Structural studies of ferrofluids in bulk and interface by neutron scattering

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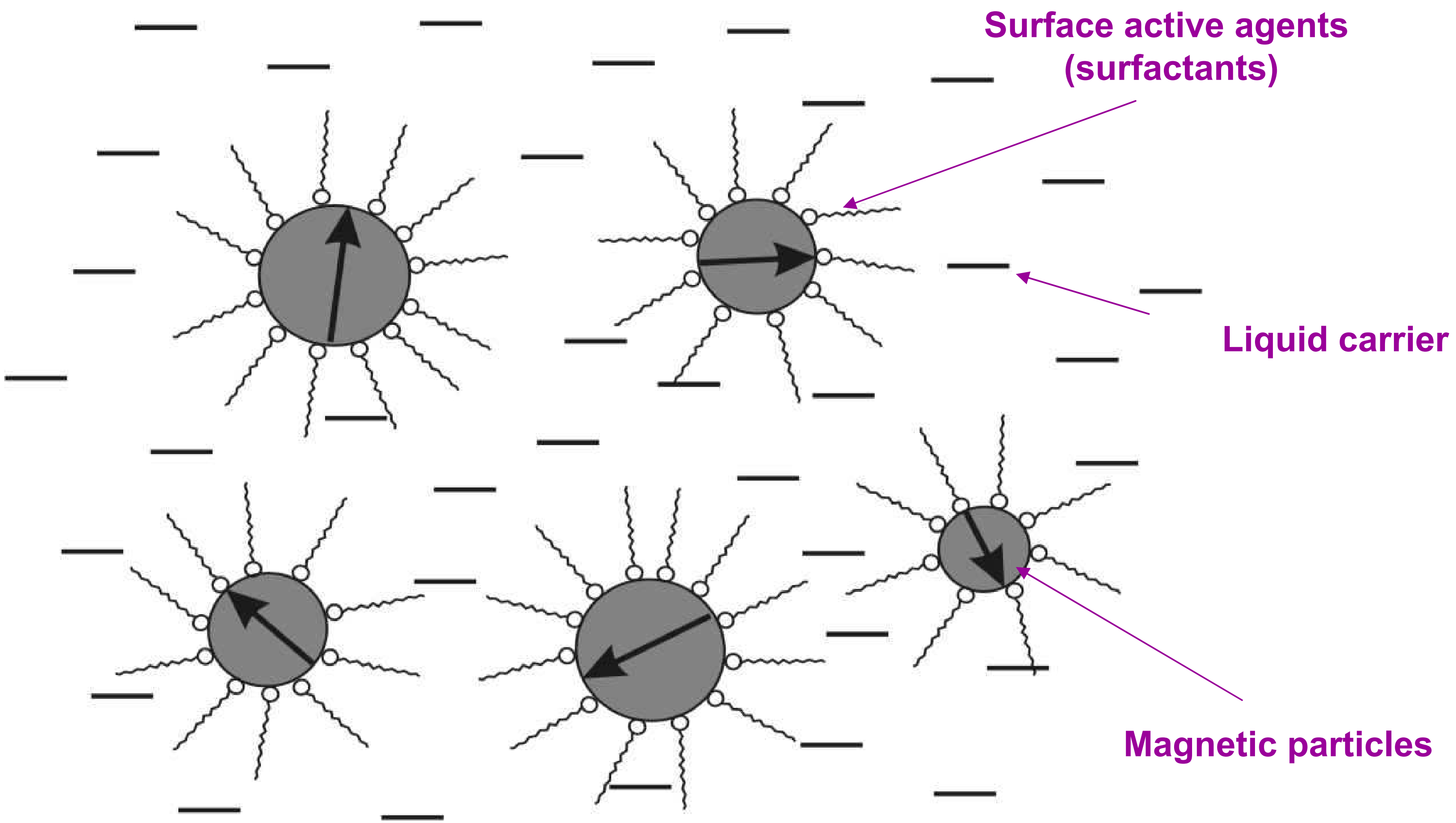
Magnetic colloids

R.E.Rosenweig, 1966



Condition of stability

Attraction

Dispersion forces

$$E_B \sim r^{-6}$$

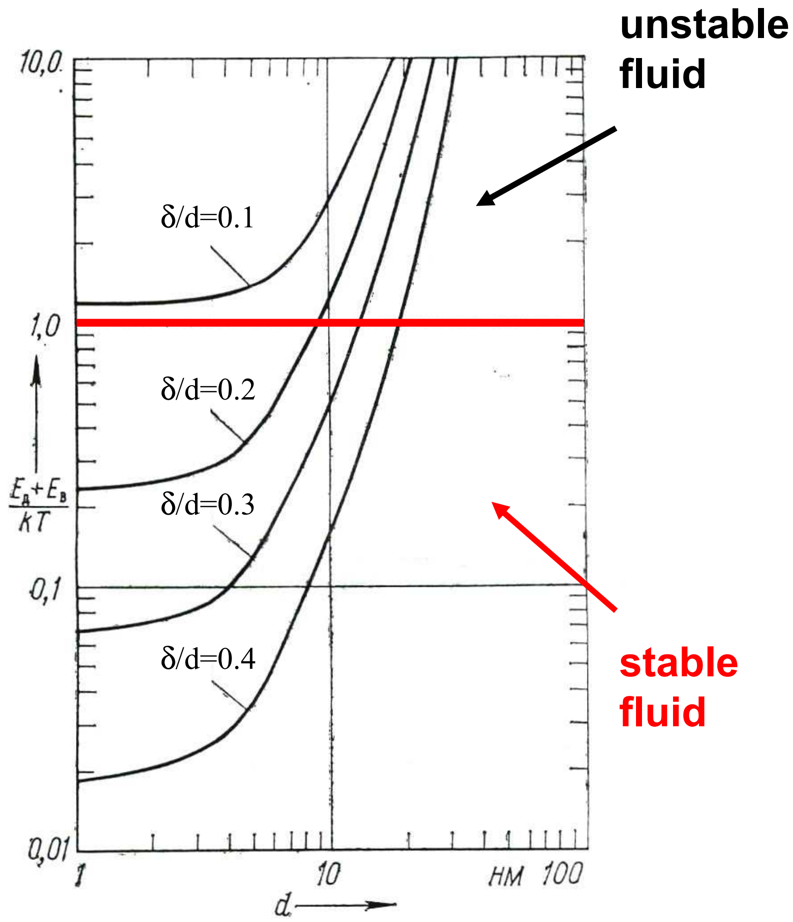
Dipole-dipole interaction of magnetic moments oriented by the external magnetic field

$$E_\partial \sim r^{-3}$$

Repulsion

Brown repulsion

$$E \sim kT$$



Parameter of stability at the contact of particles from magnetite (Fe_3O_4), M_S=478 кА/м, covered by the surfactant shell (thickness δ) as a function of the particle diameter, d. T = 300 K.

