Workshop Romania-Hungary
3 Mars 2009

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Neutron Scattering in Romania

- The neutron physics in Romania started along with VVRS Nuclear Reactor (1957).
- Unfortunately this machine was not upgraded and was shut down in1997. At present time the majority of Romanian researchers are working abroad. However the neutron physics activity had continuity in Romania especially due to constantly collaboration with JINR-Dubna, Russia.

  Some more representative results obtained by Romanian physicists along the time:
- *The development of high performance instruments by using focusing effects*
- *Critical magnetic scattering*
- *Advancements in theory of Neutron Diffraction*
- *Dynamics of gases adsorbed on activated charcoal*
- *Dynamics of simple and molecular liquids by Neutron Scattering*
- *SANS studies of super-paramagnetic particle and magnetic fluids*
- *Phase transition in hydrogen bonded molecular crystals by QENS*

Neutron Scattering in Romania

- These results are only a part of may other achievements that we remember now. At present time the people that are working in this research field belong to the Romanian Neutron Scattering Society which has been founded in 2003 and has been affiliated to European Neutron Scattering Association (ENSA), as fully member, in the same year.
- **Romania desires to continue Neutron Scattering activity and boosts the construction of European Spallation Source, intending to attract more scientists and students in this field in the future.**

Neutron Scattering in Romania

In the present the neutron scattering research in Romania is developing in three main directions:

- 1.The implementation of a new concept of high resolution focussing configuration and the realization of new neutron crystal diffractometer having a configuration that is estimated to have a real high resolution.

- 2. Investigation of Nanosystems and Novel Materials by SANS and Neutron Depolarization Methods:

  - Investigation of the ferrofluids microstructure; nuclear and magnetic structure; particle concentration effects; Investigation of the microstructure of magnetic elastomers; Investigations of superparamagnetic particles produced by bio-engineering procedures.

- 3. Elastic, Quasielastic, and Inelastic Neutron Scattering on biomolecules-biopolymers-water systems
- - Molecular dynamics in polysaccharide hydrogels
- - Dynamics in free and immobilized enzymes by neutron scattering

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Institute for Nuclear Research PITESTI

TRIGA REACTOR INSTRUMETS FOR STRUCTURE ANALYSIS

Dr.Ion Ionita & Group

1. ***FOCUSING CONFIGURATION IN CRYSTAL NEUTRON DIFFRACTOMETRY; FOCUSING HIGH-RESOLUTION NEUTRON DIFFRACTOMETER DIR1***

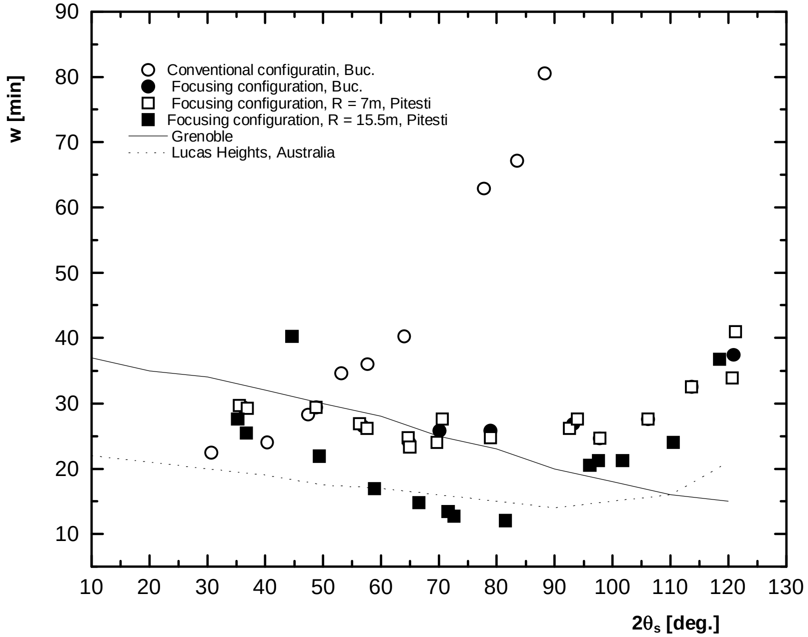
2. SANS FACILITY AT THE PITESTI 14MW TRIGA REACTOR

References

- **M.Popovici, A.D.Stoica and I.Ionita**, J.Appl.Cryst.,20,1987,pp.90
- **M.Popovici, W.B.Yelon, R.Berliner, A.D.Stoica, I.Ionita, R.Law,** Nuclear Instr. & Meth. , **A338**, 1994,
- **I.Ionita, A.D.Stoica, M.Popovici, N.C.Popa,** Nuclear Instr. & Meth. **, A431**, 1999, p.509-520

1.The focusing high-resolution configurations characteristics

- the absence of the Soller collimators
- the use of the perfect crystals in asymmetric reflexion
- a take-off angle shorter than 900or greater than 1300
- high resolution, around 20 minutes,for the whole range of the scattering angles values
- the sample rotation during the diffraction pattern raise, to achieve the focusing conditions for every value of the scattering angle
- taking account of the reflectivity dependence on the crystal radius of curvature a fixed radius of curvature should be used, adapted to the experimental conditions; as a general rule this value should be the optimum radius of curvature for the higher value of the scattering angle



Resolution performances of the DIR1 diffractometer

2. SANS FACILITY AT THE PITESTI 14MW TRIGA REACTOR

ISSN 1063-7745, Crystallography Reports, 2006, Vol. 51, Suppl. 1, pp. S27–S31. © Pleiades Publishing, Inc., 2006.

DIFFRACTION AND SCATTERING
OF IONIZING RADIATIONS

The SANS Facility at the Pitesti 14MW TRIGA Reactor[1]

I. Ionita[a], B. Grabcev[b], S. Todireanu[b], F. Constantin[c], V. Shvetsov[d], E. Anghel[a], G. Popescu[e], M. Mincu[a], and A. Datcu[a]

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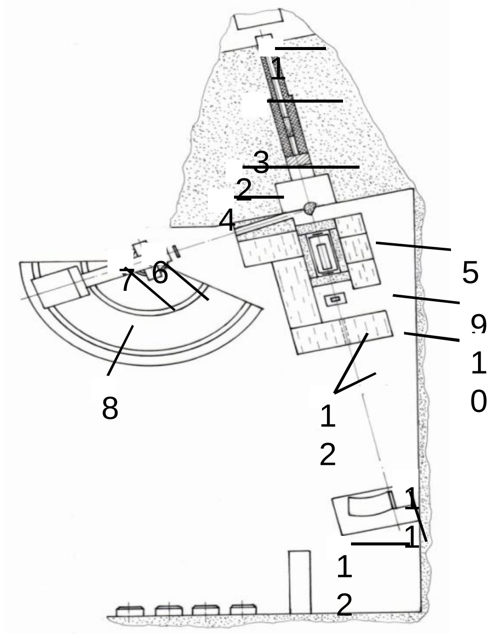
[e] *National College Alexandru Odobescu, Pitesti, Romania*

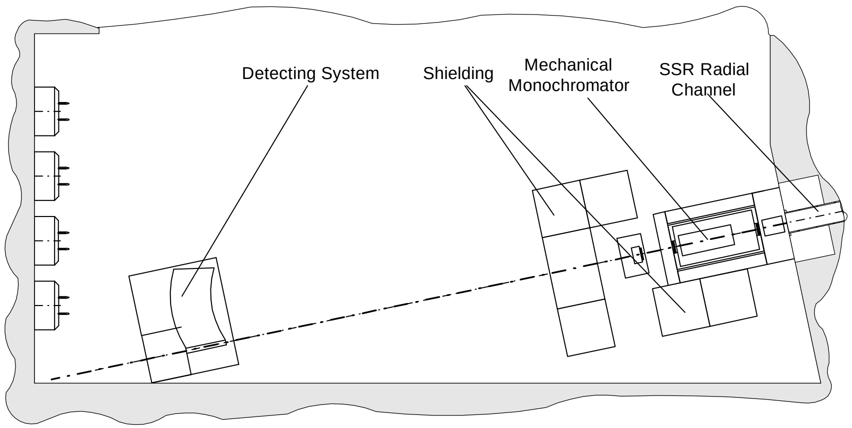
Received June 6, 2006

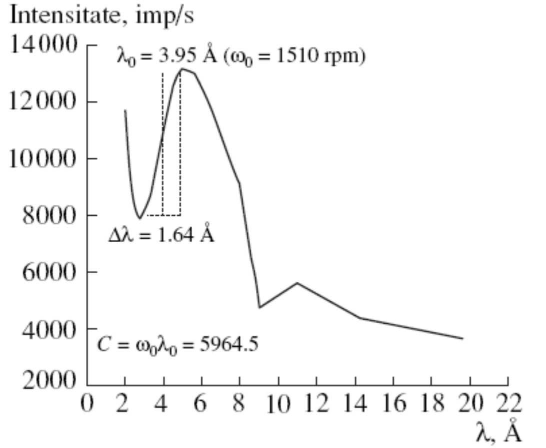
Abstract—The SANS facility existing at the Pitesti 14MW TRIGA reactor is presented. The main characteristics and the preliminary evaluation of the installation performances are given. A monochromatic neutron beam with 1.5 Å ≤ λ ≤ 5 Å is produced by a mechanical velocity selector with helical slots. A fruitful partnership was established between INR Pitesti (Romania) and JINR Dubna (Russia). The first step in this cooperation consists in the manufacturing in Dubna of a battery of gas-filled positional detectors devoted to the SANS instrument.

PACS numbers: 14.60.Lm

DOI: 10.1134/S1063774506070066







Transmitted spectrum with a discontinuity at λ = 0.395 nm

Neutron Scattering in Romania

In the present the neutron scattering research in Romania is developing in three main directions:

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  - Investigation of the ferrofluids microstructure; nuclear and magnetic structure; particle concentration effects; Investigation of the microstructure of magnetic elastomers; Investigations of superparamagnetic particles produced by bio-engineering procedures.

- 3. Elastic, Quasielastic, and Inelastic Neutron Scattering on biomolecules-biopolymers-water systems
- - Molecular dynamics in polysaccharide hydrogels
- - Dynamics in free and immobilized enzymes by neutron scattering

Members of NIPNE Neutron Scattering Research Group

Vasile Tripadus Ph.D, Maria Balasoiu Ph.D, Dorina Aranghel Ph.D, Mihai Statescu Drd., Raul Erhan Drd

Neutron facilities:

- BENSC, HMI, Berlin,Germany
- SINQ, PSI, Villigen, Swittzerland
- Reactor Orphee, LLB-CEA, France
- IBR-2 Dubna, Russia
- Budapest Nuclear Reactor, Hungary

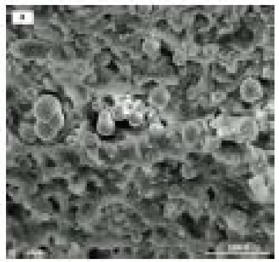
Neutron spectrometers:

- NEAT, FOCUS, MIBEMOL Time of Flight spectrometres
- YUMO, SANS diffractometers.

Investigation of Nanosystems and Novel Materials by SANS and Neutron Depolarization Methods

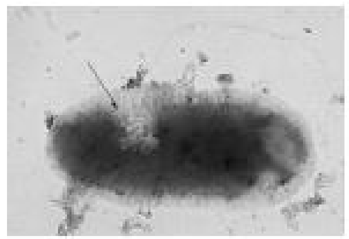
• Investigation of the ferrofluids microstructure; nuclear and magnetic structure; particle concentration and temperature effects; stabilization using different chain length mono-carboxylic acids.

