Magnetic fluids and elastomers: Structural studies for innovative applications

Maria Balasoiu[1,2]

[1]Frank Laboratory of Neutron Physics, JINR, Dubna, Russia
[2]Horia Hulubei Hational Institute of Physics and Nuclear Engineering, Magurele, Romania

Program Advisory Committee for Condensed Matter, JINR, Dubna,

28.06.2021

Outline

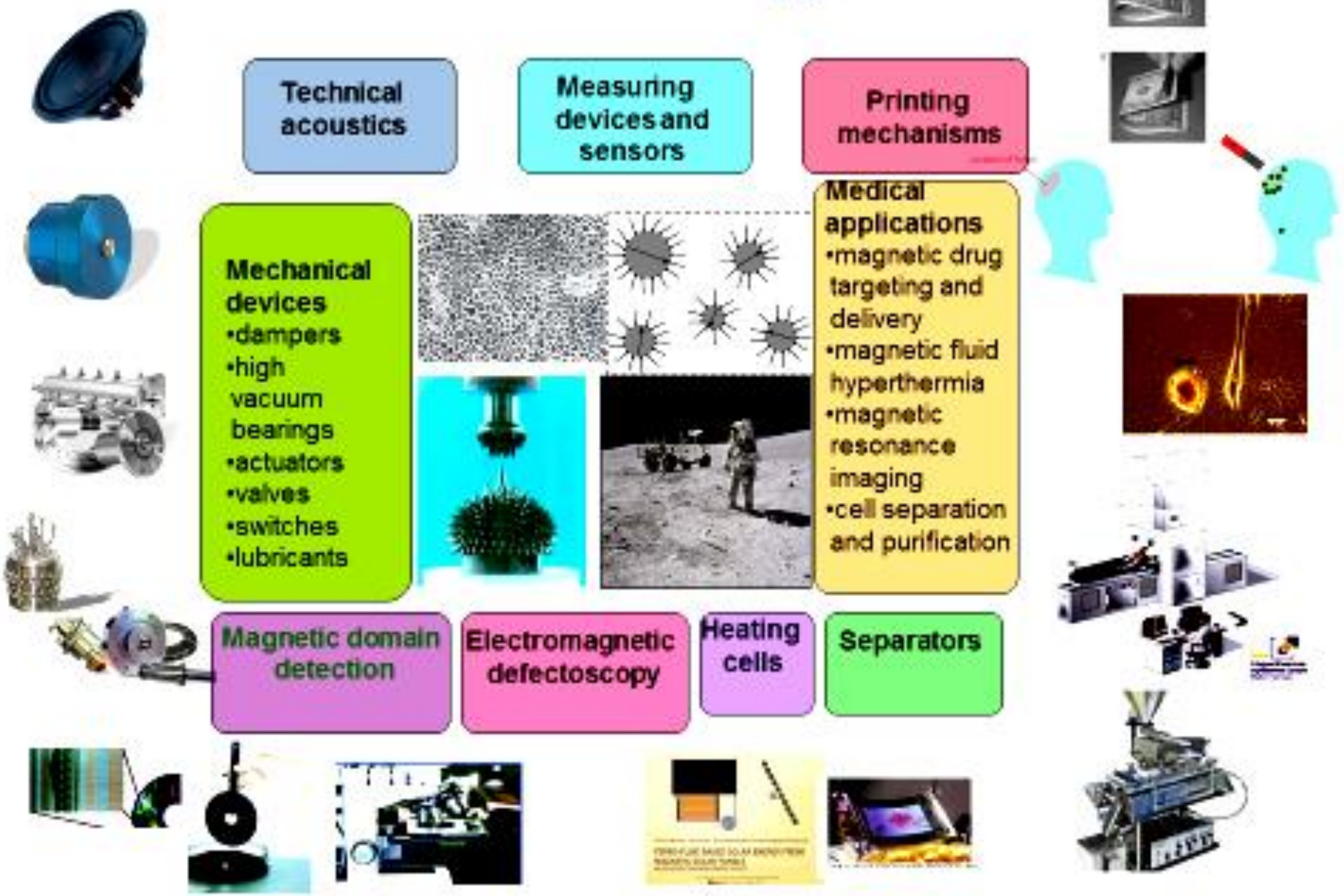
- ❑ **Ferrofluids and their applications**
  - Examples of applications
  - Publication statistics
  - Structural investigation: SANS, SAXS

- ❑ **Magnetic and magnetorheological elastomers (MEs and MREs)**
  - Examples of applications
  - Statistics
  - Structural investigation: SANS, SAXS, ND

  - ❑ Neutron Centers and used facilities
  - ❑ Accessible complementary methods

- ❑ **Acknowledgements**

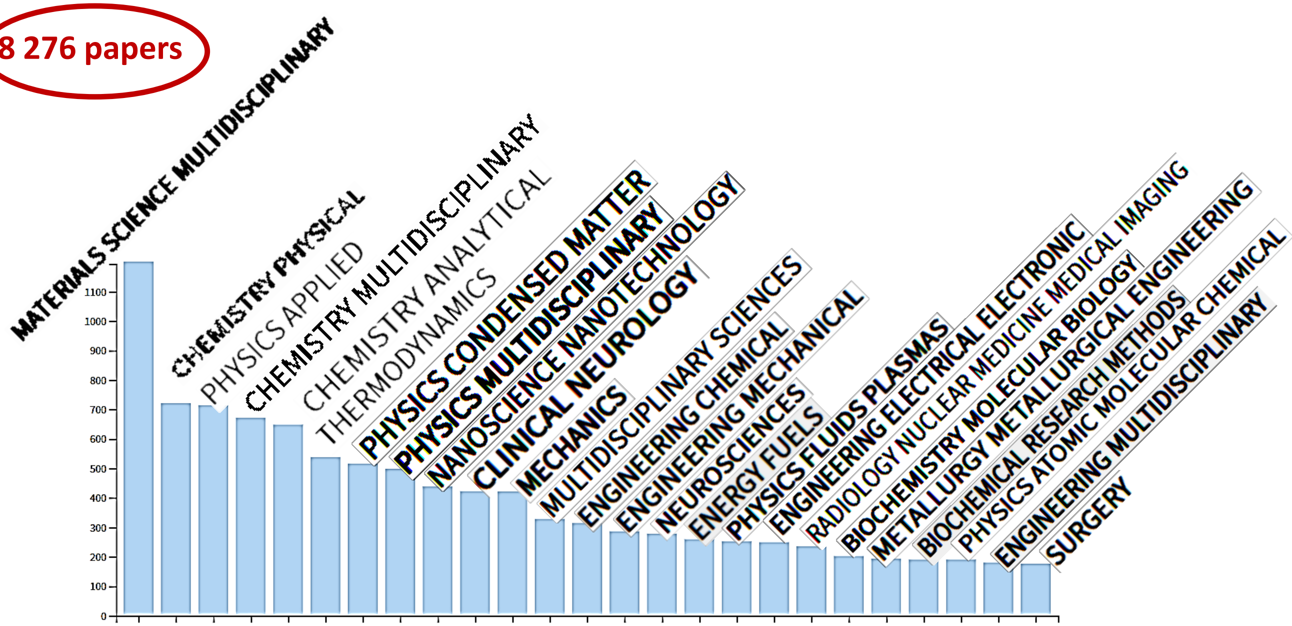
Ferrofluids and their applications



Web of Science Paper Topic Statistics in 2020 year

Ferrofluids, ferrocolloids, magnetic fluids, magnetic liquids

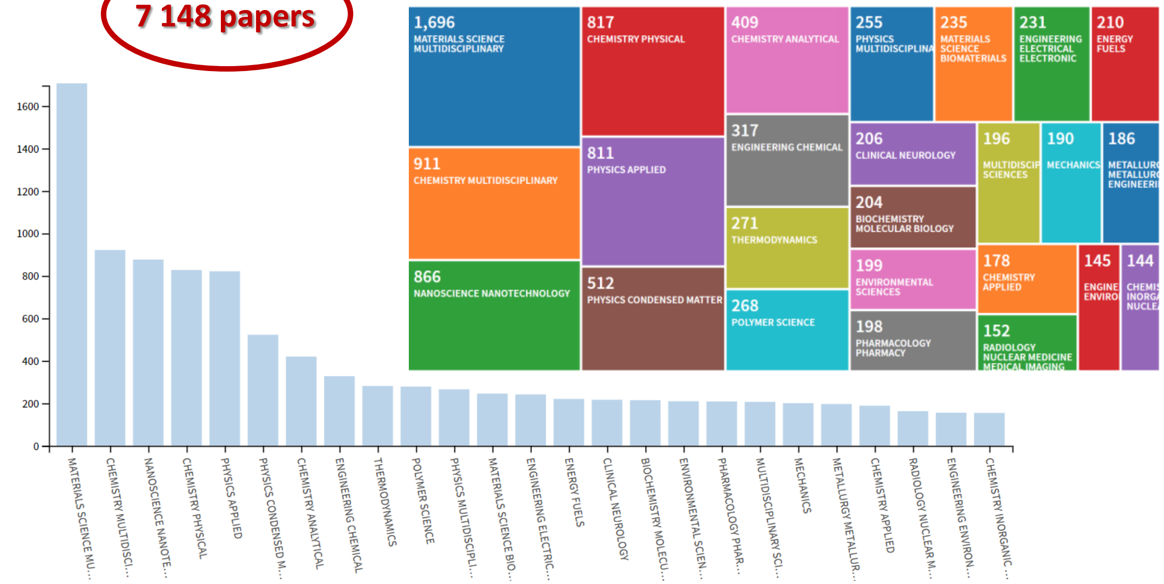
8 276 papers



Web of Science Paper Topic Statistics in 2021 year

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

7 148 papers



Neutron scattering is a perfect tool to investigate the ferrofluids due to the specificity of neutron interaction with the condensed matter, both nuclear and magnetic.