Structural characteristics

Dispersed materials

Fe_3O_4, γ-Fe_2O_3, $MnFe_2O_4$, Co, $CoFe_2O_4$

Size distribution

$$D_N(R) = \frac{1}{RS\sqrt{2\pi}} \exp\left(-\frac{\ln^2 (R/R_0)}{2S^2} \right)$$

$3 < R < 15$ nm; $R_0 = 4 \div 6$ nm; $S = 0.2 \div 0.6$

⇓

one domain state

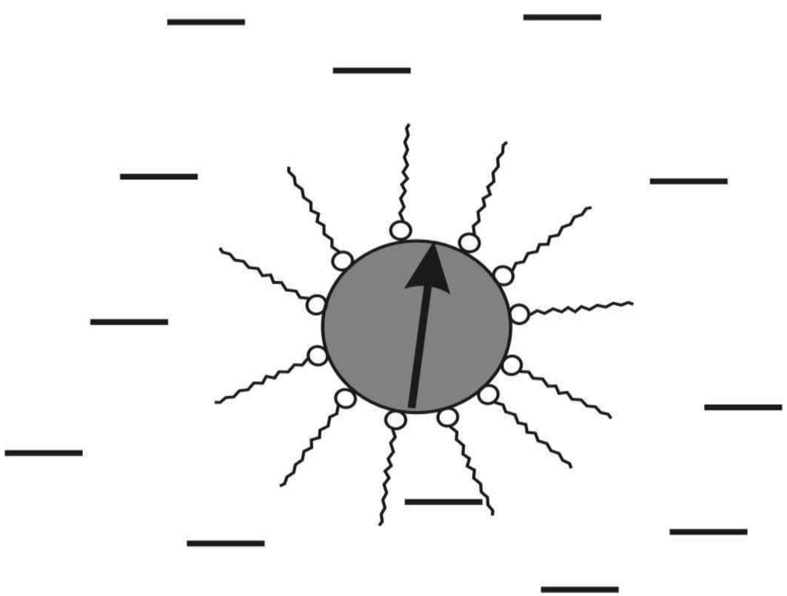
⇓

superparamagnetic systems

Liquid carrier	Saturation magnetization, кGs
Polar liquids	
Alcohols	0.8-0.9
Water	0.4-0.6
Pentanol	1.5
Non-polar liquids	
Hexane	0.8-0.9
Benzene	1 - 2
Kerosene	1.2
Transformer oil	1.1
Vacuum oil	0.6-0.8

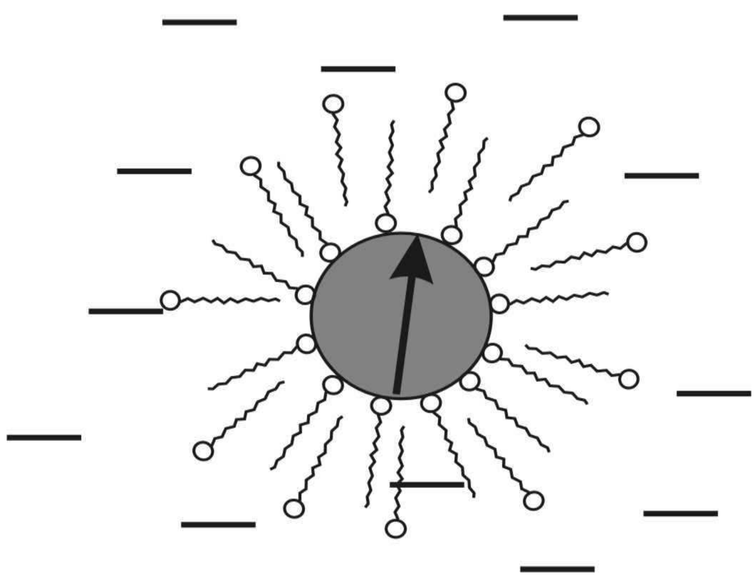
Non-polar and polar ferrofluids

Non-polar carrier



single surfactant layer
(e.g. oleic acid, δ ≈ 1.8 nm);
chemisorption;
optimum content of the surfactant;

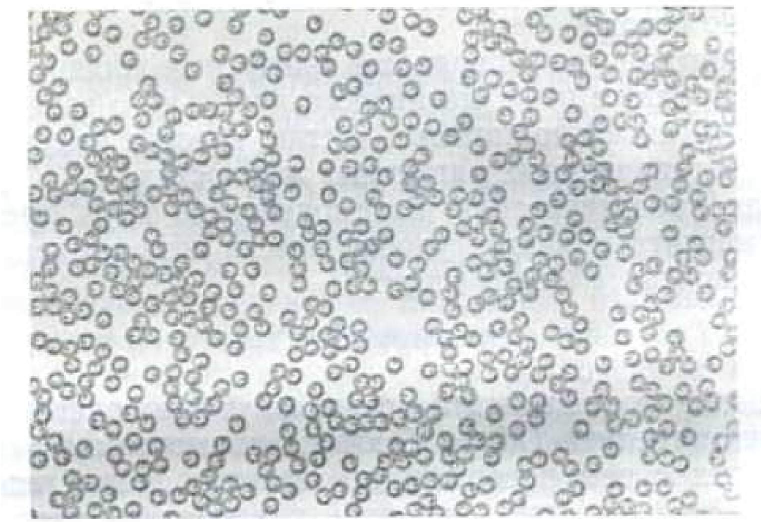
Polar carrier



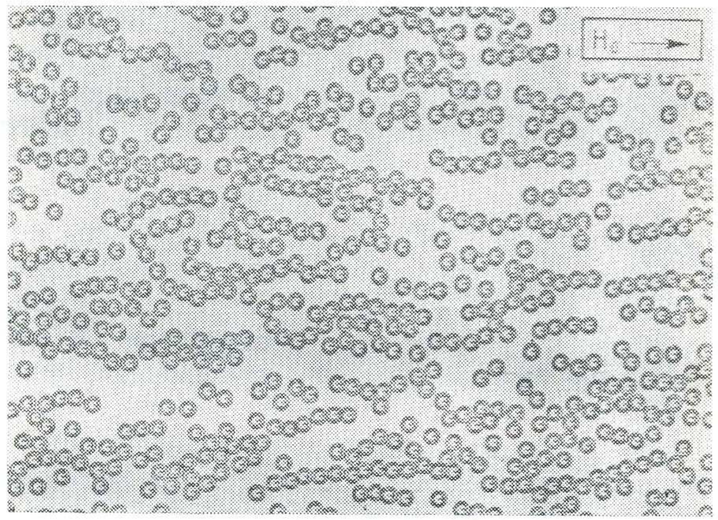
double surfactant layer
(e.g. oleic acid + DBS, δ - ? nm);
chemisorption + physical adsorption;
excess of the surfactant;

