India-JINR Meeting
16-19 October 2023

Small-angle scattering investigations of ferrofluids with anisometric nanoparticles

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16 October 2023

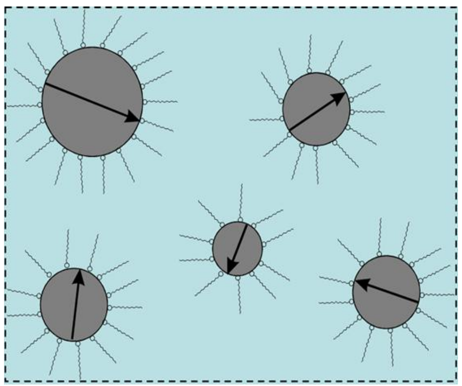
OUTLOOK

- About the subject of ferrofluids:
  - What are they and what can they be used for?
  - Information on the relevance of the topic
- Small angle neutron scattering method in the investigation of ferrofluid structural properties
- About the goal of present project
  - Development of new ferrofluids with enhanced magneto-optical properties
- SAS investigations to determine the nanostructural features for helping the chemists to choose or to improve their preparation methods or protocols
- Conclusions

What are ferrofluids and what can they be used for?

Mechanical devices
- dampers
- high vacuum bearings
- actuators
- valves
- switches
- lubricants

Technical acoustics
Measuring devices and sensors
Magnetic domain detection
Electromagnetic defectoscopy
Heat transfer
Materials Separators
Printing mechanisms
Bio-medical applications
………

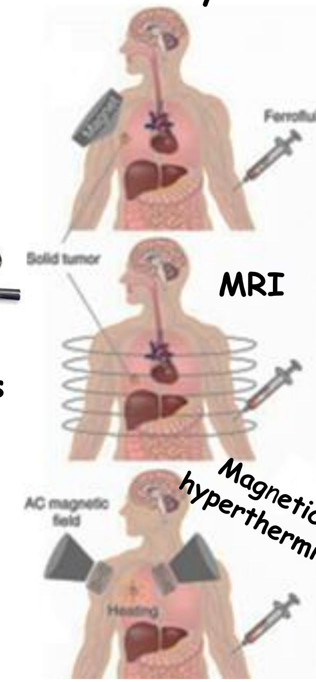


- ❑ **Magnetic particles**: Fe_3O_4, γ-Fe_2O_3, $CoFe_2O_4$, Co, $MnFe_2O_4$, Fe, etc.
- ❑ Mean diameter about 10nm;
- ❑ Log-normal size distribution;

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

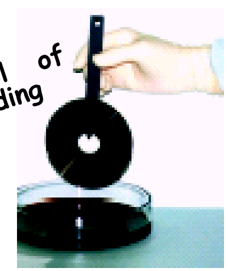
- ❑ One magnetic domain state;
- ❑ **Stabilizing layer**: surfactants, polymers, etc.
- ❑ **Liquid carrier**: hydrocarbons; alcohols, dieters, oils, etc.; water, biological serum

Magnetic drug delivery



Seals

Quality control of magnetic recording



Magnetic inks

Dampers

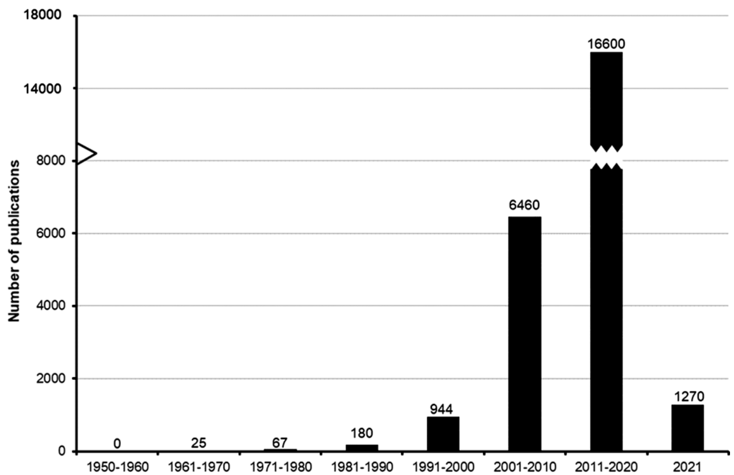
High vacuum bearings

Loudspeakers

Water treatment

On the relevance of the ferrofluid topic

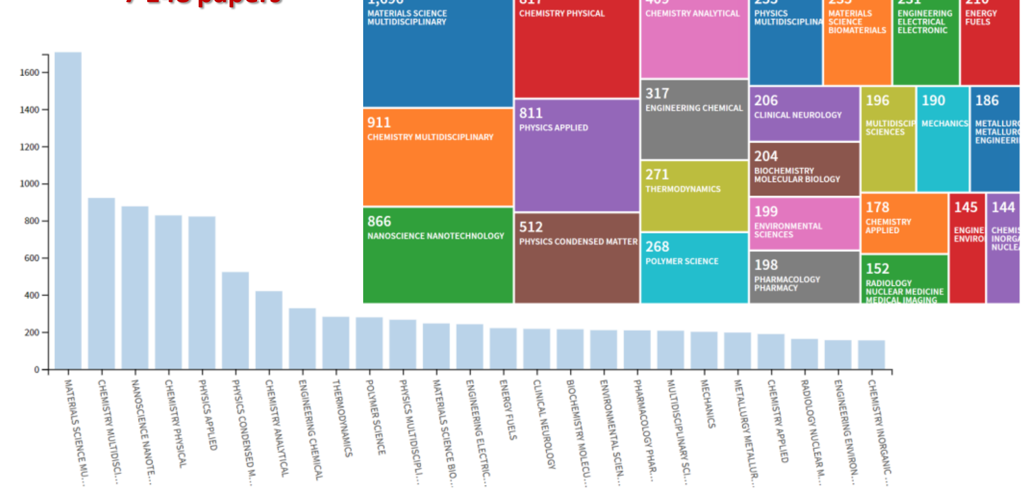
Number of scientific publications in the synthesis of ferrofluids over the years