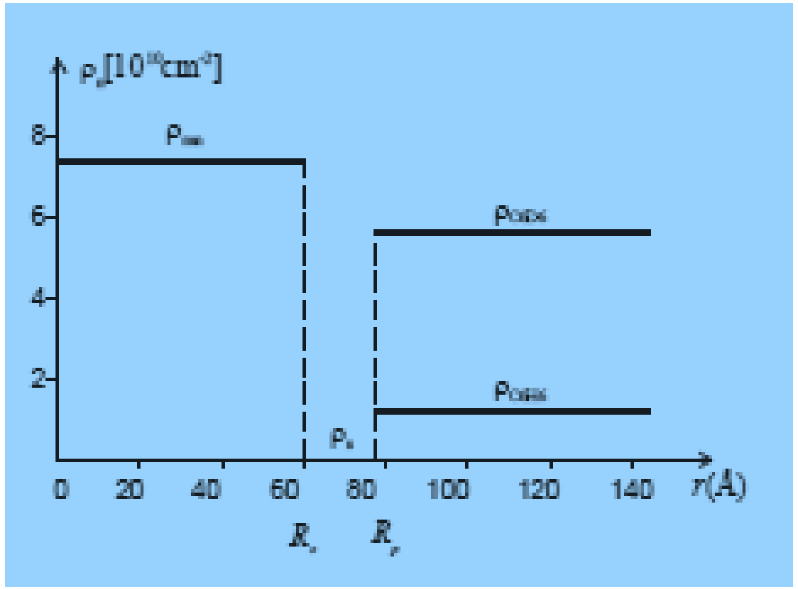
Determination of the nuclear structure

- parameters of the particle size distribution
- thickness and composition of the surfactant shell
- micelle formation in ferrofluids
- interparticle interaction
- particle aggregation
- variation of the microstructure with the temperature

Determination of the magnetic structure

- magnetic size of particles and aggregates
- magnetic corelations between particles

Determination of the nuclear and magnetic component of the SANS of nonpolarized neutrons in the Guinier range by means of the contrast variation method - MURN (YuMO) facility in function at the IBR-2 reactor



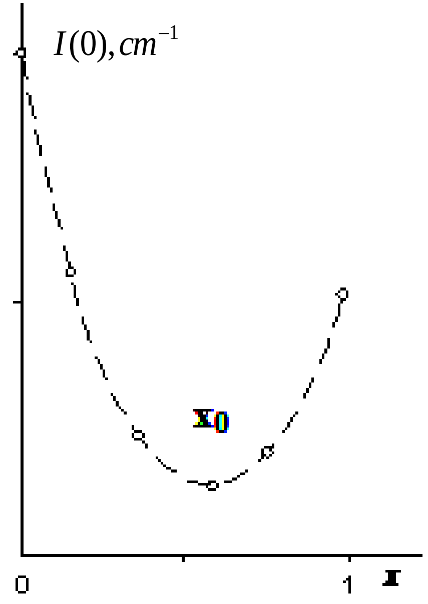
$$I(q) = I_n(0)\exp\left[\frac{R_{gn}^2 q^2}{3}\right] + I_m(0)\exp\left[\frac{R_{gm}^2 q^2}{3}\right]$$

$$I_n(0) = n_p(\rho_n V_n)^2$$

$$\rho_n = \langle \rho_p - \rho_c \rangle$$

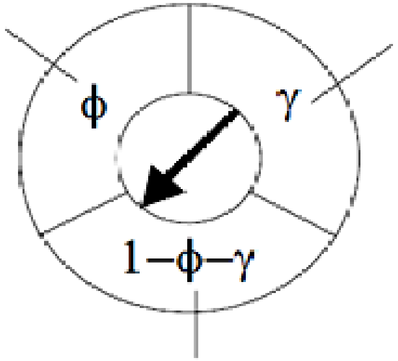
$$\rho_c = x\rho_{cd} + (1-x)\rho_{cД}$$

$$I_m(0) = n_p(\rho_m V_m)^2$$



Surfactant shell

Surfactant

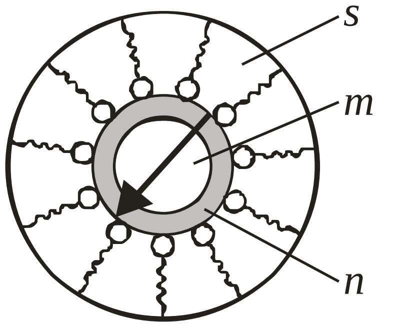


Liquid base

Empty volume

$$R_{gn} = 4.6 \pm 0.2nm$$

$$R_{gm} = 3.6 \pm 0.2nm$$



Magnetic core

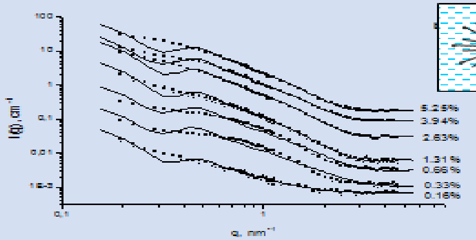
Nonmagnetic layer

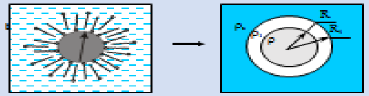
B. Grabcev, M. Balasoiu, D. Bica, A.I. Kuklin, Magnitnaia Gidrodinamica 10(2) (1994) 156-162

B. Grabcev, M. Balasoiu, A. Tarziu, A.I. Kuklin and D. Bica, *J. Mag. Mag. Mater.* 201 (1999) 140-143

Water-based ferrofluids

D_2O/DBS+DBS/Fe_3O_4



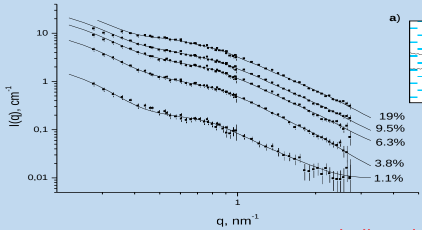


<R> ~6.6 nm; <R_1 - R> ~3.5 nm; ΔR/<R> ~0.5

•significant effect of interaction between colloidal particles in the solution

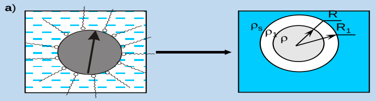
Structure of ferrofluids on non-polar organic carriers

Experimental curves



Model

non-interacting particles:



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

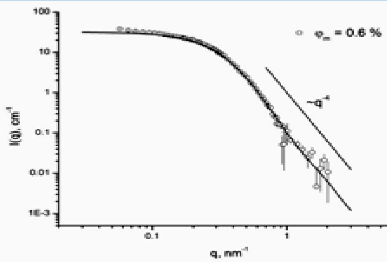
•core-shell model works well !

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

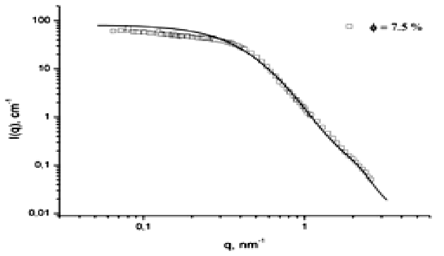
•effect of magnetic scattering contribution on resulting parameters does not exceed 15 % for d-carriers !

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

H-pentanol/AO+DBS/Fe_3O_4



H-benzene/AO/Fe_3O_4

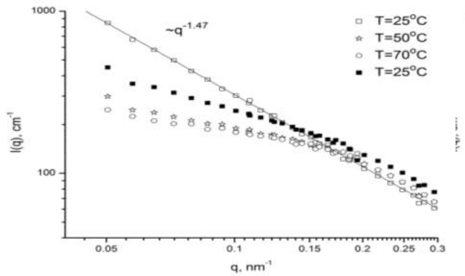


•Structures of the two types of ferrofluids are similar

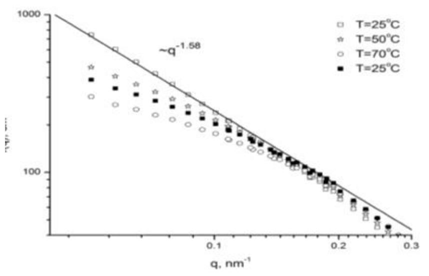
•interaction effect in polar ferrofluids is stronger

Water-based ferrofluids: temperature effect

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



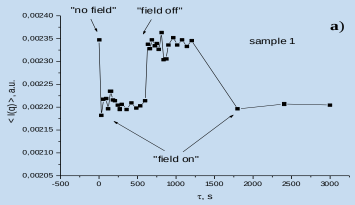
H_2O/DBS +DBS/Fe_3O_4 $\varphi_m = 2.0$ %



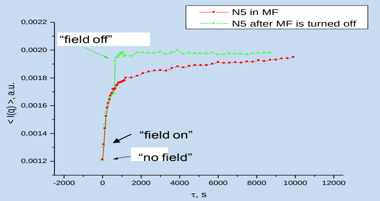
•Temperature increase results in destroy of secondary aggregates

•At once temperature returns to RT the aggregation starts again

Aggregation in ferrofluids under magnetic field



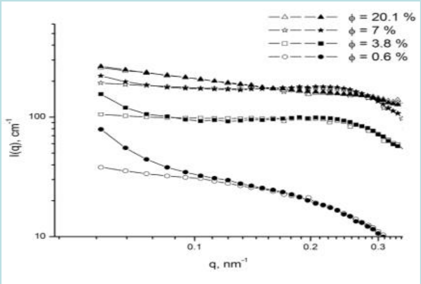
Changes in the mean scattering intensity in time under magnetic field for benzene-based fluid ($\varphi_m = 5$ %) due to formation of aggregates. No anisotropy in 2D scattering is observed.



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

25ºC 85ºC

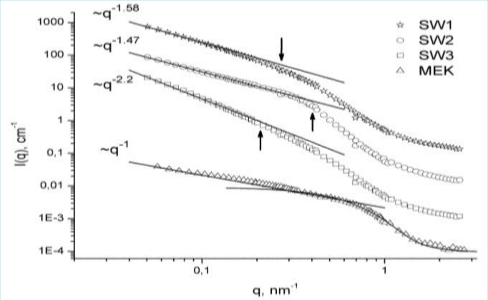


•Desorption of the second surfactant layer starts at T ~ 80ºC

•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.