• Investigation of the microstructure of magnetic elastomers, magneto-rheological elastomers, shape-memory magnetic polymers



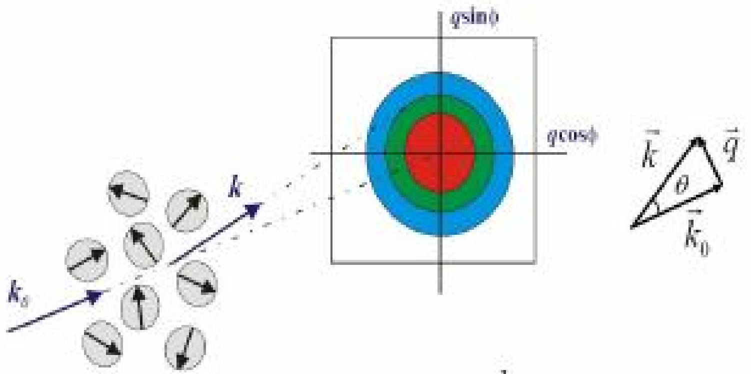
• Investigations of superparamagnetic particles produced by bio-engineering procedures.

Bacteria *Klebsiella oxytoca* producing iron oxide nanoparticles



SMALL ANGLE NEUTRON SCATTERING

Non-polarized neutrons.



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

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

For low concentrated fluids (< 3 vol. %)

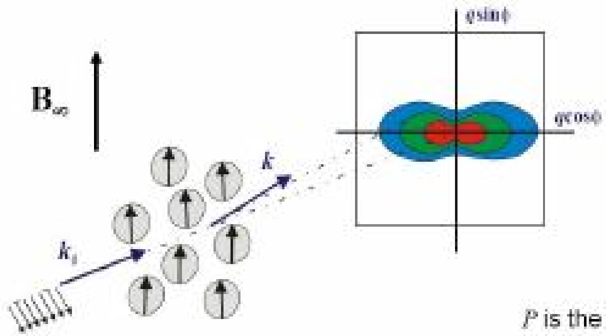
$$\frac{d\sigma}{d\Omega}(\vec{q}) \approx F_N^2(q) + \frac{2}{3}F_M^2(q) \approx F_N^2(q)$$

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

F_N is nuclear scattering amplitude

F_M is magnetic scattering amplitude

Polarized neutrons.



P is the rate of polarization

ε is the spin-flipper efficiency

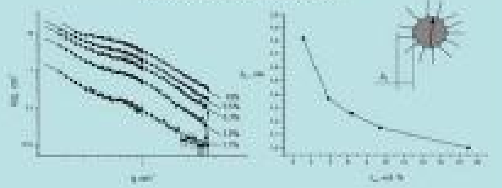
$$\frac{d\sigma^+}{d\Omega}(\vec{q}) \approx F_N^2(q) + \{F_M^2(q) - \underline{2PF_N(q)F_M(q)}\}\sin^2\varphi$$

$$\frac{d\sigma^-}{d\Omega}(\vec{q}) \approx F_N^2(q) + \{F_M^2(q) + \underline{2\varepsilon PF_N(q)F_M(q)}\}\sin^2\varphi$$

Investigation of the ferrofluids microstructure

Concentration effect in magnetite/oleic acid/d-benzene

thickness of surfactant shell



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.

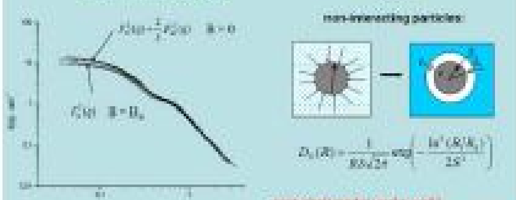
Surfactant shell thickness as a function of the magnetite volume fraction as revealed by SANS

M.V. Avdeev, M. Balasoiu, D. Bica, L. Rosta, Gy. Török, L. Vekas, **Materials Science Forum**, Vols 373-376 (2001) 457-460
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

Experimental curves — Model

non-interacting particles:

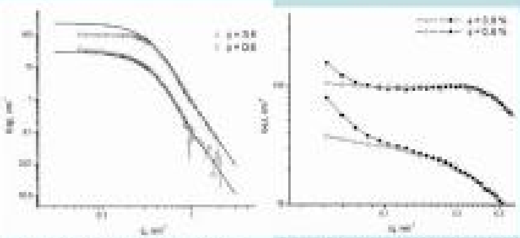


Experimental (points) and model (solid lines) SANS curves for fluid magnetite/oleic acid/d-benzene (φ_m=4.8 %). Resulting thickness of the surfactant shell is Δ=1.34 nm and Δ=1.15 nm for the curves at B = 0 and B = B_s, respectively.

- core-shell model works well !
- interaction effect on the scattering is small for φ_m < 5 % !
- effect of magnetic scattering contribution on resulting parameters does not exceed 15 % for d-carriers !

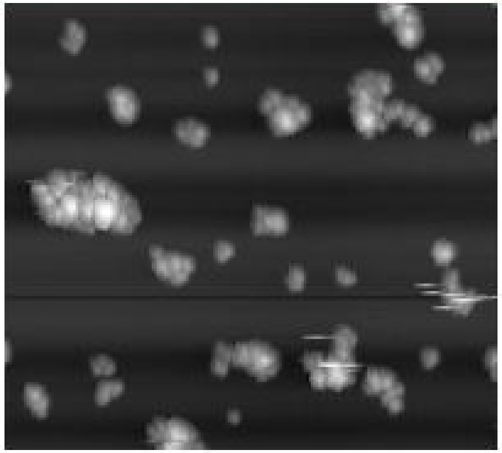
Structure of stable ferrofluids on polar carriers

highly stable fluid magnetite/OA + DBS/h-pentanol



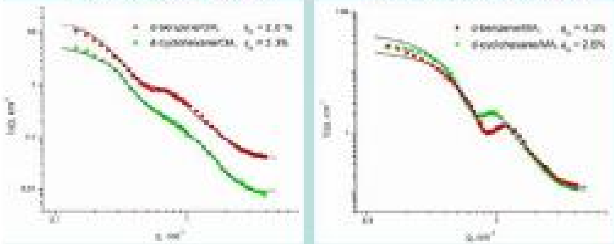
Experimental SANS curves for different volume fraction of magnetite. Lines correspond to the model of polydisperse spheres. Treatment to take into account the interaction effect is in progress.

Temperature effect at smallest q-values points out the formation of large aggregates as a result of desorption of the second stabilizing surfactant layer. Open and solid symbols correspond to experimental points obtained at 20 and 80°C, respectively. Solid lines are plotted to guide the eyes.



Effect of surfactant length

Oleic acid (OA): $C_{18}H_{34}O_2$ — Myristic acid (MA): $C_{14}H_{28}O_2$

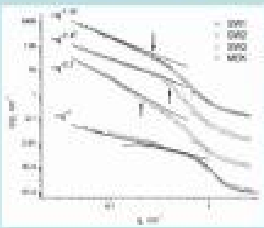


Results of fits of the core-shell model:
→ R_0 = 4.6 nm; $\Delta R/R_0$ = 0.38; Δ_1 = 1.31 nm
→ R_0 = 4.1 nm; $\Delta R/R_0$ = 0.4; Δ_1 = 1.67 nm

Results of fits of the core-shell model:
→ R_0 = 2.4 nm; $\Delta R/R_0$ = 0.4; Δ_1 = 1.28 nm
→ R_0 = 3.1 nm; $\Delta R/R_0$ = 0.28; Δ_1 = 1.38 nm

M.V. Avdeev, D. Bica, L. Vekas, O. Marinica, M. Balasoiu, V.L. Aksenov, L. Rosta, V.M. Garamus, A. Schreyer, Journal of Magnetism and Magnetic Materials

Water-based ferrofluids: aggregation effects



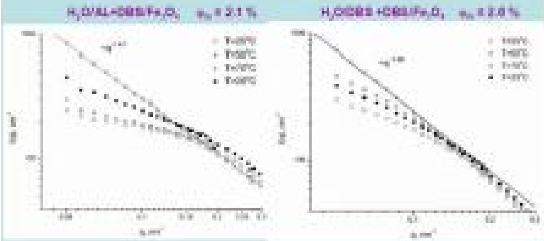
Experimental SANS curves for different water-based ferrofluids and MEK ferrofluid. For convenient view data are divided by factors of 10 (SW2), 100 (SW3) and 1000 (MEK). The scattering levels are observed. Straight solid lines correspond to the power law.

SW1: $H_2O/AL+DBS/Fe_3O_4$, φ_m = 2.1 %
SW2: $H_2O/DBS+DBS/Fe_3O_4$, φ_m = 2.0 %
SW3: ...
MEK: ...

- Specific aggregation in initial ferrofluids takes place
- Formation of secondary fractal aggregates is detected

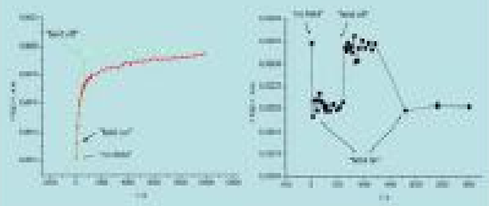
Water-based ferrofluids: temperature effect

$H_2O/AL+DBS/Fe_3O_4$, φ_m = 2.1 % — $H_2O/DBS+DBS/Fe_3O_4$, φ_m = 2.0 %



- Temperature increase results in destroy of secondary aggregates
- At once temperature returns to RT the aggregation starts again

Aggregation in water-based ferrofluids under magnetic field



Changes in the mean scattering intensity in time under magnetic field for water-based fluid (φ_m = 0.9 %) due to formation of aggregates. No anisotropy in 2D scattering is observed.

Changes in the mean scattering intensity in time for stable concentrated h-pentanol-based fluid (φ_m = 10 %) under magnetic field due to anisotropy in 2D magnetic scattering.

V.L. Aksenov, M.V. Avdeev, M. Balasoiu, D. Bica, L. Rosta, Gy. Török, L. Vekas, **J. Mag. Mag. Mater.** (2003)

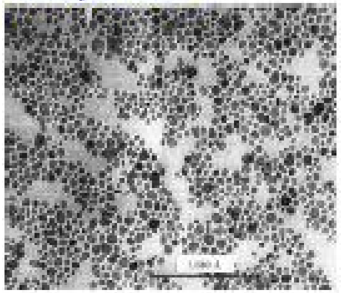
Magnetic elastomers, magneto-rheological elastomers, shape-memory magnetic polymers, ….

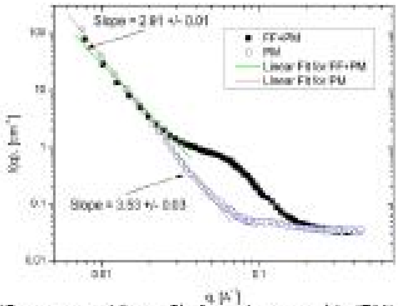
A new class of engineering materials whose mechanical, thermomecanical, electrical properties can be controlled by a magnetic field.

Examples of applications:

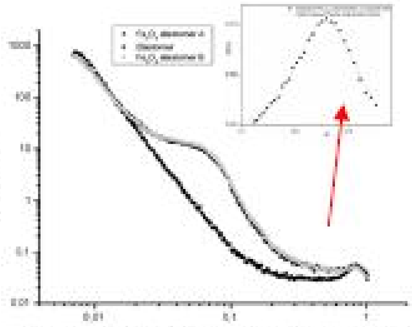
- Automotive applications – due to the ability to change their viscoelastic properties under application of a magnetic field.
- High application potential in medicine
- Smart implants or instruments could enable surgeons to perform mechanical adjustments in noncontact mode

Nanoparticles



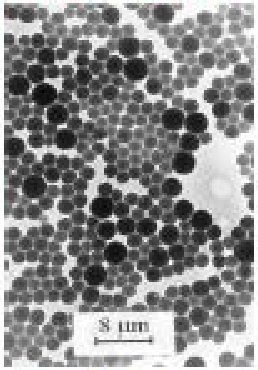


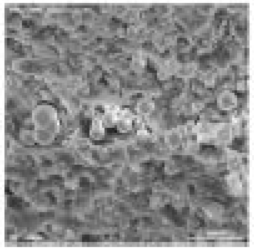
SANS curves and linear fits for polymer matrix (PM) and polymer matrix with embedded Fe3O4 ferrofluid (FF+PM) obtained at YUMO, Dubna

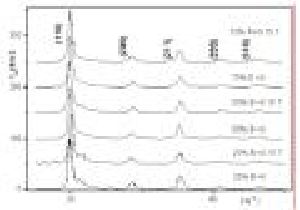


SAXS experimental curves from elastomer samples and simple elastomer obtained at Rigaku spectrometer in function at IMC, Prague.