Aggregation in applied magnetic field

Modelling of a concentrated ferrofluid with monodisperse Co particles



H=0



H ⟶

Parameters of magnetic fluids sensitive to the external magnetic field

- ***Density***
- ***Viscosity***
- ***Dielectric permeability***
- ***Magnetic permeability***
- ***Conductivity***
- ***Inductivity***
- ***Heat conductivity***
- ***Heat capacity***
- ***Surface tension***
- ***Ultrasound absorption***
- ***Optical absorption***
- ***Refraction index***
- ***Reflection index***

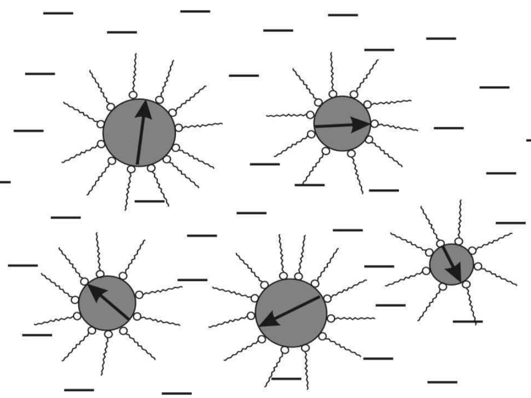
Applications of ferrofluids

Technical acoustics

Measuring devices and sensors

Printing devices

Mechanical devices
- dumpers
- bearings
- actuators
- valves
- switchers
- lubricants
- polishers



Medical applications
- drug delivering and targeting
- hyperthermia
- magnetic resonance imaging
- cell separation and cleaning

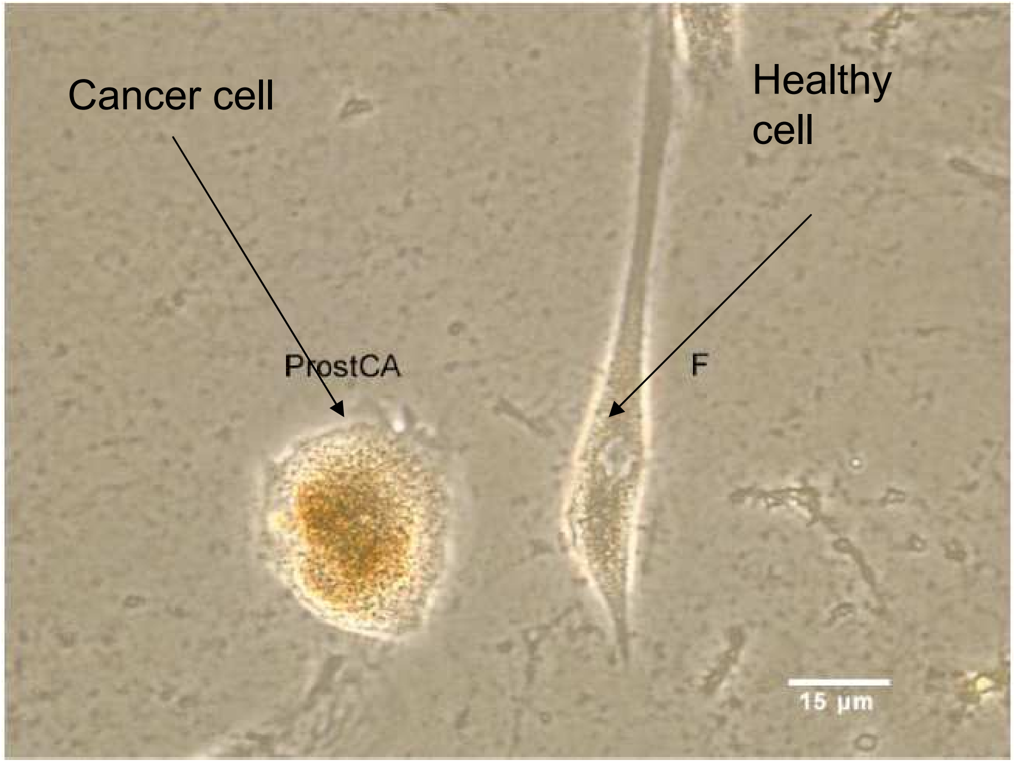
Electromagnetic defectoscopy

Heating cells

Separators

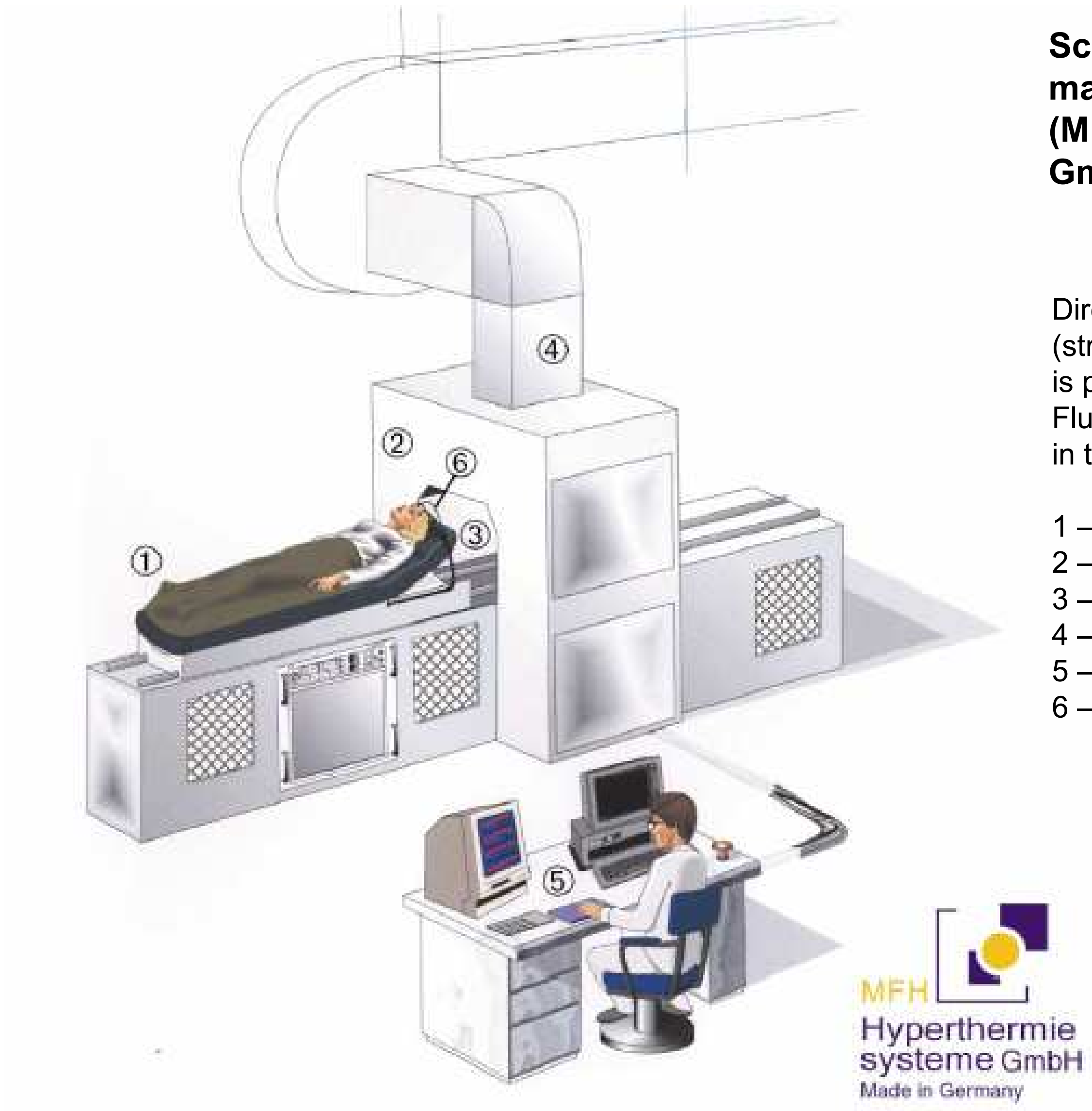
Magnetic hyperthermia in cancer treatment