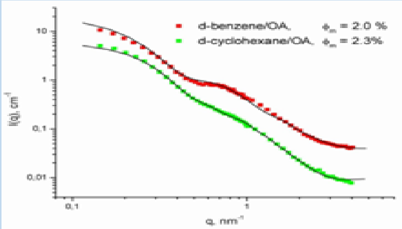
SW1: H_2O/AL+DBS/Fe_3O_4 $\varphi_m = 2.1$ %
SW2: H_2O/DBS +DBS/Fe_3O_4 $\varphi_m = 2.0$ %
SW3: sap/AO+AO/Fe_3O_4 $\varphi_m = 2.1$ %
MEK: MEK/AO+DBS $\varphi_m = 5.7$ %

•Specific aggregation in initial ferrofluids takes place

•Formation of secondary fractal aggregates is detected

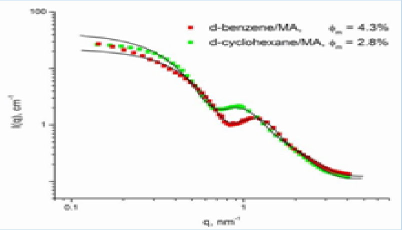
Effect of surfactant length

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



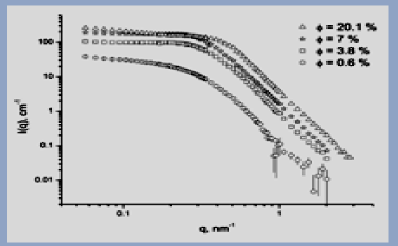
Results of fits of the core-shell model:
□ R_0 = 4.6 nm; ΔR/ R_0 = 0.35; δ_1 = 1.31 nm
□ R_0 = 4.1 nm; ΔR/ R_0 = 0.4; δ_1 = 1.67 nm

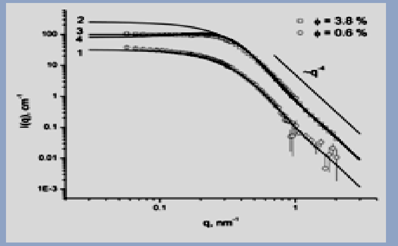
Myristic acid (MA): $C_{14}H_{28}O_2$



Results of fits of the core-shell model:
□ R_0 = 2.4 nm; ΔR/ R_0 = 0.4; δ_1 = 1.28 nm
□ R_0 = 3.1 nm; ΔR/ R_0 = 0.25; δ_1 = 1.38 nm

Pentanol-base ferrofluids: concentration effect





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

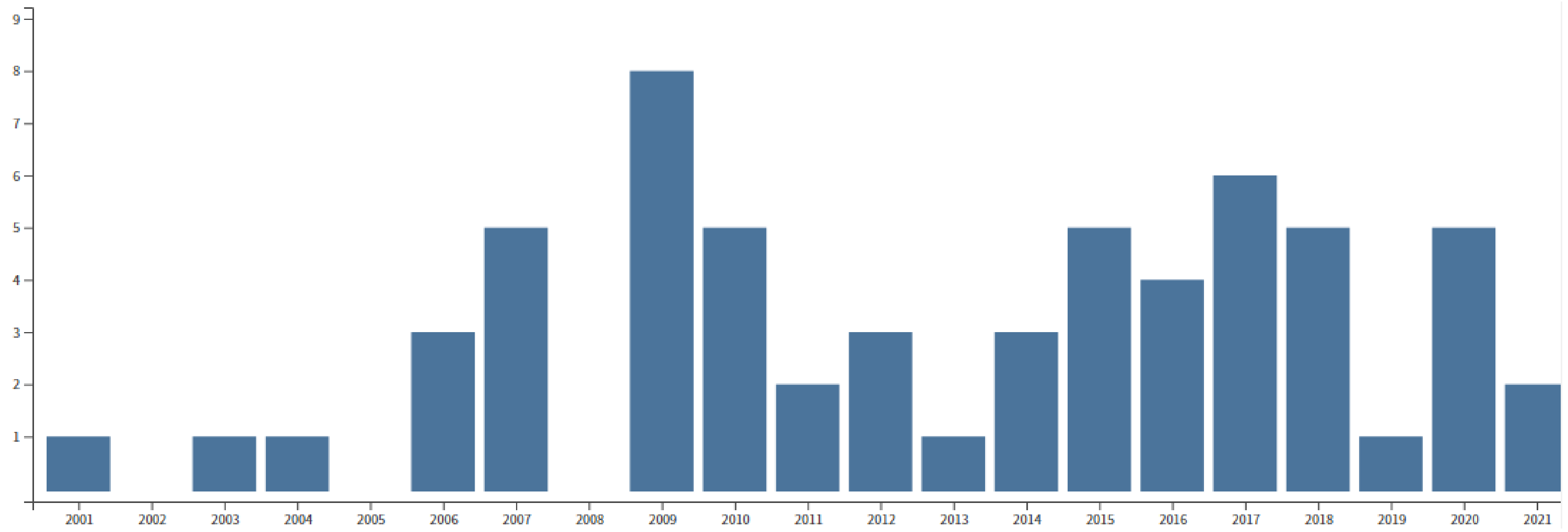
•Model of hard spheres interaction: 1 % < $\varphi_m < 5$ %

•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

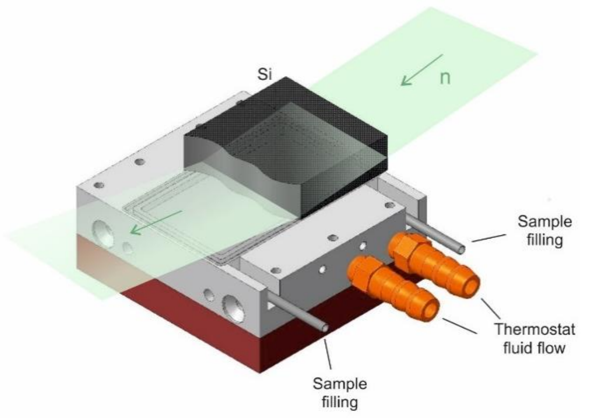
M.V. Avdeev & Group

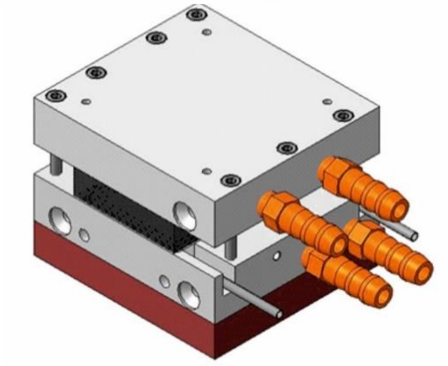
>60 Papers

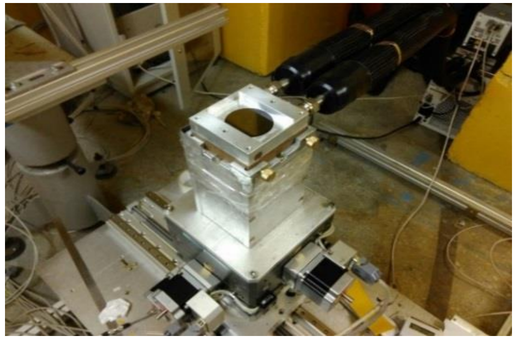


Interfaces of ferrofluids with silicon substrates by neutron reflectometry

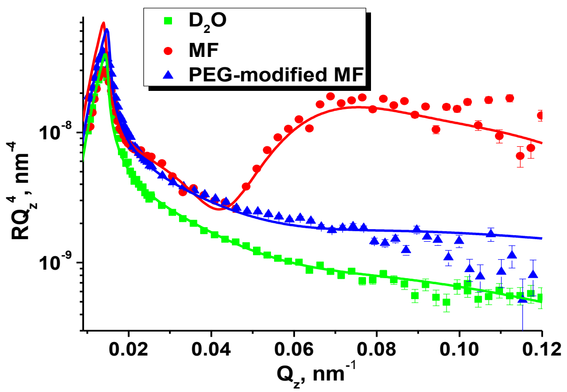
Experimental cell at horizontal reflectometer GRAINS, IBR-2

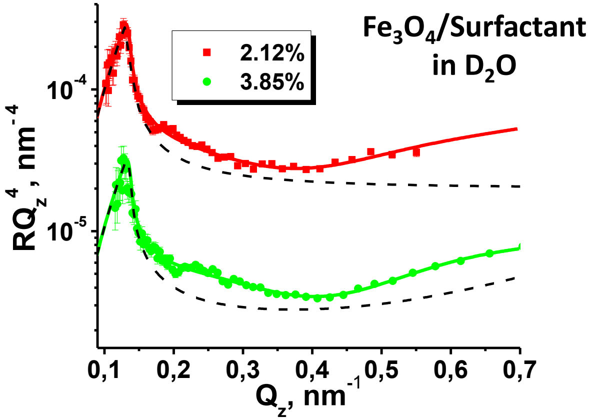


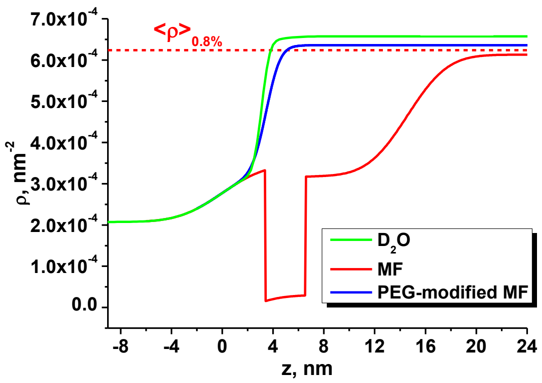


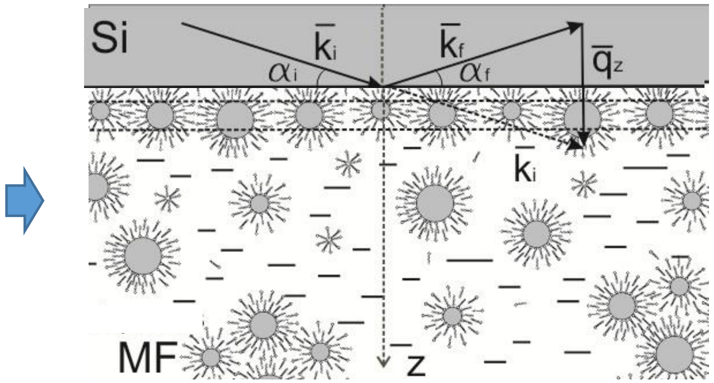


Detection of adsorption layers on substrates









M.V. Avdeev, V.I. Petrenko, I.V. Gapon, L.A. Bulavin, A.A. Vorobiev, O. Soltwedel, M. Balasoiu, L. Vekas, V. Zavisova, P. Kopcansky, *Appl. Surf. Sci.* 352 (2015) 49

M.Kubovcikova, I.V.Gapon, V.Zavisova, M.Koneracka, V.I.Petrenko, O.Soltwedel, L.Almasy, M.V. Avdeev, P.Kopcansky, *J. Magn. Magn. Mater.* 427 (2017) 67