Web of Science Paper Topic Statistics in 2021 year

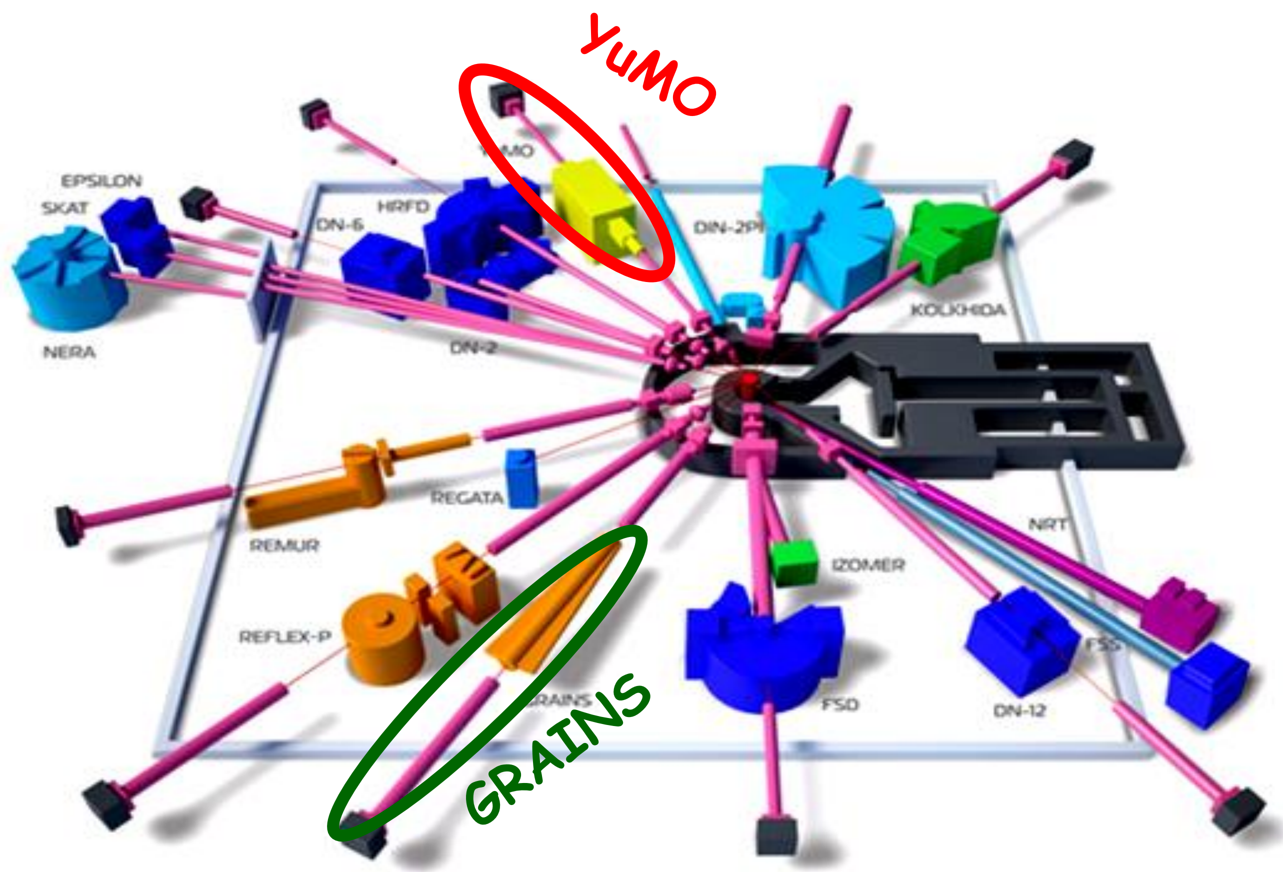
Ferrofluids, ferrocolloids, magnetic nanoparticles, magnetic fluids, magnetic liquids and structure

7 148 papers



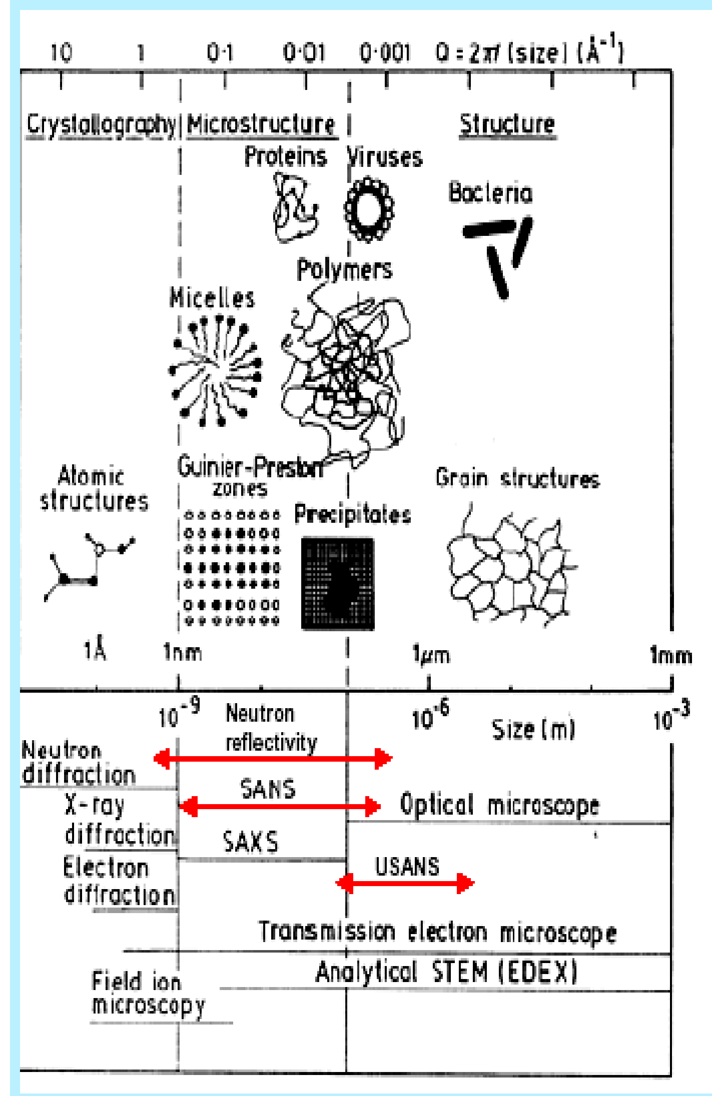

ICMF23
16th International Conference on
Magnetic Fluids
Granada (Spain), 12-16 June 2023

IBR-2 Experimental Hall
(JINR, Dubna)