A.Jordan, et al., J. Mag. Mag. Mater., 2001



Adsorption of nanoparticles by a cancer cell

Magnetic hyperthermia in cancer treatment

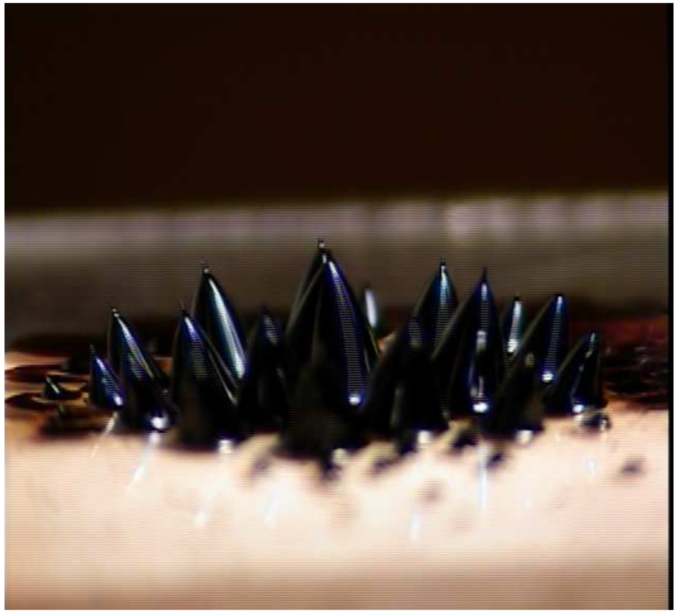


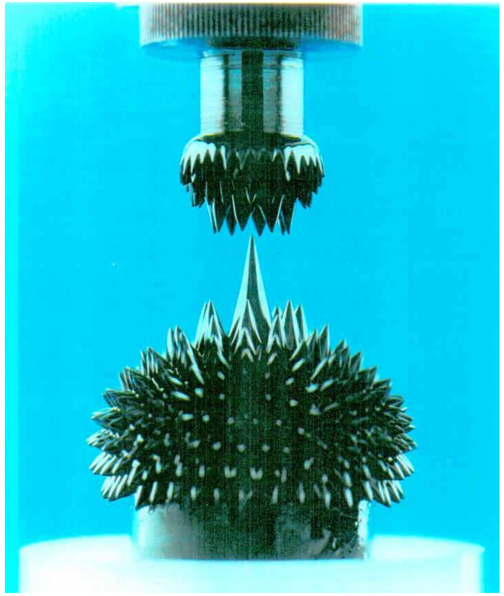
Scheme of the prototype system on magnetic hyperthermia (MFH Hyperthermiesysteme GmbH,Berlin,Germany).

Direction of alternating magnetic field (strength 0-15 кA/m, frequency 100 kHz) is perpendicular to the plain of couchette with a patient. Fluorescent-optical temperature sensors are embedded in the tissue.

1 – couchette with a patient
2 – ferrite applicator
3 – vertical aperture 30×50 cm^2
4 – cooling system
5 – system of control and monitoring
6 – basic thermosensors outside the patient

Free surface phenomena in ferrofluids





Rosenzweig instabilities as a result of competition
between magnetic and gravitation fields and surface tension

Problems for neutron scattering in structural study of ferrofluids

Determination of the nuclear structure in bulk and interface (non-polarized neutrons):

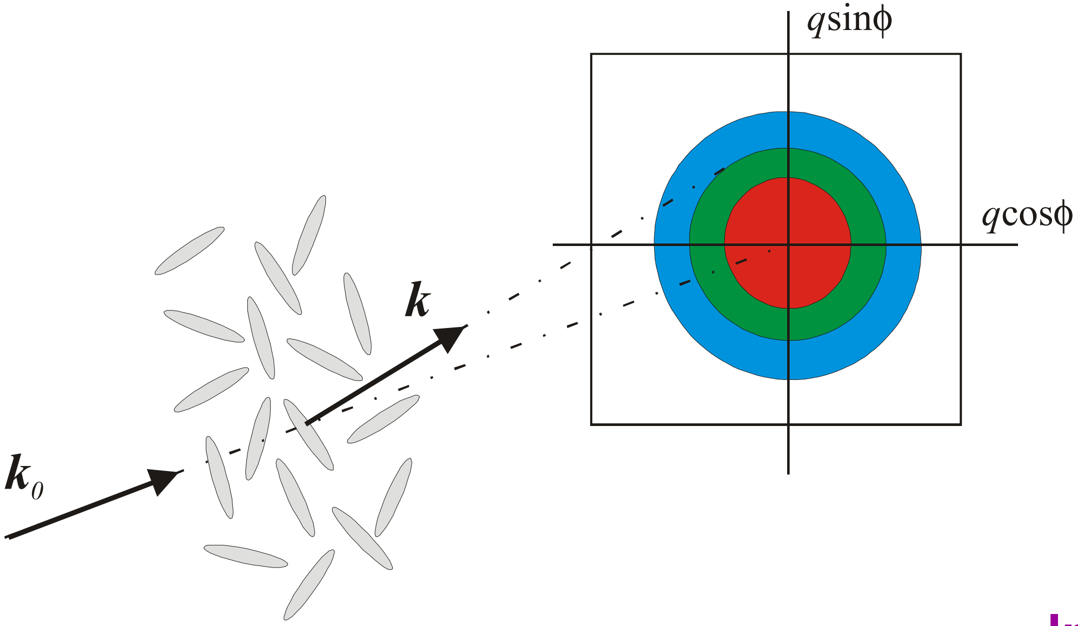
- parameters of the particle size distribution
- thickness and composition of the surfactant shell
- micelle formation in ferrofluids
- interparticle interaction
- particle aggregation in different conditions