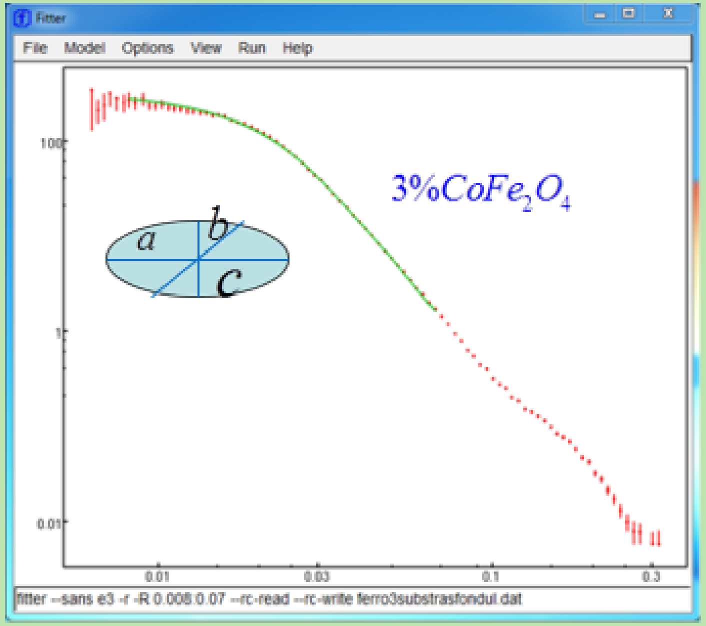
I.V.Gapon, V.I.Petrenko, L.A.Bulavin, M.Balasoiu, M.Kubovcikova, V.Zavisova, M.Koneracka, P.Kopcansky, M.V.Avdeev, *J. Phys. Confer. Series* 848 (2017) 012015

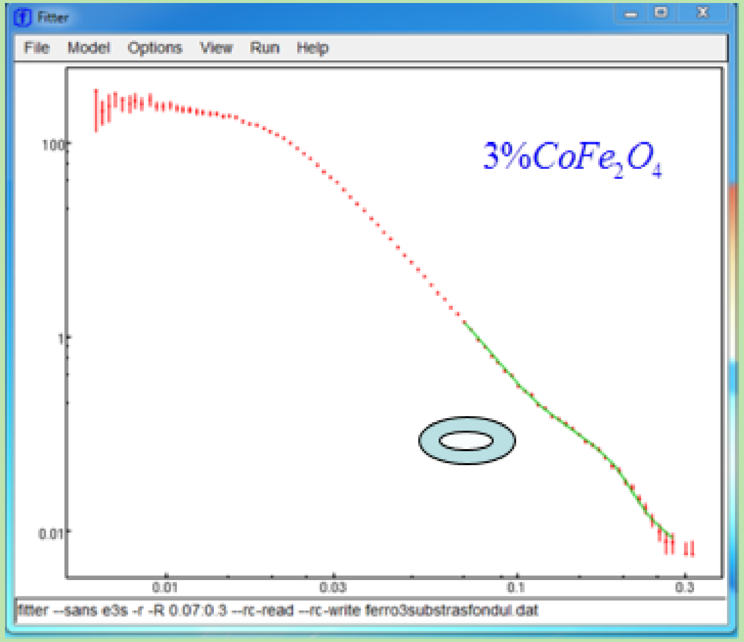
A.V. Nagornyi., V.I.Petrenko, M.Rajnak, I.V.Gapon., M.V Avdeev., B Dolnik., L.A.Bulavin, P.Kopcansky,, M.Timko, *Appl. Surf. Sci.* 473 (2019) 912

SANS investigation of $CoFe_2O_4$/lauric acid/DDS-Na/H_2O ferrofluid - YuMO) facility in function at the IBR-2 reactor

Collaboration with LIT

FITTER Program





Triaxial ellipsoid model with half axes

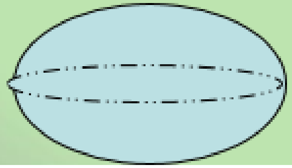
$a = (15.2 \pm 0.4) nm$

$b = (10.85 \pm 0.2) nm$

$c = (5.0 \pm 0.1) nm$

$R^2_g = [(a/2)^2 + (b/2)^2 + (c/2)^2]/5$

$2R_g = (8.63 \pm 01) nm$



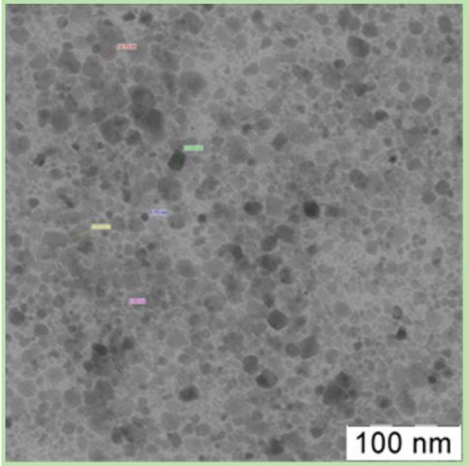
Triaxial ellipsoidal shell model

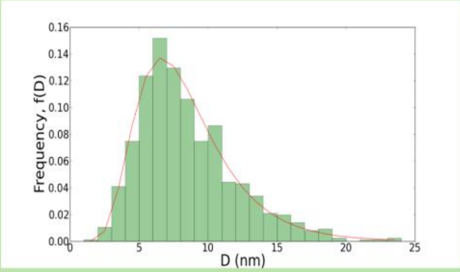
$a_{core} = (1.5 \pm 0.02) nm$

$b_{core} = (3.2 \pm 0.02) nm$

$c_{core} = (5.2 \pm 0.2) nm$

$t_{shell} = (3.3 \pm 0.1) nm$





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

$\mu = 2.056 \quad \sigma = 0.164$

$\bar{D} = 8.48 nm$

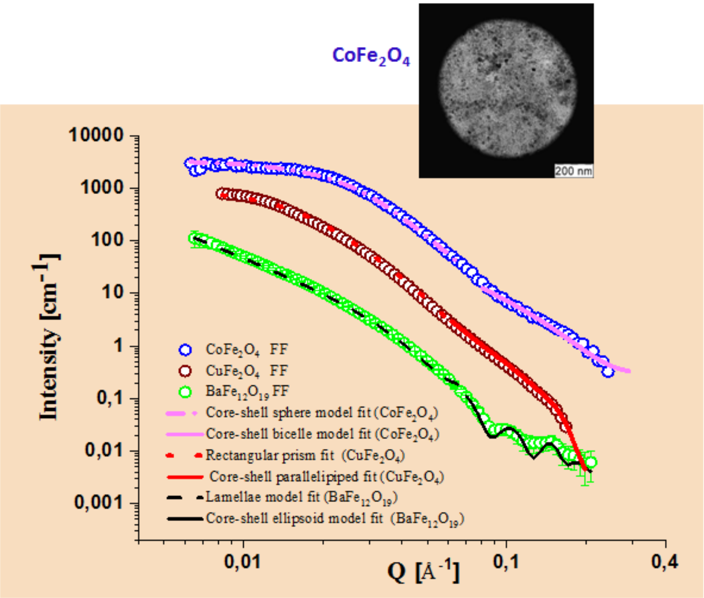
M. Balasoiu, O. I. Ivankov, D.V. Soloviov, S.N. Lysenko, R.M. Yakushev, A-M. Balasoiu-Gaina, N. Lupu, "Microstructure investigation of a $CoFe_2O_4$/lauric acid/DDS-Na/H_2O ferrofluid", *J. Optoelectron. Adv. Mater.* 17(7-8), 1114-1121 (2015)

A. G. Soloviev, T. N. Murugova, A. H. Islamov, A. I. Kuklin, J. Phys.: Conf. Ser. 351, 012027(15) (2012)

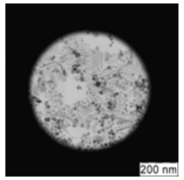
Investigation of the structure of ferrofluids with anisometric particles using SANS and SAXS

Collaboration with Institute of Technical Chemistry, Perm, Russia

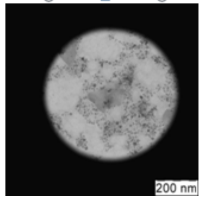
$CoFe_2O_4$

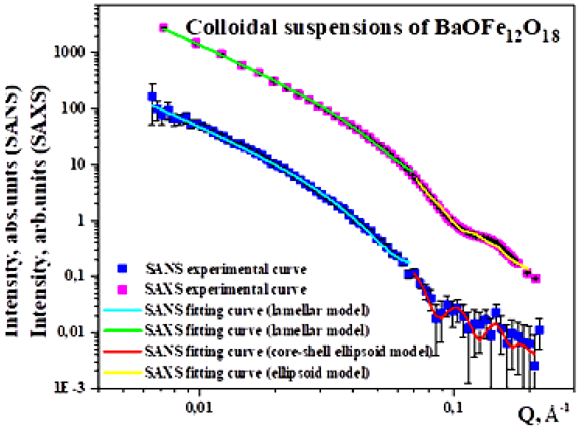


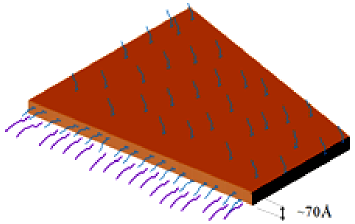
$CuFe_2O_4$

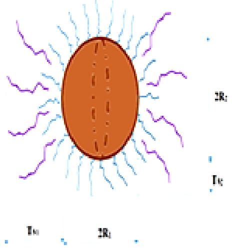


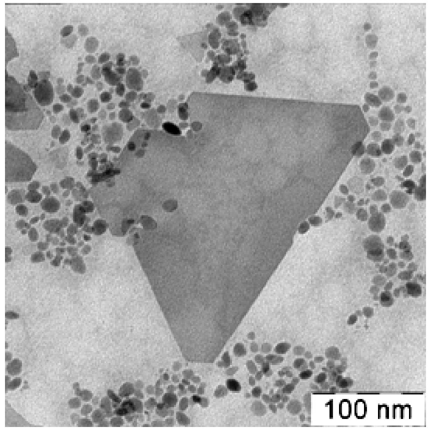
$BaFe_{12}O_{19}$







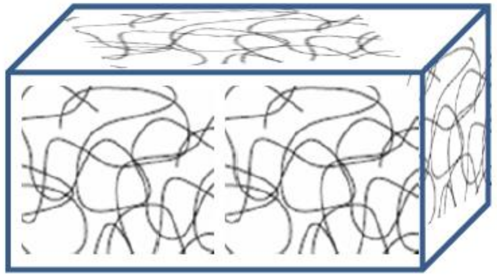




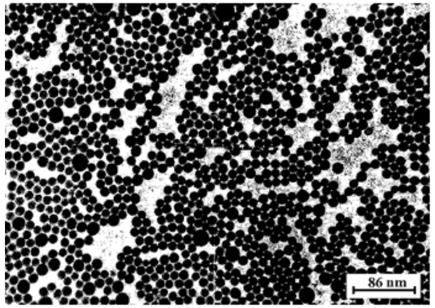
For data processing SASView and FITTER Programs have been used