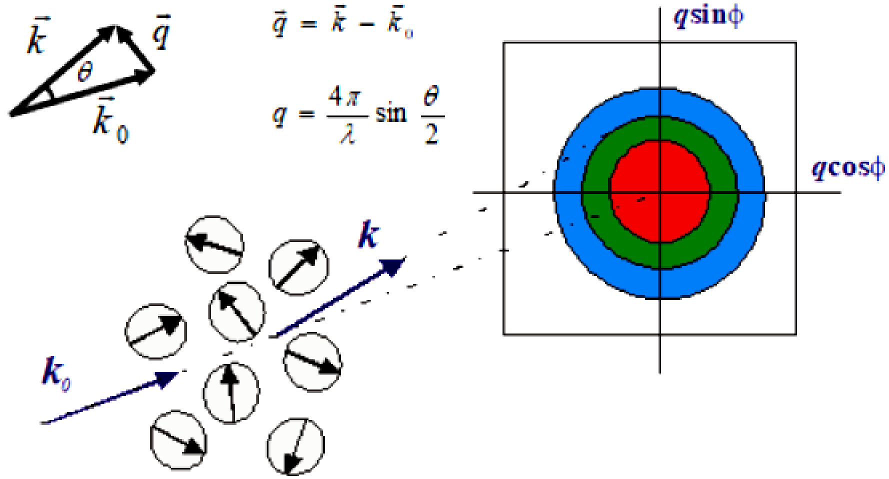


Small-angle neutron scattering (SANS)

- ❑ SANS resolves structures on scales from 1 to 1000 nm;
- ❑ Neutrons can be used to study bulk samples
(1-2 mm thick);
- ❑ SANS is sensitive to light elements such as H, C and N;
- ❑ SANS is sensitive to isotopes such as H and D.



Small-angle neutron scattering (SANS). Non-polarized neutrons.



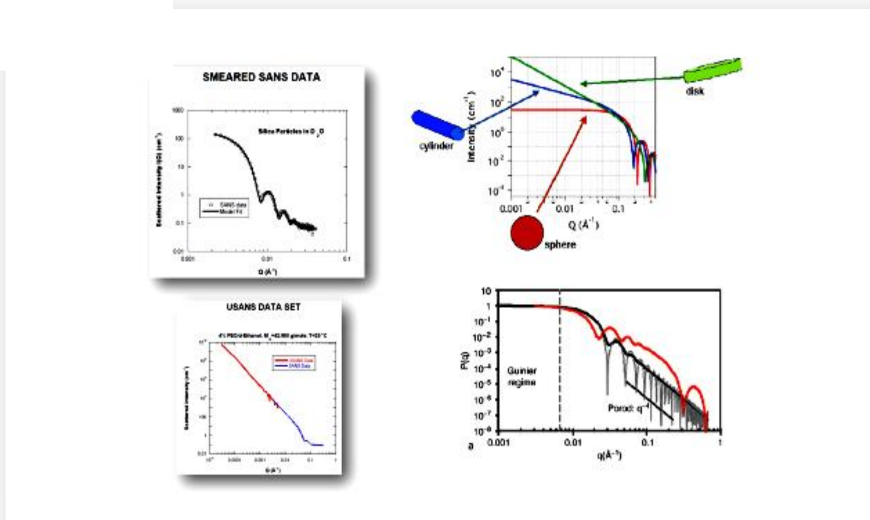
For low concentrated fluids (< 3 vol. %)

$$\frac{d\sigma}{d\Omega}(\vec{q}) \approx F_N^2(q) + \frac{2}{3}F_M^2(q) \approx F_N^2(q)$$

$\frac{d\sigma}{d\Omega}$ is differential scattering cross-section

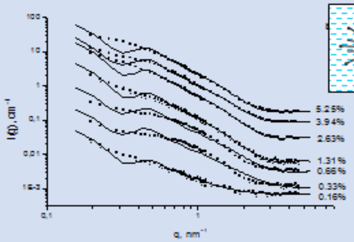
F_N is nuclear scattering amplitude

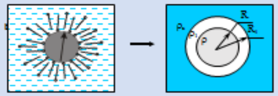
F_M is magnetic scattering amplitude



Water-based ferrofluids

$D_2O/DBS+DBS/Fe_3O_4$



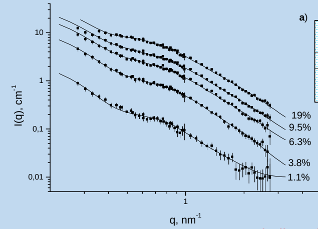


$\langle R \rangle \sim 6.6$ nm; $\langle R_1 - R \rangle \sim 3.5$ nm; $\Delta R/\langle R \rangle \sim 0.5$

•significant effect of interaction between colloidal particles in the solution

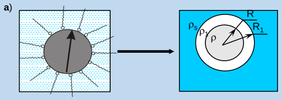
Structure of ferrofluids on non-polar organic carriers

Experimental curves



Model

non-interacting particles:



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

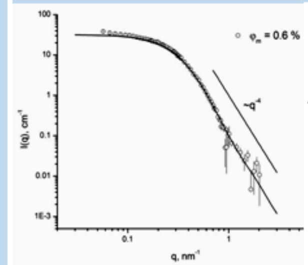
•core-shell model works well !

•interaction effect on the scattering is small for $\varphi_m < 5$ % !

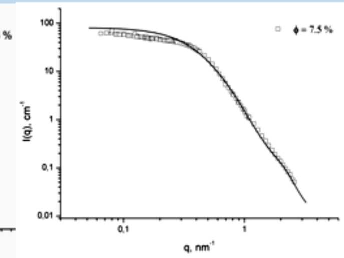
•effect of magnetic scattering contribution on resulting parameters does not exceed 15 % for d-carriers !

Pentanol-base ferrofluids: comparison with highly stable non-polar MF

H-pentanol/AO+DBS/Fe_3O_4



H-benzene/AO/Fe_3O_4

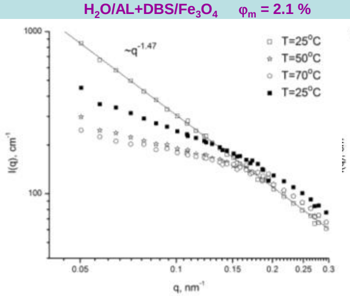


•Structures of the two types of ferrofluids are similar

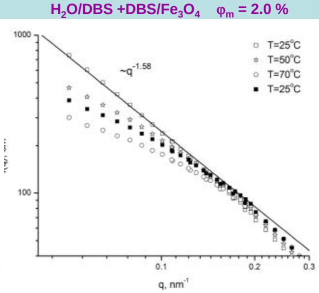
•interaction effect in polar ferrofluids is stronger

Water-based ferrofluids: temperature effect

$H_2O/AL+DBS/Fe_3O_4$ $\varphi_m = 2.1$ %



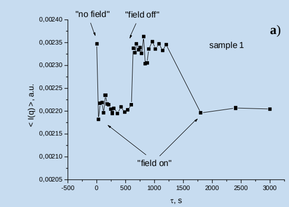
$H_2O/DBS+DBS/Fe_3O_4$ $\varphi_m = 2.0$ %



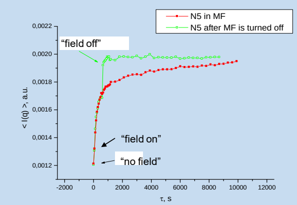
•Temperature increase results in destroy of secondary aggregates

•At once temperature returns to RT the aggregation starts again

Aggregation in ferrofluids under magnetic field

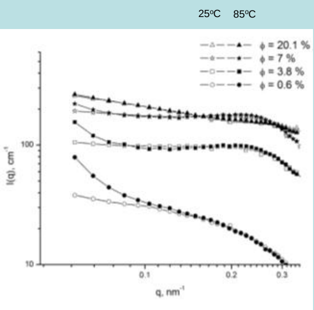


Changes in the mean scattering intensity in time under magnetic field for benzene-based fluid ($\varphi_m = 5$ %) due to formation of aggregates. No anisotropy in 2D scattering is observed.