Determination of the magnetic structure in bulk and interface (polarized neutrons):

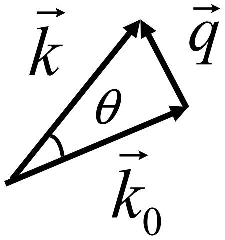
- magnetic size of the particles and aggregates
- magnetic correlation between particles

Study of surface instability

Small-angle neutron scattering (SANS). Isotropic case.



$$\left\langle \frac{d\sigma}{d\Omega} \right\rangle_{\Omega} = f(q)$$



$$\vec{q} = \vec{k} - \vec{k}_0$$

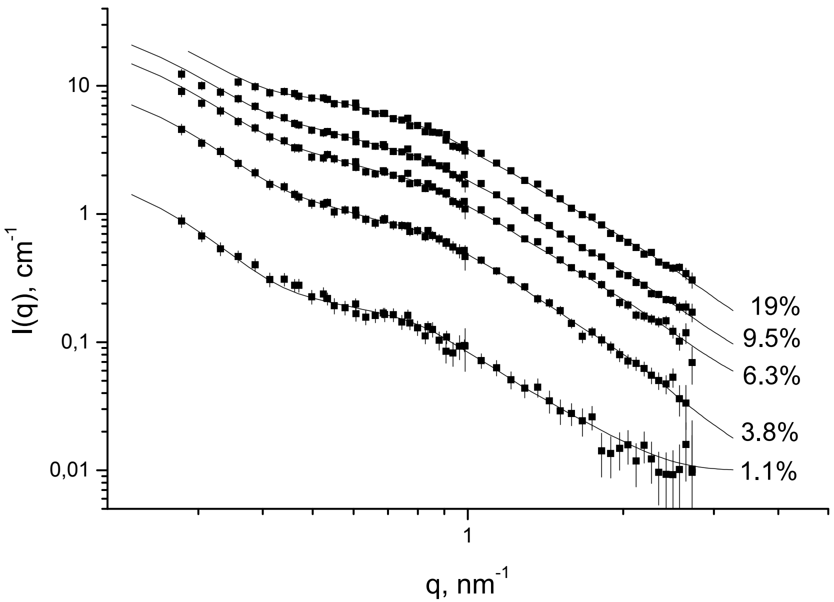
$$q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}$$

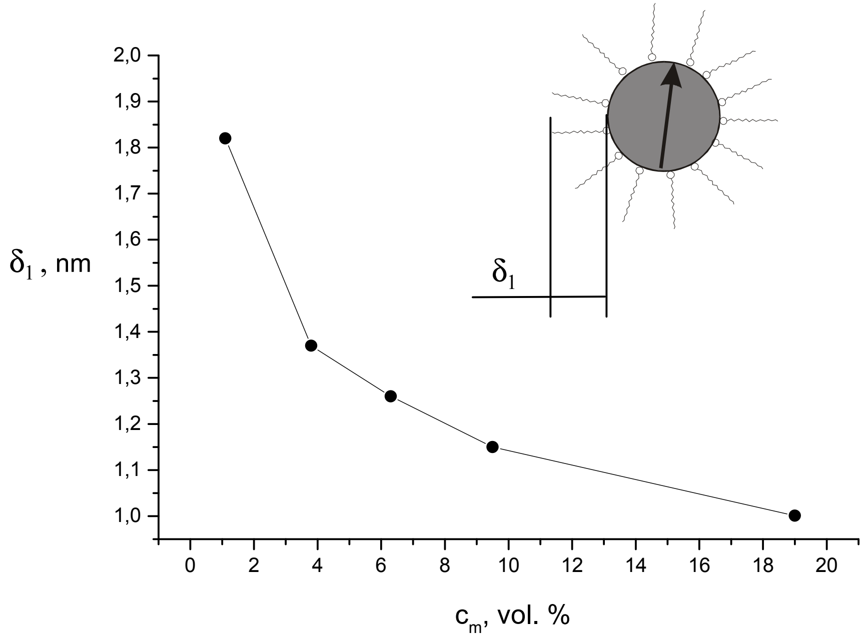
Instruments

YuMO time-of-flight setup,
IBR-2 Reactor, FLNP, JINR, Dubna

Yellow Submarine steady-state setup,
Budapest Research Reactor, BNC

SANS study of concentration effect in the ferrofluid magnetite/oleic acid/benzene





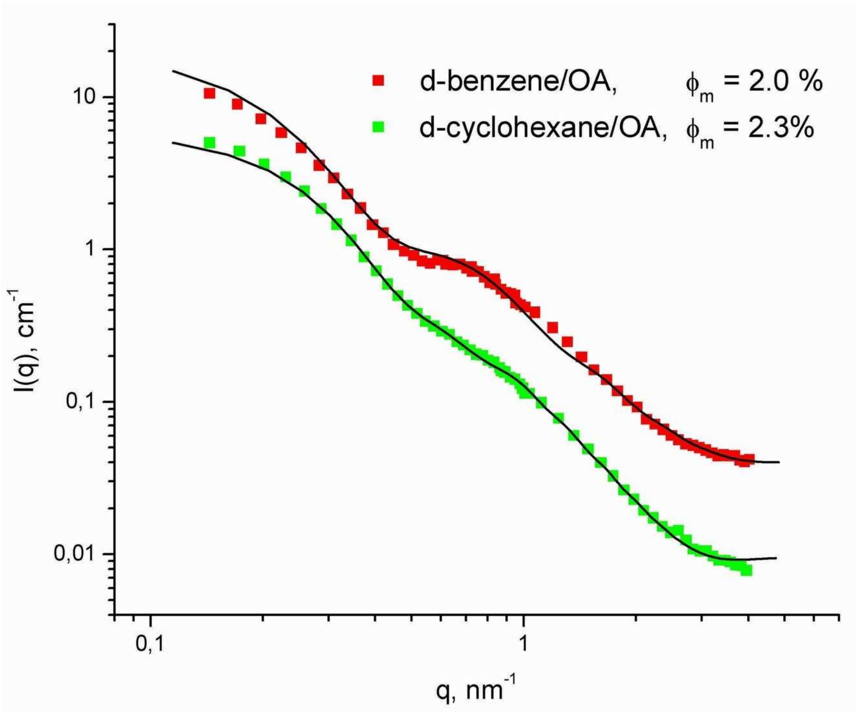
Experimental SANS curves for different values of magnetite volume fraction and fits of the model of non-interacting core-shell particles. The magnetic scattering contribution (< 10 %) is neglected.