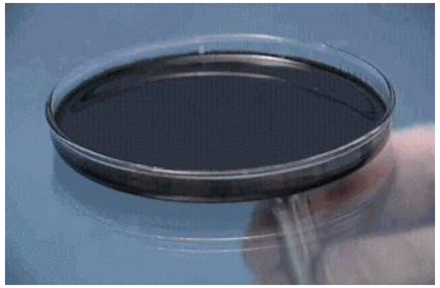
S. Lysenko, A. Lebedev, S. Astaf'eva, D. Yakusheva, M. Balasoiu, A. Kuklin, Yu. Kovalev, V. Turchenko, Preparation and magneto-optical behavior of ferrofluids with anisometric particles, Physica Scripta 95 044007 (2020)

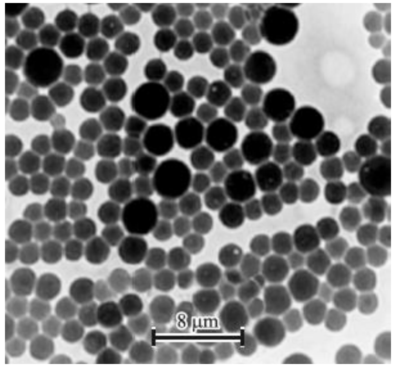
Magnetic and magnetorheological elastomers (MEs and MREs)

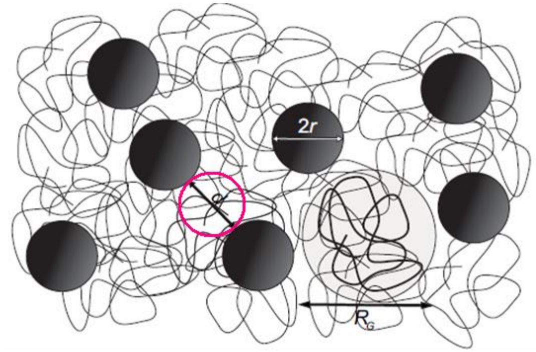


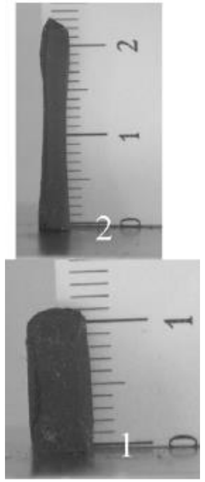
Proba U $\bar{d} = 11nm$





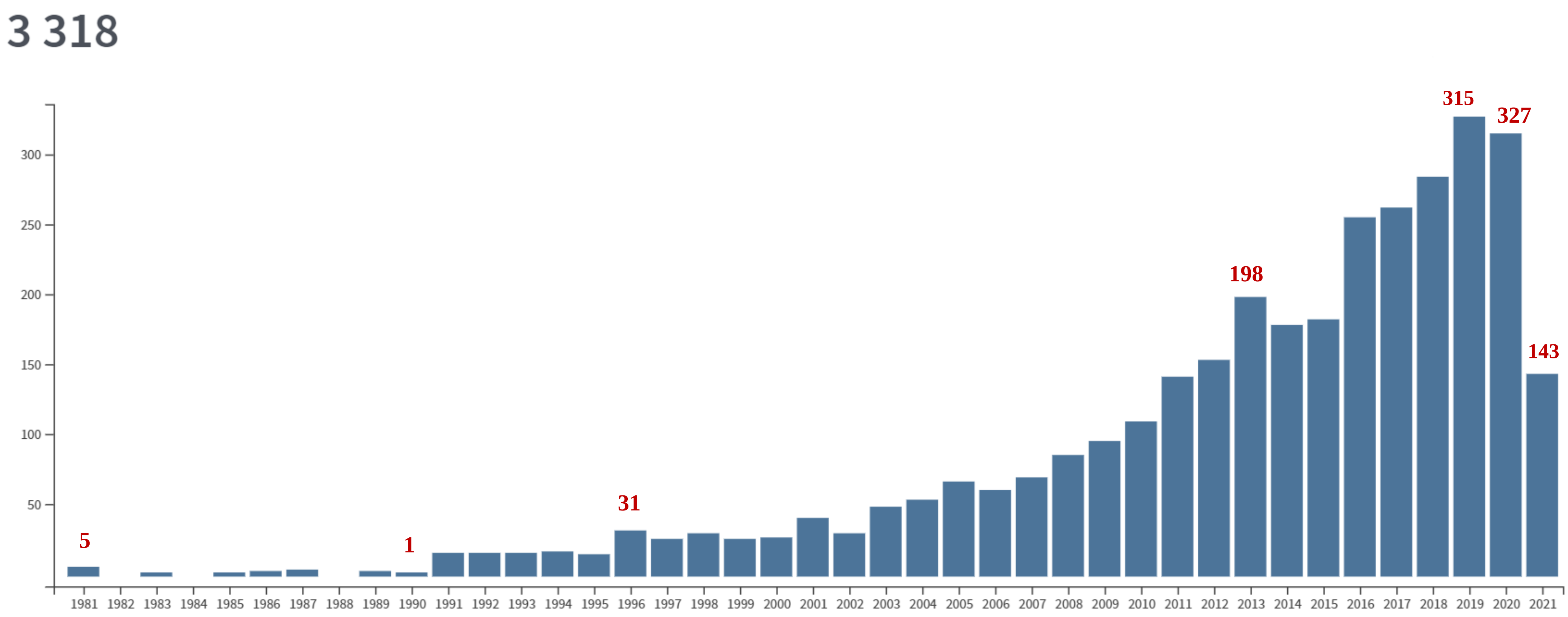






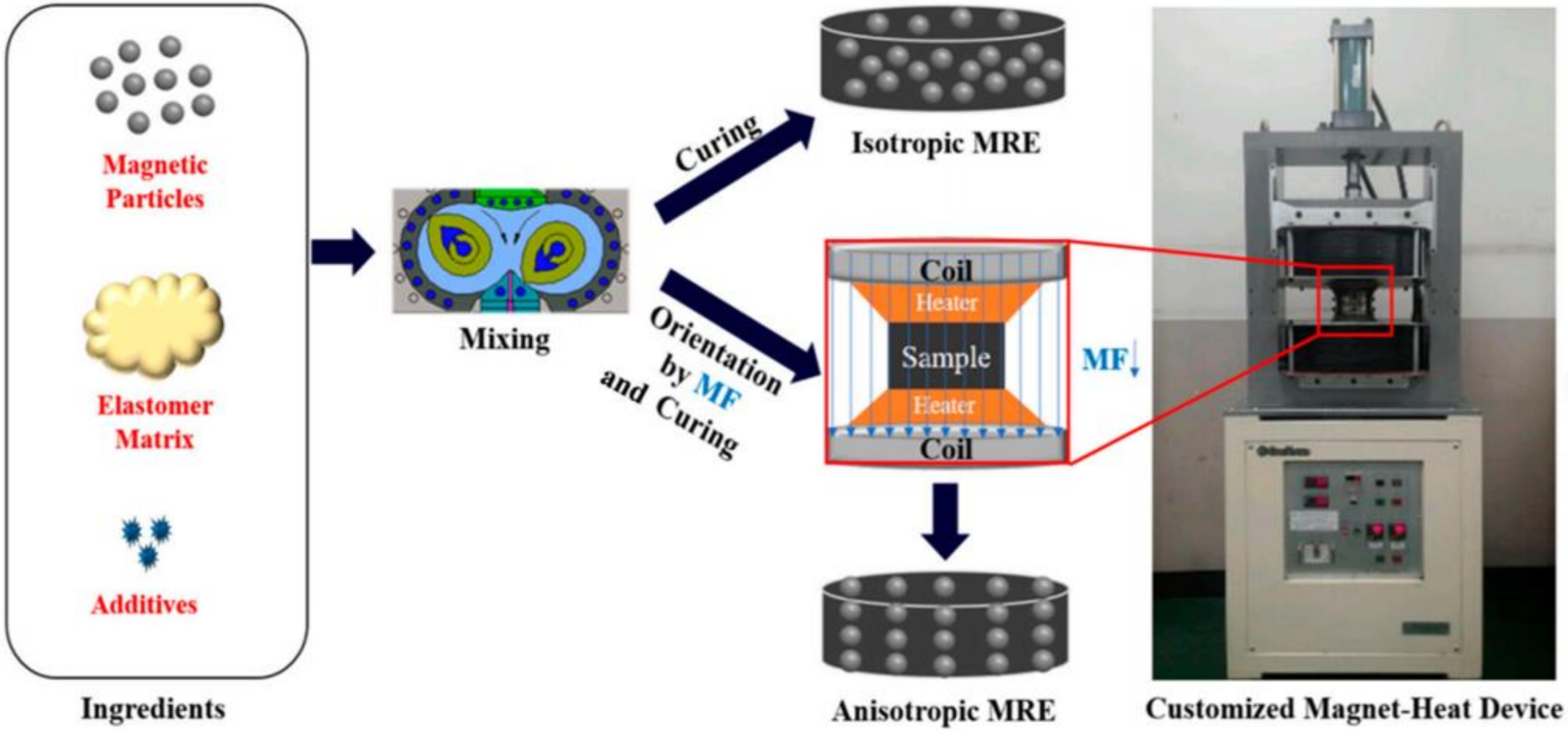
Web of Science Paper Statistics

Magnetic elastomers, ferrogels, magnetorheological elastomers, magnetoactive elastomers



Jolly, Carlson, Munoz, *Smart Mater. Struct.*, 1996, 5, 607.
Zrinyi, Barsi, Buki, *J.Chem.Phys.*, 1996, 104, 8750.

Preparation



Schematic diagram of fabrication process of isotropic and anisotropic magnetic and magnetorheological elastomers (MEs and MREs)

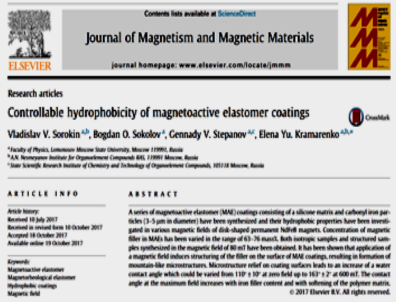
Seung Hyuk Kwon , Jin Hyun Lee and Hyoung Jin Choi, *Materials* 11, 1040(22) (2018)

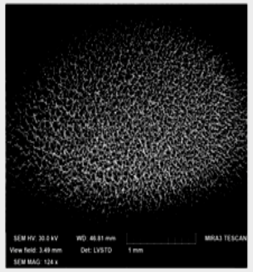
Applications

Magnetoactive elastomer application in energy-absorbing vehicle bumper construction

The bumper – is the first vehicle construction element which touches the obstacle during impact. In accordance with the modern requires to the transport there is seeking to protect not only the driver and passengers but also the pedestrians in case of a potential clash.