Changes in the mean scattering intensity in time under magnetic field for water-based fluid ($\varphi_m = 5$ %) under magnetic field due to anisotropy in 2D magnetic scattering.

Pentanol-based ferrofluids: temperature effect

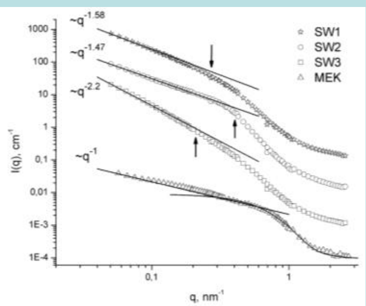


•Desorption of the second surfactant layer starts at T ~ 80ºC

•Desorption is higher for smaller particle concentration

•Formation of micelles in the systems and change in the structure of particles with concentration and temperature are unlikely

Water-based ferrofluids: aggregation effects



Experimental SANS curves for different water-based ferrofluids and MEK ferrofluid.

SW1: $H_2O/AL+DBS/Fe_3O_4$ $\varphi_m = 2.1$ %

SW2: $H_2O/DBS+DBS/Fe_3O_4$ $\varphi_m = 2.0$ %

SW3: sap/AO+AO/Fe_3O_4 $\varphi_m = 2.1$ %

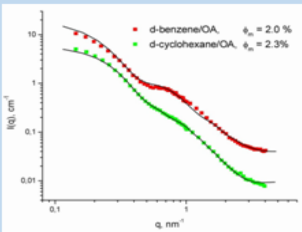
MEK: MEK/AO+DBS $\varphi_m = 5.7$ %

•Specific aggregation in initial ferrofluids takes place

•Formation of secondary fractal aggregates is detected

Effect of surfactant length

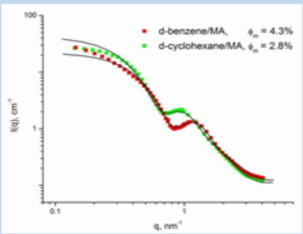
Oleic acid (OA): $C_{18}H_{34}O_2$



Results of fits of the core-shell model:

- $R_0 = 4.6$ nm; $\Delta R/R_0 = 0.35$; $\delta_1 = 1.31$ nm
- $R_0 = 4.1$ nm; $\Delta R/R_0 = 0.4$; $\delta_1 = 1.67$ nm

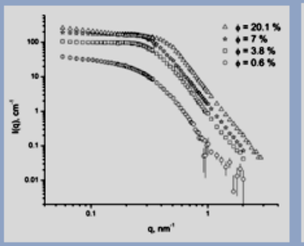
Myristic acid (MA): $C_{14}H_{28}O_2$

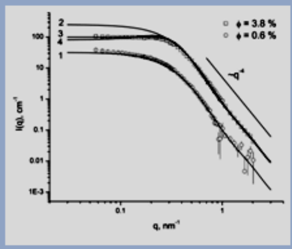


Results of fits of the core-shell model:

- $R_0 = 2.4$ nm; $\Delta R/R_0 = 0.4$; $\delta_1 = 1.28$ nm
- $R_0 = 3.1$ nm; $\Delta R/R_0 = 0.25$; $\delta_1 = 1.38$ nm

Pentanol-base ferrofluids: concentration effect





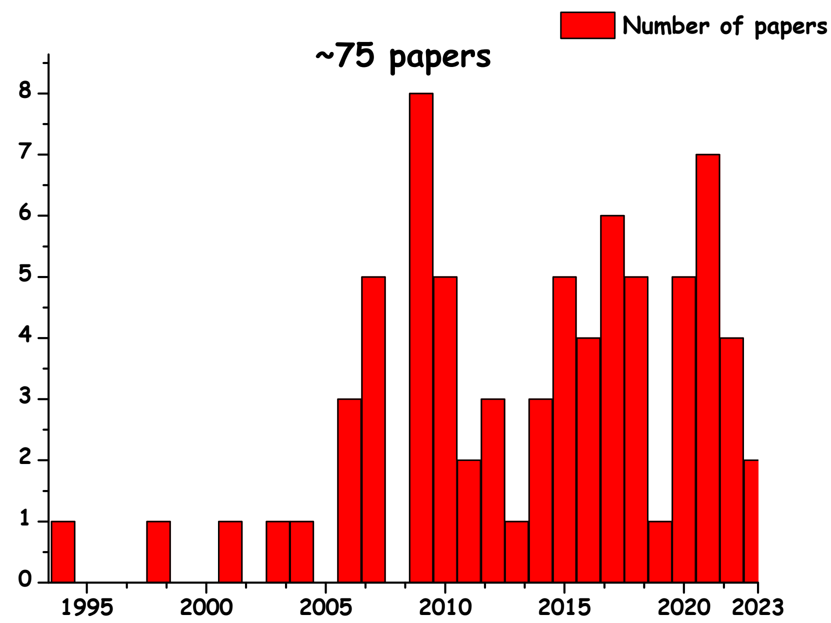
•Model of non-interacting spheres: $\varphi_m < 1$ %

•Model of hard spheres interaction: $1 \% < \varphi_m < 5$ %

•Soft interaction (surfactant shell) or magnetic attraction : $\varphi_m > 5$ %

Collaborations with:

- Romanian Academy Timisoara Section,
- Institute of Experimental Physics SAS, Košice, Slovakia,
- Biology Centre CAS, České Budějovice, Czech Republic,
- Faculty of Physics, Taras Shevchenko National University of Kyiv, Ukraine
- Institute of Technical Chemistry of Russian Academy of Sciences, Perm
- West University of Timisoara, Romania

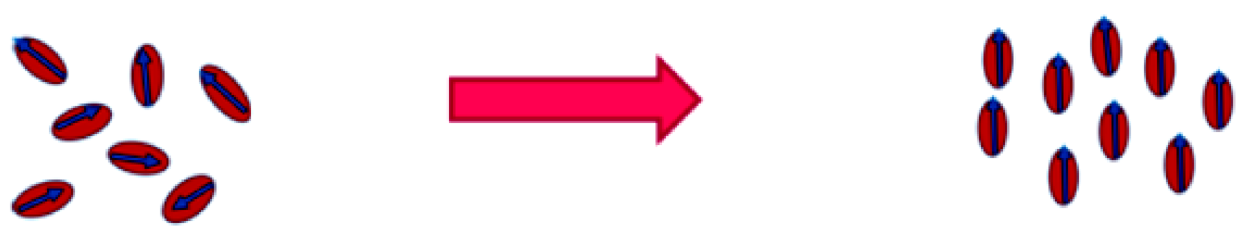


❖ Development of new magneto-optical systems for the control of optical fluxes in optoelectronics

Ferrofluids with an increased magneto-optical response in comparison to the already known effects was addressed.