Surfactant shell thickness as a function of the magnetite volume fraction as revealed by SANS

M.Avdeev, M.Balasoiu, Gy.Török, D.Bica, L.Rosta, V.L.Aksenov, L.Vekas, **J. Mag. Mag. Mater.** (2002)
V.Aksenov, M.Avdeev, M.Balasoiu, L.Rosta, Gy.Török, L.Vekas, D.Bica, V.Garamus, J.Kohlbrecher, **Appl. Phys. A** (2002)

Structure of ferrofluids on non-polar organic carriers

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

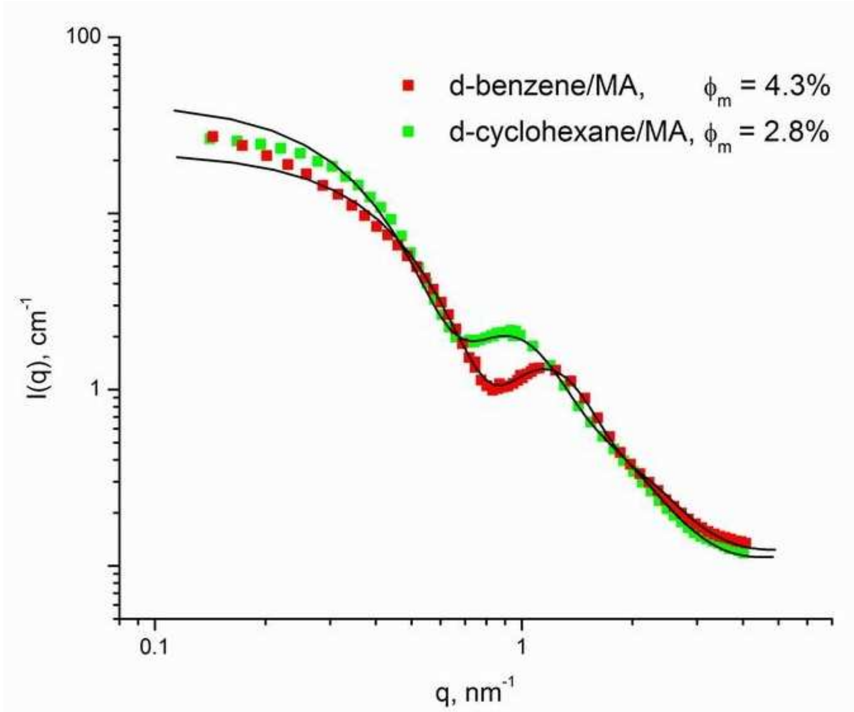


Results of fits of the core-shell model:

→ R_0 = 4.6 nm; $\Delta R/R_0$ = 0.35; δ_1 = 1.31 nm

→ R_0 = 4.1 nm; $\Delta R/R_0$ = 0.4; δ_1 = 1.25 nm

Myristic acid (MA): $C_{14}H_{28}O_2$



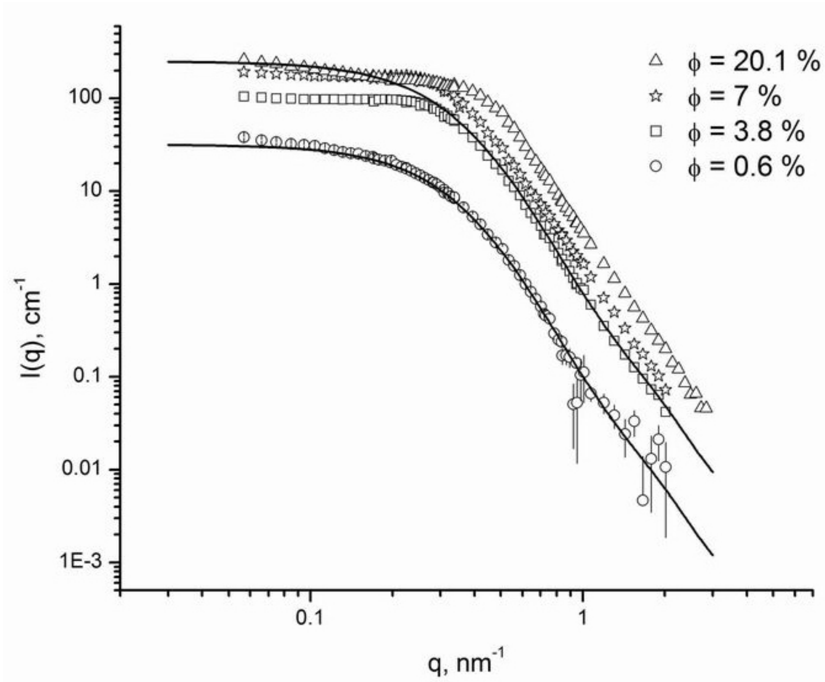
Results of fits of the core-shell model:

→ R_0 = 2.4 nm; $\Delta R/R_0$ = 0.4; δ_1 = 1.31 nm

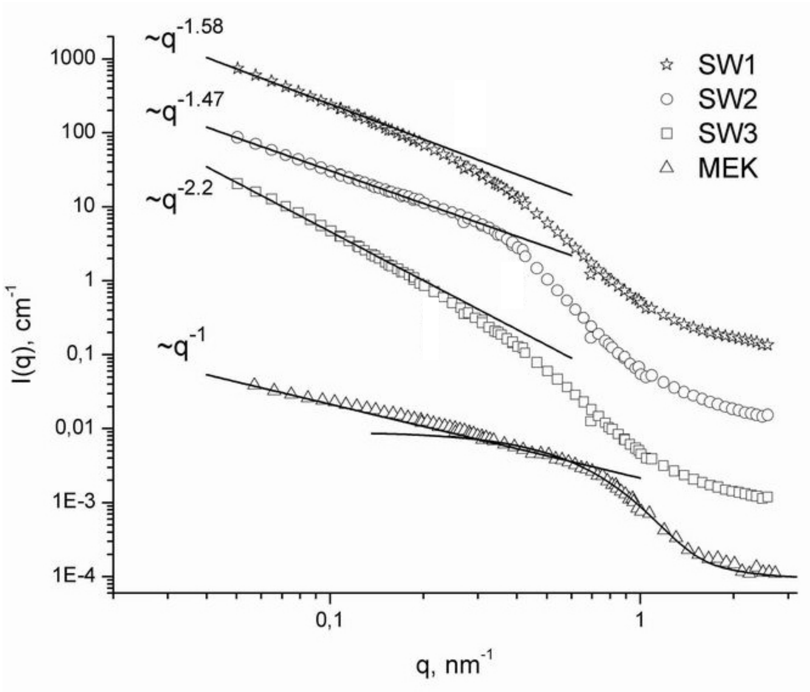
→ R_0 = 3.1 nm; $\Delta R/R_0$ = 0.25; δ_1 = 1.25 nm