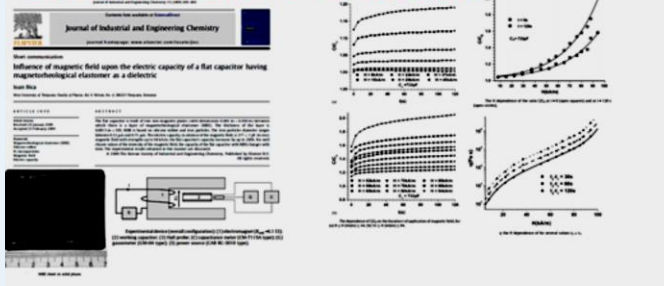
Magnetoactive elastomer coatings



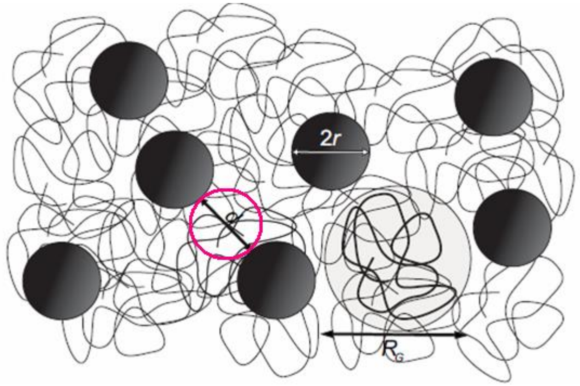


SEM image of MAE coating containing 70% of carbonyl iron particles and 66% of plasticizer in the magnetic field of one NdFeB magnet.

Magnetically controlled electric capacity of a flat capacitor with a MRE as dielectric



(1) The MRE-based flat capacitor modifies its capacity considerably with the intensity H of the applied magnetic field; (2) from the moment of application of H, C increases, and after a certain interval of time, it remains quasi-constant;

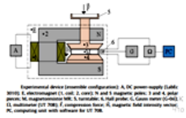


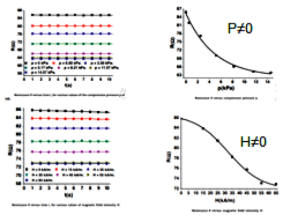
Our aim

To find correlations between macroscopic features and microstructural changes for learning to control them during the fabrication process!

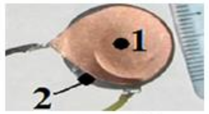
Hybrid electro-conductive magnetorheological elastomer

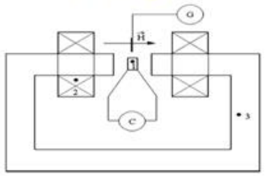
Iron (small) and graphite (large) microparticles embedded in the macro-cells formed as a result of silicone polymerization.

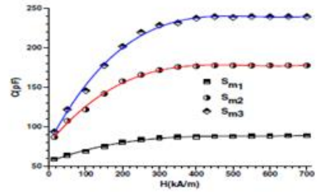




Magnetic field influence on the capacitance value of a plane capacitor with MR elastomer-based dielectric







Capacitance C of a plane capacitor with MR elastomer-based dielectric with different concentration of magnetic particle SM$_i$ (i=1,2,3) is sensibly influenced by the applied magnetic field and particle!

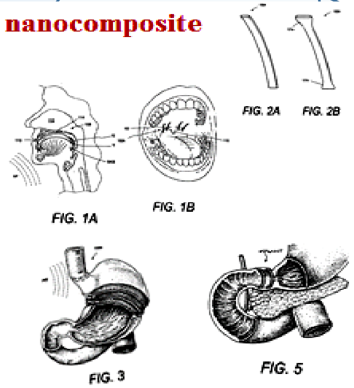
Experimental device: (1) plane capacitor with MR elastomer-based dielectric; (2) coil; (3) magnetic yoke; (C) capacitance meter; (G) gauss meter

I. Bica, Y.D. Liu, H.J. Choi, Colloid. Polym. Sci. 2012 (doi:10.1007/s00396-012-2627

Elastomeric magnetic nanocomposite biomedical devices

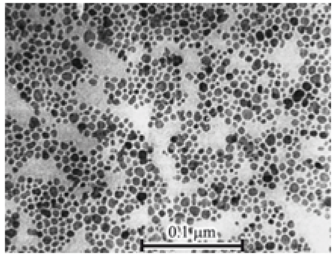
US Patent 20050267321 A1

A biomedical device of a smart class of low modulus elastomers with dispersed, aligned magnetic nanoparticles therein that allow for controlling the flexural modulus of the device and engaged tissue in response to an applied magnetic field.



http://www.google.com/patents/US20050267321

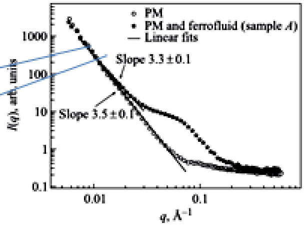
Stomaflex + Fe_3O_4 ferrofluid/Fe microparticles. Influence of particle concentration and intensity of magnetic field applied during the polymerization process



SANS

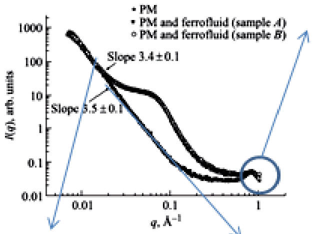
$D_s = 2.5 \pm 0.1$

$D_s = 2.7 \pm 0.1$

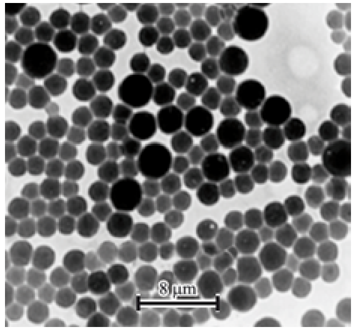


SAXS

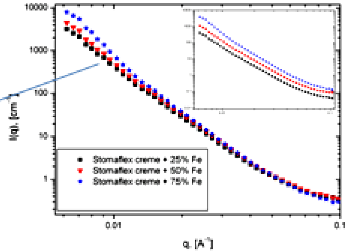
Pseudo-Voigt profil



$D_s = 2.5 \pm 0.1$ $D_s = 2.6 \pm 0.1$



SANS



M. Balasoiu, M.L. Craus, E.M. Anitas, I. Bica, J. Plestil, A.I. Kuklin, Physics of Solid State 52, 861-865 (2010)

Polymer matrix exhibits the behavior of a fractal object with the surface fractal dimension:

$$D_s = 2.5 \pm 0.1$$

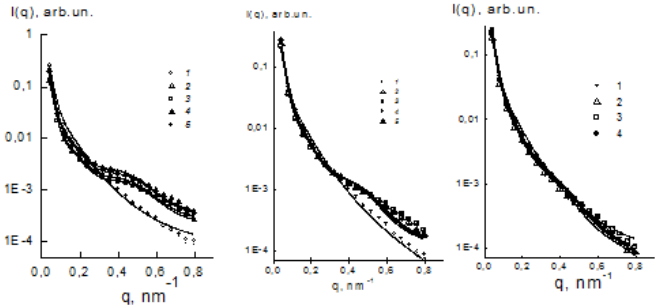
The profiles of the curves are the same for each concentration showing that for these sizes of particl in a **q-range of** **0.006 – 0.1 A^{-1}** t microstructure of magnetic elastomers is the same, t curves being determined by the contribution of t components parts through addition.

Using **Porod law** - mean radius for particl **R = 2.00 +/- 0.25 μm**

$$I = \frac{2\pi\rho^2}{Q^4} S$$

- good agreement with scanning electron microsco data.

5.88% 3.9% 1.27%



M. Balasoiu, V.T. Lebedev, D.N. Orlova, I.Bica, Crystallography Reports 56(7) (2011) 93-96

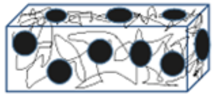
Two-level structure model

$$I(q) = I_{01}\exp[-(qR_g)^2/3] + I_{02}[1+(qR_c)^2]^{-2}$$

R_g polymer large scale inhomogenities (structures);
R_c smaller globular object (correlation radius)

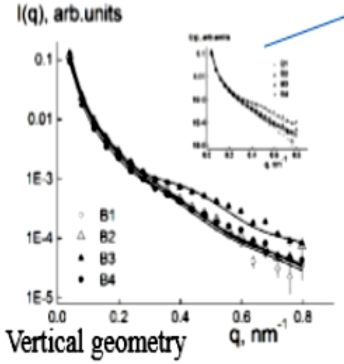
$$I(q) = I_{01}\exp[-(qR_g)^2/3] + I_{02}[1+(qr_c)^2]^{-2}[1+n\sin(qL)/(qL)]$$

r_c - correlation radius (magnetic particles)
L – distance between particles of the order of small polymer domain size ($2R_c$).
n - is the average number of particles correlated with a given particle at a characteristic distance L.



The implicit effect of texturizing field on the elastic properties of magnetic elastomers revealed by SANS

Horizontal geometry



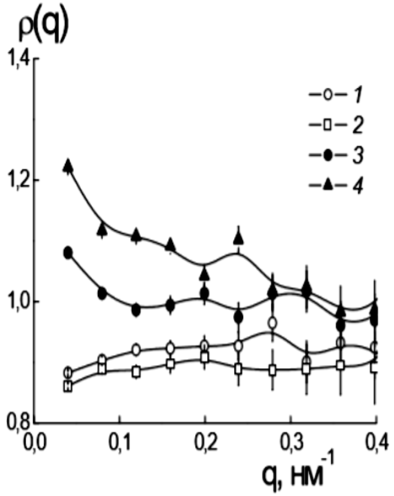
Vertical geometry

$$I(q) = I_{01}\exp[-(qR_G)^2/3] +$$
$$+I_{02}[1+(qR_c)^2]^{-2}[1+n\sin(qL)/(qL)]$$

№ of sample/ B, Gauss	I_{01}, arb. un.	R_G, nm 	$I_{02}\cdot 10^5$, arb.un.	R_C, r_C, nm 	n	L, nm
B_2	0.224±0.001	39.8±0.3	1711±65	5.79±0.09	0.60±0.09	15.7±0.4
B_3	0.250±0.001	38.7±0.6	719±16	3.64±0.04	1.29±0.04	16.6± 0.2
B_4	0.176±0.001	39.2±0.2	937±30	4.92±0.07	0.84±0.04	18.7± 0.3

M. Balasoiu, V.T. Lebedev, Yu.L. Raikher, I. Bica, M. Bunoiu, Journal of Magnetism and Magnetic Materials 431 (2017) 126–129

$$\rho(q) = I_h(q)/I_v(q)$$



- No magnetic field during polymerization: the intensities ratio is

ρ (q) ~ 0.9 <1.