Optical fluxes can be controlled if the properties of an anisotropic medium are affected by external electric or magnetic fields.

characteristic time of about ~ 10 ms



characteristic time of about ~ 50 μs !

Preparation of anisometric copper ferrite nanoparticles

(co-precipitation method)

Preparation of initial solution

$FeSO_4$

$CuSO_4$

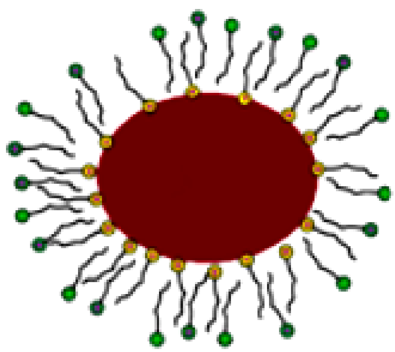
Adding $(NH_2OH)_2 \cdot H_2SO_4$ for oxidation of Fe(II) to Fe(III)

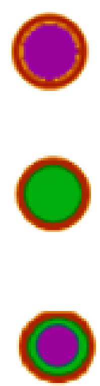
Adding NaOH and vigorous stirring; heating up to the boiling point at stirring and again adding NaOH; boiled 10 min

Washed with water to pH=8; added HCl until pH=4

For neutral medium, the precipitate is washed with deionized water and separated using a magnet

Stabilization by double layer in water





Lauric acid (LA)
$C_{11}H_{23}COOH$

Sodium dodecyl sulphate (SDS)
$CH_3(CH_2)_{11}OSO_3Na$

SDS : LA (1:1)

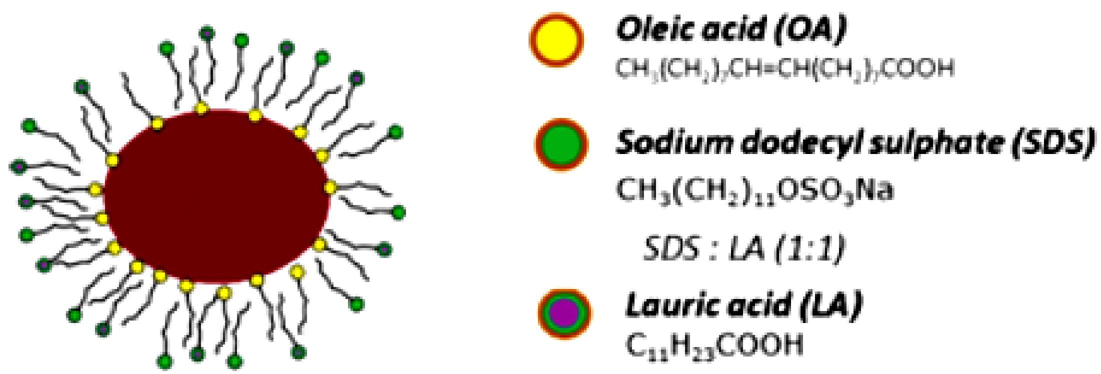
Lauric acid (LA)
$C_{11}H_{23}COOH$

Particles stabilized by surfactant double layer composed from 3 surfactant compounds

Preparation of lamellar barium hexaferrite nanoparticles

(hydrothermal synthesis)

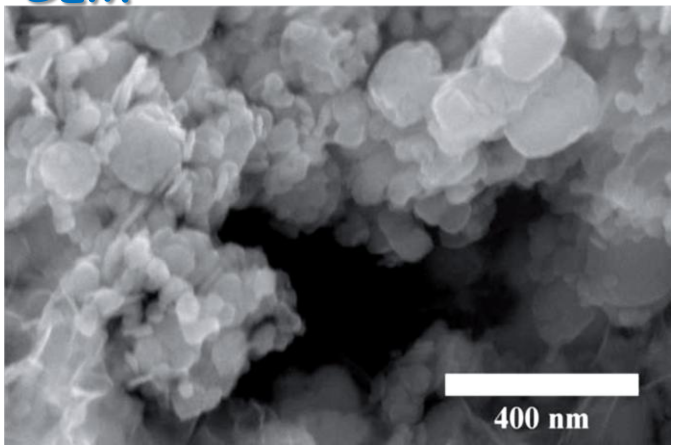
- Preparation of initial solution
  - $Fe(NO_3)_3$
  - $Ba(NO_3)_2$
- Adding NaOH for coprecipitation of hydroxides
- Autoclaving at 160°C
- Stabilization by oleic acid in ammonium medium
- Peptization in petroleum ether and centrifuging for "small" particle separation
- Stabilization by double layer in water



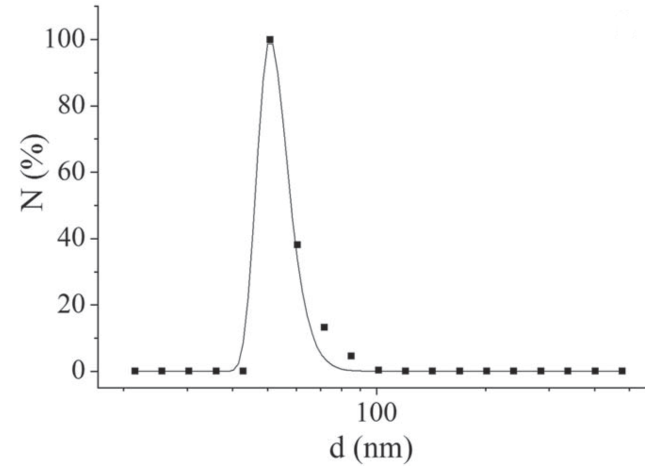
Particles stabilized by surfactant double layer composed from 3 surfactant compounds