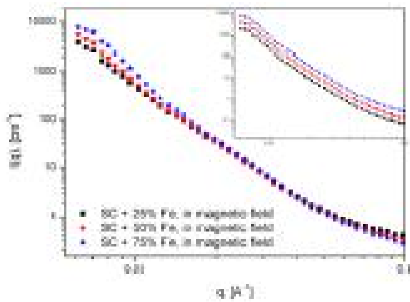
Microparticles







Diffractograms of elastomers with Fe microparticles (in various concentrations) by using MoKα radiation.



Diffractograms of elastomers with Fe microparticles (in various concentrations) by using MoKα radiation.

Conclusions

- ✓ It was found that the elastomer is fragmented into small particle ordered at short distance.
- ✓Doping with Fe_3O_4 particles leads to a significant change of the local structure of elastomer, meaning the decrease of the micro-strains into the matrix.
- ✓Polymer matrix exhibits the behavior of a fractal object with the surface fractal dimension D_s = 2.47 +/- 0.01.
- ✓After introducing the ferrofluid, the obtained magnetic elastomer became a fractal object with a mass fractal dimension; the mass fractal dimension is decreasing in the magnetic elastomer polymerized in magnetic field.

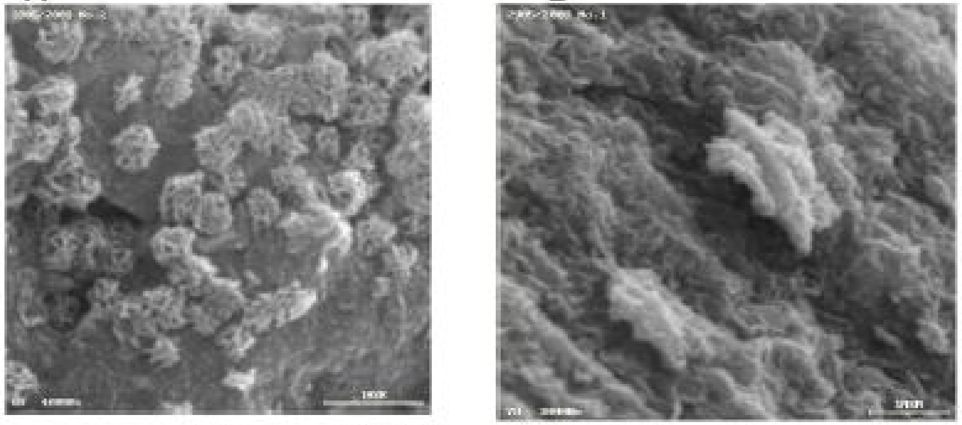
- ✓Using Porod law have been determined the mean radius for particles of R = 2.00 +/- 0.25 µm, in very good agreement with scanning electron microscopy data.
- ✓For the elastomer filled with a large amount of Fe microparticles (75% particle concentration) a texture effect is detected; for the samples polymerized in magnetic field the texture effect is higher. Surface fractal property is obtained for all the microparticle concentrations.

Further SANS, USANS and neutron depolarization of polarized neutrons studies needed!

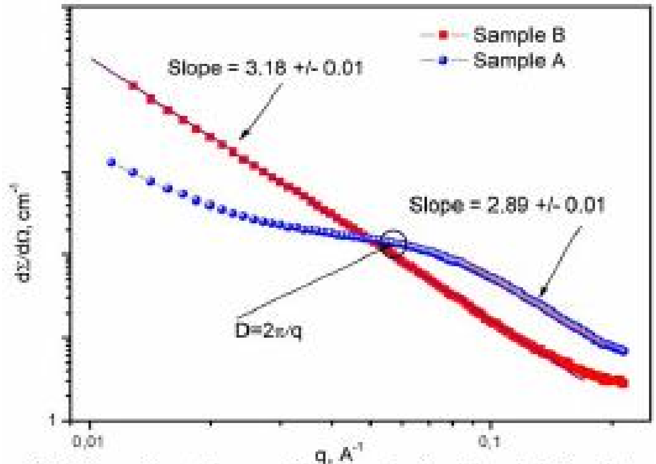
Balasoiu M., Craus M. L., Kuklin A. I., Plestil J., Haramus V., Islamov A. Kh., Erhan R., Anitas E. M., Lozovan M., Tripadus V., Petrescu C., Savu D., Savu S., Bica I., **Journal of Optoelectronics and Advanced Materials**, vol.10, No.11**(2008)**2932-2935.

Investigation of biogenic iron containing nanoparticles (ferrihydrite) produced by bacteria *Klebsiella oxytoca*

Preliminary results on morphology and structure of iron oxide particles formed inside *Klebsiella oxytoca* bacteria are obtained - effect of the bacteria age (the duration of growth) on the particles properties is studied.



JEOL type JSM-840 scanning electron microscope images of Samples A and B.



SAXS experimental curves from sample 1and 3 and obtained at Brucker Nanostar SAXS spectrometer in function at the Institute of Synthetic Polymer Materials RAS, Moscow.

Results

✓Sample **A** in the q range 0.08 ÷ 0.11 $Å^{-1}$ a mass fractal structure with the mass fractal dimension D_m = **2.89 ± 0.01** is obtained.

✓For Sample B, the system structure is characterized by a fractal dimension of D_s = **2.82 ± 0.01** that is specific to highly branched surface fractals. These conclusions agree with the evidence from SEM images.

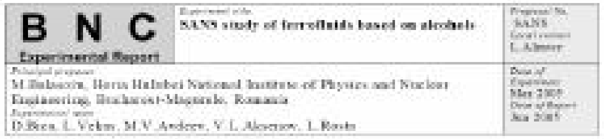
✓The maximum observed on the experimental curve of Sample A at $q \approx 0.06$ $Å^{-1}$ points out the presence of nanoparticles with the size about 100 Å.

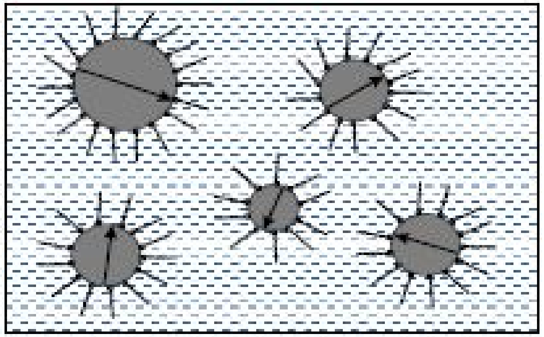
Further SANS studies of structural and micromagnetic properties of the bacterial ferrihydrite samples in function of the growth conditions and the duration of the preparation processes are required!

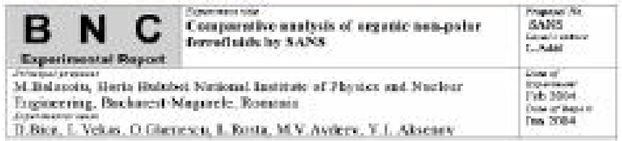
M.Balasoiu, A.I.Kuklin, O.Orelovich, Yu.S.Kovalev, G.M.Arzumanian,T.S.Kurkin, S.V.Stolyar, R.S. Iskhakov, Yu.L.Raikher, *JINR Comunication E14-2008-200* (in press)

SRFN

Structural studies of ferrofluids by small-angle neutron scattering.
Romanian - Hungarian - JINR Cooperation







Some resulted works and papers

Aspects of the magnetic fluids microstructure, M.Balasoiu, **PH.D Thesis, 1998**, Institute of Atomic Physics, Bucharest.

Influence of particle concentration on ferrofluids microstructure studied by SANS; M.V.Avdeev, M.Balasoiu, D.Bica, L.Rosta, G.Torok, L.Vekas; **Materials Science Forum,** Vols.373-376 (**2001**) 457-460

Magnitizable colloids on strongly polar carriers – preparation and manifold characteriziation; D.Bica, L.Vékás, M.V.Avdeev, M.Balasoiu, O.Marinică, F.D. Stoian, D.Susan-Resiga, Gy.Török, L.Rosta; **Prog. Colloids Polymer Sci.**, Vol. 125, (**2004**) 1-9

Structural studies of ferrofluids by small-angle neutron scattering; M. Balasoiu, M.V.Avdeev, A.I.Kuklin, V.L.Aksenov, D.Bica, L.Vekas, D.Hasegan, Gy. Torok, L.Rosta, V.M.Garamus, J.Kohlenbrecher; **Magnetohydrodynamics,** Vol.40, No.4, (**2004**)359-368

Use of small-angle neutron scattering in testing the stability of ferrofluids; M.Balasoiu, L.Vekas, M.V.Avdeev, V.L.Aksenov, A.A.Khokhryakov, D.Bica, D.Hasegan, Gy.Torok, L.Rosta; **Romanian Reports in Physics**; Vol.57, No.2 **(2005)** 261-265

Interaction effects in non-polar and polar ferrofluids by small-angle neutron scattering;Gy. Török, A. Len, L. Rosta, M. Balasoiu, M. V. Avdeev, V. L. Aksenov, V. Ghenescu, D. Hasegan, D. Bica, L. Vékás; **Romanian Reports in Physics**; Vol. 58, No.3, (**2006**) 293-299

Comparative analysis of the structure of sterically stabilized ferrofluids on polar carriers by small-angle neutron scattering; M.V. Avdeev , V.L. Aksenov, M. Balasoiu, V.M. Garamus , A. Schreyer , Gy. Török, L. Rosta , D. Bica, L. Vékás; **Journal of Colloid and Interface Science** , Vol. 295, Issue 1 (**2006**) 100-107

On the possibility of using short chain length mono-carboxylic acids for stabilization of magnetic fluids, M.V.Avdeev, D.Bica, L.Vekas, O.Marinica, M.Balasoiu, V.L.Aksenov, L.Rosta, V.M.Garamus, A.Schreyer, **Journal of Magnetism and Magnetic Materials**, Vol.311(**2007**) 6-9

The main topics tackled by the NIPNE-JINR Neutron Scattering Group in the last years

- Order-disorder phase transitions in molecular crystals connected with thermodynamic properties of the system

- Proton dynamics in biopolymer-water systems (NIPNE- LLB, Saclay, CEA France)

1.Order disorder phase transitions in molecular crystals

1.The ferroelectric-paraelectric phase transition in triglycine sulphate-TGS

Reference:

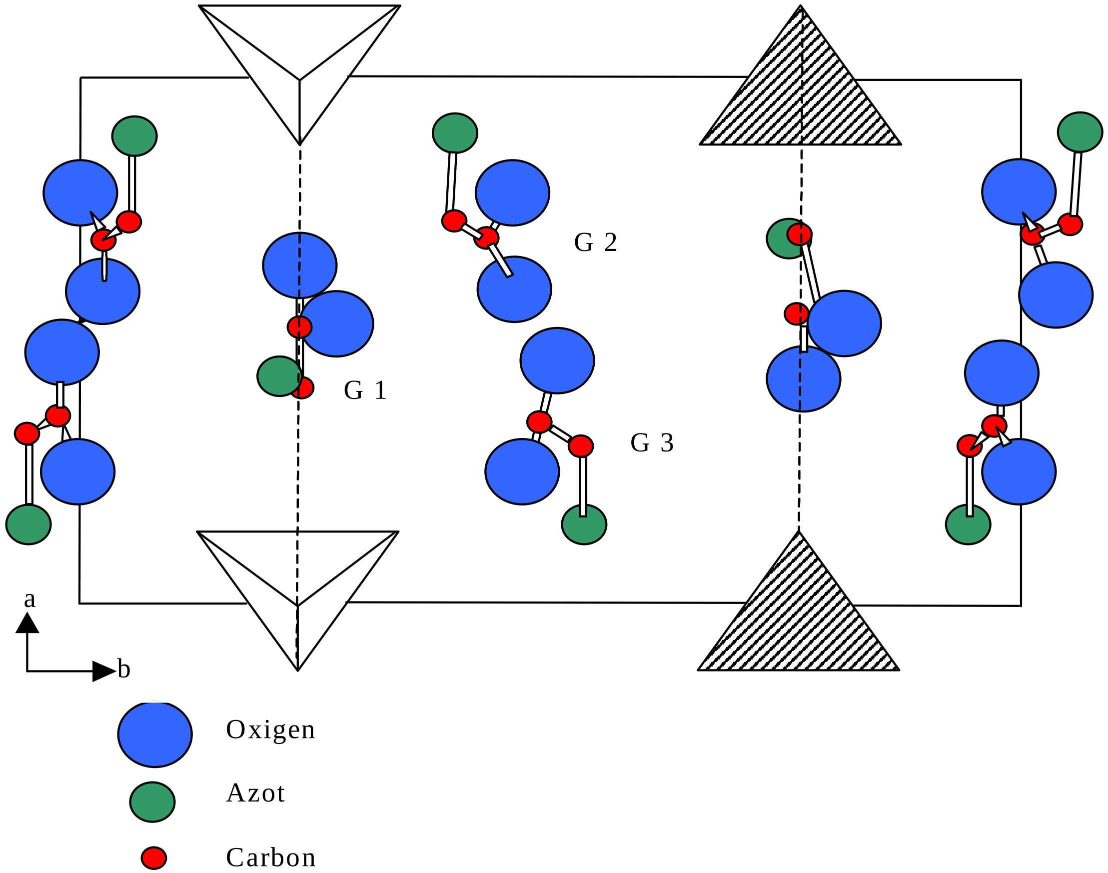
V.Tripadus, A Radulescu, J.Pieper, A. Buchsteiner, A.Podlesniak, S.Janssen, A.Serban

"*Molecular dynamics in triglycine sulphate by cold neutron spectroscopy*"

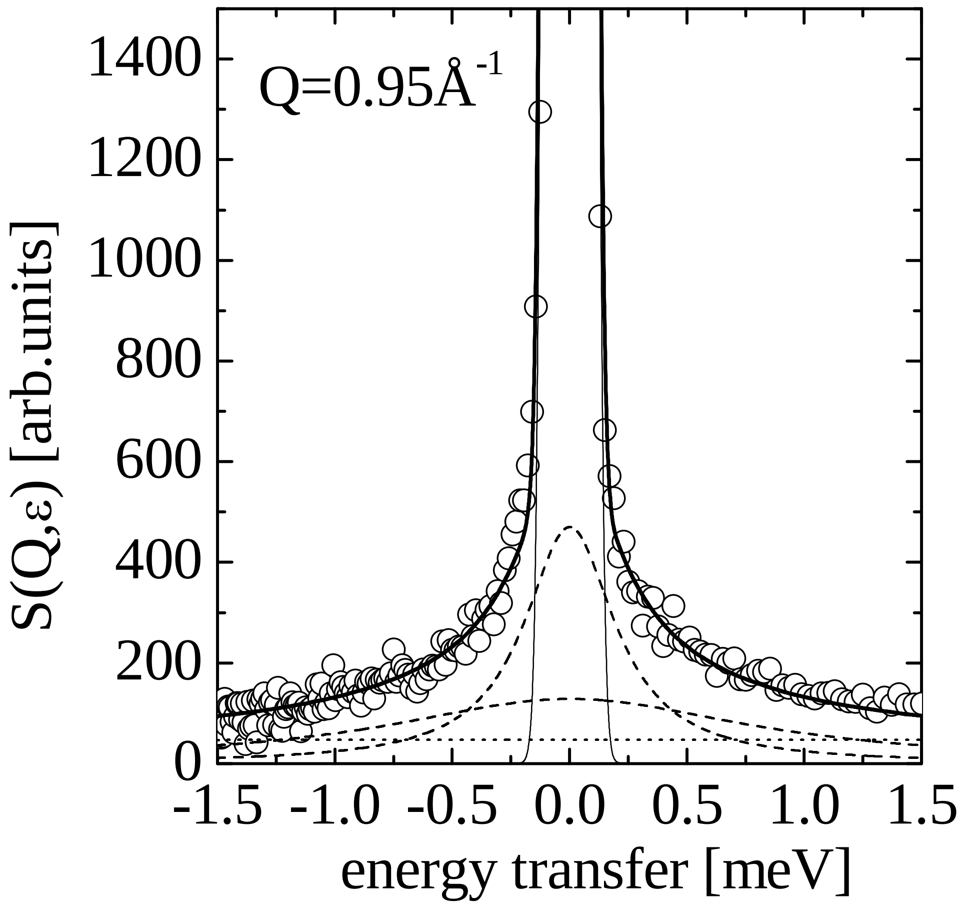
Elsevier "Chemical Physics" 322, p. 323-330, (2006)

- Chemical formula- $\mathbf{(NH_2CH_2COOH)_2\ H_2SO_4}$
- Ferroelectric material that exhibits an order-disorder phase transition at 49.2^0 C
- Crystalografic group: monoclinic
- Symmetry group in ordered phase: P_21
- Symmetry group above Tc: P_21/m

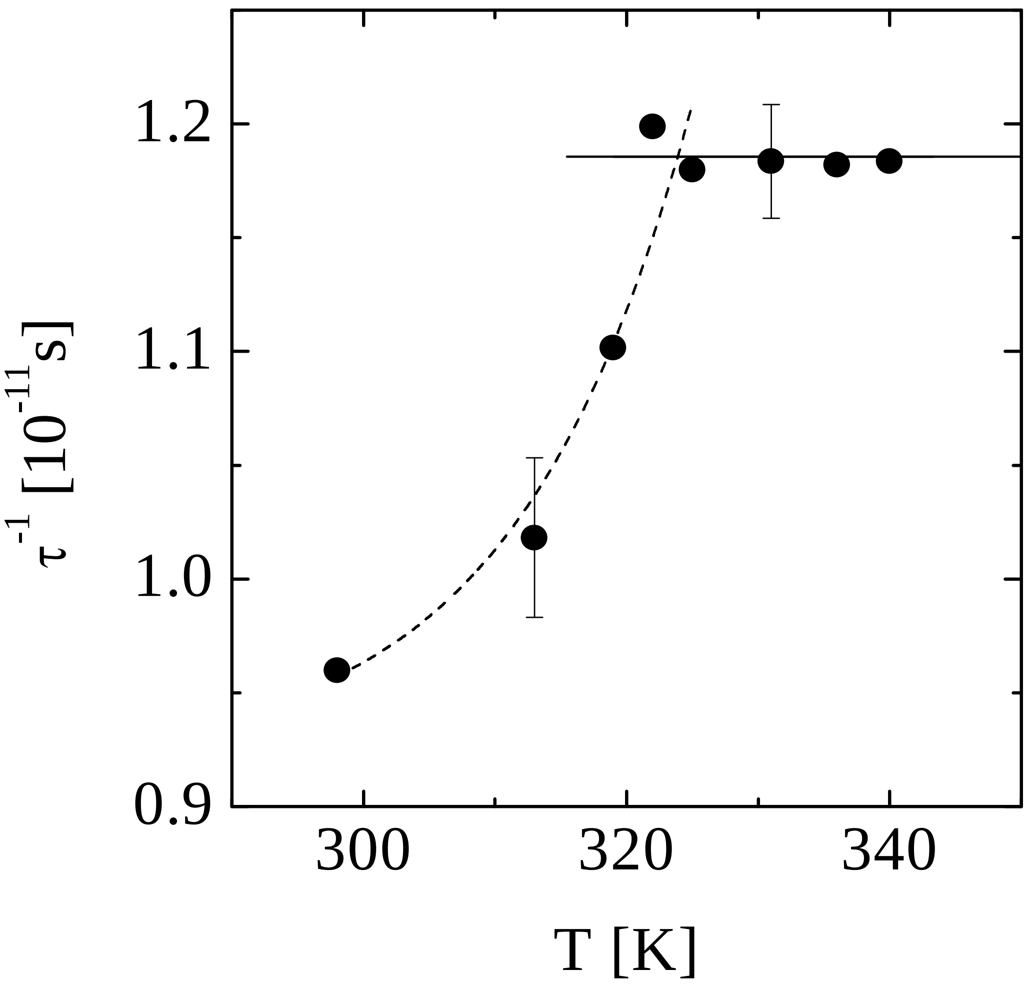
TGS unit cell, the SO_4 group is represented by tetrahedron



The TGS quasielastic line two lorentzians fit obtained at PSI-FOCUS spectrometer: the narrower lorentzian is given by amino flipping while the wider one by its reorientational motion



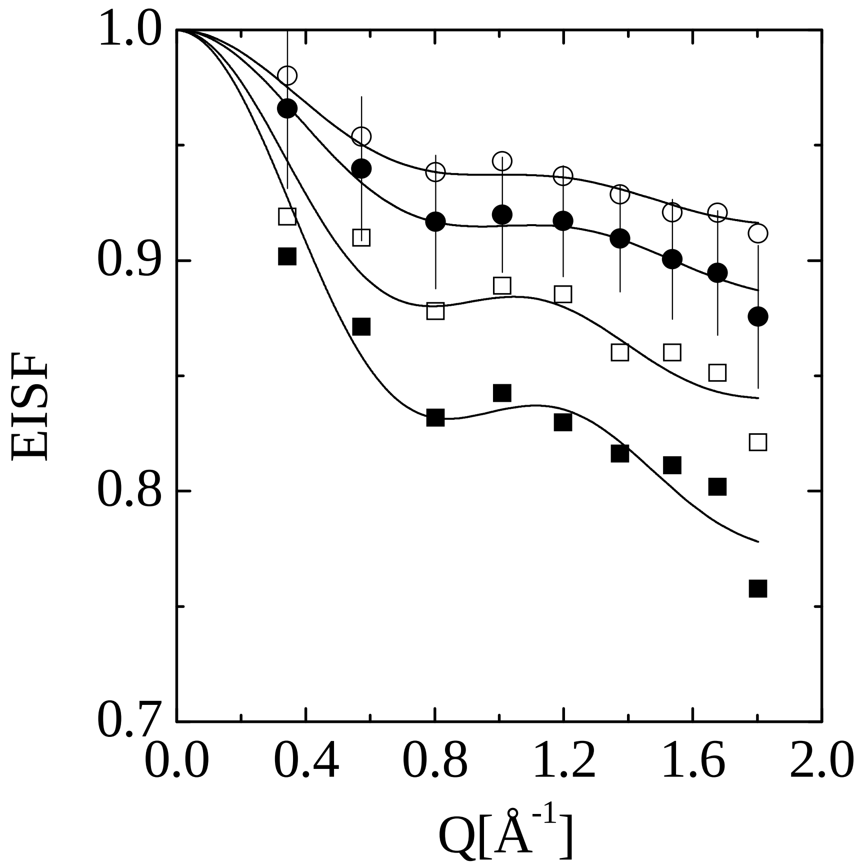
The temperature dependence of the flip frequency of NH_3 group. The discontinuity at $T=T_c= 322.25K$ is connected with the asymmetry of the ferroelectric order parameter introduced by the asymmetry of double minimum potential