Magnetic field is applied, the ratio

ρ (q)> 1

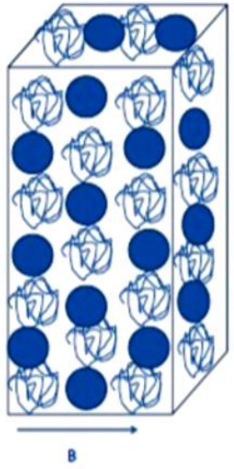
increases with decreasing of momentum transfer.

-

A change of the shape (anisotropy) of large polymer clusters, scattering at small momenta transfer q ≤ 0.4 nm^{-1} is detected.

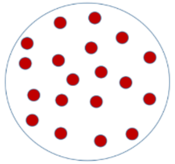
- In the initial matrix (pure rubber) and the ME, prepared without a magnetic field, SANS reveals a substantial number of large polymer coils (blobs) which are vertically prolate: $\rho(q) \sim 0.9 < 1$.

- For polymerization in magnetic field $\rho(q) > 1$ increases with q decreasing



SANS data indicates that in the case of MEs polymerized under the magnetic field the blobs are preferably elongated in the direction normal to the field.

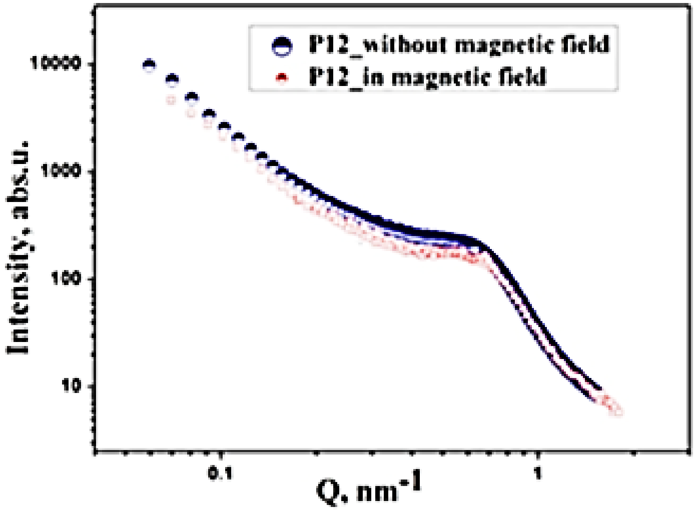
SANS measurements of samples polymerized in ZF. Measurements accomplished in magnetic field



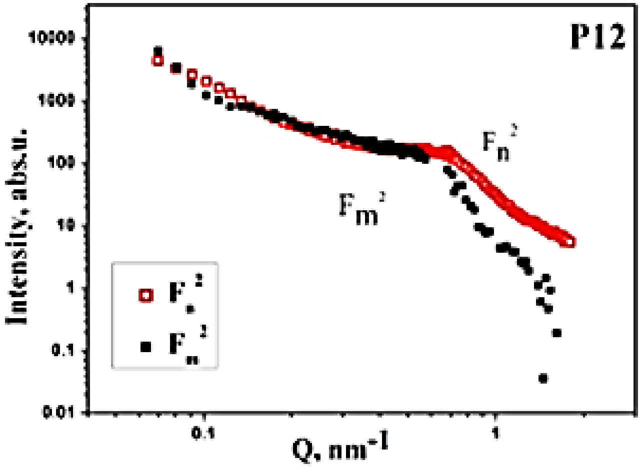
Isotropic sample

$$I = F_n^{\,2} + \frac{2}{3} F_m^{\,2} \qquad H = 0$$

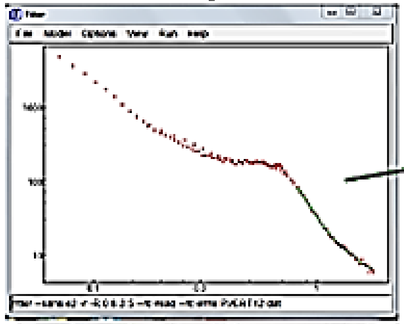
$$I = F_n^{\,2} \qquad H \neq 0 \quad \vec{H} \perp \vec{q}$$

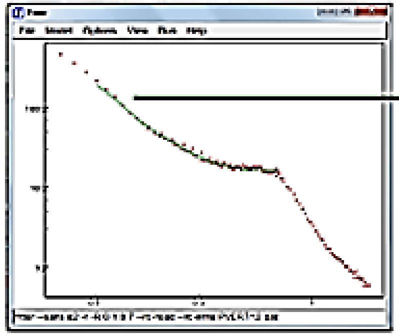


Sample	Content of Fe_3O_4, % mass.	B, Gauss
P12	5.88	0

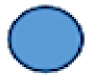


FITTER Program





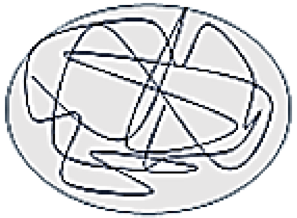
Biaxial ellipsoid model:



Axis/2=(4.49±0.01)nm
e=(0.50±0.0009)

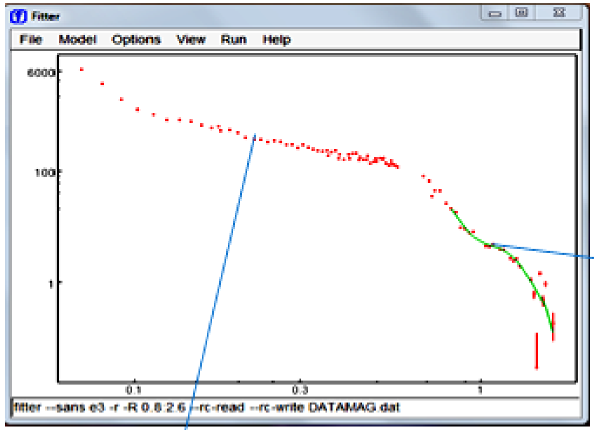
$\mathbf{F_n}$

Biaxial ellipsoid model:



Axis/2=(27.15±0.11)nm
e=(0.227±0.001)

FITTER Program



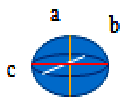
Long range magnetic correlations

Magnetic form factor

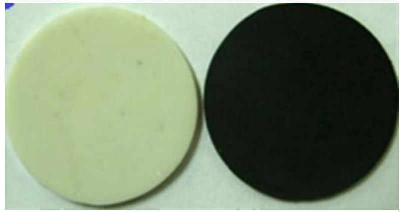
- Triaxial ellipsoid model with half axes:

a/2=(3.49±0.01)nm
b/2=(5.96±0.07)nm
c/2=(5.24±0.03)nm

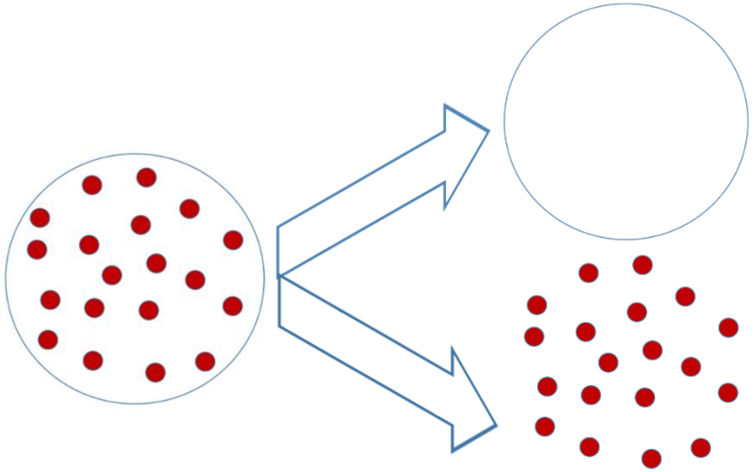
$\mathbf{F_m}$



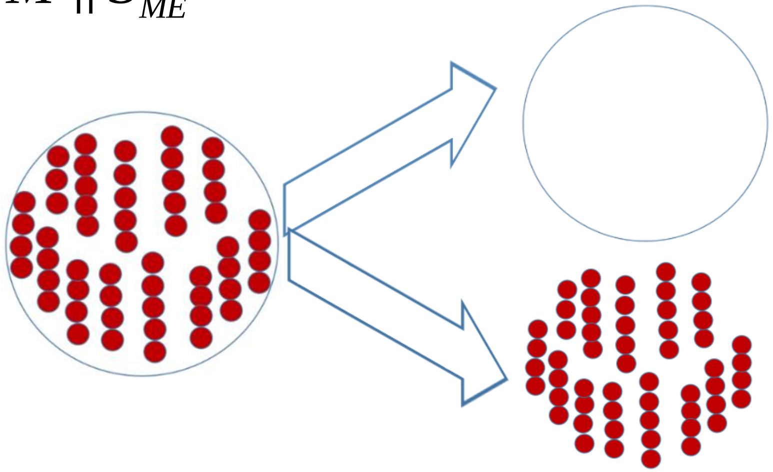
M. Balasoiu, O. M. Bunoiu, I. Bica, G. Pascu, L. Almasy, Rom. Journ. Phys. 2021, submitted