Characterization of $CuFe_2O_4$ rod-like particles

SEM

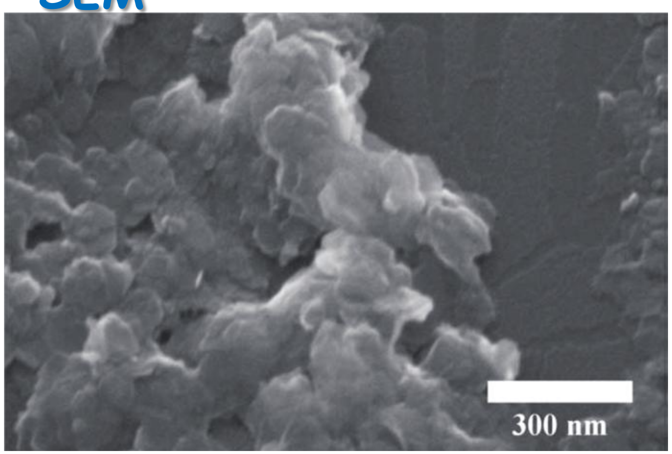


DLS

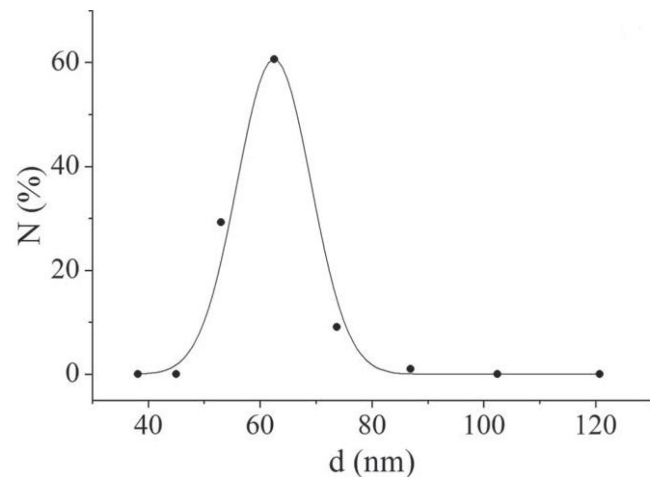


Characterization of $BaFe_{12}O_{19}$ nanoplates

SEM

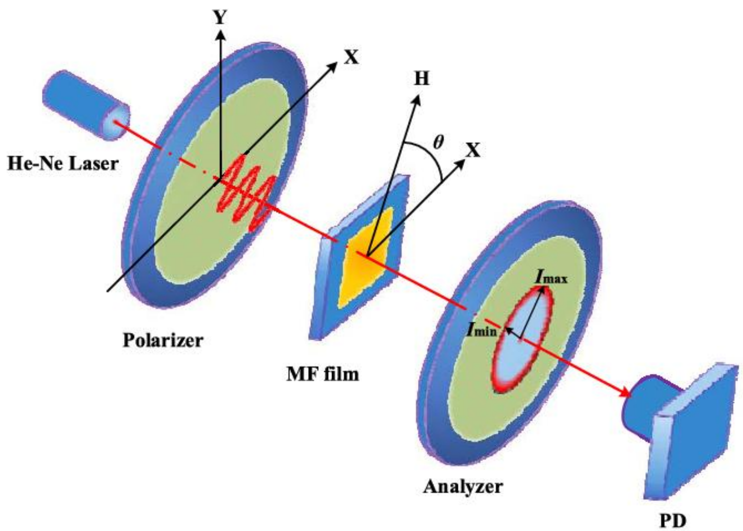


DLS

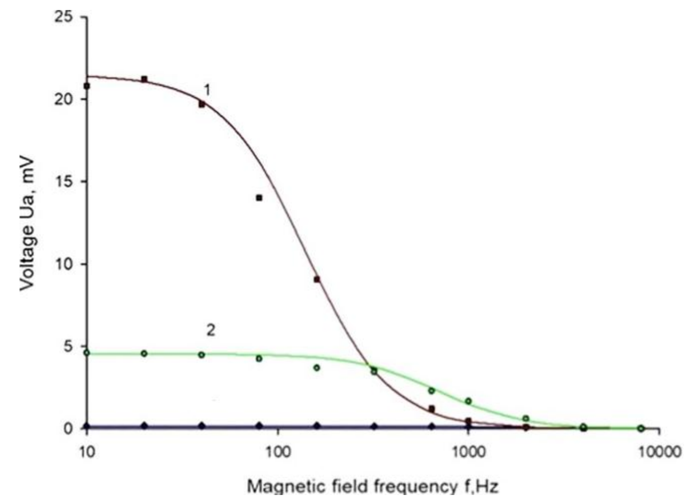


Particle size distribution according to dynamic light scattering data.

Birefringence in magnetic fluid subjected to magnetic field



General scheme of light birefringence :
The beam is split into two orthogonally polarized rays with angle θ between them.

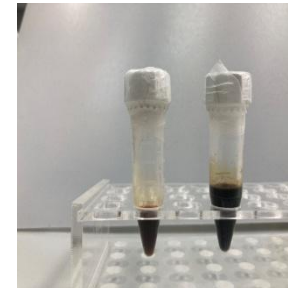


Frequency characteristics of magneto-optical signal for ferrofluids:
(1)- Ferrofluid with BaFe12O19/H2O, 'large' nanoplates;
(2)-Ferrofluid with Cu0.64Fe2O4/H2O, 'large' nanorods.

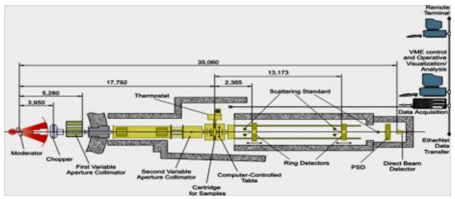
Lysenko S.N., Lebedev A. et al, Physica Scripta (2020) 95(4).