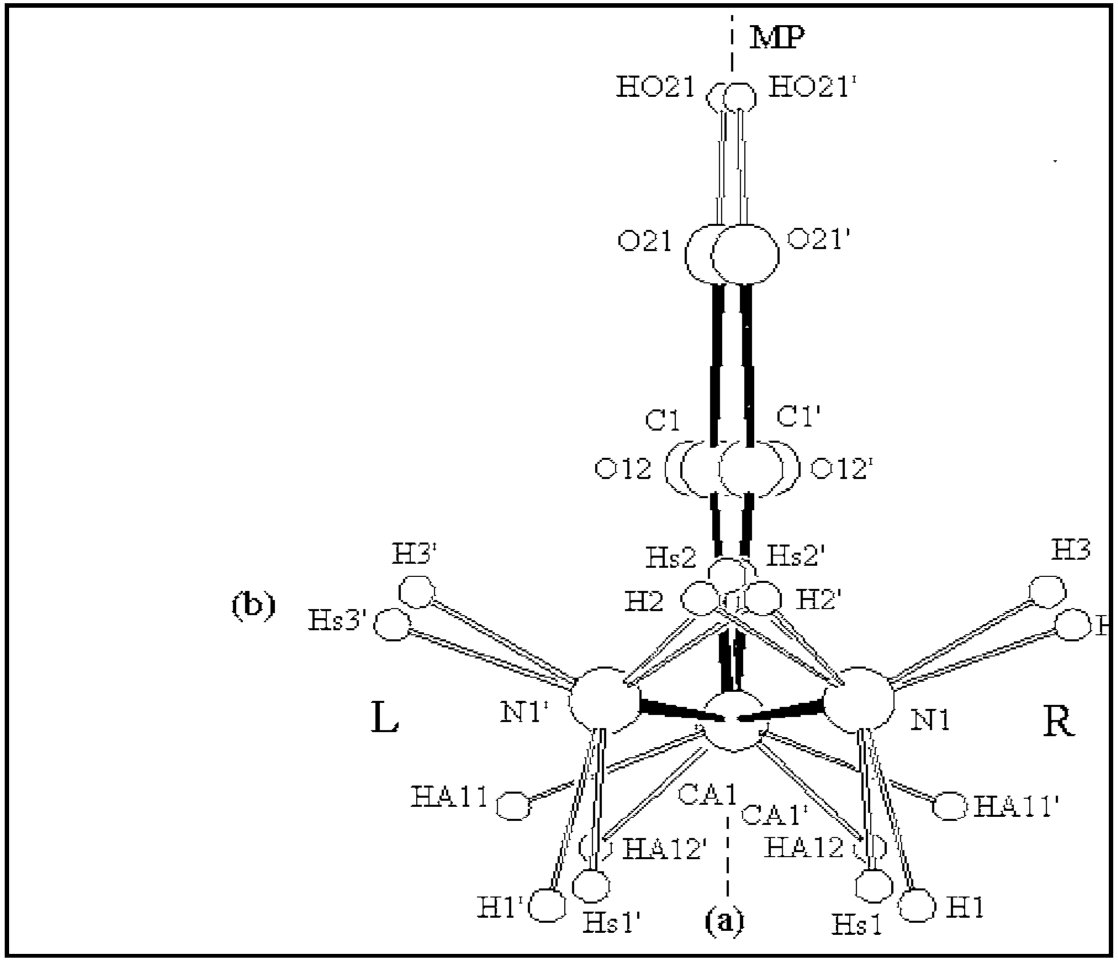
Elastic Incoherent Structure Factor for TGS at different temperatures

EISF=$1- p_1- p_2 + 0.5\, p_1(1+j_0(QR_1)) + 0.5\, p_2(1+ j_0 (QR_2))$

The data were well fitted by the proton diffusion jump between two sites

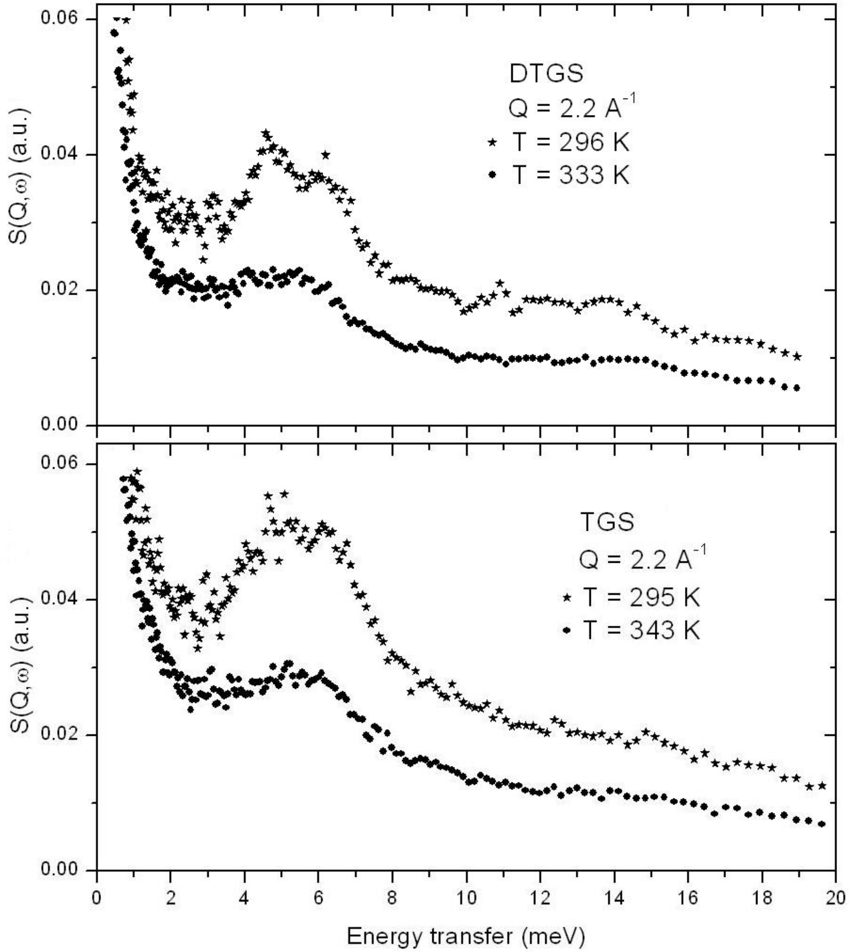


The special dynamics of GI glycine molecule



Reference: **V. Tripadus, D. Aranghel, M. Statescu, A. Buchsteiner**
"*Molecular dynamics in DTGS(ND3) by QENS and INS*",
"Chemical Physics", Chemical Physics, 353, 59-65, (2008)

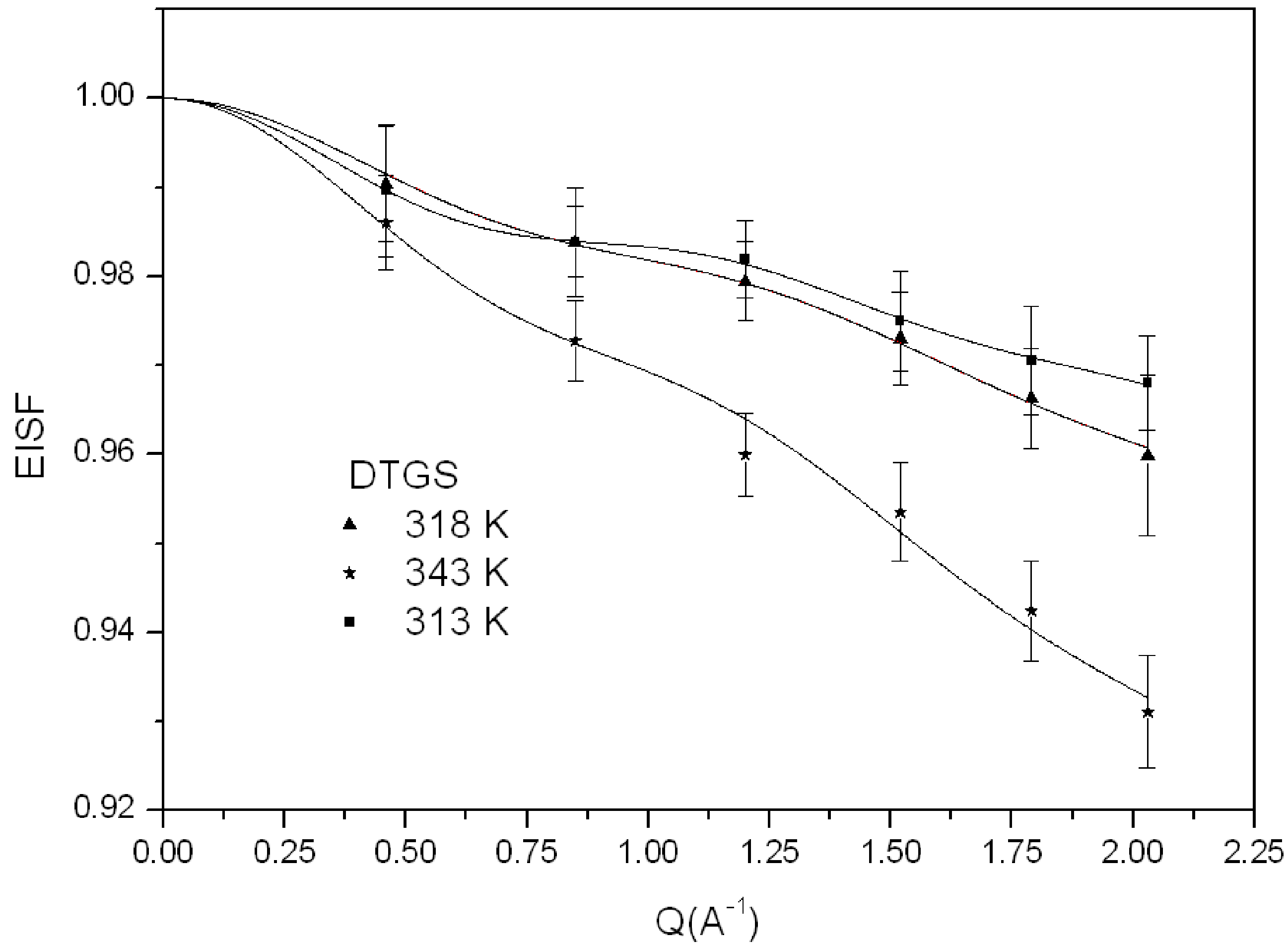
Low energy transfers dynamical structure factors S (Q, ω) for DTGS (partial deuterated TGS) and TGS measured at two temperatures: under critical point and above it. The effect of the lattice ordering is obvious.



The EISF of DTGS describing the CH_2 flipping motion

$$EISF' = 1 - p_1 - p_2 + p_1 .\ J^2_0(R1Q) + p_2\ 0.5\ [1 + J_0(R_2Q)]$$

Refernce:



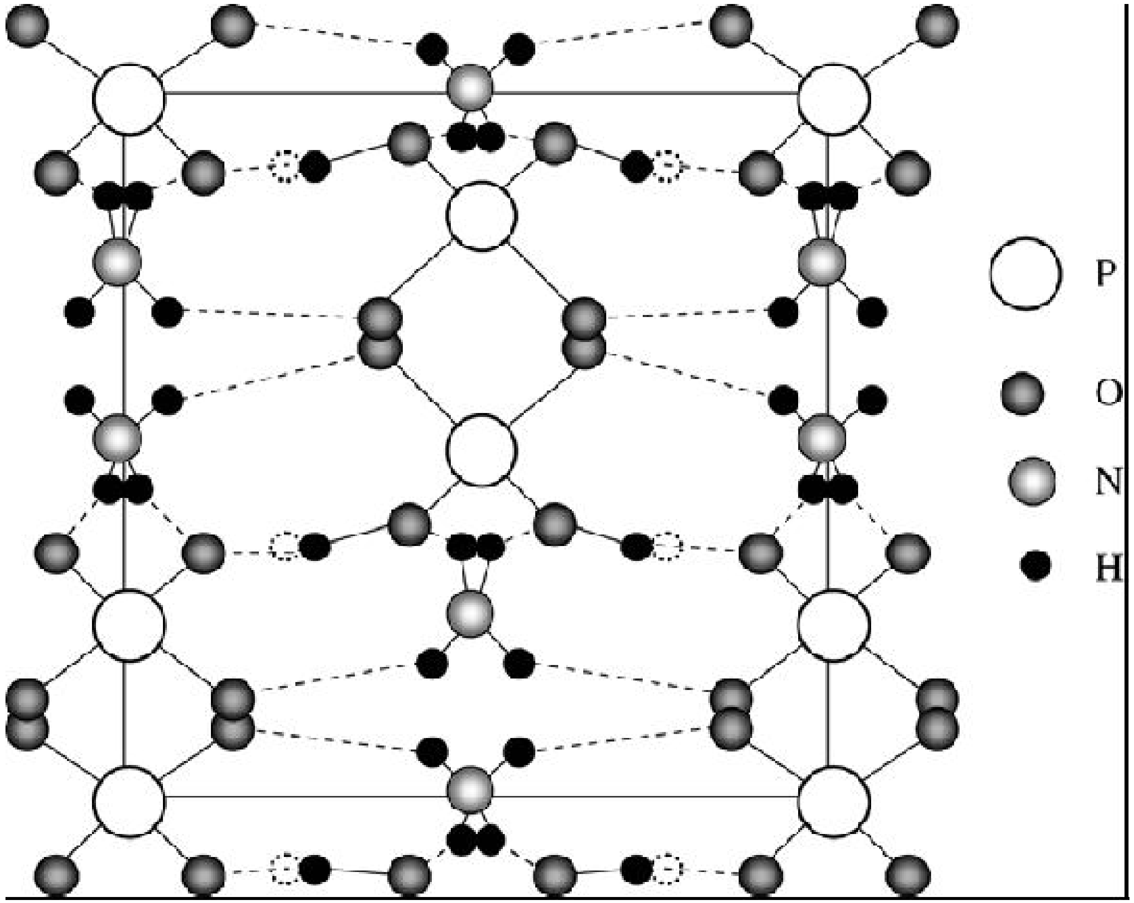
Our results describing the frequencies of TGS amino group

The flip characteristic times:

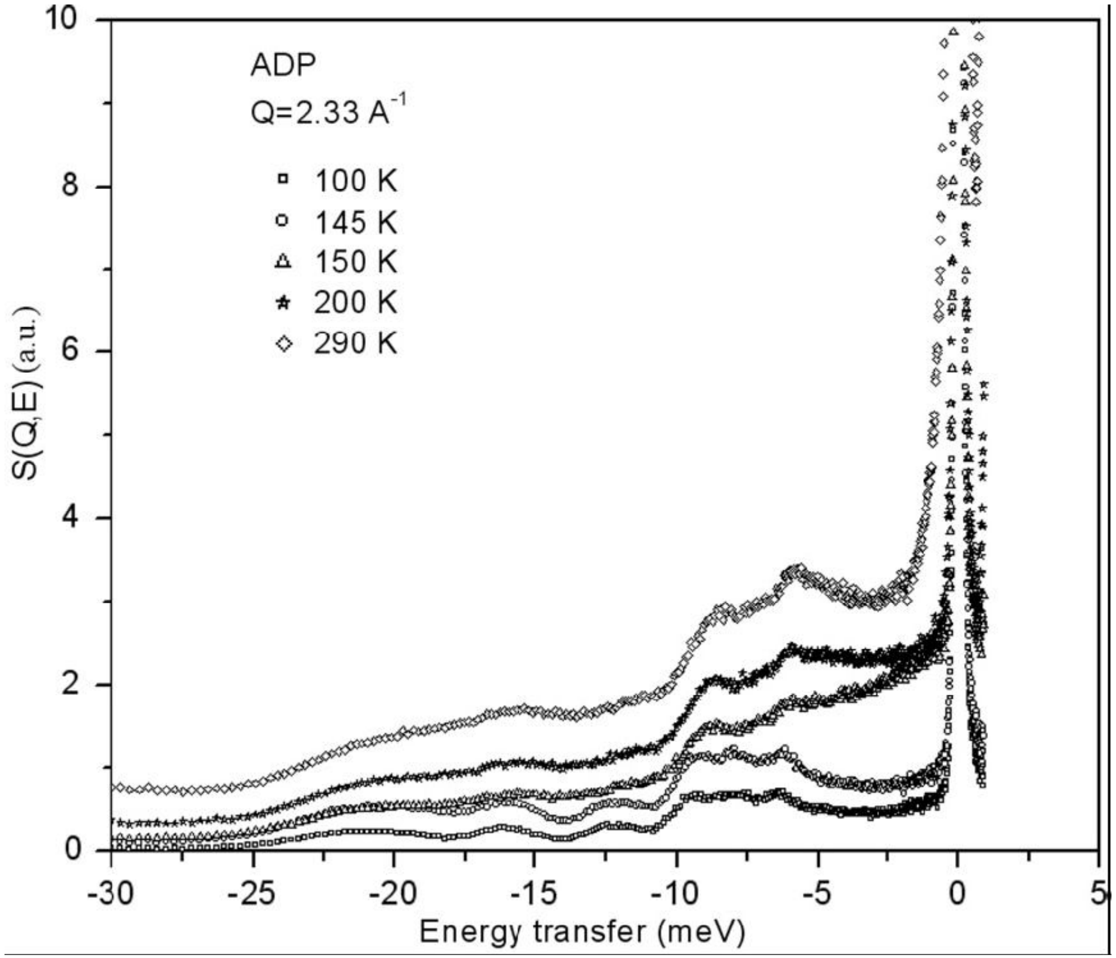
1. Flip:τ_f =0.83÷1.05 10^{-11}s,(RMN τ_f=1.2 10^{-11}s)
2. The rotational oscillations of the NH_3 group around C-N axis:τ_r= 0.23÷0.30 10^{-11} (RMN τ_r= 2.1 10^{-11}s)
3. The flipping frequencies associated with CH_2 group τ_c =0.45 10^{-11} s , (RMN τ_c =1.2 10^{-11}s)

2. *ADP ANTIFERROELECTRIC-PARAELECTRIC PHASE TRANSITION*

Reference: V. Tripadus, M. Gugiu, M. Statescu, A. Podlesnyak "*Molecular Dynamics in Ammonium Dihydrogen Phosphate using Incoherent Neutron Scattering*, Elsevier "Chemical Physics" 335, p. 233-241, **(**2007)



ADP low energy transfer neutron scattering spectrum.
The changes of the acoustic phonon group is obvious

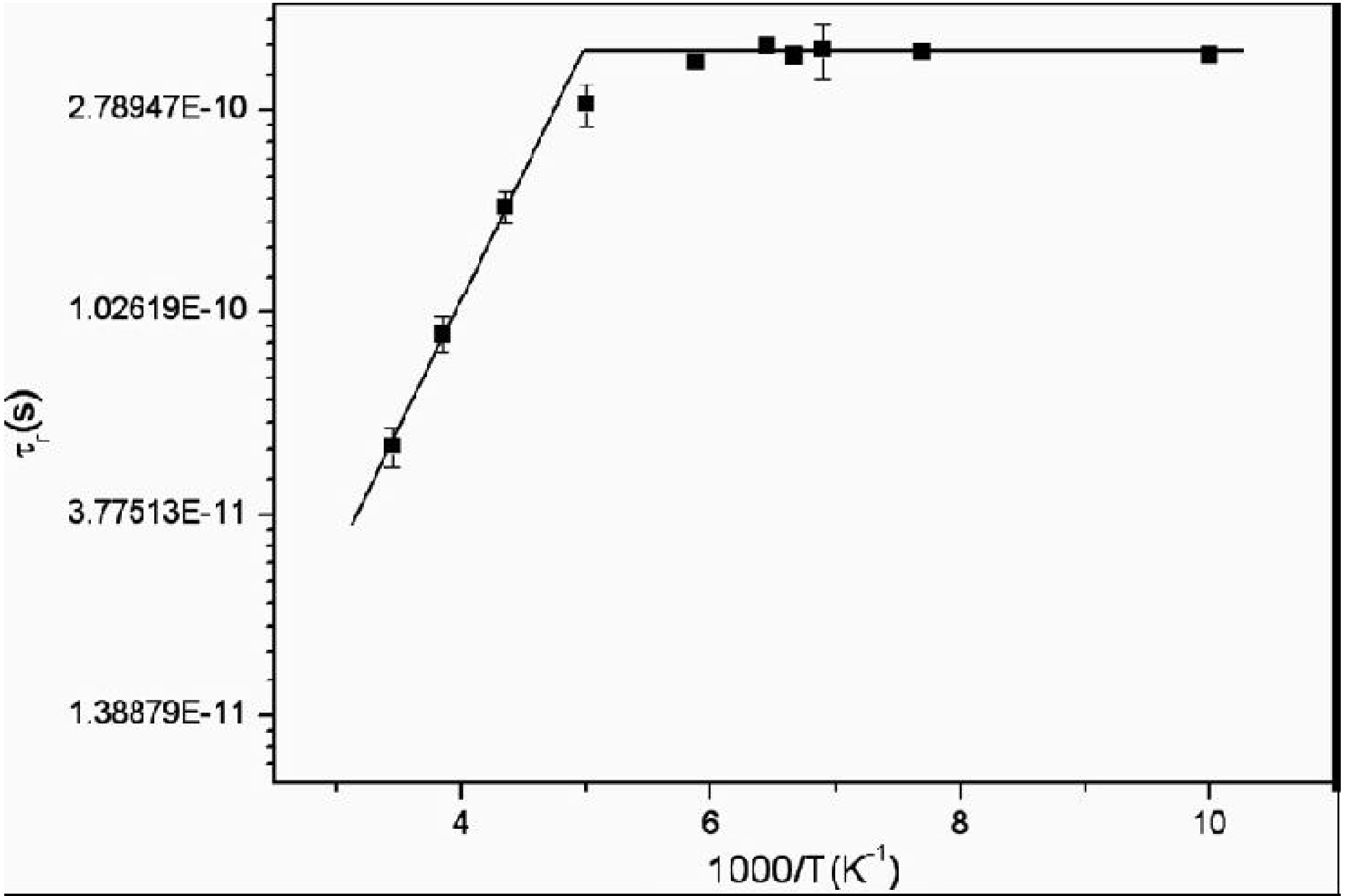


The residence time of the NH_4 jump diffusion as a function of temperature,

$\tau = \tau_0 \exp(E_a/K_BT)$ Ea = 3.5 ± 0.1kcal/mol, τ0 = 5.6 ± 0.5*10^{-14} s.

The *correlation times* obtained from NMR measurements give

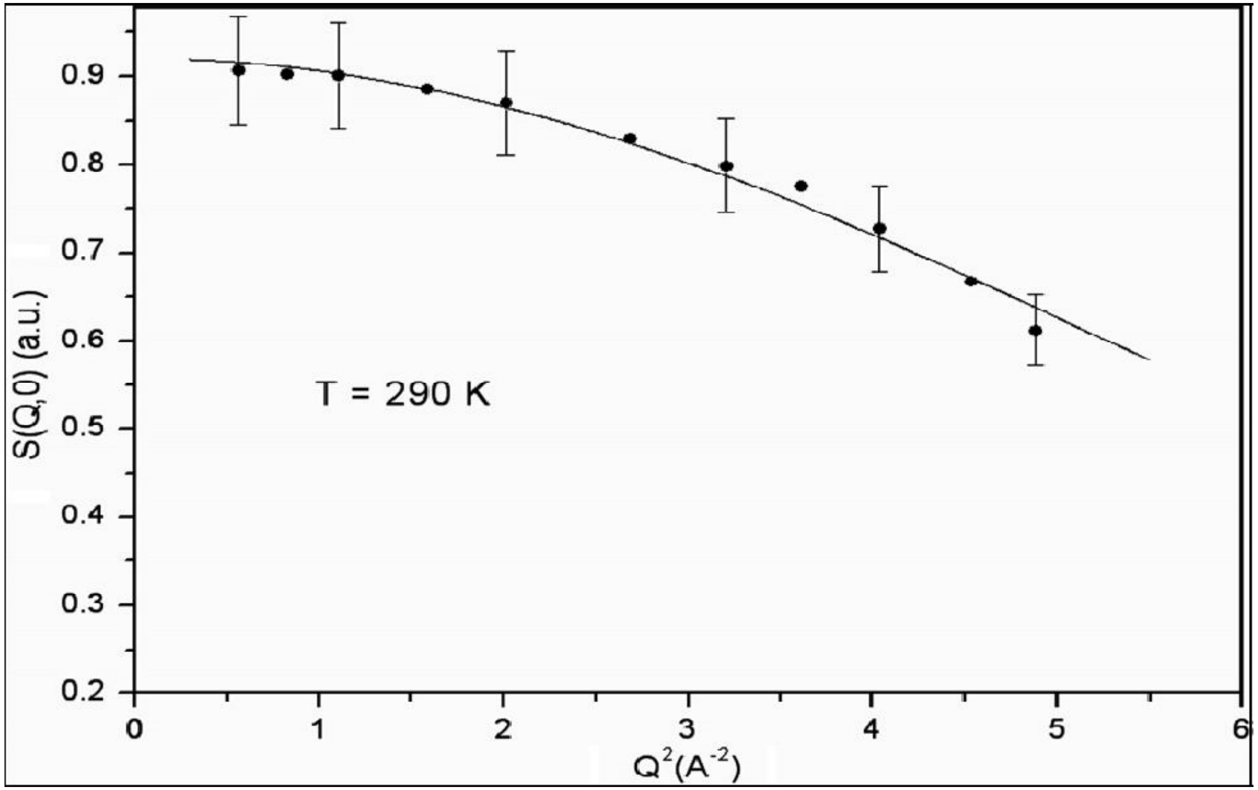
Ea = 3.7 ± 0.3 kcal/mol and τ_0 =5.0*10^{14} S.



