https://www.artfutura.org/v3/en/sachiko-kodama/

THANK YOU

FOR ATTENTION!