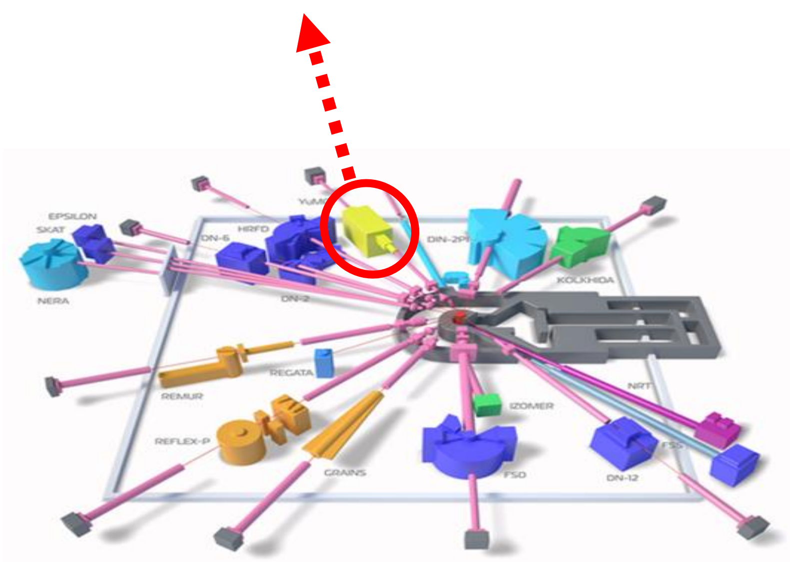
Experimental

SANS



SANS-YuMO Instrument





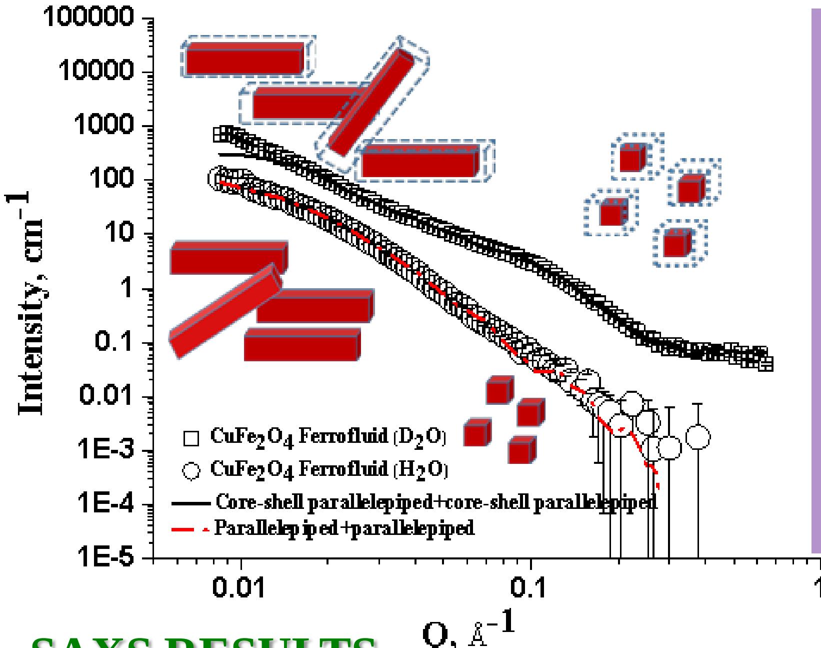
IBR-2 Experimental Hall (JINR, Dubna)

SAXS

Xeuss 3.0 (FLNP-JINR, Dubna)

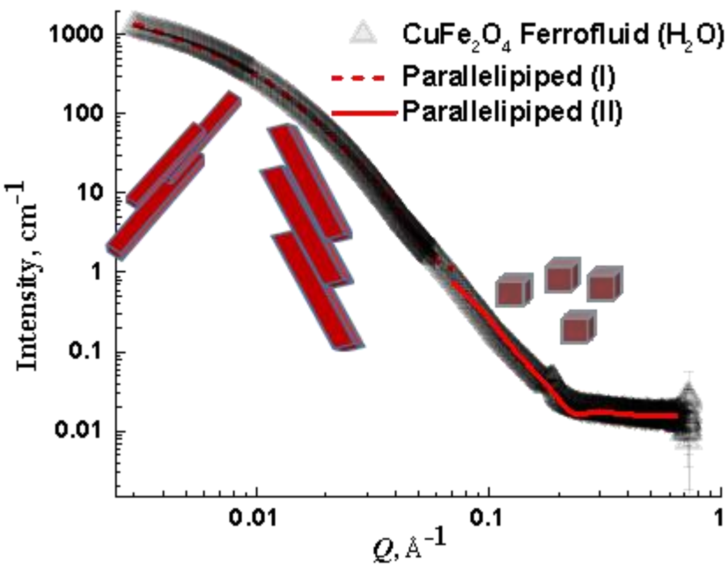
RIGAKU (MPhTI, Dolgopudnyi)

SANS RESULTS



Sample	Q-range [$Å^{-1}$]	Model fit	Dimensions [nm]
$CuFe_2O_4$/LA/LA+SDS/H_2O	0.008÷0.15	Parallelepiped + Parallelepiped	A_1~15; B_1~25 C_1~80
			A_2~13; B_2~22 C_2~8
$CuFe_2O_4$/LA/LA+SDS/D_2O	0.008÷0.52	Core-shell parallelepiped + Core-shell parallelepiped	A_1~5; t_{A1}~2 B_1~20; t_{B1}~1 C_1~60; t_{C1}~10
			A_2~5; t_{A2}~2 B_2~15; t_{B2}~2.5 C_2~20; t_{C2}~8

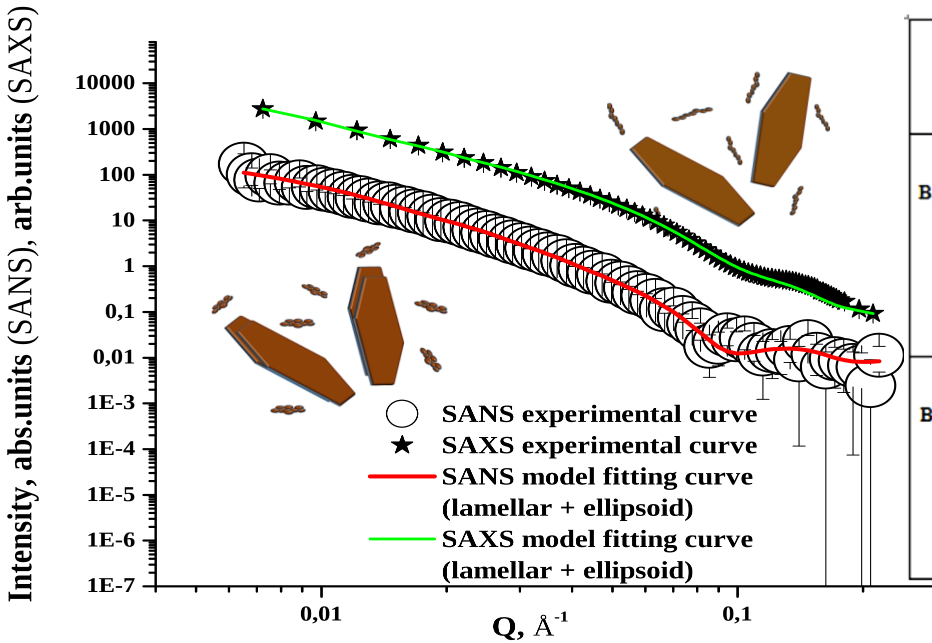
SAXS RESULTS



Sample	Q-range [$Å^{-1}$]	Model fit	Dimensions [nm]
$CuFe_2O_4$/LA/LA+SDS/H_2O	0.005÷0.04	Parallelepiped	A=10 B=30 C=220
	0.04÷0.7	Parallelepiped	a= 2.6 b=5.5 c=40