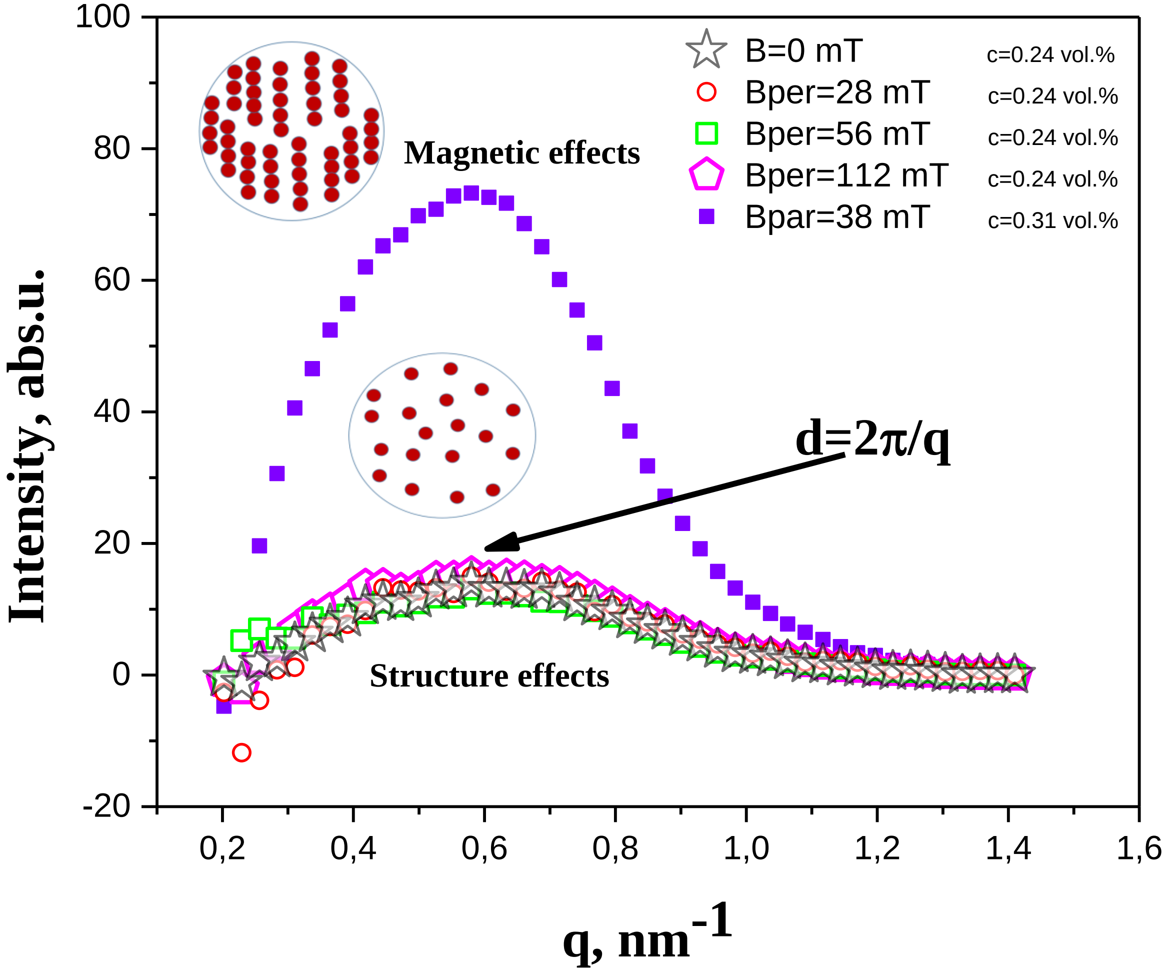


$\vec{M} = 0$ *and* $\vec{M} \perp S_{ME}$



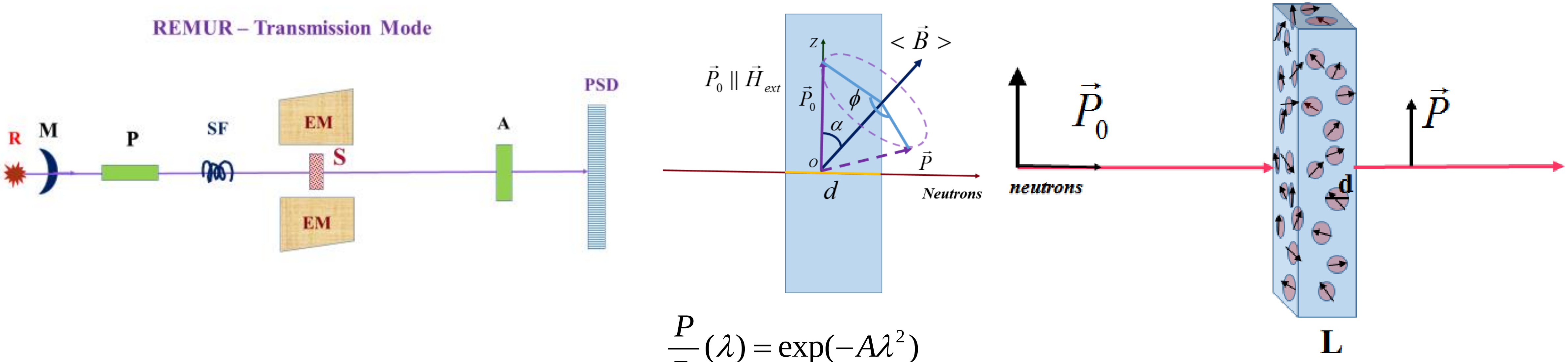
$\vec{M} \parallel S_{ME}$



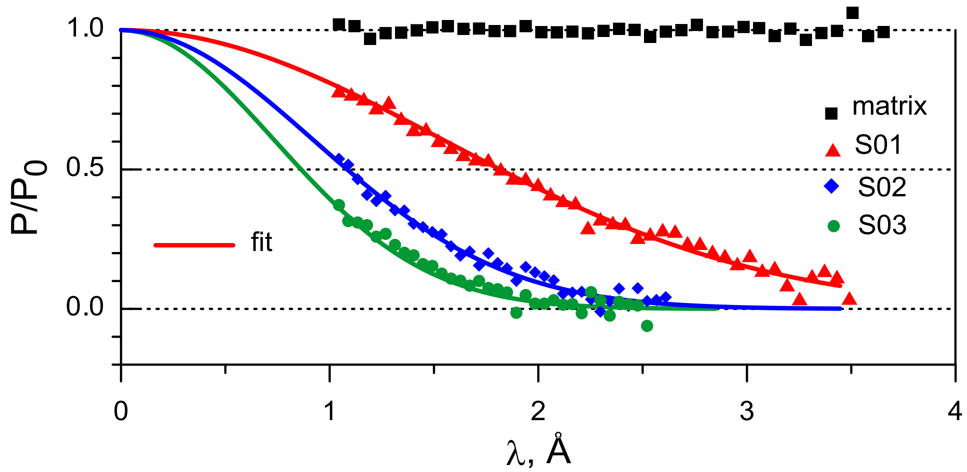


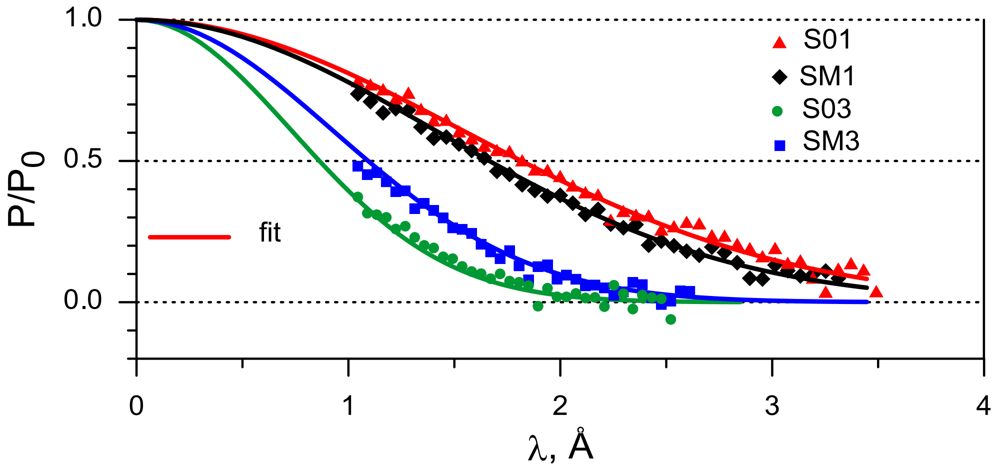
Determination of an average distance d~10.8 nm between the elongated clusters in the ME polymerized in magnetic field applied parallel to the sample plane !

INVESTIGATION OF MAGNETORHEOLOGICAL ELASTOMERS BY MEANS OF NEUTRON DEPOLARIZATION TECHNIQUE



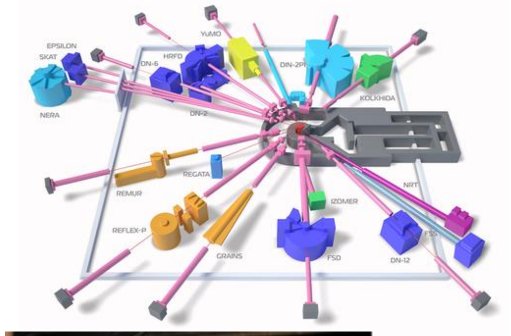
$$\frac{P}{P_0}(\lambda) = \exp(-A\lambda^2)$$





M. Balasoiu, S.V. Kozhevnikov, Yu.V. Nikitenko, G.E. Iacobescu, M. Bunoiu, I. Bica, IOP Conf. Series: Journal of Physics: Conf. Series 848 (2017) 012016

NEUNTRON CENTRES AND USED FACILITIES



- **YUMO, GRAINS, REMUR** instruments, **IBR-2** high pulsed reactor, Dubna, JINR

- **SANS II**, **SINQ** spallation source, Villigen, PSI

- **SANS I**, Geesthacht
- **Membrana** instrument **WWR-M** steady reactor, Gatchina, PN

- **Yellow Submarine**, **VVR-M** steady reactor BNC Budapest

COMPLEMENTARY METHODS

- **SAXS:** IMC, Prague; MPhTI, Dolgoprudny; FLNP-JINR, Dubna

- **muSR**: DLNP-JINR; NRC KY PNPI, Gatchina
- **XRD, TEM, SEM, AFM:** FLNP-JINR, FLNR-JINR Dubna, MSU Moscow

- **Differential Scanning Calorimetry:** FLNP-JINR, Dubna

- **Thermogravimetric analysis:** ; FLNP-JINR, Dubna
- ....

4th International Summer School and Workshop
"Complex and Magnetic Soft Matter Systems: Physico-Mechanical Properties and Structure"
held ONLINE in Timisoara, Romania, at the West University of Timisoara,
19 - 22 April 2021

ORGANISED BY

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- Byelorussian National Technical University, UNESCO Chair
- Abdus Salam International Centre for Theoretical Physics
- Horia Hulubei National Institute of Physics and Nuclear Engineering, Bucharest
- Romanian Society of Physics

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- **Registered 102;**
- **More than 120 participants;**
- **23 Invited presentations;**
- **23 Oral presentations;**
- **36 Poster presentations**
- **17 presentations of young researchers presented orally 5 min.**
- **Austria, Azerbaijan, Belarus, France, Germany, Ireland, Poland, Romania, Russia, England, Slovakia, Ukraine.**

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1. Romania, Slovakia, Czech Republic
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3. NRC KY PNPI, Gatchina
4. Institute of Technical Chemistry, Perm
5. Institute of Mechanics of Solid State, Perm
6. Federal Research Center Krasnoyarsk
7. MSU, Moscow

Special acknowledgements to the

- ❑ JINR and Laboratories Directorates and Administrative Staff.
- ❑ The works have been partially supported from Scientific projects and Grants of Romania, Slovakia, Czech Republic

Thank you very much for attention