Elastic Scattering Component

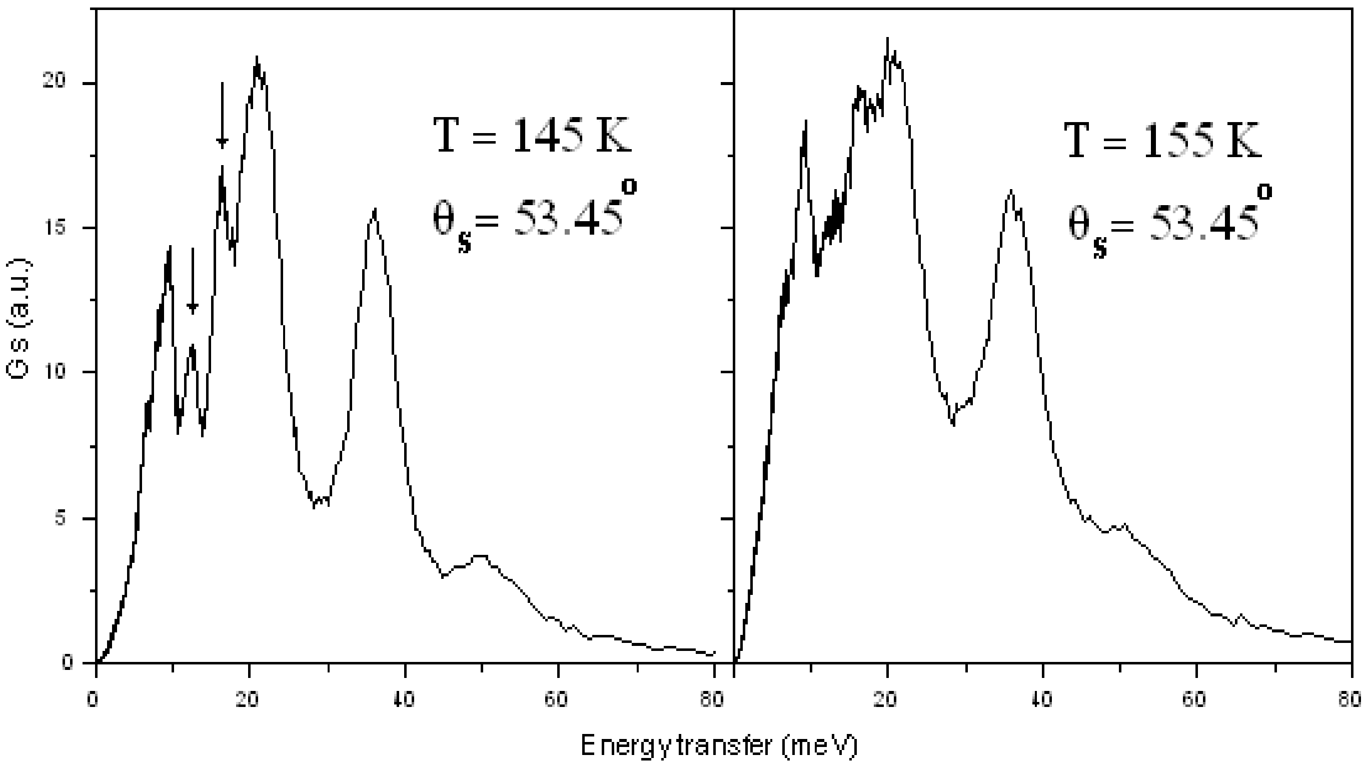
$$S(Q,\omega\approx 0) = \exp[-2W(Q)]\cdot EISF$$

- $W(Q)=Q^2\langle\Delta x^2\rangle_G/6$, $\langle\Delta x^2\rangle_G$ is the mean-square displacement of the scattering particle in harmonic approximation.
- $EISF=(1-p_1-p_2+p_1*0.25(1+3(\sin(QR))/(QR))+p_2*(1-2k_1*k_2(1-(\sin(Qd)/(Qd))))$
- p_1 and p_2 stand for the fractions of mobile and fixed protons respectively and R is the distance which connects two protons in the ammonium group
- The ammonium ion performs instantaneously reorientational jumps and the average *residence time* between two jumps is τ_r .During this interval of time the proton oscillates between two distinct wells of an asymmetric potential separated by a distance d and the occupation probabilities k_1 and k_2
- The fitting results: $\langle\Delta x^2\rangle_G$= 0.0264 ± 0.010, p_1 = 0.6 fixed, p_2 = 0.16 ± 0.02, d=0.2, R=0.3,k_1k_2=k=1 were kept fixed.



0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
S(Q,0) (a.u.)
T = 290 K
0
1
2
3
4
5
6
Q²(A⁻²)

The effect of proton ordering on AFE-PE phase transition observed in phonon density of states for ADP under critical temperature



ADP Conclusions

- The hydrogen bonds network is directly involved in the order-disorder phase transition phenomenon.
- The ordering of molecular groups connected in the molecular crystal lattice by H bonds is an essential aspect of phase transition
- QENS is turned out to be a powerful method to set off the main dynamical aspect involved in the order-disorder phase-transition

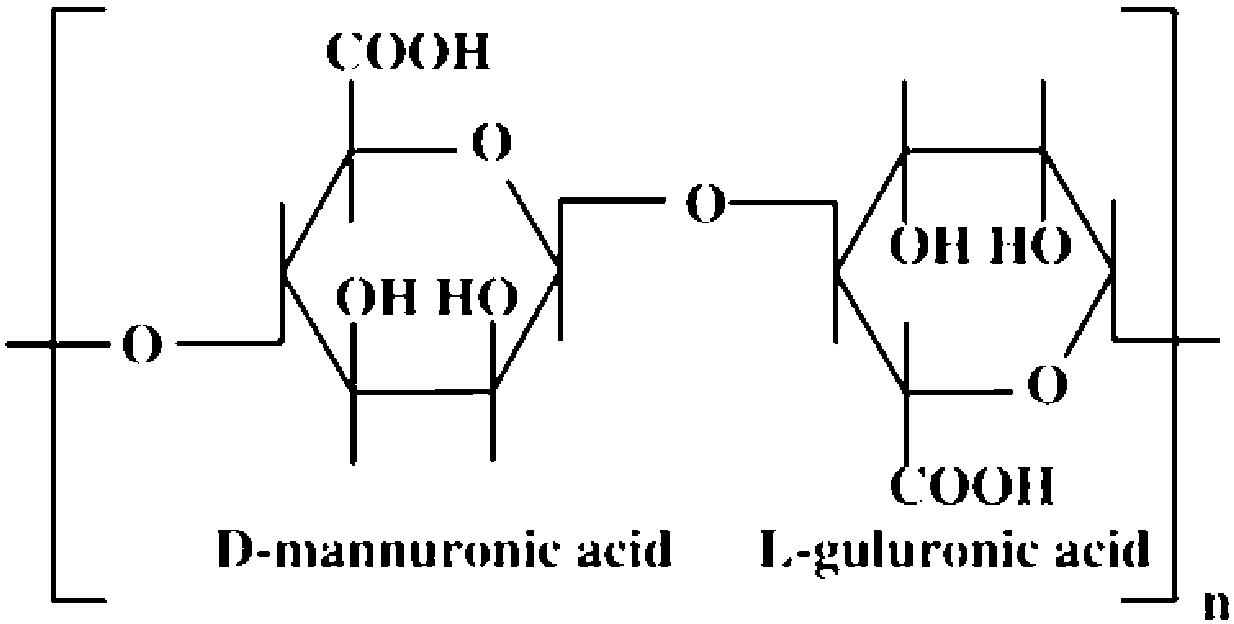
BY QENS

Reference:**V. Tripadus, J. M. Zanotti, S. Mitra, , M. Statescu, D. Aranghel, O. Constantinescu,**

"Molecular dynamics in sodium alginate using elastic neutron scattering"