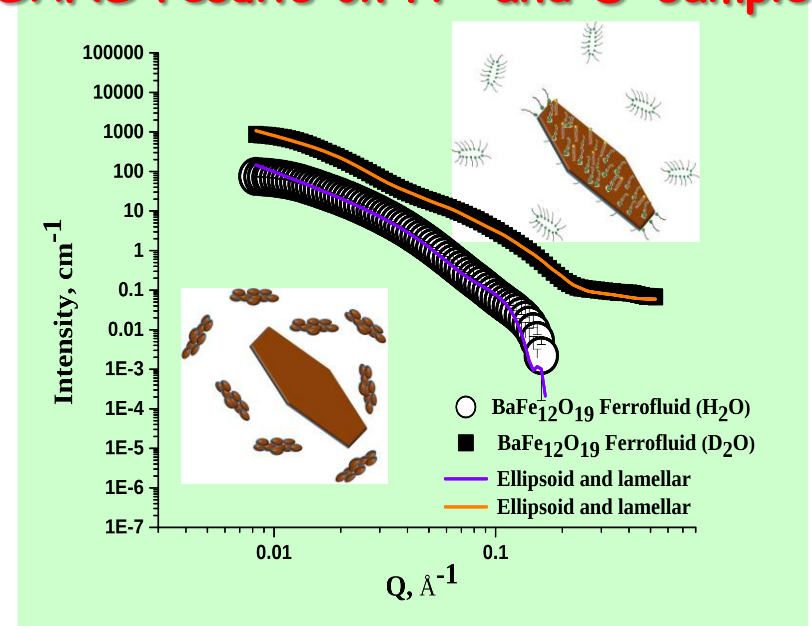
Balasoiu M., Astaf'eva S. et al., Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques 17(3), 730–737 (2023).

SAXS and SANS results on H-sample



Sample	Q-range [nm⁻¹]	Model fit	Modal parameters	Dimensions [nm]
$BaFe_{12}O_{19}$/OA/LA+SDS/H_2O	0.08÷2	Ellipsoid + lamellar-shaped particles	R_p R_e δ	3.0±0.1 14.0±0.3 7.8±0.1
$BaFe_{12}O_{19}$/OA/LA+SDS/D_2O	0.08÷2	Ellipsoid + lamellar-shaped particles	R_p R_e δ	1.5±0.1 15.1±0.1 14.2±0.1

SANS results on H- and D-samples

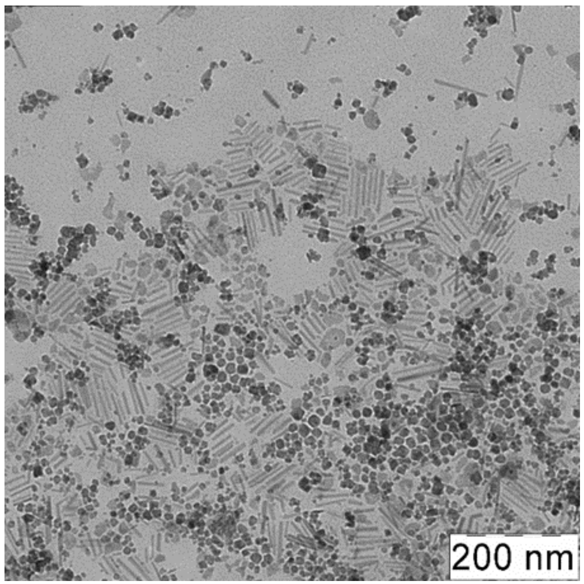


Experimental method	Q-range [nm⁻¹]	Model fit	Modal parameters	Dimensions [nm]
SAXS	0.07÷2	Ellipsoid + lamellar-shaped particles	R_p R_e δ	3.0±0.1 34.0±0.6 7.0±0.1
SANS	0.07÷2	Ellipsoid + lamellar-shaped particles	R_p R_e δ	4.1±0.1 26.1±0.7 14.1±0.6

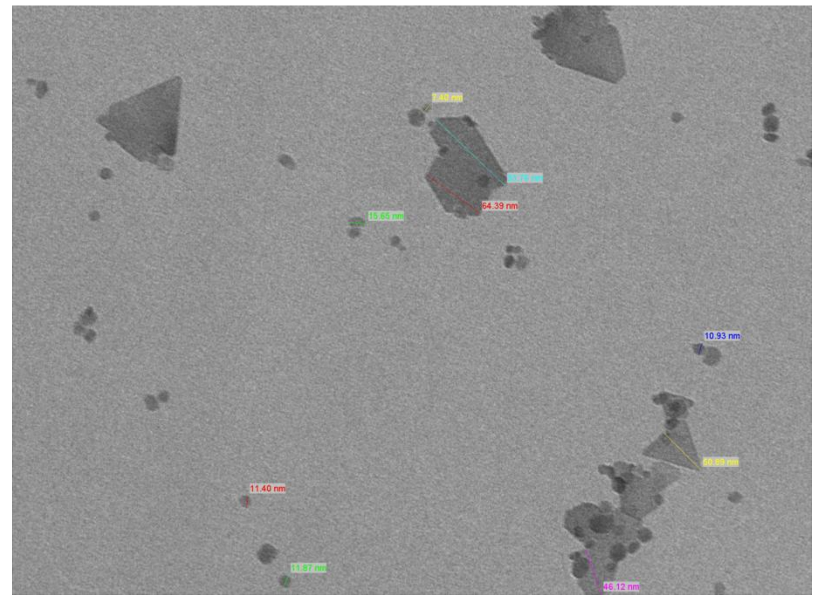
Balasoiu M., Astaf'eva S. et al., Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques (2023) (submitted).

Comparison with TEM

$CuFe_2O_4$



$BaFe_{12}O_{19}$



Conclusions

- New water based ferrofluids with anisometric particles have been synthesized for magneto-optical applications;
- The magneto-optical response of new obtained ferrite colloids ($BaFe_{12}O_{19}$ and $CuFe_2O_4$) as a function of magnetic field frequency showed a pronounced effect;
- The SANS measurements have been accomplished at the YuMO instrument in function at the IBR-2 reactor;
- SANS and SAXS analysis detected clearly system structure with combined big and small particles; the morphology and size parameters for each type have been obtained;
- The transmission electron microscopy images of the samples shows a good agreement with SANS and SAXS results.
- By combining SANS and SAXS investigations, and measurements of H- and D-based ferrofluid, complementary information on the surfactant distribution on the particles surface and structure of the system have been obtained.

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