M.Avdeev, M.Balasoiu, V.L.Aksenov, Gy.Török, L.Rosta, A.A.Vorobiev, D.Bica, L.Vekas,
X International Conference on Magnetic Fluids, August 2-6 2004, Guaruja, Brazil

Structure of ferrofluids on polar carriers



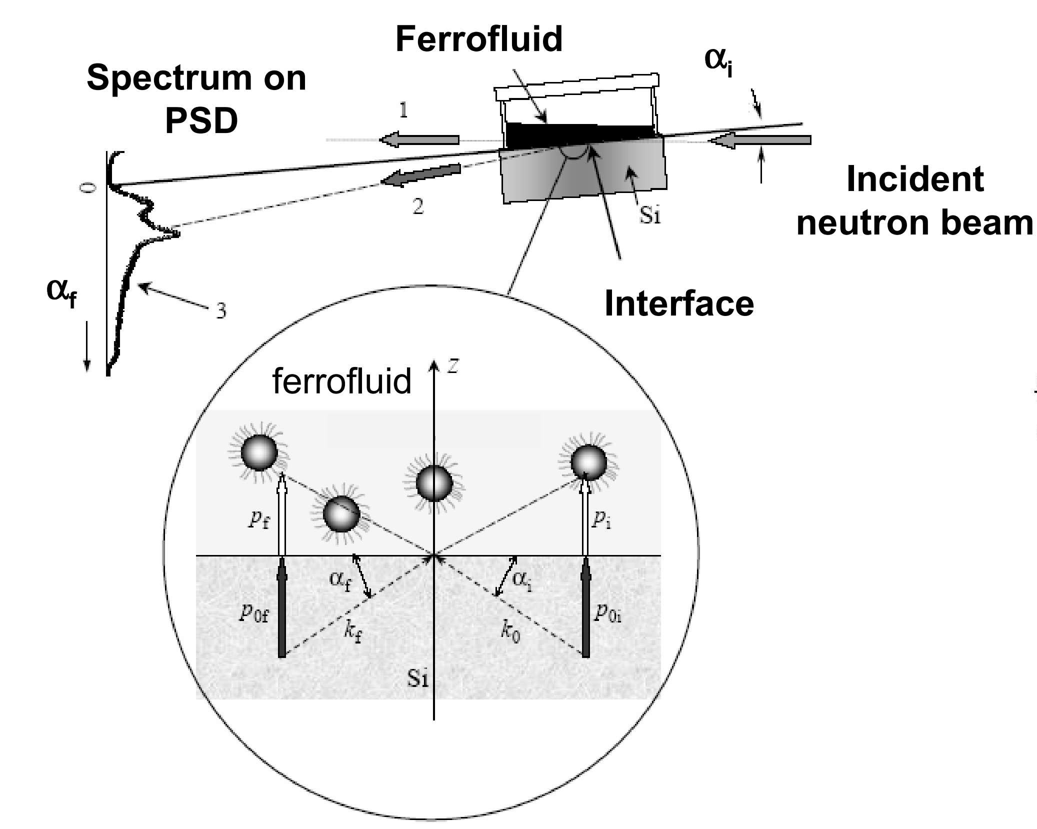
Experimental SANS curves for highly stable **pentanol-based** ferrofluids for different volume fraction of magnetite. Lines correspond to the model of polydisperse spheres.



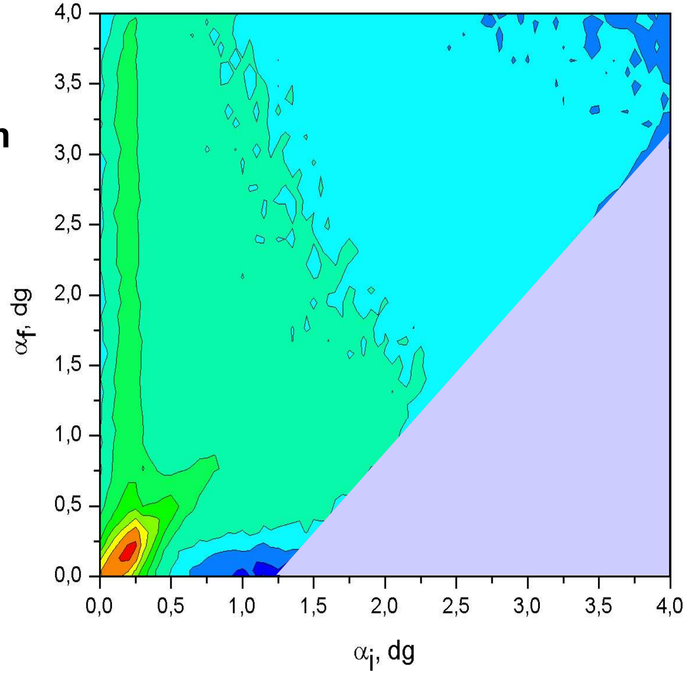
Experimental SANS curves from **water-based** (SW1-SW3) and **methylethylketon-based** (MEK) ferrofluids. Straight lines correspond to the power-law scattering from fractal clusters. The second line for the MEK sample is the calculation according to the core-shell model

M.V.Avdeev, V.L.Aksenov, M.Balasoiu, V.M.Garamus, A.Schreyer, Gy.Török, L.Rosta, D.Bica, L.Vékás, submitted to **J. Inter. Colloid. Sci.**