National Conference of Physics, Bucuresti, 2008

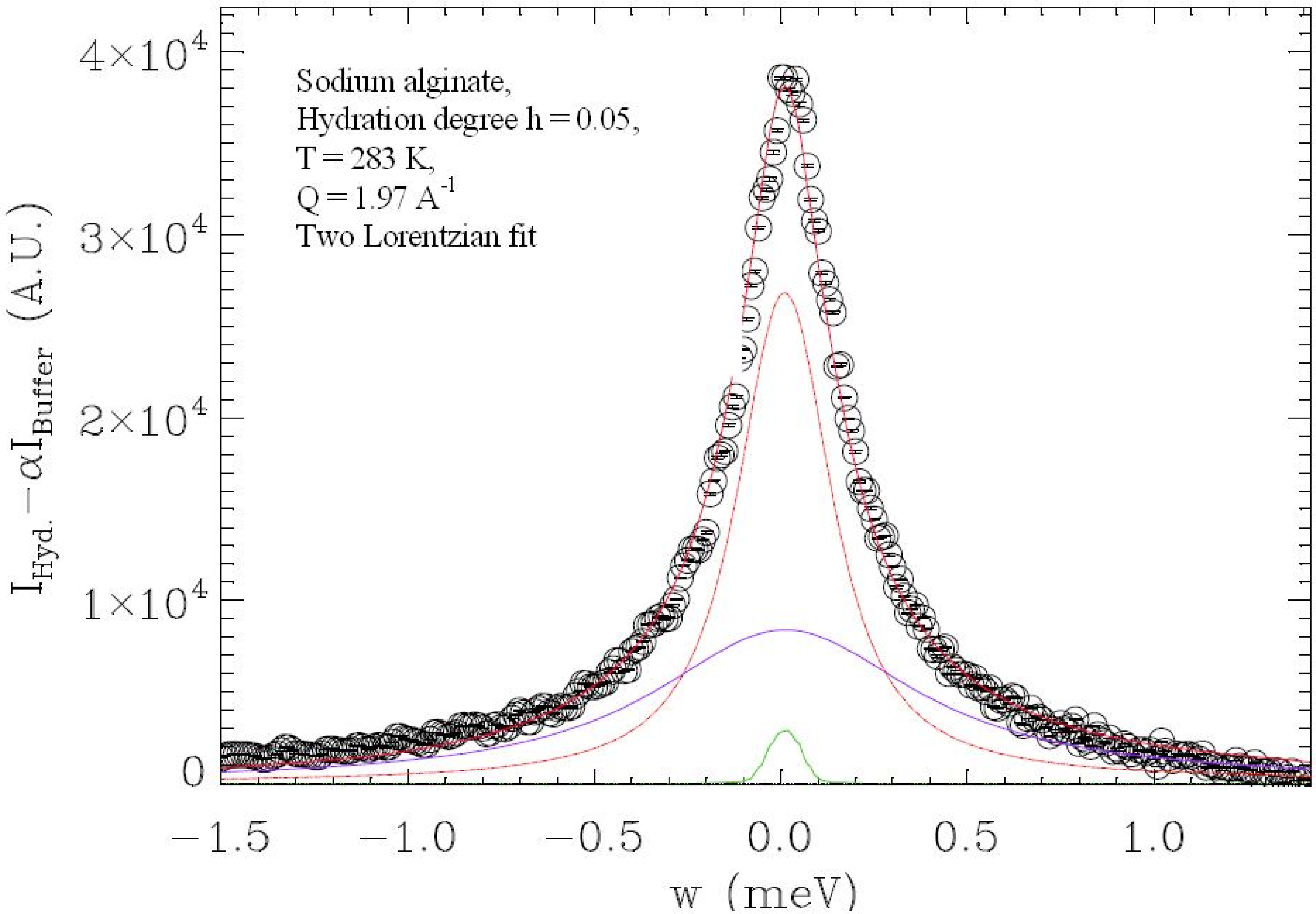
Chemical structure of alginic acid



Neutron scattering measurements on biopolymers

- The neutron scattering experiments are very suited to study the water-polysaccharides systems both for the point of view of solvent molecules dynamics and for the polymer chains dynamics. The proton motion of the solvent molecules is faster than of polymer chain protons The separation of the two contributions could be done only by a suited choosing of the experimental conditions. In order to separate the biopolymer chain protons motions from the solvent protons we have used the heavy water as solvent. In this case the quasielastic line (including the pure elastic scattering) will be given mainly by the polysaccharide non-exchangeable protons. The quasielastic line contains one or more Lorentzians, the widths of which are connected with the diffusive motion of the polysaccharide moiety.

Fig 2. Fitted quasielastic line with two Lorentzians. The green curve is the elastic line given by the resolution function.

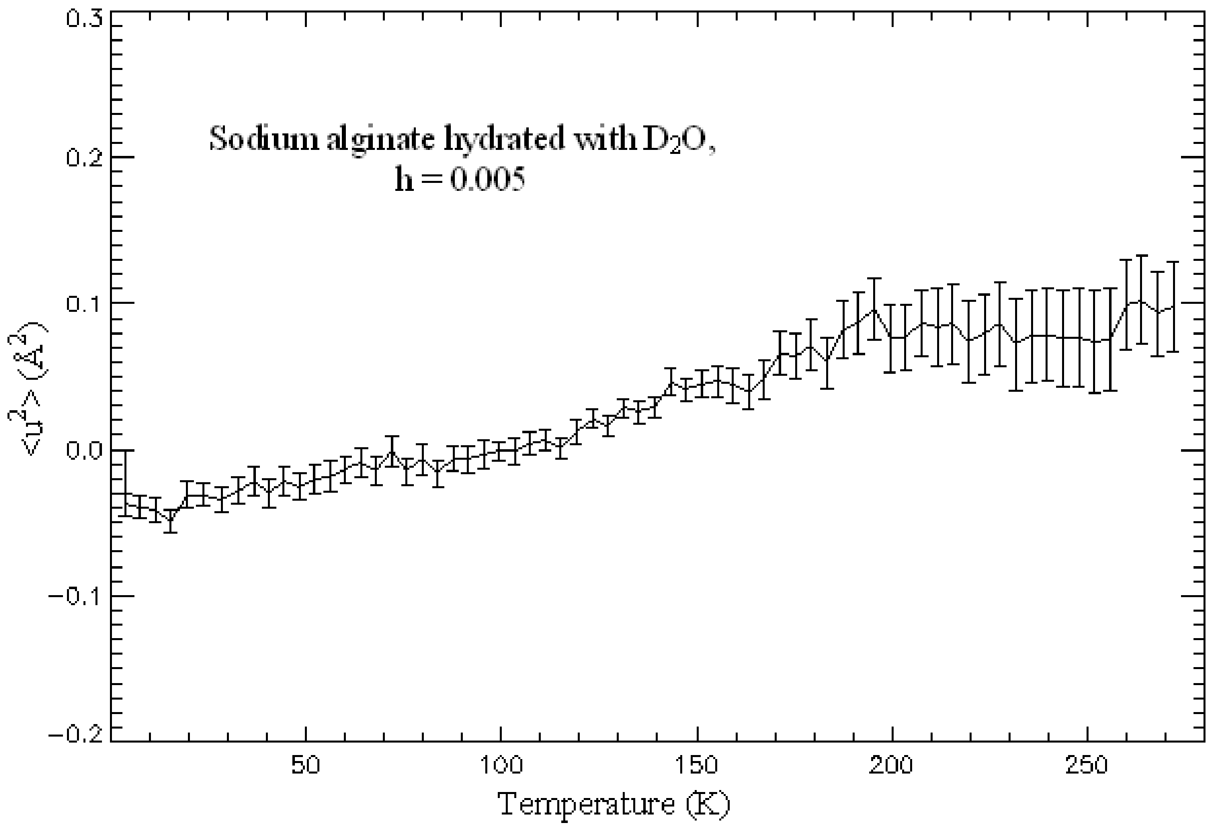


Experimental parameters

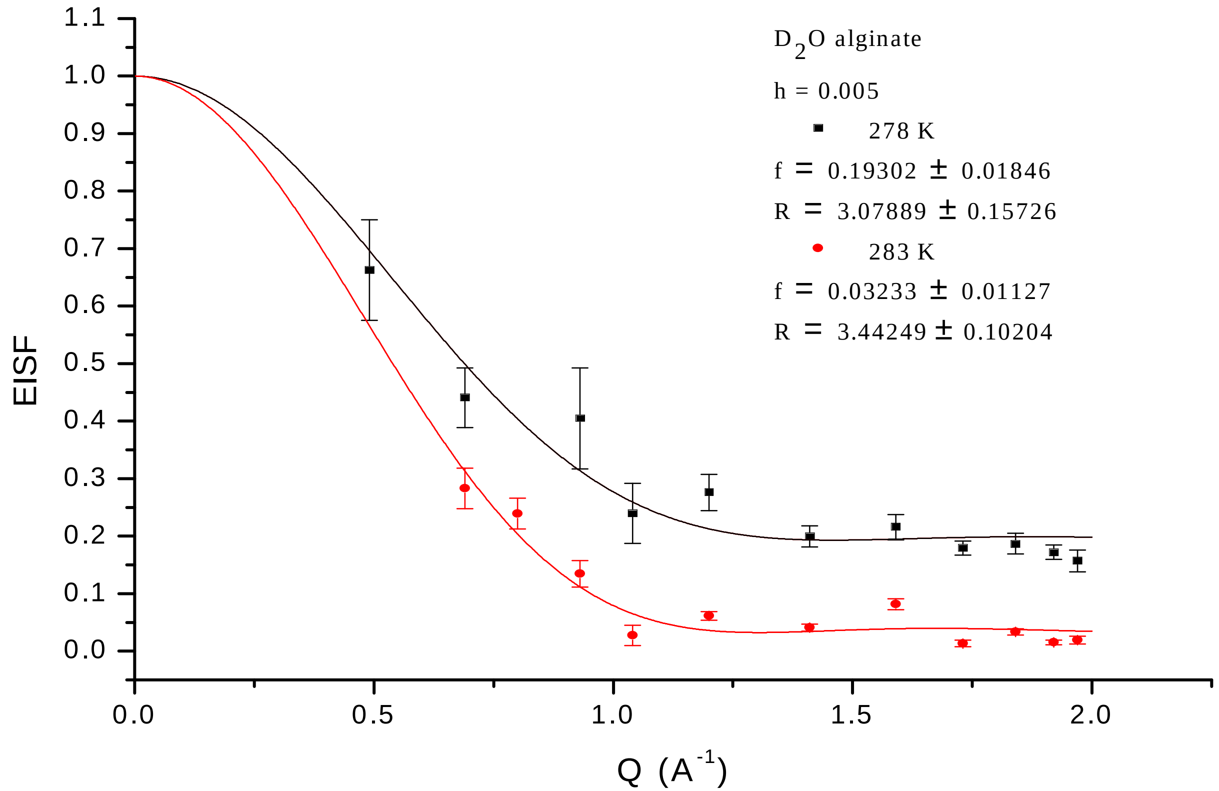
1. Neutron measurements: Nuclear Reactor ORPHE, LLB-CEA, Saclay, France
2. Neutron spectrometer: MIBEMOL-TOF
3. Incoming neutrons wavelength: λ_0=6 ´
4. Energy window: 0.1 meV
5. Timescale ≈ 6.6 ps
6. Momentum transfer interval: 0.69 ´$^{-1}$ and 1.97 ´$^{-1}$
7. The hydration levels of the samples, h= 0.005, 0.0125, 0.025, 0.05, 0.5 grams of polysaccharide/grams of water.
8. Data processing program: QENSH -MIBEMOL
9. Measuring temperature range: 4K and 310K

- **Results**

Fig.2 Mean square displacement of the protons in sodium alginate biopolymer hydrated with heavy water as a function of temperature.



Comparative presentation of experimental EISF at two different temperatures fitted with the theoretical spherical model
R- the radius of the sphere, r-mean square displacement



Conclusions

- - The protons dynamics of hydrated sodium alginate biopolymer is described by "jump diffusion in restricted volumes" models: Volino and Dianoux (1980) as well as Hall and Ross(1981).
- - The quasielastic lines were fitted generally using the QENSH program with one or two Lorentzians
- -The mean square displacement of the polysaccharide chains protons as a function of temperature presents two transition points:150K and 180K. The first transition point was connected with rotational motions release while the second transition point is connected with water molecule center of gravity translational diffusion
- - The dynamical behavior of the polysaccharide-water system is governed by the presence of the network of hydrogen bonds between water molecules and hydrophilic sites of the biopolymer.

- ***References***
- **1. V. Tripadus, D. Aranghel, M. Statescu, A. Buchsteiner**
- **"*Molecular dynamics in DTGS (ND3) by quasielastic and inelastic neutron scattering*",**
- **"Chemical Physics", Chemical Physics, 353, 59-65, (2008)**
- **2. Vasile Tripadus, Marius Gugiu, Mihai Statescu, Andrew Podlesnyak**
  Molecular Dynamics in Ammonium Dihydrogen Phosphate using Incoherent Neutron Scattering
  Elsevier "Chemical Physics" 335, p. 233-241, (2007)
- **3. V.Tripadus, A Radulescu, J.Pieper, A. Buchsteiner, A.Podlesniak, S.Janssen, A. Serban**
  Molecular dynamics in triglycine sulphate by cold neutron spectroscopy
  Elsevier "Chemical Physics" 322, p. 323-330, (2006)

4. V. Tripadus, A.Radulescu, A..Buchsteiner,S.Janssen, D. Aranghel, C..Simion
Dynamics of Amino Gl-Glycine Molecule in Triglycine Sulphate by Incoherent Quasielastic Neutron Scattering **Romanian Journal of Physics, vol.51, Nos.5-6, p.557-565, (2006)**

- **5.V.Tripadus M. Gugiu, M. Statescu, A. Podlesnyak, S.Janssen**
- ***AIP Conference Proceedings; Journal Volume: 899; Journal Issue: 1; Conference:***
- ***6th international Conference of the Balkan Physical Union, Istanbul (Turkey), 22-26 Aug 2006***
- **6. V. TripadusJ. M. Zanotti, S. Mitra, , M. Statescu, D. Aranghel, O. Constantinescu,**
- ***"Molecular dynamics in sodium alginate using elastic neutron scattering"***
- **National Conference of Physics, Bucuresti, 2008**

Thank you for your attention!

03.03.2009