Neutron reflectometry



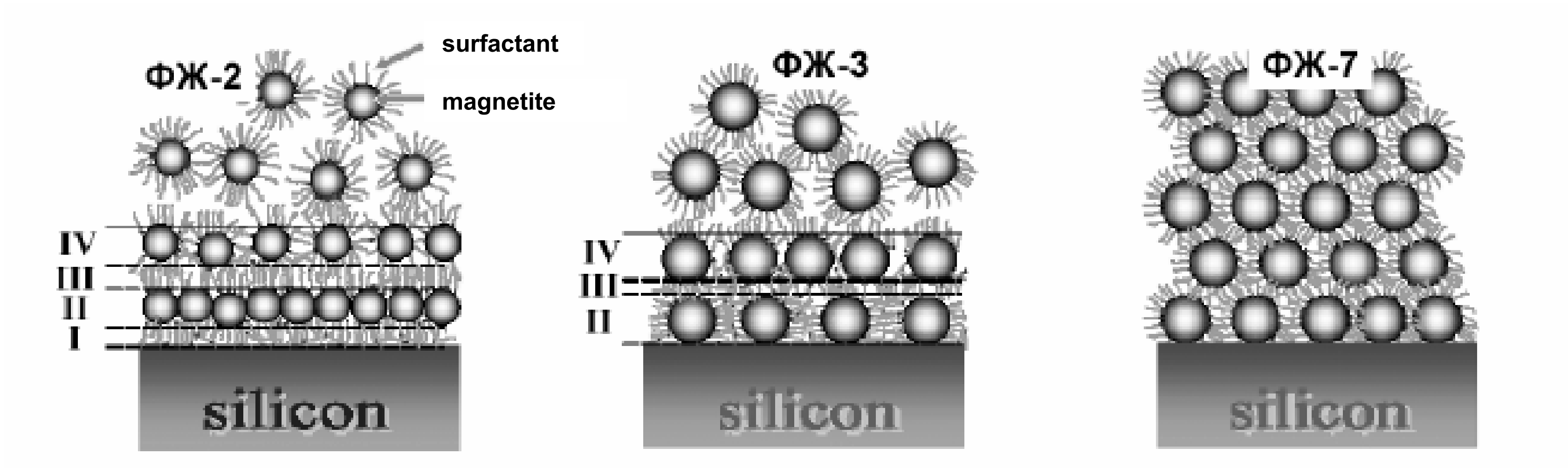
Scheme of experiment



Map of scattering intensity (diffractometer-reflectometer EVA, ILL, France)
Direction $\alpha_i = \alpha_f$ corresponds to the full reflection.

Ordering in water-based ferrofluids at interface with silicon by neutron reflectometry

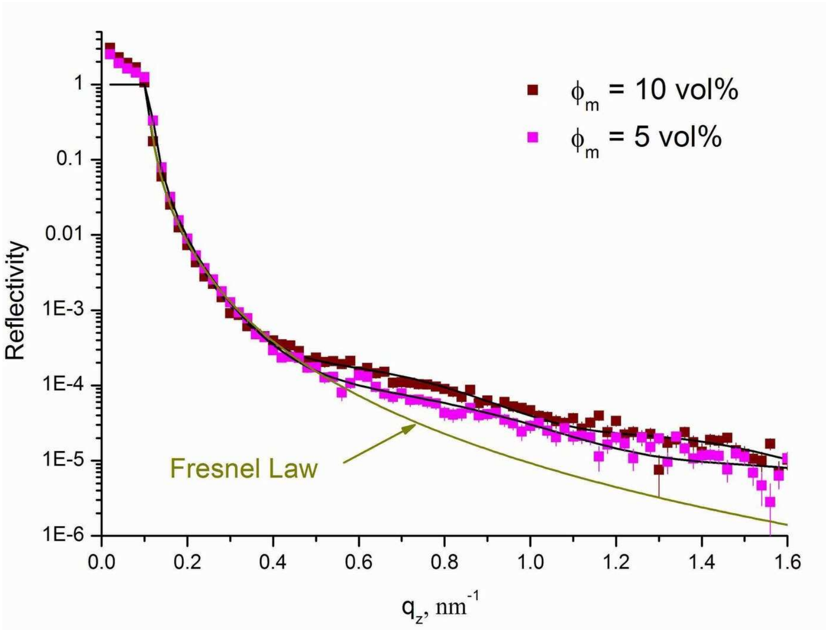
magnetite/sodium oleate/heavy water



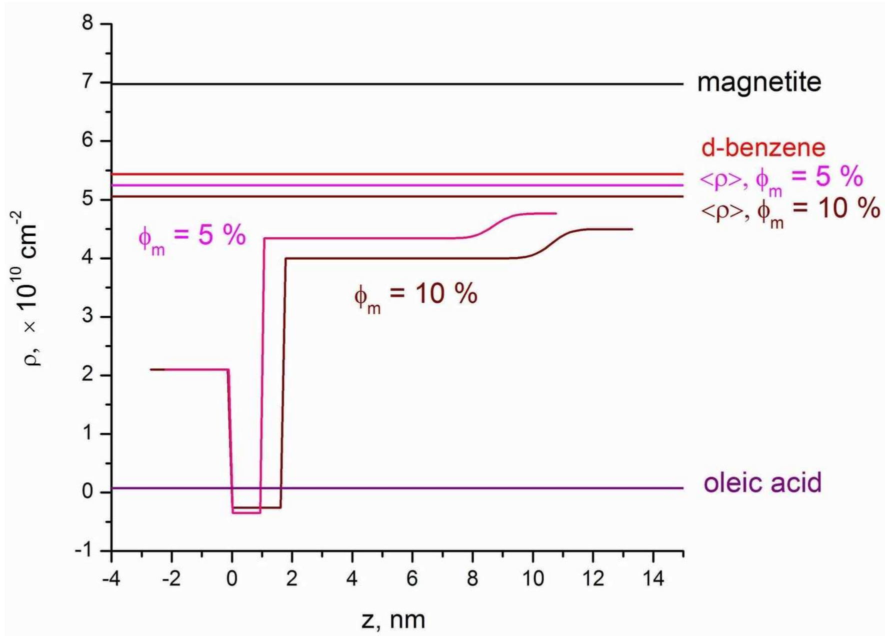
$\varphi_m = 2$ % $\varphi_m = 3$ % $\varphi_m = 7$ %

A.Vorobiev, G.Gordeev, W.Donner, H.Dosch, B.Nickel, B.Toperverg, *Physica B* (2001)
A.Vorobiev, G.Gordeev, J.Major, W.Donner, B.Toperverg, H.Dosch, *Applied Physics A* (2002)

Structure of ferrofluid magnetite/oleic acid/benzene at interface with silicon



Experimental and model reflctivity curves for ferrofluids with different volume fractions of magnetite



Scattering length density profiles obtained from the experiments and their comparison with calculated density values for different components of the fluids.

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Summary

- knowledge about microstructure of ferrofluids is very important for understanding of their stabilization mechanisms

- small-angle neutron scattering provides much information about features of microstructure of ferrofluids in bulk

- neutron reflectometry has good prospects for studying microstructure of ferrofluids at interfaces